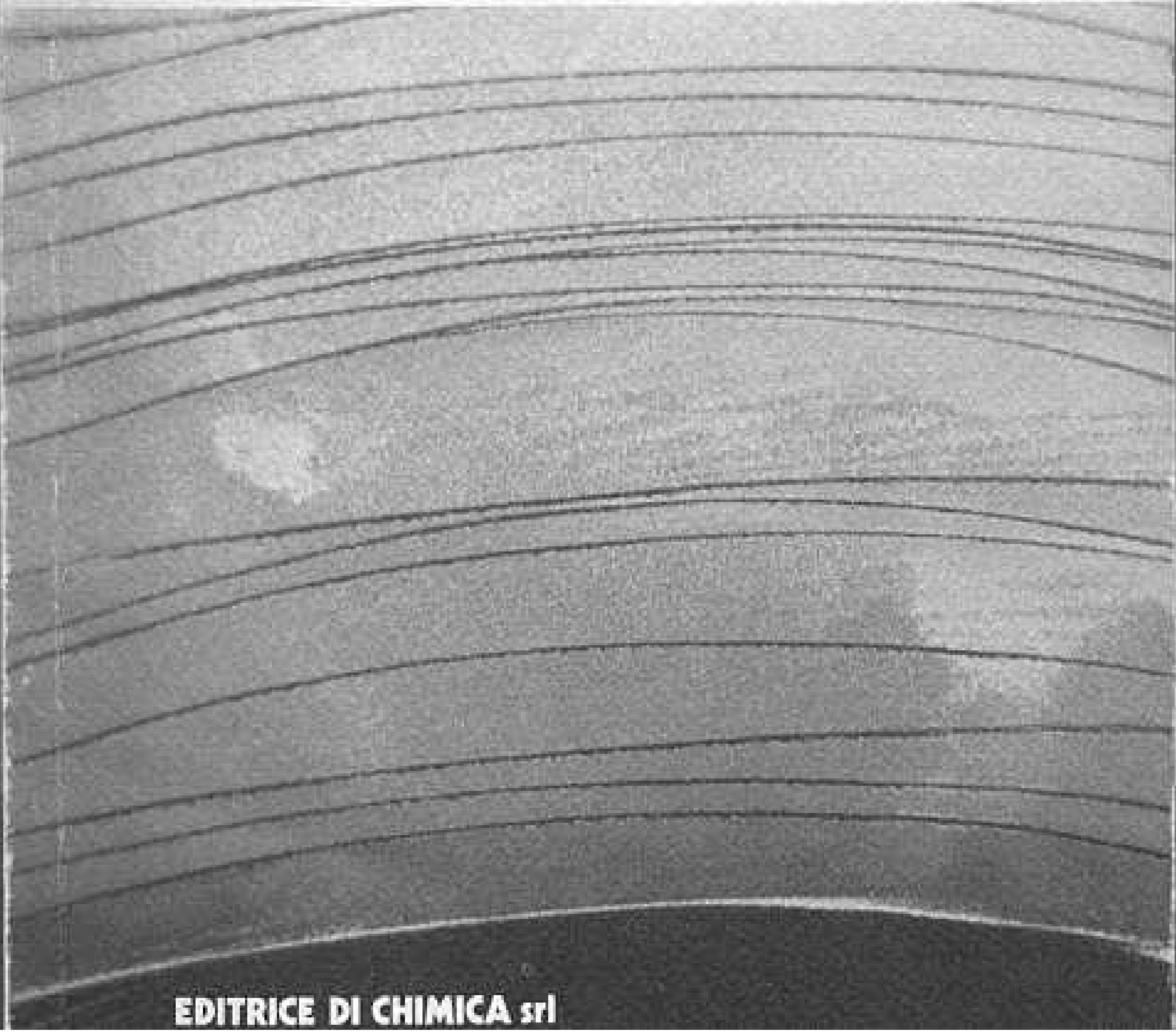
GIULIO NATTA

Present significance of his scientific contribution



EDITRICE DI CHIMICA srl

GIULIO NATTA

Present significance of his scientific contribution

EDITORS:
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FOREWORD

Giulio Natta was undoubtedly one of the most significant figures in 20th century chemistry.

In addition to his great curiosity, his natural intuition and the breadth of his knowledge (allowing him to pursue research in wide-ranging areas of chemistry and chemical engineering), he never lost sight of application possibilities.

His work is particularly characterized by the fact that his research themes are still in the vanguard of scientific and industrial significance even after several decades.

Since the choice of research themes is an essential element in their success, it seemed of interest to recall the principle lines of his research now, three years after his death. We have therefore invited specialists in these fields to illustrate them here.

These contributions are collected here in the order in which the research areas were initially considered by Prof. Natta.

These articles are preceded by the presentations made by Prof. Quilico, a fellow student and colleague, Prof. Rigamonti, one of his first assistants, and Prof. Pino, one of his collaborators at the Milan Politecnico, at a commemorative ceremony at the Politecnico in Milano.

The editors of this collection are grateful for the collaboration of the authors of the reviews, many of whom had the privilege to know and in some cases work with Prof. Natta.

The editors are also grateful to the CNR and the Italian Chemical Society for their financial support of this publication.

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Giulio Natta: the man, the scientist

Presentations made at the commemorative ceremony at the Politecnico in Milano

The Human Personality of Giulio Natta

ADOLFO QUILICO
Emeritus Professor, Politecnico, Milano

Chancellor, colleagues, ladies and gentlemen:

In my capacity as an old classmate of Giulio Natta, as well as a friend and colleague for many years, it is my privilege to say a few words about the man himself. I leave to others better qualified by virtue of their years as his students and collaborators the task of illustrating his fundamental contributions to the science of chemistry and its applications during the course of his distinguished and productive career.

However, mine is not a simple task. On the one hand, one cannot separate the man from his work; on the other, it is the adventures of thought which colour and reveal the life of a distinguished scientist, who in his private life usually is not very different from common mortals. In any case, in the brief time available, I will try to give a profile of the human personality of Giulio Natta, as I have observed him over the many years of our friendship.

Giulio Natta was born in Porto Maurizio (now Imperia) in 1903 of Ligurian parents: Francesco Natta, a judge, and Elena Crespi. After completing secondary school and the propaedeutical biennium in Genova, he enrolled in 1921 in industrial chemical engineering in our Technical University (Politecnico). In 1922 he became a student in the Institute of General chemistry directed by Giuseppe Bruni, at the request of Bruni's assistant Giorgio Renato Levi, who had a particular ability to discover early vocation for chemistry. I knew Natta since 1923 when I also became a student in the Institute. With Adolfo Ferrari and Arnaldo Corbellini, we four formed the first group of engineers who received chairs in chemistry in Italy.

To this day I remember very vividly my first meeting with Natta in our dear old centre in Piazza Cavour, where the chemistry laboratory was placed in the glassenclosed portico of an old convent. As I entered, not without a certain reverential awe in such surroundings, I met a thin young man with wavy hair and intelligent eyes who welcomed me to the Institute. We immediately became friends, and he invited me to his home in a severe and rather gloomy building in via Rugabella, where he had set up a laboratory. I was particularly impressed that he had an analytical balance, a luxury I could never afford for my own modest home laboratory.

Even as students, we were very absorbed in our research, returning many nights a week to work in the laboratory after dinner until midnight. We were good company for one another even though our work was in different areas. I recall a tragicomic episode which occurred one summer evening. While looking for a chemical in a cabinet, Natta dropped a large ampul of mercaptan, which on breaking released its typical perfume throughout the area. The vapours travelled through the open windows into the adjacent houses, spreading the alarm and waking the sleeping neighbors to unleash a chorus of curses and protests. I remember quickly dousing the lights and beating a hasty retreat.

Although Natta was an excellent student who passed his exams brilliantly, he was certainly not what the British call a « swot ». He never forgot his youth, and besides his studies had interests appropriate to his age. He was a proven skier and took part in student productions, which were at that time good healthy fun. He belonged to a student association known as the « brawling knights », whose program is suggested by its name. Their participation in the freshman's rag of 1923 was memorable: a wagon representing a « soup slicing machine ». Who would have thought that the inventors of this miraculous machine included a future Nobel prize winner!

After graduation (his in 1924, mine in 1925), we became assistants to Bruni. We remained together until 1933, when Natta won the Chair in General Chemistry at the University of Pavia and transferred there.

Up to that time, Natta's scientific activity was predominantly directed toward x-ray studies of crystal structures in what must be considered the first Italian centre for this type of work. The centre was founded in 1923 in the old Piazza Cavour laboratory where G.R. Levi, Natta and A. Ferrari worked. In 1925, he went to Freiburg to study the new techniques of electron interference in Prof. Seemann's laboratory. There he came to know Hermann Staudinger and his pioneering work on macromolecules, and so was led to applying his knowledge of x-ray techniques to the study of the crystal structure of high polymers, with great success.

After a period as Professor of Physical chemistry in Rome and of Industrial chemistry at the Turin Politecnico, Natta returned to Milan in 1939 to succeed Mario Giacomo Levi in the industrial chemistry chair at our Politecnico. This marks the beginning of the golden period of his

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The soup slicing machine.

research and teaching, which continued with increasing success until the appearance and development of his illness.

Natta's most impressive aspect was his dual personality as a scientist of deep theoretical preparation on the one hand, and as a technician concerned with the practical application of his findings on the other. He was a true industrial chemist, comparable to Claude, to Haber, to Bergius. This vocation was apparent from the very beginning when in 1926, only two years after graduation, he applied himself to the synthesis of methanol.

From a didactic point of view, although he was not blessed with particular oratorical ability and showed a certain innate timidness and reserve on contact with the public, his lessons were quite interesting and effective, packed with concepts and ideas. As soon as he returned to the Politecnico in 1939, he deeply renewed the teaching of industrial chemistry, which until then had been descriptive and informative in character, to give it a formative content which gave the fundamental principles of industrial chemistry and also considered the economic factor. This modern approach to teaching Industrial chemistry, based on the principles of thermodynamics, kinetics and catalysis, and on the study of unit operations, was shown to be particularly well suited for chemical engineers and was adopted immediately by various Italian schools.

With the help of industry, he took great pains in the renewal and reorganization of the Institute of Industrial Chemistry in our Politecnico as it was moved to a new location and equipped with all the equipment necessary for the use of the most modern methods of physical and chemical research.

Ever kind and polite in his dealings with colleagues and collaborators, he knew how to communicate to the latter his enthusiasm for research, as shown by the number and quality of his students who reached university chairs or high positions in industry.

Until his illness appeared in 1959, his private life passed calmly with his wife Rosita and his two sons. His wife gave him loving care during his sickness, and her early death in 1968 was for him a heavy blow.

He accepted his pain with stoicism and resignation. I recall one day as I visited him in his office at the Politecnico, he said he had accepted it with resignation also because it required him to remain seated at his work longer, and thus allowed him to devote himself without interruption to the large problems he was grappling with.

His work won him broad and well merited recognition on an international level, culminating in the Nobel Prize for chemistry in 1963 for his studies of stereospecific polymerization and macromolecular stereochemistry which will be discussed shortly. He was named a member of numerous foreign Academies and Chemical Societies, including the New York Academy of Sciences and the USSR Academy of Science. He was a member since 1955 of the Accademia dei Lincei and since 1964 of the Accademia dei Quaranta (Academy of the Forty). His prizes, medals and honorary degrees are innumerable.

On this occasion, Italian chemistry remembers him with honour and affection.

Natta's Work until 1949

Rolando Rigamonti
Istituto di Chimica industriale del Politecnico, Torino

In the brief time allotted in this commemoration, it is no easy task to summarize the scientific activity of Prof. Natta, since more than 500 papers in scientific journals bear his name, alone or at the head of a list of his collaborators. Therefore, I will limit myself to his work until 1949, the year in which he left the Technical University (Politecnico) of Milan to assume the chair at the Politecnico of Turin. For the sake of completeness, I will also briefly mention some of his work in subsequent years, representing the continuation of research begun in the above period. Note also that this date corresponds more or less to the beginning of the long research activity in the field of polymers which brought Natta the most coveted prize in science. My friend and colleague from Milan, Prof. Pino, will consider this period in the next address.

Very few know that Prof. Natta began his scientific career in the field of preparative organic chemistry, studying the formation of mercaptans and alkyl sulfides by reaction of alcohols with aluminum sulfide and then extending this technique to the preparation of the analogous selenium and tellurium compounds and of arsines, working with magnesium arsenide for the latter (Table 1). It is even less well known that, after graduation, he used this technique to synthesize various homologues of mustard gas during his military service at the Military Chemical Centre laboratories in Rome and that he tested these compounds on himself to prove their blistering properties. This gave him quite a reputation for heroism with his superiors and allowed him to be sent as a simple soldier on his own to Milan for several months to continue his research at the General Chemistry Laboratory of the Politecnico, which was better equipped than the laboratories in Rome. In itself this is insignificant compared to his great body of later work; however, it reveals Natta's passion for research even then.

TABLE 1 - PREPARATION OF ORGANIC SULFIDES, SELENIDES, TELLURIDES AND OF ARSINES

$Al_2S_3 + 3CH_3OH \rightarrow Al_2O_3 + 3CH_3SH$
$Al_2S_3 + 6CH_3OH \rightarrow 2Al(OH)_3 + 3(CH_3)_2S$
$Al_2Se_3 + 3CH_3OH \rightarrow Al_2O_3 + 3CH_3SeH$
$Al_2Se_3 + 3(CH_3)_2O \rightarrow Al_2O_3 + 3(CH_3)_2Se$
$Al_2Te_3 + 6CH_3OH \rightarrow 2Al(OH)_3 + 3(CH_3)_2Te$
$2AlAs + 3CH_3OH \rightarrow Al_2O_3 + (CH_3)_2AsH + CH_3AsH_2$
$Mg_3As_2 + 3CH_3OH \rightarrow 3MgO + (CH_3)_2AsH + CH_3AsH_2$
$(CH_3)_2AsH + CH_3AsH_2 \rightarrow (CH_3)_3As + AsH_3$

Following this early isolated episode, Natta began work in the field of x-ray structure determination of crystalline substances — a new or almost new area and so a very fruitful one. He devoted himself enthusiastically and intensely to this work, adding 56 publications in seven years to 16 publications in other fields for a total of 72 with which he won the General and Inorganic Chemistry Chair at the University of Pavia. These studies formed a solid and deep preparation for his later work, which led to the Nobel prize, as he himself noted on that occasion.

Using this technique, Natta studied the structure of the oxides of cobalt, lead, tin; of the hydroxides of cadmium, nickel, iron, strontium, cobalt; of molybdenum sulfide and chromium chloride; of the arsenides of aluminum, magnesium, zinc; of white phosphorus; of the cyanides of silver, sodium, potassium, ruthenium and cesium; of perowskite (calcium metatitanate), and of several antimony minerals (Table 2). He also studied substances which are liquids or gases at ordinary temperatures using a particular technique involving solidifying them on a glass capillary connected to the bottom of a Dewar flask filled with liquefied air. In this way, he obtained on the capillary the form suitable for study using the so-called « powder method ». It is interesting to note that by working in this way he was already using the freezing method in which strong and very rapid

TABLE 2 - SOLID SUBSTANCES STUDIED USING X-RAY DIFFRACTOMETRY

PbO, SnO, CoO, Co_3O_4, Co_2O_3
$Cd(OH)_2$, $Fe(OH)_2$, $Ni(OH)_2$, $Co(OH)_2$
$Sr(OH)_2 \cdot 8H_2O$, $SrO_2 \cdot 8H_2O$
MoS_2
$CrCl_3$
$AlAs$, Mg_3As_2, Zn_3As_2
white P
$AgCN$, $NaCN$, KCN, $RbCN$, $CsCN$
$CaTiO_3$
$mCaO \cdot Sb_2O_5$, $mCaO \cdot Sb_2O_5 \cdot nH_2O$
$Ca_2Sb_2O_7$, $Pb_2Sb_2O_7$, $(Sb_2O)Sb_2O_7$ $(= 2Sb_2O_4)$

cooling gives a mass of very fine crystals and prevents clumping. With this technique he studied (Table 3) benzene, thiophene, hydrogen sulfide, hydrogen selenide, krypton, xenon, phosphine, arsine, silicon tetrafluoride, hydrogen peroxide, hydrogen chloride, hydrogen bromide and hydrogen iodide. From the last three compounds, with the sharp observation that the diameter of the hydrogen ion H^+ (that is, the proton) is absolutely negligible compared to that of the chloride, bromide and iodide anions (Cl^-, Br^-, I^-), he was able to determine the ionic radii of these anions from the size of the unit cell. From these, using literature data for the dimensions of the unit cells of other compounds, he was able to determine the ionic radius of numerous cations and so correct the values found by Goldschmidt using other hypotheses. He also observed that the radii of the above three anions were equal to those of the argon, krypton and xenon atoms, with the same number of extranuclear electrons as the former.

TABLE 3 - GASES AND LIQUIDS STUDIED IN THE SOLID STATE USING X-RAY DIFFRACTOMETRY

C_6H_6, C_4H_4S
H_2S, H_2Se
Kr, Xe
PH_3, AsH_3, SiF_4
H_2O_2
HCl, HBr, HI

DIMENSIONAL ANALOGY BETWEEN HALIDE IONS AND RARE GASES

$Cl^- = 1{,}92$ Å	$Ar = 1{,}92$ Å
$Br^- = 2{,}04$ Å	$Kr = 2{,}04$ Å
$I^- = 2{,}21$ Å	$Xe = 2{,}18$ Å

TABLE 4 - COMPLEX COMPOUNDS AND SPINELS STUDIED USING X-RAY DIFFRACTOMETRY

$[Co(NH_3)_5H_2O]I_3$, $[Co(NH_3)_6]I_3$
$CsHgCl_3$, $CsHgBr_3$, $CsHgI_3$
$CsCdBr_3$, $CsCdI_3$
Cs_2PtCl_6, Rb_2PtCl_6, Cs_2TeCl_6
$CoO \cdot Al_2O_3$, $CoO \cdot Cr_2O_3$, $CoO \cdot Fe_2O_3$
$CoO \cdot Co_2O_3$, $ZnO \cdot Co_2O_3$
$2CoO \cdot SnO_2$, $2MgO \cdot SnO_2$
$CoS \cdot Co_2S_3$, $ZnS \cdot Cr_2S_3$

Natta performed a series of studies of complexes and spinels (Table 4): the cesium trihalogenomercurates and trihalogenocadmiates, the cesium ad rubidium chloroplatinates, the cesium chlorotellurite. In these studies, he demonstrated the existence of isomorphism. Spinels are formed by the union of a bivalent metal oxide with a trivalent metal oxide; Natta studied those containing cobaltous oxide and observed that spinels with cobaltic oxide are also possible. However, perhaps his most interesting contribution in this field was the recognition that certain compounds made from two molecules of bivalent metal oxide and one of tetravalent metal oxide have the same structure as spinels. These include the stannates of cobalt and magnesium, as well as some sulfur salts like zinc sulfochromite, that is compounds whose molecular formula is analogous to that of the spinels.

However, the spirit of the scientist was not directed only toward primarily theoretical or speculative questions like simple studies of crystal structures. He also sought ways to apply scientific methods and results to problems of more general and at times also practical interest.

TABLE 5 - ALLOYS AND ISOMORFISM CASES FOUND BY X-RAY DIFFRACTOMETRY

Cd-Ag, Cd-Mg
(Pb,Sn)O, (Ca,Cd)O, (Co,Mn)O, (Ca,Co)O
(Ca,Ni)O, (Ca,Mg)O
(Co,Ni) $(OH)_2$, (Ca,Cd) $(OH)_2$, (Co,Mg) $(OH)_2$
(Ni,Mg) $(OH)_2$, (Mn,Cd) $(OH)_2$, (Mg,Zn) $(OH)_2$
(Ni,Zn) $(OH)_2$, (Co,Zn) $(OH)_2$
Na(Cl,CN), Na(Br,CN), Ag(CN,Br)
$Cs_2(Pt,Te)Cl_6$, $(Cs,Rb)_2PtCl_6$
$(CaPb)_2Sb_2O_7$, $(Ca,Pb,Sb_2O)_2Sb_2O_7$

For example (Table 5), he studied cadmium-silver and cadmium-magnesium alloys using x-ray diffractometry, clarifying certain points of their state diagrams (a method later applied widely to this type of research). With the same procedure, he recognized that Rinman green and Thénard blue are spinels and that cobalt pink is a solid solution of the oxides of cobalt and magnesium. Finally, he observed the existence of phenomena of isomorphism in various pairs of oxides and hydroxides, defining the ratios between the various metal ions within which this isomorphism occurs. I will discuss below the most interesting application of x-ray diffraction: the study of catalysts.

Related to the study of crystal structures with x-rays is the use of fast electron diffraction for the same purpose: Natta turned to this technique after learning it at Freiburg with Seemann. Perhaps the best way to describe the research of that period is that Natta « amused » himself by examining very many substances with this method. This word comes to mind spontaneously when I remember the enthusiasm and almost child-like spirit of curiosity with which he applied this new research method (Fig. 1) to alkaline, ammonium and silver halides; to lead, manganese, zinc sulfides; to metals like silver, gold, platinum, palladium, iridium and ruthenium

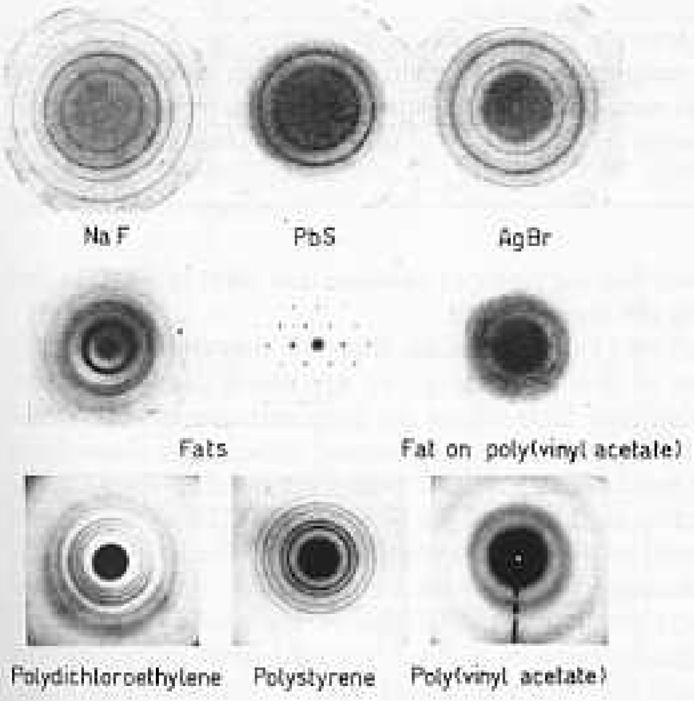

Fig. 1 - Electron-beam photograms.

deposited on thin films of collodion by reducing their salt solutions; and to many other substances which he never even published. This enthusiasm and spirit of curiosity led him to discover two very interesting facts: one about alloys, the other about polymers.

Polymers were studied using thin films obtained by evaporating a few drops of a solution of them on a water surface. The work was extended to numerous products (cellulose and its esters, vinyl derivatives, polystyrene, rubber) and led to the determination of interatomic distances typical of the polymeric chain. Natta undertook this study with the idea that, given the thinness of the films examined (10^{-5} mm) and the length of the polymeric chains, these should lie in the plane of the films themselves and so facilitate the determination of the interatomic distances. But this research was blocked from the beginning by a curious phenomenon: during the manipulations, the thin films became covered with a monomolecular layer of fats, which gave its own interference pattern to hide that of the polymer. Thus all the photograms were the same and could not be interpreted on the basis of the chemical formula of the polymer itself. The discovery of this phenomenon had great repercussions among the other European workers running

TABLE 6 - EXAMINATION BY ELECTRON RAYS OF Pt-Ag ALLOYS

	LATTICE CONSTANT
Pt	3,913 Å
Ag	4,078 Å
Pt prec. on Ag	4,065 Å
The same, overturned	4,078 Å
The same, heated to 700 °C	4,003 Å

analogous experiments, and led Natta to examine thin films of paraffin and fatty acid esters using the same method.

As regards the alloys (Table 6), Natta observed that depositing noble metals on thin sheets of less noble metal, by depositing the former from solutions of their salts, gave films not of the pure noble metal, but rather of alloys of it with the less noble metal. However, these alloys showed one particularity: if the less noble metal has a unit cell smaller than that of the metal precipitated on it, the cell of the alloy formed follows the Vegard rule, expanding proportionally to the quantity of noble metal present. If on the other hand the cell of the less noble metal is larger, the alloy formed on precipitation keeps the dimensions of that of the precipitating metal, even up to a noble metal content of 50%. Upon cold aging or heating, the cells contract, to reach the values predicted by the proportionality rules. It is also interesting that these films, even though very thin, show a different composition on each face, as shown by inverting the position of the test film in the electron rays: the side facing the precipitating metal is richer in it. This sheds light on the topochemical mechanism of their formation.

In addition to all these studies of a more speculative nature, Natta pursued an intense and highly successful activity in other more applied areas: the foremost include the synthesis of methanol (Fig. 2), effected with a particular catalyst made of smithsonite calcined at 400-450 °C, and that of higher alcohols from carbon monoxide and hydrogen. This last required a long analysis using fractional distillation, which would have been considerably accelerated by modern gas chromatography techniques.

However, in these applied studies as well Natta developed the theoretical part also. While in the synthesis of higher alcohols he studied the reaction mechanism by hydrogenating salts of carboxylic acids; in that of methanol he turned his attention to the catalyst (Table 7), studying it by x-ray diffraction as well as adsorption of hydrogen, carbon monoxide and methanol vapours. In this way, he was able to show that aging of the catalyst was due to enlargement of its crystals and that high melting promoters like alumina, or chromium, iron or nickel oxide, have a negative effect on the sintering, especially when they are partially combined with or form solid solutions with zinc oxide. In the latter case, he was also able

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$n\ CO + (n+1)\ H_2 \longrightarrow C_nH_{2n+1}OH$$

$$n\ CH_3OH \longrightarrow C_nH_{2n+1}OH + (n-1)\ H_2O$$

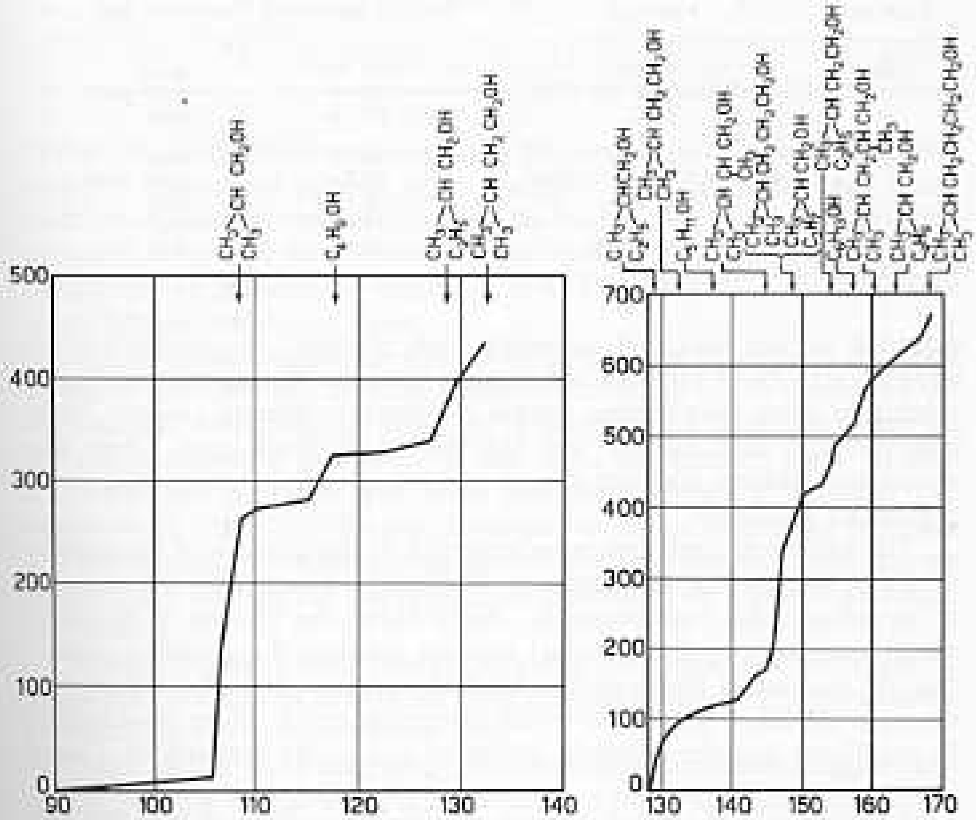

Fig. 2 - Synthesis of alcohols from carbon monoxide and hydrogen.

to show that the small quantities of nickel or iron oxides in solid solution with the zinc oxide are not reduced to the metal, so preventing the onset of side reactions in the synthesis of methanol.

Studying the structure of these catalysts led Natta to a shrewd observation: many catalysts are known to be prepared from a mother substance to be reduced with hydrogen or calcined so as to lose some of its components (water, carbon dioxide, oxygen, *etc.*) without varying its own apparent volume. In this way, a microcrystalline structure is obtained with very

TABLE 7 - STUDIES ON CATALYSTS

ZnO OBTAINED FROM	SIZE OF CRYSTALS AFTER HEATING AT 400 °C 2 h	 6 h	 15 h
Smithsonite	90 Å	110 Å	130 Å
Basic carbonate	250 »	300 »	350 »
The same with Cr_2O_3	130 »	150 »	170 »

CATALYST	SOURCE	VOLUME REDUCTION	ACTIVITY AND LIFE
Fe	Fe_3O_4	52 %	good
	97% Fe_3O_4 + 3% Cr_2O_3	50 »	very good
	Fe_2O_3	67 »	bad
ZnO	$ZnCO_3$	49,2 »	good
	95% $ZnCO_3$ + 5% Cr_2O_3	47,9 »	very good
	$Zn(OH)_2$	56,4 »	bad
	Zn oxalate	75,9 »	bad
	Zn formiate	78,2 »	bad

extended surface area and extremely high porosity. By comparing the catalytic activity of the obtained catalyst with the variation in molecular volume on going from various mother substance to finished catalyst, Natta observed that good activity was only shown in those cases where this variation in volume does not exceed 50-55% of the molecular volume of the mother substance.

The studies on methanol were extended to the kinetics of the process (Table 8), overcoming the experimental difficulties arising from the necessity of operating under high pressures. Natta found the kinetics to be determined essentially by the chemical reaction between the adsorbed phases, that the reaction is hindered by adsorbed methanol, and that the catalyst uses only the initial part of the whole adsorption curve. From these results, he concluded that the synthesis should be run in the presence of a large excess of hydrogen.

A second area of applied research was the preparation of formaldehyde

TABLE 8 - KINETICS OF SYNTHESIS OF METHANOL

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$r = \frac{f_{CO}p_{CO}f^2_{H_2}p^2_{H_2} - \dfrac{f_{CH_3OH}\,p_{CH_3OH}}{K}}{(A + Bf_{CO}p_{CO} + Cf_{H_2}p_{H_2} + Df_{CH_3OH}\,p_{CH_3OH})^3}$$

r = reaction rate
f = fugacity coefficient
p = partial pressure
K = equilibrium constant
A, B, C, D = temperature variable constants

TABLE 9 - SYNTHESIS OF FORMALDEHYDE AND COAL GASIFICATION

SYNTHESIS OF FORMALDEHYDE

$CH_3OH \rightleftharpoons CH_2O + H_2$
$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O$

COAL GASIFICATION

Water-gas (Blue gas)

$C + H_2O \rightarrow CO + H_2 - 28{,}7$ Kcal
$C + \frac{1}{2}O_2 \rightarrow CO + 29{,}2$ Kcal

Natta

$2C + 2H_2O + \frac{1}{2}O_2 \rightarrow CO + 2H_2 + CO_2 + 10{,}5$ Kcal

(Table 9), studied earlier through the dehydrogenation of methanol over catalysts made up of pure or silvered copper. One of the findings, based on thermodynamic considerations, was the favourable effect of the presence of carbon dioxide in the mixture sent over the catalyst. Later Natta studied the process by oxidation of methanol as well, developing a catalyst based on molybdenum and iron oxides.

The synthesis of methanol required the preparation of mixtures of carbon monoxide and hydrogen of compositions which could not be obtained from the classical production of water-gas. Pursuing a brilliant idea based on the chemico-physical principles of this latter production, Natta realized the gasification of carbon with water vapour and oxygen at relatively low temperatures (800 °C) to prepare a mixture of carbon monoxide, hydrogen and carbon dioxide. When carbon dioxide was then removed using known methods, the mixture had the correct composition for the above-mentioned synthesis.

Another reaction Natta studied was the dimerization of *iso*butene to *iso*octane: he achieved good yields using alumina as catalyst, in the presence of small amounts of hydrochloric acid.

Natta carried out a long series of experiments on hydrogenations (Fig. 3), in particular of glucose and other carbohydrates and furfurol. In this period, this type of reaction and catalyst was of great interest to many researchers.

From the hydrogenation of glucose Natta obtained sorbitol, glycerol, glycols and alcohols in various yields depending on the reaction conditions and determined the conditions required to obtain the highest possible yield of glycerol. He also observed that with some catalysts the reaction was preceded by the isomerization of glucose to other hexoses, and gave a justification for the composition of the reaction products based on their free energy of formation.

Furfurol also gave a series of substances: furfurylic and tetrahydrofurfurylic alcohols, amylenic glycols, amyl alcohols and methylfuran, once again in various proportions depending on the reaction conditions.

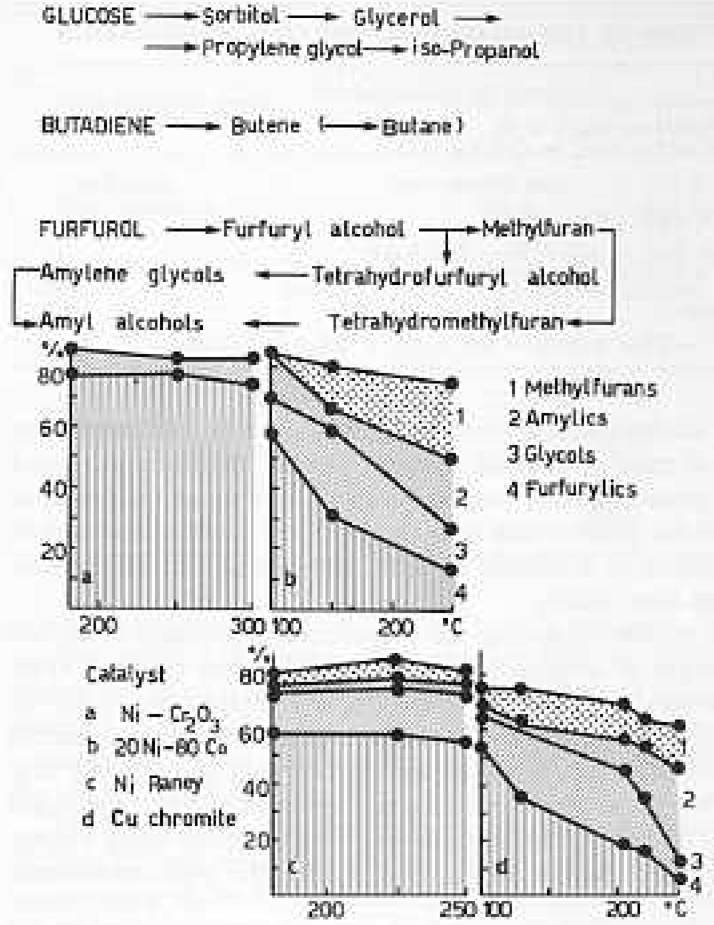

Fig. 3 - Hydrogenations.

These studies with furfurol led him to investigate the preparation of this compound according to the classical method of hydrolyzing agricultural wastes. However, he effected this hydrolysis with an ingenious process (Fig. 4) applying the principles of physical chemistry: the reaction was run in a column in which the material to be hydrolyzed, impregnated with hydrochloric acid, was made to descend against a counter-current of steam. Because of the liquid-vapour equilibria between hydrochloric acid and water, the former concentrates in one area of the column and there considerably speed up the hydrolysis reaction, while the steam immediately removes the furfurol formed, preventing resin formation and giving higher yields than other processes. By recycling the condensate after the furfurol

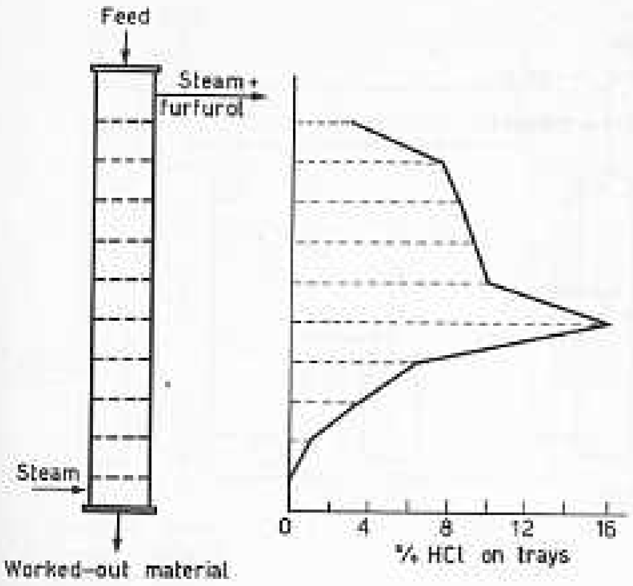

Fig. 4 - Furfurol preparation.

was distilled, Natta concentrated the acetic acid formed as by-product to allow its recovery.

Natta also studied the ammonolysis of the furfurol hydrogenation products, preparing heterocyclic bases of the pyrrole and pyridine group.

Among the hydrogenations Natta studied, the selective preparation of butene from butadiene should be remembered. He began from the principle of using a catalyst with active sites very far apart, to allow the butene molecule to be desorbed as soon as it formed, before it could be further hydrogenated to butane.

An important chapter in the history of Natta's work is the preparation of butadiene (Fig. 5), the starting material for synthetic rubber. His earlier studies of catalysts allowed him to improve, by the addition of chromium oxide as promoter, both the alumina-based catalyst in the early process starting from mixtures of alcohol and acetaldehyde as well as the subsequent one based on magnesium oxide and silica in the process from alcohol alone. The x-ray diffractometric study of the structure of the latter catalyst showed that during its preparation and use small quantities of magnesium silicate formed, lowering the yield of the reaction. Thus he could prepare catalysts capable of giving higher yields of butadiene from alcohol.

The above research led to the necessity of studying a process for separating butadiene from butenes, formed in considerable quantities as by-products. The solution to this problem came to Natta while he was

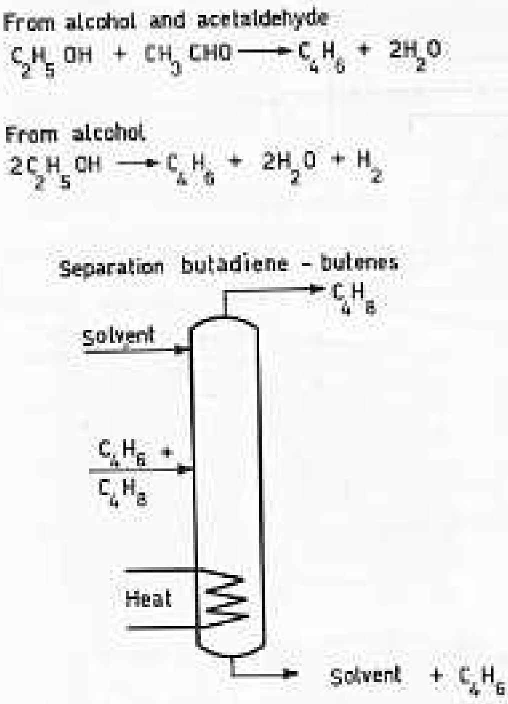

Fig. 5 - Butadiene preparation.

speaking to an assistant, walking as was his habit through a long corridor of the Institute of Industrial Chemistry in the old location of the Politecnico of Turin, later destroyed during the war. Since the use of a selective solvent had proved to be insufficient, Natta thought of using in the absorption column a flow of the most easily absorbed component from the bottom to the top, partially degassing the liquid at the base of the column by heating, obtaining in this way an additional fractionation of the gaseous mixture into its components and so better separation of the butadiene from the butene. After the war, this process, discovered also by the Americans that named it Distex, was studied by Natta from the point of view of designing the extraction column and was further perfected technologically (Fig. 6). The absorption was performed under pressure, and the desorption partially through expansion and partially through stripping with the less soluble gas, followed by recycling of the products. The study was later extended to more complex mixtures, even those containing non-absorbable gases.

Three other researches must be recalled. In the first, the fruit of an expert study, he showed the danger of an excess of water and fine sand

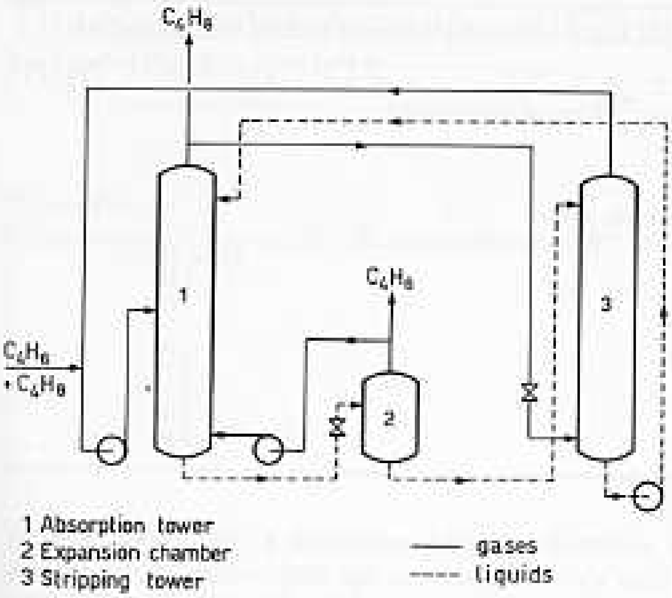

Fig. 6 - Butadiene separation.

in the composition of concrete: it leads to more porous structures in which hydrolysis and carbonation during the hardening period occur too rapidly and so prevent the increase of resistance with aging.

The second concerns the process of a chain of successive reactions (Table 10). Natta took as the test reaction one in which a compound B is

TABLE 10 - KINETICS OF SUCCESSIVE REACTIONS

$$A + B \rightarrow AB$$
$$AB + B \rightarrow AB_2$$
$$AB_n + B \rightarrow AB_{n+1}$$

$$C_{AB_n} = (-1)^n a_0 K_1 K_2 \dots K_n \left[\frac{e^{-K_1 \tau}}{(K_1 - K_2)(K_1 - K_3) \dots (K_1 - K_{n+1})} + \frac{e^{-K_2 \tau}}{(K_2 - K_1)(K_2 - K_3) \dots (K_2 - K_{n+1})} + \dots + \frac{e^{-K_{n+1} \tau}}{(K_{n+1} - K_1)(K_{n+1} - K_2) \dots (K_{n+1} - K_n)} \right]$$

$\tau = \int C_B dt$
C_B, C_{AB_n} = concentration of B and AB_n
a_0 = starting concentration of A
$K_1, K_2 \dots K_{n+1}$ = velocity constants
t = time

TABLE 11 - RATE OF ULTRA-SOUNDS PROPAGATION IN POLYMERS

$$\sqrt[3]{u}\,\frac{M}{\rho} = R = \Sigma m_i R_i \qquad \text{(Rama Rao's formula)}$$

u = ultra-sounds velocity
M = molecular weight
ρ = density
m_i = number of atoms of the i-th species
R_i = constant for the atoms of the i-th species

	FORM FACTOR
Paraffine	1.00
Polyethylene	1.00
Nylon 6,6	1.00
Poly-*iso*butylene	0.80
Polystyrene	0.82
Butyl rubber	0.65
Buna	0.82
Hevea rubber	0.90

added repeatedly to a compound A, and conducted a theoretical study of the kinetics. He was then able to determine the distribution of the various compounds in the final product as a function of the kinetic constants of the various stages of the process. The theoretical relationships found were verified experimentally in the addition of ethylene oxide to methanol. Not only was their validity confirmed, but it was also observed that the rates of the reactions after the first are higher due to the greater energy of the just formed molecule, which holds part of the thermal energy developed in the reaction. The theoretical study was also extended to consider recycling of the intermediate compounds.

In the third (Table 11), while measuring the rate of ultrasonic propagation in polymer solutions and comparing it with the theoretical one calculated with Rama Rao's formula as the sum of the contributions of the individual atoms or interatomic bonds, Natta found that the ratio between the experimental and theoretical result (called by him the « form factor ») was approximately 1 for linear chains but fell to 0.7-0.8 in the presence of branching.

With this work in 1949, Natta returned to the study of polymers begun earlier with the electron ray experiments mentioned above and started toward the large body of work which prof. Pino will now discuss. I will close here by asking your pardon if I have occasionally not mentioned the friends who collaborated with Natta in the work I discussed. They are very many, and I did not wish to mention all of them including myself. However, I am sure they will agree that this silence about our names is a real homage and thanks to the memory of our Teacher, who guided and aided us in shaping our own careers.

The Scientific Activity of Giulio Natta from 1949 to 1973

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This most significant period of the scientific activity of Prof. Natta started with his first contacts with the U.S.A. chemical industry, where a very rapid development of petrochemistry was producing substantial and unexpected changes.

The profound emotions that Professor Natta felt during his first trip to the U.S.A. are well described in a paper published in *La Chimica e l'Industria* (¹).

Since Natta had received his education in chemistry and chemical engineering in the twenties, *i.e.* when industrial organic chemistry was mainly based on coal and fermentation products, he was fascinated by the new possibilities offered to the chemical industry by the practically unlimited availability of unsaturated hydrocarbons like ethylene, propylene, butenes and butadiene easily obtainable from petroleum and he immediately recognized the industrial potential of the chemistry of aliphatic compounds.

P. Giustiniani — at that time General Manager of Terni SpA., and later Managing Director of Montecatini SpA — with whom Natta visited the U.S.A. for the first time, shared his enthusiasm. Thus, by the end of the forties, the Industrial Chemistry Institute of the Politecnico of Milan and Montecatini Company (later Montedison) established that fruitful collaboration which was to produce extremely important industrial achievements, among which the commercial production of isotactic polypropylene.

On his trip to the U.S.A., Professor Natta was impressed by the number of scientists who worked at the research laboratories and by the way in which research was organized.

In 1948 he wrote: « It often happens that the number of chemists working in those huge laboratories is 400 to 600. A few years ago it amazed us that the number of chemists working at the I.G. laboratory of Reppe was about 100, and that the research on nylon was carried out by 30 scientists. Now, compared with the present number of U.S.A. researchers, these figures seem insignificant » (¹).

In the same article he also writes: « In my life as a modest researcher there were ten at the most chemists under my direction, and to follow them all seemed to be a very hard work to me. I wonder how a single man can direct 500 to 600 researchers ».

Being highly interested in research organization, he often urged me to describe how research was carried out at the Organic Chemistry Laboratory of the Polytechnic Institute of Zürich, where I had gone in 1950 to specialize in organic chemistry under the direction of Professor Ružička, a scientist whom Natta admired for his achievements in the field of organic syntheses.

Thinking that the academic world — scarcely ready for substantial innovations — could hardly have provided young graduates with the up-to-date preparation required for the large-scale introduction of petrochemistry in Italy, and, at the same time, wishing to avail himself of a research team capable of competing with the U.S.A. teams, Natta proposed, and Mr. Giustiniani agreed, that 10-20 graduates in chemistry and industrial chemistry should be engaged every year to be trained in industrial aliphatic organic chemistry at the Industrial Chemistry Institute of the Politecnico, before they would start to work in the Montecatini laboratories.

After the didactic experience made in the more developed countries in Europe and in the U.S., the trainee would have to carry out a research project independently and attend courses on industrial organic chemistry, as well as on advanced topics of organic chemistry, physical chemistry, and instrumental analysis.

It is to Mr. Giustiniani's credit that he acceded to Natta's request without faltering. Actually, Natta's plans would never have been realized without the support of the industry.

Thanks to the careful selection of the trainees and to the high quality of the teachers (in addition to Prof. Natta himself, I wish to mention Prof. A. Quilico, Prof. G.B. Bonino, the late Prof. R. Piontelli, as well as notable industrial managers, such as G. Greco and the late F. Tredici), and to the climate in which the trainees were able to develop their scientific work, the chemists educated at the Milan Politecnico in the early fifties still constitute the supporting structure of the major laboratories of the Italian chemical industry. Some of their names and present positions are mentioned in parentheses in Fig. 1 and 6, after the description of the research works they collaborated on.

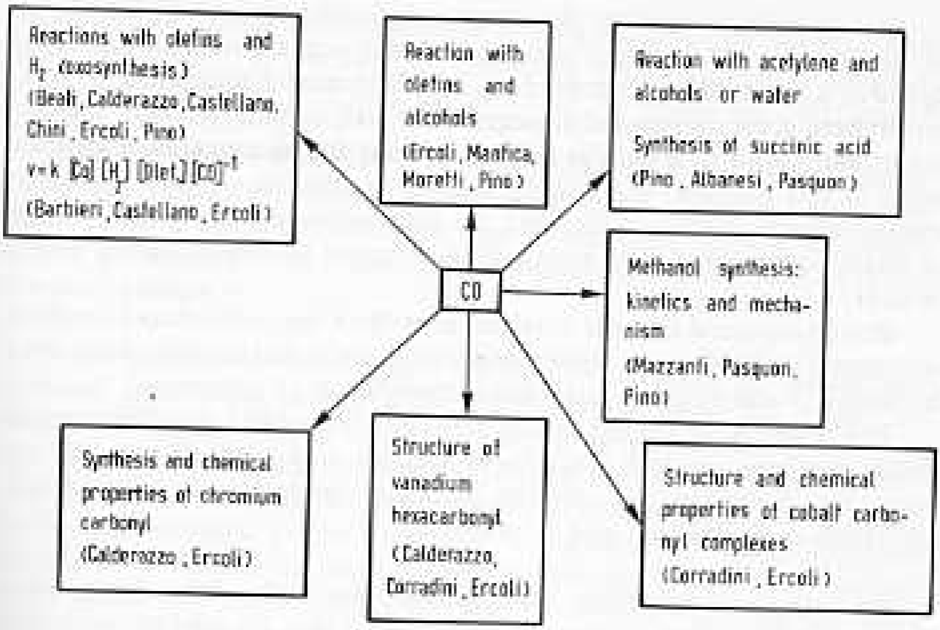


Fig. 1 - **Summary of Natta's research in the field of carbon monoxide chemistry.**

I have dwelt on this project because, in my opinion, it largely contributed to the extraordinary results that Natta achieved in the period from 1953 to 1963.

These very results were obtained also because the Institute was provided not only with modern equipments for x-ray and electron diffraction studies (the traditional field of Natta's research activity), but also with adequate equipment for IR and UV spectrography, which at the time were considered pioneering techniques.

Various research teams and services were established within the Institute, even if informally.

An important step in the life of the Institute was the creation of the Plastics Testing Laboratory, set up by Natta with the collaboration of Prof. D. Pagani, and with the financial support of Milanese firms (²).

The space available for the Institute was considerably increased with the construction of a new building and the acquisition of the building formerly housing the « Stazione Sperimentale per i Combustibili ».

The scientific activity developed by Natta from 1948 onwards followed two main trends of high theoretical and practical interest, which are still valid even if 30 years have elapsed, *i.e.* the chemistry of carbon monoxide and the synthesis and properties of macromolecular compounds.

Natta's early research on the chemistry of carbon monoxide dates back to the twenties. In the early forties he became acquainted with the « oxo-synthesis », a reaction discovered by Dr. Röhlen of Ruhrchemie.

Realizing its commercial importance, Natta investigated this reaction after 1943 [with E. Beati (3)] with the twofold purpose of extending the scope of this reaction — originally applied to ethylene only — to various organic substrates, and of studying the mechanism of the same as well as of analogous carbonylation reactions investigated by Reppe during World War II.

Being convinced that the catalytic activity of the cobalt-based catalysts discovered by Röhlen was higher than that of the nickel catalysts discovered by Reppe, Natta reinvestigated the carbonylation of acetylene.

The research he carried out in this field from 1947 to 1954 resulted finally in a new one step synthesis of succinic acid from acetylene (4). A pilot plant based on this research was later implemented with the collaboration of I. Pasquon and G. Albanesi.

As early as 1944 Natta realized that the olefins hydroformylation rate was independent of the total pressure of the 1:1 carbon monoxide and hydrogen gaseous mixture.

However, it was only after ten years that Natta succeeded in demonstrating that the said independence was connected with a reaction of first order with respect to hydrogen and of order (— 1) with respect to carbon monoxide [with the late R. Ercoli, full Professor of Industrial Chemistry, Palermo University, and S. Castellano, Carnegie Mellon Institute, Pittsburgh, Pa. U.S.A. (5)].

Natta's interest in the chemistry of carbon monoxide remained alive even in subsequent years. As a matter of fact, he investigated the preparation and reactivity of chromium hexacarbonyl and its arenic derivatives, and synthesized vanadium hexacarbonyl, thus obtaining the first carbonyl of a metal of the 5th group of the periodic table and the first paramagnetic metal carbonyl [with R. Ercoli and F. Calderazzo, now full Professor of General Chemistry, Pisa University (6,7)].

The above very important results obtained by Natta in the field of carbon monoxide chemistry correspond only to a minor part of his scientific activity. Indeed Natta obtained his most important achievements in the field of high polymers. His first research in this field started in 1932 during his stay in Freiburg im Breisgau where he met Professor H. Staudinger (8). Later, he contributed to the first production of synthetic rubber in Italy. After World War, II polymers remained to be one of his main research interests, even though after the end of the initial activity in the field of synthetic rubber no experimental research was in progress in his Institute till the end of the forties.

In the early fifties Natta started to investigate some physical properties of the polymers, e.g. the rate of ultra-sonic waves in melted polymers [with M. Baccaredda (8)] and the structure of crystalline polyethylene [with P. Corradini (9)].

However, he never ceased to be interested in the synthesis of macromolecular compounds. His talk often turned to the high-molecular-weight linear paraffins of which, during a trip to Germany, he had received a sample produced by the Fischer-Tropsch reaction in the presence of ruthenium catalysts.

Natta resumed his experimental activity in the field of macromolecular syntheses after he had attended the lecture that Professor K. Ziegler delivered in Frankfurt (1952) about the ethylene polymerization in the presence of alkyl aluminium compounds [Ziegler's « Aufbaureaktion » (10)].

At the end of the above lecture, which I also attended, Natta asked for my opinion about Ziegler's research: I was most favourably impressed by Ziegler's research on such a difficult subject, but I felt doubtful about the commercial prospects for Ziegler's results. On this last point Natta's opinion was opposite to mine: being well acquainted, thanks to his previous work on synthetic rubber, with radical polymerizations, he at once realized — probably even before Ziegler himself — that the German scientist had found a completely new principle as far as the synthesis of polymer chains was concerned. In fact the polymerization of ethylene carried out by Ziegler did not occur by monomer addition to a free radical or to a free carbonium ion (Fig. 2), located at the end of a growing chain, but by monomer insertion between a metal atom and the growing chain bound to it.

In Natta's opinion this offered greater possibilities for controlling the polymer chain structure during the synthesis.

Excited by this idea, Natta suggested to the Montecatini Company to enter into a collaboration agreement with K. Ziegler, and charged me to establish at his Institute a research team entrusted with the task of repeating Ziegler's experiments, of separating ethylene polymers with as high as possible a molecular weight, and of investigating the kinetics of polymerization.

It was also envisaged to send a few members of the new team to Ziegler's Institute.

Thanks to the collaboration of a number of chemists of exceptional capacity (it is enough to mention the late Prof. P. Chini, M. Farina, now full Professor at the Milan University, R. Magri, L. Luciani, E. Giachetti), Ziegler's tests were repeated, ethylene polymers were fractionated by solvent extraction, and the study of the « Aufbaureaktion » kinetics was started.

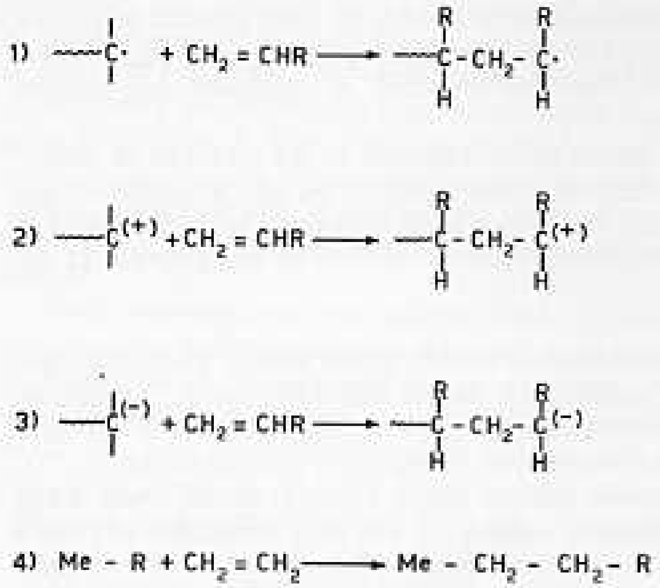


Fig. 2 - Chain growth by monomer addition to an activated chain end (1, 2, 3) or by monomer insertion into a metal-to-carbon bond (4).

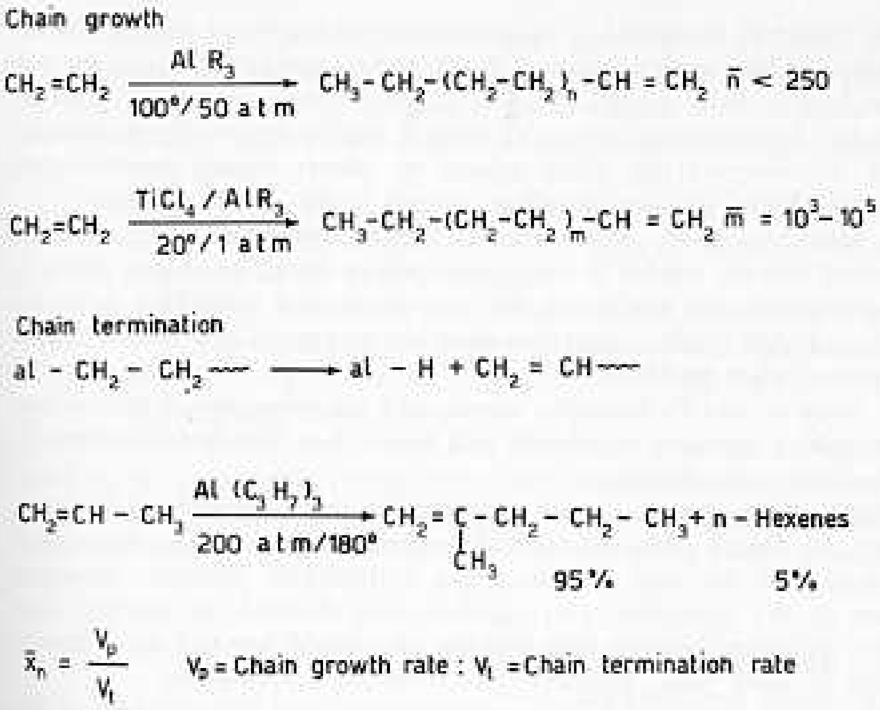
Under the agreement between Montecatini and K. Ziegler, at the beginning of 1954 Prof. Natta was given the text of Ziegler's patent on the preparation of ethylene high polymers in the presence of catalysts obtained by causing $TiCl_4$ and alkyl aluminium compounds to react. Thanks to the extensive knowledge of the aluminium alkyl chemistry already existing at the Institute, the research in the new area could immediately be started.

At this point, Natta was able to give full proof of his extremely great creative talent.

After learning of Ziegler's results, and using his great experience in the field of heterogeneous catalysis and radical polymerization, he assumed as a working hypothesis that the formation of ethylene high polymers was due to a higher rate of growth of the polymer chains, caused by the presence of a heterogeneous catalyst activating the ethylene molecule before it is inserted in the aluminium-carbon bond (Fig. 3).

Thinking that Ziegler could rapidly progress in his research on polyethylene Natta decided to prepare small quantities of the new polyethylene for the purpose of studying its structure, but at the same time, he decided to start the investigation of the polymerization of propylene.

As a matter of fact, as he knew that by reacting propylene in the presence of aluminium alkyls, dimers or at most trimers of propylene could be



Chain growth

$$CH_2{=}CH_2 \xrightarrow[100°/50\ atm]{Al\ R_3} CH_3{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH{=}CH_2 \quad \bar{n} < 250$$

$$CH_2{=}CH_2 \xrightarrow[20°/1\ atm]{TiCl_4\ /\ AlR_3} CH_3{-}CH_2{-}(CH_2{-}CH_2)_m{-}CH{=}CH_2 \quad \bar{m} = 10^3{-}10^5$$

Chain termination

$$al{-}CH_2{-}CH_2{\sim\sim} \longrightarrow al{-}H + CH_2{=}CH{\sim\sim}$$

$$CH_2{=}CH{-}CH_3 \xrightarrow[200\ atm/180°]{Al\ (C_3H_7)_3} \underset{95\%}{CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2{-}CH_2{-}CH_3} + \underset{5\%}{n{-}Hexenes}$$

$$\bar{x}_n = \frac{V_p}{V_t} \qquad V_p = \text{Chain growth rate} : V_t = \text{Chain termination rate}$$

Fig. 3 - Chain growth and chain termination in ethylene polymerization and propylene dimerization with organometallic catalysts.

obtained, he hoped that the new heterogeneous catalysts found by Ziegler might give, as in the case of ethylene, propylene high polymers, which would be suitable for application in the field of synthetic rubber with which he was so well acquainted.

Somewhat reluctantly — we were all engaged in research in other fields — we started to prepare and purify propylene to be used in the polymerization experiments.

At the beginning of March 1954, P. Chini obtained a small quantity of a yellow-brown gummy product which clearly was nonhomogeneous.

The polymerization of propylene immediately became the most important subject of our research; in particular, G. Mazzanti, who at the time was at the head of Montecatini's trainees, dealt with the problem with P. Longi and E. Giachetti.

The tests were repeated using a higher pressure; the gummy product was extracted with the solvents we had used for polyethylene fractionation, and four different fractions were obtained: the first was oily, the second was similar to an uncured rubber, the third looked like a vulcanized rubber, and finally the fourth fraction, which at times amounted to 40% of the reaction product, was a white powder whose melting point exceeded 160 °C.

All resources Natta had at his Institute were employed for the characterization of the new polymers. P. Corradini performed x-ray investigations, and a high crystallinity was found in the less soluble polymer fractions. Furthermore, after determining the polymer chain identity period, he observed that there existed no planar zig-zag conformation of the type found in linear paraffins, at least in the crystal state.

E. Mantica with M. Peraldo and L. Bicelli carried out the IR analyses and found that the methyl to methylene ratio in the polymer was about 1.

Furthermore, the spectra of the amorphous and crystalline polymers were found to be similar, except for some bands, present in the latter which disappeared upon melting.

F. Danusso and G. Moraglio investigated the behaviour of the various polypropylene fractions in solution and found that they had substantially different molecular weights.

Natta's early idea was to use propylene for the production of synthetic rubber: in March 1954 he insisted on copolymerizing propylene with butadiene with the idea of obtaining a vulcanizable product. However as soon as the crystalline polypropylene was isolated, he realized that the new polymer, being a high melting one, could be used as a plastic material in many fields, different from those for polyethylene.

By availing himself of very simple apparatus, and with the help of Mr C. Origgi, a technician of exceptional skill who directed the workshop of the Institute, in May 1954 Natta succeeded in making the first fibre from polypropylene. The mechanical characteristics of the fibre were studied at the Plastics Testing Laboratory with G. Lutzu.

At the same time, Natta and his collaborators started to discuss the structure of polypropylene and the reasons for the crystallinity of the heptane-insoluble fractions.

At first, the difference between the crystalline and noncrystalline fractions was assumed to depend on the different molecular weights. However, Natta was not fully satisfied with this explanation: as a matter of fact, the molecular weights did not undergo a regular variation with the decreasing of the fractions solubility in the organic solvents, but were considerably different in the crystalline and the non-crystalline fractions.

Natta liked repeating the saying « *Natura non facit saltus* » and urged us to look for other reasons on which the said differences might be based.

From a thorough bibliographic investigation we were able to ascertain that some crystallinity had been previously observed in a vinyl polymer, the poly(*iso*butylvinylether), obtained by C.E. Schildknecht in 1948 by cationic polymerization in heterogeneous phase. This polymer exhibited a very low crystallinity, lower than that of non-fractionated polypropylene (11).

On the basis of the x-ray diffraction spectra, whose interpretation was difficult just because of the low crystallinity of the samples, Schildknecht and collaborators had set forth the hypothesis that the polymer chains in the crystals had a planar zig-zag conformation, which was inconsistent with what P. Corradini had found for polypropylene.

Schildknecht's work focused the attention of Natta and his group on the relevance of the steric regularity in the polymer main chain to the physical properties of the vinyl polymers.

After countless discussions the hypothesis was formulated that the crystalline and non-crystalline polypropylene fractions were different because of the existence in the crystalline polymer of steric regularity in the main chains of the macromolecules.

In his first paper on the topic ([17]), Natta stated that in the crystalline fractions the asymmetric carbon atoms may have the same steric configuration at least for long chain portions, and proposed to call the said carbon atoms, and consequently the polymers containing them, « isotactic » (Fig. 4).

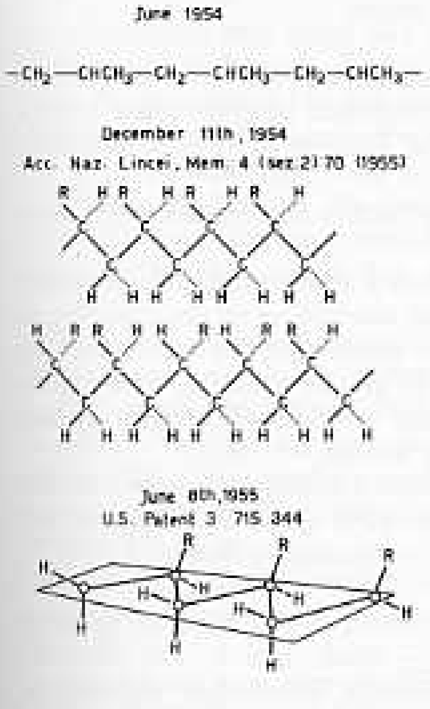


Fig. 4 - First representations of an isotactic polymer chain.

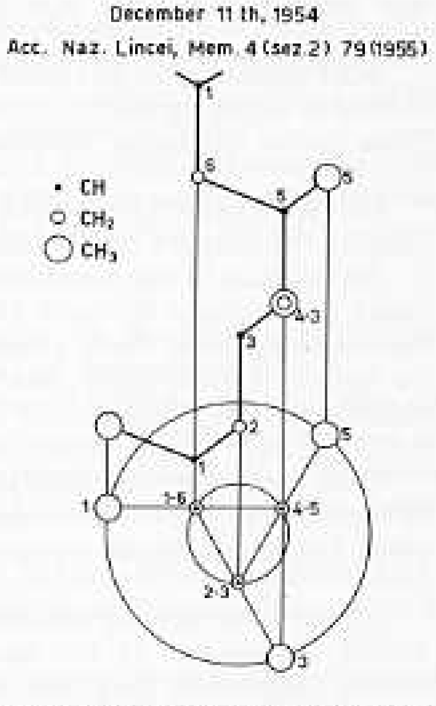


Fig. 5 - First representation of the 3/1 helix of isotactic polypropylene.

The determination of the molecular structure of polypropylene paved the way for the discovery that some catalysts based on titanium halides and aluminium alkyls — found by Ziegler — had a very important and quite unexpected property: the stereospecificity, which we now know to be exceptionally high, *i.e.* equal to or even higher than that of enzymes.

To fully appreciate the level of Natta's creative skill, it is enough to point out that only three months elapsed from the first synthesis of crude polypropylene to the first patent application conveying all data about isotactic polypropylene.

To give a few examples, Ziegler obtained his first crude nonfractionated polypropylene eight-nine months after his first patent on polyethylene. Some U.S.A. industrial laboratories (e.g. Standard Oil of Indiana and Phillips Petroleum), succeeded in obtaining from propylene, by methods other than Natta's, mixtures of polypropylenes with different stereoregularities but they did not fully understand the structure even after years of research. Finally, the DuPont Company that in August 1954 — approximately two months after the first patent of Natta — had filed a patent on the preparation of a polypropylene mixture with catalysts similar to Ziegler's, only obtained isotactic polypropylene from the said mixture in 1955, *i.e.* after becoming acquainted with Natta's papers.

After submitting his first patent application on polypropylene (13), Natta decided to develop research on the polymerization of other alpha olefins. These studies resulted in the patenting of many new isotactic polymers.

He then focused his attention on the factors determining the stereospecificity of Ziegler's catalytic systems.

On the basis of the hypothesis that it is a transition metal solid compound that activates the olefin before the occurrence of the insertion in the metal-alkyl bond, Natta assumed that stereospecificity was caused by the surface regularity of the solid. With the aim of obtaining more regular catalytic surfaces, Natta decided to prepare the catalysts using crystalline $TiCl_3$, insoluble in the reaction medium, instead of $TiCl_4$.

Once again Natta's intuition proved true: the isotactic polymer content in the crude polymer was increased from 40% to 85%. The way was paved for the commercial production of the isotactic polymer.

I have dwelt on the discovery of isotactic polypropylene as being Natta's masterpiece. In this research — more than in any other — Natta's imagination, deep and wide scientific knowledge, decisiveness, perseverance, and incredible skill blended harmonically.

After this discovery, Natta developed a series of research projects of outstanding importance in the new field. Indeed, Sir Robert Robinson wrote that Natta « developed the theme of polymerization as a grandiose fugue » (14).

G. Natta: **Evolution des recherches sur les hauts polymères à l'Ecole Polytechnique de Milan,** *Chim. Ind. (Paris) 89*, 545 (1963).

1) First stereospecific syntheses of isotactic poly(alphaolefins) (Corradini, Danusso, Longi, Mazzanti, Pino).
2) Conjugated polyolefins (Porri; Crespi).
3) Kinetic study of olefins polymerization (Giachetti, Pasquon; Danusso, Sianesi).
4) Investigations on the catalysts (Giannini, Mazzanti, Pino; Pasquon, Zambelli; Porri, Corradini).
5) Syndiotactic polypropylene (Pegoraro; Pasquon, Zambelli).
6) Non-hydrocarbon polymers (Mazzanti, Longi, Dall'Asta, Bernardini, Farina).
7) Synthesis and characterization of di-isotactic polymers (Farina, Peraldo).
8) Asymmetric syntheses (Farina; Porri).
9) Crystalline copolymers: a) Alternate copolymers (Dall'Asta, Mazzanti, Pasquon, Pregaglia); b) Copolymers with a statistical distribution (Danusso, Sianesi; Porri).
10) Saturated elastomers (Crespi, Mazzanti, Sartori, Valvassori).
11) Grafted polymers (Beati, Severini).
12) Chemical-physical methods of analysis and separation (Allegra, Bassi, Corradini; Danusso, Moraglio; Pegoraro; Giuffrè; Ciampelli, Mantica, Peraldo, Zerbi; Lombardi).

Fig. 6 - Development of the research of Natta and co-workers on stereospecific polymerization.

The results that Natta and his collaborators obtained concerning the stereospecific polymerization and related fields can hardly be listed. However, the development of this research may be inferred from Fig. 6, drawn from a summarizing paper that Natta published in 1963 (14).

The research that Natta developed in the sixties followed the main trends described above. He continued to direct the research at his Institute till 1973, when having reached retirement age, Natta left the Institute he had directed for more than 35 years.

The importance of Natta's discoveries for the progress of polymer science was immediately understood on an international scale.

As early as in January 1955, Professor P.J. Flory made the following comments on Natta's first paper on isotactic polymers submitted to JACS (15a): « The results described in your manuscript are of extraordinary interest; perhaps one should call them revolutionary in significance » (15).

This was also the opinion of Prof. Tobolski of Princeton University when he published his paper « Revolution in Polymer Chemistry » in 1957 (16).

In addition to a large number of international awards, in U.S.A., Soviet Union and Europe, in 1963 Natta was awarded the Nobel Prize, shared with K. Ziegler.

However he considered the best aknowledgments for his research to be the data he often received about the commercial production of the new

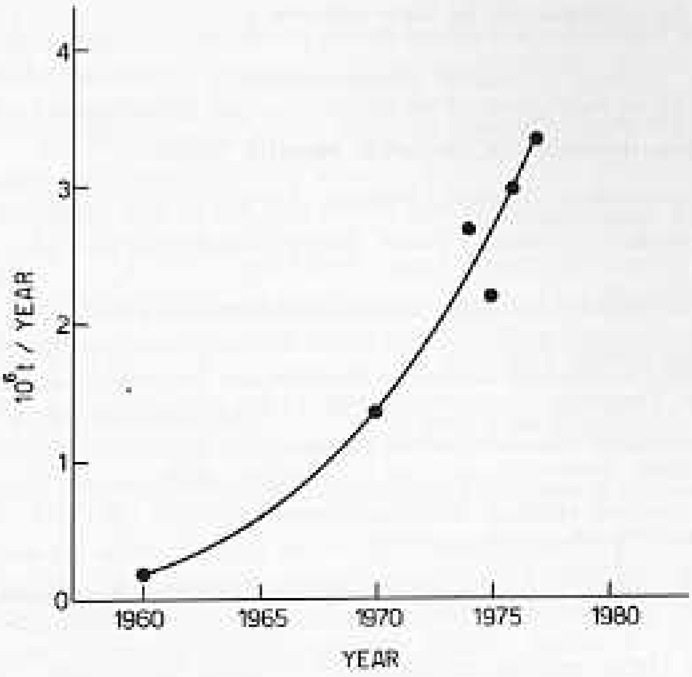


Fig. 7 - World production of isotactic polypropylene.

polymers, and the news about the progress of the scientific and industrial research in the area he had started.

In twenty years the rise in the commercial production of isotactic polypropylene has been impressive: the present production amounts to more than 3 million tons per year (Fig. 7).

Concerning the rapid development of stereospecific polymerization, he was very proud of the number of patents that researchers all over the world had applied for, in the field, in the period from 1954 to 1960 ([15]): 4 in 1954 (when the discovery took place), 25 in 1955, approx. 150 in 1956, about 200 in 1957, 1958, 1959, 1960, for a total of about 1000 patents in six years!

Now, I wish to briefly hint at the activity of Prof. Natta as an educator and at the impetus he gave to the progress of macromolecular chemistry in Italy.

In 1960 he succeeded in persuading CNR (Italian National Council for Research) to establish a National Centre of Macromolecular Chemistry, consisting of eight sections located in Milan, Padua, Turin, Genoa, Pisa (two sections), Rome and Naples.

In the sixties, thanks to this Centre, macromolecular chemistry in Italy reached a high level on an international scale. The former Sections were later replaced by an Institute, some Laboratories, and some Research Centres.

The activity of Giulio Natta as an educator over almost 40 years has been so successful that it seems unnecessary to recall it here.

While he was convinced that the formal lectures were of little use for the education of the young students, Natta deeply believed in the formative value of discussions on specific research topics, and in particular in the formative value of the experimental research work and of the mastering of the theory necessarily connected to it.

He had an admirable faith in research: « Scientific research is truly fascinating, and those who do it are interested in every new application », he wrote (16) to conclude his last paper dated 1972. « As far as I am concerned, should I begin anew, I would devote my life to research ».

He followed his scholars with the greatest interest, and although he was somewhat critical of their work, particularly from the point of view of the practical importance of their research, he was very proud and happy for their success.

It was his opinion that success in research may be achieved by those who make a careful choice of the research subjects and who never neglect the possible application for the results obtained. The research subjects chosen should be dealt with through hard work, utmost scientific exactitude, and criticism. « In this way only », he used to say smiling, « if fortune smiles on us, any success is possible ».

The importance of Natta's school for the Italian university and industry may be inferred from the following.

Of his scholars, about twenty have been appointed as full university Professors in Italy and abroad.

The number of those who attained outstanding positions in the industry is certainly higher; I only recall the few with whom I was more closely acquainted: G. Mazzanti, the former President of ENI; M. Bruzzone and W. Marconi, heading Assoreni's laboratories; G. Crespi, coordinator of Montedison's research; G. Pregaglia, head research and technology of Montedison Petrolchimica, and former President of the Italian Chemical Society; A. Valvassori, Managing Director of Donegani Institute SpA; A. Palvarini, head of Farmoplant's research; B. Calcagno, of the Pirelli Company; G. Dall'Asta, former head of Snia Viscosa's research Centre of Colleferro; P. Longi, M. Ragazzini, E. Giachetti, G. Paleari, G. Negri, I. Ronzoni, U. Soldano, and many others.

Their professional and human qualities hold in honour the School in which they were formed.

By his example and work, Giulio Natta left a message that everybody should ponder and convey to the young researcher who did not have the luck to meet him — a message of faith in research and in the benefits deriving to mankind from science and technology.

Natta's optimism about the beneficial effects of science and technology for the future of mankind was the result of the events he had witnessed and of the successes he had attained: the synthesis of ammonia — on which industry of fertilizers is based — through which the ever increasing world population may be provided with food; the progress achieved is certainly higher; I only recall the few with whom I was more closely in the knowledge of biochemical mechanisms on which life in our world is based; of the discovery of new materials, often useful and sometimes necessary for the sort of life mankind wants to lead at the present time.

Natta's message should especially be considered by all those who seek any opportunity to attack research and the chemical industry under the guise of philosophical and ecological motivations that they do not care to analyse in a critical and conscious way.

Acknowledgement

I wish to thank Mrs R. Lamma Fontani, who for many years was Prof. Natta's faithful secretary, for her help in finding the documentation necessary for this commemorative paper.

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Giulio Natta: the themes

The Chemistry of Carbon Monoxide

The first paper of Professor Natta on this subject has been published in 1930 [G. Natta, M. Strada, *Giorn. Chim. Ind. Appl. 12*, 169 (1930)].

His activity in this field is proved by many publications. We quote, for instance: G. Natta, E. Beati, *Chim. Ind.* (*Milan*) *27*, 84 (1945); G. Natta, P. Pino, *Chim. Ind.* (*Milan*) *31*, 109 (1949); G. Natta, P. Pino, *Chim. Ind.* (*Milan*) *31*, 245 (1949); G. Natta, P. Pino, *Chim. Ind.* (*Paris*) 63, 467 (1950).

Prof. Irving Wender who is particularly expert in the mentioned subject has been requested to give a contribution to the volume. The contribution is entitled: *Chemicals and Fuels from Synthesis Gas.*

Chemicals and Fuels from Synthesis Gas

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The chief purpose of this paper is to present, in broad view, the present state of knowledge and future roles of synthesis gas, with some emphasis on the chemistry of carbon monoxide. The chemistry and uses of synthesis gas are rapidly expanding fields and an attempt will be made to sketch the role that synthesis gas will play in the next two decades. Professor Natta's contributions to the kinetics and mechanism of the synthesis of methanol (1-3) and of higher alcohols (4-6), furnished sound bases for the commercial exploitation of these syntheses, which are now of increasing importance. His work on the hydroformylation (oxo) and related reactions helped build the industries which use these versatile reactions (7-9). Details of the mechanisms of synthesis gas reactions will not be discussed; rather the interplay of synthesis gas as a source of chemicals and as a source of fuels will be examined.

For the past thirty years, petroleum and natural gas have been the most abundant and inexpensive sources of fuels and chemicals. The oil embargo in 1973, and more recent socio-political events, have not only increased the costs of these raw materials but also clearly shown the risks involved in depending, to a large extent, on oil and gas supplies from a single geographical area. In response to these events, industry and government have initiated a gradual, deliberate shift from petroleum and natural gas, both for fuels and for chemical feedstocks, toward other fossil fuel resources, namely coal, shale oil, tar sands, heavy oils, biomass, organic wastes, *etc.*

Industry has been using synthesis gas as a chemical feedstock for many years. Almost all of the synthesis gas in the United States has been made by the steam reforming of methane:

$$CH_4 + H_2O \xrightarrow[750\text{-}900\ ^\circ C]{Ni} 3H_2 + CO \qquad [1]$$

In Europe (where natural gas was not cheap or available) synthesis gas was made also by the catalytic steam reforming of naphtha or light gas oil. For petroleum-derived feedstocks boiling above about 340 °C, partial oxidation using steam and oxygen has been used to produce synthesis gas. Since the world's proven reserves of coal far exceed those of petroleum and natural gas, the partial oxidation of coal will very likely be the source of synthesis gas in the future. It is of interest that the first synthetic fuel plant to be built in the United States will probably be the American Natural Resources Co. (ANR) lignite to synthetic natural gas (SNG) plant to be erected in North Dakota. ANR plans to process 14,000 tons of coal into about 125 million cubic feet of SNG every day. ANR will also produce two million gallons of methanol per year; the methanol will be used to scrub sulfur oxides from the SNG. The same company is exploring the possibility of converting part of the synthesis gas produced to methanol for conversion to gasoline using Mobil's zeolite catalysis.

Many plants for the conversion of coal to synthesis gas are already in operation outside of the U.S.; some for many years. These include the Lurgi fixed bed gasifier (10-11), which is used by SASOL and will also be used in the above-mentioned ANR plant, the Koppers-Totzek entrained bed process (12-13) and the Winkler fluidized bed process (12-14). There is a large amount of work now being carried out on so-called second generation coal gasifiers which operate at higher pressures with greater throughputs. The Texaco and Shell-Koppers processes, along with the British Gas Slagging Lurgi seem most advanced although there are a number of other gasifiers that appear promising, including Saarburg-Otto, U-Gas, the Westinghouse gasifier and the High-Temperature Winkler, among others.

There is a coming turn that seems inevitable in the future large-scale uses of synthesis gas. In places where methane or naphtha have been cheap, they have been used as the source of synthesis gas, mostly for the production of chemicals. However, a small plant (SASOL 1) in South Africa has been using the Fischer-Tropsch process to convert coal to liquids for motor fuels and to chemicals; this plant has been in operation for over 25 years using Lurgi gasifiers, suitable for the gasification of low-rank coals. In the U.S., almost a half-million barrels of oil equivalent per day of natural gas have been used to-produce synthesis gas for chemicals. But most of the natural gas produced in the U.S. has been fed into the network of pipelines for distribution throughout the country.

However, natural gas pipeline networks have been built in many countries where the gas has only lately become available; these include the United Kingdom, Germany, Holland, Denmark, Italy and other countries. These countries intend to keep their pipelines full and so, in the next decades, many of them will undoubtedly gasify coal to synthesis gas which will then be methanated to SNG. This amounts to a reversal of what has been the usual procedure (see eq. 1); instead of reforming natural gas to synthesis gas, synthesis gas will be methanated to produce synthetic natural gas (SNG or high BTU gas) (eq. 2):

$$3H_2 + CO \xrightarrow[350\ °C]{Ni} CH_4 + H_2O \qquad [2]$$

But this is only the tip of the iceberg. In the long term, synthesis gas, presently chiefly a source of chemicals, will be used in large amounts directly as a fuel gas, converted to SNG for fuel use, converted to liquid fuels such as gasoline and diesel fuel, or be used to generate electricity in what promises to be both an environmentally acceptable and efficient way (coal gasification-combined cycle). As we shall see, even a number of chemicals made from synthesis gas, such as methanol and ethanol, may well find larger volume uses as fuels than as chemicals. And a major source of the synthesis gas will undoubtedly be coal.

We shall examine the uses of synthesis gas by:

i) - looking first at its individual components, hydrogen and carbon monoxide;

ii) - as a source of chemicals (which will also have fuel uses);

iii) - as a source of gaseous and liquid fuels (which leads also to chemicals);

iv) - and lastly as a direct gaseous fuel for industrial use and for the generation of electricity.

1. Hydrogen and Carbon Monoxide

1.1. HYDROGEN

Probably the chief use of synthesis gas at present is to make hydrogen. Carbon monoxide in the synthesis gas is reacted with steam to yield more hydrogen (the water-shift reaction):

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad [3]$$

Most of the hydrogen from synthesis gas is combined with nitrogen over a promoted iron catalyst at about 450 °C and 150-350 bars to make ammonia. Hydrogen is also consumed extensively in various petrochemical and refining processes such as hydrocracking, hydrorefining, and the hydrogenation of various unsaturated substances. Also, immense amounts of hydrogen may be needed after about 1990 for the direct hydrogenation of coal to clean liquid fuels by advanced versions of the old Bergius process used by Germany during World War II. This hydrogen will be made by partial oxidation of coal liquefaction bottoms or of coal itself or by reforming of light gases made during the direct hydrogenation of coal. In each case, the water gas shift reaction will be used to convert the CO in the synthesis gas to more hydrogen.

1.2. CARBON MONOXIDE

Carbon monoxide as such has a very large number of uses in chemical manufacture; it also is used in ore reduction. Some important uses of CO will be discussed below; other uses, along with the mechanisms of carbonylation reactions, have been reviewed by many Authors (15-22).

2. Synthesis Gas as a Source of Chemicals and Fuels

This area of research, development and commercialization is so large that it is best understood by dividing it into three parts: (1) *direct* synthesis from carbon monoxide and hydrogen; (2) *indirect* synthesis where methanol is used as an intermediate; and (3) syntheses involving a third chemical (an olefin, a hydrocarbon, a nitrogen-compound, *etc.*) which reacts with synthesis gas or with carbon monoxide. This third class will not be discussed in detail (15-22). It is obvious from Table 1 that the synthesis of chemicals and fuels are very much intertwined.

TAB. 1 - SOME CHEMICALS AND FUELS FROM SYNTHESIS GAS

Fuel Gas —— $CO + H_2$ —— Combined Cycle Power Generation

DIRECT SYNTHESES	INDIRECT SYNTHESES (via methanol)	SOME SYNTHESES WITH A CHEMICAL NOT DERIVED FROM SYNTHESIS GAS	
methane *	formaldehyde	olefins	aldehydes
methanol *	ethanol *		alcohols *
ethylene glycol	methyl acetate *	toluene	terephthalic acid
ethanol *	methyl formate		styrene
higher (C_2-C_5) alcohols *	acetic acid	nitroaromatics	isocyanates
gasoline *	acetaldehyde		
diesel fuel *	acetic anhydride	ammonia	amines
C_2-C_4 olefins	vinyl acetate		
isobutane *	C_1-C_4 alcohols *		acetonitrile
ethylene	gasoline *		
BTX *,b	diesel fuel *		
ammonia	ethylene		
	propylene		
	BTX *,b		
	methyl *t*-butyl ether *		

* Has use as a fuel.
b Benzene, toluene and xylenes.

In the past, manufacturers of chemicals have been comfortable in the fact that the value added to petrochemical feedstocks has enabled them to pay higher prices for raw materials. But as the value of chemicals as fuels increases and as the possibility that governments will allocate raw material resources for fuel use grows more likely, this advantage may be threatened.

Space does not allow an examination of all the reactions leading to the products listed in Table 1. Short discussions of some of the syntheses involved with emphasis on some pertinent examples will be all that is possible.

2.1. CHEMICALS AND FUELS BY DIRECT SYNTHESIS

We have already discussed the synthesis of methane or synthetic natural gas (SNG).

There are a number of well-worked out processes for the synthesis of methanol (1,23-27). Almost 4 million tons per year or about 70,000 barrels/day of methanol are now produced in the U.S., accounting for about 40% of world production.

The Union Carbide Co. has been working on the synthesis of ethylene glycol using a soluble rhodium catalyst (28):

$$\begin{aligned} H_2 + CO \xrightarrow{\text{Rh complex}} \underset{78\%}{HOCH_2CH_2OH} + \underset{11\%}{CH_3CHOHCH_2OH} + \\ + \underset{11\%}{HOCH_2CHOHCH_2OH} \end{aligned} \qquad [4]$$

Under certain conditions, methanol, rather than ethylene glycol, can be synthesized in high yield in the same system. While initial work was conducted at very high pressure (20,000 psi), recent work by Union Carbide indicates that the reaction pressure can be lowered to 5,000 psi or below using a homogeneous ruthenium catalyst in acetic acid as solvent. Dupont and others are also working on similar processes. Since the price of ethylene, the present major source of ethylene glycol (via ethylene oxide) has been rising steadily and its availability may decrease, this process, starting with an equimolar mixture of carbon monoxide and hydrogen, could have a significant impact on ethylene requirements.

Ethanol can be synthesized directly from synthesis gas although these processes are at early stages of development. Union Carbide (29), Sagami Chemical (30), the Institute Français du Pétrole (IFP) (31) and the Phillips Petroleum Co. (32) as well as other companies are investigating this reaction.

The Fischer-Tropsch process has been used to manufacture a wide array of paraffins, olefins, and oxygenates at the SASOL 1 plant in South Africa for over 25 years. Ten Lurgi gasifiers operating at 25 atmospheres gasify coal to furnish the synthesis gas. Most of the product consists of straight-chain molecules with about 15% of methyl branching. No bifunctional compounds such as glycols are formed.

In SASOL 1, two parallel processes are used (35-37). In a fixed bed (Arge) process run at 220-240 °C, 26 atm and H_2:CO = 1.7 with a promoted Fe catalyst, the product contains approximately 22% C_1-C_4 gas, 25% C_5-C_{11} gasoline, 15% C_{12}-C_{20} middle distillate and 35% C_{20+} with these fractions being typically 50% olefinic. An entrained bed (a recirculating fluidized bed) reactor called the Synthol reactor, operates at 320-340 °C, 22 atm and H_2:CO = 3 with a promoted pulverized melted magnetite catalyst. The product from this reactor is much lighter (about 52% gas, 33% gasoline, 5% middle distillate); it is about 70% olefinic and contains some 10% of oxygenated products. The best gasoline selectivity is 40% and that of diesel fuel is 20%.

SASOL 2, some ten times larger than SASOL 1 and using only Synthol reactors, started operation in early 1980. When fully on line, SASOL 2 will convert about 40,000 tons of coal per day into about 58,000 barrels per day of liquid products. SASOL 2 uses 36 advanced higher capacity Lurgi gasifiers to convert coal to synthesis gas. SASOL 3 will be completed in 1982. The entire complex will use 75,000 tons of coal per day, furnishing about half of South Africa's oil needs.

Hoogendoorn (37) estimated the following distribution of products from SASOL 2 (in millions of tons per year)

Motor Fuels	1,500,000
Ethylene	185,000
Chemicals	85,000
Tar products	180,000
Ammonia (as N)	100,000
Sulphur	90,000
Total Saleable Products	2,140,000

SASOL 2 would have seven Fischer-Tropsch reactors consuming 1,900,000 cubic meters of synthesis gas per hour.

The Isosynthesis, no longer practiced but of considerable interest in terms of potentially new routes to desirable products, is different from the Fischer-Tropsch process in that difficultly reducible oxides are used as catalysts (38-41). Secondly, these catalysts give saturated, branched-chain, aliphatic hydrocarbons containing 4 to 8 carbon atoms. The reason for originally developing this process was to produce *iso*butane for high-octane gasoline. The most effective catalysts are the tetravalent oxides, thoria, zirconia, and ceria; other oxides, such as tungstic, zinc, chromia, manganese, and titania are not as effective in producing *iso*butane.

Thoria was found to be the best catalyst, producing a C_3-C_4 fraction containing large amounts of *iso*butane. Temperature of operation was between 375-475 °C and the pressure was high (300 atm). The amount of *iso*butane could be increased by the addition of 20% of alumina to the thorium oxide.

The most active divalent oxide, zinc oxide, produced no liquid hydrocarbons but gave mainly methane and alcohols. This Isosynthesis should be explored more fully — catalysts operating at milder conditions are the primary target.

Ethylene, propylene and butylenes, C_1-C_5 alcohols and BTX may also be synthesized directly from synthesis gas; these will be discussed under the reactions of methanol (indirect syntheses).

The literature indicates that hydrocarbon chain growth in Fischer-Tropsch reactions can be modeled as a polymerization process ([36,42-44]). This suggests that product distribution should be broad and that it would not be possible to achieve high selectivity to many desirable products. Polymerization modeling, for instance, indicates that maximum selectivity to ethylene is 30%, to C_2-C_4 olefins is 56% and to C_5-C_{11} gasoline is 47% ([30,31]).

Kugler ([45,46]) reasoned that poor hydrogenation catalysts and relatively low hydrogen concentrations should be used to increase selectivity to light olefins at the expense of methane production. He confirmed his predictions using ruthenium catalysts modified by strong metal support interactions. A necessary characteristic of the support was its poor abiliy to chemisorb hydrogen ([47]).

To shift the product distribution toward lighter olefins, Kugler used Ru on titania or Ru on manganese oxide, raised the reaction temperature above 250 °C and reduced the $H_2:CO$ ratio. At 350 °C, one atm, and an $H_2:CO$ ratio of 0.5, using Ru on manganese oxide, he obtained a selectivity to C_2-C_4 olefins of about 72 wt.% with 19 wt.% of methane present.

Ruhrchemie has been investigating Fischer-Tropsch catalysts, including iron-manganese catalysts, in an attempt to produce low molecular weight hydrocarbons in amounts greater than predicted by the Schulz-Flory polymerization equation. The main product desired is ethylene and Ruhrchemie has been achieving some success. Evidently olefins desorb from the catalyst fairly easily. One reported breakdown of products formed from synthesis gas by Ruhrchemie, in wt.%, is: methane 9.0; ethylene 31.3; propylene 22.2; butenes 17.4; C_2-C_4 paraffins 15.7; C_{5+} paraffins 3.8 ([48]).

2.2. INDIRECT SYNTHESES FROM METHANOL

About 40% of the world's production of methanol is converted into formaldehyde by a combination of dehydrogenation and oxidation reactions. The Dupont Company produced ethylene glycol from HCHO and synthesis gas until 1968 (49). This process or a variant (50,51) may be revived because of rising ethylene costs.

Monsanto has commercialized the homogeneously catalyzed reaction of methanol and carbon monoxide to form acetic acid in 99% selectivity using a rhodium complex as the catalyst (52,53). The conventional route to acetic acid involves the palladium-catalyzed oxidation of ethylene but the lower price of the feedstock has led to widespread adoption of the methanol-based process. About 40% of the world acetic acid production is now made by the Monsanto process.

Methanol can be converted to ethanol by treatment with synthesis gas in the presence of a homogeneous cobalt or rhodium catalyst (54-57). Although a variety of low molecular weight products are also formed, molar selectivities to ethanol as high as 82% have been achieved using $Co_2(CO)_8$ as the catalyst in the presence of small amounts of sodium iodide and ruthenium trichloride (58); only about 4% of propanol is formed and about 0.5% of butanols. The ethanol can be dehydrated to ethylene and this route to ethylene involves only synthesis gas as the starting material. Gulf Research and Development Co. (59) has homologated methanol to ethanol with the only significant by-products being ethyl ether and methyl acetate plus smaller amounts of methyl ether. It may be possible to use this mixture as a gasoline additive.

2.2.1. *Acetic anhydride synthesis*

It is of historical interest to note that the last unit to use coal as a raw material for methanol synthesis in the U.S. employed a Babcock and Wilcox/Dupont oxygen blown gasifier (60). A commercial scale coal partial oxidation unit was installed at Belle, West Virginia in 1955. It operated for about 15 months, gasifying about 400 tons per day of coal to give 24 million standard cubic feet per day of synthesis gas. In pilot plant work that led to this commercial plant, Dupont began production of a number of other products based on carbon monoxide, hydrogen, methanol and ammonia. Among these products were ethylene glycol, methyl methacrylate, urea and nylon intermediates (61).

The synthesis of acetic anhydride is of particular interest at the moment because it may be the first chemical intermediate that will be made using synthesis gas obtained by the gasification of coal in the U.S. since 1956. The Tennessee Eastman Co. (62) plans to use a Texaco entrained coal gasifier to produce acetic anhydride by the carbonylation of methyl acetate; this chemical will be made from methanol and acetic acid, both produced from synthesis gas. This route is a net consumer of methanol and CO, not acetic acid, and again obviates the use of ethylene. The acetic anhydride will be used to synthesize cellulose acetate, an important polymer used by Tennessee Eastman. Equations for the reaction can be written:

$$CH_3OH + CH_3COOH \longrightarrow CH_3COOCH_3 \qquad [5]$$

$$CH_3COOCH_3 + CO \xrightarrow[\text{catalyst}]{\text{Rh or Ni}} (CH_3CO)_2O \qquad [6]$$

$$(CH_3CO)_2O + (C_6H_{10}O_5)_n \longrightarrow \text{cellulose acetate} + \underset{\text{(recycled)}}{CH_3COOH} \qquad [7]$$

The new process is essentially a replacement of ketene (made by pyrolysis of acetic acid) by methanol and carbon monoxide.

2.2.2. *Ethylidene diacetate and vinyl acetate*

Halcon International Inc. (63) has developed a synthesis of ethylidene diacetate by the reductive carbonylation of either methyl acetate or dimethyl ether. The reaction is carried out under anhydrous conditions. The catalyst system resembles those used by Halcon International Inc. for the synthesis of acetic anhydride, but the presence of some hydrogen mixed with the CO favors the formation of the ethylidene diacetate. This compound yields vinyl acetate on thermal treatment with regeneration of a molecule of acetic acid. This could be an attractive route to the formation of vinyl acetate (64).

2.2.3. *Methanol as a fuel*

One commercial plant in South Africa produces methanol from coal but it is anticipated that there will be many such plants built in the next two decades. Essentially all the methanol produced today is of high purity and is used as a chemical. The growing world shortage of petroleum has resulted in great interest in the use of methanol as a fuel.

The Electric Power Research Institute (EPRI) has been studying the use of methanol as a presently high-priced, high-quality fuel suitable for use in peaking turbines. The use of methanol as an automotive fuel, either alone or as a blending agent in gasoline in quantities up to 10 to 15% by volume, has been proposed by many. Methanol mixed with gasoline has the advantages of raising the octane rating, saving gasoline, and perhaps lowering emissions. But there are disadvantages: phase separation due to the addition of water which would be difficult to prevent in a distribution system, some possible corrosion problems, *etc.* But the methanol-gasoline blend is being used in several countries.

An ethanol-gasoline blend has gained wide acceptance and is sold as « gasohol » in the U.S. The ethanol is made mostly from biomass. Several companies are developing syntheses of C_1-C_4 alcohols as fuel additives or as gasoline substitutes (29-32,65).

2.2.4. *The Mobil Methanol-to-Gasoline* (MTG) *process*

In this process, developed by the Mobil Research and Development Corporation (66-68), methanol is converted to gasoline and water using a shape-selective artificial zeolite catalyst such as H-ZSM-5 of controlled pore size. Gases in the C_3 and C_4 range, formed during the reaction, can be fed to an alkylation unit to produce high-octane gasoline, adding to the overall gasoline yield. Molecules larger than about C_{10} reform in the catalyst cavities until they are small enough to emerge. Coke formation is prevented since polynuclear aromatics are not formed. The distribution of products from the Mobil process is compared with products from the SASOL Fischer-Tropsch reaction in Table 2 ([69]).

TAB. 2 - FISCHER-TROPSCH (SASOL) AND MOBIL (MTG) PRODUCTS

PRODUCT	PROCESS	
	SASOL I (SYNTHOL)	MOBIL
Light gas C_1-C_2	20.1	1.3
LPG C_3-C_4	23.0	17.8
Gasoline C_5-C_{12}	39.0	80.9
Diesel C_{13}-C_{18}	5.0	0
Heavy Oil C_{19}^+	6.0	0
O-Compounds	7.0	0
Aromatics, % of gasoline	5	38.6

The Mobil process is more selective than the Fischer-Tropsch route for converting synthesis gas to hydrocarbons. No separation of oxygenates is required. Mobil has operated 4 barrel a day fixed-bed and fluid-bed reactors converting crude (17% water) methanol into about 1.5 barrels of gasoline per day. A 100 barrel per day fluid-bed pilot unit, sponsored by the U.S. Department of Energy, The Federal Republic of Germany, German industrial participants and Mobil, is under construction in West Germany. Yields from the fluid-bed process appear to be significantly higher than those from the fixed-bed unit.

About 70% of the cost of producing Mobil's high octane gasoline from coal is in the gasification of the coal, about 15% of the cost is in the conversion of the synthesis gas to methanol and about 10% is in the conversion of methanol to gasoline.

If desired, the Mobil process conditions can be varied so as to yield a product which contains more than 80 wt.% of aromatics.

Both Mobil ([70]) and BASF ([70,71]) are investigating catalytic systems to produce ethylene, propylene and butylenes from synthesis gas using zeolites as catalysts. Since these olefins are primary reaction products ([72]), operating at high space velocities will increase their yield. The yields of these olefins approach 90% when water is added to the methanol feed.

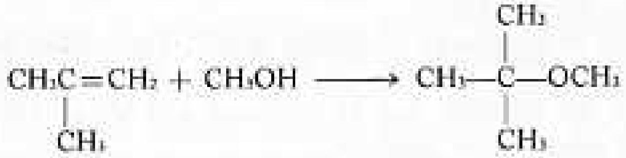
While methanol is now being used as the feed in the MTG process, it may be possible to go directly from synthesis gas to olefins without using methanol as an intermediate. Physical mixtures of Fischer-Tropsch catalysts and zeolites can be used to convert synthesis gas directly to gasoline and this route is being explored in several laboratories. Fischer-Tropsch catalysts, such as iron or ruthenium, either as part of the silica-alumina molecular sieve or placed within its pores, are also being investigated as systems to produce gasoline, aromatics or low-molecular weight olefins directly from synthesis gas.

Researchers at Mobil have developed a heterogeneous Ru catalyst system that converts synthesis gas to high octane gasoline in a single step (73). Ru metal and an intermediate pore zeolite are used; the Fischer-Tropsch intermediates are apparently intercepted in situ and converted to gasoline. Nijs, Jacobs and Utterhoeven (74) compared synthesis gas reactions over a RuNaY zeolite, with all the Ru encaged in the zeolite, with a reference Fischer-Tropsch Ru on SiO_2 catalyst. Under « identical » conditions, (252 °C, $H_2 : CO = 3 : 2$) 60% of the reaction products with the Fischer-Tropsch catalyst were in the C_{11+} range; with the RuY catalyst, less than 1% of the product was in the C_{11+} product range.

2.2.5. *Methyl Tert-Butyl Ether* (MTBE)

MTBE is a high-octane blending stock (75,76), with a research octane number (RON) of 117 to 118 and a motor octane number of 101. Methanol can also react with *iso*amylenes to produce *tert*-amyl methyl ether (TAME) which also is a high-octane compound for upgrading gasoline. Initial activity in blending MTBE and similar octane extenders occurred in Italian and West German plants about 5 years ago (77).

MTBE was approved for use by the U.S. Environmental Protection Agency (EPA) in February, 1979. It can be used as an octane booster to replace lead or manganese anti-knock compounds. The ether is produced by reacting *iso*butylene and methanol in the liquid phase over an ion exchange resin catalyst (76,77):



$$\underset{\displaystyle CH_3}{\underset{|}{CH_2C}}{=}CH_2 + CH_3OH \longrightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}OCH_3$$

An estimate of potential MTBE production for the U.S. has been made, in millions of pounds per year: 1983, 650; 1985, 700; 1990, 1400 (78).

2.2.6. *Formic acid*

About 60% of the world production of formic acid (about 100,000 tons) is obtained as a by-product of the oxidation of light naphtha or butane to form acetic acid. Since most new plants make acetic acid by carbonylation of methanol, formic acid has become less available via this oxidative route. More formic acid therefore will be made in the future by sodium methylate catalyzed reaction of CO with methyl alcohol to give methyl formate. Synthesis gas can be used instead of pure CO. The ester is treated with bases to displace the equilibrium toward the alkali formate which is then acidified. The Leonard Process, using a modification of this method of synthesizing HCOOH, will be used by Kemira Oy in Finland; their plant to make 20,000 tons of HCOOH per year should be in operation in late 1981 (78).

Since retro-esterification can occur easily during workup of the CH_3OH/HCOOH mixture, the methyl formate is often treated with ammonia to form formamide. The formamide is then hydrolyzed to give HCOOH.

3. Synthesis Gas as a Fuel

Synthesis gas (medium BTU gas) is an excellent fuel by itself — it has a heating value of 300-400 BTU per standard cubic foot, depending on the amount of methane or other combustible material that is formed during synthesis. The processes for producing intermediate BTU gases are less complex and costly than those for producing high BTU gas of pipeline quality. Actually, synthesis gas is the aristocrat — the blueblood — of coal gasification products. It yields more BTU per ton of coal, has a higher flame temperature, smaller volume of combustion products and a higher percentage of usable heating value than SNG (79). It can be transported by pipeline up to 100 miles and can be used to furnish industrial gas for a wide area. Plants for supplying industrial fuel gas (IFG) from coal are currently being planned in Memphis, Tenn. in the U.S. using U-Gas fluidized bed gasifiers. Here it will undergo a minimum of clean-up; in fact only H_2S will be removed. Another IFG plant is planned for Katowice, Poland; here Koppers-Totzek gasifiers will be used to gasify the coal. So large central coal gasifiers will probably be used to supply synthesis gas as both a fuel and a chemical feedstock in the future.

Coal gasification-combined cycle (GCC) power plants represent a major and promising new alternative for using coal as a source of electric power (80). In this use, the coal gasification system is directly integrated with a combined cycle power plant. The synthesis gas is combusted under pressure to drive a gas turbine; the hot exhaust is then used to heat water for a steam turbine. Both turbines are coupled to generators and their combined efficiencies can yield a system efficiency of 37-39%, coal to busbar. Cost and performance estimates indicate that a 1000 MW Texaco gasifier based plant should be competitive with conventional pulverized coal-fired plants that meet standards set by EPA in 1978. If emission standards are further tightened, then GCC plants would become increasingly attractive. The Electric Power Research Institute (EPRI) and Southern California Edison have been exploring this route for baseload use in electricity generation.

In some places in the world, there is an excess of natural gas and no pipelines exist for its distribution; the gas is often flared. These include New Zealand, Alaska and the Middle East.

New Zealand recently announced the selection of the Mobil MTG process as the core of a 13,000 barrel per day liquid fuels complex to be fed by the giant Maui gas field 30 miles off New Zealand's shore. Natural gas will be reformed to synthesis gas which will be converted to methanol. The methanol will be converted to gasoline using Mobil's fixed bed reactor process. New Zealand estimated that the Mobil process is more thermally efficient than the SASOL process (57% as compared to 48%) and has lower investment costs. The cost of Mobil gasoline would be about $ 23 per barrel compared with $ 34 to $ 36 per barrel for the Fischer-Tropsch product. The refining requirements of the SASOL/Fischer-Tropsch process add about 20% to total investment costs; the Mobil process yields gasoline without the need for extensive upgrading. As mentioned above, natural gas, not coal, would be the source of synthesis gas in this case.

In September, 1980, Gulf Oil and Gulf Canada and Dome Petroleum outlined to the U.S. Department of Energy a $1 billion plan to produce 63,000 barrels a day of methanol from natural gas in the high Arctic Islands of Canada (8). The methanol could be transported to southern markets in tankers as early as 1985. Company officials believe that the methanol could compete effectively with petroleum products in the transportation and electric utility peaking turbine markets and possibly in space heating and industrial boiler markets as well. Introducing 63,000 barrels a day of methanol into the U.S. market would have its problems since the current U.S. market for methanol is about 70,000 barrels a day. But EPA has granted authority to Atlantic Richfield and to Sun Oil to test a mixture of *tert*-butyl alcohol and methanol in gasoline; this application alone, even with a modest 2.5% methanol concentration used, could easily soak up the potential new supply.

Worldwide, trillions of cubic feet of natural gas are flared each year. In the Middle East, plans are also afoot to convert this gas to synthesis gas which would be used to make the easily transported methanol, along with other products.

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Heterogeneous Catalysis

The first paper of Professor Natta on this subject has been published in 1930 [G. NATTA, *Giorn. Chim. Ind. Appl. 12*, 13 (1930)].

His activity in this field is proved by many publications. We quote, for instance: G. NATTA, E. CASAZZA, *Giorn. Chim. Ind. Appl. 13*, 173 (1931); G. NATTA, N. AGLIARDI, *ACC: Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat. 2*, 387 (1947); G. NATTA, *Bull. Soc. Chim. France 16*, 132 (1949); G. NATTA, « Synthesis of methanol » in « Catalysis », III, P.A. Emmett ed., Reinhold, New York 1955.

Prof. Gabor A. SOMORJAI who is particularly expert in the mentioned subject has been requested to give a contribution to the volume. The contribution was given with the participation of Prof. P.R. Watson and is entitled: *Recent Advances in Heterogeneous Catalysis*.

Recent Advances in Heterogeneous Catalysis(*)

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1. Introduction

The study of heterogeneously catalyzed reactions is, despite its long and varied history, an area of active and tremendous concern for both academic and industrial researchers. The events of the last decade have shown us that we cannot rely on traditional feedstocks for the future. As a result the chemical industry worldwide has embarked on programs of catalytic research aimed at tailoring catalysts that can more efficiently crack poorer grades of crude oil or are able to catalyze the formation of fuels and commodity chemicals from new carbon sources such as biomass and synthesis gas, CO and H_2. Environmental concerns have resulted in new breeds of catalysts such as are used in automobile exhaust systems.

Paralleling these new technical developments there has been a resurgence of interest in providing microscopic descriptions of catalyst structure and behavior. Much of the impetus for this revitalization in heterogeneous catalysis research has been the rapid and impressive development, both in an instrumental and theoretical manner, of experimental tools that are sensitive to various atomic scale properties of surfaces.

Many of the electron and photon spectroscopies have been developed by surface scientists are being employed with increasing regularity and success for both model and actual catalysts. As a result it is becoming clear that we can achieve a detailed microscopic description of the surface properties of a catalyst and start to find correlations between these properties and catalytic performance and new insights into the catalytic process. Thus we are standing at an exciting time in the history of heterogeneous catalysis. Many bold new technical developments are underway, and it appears that in some cases we are drawing ever closer to the catalytic

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chemists' dream of having a sufficently detailed understanding of atomic scale factors that determine the performance of a catalyst and the mechanistic details of the catalytic performance to be able to tailor new catalysts with suitable properties to perform specific functions.

In view of this wealth of information this survey limits us by its size to the discussion of a few selective areas of modern catalysis science. Selection of topics and their treatment reflect the interests of the authors, and it is certainly not complete since we neglect, for example, some important aspects of modern catalysis science such as carbon monoxide chemistry as it is already covered in this volume. However, the subjects we have chosen we consider to represent an interesting selection of recent discoveries which show to advantage the cutting edge of both new technological and scientific advances.

2. New techniques of catalysis research

Over the past 15 years a very large number of experimental techniques have been developed that can inspect heterogeneous catalyst surfaces on the atomic scale (1). Many of these techniques are directly applicable to the investigations of the small catalyst particles in a configuration that is very similar to that used in the industrial technology. These systems contain catalyst particles of 20-150 Å in size that are dispersed on high surface area supports. Photoelectron spectroscopy (XPS) can determine the composition of the particles and the oxidation states of surface atoms as many successful experiments testify. Extended x-ray absorption fine structure studies (EXAFS), using x-rays from the high intensity synchrotron or rotating anode sources, can determine the coordination number of surface atoms of the small atomic clusters and the surface composition.

Most of the other surface sensitive probes must be employed using external surfaces as they cannot find their way inside the small pores of the catalyst suports or they cannot back scatter readily. These probes are usually low energy electrons or ions instead of photons that must also be employed in high vacuum to obtain reproducible results. These surface techniques are utilized on model catalyst systems that are fabricated by the deposition of small particles on the external surfaces of oxide films. Often single crystal surfaces of metals or oxides, catalysts with well defined structure and composition are used in these investigations. Low energy electron diffraction (LEED) determines the atomic surface structure of the clean surface and of monolayers of adsorbates as long as the surface species are well ordered. High resolution electron energy loss spectroscopy (HREELS) determines the vibrational spectra of adsorbed atoms and molecules and can readily detect hydrogen on surfaces. Auger electron spectroscopy (AES) determines the surface composition along with XPS. Ion scattering spectroscopy (ISS) and secondary ion mass spectroscopy (SIMS) are sensitive probes of the surface composition. These are perhaps the most frequently used techniques of modern surface science for studies of catalysts that joined many other techniques in this field (infrared spectroscopy, isotope labeling, electron spin resonance, Mossbauer spectroscopy, to name a few) to provide a picture of the catalyst surface structure and composition on the molecular scale.

Catalysis is a kinetic phenomenon, and studies in this field require the determination of rates and product distribution. Usually these studies have to be carried out at high pressures and high temperatures. In order to bridge the pressure gap that exists between the conditions necessary to analyze the surface structure and composition (high vacuum) and those required for catalytic reaction studies a low pressure-high pressure reaction cell was developed which combines surface science and catalytic studies (^{2}). The sensitivity of this small reactor is so high that it can readily determine reaction rates and product distributions for sample catalysts no larger than 1 cm^2 in surface area. Such small area samples can be prepared with uniform structure and composition that is usually difficult with high surface area catalysts. Thus the correlation between the catalyst surface structure and the composition on one hand, and its reaction rate and product distribution on the other can be reproducibly studied and determined. As a result, the atomic scale characteristics of complex catalysts that make them active and selective are being uncovered.

3. New-observations and concepts emerging from surface science studies

3.1. SURFACE IRREGULARITIES, STEPS, AND KINKS ARE ACTIVE SITES FOR BREAKING CHEMICAL BONDS

Studies of transition metal crystal surfaces revealed the importance of atomic height steps and kinks to break H-H, C-H, C-C, and C-O bonds with near zero activation energies (^{3}). On terrace sites of higher symmetry there is often a small activation energy for bond scission that decreases the rates of these elementary surface chemical processes as compared to the chemical reaction rates at the surface defects. By suitable manipulation of the surface structure, the relative concentrations of the various surface irregularities can be altered that, in turn, can change the rates of competing surface reactions and thus the product distribution. By blocking some of these small concentration surface sites with sulfur or other chemically inert metals, the reaction selectivity can often be improved.

3.2. THE OXIDATION STATE OF SURFACE ATOMS CAN STRONGLY INFLUENCE THE SELECTITY OF CATALYTIC REACTIONS

Recently the catalyzed hydrogenation of CO has been investigated on transition metal and metal oxide surfaces (4). Very different rates and product distributions were found as the oxidation state of the surface atoms are altered. Rhodium metal produces largely methane from CO and H_2, while Rh_2O_3 produces olefins and oxygenated products such as acetaldehyde. $LaRh_2O_3$ yields alcohols in high concentrations. Iron metal is readily poisoned by the building of a multilayer of carbon during the CO-H_2 reaction; Fe_3O_4, on the other hand, remains active and selective and exhibits a product distribution very different from that of iron.

It appears that the changing binding energies and dissociation probabilities of adsorbed molecules as the oxidation states of surface atoms are changed strongly influence the surface concentrations of adsorbed species and the nature of the reaction intermediates. As a result, the reaction rates and product distribution are also altered.

3.3. MONOLAYERS OF CARBONACEOUS DEPOSITS ON THE CATALYST PLAY IMPORTANT ROLES IN DETERMINING CATALYTIC ACTIVITY AND SELECTIVITY

There are many hydrocarbon reactions that occur at relatively low temperatures (< 200 °C); these are hydrogenation, dehydrogenation, and isomerization to name a few. These reactions occur with high turnover numbers while others need higher temperatures (> 200 °C). These reactions include dehydrocyclization and hydrogenolysis. ^{14}C isotope labeling experiments revealed that carbonaceous overlayers form on the catalyst surface in both temperature regimes (5). During the low temperature reactions, the carbonaceous deposits rehydrogenate at a rate that is faster than the turnover number. Thus the catalytic reactions take place on the metal surface in this circumstance. However, at high temperatures, the rate of rehydrogenation of the carbonaceous deposits is much slower than the turnover number of the hydrocarbon reactions. As a result the reaction must take place on top of the carbonaceous layer — not on the metal surface. This finding necessitates the rethinking of many of the reaction schemes that assumed the surface reactions to occur only on the metal surface. The importance of the chemical bonding of the adsorbates to the carbonaceous fragments and the hydrogen transfer between the fragments and the adsorbed molecules is clearly indicated by these studies and influence reactivity and selectivity of hydrocarbon reactions.

3.4. THE ROLE OF ADDITIVES, ELECTRON DONORS AND ACCEPTORS DURING CATALYTIC REACTION

The formulation of many catalysts include the addition of electron donors, mostly alkali metals or electron acceptors, halogens or oxygen. For example, alkali salts are added to iron catalysts used in ammonia synthesis or to the iron catalyst used for the hydrogenation of carbon monoxide. Chlorine is added to platinum reforming catalysts that are dispersed on alumina support.

These additives play several important roles through which they influence reactivity and selectivity. These roles are being verified by recent surface science studies. Potassium helps to remove carbon from iron surfaces as CO_2 by a catalytic side reaction that involves the formation of KOH and perhaps also K_2CO_3. Potassium increases the heat of adsorption of N_2 on iron, and increases the activation energy for dissociation of N_2 to atomic nitrogen. It also increases the dissociation probabilities of carbon monoxide on iron and the heat of adsorption of carbon monoxide on platinum.

Charge transfer between the additives and the catalyst leads to charge redistribution that can modify the oxidation states of surface atoms. Chlorine is know to facilitate the redispersion of noble metal particles. Thus the surface structure of catalysts can be altered by additives most likely through their effect of the changed relative surface free energies of the various crystal faces. Oxygen adsorbed at a kink site on platinum surfaces was found to exhibit enhanced catalytic activity in hydrogenolysis reactions.

4. Building of New Catalysts

4.1. ADVANCES IN ALLOY CATALYSIS. BIMETALLIC CLUSTERS

There has been a long-standing interest in exploring the electronic factor in catalysis through the use of bimetallic catalysts (6). New developments in the preparation and characterization of highly dispersed bimetallic cluster catalysts have resulted in successful commercialization (7). A supported bimetallic catalyst can be made quite simply by impregnating a high surface area support, such as silica or alumina, with an aqueous solution of salts of the two metals of interest. The dried material is then reduced in hydrogen to provide highly dispersed particles. Alternatively, the starting point can be a molecular complex containing two metal atoms already bound together. An example is the use of SiO_2 impregnated with $(Co_2Rh_2)(CO)_{12}$ as a catalyst precursor (8). These procedures result in the formation of very small metal clusters dispersed on the surface of the carrier. An interesting question is whether the clusters will be monometallic or contain atoms of both metals. On statistical grounds we might expect them to be bimetallic, and this has been shown experimentally even for cases in which individual metals show very low bulk miscibility.

Direct experimental verification has emerged in various ways. First, a catalytic reaction is used to probe the interaction between the two metallic components. A favorite reaction has been the hydrogenolysis of ethane to methane. An example of this type of investigation has been performed by SINFELT for the Cu-Ru and Cu-Os systems supported on silica (9). In these cases addition of copper to the Group VIII metal markedly reduced the hydrogenolysis activity. Experiments of this type demonstrate clearly that the two metals are not isolated from each other on the carrier surface and provides evidence for the existence of bimetallic clusters. From the point of view of practical catalysis, such systems are of interest as inhibition of hydrogenolysis may improve the selectivity to more desirable reactions such as dehydrocyclization and isomerization.

The second approach to characterizing the bimetallic nature of these cluster catalysts has been that of x-ray diffraction which has been applied with some success to naphtha reforming catalysts containing two Group VIII metals (e.g., Pt-Pd, Pt-Rh, Pt-Ir) (10).

Platinum and iridium crystallize in the f.c.c. structure and form solid solutions in all proportions in the bulk. The lattice parameter is a function of the composition and hence can be used to demonstrate the presence of bimetallic clusters in silica supported Pt-Ir catalysts. The x-ray diffraction pattern from a mixture of 10% Pt-SiO_2 with 10% Ir-SiO_2 shown a broad line due to the overlapping of lines from individual clusters of Pt and Ir, estimated to be 56 Å and 27 in size, respectively. The pattern from a bimetallic cluster catalyst (10% Pt, 10% Ir-SiO_2) shows a single symmetric line corresponding to clusters of 49 Å size and a lattice parameter corresponding to a 1 : 1 mixture of Pt and Ir, in agreement with the overall composition.

The application of x-ray diffraction to more highly dispersed catalysts becomes very difficult. In order to obtain information on more highly dispersed clusters a third technique, that of extended x-ray absorption fine structures (EXAFS), has been developed (see section 2). EXAFS results on a 1% Ru-Cu on silica catalyst (11) indicate that the ruthenium component is very similar to the ruthenium in a silica-supported ruthenium reference catalyst with an average coordination number of 11 ± 1. The ruthenium atoms are coordinated mainly to other ruthenium atoms and only to a minor extent to copper atoms. However, the copper component of the bimetallic cluster has an average coordination number of 9 ± 2.5 and appears to have a more equal distribution of copper and ruthenium nearest neighbors. These results are consistent with a cluster in which the copper is present on the surface of a small core of ruthenium atoms.

The ruthenium-copper catalyst is complex in the sense that a distribution of cluster sizes is observed by electron microscopy which may exhibit some variation in shape. The EXAFS results, especially the average coordination number of ruthenium close to 12, indicate that the majority of the clusters have a three-dimensional form and that rafts of two atomic layers are only a minor component, which had been suggested previously.

4.2. AUTOMOTIVE EXHAUST CATALYSTS

The use of catalytic converters to reduce the emissions of unburned hydrocarbons, CO and nitrogen oxides in exhaust gases, has a history going back over 40 years. As early as 1949, Houdry (12) developed mufflers for trucks used in confined spaces such as mines and warehouses. Remarkably, one of these anticipated developments that were to occur on a large scale in the 1970's was a catalyst of monolith-porcelain rods with an alumina washcoat on which platinum was deposited.

The impetus that opened up this new field of catalytic chemistry was given by the United States Federal Clean Air Act of 1970 which set standards of emission that could not readily be met by the existing technology of internal combustion engines and spurred an intensive research effort. The initial maximum concentration of emissions were specified to reduce carbon monoxide and hydrocarbon emissions by 90% or more of those previously emitted. Control on nitrogen oxide emissions came somewhat later. Enforcement of the law was delayed and interim standards adopted, but all new cars (with the exception of Honda which uses an improved combustion system) sold in the U.S. since 1976 have been equipped with catalytic converters.

4.2.2. *Exhaust gas composition*

Ideally, the automotive engine receives a stoichiometric mixture of air and gasoline (14.7 : 1 by weight) which is completely combusted to CO_2, H_2O, and N_2. In practice, lean mixtures (16:1) are desirable for economical cruising, and rich mixtures (12 : 1) for starting and acceleration. The combustion process is never complete so that the exhaust gases contain carbon monoxide, hydrocarbons, hydrogen, and oxygenated organics such as formaldehyde. Some of the nitrogen in the air is oxidized to nitrogen oxides during combustion.

The major problems associated with designing catalytic converters is not just one of finding a catalytic system that will produce the required reductions in emissions, but one that will keep on doing its job for many thousands of miles and under an extremely wide range of operating conditions.

The major difficulty is the requirement of efficient operation under transient conditions. In most major catalytic processes employed in the chemical industry, continuous steady-state operating conditions are utilized. In the urban car we have to deal with start-up conditions and with the recurring transient conditions of stop-and-start urban driving. The concentrations of the major pollutants can change drastically with air-to-fuel ratio during acceleration. The exhaust gas temperature may vary between 300 and 1000 °C (^{13}) while the gas flow rate may change by an order of magnitude or more, and typically affords a contact time with the catalyst of only a few milliseconds (^{14}).

Further constraints on the choice of catalyst are that the oxidizing atmosphere of the auto exhaust contains not much more than a stoichiometric amount of oxygen and about 15 mole-% water. The catalyst should also have a lifetime that is a substantial fraction of the lifetime of the car. An efficient automotive catalytic converter must operate well within narrow ranges in the four variables: gas flow rate, temperature, gas composition, and poison concentration. The catalytic system can tolerate occasional excursions from these ranges, but prolonged variations are not permitted.

4.2.3. *Catalyst strategies*

A large research effort has gone into finding suitable catalysts that will lower nitrogen oxide, carbon monoxide, and hydrocarbon emissions, within the constraints detailed above. The catalytic reduction of NO by a reducing agent such as CO or H_2 proceeds at reasonable rates on a number of catalysts, but if oxygen is present it will be preferentially reduced. Therefore, it is necessary to provide a net reducing atmosphere to reduce NO to nitrogen. This is in contrast to the oxidizing conditions needed to convert CO and hydrocarbons to CO_2 and water.

Of the many types of catalysts tested, the most successful for both oxidation and reduction appear to be the platinum group metals. These are usually dispersed as small crystallites on alumina. Three major support shapes are spheroids, wire mesh, and monolithic honeycombs. A washcoat of high surface area alumina is usually placed on the ceramic surface to act as the substrate for the metal. Unfortunately, the use of such catalysts places a heavy demand on the continued availability of noble metals which are principally mined in the Soviet Union and South Africa. Research to find a suitable non-noble metal catalyst substitutes for the presently used platinum based catalysts is an active and important area of research at present (15).

The most successful automobile emission catalyst is the « 3-way redox » system. Simultaneous oxidation and reduction can take place in a single catalytic bed, provided that the air-to-fuel ratio is maintained close to the stoichiometric 14.7:1. In this window NO_x conversion to N_2 is still high, while CO and hydrocarbon is still over 80%. In order to achieve the precise metering necessary to maintain the stoichiometric ratio, a feedback control mechanism, equipped with an oxygen sensor to measure oxygen pressure in the exhaust gas, must be provided. The prime catalysts for the redox system are rhodium, platinum, palladium, or rhodium-platinum catalysts. This catalyst is the workhorse of the auto emission control technology at present.

4.2.4. *Poisoning*

The use of platinum-type emission catalysts necessitate the elimination of potential poisons from gasoline, most prominently lead compounds. All automobiles equipped with catalytic converters must use unleaded gasoline. This means that the octane number of the gasoline must be boosted by catalytic reforming or cracking and by additives other than tetramethyl or tetraethyl lead. In turn, more crude oil must be processed since the yield of gasoline from the crude decreases with increasing octane requirement.

4.3. STRONG METAL SUPPORT INTERACTION (SMSI)

In many important applications such as automotive exhaust purification, gasoline octane improvement, and the manufacture of fats and oils, the catalyst consists of small metal particles distributed in the pores of a porous inorganic oxide. These support oxides, such as alumina or silica, have high surface areas, often greater than 200 square meters per gram. A dilute solution of a metal salt can be dispersed over this large area and, subsequently, reduced, resulting in very small metallic particles of the order of 20 Å in size. As a result, most of the catalyst atoms are surface atoms and, as the catalytic reactions occurs on the catalyst surface, this represents a more efficient catalytic utilization of the available metal, a particular economic benefit in the case of expensive catalysts such as the noble metals.

The function of the catalyst support is, therefore, to provide an efficient dispersion of the metallic catalyst and to maintain it under processing conditions by keeping the particles far enough apart to prevent agglomeration. This view of the function of the support being a merely physical role has been borne out in large measure in practice. In general, the support has not been thought to exert profound effects on the activity or selectivity of supported-metal catalysts (8), and there has been no need to invoke any large degree of metal-support interaction. However, the intimate association of metal and support provides a potential for such an interaction and, in some cases, it has been shown that the nature of the support can influence catalytic activity.

More recently, there has appeared evidence for a type of metal-support interaction of a more pronounced nature. This has been termed, « strong metal-support interaction », or SMSI in which there is direct physical evidence of strong bonding as well as alterations of catalytic properties.

4.3.1. *Characteristics of* SMSI

The most obvious characteristics of a system exhibiting SMSI are shown in the strongly altered chemisorption properties. The chemisorption of H_2 and CO are used on routine basis to measure both the dispersion of the

TAB. 1 - HYDROGEN CHEMISORPTION ON TiO_2 SUPPORTED GROUP VIII METALS
H/M is the ratio of hydrogen atoms adsorbed to total metal atoms

METAL (2 WT%)	H/M	
	REDUCTION @ 200 °C	REDUCTION @ 500 °C
Rh	0.71	0.01
Pd	0.93	0.05
Pt	0.88	0.00

TAB. 2 - SUPPORTS SHOWING SMSI ACTIVITY WITH Ir

SMSI SUPPORTS	NON-INTERACTING SUPPORTS
TiO_2	Al_2O_3
V_2O_3	SiO_2
MnO	Sr_2O_3
Nb_2O_5	HfO_2
Ta_2O_5 *	MgO
	ZrO_2
	Y_2O_3
	Cr_2O_3 §

* Sluggish.
§ Some slight suppression of H_2 chemisorption.

metal to allow rate measurement on the basis of surface instead of total metal atoms, and in the case of CO to gain chemical information from studies of the CO stretching frequency. The indicator of SMSI behavior is a severely depressed ability for the supported metal atoms to chemisorb H_2 or CO. The noble metal impregnated TiO_2 is first reduced in H_2 and then evacuated before chemisorption measurements are made. After reduction at 200 °C, the hydrogen chemisorption values (expressed as ratio of hydrogen atoms adsorbed to toal metal atoms) are typical of those found on familiar supports such as alumina or silica. Reduction at 500 °C, however, leads to a drastic reduction in the ability of the metals to adsorb hydrogen, reducing the chemisorption to all but undetectable levels. Similar behavior is seen for CO chemisorption. Explanations such as agglomeration of the metal, due to structural collapse in the presence of strongly bound hydrogen molecules from the reduction process, were discounted by careful experimental procedures.

Titanium oxide is not the only support to show such behavior, nor is activation at 500 °C a necessary prerequisite for SMSI behavior. The oxides of titanium, vanadium, manganese, and niobium are able to suppress the chemisorption of hydrogen onto iridium by an order of magnitude when activated in hydrogen for one hour at 350 °C. The ratio of hydrogen atoms adsorbed to metal atoms continues to decline as the reduction temperature is raised. The supports which have been tested for SMSI behavior are listed in Table 2. For supports such as alumina and silica, hydrogen chemisorption continues at a high level for reduction temperatures up to 500 °C. If the temperature is raised to 700 °C, hydrogen chemisorption drops slightly due to particle agglomeration. Thus several binary transition oxides show striking metal-support interactions, whereas others do not. A possible explanation for this can be found by examining the reducibility of the oxides to metal or a lower oxide. A clear correlation can be traced between SMSI behavior and reducibility. Those transition metal oxides that are highly resistant to reduction do not show a strong metal support interaction. Those that are easily reducible (TiO_2, or Nb_2O_5), or are already unsaturated (MnO, V_2O_3) do. The sluggish behavior of Ta_2O_5, which only shows a substantial SMSI effect if reduced at > 400 °C, can be correlated with its intermediate reducibility.

4.3.2. *Metal-substrate bonding*

The effect of SMSI supports on the supported metal atoms has been seen directly using an electron microscope in a series of elegant experiments by Baker *et al.* (^{11}). A clearer difference was seen for Pt/TiO_2 than for other supports such as alumina, silica, and carbon. Much smaller particle diameters were seen for reduction on titania; moreover, the particles were thin and flat, only a few atoms thick as opposed to the usual hemispherical aggregates. High temperature oxidation transformed the thin particles to thicker hemispheres. Reduction would reverse this behavior with melting of the thickened platinum aggregates into thin rafts. Clearly, the support metal interaction must be sufficient to outweigh the cohesive forces within the metal aggregates. At the same time, the TiO_2 support reduced to Ti_4O_7 which could be reoxidized. The changes in chemisorption and structural properties which characterize the SMSI state are strongly suggestive of a substantial electronic interaction at the metal-oxide interface. Consideration of experimental results with theoretical studies, using molecular orbital methods (^{5}), suggests that two important needs have to be satisfied to allow SMSI behavior.

1. Oxygen anions must be removed from the surface to allow a close approach of a metal atom to a surface cation.

2. The surface transition metal cations of the support must be reduced thereby acquiring *d*-electrons. The concomitant loss of surface anions allows a metal-cation approach with electron transfer to the metal resulting in an ionic attractive interaction.

Thus surface reduction fulfills the twin needs of removing oxygen and reducing the support cation, e.g. Ti^{4+} to Ti^{3+}. Clearly these supports that contain metal cations which are highly resistant to reduction, e.g. Al_2O_3, would not be able to exhibit this type of behavior. This interpretation is supported by x-ray photoelectron studies which show charge transfer from reduced surface cations to the supported metal in Pt/TiO_2 (^{21}) and $Pt/SrTiO_3$ (^{22}).

The observed suppression of H_2 and CO chemisorption on SMSI catalysts is rather difficult to account for. Present explanations center on the unusual and flat topography of the metal particles which do not provide the correct ensemble of metal atoms for effective adsorption and the altered oxidation states of the metal ions at the surface.

4.3.3. SMSI *catalysts*

As chemisorption must be an essential step in any catalytic reaction, we might expect the strongly altered chemisorption characteristics of supported metal catalysts in the SMSI state to be reflected in different catalytic properties. In particular, for CO-H_2 synthesis gas chemistry, the repression of CO and H_2 chemisorption might lead us to expect lowered activity, different selectivities, and decreased deactivation rates as compared to non-SMSI catalysts. Indeed, there are several selective SMSI catalysts under intense experimental scrutiny at present. Unfortunately, published catalytic data for SMSI catalysts is as yet meager. Studies of methane production from CO and H_2 by Vannice and Garten (23), using supported nickel and ruthenium catalysts, have shown up to 10-fold greater activity when the metals were dispersed on a titania support rather than on alumina, silica, or carbon. *In situ* infrared studies showed only small amounts of CO on the titania supported metal, but larger amounts if the carrier was silica or alumina. In general, the SMSI catalysts showed a lower selectivity for methanation and a higher yield of olefins. Clearly, a weakened surface-substrate interaction can lead to many beneficial catalytic effects.

The nature of the strong metal-support interaction still poses some important questions, particularly as to how the oxide-support-to-metal charge transfer changes from system to system. If we can understand the details of such variation and the response in terms of catalytic efficiency and product distribution, it may well be possible to design new catalysts with improved properties.

4.4. NEW ZEOLITE CATALYSTS

Zeolites are the largest volume catalyst used presently in the petroleum refining and chemical technologies (24). These alumina-silicates are prepared with various concentrations of aluminum ions in the tetrahedral silica framework. The Brønsted acidity of the catalyst can be correlated with the Al^{3+} concentration in the crystal lattice. By using clever synthetic routes, zeolites with variable pore sizes are prepared that permit one to carry out « shape selective » catalysis. Molecules that are small enough to enter the channels in the crystal lattice which are of molecular dimensions (~ 12-22 Å range) will react, undergo hydro-cracking, and isomerization, while molecules which are too large to enter the pores remain unreacted. These catalysts are of very large internal surface area and exhibit ordered lattice structures and high thermal stability.

Recently, researchers from the Linde Division of Union Carbide, and from Mobil Oil Corporation have reported the synthesis of a new class of zeolites with very large silicon to aluminum ion ratio chemical composition. The materials are made of silicon and oxygen atoms almost exclusively, but the removal of the aluminum ions does not prevent the formation of the large internal surface area structures. These new zeolites, one of which is named sylicalite by the Union Carbide researchers, are often hydrophobic, rejecting water while adsorbing hydrocarbons. The small concentration of aluminum ions left behind in the silica framework can be used to ion exchange metals of various types into the structure, thus producing a new class of catalysts with low Bronsted acidity.

The most successful new zeolite is called ZSM-5 by the Mobil researchers. The catalyst has been employed in a new technology to produce high octane gasoline with a large concentration of aromatic molecules from methanol. Since methanol can be readily produced from CO and H_2, this new technology represents a breakthrough for indirect liquification of synthesis gas, CO and H_2 to high octane fuel. ZSM-5 has also been used to isomerize toluene and for various selective reactions of olefins. The new catalyst is much more resistant to coking than the more acidic zeolites, and maintains the same thermal stability.

At present, zeolites provide new and exiciting opportunities to develop catalytic technologies of great importance, both in the chemical and petroleum industries. As a result of new advances of catalyst synthesis, it is likely that an entirely new family of zeolites with intriguing chemical properties will become available in the near future.

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Elastomers

The first paper of Professor Natta on this subject has been published in 1942 [G. NATTA, *Chim. Ind.* (*Milan*) *24*, 419 (1942)].

His activity in this field is proved by many publications. We quote, for instance: G. NATTA, P. CORRADINI, *Angew. Chem. 68*, 615 (1956); G. NATTA, *Rubber Plastics Age 38*, 495 (1957); G. NATTA, C. CRESPI, *Chim. Ind.* (*Milan*) *41*, 123 (1959).

Prof. Mario BRUZZONE who has collaborated with Giulio Natta in this field from the beginning has been requested to give a contribution to the volume. The contribution is entitled: *Synthetic Hydrocarbon Rubbers.*

Synthetic Hydrocarbon Rubbers

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1. History

Synthetic hydrocarbon rubbers (SHRs) are based on hydrocarbon monomers, *i.e.* monomers which contain only carbon and hydrogen atoms.

The first SHRs were synthesized with the aim of obtaining a substitute for natural rubber during its shortage for war reasons (First and Second World Wars).

After the Second World War, SHRs showed a spectacular growth which continued in spite of the restoration of the natural rubber supply, so that nowadays they hold an unquestionable first position in total rubber consumption (Fig. 1).

The reasons for the SHR success after the Second World War are:

the development of petrochemistry and the related abundant supply, at a lower cost, of monomers formerly obtained from agricultural products or from carbochemistry;

the tremendous expansion of the automotive industry on a worldwide basis, and the consequent impossibility, for natural rubber, to cope with the fast growing demand;

the technical-economical advantages of SHR with respect to natural rubber in several applications.

As a consequence, SHRs consumption overcame that of natural rubber and this situation is likely to last in the future, in spite of the increasing price of petroleum.

As a matter of fact, notwithstanding the excellent properties of natural rubber, some of which are not yet overcome by any existing SHR, some important factors stand against a massive recovery of natural rubber.

Among these factors are the long term investment and the high labour intensity of natural rubber and the possibility of land utilization for more profitable productions.

A *Hevea Brasiliensis* tree requires in fact approximately 7 years before beginning the production of rubber, and the productivity per employee and per year is about only 2 tons, as compared with 500-600 tons of a *cis*-1,4-polyisoprene plant with a nameplate capacity of 30,000 tons per year.

In favour of natural rubber the advantages of a low requirement of fossil energy (for fertilizers, chemicals and processing) and of low environmental pollution are claimed, however.

Another competitor of SHRs could have been represented, in principle, by other synthetic rubbers that contain heteroatoms (*i.e.* atoms different from carbon and hydrogen) in the main chain or as side groups.

In fact, several monomers which contain heteroatoms such as oxygen, sulphur, nitrogen, chlorine and so on are supplied by the petrochemical industry at a reasonable price, comparable at least to that of some hydrocarbon monomers.

However, the heteroatoms containing rubbers have not succeeded so far in displacing hydrocarbon rubbers (*i.e.* SHRs and natural rubber) from the tyre field, that has hegemonized till now the rubber consumption (Fig. 2), and were confined to limited, albeit indispensable, applications.

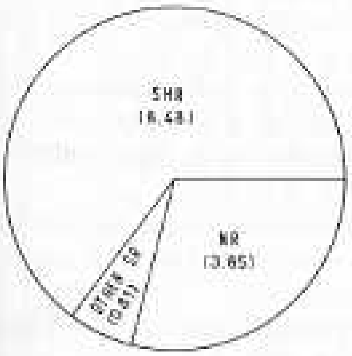


Fig. 1 - World rubber production in 1979 (million tons). SHR = SBR **(5,546) + +** BR **(1,208) +** IR **(0,836) +** EPDM **(0,372) +** IIR **(0,520). Other synthetic rubbers =** CR **(0,464) +** NBR **(0,343). Data in parenthesis: production expressed in million tons for each type. Consumption:** SHR **consumption in 1979 reached 8,23 million tons (97% of production).**

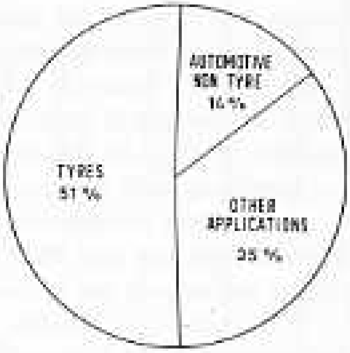


Fig. 2 - Percentage world rubber consumption (SR + NR) **for « tyres », for «automotive non tyre» and «others» applications.**

After WW II, the only SHRs available were SBR (styrene-butadiene rubber) and butyl rubber (*iso*butylene-isoprene rubber), but approximately ten years after the war the organometallic chemistry and the stereospecific polymerization, with the outstanding contribution of K. Ziegler and G. Natta, opened the way for a host of new molecular and macromolecular structures.

Up to now, as will be outlined later on, we have only begun to tackle some of the possibilities offered by organometallic chemistry and by stereospecific polymerization, but most is still to be done.

2. Hydrocarbon monomers

Most of the monomers used nowadays for production of SHRS come, directly or indirectly, from naphtha cracker or from refinery streams.

However, only the C_4 and, potentially, the C_5 fractions have a substantial outlet in SHRS.

In C_4 fraction butadiene, *iso*butylene and butene-1 are already present and need only to be separated by extractive distillation.

In the C_5 fraction isoprene, *cis* and *trans* piperylene and cyclopentadiene (which transforms into the dimer) are present.

Dicyclopentadiene can be easily reverted to cyclopentadiene, and after partial hydrogenation cyclopentene is obtained, another interesting hydrocarbon monomer.

In general, monomers obtained by separation are cheaper than monomers obtained by synthesis. However, the difficulty of collecting sizable quantities of C_5 fraction and the problem of isomer separation (that of course worsens, as the number of carbon atoms increases) compels the production of some monomers by synthesis.

A relevant factor in a hydrocarbon monomer is its purity, particularly when the monomer is polymerized in the presence of a small quantity of catalyst (high yield processes) or when the impurity has a high tendency to coordinate with the catalytic centre.

Sometimes, purification is as important as polymerization for the overall process economy and therefore improved monomer separation and purification techniques are a challenge for future work.

The monomers directly used today for commercial production of SHRS are listed in Table 1, in order of increasing carbon atoms.

Another monomer present in the C_5 cut of naphtha cracker, *i.e.* piperylene (*cis* and *trans* isomers) has not been included in the table; its possible use as a monomer for production of a new SHR has been recently pointed out (see below).

Among the monomers indicated in Table 1, butadiene and styrene are used in large quantities for SHR. Isoprene, *iso*butylene, ethylene and propylene are used in sizable quantities and 1,4-hexadiene, 5-ethyliden-2-norbornene and dicyclopentadiene in small quantities, as co-monomers.

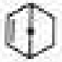
An economic synthesis of isoprene is still a challenge for the chemist, notwithstanding the long list of possible synthetic routes already available, indicated in the table.

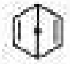
Besides the monomers listed in Table 1, a host of new monomers have been recently synthesized, as shown in Table 2. Most of these syntheses

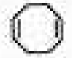
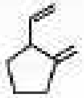
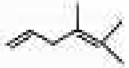
TABLE 1 - COMMERCIAL HYDROCARBON MONOMERS

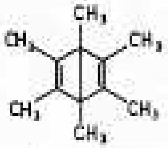
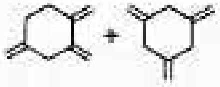
CARBON ATOMS	FORMULA	NAME	HOW MADE
C_2		Ethylene	Cracking various hydrocarbons from ethane to gas oil by catalytic processes or in the presence of steam
C_3		Propylene	Recovered from cracked gas streams of oil refineries and coproduct streams of steam-cracking ethylene plants
C_4		1,3 butadiene	Extraction from C_4 fraction of naphtha cracker - Dehydrogenation of butenes (refineries) and butane (natural gas)
		Isobutylene	Extraction from C_4 fraction of naphtha cracker or from mixed butylene streams of refinery catalytic crackers
C_5		Isoprene	Extraction from C_5 fraction of naphtha cracker - Synthesis from isobutylene and formaldehyde - Dehydrogenation of isoamilenes - Dimerization of propylene and demethanation - Synthesis from acetylene and acetone - Hydrocarbonylation of butene 2 with synthesis gas
C_6		1,4 hexadiene	Synthesis from butadiene and ethylene
C_7		Norbornene	Diels Alder addition of cyclopentadiene and ethylene
C_8		Styrene	Dehydrogenation of ethylbenzene made by alkylation of benzene with ethylene or recovered from refinery reformate
C_9		5-ethyliden-2-nor-bornene	Diels Alder addition of cyclopentadiene and butadiene and isomerization
		alphamethylstyrene	Benzene alkylation with propylene and dehydrogenation
C_{10}		dicyclopentadiene	Obtained by naphtha cracker stream as a monomer or as a dimer

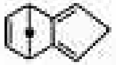
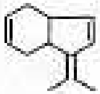
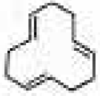
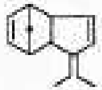
TABLE 2 - SOME LESS COMMON HYDROCARBON MONOMERS

CARBON ATOMS	FORMULA	HOW MADE	CATALYST	CONVERSION %	SELECTIVITY %	REF.	NOTES
	MONOLEFINS						
C_6		2 	$NiCl_2+PR_3+AlR_3$			1	
"		"	$NiCl_2+P(C_6H_{11})_3+AlR_3$		67	1	
"		"	$NiCl_2+PØ_3+AlR_3$	95	75	1	
C_7			Δ	70		2	
C_{10}			$[Pd(ØCH=CH_2)Cl_2]_2$		high	3	
	DIOLEFINS						
C_6		2 	$(Ø_2PC_2H_4PØ_2)Ni(CO)_2$	60	60	4	
"			KOH, Pd, Al_2O_3	95	70-90	5	R = CH_3, C_2H_5
"			CoX_2+AlR_3 $CoX_2+M_1M_2H_4+ROH$	35	100	6 7	M_1 = Na, Li; M_2 = B, Al
"		" "	$RhCl_3 \cdot 3H_2O+ROH$ $NiCl_2 \cdot 2PR_3+AlR_2Cl$		80	8 9	

CARBON ATOMS	FORMULA	HOW MADE	CATALYST	CONVERSION %	SELECTIVITY %	REF.	NOTES
C_6			$FeA_3 + AlR_3 (RMgX)$ $FeCl_3 + AlR_3 + R_2P(CH_2)_2PR_2$ $CoA_3 + AlR_2Cl + R_2P(CH_2)_2PR_2$	40 70 70	90 100 100	10 11 11	A = acac A = acac
″			$RhCl_3 \cdot$ $CoCl_2(\varnothing_2PC_2H_4P\varnothing_2) + AlR_3$		 97	8 12	
″			$FeCl_3 + P\varnothing_3 + AlR_3$	10	35	13	
C_7			$FeA_3 + \varnothing_2PC_2H_4P\varnothing_2 + AlR_2Cl$		75	11, 14	A = acac
″			$(PR_3)_2NiCl_2 + AlR_2Cl$	30	80	15	
″		″ ″	$CoCl_2 + P(OR)_3 + AlR_3$ $FeA_3 + \varnothing_2PC_2H_4P\varnothing_2 + AlR_2Cl$	90	90 85	11 11	 A = acac
″			$RhCl_3$	95	90	16	
″			$CoCl_2 + PCl_3 + AlR_3$	60	83	17	
″		″ ″	$CoCl_2 \cdot (\varnothing_2PCH_2)_2 + AlR_3$	60	high	12	
″			Δ	45		18	
C_8			$NiCl_2–PR_3 + AlR_2Cl$	70	83	15	

CARBON ATOMS	FORMULA	HOW MADE	CATALYST	CONVERSION %	SELECTIVITY %	REF.	NOTES
C_8			$(P\text{Ø}_3)_2Ni(CO)_2$	43	(3:2)	19	
"		2 	$C_5H_5Fe(CO)_2NO$	97	high	20	
"		2 	$Ni(COD)_2+P(OA_r)_3$	100	97	21	
"		"	$(C_3H_5)Ni(PEt_3)_2Cl+MeOH$	50	95	22	
"			FeA_3+Et_2AlOEt	78	100	11	$A =$ acac
"			$FeA_3+\text{Ø}_2PC_2H_4P\text{Ø}_2+$ $+AlR_2Cl$	90	92	11	$A =$ acac
"			$CoCl_2+\text{Ø}_2PC_2H_4P\text{Ø}_2+AlR_3$	37	85	12	
"			" "	40	55	12	
C_9			$Ni^0+P(OAr)_3$	low	high		

CARBON ATOMS	FORMULA	HOW MADE	CATALYST	CONVERSION %	SELECTIVITY %	REF.	NOTES
C_9			Δ (V_2O_5—Al_2O_3)	40-70		23	
C_{11}			$MnA_2 + RMgCl$	20	40	31	A = acac
C_{12}			$FeA_3 + AlR_3$	80	52	11	A = acac
"		3 —≡—	$AlCl_3$	80	70	36	
	TRIOLEFINS						
C_8		2 	$FeCl_3 + PØ_3 + AlR_3$	65	70	24	
"		"	$(PØ_3)_2Pd(C_4H_2O_3)$	85	100	25	
"		"	$Pd(PR_3)_2$	80	92	26	
"		"	$Co(CO)_4 + AlR_3$	60	90	27	
C_9		3 ══	$(PØ_3)_2Ni(CO)_2$	40		28	

CARBON ATOMS	FORMULA	HOW MADE	CATALYST	CONVERSION %	SELECTIVITY %	REF.	NOTES
C_{10}			SeO_2, Al_2O_3	30	-	29	
″		2 	$Zr(\pi C_3H_5)_4 + Al_2Et_3Cl_3$	66	78	35	
C_{11}			$CoA_3 + AlR_3$	50	98	31	
C_{12}			Δ	60	99	30	
″		3 	$MnA_3 + RMgCl$	35	100	32	A = acac
″		3 	$TiCl_4 + AlEtCl_2 + Me_2CO$	90	97	34	
C_{15}			Δ	33	99	30	
C_n				65	95	33	

have been made possible by the progress of organometallic chemistry, and often specificity and yield are excellent.

Table 2 gives only an idea of the manyfold possibilities for synthesis of new or modified SHRs by using less conventional monomers.

3. Polymerization processes

Polymerization processes for production of SHR can be listed as:

i) - emulsion processes
ii) - solution processes
iii) - slurry processes
iv) - bulk processes.

Emulsion processes are performed by emulsifying monomers in water. Polymerization is performed in the presence of catalysts (in particular radical catalysts).

At the end of the polymerization step the rubber emulsion is coagulated in the form of small crumbs by addition of coagulation agents. The crumbs are collected by filtration and then dried and baled.

Of course emulsion processes are not suitable for catalyst systems incompatible with water, such as most ionic catalysts, and in particular with most stereoregulating catalyst systems.

An exception is represented by some rhodium based catalysts, that polymerize butadiene to a high *trans* polymer in water emulsion (7).

The emulsion process is used for the synthesis of the most important SHR, *i.e.* SBR, a styrene butadiene copolymer based on radical catalysts of redox type.

A certain stereoregulation of butadiene addition is obtained also with radical catalysts, by lowering the polymerization temperature (8).

Solution processes are performed by adding a catalyst to a monomers solution, normally in hydrocarbon solvents. The nature of the solvent (aliphatic or aromatic, polar or apolar) has frequently an important effect on the course of polymerization.

Depending on the initial monomer content, on the degree of monomer conversion into polymer and on the polymer molecular weight, the solution viscosity increases and eventually reaches a limit beyond which it is very difficult to handle it for mass and heat transfer problems (polymerization is in general exothermic).

Owing to the fact that a high molecular weight is mandatory for rubber performance, monomer conversion must be stopped to avoid an excessive viscosity when the rubber content in the solution attains a limit of 15-20 wt %.

This fact imposes an expensive recycle of solvents and of unreacted monomers. In the next step the rubber solution is steam stripped or desolventized. After stripping, rubber is obtained in the form of small crumbs that are dried in an air oven or in a mechanical dryer and baled.

In some cases, before the stripping section, also a washing section is provided, in which the rubber solution is washed with water for extracting the catalyst residues that could affect the rubber properties.

In a slurry process, the rubber is partially insoluble in the reaction medium, so that a separation occurs during the polymerization step. This fact is favourable in that the solution viscosity is reduced allowing a higher rubber content to be reached at the end of polymerization.

However, due to the intrinsic sticky nature of many rubbers, rubber separation can involve problems of reactors and equipments fouling.

A slurry process is used for butyl rubber production and, in some cases, for (ethylene co-propylene) polymers and terpolymers.

Bulk polymerization, *i.e.* monomers polymerization in the absence of solvents and of polymerization medium, has a historical background, in that it was used for SHR production till to WW II.

Apparently, apart from some literature and patent quotation, this type of polymerization has not been resumed for SHR production.

However, a reconsideration of bulk polymerization of SHR, by taking advantage of new catalyst systems and equipments, seems to be of interest for simplifying the process and for reducing its energy requirement.

A step in this direction (*i.e.* solventless polymerization processes) has been already taken by the plastics industry.

4. Rubber structure and physical properties

Before dealing with the properties of different SHRS, that will be the subject of the next paragraphs, some elements of rubber physics are necessary in order to understand the relation between properties and structure of SHR.

4.1. PRIMARY PROPERTIES OF SHR

The primary properties of a SHR are:

i) - high elongation (*i.e.* up to 1000%)

ii) - substantial recovery of the initial length upon removal of stress

iii) - retractive force substantially arising from entropy change induced by elongation, at difference with elastic, but non rubberlike, materials.

These properties ask for a structure based on long-chain molecules, possessing many freely rotating links, with weak interactions among different chains except at a few places along their length where they are interlocked to form a three-dimensional network.

The parent macromolecules, from which the network is obtained, are called « primary chains », the network junctions « crosslinks » and the chains between two consecutive crosslinks « network chains ».

When deforming the above mentioned network, e.g. by stretching it, a retractive force builds up, arising from the entropy lowering induced by elongation.

Only a rather small component of force comes from *intra*molecular energy changes.

The entropic component of retractive force springs out from the reduction of the number of possible chain conformations imposed by elongation.

The meaning of the above mentioned facts from the standpoint of elastomer synthesis is that the primary molecular weight should be high (up to 10^6 g/mol), that the high primary molecular weight should not be obtained by branching the chain, that the monomer units should be chosen in order to allow a reasonable rotation of the main chain bonds, that any *inter*molecular interaction (crystallization, for example) should be avoided.

Also the network chain length should be high, so as to preserve the possibility of attaining a high elongation.

In fact the maximum theoretical extension of the network chain is related to the square root of the number of network chain links, that in its turn is inversely proportional to the crosslinking density of the network.

The primary molecular weight (M) should be at least a decade larger than that of a network chain (M_c) in order to avoid an elastically inefficient network to be formed [when $M/M_c = 20$ the efficiency loss is roughly 10% (38)].

The secondary properties (secondary in the sense that they are not always compulsory, and that they are not requested to be present simultaneously at the highest level) of a SHR are:

iv) - high strength

v) - good dynamic properties

vi) - good ageing resistance

vii) - good processability.

4.2. STRENGTH

As to the meaning of strength, tensile strength, tear strength, fatigue resistance, flex cracking resistance, abrasion resistance *etc.* are intended for, depending on the application.

The most studied form of strength, in terms of a property/structure relationship, is monoaxial tensile strength.

Unfortunately, a pure tensile fracture is experienced very seldom in a rubber object.

The ascertained ways for increasing tensile strength by acting on rubber structure (and therefore excluding the action of reinforcing fillers) are:

a) - a decrease of crosslinking density of the network. An adverse effect on elastic recovery and on dynamic properties ensues;

b) - a choice of a rather weak crosslink for building the network. In other words, a crosslink able to creep when over-stressed. The drawbacks are similar to that of point a);

c) - a decrease of chain internal mobility, for example by hindering the rotation of some main chain bonds. The tensile strength is increased through a dissipative viscoelastic process, that, however, is effective only in a narrow range of temperatures or extension rates (40);

d) - the synthesis of a block copolymer able to give rise to hard domains, dispersed in a rubbery phase (40);

e) - the synthesis of a regular molecular structure, amorphous from zero up to a moderate elongation but able to undergo a fast crystallization at high strain.

The last form of reinforcement seems to be the cleverest one, in that crystallization reinforcement is operative only when, and where, the elastomer experiences an overstrain.

In the normal low strain condition the elastomer is amorphous and its dynamic behaviour can outperform that of filler-reinforced elastomers.

However, the requirements in terms of molecular structure for a strain crystallizable SHR are not yet completely clarified and deserve some additional remarks.

A strain induced crystallization involves a transition from amorphous state into a particular crystalline state in which the chains are extended and substantially oriented in the strain direction (extended chain crystalline state) whereas the crystallization in a isotropic (non extended) or nearly isotropic (low extended) states takes place in a folded way (folded chain crystalline state).

The distinction between the two crystalline states is important in that extended chain crystallization is a favourable phenomenon for rubber performance, whereas folded chain crystallization is not.

In fact, extended chain crystallization contributes to rubber reinforcement under strain and eventually to strength, whereas folded chain crystallization causes an indesirable hardening of rubber at low temperature and a (reversible) loss of elastomeric properties.

A « state diagram » including the above mentioned crystalline states and the amorphous state has been theoretically predicted (41) and represented in Fig. 3.

The borderline between amorphous and crystalline extended chain state complies substantially with Flory's equation (42):

$$\frac{1}{T_m^0} - \frac{1}{T_m} = - \frac{R}{2N_u \Delta H_u} F(\alpha)$$

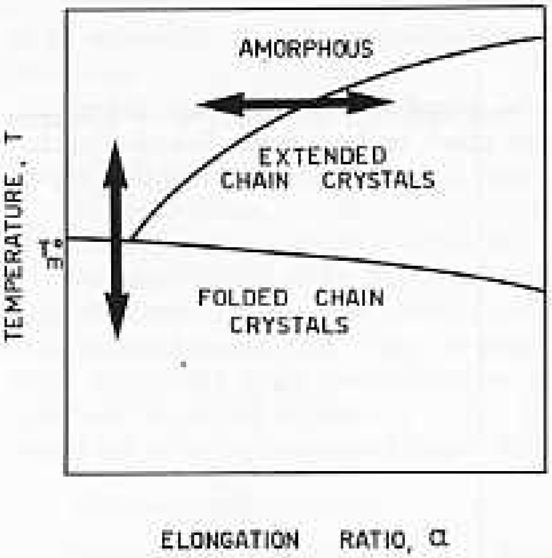


Fig. 3 · «State diagram» of crystallizable SHR. The three areas of diagram represent «amorphous», «crystalline extended» and «crystalline folded» states, in function of temperature and $\alpha = L/L_0$. Orizontal arrow: transition experienced by stretching the rubber at constant temperature. Vertical arrow: transition experienced by cooling the rubber in a low strained, or non strained state. Theoretical calculations according to (41), by assuming $N_c = 100$, $S = 2$, $\Delta H_u = 9.22$ kJ mol^{-1}, $T_m = 273$ K.

where:

$F(\alpha) = \alpha^2 + \dfrac{2}{\alpha} - 3$

ΔH_u = melting enthalpy

N_c = number of monomer units per network chain

α = L/L_0 = elongation ratio

R = gas constant

T_m^o = isotropic melting temperature

T_m = melting temperature under strain.

This equation predicts that the lower is the melting enthalpy, the higher is the effect of strain in increasing the melting point.

The increase of melting point has also a positive effect on crystallization kinetic in that it enhances the nucleation rate (43).

In conclusion, as an indication for the synthesis of improved crystallizable SHRS, a low melting enthalpy seems necessary in order to achieve a fast crystallization upon strain, also at rather high temperature. However, no theoretical predictions as to the structural features for achieving a low melting enthalpy in a macromolecule are available till now. The melting enthalpies and the isotropic melting point of a few crystallizable SHRS are reported in Table 3.

As to the folded chain crystallization, it has been shown that this unfavourable phenomenon can be at least slowed down by controlling the segmental friction (e.g. by a moderate increase of glass point) of the macromolecule (44).

TABLE 3 - THERMODYNAMIC CHARACTERISTICS OF CRYSTALLIZABLE ELASTOMERS

	MELTING POINT (°C)	GLASS POINT (°C)	MELTING ENTHALPY (kJ mol^{-1})	REPEATING UNITS PER SEGMENT
Cistactic polybutadiene (97% *cis*)	+ 11,5	— 102	9,22	2
Cistactic polyisoprene (NR)	+ 28	— 73	4,36	1,5
Poly(*trans* butadiene co-piperylene) (piperylene 22-35% mol)	from + 20 to 0	from — 70 to — 75	form I 6,3-13,8 form II 3,6-4,6	—
Transtactic polypentenamer (85% *trans*)	+ 34	— 95	12	2
Poly(*iso*butylene co-isoprene)	—	— 71	—	—

Data from ref. ([illegible]).

However, a basic research effort also on this important point seems to be opportune, for a better orientation of the synthesis toward improved structures.

Beyond the ascertained influence of strain crystallization on tensile strength, its influence on other forms of strength, such as tear strength, fatigue resistance, flex cracking has been demonstrated.

On the contrary, the abrasion resistance of a rubber does not appear to be related with its ability to crystallize upon strain (45).

We have omitted so far the influence of fillers on strength, in that this type of reinforcement is not directly connected with elastomer structure. It is known however that rubber in almost every application is used in a filled form. We shall limit ourselves only to point out that strength achieved by use of reinforcing fillers, important though it is, does not erases the effect on strength of factors listed above in points from a) to e).

4.3. DYNAMIC PROPERTIES

Dealing now with point iv), *i.e.* dynamic properties of SHR, a comprehensive approach is that of determining some basic viscoelastic parameters of rubber in a range of frequencies and of temperatures by mechanical spectrometry. Within the limit of linear viscoelasticity (*i.e.* small deformation), by applying the method of reduced variables (46) it is possible to extend the evaluation of the above mentioned viscoelastic parameters to a much wider range of temperature or of frequencies.

We shall limit ourselves to a few considerations on some plots of viscoelastic parameters in function of frequency and of temperature, in order to give an idea of their utility in foreseeing some rubber properties.

In Fig. 4 storage modulus (G') and loss modulus (G'') are reported in function of temperature for three different raw elastomers; cistactic polybutadiene, cistactic polyisoprene and a chlorinated butyl rubber.

G' changes with temperature from 10^3 MPa (glassy state) down to less than 1 MPa (rubbery state). G'' shows a peak in correspondence with the transition from glassy to rubbery state. Cistactic polybutadiene shows a lower glass point in respect to the other two elastomers.

Moreover, G' plot tell us that the transition glassy-rubbery state of elastomers with similar glass point (*i.e.* cistactic polyisoprene and chlorinated butyl rubber) can be more or less abrupt in function of temperature. Another point of interest is the singular bulging (see arrow) shown by cistactic polybutadiene, due to a partial crystallization of the polymer. This bulging disappears when the polymer is quenched, or when the cistacticity is decreased.

In Fig. 5 G' and loss factor ($\tan \delta = G''/G'$) are reported in function of frequency for the same raw elastomers. The curves of G' show a zone in which G' in nearly constant (rubbery plateau) included between two zones in which G' increases abruptly with frequency.

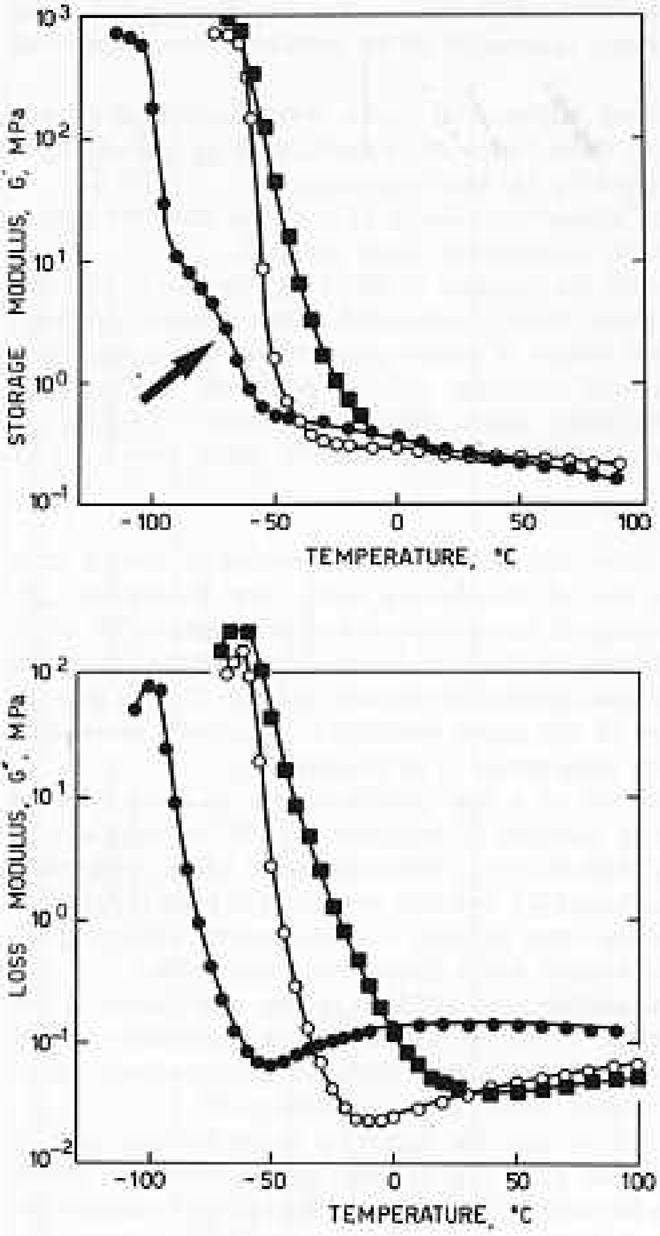


Fig. 4 - Storage and loss moduli in function of temperature. (Mechanical spectrometer, Rheometrics, frequency = 1 Hz). Filled dots: cistactic polybutadiene; void dots: cistactic polyisoprene; squares: brominated butyl rubber.

The height of the rubbery plateau of a raw elastomer is a function of the topological interactions (entanglements) of elastomer chains. Topological interactions of chains are connected with their structure even if this connection has not yet been clarified. Since topological interactions are not connected with glass point (see Table 4) or other customary parameters, their determination (e.g. from rubbery plateau height or other experiments) should be included in every new elastomer evaluation.

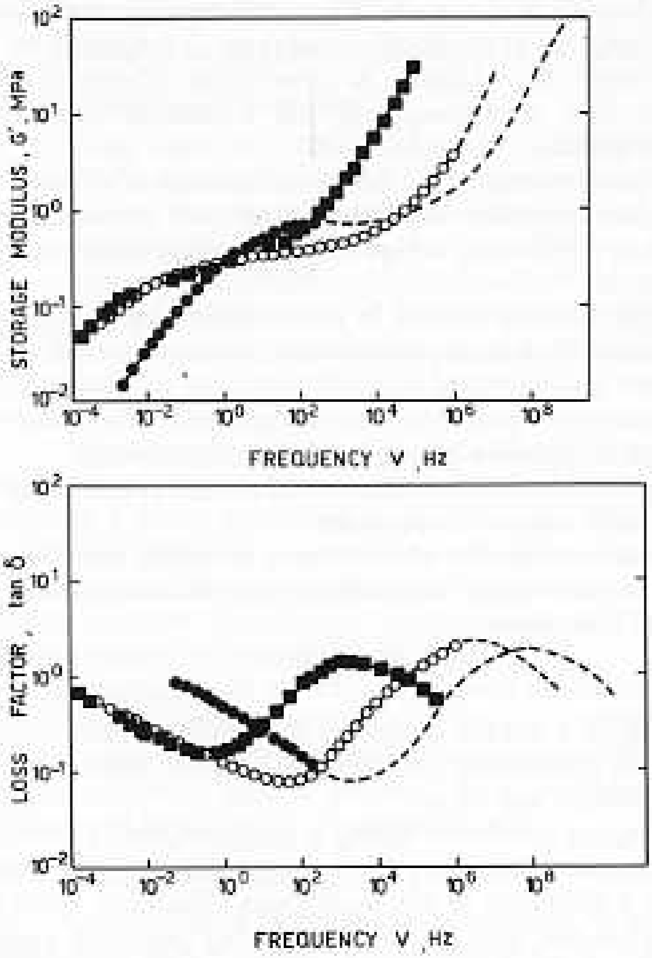


Fig. 5 - Storage modulus and lossfactor in function of frequency. (Mechanical spectrometer, Rheometrics temperature 25 °C). Filled dots: cistactic polybutadiene; void dots: cistactic polyisoprene; squares: brominated butyl rubber.

TABLE 4 - GLASS POINTS AND TOPOLOGICAL INTERACTION OF SOME POLYMERS

	M_e	Tg(K)
Poly(ethylene)	4 000	148
Poly(ethylene co-propylene) (56/44 mol)	4 000-7 000	~ 213
Cistactic polybutadiene	7 000	171
Cistactic polyisoprene	14 000	200
Poly(isobutylene)	17 000	202
Polydimethylsiloxane	29 000	146
Polystyrene	35 000	373

The table shows that there is not correlation between M_e (molecular weight between two consecutive entanglements) and Tg.

Data from ([illegible]) and ([illegible]).

As to the zones in which G' increases abruptly with frequency, the low frequency zone is the « flow zone ». Its position and shape is important for elastomer processing. When the elastomer is cross-linked (chemical or physical cross-links) the flow zone disappears and transforms into an extension of the rubbery plateau.

The abrupt high frequency zone of G', likely the maximum of $\tan \delta$, is connected with the glass transition (as already mentioned, temperature and frequency are interconvertible and a high frequency corresponds to a low temperature).

From the height of the rubbery plateau in the G'/frequency plot, the lower topological interaction of cistactic polyisoprene in respect to cistactic polybutadiene is inferred.

Several additional elastomer properties can be desumed from viscoelastic parameters plotted in function of temperature and frequency.

Among others, the rubber coefficient of friction and the gas permeability can be desumed in a suitable zone of frequencies.

However, other dynamic properties of elastomers in which viscoelasticity exceeds a linear behaviour (high deformation, crystallization) should be determined by specific experiment.

4.4. AGEING RESISTANCE

The ageing resistance of a rubber [point v) of paragraph 4.1] encompasses a large range of phenomena such as oxygen, ozone, light, heat, corona effect resistance, fatigue and so on.

In general, the resistance of a rubber to ageing is connected with a structure in which the unsaturations (necessary for rubber vulcanization with sulphur) are reduced to a minimum in the main chain. An even better resistance is obtained when the main chain is completely saturated and the unsaturations are situated, when present, in side groups. Also the case of unsaturated cycles inserted in the main chain has been studied: in this case the « invulnerability » of rubber to, for example, ozone, is due to the fact that the unsaturation is by-passed by a saturated chain.

In considering ageing resistance one should take into account not only the chain resistance, but also the cross-links resistance. A carbon-carbon bond, obtained by a peroxide cure or by radiation is stronger than a monosulphidic bond (efficient cure), and the last is stronger than a disulphidic bond.

At a very high temperature, in the presence of oxygen, also the higher tendency of tertiary carbon atoms to form hydroperoxides (and eventually to chain scission) in respect to secondary and primary carbon atoms is to be considered. Of course, the ageing resistance is improved by suitable additives (antioxidants, antiozonants, antifatigue, antimetal additives) but the intrinsic resistance of the molecular chain to environment is not erased by the addition of any antiageing chemical.

4.5 PROCESSABILITY

Rubber processability is connected with several interrelated factors.

4.5.1. *Rheological behaviour*

Among these, rheological behaviour of the viscoelastic material, represented by a raw elastomer or its compounds, controls the resistance to deformation, the energy consumption for imposing a flow and the elastic recovery that follows a deformation or a flow.

A viscoelastic behaviour is beneficial, unlike a pure viscous one, for achieving a good dispersion of fillers and additives in the rubber.

Owing to the large deformations generally imposed by processing, a large-strain or non linear theory of viscoelasticity must be applied in several cases.

The customary measure for evaluating elastomer processability is its bulk shear viscosity, and in particular the Mooney viscosity. In order to achieve a better prediction of processability and, moreover, to get some indication as to the structural features influencing processability, Mooney viscosity can be implemented with measurements of shear viscosity in a wide range of shear rates, measurements of transient shear viscosity, measurements of elongation viscosity.

The elasticity of the raw rubber and its connection with structure can be evaluated by topological interactions (see paragraph 4.3) and by maximum relaxation time (4) that are connected with elastic memory (maximum relaxation time is desumed from relaxation times spectrum $H(\tau)$, calculated by G' or G'' of paragraph 4.3).

4.5.2. *Ultimate properties*

A second factor of paramount importance for processing is the ultimate properties of raw rubber or its compounds. In other words, the cohesion of rubber during processing should be sufficient to bear the stresses imposed by the rheological conditions of process without fracturing. In fact a material that fractures tears or crumbles is unprocessable.

The structural features governing the ultimate properties of a raw elastomer are some of those already indicated for vulcanized rubbers [points c) and e) of paragraph 4.2]. In particular, strain induced crystallization has an outstanding favourable effect in increasing the ultimate properties of a raw rubber during processing. The « green strength » obtained by a crystallization mechanism is of particular importance for some particularly demanding rubber processes (e.g. radial tyres).

5. Synthesis and properties of SHRs

From the considerations made so far on the importance of the role of crystallization on elastomer processing and properties, and on the importance of stereospecific catalysis in supplying regular structures able to undergo a strain induced crystallization, the opportunity stems out of classifying SHRS as follows:

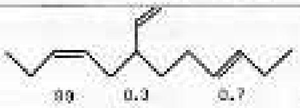
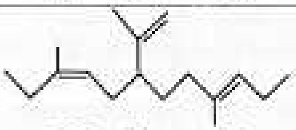
i) - amorphous SHRS: amorphous and monophasic both in unstretched and stretched state;

ii) - crystallizable SHRS: amorphous and monophasic in unstretched state, show crystalline domains in an amorphous matrix upon stretching;

iii) - biphasic SHRS: show a hard (glassy or crystalline) phase in an amorphous matrix both in unstretched and stretched state.

The last SHRS are particular block copolymers (thermoelastomers) that will be described later on.

TABLE 5 - CRYSTALLIZABLE HYDROCARBON SYNTHETIC RUBBERS

	ACRONYM	STRUCTURE (% MOL)	NOTE
Cistactic polybutadiene	BR	 99 0.3 0.7 98 0.5 1.0 97 1.0 2.0 94 4.0 2.0	U catalyst Nd catalyst Co, Ni catalyst Ti catalyst
Cistactic polyisoprene	IR	 96.0 3.5 0.5 92.5 6.0 1.5	Ti catalyst Li catalyst
Transtactic polypentenamer	TPA	 85 15	W catalyst
Poly(trans butadiene co piperylene)		 70 20 10	V catalyst
Transtactic polybutadiene and related styrene copolymers		 79 7 14	Ba catalyst
		 75 4.5 13.5 5	Ba catalyst
Poly isobutylene			

5.1. CRYSTALLIZABLE SHR

Several crystallizable SHRS, both commercial or experimental, are listed in Table 5. These SHRS are characterized by the fact that their structural regularity allows a strain crystallization to be obtained, at least in certain conditions of strain and temperature.

As it can be inferred from the table, there are different ways as to obtain crystallizable SHRS.

The first one is based on regular (tactic) homopolymers. By using different catalyst systems it is possible to obtain small changes of tacticity, and hence of melting point. These small changes have an important effect on SHR properties.

The second one is based on high melting point, tactic structures in which suitable comonomer units have been placed in order to decrease the melting point down to near room temperature.

The third one is based on regular alternating copolymers, which can be considered as new regular homopolymers in which repeating units are composed of a couple of different monomers.

5.1.1. *Cistactic polybutadienes*

Cistactic polybutadienes of different tacticity are obtained with Ziegler-Natta catalyst systems (Table 6).

TABLE 6 - CATALYST SYSTEMS FOR CISTACTIC POLYBUTADIENES

	CATALYST SYSTEM	SOLVENT	*cis* %
3*d* block	$TiJ_4 + AlR_3$ $TiJ_2Cl_2 + AlR_3$ $TiCl_4 + AlR_2J$ $TiCl_4 + AlJ_3 + AlR_3$	aromatic	92-95
	$CoCl_2py + AlR_2Cl$ $Co(acac)_2 + AlR_2Cl$ $CoCl_2 + AlR_2Cl$ + activator $CoCl_2 + AlCl_3$ + thiophene $Co(acac)_2 + AlHCl_2.B + AlBr_3$	aromatic	97
	$Ni(COOR)_2 + AlR_3 + BF_3$ $Ni(COOR)_2 + AlR_2F + TiCl_4$	aromatic or aliphatic	97
4 and 5*f* block	$Ce(COOR)_3 + AlR_3 + AlRX_2$	aliphatic	98
	$Nd(OR)_3 + AlR_3 + AlRX_2$ $Nd(COOR)_3 + AlR_3 + AlRX_2$	aliphatic	98
	$U(allyl)_3X + AlRX_2$ $U(OR)_4 + AlR_3 + AlRX_2$	aliphatic	99

Note: X = halogen.

Catalyst systems are characterized by the transition element used; however, other factors such as the ligands nature, the co-catalyst, the presence of Lewis bases or acids, the polymerization medium (aliphatic or aromatic hydrocarbon) have a paramount importance on the activity and specificity of a catalyst system.

Among the catalyst systems listed in Table 6 the ones based on titanium, cobalt and nickel have been applied in commercial production of rubber.

The systems based on cerium have been abandoned for the adverse effect of this metal on the elastomer ageing.

Also the newest catalyst systems are based on transition elements of the *f*-block of periodic table [*i.e.* neodymium ([illegible]) and uranium ([illegible])]. Neodymium, unlike cerium, has not a variable electronic structure (due to possibility of the inner 4*f* level electrons of the last element to occupy a valence electronic level). Therefore both neodymium and uranium ar not objectionable for promoting rubber oxidation. A peculiarity of catalysts based on *f*-block elements is their extremely high stereospecificity in butadiene polymerization. The high stereospecificity is maintained in spite of rather wide temperature variations and is practically independent on the nature of halogen ligand (see Table 7).

TABLE 7 - DEPENDENCE OF POLYBUTADIENE CISTACTICITY (%) ON THE NATURE OF HALOGEN LIGAND FOR DIFFERENT CATALYST SYSTEMS

	TRANSITIONAL METAL	HALOGEN				
		F	Cl	Br	I	Ref.
3d-block	Ti	35	75	87	93	([illegible])
	Co	93	98	91	50	([illegible])
	Ni	98	85	80	10	([illegible])
4 and 5f block	Ce	97	98	98	98	([illegible])
	Nd		98	98	98	(*)
	U		98,4	98,5	98,5	([illegible])

(*) Unpublished data of our laboratories.

Melting points of polybutadienes obtained with catalyst systems based on different transition metals are reported in Table 8.

Catalyst systems described so far are very active in promoting butadiene polymerization, and the transition metal content in the final rubber (in absence of a washing step) ranges from some ten to some hundred ppm.

A particularly useful peculiarity of the *f*-block catalysts is that the

TABLE 8 - MELTING POINT AND HALF-CRYSTALLIZATION TIMES OF CISTACTIC POLYBUTADIENES

CATALYST TRANSITION METAL	1,4 *cis* %	MELTING POINT (°C)	HALF CRYSTALLIZATION TIME (min.)
U	99	+ 2,2	5
Ni	97	— 1,0	30
Co	97	— 3,0	40
Ti	94	— 8,0	900-5 000

Data from ref. ([illegible]).
Crystallization temperature: — 20 °C.

polymerization can be performed in aliphatic solvent, that are safer than aromatic ones.

As to the elastomer properties, it has been observed that also relatively small increases of tacticity have a substantial effect on processability, tack, green strength and other valuable characteristics of the elastomer in a raw state (Table 9) ([illegible]).

TABLE 9 - TACTICITY AND PROCESSABILITY OF POLYBUTADIENES

CATALYST SYSTEM		Li	Ti	Co	Ni	U
1,4-*cis* %			94	97	97	99
Mill processability (raw elastomer)	25 °C	B	G	G	G	G
	40 °C	B	F	G	G	G
	60 °C	B	B	F	G	G
	75 °C	B	B	B	F	G
Mill processability (black stock)	25 °C	B	G	G	G	G
	40 °C	B	F	G	G	G
	60 °C	B	B	F	F	G
	75 °C	B	B	B	F	F
Tackiness (kg/cm^2)	—	—	1,5	2	2	3

G = good F = fair B = bad

Data from ref. ([illegible]).

Also the elastomer properties after vulcanization are favourably affected by an increase of cistacticity.

Tensile strength and elongation at break of cross-linked, unfilled polybutadienes of different tacticity are reported in function of cross-linking density in Fig. 6 and of temperature in Fig. 7. Similar improvements due

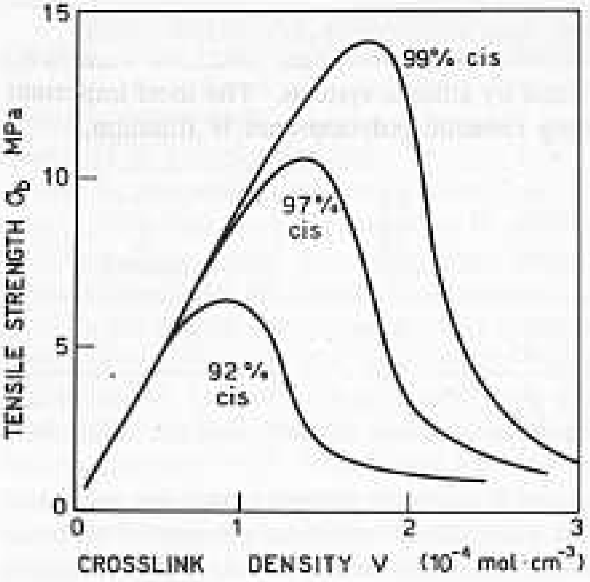
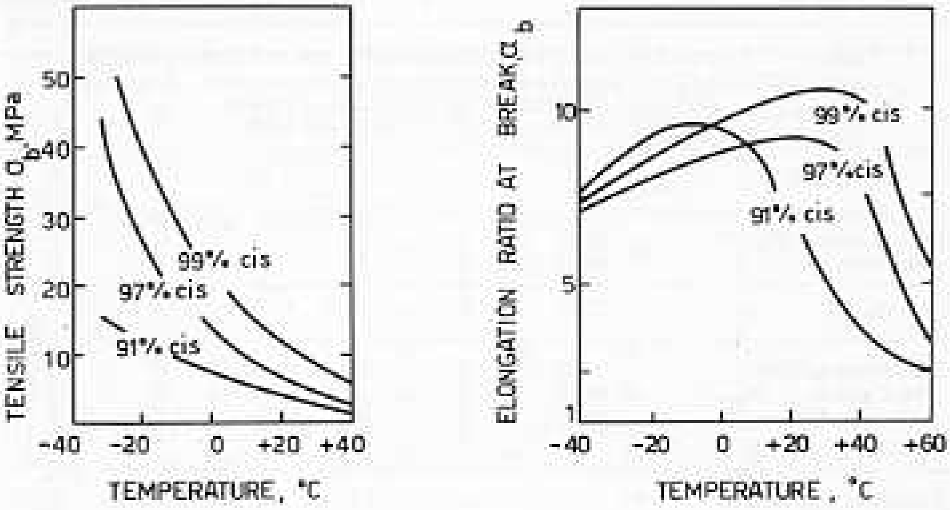


Fig. 6 (on the left) - Tensile strength of cistactic polybutadienes of different tacticity in function of crosslinking density. Pure gum vulcanizates.

Fig. 7 (below) - Tensile properties of cistactic polybutadienes of different tacticity in function of temperature. Pure gum vulcanizates. Crosslinking density 1.10^{-4} mol cm^{-3} for all samples.



to tacticity are noticed also when the elastomers are reinforced with fillers.

A certain susceptibility of cistactic polybutadienes to undergo a crystallization at low temperature in isotropic (*i.e.* unstrained) state has been found. This susceptibility is higher in respect to natural rubber and cistactic polyisoprenes.

The first experimental production on an industrial scale of extremely high cistactic polybutadienes based on *f*-block elements has been performed by ANIC of Italy in 1980. The catalyst has been developed by the Author and his associates.

5.1.2. *Cistactic polyisoprenes*

Cistactic polyisoprenes of different tacticity are obtained both with Ziegler-Natta catalyst systems and by anionic systems. The most important transition element for obtaining cistactic polyisoprenes is titanium.

On this element are based the catalyst systems for commercial production of highly cistactic polyisoprene, in conjunction with aluminum alkyls (51), or with aluminum hydride derivatives (52).

Other transition metals suitable for obtaining highly cistactic polyisoprenes are the *f*-block elements, *i.e.* some lanthanides and uranium (53). These catalyst systems have not been commercialized till now.

A cistactic polyisoprene, with a somewhat lower tacticity in respect to Ziegler-Natta catalysts is obtained by anionic catalysts, such as lithium alkyls.

In Table 10 some typical catalyst systems, used for production of cistactic polyisoprenes are reported.

TABLE 10 - CATALYST SYSTEMS FOR CISTACTIC POLYISOPRENES

CATALYST SYSTEMS	SOLVENT	MICROSTRUCTURE %			
		cis	*trans*	1,2	3,4
1) - $TiCl_4 + AlR_3$ + anisole + CS_2	aliphatic	96,0	0,5	—	3,5
2) - $TiCl_4 + (HAlN\text{-}i\text{-}C_3H_7)_6$	aliphatic				
3) - Li alkyls	aliphatic	92,5	1,5	—	6,0

$(HAlN\text{-}i\text{-}C_3H_7)_6$ or hexa(*iso*propyliminoalane) is a cage-structured compound (52), obtained by reacting aluminum and *iso*propylamine in the presence of hydrogen and of a catalyst.

In spite of the fact that a lower cistacticity has an unfavourable effect or rubber processability and properties, likewise to cistactic polybutadienes, in favour of anionic catalysis stands the absence of transfer and termination reactions. The molecular weight of rubber can be increased virtually at will, without facing problems of long branching or gel formation. In comparison with cistactic polybutadiene, a polyisoprene process has to deal with very severe chemical and technological problems.

Apart from the above mentioned importance of reaching the highest cistacticity, a cistactic polyisoprene should be synthesized at the highest molecular weight (at difference with cistactic polybutadiene, whose molecular weight has a upper limit due to processability), avoiding any long branching formation.

At equal molecular weight the more linear are the chains and the narrower is the MWD, the better are the dynamic properties of the network, at equal cross-linking density.

For the above considerations a polyisoprene process is designed in order to produce a very high molecular weight and linear product (and hence to deal with very viscous solutions).

The suitable molecular weight for a correct compromise between processability and properties is then obtained by the customer by mechanical degradation. In fact, at difference with cistactic polybutadiene, cistactic polyisoprene is easily degraded by mechanical break-down, whose characteristic is that of breaking preferentially the longer chains and furthermore to break them in the middle. The resulting MWD is therefore very different from the one obtained by regulating the molecular weight during the synthesis.

The above requirements of high cistacticity, high molecular weight, low branching, low gel, low oligomer content are in a good deal solved by a careful control of the catalyst system, that in some cases is based on a complex catalyst mixture [see 1) of Table 10] and in other cases on a single, well defined co-catalyst [see 2) of the same Table]. On the last catalyst, developed in our laboratories, is based the Snamprogetti process (10).

A last but nonetheless important point for a cistactic polyisoprene process is the control of the catalyst residues, in relation to the well known sensitivity of cistactic polyisoprene (natural and synthetic) to certain metal poisons.

As to the properties of cistactic polyisoprenes, cistacticity affects, likewise cistactic polybutadienes, both processability and properties. In the case of cistactic polyisoprenes the effect of tacticity is even more important, in that it allows very high mechanical properties, also in the absence of reinforcing fillers, to be reached.

Some mechanical properties of different cistactic polyisoprenes in function of crosslinking density and of temperature (4) are reported in Fig. 8 and Fig. 9.

They show that, also at a rather low level of tacticity, polyisoprene is able to crystallize upon stretching, as shown by the high value of tensile strength attained by the peak of the 92.5% cis polymer shown in Fig. 8. However, the narrow range of cross-linking densities in which such high tensile strength is obtained and the rather low temperature beyond which the polymer behaves as amorphous, stand for as serious limits in the performance of a « low » cistactic polyisoprene.

Also in the raw state a « low » cistactic polyisoprene shows inferior processability, tack, green strength in comparison to high cistactic polyisoprenes. This behaviour matches that of cistactic polybutadienes, in function of tacticity.

Another interesting property of cistactic polyisoprene, not connected with crystallization, is its low tendency to entangle. As pointed out in chapter 4, this fact is relevant for achieving good dynamic properties and good processability.

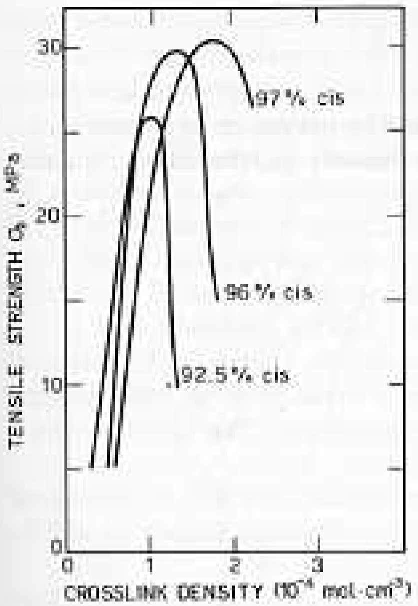
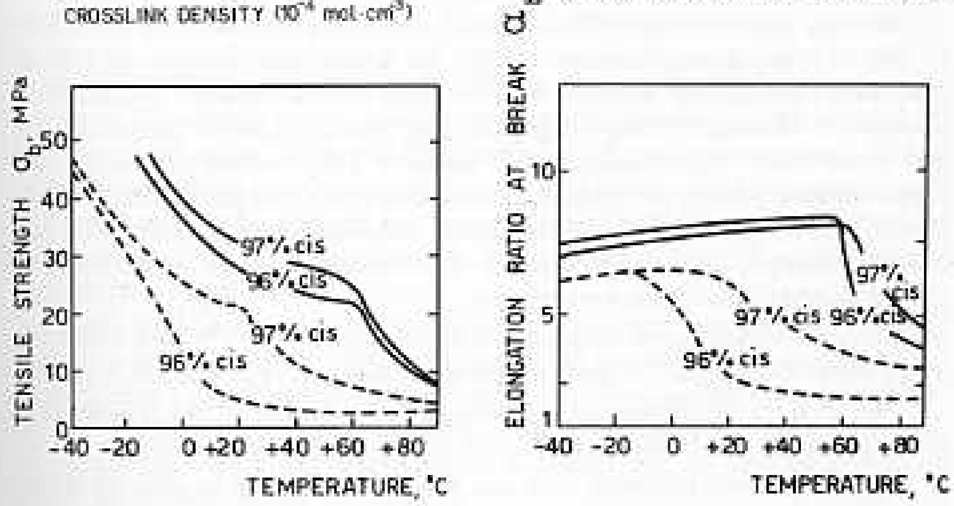


Fig. 8 (on the left) - Tensile strength of cistactic polyisoprenes of different tacticity in function of crosslinking density. Pure gum vulcanizates.

Fig. 9 (below) - Tensile properties of cistactic polyisoprenes of different tacticity in function of temperature. Pure gum vulcanizates. Crosslinking densities: solid line 97% cis: $1.6 \cdot 10^{-4}$ mol cm^{-3}. Solid line 96% cis: $1.4 \cdot 10^{-4}$ mol cm^{-3}. Dotted lines 97% and 96% cis: $2.1 \cdot 10^{-4}$ mol cm^{-3}.



5.1.3. *Transtactic polypentenamers*

*Trans*tactic polypentenamers are obtained with particular Ziegler-Natta catalyst systems based on tungsten or molibdenum, that are able to open the cyclopentene ring (53). Various schemes have been put forward as to the mechanism of ring opening polymerization, that has been generalized to many cycloolefins. Unlike other addition polymerizations the polymerization enthalpy of cyclopentene is very low, as suggested by the fact that the total number of single and double bonds does not change during polymerization. The rather small negative polymerization enthalpy comes from the release of ring tension that is still present in cyclopentene.

Since the polymerization entropy of cyclopentene is negative, likewise most addition polymerizations, the only driving force toward polymer formation comes from the said ring tension, and the ceiling temperature (the maximum temperature at which polymerization is possible) is rather low.

The polymerization process can be performed in solution or in bulk. In order to increase conversion and polymerization rate, an activator in the catalyst system is necessary. Particular care is needed in order to avoid side cationic reaction, and to control the isomerization from *trans* to *cis* of the double bonds of the chain. A certain presence of *cis* double bonds is however necessary for reasons that will be explained later.

The molecular weight of the polymer can be controlled by addition of non-cyclic olefins during polymerization or by addition of small quantities of water, that is claimed to have a beneficial effect also on MWD and hence on processability.

As to the properties of *trans* polypentenamer, they are in agreement with those one should expect from some thermodynamic properties of this polymer.

Melting point is higher than that of cistactic polybutadiene and close to that of cistactic polyisoprene (Table 3). Glass point is close to that of cistactic polybutadiene and much lower than that of cistactic polyisoprene (Table 3). Melting enthalpy is higher than that of cistactic polybutadiene and much more higher than that of cistactic polyisoprene (Table 3). As a consequence, from the considerations made in chapter 4, this crystallizable SHR should show a high tendency to crystallize at low temperature, also in isotropic (unstretched) state. In a stretched state, crystallization should depend heavily on temperature.

The above facts have been confirmed by experiment (34) and stand for as the main limitations for *trans* polypentenamer in its application as a SHR.

The high crystallization rate of *trans* polypentenamer at low temperature is shown in Fig. 10 in comparison with other elastomers.

The above crystallization rate can be decreased by lowering the transtacticity of the polymer, but this is obtained to the detriment of mechanical properties.

In fact, a compromise has been found by setting the *trans* content at approximately 85%.

In conclusion, *trans* polypentenamer shows the same drawbacks, albeit in a larger extent, of cistactic polybutadiene in comparison to cistactic polyisoprene. This fact and the doubtful monomer availability and cost have held back the rubber producers till now from synthesizing on a commercial scale this interesting crystallizable rubber.

As to other crystallizable polyalkenamers (and particularly those with more than 5 carbon atoms in the cycle), the reader is directed to specialized publications in this field (35).

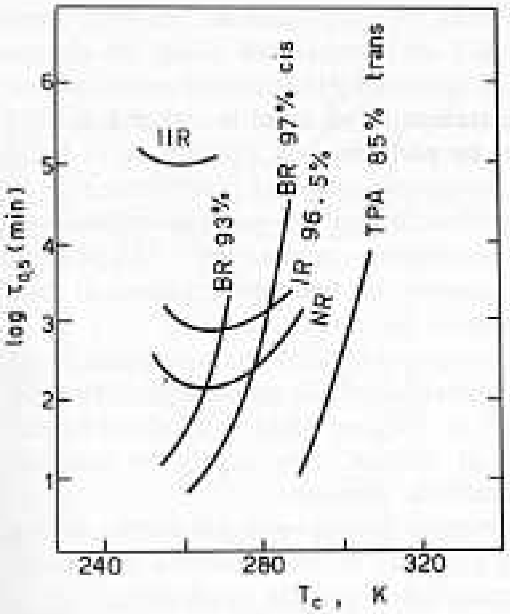


Fig. 10 - Semicrystallization time in function of crystallization temperature for different SHR. BR = cistactic polybutadiene (tacticity as indicated); IR = cistactic polyisoprene; NR = natural rubber; TPA = transtactic polypentenamer; IIR = poly(isobutylene co-isoprene).

5.1.4. *Poly(trans butadiene co-piperylene)*

Some interesting properties of *trans* polypentenamer, such as its very high green strength, attracted the attention of some researchers of our laboratory, looking for an improvement of this property, in connection with the widespread adoption of the radial tyre technology in the last years, but looking also for a more straight and economic way of synthesizing a high green strength SHR.

They found eventually a possibility of reaching this aim by resuming former work (55) on the copolymerization of butadiene, in *trans* configuration, with 1,3-pentadiene (piperylene). On the grounds of the improvements obtained in the synthesis and in the properties of the copolymers, poly(*trans*-butadiene co-piperylene) now stands for as one of the more viable high green strength SHRs (56).

The principle of the approach for obtaining crystallizable rubbers from transtactic polybutadiene structures is based on the well known Flory's equation

$$\left(\frac{1}{T_m}\right)_c = \left(\frac{1}{T_m}\right)_h - \frac{R}{\Delta H_u} \ln X_A$$

where

$(T_m)_c$ = copolymer melting point
$(T_m)_h$ = homopolymer melting point
ΔH_u = melting enthalpy
X_A = mole fraction of parent polymer

that predicts a lowering of melting point of a crystallizable polymer, when non co-crystallizable comonomer units are interspersed along the chains.

It is outside the scope of this work to consider the cases of a non random comonomer distribution and the possibilities of insertion of the foreign comonomer within, or outside, the crystal lattice.

It is only necessary to say that piperylene, or better piperylene units in certain configuration, are able to decrease the melting point of a transtactic polybutadiene from 145 °C down to ambient temperature. The absence of crystallinity in the vulcanized, isotropic or moderately extended, state is of course an unavoidable requirement for rubber elasticity.

The catalyst systems used for poly(*trans*-butadiene co-piperylene) are based on vanadium chelates and aluminum alkyl halogenides [also titanium catalysts have been later reported (7)]. Polymer yield is excellent (under 3.5 mol of transition metal per ton of rubber). Any copolymer composition can be obtained without any particular problem.

The reactivity of piperylene is higher than that of butadiene, during their copolymerization. The melting point can be easily tailored by controlling the copolymer composition in compliance with the application.

The process can be in solution (aromatic hydrocarbons) or in bulk. Only the *trans* isomer of piperylene is polymerized (stereoelective polymerization). The *cis* isomer and isoprene behave as diluents.

Even cyclopentadiene acts only as a moderate poison in this polymerization, at difference with polyisoprene. Therefore, also some C_5 cuts can be used as comonomers without any difficult and expensive separation problem.

As far as the economics of the process are concerned, they depend on the availability of suitable C_5 cuts. It should be pointed out that the more interesting copolymer compositions for obtaining crystallizable SHR, need only 30% wt of piperylene, the remaining being butadiene. Therefore, at difference with polypentenamers, only 1/3 in wt of C_5 monomer is requested and, moreover, the comonomer is obtained merely by extraction and does not need any further chemical transformation.

The process has not been commercialized till now. It has been tested successfully in a pilot plant scale in our laboratory with C_5 cuts of different sources.

As to the properties, beyond the above mentioned excellent green strength (Fig. 11), also tack and other valuable processing properties show the beneficial effect of strain induced crystallization. Particularly interesting are the blends with synthetic cistactic polyisoprene, in order to achieve a synergism of properties: poly(*trans*-butadiene co-piperylene) improves the green strength of synthetic cistactic polyisoprene and the last one imparts to the blend its unique ability to crystallize also in adverse conditions (high strain rates, high temperatures).

Among the others valuable characteristics of poly(*trans*-butadiene co-

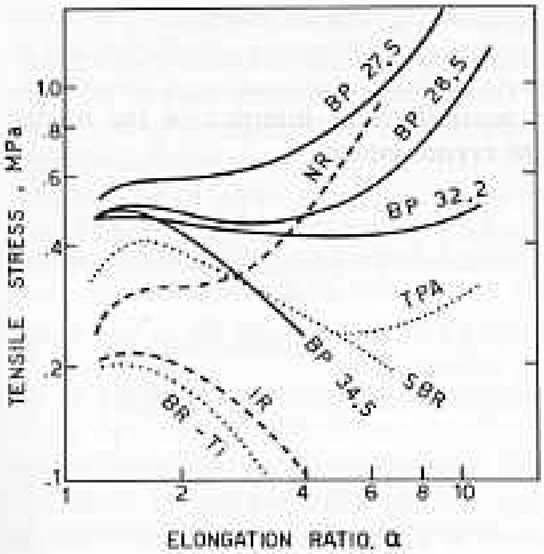


Fig. 11 - Green strength of crystallizable elastomers. Stress strain curves of uncured elastomers compounded with 35 phr SRF carbon black. BR-Ti = cistactic polybutadiene (93% cis, ML(1+4): 63); IR = cistactic polyisoprene (96% cis, ML(1+4): 41); NR = natural rubber (SMR 5, ML(1+4): 47); SBR = 1500 type (ML(1+4): 52); TPA = transtactic polypentenamer (85% trans ML(1+4): 96); BP = poly(transbutadiene co-piperylene). Piperylene content (mol) shown in brackets, ML(1+4): 87, 79, 73, 77 in order of increasing piperylene content. Data from ref. (96).

piperylene) is the fact that the non co-crystallizing piperylene units increase the glass point of transtactic polybutadiene (which is close to that of cistactic polybutadiene) and, as a consequence, the skid resistance of the copolymer is improved in respect to cistactic polybutadiene.

5.1.5. *Transtactic polybutadienes and their styrene copolymers*

Independently from what has been said in point 5.1.4, other research groups tried to obtain useful, high green strength rubbers from transtactic polybutadiene structures. Crystallizable elastomers have been obtained both by transtactic polybutadiene homopolymers and by poly(*trans*-butadiene co-styrene). In the last case, the copolymers were random and the styrene content for obtaining the best results ranged approximately between 2.5 and 7.5 mol % (107).

The catalyst system was based on a complex of barium alkoxides, water and butyl lithium.

The 1,2- content obtained with the above catalyst system was about 1/3 of that obtained with alfin catalysts.

In respect to a butyl lithium catalyst, operating in hydrocarbon solution, the cistacticity is lowered from 35% to 14%.

A typical microstructure of homo and copolymers of butadiene obtained with the barium based catalyst system is given in Table 5.

The polymerization process is done in aromatic hydrocarbon solution and gives a very broad MWD. A rather low polymerization temperature (22 °C) is necessary for reaching the highest (80%) transtacticity.

As to the properties of the rubber, they appear to be close in some respect to those of (*trans*-butadiene co-piperylene) polymers described in paragraph 5.1.4.

5.1.6. *(Trans-butadiene co-monoolefin) alternating polymers*

Regular macromolecular structures, potentially interesting as crystallizable SHRS, can be obtained by alternating copolymerization of two different monomers or by polymerization of the same monomer in two alternate configurations (equibinary polymers). An alternating copolymerization allows a new chain, *i.e.* composed of new repeating units, to be obtained. The repeating unit can be composed for example of subunit couples such as: ethylene-*trans*-butadiene, propylene-*trans*-butadiene, *cis*-butadiene-*trans*-butadiene.

In the first two cases, the repeating unit encompasses six carbon atoms whereas in the last one up to eight carbon atoms.

Therefore, the repeating unit length is well above that obtained in the customary 1,2 or 1,4 addition.

Other possibilities for increasing beyond four carbon atoms the repeating unit length, are offered by ring opening polymerization of cycloalkenamers with 5 or more carbon atoms in the ring (see paragraph 5.1.3) or by the 1,6 addition of conjugated trienes.

However, alternating polymerization is particularly interesting in that it allows the above said new repeating units to be obtained also from relatively abundant and cheap monomers.

In the last ten years, two alternating structures have attracted particular attention as possible new SHRS. They are poly(*trans*-butadiene co-ethylene) and poly(*trans*-butadiene co-propylene). Of course, many other structures can be synthesized, provided that a suitable catalyst system is found.

Both the above mentioned copolymers are not synthesizable via ring opening polymerization, in that cyclohexene ring is refractory to this reaction.

Poly(*trans*-butadiene co-ethylene) is crystalline also at rather high temperature, so that it cannot be used as a SHR, unless transtacticity, or alternation degree, are reduced to a certain extent.

Poly(*trans*-butadiene co-propylene) has been more thoroughly studied up to a pilot plant scale (58). The catalyst is a modified Ziegler-Natta catalyst based on vanadium or titanium (59). It is characterized by the fact that the transition metal component and the aluminum alkyl derivative are reacted at a very low temperature (— 70 °C) in order to give a suitable catalyst. The presence of halogens as ligands and carbonyl compounds are claimed as necessary in order to enhance the catalyst activity and the polymer molecular weight. It seems that the polymerization proceeds through an alternating coordination of each monomer to the catalyst centre.

The alternation degree is very high (more than 79%). Termination occurs preferably at a propylene terminal unit by hydrogen beta elimination. Also the polymerization should be carried out at low temperature somewhat to prejudice of polymerization rate and yield.

The ability of this alternating polymer to crystallize upon stretching is not clearly demonstrated and in a recent publication ([illegible]) the crystallization of this polymer in a unstretched state has been ruled out. However, some characteristics such as green strength, mechanical properties and x ray pattern seems to indicate ([illegible]) the possibility of an effect of the polymer regularity in the degree of chains orientation in a vulcanized, stretched sample.

The glass point is low (— 74.5 °C). The cure rate is slower in respect to conventional diene rubbers, as expected by the lower unsaturation content. The aging resistance is improved accordingly.

5.1.7. *Polyisobutylene*

Poly*iso*butylene is the first man made crystallizable SHRs. It is practically not crystallizable in the isotropic state. However, it undergoes a ready crystallization upon stretching. In order to stretch the chains, a network is necessary however and this, in its turn, requires a certain amount of unsaturation, provided, for example, by a diene comonomer. In fact a peroxide cure of poly*iso*butylene is not possible and a sulphur cure requires such an unsaturation (see paragraph 5.2.4). Notwithstanding the above mentioned good characteristics as a crystallizable SHRs, poly*iso*butylene crystallization is very sensitive to the comonomer content, so that it behaves as an amorphous rubber beyond a certain content of comonomer units. Moreover, the strain crystallization of poly*iso*butylene vanishes at rather low temperature.

We shall deal with amorphous *iso*butylene copolymers in the next chapter.

5.2. AMORPHOUS SHRS

Amorphous SHRs are unable to crystallize both in the isotropic and strained state. The structure of amorphous rubbers is generally irregular but also cases of regular, yet substantially amorphous structures are known (e.g. isotactic polyhexene-1).

An homopolymer can be irregularly structured for constitutional irregularities (head-tail and tail-head addition of monomer, 1,2 addition and 1,4 addition *etc.*) for geometric irregularities (random presence of *cis* and *trans* units) or for stereo irregularities (irregular sequencies of asymmetric carbon atoms in the chain).

Another way for obtaining irregular structures is based on the random copolymerization of two or more monomers.

As it has been said in chapter 4, a way for improving the mechanical properties of an amorphous rubber (in both vulcanized and unvulcanized state) is that of decreasing the chain mobility, by hindering the rotation of some main chain bonds. This can be achieved, for example, by inserting in the chain monomers with bulky side groups.

The mechanical properties (e.g. tensile strength) can be improved in this way, by a mechanism of viscoelastic reinforcement at least in a range of temperatures and strain rates.

However, this type of reinforcement is not sufficient in the absence of reinforcing fillers.

The description of the action of this extremely important component of a rubber recipe is outside the scope of this work.

It is only necessary to say here that an amorphous rubber is so weak, that its practical application would be impossible without reinforcing fillers.

It has been postulated that the viscoelastic behaviour of an amorphous SHR could be predicted, provided that its glass transition temperature is known (61). The « shift factor » able to reduce the viscoelastic behaviour of any SHR to a single master curve, is related with glass transition temperature by the equation (WLF equation):

$$\ln \alpha_T = -\frac{40.0\,(T - T_g)}{52 + (T - T_g)}$$

where

α_T = shift factor
T_g = glass point

However, the failure of the above equation to explain some deviations of great importance in the rubber behaviour, suggests its use only as a first approximation, submitting to the experiment the final evaluation of the viscoelastic behaviour of a new macromolecular structure and its connection with properties.

The forecasting of T_g instead is considered sufficiently reliable, on the basis of empirical equations based on group contributions (62).

In characterizing a new macromolecular structure, and particularly an amorphous SHR, also its characteristic topological interaction should be taken into account, and not merely the glass point, as customary.

In chapter 4 the importance of this parameter, that is not correlated to the glass point, has been already pointed out.

In Table 11 structures of several amorphous SHRS are reported.

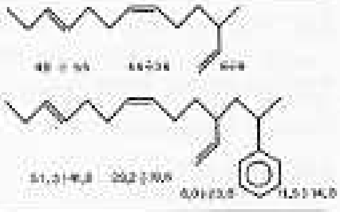
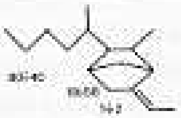
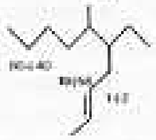
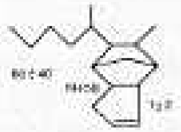
5.2.1. SBR

For SBR is intended here only poly(butadiene co-styrene) obtained in emulsion by radical catalysts. Other poly(butadiene co-styrene) obtained in solution by anionic catalysts will be dealt with in the next section.

SBR is the most important SHR. Its world capacity was as high as 6.5 million tons in 1979.

SBR is a random copolymer of butadiene and styrene, generally containing 13.4 mol % of styrene (23 wt %). The butadiene units in a « cold SBR » are in a 68/14/18 ratio for *trans*/*cis*/vinyl isomer units.

TABLE 11 - AMORPHOUS HYDROCARBON SYNTHETIC RUBBERS

	ACRONYM	STRUCTURE (% MOL)
Poly(butadiene co-styrene) (redox catalysts)	SBR	
Lowtactic polybutadienes and related styrene copolymers (anionic catalysts)	Solution SBR (low and high vinyl)	
Atactic, high vinyl polybutadienes (anionic and Ziegler-Natta catalysts)		
Poly(isobutylene co isoprene)	IIR	
Poly(ethylene co-propylene) co and terpolymers		  
Poly(norbornene)		

The catalyst system of the most common SBR to-day is a free radical redox system that allows high polymerization rates to be achieved also at low temperature (5 °C). Therefore, the resulting rubber has been named « cold rubber ».

The catalyst recipe reported in Table 12 gives only an idea of the tremendous amount of sofistication reached by this technology, and of the related work of so many scientists.

TABLE 12 - POLYMERIZATION RECIPE OF SBR 1500 (« COLD RUBBER »)
(parts in wt)

1,3-Butadiene	72	Monomers
Styrene	28	
Water	180	Reaction medium
Fatty acid and or rosin soap	4,5	Emulsifier
KCl	0,3	Emulsion stabilizers
Auxiliary surface active agent	0,3	
t-dodecyl mercaptan		MW control
p-menthane hydroperoxide	0,063	Redox catalyst
$Fe_2SO_4 \cdot 7H_2O$	0,010	
Ethylendiamine-tetraacetic acid salt	0,050	Fe ions complexing agent
Sodium formaldehyde sulfoxylate	0,050	Ferric → ferrous ions reducing agent

In the Table, the main functions of different ingredients are indicated.

As to the process, we shall limit ourselves to point out that the concept of emulsion polymerization, besides having been one of the more fascinating achievement of polymer chemistry, represents also to-day the most elegant way for synthesizing high molecular weight molecules (such as those of SBR, that exceed that of many plastics of one, and in certain cases of two, orders of magnitude) without meeting any problem connected with solution or bulk viscosity, intrinsically connected with a high molecular weight.

Moreover, water is hardly surmountable, as a heat transfer medium.

As to the copolymerization reaction, the reactivity ratios of butadiene and styrene in a radical initiated polymerization are sufficiently close as to avoid any problem of homogeneity within a polymerization reactor, also when the polymerization reaction is performed in continuous. It should be pointed out that $r_1 r_2 \simeq 1$ and therefore the polymerization allows a random addition of the two monomers.

Another relevant aspect of the radical emulsion polymerization is that, in a batch polymerization, in the central part of the curve representing the conversion in function of time, the conversion rate is practically constant. This is at difference with a batch solution polymerization, in which a continuous lowering of conversion rate in function of time is noted according to a first order kinetic dependence on monomer concentration. The finishing step of an emulsion process is of course different from that of a solution process. After stripping out the unreacted monomers from the rubber emulsion and adding an antioxidant, the rubber is recovered by controlled coagulation in the form of crumbs. The crumbs are dewatered and dried in a hot air oven or in a mechanical dryer.

The final rubber contains, in a rather high amount in respect to a solution process, non rubber constituents coming from emulsifier residues, stabilizer and coagulation agents, that should comply with specifications.

As to the properties, SBR has covered till now most of tyre and a good part of non-tyre application of rubber. It has allowed the tremendous expansion of the automotive industry by complying with the fast growing demand of rubber, and by filling the gap left by natural rubber supply.

Some of its properties in tyre application are essential; among those, its high coefficient of friction, coupled with a low wear, place it also to-day among the best rubbers for safe and long lasting tyre treads.

However, in the last years, the tyre technology change from a biased to a radial tyre, the incoming in the non tyre field of other SHR have somewhat eroded the growth rate of SBR. Anyway, this work-horse of SHR has demonstrated, also in the past, to be able to face out the most pessimistic previsions.

We realize that the space left for SBR presentation here does not do justice to the historical, scientific and economical importance of this dean of SHR. The interested reader is addressed therefore to the many excellent reviews existing on this important subject ([illegible]).

5.2.2. *Low tactic polybutadienes and their random styrene copolymers*

As it has been pointed out in paragraph 5.1.2, lithium alkyls initiators promote isoprene polymerization to a rather high *cis* polymer in hydrocarbon solvents.

On the contrary butadiene, in the same conditions, is polymerized to a low tactic polymer, with a 48/44/8 ratio for *trans/cis*/vinyl monomer units. Therefore, anionic initiators and, among them, lithium alkyls, are not suitable for obtaining crystallizable, butadiene based elastomers.

In spite of this fact, a set of features of anionic catalysis is unique and gives the reason for the continuous growth of its application, side by side with Ziegler-Natta catalysis.

One of these features is that of allowing a broad range of microstructures to be obtained in the polymer, starting from the above said 48/44/8 *trans/cis*/vinyl up to a practically 100% vinyl atactic polybutadiene.

The microstructure variation is obtained by adding electron donor solvents or by modifying the catalyst system with suitable additives.

The second feature is that of a facile copolymerization with styrene. Any styrene composition can be obtained with a rather good control of the microstructure of butadiene units, within the limits above indicated for butadiene homopolymers. The copolymerization with styrene can be performed in such a way as to obtain random or block copolymers. Block copolymers will be dealt with in paragraph 5.3.

The third feature, connected with the « living » character of lithium initiated polymerization in particular conditions, is that of allowing a very good control of molecular weight, from low to extremely high, without any chain transfer reaction. In a living polymerization all the chains grow simultaneously and molecular weight is in stoichiometric relation with the initiator. As a consequence, a particularly narrow MWD (Poisson distribution) is obtained in the polymer.

The first commercial production of a 44/48/8 *trans*/*cis*/vinyl butadiene homopolymer begun in the fifties (Firestone Tire & Rubber Co., USA) and its growth has not been hampered by cistactic polybutadienes.

Mechanical properties and several processing characteristics of this polybutadiene are inferior to that of cistactic polybutadienes, due to the absence of crystallization.

However, dynamic properties and other properties related to them (abrasion, coefficient of friction for example) are similar, in that they depend on the total content of 1,4 addition (*cis* + *trans*). An advantage of high 1,4 (*cis* + *trans*) lithium initiated polybutadiene is its suitability as a rubber for extremely low temperatures, owing to its low glass point and to its intrinsic resistance to low temperature crystallization.

Another advantage is its narrow MWD and its clarity that make it an ideal reinforcing agent for high impact polystyrene.

Besides the above mentioned lithium initiated butadiene homopolymer, also anionic, random butadiene styrene copolymers have obtained a rather good commercial success. These so called « solution SBR » have a butadiene units microstructure similar to that of the above mentioned butadiene homopolymer (see Table 11) and a styrene content close to that of a conventional emulsion SBR.

The fact that the properties of several poly(butadiene co-styrene) as SHR depend on their glass point, independently from the fact that a certain glass point has been obtained by increasing the styrene content or the vinyl addition, has been recently pointed out (64). The effectiveness of vinyl units in respect to that of styrene units (both measured as wt %) in increasing the glass point in approximately 0.8.

By taking advantage of the versatility of the anionic catalysis and of the above mentioned substantial convertibility of styrene and vinyl units contents, high vinyl butadiene homopolymers and their random styrene copolymer are covering nowadays a very broad spectrum of characteristics, tailored to the application.

As to the polymerization process, it is generally performed in solution. The importance of solvent in regulating the butadiene units microstructure has been already pointed out.

Also the function of solvent as a chain transfer agent should be taken in due account.

A chain transfer solvent (such as toluene) should be avoided in order to reach very high molecular weight polymers, or very narrow MWD. A certain amount of chain transfer is instead beneficial in order to control the molecular weight, without resorting to an increase of the rather expensive anionic initiator.

The polymerization process temperature is in general higher than that of a Ziegler-Natta polymerization and a semi-adiabatic polymerization is common, due to the already mentioned absence of transfer reactions and to the irrelevance of small microstructure variations caused by temperature. The reader interested in anionic polymerization applied to the synthesis of SHR, is directed to the many good reviews existing on this subject [see, for example, ref. ([illegible]) and ([illegible])].

5.2.3. *Isobutylene copolymers and their derivatives*

As it has been pointed out in paragraph 5.1.7, when in a *iso*butylene chain comonomer units are inserted, such as isoprene units, the tendency of the rubber to crystallize by strain decreases and eventually vanishes.

The most important copolymer of *iso*butylene is poly(*iso*butylene co-isoprene), *i.e.* the well known butyl rubber. Isoprene content is normally low (0.8-4.2 mol %) and isoprene units are mainly in *trans* 1,4 configuration.

The catalyst used for production of butyl rubber is $AlCl_3$ in methyl chloride. The reaction is performed at a very low temperature (— 100 °C). The initiation step is very fast and leads to the formation of carbonium ions. The propagation step is also very fast and proceeds may be via free ions (a carbocation at the tip of the growing chain) or via a carbocation/gegenion pair.

Termination and transfer reaction should be minimized in that the good properties of *iso*butylene chains are fully exploited, as a SHR, only when molecular weight is very high (*i.e.* more than 150,000 up to 1,000,000).

Termination and transfer reactions to the monomers are reduced by performing the polymerization at low temperature, that is also mandatory for increasing the rate and the polymer yield. Great attention is deserved to impurities (e.g. butene-1, for example) that act as chain terminators or as chain transfer agents.

Also the comonomer, necessary for introducing unsaturations in the chains, is a chain transfer agent. Therefore it is chosen, among the dienes, bearing in mind also this aspect of polymerization beside its reactivity with *iso*butylene.

As to the process, that of butyl rubber represents a brilliant achievement of chemical engineering. The polymerization is very fast and is completed in a matter of seconds. A very efficient heat exchanger and a powerful and efficient stirrer is necessary in order to maintain the temperature at — 100 °C. The ratio between monomers and polymerization medium (methyl chloride) is 30/70 wt. The reactor is cooled with liquid ethylene, flowing in the reactor jacket and in a internal heat exchanger. Another feature of the butyl rubber process is that rubber is produced as a slurry, suspended in the reaction medium. As butyl rubber is very sticky, also problems of reactor fouling are present.

The slurry is flashed in hot water and unreacted *iso*butylene is recycled. The rubber is added with acid scavenger and stabilizers and dried.

As to the product, butyl rubber holds a limited but qualified part of SHR market.

Its main characteristics are: low gas permeability (inner tubes and inner liners of tyres), high heat and oxidation resistance (automobile radiator hoses, « bags » for tyre vulcanization *etc.*) low resilience (mechanical shocks dampers *etc.*), high resistance to ozone and corona effect (high voltage cables insulation).

The low resilience of butyl rubber is unique among SHRS, in that it is coupled with a very low glass point (47).

Some of the above mentioned butyl rubber applications are threatened however by other SHR, and in particular by poly(ethylene co-propylene) co- and terpolymers.

Some novel, recent improvements in the field of butyl rubber are worth mentioning. They deal with improvements of butyl rubber process and products. As to the process, research groups have worked independently in USA and in our laboratories (48) in order to reduce the energy and the investment required by the conventional process, operating at — 100 °C. A considerable amount of energy is required for providing the frigories at — 100 °C in order to balance the polymerization enthalpy and the reactor stirring energy and, moreover, for cooling down the feeds entering the reactor. As to the first two terms, the energy saving obtained by operating the reactor at — 50 °C instead of — 100 °C, as customary, is theoretically (Carnot cycle):

$$\frac{W_{(-100\,°\mathrm{C})} - W_{(-50\,°\mathrm{C})}}{W_{(-100\,°\mathrm{C})}} = 1 - \frac{173\ \mathrm{K} - \alpha}{223\ \mathrm{K} - \alpha} \qquad \text{where } \alpha = \frac{173 \cdot 223}{T_A}$$

where T_A is the ambient temperature. Putting $T_A = 296$ K, the energy saving should be as high as 54%.

As mentioned above, both in U.S.A. and in our laboratories improved catalyst systems have been found (syncatalysts) based on aluminum alkyls or alkyl halides and a co-catalyst that can be a proton source (e.g. HCl), a carbonium ion source (e.g. *t*-butylchloride), a chloronium ion source (e.g. chlorine) that allows high molecular weight butyl rubber to be obtained also at a moderately low temperature (— 50 °C).

The syncatalyst process has not been developed till now.

As to the product improvement, a great deal of research has been directed to the improvement of co-vulcanization of butyl rubber with diene rubbers.

Apparently this can be done in the synthesis step by increasing the unsaturations (69) but has not yet been applied. The co-vulcanization is currently achieved by post- modifying butyl rubber by chlorination or by bromination. Both chlorinated and brominated butyl rubber have been commercially exploited for many years. The last improvements in the field of butyl rubber, at a laboratory level, are:

— butyl rubbers « immune » to ozone attack. The isoprene comonomer is substituted by cyclopentadiene. Cyclopentene rings are inserted in the main chain and therefore the unsaturation (site of ozone attack) is by-passed by a saturated chain. Also β-pinene has been suggested as a comonomer (70);

— butyl rubber with more active unsaturation sites. Instead of increasing the unsaturation content, more active conjugated double bond systems are inserted in the chain. This was done independently in USA by dehydrochlorination of a chlorinated butyl rubber (71) and in our laboratories (72) by using new triene comonomers (such as 1,3,5-hexadiene, *i.e.* the vinylog of 1,3 butadiene) that are also very reactive in polymerization.

5.2.4. *Poly(ethylene co-propylene) co- and terpolymers*

The history of poly(ethylene co-propylene) co- and terpolymers is rather recent. It begun in 1955, *i.e.* a quarter of a century ago. Also this achievement of macromolecular science is marked by the outstanding contribution of Natta and his school. Immediately after the discovery of isotactic polypropylene it was found that isotactic polypropilene contained a rather large amount of atactic (amorphous) polypropylene that could be extracted by low boiling solvents. The amount of atactic polymer was quite high in the early isotactic polypropylenes and therefore Natta stimulated the author of this review to find a possible use as a rubber of this « sub-product ».

After some unsuccessful tentatives of crosslinking it with peroxides (also atactic polypropilene, likely *iso*butylene, shows a too high scission rate to be crosslinked in this way) we found a possibility of crosslinking it via chlorosulfonation and curing with metal oxides (73). This way had been already exploited by Du Pont for crosslinking a chlorinated and chlorosulphonated polyethylene (Hypalon).

At difference with Hypalon, we tried to avoid as much as possible the chain chlorination since atactic polypropilene was already amorphous. However, the elastic properties of chlorosulphonated atactic polypropylene turned out to be unsatisfactory and we realized that this fact was due to an excessive presence of side groups (*i.e.* methyl groups) along the chain, also in the absence of a chlorination.

In order to reduce the number of methyl groups along the chain a possibility was offered by the copolymerization of ethylene with propylene.

As soon as suitable catalysts for synthesizing a sufficiently amorphous copolymer were found, the copolymer was chlorosulphonated and cured and gave rise to the first ethylene propylene rubber (74). According to our expectations, the dynamic characteristics were tremendously improved in respect to that of atactic polypropylene, in function of the ethylene content of the copolymer.

This discovery lead to a frantic work both in the synthesis laboratory, in order to find a suitable termonomer able to achieve a sulphur crosslinkable ethylene-propylene rubber, and in the curing laboratory in order to find a viable method for curing the copolymer already obtained.

The copolymer was cured with peroxides (75), with peroxides and sulphur (76), with peroxides and maleic anhydride (77), with peroxides and difunctional hydrocarbon monomers (78).

Other viable routes were that of chlorinating and dehydrochlorinating the copolymer (79) in order to achieve unsaturations in the polymer chain and that of sulphonating the chains with SO_3 complexes (80).

The synthesis of a sulphur crosslinkable terpolymer succeded later on, when a research group of Dunlop found that dicyclopentadiene was able to terpolymerize easily with ethylene and propylene (81). The explanation was that the unsaturation of the « cyclohexene ring » of dicyclopentadiene was activated by the strain imposed by the endomethylenic group. Of the two dicyclopentadiene isomers, exo dicyclopentadiene was found more suitable than endodicyclopentadiene (82).

Another important feature of dicyclopentadiene as a termonomer was that the second unsaturation of the termonomer (*i.e.* that of « cyclopentene ring ») was substantially unaffected during polymerization, and therefore it was inserted in the chains as a crosslinking site.

Independently, a research group of Du Pont found that also 1,4-hexadiene was a suitable termonomer. In this case, the vinyl group of the termonomer was used for achieving the terpolymerization, whereas the internal unsaturation was unaffected during polymerization and remained as a crosslinking site in the chain.

The catalyst systems used nowadays for producing poly(ethylene co-propylene) co- and terpolymers are not substantially different from the best catalysts found in the early work at the Politecnico of Milan (83).

They are based on hydrocarbon soluble vanadium compounds and aluminum alkyls or aluminum alkyl halides. The presence of halogen ligands in the catalyst system seems necessary also in this case.

Among the vanadium compounds, $VOCl_3$ is preferred for stability and price.

When the vanadium compound is put in contact with aluminum alkyls, a fast reduction of the first takes place and the catalyst site is formed. However, at difference with other catalyst systems, a fast decay of catalytic activity is noted in function of time.

The catalyst activity decay has been explained in terms of an over-reduction of vanadium. The over-reduction can be hampered by including in the catalyst recipe specific vanadium reoxidizing agents.

A typical feature of ethylene propylene copolymerization is that the reactivities of ethylene and propylene are quite different.

Reactivity ratios values of 15-30 have been reported for ethylene and of 0.06-0.03 for propylene.

As to the process, the aforementioned difference of reactivity of ethylene and propylene should be taken into account.

In order to reduce the perturbing influence of monomer feed composition on monomer reactor composition (related to the difference of monomers réactivity) the monomer conversion of the reactor is generally kept at a rather low level.

As this fact is detrimental to termonomer « utilization », an arrangement of a series of reactors is opportune. Of course, an efficient stirring of reactors is mandatory in order to achieve a sufficient reactor homogeneity.

Poly(ethylene co-propylene) solutions are very viscous also at low polymer content: a content of more than 8% wt is hardly achieved. A possible way for increasing this figure is that of performing the copolymerization in the absence of solvents (8). Liquid propylene performs in this case both as a monomer and as a polymerization medium. The copolymer, insoluble in liquid propylene, precipitates as a slurry and this fact allows an increase of polymer content to be obtained, at a reasonable slurry viscosity. The process temperature is also important, in that a compromise should be reached between polymerization rate and vanadium catalyst deactivation.

The polymerization temperature is generally below 40 °C.

Also the finishing section of the process (catalyst deactivation and catalyst residues removal) deserves particular attention. Any cationic side reaction should be controlled in order to avoid a branching and even a crosslinking of the terpolymer.

Moreover co- and terpolymers should be free of vanadium residues in order to avoid a possible oxidative degradation and discolouring of the polymer.

As to the properties, poly(ethylene co-propylene) co- and terpolymers are unique among SHR in that they display an excellent ageing resistance coupled with very good dynamic properties. Their ageing and ozone resistance excels that already good of butyl rubber, in relation to the fact that the unsaturations are located in side groups and not in the main chain. In relation to these good characteristics and to the unlimited availability of ethylene and propylene monomers, the future of this SHR looks particularly promising.

The properties of (ethylene co-propylene) polymers and terpolymers depend upon:

— ethylene content
— ethylene distribution (copolymer randomness)
— MWD
— termonomer type.

Copolymer randomness is important in achieving good elastomeric properties also at rather high ethylene content. The higher the ethylene content is, the better are the dynamic properties, provided that long ethylene sequencies are avoided, which could give rise to an undesirable crystallinity. MW and MWD control (hydrogen is suitable as a chain transfer agent) are of paramount importance for achieving a sufficient level of processability. Processability is considered the weak point of poly(ethylene co-propylene) co- and terpolymers. This fact could be related to the unusually high topological interaction shown by ethylene propylene chain (27). Only by decreasing MW it is possible to decrease the raw rubber elasticity originated by topological interaction. A good MWD control allows a compromise to be found between processability and dynamic properties of the vulcanizate.

As to the termonomer choice, it depends both on its behaviour in the polymerization stage and in the curing stage.

As to the polymerization stage, as already pointed out, the termonomer should:

— have two reactive sites with specific functions, without any functional interference between them. The first site should allow a fast, complete and random terpolymerization with ethylene and propylene. The second site should be inactive during polymerization.

— be sufficiently stable.

— be low in molecular weight for a favourable unsaturation/weight ratio and for easing the recovery of the non reacted monomer.

As to the curing stage the termonomer should:

— give high and constant moduli (at equal termonomer content) in a reasonable time at a reasonable vulcanization temperature. A decay of moduli (reversion) or a continuous increase of them during a prolonged cure (marching modulus) are considered unsatisfactory.

— reach the above mentioned moduli plateau in a short time (high cure rate). Of course, cure rates should be compared at equal level of moduli plateau or at equal termonomer content.

— do not give a premature vulcanization (scorching) during storage and processing.

Most of the above specifications are met by the three commercial termonomers used to-day. They are (Table 1) 5-ethylidene-2-norbornene, dicyclopentadiene and 1,4-hexadiene.

5-ethylidene-2-norbornene is considered one of the best termonomers: it has the same reactive norbornene « head » of dicyclopentadiene, but its ethylidene « tail » is both more inert in polymerization step and more reactive in curing step.

Molecular weight of 5-ethylidene-2-norbornene is intermediate between dicyclopentadiene (10 carbon atoms) and 1,4-hexadiene (6 carbon atoms).

The cure rates of the above mentioned termonomers have been compared (86). The rating is, in order of decreasing cure rate constant HD > ENB > DCP. Other highly reactive new termonomers have been recently proposed. They are based on a norbornene « head » with a conjugated double bond system in the « tail » (72) (fig. 12).

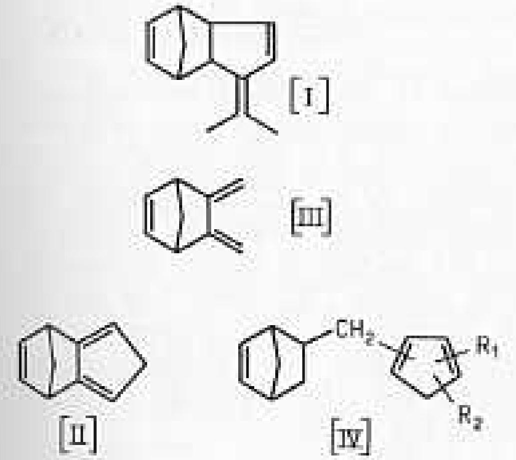


Fig. 12 - Triene termonomers containing a conjugated double bond system in transoid [I] and cisoid [II] [III] [IV] conformation. [I] 1-*iso*-propylidene dicyclopentadiene (3-*iso*-propylidene-tricyclo-$[5.2.1.0^{2,6}]$-4,8 decadiene; [II] dehydro-*iso*-dicyclopentadiene(tricyclo-$[5.2.1.0^{2,6}]$-2,5,8 decatriene); [III] 5,6 dimethylene-2-norbornene; [IV] cyclopentadienyl-5-endo-norborn-2-enyl-methane derivatives.

By using these termonomers, the chains are provided with very reactive double bond systems, useful for polymer postmodifications such as grafting, functionalization and so on.

Owing to the reactivity of these termonomers, their content can be kept below the customary value of 1-2 mol %, used for conventional termonomers. The reader interested in deepening the subject of poly(ethylene co-propylene) and of related terpolymers (EPM and EPDM) is directed to the recent excellent reviews, such as (87-89).

5.2.5. *Polynorbornene*

Recently, another amorphous SHR has been produced on a commercial scale, *i.e.* polynorbornene or poly(bicyclo [2.2.1] heptene-2).

By tungsten based catalyst, one ring of norbornene is opened (90), so that a chain containing 1,3-cyclopentylene alternated with vinylene groups (in *cis* and *trans* configuration) is obtained (Table 11).

The glass transition is rather high (35-45 °C) so that a reduction of glass transition with plasticizers is necessary.

The high molecular weight, (up to 2 millions) allows a high quantity of oil and filler to be added still maintaining rather good mechanical and dynamic properties.

The unsaturations in the chain provide the reactive sites for a sulphur vulcanization.

The literature data on the polymer properties are not yet sufficient for a conclusion on the application possibilities of this new SHR, in competition with the already existing ones.

5.2.6. *Other amorphous* SHRS

Among the host of possible amorphous SHRS we shall limit our attention to *cis*tactic polypentenamer, poly(*cis*-isoprene co-*cis*-butadiene), and hexene-1 copolymers.

*Cis*tactic polypentenamer is obtained by ring opening polymerization of cyclopentene with a two components catalyst system based on $MoCl_5$ and $AlEt_3$ (47). The polymerization is performed in bulk, below — 10 °C in order to preserve a high *cis* tacticity. At — 40 °C the polymer *cis* tacticity is above 99%. At this temperature, a conversion of 50% is obtained in 8 h. The glass point of the polymer is claimed to be very low [— 135 °C, measured by flexural modulus (48)], lower than that of transpolypentenamer and of cistactic polybutadiene. The melting point is so low (— 41 °C) and the crystallization so slow that the rubber can be considered amorphous. The exceptionally low glass point suggests its use as a rubber for applications at extremely low temperature.

Poly(*cis*-isoprene-co-*cis*-butadiene) can be synthesized by uranium (49) and rare earths (50) based catalysts.

The *cis* tacticity is high, the copolymers are homogeneous and random. Molecular weight, particularly with neodymium catalysts, can reach a very high value. An isoprene content of approximately 15% wt is sufficient for obtaining an amorphous polymer also at low temperature or in a stretched state. Any copolymer composition can be obtained, depending on the monomers ratio.

The interest of this copolymer stems from the possibility of its use as a compatibilizing agent for cistactic polyisoprene and cistactic polybutadiene, that are incompatible.

Polymers, copolymers and terpolymers of hexene-1 have been produced recently (51).

By early work of Natta and co-workers it was known that the glass points of polyalphaolefin homopolymers showed a maximum for polypropylene and polybutene-1 and then decreased again for polypentene-1 and polyhexene-1. The glass transition of polyhexene-1 is rather low (— 50 °C).

The use of hexene-1 co- and terpolymer as a new SHR has been recently tested by Goodyear (75). In particular the copolymers of hexene-1 with 1,4-hexadiene (in order to provide unsaturations for sulphur cross-linking) and the terpolymers with butene-1 (apparently in order to reduce the cost) were tested.

These copolymers and terpolymers are claimed to have an exceptionally high resistance to flex cracking.

A low Mooney viscosity also for very high molecular weight has been found.

5.3. MULTIPHASE SHRS

From a physical standpoint, multiphase SHRS are SHRS which do not need a chemical cross-linking step for forming a network: the network is formed only by physical interaction among segments (hard sequencies) of several molecular chains.

The meaning of the definition « hard sequencies » will be explained later on.

The physical interaction among hard sequencies should weaken above a certain temperature, in order to allow an easy processing of the rubber, and to strengthen below it, in order to provide a strong anchoring point (physical cross-link) for the soft sequencies of the molecular chain.

The soft sequencies should be connected at both ends with hard sequencies in order to perform as effective network chains (see paragraph 4).

The length and the physical characteristics of the soft sequencies (e.g. glass point *etc.*) are subjected to the same requirements of a conventional network chain, and therefore they do not need any particular explanation. Some additional remarks appear to be opportune instead as to the structure and function of hard sequencies.

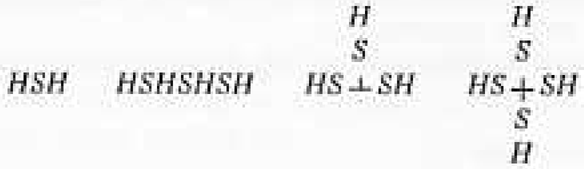
In a multiphase SHR the physical interaction among hard sequencies is based on van der Waals forces, that are quite weak in comparison to a chemical bond. In order to increase the mechanical resistance of the physical cross-link, the hard sequencies should be sufficiently long, in order to increase the overall van der Waals interaction among chains. Secondly, a dense packing of hard sequencies is necessary for increasing the above mentioned interaction and for avoiding as much as possible their interference with the function of the soft sequencies.

The dense packing of hard sequencies calls for their separation as microdomains, dispersed in a rubbery phase made of soft (and possibly only soft) sequencies.

The microdomains formed by hard sequencies, are given the adjective of « hard » in that they are below their melting point or their glass point. The melting or the glass point of hard microdomains should be chosen as a compromise between the temperature range of processing and the temperature range experienced by rubber during its use.

In conclusion:

1) - The chain structure of a multiphase SHR should be composed of hard and soft segments. The soft segments should be always bonded at both ends with hard segments. Calling H the hard segments and S the soft segments, structures such as:



$$HSH \qquad HSHSHSH \qquad HS\overset{\overset{H}{S}}{\perp}SH \qquad HS\overset{\overset{H}{S}}{\underset{\underset{H}{S}}{+}}SH$$

are allowed, whereas structures such as

$$HS \qquad SHS \qquad HSHSHS \qquad SHSHSHS \qquad HS\overset{S}{\perp}SH$$

are not ($\perp$ and $+$ are chemical tri and tetrafunctional bonds).

2) - The soft sequencies should have length and physical characteristics (T_g) suitable for a rubbery network chain.

3) - The hard sequencies should have length and physical characteristics as to separate from the rubbery phase in form of microdomains, whose melting point or glass point should be a suitable compromise between rubber processability and upper temperature limit of use.

From a technological standpoint, multiphase SHR show the following advantages:

— do not need chemical cross-linking agents and allow time and cost of compounding and cross-linking steps of a conventional SHR to be avoided;

— since the physical cross-link is reversible with temperature, a reutilization of scraps is possible;

— also very bulky rubber objects can be made inexpensively by injection molding, whereas a chemical cure should require unacceptable long curing times in a press, for heat transfer reasons;

— the physical cross-link allows a certain network relaxation that improves the mechanical properties of the rubber, also in the absence of a strain crystallization of the soft segments.

The disadvantages are related to:

— an inferior resistance of the physical cross-link, compared to a chemical one, when subjected to a thermal or mechanical stress. In particular multiphase SHRs are prone to creep in unfavourable temperature/stress-duration conditions;

— an inferior aging resistance in comparison to a chemical cross-linked rubber, at equal composition of soft sequencies, has been noticed.

From the physical considerations put forth just now, multiphase SHRs can be classified on the basis of the characteristics of the hard domains as:

1) - multiphase SHRs with glassy microdomains
2) - multiphase SHRs with crystalline microdomains.

We shall deal with multiphase SHRs by following this order, in relation to their present commercial importance. However, also the second type of multiphase SHRs has gained recently a remarkable success.

5.3.1. *Multiphase* SHRs *with glassy microdomains*

A great deal of multiphase SHRs that have obtained a large commercial success is based on anionic polymerization. They are generally related to as « block polymers » or « thermoplastic elastomers ».

A typical, if not unique, feature of anionic polymerization is that of being, in certain conditions, termination and transfer-free, as pointed out early by Ziegler ([illegible]).

The potential of this fact in obtaining block polymers with pre-determined sequencies was pointed out by Szwarc, who coined for this kind of polymerization the suggestive term of living polymerization ([illegible]).

The existence of a living chain end allows the length, and the position along the chain of sequencies of two (or more) monomers to be controlled, complying with the primary requirements of a multiphase SHR.

In 1965 Shell ([illegible]) followed in 1968 by Phillips ([illegible]) begun in U.S.A. the commercial production of (butadiene co-styrene) block polymers.

The choice of hydrocarbon monomers susceptible of anionic polymerization is quite limited. The more common ones are indicated in Table 13.

TABLE 13 - HYDROCARBON MONOMERS FOR BLOCK POLYMERS BY ANIONIC POLYMERIZATION

Monoolefins (for hard sequences)	Styrene, *p.tert*-butylstyrene, α-methylstyrene
Diolefins (for soft sequencies)	Butadiene, isoprene, other dienes

The main routes for obtaining anionic block copolymers suitable as SHR are:

A) a three steps process with monofunctional initiators;

B) a two steps process with difunctional initiators;

C) a two steps process with monofunctional initiators, followed by a coupling reaction.

A. Three steps process with monofunctional initiators

In compliance with the structural requirement of a block copolymer suitable for SHR, the simplest structure is:

$$HSH$$

where H is a hard sequence and S a soft sequence. When styrene is chosen as the monomer for the H sequence, it should be polymerized first, in the presence of the anionic initiator. One of the best initiator is *sec*-butyl lithium, in that it is more active than other butyl lithium isomers in providing a sufficiently fast rate of initiation of styrene also in apolar, hydrocarbon solvents.

Apolar, hydrocarbon solvents are necessary so as to avoid that during the synthesis of the second segment based on a diene, this could add in a configuration different from 1,4 (*cis* + *trans*) and therefore unsuitable for an elastomer.

At the end of the first step, the initiator should be completely utilized, the styrene monomer should be depleted and only styryllithium species at the end of living chains should be present.

At this point the second step takes place with the addition of the second monomer (e.g. butadiene). The initiation of butadiene polymerization by styryllithium species is quite rapid (the cross over rate constant $K_{S\rightarrow B}$ is high, where S is for styrene and B for butadiene). Butadiene is polymerized until depletion and then styrene is added (third step).

At difference with the cross over rate constant $K_{S\rightarrow B}$ the opposite cross over constant $K_{B\rightarrow S}$ is rather slow, but can be accelerated by the addition of small amount of polar substances, such ad diethylether, tetrahydrofuran, dimethoxyethane *etc*.

B. Two steps process with difunctional initiators

The three steps process is complicated and time consuming. Moreover, every monomer addition can give rise to an introduction of poisons in the polymerization reactor, with the result of obtaining, instead of a pure triblock polymer, a mixture of it with its parent polymers.

Some particular dilithium derivatives, such as 1,4-dilithio-1,1,4,4,-tetraphenylbutane (8) are sufficiently pure and soluble in hydrocarbon media (necessary for the reasons already pointed out) for obtaining the three block copolymer (exemplified in the three step process) in only two steps.

The dilithium initiator is put in contact with the first monomer, that is in this case the diene. A chain is obtained bearing at both growing ends dienyl lithium species.

The second step involves the addition of the monomer necessary for synthesizing the hard segment (e.g. styrene, α-methylstyrene).

The final product is similar to that obtained with a three step process, with the advantage of a simplified and faster procedure.

The two steps process based on difunctional initiator is the process of choice when one of the cross over rate constants is zero, which makes impossible to synthesize a *HSH* block polymer by a three steps process.

C. Two steps process with monofunctional initiators, followed by a coupling reaction

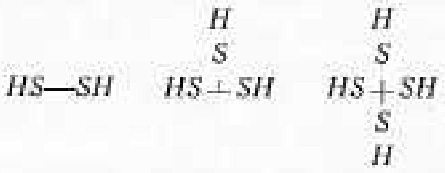
This process has gained wider acceptance in that it allows the same polymer of the « three steps process » to be obtained yet reducing the polymerization time to one half. Moreover, the danger of unwanted terminations due to impurities introduced with the feeds is reduced, likely the preceding process *B*.

The first two steps are similar to the « three steps process » *A*.

A diblock chain is obtained with lithium dienyl species at one end.

At the end of the second step, a coupling agent, provided with two or more electrophilic functions, is added.

By reaction of the electrophilic species with the carbanionic ones present in the system a block copolymer is formed with a linear, a trifunctional branched, a tetrafunctional branched structure:



$$HS{-}SH \qquad \begin{array}{c} H \\ S \\ HS \perp SH \end{array} \qquad \begin{array}{c} H \\ S \\ HS + SH \\ S \\ H \end{array}$$

depending on the functionality of the coupling agent. In other words, the first structure from left is obtained with a difunctional coupling agent, whereas the second one with a trifunctional agent and the third one with a tetrafunctional agent.

Of course, the functionality of the coupling agent can be increased beyond 4. Polystyrenes with degrees of branching up to 11 have been obtained.

The coupling agent can be chosen among a long list of di- or multifunctional electrophilic chemicals (such as, for example, dibromomethane, chlorosilanes and so on).

The main requirements of a good coupling agent are a high coupling efficiency, that depends also on the nature of the lithiated species, and the absence of side reactions, in particular of radical side reactions that give rise to an unwanted random branched polymer.

Among multiphase SBRs with glassy microdomains particular attention deserves a class of polymers obtained from styrene-butadiene-styrene or from styrene-isoprene-styrene copolymers by hydrogenation of the polydiene segment.

By a post polymerization hydrogenation, a styrene-butadiene-styrene block copolymer is transformed in a styrene-EB-styrene copolymer in which EB means a random copolymer of ethylene and butene-1. The butene-1 units come from the vinyl butadiene units of the parent polybutadiene block.

The glass transition of the soft block of the hydrogenated polymer is sufficiently low, depending on the vinyl addition of the parent polymer, and the ageing resistance is improved.

The hydrogenated block copolymer has been commercialized by Shell Chemical Corp. under the trade mark of Kraton G.

The hydrogenation post reaction is performed with hydrogen in the presence of catalysts (for example cobalt or nickel salts) in mild conditions (50 °C, 3.5 kg/cm^2) in order to achieve a complete hydrogenation of the polydiene block, avoiding any hydrogenolisis of the chains and any hydrogenation of the styrene rings. Also hydrogenated block polymers show very good mechanical properties likely the parent polymer, also in the absence of reinforcing fillers (see paragraph 4.2).

5.3.2. *Multiphase* SHRs *with crystalline microdomains*

The first multiphase SHR with crystalline microdomains (stereoblock polymer) appears to be that claimed in an early patent (99), by Natta and collaborators. It was a partially isotactic polypropylene, or polybutene-1, obtained by extraction of the raw polymer. The elastomeric properties were improved by a partial chlorination.

In these multiphase SHRs the crystalline domains were associations of isotactic sequencies whereas the soft segments were atactic sequencies. Both the length of the isotactic and atactic sequencies, and their succession were not controlled. Moreover, the elastic properties of the atactic propylene or butene sequencies were not good. In spite of that, the mechanical properties of this ancestor of polyolefin multiphase SHRs have been found outstanding, also in the absence of reinforcing fillers.

Uniroyal developed the first polyolefin thermoplastic elastomer (100,101), based on blends of polypropylene and poly(ethylene co-propylene) followed by several other Companies. Depending on the patents disclosed till now, the blending of a crystalline and of a rubbery olefin polymer may require or not a cross-linking step. However, some cross-linking and grafting reactions can result from a mere mechanical action during the blending step of the polymers.

Of course, the mechanical-dynamic characteristics of these blends cannot outperform those of well defined block polymers obtained by anionic polymerization. However, the low cost and the high ageing resistance of polyolefin blends, together with their acceptable mechanical characteristics, has gained to them a remarkable success in a sector of the market at mid-way between the plastics and the elastomer sectors.

A typical application of polyolefin blends is that of automotive bumpers; however, the application field of these versatile materials is expanding at a fast pace.

The newcomer, among multiphase SHRs with crystalline microdomains, seems to be syndiotactic 1,2 polybutadiene with low crystallinity. This polymer has been commercialized by Japanese Synthetic Rubber, in 1975 (102).

6. Perspectives

As pointed out in chapter 1, the main outlet of SHR is, and is likely to continue to be, the tyre sector.

Among the main requirements of the tyre sector, in terms of rubber structure, are improved SHR for radial tyre technology and for low rolling resistance tyres. Both these requirements seem to be compliable, at least to a certain extent, by new crystallizable and amorphous SHRs.

Beside the tyre sector, other applications of SHR are likely to show good perspectives for the years ahead.

The past decades have been marked by the transport of energy resources in the form of gas or liquids. The next decades will deal with the transport of tremendous amounts of solids: e.g. coal and low grade ores.

It seems a reasonable forecast that rubber, and in particular SHR, will play an important role in this change. Also the rubber structure should be specifically designed to comply with this application (e.g. high abrasion resistance, good dynamic properties for low power requirements and so on).

Other new outlets rely upon the ingenuity and fantasy of the rubber scientists and technicians. As an example, I would mention here the solar heat exchanger that has been recently proposed (106) and that takes advantage of a SHR with outstanding environmental resistance.

No doubt many other broad-use applications of SHRs can be discovered in the future.

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Vinyl Polymers

The first paper of Professor Natta on this subject has been published in 1934 [G. NATTA, *Giorn. Chim. Ind. Appl. 16*, 285 (1934)].

His activity in this field is proved by many publications. We quote, for instance: G. NATTA, R. RIGAMONTI, *Atti Acc. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat* (6) *24*, 381 (1936); G. NATTA, P. CORRADINI, I.W. BASSI, *Makromol. Chem. 18*, 455 (1956); G. NATTA, G. DALL'ASTA, G. MAZZANTI, U. GIANNINI, S. CESCA, *Angew. Chem. 71*, 205 (1959).

Prof. Paolo CORRADINI who has collaborated with Giulio Natta in this field from the beginning has been requested to give a contribution to the volume. The contribution is entitled: *The Role of the Discovery and Investigation of Stereoregular Polymers in Macromolecular Chemistry.*

The Role of the Discovery and Investigation of Stereoregular Polymers in Macromolecular Chemistry

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The discovery and utilization of the properties of matter has marked since the beginning of mankind's history the various steps of the civilization process: this fact is explicitely aknowledged when we talk of stone age or iron age.

Even earlier in his history the mankind had learned to utilize for his needs various species of macromolecular materials of natural origin, such as wood, leather, various fibers.

Yet the scientific understanding of the common chemical and molecular basis of the most relevant characteristics of these materials, which is the object of the macromolecular science, started, however, only in the 20's with the work of Staudinger: less than sixty years ago.

It may be interesting to go back for a moment to that period, in order to better understand the meaning of the discovery and scientific investigation of stereoregular polymers by Giulio Natta and his school.

The possible existence of long chain molecules was indeed already implicit in the second half of the past century in the ideas of valence formulated by Kekulé and others; this idea was, however, overlooked in the following years because chemists were concerned to deal only with small molecules having defined and unique formulas. The habit to think of polymeric substances in terms of formulas corresponding to relative molecular masses not too high, usually cyclic, was, in fact, more corresponding to the prevailing paradigms of the scientific community of the time, that considered as purpose of the chemist the preparation and isolation of pure substances, a pure substance being one containing all identical molecules. The scientists were thus lead, at the beginning of this century, to the wrong opinion that natural rubber should be mainly constituted by dimeric rings of isoprene, while cyclic formulas containing a variable but small number of monomers were proposed for the synthetic polymers of styrene.

The formation of colloidal solutions should have been considered as an evidence in favour of much higher molecular masses. This phenomenon was, however, explained in terms of aggregation of the cyclic oligomers in larger entities through the action of secondary or partial valences, whose nature was, however, unexplained.

The term « macromolecule » was proposed firstly by Staudinger in 1922 (1); the fact that polymers are constituted by very large molecules (macromolecules), each formed by hundreds or thousands of constitutional units, was accepted by the scientific community only in the following years, when new evidence in favour of Staudinger ideas was continuously gained.

The x-ray investigation of some natural polymers (cellulose, natural rubber, guttapercha) was a new important contribution to a better understanding of the concept of macromolecule; it was thus possible to demonstrate that the results of the x-ray diffraction of cellulose fibers are in complete agreement with a chain formula, containing a very large number of identical structural units. As shown in Fig. 1, which is taken from a paper by Meyer and Mark (1928) (2), these units play in the crystals of a polymer a role very similar to that of low molecular weight molecules in their unit cell; the macromolecules thus cross successive cells through the whole crystal lattice.

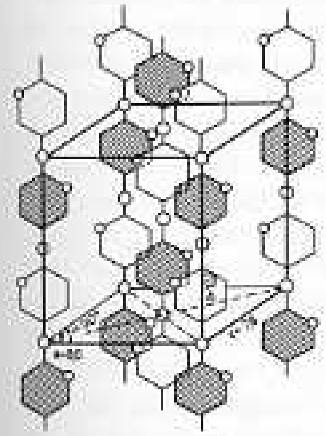
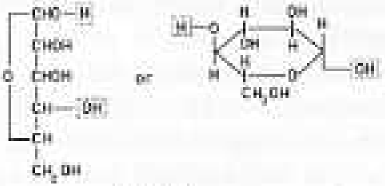
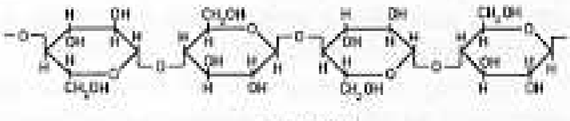


Fig. 1 - Representation of cellulose chains in the crystals as given by Meyer and Mark in 1928.



GLUCOSE



CELLULOSE

Fig. 2 - Monomer units (above) and the polymeric structure of cellulose as reported by Carothers in 1931.

The identity of the structural units along the chain of a crystalline polymer may be granted if the chemical structure of the polymer is regular: as shown in Fig. 2, which is taken from a paper of Carothers (1931) (3), the chain of cellulose is composed of units which are all β-glucose units and all in a 1,4 sequence.

Analogously, the constitutional units present in the chain of the natural polyisoprenes are all equal and correspond to a 1,4 enchainement; the double bonds are always in the *trans* configuration in guttapercha and in the *cis* configuration in natural rubber (Fig. 3).

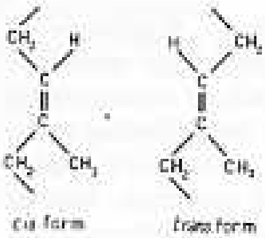


Fig. 3 - Stereoisomerism of the repeating units in natural polyisoprene polymers as reported by Carothers in 1931.

We define today as a *regular polymer* a linear polymer whose molecules can be substantially described by a unique species of constitutional units in a unique sequential arrangement. We define a polymer as *stereoregular* if the succession of configurations is regular too (we mean by configuration the spatial arrangement of the various bonds, without considering the multiplicity of arrangements, which arise from rotation around single bonds).

Cellulose, guttapercha and natural rubber are examples of stereoregular polymers, which nature is able to synthesize. The researches conducted in the three decades past 1922, when Staudinger firstly proposed the term « macromolecule », led to the synthesis of semicrystalline polymers — as the nylons by polycondensation and low density polyethylene by polyaddition — all polymers of great practical importance. These are regular polymers, whose constitutional units can have only a unique configuration; consequently, they do not show problems of stereoregularity. On the other hand, the vinyl polymers already known at the time — as poly(vinyl chloride) or polystyrene, obtained by radical polymerization processes — resulted amorphous at a roentgenographic examination, even if they had a quite regular constitution.

Anyway, the researchers of those years did not recognize that the lack of crystallinity was to be related to the lack of regularity in the succession of configurations, as we will discuss later on.

The discovery of how to synthesize stereoregular polymers was made by Natta and his co-workers in 1954. It may be interesting to recall some aspects of this fascinating history.

Crystalline polymers of α-olefins were unknown at the time. In 1947 Schildknecht (4) obtained crystalline polymers from vinyl alkyl ethers using a process of cationic polymerization at low temperature. These crystalline polymers could be molded giving rise to plastic materials of some rigidity, differently from the amorphous polymers previously obtained from the same vinyl alkyl ethers, much more soluble, rubbery and sticky.

Schildknecht published also some x-ray diffraction patterns of the polymers he had obtained, but he did not give them a correct interpretation, nor emphasized he the problem of stereoregularity as clearly as later did Natta and co-workers, who — for the first time — studied and determined (after the discovery of the isotactic vinyl polymers) the steric structure — still isotactic — of the Schildknecht's polymers (5).

In the early 50's, there was the quite contemporary discovery — in three different laboratories — of processes for the polymerization of ethylene at low pressures using solid catalysts: the catalyst used by the Standard Oil of Indiana was molibdenum(VI) oxide supported on aluminum oxide; the one by Phyllips Petroleum, chromium(VI) oxide still supported on silica/alumina; the catalyst studied by Ziegler and his co-workers, at the Max Planck Institute at Mühlheim, resulted from the reaction between triethylaluminum and titanium tetrachloride. Nowadays it is hypothesized that the mechanism of polymerization is quite similar for all three catalysts.

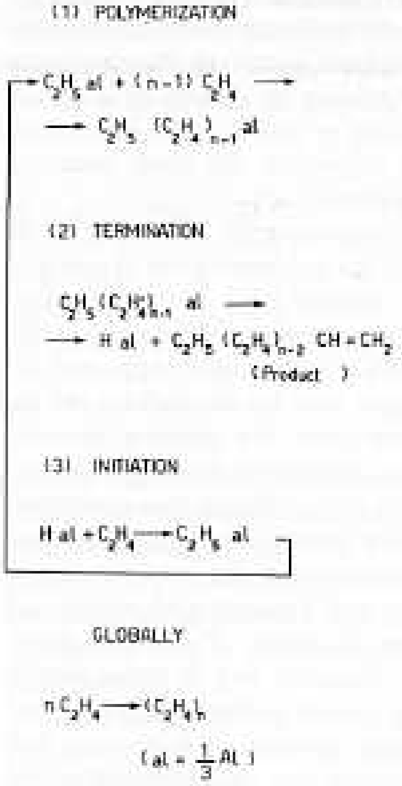
The polyethylene obtained is more highly crystalline, more rigid and dense and has a much more regular structure than the one previously known obtainable at very high temperature and pressure and which had been industrially produced in the previous 15 years. The latter shows macromolecules with both long and short branches and is consequently less crystalline than the almost completely linear polyethylene obtained with the catalytic processes mentioned above. Anyway, it is obvious that polyethylene does not present tertiary carbon atoms in its constitutional unit, hence it does not show problems of stereoisomerism.

It may be worth describing in some detail how the catalysts based on titanium chloride and aluminumalkyls for the polymerization of ethylene were discovered by Ziegler and co-workers.

They discovered firstly the reaction of growth of alkyl chains with ethylene on aluminumalkyls (Scheme), as shown in [1]. The reaction is a catalytic one; after several additions the intermediate product, as it can be seen in [2] in the scheme, gives rise to a hydride and an olefin and, due to the addition of a new olefin to the hydride — as shown in [3] — the cycle starts again (6).

In the presence of propylene, the reaction stops leading to the formation of a well-defined dimer. This fact, discussed by Ziegler during a lecture given in Frankfurt in 1952, struck Prof. Natta, who was in the audience. In particular Natta was impressed by the specificity (not yet stereospecificity) of the reaction which — due to the use of organometallic catalysts — made it possible to obtain, starting from propylene, a unique dimer; while it was well known that the usual dimerization catalysts, which act through a cationic mechanism, give complex mixtures of isomers (7).

Scheme



The growth reaction of alkyl chains with ethylene on aluminum alkyls according to Ziegler.

In the same year, Ziegler was struck by a casual observation which revealed itself afterwards to be of a great importance: the oligomerization of ethylene stopped with the dimer, to give butene-1, in the presence of a small amount of nickel. The nickel seems to have been deposited by mistake on the walls of a not well-cleaned autoclave. Starting from this observation, Ziegler considered the possible influence that small amounts of other elements could have on the reaction of oligomerization of ethylene. It was this research that, at the end of 1953, gave striking results. In the presence of a catalyst formed by the reaction between titanium tetrachloride and triethylaluminum, in a hydrocarbon medium, ethylene is rapidly absorbed, even at atmospheric pressure, to give a high polymer.

While the first discovery of catalysts based on transition metal halides and aluminumalkyls must be attributed to Ziegler, on the other hand the merit of the most important subsequent developments in the field of the science of macromolecules is to be attributed to Natta and his school. The thread line that led Natta to his discoveries is different from Ziegler's. Both

Natta and Ziegler had a great sensibility towards the problems of industrial chemistry but Ziegler was mainly a great organic chemist, while Natta's interests had been directed at physical and structural chemistry since the beginning of his career.

Natta graduated in engineering when very young. His works were initially directed towards the study by x-ray diffraction techniques of the structure of crystals and towards the resolution of various structural problems. In 1932 he met Staudinger at Freiburg, and since then he was attracted by the study of linear high polymers, with the aim of determining their lattice structure by means of electron scattering diffraction from thin films. In 1938, after having studied in the laboratory, from a chemical and structural point of view, the catalytic processes for the synthesis of methanol and of higher alcohols, he was charged with the direction of the researches and the study of synthetic rubber production processes in Italy. These studies led to the first Italian industrial realization of butadiene-styrene copolymers.

Quite at the same time Natta began to study — at the Politecnico of Milan — the possible applications of petroleum derivatives, and in particular of olefins, as raw materials for chemical syntheses, as, for example, the oxosynthesis of aldehydes.

In 1952 Natta was at Frankfurt for a lecture given by Ziegler, and — as I already reported — he was impressed by the presented results. With the cooperation of Prof. Pino, who was his assistant at the time, and of some researchers of the Montecatini Company, he began to study the kinetics of polymerization of ethylene in the presence of aluminumalkyls.

At the end of 1953, Ziegler discovered the process of polymerization of ethylene at low pressure. I remember, as personally lived, those charming days dense of fascinating outcomes at the beginning of 1954, when it was found in our laboratories that the Ziegler catalysts could polymerize (besides ethylene) propylene, styrene and several α-olefins to high linear polymers; these polymers appeared crystalline when examined by x-ray diffraction techniques, and were able to give oriented fibres.

I remember the enthusiasm and the restless activity which urged Natta and his young co-workers to the synthesis and structural characterization of the new products.

After twentyfive years, we may ask the reason why the stereospecific polymerization was discovered in a laboratory with no great experience (at least in comparison with other laboratories) in the field of the synthesis of polymers; I think that a series of favourable circumstances determined this discovery:

i) we were in a University laboratory, with a mentality concerning the fundamental research more open than in an industrial laboratory, but not insensible to applicative problems;

ii) we had in this laboratory small groups of very good scientists, with experience in the fields of organic, industrial organic, organometallic and structural chemistry; this complexity of different experiences was at that time hardly available in other more specialized laboratories;

iii) with the aim to characterize the ethylene oligomers, various processes of extraction and roentgenographic characterization had been implemented; these processes were particularly suitable for the new polymers;

iv) through an agreement with the Montecatini Company, about fifteen post-graduates, selected among the best ones in all the Italian Universities, were each year sent to the laboratory to attend courses of specialization in organic aliphatic chemistry and to collaborate to the various research projects: it was thus very easy, after the first discovery, to have a quite high number of researchers in the new field;

v) the laboratory was directed by Prof. Natta, fertile and productive mind, a well known and internationally recognized expert on the two essential aspects of the problems to be tackled: structural chemistry and catalytic synthesis;

vi) the Montecatini Company was able to give a ready and large financial support.

This series of favourable circumstances (financial support, researchers, interdisciplinary approach) determined the fact that, while other laboratories (Ziegler's in Mühlheim and the industrial laboratories of Phyllips Petroleum and Standard Oil of Indiana) dealt earlier than Natta with catalysts able (at least partially) to polymerize α-olefins in an ordered manner, they did not succeed in recognizing in time the value of the new polymerization processes and to implement the catalytic systems; they did not have, on the other hand, the possibility to characterize from the structural point of view, with the same rapidity, the crystalline polymers which could be obtained and to extend the investigation to new monomers.

In less than one year since the preparation of the first polymer of propylene, Natta was able to communicate, in the meeting of the Accademia dei Lincei of December 1954, that a new chapter had been disclosed in the field of macromolecular chemistry, due to the discovery of processes which allowed to obtain polymers with an extraordinary regularity in their structure from both the points of view of their chemical constitution and the configuration of the successive monomeric units along the chain of each macromolecule (⁸).

The clarity and depth with which the results were presented are worth to be remembered. Vinyl polymers may be considered to be constituted of structural units containing a tertiary carbon atom (Fig. 4) so that in a polymer with a finite length this carbon atom may be looked at as asymmetric: hence it is possible to have two kinds of enantiomeric units. There-

Fig. 4 - The two enantiomeric units in a regular vinyl polymer:

$$\ldots\ -\underset{\displaystyle R}{CH}-CH_2-\underset{\displaystyle R}{CH}-CH_2-\underset{\displaystyle R}{CH}-\ \ldots$$

fore, it was convenient to examine whether the observed crystallinity could have been determined by a regular succession of steric configurations for each monomeric unit.

The x-ray examination allowed to determine the lattice constants of crystalline polypropylene, polybutene-1 and polystyrene. The identity period along the chain axis — as determined by fibre diffraction patterns — resulted to be of the order of 6.5 Å, and could be attributed to a chain segment containing three monomeric units. Therefore, it was to be excluded that the crystallinity could have originated from a regular alternance of monomeric units characterized by enantiomeric steric configurations. On the contrary, it was evident that the polymeric chains had to be constituted by regular successions of monomeric units with the same steric configuration (9). This kind of structure was given the denomination « isotactic » (from the greek words « isos », the same, and « tasso », to put in order). The examination of the crystal structure of isotactic polymers — expecially polypropylene — showed that the chain conformation of these polymers is always helical. Fig. 5 shows the chain conformation of isotactic crystalline polypropylene as reported in a paper presented by Natta and Corradini to the Accademia dei Lincei in 1954.

Fig. 6 shows a more detailed model (comprising also the hydrogen atoms) of the chain of polypropylene, in two orthogonal projections, along the axis and perpendicularly to the axis of the chain.

It is seen that a ternary helix with three monomeric units per repeating unit is formed by the alternation of carbon-carbon bonds in *gauche* and *trans* conformations. Helicoidal chain structures in a polymer allow the repetition of identical configurational units in such a way that they take equivalent conformations in respect to an axis. It may be interesting to recall that at the beginning of the fifties the application of similar principles led Pauling to suggest the α-helix model for polyaminoacid and Watson and Crick to the double helix model for DNA.

As an example, Fig. 7 shows a comparison of the chain conformation of an isotactic polymer having 3.5 monomeric units per pitch (poly-4-methylpentene) with that of an α-helix having 3.7 aminoacid residues per pitch.

Soon after the discovery of isotactic polypropylene the research in Italy started to be directed along three different lines (10).

Fig. 5 (below) - Chain conformation (in two orthogonal projections) of the isotactic polypropylene chain as reported first in 1954.

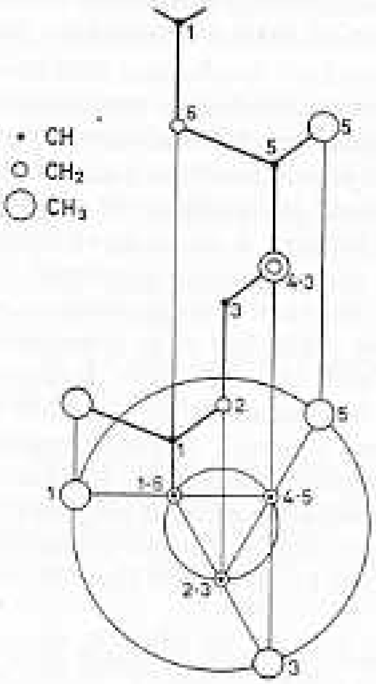
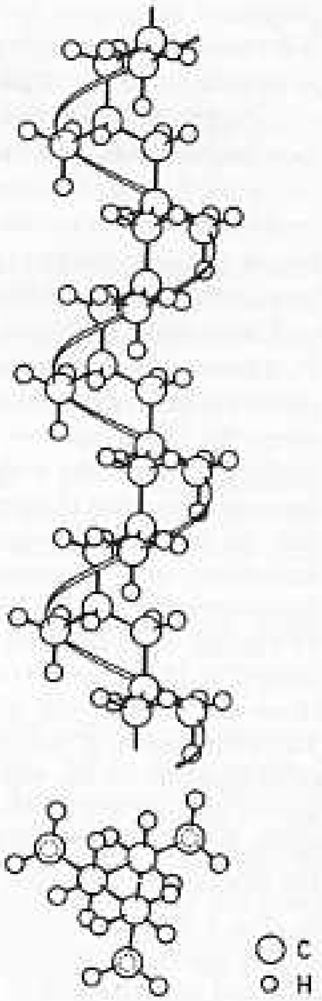


Fig. 6 (on the right) - Chain conformation of isotactic polypropylene comprising hydrogen atoms.



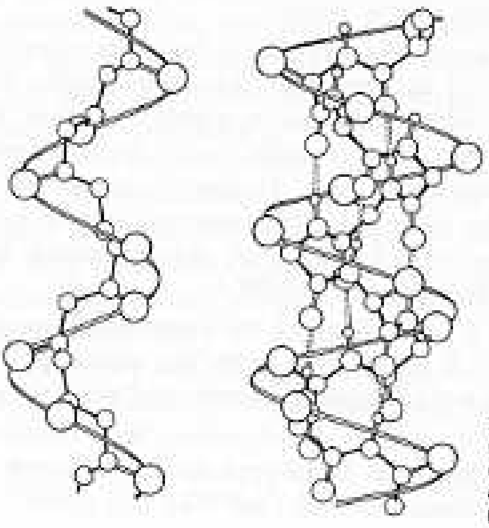


Fig. 7 - Chain conformation of an isotactic polymer with 3.5 units per pitch (on the left) compared with the chain conformation of Pauling's α-helix (on the right).

i) study of the synthesis of other types of stereoregular polymers from monomers with a chemical structure other than that of the simpler α-olefins;

ii) improvement of the study of the possible configurational successions in the new polymers and establishement of the relationships between chemical structure and macromolecular conformation;

iii) study of the most favourable conditions for the synthesis of olefinic and diolefinic hydrocarbon polymers in high yields and with high stereoregularity and study of the polymerization reaction mechanism.

These lines have, indeed, proved very fruitful and have contributed enormously to enlarge the field of macromolecular chemistry.

Remarkàble results were obtained, for instance, in the study of diene polymers. It was possible to obtain and characterize from the structural point of view isoprenic polymers with a 1,4 sequence having the double bonds always in the *cis* or in the *trans* configuration, as in the case of the well known natural polymers, rubber and guttapercha. The discovery of the stereospecific catalysis of polymerization has thus allowed mankind to disclose a new field which had always been thought to be in absolute control of nature.

In the case of the butadiene polymers, it was feasible to isolate and to characterize from the structural viewpoint all the four possible stereoregular polymers, two with 1,4 and two with 1,2 enchainement.

Fig. 8 shows the projection along (lower) and perpendicularly to the

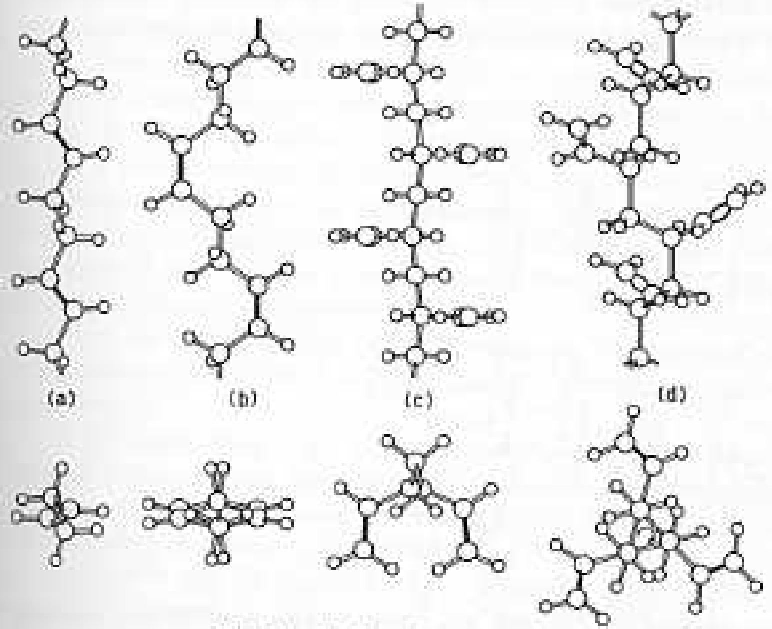


Fig. 8 - Conformations in the crystalline state of the four possible stereoregular chains of polybutadiene (a) 1-4 *trans*; b) 1-4 *cis*; c) 1-2 syndiotactic; d) 1-2 isotactic).

chain axis (higher) of their chain conformations in the crystalline state (11). The melting point of the 1,4-*trans* polybutadiene (Fig. 8,a) is higher than that of polyethylene, while the 1,4-*cis* polybutadiene (Fig. 8,b) is amorphous at room temperature and can be crystallized only if stretched. The latter is a particularly good synthetic rubber.

Two different kinds of stereoregular polymers can be obtained with butadiene when the sequence of monomeric units is of the 1,2 type. The first of them (Fig. 8,c), crystallizes with a chain conformation of ternary helix very similar to that previously shown for polypropylene; it is an isotactic polymer, characterized by the repetition of monomeric units with the same configuration. The second, on the other hand (Fig. 8,d) is characterized by the alternation of monomeric units which are chemically equivalent, but are in an opposite steric configuration. The latter kind of sequence of configurations was given the name of « syndiotactic », from the greek words « syn dyo », every two, and « tasso », to put in order.

This discovery led to recognize that even the long time known poly(vinyl chloride) exhibited a small degree of crystallinity due to the presence of short sequences of syndiotactic configurations (12).

Fig. 9 shows the first representation proposed for distinguishing easily the different types of stereoisomerism present in vinyl polymers, viewing the main chains as lying down on a plane: i) isotactic sequence of configurations; ii) syndiotactic sequence of configurations; iii) no order present, atactic sequence of configurations.

Besides the stereoregular polymers of dienes, the thorough investigation of the possibilities offered by the Ziegler-Natta catalysts in particular and

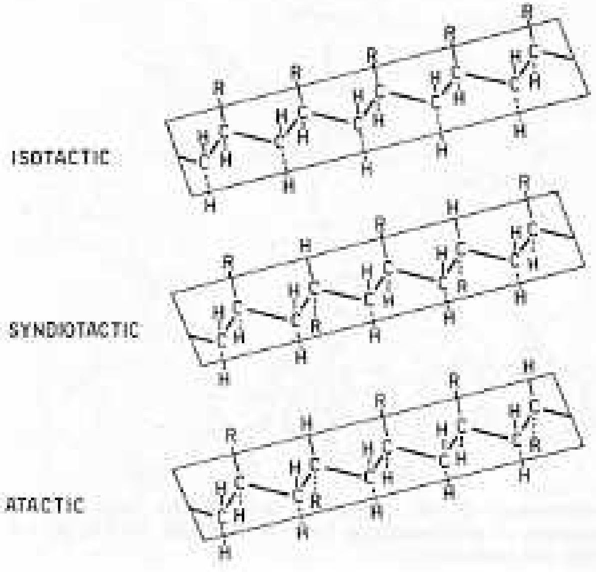


Fig. 9 - Schematic representation of the configuration of isotactic, syndiotactic and atactic vinyl polymers.

of the stereospecific polymerization catalysis in general has led to the acquisition of new classes of polymers, too numerous to be discussed here. I shall briefly mention, because of their importance as elastomers, only the ethylene-propylene copolymers and the stereoregular polymers obtained by a metathesis reaction through the opening of the cyclopentene ring. Among the most recent predominantly scientific investigations on the mechanism of stereoregulation, I will recall those on the polymerization of alkenes having a chiral center in the side chains, which have been carried on mainly by the school of Pino (13).

The need of a better understanding of how the sequences of configurations could affect the physical properties of the new polymers has led to a more careful investigation of the relationship among chemical structure, conformation and organization of macromolecules and physical properties.

As I have already mentioned, one of the strong points of Natta's school — especially at the beginning of the researches in the field of the stereospecific polimerizations — was the use of solvent fractionation on the crude polymers obtained. Unlike polymers obtained with different polymerization procedures known before, it soon became evident that, in the case of propylene polymers, the fractionation, at least under certain conditions, did not take place according to the molecular masses. Of the fractions with comparable intrinsic viscosities, those insoluble in ether, were clearly crystalline for temperatures below at least 130 °C, while the ones insoluble in acetone, but soluble in ether, were completely amorphous, even at low temperature.

The fraction insoluble in boiling *n*-heptane showed a melting point higher than 160 °C. The crystallinity increased with increasing melting point and insolubility, as it results from the x-ray diffraction patterns shown in Fig. 9. The explanation of these phenomena was correctly identified by Natta and co-workers in the presence, in the various extracted fractions, of different distributions of configurations. With the improvement of nuclear magnetic resonance techniques, this conclusion was fully confirmed, and allowed also to give a deeper insight into several aspects concerning the polymerization mechanism (14).

It can be useful, at this point, to represent the possible successions of configurations for a vinyl polymer, on the ground of relative local configurations.

At it results from Fig. 10, two monomeric units in sequence (constituting a « dyad ») can have too non-equivalent relative configurations; in analogy with the classic case of tartaric acids, these relative configurations are indicated as « meso » and « racemic » respectively.

A polymer will be ideally isotactic if all the dyads are meso; it will be ideally syndiotactic if all the dyads are racemic; in general, and according to the catalytic system, intermediate situations can occur.

Let us suppose now that, in the heterogeneous catalytic system orig-

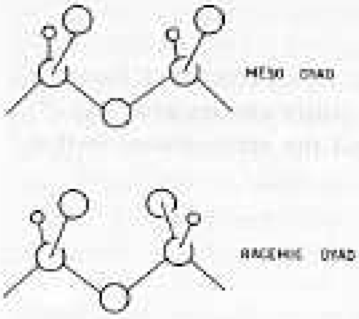


Fig. 10 - Meso and racemic relative configurations in a head-to-tail vinyl polymer.

inated by the reaction between $TiCl_4$ and aluminumalkyls, active sites of a different nature can be found; these active sites could differ both in their regiospecificity and capability of stereoregulation. If that is true, some active sites could have an extremely high capability of stereoregulation, giving rise to macromolecules insoluble in boiling *n*-heptane, with a percentage of « meso » dyads not far from 100%, while other active sites could have a lower capability of stereoregulation, so justifying the existence of fractions with increasing solubility, till the complete amorphous fractions even soluble in ether (Fig. 11).

The correct understanding of the reasons why it is possible to find fractions with different stereoregularity allowed to reach an immediate outcome of great technological importance, that is the synthesis of polypropylenes characterized — even unfractioned — by an extremely high degree of iso-

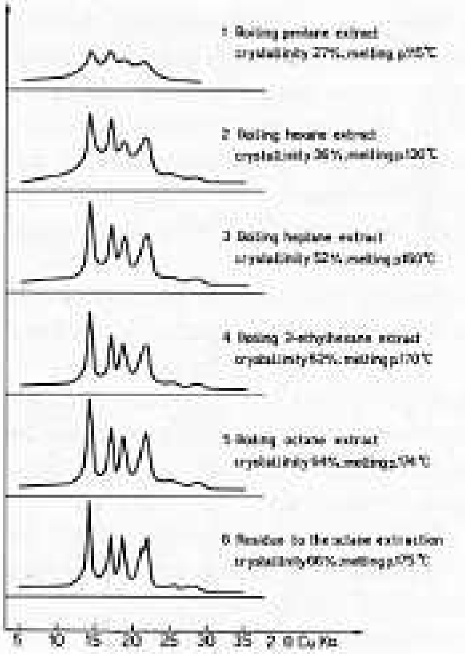


Fig. 11 - X-ray spectra of polypropylene fractions with increasing melting points and decreasing solubilities.

tacticity. This is possible starting, rather than from liquid $TiCl_4$ (the catalyst used by Ziegler for polyethylene), from solid $TiCl_3$, with a high degree of subdivision, in its violet polymorphic layer-structured forms α, γ or δ (the last two structurally characterized by Natta and co-workers) (^{10}). The extensive use of fractionation techniques and the comprehension that, in some catalytic systems, the presence of active sites characterized by extremely different capabilities of stereoregulation is possible, led sometimes to the identification and characterization of stereoregular polymers of a completely new kind. On the other hand, the synthesis and characterization of such polymers were the obvious starting point for the preparation of « ad hoc » catalytic systems for the production of polymers with satisfactory yields and steric purity.

The first polybutadiene with a structure mostly of the 1,4-*cis* type was isolated and identified, by means of x-rays, by extraction from a crude polymer containing equal percentages of 1,4-*trans* and 1,4-*cis* units; the syndiotactic polypropylene was firstly isolated in quantities of about 1% of the starting crude polymer (mostly isotactic and prepared by catalytic systems constituted by $TiCl_4$ and lythiumalkyls), starting from the observation that, at the x-ray examination, the hexanic extract was characterized by both the classic diffraction lines for isotactic polymers and one anomalous line, not particularly intense, corresponding to a Bragg distance of 5.4 Å.

The successive synthesis in high yields of syndiotactic polypropylene using homogeneous catalysts (different from the heterogeneous ones for the synthesis of isotactic polypropylene) constituted by VCl_4 and diethylmonochloridealuminum allowed its complete structural characterization. The syndiotactic polypropylene can crystallize in two different crystalline modifications arising from a different chain conformation. Fig. 12 shows

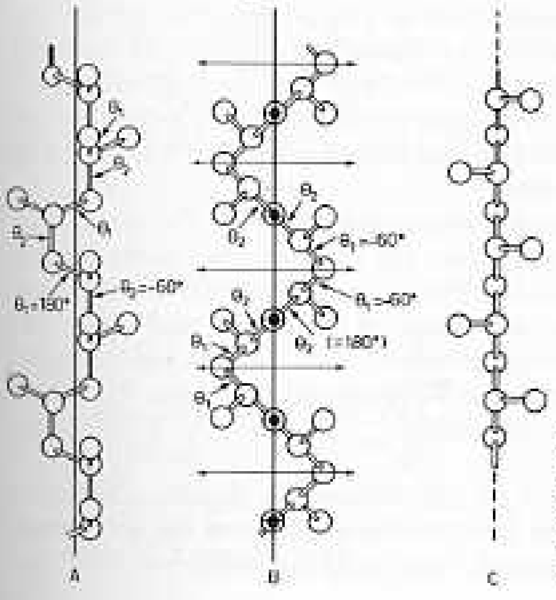


Fig. 12 - Comparison among the chain conformations of stereoregular polypropylenes: A) isotactic polypropylene; B) syndiotactic polypropylene, helicoidal modification; C) syndiotactic polypropylene, nearly zigzag planar modification.

a comparison between the models for the isotactic polypropylene chain (a ternary helix along which the chain bonds assume alternatively a *trans* and a *gauche* conformation) and the two possible syndiotactic polypropylene chain conformations: a planar zig-zag conformation, at the right hand side of the figure, corresponding to an all-*trans* bond sequence, and a helicoidal conformation, in the middle of the figure, in which bond pairs in *trans* ($\theta_1 = 180°$) conformation alternate with bond pairs in *gauche* ($\theta_2 = -60°$) conformation. It was possible to demonstrate that the chain conformations experimentally found for both these and other stereoregular polymers are in excellent agreement with the conformations foreseeable on the ground of the minimization of the internal energy (once the configuration has been assigned) under the condition of the repetition along one axis.

Without this condition, it is possible to foresee the conformation distribution for unperturbed chains, both in Θ solvents and in the melt.

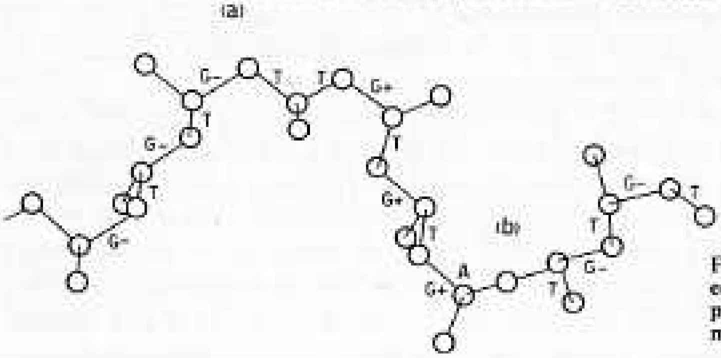


Fig. 13 Short spiralized sections of a polypropylene chain in the melt or in solution.

The isotactic polypropylene chain (Fig. 13) corresponds — in the melt — to a succession of short spiralized segments, alternating in opposite senses (16). Even if it is not possible here to give a deeper insight into the spatial conformation of polymeric chains, whose study was greatly promoted by the discovery of stereoregular polymers, and into the implications between molecular organization and physical properties, it may be appropriate to cite two meaningful sentences from the lecture given by Prof. P.J. Flory in the occasion of his Nobel prize (17).

> « Comprehension of the spatial relationship between the atoms of a molecule is a universal prerequisite for bridging the connection between the graphic formula and the properties of the substance so constituted. If the marked differences in properties that distinguish the great variety of polymeric substances, both natural and synthetic, are to be rationally understood in fundamental molecular terms, this must be the focus of future research ».

It may be of interest now to shortly discuss the possible mechanism that leads to the extremely high stereoregularity observed for polypropylenes. As we have already reported, high stereoregularity had been previously found only in natural polymers, obtained by enzymatic catalysis.

For some catalytic systems based on layered $TiCl_3$ it was found, by means of nuclear magnetic resonance studies that the resulting polypropylene macromolecules may show a fraction of « meso » dyads higher than 99%, and that in such polymers the « racemic » dyads appear always to be in pairs. With reference to the lower part of Fig. 14, the few inversions of configuration seem to happen according to the model a) rather than according to model b).

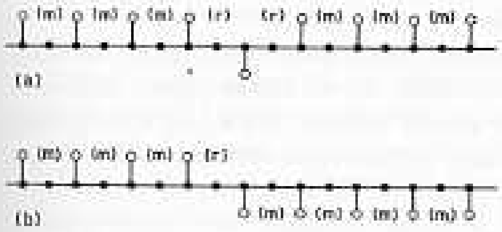


Fig. 14 - Possible inversions of configuration along the chain of a prevailingly isotactic polymer.

The monomer molecules show a strong tendency to be inserted on each catalytic site always with the same configuration. The hypothesis that the chirality of the chain which is growing on a metal-carbon bond influences the reactivity of the prochiral faces of the olefin can be excluded, because this hypothesis would be in agreement with model b) and not with model a). The structural investigation of the isotactic polymers of *cis* and *trans* 1-d_1-propylene shows, on the other hand, that the addition mechanism of the double bond is always *cis*. A possible model of the catalyst's surface ($TiCl_3$ in layers) which could be in good agreement with the high stereospecificity observed is shown in Fig. 15 (18).

Suppose that on a surface titanium atom are bound the growing chain and an olefin molecule in the proper orientation to give a primary insertion by *cis* migration. The intrinsic chirality of the catalytic site (in the case of the figure, Λ) would determine a shew orientation of the first carbon-carbon bond of the growing chain: the insertion of the olefin is thus more

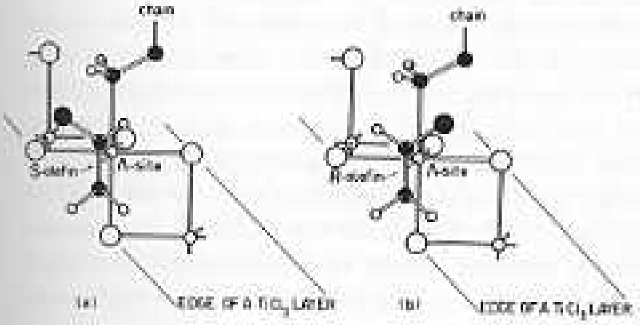


Fig. 15 - Possible model of a catalytic Λ site at the $TiCl_3$ surface: while the chain is bound to assume a chiral orientation, the preferred coordination of the olefin is with the S-face (case a).

difficult in model b) (because of steric interactions among the methyl group of the olefin and the chain atoms), while the insertion is easier in model a). The models a) and b) differ mainly with respect to the coordination face (*R* or *S*) of the olefin on the titanium atoms. We would have then a preferential insertion of the olefin with a given chirality on a given site, and this kind of insertion would be reproduced again even if an error occurred. This is confirmed by the synthesis of macromolecules, starting from racemic mixtures of optically active monomers, in which the monomeric units have a specific prevalence of chirality, according to the chirality of the site on which they have grown.

The various points already discussed in this paper have given an idea of the enormous consequences that the discovery of stereoregular polymers has produced in the field of macromolecular science; it may be appropriate at this point to try to give a quick flash on the most recent improvements of the stereospecific catalysts, on the technological versatility of polypropylene — the most important of the polymers obtained with stereospecific catalysts — and on the weight that the new synthetic processes have had on the industrial productions.

Some years ago, the feeling was that nothing better than a clarification and a better control of the stereospecificity mechanism could be obtained in the research on the catalysts. The art (if not the science) of preparing $TiCl_3$ catalysts with the highest possible surface activity appeared to be well consolidated.

At the end of the Sixties, however, new catalytic systems for the polymerization of ethylene were implemented, in which the titanium chloride is supported on a matrix, as, for instance, magnesium oxide or chloride. These new catalysts show a very high activity in the polymerization of ethylene, with yields of the order of 10^6 instead of 10^4 grams of polymer per gram of titanium. In the second generation plants for the production of high density polyethylene, the use of these catalysts avoids the expensive process of separating the catalyst from the polymer.

The new catalysts however were unsatisfying in the polymerization of propylene, where a control of the succession of the meso *versus* the racemic configurations along the polymer chain is necessary. The isotacticity index (the insoluble fraction in boiling *n*-heptane) of polypropylenes which can be obtained with high yields using catalysts for ethylene polymerization of the above kind, is in fact in the range 30-60%. This means that approximately one half of the macromolecules have a fraction of relative meso configurations lower than 95%, so that the most interesting technological characteristics of the polymer are heavily damaged. More recently, the research to design a high yield supported catalyst also for the isotactic polymerization of propylene too has led, with the help of the previous experience in the field, to the implementation in the Montedison research laboratories of a new catalytic system which is capable of so high yields

(300 000 g of polymer per gram of titanium) that the depuration process can be eliminated in the production plants; on the other side, the isotacticity is so high, that the heavy cost of the extraction of the amorphous fraction can be considerably reduced.

The research efforts to a better comprehension of the action mechanism of the Ziegler-Natta catalysts, of the nature of the catalyst surface and of the influence of various chemical agents are now paying back, in this way, also in terms of a simpler industrial process.

At the same time, studies intended to a better comprehension of the relationship between structure and properties have also advanced. The use of synthetic polymeric materials — and of composites in which the polymers are present — is always increasing, in substitution (at time, ameliorative) of natural, metallic or ceramic materials. In the near future, considering also the increasing consciousness of the limitation of the available resources and the need to increase the added value of the productions, it may be foreseen that the efforts of the producers of polymeric materials will be shifted from the concept of quantity to that of quality and aptness of the products to their specific usage. It is realized that the properties which allow to design a polymeric material for a certain usage depend, sometimes in a very complex way, also on the physical structure of the material and on its evolution in the time.

We can speak of « tailor-made » polymers — using an expression dear to Prof. Mark — in referring to specific chemical structures, designed to a certain usage. However, also differences in physical structure of the same material, obtained with a suitable treatment, or very small differences in chemical structure for materials which are practically identical from the chemical viewpoint, can result in noticeable differences in the manufacture and in the mechanical properties of the final products.

The manner of organization of the crystalline and amorphous phases in a polymeric solid with a given chemical structure is heavily dependent on the thermal and mechanical history of the sample. Fig. 16 shows the complexity of the molecular organization in a semicrystalline polymer. The crystals of a polymer appear to be as lamellas; the short axis of the lamellas is coincident with the axis of the macromolecular chains. Each chain is folded many times inside a single crystal (obtained from dilute solution) as shown in the upper part of the figure, but it may belong to many different crystals in the bulk of a polymer (lower part). The crystals and the amorphous regions can be oriented, depending on the manufacture process.

The amorphous regions are placed among the crystals; they can contain entire macromolecules (usually with lower molecular weight and tacticity), portions of macromolecules (a few decads of constitutional units) which belong to chain folds on the surface of the crystalline lamellas or to tie chains interconnecting adjacent crystals. Without giving more details, a significant

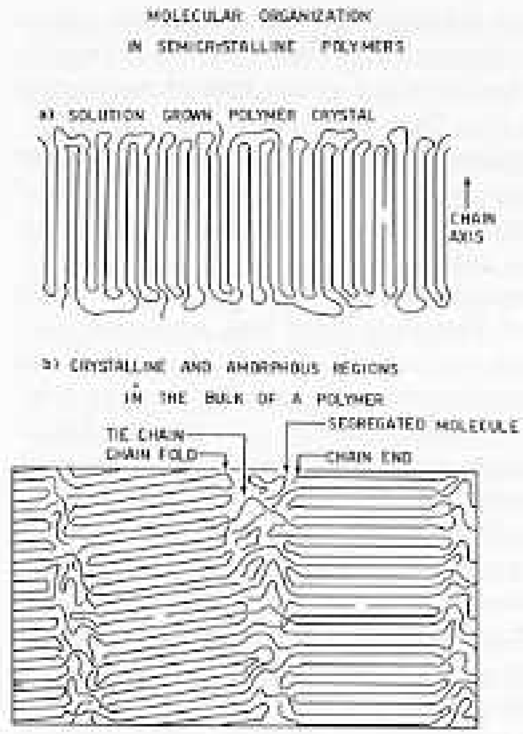


Fig. 16 - Schematic model of the molecular organization in semi-crystalline polymers.

example of the influence of the manufacturing process and of the resulting regulated morphology on the mechanical properties is provided just by isotactic polypropylene. Depending on the process we can obtain from a single material with given chemical structure (19):

i) strong fibres, which require high stresses to undergo small deformations and then break;

ii) ductile fibres, capable to sustain very high deformations (1 000%) before breaking;

iii) fragile fibres, which break up soon with very small deformations;

iv) elastic fibres, capable to deform up to 100% with the total recovering of the original length when the applied stress is removed.

From a single polymeric material it is possible to obtain extremely different mechanical behaviors. It is not possible to observe such extremely different behaviors in metallic or ceramic materials.

Similar considerations can be made in the case of polymeric films, with reference to the optical and mechanical properties, to their permeability to gases and to their weldability.

It is possible to speak today not only of « tailor made » chemical structures but also of « tailor made » physical structures.

The progress of the scientific and technological investigation of polymers, marked by the important discoveries of polymerization processes with coordinate catalysis, has led the industrial production of polymeric materials in the world to more than 50 million tons per year; this quantity is 10 times lower in mass, but of the same order in volume, than the world production of raw steel. It is important to underline that the production of synthetic polymeric materials was 500 times lower 50 years ago and 30 times lower 30 years ago than the present production. Today in the West Europe, the consumption of polymeric materials is more than 50 kg per year *pro capite*.

Is this an unending increase?

The oil crisis has led to a decrease, but not to a stop of the growth rate of production; on the other side the global needs of energy and petroleum (as a starting material) for the production of polymeric materials, at least in volume compare favourably with the production needs of other materials, as for instance, aluminum or steel (Table 1). Table 2 shows data on the 1978 consumption of the five main thermoplastic materials in the West Europe and all over the world (20).

TAB. 1 - ENERGY NEEDS FOR THE PREPARATION OF SOME INDUSTRIAL PRODUCTS (1976)

	PER UNIT MASS kJ/g	PER UNIT VOLUME kJ/cm^3
Aluminum	245	660
Steel	45	340
Glass	20	50
Paper	60	80
Polystyrene	140	150 (60)
Poly(vinyl chloride)	90	120 (35)
Polyolefins	100	95 (45)

The reported values comprise the energetic content of raw materials, such as petroleum (in parentheses).

The five main thermoplastic materials (which cover more than 50% of the overall industrial production of polymeric materials), are low and high density polyethylene, polypropylene, polystyrene and poly(vinyl chloride).

Two of them, the high density polyethylene and polypropylene, are produced using anionic catalytic processes of the Ziegler-Natta kind. Among the thermoplastic materials for which a sensible growth rate can still be foreseen we find the isotactic polypropylene, which represents today the 10% of the overall production and could increase, according to reliable estimates, to a 15% in the next ten years. A high increase can be in particular expected for polypropylene polymers in composites with glass fibres, or modified by blending or copolymerization with ethylene to give

TAB. 2 - CONSUMPTION OF THERMOPLASTIC MATERIALS
IN WESTERN EUROPE AND IN THE WORLD (1978)

	WESTERN EUROPE		WORLD (estimated)	
	CONSUMPTION $(\times 10^3 t)$	CONSUMPTION *pro capite* (kg/year)	CONSUMPTION $(\times 10^3 t)$	PERCENTAGE
Polyethylene (l.d.)	3 720	10.3	10 400	27.4
Polyethylene (h.d.)	1 380	3.9	4 180	11.0
Isotactic polypropylene	1 100	3.1	4 000	10.5
Polystyrene and cop.	2 060	5.8	6 900	18.2
Poly(vinyl chloride) and cop.	3 650	10.2	10 600	27.9
Others				~ 5

polymers more flexible and resistant at low temperature. Formulations of polypropylene with ethylene-propylene copolymers may result, finally, in thermoplastic elastomers (which are plastic at higher temperatures and rubbers at room temperature), which should be increasingly used in the automobile industry.

The present trends of macromolecular science fit into the scenery just sketched and are conditioned to some extent by the world wide tendency to enlarge the fields of usage of the *existing* polymeric materials (with the largest increments in the fields of housing, agriculture, transportation), by specializing their quality in relationship to uses. It is evident that macromolecular chemistry is becoming presently a mature science, and to this end, great has been the role of the discovery and investigation of the stereospecific polymerization and of the stereoregular polymers, marked by the genius of Prof. Giulio Natta.

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Stereospecific Polymerization of α-Olefins

The first paper of Professor Natta on this subject has been published in 1955 [G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* *77*, 1708 (1955)].

His activity in this field is proved by many publications. We quote, for instance: G. Natta, *Nuovo Cimento 15* (10) Suppl. 1, 9 (1960); G. Natta, M. Farina, M. Peraldo, *Makromol. Chem.* *38*, 13 (1960); G. Natta, I. Pasquon, A. Zambelli, *J. Am. Chem. Soc.* *84*, 1488 (1962); G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, *J. Am. Chem. Soc.* *83*, 3345 (1961); G. Natta, *Chim. Ind.* (*Milan*) 46, 397 (1964).

Prof. Adolfo Zambelli who is particularly expert in the mentioned subject has been requested to give a contribution to the volume. The contribution is entitled: *Some Aspects of the Mechanism of Stereospecific Polymerization of α-Olefins.*

Some Aspects of the Mechanism of Stereospecific Polymerization of α-Olefins

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1. Introduction

Stereospecific polymerization of α-olefins has been extensively reviewed few years ago in an excellent book (1).

As a consequence this article will just consider some topics concerning the different mechanisms of stereoregulation and the structure of polymeric materials obtained in the presence of different catalysts.

Fig. 1 shows the Fischer projections of three different stereoregular forms of polypropylene. Isotactic and syndiotactic polypropylenes (Fig. 1a and b) are obtained by homopolymerization of propene in the presence of suitable catalysts, e.g. $TiCl_3$-$Al(C_2H_5)_2Cl$ and VCl_4-$Al(C_2H_5)_2Cl$ respectively (2,3).

Head-to-head-tail-to-tail *erythro* diisotactic polypropylene (Fig. 1c) is

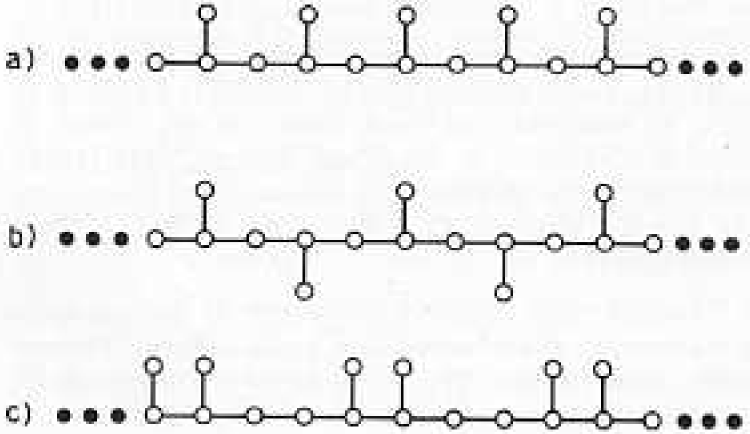

Fig. 1

obtained by copolymerization of *cis*-2-butene with ethylene in the presence of VCl_4-$Al(C_2H_5)_3$ (4).

In order to succeed in preparing isotactic and syndiotactic polypropylene, regiospecific and stereospecific processes are required.

For the preparation of head-to-head-tail-to-tail *erythro* diisotactic polypropylene it is required that:

i) - the overall stereochemical mechanism of addition to the double bond of *cis*-2-butene is *cis*;

ii) - the addition of 2-butene molecules to a given growing chain produces monomer units having constant configuration;

iii) - that alternate copolymerization with ethylene is achieved.

In the following sections some aspects of the polymerization mechanisms are considered in order to understand how the previous requirements are met in the presence of the quoted catalytic systems. Ethylene-propene copolymerization is also briefly considered.

2. Isotactic polypropylene

Isotactic specific polymerization of propene is typically performed in the presence of heterogeneous catalytic systems consisting of a halide of early transition metals (in bulk or supported) and of a base metallorganic compound (2). Polymerization occurs on the surface of the solid cocatalyst and the analysis of the end groups of the polymer shows that chain growth involves insertion of the monomer on reactive metal-carbon bonds (5,6).

A number of evidences show that the active metal is the transition one (7). It has also been experimentally observed that:

i) - the overall stereochemical mechanism of addition to the double bond of the monomer is *cis* (8);

ii) - the regiospecificity of the monomer insertion is primary (or metal to C_1) (5,6):

$$Mt \ldots \xrightarrow{+\ C_3H_6} Mt\,CH_2CH(CH_3) \ldots$$

primary insertion of propene

$$Mt \ldots \xrightarrow{+\ C_3H_6} Mt\,CH(CH_3)CH_2 \ldots$$

secondary insertion of propene

iii) - the stereochemical sequence of the configurations of the substituted carbons is accounted for by the « enantiomorphous sites » model (9,10).

This model assumes that the whole catalyst is a racemic mixture of enantiomorphous catalytic sites (D preferring sites and L preferring sites).

The probability that the addition of the monomer gives a monomer unit having D (L) configuration is $P_{DD}(P_{LL})$ for the D(L) preferring sites. The probability of having L(D) configuration is $P_{DL}(P_{LD}) = 1 - P_{DD}(P_{LL})$. Of course $P_{DD} = P_{LL}$.

It is important to point out that the D or L preferring character of the active sites is not related to the last unit of the growing chain end.

As a consequence, the more recurrent irregularity in the stereochemical sequence of the isotactic homopolymers is ... *m m m r r m m m* ... (10) and in ethylene propene copolymers prepared in the presence of isotactic specific catalysts, isolated ethylene units span propylene units of the same configuration (Fig. 2) (11).

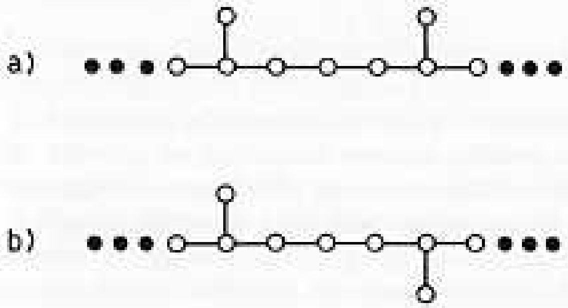

Fig. 2

Indeed Arlman and Cossee (12) observed that the transition metal atoms at the surface of the solid cocatalyst are in asymmetric environment, and suggested that stereoregulation arises from the non bonded interaction of the prochyral monomer with the ligands of the active sites.

Corradini and co-workers (13) suggested that stereoregulation could ultimately arise from the chyral orientation of the bond between the CH_2 and the $CH(CH_3)$ of the growing chain end.

3. Syndiotactic polypropylene

Syndiotactic polymerization of propene occurs in the presence of homogeneous catalytic systems, e.g. VCl_4-$Al(C_2H_5)_2Cl$ (5). Also in this case many evidences suggest that propagation involves insertion of the monomer on reactive transition metal carbon bonds (14). The overall stereochemical mechanism of addition to the double bond is *cis* (15) like in isotactic polymerization.

The regioregularity of syndiotactic polypropylene is lower than that of isotactic polypropylene and none of the four possible insertion steps:

$$Mt \vdash\!\bullet \ldots \xrightarrow{+\ C_3H_6} Mt \vdash\!\bullet \vdash\!\bullet \ldots 1\ 1$$

$$Mt \vdash\!\bullet \ldots \xrightarrow{+\ C_3H_6} Mt \bullet\!\dashv \vdash\!\bullet \ldots 1\ 2$$

$$Mt \bullet\!\dashv \ldots \xrightarrow{+\ C_3H_6} Mt \bullet\!\dashv \bullet\!\dashv \ldots 2\ 2$$

$$Mt \bullet\!\dashv \ldots \xrightarrow{+\ C_3H_6} Mt \vdash\!\bullet \bullet\!\dashv \ldots 2\ 1$$

is negligible (11,16). (Mt = metal atom of the catalytic complex, $\vdash\!\bullet$ = CH_2-$CH(CH_3)$, $\bullet\!\dashv$ = $CH(CH_3)$-CH_2).

It has been reported in the literature (11,17) that $k_{22}/k_{21} > k_{11}/k_{12} > 1$ (where k_{ij} is the kinetic constant relative to step ij) so that step 22 accounts for most of the monomer polymerized, and that step 22 is the only syndiotactic specific one (6,11). The stereospecific propagation process 22 occurs according to the symmetric Bernoullian model proposed by Bovey and Tiers (17).

According to this model

$$P_r = [r] \qquad P_m = 1 - P_r$$

where $[r]$ = molar fraction of syndiotactic dyads in the polymer (neglecting the effect of the regioirregularity). (P_r = propagation probability of syndiotactic dyads, P_m = propagation probability of isotactic dyads).

The regio- and stereochemical structure of both the homopolymers of propene and the ethylene-propene copolymers prepared in the presence of syndiotactic specific catalysts is in agreement with the previous considerations on the propagation mechanism (*i.e.* Markovian model of the regiospecific propagation, symmetric Bernoullian model for the stereospecific propagation according to step 22).

A consequence of this propagation model is that steric control ultimately arises from the asymmetric configuration of the last unit of the growing chain end (18). A detailed reaction mechanism for syndiotactic polymerization has been proposed in the literature (19). All the previous observations are accounted for by assuming homogeneous catalytic complexes consisting of a pentacoordinate vanadium atom bearing a σ metal-carbon bond, three chlorine ligands and a coordinated monomer. The V is assumed to be essentially achiral.

4. Erythro diisotactic head-to-head-tail-to-tail polypropylene

As pointed out in sect. 1 this unusual polypropylene can be obtained from alternate copolymerization of *cis* 2-butene with ethylene, in the presence of the catalytic system VCl_4-$Al(C_2H_5)_3$ (4). Polymerization occurs by insertion of the monomers on reactive metal-carbon bonds.

$$Mt \vdash\!\dashv \quad \ldots \xrightarrow{+\ C_2H_4} Mt \vdash\!\dashv \vdash\!\dashv \qquad \ldots 1'\ 1'$$

$$Mt \vdash\!\dashv \;\ldots \xrightarrow{+\,C_4H_8} Mt \bullet\!-\!\bullet \vdash\!\dashv \;\ldots 1'2'$$

$$Mt \bullet\!-\!\bullet \;\ldots \xrightarrow{+\,C_4H_{10}} Mt \bullet\!-\!\bullet \bullet\!-\!\bullet \;\ldots 2'2'$$

$$Mt \bullet\!-\!\bullet \;\ldots \xrightarrow{+\,C_2H_4} Mt \vdash\!\dashv \bullet\!-\!\bullet \;\ldots 2'1$$

where Mt = metal atom of the catalytic complex, $\vdash\!\dashv$ = CH_2-CH_2, $\bullet\!-\!\bullet$ = $CH(CH_3)$-$CH(CH_3)$.

It is possible to obtain alternating copolymers because $k_{2'2'} = 0$ ($k_{2'2'}$ is the kinetic constant of copolymerization step 2'2').

Since $k_{1'1'} \gg k_{1'2'}$, $k_{2'1'}$, a very high C_4H_8/C_2H_4 ratio is needed in the feed.

The *erythro* structure of the polymer is a consequence of the *cis* opening of the double bond. Of course the regiospecificity is out of question due to the symmetry of the monomers.

It may be worthwhile to observe that:

i) - the catalyst system used in stereospecific alternate copolymerization (VCl_4-$Al(C_2H_5)_3$) is not stereospecific in polymerization of propene (19);

ii) - in the presence of heterogeneous catalysts, isotactic specific in the polymerization of propene, alternating copolymerization has not been achieved due to the low relative reactivity of 2-butene (9);

iii) - in the presence of syndiotactic specific catalysts alternating copolymerization can be achieved but the polymer lacks in stereoregularity (9).

The isotactic structure of the polymer obtained in the presence of VCl_4-$Al(C_2H_5)_3$ could arise, in principle, either from the asymmetry of the last 2-butene unit of the growing chain end or the possible asymmetry of the catalytic complex.

The previous observations [particularly iii] and the fact that the closest asymmetric carbon is two bonds apart from the metal carbon bond, when the insertion of 2-butene occurs, seems to disfavour the first hypothesis concerning steric control.

5. Ethylene-propene copolymers

Structure and properties of ethylene-propene copolymers are greatly influenced by the catalyst used in copolymerization. This is quite obvious for block copolymers which have intermediate properties between polyethylene and the corresponding polypropylene.

Statistic copolymers of ethylene with propene having elastomeric properties are also produced (20). Introduction of methyl substituents amorphises polyethylene chains to a degree depending on the amount and the distribution statistic. In order to optimize the elastomeric properties it is necessary to amorphise completely the copolymer chains with an amount of propene units as low as possible. The needed amount of propene units depends on the monomer sequence distribution which, in turn, depends on the catalyst used to perform copolymerization.

As discussed in sect. 3, in the presence of syndiotactic catalysts, propagation of propene chains is sensitive to the non bonded interactions between the growing chain and the monomer. The same is true for ethylene-propene copolymerization. As a consequence these catalysts ensure the best distribution of comonomer units (21).

6. Conclusion

The ultimate goal of a discussion concerning the mechanism of stereospecific polymerization is a correlation between the structure of the catalysts, the reaction mechanism and the structure of the reaction products.

Unfortunately the direct evidences concerning catalytic centers are scanty. It seems well established that all the considered catalysts are organometallic complexes of the early transition metals. Most probably monomer coordinates to the transition metal before insertion on the reactive metal carbon bond.

The different regiospecificity of isotactic and syndiotactic polymerization of propene could be due to a different coordination number around the transition metal atom of the catalytic complexes.

An essentially hexacoordinate transition metal atom has been proposed for the isospecific catalytic centers (12). On such highly hindered centers primary insertion of the monomer should be favoured. In such case the substituted carbon of the last unit of the growing chain end should be far enough as not to interfere with the steric control arising from the (asymmetric) transition metal.

Pentacoordinate transition metal atoms have been proposed for the syndiospecific catalyst (19). The lower coordination should leave enough room around the metal for secondary insertion of propene (20).

The presence of a substituted carbon α to the metal should be a necessary requirement for syndiotactic steric control.

Insertion of 2-butene on the highly hindered isotactic specific centers is impossible.

On syndiotactic specific complexes 2-butene insertion is possible because of the lower coordination number (at least when the last unit of the growing chain end is ethylene), but it is not stereospecific since the environment of the catalyst is essentially symmetric (20) and the substituted carbon is too far from the reactive metal carbon bond.

The catalyst for alternate stereospecific copolymerization of *cis* 2-butene with ethylene should be asymmetric but less sterically hindered than those affording isotactic polymerization of propene.

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Stereospecific Polymerization of Polyolefins

The first paper of Professor Natta on this subject has been published in 1956 [G. Natta, P. Corradini, L. Porri, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.* (8) *20*, 728 (1956)].

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Prof. Lido Porri who collaborated with Giulio Natta in this field from the beginning has been requested to give a contribution to the volume. The contribution is entitled: *Stereospecific Polymerization of Dienes: Achievements and Perspectives.*

Stereospecific Polymerization of Dienes: Achievements and Perspectives

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Conjugated diolefins were the 2nd class of hydrocarbon monomers to be polymerized with transition metal catalysts. Work on diolefin polymerization began in 1954 soon after the first results on the polymerization of propylene and other α-olefins were obtained.

Methods for the polymerization of diolefins had long been known in 1954, but none had yielded polymers with a high regularity of structure from the most common diolefins.

With Na or K catalysts polymers consisting predominantly of 1,2 units could be prepared, in some cases above 95%. However, no crystallinity was detected in these polymers by x-ray, because of a lack of configurational order at the tertiary carbon atoms of each macromolecule (1).

It is now known that, among alkali metals, lithium and its derivatives can give isoprene polymers consisting of 90-92% *cis*-1,4 units, which are thus capable of crystallizing on stretching. However, these stereospecific properties of lithium catalysts were observed only after the discovery of coordination catalysts (1,2). So, it may be said that no polymer with a regular structure was synthesized by alkali metal catalysts before 1954.

Cationic initiators gave diolefin polymers with a very irregular structure, due to cross-linking or cyclization (3).

Polymers with some structural regularity were obtained with radical initiators, but only from some particular diolefins. Polybutadienes consisting of ca. 80% *trans*-1,4 units were obtained with radical initiators at low polymerization temperature (4). When examined stretched below 0 °C (5), these polymers exhibit a low degree of crystallinity due to the presence of *trans*-1,4 sequences in the chain. Poly(chloroprene) consisting of ca. 95% *trans* units and exhibiting a good degree of crystallinity at room temperature, was obtained with radical initiators (6), operating below 0 °C.

The introduction of the so called « Alfin » catalyst, a heterogeneous system consisting of a combination of sodium allyl, sodium isopropoxide and sodium chloride, is a step forward from the previous systems in its ability to yield regular diolefin polymers. With this system A.A. Morton in 1947 prepared a polybutadiene consisting of 72-75% *trans*-1,4 units, and exhibiting at room temperature, in the unstretched state, some degree of crystallinity attributable to sequences made up of *trans*-1,4 units only (7). It was later found that the Alfin catalyst yields crystalline isotactic polymers from styrene (8). This system may therefore be considered as the first example of a stereospecific organometallic polymerization catalyst.

The radical polychloroprene and the Alfin polybutadiene were the only two synthetic diolefin polymers exhibiting crystallinity at room temperature in the unstretched state known before 1954.

The only two highly regular polymers of polydiolefin structure known at that time were the two natural polymers guttapercha and natural rubber, a *trans*-1,4 and a *cis*-1,4 polyisoprene respectively.

The introduction of the transition metal catalysts had a dramatic effect on the field of diolefin polymerization. The new catalysts were found capable of yielding macromolecules consisting almost exclusively of monomeric units of the same type (1,2; *trans*-1,4; *cis*-1,4) in a regular head-to-tail arrangement. Moreover, macromolecules with a very high degree of steric regularity were obtained from monomers that give monomeric units containing asymmetric carbon atoms. Various types of dienes have been polymerized with the new organometallic catalysts. Besides butadiene, monosubstituted butadienes of the type $CH_2{=}CH{-}CH{=}CHR$ or $CH_2{=}CR{-}CH{=}CH_2$ have been polymerized, as have disubstituted butadienes (with the substituents at position 2-3, 2-4 or 1-4). Various types of allene monomers have also been used.

Highly stereoregular crystalline polymers have been prepared from each of these classes of monomers. The following chapters report a review of the most significant results obtained in transition metal catalyzed diolefin polymerization.

Stereoregular polymers from 1,3-dienes

Four different highly stereoregular polymers were obtained from butadiene (Table 1). A highly crystalline *trans*-1,4 polymer was obtained at the beginning of 1955 (9), a 1,2-syndiotactic polymer a few months later (10). Syndiotactic polybutadiene was the first highly crystalline polymer with a syndiotactic structure. The term syndiotactic was coined when it was first prepared.

In April 1956 another crystalline 1,2-polybutadiene, with an isotactic structure, was prepared (11). Butadiene was the first monomer from which both an isotactic and a syndiotactic polymer were prepared. Approximately at the same time a *cis*-1,4 polybutadiene was also obtained (12).

TAB. 1 - STEREOREGULAR POLYMERS FROM SOME COMMON 1,3-DIENES

MONOMER	POLYMER *	CATALYST SYSTEM	REFERENCES
Butadiene	*trans*-1,4 (1955)	Al*Et*$_3$-αTiCl$_3$; Al*Et*$_3$-VCl$_3$; Al*Et*$_2$Cl-V(acac)$_3$; [η^3-(C$_4$H$_7$)NiI]$_2$	(9), (30), (53), (61), (63)
	1,2-syndiotactic (1955)	Al*Et*$_3$-V(acac)$_3$; Al*Et*$_3$-Cr(acac)$_3$; Al*Et*$_3$-Mo(acac)$_3$	(10), (47), (46)
	1,2-isotactic (1956)	Al*Et*$_3$-Cr(acac)$_3$; Al*Et*$_3$-Cr(CN*Ph*)$_6$	(11), (48)
	cis-1,4 (1956)	Al*Et*$_3$-TiI$_4$; Al*Et*$_2$Cl-Co(acac)$_2$-H$_2$O; Al*Et*$_3$-BF$_3$-Ni(OCO*R*)$_2$; Al*Et*$_2$Cl-Nd(OCO*R*)$_3$-Al(*i*-*Bu*)$_3$	(12), (53-7), (60), (45)
Isoprene	*cis*-1,4 (1954)	Al*Et*$_3$-TiCl$_4$ (Al/Ti = 1)	(14), (62)
	trans-1,4 (1955)	Al*Et*$_3$-VCl$_3$; Al*Et*$_3$-αTiCl$_3$	(9), (30-2)
	3,4 (1955)	Al*Et*$_3$-Ti(O*R*)$_4$	(15)
Pentadiene	*trans*-1,4-isotactic (1955)	Al*Et*$_3$-αTiCl$_3$; Al*Et*$_3$-VCl$_3$	(9), (16)
	cis-1,4-syndiotactic (1962)	Al*Et*$_2$Cl-Co(acac)$_2$-H$_2$O	(17), (38)
	cis-1,4-isotactic (1963)	Al*Et*$_3$-Ti(O*R*)$_4$; Al*Et*$_2$Cl-Nd(OCO*R*)$_3$- -Al(*i*-*Bu*)$_3$	(18), (39)
	1,2-syndiotactic (1965)	Al*Et*$_2$Cl-Co(acac)$_2$-heptane	(19)

* The date reported is that of the first patent application or of the first paper.

The first three polymers (*trans*-1,4; 1,2-syndiotactic; 1,2-isotactic) were prepared and characterized by the group in Milan. A high-*cis* polybutadiene, capable of crystallizing at room temperature upon stretching, was also prepared and characterized by this group in July 1956, but the first patent on the preparation of this polymer was filed by Phillips Co. three months previously (12). The crystalline structure of the *cis* polybutadiene was, however, determined by the Milan group and published in the second half of 1956 (13).

The preparation of the four stereoregular polymers of butadiene has certainly been one of the most brilliant achievements of stereospecific polymerization with transition metal catalysts.

Stereoregular polymers were also obtained from isoprene (Table 1). A *cis*-1,4 polymer, practically identical to natural rubber, was prepared in Dec. 1954 in the Goodrich laboratories (14), while a *trans*-1,4 polymer identical to natural guttapercha, was prepared by the Milan group at the beginning of 1955 (9). A 3,4-polyisoprene was also obtained; this, however, was found to be amorphous by x-ray at room temperature, due presumably to low stereoregularity (15).

Several stereoregular polymers were obtained from 1-substituted butadienes, in particular from 1,3-pentadiene (Table 1). Monomers of this type give 1,4- units, $-CH_2-CH=CH-\overset{*}{C}H(R)-$, each containing an asymmetric carbon atom, and hence two types of stereoregular *cis*-1,4 or *trans*-1,4 polymers are possible, isotactic and syndiotactic.

Three crystalline polymers with a 1,4 structure [*trans*-1,4-isotactic (16); *cis*-1,4-isotactic (17); *cis*-1,4-syndiotactic (18)] and a polymer with a 1,2-syndiotactic structure (19) were obtained from pentadiene.

Among the 1,4-disubstituted butadienes, only 2,4-hexadiene and two deuterated diolefins [(*Z*,*Z*)-1,4-d_2-1,3-butadiene; (*E*,*E*)-1-d_1-1,3-pentadiene] have been studied. Stereoregular polymers with a *trans*-1,4-*threo*-diisotactic structure have been obtained from each of these monomers (20-23,41), while stereoregular *cis* polymers with a *threo* disyndiotactic structure have been obtained from the deuterated butadiene (22) and pentadiene (23).

This rapid review gives a clear idea of the impact of transition metal catalysts on 1,3-dienes polymerization. There is no doubt that polymerization of conjugated diolefins, much more than that of other monomers, has shown the power of transition metal catalysts to stereoregulate a polymerization.

Other polymers from 1,3-dienes

EQUIBINARY POLYDIOLEFINS

In addition to the stereoregular polymers reported in the preceding section, transition metal catalysts have been found to yield a particular type of diolefin homopolymers, characterized by the fact that they consist of two types of monomeric units, in a practically 1 : 1 ratio. These homopolymers have been called « equibinary » polydiolefins by Teyssié and co-workers, who first described a 1,4 polybutadiene consisting of about 50% *cis*-1,4 and 50% *trans*-1,4 units (24). Polybutadienes consisting of about 50% *cis*-1,4 and about 50% 1,2 units have later been prepared by Furukawa (25-27). A polypentadiene consisting of about 50% *trans*-1,4 and about 50% 1,2 units has also been reported (41,42).

All the equibinary polymers prepared are amorphous by x-ray and IR examination, and hence they may not be considered as stereoregular polymers. They are formed when a catalyst can yield two types of monomeric units, with an equal probability.

Homopolymers of this type have been obtained only with transition metal catalysts, and therefore it seems appropriate to mention them in this review.

ALTERNATING MONOOLEFIN-DIOLEFIN COPOLYMERS

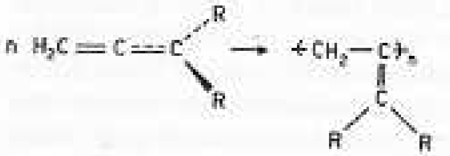
Some alternating monoolefin-diolefin copolymers have been prepared with transition metal catalysts, e.g. ethylene-butadiene (28), propylene-butadiene (29), propylene-isoprene (29). The mechanism of formation of these copolymers differs from that of other alternating copolymers prepared by radical initiators (e.g. the copolymers containing maleic anhydride as comonomer) or by transition metal catalysts (e.g. ethylene-cyclopentene, ethylene-but-2-ene copolymers).

All the alternating olefin-olefin copolymers so far known are characterized by the fact that one comonomer, for steric reasons, does not homopolymerize. The alternating olefin-diolefin copolymers differ in that each comonomer can homopolymerize with the catalyst systems used (e.g. $AlEt_3$-$VO(OR)_3$-Lewis base).

The driving force for the formation of these alternating copolymers is likely to be found in the particular situation of the coordination sphere of the transition metal of the catalyst. Presumably, when the last polymerized unit is the monoolefin two coordination sites are available, and this favors the coordination of the diolefin with the two double bonds, whereas when the last polymerized unit is the diolefin (which is bonded to the transition metal by an allylic bond) only one coordination site remains available, and this favors the coordination of the monoolefin. The formation of this type of alternating copolymers is, therefore, peculiar to transition metal catalysts.

Stereoregular polymers from allene monomers

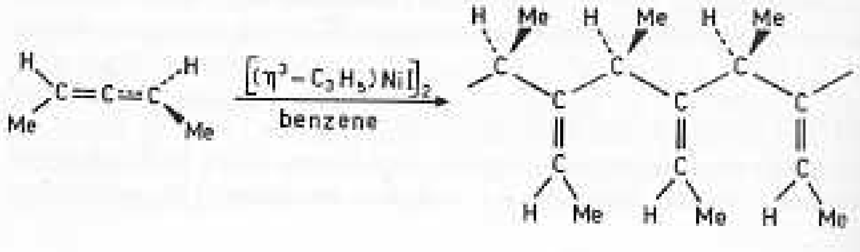
Allene and 1,1-disubstituted allenes have afforded with transition metal catalysts highly crystalline polymers consisting of a regular head-to-tail arrangement of 1,2 monomeric units:



(R = H or alkyl group)

Several catalysts have been used but the most regular polymers have been obtained with catalysts derived from nickel and rhodium (30,31).

Polymers characterized by some degree of stereoregularity have been obtained from dyssimmetric monomers, such as 1,3-dimethylallene. The optically active monomer afforded a polymer with stereoregular sequences of the following type (32):



These sequences contain two type of configurational order: one at the asymmetric carbon atoms of the main chain, which is of the isotactic type, the other at the configuration of the double bonds attached to the main chain. If the macromolecule is stretched on the plane, the methyl groups are all on the same side, with respect to the double bond. The polymer of 1,3-dimethylallene is the first (and so far only) example of this new type of stereoregularity.

Mechanistic interpretation of diene polymerization

The intensive work carried out since the beginning of the sixties has clarified some basic aspects of the mechanism of diolefin polymerization.

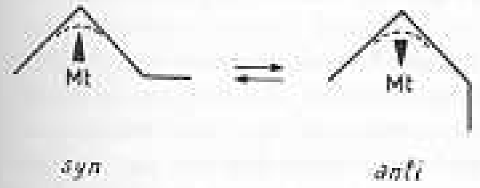
The following pages examine the current understanding of the factors that determine the formation of stereoregular diolefin polymers.

It was soon recognized (in 1963) that the bond between the transition metal and the growing chain is of the allylic type. Some peculiar features of the polymerization of dienes, with respect to that of α-olefins, are attributable to the particular properties of this type of bond.

In 1954, at the beginning of stereospecific polymerization, no allyl complex of a transition metal was known. Work on this field began in 1960 and soon led to the clarification of the nature and properties of this type of bond and also to the isolation of very simple and relatively stable allyl complexes of various transition metals. The importance of these compounds as catalysts for the polymerization of diolefins or as model compounds for mechanistic studies was soon realized. In 1964 three different groups ($^{33-35}$) reported on the polymerization of butadiene to *cis*-1,4, *trans*-1,4 and 1,2 polymers using as catalysts simple η^3-allyl derivatives of Ni, Cr, Co. The work on allyl complexes of transition metals by organometallic chemists, and the use of these complexes as polymerization catalysts by polymer chemists, has fundamentally contributed to the elucidation of some basic aspects of the catalysis of diolefin polymerization.

One cannot understand the mechanism of diolefin polymerization without considering the following properties of the η^3-allyl-metal bond.

1) Two isomeric forms are possible for a terminally substituted allyl group, *anti* and *syn*, which are in equilibrium:

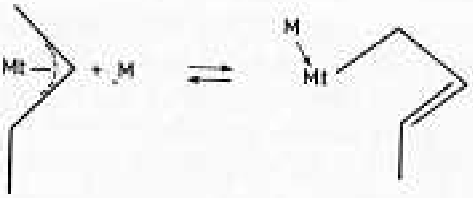


(Mt = transition metal)

Evidence for these two isomers was first reported in 1961 (^{36}); the implications of this isomerism on the stereospecific properties of transition metal catalysts were recognized a few years later (37-40).

2) Insertion reactions into an η^3-allyl-metal bond in general, (and monomer insertion in particular) occur in two steps.

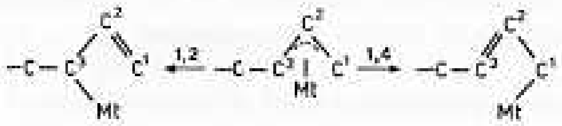
The first step is the formation of an η^1-allyl, as a result of the coordination of the monomer (or of any other reactant molecule, e.g. CO, an olefin and s.o.) to the transition metal:



(M = monomer)

The 2nd step is the actual insertion process into the Mt-C σ bond (this point will be examined later). Various types of evidence favor the formation of an η^1-allyl by interaction of electron donors with η^3-allyl complexes. The monomer-promoted formation of an η^1-allyl, with rapidly reversible monomer coordination, was clearly demonstrated by NMR in the case of the insertion of butadiene into η^3-butenyl-Pd-Cl (41,42).

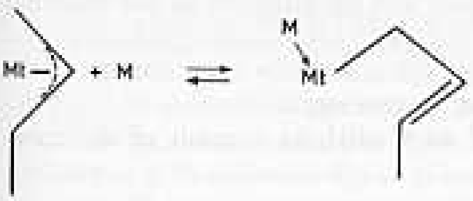
3) An η^3-allyl-metal bond has two reactive points, C^1 and C^3. The investigation of insertion reactions of various compounds (1,3-dienes, allenes, CO, CO_2, *etc.*) into allyl complexes has clarified this point. In polymerization, reaction of incoming monomer at C^1 gives a 1,4 unit, while reaction at C^3 gives a 1,2 unit. The following scheme shows the η^1-allylic intermediate in each case:



FORMATION OF STEREOREGULAR 1,4 POLYMERS

As shown in Table 1, all *trans*-1,4 and all *cis*-1,4 polymers have been obtained from various diolefins.

The formation of a *cis*-1,4 or of a *trans*-1,4 unit depends on the structure, *anti* or *syn*, of the last polymerized unit at the moment of monomer insertion. As indicated previously, when the new monomer coordinates to the transition metal an η^1-allylic species is formed; the configuration of the double bond of this species is related to the structure of the last polymerized unit:



(*M* = monomer)

The 2nd step consists of a transfer of the *Mt*-C σ bond to the coordinated monomer. A diolefin can coordinate with only one or both double bonds, depending on the coordinative unsaturation around the transition metal and also on the structure of the monomer (for some diolefins, e.g. (Z)-1,3-pentadiene, the cisoid conformation is unfavored). Coordination with one double bond gives rise to a new *syn* allylic complex, while coordination with both double bonds gives rise to a new *anti* complex.

Fig. 1 shows a scheme for the formation of a *trans*-1,4 (*cis*-1,4) unit from a *syn* (*anti*) complex. A 1,4-substituted monomer is used to show the stereochemistry of monomer insertion, which will be discussed later in this section.

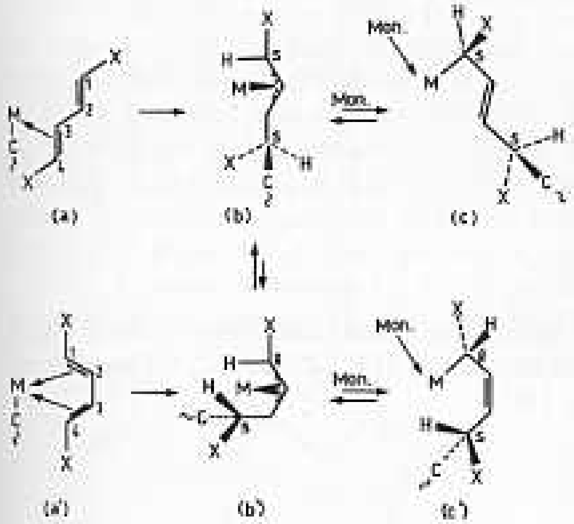


Fig. 1

The above interpretation is the result of considerable research carried out by various groups; however the basic concepts of this interpretation were already clear at the beginning of the sixties. In a scheme proposed by the Milan group in 1964 for the formation of *cis*-1,4 syndiotactic polypentadiene, the allylic group is in the *anti* configuration, the monomer is coordinated as a bidentate to give an *anti* allylic group and the insertion is conceived as a transfer of the *Mt*-C σ bond to the coordinated diene (31).

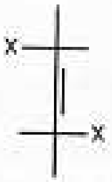
Other groups have independently proposed a relationship between the structure of the allylic group, *syn* or *anti*, and the structure of the resulting monomeric unit, *trans* or *cis* (18,40).

The validity of the scheme of Fig. 1 has recently been supported by the polymerization of 1,4-disubstituted butadienes. Monomers of this type give, on insertion, an allyl group in which two asymmetric carbon atoms are present, C^1 and C^4. As shown in Fig. 1, if insertion of a symmetric diolefin occurs via a *cis*-addition, in the *syn* complex C^1 and C^4 have the same chirality, while in the *anti* complex C^1 and C^4 have opposite chirality.

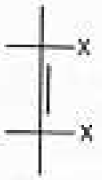
Anti ⇄ *syn* isomerizations are possible; it has been shown that these occur with inversion of chirality at C^1, so that in a *syn* complex C^1 and C^4 have the same chirality independently of whether it derives from monomer coordination with only one double bond (a → b, Fig. 1) or from and *anti* ⇄ *syn* isomerization (a' → b' → b, Fig. 1).

When a new monomer coordinates to the transition metal, the *syn* complex gives a *trans*-1,4 unit in which C^1 and C^4 have the same chirality, while the *anti* complex gives a *cis*-1,4 unit in which C^1 and C^4 have opposite chirality (21).

In other words, according to the scheme of Fig. 1, a symmetric 1,4-disubstituted butadiene, *X*CH=CH—CH—CH*X*, should give *trans*-1,4 units of type A and *cis*-1,4 units of type B (the units are represented in the Fisher projections):

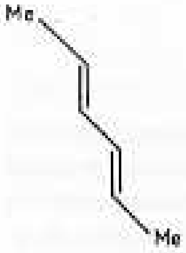


A (*trans* unit)

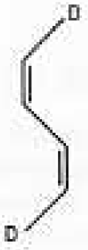


B (*cis* unit)

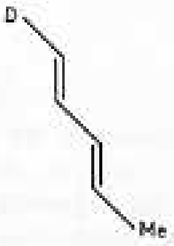
The following terminally substituted butadienes have recently been polymerized (20-22,43,44): (*E*,*E*)-2,4-hexadiene, [I]; (*Z*,*Z*)-1,4-d_2-1,3-butadiene, [II]; (*E*,*E*)-1d-1,3-pentadiene, [III].



[I]



[II]



[III]

These monomers afforded several stereoregular polymers, as shown in Table 2. The structure of the polymers is fully consistent with the scheme

TAB. 2 - STRUCTURE OF STEREOREGULAR POLYMERS OBTAINED FROM MONOMERS 1-3 WITH SOME CATALYST SYSTEMS

MONOMER	CATALYST SYSTEM			REFERENCES
	AlEt_3-VCl$_3$	AlEt_2Cl-Co(acac)$_2$	AlEt_2Cl-Nd(OCOR)$_3$-Al(i-Bu)$_3$	
1		*trans-threo* diisotactic	*trans-threo* diisotactic	(20), (21), (42)
2	*trans-threo* diisotactic	*cis-threo* disyndiotactic		(22)
3	*trans-threo* diisotactic	*cis-threo* disyndiotactic	*cis-erythro* diisotactic	(44)

of Fig. 1, in the sense that the *trans* polymers are made up of monomeric units of type A, while the *cis* polymers are made up of monomeric units of type B.

In the case of butadiene or isoprene polymerization, it is a sufficient condition for formation of all-*cis* or all-*trans* polymers that the last polymerized unit always has an *anti* or a *syn* structure during the growth of the macromolecule. This condition is no longer sufficient for formation of *trans* or *cis* stereoregular polymers from 1- or 1,4-substituted butadienes. Monomers of this type have two prochiral faces and they must react always with the same prochiral face to form an isotactic polymer or alternatively with one prochiral face and the other to form a syndiotactic polymer.

The factor that determine reaction of incoming monomer with one prochiral face rather than with the other have not yet been entirely clarified. It is possible, however, to determine from the structure of the polymer (*erythro* or *threo*) which prochiral face actually reacts.

Fig. 2 reports a scheme for the formation of a *trans-threo*-diisotactic polymer from monomer [II] with the AlEt_3-VCl$_3$ system.

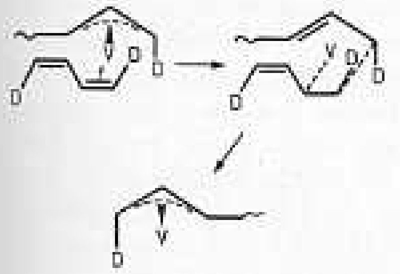


Fig. 2

In this scheme the last polymerized unit (the allylic group) is below the plane of the figure, the incoming monomer is above, and the vanadium atom is on the plane.

With the mode of presentation indicated a *threo* polymer is formed, while reaction with the other prochiral face would give an *erythro* polymer

Furthermore, with the mode of presentation indicated, the new monomer gives, after insertion, an allylic group superimposable on the preceding one, and hence an isotactic polymer, as actually found.

Fig. 3 reports a scheme for the formation of a *cis-threo*-disyndiotactic polymer from monomer [II] with the homogeneous AlEt_2Cl-Co(acac)$_3$ system.

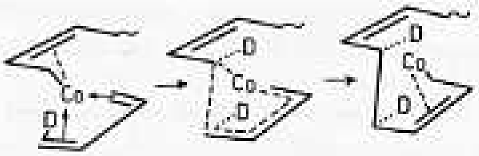


Fig. 3

The monomer, with the mode of presentation indicated, forms a *threo* polymer, and gives rise to an allylic group which is enantiomorphous with respect to the preceding one. Hence a *threo* disyndiotactic polymer will result. In this particular case the mode of monomer presentation is probably determined by the influence of the last polymerized unit.

The two above cases give an idea of the present understanding of the formation of stereoregular 1,4 polymers from terminally substituted butadienes. While we know which prochiral face of the monomer reacts with the catalyst, the factors causing the monomer to react in that way are still the object of hypotheses.

FORMATION OF STEREOREGULAR 1,2 POLYMERS

Several stereoregular polymers with a 1,2 (or 3,4) structure have been prepared from various diolefins [butadiene (43,48), isoprene (25), pentadiene (19), 4-methylpentadiene (60)]. As previously indicated, a 1,2 (or 3,4) unit is formed when the incoming monomer reacts at C^3, rather that at C^1, of the allylic group. Reaction at C^3 may be determined by steric, geometric or ionic factors, depending on the particular catalyst and monomer used.

The polymerization of 4-methyl-1,3-pentadiene to 1,2-isotactic polymers is an example of formation of 1,2 units determined by steric factors due to the presence of substituents in the allylic group. The AlEt_3-αTiCl$_3$ system is the most stereospecific for this polymerization; the same system gives *trans*-1,4 polymers from butadiene. The two monomers give different allylic groups, as shown in Fig. 4: C^1 of the allylic group derived from butadiene has no substituent, while C^1 of the allylic group derived from 4-methyl-pentadiene bears two methyl groups. As a consequence, butadiene reacts at C^1 (less substituted than C^3) to give a *trans*-1,4 unit, while 4-methylpentadiene reacts at C^3 (less substituted than C^1) to give a 1,2 unit.

Another case in which steric factors are clearly predominant in directing reaction to C^3 is the polymerization of 1,3-pentadiene by the homogeneous AlEt_2Cl-V(acac)$_3$ system (61).

The situation is different in the case of formation of 1,2 units from butadiene. Evidence from reaction of butadiene with η^3-butenyl complexes

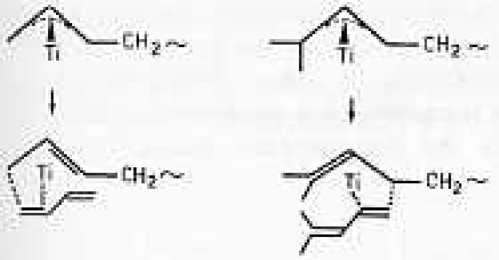
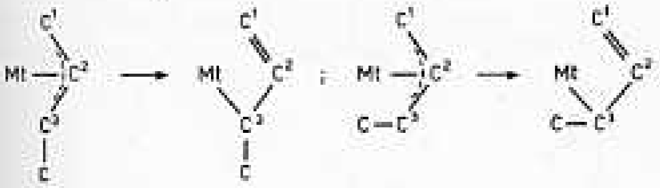


Fig. 4

of transition metals indicates than a 1,2-butadiene unit can derive either from an *anti* or from a *syn* butenyl group:



In both cases the new monomer must react at C^3, that is at the most substituted carbon of the allylic group to give a 1,2 unit. In the case of butadiene geometric factors determine reaction at C^3, in the sense that the geometry of the catalytic complex is such that one terminal carbon atom of the coordinated monomer is at bonding distance from C^3 rather than from C^1 of the allylic group.

There are several catalysts that can give 1,2-polybutadiene and the steric situation around the transition metals obviously differs from one catalyst to the other.

For a vast class of catalysts (those derived from alcoholates or acetylacetonates of Ti, V, Cr, Mo, Co), however, the mode of formation of 1,2 units may be visualized. The following observations are pertinent to the catalysts of this class:

1) they give 1,2 polybutadienes in which the non-1,2 units are predominantly *cis*-1,4 (44,47);

2) some catalysts [e.g. $AlEt_3$-H_2O-$Co(acac)_2$; $AlEt_3$-$Mo(OR)_3Cl_2$] yield polybutadienes consisting of 1,2 and *cis*-1,4 units in a practically 1 : 1 ratio (21-27). Other catalysts [e.g. $AlEt_3$-$Ti(OR)_4$] yield 1,2 polymers from butadiene, but *cis*-1,4 polymers from pentadiene (15,58).

The above facts suggest that with the above catalysts a 1,2 unit derives from the same situation as a *cis*-1,4 unit, that is from an *anti* allylic group and from a coordination of the monomer with the two double bonds.

Fig. 5 shows a possible scheme for formation of 1,2-polybutadiene, which is consistent with all the above experimental data. In this scheme the last polymerized unit is below the plane of the figure, the coordinated monomer is above, while the transition metal is on the plane.

A situation similar to that shown in Fig. 5 arises in some complexes of transition metals (44,45), to support the proposed scheme.

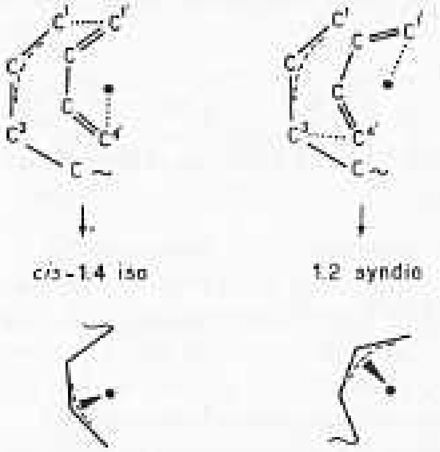


Fig. 5

Formation of the new C—C bond between C^1 and $C^{1'}$ or between $C^{4'}$ and C^3 gives rise to *cis*-1,4 or 1,2 units.

Small variations in the geometry of the complex due to the nature of the ligands bonded to the transition metal may lead to the preferential formation of one type of monomeric unit. With some catalysts [e.g. those derived from $V(acac)_3$, $Ti(OR)_4$] 1,2-butadiene units are predominantly formed. With other catalysts [e.g. $AlEt_3$-$Mo(OR)_3Cl_2$] the situation is less rigid and the formation of 1,2 and *cis*-1,4 units becomes equally probable.

Small variations in the geometry of the complex may also depend on the type of diolefin coordinated, and this may account for the formation of *cis*-1,4 polypentadiene and of 1,2-polybutadiene with the $AlEt_3$-$Ti(OR)_4$ system.

It should be noted that the formation of *cis* units according to the scheme of Fig. 5 leads, after incorporation of the coordinated monomer, to an allylic group which is superimposable on the preceding one, and hence to an isotactic polymer. On the other hand, the formation of a 1,2 unit according to this scheme leads to an allylic group which is enantiomorphous with respect to the preceding one, and hence to a syndiotactic polymer. All this is consistent with the results obtained with the $AlEt_3$-$Ti(OR)_4$ system, which yields, as previously indicated, a *cis*-1,4 isotactic polypentadiene and a 1,2 syndiotactic polybutadiene.

In some particular cases ionic factors are involved in the formation of 1,2 units. The $AlEt_2Cl$-$Co(acac)_2$ system gives a *cis*-1,4 polymer (98%) from butadiene, but it gives a polymer consisting of about 65% *cis*-1,4 and 35% 3,4 units from isoprene. In the case of isoprene two modes of presentation are possible, a shown in Fig. 6.

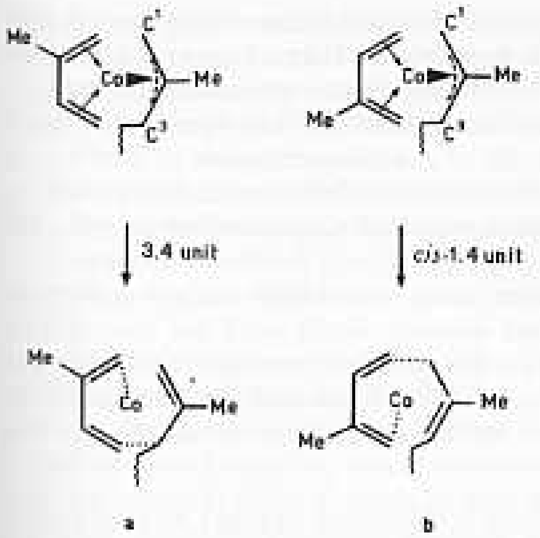


Fig. 6

Isoprene has a high tendency to give, with transition metal catalysts, a methallyl rather than an allyl group, due to the higher stability of the former. This means that the mode of presentation of Fig. 6a will give a 3,4 unit, while that of Fig. 6b, will give a *cis*-1,4 unit. The modes of coordination of Fig. 6a and b occur with equal probability, but since C^3 is more substituted than C^1 (and hence less reactive) the formation of a 3,4 unit is slower than that of a 1,4 unit. This accounts for the lower percentage of 3,4 units in the polymer.

In the above case ionic factors are clearly involved in directing reaction of the incoming monomer to C^3.

In conclusion, it is now evident that various factors can determine the formation of 1,2 (or 3,4) monomeric units, those examined above being the most important ones.

Perspectives

26 years since the discovery of transition metal catalysts, research work is still intense in the field of diolefin polymerization. The attention is focused on the following topics: 1) mechanistic studies; 2) improvement of existing catalysts and search for new ones; 3) development of new products.

1) Although some basic aspects of the mechanism of transition metal catalyzed polymerization of dienes are now clear, several points are still obscure or need further work.

With regard to the factors that determine stereospecificity, one is now in a position to propose plausible hypotheses. These, however, must to be proven. Advances in this field will come from organometallic chemistry and in particular from investigation of reactions of dienes with model compounds rather than from studies of the polymerization.

Other mechanistic aspects still to be clarified concern the process of initiation with some catalysts and the process of termination as well. On the latter point very little is known.

The influence of the aluminum compound on the catalytic activity is one area in which ideas are rather obscure. Much work has been carried out in this field, and it is known that catalysts prepared from different aluminum compounds ($AlEt_2Cl$, $Al_2Et_3Cl_3$, compounds containing AlOAl bonds) have a different activity, but no satisfactory explanation for this has been proposed as yet.

2) Much work is being devoted to improving catalysts already known and to developing new ones. The interest is focused on catalysts for *cis*-polymerization of butadiene and isoprene, due to their industrial interest.

After the 1st generation of catalysts (those derived from titanium) and the 2nd (those derived from cobalt and nickel), a 3rd generation is now being studied. These new catalysts are based on elements of the series of lanthanides and actinides. The $AlEt_2Cl\text{-}Nd(OCOR)_3\text{-}Al(i\text{-}Bu)_3$ system (R = alkyl or cycloalkyl group) appears extremely promising for the *cis*-polymerization of butadiene and is now being tested on a pilot plant scale.

At present, different catalysts are used for the *cis* polymerization of isoprene ($AlEt_3\text{-}TiCl_4$, $AlEt_2Cl\text{-}Ti(OR)_4$) and of butadiene ($AlEt_3\text{-}BF_3\text{-}Ni(OCOR)_2$). It seems likely that research work now in progress will lead to the development of a unique catalyst for the *cis* polymerization of both monomers.

3) The possibilities offered by transition metal catalysts have not been completely explored. One can foresee that new products, some with potential practical interest, will be prepared in the near future, especially in the field of copolymers. In Italy ENI is now evaluating butadiene-pentadiene copolymers, which have interesting elastomeric properties. The neodymium catalysts seem to be particularly suitable for preparing block copolymers, some of which could be of interest in the field of thermoplastic elastomers.

The industrial development of possible new products appears, however, rather uncertain. Of the many diolefin polymers prepared with transition metal catalysts, only those with elastomeric properties have a practical interest (*cis* polybutadiene; *cis* polyisoprene; butadiene-propylene copolymers). However, of these, only *cis* polybutadiene is currently produced on an industrial scale, although in an amount that is not comparable to that of polypropylene. Synthetic *cis* polyisoprene is not price competitive with natural rubber and its industrial production is now extremely limited. The situation may change in the future if isoprene monomer drops in price.

Propylene-butadiene copolymers have been produced on a pilot plant scale, but no large scale production has followed because of the problems encountered in their preparation.

The butadiene-pentadiene copolymers mentioned above are very promising, but pentadiene monomer is not easily available, at least at present.

It appears, therefore, that new diolefin products are certainly possible, but their industrial development is rather uncertain.

As a concluding remark of this review it may be said that the transition metal catalyzed polymerization of diolefins has provided a variety of new products and probably represents, from the scientific point of view, the richest and most interesting area of stereospecific polymerization. However, from the practical point of view, at least at present, its industrial interest is inferior to that of the polymerization of propylene.

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Asymmetric Polymerization

The first paper of Professor Natta on this subject has been published in 1960 [G. Natta, M. Farina, M. Donati, M. Peraldo, *Chim. Ind. (Milan)* *42*, 1363 (1960)].

His activity in this field is proved by many publications. We quote, for instance: G. Natta, L. Porri, A. Carbonaro, G. Lugli, *Chim. Ind. (Milan)* *43*, 529 (1961); G. Natta, L. Porri, S. Valente, *Makromol. Chem.* *67*, 225 (1963); G. Natta, M. Farina, *Tetrah. Letters* 703 (1963); G. Bressan, M. Farina, G. Natta, *Makromol. Chem.* *93*, 283 (1966); M. Farina, G. Audisio, G. Natta, *J. Am. Chem. Soc.* *89*, 5071 (1967).

Prof. Mario Farina who is particularly expert in the mentioned subject has been requested to give a contribution to the volume. The contribution is entitled: *Asymmetric Polymerization.*

Asymmetric Polymerization

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From the start, synthesis of stereoregular polymers posed complex problems of stereochemistry because of the difficulty of inserting the new phenomena into the interpretative structures which were most widely accepted at the time. One of the most intricate aspects was the lack of chirality of polypropylene and of the other isotactic vinyl polymers. The process generating these may be taken to be a multiple asymmetric synthesis (the monomer reacts with the chain-end or with a chain-catalyst complex which, whatever the specific mechanism, is of an asymmetric character) and yet the structure of the polymer is incapable of existing in optically active forms. The problem becomes even more complicated if we observe that a single (achiral) macromolecule of isotactic or syndiotactic polypropylene may be coiled into a dextro or laevo helical conformation.

On the other hand, the extremely widespread presence of optically active biopolymers (polysaccharides, proteins, nucleic acids) in living organisms, and the existence in each class of a single series of antipodes (dextro or laevo) with practically quantitative enantiomeric purity would seem to suggest a close relationship between life and optical activity. One of the most fascinating problems still to be solved in the natural sciences, the origin of optical activity on earth, might find in the study of the processes of asymmetric polymerization some decisive answers.

The logical and experimental difficulties met with in the attempt to produce an optically active polymer from a non-chiral monomer and the theoretical and practical implications of such a process, made the study of this topic extremely interesting. This task was handed over to me by Professor Natta towards the end of the 1950's.

Though at a rational level the situation at the time was less than perfectly clear, the first attempts aimed at very reasonable goals: the synthesis of propylene oligomers carried out in a chiral environment and the preferential formation of one of the two helices of isotactic polypropylene. At the time the helix inversion mechanism had not yet been cleared up and it might be imagined that the energy barrier involved in this process was high enough to permit at least temporary observation of the optical activity due to the helical conformation.

My attempts did not succeed, partly for experimental reasons, partly because of a still-too-rough knowledge of the subject. We shall see further on that there exist optically active polymers the chirality of which depends solely upon conformational factors, and also that it is possible to produce a « conformational asymmetric synthesis ». These possibilities do not however include propylene or other simple vinyl monomers known at that time.

In the spring of 1960, Professor Natta asked me to make a summing-up of all the fruitless attempts made until then, with an eye to publication. My reluctance to write of unpleasant things turned out to be providential, because, within only a few months, at the Milan Politecnico three examples were realized of asymmetric polymerization, and these were totally different from one to another as regards the type of monomer, the structure of the polymer, the mechanism of polymerization and the mode of transmission of the asymmetric induction.

This success derived essentially from two facts: the development of research on stereoregular polymers of olefins and diolefins carried out by the Milan group, and the in-depth examination of some literature. In the following pages I intend to describe, trusting in my memory and my notes, the elements which influenced this research most directly, without the pretence of presenting a complete review of the subject. I shall then deal with some of the more interesting and recent developments in this field.

The state of the art at the end of the 1950's

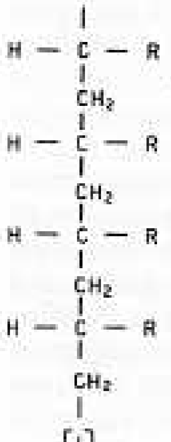
In 1953, Frisch, Schuerch and Szwarc published a statistical treatment of asymmetric polymerization (1) which formed a starting-point for all successive developments. The principal conclusion were: determination of the simplest mechanisms of propagation of asymmetric induction and recognition of the non-chiral nature of vinyl polymers. These Authors proposed two extreme mechanisms for obtaining optically active polymers. The first is based upon a reaction of asymmetric initiation and of stereoregular symmetric growth; in other words upon a process in which the asymmetric agent influences only the first stage of reaction and induces the formation of a D chain with a probability different from that of the L ($I_D \neq I_L$). After the first stage, the conditional probability of the formation of a new monomeric unit having the same sign as the preceding one is equal in the two enantiomeric cases (DD = LL).

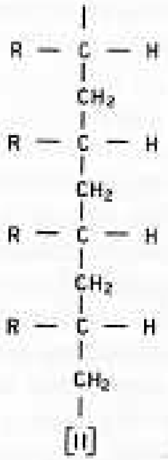
In the second hypothesis there exists a mechanism of asymmetric growth in which, in all the stages of propagation, the conditional probability of a sequence is different from that of its antipode (DD ≠ LL). In this case an asymmetric catalyst, or more in general a chiral environment is required, the action of which must extend along the whole course of the polymerization.

It has been stated that only with the second mechanism is it possible to obtain high molecular weight polymers of high rotatory power (this being in fact independent of the degree of polymerization), whilst with a mechanism of asymmetric initiation the optical activity falls off rapidly as the degree of polymerization increases — unless there is a very high degree of stereoregularity — due to the inability of the system to correct configuration errors which have come about during polymerization.

With regard to chirality, it has been stated that a vinyl polymer composed of units of a single configuration will be superposable on its mirror image, if a justified assumption is made that the effects due to the chain length and end groups are negligible, and consequently it is not optically active.

A demonstration of the non-chirality of stereoregular vinyl polymers has also been provided by Natta, Pino and Mazzanti (2) and by Arcus (3) in ways which substantially coincide. In accordance with one of the possible models, the high molecular weight polymers may be considered to be chains of infinite length. In this case apparently enantiomeric chains such as [I] and [II] are indistinguishable from each other, as can be seen by rotating one of the Fischer projections through 180° on paper.

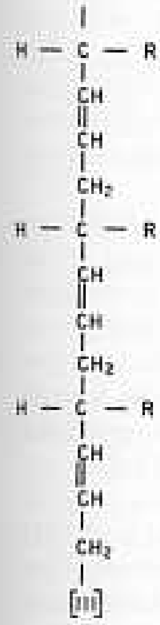

[I]


[II]

Isotactic vinyl polymers of finite length with identical terminal groups are also inactive by internal compensation, whilst a weak optical activity was attributed to the single isotactic molecules having different terminal groups. It is however known that optical activity is a short-range phenomenon, whence it can reasonably be supposed that the effect of the chirality due to the tertiary carbon atoms adjacent to the terminal groups is observable only in the fractions of lower molecular weight.

Arcus extended his treatment also to disubstituted ethylenes of the $CHA=CHB$ type and to symmetric cyclic olefins (such as acenaphtylene) or non-symmetric ones (such as indene) and correctly predicted the chirality of the di-isotactic polymers of the cyclic olefins (3). Unlike the case of non-cyclic monomers, chirality is in this case observable also in chains of infinite length. Arcus later undertook a systematic examination of the chirality of alternate copolymers (4) and, taking up an observation first made by Frisch, Schuerch and Szwarc (5) showed how optically active copolymers could be obtained, on principle, from the copolymerization of a vinyl monomer with a disubstituted ethylene ($CH_2=CHX$ plus either $CHA=CHB$ or $CHA=CHA$).

Meanwhile, during the study of the polymerization of substituted butadienes, carried out by Natta, Porri and Corradini, it was recognized that the 1,4-isotactic polymers of pentadiene and similar monomers have a chiral structure (see formulae [III] and [IV]) (6). The tertiary atoms in the chain are truly asymmetric and not pseudo-asymmetric as in the case of polypropylene. 1,3-Pentadiene may even form two different isotactic chiral polymers, characterized by the different configuration (*cis* or *trans*) of the double bond in the chain.



[III]

[IV]

In my laboratory research into the stereochemistry of the polymerization of $CHA=CHB$ disubstituted ethylenes had been under way since 1958, under the guidance of Professor Natta and with the collaboration of M.

Peraldo. Starting from the *cis* and *trans* 1d$_1$ propylene, $\mathrm{CH_3}$—CH=CHD, in the presence of $\mathrm{TiCl_3}$ and AlEt_3 the first di-isotactic polymers were obtained (6), respectively in the *erythro* and *threo* forms. Other monomers taken into consideration were the alkenylethers R—CH=CH—O—R' (7), which polymerize cationically, and the crotonates $\mathrm{CH_3}$—CH=CH—COOR (8), which on the contrary polymerize anionically.

A requisite for the stereoregular polymerization of the disubstituted ethylenes is to use the monomers in their pure stereoisomeric forms. To achieve this, it is often necessary to submit the *cis-trans* mixture of the monomers or of their precursors to difficult separations, as in the case of the deuterated propylenes and alkenylethers. In more lucky circumstances a single stereoisomer already in the pure state is obtained directly during synthesis, as in the case of crotonates.

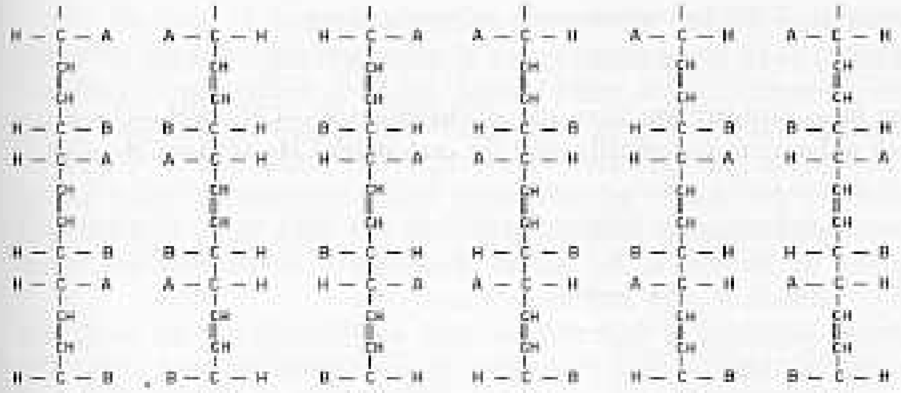
The problems and considerations set out in these pages were well known at that time, but no experimentally valid solution could be found, until the problem was cleared up quite suddenly. As is so often the case, this came about thanks to a stroke of luck.

I was reading a review of the stereochemistry of olefins (9) when a simple phrase caught my attention: « Sorbic acid has the *trans-trans* structure ». At that moment I perceived with certainty that asymmetric synthesis of polymers was destined to succeed.

Sorbic acid, or rather its esters ($\mathrm{CH_3}$—CH=CH—CH=CH—COOR), though they had never been polymerized, appeared to me to be the ideal monomers for the purpose: they were substituted butadienes, like pentadiene, and would produce chiral isotactic polymers; their reactivity being analogous to that of crotonates, it would be possible to polymerize them anionically, and they existed in only one of the four possible stereoisomeric forms.

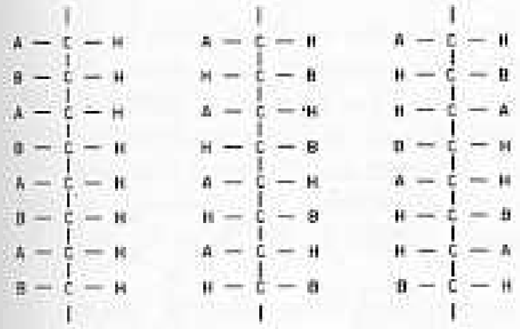
Stereoregular polysorbates present the most complex type of tacticity observable to date in synthetic polymers. They have been said to be tritactic because their monomeric unit contains three sites of stereoisomerism, two tertiary carbon atoms and the double bond. Considering only the structures obtained by 1,4 addition, the existence of 12 different types of macromolecules can be predicted, 6 with *cis* and 6 with *trans* insaturation. For each series the number of structures is double that predicted for the polymers of CHA=CHB disubstituted monoolefins ([V]-[X] and [XI]-[XIII] respectively).

In fact, the *erythro* and *threo* di-syndiotactic polymers ([IX] and [X]) can be distinguished one from the other (unlike the case of monoolefins, in which a single di-syndiotactic polymer [XIII] exists); in addition both the *erythro* and the *threo*-di-isotactic polymers consist of pairs of antipodes ([V] and [VI], and [VII] and [VIII] respectively). The chirality of the di-isotactic polymers of the sorbates is observable in chains of infinite length, and the tertiary carbon atoms are truly asymmetric, being bonded



[V] [VI] [VII] [VIII] [IX] [X]

erythro-di-isotactic threo-di-isotactic erythro-di-syndiotactic threo-di-syndiotactic



[XI] [XII] [XIII]

erythro-di-isotactic threo-di-isotactic di-syndiotactic

to four different substituents in the immediate vicinity of the atom under consideration.

It took only a month to obtain soluble and partially crystalline polymers of methylsorbate and of other sorbates by anionic polymerization (butyllithium in toluene at — 40 °C) (30). On the evidence of the experimental findings available at that time, an *erythro*-di-isotactic structure was attributed to such polymers (31). The validity of this affirmation today requires some retrenchment, since the use of NMR spectroscopy has shown the existence of some steric disorder and the microtacticity of these polymers is a problem still to be resolved. Nonetheless, the working hypothesis then put forward, *i.e.*, the chirality of such polymers, is still fully valid.

Realization of the first asymmetric polymerizations

Exactly twenty years ago, in the autumn of 1960, research on asymmetric polymerization reached a turning-point. In my laboratory two lines of research had been set up after much discussion with Professor Natta and M. Peraldo and conducted by myself, by M. Donati and by G.C. Bressan: one on the anionic polymerization of sorbates, and the other on the cationic polymerization of benzofuran. At the same time, L. Porri and his group set themselves the task of obtaining the asymmetric polymerization of pentadiene with coordination catalysts.

At the beginning of december our goal was reached and the result was immediately communicated to students at an international level (12,13). The first result was obtained starting from methylsorbate: in the presence of an optically active organometallic catalyst, 2-methylbutyllithium, it was converted into a polymer analogous to that obtained in racemic form some months before, but undoubtedly having optical activity ($[\alpha]_D = -3^\circ$; I remember reading a rotation of 0.31° in a 40 cm tube with a Lippich-Landolt visual polarimeter).

The fundamental aspect of the process is the transformation by a catalytic process of a non-chiral monomer (methylsorbate has a plane of symmetry) into a chiral polymer, with a small but significant prevalence of monomeric units of a given sign with respect to those of opposite sign.

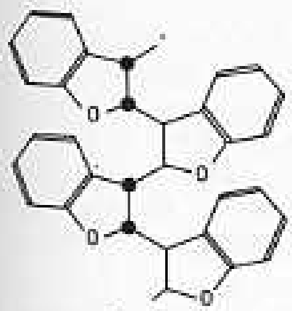
From the point of view of Frisch, Schuerch and Szwarc's treatment (1), this is probably a process of asymmetric initiation, since in anionic polymerizations the organic residue originally bonded to the metal is found in the polymer as end-group.

Immediately after this result we examined other catalytic systems in the hope of obtaining higher rotatory powers, thanks to a presumably different mechanism of transmission of asymmetric induction. Optically active polysorbates were also obtained in the presence of butyllithium complexed with an asymmetric ether such as menthylethylether (14). In this case the chiral agent is not situated at the end of the polymeric chain and its action would have influenced the entire polymerization. The values of optical activity are comparable to those of the preceeding case, but it was not possible to shed light on the type of mechanism acting in this case.

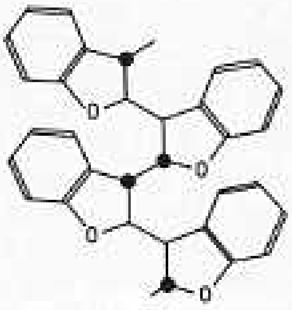
Meanwhyle, we also succeeded in carrying out the asymmetric polymerization of benzofuran (15-17). Polymerization takes place with a cationic mechanism and is promoted by various combinations of a Lewis acid ($\mathrm{Al}Et\mathrm{Cl}_2$) with an asymmetric agent (camphorsulphonic acid, alkaloids, aminoacids, etc.). The best catalysts turned out to be the complexes with (—) or (+) phenylalanine: polymers obtained in their presence at — 80 °C in toluene have optical activity greater than 30° (*).

(*) Unless specifically indicated otherwise, measurement was carried out with the sodium D light.

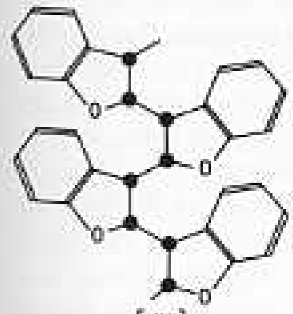
In the case of benzofuran both the *erythro*- and *threo*-di-isotactic structures are chiral and may exist in enantiomeric forms [XIV]-[XV] (2). The lack of crystallinity made it impossible to assign a structure to the polymer by diffractometric methods, nonetheless the isotactic disposition was clearly established on the basis of its optical activity. Apart from [XIV] and [XV], no other simple chiral structures exist (the *erythro*- and *threo*-di-syndiotactic forms [XVI] and [XVII] are achiral because of the presence of a mirror glide plane).



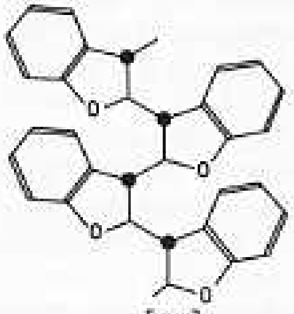
[XIV]



[XV]



[XVI]



[XVII]

Still at Milan Politecnico, at the beginning of 1961 L. Porri and his group obtained a new example of asymmetric polymerization (11). *trans*-1,3-Pentadiene was polymerized in the presence of VCl_3 and an optically active organometallic compound, tris ((*S*)-2-methylbutyl) aluminium; the polymer has a 1,4-*trans*-isotactic structure and presents a rotatory power of about — 1°. Despite the low optical activity and the fact that it is supposed to have incomplete stereoregularity, this polymer represents a considerable step forward in the field, since for the first time asymmetric induction was obtained on a hydrocarbon monomer using a typical coordination catalyst.

Developments after 1961

Developments in asymmetric polymerization after 1961 have been reviewed by various authors (19-24) as part of the wider field of research on the synthesis of optically active polymers. The requisites for the chirality of such polymers were also set out several times (22-26), using the infinite chain model or that, equivalent to the former, of cyclic oligomers. The reader will find a full treatment in the articles quoted. Here I would like to discuss some developments of the research already illustrated in the last chapter.

Of the various types of asymmetric polymerization, that of cyclic monomers has attracted most attention. Simultaneously with our research on benzofuran, Schmitt and Schuerch studied various cyclic monomers (27): indene, 1-methylcyclopentene, 4,5-dihydro-1-methylfuran, α-angelicalactone. Their line of research, parallel to that followed by us, was based on the use of Lewis acids (BF_3) and optically active cocatalysts. Unfortunately these efforts had a negative outcome, either because of the lack of isotacticity in the polymers or because of the insufficient power of asymmetric induction on the part of the specific catalytic system used.

In our work, the replacement of $\mathrm{Al}Et\mathrm{Cl}_2$ by $AlCl_3$, while still using phenylalanine as cocatalyst produced a considerable increase in the optical purity of the polymer. From the 30° of the first polymers we reached 75° (28) and even 90°, as an instantaneous value (29-30). Fractionating the polymer obtained at low conversion showed that rotatory power is practically independent of the length of the chain. Consequently it may be supposed that there is a mechanism of asymmetric growth in which each stage is influenced by the optically active counterion. In high conversion polymers an increase of optical activity with molecular weight is observed, a phenomenon attributed to a deterioration of the counterion linked to chain transfer or termination reactions.

Other experiments conducted at low monomer concentration showed an increase of asymmetric induction with time, which may be taken to be an autocatalytic process. The highest values of optical activity were in fact obtained not at the beginning of polymerization, but after a certain degree of conversion (29-30). On the other hand polymerization experiments performed in the presence of a preformed polymer produced, from the very first instant, a polymer having extremely high optical activity ($[\alpha]_D = 90°$). In this case the sign of the optical activity depends solely upon the configuration of the phenylalanine used, and not upon that of the polymer introduced.

These facts were the object of long critical discussions and of various experiments aimed at verifying the hypotheses which were gradually coming to light. The interest of Professor Natta for this work was intense, such indeed that he recalled these questions in the title of his Nobel Prize Lecture: *From the Stereospecific Polymerization to the Asymmetric Autocatalytic Synthesis of Macromolecules* (31). The interpretation we finally developed envisages a chemical (not stereochemical) interaction of the polymer on the catalyst such as to vary its composition and increase its asymmetric power by an indirect way.

The chemical nature of polybenzofuran made it for a long time impossible to determine the relative configuration (*erythro* or *threo*) of the chain, as also its absolute configuration and optical purity. G.C. Bressan, towards the end of the 1960's, succeeded in cristallizing the polymer by non-conventional techniques (32,33), yet it was impossible to obtain drawn fibers suitable for x-ray examination. A recent study of the microstructure of polybenzofuran suggests that the most probable is a *threo*-di-isotactic structure, based on conformational analysis and NMR spectra (34).

A polybenzofuran endowed with a high degree of optical activity ($[\alpha]_D = + 73.8°$) was obtained by Takeda, Fueno and Furukawa (35) using a catalyst composed of $AlCl_3$, Et_3SnCl and (—)menthyl-O-$Sn\mathit{Et}_3$. The same Authors also studied the statistical aspect of asymmetric polymerization (36) extending and generalizing the schema previously put forward by Frisch, Schuerch and Szwarc (3).

As an extension of the earlier research conducted in Milan, mention must also be made of the asymmetric polymerization of α- and β-naphthofuran, carried out in the presence of the $AlCl_3$-phenylalanine complex (37). The polymers have respectively $[\alpha]_D = 41°$ and 145°; this latter value was for a long time the highest value of rotatory power obtained by asymmetric polymerization.

Asymmetric polymerization of sorbates and analogous monomers (β-vinylacrylates, β-stirylacrylates (38,39) has undergone completely different developments, in relation to the higher reactivity of such products. We succeeded, in fact, in determining the absolute configuration and the minimum entity of asymmetric synthesis by demolition of the polymer to methylsuccinic acid (40). The attribution of chirality, however, regards only one of the two asymmetric carbon atoms (the information relating to the other atom is lost during the demolition process), and can be extended to the entire polymer only under the hypothesis of a well defined structural relationship. As already mentioned, the original attribution came under discussion in the light of NMR spectrum analysis and of more accurate demolition studies (41). Slight modifications of the catalytic system, for instance the addition of electron-donor compounds, alter the microstructure of the polymer, which may range from a prevalently *erythro* structure to one prevalently *threo*. Consequently the optical purity of methylsuccinic acid (= 6%) cannot be correlated directly, and is almost certainly lower than that of the polymer.

Important progress was also made on the polymerization of hydrocarbon monomers, in particular pentadiene. In 1963 Natta, Porri and Valente obtained a polypentadiene having high optical activity ($[\alpha]_D = — 22.8$)

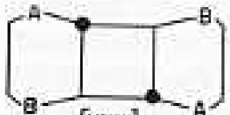
with a prevalently 1,4-*cis*-isotactic structure (42). Though the diastereoisomeric purity was not especially high (its content in 1,4-*cis* units is below 80%), the asymmetric induction acting on the single monomer unit is very high and is effective in every stage of the reaction. The catalyst is composed of $AlEt_3$ and $Ti(O\text{-menthyl})_4$. If the chiral agent is instead placed on the aluminium, as in the catalyst tris((R)-2-methylbutyl)-aluminium + $Ti(O\text{-butyl})_4$, no asymmetry at all is obtained, even with a polymer structure practically identical to the precedent one. From these facts it was deduced that the chain grows on the titanium, or at least that the monomer coordinates to the titanium before being incorporated in the growing chain.

FREE RADICAL ASYMMETRIC POLYMERIZATION

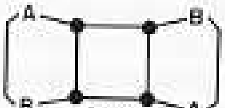
The asymmetric polymerizations hereto described proceed by an ionic or coordination mechanism. All attempts at asymmetric synthesis by free radical processes had met with failure. It must however be said that most had been attempted before the structural requisites for chirality in polymers had been defined. Furthermore, the lack of stereoregularity commonly observed in free radical polymerizations seemed to preclude any possibility of success with this type of process.

The problem of radical asymmetric polymerization was resolved in 1967 at Milan Politecnico by a process far different from the traditional ones, *i.e.*, by solid-state polymerization in chiral inclusion compounds.

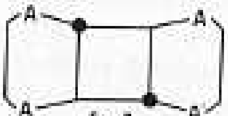
The origins of this discovery date from a few years earlier and the fundamental hypotheses are far reaching. As soon as the asymmetric polymerization of benzofuran had been accomplished, it was realized (25) that the chirality of the asymmetric carbon atoms in the chain could not be specified by Cahn Ingold and Prelog's rules as set forth in the 1956 edition (43). It was seen that the fact had a more general bearing and that analogous phenomena also existed in organic chemistry, for example, in polycyclic compounds of the [XVIII]-[XX] type (44). We turned our attention to the *trans-anti-trans-anti-trans* stereoisomer of perhydrotriphenylene [XXI], which had not as yet ever been described, and succeeded in synthesizing it in 1963 (45).



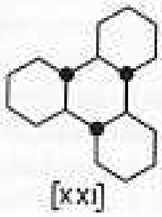
[XVIII]



[XIX]



[XX]



[XXI]

This compound turned out to be of such interest that even today research into its behaviour is of considerable interest. The issue of nomenclature which we proposed was widely discussed and inserted into the latest edition of Cahn, Ingold and Prelog's rules (46).

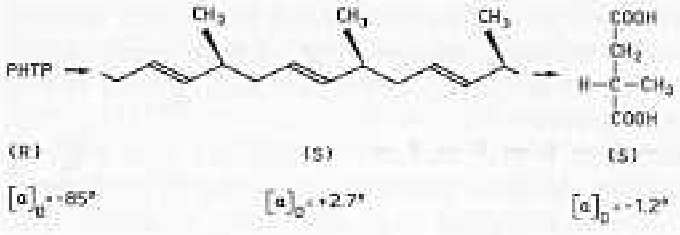
The perhydrotriphenylene (PHTP) molecule is endowed with high rotational symmetry, but with no mirror symmetry. It belong to point group D_3 and is one of the gyrochiral organic molecules (chiral molecules with high rotational symmetry) most studied from the stereochemical point of view (26,47,48). In particular it was resolved into antipodes by G. Audisio and myself in 1967 (49,50).

The high rotational symmetry of PHTP is also responsible for its behaviour in the crystal state. It shows polymorphism when it crystallizes in the pure state (51), but above all possesses an exceptional ability to form inclusion compounds with numerous substances of low and high molecular weight (52,53). As shown by the results obtained by G. Allegra and his group at Milan Politecnico, these inclusion compounds are similar to the crystalline adducts formed by urea and thiourea (8); in particular the guest molecules are arranged inside channels bounded by the host molecules superimposed on one another. However, they show a far greater facility of formation and a higher stability. The explanation of this fact was made possible by a study of the phase diagrams of binary mixtures between PHTP and guests of high and low molecular weight, recently carried out in my laboratory by G. Di Silvestro and M. Grassi (54,55), and is essentially linked to the behaviour of the two components in the liquid phase in equilibrium with the inclusion compound. The liquid phase has practically ideal behaviour in the case of PHTP, whilst there is an extensive miscibility gap in the case of urea.

As already observed in the case of urea and thiourea (56,57), a stereoregular polymerization promoted by high energy radiation is also observed in PHTP inclusion compounds with various vinyl and diene monomers (53,58-61), polymerization which proceeds according to a free radical mechanism (62).

In particular *trans*-1,3-pentadiene yields a 1,4-*trans*-isotactic polymer of extremely high regularity, even higher than that obtained in the presence of coordination catalysts. As already observed, this polymer is chiral; therefore the PHTP-pentadiene system lends itself on principle to the study of our problem.

As soon as it had been obtained in optically active forms, it was seen that the single enantiomers of PHTP also formed inclusion compounds analogous to the racemic one, but having no elements of mirror symmetry. When an inclusion compound between (—)PHTP and pentadiene was submitted to radiation, an optically active polymer of opposite sign to that of PHTP was obtained. Conversion to methylsuccinic acid made it possible to determine the absolute chirality and the enantiomeric purity of the polymer (63).



OPTICAL YIELD = 7%

[XXII]

This finding marks a very important step in the development of asymmetric syntheses. It was in fact shown for the first time that asymmetric synthesis may take place inside crystals. Until that moment known examples, which in any case were controversial (64), only involved reactions taking place on the surface of crystals.

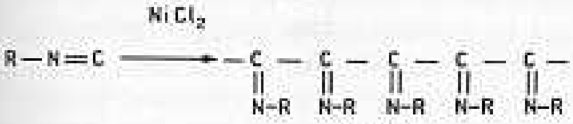
A further example of free radical asymmetric polymerization was recently reported by Doiuchi, Minoura and Kubouchi (65,66). These Authors prepared optically active copolymers starting from styrene and maleic acid or anhydride, in the presence of potassium persulfate or benzoyl peroxide as initiators and lecithin as a chiral agent. Chirality is related to the alternance of mono- and disubstituted monomeric units, in agreement with the treatment already discussed (1,4). Polymerization occurs in emulsion, and asymmetric induction has been attributed to the chiral nature of the micelles and more specifically to electrostatic interactions between the polar monomer and lecithin.

FROM « CONFORMATIONAL » ASYMMETRIC POLYMERIZATION TO « THROUGH SPACE » ASYMMETRIC INDUCTION

As observed by other Authors (24), the years from 1960 to 1970 were the most fertile in the development of the synthesis of optically active polymers. Interest for these problems has however reawoken in recent years and some recent findings, for their importance and significance, go beyond the specific field of macromolecular chemistry and constitute fundamental contributions to stereochemistry in general.

One of these findings regards the synthesis of optically active polymers, the chirality of which is due exclusively to the helical conformation. I have already mentioned that one of the first attempts carried out at Milan Politecnico involved the isolation of a single helix of isotactic polypropylene. The result which we were not able to obtain at the end of the 1950's, was obtained twenty years later on a polymer with much bulkier side groups, polytriphenylmethylmethacrylate, by Okamoto, Suzuki, Hatada and Yuki (67).

Before discussing this exceptional result I would like to recall that the first optically active polymers lacking configurational elements of chirality (asymmetric carbon atoms) were the polyalkylimminomethylenes.

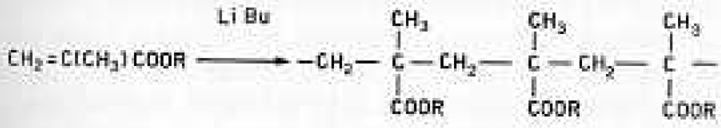


$$R{-}N{=}C \xrightarrow{NiCl_2} -\underset{\underset{N-R}{\|}}{C}-\underset{\underset{N-R}{\|}}{C}-\underset{\underset{N-R}{\|}}{C}-\underset{\underset{N-R}{\|}}{C}-\underset{\underset{N-R}{\|}}{C}-$$

[XXIII]

These polymers, obtained from isonitriles, have a rigid helical conformation (68-70); their chirality has been ascertained by chromatographic resolution on a chiral support, obtaining fractions of opposite rotation, which were enriched up to a constant value ($[\alpha]_D$ max = ± 56°) (71). No attempts at a catalytic synthesis of these polymers have to date been published. Optically active polyimminomethylenes have also been obtained starting from optically active isonitriles (*i.e.*, *sec*-butylisonitrile) (70). In these polymers a lateral group chirality and a helical chirality exist at the same time. The situation is substantially analogous to that used for the stabilization of a particular sense of the helix in the optically active poly-α-olefins, investigated by Pino, Lorenzi and Lardicci (72,73) and successively by numerous other workers (19-24). In both cases the diastereomeric relationship existing between the lateral chiral substituent and the chain conformation means that the two senses of the helix are not energetically equivalent. Hence the existence of a preferential sense of the helix is of thermodynamic origin.

The asymmetric synthesis of polytriphenylmethylmethacrylate thus represents an absolutely new instance:



$$CH_2{=}C(CH_3)COOR \xrightarrow{Li\,Bu} -CH_2-\underset{COOR}{\overset{CH_3}{C}}-CH_2-\underset{COOR}{\overset{CH_3}{C}}-CH_2-\underset{COOR}{\overset{CH_3}{C}}-$$

$R = CH(C_6H_5)_2$

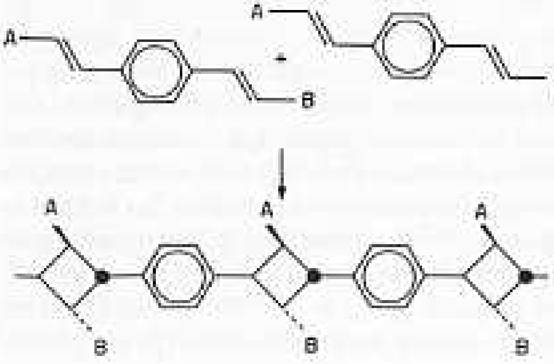
[XXIV]

It was obtained starting from a non-chiral monomer in the presence of an optically active catalyst (butyllithium + spartein) analogous to that already used by the same Authors in the enantioselective (or stereoelective) polymerization of (*R*/*S*)-methylbenzylmethacrylate (74) and in the copolymerization of this monomer with triphenylmethylmethacrylate (75). It may be deduced from the NMR spectra that the polymer has a practically pure isotactic structure; its optical activity is extremely high ($[\alpha]_D$ = + 380°, max value measured on isolated polymer, $[\alpha]_D$ = + 580° estimated value based on measurements carried out during polymerization) (67). It should be borne in mind that the isotactic vinylidene polymers of non-chiral monomers, analogously with the vinyl ones, are not chiral; hence the optical activity must be attributed to the existence of chiral helical conformations, kinetically stabilized by the interaction between adjacent triphenylmethyl groups. The few data so far available do not make possible to know the height of the barrier opposing the conformational racemization. Even data relating to the chirooptic properties are not available; this will certainly be of the utmost interest.

So far as I know, this is the first example of « conformational » asymmetric synthesis on acyclic compounds, in which the most important phenomenon in play is the insertion of the monomer units into the chain according to a helical geometry (translation + rotation).

The second group of research findings which I would like to mention here involve solid-state asymmetric polymerization. This can be divided into two parts: polymerization of pure crystalline monomers and polymerization of monomers trapped in a crystal lattice. I have already mentioned the latter with reference to PHTP. Along the same line, but with much more significant results on the quantitative plane, are the studies carried out by Audisio and Silvani (76) and by Miyata and Takemoto (77,78) into the polymerization of substituted dienes (*cis*-1,3-pentadiene and *trans*-2-methyl-1,3-pentadiene respectively) inserted as guests in the inclusion compounds of deoxycholic acid. The optical activity ($[\alpha]_D = -21°$ and $+250°$ in the two cases) indicates considerable enantiomeric purity, whilst the diastereoisomeric purity is not very high. This may indicate that in deoxycholic acid the correlation between single stages of polymerization is slight or negligible (79).

On solid state asymmetric polymerization I would like to mention the splendid research carried out at Weizmann Institute by Lahav and Addadi (80-85). Their line of research consists in converting the chirality from the crystal level to the molecule by means of a topochemical polymerization. Suitable monomers for this process turned out to be the substituted benzene-1,4-diacrylates which by photopolymerization give dimers, trimers and higher oligomers containing cyclobutane rings according to the scheme:



[XXV]

The constitutional, diastereomeric and enantiomeric structure of the products depends upon spatial arrangement of the monomers in the crystal lattice. In appropriate conditions such products have high — in some cases quantitative — optical purity.

The key stage of the process consists in the preparation of chiral monomer crystals. This was achieved by choosing suitable crystal nucleation and growth conditions and introducing a *sec*-butyl group as a desymmetrizing agent. An accurate analysis of phase diagrams, NMR spectra and rotatory power has shown that the influence of the *sec*-butyl group is limited to the induction of preferential crystallization of the monomer in dextro or levo crystals but does not take part in the successive reaction. In fact, products with practically identical optical purity are obtained throughout the field of stability of crystals of a given chirality, even when these contain considerable quantities — up to 40% — of monomer having, as a molecule, the opposite sign.

The crystallization of a racemic *sec*-butyl ester in particular conditions produces a metastable phase in which crystals of opposite chirality contain equal amounts of the two molecular enantiomers. The photopolymerization of single metastable crystals has produced oligomers with significant values of optical activity — up to about 30% — thus obtaining an « absolute » asymmetric polymerization.

The demonstration of the feasibility of asymmetric polymerization under the control of the chirality of the crystal lattice and not of the molecular chirality, which represents one of the central points of the research carried out by Lahav and Addadi, was also obtained in inclusion polymerization in PHTP by using a completely different approach. This problem was quite clear right from the publication of the first article in 1967 ([illegible]). Our conclusion were then as follows:

> « Our experiments show that optical activity may be induced in simple chemical systems under rather primitive and scarcely selective conditions, as the use of ionizing radiation and the absence of complex reagents or catalysts. We are at present investigating whether the polymerization starts from asymmetric radicals or ions obtained by irradiation of PHTP, or if it involves exclusively the guest molecules. In the latter hypothesis this reaction differs sharply from the other asymmetric syntheses known so far; actually only weak Van der Waals forces are responsible for the geometric arrangement that favours one of the sequences (e.g., DDD...) with respect to the other ».

This investigation turned out to be very difficult. In fact, the presence of a chiral end group derived from PHTP had been ascertained by radiochemical means ([illegible]). In any case, the limited availability of optically active host (and hence of polymer), the low value of optical activity and the extremely high diastereomeric purity of the polymer made it problematical to study the variation of rotatory power with the degree of polymerization.

A different approach to the problem was first seen when we managed to prove the living character of the inclusion polymerization in PHTP ([illegible]) and succeeded in preparing block copolymers ([illegible]). The aim was thus to produce a non-chiral/chiral two-block copolymer so as to eliminate any influence deriving from the terminal group linked to the non-chiral block. In experiments conducted in my laboratory by G. Di Silvestro and P. Sozzani, isoprene was chosen as the first monomer and *trans*-1,3-pentadiene as the second (I recall that isoprene polymerizes in the 1,4 mode, not giving rise to chiral units). The structure of the copolymer can be represented as follows:

$$\text{PHTP}^{*}\text{—(CH}_2\text{—CH}=\text{C(CH}_3\text{)—CH}_2\text{)}_m\text{—(CH}_2\text{—CH}=\text{CH—CH}^{*}\text{(CH}_3\text{))}_n\text{—}X$$

In this way a portion of chain not endowed with chirality for several hundred angstrom was inserted between the PHTP radical and the pentadiene monomer units. The presence or the absence of asymmetric induction was to be the test of the two conflicting hypotheses.

The result obtained was highly significant: not only is the copolymer optically active, but the enantiomeric purity of the polypentadiene segment in the copolymer was equal to that observed in the homopolymer ([illegible]). In this case too, asymmetric induction is controlled solely by the chirality of the crystal. The chemical nature of the system employed suggests another consideration, already advanced as hypothesis years earlier: asymmetric induction is possible even only in the presence of weak and non-specific interactions such as those involved in the crystal lattice of a saturated hydrocarbon. I have used the term « through space induction » to define this kind of asymmetric induction, in contrast with the « through bond induction » characterizing the most common and most efficient asymmetric syntheses involving covalent bonds or hydrogen bonds, formation of complexes, specific solvations and other relatively strong interactions between chiral agent and substrate.

At least for the moment, the journey begun twenty years ago under the guidance of Giulio Natta ends at this point. To his memory I dedicate this my latest work, with gratitude for having pointed out to me a goal worthy of being pursued and for having supplied me with the means to reach it, for having left me complete freedom to decide and make plans, for having followed my work for years with lively interest and penetrating criticism. And, above all, for having taught me an absolute respect for experimental results and for having shown me how the most profound and far reaching conclusions are to be drawn from experimental findings.

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Conformation of Macromolecules

The first paper of Professor Natta on this subject has been published in 1925 [G.R. Levi, G. Natta, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat. 2*, 1 (1925)].

His activity in this field is proved by many publications. We quote, for instance: G. Natta, *Atti Accad. Naz. Lincei, Mem., Classe Sci. Fis. Mat. Nat. 4*, 61 (1955); G. Natta, *Polymer Sci. 16*, 143 (1945); G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Moraglio, *J. Am. Chem. Soc.* 77, 1708 (1955); G. Natta, L. Porri, P. Corradini, D. Morero, *Chim. Ind.* (*Milan*) *40*, 362 (1958).

Prof. Giuseppe Allegra who is particularly expert in the mentioned subject has been requested to give a contribution to the volume. The contribution is entitled: *Conformations and Dynamics of Macromolecules*.

Conformations and Dynamics of Macromolecules

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In the last few years diffraction experiments at the molecular level revealed an important new possibility: through the measurement of the Doppler effect, *i.e.*, the loss or gain of radiation energy upon diffusion (dynamic scattering), it is possible to obtain information about the molecular motions (1). Let's specify that these do neither involve the vibrational nor the rotational motions which are generally studied by means of infrared or microwave spectroscopy, whose characteristic frequencies are usually larger than $10^{12}s^{-1}$. The frequencies investigated by dynamic scattering are usually smaller than $10^{10}s^{-1}$; otherwise said, the relevant characteristic times are longer than $10^{-10}s$. In the case of linear macromolecules, within these observation times we may observe chain motions of a conformational origin, *i.e.*, due to rotations around single bonds, while the radiation adopted consists of monochromatic neutron beams (typical wavelength ~ 2 Å), the energy of which is close to the thermal level (2). If we are interested to cooperative motions of long macromolecular sequences or to the diffusion of the whole chain in a dilute solution, the scattering of light may be used, with characteristic times of order $10^{-4}s$ or longer (1).

Other sources of information on the internal motion of macromolecules are sensitive to observation times, or chain sequences, which are not so short as those investigated by neutron diffraction; among these, the complex viscosity $\eta^* = \eta' - i\eta''$ is particularly important, *i.e.*, the contribution provided by the chains to the overall viscosity when the solution is submitted to an oscillatory shear stress (3). The η' component, in phase with the imposed deformation, gives the *elastic* response of the chains, while η'' which is at 90°, represents the *viscous* response. Since it is apparent that the viscoelastic behaviour of a system exclusively depends on its internal dynamics, the knowledge of η' and η'' at different ω frequencies produces important information on the conformational motions, although the upper experimental limit of ω (around $10^9 s^{-1}$) restricts the analysis to fairly cooperative motions, such as those involving at least a few tens of chain atoms.

In the present chapter some relevant physical factors influencing the conformational dynamics of macromolecules will be discussed and, through the analysis of the equations of motion, their effect will be evaluated and compared with the experimental data; on the contrary, the several aspects of the experimental methods will not be discussed except for the general mentions previously made. Being impossible to discuss the matter in detail in an introductory chapter like the present one, we will mainly try to define the general ideas, sending the reader to more specialized publications for the mathematical details. Finally, we anticipate our apologies to the reader if contributions to the subject provided by the author and his group will probably be overemphasized.

Equations of motion

The mathematical description of the motion of a polymer chain is usually given in terms of the Rouse equivalent model (4). The macromolecule is conceived as an ensemble of beads serially connected by ideal springs; these are devoid of mass and exert a perfectly elastic force of an entropic origin, while both the mass and the interaction with the solvent are concentrated on the beads; the solvent is seen as a continuous viscous medium. The springs do not interact among themselves; their number and force constant (related with their average amplitude of oscillation), are so determined as to reproduce the mean-square distance, and therefore the mean-square radius of gyration, of the real macromolecule (5). In practice, it is often convenient to identify the beads with the chain statistical segments, *i.e.*, the shortest sequences after which no correlation exists between bond orientations in space. In the case of polyethylene around 100 °C the number ν of bonds per statistical segment is about 10.

In dilute solution and disregarding the chain ends, the forces acting on the k-th bead are, in projection on a general x axis:

1) the elastic force $F_{el}(k,t) = \alpha[x(k+1,t) - 2x(k,t) + x(k-1,t)]$, where $\alpha = 3k_BT/b^2$ is the spring force constant, while b^2 is its mean-square amplitude of oscillation. With reference to the statistical segment, $b^2 = C_\infty \nu l^2$, where C_∞ is the macromolecular characteristic ratio (5), l is the C—C bond length while ν is ~ 10 as above said;

2) the friction force $F_{fr}(k,t) = -\zeta_s \dot{x}(k,t)$, where ζ_s is the friction coefficient of the statistical segment;

3) the random Brownian force $X(k,t)$, due to the bumps exerted by the solvent. These rapidly fluctuate in time, with an independent effect over different statistical segments;

4) the inertial force $F_{in}(k,t) = -\mu\ddot{x}(k,t)$ (μ = segment mass), which has a very slight effect in the frequency field under consideration ($< 10^{12} s^{-1}$);

5) the hydrodynamic interaction. This is actually the dragging effect exerted by the macromolecule upon the solvent, leading to a reduction of the friction force defined at point 2), because the *relative* velocity between the segment and the solvent is smaller than $\dot{x}(k,t)$. In practice, it can be taken into account by keeping the same definition for F_t and suitably reducing the friction coefficient (see [37]).

Neglecting at present the hydrodynamic interaction (the inertial force will never be taken into account) the equation of motion of the k-th segment is:

$$\alpha[x(k+1,t) - 2x(k,t) + x(k-1,t)] - \zeta_s\dot{x}(k,t) + X(k,t) = 0 \qquad [1]$$

$(\alpha = 3k_BT/b^2)$.

We have thus a system of linear differential equations for the unknowns $x(k,t)$, the resolution of which requires the definition of suitable independent coordinates of motion (normal modes in the statistical sense). Let us now define, according to Ronca (6),

$$\widetilde{x}(q,t) = \sum_{k=1}^{n} x(k,t)e^{iqk}$$
$$\widetilde{X}(q,t) = \sum_{k=1}^{n} X(k,t)e^{iqk}, \qquad [2]$$

where $\{q\} = 0,\ \frac{1}{n}\,2\pi,\ \frac{2}{n}\,2\pi \ldots \frac{n-1}{n}2\pi,$

hence
$$x(k,t) = \frac{1}{n}\sum_{\{q\}}\widetilde{x}(q,t)e^{-iqk}$$
$$X(k,t) = \frac{1}{n}\sum_{\{q\}}\widetilde{X}(q,t)e^{-iqk}, \qquad [2']$$

and suppose for simplicity that the chain be connected ringwise so that $x(n+1) = x(1)$, $x(n+2) = x(2)$ *etc.* By multiplying the general equation [1] by e^{iqk} and summing over all k's, we get:

$$2\alpha(1 - \cos q)\widetilde{x}(q,t) + \zeta_s\dot{\widetilde{x}}(q,t) = \widetilde{X}(q,t). \qquad [3]$$

The $\widetilde{x}(q,t)$'s are the normal mode variables, since in eqs. [3] they are separated hence independent; we obtain (6)

$$\widetilde{x}(q,t) = \frac{1}{\zeta_s}\int_{-\infty}^{t}\widetilde{X}(q,t')\cdot e^{-\frac{2\alpha(1-\cos q)}{\zeta_s}(t-t')}dt'. \qquad [4]$$

It is now advisable to suggest a conceptual interpretation of the mathematical results. The $x(k,t)$ displacement of the general segment at time t has been expressed as a sum of different $\tilde{x}(q,t)$ contributions (the normal modes, see eq. [2']), each of which may be considered as a wave with a repeat length comprising $2\pi/q$ segments along the chain contour. On its turn, each $\tilde{x}(q,t)$ is the sum over different times $t'(< t)$ of random terms $\tilde{X}(q,t')/\zeta_*$ (see [4]) relaxing as $e^{-t/\tau(q)}$, where

$$\tau(q) = \frac{\zeta_*}{2\alpha(1 - \cos q)} \qquad [5]$$

is the relaxation time of the normal mode. In practice, after a time interval of order $\tau(q)$, the $\tilde{x}(q,t)$ amplitude bears no resemblance with itself because of the effect of the Brownian forces $\tilde{X}(q,t)$. It is obvious that the latter are needed to reestablish the chain thermal energy, which otherwise would gradually be cancelled by the friction force $-\zeta_*\dot{x}(k,t)$, as it may be seen in eq. [1]. This implies that there must exist a connection between the Brownian force, the absolute temperature T and the ζ_* friction coefficient; the relationship may be expressed as follows

$$< \tilde{X}(q,t)\tilde{X}(q',t') > = 2nk_BT\zeta_* \cdot \Delta(q + q') \cdot \delta(t - t'), \qquad [6]$$

where Δ and δ are the Kronecker and Dirac deltas respectively, while the average is to be taken over all possible values of the Brownian forces. Eq. [6] is a mathematical representation of the so-called « fluctuation-dissipation theorem » (7).

It has been recently possible to overcome some of the limits of the Rouse bead-and-spring model, proposing more realistic descriptions (8,9). The model suggested by the Author in collaboration with Ganazzoli (9) is based on the statistical behaviour of the following vectors:

$$\tilde{\mathbf{l}}(q) = \sum_{k=1}^{N} \mathbf{l}(k)\exp(iqk); \qquad \left(\mathbf{l}(k) = \frac{1}{N}\sum_{(q)}\tilde{\mathbf{l}}(q)\exp(-iqk)\right), \qquad [7]$$

where $\mathbf{l}(k)$ is the vector associated with the k-th bond, while the q variable may take on all the values given in eqs. [2] by replacing N (No. of chain bonds) for n (No. of beads or statistical segments). It is possible to prove that:

i) - the vectors $\tilde{\mathbf{l}}(q)$ are statistically distributed with a Gaussian law,

ii) - they are statistically independent up to the second order, inasmuch as:

$$< \tilde{\mathbf{l}}(q) \cdot \tilde{\mathbf{l}}(q') > = Nl^2C(q) \cdot \Delta(q + q'), \qquad [8]$$

where l is the C-C bond length while $C(q)$ is the generalized characteristic ratio. The latter for $q = 0$ reduces to the ordinary characteristic ratio C_∞ (5).

For the general value of q we have

$$C(q) = 1 + 2 \sum_{h=1}^{\infty} \frac{< \mathbf{l}(k) \cdot \mathbf{l}(k+h) >}{l^2} \cos(qh), \qquad [9]$$

which may be evaluated for any polymer through essentially the same formalism producing C_∞, once the conformational energy maps are obtained (8a). Fig. 1 gives $C(q)$ *vs.* q for polyethylene at 400 K. The joint probability distribution $W\{\tilde{\mathbf{l}}(q)\}$ for all the normal modes may be expressed as:

$$W\{\tilde{\mathbf{l}}(q)\} = (\text{constant}) \cdot \exp\left(-\frac{3}{2} \sum_{(q)} \frac{< \tilde{\mathbf{l}}(q) \cdot \tilde{\mathbf{l}}(-q) >}{Nl^2 C(q)}\right). \qquad [10]$$

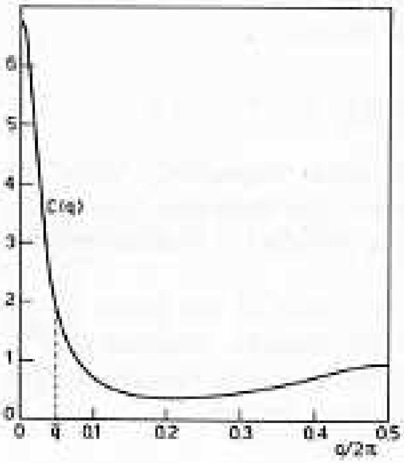

Fig. 1 - **The generalized characteristic ratio $C(q)$ for polyethylene (see eq. [9]; T = 400 K; internal rotation angles: T = 180°, G^+ = 60°, G^- = 300°; $G^\pm$ $G^\mp$ sequences not allowed; bond angle C-Ĉ-C 109°28′; energy difference between *gauche* and *trans* states = 0.5 kcal/mol).**

It is worth pointing out that the above mentioned distribution is not rigorous, although being much more accurate than that corresponding to the Rouse model. While the terms within the exponential depend quadratically from the chain coordinates, the existence of higher-order interactions among the normal modes implies that the exact expression should also contain terms of the fourth, sixth... degree. Otherwise said, we are confining our approach within a *generalized Gaussian approximation*, the limitations of which will be duly taken into account in the following.

The physical meaning of [10] is not restricted to the probability distribution of chain coordinates (through [7]); it also contains an important energetic aspect. In fact, $-k_BT \ln W\{\tilde{\mathbf{l}}(q)\}$ may be interpreted as the Helmholtz free energy $A\{\tilde{\mathbf{l}}(q)\}$ of the general conformation (10), whence the intramolecular force acting on the k-th chain atom can be calculated. It may be proven that the dynamic normal-mode equation corresponding to [3] becomes:

$$2\alpha(q)\,(1-\cos q)\widetilde{x}(q,t)+\zeta\,\dot{\widetilde{x}}(q,t)=\widetilde{X}(q,t), \qquad [11]$$

where all magnitudes are now referred to the chain atoms instead of to the beads of Rouse model. The elastic force constant $\alpha(q)$ depends on the normal mode according to the relationship:

$$\alpha(q)=\frac{3k_BT}{C(q)l^2}\,. \qquad [12]$$

Because of the inverse dependence on $C(q)$ (see Fig. 1), for the collective modes ($q \simeq 0$) the chain behaves in a relatively flexible way, while being more rigid for the localized modes, since $\alpha(q)$ increases up to twenty times compared with $\alpha(0)$. This is clearly shown from comparison of the relaxation time:

$$\tau(q)=\frac{\zeta}{2\alpha(q)\,(1-\cos q)}=\frac{C(q)}{6(1-\cos q)}\,t_0;\ \left(t_0=\frac{\zeta\,l^2}{k_BT}\right), \qquad [13]$$

with the corresponding time for the Rouse chain (see [5]). Since the latter has the same elastic constant whatever is the q value, for localized modes we should expect comparatively longer relaxation times than for the real chain. This effect can be observed in Fig. 2, where the relaxation

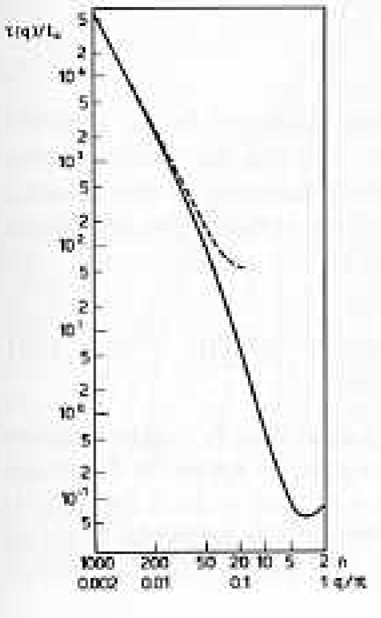

Fig. 2 - The relaxation time $\tau(q)$ for the real chain (continuous line) and for the Rouse chain (dashed line); $n = 2\pi/q$ is the number of atoms included in the wavelength of the q-th normal mode. The parameters are as in Fig. 1, the t_0 time unit is defined in eq. [13]. For the Rouse chain, a statistical segment contains 10 atoms ($= \nu$).

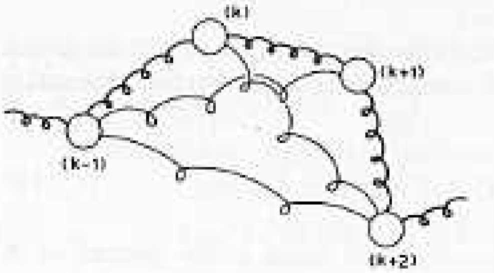

Fig. 3 - Elastic forces affecting the general atom are visualized as springs connecting with all the other chain atoms. The more the two atoms are separated, the weaker the spring is (see eq. [14]).

times calculated for the two models are compared. Incidentally, it should be pointed out that the shortest normal-mode wavelength for the Rouse model comprises about 20 chain atoms (corresponding to two statistical segments), which prevents from taking into account *all* the conformational degrees of freedom within such a model. The greater stiffness of the real chain in comparison with the Rouse model may also be seen in Fig. 3. As it can be inferred from the intramolecular potential $- k_B T \ln W\{\tilde{\mathbf{l}}(q)\}$ (eq. [10]), each atom may be considered as connected by ideal springs with any other (and not only with the nearest neighbours as in the Rouse model), although the elastic constants of these springs tend to diminish rapidly as the topological distance increases. Namely, for two atoms separated by k bonds the force constant of the connecting spring is given by:

$$K(k) = - \frac{3k_B T}{\pi l^2} \int_{-\pi}^{+\pi} \frac{(1 - \cos q) \cdot \cos (qk)}{C(q)} \, \mathrm{d}q \qquad [14]$$

In the ideal case where there is no bond correlation, the Rouse model would be recovered. In fact, from [9] $C(q) = 1$; hence $K(\pm 1) = 3k_B T/l^2$, otherwise $K(k) = 0$.

The dynamic structure factor

From the measurement of the Doppler effect displayed by the neutrons scattered by the macromolecules, it is possible to obtain the *dynamic structure factor*, $S(Q,t)$ ($Q = 4\pi \sin(\theta/2)/\lambda$, θ deflection angle, λ wavelength), which may be defined as the mutual interference between the macromolecular conformations at time zero and at time t:

$$S(Q,t) = N^{-2} \sum_{j,k=1}^{N}\sum < \exp [- i\mathbf{Q} \cdot (\mathbf{r}(j,t) - \mathbf{r}(k,0))] >; \qquad [15]$$

$\mathbf{r}(j,t)$ is the vector defining the j-th atom position at time t. Let us suppose that the probability distribution of $\Delta\mathbf{r}(j\text{-}k,t) = \mathbf{r}(j,t) - \mathbf{r}(k,0)$ be Gaussian, which is approximately true when the time t is $> 6 \div 10\, t_0$ (see [13]) and/or when j-k is higher than $50 \div 70$ units (**). In this case [15] reduces to:

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$$S(Q,t) = N^{-2}\Sigma\sum_{j,k=1}^{N} \exp\left[-\frac{1}{6}\,Q^2 \cdot B(j\text{-}k,t)\right], \qquad [16]$$

where

$$B(j\text{-}k,t) = <\Delta r^2(j\text{-}k,t)> \qquad [17]$$

is known as the *correlation function*. For isotropic conformational motions this may be expressed as [putting j = 0]

$$B(k,t) = 3 < [x(k,t) - x(0,0)]^2 >. \qquad [18]$$

From the combined use of [11] and [2] as well as of the fluctuation-dissipation theorem ([6]), the following general expression for the correlation function is obtained:

$$B(k,t) = \frac{l^2}{2\pi}\int_{-\pi}^{\pi} C(q)\,[1 - \exp(-t/\tau(q)) \cdot \cos(qk)]/(1 - \cos q)\,\mathrm{d}q. \quad [19]$$

The relaxation times $\tau(q)$ are given by [13]. The corresponding result for the Rouse model is obtained from [19] by putting $C(q) \rightarrow C_\infty$ $(=C(0))$, $\zeta \rightarrow \zeta\nu$, (where $\nu = 10$ is the number of chain atoms per statistical segment), $\alpha(q) \rightarrow \dfrac{3k_BT}{C_\infty \nu l^2}$. Fig. 4 shows the $B(k,t)$ plots for both models, within the time interval where the conformational characteristics

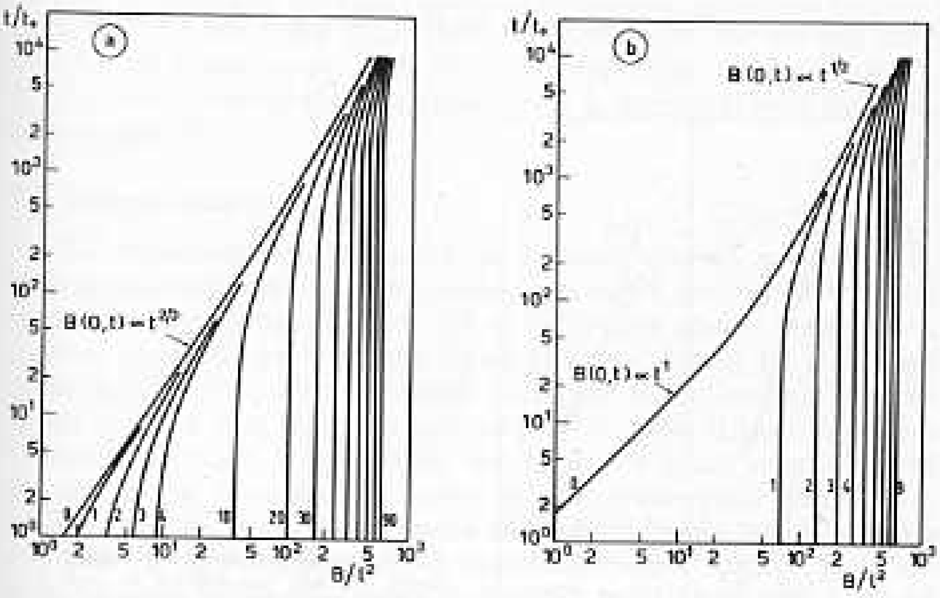

Fig. 4 - The correlation function $B(k,t)$ (see eqs. [17]-[19]) as a function of t at different k's (numbers on the curves) for the real a) and for the Rouse chain b). $B(k,t)$ is in unit l^2 ($l = 1.54$ Å is the C—C bond length), t is in unit t_0, see eq. [13].

of the real chain are most relevant. The influence of these results on the dynamic structure factor may be more easily discussed with reference to the *incoherent* scattering (^{1}), that is produced by those nuclei (e.g. ^{1}H) imparting a random phase change to the scattered neutrons. Under these circumstances, the dynamic structure factor only depends on the self-correlation function $B(0,t)$:

$$S_{inc}(Q,t) = \exp\left(-\frac{1}{6}\, Q^2 B(0,t)\right). \qquad [20]$$

For a given value of the scattering coordinate Q, it is convenient to associate two distinct characteristic times to $S_{inc}(Q,t)$, *i.e.*, the half-peak time $t_{1/2}$ and the initial decay time τ_Q, defined by the relations:

$$\begin{aligned} &\text{a)}\quad S_{inc}(Q,t_{1/2}) = 0.5\, S_{inc}(Q,0) = 0.5, \\ &\text{b)}\quad \lim_{t\to 0} S_{inc}(Q,t) = \exp(-t/\tau_Q). \end{aligned} \qquad [21]$$

Their dependence on Q is shown in Fig. 5 within the interval $0.1 < Q < 0.4$ Å^{-1} (the so-called intermediate scattering range). These functions are often represented by a power law of the type

$$t_c \cdot Q^\beta = \text{constant}, \qquad [22]$$

where t_c may be either $t_{1/2}$ or τ_Q. If the $B(0,t)$ function (for $t > t_0$) depends

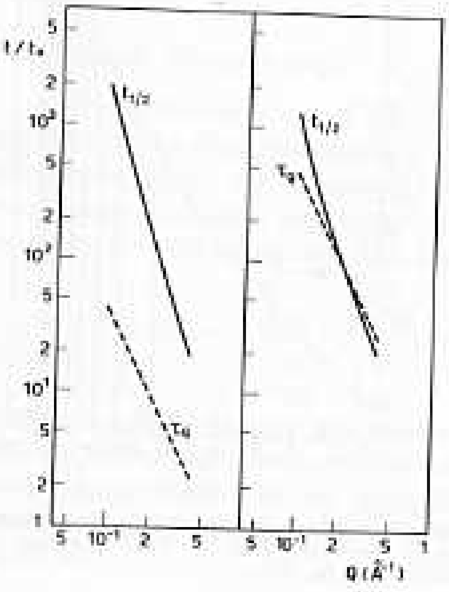

Fig. 5 - Incoherent scattering: characteristic times $t_{1/2}$ and τ_Q, defined in eqs. [21], reported vs. Q for the real chain (on the left) and for the Rouse chain (on the right). The time unit is t_0 as in Figs. 2 and 4.

VALUES OF THE EXPONENT β FOR THE POWER LAW $t_c \cdot Q^\beta = const$
(see eqs. [21] and [22], $0.1 < Q < 0.4$ Å^{-1})

CHARACTERISTIC TIME t_c	EXPONENT	
$t_{1/2}$	3.2	coherent scattering
τ_0	3.6	
$t_{1/2}$	3.1	incoherent scattering
τ_0	2.0	

on its turn on a power of time:

$$B(0,t) = (\text{constant}) \cdot t^\alpha, \qquad [23]$$

(see Fig. 4), from comparison of equations [20] and [21a] it is easy to see that $\beta = 2/\alpha$. As it may be seen in the Table, for the real chain the resulting value of β is constant and very close to 3, in agreement with several experimental data (11); on the contrary, for the Rouse chain it varies between 3.5 (for $Q = 0.1$ Å) and 2.4 (for $Q = 0.4$ Å^{-1}). Analogous conclusions hold for coherent scattering, in which case the structure factor also depends on the interatomic correlation functions (see [16]). As far as τ_0 is concerned, the most significant information which can be drawn from Fig. 5 is the $t_{1/2}/\tau_0$ ratio, which is much larger for the real chain than for the Rouse model. This shows that the initial relaxation time of $S_{inc}(Q,t)$ is much faster than the average one, in agreement with the experimental data (12).

The internal viscosity

The experimental behaviour of the complex viscosity $\eta^* = \eta' - i\eta''$ of some polymers in solution like polystyrene, shows that at relatively high frequencies (approximately from 10^2 to $10^5 s^{-1}$) the elastic component η' tends to a constant value, suggesting an increased rigidity for the macromolecules (13). This effect is usually attributed to the internal viscosity, which is still a very much debated subject (14). The original hypothesis by Kuhn and Kuhn (15) concerned the dissipative effect connected with the overcoming of rotational barriers in a conformational transition, in analogy with the heavy-sphere model adopted by Eyring for the viscosity of liquids (16). It was translated into quantitative terms, although in a semi-empirical way, with some success by Cerf (17) and Peterlin (18). Later on, Iwata (19), Cerf himself (20) and Mac Innes (21) used more refined statistical models, while de Gennes (22) suggested that internal viscosity might originate from the intramolecular friction between different segments. A different interpretation was given by Adelman and Freed (23) who attributed the rigidity effect at high frequencies to the anharmonicity of the intramolecular potential, and by Adler and Freed (24) who obtained analogous results within a quadratic-potential approximation by introducing an interaction energy between the side chains. Fixman, by means of molecular-dynamics simulations, was able to reproduce the viscosity « plateau » at high frequency (25).

This Author, through non-equilibrium statistical-mechanical considerations, suggested that the internal viscosity force acts on a chain sequence when its head-to-tail distance differs from the average value expected from the existing ratio of rotational isomeric states (in the case of polyethylene, *trans* and *gauche* states) (26). Let us still consider for a while the bead-and-spring model, assuming again the beads to coincide with the statistical segments. Since there can be no instantaneous, long-range transmission of tensile force in a « soft » system like a polymer coil, a sudden pull applied to the chain ends along the x axis first gives rise to an elongational deformation of the terminal segments, and then propagates to the inner sequences. The phenomenon takes a finite time since it involves rotations of the torsional angles, which cannot happen instantly. As a consequence, the k-th segment is submitted to a non-equilibrium force $\Phi(k,t)$ (internal viscosity) which has to be balanced by the elastic force transmitted by the neighbouring segments. If the stress propagates toward increasing k's, ignoring at first both the friction with the solvent and the Brownian forces, we have (27):

$$\text{a)}\quad [x(k+1,t)-x(k,t)]-[x(k,t)-x(k-1,t)]+\varphi(k,t)=0$$

$$\text{b)}\quad \frac{1}{\bar{\tau}_0}\varphi(k,t)+\dot{\varphi}(k,t)=\frac{2}{3}[\dot{x}(k+1,t)-\dot{x}(k-1,t)], \qquad [24]$$

where

$$\text{c)}\quad \varphi(k,t)=\Phi(k,t)/\alpha,$$

and the elastic constant α is the same as given in [1]. The rotational relaxation time $\bar{\tau}_0$ is given by (26):

$$\bar{\tau}_0=\frac{\exp(\Delta/k_BT)}{2A}\left(\frac{f_G^0\,f_T^0}{2}\right)^{1/2}; \qquad [25]$$

A is a frequency factor, Δ is the effective (average) energy barrier between *gauche* and *trans* states, while f_G^0 and f_T^0 are the respective equilibrium probabilities. It is possible to show that eqs. [24] represent a perturbation proceeding along increasing values of k with a damping amplitude.

The rate of $d_1 = [x(k+1,t) - x(k-1,t)]$ is given by the difference d_2 between the projections $[x(k+1,t) - x(k,t)]$ and $[x(k,t) - x(k-1,t)]$; if d_1 were constant in time, then d_2 would relax as $e^{-t/\bar{\tau}_0}$. Since it is presumed that a given segment undergoes a uniform conformational change in order to reach the same extension as the previous one, it is implicit in the above picture that a uniform extension should be simultaneously transferred to all of its bonds. In other words, a sort of rigidity would be associated to the whole segment, which seems to be in contrast with the existence of several conformational degrees of freedom within it. We shall see later how this limitation may be overcome.

Integrating eq. [24b] over the time variable and replacing $\varphi(k,t)$ into [24a], we get

$$\begin{gathered} x(k+1,t) - 2x(k,t) + x(k-1,t) + \\ + \frac{2}{3} e^{-t/\bar{\tau}_0} \int_{-\infty}^{t} e^{t'/\bar{\tau}_0} [\dot{x}(k+1,t') - \dot{x}(k-1,t')] \, dt' = 0. \end{gathered} \qquad [26]$$

If the perturbation imparted to the chain is a harmonic oscillation with an angular frequency $\omega \ll \bar{\tau}_0^{-1}$, it is easy to verify that the stationary solution of eq. [26] is given by:

$$x(k,t) = H \cdot \exp\left[i \left(\frac{2\pi k}{\lambda} - \omega t \right) - kK \right], \qquad [27]$$

where

$$\lambda(\text{in segments}) = \frac{3\pi}{2\omega\bar{\tau}_0}; \quad K = \frac{4}{3} \omega^2 \bar{\tau}_0^2 . \qquad [28]$$

Eq. [27] represents a stationary wave propagating and damping off toward increasing k values, with a velocity

$$\nu(\text{in segments}/s) = \omega\lambda/2\pi = \frac{3}{4\bar{\tau}_0}. \qquad [29]$$

It is interesting to remark that, except for $\bar{\tau}_0$, eq. [26] does not contain any reference to sequences which should homogeneously relax (e.g., statistical segments), although it was originally derived from this very hypothesis (26). This suggests that the equation itself has a more general validity; in fact it may be extended to the chain single bonds, which gives the advantage that all the degrees of freedom are taken into consideration (27). As a consequence, once again $x(k,t)$ will refer to the k-th *atom* coordinate at time t. The rotational relaxation time *per bond* will be denoted as τ_0 in order to distinguish it from $\bar{\tau}_0$, *i.e.*, that pertaining to the statistical segment. It should be noticed that at frequencies such as $\omega\tau_0 \ll 1$, the two descriptions are equivalent if the correspondence $\tau_a = \bar{\tau}_0/\nu$ is established, where ν (No. of chain atoms/statistical segment) is ~ 10. By introducing into [26] the friction and the Brownian forces and making recourse again to the normal modes defined in [2], we get

$$2\alpha(q)\,(1 - \cos q)\widetilde{x}(q,t) + \frac{4}{3}\,i\alpha(q)\sin q \int_{-\infty}^{t} \dot{\widetilde{x}}(q,t')\,e^{-\frac{t-t'}{\tau_0}}\,dt' +$$

$$+ \zeta\dot{\widetilde{x}}(q,t) = \widetilde{X}(q,t), \qquad [30]$$

where the internal viscosity force $\widetilde{\Phi}(q,t)$ is obviously to be identified with the term containing the integral, otherwise the equation being equivalent to eq. [11]. In the special case when τ_0 is very small compared with the relaxation time of the normal mode, we have

$$\widetilde{\Phi}(q,t) = -\frac{4}{3}\,i\alpha(q)\sin q \cdot \tau_0 \cdot \dot{\widetilde{x}}(q,t). \qquad [31]$$

At first inspection this analytical form resembles other expressions already suggested for the internal viscosity [see, e.g. references (17) and (18)], but it basically differs because of the presence of the imaginary unit, imparting a 90° phase shift with respect to the friction force $-\zeta\dot{\widetilde{x}}(q,t)$. This produces a peculiar relaxation of the normal modes, which behave as damping travelling waves. More specifically, Fig. 6 shows that each mode

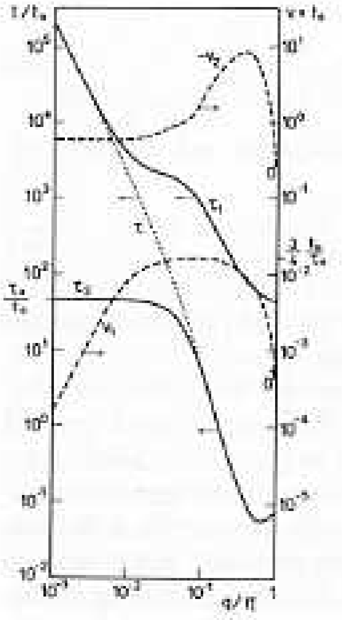

Fig. 6 - Relaxation times (τ_1 and τ_2) and propagation velocities of the respective damping waves (ν_1 and ν_2, chain atoms/s) for the general normal mode $\widetilde{x}(q,t)$ in the presence of internal viscosity (see eq. [30]); the time unit t_a is as in Fig. 5, $\tau_a = 46.7\ t_a$. For comparison, the dotted line shows the relaxation time $\tau(q)$ in the absence of internal viscosity (see Fig. 2).

consists of the superposition of two waves, relaxing with different times $\tau_1(q)$ and $\tau_2(q)$ while moving with different velocities toward opposite directions. The effect of the internal viscosity on the dynamics of the chain is mainly related with the $\tau_1(q) - \tau(q)$ difference, which is negligible for very small q and increases up to $q \sim \pi/2$, as shown in the figure; this type of behaviour corresponds to what found by several authors (17,18,21).

It may be also worth pointing out that the propagation velocity v_1 of the component relaxing more slowly, (*i.e.*, with the relaxation time τ_1) is always lower than the limit $\frac{3}{4\tau_0}$ that would be reached only in the case when $q \to 0$ and $\zeta/\tau_0 \to 0$ (cfr. eq. [29], obtained under these hypotheses). Finally, it should be stressed that the normal mode waves travelling toward increasing k's, considered hitherto, are always associated with equal probability to those moving toward the opposite direction.

The internal viscosity and the complex modulus

The complex modulus G^*, defined as

$$G^* = i\omega\eta^* = i\omega(\eta' - i\eta'') = G' + iG'', \qquad (G' = \omega\eta'', \quad G'' = \omega\eta'), \tag{32}$$

is obviously connected with the complex viscosity η^* but it is preferred sometimes in current practice. Let us suppose that the polymer solution be submitted to a periodic shear stress in the plane (x,y) along the x direction, so that the solvent velocity in the same direction is

$$v_x^{(0)} = \gamma e^{i\omega t} \cdot z, \tag{33}$$

where z is perpendicular to (x,y). Under these circumstances the complex viscosity is given by

$$\eta^*(\omega) = \eta_s + \frac{c}{\gamma e^{i\omega t}} N < f_x(k,t) z(k,t) >_k, \tag{34}$$

where η_s is the solvent viscosity, c is the polymer concentration (number of chains/volume), N is the number of carbon atoms/chain and $f_x(k,t)$ is the force exerted by the k-th atom on the solvent, corresponding to the first two terms of eq. [30]. Starting from [30], [32] and [33] and using the fluctuation-dissipation theorem (7) which in the present case reads (compare with [6], $\tau_0 = 0$)

$$< \widetilde{X}(q,t)\widetilde{X}(q',0) > = \\ = Nk_BT \left\{ 2\zeta\delta(t) + \frac{4}{3}\, i\alpha(q) \sin q \, e^{-t/\tau_0} \widetilde{X}(q,0) \right\} \cdot \Delta(q + q'). \tag{6'}$$

it is possible to calculate $\eta^*(\omega)$. Without giving the complete expression (27), in this context we shall limit ourselves to the special case where $\omega\tau_0 \ll 1$, so that the approximation [31] may be adopted. The result is

$$\eta^*(\omega) = \eta_s + c \cdot k_B T \sum_{(q)} \frac{\zeta}{4\alpha(q)\,(1 - \cos q)} \; \frac{1 + i\omega \dfrac{8\alpha(q)\tau_0^2}{9\zeta}(1 + \cos q)}{1 + i\omega\bar{\tau}(q)/2}, \qquad [35]$$

where

$$\bar{\tau}(q) = \frac{\zeta^2 + \left(\dfrac{4}{3}\sin q \cdot \alpha(q)\tau_0\right)^2}{2\zeta\alpha(q)\,(1 - \cos q)} \qquad [36]$$

is the effective relaxation time. It can be seen in [35] that for large ω's (provided $\omega\tau_0 \ll 1$), η^* is given by a sum of real contributions tending to constant values, so that it ultimately reduces to a constant η', in accordance with the experimental data.

Fig. 7 shows the two components of the complex modulus $G^*(\omega)$ (see [32]), calculated with no approximation for two different molecular weights; the τ_0 value has been so chosen as to reproduce at best the experimental data obtained from dilute polystyrene solutions (13). It should be remarked that here we are unduly extending to polystyrene the conformational properties of polyethylene as embodied in the generalized characteristic ratio $C(q)$ (see [9]), although the error involved should be

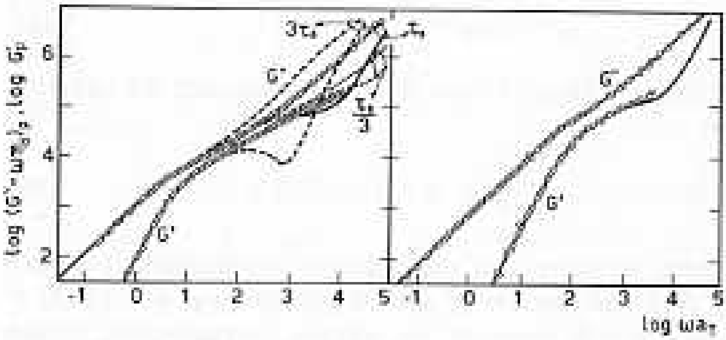

Fig. 7 - Experimental values (circles) of the reduced complex modulus (G', G'') of polystyrene solutions (13). The molecular length is 5100 and 980 carbon atoms on the left and on the right, respectively.
The calculated curves giving the best agreement (continuous lines) correspond to 8000 and 1300 carbon atoms in the main chain, $\zeta = 10^{-4}$ g s^{-1}/chain atom (corresponding to a solvent viscosity $\eta_s = 1$ P), $T = 400$ K, $t_0 = \zeta l^2/k_B T = 4.3 \times 10^{-7}$ s, $\tau_0 = 46.7\ t_0$ as in Fig. 6. The coefficient of hydrodynamic interaction h_0 (see eq. [37]) has been set equal to 0.03. In the left-side plot the curves calculated for τ_0 equal to three times (dashed lines) and to one third (dotted lines) the optimal value are also reported, showing that the true value cannot be very different from that assumed by us.

very small at least in this frequency range. Besides, the *hydrodynamic interaction* has been taken into account, according to Ronca's approach, which only modifies the ζ friction coefficient for each normal mode (28):

$$\zeta \rightarrow \zeta(q) = \frac{\zeta}{1 + h_0 N^{1/2} \pi \cos(qN/2) J_0(qN/2)} . \qquad [37]$$

In the above, J_0 is the Bessel function of zero order, while h_0 is the hydrodynamic interaction coefficient that we have considered as an adjustable parameter, according to current practice.

As it can be observed from the figure, the agreement between the experimental and calculated curves is fairly good. In the double-logarithmic representation, the η' plateau toward the high frequencies shows up as a constant, unitary slope of G'' (see [32]). For frequencies close to τ_0^{-1} the calculated G' and G'' curves intersect one another, but the experimental data do not allow to verify this theoretical prediction; however, discrepancies between theoretical and experimental data of G' may be observed in this region. As it can be noticed in the left-side plots, the calculated curves are rather sensitive to the value chosen for τ_0, so that the order of magnitude of this characteristic time should be considered as correct.

The internal viscosity and the dynamic structure factor

Proceeding in analogy with the 3rd section of the chapter, but adopting the full equation of motion [30] with the parameters already used for the calculations reported in Figs. 6 and 7, we have evaluated the correlation functions $B(k,t)$ shown in Fig. 8. The hindering effect exerted by the internal viscosity, especially at times around τ_0, is apparent when comparing with the results for $\tau_0 = 0$; besides, a tendency to stronger correlation in the motion of neighbouring atoms is observable. Fig. 9 shows the behaviour of the coherent dynamic structure factor $S(Q,t)$ (see [16]), for the extreme values of the interval $0.1 < Q < 0.4$ Å^{-1}, calculated with and without the internal viscosity. Its effect is particularly noticeable for $Q = 0.4$ Å^{-1} because in this case the half-peak time $t_{1/2}$ is close to τ_0 and from Fig. 6 it can be seen that a high concentration of relaxation times exists in the proximity of τ_0. From the figure it can be noticed that in both cases the initial slope is independent from the internal viscosity, in accordance with what observed by Fixman through simulation computations carried out on model chains containing rotational energy barriers (25). Since these calculations are controlled by Kirkwood's diffusion equation, it may appear that the present theory of internal viscosity is implicitly contained therein, although the question is still open.

As for the behaviour of the relaxation times $t_{1/2}$ and τ_0 *vs.* Q (see eqs. [21] and [22]), while the latter is insensitive to the internal viscosity, the exponent β for $t_{1/2}$ is made to decrease from 3.2 to 2.8 and from 3.1 to 2.4 in

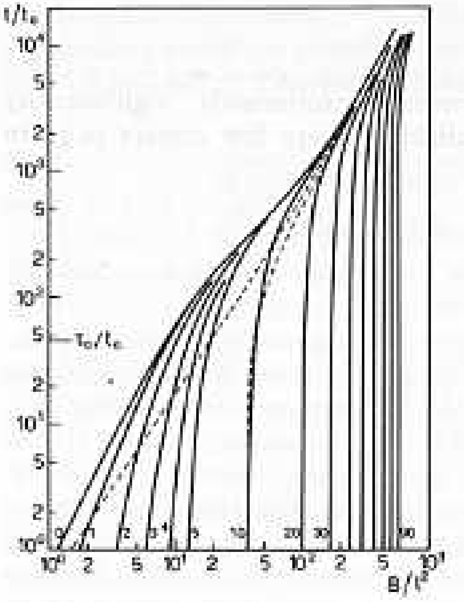

Fig. 8 - Correlation function $B(k,t)$ in the presence of internal viscosity (as in Figs. 6-7) but ignoring the hydrodynamic interaction ($h_0 = 0$). Other parameters as in Fig. 4. The dashed lines correspond to $k = 0$ and $k = 10$, $\tau_0 = 0$ (see Fig. 4).

the respective cases of coherent and incoherent scattering ($0.1 < Q < 0.4$ Å^{-1}). It should be remarked, though, that our results depend on the best-fitting value of τ_0 for the experimental data for polystyrene, where the side phenyl groups give rise to remarkable hindrance to the rotation around chain bonds. The corresponding value for polyethylene should be smaller, and therefore the value of β closer to 3.

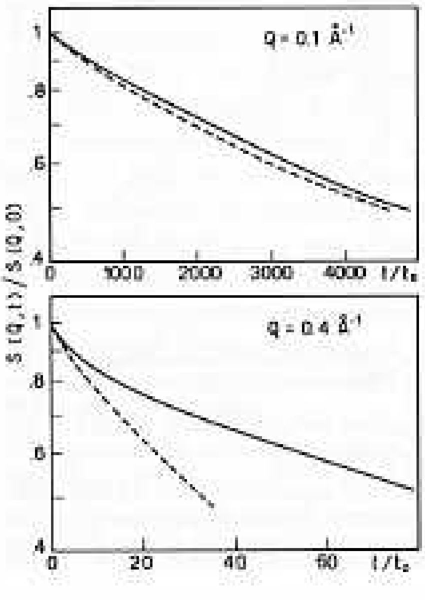

Fig. 9 - The coherent dynamic structure factor (see eq. [16]) vs. t for two typical values of $Q(= 4\pi \sin(\theta/2)/\lambda)$. Continuous lines with $\tau_0 = 46.7\ t_0$, dashed lines with $\tau_0 = 0$; $h_0 = 0$.

Concluding remarks

Most of the theoretical results reported in this paper are still waiting an accurate comparison with experiment. Unfortunately, high-intensity neutron beams are required, only available in very few centers (e.g., in Grenoble), which seriously limits today's availability of dynamic scattering results. On the other hand, the neutron spin-echo technique appears to be very promising for the near future (12).

However, some theoretical verifications seem to be rather sound already. The experimental value close to three of the β exponent for $t_{1/2}$ (see [22] and Table) in the intermediate scattering range is well interpreted by the model proposed by us. Incidentally, we predict that for macromolecules with a particular stiffness, possibly ascribable in part to internal viscosity, the exponent should be lower than three, which seems to agree with experimental observations on (relatively stiff) polystyrene on one side (< 3) and on (relatively flexible) polydimethylsiloxane on the other (~ 3) (29). As for the internal viscosity, besides the reasonable quantitative interpretation of the experimental data on the complex modulus (see Fig. 7), it is important to remark that the order of magnitude of τ_0 adopted in our calculations agrees with that of the rotational relaxation times found by Matsuo, Kuhlman, Yang, Gény and Stockmayer from nuclear relaxation experiments on polystyrene, taking into account the different solvent viscosities (30,27). These are some of the elements encouraging to proceed along this fascinating field of investigation, where the conformational-statistical study of macromolecules seems to find one of its most important new areas of application.

The Author wishes to express his deep gratitude to Dr. Giorgio Ronca of the Politecnico of Milan, for precious suggestions offered during long discussions. He also thanks his coworker, Dr. Fabio Ganazzoli, for important help received during his attendance to the « Scuola di Perfezionamento in Scienza delle Macromolecole Giulio Natta », at the Politecnico of Milan.

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Organometallic Catalysts

The first paper of Professor Natta on this subject has been published in 1957 [G. NATTA, P. PINO, G. MAZZANTI, U. GIANNINI, *J. Am. Chem. Soc.* 79, 2975 (1957)].

His activity in this field is proved by many publications. We quote, for instance: G. NATTA, G. MAZZANTI, *Tetrahedron 8*, 86 (1960); G. NATTA, G. DALL'ASTA, G. MAZZANTI, *Angew. Chem. 76*, 765 (1964); G. NATTA, U. GIANNINI, P. PINO, A. CASSATA, *Chim. Ind.* (*Milan*) *47*, 524 (1965).

Prof. Yves CHAUVIN who is particularly expert in the mentioned subject has been requested to give a contribution to the volume. The contribution is entitled: *Olefin Metathesis*.

Olefin Metathesis

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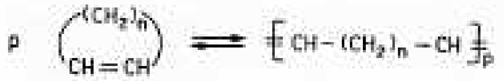
1. Introduction

When treated with selected transition-metal complexes, olefins may undergo a selective « alkylidenolysis » reaction (also called « metathesis », « dismutation » or « disproportionation »), *i.e.* a breaking of the carbon-carbon double bond and redistribution of the alkylidene moieties. Depending on the nature of the starting olefin, this reaction may give rise to various products:

— cyclic olefins yield unsaturated high-molecular-weight polymers (called « polyalcenylenes »).



$$p \left(\overset{(CH_2)_n}{\underset{CH=CH}{}} \right) \rightleftharpoons \left[CH-(CH_2)_n-CH \right]_p$$

— unsymmetric acyclic olefins afford mixtures of symmetric olefins:

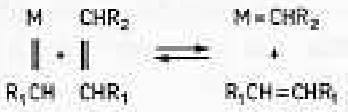
$$R_1CH{=}CHR_2 \rightleftharpoons R_1CH{=}CHR_1 + R_2CH{=}CHR_2$$

— cross-reaction of cyclic and acyclic olefins leads to a telomerization reaction with the acyclic olefin playing the part of a telogen the cyclic olefin being the taxogen:

$$p \left(\overset{(CH_2)_n}{\underset{CH=CH}{}} \right) + R_1CH{=}CHR_1 \rightleftharpoons R_1CH \left[CH-(CH_2)_n-CH \right]_p CHR_1$$

All these transformations have the following common features:

— They involve an unprecedented mode of activation of the olefinic double bond. Various experimental data provide evidence that the catalytic process involves a metathetic exchange of the alkylidene moieties of the olefin with a metallo-carbene species:



— There is no change in the nature and the number of the chemical bonds initially present in the reactants, and the reaction is characterized solely by a change in the molecular weight of the products. Thus the reaction is nearly thermoneutral with a small enthalpy contribution eventually arising from the relief of ring strain, steric hindrance or conjugation effects, and the equilibrium distribution of products is entirely (or mainly) controlled by entropy.

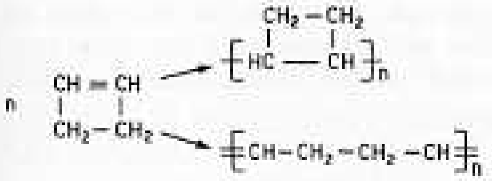
— Most of these reactions may be catalyzed either by homogeneous or heterogeneous catalysts. However it must be remembered that each catalyst keeps its own characteristics.

2. Historic account

During a systematic study of the reactivity of olefins with an internal double bond in regard to anionic coordination catalysts, G. Natta and co-workers (1) observed that cyclobutene can give rise to two modes of polymerization:

i) - either by the opening of the double bond with formation of « polycyclobutene », or

ii) - by ring cleavage to form an unsaturated polymer of the « polybutenylene » type:



Then attemps were made to homopolymerize higher cycloolefins, especially cyclopentene, and it was surprisingly found that molybdenum or tungsten based catalysts (e.g. WCl_6-$Al(C_2H_5)_3$ or $MoCl_5$-$Al(C_2H_5)_3$) afford, with high yield and high activity, pure polypentenylene containing either *trans* or *cis* double bonds (2). These polymers possess good elastomeric properties, closely related to those of *cis* 1,4-polybutadiene or -isoprene.

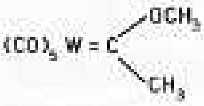
Other cycloolefins such as cyclodecene were subsequently polymerized, and the physical properties of the polymers were carefully analyzed.

At the same time, R.L. Banks and co-workers (3), seeking heterogeneous catalyst systems for paraffin-olefin alkylation or olefin polymerization, observed that alumina impregnated with molybdenum or tungsten carbonyls can transform 1-butene into a mixture of 2-pentene and propylene. In the same way propylene affords ethylene and 2-butene:

$$2CH_3-CH=CH_2 \rightleftharpoons CH_2=CH_2 + CH_3-CH=CH-CH_3$$

It was not immediately recognized that the discoveries by G. Natta and R.L. Banks were in fact the same reaction (the common features of the two reactions were the conservation of the double bonds and the nature of the transition metals used in the catalysts). The parallels were drawn only later, in part by N. Calderon and co-workers (4) who used an anionic coordination catalyst for the disproportionation of 2-pentene.

It was also in the same year, 1964, that E.O. Fischer described the first stable metal-carbene complex (5):



a species which probably plays a major role as an intermediate in metathesis.

3. Consequences of Thermodynamics and Mechanism on the Reactivity of Olefins

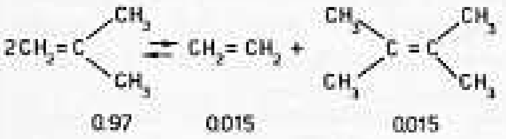
3.1. ACYCLIC OLEFINS

The metathesis of acyclic olefins ultimately affords a thermodynamic equilibrium, the position of which depends essentially on the nature of the reactants. Thus, unbranched olefins with an internal double bond (e.g. 2-pentene) give a statistical distribution of the olefins with a random scrambling of the alkylidene groups:

$$\underset{0.5}{2CH_3-CH=CH-CH_2-CH_3} \rightleftharpoons \underset{0.25}{CH_3-CH=CH-CH_3} + \underset{0.25}{CH_3-CH_2-CH=CH-CH_2-CH_3}$$

The redistribution process and the prevalence of entropy have been verified with deuterated olefins and complex mixtures (e.g. 2-pentene and 6-dodecene yield 2-butene, 3-hexene, 2-octene and 3-nonene).

However, in the case of branched olefins the enthalpy contribution is no longer negligible, and equilibrium exhibits considerable deviation from randomness, e.g. at 20 °C the following equilibrium may be observed:



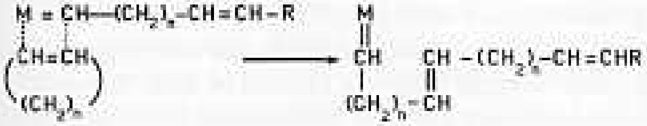
As expected such an equilibrium may be shifted by varying the concentration of one of the reactants, and a pure olefin can be obtained by the continuous elimination of one of the components. For example, if ethylene is continuously removed from the liquid phase of an α-olefin, a pure symmetric olefin can be recovered quantitatively:

$$R{-}CH{=}CH_2 \longrightarrow R{-}CH{=}CH{-}R + CH_2{=}CH_2 \uparrow$$

3.2. CYCLIC OLEFINS

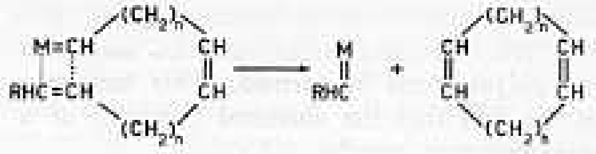
As discovered by Natta, the ring-opening polymerization of cyclopentene (or cyclobutene) affords high-molecular-weight polyalcenylene. On the other hand the polymerization of cyclooctene (or cyclododecene for example) generally gives a complex mixture of high- and low-molecular-weight polymers. Furthermore, whatever the cycloolefin, all the monomers cannot be converted to polymers. In fact, as will now be discussed, the behavior of various cycloolefins depends to a great extent on the ring size.

The growing step of cycloolefin polymerization may be represented as a formal insertion of the olefinic double bond into a metal-carbene compound, affording a high-molecular-weight carbene species:



In this way this mechanism parallels the growing step of conventional olefin polymerization by a Ziegler-Natta catalyst in which the double bond is inserted into a metal-carbon σ-bond:

However, unlike conventional polymerizations, the growing chain may compete with the monomer for the carbene, giving macrocycles:



The size of the macrocycles which is obtained through the intramolecular reaction (« back-biting » reaction) essentially depends on the value of « n ». In this way the behavior of cyclic olefins is quite similar to the condensation reaction of lactams, lactones or cyclic ethers, which has been thoroughly discussed by J.P. Flory ([illegible]); so, for a linearchain polymer the ease of cyclization goes from a maximum for the five-membered ring, to a minimum for the nine-membered ring, then slowly rise to a broad maximum value occurring around 18 atoms (Fig. 1).

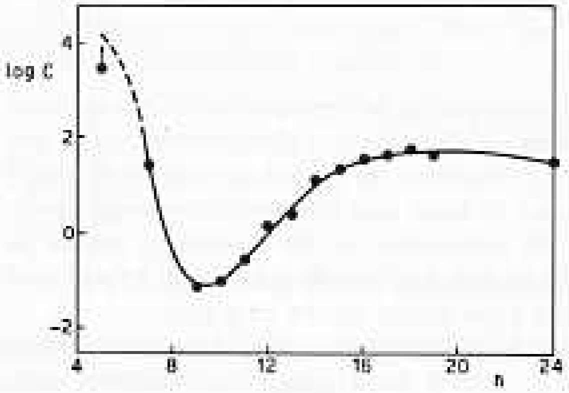


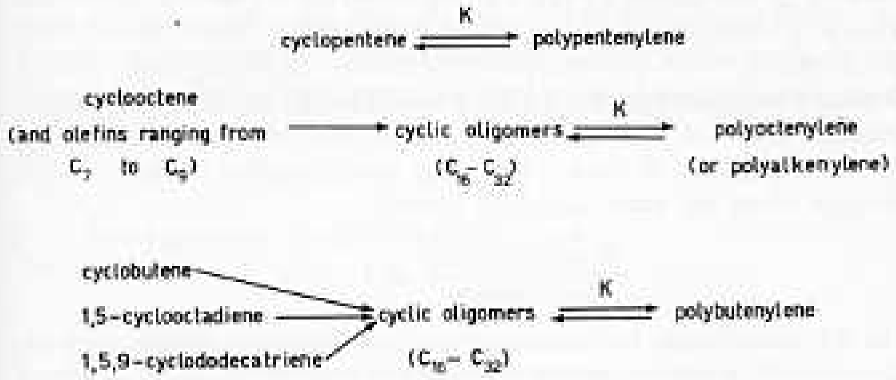
Fig. 1 - Log of the cyclization constant for the lactonization of ω-hydroxy-acids vs. ring size (P.J. Flory).

This readily explains the reversible depolymerization of high-molecular-weight polypentenylene to nearly pure cyclopentene and the fact that polymerization of cyclic olefins such as cyclooctene gives not only high polymers but also cyclic oligomers ranging from C_{16} to C_{32}. In turn the depolymerization of polyoctenylene does not give any cyclooctene but only cyclic oligomers.

A quite similar behavior is observed with cyclic unconjugated multi-olefinic compounds such as 1,5-cyclooctadiene or 1,5,9-cyclododecatriene which afford a mixture of cyclic oligomers (C_{16} to C_{32}) and high-molecular-weight polybutenylene (« 1,4-polybutadiene »), all formally derived from cyclobutene.

Due to the low enthalpy contribution, an actual equilibrium is observed at room temperature between high polymers and either monomer (in the case of cyclopentene) or cyclic oligomers (in the case of higher cycloolefins). The concentration of the low-molecular-weight species does not depend on the amount of polymer formed and depends only on the temperature. For a given temperature this concentration may be considered as a threshold concentration below which no polymer can be formed. This has been ascribed by J.P. Flory ([illegible]) to the fact that the chemical potential of a structural unit (monomer or oligomer unit) reaches a finite value (greater than zero) even when its concentration is zero, provided the chain length is infinite.

All this may be roughly summarized as in the scheme:



For a given temperature, all these equilibria are governed by the following relationship:

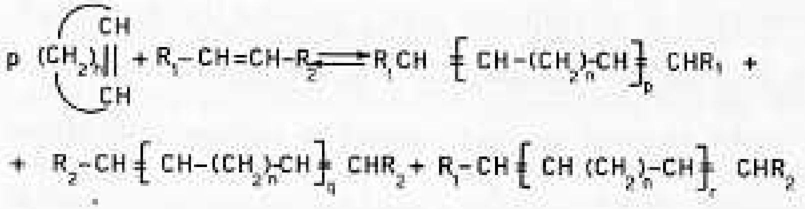
$$K = \frac{1}{[\text{low molecular weight species}]}$$

The threshold concentration of a given cyclic species may be substantially lowered by copolymerization with a readily polymerizable cycloolefin. Thus cyclohexene, which does not polymerize under normal conditions due to the largely positive value of free energy of polymerization (threshold concentration higher than 10 moles/liter), does copolymerize with cyclopentene.

As a consequence of the « back-biting » reaction of the growing chain, catenanes are also formed in small quantities:

3.3. CROSS METATHESIS OF A CYCLIC OLEFIN. METATHESIS OF UNCONJUGATED ACYCLIC POLYENES

Telomers are obtained by cross metathesis:



$$p\ (\text{CH}_2)_n\!\left(\begin{matrix}\text{CH}\\ \|\\ \text{CH}\end{matrix}\right) + \text{R}_1\text{-CH=CH-R}_2 \rightleftharpoons \text{R}_1\text{CH} \left[\text{CH-(CH}_2)_n\text{-CH}\right]_p \text{CHR}_1 + \text{R}_2\text{-CH}\left[\text{CH-(CH}_2)_n\text{-CH}\right]_q \text{CHR}_2 + \text{R}_1\text{-CH}\left[\text{CH (CH}_2)_n\text{-CH}\right]_r \text{CHR}_2$$

Besides the expected products arising by self-metathesis of acyclic olefins, the reaction provides three series of polyenes also of the symmetric and unsymmetric type. In the case of internal acyclic olefins ($R_1R_2 \neq \text{H}$) the distribution obeys the same statistical law:

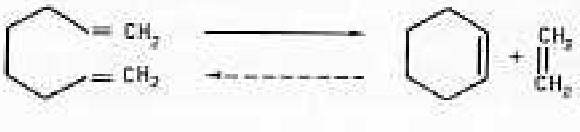
$$\frac{\Sigma \text{ unsymmetric}}{\Sigma \text{ symmetric}} = 1 \, .$$

On the other hand, the concentration of p, q and r species depends on the ratio of acyclic to cyclic olefins. For example a large excess of acyclic olefins favors the formation of dienes (p, q, $r = 1$), but in low concentrations the acyclic olefin acts as a chain-regulating agent for the polymerization of cycloolefins.

Cross metathesis of α-olefins provides mainly unsymmetric type products. Entropy is no longer the controlling factor, and mechanistic parameters can be taken in account.

The cross-metathesis of unconjugated multiolefinic compounds such as 1,5-cyclooctadiene or high-molecular-weight polyalcenylene ultimately gives, as expected, equilibrated telomers all derived from $R\text{CH ǂ CH-(CH}_2)_n\text{-CH ǂ CH}R$ moieties. (This reaction providing easily identified diolefins has been used to analyze the structure of various unsaturated and even partly cross-linked polymers).

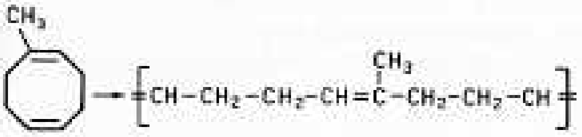
In the same way the inter- and intramolecular reaction of unconjugated acyclic diolefins ultimately affords the same olefin mixture as above, and the product distribution can be predicted on the basis of thermodynamic stability and the concentration of various components, e.g. the following equilibrium may be shifted at will:



4. Synthetic Aspects of Metathesis

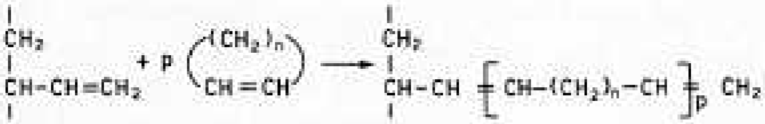
Metathesis is a powerful tool for the synthesis of various olefinic compounds.

Unsaturated high molecular weight polymers, with *cis* or *trans* double bonds, depending on the catalyst systems and polymerization conditions, being either elastomers, crystalline or amorphous materials, are obtained from nearly all cycloolefins, not only cyclopentene, cyclooctene [polyoctenylene is manufactured on an industrial scale (*)], 3-methylcyclooctene, cyclododecene and 3-methylcyclododecene, but also from various polycyclic olefins such as dicyclopentadiene, norbornene [« polynorbornene » is produced at the rate of approx. 15,000 t per year (**)]. Due to the low reactivity of tri- or tetrasubstituted double bonds, perfectly regular polymers are formed from unsymmetrical substituted cyclodiene, e.g.:

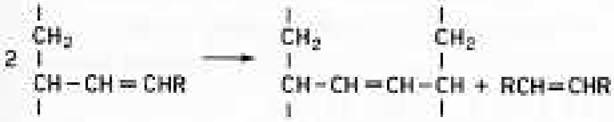


In addition, miscellaneous linear unsaturated copolymers with specific mechanical properties are obtained by the cross-reaction of various cycloolefins or by the reaction of cycloolefins with unsaturated polymers such as 1,4-polybutadiene, 1,4-polyisoprene (polymethylbutenylene) or their copolymers.

The cross-metathesis of cycloolefins with polymers having pendant double bonds such as 1,2-polybutadiene affords grafted copolymers:



With specific conditions crosslinked polymers may also form:



$$2\,\underset{|}{\overset{\overset{|}{CH_2}}{\overset{|}{CH}}}-CH=CHR \longrightarrow \underset{|}{\overset{\overset{|}{CH_2}}{\overset{|}{CH}}}-CH=CH-\underset{|}{\overset{\overset{|}{CH_2}}{\overset{|}{CH}}} + RCH=CHR$$

Macrocyclic oligomers, selectively formed below the threshold concentration, are useful intermediates.

(*) Chemische Werke Hüls.
(**) Charbonnages de France.

Metathesis of acyclic provides interesting routes for the synthesis of many specialty olefins or for balancing various olefin streams. Practically all olefins react with the conditions being more drastic as the olefins are more substituted. Heterogeneous catalysts prove to be particularly suitable because they are stable at high temperature.

Thus the disproportionation of propylene to ethylene and *n*-butenes has found commercial applications in some petroleum refineries and chemical plants (*).

In a general way, if the catalyst system possesses activity for shifting the double bond, long-chain linear olefins can be produced from any short-chain linear olefins such as propylene, *n*-butenes, *n*-pentenes, *etc*. Ethylene is the by-product:

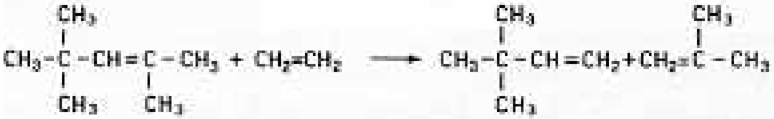
$$CH_3-CH=CH_2 \xrightarrow{\text{Metathesis}} CH_3-CH=CH-CH_3+C_2H_4 \xrightarrow{\text{Isomerization}}$$

$$CH_2=CH-CH_2-CH_3 \xrightarrow{\text{Metathesis}} CH_3-CH_2-CH=CH-CH_2-CH_3+C_2H_4$$

$$\longrightarrow \text{etc} \ldots..$$

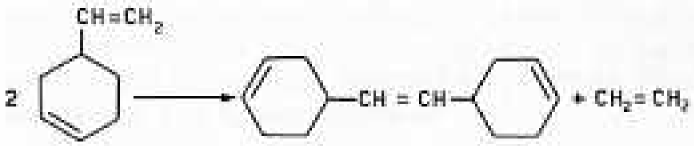
Isomerization and metathesis may also be achieved in two separate steps. This technique is used on an industrial scale to balance long-chain α-olefins produced by ethylene oligomerization (**).

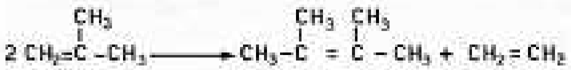
The reaction of ethylene with internal olefins provides a general route to the synthesis of α-olefins (this reaction is called « ethenolysis »). In this way neohexene and various α,ω-diolefins such as 1,5-hexadiene, 1,6-heptadiene and 1,9-decadiene are produced on a semiworks scale:



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH=\underset{CH_3}{\underset{|}{C}}-CH_3+CH_2=CH_2 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH=CH_2+CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3$$

Technology has also been developed on a small scale for the production of various olefins, e.g.:





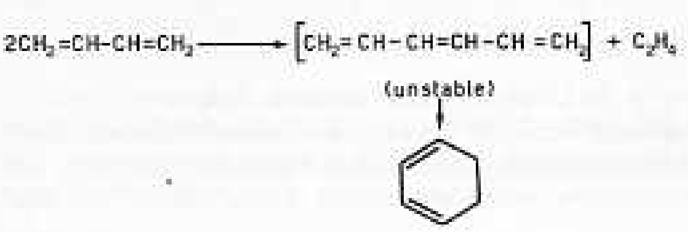
$$2\,CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3+CH_2=CH_2$$

(*) Phillips Petroleum Company.

(**) Shell International Research Maatschappij.

Due to the high selectivity of some catalysts, metathesis can be used for synthesizing isotopically-labeled products from ^{14}C- or ^{2}H-labeled olefin.

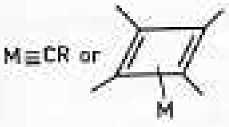
Conjugated dienes react only at high temperature. Under such conditions the expected hexatriene yields cyclohexadiene:



Surprisingly alkynes may also be metathesized, e.g.:

$$CH_3-C\equiv C-CH_2-CH_3 \rightleftharpoons CH_3-C\equiv C-CH_3 + CH_3-CH_2-C\equiv C-CH_2-CH_3$$

In this case specific intermediate species must be involved such as metal-carbyne or metal-cyclobutadiene complexes:



4.1. METATHESIS OF SUBSTRATE BEARING POLAR GROUPS

The metathesis of olefins substituted with functional groups should considerably extend the usefulness of the reaction. However, major difficulties may arise for two reasons:

i) - the deactivation of the double bond toward metathesis by the substitution of vinylic or allylic hydrogen;

ii) - the poisoning effect of electronegative atoms (such as O, N or S) on most known catalysts.

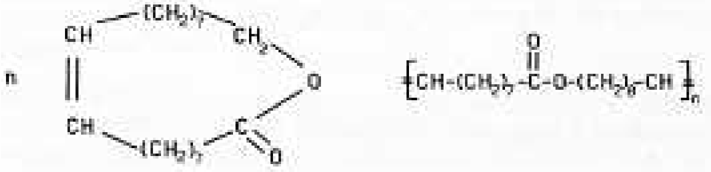
Numerous catalysts are capable of tolerating halogenated compounds, as either solvent or reactant. Thus 1-chloro 1,5-cyclooctadiene polymerizes readily (probably by the unsubstituted double bond), but vinyl chloride does not give ethylene.

Concerning the second point no progress was made until the discovery by C. Boelhouwer *et al.* who succeeded in the metathesis of various unsaturated esters with special catalysts based on tungsten or rhenium and Sn*Me*$_4$ (⁷). Later, additional catalyst systems were discovered, which are effective for the metathesis of acyclic unsaturated nitriles, ketones, ethers, amides, oxysilanes, amines and esters of unsaturated alcohols. This open the way to the synthesis of difunctionalized compounds, e.g.:

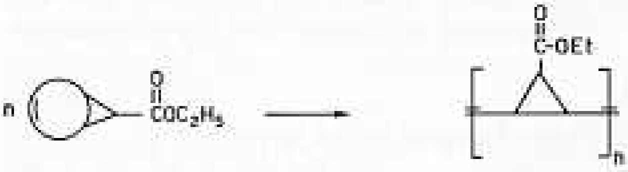
$$2CH_2{=}CH{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow CH_3O\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}CH{=}CH{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}OCH_3 + C_2H_4$$

The position of the double bond in relation to the functional group is crucial, and generally acrylic and allylic derivatives do not react. On the other hand, up to now, unsaturated acids have failed to disproportionate.

Unsaturated lactones polymerize to unsaturated polyesters; e.g., ambrettolide, a naturally occurring lactone:

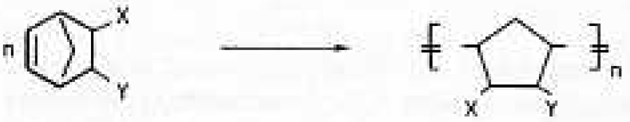


In the same way cycloolefins bearing cyclopropane esters afford polymers with pendant ester groups:



However, at the present time, the usefulness of the reaction is restricted due to the low activity of most catalysts.

Surprisingly the inhibitory effects of polar functional groups are much less pronounced when the substituent is attached to a strained cycloalkene such as norbornene derivatives which are very easily polymerized;



Substituants such as ester, nitrile, amide, anhydride, pyridyle and imide in an « endo » or « exo » position do not deactivate most conventional catalysts. This unexpected behavior has been ascribed to the release of ring strain. However this explanation appears unsatisfactory since polymers themselves readily react with other polyalkenylenes to afford random copolymers. It must be underlined that noble metal catalysts (Ir, Ru, Rh) in protic solvents polymerize all functionalized norbornenes, even ones bearing a hydroxy group. Like polynorbornene itself, many of these polymers have some potential for commercialization.

5. Catalyst Systems

The metathesis reaction was discovered at a time there was still a rigid frontier between homogeneous and heterogeneous catalysts. Actually, the main difference does not lie in the heterogeneous character of the system but mainly in the preparation methods and, above all, the thermal stability.

All metathesis catalysts are derived from transition-metal compounds in group IV to VIII, with the less active being those of the first transition series. The most active are tungsten, molybdenum and rhenium. But it must be emphasized that there is often a specificity between an olefinic structure and a given transition metal. So, noble metals such as ruthenium are very reactive towards cycloolefins with considerable ring strain (cyclobutene, norbornene) and unreactive towards acyclic olefins. On the other hand, for a given transition metal, there is often an effect of the environment on the relative reactivity of cyclic olefins to acyclic ones or of α-olefins to internal olefins.

Typical *heterogeneous* systems are obtained by impregnating (in an aqueous or non aqueous way) refractory supports such as alumina, silica or magnesia, with carbonyls, oxides, sulfides of molybdenum, tungsten, rhenium, *etc*. Generally these systems require activation at high temperature in a stream of various gases such as oxygen and or nitrogen. Pretreatments can modify activity and selectivity. Thus neutralizing the acid-type sites by small amounts of alkali reduces the isomerization activity of the catalysts.

Rhenium based systems are reactive at room temperature. In contrast, catalysts containing molybdenum and tungsten require higher temperature (up to 500 °C in the case of silica supported catalysts). But when operating at such temperatures, they are more resistant to poisoning by polar impurities and can disproportionate highly complexing olefins such as conjugated dienes or styrene. This may also enable them to work in more favorable thermodynamic conditions.

Contrary to their homogeneous counterparts, heterogeneous systems are active and selective in the disproportionation of *iso*butene and highly branched olefins. Being easily recovered and regenerated, they have found a wide range of applications for the metathesis of acyclic olefins.

All the *homogeneous* (or microheterogeneous) catalysts derived from the first systems used by Natta, *i.e.* a mixture of soluble transition-metal halides (WCl_6, $MoCl_5$, *etc.*) and organometallic derivatives of main group elements ($Al(C_2H_5)_3$, $AlCl(C_2H_5)_2$, C_4H_9Li, C_4H_9MgCl...). As for conventional Ziegler-Natta catalysts, the recipes are countless. The organometallic compound may have the usual triple function:

— as an alkylating agent to provide a transition metal-carbon bond responsible for the catalytic activity;

— as a reducing agent, by homolytic decomposition of some of the transition metal-carbon bonds formed in the first step;

— as a Lewis acid, with the removal of a halide ion providing an additional vacant coordination site for the incoming olefin.

Each of these three functions is not essential, but the most active catalysts generally contain an alkylaluminum halide derivative (alkylating agent having a Lewis acid character), e.g. WCl_6-$Al(C_2H_5)Cl_2$. It has been frequently reported that oxygenated compounds such as ethanol, water or dioxygen increase the catalytic activity. So, the oxygen-metal bond may play an important role in the active species.

Many other active catalysts may be obtained by reacting a Lewis acid ($AlCl_3$, $TiCl_4$...) with a transition metal complex whatever is its valence state may be ($W^0 \rightarrow W^{VI}$) e.g. $W(CO)_5L$-$TiCl_4$ or WO_3-$AlCl_3$.

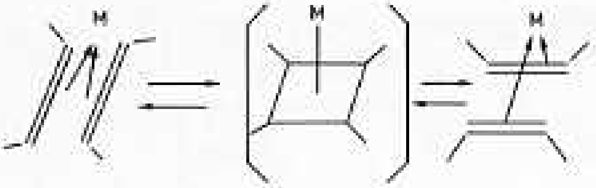
All these recipes are generally very sensitive to the presence of Lewis bases. However catalysts not containing Lewis acids [e.g. WCl_6-$Sn(CH_3)_4$] may accomodate various functions and have been used for the metathesis of olefins possessing polar functionalities. Hydrates of $RuCl_3$ or $IrCl_3$, which are active ring-opening catalysts for highly strained cycloolefins, have been used in ethanol solution and can accomodate a wide range of functional groups.

Homogeneous systems are by far the most active catalysts (the average turnover number for high conversions is sometimes greater than 10^6 mol/mol/hour), but they are often sensitive to impurities, are not very stable even at moderate temperature and cannot be easily regenerated. They find their main utilizations in the field of polymerization.

As for other catalyst systems, attemps have been made to apply the techniques of homogeneous catalysis to the heterogeneous phase. So transition metal complexes such as π-allylic or carbonyl have been grafted either onto inorganic supports (alumina, silica) or onto crosslinked polymers bearing suitable ligands. In another approach typical heterogeneous systems (WO_3-SiO_2, Re_2O_7-Al_2O_3) have been activated by organometallic compounds of the main series. This combines the advantages, but unfortunately often the drawbacks, of the two catalyst types.

6. Mechanistic aspects

The first proposed scheme for the transalkylidenation process assumed a pairwise scrambling of the alkylidene moieties, involving initially a *bis*-olefin metal entity bearing two olefinic ligands in a *cis* configuration about the metal. The key intermediate was suspected to be a quasi-cyclobutane complex:



Other types of symmetric transition states have been proposed such as tetramethylene-metal and metallocyclopentane complexes.

Lately it appears that some experimental data were incompatible with the existence of a symmetrical intermediate, especially:

— the high-molecular-weight polymer formed during the initial stage of cycloolefin polymerization;

— the telomer distribution in the cross-metathesis reaction of cyclic and acyclic olefins;

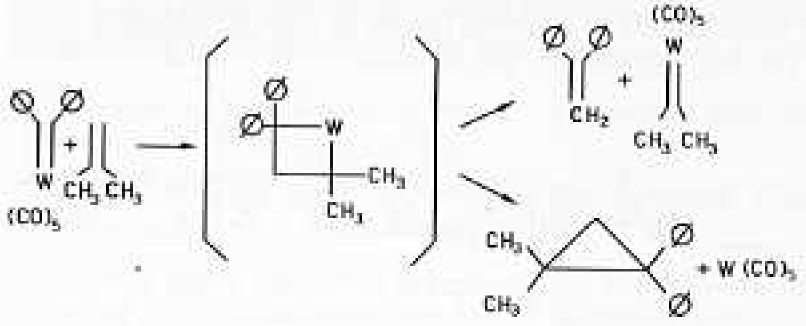
— the deuterium distribution in the products from the metathesis of partially deuterated α,ω-dienes.

It is now widely recognized that most of these features are better explained by a non pairwise mechanism based on the interaction of a carbene-bearing metal complex with an incoming olefin, with the crucial intermediate being a metallocyclobutane species. This mechanism is strongly supported by model experiments with stable carbene complexes similar to the first carbene complex isolated by E.O. Fischer. It has been shown by C.P. Casey *et al.* (^{8}) that pentacarbonyl diphenylcarbene tungsten reacts with *iso*butene to give a mixture of metathesis products and a cyclopropane derivative. This clearly demonstrate that a metallocycle may be an intermediate for both reactions of the scheme on the top of the next page.

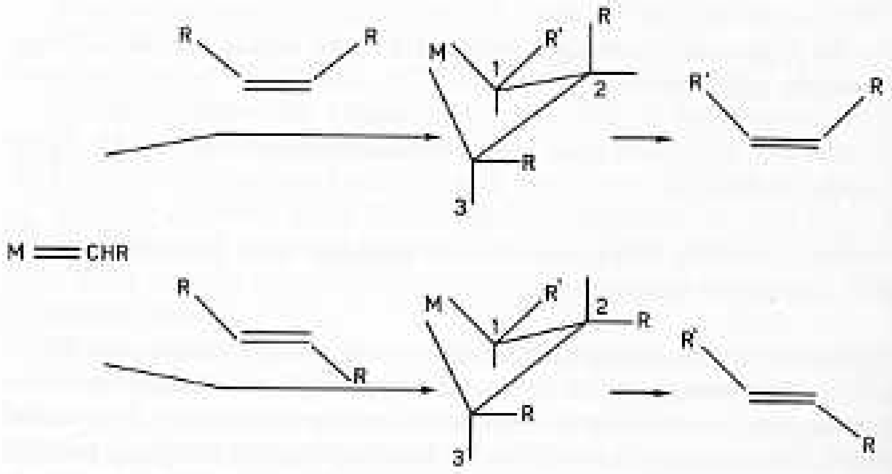
(In fact the formation of cyclopropane was noted in early experiments by R.L. Banks).

Furthermore the same carbene complex, although sluggish, may also be used as a metathesis catalyst for the polymerization of cycloolefins.

Scheme

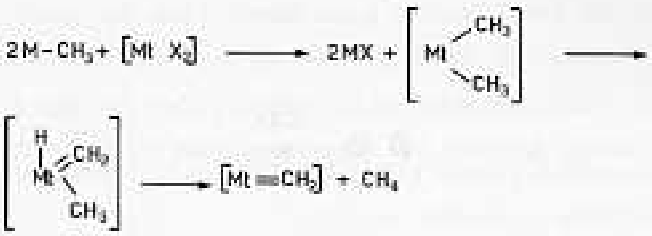


The stereochemistry of olefin metathesis has been tentatively related to the relative stabilities of the puckered metallocycle intermediate, and the favored pathway is that which minimizes the 1,3-diaxal interactions:

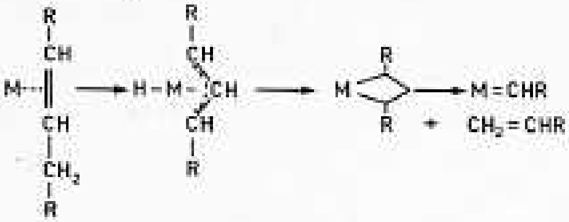


Such a scheme is however unsatisfactory and interaction with metal ligands and the coordination steps of the incoming olefin have to be taken into account.

Very little is known about the formation of the initial carbene-metal entity. For catalysts activated by organometallic compounds not bearing β-hydrogen, the possibility of abstraction of α-hydrogen from the transition metal-carbon σ-bond seems to be clearly demonstrated, e.g.:



In the other cases only hypotheses have been put forward, such as the formation of π-allylic intermediates:



Lastly, the role of the Lewis acid in the activation of carbene ligands is not yet clearly understood.

7. Conclusion

The discovery of the metathesis reaction is not only important by itself, *i.e.* as an entirely new method for the synthesis of polymers or unsaturated hydrocarbons, but it opens up new horizons concerning the reactivity of possible intermediates in various reactions such as the polymerization of acyclic acetylenic compounds or the selective dimerization of olefins (⁹).

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