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Stereospecific Catalysis in the Field of Optically Active Polymers

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The present review examines a new field of polymerisation catalysis—the catalytic synthesis of optically active polymers of various classes: (1) poly-α-alkenes under the influence of dissymmetric catalysts, acting as anionic or cationic catalysts, and (2) poly-oxides and poly-imines under the influence of both heterogeneous and homogeneous coordination catalysts. The stereospecific polymerisation of optically active alkenes and the stereoselective polymerisation of racemic alkenes using optically active catalysts are examined. The bibliography contains 127 references.

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I. INTRODUCTION

Progress in stereospecific catalysis has been particularly extensive in the field of optically active polymer synthesis. In recent years, fundamentally new stereoselective and stereo-elective processes have been carried out, and the advantages of the use of optically active compounds in the study of the mechanism of stereospecific catalysis have been demonstrated. Work has also begun on the directed synthesis of optically active polymers with required structure for use as dissymmetric adsorbents and catalyst components[1,2].

The present review is restricted to an examination of the conditions of the catalytic synthesis of optically active polymers, the part played by heterogeneous dissymmetric catalysts in the stereospecific polymerisation of α-alkenes, propene oxide, and imines, and the catalytic stereo-elective polymerisation of propene oxide and poly-α-alkenes.

The large amount of experimental material examined in the present review has been obtained chiefly by Natta, Furukawa, Tsuruta, and their schools, and demonstrates convincingly the part played by asymmetric adsorption and complex formation in asymmetric polymerisation catalysis; this is of considerable interest for an understanding of the mechanism of heterogeneous and homogeneous dissymmetric catalyst action.

II. THE ROLE OF HETEROGENEOUS CATALYSTS IN STEREOSPECIFIC POLYMERISATION

The presence of the surface of a heterogeneous catalyst in a reacting system decreases the number of symmetry elements compared with a homogeneous reaction, so that we should expect the production of greater stereoregularity in the polymerisation products in the presence of heterogeneous catalysts. Stereoregular polymers may also be formed, however, in homogeneous radical polymerisation under certain conditions.

Heterogeneity of the catalytic system, which is essential for the preparation of stereoregular poly-α-alkenes, apparently becomes superfluous in the polymerisation of other monomers (aldehydes, dienes, and acrylates). According to Schildknecht[3], stereoregular poly(vinyl isobutyl ether) may also be formed in the absence of a solid surface with soluble catalysts[4]. In this instance, however, the structure of the monomer and the conditions of polymerisation are of particular importance. The monomers should contain not less than two functional groups interacting electronically with one another, the reaction must be carried out at low temperatures to reduce the freedom of rotation of the chains, and the presence of large bulky groups in the monomer leads to rigidity of the chains and high stereoregularity[5]. Since stereospecificity is determined by the atomic configuration surrounding the ends of the chain and situated not more than 20 Å from it, and since this corresponds to the dimensions of large complexes, the production of stereospecificity, according to Szwarc and Smid[6], requires the presence of a macroscopic surface. Thus isotactic polystyrene can also be obtained in homogeneous solution with $n\text{-}C_4H_9Li$ as initiator at −30°C. The solvent also has a considerable influence: in toluene, methyl methacrylate gives an isotactic polymer with a fluorenyllithium catalyst, but a syndiotactic polymer in dimethoxyethane. If we ignore particular instances, however, heterogeneity of the system remains a necessary condition (particularly in the polymerisation of α-alkenes) for the production of stereoregular polymers. With heterogeneous catalysts, stereospecificity depends to a significant extent on the stage involving adsorption of the monomers at the active centre on the solid catalyst surface. Stereoregular polymers are obtained on catalysts acting by an ion-coordination mechanism (anionic and cationic). These contain metals capable of coordinating molecules of the monomer before the stage corresponding to their introduction into the growing chain. A specific action is shown by metals with small ionic radius (Al, Be, and Li) and compounds of the transition metals. The steric effect of bulky groups in the coordinating monomer is also significant. This factor cannot be decisive in stereospecific polymerisation, however, and it can lead only to stereoregularity of the syndiotactic type.

Different authors have different views on the mechanism of Ziegler–Natta catalyst action (see Tsuruta's monograph[7]), but in one respect they agree: the structure of the macromolecule is determined by the stage in which the monomer is adsorbed on the surface of the heterogeneous catalyst. The active centre on the surface may contain metal alkyls adsorbed on $TiCl_3$ or $TiCl_2$ (Friedlander), and the mechanism of chain growth is a form of matrix polymerisation, when both ends of the chain are attached to the surface. According to Nenitzescu, the organotitanium compounds, which undergo splitting to form radicals, act as the catalyst. Natta considers that in coordination anionic polymerisation, adsorption of AlR_3 takes place on the surface of the $TiCl_3$ crystals with the formation of active centres, the number of which can be determined, for example, by using AlR_3 labelled with ^{14}C.

Asymmetric centres are formed with the participation of aluminium atoms and the spatial configuration of the chain is determined by the way in which the monomer molecule approaches between Al and R. Since two approaches are possible, the resulting polymer (isotactic) consists of a mixture of DDD- and LLL-structures.

When two of the coordinating groups are of different chemical character, enantiomorphic structures are possible in the surface complexes. High stereospecificity in such a catalyst should be produced when it is joined to a growing chain (Natta[4]).

The problem of the nature of the active centres has been the subject of detailed discussion. According to the data of Carrick and coworkers[8], and contrary to Natta's opinion, growth takes place at transition metal active centres without direct participation of the reducing agent (AlR_3). Cossee[9] suggests that polymerisation takes place at a titanium ion on the surface of the $TiCl_3$ (or $TiCl_2$) lattice, in which one of the chlorine atoms has been replaced by an alkyl group R, and beside which there is a vacant site on which adsorption of the monomer molecule takes place. After this stage, the Ti–Al bond and the vacant site are preserved in the active centre, and only their positions change.

Polymerisation by the anionic mechanism is influenced considerably by steric factors, because of the small radius of the coordinating metal cation. The stereoregulating power of these catalysts is greater than that in cationic polymerisation, and steric factors are decisive. It is considered that the monomer molecule being attached should be orientated beforehand, but the essential features of the transition state have not yet been determined.

According to Cossee[9], the active centre of heterogeneous Ziegler–Natta catalysts is a transition metal ion with octahedral configuration. When the α-alkene molecule is adsorbed on the surface, its position is such that it forms a π-bond with the titanium ion and occupies the vacant site in such a way that the CH_3 group (in the case of propene) is directed away from the surface, and the CH_2 group is directed towards the surface of the catalyst.

This orientation of the monomer molecule explains the "head-to-tail" addition. The action of AlR_3 reduces to alkylation of the catalyst surface. This scheme explains the formation of isotactic polymers and the fact that alkenes with a non-terminal double bond and with a large R group do not undergo polymerisation at all. Moreover, compounds such as acetylene, water, and CO act as poisons, since they are firmly bound to the catalyst on the vacant sites.

Cram[10] explains stereospecific polymerisation on the basis of steric repulsion between the substituents in the monomer and the penultimate link in the chain. The growing chain takes its origin from the edge of the catalyst crystal. The monomer entering the chain will react with least steric hindrance when R is on the same side as H— on an asymmetric carbon atom.

It is evident that we should expect a much greater part in this process to be played by a dissymmetric catalyst capable of forming surface diastereoisomers on asymmetric adsorption. Cossee's scheme readily explains the formation of these "diastereoisomers".

These ideas were used by Krylov and Livshits[11-13] to explain the asymmetrising action which they observed for the heterogeneous catalyst magnesium d-tartrate in the polymerisation of propene oxide.

Ideas about the existence of asymmetric centres on the catalyst surface were put forward in general form by Hartung and coworkers[14]. They examined various types of centre on the surface of a catalyst on the basis of Ogston's "three-point adsorption"[15] and Balandin's multiplet theory of catalysis[16].

If two enantiomorphic centres are present in different quantities, stereospecificity is not observed. In the examination of this problem, however, Hartung and coworkers[14] reached an incorrect conclusion by assuming that in the hydrogenation of, for example, (–)-α-oximinopropiophenone the optically active product is formed as a result of the action of only one type of centre[17], whereas this result is due to purely steric interaction as a consequence of asymmetric synthesis under the influence of the original asymmetric centre in the molecule.

To investigate the problem of the properties of the enantiomorphic complexes formed between the dissymmetric centres of the catalyst and the monomer molecule, it is convenient to use the approach proposed by Pajaro, Corradini, and coworkers[18,19], who studied diastereoisomeric complexes of alkenes with optically active complex compounds.

An alkene with unsymmetrical structure can be coordinated by means of a $\sigma\pi$-bond to a transition metal complex with the formation of two enantiomorphs. If the transition metal compound contains an optically active ligand, the diastereoisomers formed with the alkene may be separated. The complexes $PtCl_2$[(–)-(*S*)-α-phenylethylamine]X, where X = styrene, propene, *trans*-but-2-ene, or *cis*-but-2-ene, have in fact been prepared and separated. The following values of $[M]_D^{18}$ were obtained for the first three diastereoisomers: $+1200° \pm 150°$, $-300° \pm 50°$, and $-280° \pm 20°$ As expected, the complex with *cis*-but-2-ene did not give diastereoisomers, because of the symmetry of the molecule.

Asymmetric induction arises on coordination of an alkene to the surface of a heterogeneous catalyst in which asymmetric centres have been produced beforehand.

III. DISSYMMETRIC POLYMERISATION CATALYSTS

1. The Catalytic Asymmetric Synthesis of Poly-α-alkenes

The polymerisation of α-alkenes is the most widely studied field of stereospecific vinyl polymerisation. Isotactic poly-α-alkenes have been prepared only using heterogeneous catalysts, and high stereospecificity has been observed when the organometallic component has been deposited (according to Natta) on the carrier—crystalline modifications of $TiCl_3$, with a layer lattice. The use of other carriers, for example, β-$TiCl_3$, which has a different lattice, or metal oxides, gives polymers with low regularity.

We should expect a greater structural regularity in optically active polymers than in the corresponding polymers formed from their racemic monomers, since the presence of the asymmetric centres in the monomer, as a result of their steric influence, will facilitate the predominant formation of one chain configuration.

An incorrect understanding of the role of the asymmetry of the atoms in the polymer chain has led to attempts to prepare optically active vinyl poly-α-alkenes.

Murahashi and coworkers [20] polymerised styrene under the influence of a catalyst consisting of $TiCl_3$ + tri-(2-methylbutyl)aluminium at 70°C and obtained polystyrene which was identical with the polymer obtained with a racemic catalyst. The polymerisation of styrene with optically active 2-methylbutylsodium also gave an inactive polymer. Braun and Kern [21] found, however, that polystyrene obtained using the optically active 2-methylbutylsodium (optical purity 85%) exhibited slight rotation (up to 0.120°; $[\alpha]_D^{20}$ + 0.60°). Calculation of the contribution of the terminal groups to the polymer chain showed that the optical activity of the polymer does not exceed the values due to the formation of $C_5H_{11}-CH_2CH(C_6H_5)-$ groups at the ends of the chain. This contribution is greater for the amorphous fractions with low molecular weight, where the macromolecule contains one 2-methylbutyl group (0.120° for M = 5400) and is smaller for the isotactic fractions (0.011° for M = 28 800). The use of rotatory dispersion enabled larger rotations to be observed for amorphous polymers.

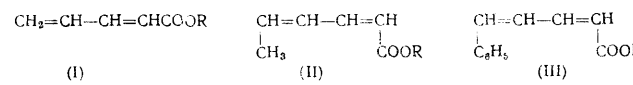
Thus, although in this example of heterogeneous catalysis we might expect steric control of the monomer orientation in the initiation stage at the catalyst surface, these results indicate that polymerisation begins with the alkyl anion of the catalyst.

Fray and Robinson [22] hoped to prove the presence of optical activity in polypropene obtained using (+)-tri(2-methylpentyl)aluminium (optical purity 38%), by subjecting the polymer to pyrolysis. It was expected that optical activity would appear in the chain fragments with low molecular weight, both as a result of the presence of asymmetric atoms and as a result of "spiralisation" of the chain. The results were negative, however.

It has been known for a long time (pp. 109 and 186 of Ref. 1) that an optically active solvent may have an asymmetrising action in the synthesis and separation of racemates. Theoretical examination of this problem by Amaya [23] showed that the probability of formation of optically active polymers under the influence of an optically active solvent increases with decrease in temperature and concentration. An attempt to induce "spiralisation" of the chain by polymerising propene using (+)-tri(2-methylpentyl)aluminium under the asymmetrising influence of (+)-pinane as solvent was unsuccessful, however [20].

Studies in the field of optically active poly-α-alkenes are associated chiefly with the names of Natta and Pino. Natta and coworkers [24] carried out the asymmetric catalytic synthesis of tritactic polymers from optically inactive monomers using dissymmetric catalysts. The dissymmetric catalyst 2-methylbutyl-lithium with methyl *trans-trans*-sorbate gave polymethyl sorbate [25] with $[\alpha]_D$ equal to −3.1° (α_D = −0.235°, c = 2.55, l = 3); $[M]_D$ = 3.9°; and $[M]_{375}$ = −13.5°. The original *trans-trans*-sorbate gives only *erythro*-di-iso-*trans*-tactic polymethyl sorbate. The other possibilities (*trans-threo*, *cis-threo*, and *cis-erythro*) are not realised. Its optical activity is much greater than that which might have been expected from the contribution of the terminal groups to the rotation and is close to the value for the model compound. It was proved by chemical methods [25,26] and by using ^{14}C that terminal groups from the catalyst are not present in the polymer. The comparatively low value of α indicates that there is no spiralisation of the chain, as was suggested for poly-α-alkenes, and is due entirely to the asymmetric atoms in the main chain.

Highly crystalline 1,4-*erythro*-di-iso-*trans*-tactic polymers exhibiting optical activity have been prepared from esters of vinylacrylic (I), sorbic (II), and styrylacrylic (III) acids:



(I) (II) (III)

Table 1 gives data on the optical rotation of polymers obtained by polymerisation of these esters with a catalyst containing an optically active group [(+)-2-methylbutyl-lithium] and also using the complex of butyl-lithium with the asymmetric Lewis base, (−)-menthyl ethyl ether.

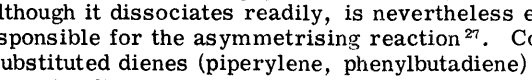
Table 1.

Monomer	Catalyst	Optical rotation of polymer in chloroform		$[M]_D$
		α_D, deg	$[\alpha]_D$, deg	
Methyl sorbate	(*R*)-2-methylbutyl-lithium	−0.70	−7.95	−10.0
Butyl sorbate		+0.36	+3.3	+5.5
Butyl β-styrylacrylate		+0.31	+2.0	+4.6
Methyl β-vinylacrylate	butyl-lithium-(−)-ethyl-menthyl ether		+7.2	
Methyl sorbate		0.27	+6.4	+3.0
Butyl sorbate		0.57	+8.4	+14.1
Butyl β-styrylacrylate		0.42	+3.7	+8.5

The mechanism of action of the first catalyst—the optically active organometallic compound R*Li—apparently involves the introduction of R* into the first monomeric unit, with subsequent transfer along the growing chain.

The second type of catalyst induces asymmetry in the first unit without the formation of a σ-bond between the dissymmetric agent in the catalyst and the chain.

When the catalyst $C_5H_{11}Li$ is used, the polymer contains one alkyl group for every 150–250 monomeric units, so that the optical activity cannot be due to their contribution to the total rotation (the value of $[\alpha]_D$ due to the terminal groups is smaller by a factor of 100 than the observed value of the rotation). Thus the optical rotation is due entirely to the asymmetric atoms in the chain. The same is true of the complex catalyst C_4H_9Li–menthyl ethyl ether, which, although it dissociates readily, is nevertheless entirely responsible for the asymmetrising reaction [27]. Conjugated substituted dienes (piperylene, phenylbutadiene) polymerise with dissymmetric catalysts to form optically active polymers with asymmetric centres in the main chain:



Starting from piperylene, Natta and coworkers [28] prepared *cis*-1,4-polypentadiene in which isotactic chains predominated. They used $AlR_3-Ti(OR)_4$ catalysts; in the system with R = (+)-2-methylbutyl and R = n-butyl, the polymer with high molecular weight did not show optical activity, and only the fraction with low molecular weight gave α_D = 0.03° ($[\alpha]_D$ = 1.76°), possibly due to the introduction of the terminal group from the catalyst.

The action of (+)-$Al(C_5H_{11})_3-VCl_3.(C_2H_5)_2O$ on *trans*-penta-1,3-diene [29] gives 1,3-*trans*-isotactic polypentadiene

with $[\alpha]_D = -1.05°$ ($\alpha_D^{18} = 0.11°$). The optical activity decreases with increase in molecular weight, indicating the occurrence of asymmetric induction in the initial stage of chain growth.

For the $Al(C_2H_5)_3$–(−)-tetra(menthoxy)titanium system, optically active *cis*-1,4-isotactic polypentadienes with maximal specific rotation of −22.8° and $[\eta] = 6.8$ (78% *cis*-chains) have been obtained.

This example is interesting since as well as optical activity due to the asymmetric atoms in the chain possibly there are also conformational factors: α increases with increase in the proportion of isotactic *cis*-1,4-structures. Moreover, the fact that an asymmetrising action is shown by a catalyst containing the asymmetric menthyl group joined to a titanium atom indicates that the transition metal is included in the active centre in the coordinating catalyst. The monomer is coordinated to this centre, and growth takes place on the surface of the heterogeneous catalyst.

Similarly, *trans*-pentadiene under the influence of the catalytic complex [VCl_3–(+)-tri-(2-methylbutyl)aluminium] gives optically active *trans*-1,4-isotactic polypentadiene[29].

Aliev[30,31] studied the asymmetric polymerisation of *trans*-1-phenylbuta-1,3-diene with (+)-2-methylbutyl-lithium and reported slight optical activity ($\alpha_D^{25} = 0.014$–$0.018°$ for $l = 1.55$), but this lies within the limits of experimental error. The use of rotatory dispersion did not permit a convincing demonstration of asymmetric synthesis, since although the value of $[\alpha]$ for $\lambda = 390$ nm increased by a factor of 2.5–3 compared with that for $\lambda = 589$ nm, the errors in the measurements showed a simultaneous increase, and this was not analysed.

Table 2.

Monomer/lithium ratio	Polyphenylbutadiene [η]	[α]390, deg	[α]390 M	Solvent	Monomer/lithium ratio	Polyphenylbutadiene [η]	[α]390, deg	[α]390 M	Solvent
37.6	0.075	+0.982	42.2	toluene	54	0.195	0.838	88.0	heptane
54	0.23	0.524	49.8	heptane	37.6	0.095	1.272	63.6	toluene
27	0.18	1.022	74.6	ditto	27	0.124	1.595	104	heptane

The polymerisation of phenylbutadiene on the complex catalyst butyl-lithium–(−)-menthyl ethyl ether at 0° and 15°C in heptane and toluene gave polymers with considerable activity and low characteristic viscosity (Table 2).

The highest optical activity in the polymers was observed at a ratio ether : butyl-lithium = 2. Decrease in the reaction temperature and increase in the solvent polarity lead to a decrease in the optical activity of the polymer. The optical rotation of the polymer specimens is independent of molecular weight, suggesting a mechanism of asymmetric growth, in which the asymmetric synthesis takes place as a result of the configurational orientation of the monomer on coordination to the lithium atom, through interaction with the asymmetric ligand—ethyl menthyl ether.

2. Asymmetric Cationic Polymerisation

In the polymerisation of cyclic monomers (benzofuran[32]), use is made of cationic catalysts, which form a complex with the optically active counter-ion, whose configuration determines, together with the growing chain, the spatial configuration of the first unit, and exercises steric control over chain growth. To intensify the stereospecificity of the action[23], the reaction is carried out between −75° and −100°C in toluene under the influence of, for example, the complex catalyst $C_2H_5AlCl_2$–(−)-β-phenylalanine (Table 3).

In each monomeric unit there are two asymmetric atoms; the polymer does not contain terminal groups from the catalyst, as proved by using phenylalanine labelled with ^{14}C.[33–36]

Table 3. Polymerisation of benzofuran on cationic catalysts.

Catalyst	Asymmetric co-catalyst	Polymer, $[\alpha]_D$, deg (benz.)	$[M]_D$, deg (diox.)	α_D
$AlCl_2 \cdot C_2H_5$	(−)-β-phenylalanine	−33.1	−39.1	−2.65
$AlCl_2 \cdot C_2H_5$	(+)-β-phenylalanine	+13.1	+15.5	
$AlCl_2 \cdot C_2H_5$	(+)-camphor-10-sulphonic acid	−3.8	−4.5	−0.68
$AlCl_2 \cdot C_2H_5$	(+)-tetramethylammonium camphor-10-sulphonate	−2.4	−2.8	
$AlCl_2 \cdot C_2H_5$	(−)-brucine	+2.8	+3.3	0.47
$AlCl_3$	(−)-phenylalanine	−28.5		

The polymer has a high conformational stability: it does not undergo racemisation even when heated in decalin at 200°C for several hours. This is also confirmed by the low temperature coefficient of optical rotation: +0.04° ± 0.01° deg^{-1}.

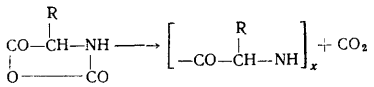
Although the optical activity is associated with the stereoregularity of the three-dimensional structure of the polymer chain, it does not necessarily lead to a tendency for the polymer to crystallise. Thus isotactic or di-isotactic polymers (for example, polybenzofuran) are obtained in amorphous form, although they are optically active. Sterically regular but amorphous polymers, for example, isotactic polymers, can be crystallised in the form of their derivatives, in which they retain their steric configuration: it is probable that, as for example in polybenzofuran, the steric conformation of the polybenzofuran chain is such that it does not permit regular packing of the chains in the crystal lattice[5,32]. It has been suggested that polybenzofuran is partly isotactic, since the optical activity in the main chain cannot be associated with a syndiotactic structure because of internal compensation. The optical activity of polybenzofuran remains constant with time. The rotatory dispersion curve shows a maximum at 303 nm: $[M]_{303} = -800°$.

The asymmetric synthesis is due to the orientating influence of the negative counter-ion situated on the growing end of the polymer chain. The efficiency of this asymmetric synthesis (calculated for unit linkage) is much greater than that for compounds with low molecular weight and approaches that of enzymatic asymmetric syntheses[33]. The mechanism, unlike that of the catalytic synthesis, evidently involves the transfer of asymmetric induction along the chain by means of the asymmetric counter-ion, the monomers being attached predominantly in one configuration. This mechanism is confirmed by the fact that the optical activity is independent of the molecular weight of the polymer[37,38].

Farina, Natta, and Bressan[38] established that the asymmetric polymerisation of benzofuran is autocatalytic. The optical activity depends to a marked extent on the monomer concentration, and from an initial value of 25–30° it passes

through a maximum in the course of the polymerisation, to a constant final value. If, at the start of the reaction, small quantities of previously formed or added polymer are already present, the value of $[\alpha]$ for the polybenzofuran formed is equal to the constant terminal value from the start of the reaction: $[\alpha]_D = 85-90°$. This suggests an autocatalytic reaction under the influence of the polymer formed. Three stages are observed in the polymerisation: (1) the formation of a polymer with low molecular weight and low value of $[\alpha]$, (2) increase in molecular weight and $[\alpha]$, and (3) new formation of fractions with low molecular weight. The second stage is autocatalytic[39]. In actual fact, the introduction of prepared polymer into the reaction sphere decreases the rate of the process by a factor of 5 to 10, but increases the asymmetrising effect, which is independent of both the sign and the magnitude of the rotation of the added polymer, and depends only on the asymmetry of the catalyst—the (+)-polymer is obtained using (+)-β-phenylalanine. The polymer formed probably intensifies the steric influence of the catalyst $AlCl_3$.(β-phenylalanine). Polybenzofuran, because of the presence of its oxygen atoms, can itself act as a Lewis base and modify the structure of the counter-ion. In the catalytic complex at a ratio $AlCl_3$: phenylalanine $\simeq$ 3, one mole of $AlCl_3$ is apparently held much less strongly, and the polymer formed produces a complex with $AlCl_3$, leading to modification of the catalyst. A polymer with high value of $[\alpha]$ is then formed under the influence of this catalyst. Thus as suggested by Natta and coworkers[38] the autocatalytic action is not steric but chemical in character.

This asymmetric autocatalysis shows a close analogy with enzymatic asymmetric syntheses in nature. A similar picture is also observed, for example, in the polymerisation of Leuch's anhydrides[40].



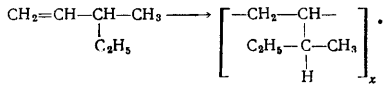
The kinetics of this reaction show a number of characteristic features: the rapid initiation stage is accompanied by chain growth processes which are at first slow (formation of a polypeptide with low molecular weight) and then rapid (conversion into a polypeptide with high molecular weight). According to Doty, a coil (β-peptide) is formed in the first stage, whereas in the second stage an α-spiral, which grows much more rapidly, is formed. If the reaction is initiated by an α-peptide, the first stage is not observed at all, but if the reaction is carried out in dimethylformamide, in which spirals are not formed, the second stage disappears. This mechanism is confirmed by study of the kinetics of the polymerisation of optically pure isomers of Leuch's anhydride and mixtures of the isomers. The homogeneous α-spiral is stable: the introduction of residues with opposite configuration decreases its stability. Thus the racemic mixture polymerises much more slowly than the optical isomer. The decrease in the rate of polymerisation of the latter when the antipode is added, however, is much greater than that when each isomer is polymerised separately. This is attributed to the fact that the polymerisation of, for example, the *d*-isomer, initiated by α-peptides obtained from the *l*-isomer, takes place slowly at first, and rapid polymerisation begins only when a sufficient number of *d*-units for the formation of a spiral are attached to the initiator. The role of the *d*-units (or other rigid conformations) can be seen from the fact that, for example, the addition of only 5% of the *d*-isomer to the *l*-anhydride is sufficient to decrease the rate constant by a factor of 3. The rate of polymerisation of the racemate is slower than that of the optical isomers by a factor of 17. Thus the polymerisation of the L-*N*-carboxyanhydride of γ-benzyl-L-glutamic acid takes place at a high rate when the polymer of γ-benzyl-L-glutamic acid is added as initiator. The reaction rate for the racemate of the anhydride is smaller by a factor of 2. In the system formed by the D-anhydride with L-polymer as initiator, the D-units are first introduced into the right-hand spiral of the L-polymer without altering its shape, but as the D-units accumulate, inversion of $[\alpha]$ is observed with an increase in rate as a result of the conversion of the α-spiral of the L-polymer into the left-hand spiral of the D-polymer.

Comparison of the relative rates of attachment of the D- and L-isomers to the right-hand α-spiral of the L-polymer showed that the L-anhydride is almost five times more active than the D-antipode[40].

IV. THE STEREOSELECTIVE POLYMERISATION OF OPTICALLY ACTIVE α-ALKENES

In the polymerisation of α-alkenes using an organometallic catalyst containing optically active alkyl groups[5] it was found that the active alkyl groups to some extent enter the polymer chain, and if the proportion of these groups is sufficiently large, optical rotation is observed in the low-molecular weight fractions. If optically active monomers are used as starting materials, however, the use of the same optically active catalyst leads to the formation of a polymer whose rotation may be 5–30 times greater than the optical rotation of the model compound, that is, a molecule with the structure of a unit in the polymer chain.

Bailey and Yates[41] at an American Chemical Society conference (1960) described a study of the effect of asymmetric atoms in the side groups of a poly-α-alkene on its crystallinity. The polymerisation of (+)-3-methylpentene ($[\alpha]_D^{25} = +33.49°$) with $TiCl_4$–$Al(n\text{-}C_4H_9)_3$ in xylene at 120–132°C for 7 days gave two polymer fractions: an atactic fraction with $[\alpha]_D^{23} = +94.9°$, and an isotactic fraction with $[\alpha]_D^{23} = -257°$ and m.p. 271–278°C, soluble only in 1,1-ditolylethane. (+)-3-Methylpentene with 4-methylpentene gave a copolymer with $[\alpha]_D^{26} = +112.4°$ and m.p. = 190°C, containing the monomers in the ratio 60 : 40. These authors attributed the marked increase in optical rotation in the polymer compared with the monomer to spiralisation of the chain

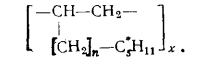


The polymer from *dl*-3-methylpentene had m.p. = 229–237°C, dissolved in 1,1-diphenylethane, and consisted of equal quantities of amorphous and crystalline phases.

An extensive series of papers on the polymerisation of optically active α-alkenes has been published by Pino and coworkers[42-55]. From optically active monomers they prepared optically active poly-α-alkenes with asymmetric centres in the side-chain. These reactions were carried out with ordinary Ziegler–Natta catalysts, and also with optically active organometallic catalysts. The latter were used to carry out stereo-elective polymerisation—selective polymerisation of one of the optical antipodes in a racemic monomer.

The polymerisation of α-alkenes on heterogeneous complex catalysts of the type $TiCl_4$–R_3Al gives polymers with a high degree of stereoregularity. A number of their characteristic properties led Pino and Natta to suggest that in the polymers, secondary structures of a spiral type,

similar to the α-spirals in proteins and polypeptides, are formed. The possibility that spiral structures are present in vinyl polymers was pointed out by Natta as early as 1954, but proof of their existence in solutions and in melts has not yet been obtained. The detailed studies of Pino have been of considerable assistance in the elucidation of the nature of the secondary structures of poly-α-alkenes. Evidence in support of the suggestion that spiral structures are present is provided by the high degree of stereoregularity, the high melting points, and the increased values of $[\alpha]_D$, which exceed the values for the monomers and model compounds by a factor of 5–30. The magnitude of $[\alpha]$ depends to a marked extent on the stereoregularity of the polymers and tends towards a limiting value[53] with increase in stereoregularity. For stereoregular specimens, the optical rotation is less sensitive to change in the regularity of the structure[53]. The absolute value of $[\alpha]_D$ for polymer solutions decreases with temperature, and the isotactic fractions show an unusually high temperature coefficient, close to the values found for solutions of proteins and polypeptides (for example, 0.30 for silk fibroin). The magnitude of $[\alpha]_D$ depends on the structure of the side-chain of the polymer, and there is an optimal distance (n = 1) between the asymmetric centre in the side group and the main chain:



Pino regards all these facts as confirmation of the existence of secondary formations analogous to the α-spirals of proteins or polypeptides[56] in solutions of poly-α-alkenes, in melts, and in the solid state.

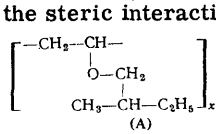
Since the contribution of the spiral structures to the total rotation increases the total rotation, decrease in $[\alpha]$ may serve as an indication of a decrease in the stereoregularity of the main chain of the polymer structure; this is also indicated by a marked negative temperature coefficient $\Delta[\alpha]/\Delta t$, characterising the reversible disappearance of regular spiral segments in the macromolecular chain with increase in temperature.

Calculation by Brewster's semiempirical method[57] established that monomers with the (*R*)-configuration form isotactic polymers in which right-hand spirals predominate.

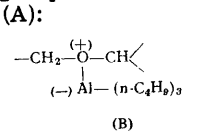
Despite the fruitfulness of this interpretation of the characteristic features of the structure of poly-α-alkenes, however, increasing doubt has recently been cast on the correctness of this interpretation[58] and it has been suggested that hindered conformations, and not spirals, are present.

Experimental data obtained by Pino and coworkers on optically active poly-α-alkenes and vinyl ethers in the presence of dissymmetric catalysts are given below.

The existence of rigid conformations, possibly of a spiral type, was suggested by Pino and coworkers[46] for the polymerisation of (*S*)-2-methylbutyl vinyl ether ($[\alpha]_D^{20}$ = +6.68°). In toluene solution, the polymer had a low rotation ($[M]_D^{25}$ = +1.1°), which was independent of the stereoregularity (infrared spectra and X-ray diffraction data) of the polyether and changed little with temperature ($\Delta[M]/\Delta t$ = +0.02). This behaviour was attributed to the presence of the ether oxygen between the asymmetric group and the main chain, weakening the steric interaction (A):



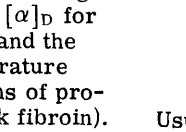
(A)



(B)

As a result, according to Pino[47], formation of a secondary structure takes place in the chain. If, however, the effect of the ether oxygen is eliminated by binding the group in a complex with $Al(n\text{-}C_4H_9)_3$, the polymer shows a sharp increase in $[M]_D$, and the temperature coefficient acquires a negative sign and a high value (up to −0.37), close to the values found for poly-α-alkenes (for example, 0.28 for poly-[*S*]-5-methylheptene). Moreover, a clearly defined dependence of $[M]_D$ on the stereoregularity of the structure is observed. All this suggested that in the "complexed" polymer one of the spiral structures predominates, as a result of the restriction of the free rotation about the C–O–C bonds in the complex (B).

A large amount of experimental material[40,59] has accumulated on the catalytic synthesis of optically active polyalkenes of general formula:



Usually, optically active monomers were employed as starting materials, and complex catalysts $Al(n\text{-}C_4H_9)_3$–$TiCl_3$ were used. The polymers were fractionated and the relationship between the optical rotation and stereoregularity was studied.

Table 4. Optical rotation of solutions of poly-α-alkenes.

	$[\alpha]_D$ monomer	Polymers					
		α_D, deg	$[\alpha]_D$, deg	$[M]_D^{20}$, deg	$\frac{\Delta[\alpha]}{\Delta t}$	$\frac{\Delta[M]}{\Delta t}$	$[\eta]$
Poly-(*S*)-3-methylpentene	(*S*) + 34.2		35.5	104	−0.10	−0.23	0.08
				163		−0.36	0.8
(*S*)-2,3-Dimethylpentane			−14.4	−11.4			
Poly-(*S*)-4-methylhexene	(*S*) − 2.5		28.6	+153	0.66	−0.42	1.3
				+288		−0.68	5.15
				+21.3			
				+9.9			
Poly-(*S*)-5-methylheptene	(*S*) + 9.8	0.95	56.5	58.1	−0.25	−0.34	5.80
Ditto, melt		0.96	—		−0.30		
Ditto, cryst.		1.02	59.6		−0.01		
(*S*)-2,5-Dimethylheptane				11.7			
(*S*)-3-Methylheptane				11.4			
Poly-(*S*)-6-methyloctene				+20.4	—	−0.09	3.78

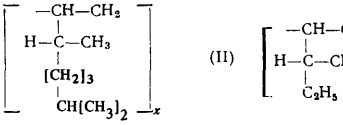
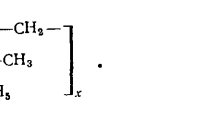
Table 4 gives data on the optical rotation of the poly-α-alkenes obtained, the monomers, and the corresponding model compounds. Sometimes, for example, for poly-(*S*)-3-methylpentene, $[\alpha]$ for the model with low molecular weight and the same absolute configuration of the asymmetric atom in the side-chain is not only smaller in magnitude, but even of opposite sign. On polymerisation, the sign of the rotation of the polymers coincides with that of the monomer, and inversion of the configuration does not take place. Inversion of the configuration is observed only for poly-(*S*)-4-methylhexene, just when there is optimal asymmetrisation of the polymer chain ($[M]_D$ = +286°).

Comparison of $[M]_D$ for model compounds (the corresponding alkanes) given in Table 4 with $[M]_D$ for the atactic fractions of poly-α-alkenes with low molecular weight shows that their rotations are of the same order of magnitude, whereas for the isotactic fractions $[M]_D$ is greater by one order of magnitude; the temperature coefficient of molecular rotation of the latter is also much greater (0.2–0.7) than that for fractions with lower stereoregularity.

The firm of Montecatini has obtained patents[48-50] on the preparation of optically active poly-α-alkenes from the corresponding monomeric (*S*)-(+)-3-methylpentene, (*S*)-(−)-4-methylhexene, (+)-3-phenylpentene, and (+)-5-methylheptene, or their antipodes, under the influence of a $TiCl_4$–$Al(n\text{-}C_4H_9)_3$ catalyst.

Pino and coworkers[44] suggest that the high optical rotation of poly-α-alkenes results from the algebraic summation of the relatively weak influences of the asymmetric atoms in the side groups and the much greater influence of the spiral structure of sections of the main chain which have identical rotation and are present in solutions.

This view appears to be confirmed by the marked dependence of the rotation on the stereoregularity of the polymers. The presence of atactic sections of chain in the polymer should decrease considerably the proportion of spirals of one sign, and hence $[\alpha]_D$. In this instance, the structure of the side group acquires considerable importance. Even when the asymmetric carbon atom is in the α-position relative to the main chain, as, for example, for poly-*R*-(−)-3,7-dimethyloctene (I), a decrease in $[M]_D$ is observed relative to the value of $[M]$ for poly-3-methylpentene (II):[51]

(I)  (II) 

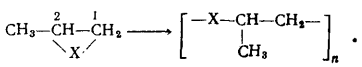
Fractionation of the poly-3,7-dimethyloctene fraction with $[\eta] = 6.52$ and $[M] = 144°$ at various temperatures (34–80°C) increased the rotation only to $[M]_D = 154°$ ($[\eta] = 6.93$).

Comparison of the properties of two groups of poly-α-alkenes, obtained by two methods: (a) by catalytic asymmetric synthesis, and (b) from the optically active monomers, shows that in the latter there is a marked increase in optical rotation as a result of the conformational contribution from the main chain, whereas the polymers obtained by asymmetric synthesis owe their optical activity to the configuration of the asymmetric atoms in the main chain.

V. STEREOSPECIFIC CATALYSIS IN THE POLYMERISATION OF PROPENE OXIDE AND IMINES

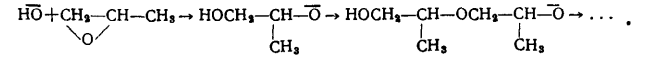
A number of problems of the detailed mechanism of polymerisation can be solved by studying the reactions of optical isomers instead of the racemates usually employed. Of particular interest are problems related to the determination of the part played by a heterogeneous catalyst in a stereoselective or stereo-elective process, the determination of the influence of the asymmetrising stages of polymerisation on the properties of the polymer produced, and the determination of the nature of the active centres of a stereospecific catalyst by comparison of the rates of polymerisation of the optical isomers and the racemate. In this connection, some success has been achieved with propene oxide—the simplest monomer capable of existing in an optically active state.

The overall polymerisation scheme assumes rupture of the epoxide ring (X = O) at the C_1–O or C_2–O bond;



If the rupture of the bonds is equally probable, as, for example, in the polymerisation of D-(+)-2,3-epoxybutane, the action of, for example, the catalytic system $Al(n\text{-}C_4H_9)_3$–H_2O in heptane gives an inactive polymer with the *meso*-diisotactic structure, with properties identical with those of the polymer from the racemic monomer[60]. Treatment of *cis*-2,3-epoxybutene with an optically active catalyst obtained from $(C_2H_5)_3Al$, acetylacetone, and *l*-menthol, however, gives a diisotactic polymer with $[\alpha]_D^{25} = +1.1° \pm 0.3°$. Inversion of the configuration of the monomer takes place in the reaction[61]. In the discussion of papers on the polymerisation of propene oxide, mention must be made of the erroneous assignment of (+)-propene oxide to the L-series[62,63]. It is more correct to relate (+)- and (−)-propene oxides to the D- and L-series respectively[64,67]. In this instance it would probably be more appropriate to use the nomenclature system of Terent'ev and coworkers[68].

The polymerisation of an optical isomer of propene oxide was first attempted by Levene and Walti[64]; the action of KOH solution gave a cyclic trimer with $[\alpha]_D^{20} = -43.0$ and a tetramer with $[\alpha]_D^{20} = -49.19$. By the action of powdered potassium hydroxide at 25°C on the D-isomer with $[\alpha] = +14.75°$, Price and Osgan[69] (1956) obtained a crystalline polymer ($\eta_{sp}/c = 0.13$; $[\alpha]_D^{25} = +25 \pm 5°$ chl., m.p. 56°C), whereas the racemic monomer gave a viscous polymer whose molecular weight, however, was similar (3000–5000), indicating a chain reaction mechanism



The use of the Pruitt–Baggett catalyst[70] ($FeCl_3$ + propene oxide) on (−)-propene oxide also gives a crystalline polymer (m.p. 72°C) with the same value of $[\alpha]_D$ as that obtained using KOH, but in addition, an amorphous fraction is always produced (from both the *l*-isomer and the racemate). Water acts as a co-catalyst, and the proportion of crystalline fraction increases in its presence. This interesting observation was subsequently applied to produce new asymmetric catalytic systems[66]. According to Price, the formation of a completely crystalline polymer from the *l*-monomer on KOH and the formation of a partly crystalline polymer on the $FeCl_3$ catalyst indicates preservation of the configuration in the first instance and partial racemisation in the second instance.

For catalysis on the $FeCl_3$ catalytic system, it was found that the rate of polymerisation is independent of the monomer concentration, but proportional to that of the catalyst, and that the degree of depolymerisation is inversely proportional to the catalyst concentration and increases with increase in the degree of conversion. This indicates that the polymerisation is heterogeneous[69], that the crystalline polymer is formed on the catalyst surface, and that the amorphous fraction is formed in solution in the presence of dissolved catalyst. This scheme presupposes asymmetric adsorption of the substrate, and this was later proved.

According to Price, the reaction mechanism involves "coordinative growth of the chain" as a result of coordination in the transition state to give a five-membered ring. The influence of water on the crystallinity of the polymer is due to its reaction with the catalyst and the creation of considerable steric hindrance in the reaction. The attachment of the first molecule of monomer takes place with preservation of the configuration of the asymmetric atom. The next molecule forms a coordinate bond with the iron atom, and this bond is formed preferentially by molecules with the same configuration. (The various reaction schemes are examined by Gaylord and Mark[71].) Other views on the mechanism of this reaction are given in a review by Bakalo and Krentsel'.[72]

Ziegler–Natta catalysts can also be used for the reaction; this gives a polymer with the same melting point as Price's polymer, indicating that the racemic polymer contains monomer chains with a single configuration[71,73].

Racemic isotactic polypropene oxide can be separated, albeit only slightly, into optically active fractions by chromatography on saccharose and on the complex formed by diethylzinc with *l*-menthol or borneol[74].

On the basis of a large amount of experimental data it is assumed that stereospecific polymerisation is facilitated by the orientating influence of the surface of a heterogeneous (or microheterogeneous) catalyst, although data have recently been published on the preparation of isotactic and syndiotactic polymers under conditions of homogeneous polymerisation by the methods of not only ionic polymerisation but also radical polymerisation[75–77]. At the same time it is known that soluble catalytic systems are less active, and the polymers obtained show a lower degree of stereoregularity[71]. This is confirmed by the data of Price and coworkers on the polymerisation of propene oxide. The fact that these microheterogeneous systems may be visually homogeneous[72] does not prove the absence of heterogeneous formations[78]. Moreover, heterogeneity may be produced in situ[71] as a result of the reduction of metal salts in the catalytic complex. The existence of active, purely heterogeneous, catalysts for the polymerisation of propene oxide also confirms this view.

Krylov and Livshits[11–13] showed that it is possible to use magnesium oxide, oxalate, and tartrate and a number of other heterogeneous catalysts for the polymerisation of propene oxide, and that the activities of Be, Ca, and Mg oxalates are comparable with that of the most effective of Price's catalysts.

A number of important problems of stereospecific catalysis have been studied for the example of the heterogeneous polymerisation of the optical isomers of propene oxide. In polymerisation on a heterogeneous catalyst, three examples of stereochemical correlation are possible: (1) the active centres of the catalyst are stereochemically indistinguishable for adsorption of the (+)- and (−)-isomers of the monomer; the probability of growth and the rate of polymerisation of the (+)-monomer are then double those for the racemate; (2) the catalyst contains equal quantities of enantiomorphic centres; the rates of polymerisation of the isomer and racemate will be equal, since replacement of the racemate by the (+)-isomer decreases the number of available centres by a factor of two but increases by a factor of two the probability of growth of the *ddd*-chains; (3) the catalyst contains centres with the same sign; the rate for one isomer will be greater than the rates of polymerisation of the other isomer and the racemate. Livshits, Krylov, and Klabunovskii[2,79,80] studied the kinetics of the polymerisation of (+)-, (−)-, and (±)-propene oxide on the heterogeneous catalyst magnesium oxalate and found that the probability of chain growth from the optical isomer [(+)- or (−)-propene oxide] is twice that for the racemate (the ratio of the first-order rate constants was ~ 2).

The results obtained (Table 5) indicate that the first situation is realised, that is, the active centres on the catalyst are indistinguishable with respect to the (+)- or (−)-isomers, and the number of accessible centres is the same for the antipode and the racemate.

In this section we must also consider the polymerisation of imines—the nitrogen analogues of propene oxide. Propeneimine isomers with $[\alpha]_D = -12.8°$ and $+12.4°$ have been polymerised in the presence of a number of catalysts [including $BF_3.(C_2H_5)_2O$] with the formation of solid polymers with $[\alpha]_D = +190.27°$ or $-101.46°$ and m.p. = 83° or 73°C respectively. Inversion of the sign of rotation takes place on polymerisation, as with propene oxide. The racemate under the same conditions gave a polymer with m.p. 17°C, although their molecular weights were similar[81].

The polymerisation of oxides and imines probably involves a succession of S_N2 reactions, in which first hydroxide ions and then alkoxide ions function as nucleophilic reagents[82]:

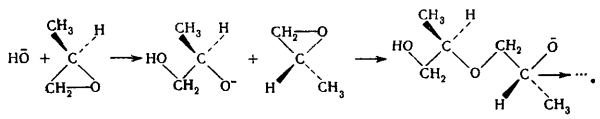
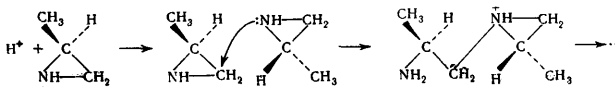


Table 5. The polymerisation of D-(+)- and L-(−)-propene oxide on magnesium oxalate and the properties of the polymers obtained.

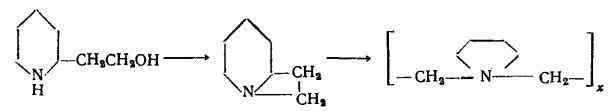
$[\alpha]_D^{20}$ for monomer, deg	Temp. of experiment, °C	Weight of MgC_2O_4, g	Duration of reaction, h	Degree of conversion, %	Polymer		Ratio of rate constants
					$[\alpha]_D$ (benz.), deg	$[\eta]$	
+9.50	83.9	0.15	33.5	74.2	−24.2	0.12	—
9.50	89.4	0.208	11.5	59.8	−23.1	0.12	1.9
9.50	93.4	0.207	14.0	54.5	−31.9	0.06	2.2
−6.95	89.4	0.242	13.5	41.1	+12.8	0.18	2.1

In the polymerisation of propeneimine we must also assume an S_N2 mechanism initiated by a proton:



Similarly, isobutylethyleneimine with $[\alpha] = -24.6°$ ($-15.4°$ [83]) gave a polymer with m.p. 56°C and $[\alpha]_D^{20} = +66.7°$ or 68° (benz.).[84] The polymer was used successfully as catalyst in an asymmetric cyanohydrin synthesis[84].

Polyconidine, prepared by Toy and Price[85], is of equal interest in connection with the use of polymers as models of enzymatic asymmetric systems. If the polymerisation is carried out in the presence of BF_3, the catalyst enters the polymer chain; the resulting polyconidine has $[\alpha]_D = +12.7°$. The action of the ether addition compound of BF_3 at room temperature gives a crystalline polymer, whose sign of rotation is the opposite of that of the monomer:



$[\alpha]_D + 11°$ $[\alpha]_D + 71°$ $[\alpha]_D - 140.8°$ m.p. 94°C

(+)-Polyconidine was obtained analogously. The racemic polymer obtained by dissolving equal quantities of (+)- and (−)-polyconidine had the same melting point as the optical isomers.

VI. THE STEREO-ELECTIVE POLYMERISATION OF DL-PROPENE OXIDE UNDER THE INFLUENCE OF DISSYMMETRIC CATALYSTS

Price and Osgan[69] found that prolonged contact between racemic propene oxide and a Pruitt–Baggett catalyst prepared using (−)-propene oxide gives a polymer containing

a crystalline fraction. This showed that under certain conditions the action of this dissymmetric catalyst may lead to a stereo-elective process, that is, the selective extraction of one of the optical antipodes of the racemate in the polymerisation. This was verified in work by Chu and Price[86]. Various catalytic systems for the polymerisation of (+)-propene oxide were studied: $Al(OC_3H_7)_3$, $ZnCl_2$, $Zn(C_2H_5)_2.H_2O$, and $FeCl_3.C_3H_6O$. All the catalysts gave crystalline polymers with similar rotations, with $[\alpha]_D$ about $-25°$, but the melting point for $Zn(C_2H_5)_2$ was much lower than that for the other catalysts, indicating a polymer with low tacticity. The polymer from the DL-monomer was even less stereoregular, however. An attempt to carry out a stereo-elective process in this way was unsuccessful.

The preparation of the catalysts involved production of the complex by the reaction of a small quantity of D-propene oxide with $FeCl_3$, after which the main bulk of the DL-monomer was added. Optically inactive products were also obtained using other dissymmetric catalytic systems: (−)-propene oxide + $Zn(C_2H_5)_2$ + H_2O; (−)-aluminium–propene glycol complex + $ZnCl_2$; and $(n\text{-}C_4H_9)_3Al$ + (−)-1-methoxypropan-2-ol.

The systems studied give less soluble and hence more stereoregular polymers from L-propene oxide than from the DL-monomer. Asymmetrisation of the catalyst by the introduction of a "seed" of the L-polymer did not give the catalyst stereo-elective properties.

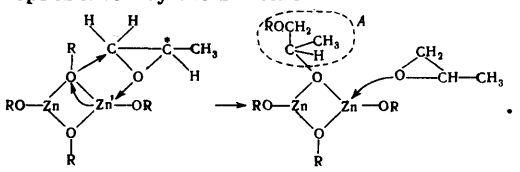
The optical activity in polypropene oxide obtained on an optically active Pruitt–Baggett catalyst was preserved only in the first hours of polymerisation at 80°C and, as shown by calculation, could be attributed entirely to the inclusion of active propene oxide from the catalyst.

The effective stereo-elective polymerisation of DL-propene oxide was carried out using a catalyst based on $Zn(C_2H_5)_2$. Polymerisation with this catalyst takes place effectively in the presence of water or alcohols. Dimeric or trimeric zinc alkoxides, whose presence was proved spectroscopically[87], are formed:

$$Zn(C_2H_5)_2 + ROH \rightarrow ROZnC_2H_5 \xrightarrow{ROH} RO{-}Zn{-}OR .$$

When an optically active alcohol is introduced into the system instead of water, we should expect this dissymmetric catalyst to have a stereospecific action and lead to the formation of an optically active polymer.

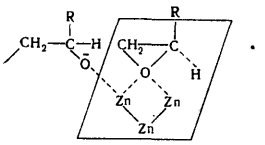
The catalytic properties of the complex are due to the presence of free coordination centres, and the zinc atom is of primary importance. For the dimer, the reaction can be represented by the scheme:



Since in the experiments the radical R was the optically active (+)-bornyl group, the introduction of each monomer molecule into the reaction sphere is sterically controlled not only by the preceding unit introduced into the chain (denoted *A* in the scheme) but also by the influence of the asymmetric centres of the bornyl group of the catalyst.

Furukawa[88] considers the polymerisation of oxides in terms of a multi-centre coordination mechanism, according to which there are two coordination centres, and the propene oxide molecule is joined through oxygen to two zinc atoms. One of the bonds is an ordinary ionic bond and involves the counter-ion.

In this coordination-anionic polymerisation, the attachment takes place at the α-carbon atom of the monomer, which contains the key atom. The stereoregulating action is brought about by the reaction of the R group in the monomer with the ligand of the catalyst or with the R group in the polymer chain. The monomer, coordinating to two catalyst centres, preserves a definite position in space relative to the end of the polymer chain and to the catalyst. The attachment of the next monomer takes place in the same configuration, with the formation of an isotactic structure. The appropriateness of this approach followed from papers by Price (1959) and the experiments of Furukawa (1962),[89] and was confirmed in work by Tsuruta and coworkers[90,91]. Asymmetric induction takes place by the stereoregular control of the reaction of the OR alkoxy-group of the optically active alcohol joined to the complex catalyst (Inoue, Tsuruta, and Furukawa[92]):



The dissymmetric catalyst was obtained, for example, by adding 0.05 M HOR [(+)-borneol, (−)-menthol] to 0.025 M $Zn(C_2H_5)_2$. At 80°C the degree of conversion in the polymerisation of DL-propene oxide amounts to 17–30%.

The crystalline polymer obtained exhibited optical activity. The conditions of the stereo-elective polymerisation, and the constants of the polymer, are given in Table 6.

Table 6. Stereo-elective polymerisation of DL-propene oxide on $Zn(C_2H_5)_2$ + co-catalyst.

Co-catalyst	Medium	% conversion	Crystalline polymer					Amorphous polymer	
				in benzene		in chloroform			
			η/c	α obs., deg	$[\alpha]_D$, deg	α obs., deg	$[\alpha]_D$, deg	η_{sp}/c	α obs., deg
(+)-borneol	toluene	27.6	5.63	−0.07	−5.9	+0.26	+7.4	—	—
ditto	hexane	25.0	3.30	−0.06	−4.6	+0.19	+6.1	1.48	±0.01
ditto	benzene	30.0	3.65	−0.06	−3.7	+0.04	+2.5	1.70	±0.01
(−)-menthol	ditto	17.3	0.59	−0.02	−3.6	+0.07	+2.2	—	—

A noteworthy feature is the very low values of the rotation, which lie, for example when the (−)-menthol co-catalyst is used, at the limits of error of the measurement (−0.02°). In chloroform, however, the magnitude of the rotation increases and its sign changes, confirming the presence of an optically active polymer. The amorphous fraction of the polymer did not exhibit optical activity. The molecular weights of the polymers were sufficiently large to exclude the influence of terminal groups on the total rotation, and the sign of the rotation was opposite to that of the bornyl or menthyl ether, confirming that the fragments of the optically active alcohol had almost no influence on the rotation of the polymer, although the introduction of terminal groups from the catalyst into the polymer was subsequently proved. It was also confirmed using the catalyst 9,10-di(hydroxymethyl)anthracene–dibutylzinc. The polymer obtained contained alkoxy-groups, which were identified from their ultraviolet fluorescence.

The observed inversion of the optical rotation of poly(propene oxide) from negative in benzene to positive in

chloroform is a characteristic feature, which was also observed by Price for the (−)-polymer. The curves for the dispersion of the rotation, recorded in these solvents, are completely symmetrical. It may be assumed that this sensitivity of the optical rotation to the nature of the solvent is due to the contribution of the molecular asymmetric structures of the polymer to the total rotation[92].

The magnitude and sign of the rotation are influenced considerably not only by the solvent but also by the concentration of the polymer in chloroform. This is possibly due to the formation of hydrogen bonds between the oxygen atom in the polymer and the chloroform[13]. The point of inversion lies at about 2.2 g in 100 g solution; the negative rotation increases with increase in the concentration of polymer in chloroform.

As expected, the unreacted propene oxide isolated after polymerisation acquires optical activity. Thus when the diethylzinc–(+)-borneol system was used, the monomer remaining had $[\alpha]_D^{20} = -0.98° \pm 0.05°$ so that the (+)-isomer in the racemate reacted more rapidly, enriching the monomer in the (−)-isomer[93].

If k_i and k_p are the rate constants for the initiation and propagation of the chain, it follows that if the catalyst centres are equivalent $k_{il} = k_{id}$, a mixture of *d*- and *l*-polymer chains in equal proportions is formed. On a dissymmetric catalyst, containing, for example, (+)-borneol, $k_{id} > k_{il}$ and the polymer contains more D-units than L-units. Thus more of the D-(+)-isomer is withdrawn from the racemate during polymerisation.

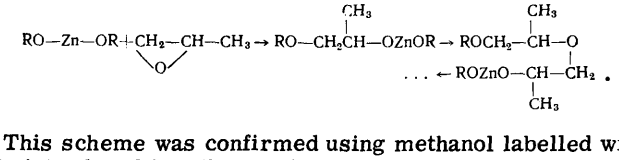
Analysis of the material balance from the optical rotation of the polymer and the activated monomer indicated that in the amorphous fraction of the polymer the influence exerted on the rotation by the bornyl group entering the polymer as terminal group cannot be neglected, since the molecular weight of this fraction is low. For the crystalline polymer, on the other hand, this influence can be neglected, in view of the high molecular weight.

The calculation is based on the formula[62,94]:

$$A\alpha_M = KP_x[\alpha_x],$$

$$K = \frac{[\alpha_{ML}]}{[\alpha_{pL}]} \cdot \left(1 + \frac{P_S[\alpha_S] + P_A[\alpha_A]}{P_x[\alpha_x]}\right),$$

where $[\alpha_{ML}]$ and $[\alpha_{pL}]$ are the specific rotations of the pure L-monomer and the polymer, A the ratio of the returned monomer to the original monomer, P_x, P_S, P_A and $[\alpha_x]$, $[\alpha_S]$, $[\alpha_A]$ the yields in per cent and the specific rotations of the crystalline, semi-crystalline, and amorphous fractions of the polymer; and $[\alpha_M]$ the specific rotation of the returned monomer. Calculation on the basis of the experimental data[62,94] showed that the plot of $P_x[\alpha_x]$ against $M[\alpha_M]$ is a straight line, indicating that K in the equation is constant, and hence that the optical activity of the polymer appears as a result of the polymerisation of the (+)-isomer in the racemate. The fact that the (+)-bornyl group can enter the fraction with low molecular weight in the polymerisation process follows from the mechanism of the initiation:



This scheme was confirmed using methanol labelled with ^{14}C, introduced into the catalytic system.

The radioactivity was found chiefly in the fraction with low molecular weight ($\bar{M}_n$ = 6100) and to a slight extent in the fraction with high molecular weight ($\bar{M}_n$ = 50 000). Thus the alcohol radical enters chiefly the amorphous fraction of the polymer. Its optical activity is due to the introduction of the bornyl group, whose rotation in chloroform is positive, like that of bornyl alkyl ethers.

Experimental data[90] obtained with the $Zn(C_2H_5)_2$–(+)-borneol catalytic system show that the optical activity of the monomer increases with time as far as 70 h, and then decreases, like the proportion of crystalline fraction. The optical activity of the polymer, however, increases slightly with duration of polymerisation, and the value of $[\eta]$ does not show a definite pattern, although it changes in the same sense as the change in the specific rotation of the polymer.

Livshits and Krylov[11–13], following Price, tried to initiate the stereo-elective polymerisation of DL-propene oxide by modifying magnesium oxalate with the (−)-isomer of propene oxide or the (−)-polymer.

The influence of added polymer on the rate of polymerisation was examined above; this is also observed in the polymerisation of benzofuran[32,95], but the effect can evidently also be expected when stereoregular structures with sufficiently high molecular weight are formed in polymerisation. In this instance there is in fact an intensification of the stereospecificity of the action of the catalytic system when the optically active polymer is introduced during polymerisation.

In the example studied[11–13], the addition of polymer to the catalyst did not lead to asymmetric polymerisation, but it nevertheless facilitated the formation of a crystalline stereoregular structure in the optically inactive polymer.

Magnesium oxide and iron oxide modified with D-tartaric acid polymerised DL-propene oxide in 18% yield with the formation of a crystalline fraction of polymer with low optical activity: $[\alpha]_D^{20} = 1.4° \pm 0.3°$ and $[\eta] = 0.57$. Magnesium oxalate was modified with D- and L-propene oxide and used in the polymerisation of the racemic epichlorohydrin. This did not lead to a stereo-elective process; the polymerisation of each monomer was kinetically independent. Only magnesium tartrate proved to be an effective catalyst (Table 7).

Table 7. Stereo-elective polymerisation of DL-propene oxide on magnesium tartrate[11–13].

Magnesium tartrate, g	*dl*-Propene oxide, g	Degree of conversion, %	Polymer	
			$[\alpha]_D$, deg	$[\eta]$
0.223	4.352	10.3	−9.2	0.03
0.153	4.472	4.32	−15.6	0.24
0.690	8.368	1.67	−27.4	0.11
0.816	6.764	2.08	16.1	0.53

In the first stages of the reaction, the polymer obtained is optically pure, but its optical purity subsequently decreases. An analogous phenomenon was also observed in the polymerisation of benzofuran[96], and this can be attributed to the stage of asymmetric initiation, and not asymmetric growth. Attempts to carry out the stereo-elective polymerisation of DL-propene oxide on iron tartrate and magnesium glutamate were unsuccessful. Magnesium tartrate proved to be an effective dissymmetric catalyst, capable of bringing about not only the polymerisation of optical isomers, but also the stereo-elective polymerisation

of racemate with the formation of polymers with a high degree of optical purity (Table 7). (The specimen obtained by Price[86], with $[\alpha]_D = -28.6°$, was taken as the optically pure polymer.) In the series of catalysts magnesium oxide–magnesium oxalate–magnesium tartrate, the specific catalytic activity decreases (30 : 20 : 1), due to the increasing degree of screening of the magnesium ion, which is regarded as the active centre[11], by the organic anion. A coordination reaction mechanism, involving chemisorption of the monomer molecule and the formation of a bond between the oxygen of the ring and the coordinatively unsaturated metal ion on the catalyst surface, is assumed. Because of steric hindrance, coordination and growth are possible only when anion vacancies are present. In the oxalate these vacancies are symmetric, whereas in the D-tartrate the vacancies are dissymmetric, and this is responsible for the stereo-elective character of the polymerisation of propene oxide. The importance of anion vacancies is also emphasised in the examination of the mechanism of action of Ziegler–Natta catalysts[9,97]. This view differs essentially from earlier views[98], according to which the stereospecificity of heterogeneous polymerisation catalysts is associated with a regular crystal lattice, and lattice defects can have only a negative influence on the stereospecificity of the catalyst.

Japanese workers were able to obtain reproducible results in the stereo-elective polymerisation of DL-propene oxide on a diethylzinc–borneol catalytic system, and this enabled them to undertake a detailed study of the mechanism of stereospecific catalysis and an investigation of the part played by asymmetric adsorption.

Tsuruta and coworkers[63] studied the "copolymerisation" of the D- and L-isomers using a stereo-elective catalytic system and, for comparison, using the non-specific catalyst KOH. Neither KOH nor $Zn(C_2H_5)_2$–CH_3OH exhibit stereoselectivity, and in the polymerisation of (+)-propene oxide the original monomer and the returned monomer have the same specific rotation. The plot of $[\alpha]_D$ for the non-fractionated polymer against $[\alpha]_D$ for the original monomer is a straight line for both catalysts, and if racemisation takes place in the reaction, it does so to an equal extent on KOH and $Zn(C_2H_5)_2$–CH_3OH.

When $FeCl_3.C_3H_6O$ was used as catalyst, the monomer with $[\alpha]_D = +15°$ gives a polymer with $[\alpha]_D^{20} = +17°$ (chloroform), that is, with a higher degree of racemisation than that in the example studied[63]. If the polymer is fractionated, the more crystalline fraction has a higher specific rotation than the amorphous fraction, so that the quantity of D-isomer entering the crystalline polymer is greater than that corresponding to the D/L ratio in the original monomer.

This is due to the fact that for a ratio D/L > 1 in the monomer, the rate of formation of a bond between the D-molecule and the active centre D* will be greater than the rate of formation of a bond between the L-molecule and this centre, so that $k_{DD}* > k_{LD}*$, despite the fact that the numbers of D*- and L*-centres on the non-specific catalyst [KOH or $Zn(C_2H_5)_2$–CH_3OH] are equal[63]. As a result, the ratio D/L in the polymer is greater than that in the monomer. Thus on a non-stereospecific catalyst $k_{DD}*k_{LD}* = k_{LL}*k_{DL}*$, whereas on a specific catalyst this equality is not observed, and the distribution of the D*- and L*-centres will be unsymmetrical.

Not only alcohols, but also ethers and amines[99], can be used as optically active modifying co-catalysts for carrying out "asymmetrically selective polymerisation".[66]

Stereo-elective power is also shown by a catalyst consisting of the reaction mixture of the partial hydrolysis of the $FeCl_3$–C_3H_6O catalyst, carried out in the presence of *d*-bornyl ethyl ether (*d*-BEE). This system was found to be highly effective and led to optical activation of the unreacted propene oxide with the formation of a crystalline polymer which, to the surprise of the authors, was found to be optically inactive. This phenomenon is so interesting that it is worth considering in more detail.

The catalyst was prepared by the Pruitt–Baggett and Price methods[69], after which *d*-BEE and water were added. The optimum Fe : H_2O : BEE ratio was found to be 1 : 1.5 : 0.5 (the returned monomer in this instance had $[\alpha]^{13} = +1.94°$, but the crystalline and amorphous fractions of the polymer were optically inactive). The rotation of the monomer increased with time, from +0.22° (1.4% activation) to 1.19° (7.9% activation).

Thus the (−)-isomer polymerises more rapidly, but the numbers of units with the *d*- and *l*-configurations in the polymer are equal and the polymer does not show optical activity.

The discovery by Furukawa and coworkers[66] of asymmetric adsorption on the catalytic system studied is of extreme importance. When DL-propene oxide was added to the system at −20°C, the excess distilled off in a vacuum, and the adsorbed quantity displaced by the addition of triethylamine, the propene oxide fractions obtained had optical rotations with different sign: $[\alpha]'_D = +0.084°$ and $[\alpha]''_D = -0.42°$.

It can thus be seen that the concentration of (−)-isomer on the surface of the complex is greater than that of the (+)-isomer, and the sign of rotation corresponds to the antipode which is polymerised at a greater rate by the given catalytic system. Thus asymmetric adsorption is one of the chief factors determining the reactions of *d*- and *l*-isomers. Kinetic treatment of the results showed that the ratio of the rates of polymerisation is close to the ratio of the isomers adsorbed on the catalyst.

The reaction takes place by a coordination-anionic mechanism, in which the monomer is first coordinated to the active centre (activated by adsorption), after which opening of the epoxide ring takes place. This can be represented by the scheme:

$$D \underset{}{\overset{K_D}{\rightleftarrows}} D_{ad} \xrightarrow{k_D} \text{polymer}$$

$$L \underset{}{\overset{K_L}{\rightleftarrows}} L_{ad} \xrightarrow{k_L} \text{polymer}$$

where K_D and K_L are the constants for the adsorption equilibrium, and k_D and k_L the rate constants for opening of the ring.

The rate of polymerisation is proportional to the concentration of adsorbed monomer, that is

$$\frac{dD}{dL} = \frac{k_D[D_{ad}]}{k_L[L_{ad}]} = \frac{k_D K_D[D]}{k_L K_L[L]},$$

or

$$\ln\frac{D}{D_0} = \frac{k_D K_D}{k_L K_L}\ln\frac{L}{L_0} = r\ln\frac{L}{L_0},$$

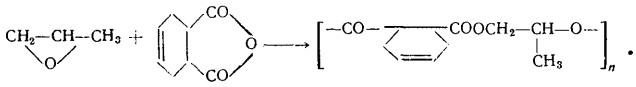
$$r_0 = \frac{k_D K_D}{k_L K_L},$$

where D_0 and L_0 are the initial concentrations of the isomers of the monomer, and r the selectivity index of the process. The inequality of the rates of polymerisation of the *d*- and *l*-isomers is controlled chiefly at the coordination (adsorption) stage. The selectivity index of the process depends essentially on the composition of the catalyst. The optimum Fe : H_2O : *d*-BEE ratio is 1 : 1.5 : 0.5, at which $r = 1.71$. The selectivity of the catalyst r increases with

increase in the water concentration and decreases with increase in the concentration of $FeCl_3$ and *d*-BEE. A second interesting observation made by Furukawa and coworkers[66] was the absence of optical activity in the polymer. Since there can be two forms of adsorption: (1) selective adsorption, when there are unequal quantities of D- and L-centres on the catalyst surface, and (2) non-selective adsorption, when the entire surface of the catalyst is equally accessible to the D- and L-molecules of the adsorbate, four states are possible, depending on whether the quantities of adsorbed D- and L-molecules are equal or unequal (non-equilibrium). Moreover, at the stage of ring opening there are four possibilities: (1) preservation of the configuration, (2) inversion of the configuration, (3) racemisation and stereospecific growth of the chain, and (4) racemisation and non-stereospecific growth of the chain. ("Racemisation" here denotes not conversion of an isomer of the monomer into the racemic monomer, but the formation of equal quantities of *d*- and *l*-units in the chain from the *d*- or *l*-monomers.) Path (3) gives equal quantities of the *d*- and *l*-polymers, whereas path (4) gives a stereoregular polymer consisting of equal quantities of *d*- and *l*-units.

In the diethylzinc–(+)-borneol and diethylzinc–water–(+)-BEE systems, processes of selective non-equilibrium coordination take place with preservation of the configuration (the formation of optically active monomer and polymer with regular structure) and racemisation with non-stereospecific growth of the chain (the formation of optically active monomer and inactive and non-regular polymer).[109]

Since propene oxide readily undergoes asymmetric selective polymerisation, it may be expected that asymmetric copolymerisation of propene oxide with another monomer having an asymmetric carbon atom will take place successfully[101]. Thus DL-propene oxide and 3-phenyl-Δ^4-tetrahydrophthalic anhydride copolymerise under the influence of 2% diethylzinc–(+)-borneol catalyst in toluene at 80°C. The copolymer (yield 49.9%) had $[\alpha]_D^{25} = +2.9°$ for a duration of reaction equal to 108 h. The rotation of the polymer, and its viscosity, increase with duration of the reaction.



The unreacted propene oxide and the propene glycol obtained by hydrolysis of the polymer were optically inactive, whereas the unchanged anhydride (isolated as the monomethyl ester) had a rotation between +1.4° and +1.7°. The dicarboxylic acid obtained by hydrolysis of the polymer was also optically active (between −0.4° and −0.5°). This unexpected result is most readily explained by assuming that the asymmetric centres of the catalyst directly activate the anhydride, which displaces the propene oxide from the D- and L-centres by adsorption.

Tsuruta and coworkers[102–105] extended stereo-elective polymerisation to the synthesis of optically active polyalanine from *N*-carboxy-DL-alanine anhydride (I), which polymerises under the influence of compounds containing active hydrogen, to form a water-soluble polypeptide. Organometallic compounds were recently used for the polymerisation of L-(I) to give a high polymer[106]. It was found that the use of even one component of the catalytic systems studied, for example, (+)-borneol or (−)-menthol as catalyst made it possible to obtain, from DL-(I), a macromolecular optically active polyalanine, which was (+) in dichloroacetic acid (DCAA) and (−) in a chloroform–DCAA mixture; the water-insoluble fraction had a high rotation (+1.3° and −1.0°).

The use of the triethylaluminium–(+)-borneol (in the ratio 1 : 2) system gave the same results: a water-insoluble fraction with $[\alpha]_D = +1.2°$ (DCAA) and $[\alpha]_D = -0.4°$ (chloroform–DCAA) was obtained in 29.5% yield.

VII. THE STEREO-ELECTIVE POLYMERISATION OF DL-α-ALKENES

Stereo-elective polymerisation has also been used successfully in the field of poly-α-alkenes. Here, two mechanisms are possible: (1) the "selection" of one of the enantiomorphs of the monomer is regulated by the asymmetric group of the chain—the alkyl group of the catalyst or the first monomeric unit, and (2) the difference in the rates for the enantiomorphs is due to the asymmetry of the active centre of the catalyst, produced as a result of appropriate arrangement of the surface atoms or by inclusion of asymmetric organic groups in the active centre.

The first possibility might be verified by comparing the optical activity of polymers from racemic 4-methylhexene and propene on an optically active catalyst. In actual fact, using a $TiCl_3$-[(+)-(*S*)-2-methylbutyl]$_3$Al.O$(C_2H_5)_2$ catalyst (optical purity 91%), Pino and coworkers[52] were able to detect optical activity in polypropene and polystyrene. Although the values found for the rotation of polypropene and polystyrene are very small, they are slightly greater than the values given by Braun and Kern[21]: +0.1 ± 0.003° for isotactic polystyrene and 0.12° for amorphous polystyrene. It should be noted that earlier, Murahashi and coworkers[20] had not detected rotation under these conditions, and Fray and Robinson[22] had not observed rotation for polypropene, either in the polymer or in the fragments obtained by pyrolysis of the polymer. Pino[52] attributed the discovery of slight activity in polypropene and polystyrene to the high optical purity of the 2-methylbutyl group in the catalyst which he used, and to the more successful selection of polymerisation conditions. In experiments at atmospheric pressure, the polypropene fractions with low molecular weight had $\alpha_D = +0.025°$ (*l*1) and $[\alpha]_D = +3.9°$, whereas the corresponding values at 10 atm were $\alpha_D = +0.05°$ (*l*1) and $[\alpha]_D = +0.90°$. For polystyrene with (*R*)-2-methylbutyl-lithium/tris(acetylacetonato)chromium catalyst the values $\alpha_D = +0.105°$ (*l*2) and $[\alpha]_D = +0.6°$ were obtained for the fraction with low molecular weight.

The stereo-elective polymerisation of racemic 4-methylhexene on a $(C_5H_{11})_3Al$–$TiCl_3$ catalyst gave an optically active polymer whose $[\alpha]_D$ value did not depend on the stereoregularity, but only on the monomer: $(C_5H_{11})_3Al$ ratio (the best result was obtained at a ratio 1 : 4) and on the molecular weight: $[\alpha] = 1.1°$ at $[\eta] = 0.15$ and falls to zero with increase in $[\eta]$ to 2.05. The highest rotation was found in the amorphous fraction, soluble in acetone: $\alpha_D = +0.095°$, $[\alpha]_D = +7.1°$.

Since one antipode entered the racemate preferentially during polymerisation, activation of the unreacted monomer due to the excess of the antipode remaining might have been expected. It was found, however, that the monomer remained inactive. Other dissymmetric catalysts were studied: [(*R*)-2-methylbutyl]Li–$TiCl_4$, [(*S*)-2-methylbutyl]$_2$Zn–$TiCl_4$, and [(*S*)-4-methylhexyl]$_3$Al–$TiCl_4$. The specific rotation of the poly-4-methylhexene fraction soluble in acetone had the values +0.7°, 13.6°, and 4.6° respectively.

Fractionation of the polymer obtained using the [(*S*)-C_5H_{11}]$_2$Zn–$TiCl_4$ catalyst gave an amorphous fraction with

$\alpha_D = +1.385°$ (*l*1) and $[\alpha]_D = +15.2°$, and a fraction with high molecular weight, with $\alpha_D = +0.030°$ and $[\alpha]_D = +1.7°$. The unreacted monomer had $\alpha_{350} = +0.045°$.

Examination of these results shows that the optical activity in polypropene and polystyrene can arise only from the introduction of terminal groups from the catalyst. At a high catalyst: monomer ratio, optical activity may appear not only in the amorphous fractions but also in the isotactic fractions. Thus the optical activity in the polymers depends not on the stereoregularity, but chiefly on the molecular weight of the fractions.

The fact that the poly-(4-methylhexene) obtained by stereo-elective polymerisation from the racemic monomer had a value of $[\alpha]_D$ comparable with the values for polypropene and polystyrene, and smaller by a factor of 10–100 than the value for poly-(*S*)-4-methylhexene obtained from the optically active monomer, and also the absence of rotation in the unreacted monomer, evidently indicate that the reaction rate is the same for both antipodes and that the catalyst groups are introduced as alkyl terminal groups into the polymer chain. Moreover, for the experiments using $TiCl_4$–$Zn(C_5H_{11})_2$ catalyst, when the greatest rotation of the polymer was observed, it may be assumed that the terminal groups themselves also have an influence by asymmetric induction, which according to calculation by Brewster's method[57] should be considerable. Despite its low efficiency, a method for the stereo-elective polymerisation of poly-α-alkenes has been patented[48–50].

The polymerisation of racemic 3,7-dimethyloctene and 3-methylpentene on a $(C_5H_{11})_2Zn$–$TiCl_4$ catalyst is stereo-elective, and the unreacted monomer remaining shows appreciable optical activity[54]. The optical activity of the polymer fractions increases with increase in stereoregularity, in contrast with cases where the activity decreases and is due to terminal groups.

Table 8. Stereo-elective polymerisation of racemic 3-methylheptene and 3,7-dimethyloctene on a $TiCl_4$-di-(+)-2-methylbutylzinc catalyst.

Monomer	Unreacted monomer		Polymerised monomer			Optical purity of polymer, %
	α_D^{25}	$[\alpha]_D^{25}$	(*S*)	(*R*)	(*S*)/(*R*)	
3-Methylheptene	−0.07 (*l* 2)	−0.75	0.15	0.10	1.5	5.5
3,7-Dimethyloctene	−0.20	−0.28	0.20	0.16	1.25	9.97
	−0.36	−0.52	0.46	0.37	1.24	1.6

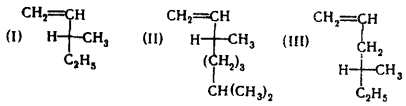
The sign of rotation of the monomer indicated that the polymerisation involves the (*S*) antipode, which has the same absolute configuration as the optically active (*S*)-2-methylbutyl group in the catalyst, whereas the excess of monomer remaining has the (*R*) configuration (see Table 8).

The (*S*)/(*R*) ratio characterises the rates of polymerisation of the antipodes in the racemate. Fractionation of poly-(3,7-dimethyloctene) gave a polymer insoluble in diisopropyl ether and soluble in cyclohexane, with $[\eta] = 0.91$ and $\alpha_D = 0.11°$ ($[\alpha]_D = +18.0$). After the fractionation of poly-(3-methylpentene), the most stereoregular fraction had $\alpha_D = 0.17°$ and $[\alpha]_D = +13.4$, whereas the fractions with low molecular weight had high rotation (+16.9°).

It was previously found that the stereo-elective polymerisation of racemic poly-(4-methylhexene) gives a polymer from which fractionation gives fractions whose optical activity decreases with increase in stereoregularity.

Stereo-elective polymerisation was achieved by Goodman and coworkers[107] using a catalyst obtained by the action of $LiAlH_4$ on *R*(−)-3,7-dimethyloctene (formation of the compound $LiAlR_4$) in its compound with $TiCl_4$. The action of this catalyst on racemic 3,7-dimethyloctene led to selective polymerisation, which depended on the value of $[\alpha]$ (between −8.3° and −11.74°) of the monomer in the catalyst, and the monomer/catalyst ratio (from 7.6 to 84.0). The specific rotation of the polymer increased from −49.6° to −83.3°.

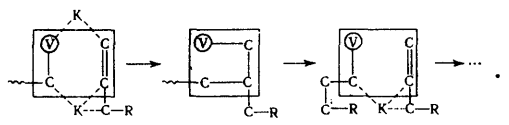
These results show that the structure of the monomer plays an important part in stereo-elective polymerisation. The catalyst is able to selectively remove one antipode from the racemate if the asymmetric atom is in the α-position to the double bond, for example, in 3-methylpentene (I) and 3,7-dimethyloctene (II); asymmetric stereo-elective polymerisation does not take place if the asymmetric atom in the side-chain is in the β-position, as in 4-methylhexene (III):



The problem of the detailed mechanism of asymmetrisation in stereo-elective polymerisation can be resolved by accumulating sufficient experimental data, but it can already be assumed that of the two mechanisms: (1) that in which the (*S*)-C_5H_{11}-group in the catalyst takes direct part in the asymmetric initiation of the polymer chain, and (2) that in which the (*S*)-C_5H_{11}-group modifies the active centre of the catalyst on which the preferential adsorption of one antipode of the monomer takes place on the transition metal, the latter is to be preferred[55], since this does not require the introduction of the concept of highly efficient 1,3-asymmetric induction with transfer along the chain of 1,3-carbon atoms. This is necessary, however, if we adopt the first scheme, which is similar to Cram's model of 1,3-asymmetric induction[108].

In actual fact, vinyl polymerisation gives 1,3-pseudo-asymmetric atoms in the chain; a polymer formed by a mechanism of 1,3-asymmetric induction will show the sequence $(ddd\ldots)_n(lll\ldots)_m$, whereas for induction due to the asymmetry of the catalytic asymmetric centre the sequence $(ddd\ldots)_n l(ddd\ldots)_m$ should predominate, that is there should be a much higher probability (p) of formation of sequences with the same configuration ($p_{dd} \gg p_{dl}$ or $p_{ll} \gg p_{ld}$), and with stereo-isomeric centres in the catalyst $p_{dd} \neq p_{ll}$.[109]

If we accept Cossee's ideas[9] regarding the part played by vacancies in polymerisation catalysis, we can picture the following mechanism, using the multiplet theory of catalysis:



Ⓥ - represents a vacancy

For α-alkenes, the adsorption of the C of the asymmetric centre outside the index is small, and the polymer is formed with preservation of the configuration[110].

Propene oxide, as a result of the strong adsorption of a carbon atom on a centre close to a vacancy, undergoes inversion of configuration (always observed for alkylpropene oxide and polypropeneimine) and the efficiency of the stereo-elective process should be slightly greater.

The concept of modification of the active centres of the catalyst by the asymmetric component is apparently more correct. This is confirmed, for example, by the stereo-elective polymerisation of racemic propene oxide when previously prepared active poly(propene oxide) is introduced on to the catalyst, as indicated above. "Autocatalysis" with benzofuran is also apparently due to some extent to this modification. The stereo-elective copolymerisation of racemic (*R*)(*S*)-3,7-dimethyloctene and (*R*)-(+)-methylpentene† can probably also be attributed to this morphological catalysis. In this connection, mention should be made of the production of asymmetrising properties in Raney nickel catalyst after modification with optically active compounds[111-113].

In conclusion, it should be noted that the high efficiency of stereoselective and stereo-elective polymerisation and the chromatographic separation of racemic polymers on other optically active polymers under conditions in which compounds with low molecular weight did not give these effects, apparently confirms Pasynskii and Pavlovskaya's view[114] that in nature, asymmetry has developed not by the formation of optically active compounds with low molecular weight, which then act as monomers, but initially by a process in which stereospecific polymerisation has led to the formation of stereoregular and then dissymmetric catalysts, on whose basis the optical asymmetry of compounds with low molecular weight began to develop, so that the origins of the latter are secondary.

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Since the present manuscript was submitted for publication, a number of new papers on asymmetric catalysis in the field of optically active polymers, including a number of particular interest[122-127], have been published[115-121].

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Macromolecular Complexes as Chemical Reaction Catalysts

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The wide potential applications of catalysis by macromolecular compounds have aroused universal interest in this relatively new branch of chemical science: the number of publications devoted to this problem has been growing continuously since the 1950's. Thus, many papers have dealt with the use of sulphonic acid resins as catalysts for hydrolysis and esterification, hydration and dehydration, alkylation, and also various condensations (see review by Polyanskii[1], recent Japanese work[2], etc.). A substantial fund of knowledge has accumulated also on the use of macromolecular catalysts and initiators in polymerisation reactions. For example, the above sulphonic acid resins have been used as polymerisation catalysts for isopentene, butene, dienes[1] and vinyl alkyl esters[3]. Macromolecular radicals obtained by chain transfer reactions[4], illumination, mechanical methods[5], or by chemical changes of reactive groups[6] are already used extensively in the synthesis of graft or block copolymers. These and other polymer systems can be synthesised also on macromolecular anions obtained as macromolecular Ziegler-Natta catalysts[7], macromolecular anion-radicals, or dianions[8], on macromolecular organometallic compounds of the polylithiumpolystyrene[9] or polylithiumpolyethylene[10] type, etc.
Papers on the catalysis of reactions by macromolecular complexes relate to the same field of research. The present review, without attempting to be fully comprehensive, deals with the most important papers (published up to 1968) on the catalysis of organic and of inorganic reactions by macromolecular complexes. For comparison, low-molecular-weight complexes are considered in a number of instances. 84 references.

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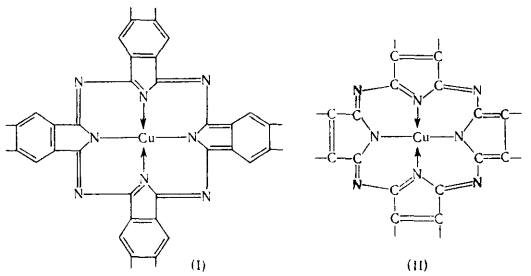
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1. REDOX REACTIONS AND DECOMPOSITIONS

Since the earliest days of the study of catalysis by macromolecular complexes, the catalytic action of these materials towards various oxidation–reduction reactions has attracted most attention†. Among the first papers to be published in this field were those of Roginskii and coworkers[11,12], who studied the catalytic properties of macromolecular chelates with a system of conjugated bonds.

Thus, Roginskii and coworkers[11] investigated the activity of a series of poly(copper phthalocyanines) having different electrophysical properties towards the decomposition of H_2O_2. The greatest catalytic activity was found in the polyphthalocyanine which had the highest electrical conductivity at room temperature and the lowest activation energy for electrical conduction. The lowest activity was observed with the polymers of lowest electrical conductivity and highest E_{act}. The authors attempted to correlate the electrophysical properties and the catalytic activity of these polyphthalocyanines. They also attempted a correlation in their study of the oxidation of alkylaromatic and cyclic hydrocarbons on macromolecular phthalocyanines[12].

These workers compared the rates of oxidation of various hydrocarbons on copper phthalocyanines of type (I), and also the catalytic activity of polymeric and monomeric copper phthalocyanines towards the oxidation of cumene to the hydroperoxide, with the activity of polymeric complexes of tetracyanoethylene and copper, which are presumably macrocyclic azoporphyrin structures of type (II):



(I) (II)

It was found that the polyphthalocyanines are more active than their monomeric analogues and that the tetracyanoethylene polymers are more active than the polyphthalocyanines: the underlying reasons were not discussed. Manecke and coworkers[13] also examined polychelates of this type, prepared from metal acetylacetonates and tetracyanothiophen (or tetracyanofuran), *p*-phenylenedimalononitrile, or *o*-phthalodinitrile.

To explain the mechanism of the catalytic action of macromolecular complexes with conjugated bonds, Berlin and coworkers[14] suggest that the presence of acetylacetonate residues in the azoporphyrin structures (II) causes initiation of a chain decomposition of the polymer with formation of peroxide radicals. These workers conclude that in the oxidation of, for example, cumene, in the presence of poly(copper phthalocyanine), oxygen must be present as

† Data on the catalytic properties of low-molecular-weight complexes have long been available: for convenience in presentation we shall discuss them and compare them with the catalytic properties of macromolecular complexes of similar structure;