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## Abstract

## Full Text

## Chemistry

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# ON THE MECHANISM OF POLYMERIZATION OF EPICHLOROHYDRIN ON THE CATALYTIC SYSTEM $FeCl_3$ × PROPYLENE OXIDE

In studying the process of polymerization of epichlorohydrin on the catalytic system $FeCl_3$× p.o., we showed ([8]) that the molar ratio monomer : catalyst regulates not only the average molecular weight but, probably, also fine details of the polymerization kinetics. It is assumed that at low catalyst concentrations the process develops in two stages: first, on the primary catalytic centers, a comparatively rapid growth of chains occurs, accompanied by gradual inactivation of the primary centers. Polymerization begins on a catalyst obtained from anhydrous ferric chloride and propylene oxide. However, as a result of the accompanying termination of the kinetic chain from the primary active centers, a new catalytic complex [$FeCl_3$ × epichlorohydrin] arises, also capable of initiating polymerization, but at a substantially different rate ([1]). So long as centers of the first kind exist, they practically completely suppress this secondary process. But with increasing degree of conversion (which increases approximately inversely proportionally to the instantaneous concentration of primary active centers), the role of the secondary centers increases and eventually becomes dominant. At high initial catalyst concentrations, the primary centers simply do not have time to be consumed during the process, and therefore one may expect that polymerization proceeds only on the primary active centers ($FeCl_3$ × p.o.).

To test this assumption, an investigation was undertaken of samples of polyepichlorohydrin obtained, other conditions being equal, at catalyst weight concentrations of 2, 5, and 10% relative to the monomer. In doing so, we expected that in those cases where two systems of active centers coexist or act successively in the polymerizing system, the corresponding molecular-weight distribution should be bimodal ([2]).

Figure 1 gives the distributions by sedimentation coefficients obtained in an ultracentrifuge under identical conditions ($C = 0.5\%$, $T = 25^\circ$, $n = 60{,}000$ rpm), without taking into account concentration effects and diffusion. For purposes of comparison these conditions are quite sufficient, since the outlines of the sedimentation curves provide the necessary information for confirming or refuting the basic hypothesis.

Fig. 1. Distribution by sedimentation constants of polyepichlorohydrin samples: a –No. 1936 (5% catalyst), $[\eta] = 0.976$; b –No. 1938 (10% catalyst), $[\eta] = 0.985$; v –No. 1937 (2% catalyst), $[\eta] = 1.33$

Figure 1: Fig. 1. Distribution by sedimentation constants of polyepichlorohydrin samples: a –No. 1936 (5% catalyst), $[\eta] = 0.976$; b –No. 1938 (10% catalyst), $[\eta] = 0.985$; v –No. 1937 (2% catalyst), $[\eta] = 1.33$

Fig. 2. Dependence of reduced viscosity on concentration. Designations as in Fig. 1 (origin of ordinate axis 0.9)

Figure 2: Fig. 2. Dependence of reduced viscosity on concentration. Designations as in Fig. 1 (origin of ordinate axis 0.9)

## Experimental Part

**Preparation of the monomer.** The commercial product was dried for five days over anhydrous calcium chloride and then fractionated on a column of 30 theoretical plates efficiency. The fraction boiling at 114–115° (760 mm Hg) was studied. Epichlorohydrin had the following

constants: $n_D^{20}$ 1.4370, $d_4^{20}$ 1.1806, $MR_D$ found 20.54, calculated 20.61. Literature data ([3]): $n_D^{20}$ 1.4364, $d_4^{20}$ 1.1801.

**Synthesis of the catalyst.** It was prepared from sublimed ferric chloride and propylene oxide according to the procedure described in the literature ([4]). A dark-brown viscous paste, having the composition: Fe 15.06%, C 37.33%, H 6.49%, dissolved in anhydrous chemically pure acetone. Catalyst concentration: 0.6 g/ml.

**Fig. 1.** Distribution by sedimentation constants of polyepichlorohydrin samples: **a** –No. 1936 (5% catalyst), $[\eta] = 0.976$; **b** –No. 1938 (10% catalyst), $[\eta] = 0.985$; **v** –No. 1937 (2% catalyst), $[\eta] = 1.33$.

**Polymerization procedure.** A catalyst solution of known concentration was placed in a glass ampoule, previously dried in vacuum and filled with nitrogen. The acetone was removed by evacuation at room temperature. Then monomer was introduced into the ampoule, it was again filled with nitrogen and sealed. The ampoules were placed in jackets and thermostated at a temperature of 80° for 24 h.

**Fig. 2.** Dependence of reduced viscosity on concentration. Designations as in Fig. 1 (origin of the ordinate axis 0.9).

**Treatment of the polymer.** The crude polymer was dissolved in hot acetone; the solution was acidified with HCl (to separate iron in the form of $FeCl_3$). After cooling, the acetone solution with the precipitated high-molecular-weight fraction was diluted with a large volume of water (low-molecular-weight fractions, which are soluble in cold acetone, also precipitated in this process). The

polymer was filtered off and dried to constant weight in vacuum at 50°. For sedimentation, 0.5% solutions of polyepichlorohydrin in tetrahydrofuran were prepared.

**Sedimentation.** Experiments to determine the distribution function with respect to sedimentation constants were carried out in a large Svedberg oil ultracentrifuge at $6 \cdot 10^4$ rpm. Sedimentation was observed using the Philpot-Svensson optical system with a phase-contrast plate. The experiments were conducted at $25 \pm 0.5°$. The sedimentation photodiagrams obtained were processed according to the usual procedure ([5]).

The intrinsic viscosity was determined at 25° in an Ostwald viscometer with a suspended level. The efflux time of the solvent (tetrahydrofuran) was of the order of $\sim$ 100 sec. Extrapolations to a zero velocity-gradient were not made because of the relatively low ($\sim 10^5$) molecular weights of the samples studied ([6]).

The partial specific volume of polyepichlorohydrin in tetrahydrofuran was determined pycnometrically at $T = 25°$.

## Discussion of Results

As can be seen from Fig. 1, the polymer of the highest molecular weight and greatest polydispersity is obtained at a catalyst content of 2%. The remnant of the low-molecular-weight maximum in the region $S = 1$ is quite clearly visible. A certain trapezoidal character of the distribution curve is due to the superposition of the primary and secondary distributions. The overall decrease in molecular weight (the shift of the curve as a whole toward smaller $S$) agrees with the data from measurements of intrinsic viscosity (Fig. 2). At a catalyst concentration of 10%, the secondary maximum disappears and the distribution becomes unimodal. From this it may be concluded that, in the latter case, only one (primary) mechanism of chain growth exists.

A rough estimate of the average molecular weight $M_{S\eta}$ by the Flory-Mandelkern formula ([7])

$$2.5 \cdot 10^6 = \frac{\eta_0 N_A}{1 - v\rho} S \left([\eta]/M^2\right)^{1/3},$$

where $\eta_0$ is the viscosity of the solvent; $N_A$ is Avogadro' s number; $v$ is the partial specific volume; $\rho$ is the density of the solution; $S$ is the sedimentation constant; $[\eta]$ is the intrinsic viscosity; and $M$ is the molecular weight ($M_{S\eta}$), gives $1 \cdot 10^5$ for the sample with 2% catalyst and, for the two other samples (5 and 10% catalyst), an average of $2.5 \cdot 10^4$.

Thus, on the basis of a statistical analysis of sedimentation diagrams obtained under identical conditions for three samples of polyepichlorohydrin synthesized

on the catalytic system [$FeCl_3$ × propylene oxide] at different catalyst concentrations, the hypothesis of a two-stage mechanism of this polymerization at primary and secondary catalytic centers has been confirmed.

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