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Faculty of Chemistry,
Chernovtsy State University

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SYNTHETIC OPTICALLY ACTIVE POLYMERS

I. N. Topchieva

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I. INTRODUCTION

Recently a new field of study has arisen in the chemistry of monomers, associated with the synthesis of optically active polymeric substances. Their synthesis and the study of their properties are of great theoretical and practical interest. From the theoretical standpoint, asymmetric synthesis of polymers constitutes a higher type of control of stereoregularity, compared with the synthesis of the usual regular crystalline polymers. It represents a further advance in the control of the synthesis of macromolecular materials. The synthesis of optically active polymers has introduced into polymer chemistry a new parameter — the specific rotation of polymers which is due to the presence of uncompensated asymmetry and constitutes the overall stereochemical result of the reaction. The studies of the changes in the optical rotation of the polymer as a function of polymerisation conditions makes it possible to establish the relation between the specific rotation, structural regularity, and the molecular weight of the polymer. Investigation of the optical activity of the degradation products of optically active polymers can reveal the steric relations which obtain between the monomer, the catalytic system, and the polymer.

On the other hand, successful synthesis of optically active polymers in the presence of small amounts of an asymmetric cocatalyst constitutes a first approximation to the modelling of processes in nature, where protein molecules are formed in the presence of small amounts of highly specific enzymes as a result of a series of complex consecutive reactions.

Since optically active polymers and oligomers have highly specific structures, they may prove important as components of very selective catalysts in polymerisation and polycondensation processes and they may also be used in the asymmetric synthesis of small molecules, as model systems in the study of biocatalysis, and as adsorbents for the separation of racemic mixtures.

Optically active polymers prepared from optically active monomers exhibit improved mechanical properties and thermal stability compared with polymers synthesised from the analogous racemic monomers, which is of undoubted practical interest. In recent years optically active polymers have been increasingly attracting the attention of investigators. This interest was stimulated, on the one hand, by the study of the structural features of proteins and nucleic acids in solutions and, on the other hand, by the advances in stereospecific polymerisation. Up to 1956 there were only seven papers on optically active polymers, while in 1961 alone about thirty publications appeared, including a number of reviews[1-4].

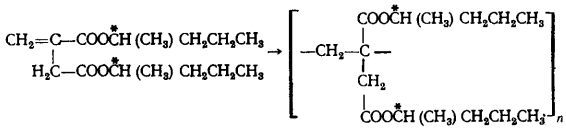
There exist three fundamental approaches to the study of optically active polymers. One of them is associated with the determination of the laws governing the asymmetric synthesis of macromolecular substances, the second deals with the study of the properties of optically active polymers, and finally, the third is concerned with the application of optically active labels in experiments designed to solve a wide range of problems in polymerisation chemistry: elucidation of the nature of active centres in catalytic systems, the conformation of macromolecules in solution, the microtactic properties of chains, the polymerisation kinetics, etc.

The author has attempted to elucidate mainly the first and the last of these problems. She wished to demonstrate the wide variety of possible uses of the optically active label; by virtue of its simplicity and availability, the procedure based on such labelling will undoubtedly form part of the arsenal of the methods available in polymer chemistry.

II. SYNTHESIS OF OPTICALLY ACTIVE POLYMERS FROM OPTICALLY ACTIVE MONOMERS AND THEIR PROPERTIES

There is nothing new in the polymerisation of optically active polymers compared with the usual stereospecific polymerisation apart from the use of the optically active monomers themselves. The resulting polymer is optically active only if the reaction does not involve the asymmetric centres of the molecule and hence racemisation does not take place.

In 1896 Walden[5] achieved the polymerisation of the optically active ester of itaconic acid, in which the asymmetric carbon atoms are located in the ester groups:



The optical rotation of the polymer is of the same order of magnitude as that of the monomer.

1. Optical Activity of High-Molecular Compounds

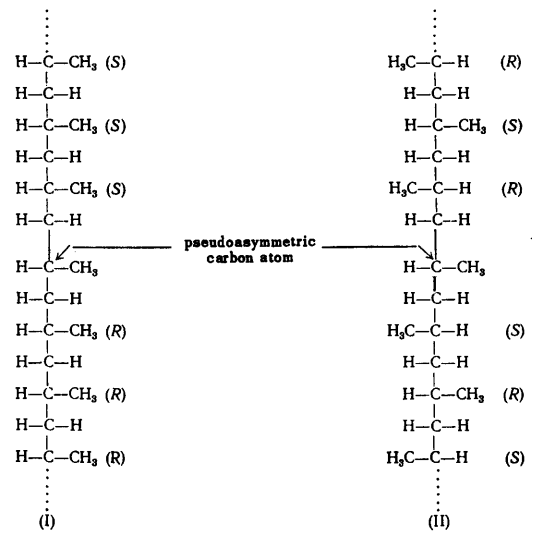
The optical activity of polymers is usually expressed in terms of the specific rotation $[\alpha]$ and the molar rotation $[M]$ which are defined by the following formulae:

$$[\alpha]=\frac{\alpha\cdot 100}{l\cdot c}\;;\quad [M]=[\alpha]\cdot\frac{M}{100}\,,$$

where α is the measured angle of optical rotation (in degrees), l the thickness of the layer of substance (in decimeters), c the concentration of the solute (in grammes per 100 ml of solution), and M the molecular weight of the polymer unit.

It should be borne in mind that the observed optical activity is a fairly complex sum of contributions due to different factors. The principal factors are as follows: optically active side groups, the primary structure determined by the covalent bonds in the chain or the configuration of the macromolecule, and the secondary structure (or chain conformation) determined by steric, non-valence interaction of the side-group.

Consideration of the chain of stereoregular polymers of the vinyl type $(-CH_2-CHR-)_n$ readily shows that, owing to the stereochemical characteristics of the asymmetric carbon atom in the main chain, the primary structures in both iso- and syndio-tactic polymers are symmetrical and cannot contribute to the optical rotation of the polymer. Indeed the chain of the syndiotactic polymer (II) formed by a regularly alternating sequence of (R)- and (S)-configurations of the asymmetric atoms† is internally compensated. In the case of the isotactic sequence of chain units (I) the asymmetry of the carbon atoms in -CHR- groups is due to the differences in the lengths of the segments of the polymeric chain joined to them. Since the immediate environment of the asymmetric atoms in each -CHR- group (apart from those nearest to the ends of the chain) is almost symmetrical, such polymers have numerous symmetry planes and are therefore optically inactive.

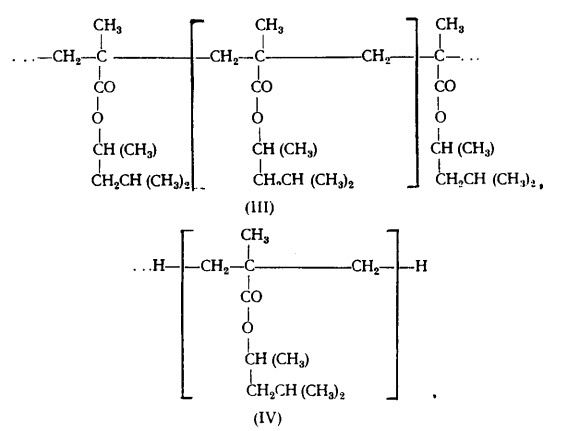


An atactic polymer formed by randomly alternating (R)- and (S)-asymmetric centres constitutes a random "meso-form" which cannot possess optical activity.

Thus comparison of the optical activities of polymer solutions with the rotation of the monomers or model compounds makes it possible, in principle, to determine the conformational contribution to the rotation and to assess on this basis the nature of the secondary structure of the macromolecule in the solution.

2. The Use of Optically Active Monomers in the Determination of the Conformation of Macromolecules in Solution

The first attempt to analyse the rotatory power of polymers was made by Arcus and West[6], who compared the optical activity of the polymers of 1,3-dimethylbutyl (+)-methacrylate (III) with the activity of the model compound 1,3-dimethylbutyl pivalate (IV). The algebraic difference between the molar rotations of the polymer and the model compound proved to be negative and equal to one third of the rotation of the model compound. The authors suggested that the observed change in rotation is associated with the presence of helical sections in the macromolecules in solution:



† For the nomenclature, see E. L. Eliel, "Stereochemistry of Carbon Compounds" (Translated into Russian), Izd. Mir, Moscow, 1965 [McGraw-Hill, 1962].

Natta and coworkers[7] showed that in the crystalline regions all isotactic polyolefins exist in the form of rigid right- and left-hand helices. In the polymerisation of olefins without optically active side-groups, the amount of different enantiomorphic forms of the helices is the same and therefore the polymer as a whole is optically inactive. On the other hand, if the polymer is crystallised under conditions which favour the preferential formation of a particular type of helix, such structures acquire optical activity[8]. Dissolution of a crystalline polymer results in the breakdown of long, well formed helices. It has been demonstrated experimentally[9] and theoretically[10] that small sections with helical conformations persist also in solution, i.e. the one-dimensional short-range order in the macromolecules in solution is in most cases similar to the one-dimensional long-range order in the crystalline state. The maintenance of one-dimensional long-range order in a free macromolecule requires the presence of intramolecular forces capable of resisting the disorienting effect of thermal motion. In polypeptides such forces are the hydrogen bonds between the repeating CO and NH groups which ensure a rigid helical structure of the macromolecules in solution[11]. The forces of steric repulsion between groups cannot by themselves fix rigidly the position of the units of the main chain and prevent the macromolecule from rolling up into a randomly twisted spherical structure.

In their study of poly-α-olefins with optically active side-groups, Pino[12-15], Bailey[16], and Nozakura[17] found that the polymers had a considerably higher optical activity than the monomers (Table 1). The absolute magnitude of the molar optical activity of the isotactic fractions of the polymers is more than ten times greater than the molecular rotation of the analogous low-molecular compounds. The sign of the optical activity of the poly-α-olefins investigated is determined by the absolute configuration of the asymmetric carbon atom of the monomer: all the polymers of (*S*)-α-olefins exhibit positive rotation while the polymers of (*R*)-α-olefins exhibit negative rotation. Goodman and Abe[18-20] observed a similar increase, compared with the monomers, in the optical activity of polymers based on aldehydes and containing the same optically active substituents as the poly-α-olefins discussed above. Very interesting results were also obtained by Ciardelli at al.[21], who reduced the optically active poly-4-methylhex-1-yne with $[\alpha]_D = +2.0°$ to poly-4-methylhexene with $[\alpha]_D = +178°$.

TABLE 1. Comparison of the optical activities of model saturated hydrocarbons with the optical activities of atactic and isotactic fractions of certain poly-α-olefins.

Low-molecular saturated hydrocarbons	$[M]_D^{25}$	Polymer	$[M]_D^{25}$ amorphous or very weakly crystalline fraction	$[M]_D^{25}$ highly crystalline fraction
(*S*)-2,3-dimethylpentane	−11.4	poly-(*S*)-3-methylpent-1-ene	+29.4	+161
(*S*)-2,4-dimethylhexane	+21.3	poly-(*S*)-4-methylhex-1-ene	+116	+288
(*S*)-2,5-dimethylheptane	+11.7	poly-(*S*)-5-methylhept-1-ene	+13.1	+68*
(*S*)-3-methyloctane	+13.3	poly-(*S*)-6-methyloct-1-ene	+12.8	+20*
(*S*)-2,6-dimethyloctane	+14.4	poly-(*R*)-3,7-dimethyloct-1-ene	−20.6	−154

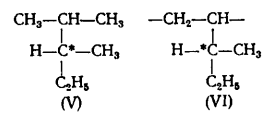
* These data refer to the most isotactic of the soluble fractions.

Pino and coworkers explain the very high optical activities of the poly-α-olefins on the basis of the above hypothesis that there is a helical short-range order in the macromolecules of isotactic polymers. When isotactic poly-α-olefins are formed, left- and right-hand helices are not energetically equivalent, since different sets of conformations of the side-group and different energies of these conformations correspond to a particular configuration of the asymmetric carbon atom in the substituent in the right-hand and left-hand helices and therefore one of the helical forms predominates in the polymers. Calculation of the molar rotation of polymers carried out in one of Pino's studies[14] by Brewster's semiempirical method[22] showed that the sign of the observed optical activity is consistent with the sign of the optical activity calculated for the helical conformation which is associated with the greatest number of rotational isomers in the side-group, i.e. has the smallest free energy.

In view of the approximate nature of the calculations by Brewster's method, the authors were unable to decide finally whether the agreement between the calculated and observed values of $[M]$ is fortuitous or real.

Birnshtein and Luizi[23] made a theoretical study of the conformational structure of the optically active poly-α--hydrocarbons which had been investigated by Pino. They showed that in macromolecules where short-range order extends over several monomer units even a small difference in the free energies of the right- and left-hand helices is sufficient to ensure that the helical conformation of lower energy predominates in the statistically twisted chains.

To elucidate the reasons for the higher optical rotation of polymers, we shall consider, from the standpoint of the conformations, the conversion of a model low-molecular optically active hydrocarbon (V) into a polymeric chain (VI):



(V) (VI)

In low-molecular hydrocarbons the number of possible conformations is fairly large and the magnitude of optical rotation is determined by the algebraic sum of positive and negative conformational rotational contributions which are of a similar value[22]. On conversion to the high-molecular compound at least one of the monomer conformations is "frozen". As a result, the equilibrium constants governing the relative amounts of dextro- and laevo-rotatory conformations in isotactic polymers and low-molecular saturated hydrocarbons differ significantly. The chromophore system of the polymer is the same as that of the monomer. The only chromophore group in these compounds is the C–H bond at the asymmetric carbon atom in the side-group. The maximum number of units in frozen conformations occurs in a helical structure, since the latter corresponds to minimum free energy.

Thus the high values of the optical rotation of poly-α--olefins are associated with the formation of preferred conformations (rigorous steric requirements) at the asymmetric atoms of the side-groups which leads to the formation of left- or right-hand helices. Pino's hypothesis does not contradict the explanation of the high values of the rotation of polymers, compared with the low-molecular

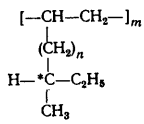
compounds, put forward by Goodman and Abe[20], who believe that the conformational rigidity of polymeric chains is due to the excess of one type of *gauche*-conformation over the others for a given isotactic sequence.

It is interesting to compare the characteristic features of the optical rotation of poly-α-olefins with the rotation of synthetic polypeptides. By virtue of the asymmetry of the helical structure itself, polypeptides, which are present in solution in a spiral conformation, behave optically as a single absorbing system and make a special "helical" contribution to the overall rotation. The optical rotary dispersion of polypeptides in solvents which do not cause appreciable breakdown of hydrogen bonds does not obey Drude's single-term equation[24] but is described by more complex expressions. The factors which influence the conformation of polypeptides (solvent, temperature, concentration of polymer, etc.) also cause a change in the optical rotation of their solutions.

In contrast to polypeptides, the optical rotatory dispersion of polyhydrocarbons in the wavelength range accessible to measurement does obey Drude's simple equation. The concentration[15] of the polymer and the solvent have little effect on the optical rotation. It is noteworthy that the temperature coefficients $\Delta[M]/\Delta T$ for polyhydrocarbons are fairly large (between -0.2 and -0.65) and depend on the stereoregularity of the fractions: they are larger for crystalline structures than for the less regular fractions.

This difference in the behaviour of the optical rotation of these two classes of "helical" polymers can be explained by the fact that the only chromophore group in polyhydrocarbons is the C–H bond at the asymmetric carbon atom in the side-group, whereas in polypeptides the chromophore system of the CO–NH unit linked by hydrogen bonds is located in the main chain. Naturally the factors which influence the stability of the hydrogen bonds in polypeptides cannot affect the conformational composition of optically active poly-α-olefins.

The optical activity of poly-α-olefins depends significantly on their stereoregularity, which is also consistent with the hypothesis of the helical structure of the polymers in solution. Comparison of the optical rotation of the most stereoregular fractions of polymers with the general formula (VII),



(VII),

where n = 0, 1, 2, and 3 shows that the molar rotation is very high for poly-(*S*)-3-methylpent-1-ene (n = 0), reaches a maximum for poly-(*S*)-4-methylhex-1-ene (n = 1), but falls appreciably in the case of higher homologues (Table 1).

Thus the study of the optical activity of polymers in solution is a very sensitive qualitative method, whereby it is possible to demonstrate whether or not sections of the helical structure of isotactic macromolecules persist in solution. Probably the secondary structure of the polymer itself influences the stereoregularity in the course of further polymerisation. Thus in the polymerisation of α-amino-acids such "stereoregulating" influence may arise on formation of an α-helix in which the isotactic distribution is preferred to the atactic distribution as a result of the better steric accommodation of the R-groups in the repeating structural unit *CHR–CONH.

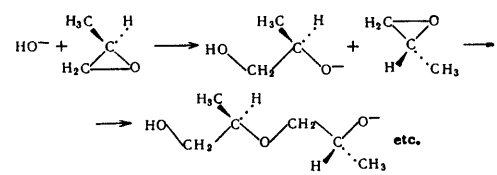
It has been shown experimentally that addition of the D-isomer in the polymerisation of the anhydride of γ-benzyl-*N*-carboxy-L-glutamic acid[11], catalysed by sodium hydroxide, decreases sharply both the rate and degree of polymerisation. This can be explained by the difficulty of incorporation of the D-isomer of the amino-acid as a unit in the growing α-helix formed from the L-amino-acid. In fact the decrease in rate is so considerable that it suggests not only that the unnatural amino-acid fails to be incorporated in the polymer chain but also that the growing chain is partially blocked on encountering the "foreign" monomer. Minoru[25] synthesised polymers by esterifying poly(vinyl alcohol) with an optically active acylamino-acid and determined the dependence of the optical activity on the degree of polymerisation and esterification. He found that the optical activity attained on introduction of a single optically active residue into the side-chain of the polymer is almost constant and independent of the degree of polymerisation and esterification of poly(vinyl alcohol).

In his study of the copolymers of styrene and (-)-menthyl acrylate, Schulz[4] found a rigorous proportionality between the optical activity and the content of the optically active component. This led him to the conclusion that there is no mutual influence of the asymmetric units in the chain. Thus the rotation of polymers and copolymers present as randomly twisted structures in solution may be used to determine their analytical composition.

The synthesis of optically active polymers containing asymmetric non-carbon atoms is of considerable interest. The only study in this field is the synthesis of the optically active poly-(+)-vinylphenyl-α-naphthylsilane achieved by Davydova et al.[26]; unfortunately the properties of the polymer are not described.

3. Polymerisation of Optically Active Propylene Oxide

One of the most thoroughly investigated optically active polymers is poly(propylene oxide) which was synthesised by Price et al. in 1956.[27] They showed that the polymerisation of the L-enantiomorph of propylene oxide takes place by an S_N2 mechanism in the presence of potassium hydroxide, first hydroxide and then alkoxide ions behaving as nucleophilic agents:



The reaction results in the formation of a fully crystalline isotactic polymer. In the presence of ferric chloride, however, a mixture of optically active crystalline and inactive amorphous polymers is obtained. Thus in the polymerisation in the presence of potassium hydroxide asymmetry is preserved to a high degree, while ferric chloride causes partial racemisation which is due to the rupture of the bond between the asymmetric carbon atom and oxygen.

Studies on the stereospecific polymerisation of propylene oxide and the relations between the type and structure of heterogeneous catalysts and the properties of the resulting polymers are of considerable interest. In this case an optically active label can also prove useful. The preservation or loss of optical activity on polymerisation of different enantiomorphs, the variation of the stereoregularity of the resulting polymers with the optical "purity" of the monomer, and also the relative rates of polymerisation of racemic and optically active propylene oxide permit the solution of a number of problems associated with the mechanism of stereoregulation (including the site where the epoxide ring is ruptured), with the chemical and stereochemical homogeneity of the active centres of the catalyst, etc.

The possible difference in the rates of polymerisation of racemic and optically active monomers was first pointed out by Kulkarni and Morawetz[28] in the polymerisation of methacryloyl and acryloyl derivatives of certain amino--acids (alanine and glutamic acid). However, a difference in the rates of polymerisation was actually observed in only one case: methacryloyl-DL-glutamic acid polymerised in the presence of benzoyl peroxide at a rate which was smaller by 5.6% than that of the polymerisation of the optically active compound.

Krylov and Livshits[29] made a theoretical analysis of the relative rates of polymerisation of the racemic monomers and the corresponding optically active compounds assuming different orders of the reaction with respect to the monomer. They demonstrated convincingly that in the stereospecific polymerisation of propylene oxide in the presence of magnesium oxide or oxalate as catalysts both enantiomorphs polymerise at the same rate which, for a first--order reaction, is twice as high as in the polymerisation of the racemate. This shows that, as was to be expected, the catalyst contains stereochemically indistinguishable centres.

To elucidate the mechanism of the asymmetrically induced polymerisation of propylene oxide on dialkylzinc—alcohol catalysts, Tsuruta et al.[30] studied the polymerisation of the monomer with different proportions of the D- and L-enantiomorphs. For comparison, the D- and L-enantiomorphs of propylene oxide were copolymerised in the presence of potassium hydroxide which is known to be a non-stereospecific catalyst. It was found that the plot of $[\alpha]_D$ for the polymer against $[\alpha]_D$ for the initial monomer is linear, both for the diethylzinc–methanol system and for potassium hydroxide. In both cases the rotation of the unreacted monomer was equal to that of the initial monomer regardless of the degree of polymerisation. To account for these results, the authors suggested that the catalytic system diethylzinc–alcohol contains two types of catalytic centre (D and L), but this cannot be regarded as evident even under the condition that "the racemisation which may occur when the monomer is incorporated in the polymer chain in the presence of the organozinc catalyst is of the same extent as in the presence of potassium hydroxide". It is interesting that the acetone-insoluble crystalline fraction of the polymer obtained on the organozinc catalyst has a higher value of $[\alpha]_D$ than the unfractionated polymer, while the soluble fraction has a lower value. The authors attribute this phenomenon to the preferential incorporation of the D-enantiomorph of propylene oxide in the crystalline polymer, so that its proportion is higher than in the initial monomer, but this is inconsistent with the hypothesis of the symmetrical distribution of the catalytic D- and L-centres.

Optically active polymers have also been obtained from propylene lactide[31], propyleneimine[32], conidine[33], and substituted caprolactams[34,35].

4. Effect of the Microtactic Structure of Macromolecules on the Optical Rotation of the Polymers

The use of optically active monomers gives rise to the possibility of a new approach to the study of the microstructure of the resulting polymers. Studies in this field have been begun recently by Schulz and Hilpert[36] who obtained a number of (-)-poly(bornyl acrylates) under conditions of radical and ionic polymerisation and investigated the curves representing the variation of the optical rotatory dispersion (ORD curves) of the polymers. Previously ORD curves were used mainly to observe the increase in the optical rotation of the polymers in the short-wavelength part of the spectrum, this serving as an indication of asymmetric synthesis of the macromolecules[37,38]. However, these curves can also provide useful information about the microstructure of the optically active polymers.

Klabunovskii et al.[39] used the data of Arcus and West[6] to find the constants A and λ_0 in the Drude equation. We may recall that the Drude equation is

$$[\alpha]_\lambda = \frac{A}{\lambda^2 - \lambda_0^2},$$

where λ_0 is the wavelength corresponding to the optically active electronic transition, λ the actual wavelength used, A the rotational constant proportional to the rotatory power associated with the transition, and to $(n^2 + 2)/3$, where n is the refractive index of the solvent.

It was shown that variation of the duration of the reaction, polymerisation temperature, and the molecular weight of (+)- and (-)-poly(1,3-dimethylbutyl methacrylates) changes slightly the rotational constant A but has no effect on λ_0. The radical initiator used has almost no influence on A and λ_0.

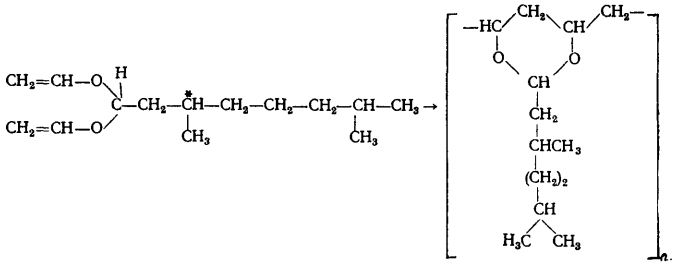
The spectropolarimetric method has been used to study the structure of polymers obtained by radical and anionic polymerisation of (+)-2-methylbutyl methacrylate[39]. It was found that λ_0 for polymers is close to the value for the monomer (about 190 nm). The values of A for the polymers obtained by radical and anionic mechanisms are significantly different and consistent with the data of Arcus and West[6].

However, Klabunovskii et al.[39] arrived at the incorrect conclusion that the stereoregularity of the polymer obtained by the radical mechanism is higher than that of the polymer obtained in the presence of a Grignard reagent. This was shown by Japanese investigators[40] in infrared and NMR spectroscopic studies of poly(methacrylic acid) obtained by the hydrolysis of the corresponding esters. By a similar treatment of ORD curves for propylene oxide polymers synthesised from L- and D-enantiomorphs in chloroform and methanol, Livshits[41] showed that the experimental curves are described by the Drude single-term equation. Polymers with greater stereoregularity give rise to higher values of A, determined by the optical activity at the sodium D-line.

The experimental data available at the present time are inadequate for the determination of the variation of the parameters defining the ORD curves as a function of the

stereoregularity of the polymers. To obtain more accurate values of the optical rotation, a correction for the dispersion of the refractive index of the medium must be applied to the observed specific rotation $[\alpha]$. Then the differences in the value of A should be consistent with the differences in the overall rotatory power associated with the optically active electronic transitions in polymers of various stereoregularities.

Abe and Goodman[42] showed that, depending on the method of polymerisation of the divinyl acetal of (+)-3,7-dimethyloctanal, the sign of the optical rotation of the resulting polymers can change:



A low-molecular polymer with optical activity close to that of the monomer and the model compound diethyl acetal of (*R*)(+)-citronellal was obtained by radical polymerisation. Cationic polymerisation in the presence of boron trifluoride–ether or aluminium chloride–ether gives solid high-molecular products with rotation of the opposite sign in the same solvent. It is interesting that the optical rotation of these polymers, like that of the (-)-poly(propylene oxide), decreases on going from benzene to chloroform solutions.

The authors attribute the difference in the rotation of substituted polydioxans to the different stereoregularity of the polymers. In this case it is reasonable to expect that the polymer obtained by the cationic mechanism has the greater stereoregularity.

The converse is also true, namely that polymers with the same chain microstructure should have the same optical rotation. Schulz[4] found that the optical activity of polyacrylates obtained by the radical mechanism and under the action of γ-radiation at -8° is the same. On this basis, he arrived at the incorrect conclusion that the polymerisation of acrylic acid esters in the amorphous, vitreous state under the action of γ-radiation involves a radical mechanism. Here the equality of the optical rotations of the polymers implies only that the microtactic structure of the chains is the same and that in both cases the polarisation is probably equally non-specific.

5. The Use of the Optically Active Label in the Study of Polymerisation Kinetics

In their study of the radical polymerisation of optically active (+)-s-butyl β-chloro(β-bromo)acrylates and vinyl (-)-β-phenylbutyrate in 1940, Marvel et al.[43] observed that the polymers have rotations which differ from those of the initial monomers by 9–12°. This difference was used to study the polymerisation kinetics.

Klabunovskii et al.[44] used a polarimetric method to study the kinetics of the radical polymerisation of the optically active esters of methacrylic and itaconic acids. The polarimetric study of polymerisation kinetics in homogeneous solutions may prove of value in certain cases, provided that the specific rotations of the monomer and the polymer differ appreciably.

III. SYNTHESIS OF OPTICALLY ACTIVE POLYMERS FROM OPTICALLY INACTIVE MONOMERS

1. The Concept of the Asymmetric Synthesis of Macromolecules

The asymmetric synthesis of macromolecules implies that in polymerisation induced by asymmetric agents there is either a selection of one enantiomorph from a monomer which consists of a racemic mixture and a fixation of these configurations in the polymer chain or formation of new asymmetric centres with a definite configuration on dissociation of a double bond or ring opening and their fixation in the macromolecular chain.

As in the case of low-molecular substances, asymmetric synthesis or asymmetric induction‡ of macromolecules can be divided into absolute and partial. By absolute asymmetric synthesis, the present author understands the synthesis of optically active substance in the absence of other optically active chemical agents (for example, under the action of circularly polarised light). Asymmetric syntheses involving the participation of auxiliary optically active substances are called partial asymmetric syntheses.

Together with partial asymmetric synthesis, in which new asymmetric centres are induced by asymmetric agents, it is also necessary to distinguish asymmetric kinetic separation. The latter term means preferential conversion or decomposition in a given reaction of one of the components of a racemic mixture because this component is formed or reacts more rapidly than the other. This follows from the fact that the two transition states are diastereoisomeric, their free energies of formation being different.

In connection with the polymerisation of racemic monomers, this means that, in the presence of optically active catalysts, preferential formation of one of the following two enantiomorphic chains is possible:

$$(R+S)\xrightarrow[\text{catalyst}]{\text{optically active}}\ \text{or}\ \begin{matrix}RRRR\ \ldots\\ SSSS\ \ldots\end{matrix}.$$

The unreacted monomer becomes enriched in the enantiomorph of the opposite sign to that incorporated in the chain. This type of polymerisation is called stereoelective[45].

When a racemic monomer is copolymerised with one of the enantiomorphs of another monomer, two chains can be formed, one of which contains only monomers in the (*R*)-configuration and the other only monomers in the (*S*)-configuration, i.e. a copolymer (*RRR'*...) and a homopolymer (*SSS*...) are formed:

$$(R+S)+R'-\begin{matrix}\nearrow RRR'R'RR\ \ldots\\ \searrow SSSSS\ \ldots\end{matrix}.$$

‡ There is no agreement in the literature concerning the use of these terms. In the present review they will be used to indicate the formation of both a new asymmetric atom and asymmetric molecular chains under conditions in which two stereoisomers are formed in unequal amounts.

This unusual type of copolymerisation is called stereoelective copolymerisation[45]. Stereoselective polymerisation must be distinguished from stereoelective polymerisation; the former consists in the polymerisation of racemic monomers in the presence of symmetrical catalysts with separation of the enantiomorphs during polymerisation and the formation of two enantiomorphic chains:

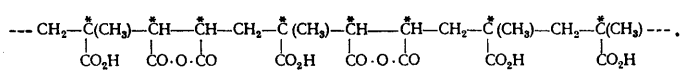
$$(R+S)\begin{cases}\nearrow RRRR\ldots\\ \searrow SSS\ldots\end{cases}$$

2. Asymmetric Synthesis of Macromolecules

Only one unsuccessful attempt to achieve absolute asymmetric synthesis, in the photo-polymerisation of styrene and copolymerisation of styrene with maleic anhydride under the action of polarised β-radiation[46], has been described. One of the possible ways of achieving partial asymmetric synthesis consists in the polymerisation of a monomer, which is optically active due to a substituent, with subsequent removal of the optically active side-groups from the final polymer. The question then arises how the optically active side-groups of the monomer influence the stereospecificity of the polymerisation. If the optically active monomer is the first unit of the growing chain, the next unit can add on either in the iso-position (DDD- or LLL-, where D and L represent the configurations of the asymmetric carbon atoms in the main chain) or in the syndio-position (DLD- or LDL-). The adducts of the monomer and the initiating radical or ion are no longer enantiomorphs but diastereoisomers, the rates of formation of which are always different. Thus the presence of optically active groups in the monomer gives rise to the potential possibility of the formation of a polymer with an optically active main chain. Whether or not the polymer or copolymer is optically active after the removal of the optically active side-groups depends on the symmetry or asymmetry of the chain formed. This problem was discussed in detail in section I, where it was shown that the primary structures of vinyl polymers are symmetrical. The secondary structure also becomes symmetrical after the removal of the optically active groups.

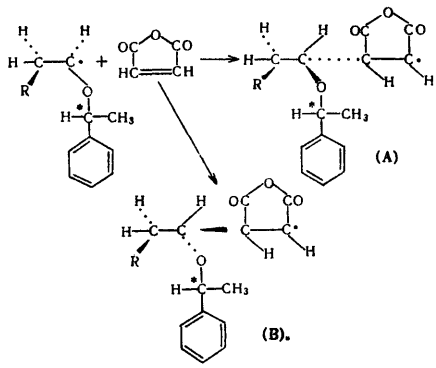
The numerous attempts to prepare optically active polymers in this way proved to be unsuccessful. Thus homopolymerisation of (+)-fluorobutyl *p*-vinylbenzoate[47], (+)-*o*-(s-butylthiomethyl)styrene[48], and (-)-1-phenylethyl methacrylate[49] and the copolymerisation of (+)-*o*-(s-butylthiomethyl)styrene with methyl methacrylate[48], followed by the removal of the optically active groups, yielded optically inactive products.

The simplest possibility of asymmetric induction is the copolymerisation of any optically active monomer with a second monomer, a disubstituted olefin, in which asymmetric carbon atoms can arise during the reaction. The copolymerisation of a usual vinyl monomer with a disubstituted olefin gives rise to three asymmetric atoms with four different substituents in its immediate vicinity. Using an optically active comonomer, it is possible to control the configuration of the induced asymmetric atoms. Thus using radical initiation, Beredjick and Schuerch[49] obtained a copolymer of L-α-methylbenzyl methacrylate and maleic anhydride which exhibited positive rotation after the removal of L-α-methylbenzyl groups:



Schmitt and Schuerch[50] obtained a laevorotatory copolymer (28.5°) by the free-radical copolymerisation of maleic anhydride with L-α-methylbenzyl vinyl ether.

The mechanism of asymmetric induction can be represented as follows:



Immediately after the first step involving the addition of two comonomers two diastereoisomeric radicals (A) and (B) are formed regardless of the configuration of the asymmetric carbon atom in the side-chain of the active component. For this reason, the rates of their formation (and further growth) must be different. During polymerisation one of the configurations of the induced asymmetric atoms is formed in excess and the corresponding copolymer exhibits optical activity even after the removal of the asymmetric side-groups. The attempt to achieve asymmetric synthesis with the aid of optically active acyl peroxides resulted in the formation of optically inactive polymers[51]. Frisch et al.[52] demonstrated theoretically that under the conditions chosen the effect of the asymmetric catalyst weakens after several chain-growth steps and therefore the specific rotation of the polymer decreases with increase in the degree of polymerisation. The situation is different in those cases where in each chain-growth step the asymmetric agent is near the growing end. This type of selection of the monomer with a specified configuration, as it approaches the growing end of the polymer chain, can be achieved by selective adsorption of the monomer on the surface or the formation of asymmetric complexes. Thus a surface or complexing agents are very important for asymmetric synthesis.

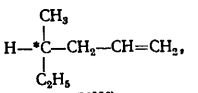
In their study of the theoretical aspects of asymmetric synthesis, Frisch et al.[52] analysed two different modes of asymmetric induction. In the first hypothesis (hypothesis of asymmetric initiation) it is assumed that the asymmetric agent influences only the first addition step and induces the formation of D-enantiomorphs with a probability different from that of the formation of the L-enantiomorphs. After the first addition step the probability of the persistance of the D- and L-configurations is the same, $k_{DD} = k_{LL}$ but $k_{DD} \neq k_{DL}$, where k_{DD}, k_{LL}, and k_{DL} are the rates of formation of the sequences DD, LL, and DL. In this case the optical activity of the polymer is inversely proportional to chain length and tends to zero for polymers with a high molecular weight.

The second hypothesis (hypothesis of asymmetric growth) postulates chain growth such that in each growth step the probability of addition in a given sequence is different from that in another sequence ($k_{DD} \neq k_{LL}$). The optical activity is independent of molecular weight and directly

proportional to the degree of asymmetric induction transmitted by the catalytic system. Qualitatively asymmetric induction should be most effective when the difference in the size of the substituents at the asymmetric centre of the molecule is large and the induced centre is as close as possible to the one already present.

3. Polymerisation of Racemic Monomers on Optically Active Catalysts

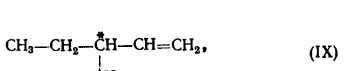
To assess the first hypothesis of asymmetric induction, Pino[53] studied the polymerisation of racemic 4-methylhex-1-ene (VIII),



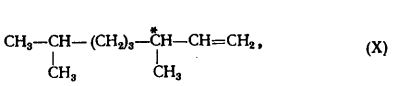
(VIII)

on a complex catalyst (based on titanium tri- and tetrachloride and optically active organometallic compounds) and compared the optical activities of the resulting polymers with the optical activity of certain polypropylene and polystyrene fractions prepared in the presence of the same catalysts. In the case of polypropylene and polystyrene only low-molecular fractions proved to be active, the optical activity decreasing rapidly with increasing molecular weight of the fraction. The optical activity of the low-molecular polymers of 4-methylhex-1-ene was much higher than that of the styrene and propylene polymers but smaller by a factor of 10–100 than the value for the optically active poly-(*S*)-4-methylhex-1-ene. The unreacted monomer proved to be inactive. The most likely explanation of the low activity of the polymers is that the optically active alkyl group of the catalyst or the first monomer unit do not determine the type of enantiomorph selected preferentially for the construction of the macromolecule, i.e. both monomer enantiomorphs are polymerised at almost the same rate. At the same time the optical activity of poly-4-methylhex-1-ene fractions obtained in the presence of catalysts based on the optically active zinc alkyl Zn(iso-C_5H_{11})$_2$ and titanium tetrachloride proved to be very high. Probably here the optical activity is not determined solely by that of the catalyst group but also by the asymmetric induction due to the first monomer unit.

The chemical structure of the monomer has a significant effect on the type of asymmetric induction. Thus in the polymerisation of racemic 3-methylpent-1-ene (IX) and 3,7-dimethyloct-1-ene (X)[54],



(IX)



(X)

where the asymmetric carbon atoms are in the α-position relative to the double bond, on the catalytic system comprising titanium tetrachloride and di[(*S*)-2-methylbutyl]zinc, polymers with considerable optical activity are formed. The optical activity of the polymer fraction increases with increasing molecular weight and melting point of the fraction, i.e. the findings are typical of asymmetric chain growth. When the degree of polymerisation of both monomers (IX) and (X) was between 7 and 22%, the unreacted monomer had appreciable optical activity. The sign of the rotation of the monomer showed that in this case the monomer enantiomorph having the same absolute configuration as the (*S*)-2-methylbutyl groups of the catalytic system was mainly incorporated in the chain. The ratios of the rates of polymerisation of the two enantiomorphs were calculated from the optical activity of the unreacted monomer and the percentage polymerisation of the monomer. It was found that the monomer with the (*S*)-configuration of the asymmetric carbon atom in the side-group polymerises 1.2–1.7 faster than the corresponding (*R*)-monomer.

The sign of the rotation of the polymers is consistent with that predicted on the basis of the absolute configuration of the preferentially polymerised monomer enantiomorph. Thus the considerable differences observed in the polymerisation of racemic 4-methylhex-1-ene, 3-methylpent-1-ene, and 3,7-dimethyloct-1-ene confirm the importance of the effect of the monomer structure on the stereospecificity of polymerisation. It may be concluded that the catalytic system titanium tetrachloride + di[(*S*)-2-methylbutyl]zinc is capable of polymerising electively one enantiomorph of a racemic α-olefin with the asymmetric carbon atom in the α-position relative to the double bond, but the electivity of this catalyst is extremely low when the asymmetric atom is in the β-position.

The stereoelectivity of the catalytic system depends also on the bond between the metal and the optically active group in the organometallic component[45]. Thus in the polymerisation of 3,7-dimethyloct-1-ene appreciable stereoelectivity is observed only with the organozinc compound [the ratio of the rates of polymerisation of the enantiomorphs in the presence of the zinc catalyst is 1.22; in the presence of organoaluminium and organoindium compounds no appreciable differences in the rates of polymerisation of (*R*)- and (*S*)-enantiomorphs are observed]. The author's explanation is that among all the organometallic compounds only the organozinc compound exchanges slowly its alkyl radical for the monomer.

In the study of the crystal structures of the polymers obtained from optically active and racemic α-olefins it was observed that the structures of poly-3-methylpent-1-enes and poly-4-methylhex-1-enes[14] are identical, but the structure of poly-(*S*)-5-methylhept-1-ene[13] is different from that of its racemic analogue. The structural identity of the polymers of (*S*)-4-methylhex-1-ene and the racemic 4-methylhex-1-ene confirms the theoretical prediction that the polymer formed from the racemic monomer is not a random copolymer of the two enantiomorphic monomers but is a mixture of two types of macromolecules. This was demonstrated by the chromatographic separation of the racemic polymer (fraction soluble in ether) on optically active poly-(*S*)-3-methylpent-1-ene[55]. On elution with ether several polymer fractions were isolated, the first having a molar rotation $[M]_D = -17.5°$ and the last being dextrorotatory with $[M]_D = +62.5°$. This study provides one of the most important demonstrations of the stereoselective polymerisation of a racemic monomer. In addition, the possibility of such separation of a polymer implies that in the isotactic growth of each macromolecule stereospecific catalysts can select preferentially one of the enantiomorphic forms of the racemic monomer, even when the asymmetric carbon atom is not directly linked to the double bond of the monomer.

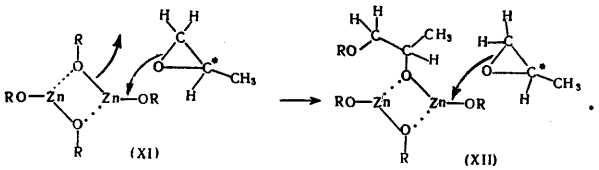
The identity of the crystal structures of the polymers obtained from different enantiomorphs and racemates of propylene oxide[27] and 2-methylbutanal[18] also indicates the stereoselectivity of the polymerisation of these monomers.

This is demonstrated directly by the successful separation of crystalline poly[(±)-propylene oxide][56] on poly[(-)menthyl glycidyl ether] into two fractions with $[\alpha]_D^{15} = -6.7° \pm 1.7°$ and $[\alpha]_D^{15} = +6.4° \pm 1.1°$.

Inoue et al.[57] described the synthesis of optically active poly(propylene oxide) using the racemic monomer and diethylzinc with optically active cocatalysts [(-)-menthol, (-)-borneol]. The optical "purity" of the polymers, determined from the specific rotation, was not more than 20%.

The occurrence of asymmetric induction was confirmed[58] by the isolation from the reaction mixture of the optically active unreacted monomer, the sign of whose rotation was opposite to that of the rotation of the monomer, preferentially incorporated into the polymer chain. It was found that, when (+)-borneol is used as the cocatalyst, L-(+)--propylene oxide is preferentially incorporated into the polymer chain.

Having analysed the optical rotations of the polymer and the unreacted monomer, Inoue et al.[59] concluded that the rotatory power of the polymer formed on the diethylzinc–(+)-borneol system is due to the preferential polymerisation of the L-enantiomorph of propylene oxide. In the initiation step propylene oxide molecules are coordinated to the catalyst, which is a cyclic dimer (XI), and are then incorporated at the site of the rupture of the Zn–O bond[60]. Chain growth proceeds according to the mechanism



(XI) (XII)

When the catalyst does not have asymmetric centres, k_{iL} should be equal to k_{iD} and the reaction should yield a mixture of polymeric molecules with a definite symmetrical distribution of tacticity in which the proportions of the L- and D-monomeric units in the chain range from 100% L to 100% D. If the catalyst contains optically active groups, the rate constant k_{iL} will differ from k_{iD}. For the system diethylzinc–(+)-borneol, $k_{iL} > k_{iD}$ and therefore L-monomeric units predominate in the polymer; also $k_{LL} > k_{LD}$. This example confirms the hypothesis of asymmetric growth.

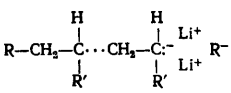
Stereoelective polymerisation of racemic propylene oxide was also achieved by Livshits and Krylov[61] on a heterogeneous stereospecific catalyst — magnesium D-tartrate. Interesting results were obtained by Furukawa and coworkers[62] in the polymerisation of racemic propylene oxide on Pruitt and Baggett's catalyst[63], prepared by the partial hydrolysis of the ferric chloride complex of propylene oxide in the presence of D-bornyl ethyl ether. The unreacted monomer was enriched in the L-enantiomorph of propylene oxide; however, the polymer did not show optical activity although it was a mixture of the crystalline isotactic fraction with a small proportion of amorphous polymer.

Observations of fundamental importance were also made in the study of the adsorption of racemic propylene oxide on an asymmetric catalytic system at a low temperature (under conditions where there is no polymerisation). After being added to the catalyst, the racemic monomer was distilled off in a vacuum. After that triethylamine was added to the residue and the volatile products were again distilled. Measurements of the optical activity showed that the propylene oxide in the first distillate was enriched in the L-monomer and in the second distillate in the D--monomer. Kinetic study of the reaction showed that the observed ratio of the D- and L-enantiomorphs of propylene oxide in the adsorbed monomer is consistent with the ratio of the rates of polymerisation of the enantiomorphs on the given catalytic system. On this basis, it was concluded that the chain growth consists of two stages, adsorption (coordination) and ring opening, and that the inequality of the rates of polymerisation of the enantiomorphs of propylene oxide is mainly due to the difference in the rate of adsorption. However, a final explanation of the lack of optical activity of the polymer was not obtained.

The polymerisation of the *N*-carboxy-anhydride of D- and L-alanine[64] in the presence of a number of asymmetric catalysts [(+)-borneol, (-)-menthol, $Al(C_2H_5)_3$–(+)-borneol, etc.] gave optically active water-soluble polyalanine fractions. Matsuura et al.[65] attempted to carry out the asymmetrically induced copolymerisation of propylene oxide and a cyclic anhydride with an asymmetric carbon atom (the anhydride of 3-phenyl-Δ_4-tetrahydrophthalic acid) on the diethylzinc–(+)-borneol catalytic system. To elucidate the possibility of the asymmetric selection of one or both monomers in the copolymerisation, measurements were made of the optical activity of the unreacted propylene oxide and the anhydride and also the hydrolysis products of the polyester which had regularly alternating propylene glycol–dicarboxylic acid ester units. It was found that the unreacted anhydride (in the form of ester) has positive rotation and the dicarboxylic acid negative rotation, while the unreacted propylene oxide and propylene glycol are optically inactive. The authors suppose that the preferential selection of one of the enantiomorphs of the anhydride is due to the specificity of the catalytic centres to a greater extent than to the "asymmetrising" influence of the preceding propylene oxide unit.

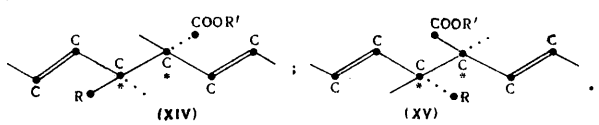
4. Asymmetric Synthesis of Polymers from Monomers without Asymmetric Centres

The preparation of optically active polymers from monomers without asymmetric centres was a considerable advance in the field of asymmetric synthesis. The polymerisation of dienes and monomers of the vinyl and acrylic types can be stereoregulated by using as catalysts lithium or sodium alkyls or aryls in a homogeneous solution. In such cases the end of the growing chain is an ionic quadrupole[66] of the type



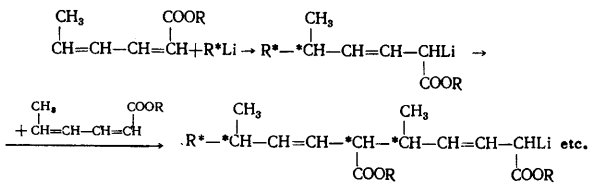
(XIII)

rather than an ion pair. The ionic quadrupole forms a complex with the monomer molecule and controls its incorporation into the growing chain. The polymerisation of dienes substituted in positions 1 and 4, in which on partial dissociation of double bonds two asymmetric carbon atoms arise simultaneously in each unit, was achieved in this way:



(XIV) (XV)

An example is the polymerisation of the esters of sorbic acid and its derivatives and of styrylacrylic acid in the presence of an optically active catalyst — methylbutyl-lithium[67] (Table 2). The polymerisation of sorbic acid esters proceeds according to the following mechanism:



The optically active group of the catalyst plays the role of the "asymmetrising" agent which effects asymmetric induction in the formation of the first asymmetric centre in the chain. Subsequently this function is assumed by the polymer chain whose end forms part of the catalytic complex during the growth process. The catalytic complex ensures the selective incorporation in the chain of units having the 1,4-*trans*-configuration and induces the formation of one of the enantiomorphic forms of the macromolecule.

It must be emphasised that both stereospecific polymerisation and asymmetric synthesis in the presence of anionic homogeneous catalysts are carried out at as low temperatures as possible (between -20° and -80°) at which the number of possible conformations of the monomer molecules is greatly reduced and the monomer–catalyst complexes are more stable. In such cases it is to be expected that the conformation of the terminal groups or of the first monomer unit will influence the configuration of the subsequent monomer units. Reduction of temperature significantly increases the stereospecificity of asymmetric synthesis also in the case of small molecules.

When the polymer was decomposed by oxidative cleavage of the double bond, optically active di- and tri-carboxylic acids were isolated, which means that the optical activity of the polymers is of a configurational type, i.e. it is related to the presence of asymmetric carbon atoms in the main chain. This method makes it possible to determine the optical "purity" of polymers, provided that oxidation is not accompanied by partial racemisation of the acids.

In the presence of racemic lithium alkyls a polymer consisting of a mixture of two enantiomorphic forms is obtained. This polymer is optically inactive.

TABLE 2. Unsaturated esters used as monomers in asymmetric syntheses.

Monomer	Formula of the monomer and the corresponding monomeric unit
Esters of β-vinylacrylic acid (pentadienoic acid)	$CH_2=CH-CH=CH-COOR$ → $\sim CH_2-CH=CH-\overset{*}{C}H(COOR)-CH_2-CH=CH-\overset{*}{C}H(COOR)\sim$
Esters of sorbic acid (hexa-2,4-dienoic acid)	$CH_3CH=CH-CH=CHCOOR$ → $\sim (CH_3)\overset{*}{C}H-CH=CH-\overset{*}{C}H(COOR)-\overset{*}{C}H(CH_3)-CH=CH-\overset{*}{C}H(COOR)\sim$
Esters of β-styrylacrylic acid (5-phenylpentadienoic acid)	$C_6H_5CH=CH-CH=CHCOOR$ → $\sim \overset{*}{C}H(C_6H_5)CH=CH\cdot\overset{*}{C}H(COOR)\cdot\overset{*}{C}H(C_6H_5)\cdot CH=CH\cdot\overset{*}{C}H(COOR)\sim$ (R = methyl and butyl)

A further advance was the use of a cocatalyst as the "asymmetrising" agent instead of the catalyst itself. This was done in the polymerisation of sorbic acid esters in the presence of an inactive catalyst and ethyl (-)-menthyl ether as an optically active additive[68]. This gave an optically active polymer with the same specific rotation as that obtained in the presence of an optically active lithium alkyl.

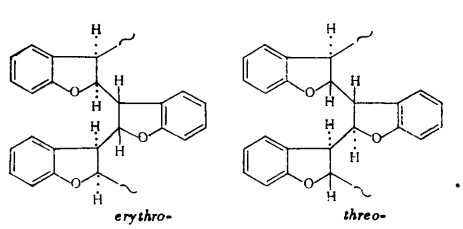
The original studies on the stereospecific polymerisation of *trans*-penta-1,3-diene using an optically active label were carried out by Natta and Porri[69]. This monomer gives rise to two types of crystalline polymer with 1,4-units. The polymerisation of the diolefin in the presence of an organometallic homogeneous catalyst yields a syndiotactic *cis*-1,4-polymer without optical activity as a result of internal compensation, while on a heterogeneous catalyst (based on vanadium trichloride and optically active tri-isopentylaluminium) the product was an optically isotactic *trans*-1,4-polymer.

Systematic study of the optical activity of the polymers obtained under different conditions in the presence of various catalysts can provide useful information about the reaction mechanism and in particular about the structure of the stereoblock-copolymers.

Another study of the same workers and Valenti[70] dealt with the elucidation of the nature of the active centres on heterogeneous Ziegler catalysts. A comparison was made of the capacities of two types of optically active catalysts of the coordination type to induce asymmetry in isotactic poly-*cis*-penta-1,4-diene: (1) (+)-tri-(2-methylbutyl)-aluminium and tetrabutoxytitanium; (2) triethylaluminium and (-)-tetramethoxytitanium. It was found that the polymers obtained in the first catalytic system were optically inactive, while polymers of both low and high molecular weight synthesised in the presence of the second catalyst did show optical activity. Thus asymmetric induction can be explained by supposing that, before being incorporated in the polymer chain, the monomer is coordinated to the organotitanium component whose asymmetric group influences the configuration of the asymmetric carbon atom in the monomer about to be incorporated.

Aliev and Krentsel'[71] achieved the asymmetric polymerisation of *trans*-1-phenylbuta-1,3-diene using two catalysts — (*R*)(+)-2-methylbutyl-lithium and a complex of n-butyl-lithium with (-)-menthylethanol. In the polymerisation with (*R*)(+)-2-methylbutyl-lithium asymmetric initiation took place, while in the presence of the optically active cocatalyst the polymerisation proceeded by the mechanism involving asymmetric chain growth. The degree of asymmetric induction was characterised by the rotational constant *A*, and it was shown that this quantity varies with the method and conditions of polymerisation.

The preparation of optically active polybenzofuran was a considerable advance in the field of asymmetric synthesis of macromolecules[72,73]:



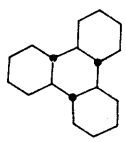
Di-isotactic polybenzofuran was obtained on the cationic catalyst $Al(C_2H_5)Cl_2$ in the presence of optically active co-catalysts: (-)-β-phenylalanine, (+)-β-phenylalanine, (-)-brucine, and others.

The polymerisation of benzofuran involving the opening of the double bond in the heterocyclic ring results in the formation of two possible diastereoisomeric units: *threo*- and *erythro*-di-isotactic units. Since polybenzofuran was not obtained in the crystalline state, the type and conformation of the chain could not be determined. However, the observed optical activity of the polymers indicates the presence of chains or sections of chains having the *erythro*- or *threo*-di-isotactic structure, since only these, among the simplest and most probable structures, would give rise to enantiomorphic chains. In *erythro*- and *threo*-di-isotactic structures all the carbon atoms in the chain are asymmetric and internally non-compensated.

The asymmetric carbon atoms of polybenzofuran exhibit an unusual type of asymmetry and cannot be assigned to the *R* or the *S* type in the nomenclature of Cahn et al.[74], whereby the configuration of the asymmetric carbon atom is established using the rule of the seniority of substituents. Indeed the carbon atom in the polybenzofuran chain in the α-position relative to the oxygen atom is linked to hydrogen, oxygen, and two carbon atoms, which are identical but belong to two different rings. A similar situation obtains also for the β-carbon atom.

To determine the seniority of the apparently identical substituents in the polycyclic compound, Farina and Bressan[75] introduced a new rule, which can be formulated as follows: if two substituents in a polycyclic compound belonging to different rings are identical in accordance with previous rules, the substituent belonging to the same ring as the given asymmetric atom is senior to the substituent linked to the external ring (the *endo*-substituent is senior to the *exo*-substituent).

We may note that a new stereochemical rule is general for polycyclic compounds (both low- and high-molecular) with the above type of asymmetry. For example, the absolute configuration of the isomers of perhydrophenylene[76], which has six asymmetric carbon atoms with a type of asymmetry similar to that found in polybenzofuran, was established on the basis of this rule:



(*R*)-*trans*-*anti*-*trans*-*anti*-*trans*-perhydrophenylene.

Best results were obtained in the asymmetric polymerisation of benzofuran using the system aluminium chloride–(-)-β-phenylalanine (component ratio 3 : 1).[75] During the polymerisation the catalyst, cocatalyst, and the end of the growing chain form part of the catalytic complex which effects asymmetric induction in each fundamental chain-growth step. In contrast to polysorbates, at the end of the reaction the macromolecules do not contain chemically combined components of the catalyst.

The product $[\alpha]n$, where n is the degree of polymerisation and $[\alpha]$ the specific rotation of a single monomeric unit, is proportional to the number of monomeric units, with rotation of a given sign, present in excess. If the hypothesis of asymmetric growth is valid, the relation between $[\alpha]n$ and n should be linear, while in the case of asymmetric initiation the relation should be represented by a curve tending to a limit.

On the other hand the quantity $W[\alpha]$, where W is the total weight of polymer per mole of catalyst, represents the total contribution of asymmetric synthesis in the polymerisation reaction. The study of the variation of $W[\alpha]$ with the amount of initiator in the polymerisation of benzofuran in the presence of aluminium chloride and (+)- and (-)-β-alanine showed that $[\alpha]$ decreases and $W[\alpha]$ tends to a limit, which confirms the hypothesis of asymmetric initiation. However, it is possible that during the polymerisation the counterion is racemised. The mechanism based on this hypothesis can explain both asymmetric growth and the disappearance of asymmetric induction, caused by the alteration in the counterion during the polymerisation process.

Schmitt and Schuerch[77] studied the cationic polymerisation of a number of unsaturated compounds: 4,5-dihydro-2-methylfuran, indene, α-angelica lactone, and cyanocyclopentene in the presence of boron fluoride and different additives, namely (-)-α-methylbenzyl alcohol, toluenesulphonyl-L-valine, and (+)-camphor. The resulting polymers contained asymmetric carbon atoms in the main chain but did not show optical activity. Examination of the molecular models of these polymers showed that in all cases syndiotactic structures are formed, which explains the absence of optical activity.

Thus we see that asymmetric synthesis of macromolecules can be achieved using the same methods of stereoregulation as in the usual stereospecific polymerisation (heterogeneous catalysis with anionic initiation for polyhydrocarbons, ionic initiation in solution at a low temperature for sorbic acid esters, benzofuran, and propylene oxide).

IV. MODIFICATION OF OPTICALLY INACTIVE POLYMERS BY LOW-MOLECULAR OPTICALLY ACTIVE COMPOUNDS

One of the methods for the preparation of optically active polymers is modification of optically inactive polymers by optically active low-molecular compounds. Thus a number of optically active polymeric salts were obtained by allowing optically active acids and bases to act upon optically inactive polyelectrolytes[4,78]. Comparison of two specimens of polyacrylic acid, obtained by the polymerisation of the monomer[79] and the hydrolysis of the anhydride of polyacrylic acid[80], shows that they are completely identical as regards infrared spectroscopic data and the content of carboxy-groups. At the same time the specific rotations of their salts with the optically active alkaloid quinine are different[4]. Probably the difference is due to the different microtactic structures of the initial polyacrylic acids. Thus the optically active label proved to be the most sensitive method for the detection of a difference in the microstructure of a polyelectrolyte.

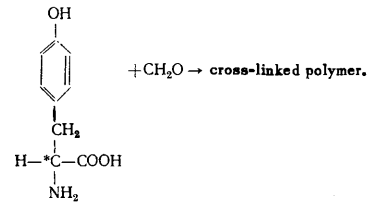
V. PREPARATION OF OPTICALLY ACTIVE POLYMERS BY POLYCONDENSATION

In principle the polycondensation method does not provide a possibility of inducing the formation of new asymmetric centres in monomers — it can only alter the environment of the already existing asymmetric atoms. There

remain two possibilities — one can use optically active monomers (pairs of monomers) or one can carry out asymmetric stereoelective polycondensation during which the optically active component incorporates selectively into the polymer chain one of the enantiomorphs of the other component which is present as a racemate:

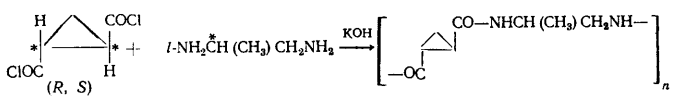
$$R + (R' + S') \rightarrow RR'RR'RR'RR' \ldots\ldots$$
$$\text{or}$$
$$RS'RS'RS'RS' \ldots\ldots$$

Losse and coworkers[81] obtained an optically active cross-linked polymer by the polycondensation of L-tyrosine with formaldehyde:



This product is insoluble in organic solvents and it is impossible to determine its rotation. It exhibits ion-exchange properties and may be used for the separation of racemates by virtue of its asymmetric carbon atoms. The use of synthetic optically active polymers for the separation of racemates has also been described by other workers[82,84]. Other examples of the synthesis of optically active polymers by polycondensation may be adduced.[85,92] The greatest interest attaches to the synthesis of polycondensation polymers by kinetic racemate separation. Several examples of successful separation of low-molecular racemic compounds by this method are described in the literature. Markwald and Meth[93] described the separation of racemic mandelic acid in the formation of its (-)-menthylamide; Markwald and McKenzie[94] achieved the separation of the same acid in its esterification with (-)-menthol and (-)-borneol.

An attempt to carry out a reaction of a similar type under polycondensation conditions was made for the first time by Topchieva et al.[95], who investigated the system (-)-propylenediamine–racemic *trans*-cyclopropane-1,2-dicarboxylic acid dichloride (containing two asymmetric centres in the molecule). The optically active polymer was synthesised by interfacial polycondensation:



In order to determine whether or not one of the enantiomorphs of *trans*-cyclopropane-1,2-dicarboxylic acid is selected kinetically, a study was made of the optical activity of the acid which failed to undergo polycondensation and the acid isolated after hydrolysis of the polymer. In both cases the optical activity proved to be zero. Control experiments demonstrated that the absence of optical activity in the acid specimens is not due to secondary racemisation processes. Thus it was established that the selection effect does not occur. Application of the usual methods of stereospecific polymerisation, reaction carried out at low temperatures, in the presence of complexing agents, and on the surface of adsorbents, also failed to give the expected results[96]. Probably further advances in the study of such a system (optically active diamine–racemic acid chloride) will involve the study of the microstructure of the polyamide which may throw light on the specific features of this reaction.

VI. OPTICALLY ACTIVE POLYMERS AS CATALYSTS

One of the most interesting applications of optically active polymers is their use as catalysts. Enzymes, which consist of proteins, i.e. optically active polymers of α-amino-acids, constitute a notable example of highly specific catalysts of chemical reactions in living organisms under very mild conditions. The catalysts employed in chemistry are only effective under more severe conditions and show little specificity.

The chemical composition of proteins does not explain this superiority of enzymes over synthetic catalysts. It is known that the groups in the side-chains of proteins (thiol, imidazole, indole, and others) can behave as catalysts in some cases, but their catalytic activity is very low. The problem arises how these groups acquire such exceptional properties when they are incorporated into the composition of a giant protein molecule.

In the attempts to find the answer to this question a number of model reactions using low-molecular compounds as analogues of enzymic systems have been discovered. The mechanisms put forward for these reactions are based on the concepts of electron density and steric hindrance adopted in organic chemistry. Probably, for a more profound understanding of model reactions, it will be of interest to use high-molecular compounds with functional groups, which are closer analogues of enzymes than low-molecular compounds.

In the light of what has been said above, the importance of the new technique based on the use of optically active polymers as catalysts of chemical reactions becomes clear.

Two ways of employing optically active polymers may be distinguished: (1) in the stereospecific catalysis of reactions involving low-molecular compounds; (2) in catalytic stereospecific synthesis of high-molecular compounds. Both these cases are realised in nature with the aid of enzymes and can also be achieved *in vitro*. It is known that enzymes acting upon substrates containing an asymmetric carbon atom usually attack only one of the two enantiomorphs[97]. The specificity of this type is as a rule absolute, i.e. the enzyme is completely incapable of reacting with the other enantiomorph. This notable property of enzymes was used by Pasteur for the separation of racemic mixtures.

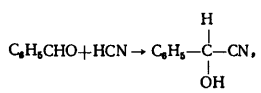
On the other hand, if the substrates consists of symmetrical molecules and the product contains an asymmetric carbon atom, then a symmetric synthesis under the influence of an enzyme results in the formation of only one enantiomorph. Thus the reduction of pyruvate in the presence of L-lactic dehydrogenase gives only L-lactate, while the product of the same reaction catalysed by another dehydrogenase is D-lactate[97].

Apart from the type of stereospecificity mentioned above, there exists yet another, namely the possibility of different behaviour of chemically identical groups in *meso*-compounds. Thus in the reaction

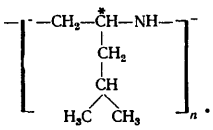
$$Cx_2yz \rightarrow Cx'xyz$$

(where primed letters denote groups attached to the carbon atom) the enzyme may act only on one of the two chemically indistinguishable x-groups. This is proved by the formation of only one enantiomorph of the asymmetric compound $Cx'xyz$. Such specificity has been observed with enzymes of the tricarboxylic acid cycle which are involved in the formation and breakdown of citric acid[98].

The generally accepted treatment of the specificity of enzymes is based on the classical "template" or "key in lock" model proposed by Fischer, Erlich, and others. In this model part of the surface of the enzyme molecule is regarded as a three-dimensional mould of a certain part of the substrate molecule. In other words, the surface of the substrate molecule is from the beginning, before reaction, complementary to the surface of the enzyme molecule. Recently the requirement of steric correspondence, which is a characteristic feature of the "template" hypothesis, has been supplemented by the "flexible" enzyme postulate, i.e. the possibility of inducing changes in the protein structure of the enzyme[99]. At the present time only one study has been made in which a synthetic optically active polymer has been successfully used as a catalyst for the asymmetric synthesis of low-molecular compounds. Tsuboyama[100] studied the synthesis of benzaldehyde cyanohydrin,



in the presence of optically active polyisobutylethyleneimine (PIBI):



The cyanohydrin synthesis involves the nucleophilic addition of the CN^- group to the carbonyl carbon atom and is catalysed by bases. On the one hand, the optically active polymer plays the role of a base which facilitates the dissociation of hydrocyanic acid and, on the other hand, by virtue of the steric effect of the isobutyl group of the polymer adjacent to the amino-group, the transition state is fixed so that the CN^- group can attack the carbonyl oxygen only in a particular direction relative to the isobutyl group.

Compared with other optically active polymeric bases, PIBI ensures the highest yield of an optically active product of the reaction (about 20%). The author concluded that the spiral structure of the polymer has a significant influence on the asymmetric synthesis.

In connection with Tsuboyama's results, it is interesting to investigate the relation between catalytic activity and the conformation of the polymer in solution and its molecular weight. Such data would bring us closer to an understanding of the nature of the "active centre" in a given catalytic system.

Another, more interesting approach involves the asymmetric synthesis of polymers in the presence of already existing optically active polymers. This problem is particularly important, since all natural biopolymers (proteins and nucleic acid) are synthesised in the living organism with the aid of appropriate optically active matrices. The attempts to achieve similar reactions with synthetic polymers have been unsuccessful. Thus in the synthesis of a polymer from racemic propylene oxide in the presence of optically active poly-(L-propylene oxide)[101] the product had a considerable optical activity even at low conversions but the activity was fully accounted for by the optically active seeding material.

Considerable advances in this field have been made by the achievement of enzymic syntheses of nucleic acids *in vitro* in the presence of templates. These include the Kornberg reaction[102] in which DNA has been synthesised on a DNA template in the presence of a universal enzyme (DNA-polymerase) from four monomeric nucleoside triphosphates; the product is a chemical copy of the primer. The catalyst in this reaction is a complex of the enzyme and the template, the former ensuring the formation of phosphodiester links, while the template is responsible for a specific sequence of the nucleosides in the reaction product.

Apart from the synthesis of DNA from all four monomeric units, Kornberg's enzyme gives the copolymer poly(A+T) on addition to a mixture of adenosine and thymidine triphosphates[103]. Without the primer the reaction is initially very slow with an induction period of several hours. After that the polymer formed initially itself serves as a template, i.e. the reaction proceeds autocatalytically. The high-molecular reaction product is a regularly alternating copolymer ATAT...

When Kornberg's enzyme is allowed to act on a mixture of monomers containing guanosine and cytidine only[103], the result is different: the products are equal amounts of the homopolymers polyguanosine and polycytidine, which form double helices by complex formation.

Apart from its template function (replication), DNA is also capable of acting as a primer for chain growth. The lower limit of the length of the primer molecule is equivalent to three nucleosides. The minimum length of the template molecule required for replication is equivalent to about twenty nucleosides. The template and primer functions may be superimposed.

Weiss and Nakamoto[104] discovered a new enzymic reaction involving the replication of RNA on DNA which behaves as a template. Enzymic systems have also been found in which polymeric RNA is synthesised from nucleoside triphosphates on an RNA (and not DNA) template[105].

The non-enzymic syntheses of polysaccharides, polynucleotides, and nucleic acids on templates are of considerable interest[106]. Thus the polymerisation of uridine monophosphate is accelerated by a factor of more than ten in the presence of polyadenylic acid. The introduction of polyarginine also accelerates the synthesis of polyuridylic acid. However, the addition of polyuridylic acid itself does not affect the reaction. The very important conclusion that there exists a mutual relation between the template acting as the catalyst and the monomer follows from

these experiments. Apparently a necessary condition which must be fulfilled in order that the polymer introduced into the reaction behaves as a template is the complementarity of the monomeric unit of the polymer and the monomeric substrate (uridine–adenine).

We shall now consider the problem of the asymmetric synthesis of polymers on templates. In this case complementarity presupposes also a correspondence between the absolute configurations of the asymmetric carbon atoms of the template and the monomeric units of the growing chain. For polymerisation to occur, the polymeric template should possess, in addition to adsorption capacity, the ability to initiate the reaction, and if this condition is not fulfilled a catalyst must be added to the reaction mixture.

The study of the adsorption of polymers from solutions on solid polymers (or association of different types of polymers) may be important for the choice of the polymeric template. Possibly, adsorbability (or capacity for association) may eventually be used as a measure of complementarity.

The problems of the adsorption of polymers on polymers are far from being elucidated. However, it is known that polymers of low molecular weight exhibit highest adsorbability. In addition, it has been observed in the chromatographic separation of isotactic poly-(*R*, *S*)-4-methylhex-1-ene[55] that adsorption interaction occurs between polymers with the same absolute configuration of the asymmetric carbon atoms and not on the principle of quasi-racemate formation.

The results obtained in the polymerisation of benzofuran[107,108], although without direct bearing on the problem of the template role of polymers, merit attention. Farina et al. found[108] that, when benzofuran is polymerised at relatively low monomer concentrations, the resulting polymer has initially a relatively low optical activity which rapidly increases with the degree of polymerisation to a maximum, and then falls slowly.

The study of the optical activity of polymers synthesised in the presence of previously prepared optically active and inactive polybenzofurans led to the hypothesis of the autocatalytic effect of polybenzofuran on asymmetric synthesis. It is interesting that the autocatalytic effect is independent of both the sign and magnitude of the optical activity of the added polymer. The sign of the optical activity of the polymer synthesised depends only on the sign of the optical activity of the asymmetric initiator employed (the sign of the optical activity of the polymer is the same as that of the optical activity of phenylalanine), while the specific optical activity is very high even at low conversions and virtually identical in many of the cases investigated.

On the basis of their results, the authors claim that autocatalysis must be attributed not to a steric effect but to a chemical effect associated with the presence of the polymer in solution. They believe that, as a result of the presence of oxygen atoms of the ether type, polybenzofuran can behave as a Lewis base in relation to aluminium chloride and can in consequence modify the structure of the conjugate ion.

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The studies on optically active polymers have only begun. The considerable theoretical importance of the problems of the asymmetric synthesis of macromolecules and also the wide variety of the possible uses of an optically active label in the investigation of polymerisation processes undoubtedly merit the attention of investigators in the field of polymer chemistry, and the relevant questions require further development.

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Faculty of Chemistry, Department of
Macromolecular Compounds,
Lomonosov Moscow State University