Chemistry

1964

SovietRxiv

Abstract

Full Text

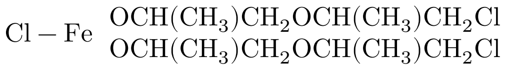
Chemistry

K. S. Kazanskii, G. I. Bandsyrev, S. G. Entelis

Structure and Properties of Propylene Oxide Polymerization Catalysts Formed upon Hydrolysis of the $FeCl_3$–Monomer Complex

(Presented by Academician V. N. Kondrat'ev, October 29, 1963)

A stereoregular crystalline polymer of propylene oxide was first obtained in 1955 on certain iron compounds, in particular, on the complex of $FeCl_3$ with the monomer (PO) (1). The composition and properties of this complex have recently been studied by many chemists (2-4), and in some cases contradictory results were obtained. The structure of the $FeCl_3$–PO catalyst was recently investigated by Bacalo (5) and has the following form:



$$\mathrm{Cl-Fe}\begin{matrix}\mathrm{OCH(CH_3)CH_2OCH(CH_3)CH_2Cl}\\ \mathrm{OCH(CH_3)CH_2OCH(CH_3)CH_2Cl}\end{matrix} \qquad \text{(I)}$$

The continuing interest in this catalyst is due to its relatively high stereospecific action even at high temperatures.

In undertaking a study of the kinetics of polymerization of organic oxides on $FeCl_3$ derivatives, we also paid attention to the study of the composition and structure of the catalytic complex $FeCl_3$–PO and, in particular, of the catalysts formed upon its partial hydrolysis; the latter, as is known from the literature, are more stereospecific (3,4,6).

The catalytic effect of water additions in the stereospecific polymerization of asymmetric α-oxides has also been observed in other systems (Me_6Al_2, Et_2Zn, Et_3Al) (7-9). The present communication sets forth the results of a study of the structure of the catalysts and some preliminary data on their catalytic properties.

Experimental Procedure

Starting materials. The monomer was dried over molten KOH and CaH_2 and distilled on a high-efficiency rectification column with a metallic packing. Purity criteria: b.p. 34.6°; d_D^{20} 0.8311; M_D^{20} 1.3664. Ethyl ether, which served as the solvent, was subjected to ordinary absolutization. Anhydrous ferric chloride was prepared by combustion of reactive metallic iron in a stream of dry chlorine according to the method (10).

The catalyst was synthesized by the reaction of anhydrous ferric chloride in ethyl ether with an excess of monomer at 0°; the ratio of components and the synthesis conditions fully corresponded to the patent (^{1}). All operations were carried out either in a stream of dry nitrogen or under vacuum. Volatile products were removed by pumping to constant weight; weighing of the vessel made it possible to determine the ratio of the catalyst components. The product was a viscous dark-brown oil.

Hydrolysis of the catalyst was carried out in acetone solution at 40°; water was introduced into the system in an amount of up to 2 moles per 1 mole

$FeCl_3$. The course of hydrolysis was monitored by electrical conductivity. The hydrolysis products were precipitated from the solution with dry heptane, decanted, and pumped down to constant weight. They were fine powders and were completely soluble in the monomer.

Study of the catalysts. The infrared spectra of the catalysts were recorded on an IKS-14: for liquid products—in a thin layer between KBr windows; for powders—in KCl pellets. The accuracy of frequency determination was 5 cm^{-1}. Molecular weights were determined by Rast' s method with camphor; ΔT values were about 15°.

Polymerization. Isolation of the polymer. Polymerization was carried out in glass ampoules placed in a thermostat ($\pm 0.1^{\circ}$). The ampoules were filled with catalyst under a stream of nitrogen and with monomer on a vacuum apparatus by condensation from the gas phase. The amounts of catalyst and monomer were determined by weighing.

After polymerization the ampoule was cooled and opened; the unreacted monomer was pumped off to determine the yield. To separate it from the catalyst, the reaction mass was dissolved in acetone and acidified with HCl; the polymer was precipitated with an excess of water and dried in vacuo.

Molecular weights were calculated from the intrinsic viscosity measured in benzene at 25°; the constants of the Mark-Houwink equation were taken from the literature (^{11}). Crystallinity was measured by the X-ray diffraction method; films for these measurements and for recording IR spectra were prepared by hot pressing.

Discussion of Results

Figure 1 gives the infrared spectra of the polymer (P), the initial complex (I), and the catalysts obtained upon its hydrolysis with one (II) and two (III) equivalents of water.

With respect to complex (I), the results we obtained confirm, in the main, the conclusions drawn in work (^{5}). Indeed, first, the molar ratio of propylene oxide to $FeCl_3$ in the complex is on average 4 : 1; second, there are no spectral manifestations of the epoxide ring; third, an entire group of vibrations belonging

Fig. 1. IR spectra of polypropylene oxide (P) and catalysts I, II, III

Figure 1: Fig. 1. IR spectra of polypropylene oxide (P) and catalysts I, II, III

Fig. 2. Conductometric titration curve of catalyst I in acetone

Figure 2: Fig. 2. Conductometric titration curve of catalyst I in acetone

to the polyether chain, observed in the spectrum of the polymer,* is present in the spectra of the catalysts; and, fourth, the spectrum of the complex contains vibrations of the C—Cl bond (700 cm^{-1}). The formation of an alcoholate bond appears quite evident both from the standpoint of the general regularities of addition of epoxides to metal halides (^{12}) and on the basis of literature data (^{5,13}); the presence of one chlorine atom at iron has been reliably shown in a number of works (^{1,3,5}). All this leads to the following

Fig. 1. IR spectra of polypropylene oxide (P) and catalysts I, II, III

structure:

$$\mathrm{ClFe}\,[(\mathrm{OC_3H_6})_2\mathrm{Cl}]_2, \qquad \text{(I')}$$

which is practically identical to (I).

Upon hydrolysis of complex (I), rupture of the Fe–Cl bond occurs: the amount of HCl evolved, measured conductometrically (Fig. 2) and by ordinary titration, is strictly equivalent to the amount of water added; vibrations characteristic of OH groups appear in the spectrum (1620 and 3385 cm^{-1}). Consequently, for complex II one may write the structure:

$$\mathrm{HO—Fe}\,[(\mathrm{OC_3H_6})_2\mathrm{Cl}]_2. \qquad \text{(II)}$$

Fig. 2. Conductometric titration curve of catalyst **I** in acetone.

With deep hydrolysis, rupture of the alcoholate bond, as the least strong one, appears most probable. In confirmation of this, in the spectrum of complex III the intensity of the vibrations of OH groups increases relative to the vibrations of, for example, CH_3 groups (1485 cm^{-1}); at the same time the ratio of the intensities of the vibrations C–O–C, CH, CH_3, C–C remains the same as in complex (II). Consequently, for complex III the following formula is valid:

$$(\mathrm{OH})_2\mathrm{Fe}\,[(\mathrm{OC_3H_6})_2\mathrm{Cl}]. \qquad \text{(III)}$$

* The spectrum of polypropylene oxide has recently been fundamentally investigated in work (^{14}).

The structures of complexes II and III derived on the basis of analysis of the IR spectra are confirmed by measurements of molecular weights:

Complex	Formula	Molecular weight, calculated	Molecular weight, found
II	$FeC_{12}H_{25}O_3Cl_2$	376	366 ± 20
III	$FeC_6H_{14}O_4Cl$	241	237 ± 16

These data also indicate the monomeric composition of the catalysts. It should be recalled, however, that in all previous studies hydrolysis of complex I was carried out either in the presence of monomer or under polymerization conditions; the composition of the catalysts under these conditions may, in principle, be different.

The catalytic properties—namely, the rate constants (k^*_{observ}), molecular weights ($\overline{M}_v$), and also the degree of crystallinity of the polymers (γ), which is a qualitative measure of the stereospecificity of the catalysts—are compared in Table 1.

Table 1

Polymerization of propylene oxide in bulk on catalysts II and III
($T = 98.6°$; 1% catalyst, $\tau = 5$ hr.)

Catalyst	α	$10^3 k_{\text{observ}}$, min^{-1}	$\overline{M}_v \cdot 10^{-4}$	γ
II	0.77	4.9	5.7	0.09
III	0.52	2.5	7.2	0.23

Thus, indeed, as the degree of hydrolysis of the $FeCl_3$—PO catalyst increases, its stereospecificity increases. The increase in the number of hydroxyl groups apparently promotes a more stringent selection of the chain configuration in the act of growth. The change in rate may be

$$^*k_{\text{observ}} = -\frac{1}{\tau}\ln(1-\alpha),$$

where α is the degree of conversion.

is associated with changes in the concentration of active centers and in their activity. For a quantitative analysis of the observed quantities, a detailed study of the kinetics of polymerization and of the properties of the polymer is necessary. The catalysts obtained are also applicable to the polymerization of ethylene oxide.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
25 X 1963

REFERENCES

1. M. E. Pruitt, J. M. Baggett, U.S. pat. 2,706,181, 1955; 2,706,189, 1955; Brit. pat. 765,054, 1955.
2. C. C. Price, M. Osgan, J. Am. Chem. Soc., **78**, 4787 (1956).
3. R. O. Colclough, G. Gee et al., J. Polym. Sci., **34**, 171 (1959).
4. G. Gee, W. C. E. Higginson, J. B. Jackson, Polymer., **3**, 231 (1962).
5. L. A. Bakalo, B. A. Krentsel' et al., DAN, **142**, 347 (1962).
6. A. B. Bortovec, U.S. pat. 2,861,962, 1958; U.S. pat. 2,873,258, 1959.
7. R. O. Colclough, G. Gee, A. H. Jagger, Symposium on Macromolecular Chemistry, **1**, 1962, p. 270.
8. J. Furukawa, T. Tsuruta et al., Makromolek. Chem., **32**, 90 (1959); Jap. pat. 3394, 1961.
9. E. J. Vandenberg, J. Polym. Sci., **47**, 486 (1960).
10. *Inorganic Syntheses*, **3**, IL, 1951, p. 179.
11. R. A. Miller, C. C. Price, J. Polym. Sci., **34**, 161 (1959).
12. M. S. Malinovskii, *Olefin Oxides*, Moscow, 1961.
13. A. B. Bortovec, J. Org. Chem., **23**, 828 (1958).
14. A. Kawasaki, J. Furukawa et al., Polymer., **1**, 315 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.