Giulio Natta, *Director of the Institute of Industrial Chemistry, Polytechnic Institute of Milan, Milan, Italy*
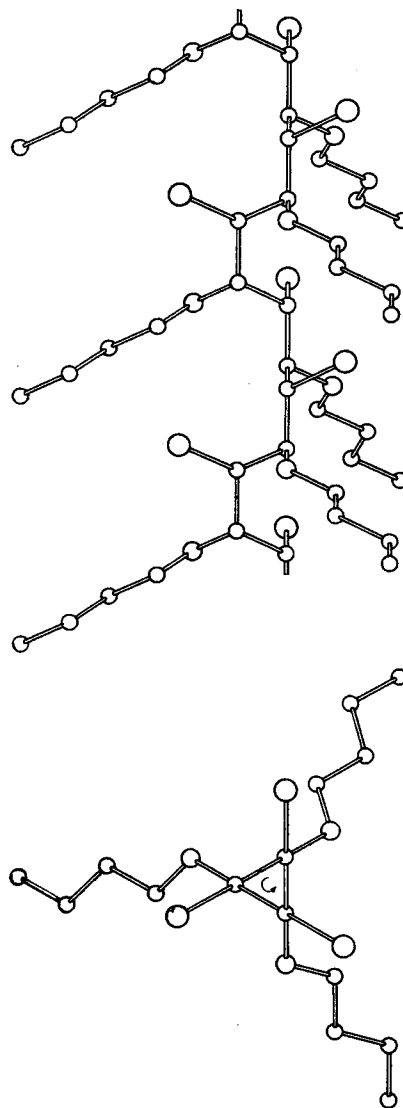
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Figure 1. Chain conformation of threo-di-isotactic poly-β-chloro-n-butyl-vinyl ether in the threefold helix form.

Complete text of the International Award Lecture

Crystallinity in High Polymers and Copolymers: a Determining Factor for their Practical Applications

Errata - Corrige

Crystallinity in High Polymers and Copolymers:
A Determining Factor for their Practical Applications

Some errors in the text of the Second International Award Lecture published in the April, 1963, issue of SPE TRANSACTIONS were brought to our attention by Professor Natta, as listed below:

1. Page 106, lines 27-31: instead of "In uneven cycles...double bound" read: "In the <u>even</u> cycles (cyclohexene, cyclooctene) the most probable conformation of the monomer molecule exhibits an axis of binary symmetry, which is normal to the double bond, as results from Figure 11."

2. Page 107, left column, line 23: instead of "...with 5..." read: "...with ...6..."

3. Page 107, left column, second to last line: instead of "...latter keeps the, read: "...latter does not necessarily keep the..."

4. Page 107, right column, line 8 and 14: instead of "di-vinylcyclobutene" read: "di-vinylcyclobutane"

5. Page 109, left column, line 4: instead of "...of asymmetrical" read: "...or asymmetrical."

The following bibliographical references are also omitted:

1. Page 108, right column, line 16, after "dimethylketene" insert (20).

2. Page 109, left column, line 7, after "paper" insert: (21).

3. Page 110, left column, line 18, after "active" insert (22).

■ *The leading worker in the field of stereospecific polymerization emphasizes the significance of this technique, which is pertinent to many phases of the polymer industry.*

Dr. Natta reviews developments in the following areas:

New Crystalline Stereoregular Polymers
Structure of these Polymers
Relationship of Crystallinity to Properties
The Possibilities and Properties of Copolymers and Alternating Copolymers
The Importance of Crystallinity in Elastomers

The discovery of stereospecific polymerization and its extension to several types of monomers, including some non-hydrocarbon monomers, has led to the identification of numerous classes of stereoregular polymers, generally crystalline, prepared from monomers which during polymerization yield asymmetic monomeric units with the ability to subsist in enantiomorphous conformations.

Before the discovery of stereospecific polymerization processes, these monomers yielded only amorphous polymers, most of them having no practical interest.

The first stereoregular polymers obtained were vinyl polymers with a hydrocarbon main chain, such as the ones prepared from alpha-olefins, conjugate diolefins and vinyl ethers (1).

Results obtained in this field were reported in a paper presented at a former SPE Meeting (2).

New Types of Crystalline Stereoregular Polymers

Stereospecific catalysis was then extended to other types of monomers, e.g. monomers with an internal olefinic double bond and monomers which polymerize as a result of the opening of other types of double bonds, such as the aldehyde or ketonic C = O bond. The polymerization of monomers having an internal olefinic double bond is also of particular theoretical interest since their stereospecific polymerization generally yields different products according to whether it starts from the *cis* or the *trans* isomer of the monomer (3). For example, in the polymerization of betachloro n-butyl-vinyl ether two crystalline polymers are obtained by stereospecific polymerization (*Table 1, Figure 1*) (4) which have different physical properties according to whether these processes start from the *cis* or the *trans* isomer of the monomer.

When starting from a trans isomer, a threo-di-isotactic polymer is obtained, while starting from a cis isomer, an erythro-di-isotactic polymer is obtained. This phenomenon confirms that in this polymerization there is a *cis*-type opening of the double bond according to *Figure 2*.

The *cis*-type opening of the double bond has also occurred in other cases, such as in alternating copolymerization of ethylene with *cis*-butene-2 or with cycloolefins (a double bond with a *cis* structure is exhibited with up to

eight carbon atoms in the ring) yielding stereoregular c talline polymers. This *cis* opening seems to occur far n frequently than the *trans* opening in other types of mc mers, also independently of whether their structure is *ci trans*. However, in the case of monomers having only double bond of the trans type, polymerization often c not occur or polymers are obtained which are not ste: regular.

Figure 3 represents schematically the structures of the isotactic polymers with a threo-di-isotactic, erythro isotactic and di-syndiotactic configuration respectively.

The formation of stereoregular di-isotactic polymers only requires that the structure of the polymerizing mc mer and the type of opening be constant, but also that manner in which the monomeric unit presents itself to growing chain be constant too, (determined by the typ attack) (4) (*Figure 4*). If on the other hand the mc meric units present themselves alternately with an oppc type of presentation, a di-syndio-tactic structure is obtai (*Table 2*).

For the catalyst to be stereospecific, it must n several requirements. In general these requisites are c found in certain initiators which act through an ionic ordinated mechanism (either of the anionic co-ordina type as in the stereospecific polymerization of hydrocar monomers, or cationic co-ordinated polymerization, as the case of vinyl ethers) (5). Whereas in the case of al[olefins and of open-chain olefinic monomers with an in

Table 1. Properties of poly-β-chloro-vinyl-n-butyl ethers

Structure of the monomer	Identity period A	Type of helix	Structure of the polymer
cis	8.6±0.1	4/1	erythro-di-isota
trans	6.5±0.1	3/1	threo-di-isotact

nal double bond, stereospecific polymerization only occurs with heterogeneous catalysts. In the case of monomers containing ether oxygen not far from the double bond, stereospecific polymerization also occurs with homogeneous systems. Prior to the poly-addition reaction, in these cases, an oriented co-ordination of the monomer with the catalyst is promoted by the presence of atoms (such as oxygen) containing a pair of free electrons which are capable of co-ordinating themselves with the metal of the electron-deficient catalytic system; this makes it possible to avoid using heterogeneous catalysts, which are necessary for the stereospecific polymerization of olefins.

Structure of Crystalline Polymers

Figures 5, 6, 7 show a few types of crystalline stereoregular polymer chains. While isotactic polymers in the crystalline state present a helical structure—as is found in many natural products (e.g. Pauling helix for certain crystalline amino acids)—syndiotactic polymers and certain stereoregular polymers with a 1,4 enchainment do not, as a rule, present any helical conformations when crystalline. X-ray investigation of the crystalline structure of many stereoregular polymers enabled us not only to determine the steric configuration of many polymers, both mono- and polytactic, but also to collect a considerable amount of structural data on new classes of crystalline polymers which were unknown till a few years ago. The abundant material collected (6) enabled us to define a few general rules which govern the conformation and the type of packing within crystals of high polymers. As already described in detail a number of general principles can be accepted:

1) All the structural units of a chain are geometrically equivalent (though not necessarily equivalent from the crystallographic point of view) with respect to a crystallographic axis. This axis coincides with the axis of the polymeric chain. Each structural unit generally coincides with a monomeric unit or with a fraction thereof.

2) In the crystalline state the chain assumes a conformation very near to that of minimum internal conformational energy which can be calculated for the free chain not belonging to the three-dimensional lattice.

The application of these concepts and the observation that the monomeric units very often also occupy mutually equivalent positions in the three-dimensional lattice obviously make it easier to predict the crystalline structure of new polymers. Principle 1) alone allows for the reduction to thirteen in theory, and to five in practice, the number of possible linear chain repetition groups (7). A further limitation for each individual case arises from the fact that an isotactic vinyl polymer must have a helical structure without centres or planes of symmetry, while a syndiotactic vinyl polymer presents either the characteristics of symmetry depending on repetition of a glide plane, or a helical symmetry of the chain with repetition of structural units containing a binary axis of symmetry.

Conformational analyses were made of the structure of free chains based on the principle of minimum internal energy, taking into account the contact distances and repulsions between atoms due to Van der Waals' forces. The most probable conformation or conformations could then be
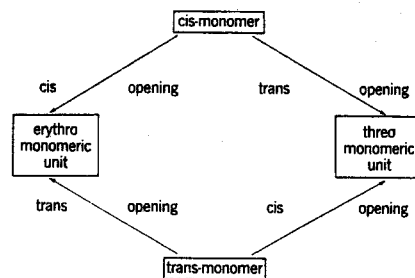
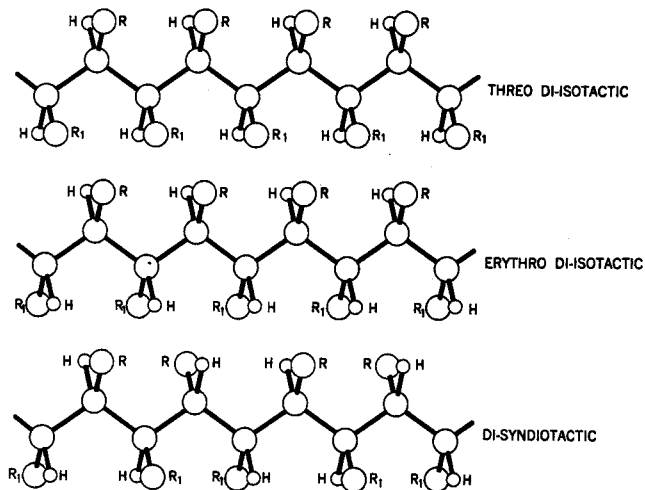**Figure 2.** Various types of double bond openings.

Figure 3. Zig-zag planar projections of threo-di-isotactic, erythro-di-isotactic and di-syndiotactic polymeric structures.
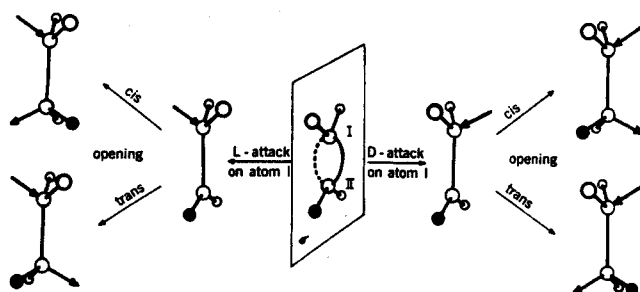
Figure 4. Scheme of a D(L) attack on a monoolefinic monomer.

Table 2. Steric relationships between the structures of the monomer and of the polymer

Monomer	Type of opening	Steric attack	Structure of the polymer
cis	cis	constant	erythro di-isotactic
trans	trans	constant	erythro di-isotactic
trans	cis	constant	threo di-isotactic
cis	trans	constant	threo di-isotactic
cis	cis	alternating	di-syndiotactic
cis	trans	alternating	di-syndiotactic
trans	cis	alternating	di-syndiotactic
trans	trans	alternating	di-syndiotactic
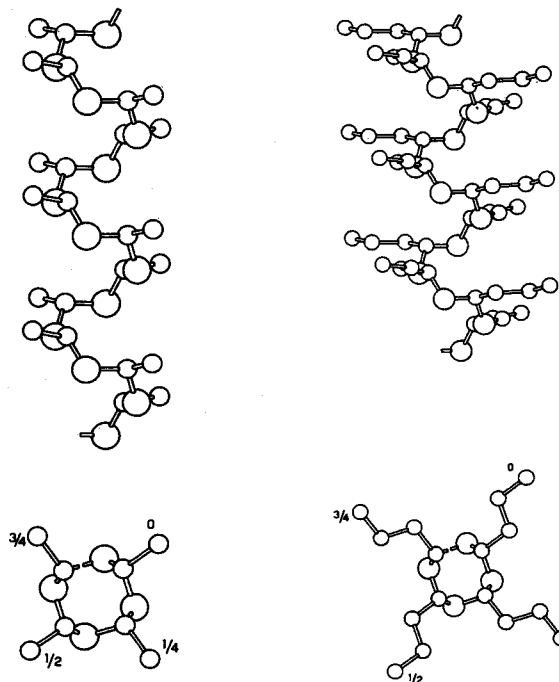
Figure 5. Chain conformation of isotactic polyacetic-aldehyde in the crystal state (side and end views).
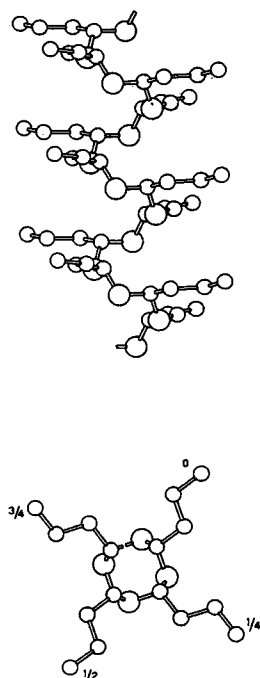
Figure 6. Chain conformation of isotactic poly-n-butyric-aldehyde in the crystal state (side and end views).

C = 5,10 Å

C = 8,43 Å
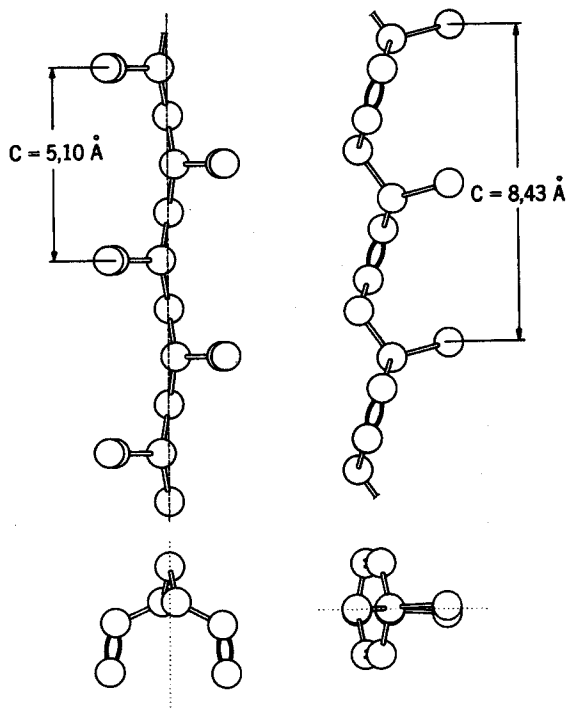
Figure 7. Chain conformations of syndiotactic 1-2 polybutadiene (left side) and of syndiotactic cis 1-4 polypentadiene(right side).

determined directly and in many cases the study of models and their optical diffraction allowed more rapid determination of the structure of polymer chains in crystals. This especially facilitated the determination of the structure of many polytactic polymers synthesized in the Institute.

The Importance of Crystallinity with Regard to Properties

Crystallinity is of great importance in macromolecular substances because it determines their physical and technological properties. The use of a high polymer as a plastic material is only possible if its melting point or its softening point is higher than the temperature of use. However, while most amorphous polymers are brittle below their transition temperature, this is not always the case with crystalline polymers, in particular when these latter are oriented. For instance, the remarkable properties of isotactic polypropylene are due to its high melting point and to its crystallinity which gives good hardness, surface gloss and excellent mechanical properties in moulded products, within a wide temperature range (from room temperature to over 100°C).

Mechanical properties depend on orientation and crystallinity. If the latter quality is present, excellent textile fibers can be obtained even from polymers which do not contain any polar groups or hydrogen bonds linking the chains which are oriented along the axis of the fibers, in the directions perpendicular to the axis of orientation. Whereas if these bonds are present even polymers of comparatively low molecular weight (in the order of 20,000 in the case of nylon) can yield textile fibers with high tensile strength. In those cases where creep is prevented by crystallinity alone, without the help of chemical bonds, higher molecular weights are required. To obtain polypropylene fibers (e.g. staple) with a tensile strength of 5-6 g/d, a polymer with an intrinsic viscosity of 1-1.5 (corresponding to molecular weights of about 150-200,000) is required (8). Tenacities of this order are more than sufficient for staple which can be produced at a high spinning rate because polypropylenes having the foregoing intrinsic viscosities can be easily extruded. It is however possible to obtain very much higher tensile strengths (10-15 g/d) by spinning—under appropriate conditions—polymers with an intrinsic viscosity higher than 2. Such high tensile strengths are of interest in the case of monofilaments and can only be obtained with highly crystalline polymers (9).

Orientation and high crystallinity can also reduce inconveniences deriving from an excessively high transition temperature, which causes brittleness as a result of the uncrystallized amorphous part present even in the most highly crystalline polymers.

Their high second order transition temperature makes several crystalline polymers difficult to use for the production of textile fibers.

Such is the case of isotactic polystyrene which has a second order transition temperature of approximately 85°C, roughly equal to that of atactic polystyrene, and a high melting point. This is due to the fact that in polystyrene crystallinity is hardly ever higher than 50%. The presence in the fibres of over 50% amorphous product, which, in addition, is not properly oriented, makes fibers brittle at room temperature.

This inconvenience can only be avoided by using highly crystalline and very well oriented polymers, but the spinning, stretching and annealing operations must be carried out at a temperature higher than that of transition. In the production of fibers it is generally preferable to employ materials whose temperature of use lies somewhere between their second order transition temperature and their melting point.

The brittleness of materials having a transition temperature close to that of use can be reduced by several methods, which, however, always involve a decrease in crystallinity. One of these methods is to employ amorphous polymer plasticizers (e.g. adding polyisobutylene to crystalline polypropylene). In certain cases, copolymerization with monomers (for instance, ethylene) whose homopolymers have a low second order transition temperature can be used. It should be borne in mind that while the second order transition temperature of amorphous copolymers (e.g. rubber obtained by copolymerizing ethylene with propylene) varies linearly with their composition, there is no such regularity in the case of crystalline copolymers. In general, addition of a monomer whose monomeric units are not isomorphous to those of the considered polymer causes the melting point to fall considerably. Changes in the brittle temperature are not governed by a simple relationship however. This phenomenon is probably also due to the fact that in copolymerization with the aid of heterogeneous catalysts it is not so easy to obtain a random distribution of the different monomeric units as in homogeneous copolymerization. However it is most probable that these different monomeric units are to be found mainly in the amorphous part, so that if brittleness is caused by the glassy state of the uncrystallized part, the effect of small quantities of the foreign monomer on the brittle temperature may be greater than in the case of an entirely amorphous copolymer having the same composition.

Crystalline Copolymers

The crystallinity of copolymers is generally lower than that of homopolymers because of the presence of the comonomer. The more the comonomer, the lower the crystallinity, and simultaneously we find a reduction in melting point, tensile strength, hardness and other mechanical properties.

When the monomeric units of the added comonomer attain 25-30% in random copolymerization, crystallinity generally disappears and the copolymer is completely amorphous. However, there are a few exceptions to this rule.

Copolymers of Isomorphous Monomeric Units

In previous papers, isomorphous monomeric units were defined as those units which can replace each other in a copolymer chain without destroying crystallinity and only causing a slight change in the lattice constants (10). This phenomenon occurs when the different monomeric units exhibit considerable similarities in shape and especially in size.

Isomorphism generally occurs when the two homopolymers present the same chain conformation and the same type of crystalline lattice but (as in the case of the di-iso-

Table 3. Modifications of trans 1-4 polybutadiene

	Identity period A	a axis A	Density
Modification I	4.92	4.54	0.97
Modification II	4.68	4.88	0.93

morphism of low formula weight ion compounds) it can also occur when the two homopolymers have a markedly different lattice structure, though the monomeric units are very similar in size and shape, as will be seen later in describing certain copolymers of conjugate di-olefins.

In cases of simple isomorphism, the properties of copolymers are, as a rule, intermediate to those of pure homopolymers and vary linearly with composition (e.g. melting point, density, lattice constants, etc.).

The first cases of isomorphism, which have been more thoroughly investigated, are those of copolymers of aromatic vinyl monomers (e.g. styrene and monofluorostyrene) (11). It was found recently that in copolymers of butadiene and 1-methyl-butadiene prepared with heterogeneous catalysts based on VCl_3 and aluminum alkyls, consisting of trans 1,4 monomeric units, the two types of butadiene and methyl-butadiene monomeric units are isomorphous, at least in forms stable at high temperatures (12). In trans 1,4 polybutadiene, this modification is characterized by a greater equatorial encumberment (Table 3) and a shorter identity period along the chain axis. This promotes the isomorphous substitution of the pentadiene unit having a methyl
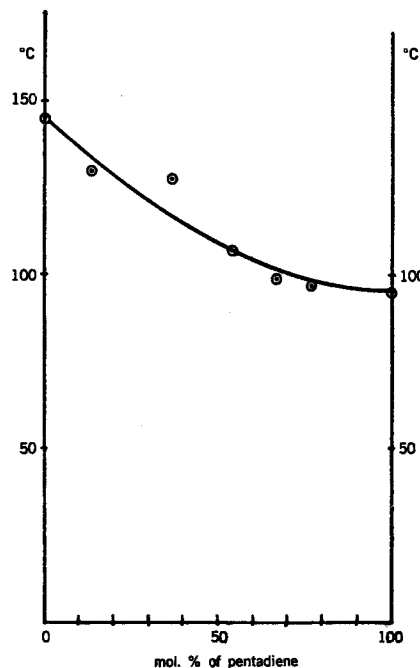
Figure 8. Melting temperature of trans 1-4 butadiene-pentadiene copolymers.

Table 4. Variation of T_t and T_m in butadiene-pentadiene copolymers obtained with the $Al(C_2H_5)_2Cl-V(Ac)_3$ soluble catalyst

Copolymer composition (C₅ mole-%)	T_t (°C.)	T_m (°C.)
0	75	145
13	47	81
14	42	74
16	37	54
19	27	46
23	—	21

$V(Ac)_3$ = vanadium triacetylacetonate

in the side chain. In effect, these copolymers have a melting point that varies with composition from 143°C (melting point of trans 1,4 polybutadiene) to 95°C (melting point of trans 1,4 poly-1,3-pentadiene) (*Figure 8*). This isomorphism does not remain in the well known modification of trans 1,4 polybutadiene which is stable at low temperatures. As the transformation temperature ($\sim 75°C$) of trans 1,4 polybutadiene drops if different monomeric units are introduced in the chain, it is possible to further lower the melting point (even one lower than room temperature) and to obtain copolymers which are still crystalline with a prevailingly trans 1,4 structure by adding small quantities of monomeric units of polybutadiene with a 1,2 enchainment. These copolymers also possess interesting elastomeric properties at room temperature and were obtained with homogeneous catalysts prepared from soluble vanadium compounds (e.g. tri-acetylacetonate) and mono-chloro-di-alkyl aluminum. The catalysts polymerize butadiene stereospecifically (all trans 1,4), but in the case of pentadiene, a small number of 1,2 units are also present (*Table 4*).

The considerable variation in the melting point owing to the presence of small quantities of monomeric units with a different structure (this variation is much greater than that

normally occurring in copolymers) is justified by the low melting enthalpy and entropy of trans 1,4 polybutadiene as evidenced by thermodynamic measurements made on that polymer. The melting enthalpy (which does not exceed 1000 cal./mole of monomeric unity) is very much lower than that of other polymers (generally of about 3000 cal/mole of monomeric units in 1-4 trans polyisoprene).

This is due to the imperfect crystalline structure of the trans 1,4 chains in the modification stable at high temperatures. If trans 1,4 polybutadiene in the form which is stable at low temperatures is heated, a change is observed in the size of the crystals at the transformation temperature (about 75°C). This change is due to a shortening of the identity period accompanied by an increase in the equatorial dimensions. The chain assumes a less regular conformation due to a statistical succession of certain angles of internal rotation between the planes containing successive chain segments.

The appearance of this disorder in the chain conformation is accompanied by a sharp change in entropy. The melting entropy decreases and therefore the melting enthalpy likewise falls. The phenomenon is identical with that occurring in globular compounds, such as camphors and neopentane. It not only is of interest from the theoretical point of view, but may lead to practical results.

In the particular case of trans 1,4 polybutadiene copolymers, this phenomenon makes it possible to obtain crystalline polymers with a trans 1,4 enchainment and a melting point below room temperature. All that is required to achieve this result is the presence of 12% 1,2 monomeric units, which on the other hand is not a sufficiently large quantity to destroy crystallinity; this latter property in fact is still found at a temperature below room temperature. Thus the elastomeric properties typical of polymers with a cis 1,4 enchainment can be extended to polymers with a trans 1,4 enchainment which usually have fewer practical applications because of their high melting point and high elastic modulus (*Table 5*).

Alternating Copolymers

In general copolymers containing 50% of each of the non-isomorphous monomeric units are amorphous and have elastomeric properties if their second order transition tem-

Table 5. Properties of vulcanizates obtained from butadiene-pentadiene copolymers prepared with homogeneous $Al(C_3H_5)Cl-V(AC)_3$ catalytic system

	Tensile strength kg/cm³	Elongation at break %	Modulus kg/cm² at 300%	Modulus kg/cm² at 700%	Hardness Shore A	Resilience % at 20°C
gum stock	165	1250	3.6	7.2	46	67
	90	1140	4.9	8.5	47	70
	87	960	5.8	12.5	47	67
black stock	215	740	36	198	66	61
	258	700	50	258	71	60

perature is lower than their temperature of use. However, several interesting cases of alternating copolymers were found, so called because they consist of alternating regular successions of the two types of monomeric units (13). If neither of the two types of monomeric units exhibits centres of asymmetry, a regular chemical structure of the monomeric units in an alternating regular head-tail enchainment is sufficient to yield crystalline polymers. But if the monomeric units exhibit centres of asymmetry, regularity in the steric structure is necessary in order to have crystalline products.

The first crystalline alternating polymers consisting of hydrocarbon monomeric units were those obtained by copolymerization of ethylene with butene-2 (14). It was observed that only by employing the cis-isomer of butene-2 and working with special catalysts (heterogeneous and stereospecific in the polymerization of alpha-olefins) a crystalline copolymer with an erythro-di-isotactic structure can be obtained (15). This confirms that the opening of the internal double bond occurs in the cis form and that at the moment of addition the monomeric unit invariably presents itself in the same orientation with respect to the growing chain in order to allow the same type of attack (Figure 4). If non-stereospecific catalysts are used instead (e.g. soluble catalysts), the copolymerization of cis butene-2, when it takes place, yields amorphous alternating copolymers, while the trans isomer of butene-2 copolymerizes much more slowly and only yields amorphous copolymers. It is interesting to note that formation of the alternating copolymer generally only occurs when operating with a large quantity of butene-2 and a very small concentration of ethylene (Figure 9). The reason is that alternating copolymerization occurs when one of the two monomers (in this case butene-2) is unable to homopolymerize in the presence of the catalyst employed—probably for steric reasons—but is able to copolymerize with the other monomer which, in turn, homopolymerizes in the presence of this catalyst. In these cases the reactivity ratios for copolymerization are, respectively, r_{11}/r_{12} very high and $r_{22}/r_{21} \simeq 0$, where monomer 1 is the one that homopolymerizes and monomer 2 the one that does not homopolymerize. It is therefore necessary to work with a high ratio of the less reactive monomer to obtain copolymers having a composition near to the alternating composition, which is the maximum amount of less reactive monomer which the copolymer can contain.

As already mentioned, copolymers with this type of composition are crystalline when they are stereoregular.

Alternating Copolymers with Cyclic Materials

Other crystalline alternating copolymers have been prepared from mixtures of ethylene and cycloolefins, such as cyclopentene and cycloheptene (16). In these cases, it is not necessary to use heterogeneous catalyst in order to obtain crystalline copolymers because the simple cycloolefins mentioned above not only have a double bond with a cis conformation, but for steric reasons can only react with a cis opening and therefore stereoregular polymerization occurs in any case (Figure 10).
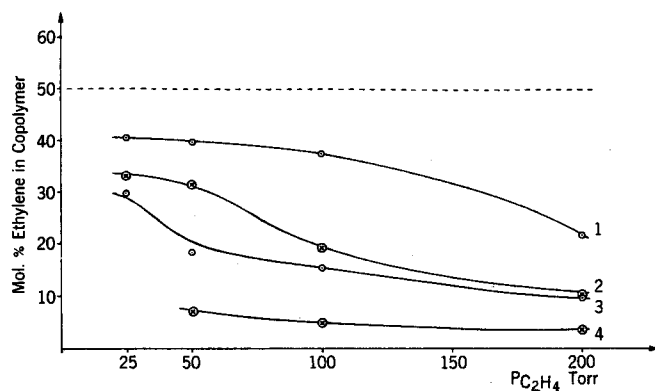
A different behavior is exhibited by certain cycloolefins

Figure 9. Ethylene content in copolymer versus ethylene pressure (curves 1-2 with cis-butene-2, curves 3-4 with trans-butene-2).
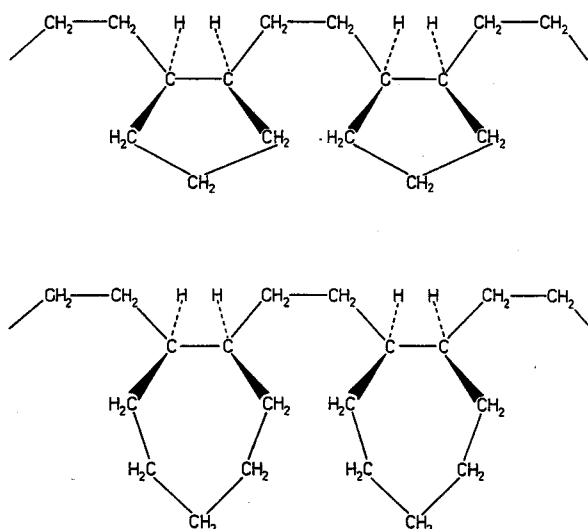

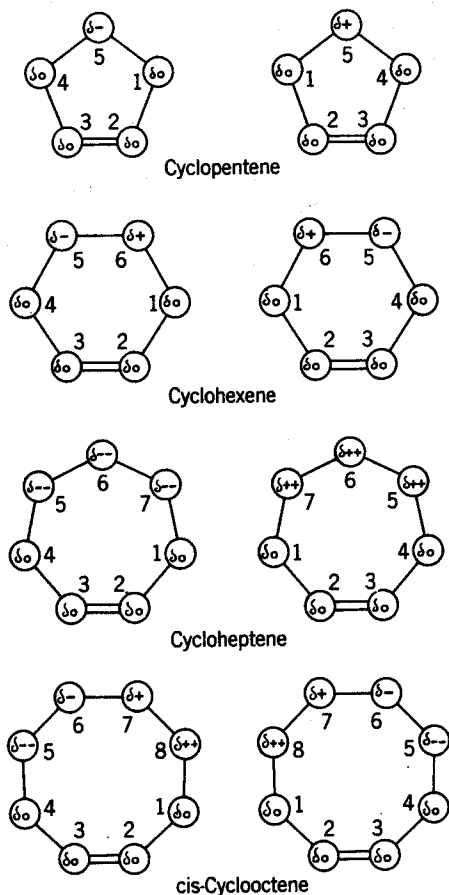Figure 10. Chains of ethylene-cyclopentene and ethylene-cycloheptene alternating copolymers.

Figure 11. Configurations of various cyclo-olefines.

with a number of carbon atoms of 3 or 4, such as cyclobutene and cyclopropene.

Cyclobutene and cyclopropene possess very high reactivity (of the same order as that of ethylene) and therefore cannot yield alternating copolymers in the above mentioned conditions. In the case of cyclobutene random copolymers with ethylene were obtained.

Cyclohexene and *cis*-cyclooctene on the other hand react much more slowly than their homologues which have an uneven number of carbon atoms and so far have not yielded any crystalline copolymers. The same is true of *trans* butene-2 which also copolymerizes very slowly (*Table 6*).

The difference in the behavior of even and uneven cyclo-olefins is discussed in greater detail in another paper (17) and must be attributed to steric reasons. The molecules of cyclopentene and cycloheptene have a *cis* structure and their most probable conformation presents a plane of symmetry normal to the double bond (*Figure 11*). If the plane containing the carbon atoms of the double bond and the two adjacent carbon atoms is considered, it is found that the other carbon atoms belonging to the cycle are all on one side of the plane under consideration. For steric reasons this promotes a constant type of opening of the double bond (*cis* opening) as well as a constant type of presentation of the molecule with respect to the catalyst linked to the growing chain. This leads to an erythro-di-isotactic stereoregular structure. In the uneven cycles (cyclohexene, cyclooctane) the most probable conformation of the monomer molecule exhibits an axis of binary symmetry which is normal to the double bond and passes through the uneven atom furthest from the double bond. This structure involves less ability

Table 6. Homopolymers and copolymers with ethylene of olefins having internal double bond (obtained with anionic co-ordinated polymerization).

Monomer	Type of catalyst	Homopolymers	Copolymers with Ethylene	
		Structure of polymer	Relative reactivity in copolymerization	Structure of copolymer containing 50% mol C_2H_4
cis butene-2	heterogeneous	not polymerizable	low	alternating	crystalline
cis butene-2	homogeneous	not polymerizable	low	alternating	amorphous
trans butene-2	heterogeneous	not polymerizable	very low	—	—
trans butene-2	homogeneous	not polymerizable	very low	—	—
cyclobutene	heterogeneous	polycyclobutyl enamer-2 or 1-4 polybutadiene	very high	random	amorphous
	homogeneous				
cyclopentene	heterogeneous	not polymerizable	low	alternating	crystalline
cyclopentene	homogeneous	not polymerizable	low	alternating	crystalline
cyclohexene	heterogeneous	not polymerizable	very low	—	—
cyclohexene	homogeneous	not polymerizable	very low	—	—
cycloheptene	heterogeneous	not polymerizable	low	alternating	crystalline
cycloheptene	homogeneous	not polymerizable	low	alternating	crystalline
cyclooctene	heterogeneous	not polymerizable	very low	—	—
cyclooctene	homogeneous	not polymerizable	very low	—	—

Note: The table above uses a six-column layout; the "Monomer" and "Type of catalyst" cells map to the first two columns, "Structure of polymer" to the third, "Relative reactivity in copolymerization" to the fourth, and "Structure of copolymer containing 50% mol C₂H₄" to the fifth/sixth visual split.
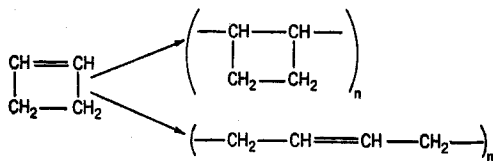
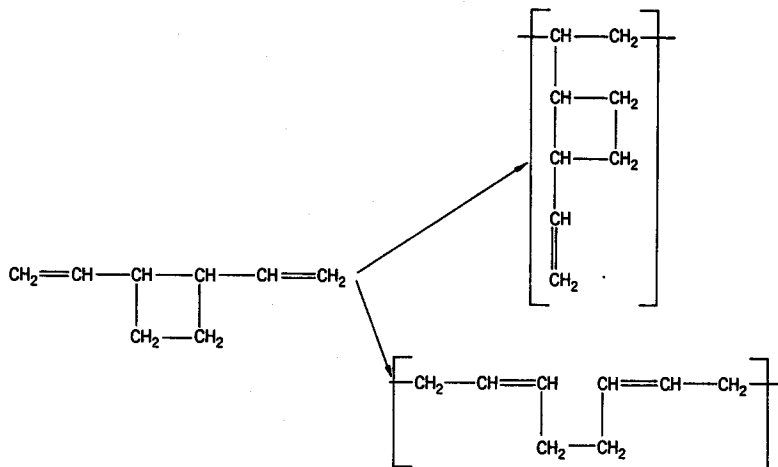**Figure 12.** Polymers from cyclobutene.

Figure 13. Polymers from trans 1-2 divinyl-cyclobutane.

to co-ordinate with the catalytic system, an equal probability of a *cis* or *trans* opening occurring and the absence of any preferred sense of presentation. A similar phenomenon occurs in *trans* butene-2. This explains not only the low reactivity of these monomers but also their inability to yield stereoregular and therefore crystalline copolymers.

The same conditions which yielded crystalline alternating copolymers, using cyclopentene and cycloheptene with ethylene, only yielded amorphous copolymers with a low content in cyclohexene monomeric units when cyclohexene was used. This is probably a result of the low reactivity of cyclohexene compared with cyclopentene and cycloheptene. The latter likewise yield amorphous copolymers when the ratio of monomeric units derived from the cycloolefin exceeds 25% but is less than the quantity required to obtain an alternating copolymer structure. Therefore possibility should not be excluded that crystalline alternating copolymers may be obtained even if cyclohexene is used, provided the operating conditions are different with extreme cyclohexene concentration in respect to that of ethylene. The lower reactivity of cyclohexene compared with the other cycloolefins considered is probably due to the greater stability of the cycloolefinic ring with 5 carbon atoms with respect to those with a different number of atoms, compared with the stability of the corresponding saturated rings.

Cyclobutene can give two types of homopolymers having different chemical structure (*Figure 12*). One of these two types is formed by opening of cycloolefinic double bonds, and therefore possesses the chemical structure of a polycyclobutylenamer-2 (nomenclatures of Huggins); the other type is formed by opening of the ring leaving the double bond unaltered, in order to have the structure of polybutadiene-1,4 (18). According to the catalyst used, the opening of the ring can give polybutadiene prevailingly 1,4 *cis* or 1,4 *trans*.

The reasons in this case are the opposite of those indicated for cyclohexene, since the reactivity of cyclobutene is very much higher than that of the cycloolefins mentioned earlier. This proves that when no part is taken in polymerization by the double bond, the latter keeps the configuration exhibited in the monomer. At present, cyclobutene

monomer is only available at a price higher than that of butadiene and since the problem of the synthesis of *cis* 1,4 polybutadiene from butadiene has now been solved, the synthesis of this latter product from cyclobutene is only of scientific interest.

Other cyclic hydrocarbons with four carbon atoms can open in polymerization conditions.[*] The *trans* 1,2 di-vinyl-cyclobutene (dimer of butadiene) polymerizes in the presence of organometallic catalysts containing titanium or vanadium with opening of the cycle and formation of monomeric units (*Figure 13*), which may be considered as constituted by two butadiene monomeric units with 1,4 enchainment. It has been demonstrated that that happens without the dissociation of di-vinyl-cyclobutene in butadiene.

The interest of these alternating copolymers, particularly those of butene-2 and its homologues, lies in the fact that this is the first example in which crystalline linear polymers have been obtained from hydrocarbons with an internal double bond.

The condition described above is based on the use of an appropriate catalytic system and of operating conditions whereby one monomer does not homopolymerize but copolymerizes with the other monomer which homopolymerizes easily. This is a necessary condition but is not sufficient to obtain alternating copolymers.

To avoid the occurrence of pairs of monomeric units of the more reactive monomer, it is sufficient in many cases to operate with very low concentrations of the latter and high concentrations of its comonomer, but in order to prevent formation of pairs of monomeric units of the comonomer, strong steric hindrances are required, such as those caused by the side groups linked to the main chain by the opening of an internal double bond in a linear or cyclic olefin. On the contrary, copolymerization of ethylene with alpha-olefins does not, as a rule, yield alternating copolymers if the catalyst employed is able to homopolymerize ethylene and to copolymerize it with alpha-olefins, but is unable to homopolymerize the latter. This is shown by the fact that in the

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* Work now in press.

Table 7. Chemical structure and physical properties of some dimethylketene-aldehyde alternating copolymers

Comonomer	Repeating unit	Approximate melting point °C	Analytical Data			Acetone	Solubility[a]		
							Ether	Chloroform	Benzene
p-chloro benzaldehyde	$-C(=O)-C(CH_3)(CH_3)-C(C_6H_4Cl)(H)-O-$	260	calc. found	Cl Cl	16.85 17.1	−	−	+	+
p-methoxy benzaldehyde	$-C(=O)-C(CH_3)(CH_3)-C(C_6H_4(OCH_3))(H)-O-$	240	calc. found	C 69.9 H C 69.7 H	6.8 6.95	−	−	+	+
m-nitro benzaldehyde	$-C(=O)-C(CH_3)(CH_3)-C(C_6H_4(NO_2))(H)-O-$	240	calc. found	N N	6.33 6.23	+	−	+++	+
furfural	$-C(=O)-C(CH_3)(CH_3)-C(C_4H_3O)(H)-O-$		calc. found	C 65.06 H C 65.21 H	6.1 6.3	++	−	+	+

[a] (+) = partially soluble at boiling point
(+ +) = soluble at the boiling point
(+ + +) = soluble at room temperature; (−) = insoluble

copolymerization of ethylene with propylene in the presence of soluble catalysts which do not homopolymerize propylene, copolymers are obtained which may contain over 50% propylene and consequently also successive pairs of propylene monomeric units. This must be attributed to the fact that the steric hindrances caused by the presence of a single methyl group are strong enough to prevent, with the above-mentioned catalysts, formation of long sequences of propylene monomeric units, necessary for homopolymerization, but are not sufficient to prevent short sequences of propylene units once polyaddition has just started or has taken place in the previous stage with an ethylene monomeric unit. Obviously, the steric hindrances which hinder polymerization in the case of an olefin with an internal double bond are much greater than the steric hindrances which occur in an alpha-olefin (19).
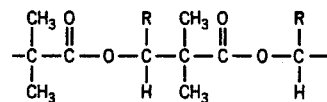
Other Types of Alternating Copolymers

Production of alternating copolymers can be extended to other types of monomers and can be expected in many cases in which the copolymerization rate of one of the monomers is very much higher than that of its comonomer and the concentration of the latter is very high in respect to that of the former.

Alternating copolymers were also obtained from non-hydrocarbon monomers, for example by copolymerizing aldehydes and ketones with di-methylketene. In this particular case, alternating copolymers were obtained even when both the monomers were capable of homopolymerizing in the presence of the catalyst. Alternating copolymers were also obtained though high concentrations of both monomers were used. A kinetic study of these copolymerizations is now in progress and will probably show that formation of alternating copolymers in these special cases is due to a higher rate of the alternating polyaddition compared with that of the non-alternating polyaddition.
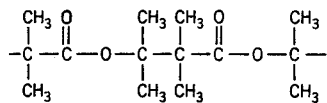
Figure 14. Dimethylketene-acetone copolymers.

Figure 15. Dimethylketene-aldehydes copolymers.

Since the monomeric units of di-methyl-ketene and ketene do not exhibit any centres of asymmetry, the alternating copolymers prepared from symmetrical ketones are crystalline (13) (*Figure 14*). But if higher aldehydes of asymmetrical ketones are used, crystallinity requires stereoregularity (*Figure 15*).

In an earlier paper a description was given of some crystalline alternating copolymers obtained by stereospecific polymerization of dimethylketene with aldehydes higher than formaldehyde (*Table 7*).

Crystallinity in Elastomers

In general all elastomers, in particular the vulcanized ones, are amorphous, at least at rest. In the field of stereoregular polymers and copolymers of diolefins, only those products having melting temperatures below the operating temperature are important as general purpose rubbers. *Table 8* shows the melting temperatures of some stereoregular polymers of diolefins.

Before the discovery of the stereospecific polymerization, the synthetic polymers of diolefins were generally amorphous. Several crystalline polymers were obtained by stereospecific polymerization, but except in some special cases and uses (trans-1,4 polyisoprene for the production of rubbers having high elastic moduli) only the polymers having, in the vulcanized state, melting temperature below room temperature have a considerable importance as general purpose rubber (natural rubber, polyisoprene and cis-1,4 polybutadiene). Such polymers, when used at temperatures even higher than the melting temperature, show the property to crystallize partially, if they are deformed by stretching. This property has an effect that can be compared to an increase of vulcanization, since it hinders the viscous flow, increasing the elastic modulus at high deformations and the tensile strength. These effects are more obvious in the use of rubbers without reinforcing fillers.

In the case of *cis* 1,4 polybutadiene, the crystallization under stretching occurs for elongations higher than 350% only in the case of a polymer having steric purity higher than 97%.

Polybutadienes with lower steric purity crystallize only for very high elongations (in analogy with the synthetic *cis* 1,4 polymers of isoprene). This inconvenience does not limit the use, if these rubbers that are sterically less pure are used in the presence of reinforcing fillers (carbon blacks) or in mixture with natural rubber.

Crystallinity is also interesting in the case of completely or prevailingly saturated elastomers.

An observation is made in the case of amorphous copolymers having elastomeric properties. By the decrease of the ratio of the amorphising comonomer, in correspondence of a determined composition, by X-ray examination, the appearance of the bands due to the incipient crystallinity is observed. If this latter is very small, it disappears during the vulcanization. The vulcanized products behave then as normal elastomers showing low initial elastic modulus.

Under stretching, however, an increase in the elastic modulus is observed (analogously to what is observed in the natural rubber and in other stereoregular polydiolefins with 1,4 enchainment). The increase of modulus and of tensile strength can be attributed to an association of the polymethylenic chain segments. This association is favored by the parallelism of chains induced by stress and is thus comparable to a beginning of crystallization.

This shows that the importance of crystallinity is not limited to plastic materials and to textile fibers but it may involve elastomers (also elastomers which do not contain unsaturations in the chain).

Conclusions

All the examples mentioned above show that the field of stereospecific polymerization has spread in recent years in several directions, not only to cover non-hydrocarbon monomers but also to include new types of regular enchainments.

A description of the main results recently obtained in our Institute was presented. It must be kept in mind that a huge amount of work has been carried out in other research institutes, in universities and in industries with interesting results. Results obtained very soon after the dis-

Table 8. Properties of stereoregular polymers of diolefins

Monomer	Configuration	Steric Purity %	Melting temperature °C	Reference
Butadiene	cis 1,4	~93	−9	(23)
Butadiene	cis 1,4	98-99	+2	(23)
Butadiene	trans 1,4	>99	145	(24)
Butadiene	isotactic 1,2	>99	128	(24)
Butadiene	syndiotactic 1,2	98-99	156	(24)
Isoprene	cis 1,4	>97	~30	
Isoprene	trans 1,4	>99	~62	(25)
Pentadiene-1,3	isotactic trans 1,4	>99	95	(26)
Pentadiene-1,3	isotactic cis 1,4	~85	43	(27)
Pentadiene-1,3	syndiotactic cis 1,4	~85	53-55	(28)

covery of the first stereospecific polymerizations indicate the tremendous scope and promise of the new fields within the sphere of macromolecular chemistry.

Since crystallinity is often associated with particular physical and technological properties, the interest of stereospecific polymerizations is not confined to the purely scientific sphere, but covers the applicational field as well, since it makes it possible to employ monomers which before the discovery of stereospecific polymerization only yielded homopolymers and amorphous copolymers of no practical use.

If the main journals of macromolecular chemistry over the last few years are consulted, it is found that a large number of papers concern stereospecific polymerization, stereoregular polymers and related problems. The recent asymmetric syntheses carried out in our Institute have made it possible to obtain optically active polymers from monomers which are not optically active. They are a special, more advanced case in stereospecific polymerization and are of interest not only because they will throw more light on the mechanism of these polymerizations, but also because they concern problems related to the formation of certain optically active macromolecules found in nature, which formation also occurs through an ionic mechanism.

Asymmetric syntheses were effected when synthesizing polytactic polymers involving asymmetric carbon atoms, whose asymmetry derived from the chemical difference between the atoms or groups bonded to the carbon atom within the monomeric unit. It is thus possible to obtain optically active polymers, unlike the case of stereoregular vinyl polymers in which the presence of enantiomorphous units is not caused by any difference in the chemical composition of the groups near to the tertiary carbon atoms but by the difference in length or configuration of the chain segments linked to those atoms.

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