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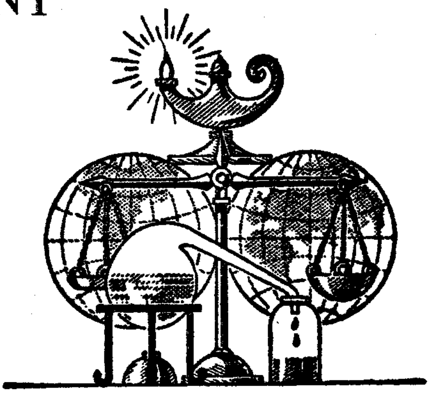
417



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PROGRESS IN STEREOSPECIFIC POLYMERIZATION AND ASYMMETRIC SYNTHESIS OF MACROMOLECULES

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INTRODUCTION

For several years I have taken the opportunity afforded by the Symposia on Macromolecular Chemistry to summarize recent research in Italy, particularly that carried out at the Institute of Industrial Chemistry of the Polytechnic School of Milan. I want to keep up this tradition this year, even though I am prevented from participating personally in the Montreal Symposium.

Our research has led to various results of some interest, especially in the field of the asymmetric synthesis, which can be considered as a particular and more advanced case of the stereospecific polymerizations.

Another branch, which was not considered by us at preceding Symposia, is the synthesis of crystalline alternating addition copolymers. This synthesis was also accomplished stereospecifically in some cases, where asymmetric carbon atoms are formed in the main chain. The X-ray diffraction methods have been particularly valuable in determining the structure of the new polymeric chains.

A further branch of research, in which we obtained results of some interest, is the stereospecific polymerizations and copolymerizations of butadienes substituted by alkyl and oxygenated groups. These studies led to the synthesis of new stereoregular polymers, which, according to the nomenclature adopted in our previous papers and recently sponsored by a sub-committee of the I.U.P.A.C. Commission on Macromolecules, are named polytactic polymers (di- and tritactic).

For lack of time I can only refer briefly to the various topics mentioned above.

THE ASYMMETRIC SYNTHESIS

Immediately after the discovery of the first stereoregular polymers, we tried to discover whether any of the tertiary carbon atoms present, which could be regarded as asymmetric under specific conditions, were able to cause optical activity. Analogous behaviour is exhibited in some natural polymers which contain tertiary carbon atoms in the main chain (linear polypeptides).

In the field of simple isotactic vinyl polymers, however, an ideal macromolecule, if assumed to be of infinite length, does not contain asymmetric

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* Paper read by Dr. Corradini.

carbon atoms and is identical with its mirror image. Isotactic vinyl high polymers of finite length, in which the influence of the end groups can be neglected, cannot show optical activity either, apart from conformational phenomena. In fact, even if one wants to consider the tertiary carbon atoms as asymmetric, their asymmetry is very slight as it is due to differences in length and configuration of the chain segments bound to each of them, and is internally compensated. Only in the case of very low molecular weight polymers can one expect a single molecule to show optical activity in solution, due to differences in the chemical structure of the end groups.

Actually, the polymerization of α-olefins with the aid of organometallic initiators containing optically active alkyls, which are found at least in part as end groups in the polymeric chains, yields polymers with a slight optical activity only in their very low molecular weight fractions. Only when starting from optically active monomers, since they contain asymmetric carbon atoms such as optically active 3-methylpentene, or 4-methylhexene, is it possible to obtain (as we are going to see in the next section) polymers showing a very high optical activity. This is due to the fact that the asymmetry of the side groups determines a preferential winding direction of the helix of the main chain. The improvement of the optical activity is therefore of a conformational nature.

Only after the discovery of the new classes of polytactic polymers, whose structure permits the existence of two enantiomorphous forms, was it possible to obtain polymers with high optical activity, starting from monomers which do not contain asymmetric carbon atoms, with the aid of catalysts containing optically active groups[1]. In all these cases, one or more tertiary carbon atoms are formed during the polymerization in each monomeric unit of the main chain. The asymmetry of these carbon atoms is due to chemical differences on the groups which are adjacent to them.

Table 1 shows some monomers and the monomeric units derived from

Table 1. Unsaturated esters employed in asymmetric syntheses, and the resulting monomeric units

Monomer	*Formulae of the monomer and of the corresponding monomeric units*
Esters of β-vinylacrylic acid (pentadienoic acid)	$CH_2{=}CH\cdot CH{=}CH\cdot COOR$ $\searrow$ $\sim\sim CH_2\cdot CH{=}CH\cdot\overset{*}{C}H(COOR)\cdot CH_2\cdot CH{=}CH\cdot\overset{*}{C}H(COOR)\sim\sim$
Esters of sorbic acid (2,4 hexadienoic acid)	$CH_3\cdot CH{=}CH\cdot CH{=}CH\cdot COOR$ $\searrow$ $\sim\sim\overset{*}{C}H(CH_3)\cdot CH{=}CH\cdot\overset{*}{C}H(COOR)\cdot\overset{*}{C}H(CH_3)\cdot CH{=}CH\cdot\overset{*}{C}H(COOR)\sim\sim$
Esters of β-styrylacrylic acid (5-phenylpentadienoic acid)	$C_6H_5\cdot CH{=}CH\cdot CH{=}CH\cdot COOR$ $\searrow$ $\sim\sim\overset{*}{C}H(C_6H_5)\cdot CH{=}CH\cdot\overset{*}{C}H(COOR)\cdot\overset{*}{C}H(C_6H_5)\cdot CH{=}CH\cdot\overset{*}{C}H(COOR)\sim\sim$ (R = methyl, butyl)

* The asymmetric carbon atoms are marked by an asterisk.

them. We have indicated chain segments containing two monomeric units linked head-to-tail.

In the case of the polymerization of 1,4-disubstituted butadienes, we obtained tritactic polymers, more precisely the highly crystalline 1,4-*erythro*-di-iso-*trans*-tactic polymer[2]. The degradation of the optically active polymers by oxidative fission of the double bonds yielded optically active bi- or tri-carboxylic acids, thus confirming that the optical activity of the polymers is of a conformational nature, due to the presence of asymmetric carbon atoms[3]. This method only allows the determination of the optical purity of the optically active polytactic polymers previously described if a partial racemization can be avoided during the oxidation and de-carboxylation processes.

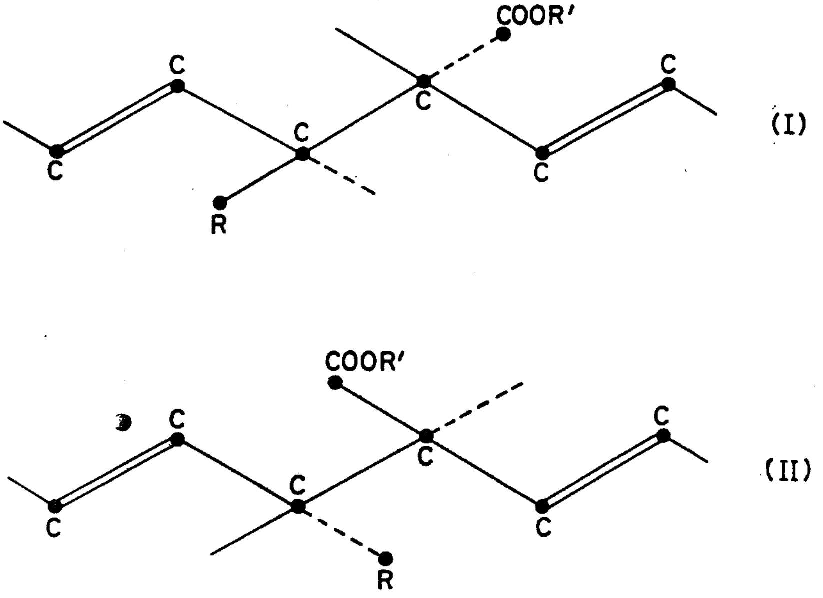


Figure 1. Schematic drawing of two enantiomorphous chains of *erythro*-di-iso-*trans*-tactic polymers (the main chain is arbitrarily stretched on a plane)

It was observed that the optical activity, though related to the regularity of the steric structure, is not necessarily related to the tendency of the macromolecules to crystallize. For instance, di-isotactic polymers, obtained from benzofuran with the aid of optically active catalysts, are optically active even though they are usually amorphous[4].

It was formerly observed that sterically regular polymers (such as those of alkyl or halogenated styrenes) do not always crystallize even though they are isotactic. This is demonstrated by the fact that they have been converted to crystalline derivatives by chemical transformations which do not alter the steric configuration[5].

In the case of optically active polymers of benzofuran, to which we attributed a di-isotactic structure, the very considerable steric factors hinder the alterations of the chain conformations (even if configurationally regular) which existed previously in the molten or amorphous state. These alterations are necessary in order to obtain a regular packing of each chain in the crystals.

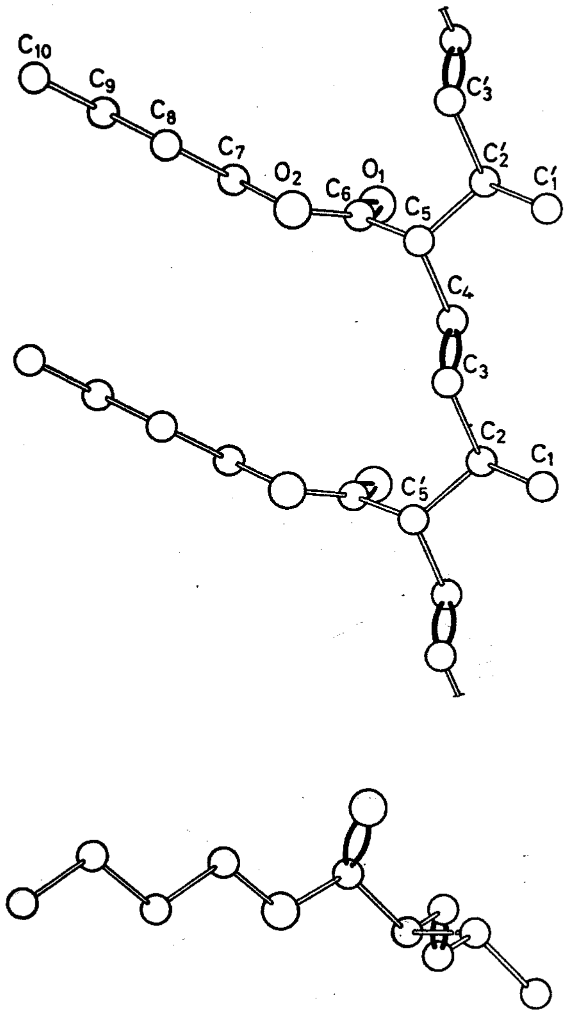


Figure 2. Side and end views of the actual conformation, in the crystalline state, of a macromolecule of poly(-*n*-butyl sorbate)

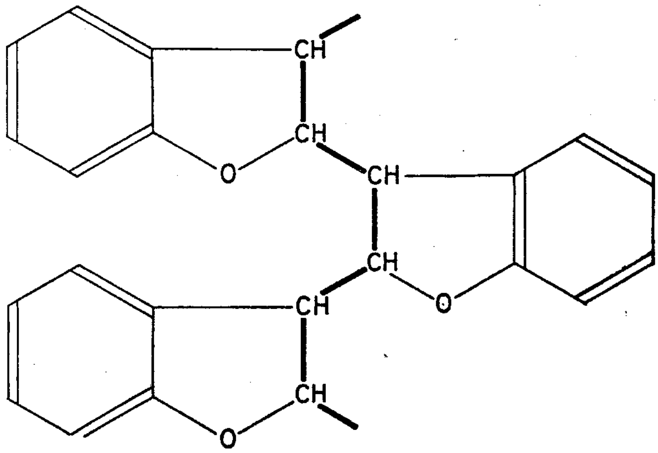


Figure 3. Head-to-tail linkage in polybenzofuran (schematic drawing)

Optically active crystalline polymers have also been obtained from diolefin hydrocarbon monomers, such as *trans*-penta-1,3-diene[6]. This monomer yields two types of crystalline polymers with 1,4 linkages. Penta-1,3-diene with the aid of organometallic homogeneous catalysts, yields a syndiotactic *cis*-1,4 polymer[7], which obviously cannot be optically active owing to internal compensations, whereas with the aid of heterogeneous catalysts, prepared from vanadium trichloride and optically active tri-isoamyl aluminium, an optically active 1,4-*trans* isotactic polymer is obtained. This melts at about the same temperature as the optically inactive polymer.

A systematic study of the optical activity of polymers obtained under different conditions, with the aid of these heterogeneous catalysts, will contribute to the interpretation of the polymerization mechanism and, in particular, to a more detailed knowledge of the structure of stereoblock polymers, possibly extending to the case of vinyl polymers.

If heterogeneous catalysts are used, the stereospecificity depends on the way in which the monomer molecule is chemisorbed by the active centre present on the surface of the solid catalyst.

Both steric purity and molecular weight depend on the chain transfer processes which, by association and dissociation, or by exchange processes of polymeric alkylated metals, are likely to be associated with the active centres of the catalyst[8].

In the stereospecific polymerizations and in the asymmetric synthesis obtained with the aid of homogeneous catalysts, it is necessary to operate at low temperatures at which the internal flexibility of the monomeric unit is strongly reduced. In these cases, the conformation of the end group or, in general, the conformation of the first monomeric unit, may exert an influence on the configuration of the subsequent monomeric units. This may be the cause of the high crystallinity of poly(alkyl sorbates) obtained with the aid of optically inactive catalysts. This high degree of crystallinity must be attributed to a high steric purity of each macromolecule.

The considerable rigidity of the chain may be considered as one of the causes of the remarkable steric regularity of poly(alkyl sorbates) when operating at low temperature. In these cases, the asymmetric synthesis may be produced by an optically active asymmetric alkyl which is present in the organometallic compound and acts as catalyst. Catalysts formed by asymmetric lithium alkyls, which have been used in the asymmetric synthesis of poly(alkyl sorbates), belong to this type.

Table 2. Asymmetric polymerization of pentadienoic esters

Monomer	*Catalyst*	$[\alpha]_D$ *in* $CHCl_3$
Methyl sorbate	(R) 2-Methylbutyl-lithium	−7·95
Butyl sorbate	,,	+3·3
Butyl β-styrylacrylate	,,	+2·0
Methyl β-vinylacrylate	(−) Menthyl ethyl ether + butyl-lithium	+7·2
Methyl sorbate	,,	+6·4
Butyl sorbate	,,	+8·4
Butyl β-styrylacrylate	,,	+3·7

The asymmetric synthesis may also be obtained when symmetric lithium alkyls are complexed with asymmetric Lewis bases[9] (*Table 2*). In these cases optically active end groups derived from the catalyst were never observed in the optically active polymer.

It is interesting to point out that the asymmetric synthesis (like the stereospecific catalysis of polymers) can be obtained only with the aid of catalysts acting through a cationic mechanism when operating at very low temperatures (from − 20° to − 80°).

In the polymerization of cyclic monomers, such as benzofuran, carried out with the aid of cationic catalysts (the same that act stereospecifically in the polymerization of vinyl ethers) complexed with optically active compounds (*Table 3*), asymmetric groups derived from the catalyst were not observed in the polymer[10]. In these cases the asymmetric synthesis can be attributed to the configuration of the asymmetric counter-ion, which can influence the configuration assumed by the first monomeric unit that is formed. This latter could help to determine the configuration of the subsequent monomeric unit, by analogy with the behaviour of each macromolecule in the stereospecific polymerization of the same monomers.

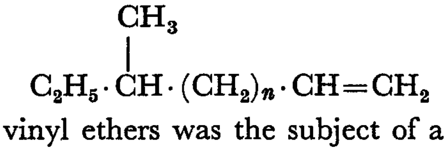
Table 3. Asymmetric polymerization of benzofuran

Catalyst	*Asymmetric co-catalyst*	*Polymerization temperature* (°C)	$[\alpha]_D$ *in benzene*
$AlCl_2C_2H_5$	(−)-β-Phenylalanine	− 75	−33·1
”	(+)-β-Phenylalanine	− 75	+13·1
”	(+)-10-Camphorsulphonic acid	− 75	− 3·8
”	(+)-Tetramethylammonium 10-camphorsulphonate	− 75	− 2·4
”	(−)-Brucine	−100	+ 2·8
$AlCl_3$	(−)-β-Phenylalanine	− 75	− 28·5

POLYMERIZATION OF OPTICALLY ACTIVE MONOMERS

It is interesting to compare the properties of optically active high polymers obtained by asymmetric synthesis from monomers having no asymmetric centres, with the properties of optically active vinyl polymers obtained from optically active monomers. In the latter case, a preferred screw sense of the helix-type conformation of the main chain of monoisotactic polymers may cause an increase in the optical activity. This increase is not observed in the polymers which are obtained by asymmetric synthesis, and which have a chain structure that does not assume a helix-type conformation; the optical activity of these polymers depends mainly on the configuration of the asymmetric carbon atoms.

The stereospecific polymerization of optically active olefins of the type:



$$C_2H_5\cdot\overset{CH_3}{\overset{|}{C}H}\cdot(CH_2)_n\cdot CH{=}CH_2 \qquad (n = 0,1,2,3)$$

and of vinyl ethers was the subject of a series of investigations carried out by Pino and his associates at the Institute of Organic and Industrial Chemistry of Pisa University[11–14]. The optical activity of the polymers obtained

Table 4. Optical activity, and its temperature coefficient, of some fractions of optically active polymers of α-olefins

Polymer	*Fraction*	*Crystallinity by X-ray exam.*	*m.p.* (1) (°C)	$[\eta]$ (2)	$[M]_D^{20}$	$\frac{\Delta[M]_D}{\Delta T}$	*Range of temperature* (°C)
poly-(*S*)-3-methylpent-1-ene	Insoluble in acetone Soluble in ether	Intermediate	65–75	0·08	+104°	−0·23	25·0–103·0
	Insoluble in acetone Soluble in decalin	Not determined	228–232	0·8	+163°	−0·36	26·5–103·0
poly-(*S*)-4-methylhex-1-ene	Insoluble in acetone Soluble in ether	Intermediate	39	1·3	+153°	−0·42	17·5–100·5
	Insoluble in ether Soluble in isoctane	High	164	7·5	+280°	−0·65	18·0–97·7
poly-(*S*)-5-methylhept-5-ene	Insoluble in acetone Soluble in ether	Low	48–52	1·4	+63°	−0·28	18·5–96·5
poly-(*S*)-6-methyloct-1-ene	Insoluble in acetone Soluble in ether	Absent	—	not det.	+19°	not det.	—

(1)—Determined by a Kofler polarized-light microscope.
(2)—In tetralin at 120°.

from a particular monomer appeared to be strongly dependent on the stereoregularity of the polymer itself. The temperature coefficient of the optical activity was much higher than that generally found in the optically active low molecular weight compounds, and of the same order as that of poly-L-glutamic acid[15] and of some proteins[16], which were assumed to have a helix-type structure in solution.

By comparing the optical activities of the most stereoregular fractions in the polymers obtained, it is possible to observe that the molar rotation, referred to one monomeric unit, is very high for poly-(*S*)-3-methylpent-1-ene ($n = 0$) and reaches its maximum for poly-(*S*)-4-methylhex-1-ene ($n = 1$) whereas it decreases very markedly for higher homologous substances.

The rather low molar optical activity of poly-(*S*)-6-methyloct-1-ene, referred to one monomeric unit, is not very different from that expected for an (*S*)-isoamyl group linked to a very high molecular weight alkyl group.

These results have been interpreted[17] by assuming that the macromolecules in solution are formed by a succession of segments of different length, each of which has a helix-type conformation, and contributes to the optical activity of the solution. The presence of optically active groups in the side chains leads to a preferential screw sense of the helix. The helix segments thus make a contribution of the same sign to the optical activity of the solution, which is therefore appreciable.

On the basis of this hypothesis, it is clear that there will be a progressive lowering of the optical activity of the polymer with decreasing stereoregularity of the main chain; moreover, the remarkable temperature coefficient of the optical activity may be interpreted as due to a decrease, with rise in temperature, of the segments of each macromolecule with a helix conformation in solution.

With regard to a prevailing screw sense, conformational analysis indicated that the isotactic polymers, derived from monomers which have an asymmetric carbon atom with an (*R*) configuration, mostly tend to assume right-handed helix conformations[18].

These results must be considered as confirmatory experimental evidence of the existence of an isotactic helix conformation in solution, at least in the case of polymers obtained from optically active monomers. Calculations made on the basis of energy considerations permitted the determination by other methods of the most probable length of the helices of the isotactic high polymers that are optically inactive[19].

With regard to crystalline structure, the polymers obtained from optically active or racemic α-olefins appeared to be identical in the case of the poly-3-methylpent-1-enes and of the poly-4-methylhex-1-enes[20], whereas the polymers of (*S*)-5-methylhept-1-ene were different[21] from those of the racemic olefin.

The structural identity of polymers of (*S*)-4-methylhex-1-ene and of racemic 4-methylhex-1-ene, bearing in mind that the crystalline racemic polymer was formed by the equal numbers of chains derived from (*S*) and (*R*) monomers, has emphasized the theoretical possibility of separating chains formed by enantiomorphous monomers. This separation was actually carried out[22] by chromatography of the racemic polymer (ether soluble fraction) on poly-(*S*)-3-methylpent-1-ene; by elution with ethyl

Table 5. Optical activities, and temperature coefficients of some samples of poly-(*S*)-2-methylbutylvinylether with different stereoregularites, and of their complexes with tri-isobutylaluminium

Polymer	*I.R. exam.* $\frac{D_B(832)}{D_B(775)}$ (1)	*Crystallinity by X-ray examination*	$[\eta]$ (2)	$[M]_D^{25}$		$\Delta[M]_D/\Delta T$ (4)	
				Non-complexed polymer	*Polymer complexed with* $Al(iso\text{-}C_4H_9)_3$ (3)	*Non-complexed polymer*	*Polymer complexed with* $Al(iso\text{-}C_4H_9)_3$ (5)
A	0·52	Absent	0·24	+4·9°	+28·0°	+0·02	−0·25
C	0·62	Low	1·00	+4·9°	+32·3°	+0·02	−0·34
D	0·73	Intermediate	0·71	+4·9°	+35·0°	Not determined	−0·36
E	0·78	Intermediate	0·19	+4·9°	+37·6°	+0·02	−0·37

(1) D_B (832) = optical density compared with the base line corresponding to a band depending on crystallinity at 832 cm $^{-1}$; D_B (775) = optical density compared with the base line corresponding to a band independent of the crystallinity and of the stereoregularity of the sample at 775 cm^{-1}; points of the base line: 761 cm^{-1} and 876 cm^{-1}.

(2) at 30° in toluene.

(3) 1·15 moles of $Al(iso\text{-}C_4H_9)$ per gram atom of oxygen present.

(4) Range of temperrture: 25–60°.

(5) 1·71–1·89 moles of $Al(iso\text{-}C_4H_9)_3$ per gram atom of oxygen present.

ether lævorotatory fractions with a molar rotation of − 17·5°, referred to one monomeric unit, were obtained initially. However, the fractions eluted at the end, appeared to be dextrarotatory with $[M]_D = + 62{\cdot}5°$. As far as we know, this is the first example of the resolution of an isotactic racemic polymer, into its respective optical antipodes. This resolution confirms that for the synthesis of each macromolecule, stereospecific catalysts are able to select preferentially one of the two enantiomorphous modifications present in a racemic monomer, even if the asymmetric carbon atom in the monomer (*e.g.* 4-methyl-hexene) is not immediately adjacent to the double bond involved in the polymerization. A chromatographic separation of stereoregular polymers with different steric structure had already been accomplished at the Polytechnic School of Milan; crystalline syndiotactic polypropylene was separated from the isotactic polymer[23].

In the polymerization of optically active vinyl ethers, contrary to that of α-olefins, it was observed that the polymers, in particular that from (*S*)-2-methylbutylvinylether, exhibit a low optical activity in toluene solution. This optical activity does not depend on the stereoregularity of the sample examined, and increases slightly with temperature (*Table 5*).

This behaviour is attributed[24] to the fact that the asymmetric induction from the s-butyl side group on the main chain, which is lessened by the presence of an ether oxygen between the side group and the main chain, is not sufficient to favour spiralling of the main chain. As a result there is no conformational contribution to the optical activity of the solution from the main chain.

The truth of this hypothesis has been demonstrated[25] by isolating the ether groups by complex formation with tri-isobutylaluminium; the complexed polymers show a much higher optical activity, depending on the stereospecificity of the sample, and a temperature coefficient of the optical activity which is of opposite sign to that found for the uncomplexed polymer, and of the same order as that observed for crystalline poly-(*S*)-5-methyl-1-heptene. It is therefore probable that in toluene solution the complexed polymers assume helix conformations which spiral predominantly in one direction.

On the whole, a research done on the polymers of optically active vinyl monomers has demonstrated the existence of a strict relationship between the stereoregularity and the conformation of the macromolecules in solution on the one hand, and the rotation, as well as the temperature coefficient of the latter, on the other hand.

Owing to the exactness and simplicity of the methods by which it is possible to measure rotations, one must believe that the study of the optically active polymers, either obtained from optically active monomers, or by asymmetric synthesis from optically inactive monomers, will make a notable contribution to the study of stereoregular polymers and of stereospecific polymerization.

STRUCTURE OF THE STEREOREGULAR POLYMERS OF SUBSTITUTED DI-OLEFINS

Ditactic Polymers

Butadienes substituted in the 4 or 1 and 4 positions undergo polymerization by 1,4 linkage, and yield polymers in which various sites of stereoisomerism are present for each monomeric unit. The monosubstituted diones (*e.g.* 4-methylbutadiene, esters of vinylacrylic acid) may yield ditactic polymers with both a geometrical and an optical tacticity.

For instance, we prepared crystalline isotactic *trans*-polypenta-1,4-[26] and crystalline syndiotactic *cis*-polypenta-1,4-dienes) from penta-1,3-diene. Poly(-1-methoxybutadiene), obtained in a crystalline modification by Breslow[27], belongs to this class.

First of all let us examine the configurational characteristics of the macromolecules with *trans* double bonds. The tertiary carbon atom can assume two configurations; therefore, the two simplest regular successions of monomeric units are those in which the tertiary carbon atoms always have the same configuration (isotactic polymer), or alternately opposite configurations (syndiotactic polymer).

Polymers of 4-methylbutadiene with a *trans*-1,4 linkage, obtained by using heterogeneous catalysts (triethylaluminium-vanadium trichloride), are isotactic, as revealed by our X-ray examination[26]. The repetition period

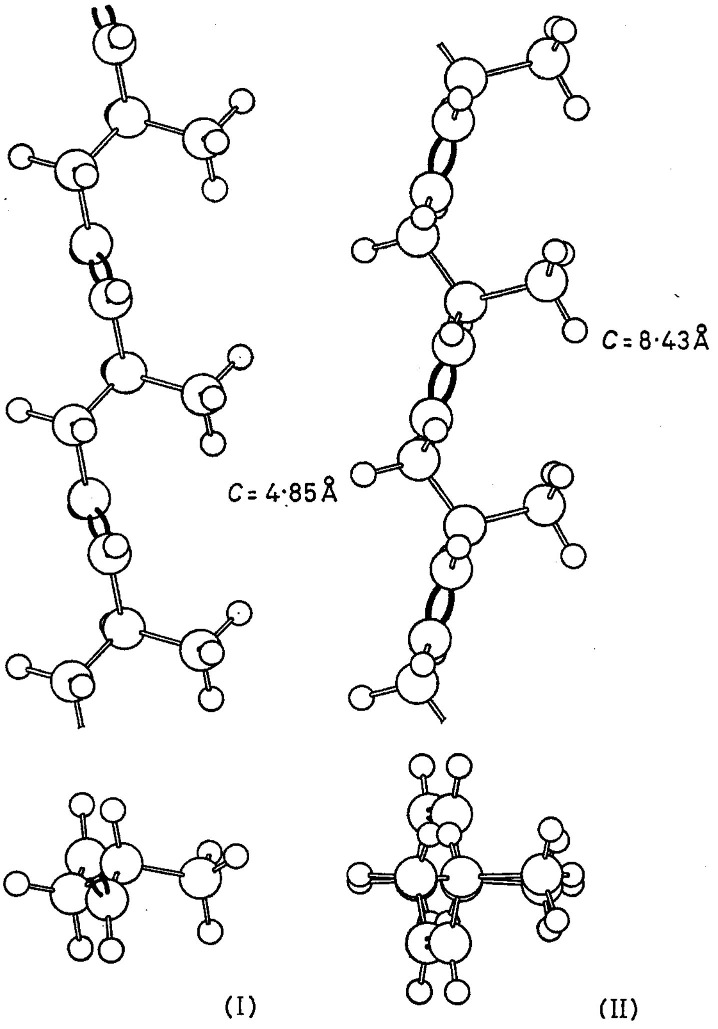


Figure 4. Side and end views of the macromolecules of isotactic *trans*-poly(-1-methylbuta-1,4-diene) (I) and of syndiotactic *cis*-poly(-1-methylbuta-1,4-diene (II) in the crystalline state

along the chain axis is 4·8 Å: this period necessarily comprises only one monomeric unit (*Figure 4*). The repetition by simple translation of successive monomeric units requires that these have the same configuration; it follows that the polymer is isotactic. A similar type of regularity has been observed by us in the case of crystalline poly(methylvinylacrylate) with a *trans*-1,4 linkage and a repetition period along the macromolecule axis which is also 4·8 Å [28].

In the case of 4-substituted butadiene polymers with *cis*-1,4 linkages, either an isotactic or a syndiotactic succession of the tertiary carbon atoms is evidently possible.

The crystalline poly(-1-methylbutadiene) obtained with the aid of some specific soluble catalysts[7] shows this last type of linkage, and has a repetition period along the macromolecule axis of 8·5 Å [29]. This period, and an accurate analysis of the diffraction spectrum, clearly indicate the presence of two monomeric units in the repetition unit, and the syndiotacticity of the succession of the tertiary carbon atoms (*Figure 4*).

Tritactic Polymers

When the monomers employed are butadienes substituted with polar groups, the stereospecific polymerization in the presence of organometallic catalysts must be carried out at low temperatures to avoid any chemical stoicheiometric reaction (mostly reduction) of the monomer with the organometallic compound. For instance, when operating with alkyllithium compounds, the esters of vinylacrylic acid yield ditactic (isotactic *trans*-1,4 polymers) whereas the esters of styrylacrylic or sorbic acids yield highly crystalline tritactic (*erythro* di-isotactic-*trans*-1,4) polymers[2].

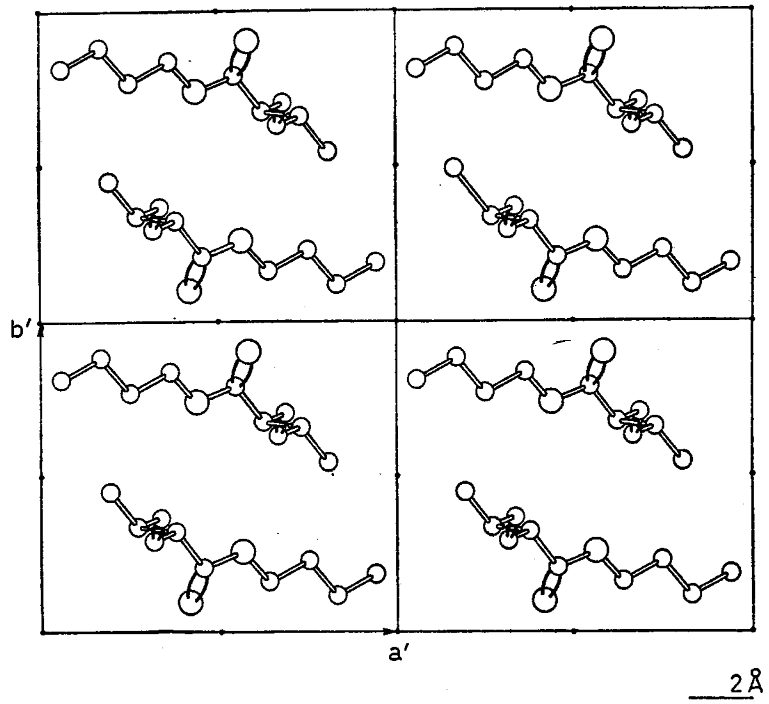


Figure 5. Projection on (001) of the crystal structure of poly(-*n*-butyl sorbate)

An accurate structural analysis was done on the isotactic poly(*n*-butyl sorbate) (*Figure 5*).

The identity period along the chain axis is 4·83 Å, and the equatorial reflections can be interpreted on the basis of a subcell with axes: $a' = 11{\cdot}36 \pm 0{\cdot}10$ Å and $b' = 9{\cdot}78 \pm 0{\cdot}10$ Å, and containing two monomeric units. The conformation of the main chain is identical with that of *trans*-polybuta-1,4-diene; and, as the identity period contains only one monomeric unit, the polymer is isotactic. Furthermore, the chain conformation found is only compatible with an " *erythro* " structure of the monomeric unit, if *cis*-type conformations are considered to be forbidden about the single bonds adjacent to the double bonds. This is confirmed by the agreement between the observed X-ray intensities and those calculated for the model shown in *Figure 5.*

BUTADIENE-PENTA-1,3-DIENE COPOLYMERS

At the Wiesbaden Conference on Macromolecular Chemistry I mentioned that copolymers of different monomers, consisting of monomeric units which are of analogous shape and size, may be crystalline; they also show lattice constants, melting points and other physical properties that are intermediate between those of the crystalline homopolymers. This contrasts with the usual observations in copolymerizations; in fact the presence of different monomeric units, distributed at random in the chain of a crystalline polymer, generally causes a lowering of the degree of crystallinity and of the melting point. The examples given in my previous lecture concerned the isotactic polymers of aromatic monomers (substituted styrenes). By analogy with the behaviour of low molecular weight substances which are able to yield solid solutions, the property of monomeric units which enables them to substitute one another in the polymer chains without destroying the crystallinity was called " isomorphism of monomeric units ". This phenomenon was also studied in copolymers of aliphatic monomers, in which it has been seldom observed so far (*e.g.* by Walter and Reding[30] with reference to branched vinyl monomers).

We observed interesting instances of isomorphism of monomeric units with conjugated di-olefins when the monomeric units corresponded to identical configurations for the same type of 1,4 linkage. However, isomorphism was not observed when monomeric units of the 1,2 or 3,4 types were copolymerized with units of the 1,4 type. An example is given by the butadiene-penta-1,3-diene copolymers having a *trans*-1,4 structure, obtained with the aid of catalysts prepared from vanadium trichloride and trialkyaluminium. They are crystalline and melt at temperatures which to a first approximation, are intermediate between those of the homopolymers (ranging from 95 to 145°)[31].

On the other hand, when 1,2 or 3,4 monomeric units are present in the chain, one can observe a fall in the melting point with respect to the homopolymers and copolymers containing them, regardless of whether these monomeric units are derived from pentadiene or from butadiene[32]. The study of these copolymers is complicated by the fact that *trans*-polybuta-1,4-diene is dimorphous, with a transition temperature of about 70°.

Owing to the low enthalpy of the *trans*-polybuta-1,4-diene modification stable at high temperature, even small amounts of monomeric units which are not isomorphous are sufficient to lower the melting point considerably and, to a lesser degree, the transition temperature. This particular behaviour is due to the fact that the modification which is stable at high temperatures has an enthalpy of about one half of that of transition. The crystallinity observed at room temperature in copolymers consisting exclusively of *trans*-1,4 monomeric units, containing less than 20 per cent pentadiene monomeric units, corresponds to the modification of polybutadiene stable at low temperatures[33]. When the proportion of pentadiene units present is greater than 25 per cent, the transition temperature falls below room temperature, and the copolymers show the structure of the *trans*-polybuta-1,4-diene modification stable at high temperatures. The presence of 1,2 monomeric units lowers the melting point; and small amounts of them are sufficient to produce amorphous products at room temperature.

Table 6 shows how the melting points of the butadiene-pentadiene copolymers vary with increasing the pentadiene content and with the corresponding decreasing of steric purity.

Table 6. Butadiene-pentadiene copolymers prepared with the aid of homogeneous catalysts: variation of T_t and T_m when varying the concentration of the pentadiene units

Composition of the copolymer pentadiene moles (%)	T_t (°C)	T_m (°C)
4	67	129
7	60	115
10	52	100
12·5	47	81
14	42	74
16	37	54
19	27	46
21·5	—	21

It is possible to prepare a complete range of copolymers composed predominantly of *trans*-1,4 monomeric units; their crystallinity, melting point and transition temperature can be varied over a wide range. Thus from these copolymers it is possible to obtain synthetic rubbers which are crystallizable under stretch and have interesting elastic moduli, elongations at break, and tensile strengths within different ranges of temperature. Vulcanization causes the disappearance of crystallinity in the slightly crystalline copolymers. Crystallinity can, however, reappear when these polymers are stretched, thus improving their mechanical properties even in the absence of reinforcing fillers.

ALTERNATING COPOLYMERS FROM HYDROCARBON MONOMERS

Polymerization processes, characterized by an anionic co-ordinated mechanism, are strongly influenced by steric factors, owing to the small radius of the co-ordinating metal cation. This is one of the causes of the regularity of chemical structure of the polymers obtained by these processes.

The regularity due to a head-to-tail linkage is greater than that which occurs at the same temperatures in cationic polymerizations. In the stereospecific polymerization of α-olefins, steric factors determine whether different monomers can polymerize, and influence their polymerization rate. The presence of bulky groups near the vinyl group slows down or inhibits the polymerization completely. Aliphatic hydrocarbon monomers containing non-terminal double bonds do not polymerize at all in the presence of the typical catalysts used in the stereospecific polymerization of α-olefins.

In some cases, however, inability to give homopolymers does not prevent the formation of copolymers, as is already known for some radical polymerizations. The formation of high molecular weight copolymers from hydrocarbon monomers containing non-terminal double bonds, which are unable to homopolymerize with the aid of organometallic catalysts, has not hitherto been known. Some monomers, such as *cis*- or *trans*-but-2-ene, pent-2-ene, and cyclopentene, do not homopolymerize in the presence of catalysts containing organometallic and transition metal compounds. This is due to the impossibility of obtaining long sequences of monomeric units composed entirely of tertiary carbon atoms carrying bulky substituents with these catalysts. However, we observed that, in the presence of a highly reactive monomer, such as ethylene, they are able to copolymerize, even though the rate constant is much lower than that of ethylene[34].

It is interesting that a polymeric growing chain with ethylene as the terminal monomeric unit may add both the monomers. The probability of adding either is related to the respective reactivity ratios ($\frac{r_{22}}{r_{24}}$ in the case of the ethylene-but-2-ene copolymerization); a growing chain in which the terminal monomeric unit is one derived from a hydrocarbon with a non-terminal double bond, may only add a monomeric unit derived from ethylene. It follows that the copolymer may contain sequences of monomeric units of ethylene, but not sequences originated by the co-monomer which is composed of isolated monomeric units, situated between two ethylene monomeric units. Consequently, the composition of the copolymers is between 0 and 50 mole per cent of the co-monomer, but cannot exceed that value.

Copolymers of ethylene containing a few per cent of monomeric units of a co-monomer, show the same type of crystallinity as polyethylene; the crystallinity decreases with increasing molar percentage of the co-monomer, and disappears when the percentage of the latter approaches 25.

It was observed that the reactivity of hydrocarbons containing non-terminal double bonds decreases with increase in the size of the molecule (but-2-ene>pent-2-ene>hex-2-ene); in the case of cyclo-olefins, the reactivity is lower for cyclohexene than for cyclopentene. Moreover the reactivity of *cis* isomers is much greater than that of the corresponding *trans* isomers[34].

As the content of some co-monomers *e.g.* *cis*-but-2-ene and cyclopentene increases one can observe the appearance of a new crystalline phase when using catalysts showing a particular stereospecificity. The crystallinity of the latter reaches a maximum at the limiting concentration of 50 per cent co-monomer[34]. When operating with a high excess of co-monomer, employed, for instance, in the liquid state under a low partial pressure of ethylene (*i.e.* one-tenth of an atmosphere), it is possible to obtain highly crystalline polymers with a composition very near to that of the alternating copolymer containing 50 moles per cent of each co-monomer. By solvent fractionation it is possible to obtain highly crystalline fractions which have almost the composition of the alternating copolymer.

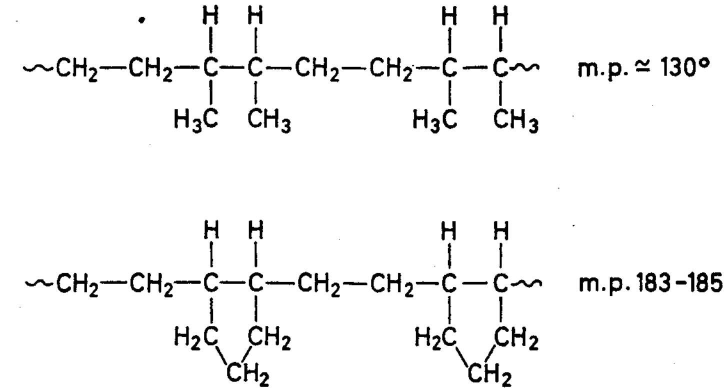


Figure 6. Chemical structure of ethylene-*cis*-but-2-ene and ethylene-cyclopentene alternating copolymers

Figure 6 shows chain segments containing two ethylene and two but-2-ene or cyclopentene monomeric units which, as we shall see, correspond to the identity period found in the crystals. The melting point of the ethylene-*cis*-but-2-ene copolymer (130°) approaches that of linear polyethylenes, whereas a much higher melting temperature (183–185°) is observed for the ethylene-cyclopentene copolymer.

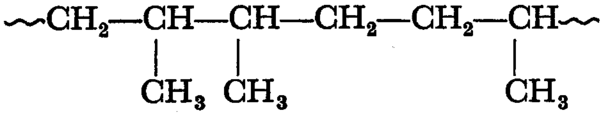
Each monomeric unit derived from the olefin with a non-terminal double bond, shows two tertiary carbon atoms for which different steric configurations are possible. As we shall see with the ethylene-*cis*-but-2-ene copolymer, the crystalline polymers show an ordered structure of the syndiotactic type.

In the case of *cis*-but-2-ene (*Table 7*), amorphous alternating copolymers are obtained with the aid of other catalysts which are not stereospecific in the polymerization of α-olefins[34].

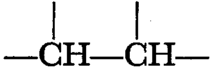
Table 7. Catalysts for alternating copolymerization of ethylene with *cis*-but-2-ene and cyclopentene

Catalyst employed	*Monomer couple*	*Polymer obtained*
VCl_4/AlR_3	Ethylene-*cis*-but-2-ene	Crystalline
”	Ethylene-cyclopentene	Crystalline
$V(acetylacetonate)_3/AlR_2Cl$	Ethylene-*cis*-but-2-ene	Substantially amorphous
” ”	Ethylene-cyclopentene	Crystalline

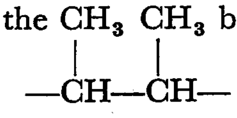
The crystalline copolymers obtained by alternating ethylene-*cis*-but-2-ene copolymerization show a regular chain structure, characterized by an identity period of about 9·15 Å. It is interesting to note that the chain of an alternating ethylene-*cis*-but-2-ene copolymer is equivalent to one of the hypothetical regular polymers of propylene, namely that with head-to-head tail-to-tail succession. Up to now this has not been obtained experimentally:



$$\sim CH_2—\underset{CH_3}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{CH}}—CH_2—CH_2—\underset{CH_3}{\underset{|}{CH}}\sim$$

It is of interest on account of the correlation that can be made between its properties and those of the two known stereoregular polymers of propylene which have regular head-to-tail (isotactic and syndiotactic) linkages. Four different regular chain configurations are possible for the alternating polymers of this type. The configuration of the  $—\overset{R_1}{\overset{|}{CH}}—\overset{R_2}{\overset{|}{CH}}—$ group may be either of the *threo* or of the *erythro* type, and the succession of these units along the chain may be either of the isotactic or syndiotactic type.

The most reliable prediction of the chain conformation for each of the four possible configurations may be made *a priori* from either the equivalent postulate, or the postulate of minimum internal energy[35]; these postulates, in the simple case of head-to-tail polypropylene, have already been justified quantitatively[36].

In the case of the ethylene-*cis*-but-2-ene copolymer, it is possible to compare the conformations of minimum internal energy, connected with each of the four possible configurations, by supposing that each of the two adjacent groups CH_3, CH and CH_2 are equivalent. The only symmetry elements along the chain allowing this equivalence are: an orthogonal axis perpendicular to the  $—\overset{CH_3}{\overset{|}{CH}}—\overset{CH_3}{\overset{|}{CH}}—$ bond in the case of a *threo* configuration, and a symmetry centre, in the case of an *erythro* configuration. In fact it is necessary to assume, for the conformation of minimum energy, that the chain satisfies the principle of staggered bonds, and this fixes all the internal rotation angles of the polymeric chain. Under these conditions it is possible to deduce, by simple methods, the conformations of minimum internal energy associated with the four regular configurations (the valence angles along the chain are assumed to be tetrahedral) (*Table 8*).

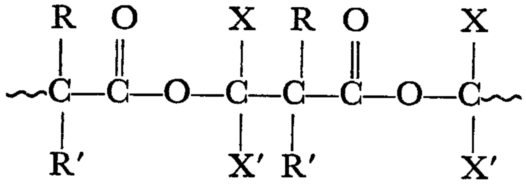
In practice, the same content of internal energy, for the free chain, must be associated with all the four models of minimum internal energy considered. From this analysis it is evident that the configuration to be associated with the polymers studied, which have an identity period of about 9·0—9·1 Å, is that of a *threo*-di-syndiotactic polymer. This has been confirmed by the structural analysis in progress for both the ethylene-but-2-ene and ethylene-cyclopentene copolymers. With regard to this last copolymer, the space group necessarily imposes the required symmetry on the chain.

Table 8. Possible regular structures of alternating copolymers with $\sim\!\sim CHR\cdot CHR\cdot CH_2\cdot CH_2\sim\!\sim$ structural units

Structure	*Symmetry*	*Internal rotation angles*		*Identity period (tetrahedral angles)*	*Monomeric units in the repetition period*
		CHR·CHR *bond*	*Other bonds*		
erythro isotactic	ti	180°	180°	5·1	1
erythro syndiotactic	tic	180°	180°	10·2	2
threo isotactic	s_2	60 or 300°	180°	12·4	3
threo syndiotactic	t2c	60 or 300°	180°	8·8	2

ALTERNATING COPOLYMERS WHICH HAVE A POLYESTER STRUCTURE

Alternating copolymers with the following general formula (corresponding to two structural and to four monomeric units):



$$\sim\!\sim\overset{R}{\underset{R'}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{X}{\underset{X'}{C}}-\overset{R}{\underset{R'}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{X}{\underset{X'}{C}}\sim\!\sim$$

have been obtained by copolymerizing some unsaturated oxygenated monomers with particular compounds containing carbonyl groups (*Figure 7*), with the aid of organometallic catalysts. For instance, in another contribution to this Symposium it is stated that ketene and substituted ketenes (*e.g.* dimethylketene) copolymerize with both aldehydes[37] and ketones[38], yielding, under specific conditions, alternating copolymers which have a polyester structure. When a symmetrical ketone (acetone) is used, highly crystalline alternating copolymers are obtained[38]. Crystalline products are obtained in the copolymerization of aldehydes only when catalysts which act in a stereospecific way are used. In these last cases, the polymers obtained contain asymmetric carbon atoms in the main chain.

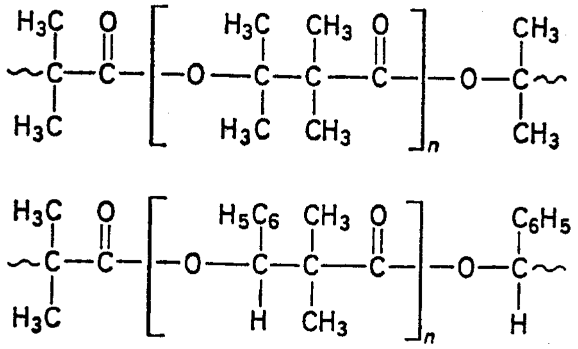


Figure 7. Chemical structure of acetone-dimethylketene and benzaldehyde-dimethylketene alternating copolymers

These copolymers are interesting because they have been obtained from simple unsaturated monomers by polyaddition, whereas the conventional polyesters have been obtained either by polycondensation processes, which seldom yield linear high molecular weight polymers, or by opening of cyclic monomers (lactones).

The acetone-dimethylketene copolymer melts at about 200° and is highly crystalline. It is very stable both thermally and chemically as it does not contain hydrogen atoms bound to secondary or tertiary carbon atoms.

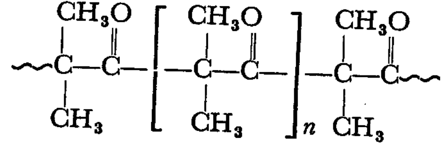
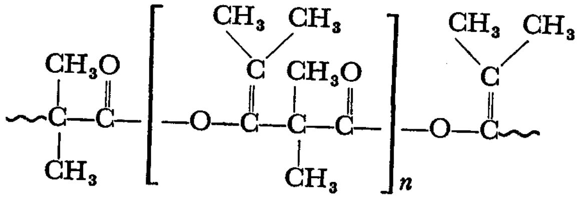
The copolymers with cyclic aldehydes (furfural, benzaldehyde, *etc.*), obtained with the aid of stereospecific catalysts, also show a polyester structure, but a higher melting point. All of them may be of interest in the production of fibres owing to their high melting points and crystallinity.

By X-ray examination, we made a thorough study of the chain conformation of the acetone-dimethylketene alternating copolymer. Crystalline and oriented fibres of copolymer have been obtained by extrusion, and subsequent stretching in hot water of the filaments obtained. From the fibre spectrum, it is possible to determine an identity period $C = 8{\cdot}8$ Å, corresponding to two structural units. The conformation of the main chain, in the crystalline state, is not planar and contains a glide plane[39].

HOMOPOLYMERS OF KETENES

As was observed in the case of conjugated diolefins, the presence of two double bonds allows the formation, depending on the stereospecific catalyst employed, of stereoregular polymers which have different chemical structures. Analogous behaviour was observed in the polymerization of ketenes which contain two cumulative double bonds[40].

Table 9. Chemical structure of polymers obtained by polymerization of dimethylketene with the aid of catalysts acting by means of cationic and anionic mechanisms

Catalyst	*Polymerization temperature* (°C)	*Poly(dimethylketene) structure*
$AlCl_3$; $AlBr_3$	Between − 80 and − 40	
$AlEt_3$; sodium naphthalenide complex	Between − 70 and − 40	

For instance, in the presence of cationic catalysts, dimethylketene (*Table 9*) yields a crystalline linear polymer with a polyketonic structure, insoluble in toluene, and melting at 240–250° [40, 41].

This polymer assumes two different crystalline modifications (*Figure 8*): one with an identity period of 4·4 Å, containing two monomeric units; the other one with an identity period of 8·8 Å containing four monomeri units[42]. Modification (α) has a helix-type chain conformation, wherea modification (β) probably consists of chains formed by small segments o two right-handed monomeric units, alternated with analogous left-hande segments.

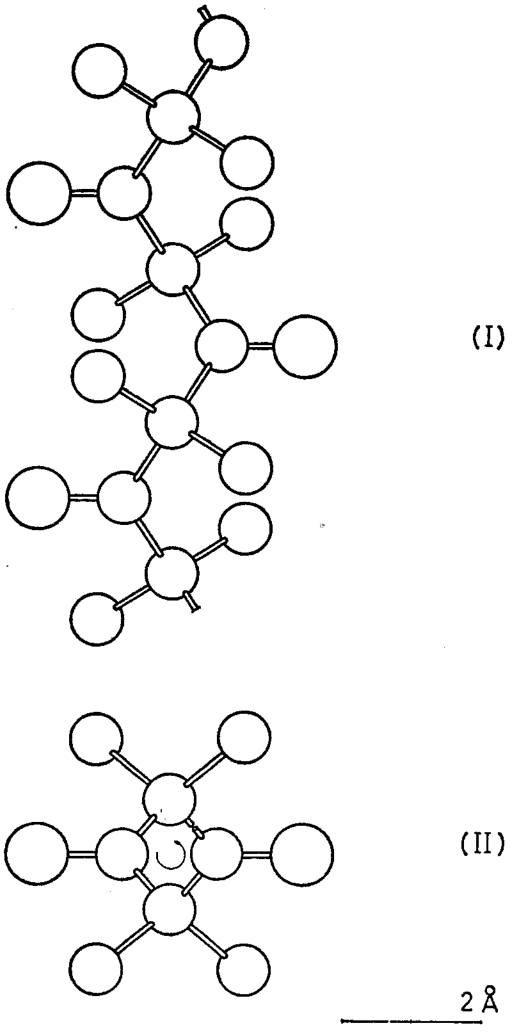


Figure 8. Side (I) and end (II) views of the macromolecule of poly(dimethylketene) crystallized in modification (α)

The use of stereospecific catalysts is not necessary to obtain this polymer because the chain does not contain carbon atoms with different side-chai substituents. The lack of hydrogen atoms directly attached to the mai chain is responsible for the high stability of the polymer, since the formatio of enolic forms is precluded. When operating with high catalyst/monome ratios, the formation of linear polymer is accompanied by the formation o a cyclic polymer (*Figure 9*) which contains three ketonic groups bonde alternately to three quaternary carbon atoms substituted with methy groups[43].

Polymers with quite different chemical structures are obtained with th aid of catalysts which act by means of an anionic mechanism. For instance sodiumnaphthalenide has been used to obtain an unsaturated polyester-type polymer which is crystalline, melts at about 170°, and is soluble both in tetralin and boiling toluene[40]. It also has a remarkable thermal stability at temperatures above the melting point.

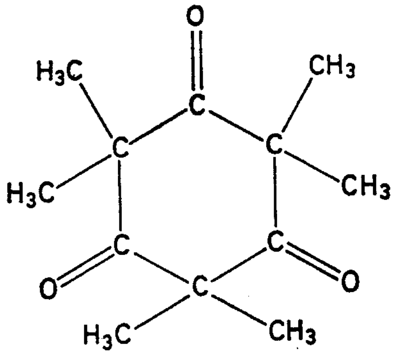


Figure 9. Cyclic trimer of dimethylketene

The difference in the behaviour of the cationic and anionic catalysts may be attributed to the different chemical reactivity of the catalysts, and to the different co-ordinating effects. With cationic catalysts the double bond of the $>C=O$ group is not opened, but is co-ordinated to the catalyst, whereas the $>C=C<$ double bond is polarized. With anionic catalysts it is likely that the $>C=O$ double bond is polarized and that the oxygen is bonded, at least in one intermediate stage of polymerization, directly to the metal present in the catalyst.

Some other topics concerning recent research in our Institute on the well-known stereoregular polymers are not referred to here, and are either already published[44] or in the press[45, 46].

In this communication we have concentrated on new types of polymers which demonstrate that stereospecific polymerization can be applied to new classes of macromolecules, thus yielding new types of crystalline polymers.

Summary

Some results, obtained at the Institute of Industrial Chemistry of Milan Polytechnic in the field of stereospecific polymerization, which had not been described at preceding Symposia on Macromolecular Chemistry, are reported here.

New classes of chemically regular and, in some cases, stereoregular polymers and copolymers were obtained by polymerizing monomers containing non-terminal double bonds; these cannot be polymerized with the aid of the most typical Ziegler-type catalysts. Beside aliphatic alkenylethers, which yield *erythro* di-isotactic polymers, heterocyclic monomers and hydrocarbon monomers containing non-terminal double bonds were also polymerized.

While it is impossible to prepare homopolymers of olefins containing an internal unsaturation with the aid of catalysts of the anionic type, we succeeded in preparing copolymers of these monomers with ethylene.

By adopting particular conditions, it was possible to prepare alternating copolymers of ethylene with hydrocarbons having a non-terminal double bond. In some cases, *e.g.* when using *cis*-but-2-ene, stereoregular polymers were obtained, which proved to be crystalline by X-ray analysis.

Two different types of crystalline polymers with polyketonic and polyester structure were obtained by homopolymerization of substituted ketenes, while the copolymerization of these with ketones (and with aldehydes) yielded copolymers having regular polyester structures and a high melting temperature.

X-ray studies contributed to determination of the structure of the new polymers and to understanding of the behaviour of certain catalysts.

Further research work on the synthesis of syndiotactic polymers of propylene was carried out.

The study of the first-order transitions of *trans*-1,4-butadiene–pentadiene copolymers allowed the determination of some thermodynamic data that justify the peculiar properties characterizing these copolymers.

New classes of stereo-ordered polymers with polytactic structure were obtained from substituted diolefins (polysorbates, alkyl styrylacrylates, *etc.*), which gave *trans*-1,4 di-isotactic crystalline polymers; their lattice structure was investigated.

The use of optically active metal-organic catalysts (or of optically inactive catalysts complexed with optically active Lewis bases) in these polymerization processes, allowed the production of optically active polymers starting from optically inactive monomers. The asymmetric synthesis was extended to mono-isotactic polymers of monosubstituted butadienes, with the aid of catalysts acting through an anionic co-ordinated mechanism.

Optically active di-isotactic polymers were obtained from oxygenated monomers, such as benzofuran, with the aid of optically active catalytic complexes acting through a cationic mechanism.

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