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V. S. Livshits, O. V. Krylov, E. I. Klabunovskii

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Abstract

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V. S. Livshits, O. V. Krylov, E. I. Klabunovskii

HETEROGENEOUS-CATALYTIC POLYMERIZATION OF OPTICAL ISOMERS OF PROPYLENE OXIDE

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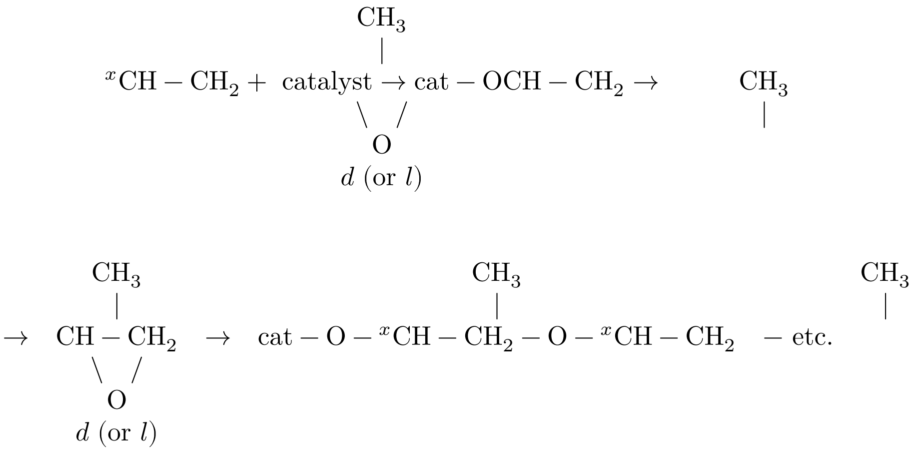
One of the comparatively simple reactions from whose study one can obtain additional information about the mechanism of the elementary act is the polymerization of propylene oxide. Propylene oxide is the simplest monomer forming polymers with an asymmetric carbon atom in the main chain.

The scheme of stereospecific polymerization of optical isomers of propylene oxide with opening of the oxide ring at the primary carbon atom may be represented as follows:



$$ {}^{x}\underset{\substack{\backslash\quad /\\ O\\ d\ (\text{or } l)}}{CH - CH_2} + \text{catalyst} \rightarrow \text{cat} - O\overset{\substack{CH_3\\ |}}{CH} - CH_2 \rightarrow $$

$$ \rightarrow \underset{\substack{\backslash\quad /\\ O\\ d\ (\text{or } l)}}{\overset{\substack{CH_3\\ |}}{CH} - CH_2} \rightarrow \text{cat} - O - {}^{x}\overset{\substack{CH_3\\ |}}{CH} - CH_2 - O - {}^{x}\overset{\substack{CH_3\\ |}}{CH} - CH_2 - \text{etc.} $$

If, upon opening of the oxide ring, the configuration of the asymmetric atom is retained, optically active polymers should be formed as a result. In the polymerization of a racemic mixture of optical isomers in the presence of a stereospecific catalyst, the same scheme is possible, but the polymer obtained will be optically inactive as a result of intermolecular compensation. If, however, the polymerization of racemic propylene oxide proceeds nonstereospecifically, then the absence of optical activity in the polymer formed will be due to the presence in the main chain of each macromolecule (with sufficiently great length) of equal numbers of asymmetric carbon atoms with opposite configuration. Depending on the degree of stereochemical heterogeneity of the catalytic surface, in the simplest case three different ratios of the rates of polymerization of the optical isomer and of the racemate may be realized.

First case. The active centers are stereochemically (for example, with respect to preferential adsorption of the *d*- and *l*-isomer) indistinguishable. The sign of the polymer chain is determined by the sign of the first monomeric unit, and the stereospecificity of the growth step follows from the different probability of addition of the *dd* or *ll* type as compared with *dl* and *ld*. In this case the number of centers accessible to the optical isomer and to the racemate* is the same, but the probability of growth of an enantiomorphic chain from the optical isomer is exactly twice as large as from the racemate (a mixture of *d*- and *l*-molecules of the monomer). Therefore, the rate of polymerization of the racemate will be half that of the optical isomer.

Second case. The stereospecificity of the catalyst is due to the presence of an equal number of active centers with opposite configuration. Therefore, on passing from the racemate to an optical isomer, the number of active centers is halved, but the probability of *dd*- or *ll*-growth is also doubled. Thus the racemate and the isomer will polymerize at identical rates.

Third case. A different probability of *ll*- or *dd*-growth of the chain, as compared with syndiotactic (*dl* or *ld*) addition, is determined by the predominance on the surface (or in soluble catalytic complexes) of active centers predominantly of one sign. Therefore the growth of chains of one sign will proceed faster than the growth of enantiomorphic chains, and an optically active polymer will be formed from the racemate, while the unreacted monomer will be enriched in the isomer of the opposite configuration. In this case the optical isomer (depending on the sign) will polymerize at a rate lower or higher than the racemate.

Similar conclusions can be reached by assuming that on the catalyst surface there exists a continuous statistical distribution of centers according to the degree of stereospecificity, and by applying the principles of the theory of catalysis on a heterogeneous surface (^{1}). In this case, instead of heats of adsorption, one must use the affinity of a given center for the monomer of a given sign, characterized by some stereochemical parameter.

Such a treatment has not previously been carried out. However, from the work (^{2}), where a zero kinetic order with respect to monomer was demonstrated, it is possible to calculate the ratio of the polymerization rates of *dl*- and *l*-propylene oxide, which is equal to 1.7. In the polymerization of *dl*- and *l*-propylene oxide on KOH, as well as in the polymerization of *dl*- and *d*-3-methylpentene-1 on a

* An idealized scheme is considered in which it is assumed that the racemate, which is a mixture of isomers, dissociates on the surface into individual isomers, which then react independently.

Fig. 1

Figure 1: Fig. 1

Ziegler—Natta catalyst (^{3}), the polymerization rates of the racemate and of the optical isomer were approximately equal.

From the data of work (^{4}) it is possible to calculate the ratio of the integral polymerization rates of *d*- and *dl*-3,7-dimethyloctane. It is equal to 1.7. In work (^{5}) equality of the rates of radical polymerization of racemic and optically active monomer was also found. However, all these data cannot be interpreted unambiguously, since in the cited works no comparative kinetic measurements were carried out under conditions identical for the optical isomer and the racemate. An exact comparison of rates is possible when the kinetic equation is known, and it will be most reliable when data are available on the polymerization rates of both optical (*d*- and *l*-) isomers and racemic mixtures.

The polymerization of $L(+)$-propylene oxide was first studied by Price and Osgan (^{2}); however, no stereochemical explanation was given in their work for the fact they observed, namely the formation of polymers of different optical purity. Below we report results on the polymerization of $D(-)$- and $L(+)$-propylene oxide on magnesium oxalate.

Magnesium oxalate dihydrate was prepared by the procedure described in (^{6}). The anhydrous salt was obtained by heating the dihydrate at 300° and a residual pressure of $1 \cdot 10^{-3}$–$1 \cdot 10^{-5}$ mm Hg. The specific surface of the catalyst, measured by low-temperature krypton adsorption, was 20 m^2/g. The $D(-)$-isomer of propylene oxide was synthesized according to (^{7}), starting from allylamine. 2-Chloroaminopropane hydrochloride was purified by crystallization from acetone. The resulting $D(-)$-propylene oxide had b.p. 35—38°, d_4^{23} 0.8330, $[\alpha]_D^{23}\ -6.95 \pm 0.10°$. $L(+)$-propylene oxide was obtained according to (^{8}) by enzymatic reduction of acetol. The conversion of L-propanediol-1,2 into propylenebromohydrin was carried out in dioxane. The $L(+)$-isomer

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Fig. 1. *a* —polymer from *l*-propylene oxide, polarizers crossed; *b* —polymer from *d*-propylene oxide.

had b.p. 35-38°, d_{20}^{22} 0.9075, $[\alpha]_D^{22} + 9.50 \pm 0.35°$ (without solvent).

The optical isomers of propylene oxide were purified from moisture and other possible impurities by repeated freezing in a vacuum apparatus over KOH. Their chemical purity was not less than 99%, as shown by analysis on a capillary chromatograph (triethylene glycol butyrate, 20°, H_2).

A preliminary study of the kinetics of polymerization of *dl*-propylene oxide by the gravimetric ampoule method showed that, in the range of monomer/magnesium oxalate ratios employed, the polymerization rate is described by a first-order equation; the apparent activation energy is 14–15 kcal/mole.

Three experiments were carried out on the polymerization of *L*(+)-propylene oxide at 89.4° (experiment 1), 93.4° (experiment 2), and 83.9° (experiment 3). The results of these experiments are given in Table 1.

Table 1

Experiment no.	Weight of MgC_2O_4, g	Polymerization time, h	Degree of conversion to polymer, %	Rate constant, min^{-1} · g^{-1} · 10^{-3}	Ratio of rate constants for isomer and racemate
1	0.208	11.5	59.8	6.3	1.9
2	0.207	14.0	54.5	4.5	2.2
3	0.150	33.5	74.2	3.9	–

The ratios obtained for the rates of the racemate and of the *L*(+)-isomer apparently indicate that here the first type of stereochemical heterogeneity of the catalytic surface, discussed above, is realized.

To confirm this hypothesis, a polymer from *D*(−)-propylene oxide, not previously described, was obtained. Thus, at 89.4° on 0.242 g of MgC_2O_4, in

Table 2

Properties of optically active propylene oxide polymers

Experiment tempera-ture, °C	Starting monomer	*l*, dm	*c*, in benzene, g/100 ml	$[\alpha]_D$	$[\eta]$, 100 ml/g	Melting point, °C
89.4	*L*	2.0	1.273	−23.1 ± 1.4	0.12	–
83.9	*L*	1.9013	1.178	−24.2 ± 0.5	0.12	74–77
93.4	*L*	1.0	2.28	−31.9 ± 0.5	0.057	–
89.4	*D*	0.9504	0.791	+12.8 ± 1.7	0.18	–
97.3	*D*	0.48	2.68	−14.3 ± 1.2 (chloroform)	–	–

13.5 h a yield of 41.1% of (+)-polypropylene oxide was obtained, which corresponds to a first-order rate constant $k = 2.71 \cdot 10^{-3}$ $\text{min}^{-1} \cdot \text{g}^{-1}$. When the polymerization of DL-propylene oxide was carried out at 89.4° on the same catalyst sample (0.193 g), $k = 1.27 \cdot 10^{-3}$ $\text{min}^{-1} \cdot \text{g}^{-1}$ was obtained. Thus, the observed kinetic isotope effect may be regarded as established.

In the polymerization of racemic propylene oxide on MgC_2O_4, in all cases a polymer was obtained that contained a considerable amount of crystalline isotactic fraction, insoluble in cold acetone, which indicates the stereospecificity of the catalytic system employed. In the polymerization of the optical isomers of propylene oxide, X-ray-crystalline polymers were obtained with unit-cell parameters corresponding to isotactic polypropylene oxide ([9]) (see Figs. 1*a* and *b*).

The results of measuring the optical activity of the unfractionated polymers obtained and some of their properties are given in Table 2. The optical activity was measured on a Hilger polarimeter, with a reading accuracy of 0.005°. The viscosity was determined in an Ubbelohde viscometer in benzene at 25°; the solvent outflow time was 90 sec. The melting temperatures of the crystallites were determined on the heating stage of an MP-7 polarizing microscope.

As is seen from Table 2, the stereospecificity of the polymerization, determined by the magnitude of the optical activity of the polymer, depends on the polymerization temperature and the molecular weight. The unreacted monomer in experiment 1 had $[\alpha]_D^{18} = +20.8 \pm 4.5^\circ$ ($c = 2.40$; $l = 1.9013$, benzene), which indicates the absence of racemization before polymerization. On allowing l-propylene oxide to stand over granulated KOH at $\sim 20^\circ$, an optically active polymer was also obtained with $[\alpha]_D^{23} = -23.3 \pm 6.7^\circ$ ($c = 0.30$, $l = 0.5$, benzene), which agrees with the data of work [2].

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Institute of Chemical Physics
Academy of Sciences of the USSR

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