Optically Active Synthetic Polymers

By H. Mark

Polytechnic Institute of Brooklyn, N.Y., U.S.A.

Dedicated to Heinrich Hopff

Optical activity or optical rotatory power is the capacity of certain materials to turn the plane of vibration of throughgoing linearly polarized light by a certain angle. There exist several physical causes for this behavior which shall be briefly enumerated in this paragraph after a short introduction into the methods of measurement.

The instruments used for the measurement of optical rotatory power—so-called polarimeters—have been greatly improved and simplified in recent years[1] and permit to measure the angle of rotation in the visible and UV range down to 0.005° (or about 15 arc sec) if favorable conditions prevail such as clarity, isotropy and absence of temperature and density gradients in the investigated sample. The *specific rotation* (α) is obtained from the measured angle of rotation $[\alpha]$ by

$$[\alpha] = \frac{1000\,\alpha}{l \cdot c}, \tag{1}$$

where l is the length of the cell (or thickness of the sample) in cm and c is the concentration of the active substance in g per 100 ml of volume. The molar rotation is obtained from $[\alpha]$ by

$$M = [\alpha]\frac{\mathrm{H}}{100}, \tag{2}$$

where M ist the molecular weight of the optically active unit. The dimension of $[\alpha]$ and $[M]$ is

$$\text{degree} \cdot \text{cm}^2 \cdot \text{g}^{-1}.$$

The phenomenon of optical activity or circular birefringence was first discovered in the domain of crystallography, where it was intensely studied for many decades and finally quantitatively explained as a dispersion effect of the second order by M. Born[1] and C. W. Oscen[2] on the basis of the spatial arrangement and polarizability of the different lattice point occupants and of their interaction or coupling. This approach made it possible to compute the absolute *values* of the optical activities of several simple crystals on the basis of their known lattice structure, the polarizability and the coupling of the different ions in the lattice.

Later, W. Kuhn[3] applied the fundamental factors of the Born-Oscen treatment to the protatory power of molecules in the solid state, in a systematic and comprehensive manner; his work represents the best and most complete treatment of this interesting and important phenomenon.

Several methods have been used to synthesize optically active polymers; they shall be briefly reviewed in this article.

(1) One of them is trivial, namely the selection of an *optically active monomer* and its use to build up by any of the known polymerization reactions the corresponding optically active polymer (or copolymer). The only restricting factor in this method is to avoid racemization of the optically active monomer during the polymerization process. Many interesting and important optically active polymers and copolymers have been prepared by this method; they have greatly improved our knowlegde of macromolecular conformation and its dependence on the molecular structure of the polymer, on solvent, concentration and temperature.

(2) The really challenging problem, however, is to use the polymerization process itself for the production of optically active centers in such a manner that a *limited amount* of optically active material—available as monomer, initiator, activator, modifier, etc.—would permit the production of a much larger amount (in principle of an unlimited amount) of optically active polymer. Several methods have recently been studied to arrive at such a progressive creation of active centers and some of them have been, in fact rather successful; they shall be briefly reviewed in this paper.

It was first of considerable importance to see whether in free radical addition polymerization the use of an optically active side chain or substituent in the monomer "induces" some structural asymmetry in the backbone chain so that the resulting polymer would display optical rotatory power[4] even after quantitative removal

---

[1] M. Born, *Physik. Z. 16* (1915) 251; *Ann. Physik 55* (1918) 177.

[2] C. W. Oscen, *Ann. Physik 48* (1915) 1.

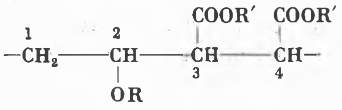
[3] Cp. e.g. W. Kuhn, *Z. physik. Chem. B 4* (1929) 14.

[4] An excellent book on Optical Rotatory Power was published by T. Martin Lowry, Dover Publications, New York 1935, second print 1964. More recent comprehensive and very complete treatises on Optically Active Polymers have been given by R. C. Schulz, *Kolloid-Z. 197* (1964) 55; Murray Goodman, Akihire Abe and You Ling Fan, in preparation; R. C. Schulz and E. Kaiser *Advances Polymer Sci. 4* (1965) 236, and P. Pino, *Advances Polymer Sci. 4* (1965) 393.

of the "inducing" asymmetric center on the side chain. MARVEL, OVERBERGER and their co-workers found[5] that in the simple *homopolymerization* of vinyl and acrylic type monomers with an optically active center in the side chain an optically active polymer resulted which *lost all its rotatory power* as soon as the active center of the side chain was quantitatively removed. Since most of these experiments were performed above room temperature and in the bulk phase it might still be interesting to explore whether at lower temperatures and/or in the presence of complex forming solvents an inducing effect can be established.

Such tests are particularly justified by the observations of BEREDJICK and SCHUERCH[6] that inducing effects can be obtained in the case of free radical induced, vinyl type *copolymerization*. It is known that vinyl and acrylic monomers can be copolymerized by the free radical mechanism with maleic or fumaric esters in such a manner that a *regularly alternating* copolymer is formed

$$\underset{A}{CH_2{=}CHOR} + \underset{B}{R'OOC{-}CH = {-}COOR'} \rightarrow$$



$$-\overset{1}{CH_2}-\underset{OR}{\overset{2}{CH}}-\underset{3}{\overset{COOR'}{CH}}-\underset{4}{\overset{COOR'}{CH}}-$$

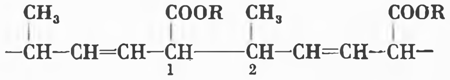
The carbon atoms 2, 3 and 4 are (in the sense of the preceding paragraph) *truly* asymmetric centers since their immediate neighbors left and right are substantially different from each other. It is true that the next neighbors of these atomes are not different from each other, but this identity cannot destroy the intrinsic configurational asymmetry of the valence skeleton in the immediate vicinity of these three carbon atoms. If neither R nor R′ possess any asymmetric character it should be expected that the random formation of the various possible transition states during the individual propagation steps will lead to a complicated diastereoisomeric meso-chain with no net effect of resulting optical activity. In fact copolymers of vinylacetate or methylacrylate with maleic and/or fumaric esters are inactive. If, however, an element of asymmetry is introduced into the system by the use of an optically active alcohol in R or R′ it is conceivable that a special transition state is so much preferred during the addition of B to A or of A to B that there is no complete cancellation of configurational asymmetry contributions along the entire chain and the polymer should remain optically active even after the *quantitative* removal of all inducing rotating centers R and R′.

This is precisely what BEREDJICK and SCHUERCH found in the copolymerization of maleic anhydrid and L-α-methylbenzylmethacrylate *vis.* L-α-methylbenzylvinylether: these systems form regularly alternating linear, 1 :1 copolymers which maintained a small, but measurably rotatory power even after all L-benzyl groups had been removed. Thus *all initially* in this synthesis invested asymmetric material is *recovered* but there still remains the newly created rotatory power of the copolymer chain. Repetition of this process allows, in principle, to produce an infinite amount of optically active polymer with a finite amount of an asymmetric starting material.

NATTA and his associates have demonstrated that the same result can be obtained by *homopolymerization* if diene type monomers are employed.[7] Considering, for example the free radical initiated 1,4-addition polymerization of sorbinic acid esters

$$ROOC{-}CH{=}CH{-}CH{=}CH{-}CH_3$$

one arrives at a chain of the form



$$-\overset{CH_3}{CH}-CH{=}CH-\underset{1}{\overset{COOR}{CH}}-\underset{2}{\overset{CH_3}{CH}}-CH{=}CH-\overset{COOR}{CH}-$$

in which the carbon atoms 1 and 2 are truly asymmetric because all their immediate substituents are substantially different and create, therefore, a strongly asymmetric valence skeleton around each of these carbon atoms all along the length of the chain.

Again, if there is no element of asymmetry introduced in this synthesis a polymeric random mesoform will result with no measurable rotatory power. But, if an optically active alcohol is used as R one might expect permanent induced net asymmetry of the backbone chain which causes optical activity of the polymer even after complete removal of the inducing asymmetric alcohol. The experiments of NATTA and his group have, in fact, verified the existence of such an effect.

These examples show that an asymmetric valence field in the side chain influences the stability of the various transition states and prefers one of them sufficiently to create a ewak, but observable net asymmetry of the backbone chain.

One should expect that *ionic initiators* which possess a counterion in close vicinity to the growing chain end should have an even more profound influence on the preference of certain transition states. This assumption is justified by the well known phenomenon of stereo-regu-

---

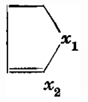
[5] Cp. e.g. C.S.MARVEL, J.DEC and H.G.COOKE, *J. Amer. Chem. Soc. 62* (1940) 3499, and C.S.MARVEL and C.G.OVERBERGER, *ibid. 66* (1944) 475.

[6] N.BEREDJICK and C.SCHUERCH, *J. Amer. Chem. Soc. 78* (1956) 2646, *80* (1958) 1933, *40* (1959) 533, and *J. Polymer Sci. 45* (1960) 313.

[7] G.NATTA *et al., Chim. et Ind. 42* (1960) 1361, *43* (1961) 161.

lation in which a certain configuration of the approaching monomer is introduced into the growing chain with a high degree of preference.

Schuerch also discussed the possibility of forming an optically active polymer from an inactive monomer such as



with the aid of a stereospecific catalysts with stereoisomeric sites at which one configuration of either *ddd* or *lll* is preferentially produced. The resulting isotactic polymer possesses true asymmetric centers in its main chain. On this basis, Schmitt and Schuerch[8] polymerized indene, 1-methylcyclopentene, 4,5-dihydro-2-methylfuran and alpha angelica lactone by a combination of boron trifluoride etherate with an optically active compound such as 1-α-methylbenzyl alcohol, tosyl L-valine or comphor. However, none of the polymers showed optical activity. Experimental evidence for Schuerch's prediction was provided by Natta, Farina and their co-workers, who polymerized benzofuran by cationic catalysts complexed with optically active cocatalysts.[7] A combination of aluminum trichloride with phenylalanine gave a polymer with high optical rotation, which, in all probability is either an erythro- or threo-di-isotactic system.

Other types of stereoregular optically active polymers were also reported by Natta and his troup[9] from optically inactive monomers by asymmetric induction. Esters of substituted butadiene carboxylic acids were polymerized with (R)-2-methyl-butyl lithium or butyl lithium complexed with (—) methyl ethyl ether as a catalyst. These high molecular weight crystalline polymers having a "tritactic" structure showed small but definitely measurable optical rotation. Polymers derived from *trans-trans* sorbates and β-styryl acrylate possess a *trans* erythro di-isotactic structure as shown by the oxidative degradation of poly-methyl sorbate.

Polymers of 1,3-pentadiene were studied in the same laboratory. The monomer, *trans*-1,3-pentadiene yielded a *cis*-1,4 isotactic polymer from a catalyst composed of a combination of trialkyl aluminium and titanium tetraalkoxide. However, optically active polymers with high molecular weight were obtained only when the alkoxide group on the titanium was optically active [(—1)-titanium tetra-methoxide and triethyl aluminium]. A combination of titanium tetrabutoxide with (+)-tri-2-methylbutyl aluminium, on the contrary, failed to produce optically active polymers with high molecular weight. From this result, Natta suggested that stereo-regulation of the monomer addition to the growing chain and probably takes place on the transition metal (titanium) through coordination of the monomer to the metal. In this connection, it is important to note that asymmetric complexes of some α-olefins with a transition metal (platinum) were resolved into two enantiomers by Pajaro and Corradini.[10] On the other hand, the *trans*-1,4 isotactic poly-1,3-pentadiene obtained with an optically active catalyst [(+)-tri-2-methylbutyl aluminium with vanadium trichloride] did not show optical rotatory power.

All attempts to obtain optically active vinyl homopolymers having asymmetric centers only in the main chain have been unsuccessful except when the immediate vicinities of carbon atoms are asymmetric such as in polybenzofuran. None of the homopolymers asymmetric sites in the side chain has shown any optical activity after the complete elimination of the optically active residues by hydrolysis of hydrogenation. Marvel and his co-workers polymerized styrene, methyl methacrylate and acrylonitrile using an optically active initiator (*l*-*p*-sec.-butylbenzoyl peroxide), with no result of optical activity. Later Frisch, Schuerch and Szwarc discussed the possibilities of asymmetric induction with an optically active catalyst. According to their mathematical treatment, the optical activity which can be induced by the use of an asymmetric initiator is negligible even when the propagation is highly stereospecific. Therefore, the propagation must be rigidly controlled to produce a significant excess of one configuration. Furthermore, they pointed out that polymers derived from such monomers as $CH_2=CHX$, $CH_2=CX_1X'$ or $CHX=CHX'$ cannot exhibit any measurable optical activity of the asymmetric carbons in the main chain even when they polymerize through a highly stereoregular course. Only at the ends of the polymer chain, the strucutural dissymmetry is similar to that of the low molecular weight analog. When both terminal groups are the same, the polymer, as a whole is meso and optically active polymers can only be expected when they contain intrinsically asymmetric carbon atoms. In some cases (e.g. syndiotactic structure), however, internal compensation of the optical activity may arise. By considering the steric factors in initiation, propagation and termination, Arcus discussed schematically various possibilities in vinyl addition polymerization.

Pino and his group[11] reported the polymerization of racemic 3-methyl-1-pentene, 3,7-dimethyl-1-octene and 4-methyl-1-hexene with asymmetric catalysts such as tris-(S)-2-methyl-butyl aluminium, bis-(S)-2-methylbutyl zinc or (R)-2-methylbutyl lithium combined with tetra- or trichloride of titanium. While poly-4-methyl-1-hexene thus formed afforded no evidence of the preferential polymerization of one antipode, both the polymer

---

[8] G. J. Schmitt and C. Schuerch, *J. Polymer Sci. 49* (1961) 287.

[9] G. Natta *et al., Makromol. Chem. 43* (1961) 251, *67* (1963) 225; also *J. Polymer Sci. 51* (1961) 463.

[10] G. Pajaro *et al., Makromol. Chem. 71* (1964) 184.

[11] P. Pino *et al., J. Amer. Chem. Soc. 85* (1963) 3883; *Makromol. Chem. 70* (1964) 182.

and recovered monomer of 3-methyl-1-pentene, when polymerized with a bis-(S)-2-methylbutyl zinc-titanium tetrachloride catalyst system, showed detectable optical rotation. On the other hand, when a combination of tetra-(R)(—1)-3,7-dimethyl-1-octyl lithium aluminium with titanium tetrachloride was employed as a catalyst, polymers derived from racemic (R)(S)-3,7-dimethyl-1-octene as well as its unchanged monomer did not exhibit any detectable optical rotation. In this last case, some racemization of the optically active alkyl group in the catalyst system was also observed on the addition of titanium tetrachloride.

Furakawa and his co-wokers[12] investigated the asymmetric polymerization of propylene oxide with different asymmetric catalyst systems. When diethylzinc/optically active alcohols, diethylzinc/water/optically active ether, or diethylzinc/optically active amine were employed as catalysts, the resulting polymer and the recovered monomer were optically active. However, using a catalyst system composed of (ferric chloride-propylene oxide) complex/water/*d*-bornyl ethyl ether, the recovered monomer was shown to be optically active while the resulting polymer was not. These authors were led to the conclusion that the propagation consists of two successive steps, coordination adsorption and ring opening, and that the relative rates of polymerization of D- and L-monomers are controlled chiefly by the coordination-adsorption step. Thus, by considering the different possibilities of the coordination-adsorption and ring opening steps, a relationship between the propagation and the nature of recovered monomer and resulting polymer can be established.

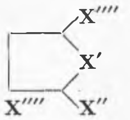
Tsuruta and co-workers[13] copolymerized D- and L-propylene oxide of various compositions with either diethylzinc/methanol or potassium hydroxide as catalyst. In each case the optical activity of the recovered monomer was found equal to that of the starting monomer and a linear relation was obtained between the optical activity of the resulting polymer and that of the starting monomer. However, the crystalline fraction showed a greater optical rotation than the amorphous fraction of the polymer prepared with diethylzinc/methanol catalyst, which is attributed to a preferred consumption of one antipode during polymerization.

The possibility of achieving asymmetric induction by copolymerizing racemic propylene oxide with another racemic comonomer in the presence of an asymmetric catalyst was examined by Matsumura and collaborators[14] through the synthesis of an optically active copolymer from D-L-propylene oxide and optically inactive 3-phenyl-Δ^4-tetrahydrophthalic anhydride using diethylzinc/*d*-borneol as catalyst. Chu and Price reported the polymerization of racemic propylene oxide with optically active catalysts such as zinc dichloride-aluminium tri-isopropoxide, diethyl zinc-water complexed with poly-L-propylene oxide or aluminium L-propylene glycolate-zinc dichloride. They attributed the optical activities of the polymers to optically active end groups derived from L-propylene oxide.

Tsuruta and his collaborators polymerized N-carboxy-DL-α-alanine anhydride by the action of D-borneol, L-menthol or tri-ethyl aluminum complexed with D-borneol. The polymers obtained were optically active. While the optical rotation of a typical polymer was dextrorotatory in dichloracetic acid, it was levorotatory in chloroform-dichloracetic acid.

Summarizing it can be stated that the following cases have been studied to date with more or less effort:

1) optically inactive monomers ($CH_2{=}CXX'$) with optically active catalysts;
2) optically active monomer ($CH_2{=}CXX'$, X or X′ optically active) with optically inactive catalysts;
3) optically inactive monomers with optically active catalysts;



4) optically inactive monomer ($XCH{=}CH{-}CH{=}CHX'$) with optically active catalysts;
5) racemic α-olefins with optically active catalysts;
6) racemic propylene oxide with optically active catalysts;
7) partially optically active propylene oxide with optically inactive catalysts; and
8) racemic propylene oxide and a racemic comonomer with optically active catalysts.

---

[12] Cp. J. Furukawa *et al.*, *Makromol. Chem. 55* (1962) 215, 230.

[13] T. Tsuruta *et al.*, *Makromol. Chem. 81* (1965) 191.

[14] K. Matsumura *et al.*, *Makromol. Chem. 81* (1965) 258.