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Stereospecific Polymerization

A revolution in polymer synthesis has occurred in the last decade.

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The great majority of synthetic polymers contain asymmetric atoms in the backbone chain. In typical vinyl polymers prepared before 1955, these asymmetric centers were arranged predominantly so that *d* and *l* units alternated. However, some sections of the polymer chain contained scrambled *d* and *l* units so that if the chain were stretched out (Fig. 1) the side-groups A would point towards or away from the viewer in a completely random way. This was the only type of addition polymer which could be prepared because chemists, as yet, had found no way to control the stereochemistry of the polymer chain.

In the last decade polymer chemistry has been revolutionized by the discovery of many methods for the synthesis of polymers in which the asymmetric centers either all have the same configuration or else vary in some orderly manner. With few exceptions these syntheses are carried out with catalysts which fix the growing polymer chain and the monomer in space in such a way that addition can only take place in one definite configuration. During this same period a revolution has also occurred in our understanding of the molecular structure and the synthesis in nature of biopolymers.

Some of the theories which have been put forward to describe the action of the catalysts for the preparation of synthetic polymers bear a formal resemblance to theories of reactions in biological systems. Where appropriate, we have drawn analogies. While some of these analogies may appear superficial, we believe they are valuable because the basic problems facing the polymer chemist studying stereospecific polymerization and the biochemist studying enzyme reactions and protein syntheses are similar. It is possible that advances in either field may inspire ideas which could shed light upon unsolved problems in the other.

Discovery of Tacticity

In 1948, Schildneckt described the preparation of a hard, dry polymer of isobutylvinyl ether, with a complex catalyst (*1*). This polymer was quite different from the glue-like polyvinyl ethers known up to that time. However, it was only later that proof was obtained that Schildneckt had carried out the first stereospecific polymerization.

In 1955, Ziegler and his group at Mulheim were studying the reaction of ethylene with aluminum triethyl. By accident it was found that in the presence of trace nickel this reaction gave a high yield of butene-1. During a systematic search for other metals which might give dimerization of ethylene, Ziegler discovered that certain transition metal salts, particularly those of titanium and zirconium, in the presence of aluminum alkyl yielded high molecular weight polyethylene (*2*). The reaction conditions were mild compared with the conventional method for preparing polyethylene which required high temperatures and pressures. Furthermore, the product had superior physical properties since it was less branched than the high-pressure material. Consequently, this was a result of great technological significance.

Of even greater scientific interest, however, was the observation of Natta in Milan that the Ziegler catalyst polymerized olefins such as propylene to polymers in which the methyl or other pendant groups were so arranged that every asymmetric carbon in the backbone had the same configuration (Fig. 2*a*) (*3*). In other words, when the chain was stretched out, every group A would be toward the viewer. Natta termed such polymers isotactic. Polymers such as those described in Fig. 1, in which some of the A groups are arranged randomly, were termed atactic.

Since 1955, many other ways have been found in which the pendant groups can be ordered along the backbone chain. For instance, polymers in which every asymmetric carbon in the chain has the opposite configuration to that preceding it have been prepared; these are termed syndiotactic (Fig. 2*b*) (*5*). Three types of polymer have been prepared from monomers of the type ACH=CHB. In one type all A and B substituents are attached to the backbone so that every asymmetric carbon has the same configuration (Fig. 2*c*). That is, both A and B point toward the viewer. In another,

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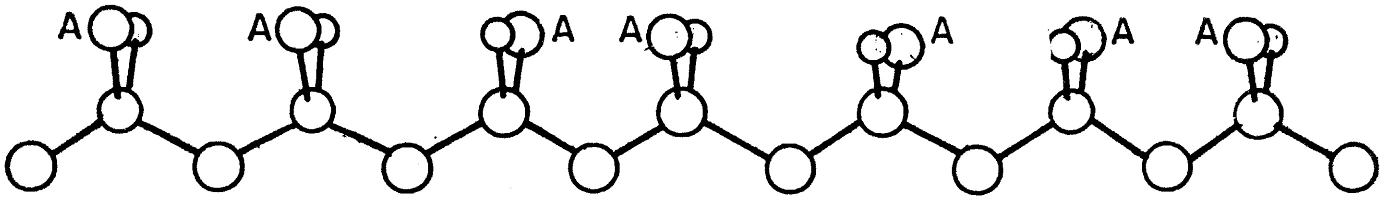


Fig. 1. Atactic polymer.

the carbons attached to B are inverted compared to those attached to A (Fig. 2*d*) so that all the A groups point toward and all the B groups point away from the viewer. The third type is the disyndiotactic polymer in which both A and B series carbon atoms are of the syndiotactic type (Fig. 2*e*) (6).

So far we have only considered saturated polymers. When polymers contain double bonds in the backbone, for example the 1,4-polymers of dienes, geometrical isomers can exist. Two poly-1,4-butadienes can theoretically exist, one in which all the double bonds are *cis* and one in which they are all *trans*. In many cases, such geometric isomerism can be controlled. For instance, Stavely in 1956 prepared a poly-1,4-isoprene in which the double bonds were almost wholly *cis* (4).

Measurement of Tacticity in Polymers

A carbon atom to be asymmetric must be joined to four different groups. In a polymer chain, two of these groups will be segments of the polymer chain of different length. This difference is not one which gives rise to any significant optical effect. As a result isotactic polymers are not normally optically active like asymmetric small molecules.

For this reason, proof that a polymer is stereoregular has generally been obtained by x-ray study. The x-ray technique is valuable because most tactic polymers, unlike the atactic variety, are crystalline solids. Apparently the orderly sequence of side groups allows the packing of the chains into a lattice. Not only can the dimensions of the unit cell be obtained in this way, but also the precise position of the atoms in the cell. From this the whole geometry of the molecule can be obtained.

Not all stereospecific polymers do crystallize, however, and in the absence of crystallinity x-ray diffraction measurements give no information on the tacticity of the polymers. Recently, tactic polymers have been studied by nuclear magnetic resonance (NMR) spectroscopy. This promises to be a powerful tool for determining the structure of stereospecific polymers, since it does not depend on the polymer being crystalline.

Geometry of Tactic Polymers

In hydrocarbons such as butane, the molecule is at its lowest energy state, and is therefore most stable when the two methyl groups are situated as far apart as possible. When tactic polymers crystallize, the side groups also tend to take up positions as far apart from one another as possible. In the case of isotactic polymers, for this to take place the polymer backbone has to assume a helical conformation. Polypropylene, for instance, crystallizes in a helix in which three monomer units form a repeating pattern (Fig. 3). In simple olefin polymers, four types of helices have been found. The most complex of these contains seven monomer units in two turns of the helix.

It is generally believed now that the helical conformation of the polymer chain is also partially retained in solution. Good evidence for this was obtained by Pino (7) and Bailey (8), who showed that isotactic polymers of alpha olefins containing asymmetric side groups had optical rotations in solution up to 28 times those expected from the structures of the side groups. This increase in optical activity was proportional to isotactic content. Apparently the asymmetric groups interact with the backbone chain in such a way that most of the helices spiral in only one direction instead of in both directions as is the case with most polymers. This causes a molecular asymmetry of the whole chain. Significantly, when the asymmetric side groups were removed from these polymers, all optical activity disappeared. Presumably in the absence of these groups the polymer now contains equal numbers of chains spiralling in each direction. Krigbaum and co-workers have also found evidence for polystyrene helices in solution by light scattering and viscosity measurements (9).

Effect of Helix Formation on Reaction Rate

The helical conformation is, of course, a common phenomenon in polypeptides. Doty found that when peptides are prepared from *N*-carboxyanhydrides the rate of polymerization is at first relatively slow and then suddenly increases fivefold (10). The acceleration occurs after eight monomer units have entered the chain. Since this is the number of units required to form a helix in this system, propagation of the helix appears to be a strong driving force for the polymerization.

That stereoregular polymers are formed in other systems because mon-

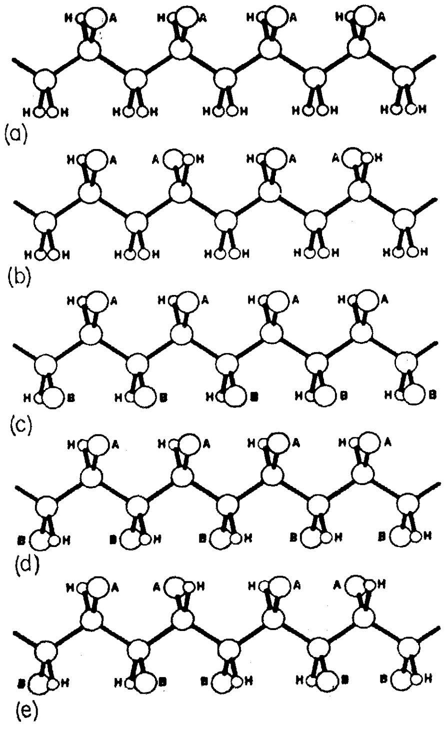


Fig. 2. Simple stereoregular polymers.

omer adds preferentially to the polymer chain in such a way as to preserve the helix has been suggested by Swarc (*11*). He assumes that there may be a much lower potential energy barrier between the monomer and the helix end when the monomer is oriented so as to preserve the helix.

In most cases, such as the polymerization of vinyl monomers, it would be difficult to observe experimentally a rate acceleration after the helix was formed, because the rate of propagation of each chain is so rapid that stopping the reaction after only a few monomer units have added is almost impossible. This problem might be overcome with flow techniques, but no work of this type appears to have been done yet. However, Natta has made the significant observation, for propylene, that the rate constant for propagation of isotactic chains is greater than that for atactic chains (*12*). Despite this observation it is doubtful if self-propagation of the helix is really the reason for the formation of tactic polymers, except possibly in cases where side groups exert unusually large steric effects. In general, the type of catalyst has a very profound effect on whether tactic polymer is obtained; hence the catalyst must influence, at the very least, the probability of the first few monomer units adding to one another so that a helix is formed.

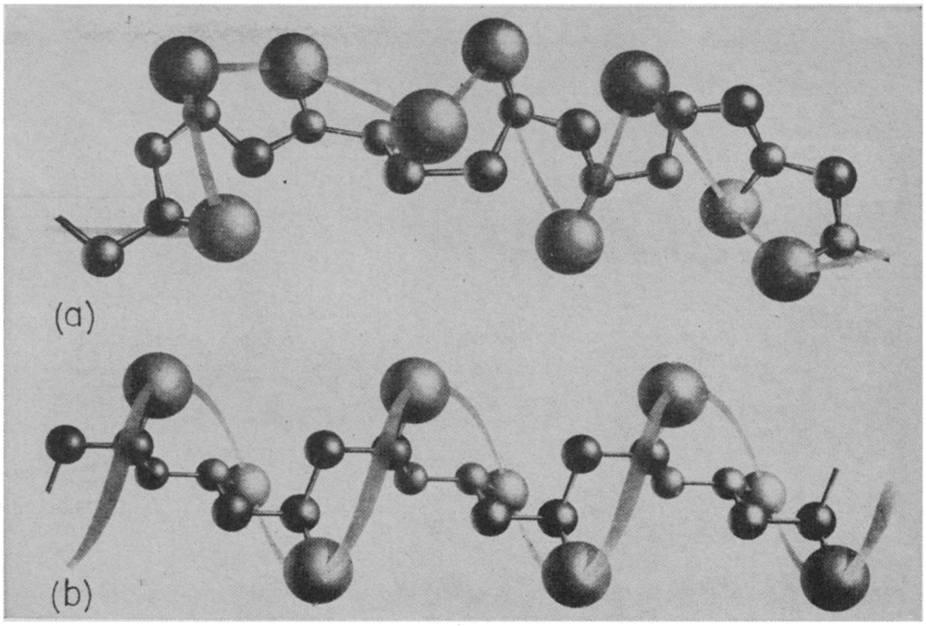


Fig. 3. Atactic polypropylene cannot form a helix (*a*) whereas isotactic does (*b*). [Max Gschwind for *Fortune*]

Stereoregulation in Heterogeneous Systems

The majority of stereoregular polymers are prepared by carrying out the polymerization on the surface of a solid catalyst. The most important of these heterogeneous systems are the Ziegler-Natta catalyst complexes formed between transition metal halides and group I to III metal alkyls. Such catalysts will polymerize nearly all 1-olefins, copolymerize internal olefins with ethylene, and polymerize some mildly polar monomers such as vinyl ethers. In all cases, isotactic polymers are formed.

There are two main types of theories for the way in which Ziegler-Natta catalysts exert steric control. In one type it is assumed that the catalyst is a titanium-aluminum compound. A typical theory of this type is due to Natta (*13*). The reaction of crystalline $TiCl_3$ and a solution of an aluminum trialkyl is postulated to result in a surface complex in which the titanium and aluminum are joined through alkyl bridges (Fig. 4). Incoming monomer is first π-bonded to titanium. The bridge titanium carbon bond then opens whereupon the π-bonded monomer unit is inserted into the chain with the pendant group, pointing away from the $TiCl_3$ surface. The steric effect of the surface, therefore, imposes stereospecificity on the polymerization. Titanium trichloride occurs in several crystalline forms. The rate of polymerization and the stereoregularity of the polymer depend upon which crystalline form is used. Presumably, the structure of the catalytic complex leading to isotactic polymer is the same in all cases, but the effective concentration on some $TiCl_3$ crystal forms is higher than on others.

In the other type of theory the aluminum alkyl is supposed to bring about some modification in the titanium halide surface causing it to become activated. The aluminum is not incorporated into the active complex, and polymer growth occurs on titanium alone. One of the most detailed theories of this type has been put forth by Cossee (*14*) who assumes that the aluminum alkyl reacts with the $TiCl_3$ surface to replace a surface chlorine atom by an alkyl group and, at the same time, to remove an adjacent chlorine atom,

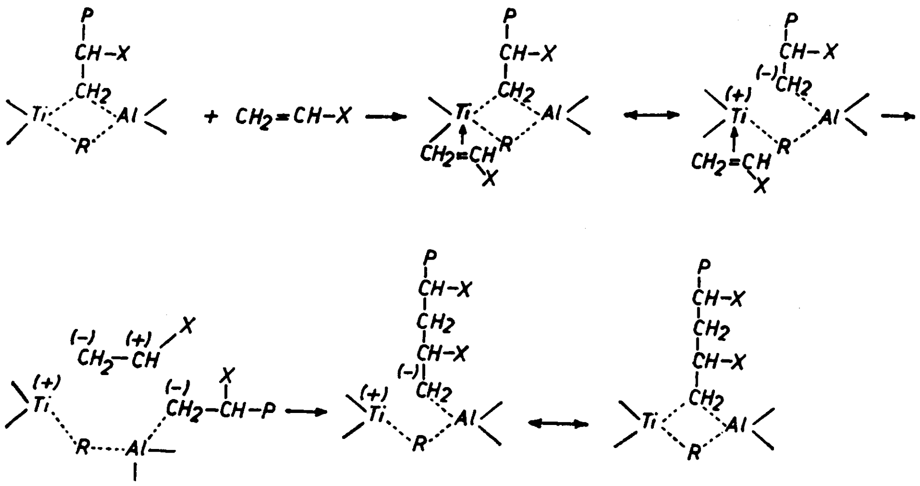


Fig. 4. Mechanism of Ziegler-Natta polymerization according to Natta.

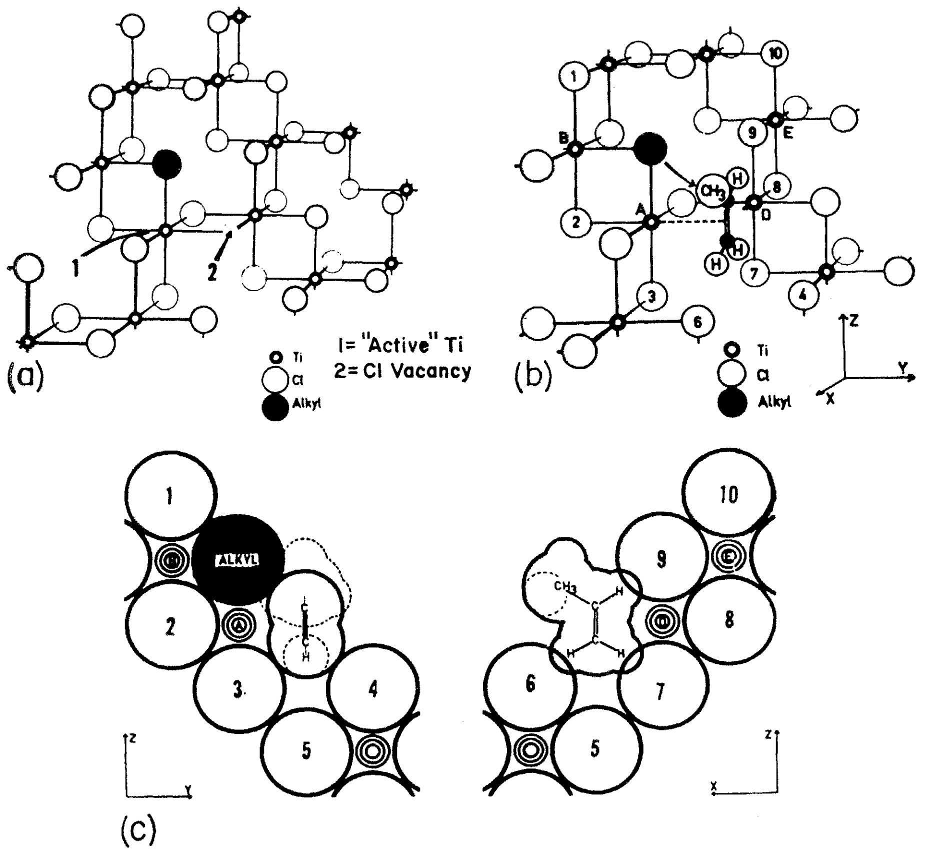
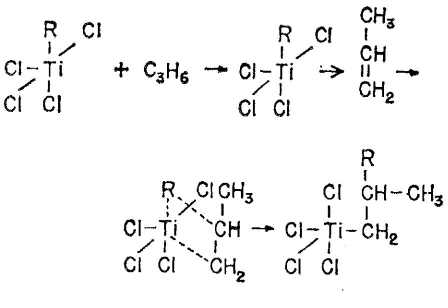


Fig. 5. Mechanism of Ziegler-Natta polymerization according to Cossee. *a*, Activated $TiCl_3$ surface; *b*, monomer π-bonded to surface; and *c*, stereochemistry of monomer-catalyst complex.

forming a hole (Fig. 5*a*). Polymerization now proceeds by way of π-bond formation of the monomer to a titanium atom (Fig. 5*b*), and then alkyl transfer.



The R group in the lattice and the hole have now changed places. It can be shown that there is only one way in which a propylene or other 1-alkene molecule can fit into the lattice and π-bond to titanium and that is with the alkyl group protruding out (Fig. 5*c*). The π-bonded molecule can only add to the chain in the above propagation scheme in one way. Every alkyl group in the polymer chain therefore has the same conformation, and the polymer is consequently isotactic.

Which of these schemes is more correct is not unequivocally proved; some considerations favor Natta's scheme and others favor that proposed by Cossee. Internal olefins cannot easily be accommodated into the active site and coordinate with titanium in Cossee's system, yet butene-2 and cyclopentene have both recently been copolymerized with ethylene by means of a Ziegler-Natta catalyst. Furthermore, when aluminum alkyl in excess of the amount required to completely cover the $TiCl_3$ surface is removed from the system immediately before addition of monomer, no polymerization takes place, and the excess aluminum alkyl has to be replaced before the reaction commences (*15*). This result is difficult to explain on the basis of an irreversible alkylation of the $TiCl_3$ surface but agrees well with the concept of an active complex formed in a reversible equilibrium:

$$TiCl_3 + AlR_3 \rightleftharpoons \text{active complex}$$

This equilibrium lies very largely toward dissociated reactants. However, it may be argued that in a scheme such as Cossee's excess aluminum alkyl is required to scavenge poisons from the system. Furthermore, a considerable body of evidence that polymer growth occurs from a titanium atom rather than an aluminum atom seems to favor propagation from an alkylated $TiCl_3$ surface rather than by an aluminum-titanium complex.

These theories which require a specific fit of the monomer into the reaction site or catalytic complex bear a formal resemblance to "template" polymerizations in biological systems and to the older theories proposed for the stereospecific reactions of enzymes. Like enzyme reactions, these polymerizations have a certain substrate specificity and are easily poisoned by substrates which can be absorbed on, but not polymerized by, the catalyst. An important difference, however, between the nature of the active site in Ziegler-Natta catalysts and those in enzyme systems is that the active site in the Ziegler-Natta catalyst is of necessity rigid, since it is on the surface of a crystalline solid, whereas evidence concerning the active sites in enzymes points to their flexibility and the capacity of the catalytic groups to "embrace" the substrate (*16*).

As in enzyme systems it is extremely difficult to obtain direct experimental evidence for the nature of the active site. The reason for this difficulty is the same in both cases: the active site constitutes such a small part of the total catalyst molecule. In enzyme systems the catalytic sites are part of the vastly larger protein molecule. In Ziegler-Natta catalysts the site is only present at the surface of a crystal made up of largely unchanged $TiCl_3$ or other metal halide molecules. In each case, one is led to look for ways to obtain indirect evidence for the structure of the catalytic species. In studying both enzyme catalysis and stereospecific polymerization, model compounds of known structure have been very useful.

For example, the enzyme papain is believed to contain carboxyl and sulfhydryl groups in the active site. Bender has shown that *o*-mercaptobenzoic acid which also contains these groups in close proximity reacts in many ways like the enzyme (*17*). Similarly, Natta and Breslau have prepared pure, crystalline compounds containing both titanium and aluminum which might be models for the catalytic complex in Ziegler-Natta polymerizations (*18*). The structure of one of these is shown in Fig. 6. This compound will polymerize ethylene to linear polyethylene but is ineffective for the polymerization of higher 1-olefins. Other complexes have yielded weakly isotactic polymers of propylene (*19*).

In neither the study of enzymes nor that of Ziegler-Natta polymerizations are the models anywhere near perfect. Although *o*-mercaptobenzoic acid is an unusually powerful catalyst for the hydrolysis of *p*-nitrophenyl acetate it is much less effective than the enzyme. And the bridge complexes containing titanium and aluminum described above do not approach the $TiCl_3/AlR_3$ catalysts in their capacity to promote stereospecific polymerization. But they are steps in the right direction, and more sophisticated work along these lines could yield valuable information.

The Ziegler-Natta type catalyst is unique in influencing the steric course of the polymerization of nonpolar mono-olefins. However, many other heterogeneous catalysts can give rise to sterically ordered polymers from monomers containing polar groups or from dienes.

Propylene oxide, for example, may be polymerized to isotactic polymers by catalysts as apparently different from each other as powdered potassium hydroxide and a complex of ferric chloride and propylene oxide (*20*). Other epoxides have also yielded isotactic materials. Since the surface features of the effective catalysts appear to have little in common, it seems unlikely that anything unique in the catalyst surface is responsible for the stereospecificity of the polymerization. Rather it appears that only a solid surface which provides a general steric hindrance in the neighborhood of the catalyst site is necessary.

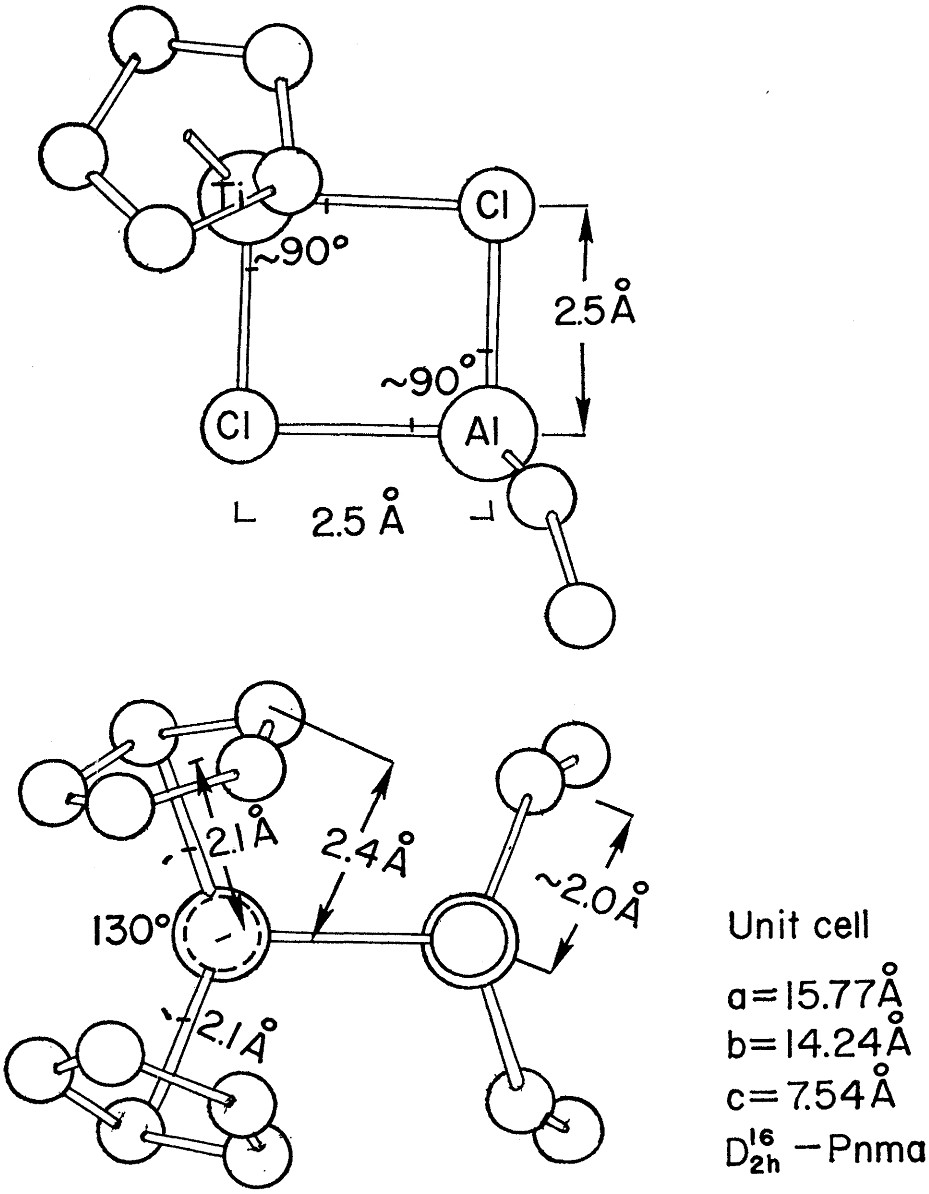
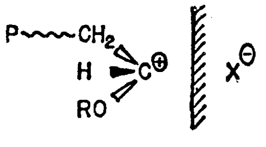
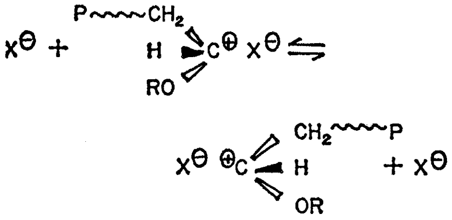


Fig. 6. Catalytic titanium-aluminum complex.

This also seems to be true of the polymerization of vinyl ethers by boron trifluoride complexes. If the catalyst is at any kind of interface, even a liquid-liquid interface, much higher stereoregularity is obtained in the polymer than when the reaction is carried out in homogeneous solution (*21*). Possibly the ion pair at the polymer end is partially tetrahedral. If the anion is embedded in an interface



the configuration of the polymer end is fixed whereas if the ion-pair is in a homogeneous phase the polymer end could invert by an exchange of anions, as

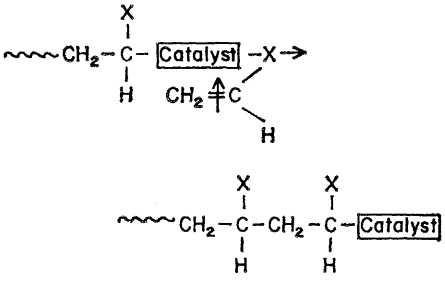


This leads to a loss of stereoregularity.

All the foregoing systems require organic solvents, and even traces of moisture destroy their effectiveness. Recently a completely different system has been described which yields all *trans* poly-1,4-butadiene (*22*). This consists of polymerizing butadiene in aqueous emulsion with rhodium chloride. If other stereospecific catalysts can be found which work in aqueous emulsion, this area may assume considerable industrial importance.

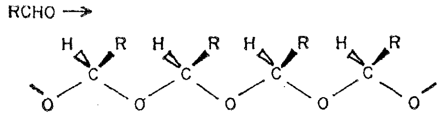
Stereoregulation in Homogeneous Systems

Natta has pointed out that if a monomer contains two or more electron-rich centers, a vinyl group and an alkoxy group for example, then the monomer should be able to coordinate directionally with a catalyst which is electron deficient. Hence, even when this catalyst is in solution, such a monomer may always have the same conformation when added to the polymer chain. A stereoregular polymer could then result even in the absence of a solid interface.



In agreement with this view, alkyl vinyl ethers have been polymerized to isotactic polymers by soluble catalysts such as aluminum alkyl halides (*23*). The polymer chain and the catalyst are either covalently bonded or else form an intimate ion pair. Coordination of the ether oxygen of the monomer with aluminum of the catalyst can consequently influence the way in which the monomer adds to the polymer. When strong Friedel-Crafts catalysts such as aluminum chloride are used, the end of the growing polymer chain is probably a free ion which is not bound strongly to the catalyst. Here the catalyst exerts no influence on the way the monomer adds and atactic polymer is formed.

Nonvinyl monomers also yield stereoregular polymers with homogeneous catalysts. Acetaldehyde and higher aldehydes are polymerized through the carbonyl group to give isotactic polyacetals (*24*).



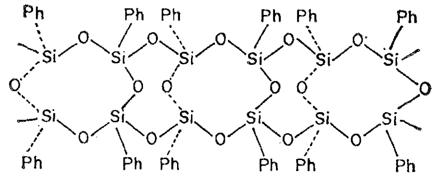
Metal alkyls, such as triethyl aluminum, are the most effective catalysts. However, Furakawa has shown that the presence of water is critical in these polymerizations—in the complete absence of water no polymerization takes place. On the other hand, more water than the optimum amount either prevents polymerization or results in atactic polymer. Furakawa has suggested that the true catalyst for stereospecific polymerization is itself a polymer produced by the hydrolysis of the metal alkyl. Such a polymer would have sites for absorption of aldehyde and initiation of polymerization along its backbone and would function somewhat like an enzyme.

Stereoregulation Induced by Means Other Than the Catalyst

In some cases, stereoregular polymers are formed because the addition of the monomer to the chain end in a stereospecific way is, inherently, the path of least energy. In other cases, stereoregularity is impressed upon the system by some externally applied constraint which only allows monomer and polymer ends to react so that stereoregular polymer is formed. In either situation, the catalyst is not the agent which is responsible for stereoregulation.

One reaction which is inherently stereospecific is the polymerization at low temperatures of methyl methacrylate by free-radical catalysts (*25*). In such a free-radical polymerization there is no catalyst residue associated with the chain end which can influence the reaction. Nevertheless, syndiotactic polymer is obtained even though the chain end is a free-propagating species. The bulky ester groups in the polymer chain and the incoming monomer interact to such an extent that there is a significant difference in free-energy between the reactions leading to syndiotactic and nonsyndiotactic placement.

Another, and perhaps the most striking, example of inherently stereospecific polymerization is the double chain or "ladder" polymer of structure



prepared from the phenylsilanetriol, $PhSi(OH)_3$. X-ray examination of the product shows that each chain has syndiotactic placement of the phenyl groups (*26*). This *cis*-syndiotactic ladder structure is the only way in which an extended network of three connected units can be formed while at the same time tetrahedral bond angles on silicon and the normal bond angles on oxygen are maintained. Brown has suggested that the stereoselectivity inherent in the formation of this network structure may throw light on the evolution of network polymer structures in living organisms (*26*).

When monomers are polymerized in the solid state one might expect that the external constraint of the crystal lattice upon the monomer would result in a polymer which had the same crystalline form as the monomer itself. Such an effect has been found in the radiation-induced polymerization of formaldehyde in the solid state. However, polyoxymethylene is not, of course, a stereoregular polymer since it contains no asymmetric centers. Most monomers which might be expected to yield stereoregular polymers—acrylamide (*27*), acrylic acid, vinyl carbazole (*28*) to name a few—yield only amorphous, atactic polymers when irradiated in the solid state. It appears that the distances between the units in the crystalline monomer and the polymer are usually so different that disruption of the monomer lattice occurs during polymerization.

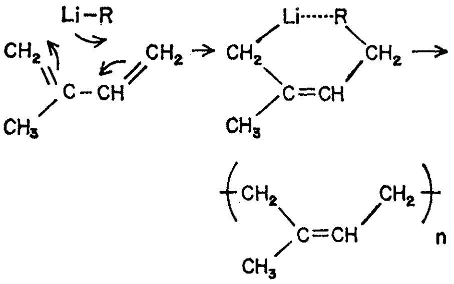
More successful results have been obtained by polymerizing monomers which are constrained within so-called "canal" complexes. These are solid addition compounds between a material which crystallizes into a lattice which has long holes or canals in it, and a material which will fit into these canals. Polymerization of a number of monomers contained as canal-complexes in thiourea and urea have been described by White (*29*). Vinyl chloride, when polymerized in urea canals, gives an all syndiotactic polymer. Poly-1,4-butadiene in which all of the double bonds have *trans* configuration has also been prepared in this way.

A possible extension of the canal-complex technique might be the polymerization of multifunctional monomers in certain clays which are known to accommodate organic liquids as monomolecular layers in the crystal lattice. In this way, large two-dimensional polymeric networks might be prepared.

Natural Stereoregular Polymers Having Simple Structures

A major difference between most natural polymers such as proteins and nucleic acids and synthetic stereoregular polymers is the complexity and large number of basic monomer units found in the former. Indeed, nature has produced very few stereoregular polymers containing only a single recurring monomer unit in the backbone chain.

One example of such a simple polymer, however, is natural rubber. This material is almost wholly *cis*-poly-1,4-isoprene. In the laboratory, the polymerization of isoprene to give this polymer (as distinct from the 1,2-polymer) is found only under carefully controlled reaction conditions (*30*). The formation of a cyclic six-membered ring in the transition state between the lithium alkyl catalyst and the 1 and 4 positions of the diene monomer accounts for the high degree of stereoregularity obtained.



Another rather simple structure, stored for energy in a large variety of bacterial cell walls, is poly-*β*-hydroxybutyric acid (*31*). The monomer, L-*β*-hydroxybutyric acid, is optically active because of an asymmetric carbon atom at the *β*-position. The polymer is highly crystalline because successive monomer units in the chain have identical configurations. Structurally it is quite analogous to isotactic polypropylene oxide already described (*20*). All attempts to synthesize a crystalline polyester from DL-*β*-hydroxybutyric acid have so far failed. It is quite possible, however, that with an appropriate catalyst a suitable synthesis may be found, perhaps one starting with a *β*-butyral lactone monomer.

Summary and Conclusions

The great flurry of activity which followed the announcement of Ziegler and Natta's initial results has led to the discovery of an enormous number of catalyst systems which are effective in stereospecific polymerization. However, there is little more understanding now than in 1955 of how most of these systems work. Now that the initial excitement has cooled, a larger amount of thoughtful work on the mechanisms of these reactions should appear. As a basis for understanding both the heterogeneous and homogeneous systems, more mechanism studies in organometallic chemistry are urgently needed. More specifically for the heterogeneous catalysts, continued attempts should be made to find better models for the active sites, and new analytical methods should be sought to provide more information concerning the active site itself. In homogeneous systems, greater understanding of the ion pairs, the structure of which is so critical, could be obtained by the preparation and study of nonpolymeric analogues.

In addition to understanding better the catalysts that we already have, we may see in the future the development of new kinds of catalysts. Some of these may be capable of producing polymers in which the units have a more complex code than in those produced by simple stereospecific catalysts. Such catalysts already exist in nature. For example, we now know that the RNA molecule functions as a multifunctional catalyst in peptide syntheses, each sequence of three bases along the backbone corresponding to a particular amino acid. The molecule consequently acts as a catalytic template which defines the order in which these amino acids polymerize into the final peptide (*32*). Synthetic RNA's have also been prepared containing only one base such as uracil along the chain (*33*).

Since three uracil units correspond to phenylalanine, the polyuracil acts as a template for the formation of a peptide containing only this amino acid. There seems no reason why, ultimately, we should not be able to synthesize polymeric catalysts of this type which can act as templates for the polymerization of specific monomers other than those found in living systems. If a number of systems such as this can be found, we will be on the road to producing catalysts which can not only control the stereochemistry of a polymer chain but also the order in which a group of different monomers can enter into it.

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