THE NATURE OF THE STEREOSPECIFIC ACTION OF HETEROGENEOUS CATALYSTS IN THE POLYMERIZATION OF PROPYLENE OXIDE

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

UDC 66.095.264+541.63+541.64

PHYSICAL CHEMISTRY

V. S. LIVSHITS, O. V. KRYLOV

THE NATURE OF THE STEREOSPECIFIC ACTION OF HETEROGENEOUS CATALYSTS IN THE POLYMERIZATION OF PROPYLENE OXIDE

(Presented by Academician V. N. Kondrat’ ev, May 18, 1965)

After the discovery of stereospecific polymerization and the study of a number of laws inherent in it, investigation of the mechanism of enzymatic catalysis can be pursued more effectively. Owing to the profound fundamental analogy between these two processes, it is desirable to seek a property sensitive to the microstructure of polymers. Such a property is optical activity, which may arise from asymmetry in the structure of a molecule or a crystal. In work (^{1}), the authors found a high stereospecific efficiency in the polymerization reaction of propylene oxide on heterogeneous catalysts: the oxalates of calcium, magnesium, and beryllium. Soon, from a study of the polymerization of optical isomers of propylene oxide on anhydrous magnesium oxalate, it was found that the active centers of this catalyst are uniform in degree of stereospecificity (^{2}). Polymerization of racemic propylene oxide on the optically active analogue of oxalate—magnesium *d*-tartrate—led to partial separation of optical isomers in the course of catalysis (^{3}). Crystalline optically active polymers were obtained in this way. The experimental results are summarized in Table 1.

Table 1

Polymerization of racemic propylene oxide on magnesium *d*-tartrate

<table>
<tr><th>Experiment</th><th>Catalyst mass, g</th><th>Mass of initial monomer, g</th><th>Polymer</th><th>Polymer</th><th>Polymer</th><th>Polymer</th><th>Polymer</th><th>Polymer</th></tr>
<tr><td></td><td></td><td></td><td>Yield, %</td><td>α_D</td><td>concentration in benzene, g/100 ml</td><td>$[\alpha]_D^{20}$</td><td>$[M]_D$ (per one monomer unit)</td><td>$[\eta]$</td></tr>
<tr><td>1-B-25</td><td>0.223</td><td>4.352</td><td>10.3</td><td>−0.190</td><td>2.07</td><td>−9.2$±0.7|−5.3|0.03||1−1 −49|0.153|4.472|4.32|−0.084|1.12|−15.6±0.6|−9.05|0.024||3−B −70|0.690|8.368|1.67|−0.847|3.09|−27.4±0.4|−15.9|0.11||4−B −127|0.816|6.764|2.08|−0.197|1.22|−16.1±$0.8</td><td>9.35</td><td></td></tr>
</table>

The accomplishment of asymmetric synthesis was confirmed by calculating the maximum possible contribution of the end groups to the molecular rotation, calculated from the molecular masses of the polymers*; by measuring the dispersion of the optical rotation of the polymers; and by isolating the unreacted monomer. The latter had a configuration opposite to that of the polymer, and its specific rotation (−0.282° ± 0.007 in experiment 1-B-25) corresponded exactly to the value calculated from the balance of optical activity.

* If it is assumed that the end groups consist of residues of tartaric acid, then for a molecular rotation $[M]_D$ of *d*-tartaric acid equal to 21.1°, their maximum contribution to the optical activity may be from +0.12 to +0.30°. The observed values of $[M]_D$ are considerably larger and differ in sign (see Table 1).

Additional facts are reported below that make it possible to give a plausible explanation of the stereospecific action of the magnesium compounds studied. The following data directly or indirectly testify in favor of a coordination mechanism for the polymerization of propylene oxide on these catalysts:

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

1) The molecular weight of the polymers formed on magnesium oxalate increases in the course of polymerization, indicating the absence of chain-length limitation as a result of a termination reaction. This in itself indicates that a radical mechanism cannot be realized under the action of unaccounted-for impurities. Moreover, it is known that, in the presence of radical initiators, propylene oxide forms only telomers (^{4}). Calculation of the number of active centers, carried out on the basis of the molecular weights of the polymers, shows that the process is accompanied by a chain-transfer reaction.

2) The polymerization rate is essentially independent of the dielectric constant of the solvent (Fig. 1). Consequently, the reaction cannot proceed by an ionic mechanism.

3) The specific catalytic activity with respect to the polymerization of propylene oxide decreases regularly in the series:
$MgO \rightarrow MgC_2O_4 \rightarrow MgC_4H_4O_6$, i.e., on passing to bulkier anions that screen the active center. If the catalytic activity of magnesium oxide, referred to unit surface area, is taken as 1, then magnesium oxalate at the same temperature (90°) will have an activity of 0.65, and magnesium tartrate 0.03. A change in temperature does not substantially alter these ratios, since the activation energies for these catalysts are approximately the same (8.5-10 kcal/mol).

Fig. 1. Dependence of the rate constant of propylene oxide polymerization on the catalyst—magnesium oxalate—on the dielectric constant of the solvent

Fig. 2. Scheme of adsorption of a propylene oxide molecule on magnesium oxalate. Below—section along the plane passing through the propylene oxide molecule

4) Hydrates of magnesium and calcium oxalates have no catalytic activity in the reaction studied. From the structure of aqueous oxalates it is known (^{5}) that water molecules in the crystal lattice of these compounds are coordinated with the central metal ion. Therefore it may be assumed that dehydration, which occurs during the preparation of the catalysts in vacuum (^{1}), frees a coordination site at the cation for the monomer.

All these facts, together with the body of data for the polymerization reaction of ethylene oxide studied previously (^{5}), compel one to accept a polymerization mechanism whose elementary act is the formation of a bond by means of an

Fig. 3. Geometrical structure of the tartrate ion, according to (13)

Figure 3: Fig. 3. Geometrical structure of the tartrate ion, according to (13)

electron pair of the oxygen in the propylene oxide molecule and a free orbital of the coordinatively unsaturated magnesium ion on the surface of the crystal.

On the basis of literature data on the planar trans-structure of the oxalate ion (7) and the structure of propylene oxide (8), a geometric model of the surface of magnesium oxalate was constructed, shown in Fig. 2.

In the upper part of this figure, on a scale of $1 : 10^8$, a portion of a crystal face is shown on which the plane of the oxalate ion coincides with the plane of the face. In the lower part of the figure a section through this face is shown with adsorbed molecules of propylene oxide. The covalent radii of the atoms and the ionic radii needed for the construction were taken from Pauling' s book (9).

It is evident from the figure that a propylene oxide molecule can be oriented on this face only in such a way that its methyl group is directed away from the surface.

In this case the magnesium atom binds the monomer molecule by means of its sixth free coordination site (five coordination positions are occupied by bonds with oxalate ions). It is easy to see from Fig. 2 that in this case the polymer molecule can form only upon adsorption of the next propylene oxide molecule on a neighboring magnesium atom. This promotes fixation of the configuration of the asymmetric atom of the monomer. The dimensions of the propylene oxide molecule and the periodicity of the magnesium ions are in fairly good geometrical correspondence (5.9 and 6.1 Å), which creates favorable conditions for regular chemisorption. The regularity of the crystal lattice of the catalyst has previously been cited (10) as a possible cause of stereospecificity. In those works, however, vacancies and other defects were regarded as the cause of the formation of nonstereoregular polymerization products. Only recently did Arlman and Cossee (11) introduce the concept of anionic chlorine vacancies to explain the stereospecific action of Ziegler–Natta catalysts.

Fig. 3. Geometrical structure of the tartrate ion, according to (13)

In an analogous way, the formation of stereoregular polymers of propylene oxide can also be imagined in anionic vacancies on the surface of magnesium oxide, without introducing the assumption of regular adsorption of several propylene oxide molecules on neighboring magnesium atoms. If oxalate anion A is removed from the surface (see Fig. 2), magnesium atoms I and II each acquire two additional coordination valences. Therefore each of them can hold both a polymer chain and a monomer molecule that has approached the magnesium atom. Thus a coordination mechanism of polymerization is realized, analogous to that described for the polymerization of ethylene oxide (12). Such an anionic vacancy can accommodate the polymer chain and either a *d*- or an *l*-molecule of monomer. The first molecule, which initiates the chain, creates asymmetry inside the vacancy, after which molecules of one and the same sign attach to the magnesium atom. However, the vacancy itself can accommodate either a *d*- or an *l*-molecule of monomer. Therefore an optically inactive polymer is formed from racemic monomer, and an optically active polymer from optically active monomer ([2]). On those faces where the plane of the anion is perpendicular to, or lies at an angle to, the plane of the face, the magnesium atoms are strongly shielded, and adsorption leading to initiation of chains can occur only in the presence of anionic vacancies; regular adsorption is altogether impossible.

As regards magnesium *d*-tartrate, as is evident from the structure of the tartrate ion ([13]) (Fig. 3), shielding of the magnesium ion lying at the intersection of planes I and II leads to the fact that polymerization can occur only in anionic vacancies. Since these vacancies themselves possess···

required asymmetry, then optically active polymers are formed on this catalyst from racemic propylene oxide. Each separately taken polymer molecule consists of monomer units of one sign of rotation. In the first stage of polymerization on magnesium tartrate (see, for example, experiment 3-B-70 in Table 1), practically all polymer chains consist of units of one sign.

As calculation of the number of active centers shows, here too the reaction is accompanied by chain transfer. In this case the growing chain possibly tears an anion out of the lattice, using it as an end group. After this the asymmetry of the environment of the magnesium ion decreases; this, evidently, accounts for the observed decrease in the yield of asymmetric synthesis with increasing degree of conversion of propylene oxide into polymer on magnesium *d*-tartrate ([3]).

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
28 IV 1965

CITED LITERATURE

[1] O. V. Krylov, V. S. Livshits, *Neftekhimiya*, **5**, 58 (1965).
[2] V. S. Livshits, O. V. Krylov, E. N. Klabunovskii, DAN, **161**, 633 (1965).
[3] O. V. Krylov, V. S. Livshits, *Tetrahedron Letters*, **17**, 1181 (1965).
[4] T. Wallace, G. Gritter, *Tetrahedron*, **19**, 657 (1962).
[5] R. W. G. Wyckoff, *Crystal Structure*, **3**, Text Table DII, N. Y., 1948.
[6] O. V. Krylov, Yu. E. Sinyak, *Neftekhimiya*, **1**, 688 (1962).
[7] *Tables of Interatomic Distances*, London, 1958, p. 125.
[8] Y. Akimoto, *Bull. Chem. Soc. Japan*, **28**, 58 (1955).
[9] L. Pauling, *The Nature of the Chemical Bond*, Moscow, 1947.
[10] A. V. Topchiev, B. A. Krentsel, L. G. Sidorova, DAN, **128**, 732 (1959).
[11] E. J. Arlman, P. Cossee, *J. Catalysis*, **3**, 99 (1964).

[12] O. V. Krylov, M. Ya. Kushnarev, E. A. Fokina, *Neftekhimiya*, **1**, 696 (1962).
[13] M. Eastrand, *Acta chem. scand.*, **1**, 178 (1947); F. Stern, C. A. Beavers, *Acta crystallogr.*, **3**, 341 (1950).

Note: Figure translations are in progress. See original paper for figures.