*Polyethers. II. Copolymerizations of Propylene Oxide with Epihalohydrins**

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Although copolymerization of vinyl monomers has been extensively studied, none of the detailed information on the copolymerization of olefine oxide or polymerizable epoxy compounds has been published. The work to be reported here was undertaken for the purpose of investigating the copolymerization of epoxides using a catalyst which commonly stereospecifically catalyzes to individual monomers.

It has been reported that propylene oxide[1-3] epichlorohydrin[4] and epifluorohydrin[4] can be polymerized by ferric chloride complex catalyst to give products which are of crystalline nature.

The present paper deals with the copolymerization of propylene oxide with epichlorohydrin using the ferric chloride complex catalyst ($FeCl_3$-PO)[1] which has been shown to be the common stereospecific catalyst. An attempted copolymerization of epifluorohydrin with propylene oxide is also contained.

Experimental

Monomers and Catalyst.—Commercial epichlorohydrin and propylene oxide were dried over a molecular sieve, fractionally distilled before use. Epifluorohydrin was prepared from epichlorohydrin and anhydrous potassium fluoride by Cryszkiewicz-Trochmowski's method[5], b. p. 85~86°C. The catalyst was prepared as previously reported by Price's procedure[1,4].

Copolymerization. — All copolymerizations were carried out, as in our previous report on the stereospecific polymerization of epihalohydrins, in sealed glass tubes containing 10 g. of the varied monomer compositions and 5% by weight of catalyst. The tubes were thoroughly flushed with nitrogen before sealing and they were maintained at 85°C in an oil bath.

Purification of Polymer. — At the end of the reaction time, tubes were cooled and opened. The products were fractionated into three parts by the following procedure.

Fraction I.—To the reaction mixture was added acidified (HCl) acetone, and the insoluble material was filtered and washed with dilute HCl-acetone and methanol successively, and then reprecipitated from a hot acetone solution with methanol.

Fraction II.—The acetone solution separated from fraction I was added dropwise under stirring to a large volume of methanol. A tacky mass, or in some cases a paste, separated out from the solution.

Fraction III.—The acetone-methanol solution separated from fraction II and the methanol washing of fraction II were combined, concentrated to a small volume and poured into a large excess of water, then centrifuged to give fraction III which was a viscous liquid.

Results and Discussion

The copolymerization of epichlorohydrin with propylene oxide was studied over a wide range of monomer compositions in the presence of $FeCl_3$-PO catalyst. Results were given in Table I. The products usually were able to be fractionally separated into three fractions; an acetone-insoluble (at room temperature) fraction (I), an acetone-soluble but methanol-insoluble fraction (II), and a methanol-soluble fraction (III).

TABLE I. COPOLYMERIZATION OF EPICHLOROHYDRIN (EpCl) WITH PROPYLENE OXIDE BY $FeCl_3$-PO CATALYST

No.	EpCl in comonomer mole %	Total conversion wt. %	Fraction %		
			I	II	III
37	100	62.5	55.0	10.7	34.3
39	85.4	35.0	27.8	15.4	56.8
30	72.2	26.3	11.2	15.9	72.9
31	48.6	26.7	0.8	14.2	85.0
32	38.6	38.9	0.1	12.4	87.5
33	29.5	—	trace	5.5	94.5
34	21.2	47.0	0.4	1.0	98.6
35	13.6	50.7	nil	nil	100
36	6.5	59.0	nil	nil	100
38	0	70.2	45.0	nil	55.0

Polymerization was carried out at 85°C in bulk for 96 hr.

The acetone-insoluble fraction (I) was a solid, the yield of which was markedly affected by the composition of epichlorohydrin in comonomer mixture. Fractions II and III were a pasty mass or a viscous liquid and their purification and

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1) C. Price et al., *J. Am. Chem. Soc.*, **78**, 4787 (1956); *J. Polymer Sci.*, **34**, 153 (1959).

2) R. Colclough et al., ibid., **34**, 171 (1959).

3) J. Furukawa et al., ibid., **34**, 541 (1959).

4) S. Ishida, This Bulletin, **33**, 727 (1960)

5) MM. E. Cryszkiewicz-Trochimowski et al., *Rec. trav. chim.*, **66**, 413 (1947).

exact fractionation and its evaluation appeared to be difficult. Accordingly in this paper only fraction I was investigated in some details, and the other fractions left untouched because of the difficulties of handling.

The relationships between mole per cent of epichlorohydrin in comonomer and the yield of total product as well as the percentage relationships of each fraction were shown in Fig. 1.

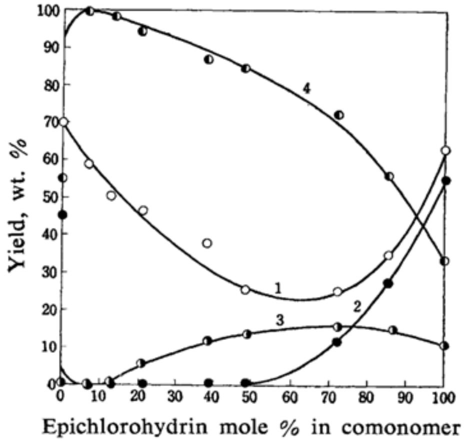


Fig. 1. The plots of yield of each fraction versus the mole % of epichlorohydrin in the comonomer.
Curve 1: total conversion, curve 2: fraction I, curve 3: fraction II, curve 4: fraction III.

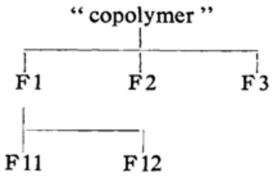
Since an amorphous polypropyleneoxide is soluble in acetone and methanol, it can hardly be suspected to be contained in fraction I. Fraction I was therefore further purified by extraction with boiling ether so as to remove the crystalline homopolymer of propylene oxide. The products thus treated were white, crystalline solids. As they were believed to be true copolymers from the following evidences, they were referred as "copolymer" and were discriminated from Fraction I. Artificial mixtures of each homopolymer (crystalline polypropylene oxide : Crystalline polyepichlorohydrin =1:1 and 1:3 by weight) could be separated completely to the original components by an extraction with boiling ether.

The further evidence that the "copolymer" was not a mixture of homopolymer of epichlorohydrin and a copolymer but a genuine copolymer, was proved by the analysis of the fractions from the "copolymer"; a successive, careful fractionation of the "copolymer" from a tetrahydrofuran solution using methanol and water as precipitants gave fractions having almost the same chlorine contents. (Table II)

All "copolymers" exhibited the X-ray patterns contributed solely by the polyepichlorohydrin part, while an artificial co-precipitated mixture

TABLE II. FRACTIONATION AND ANALYSIS OF A "COPOLYMER"

Fraction	wt. %	Cl %	EpCl mole %
"copolymer"	origin	29.89	69.3
F11	2.8	32.10	76.0
F12	27.6	29.76	67.2
F2	53.7	29.86	69.2
F3	15.9	27.47	61.9



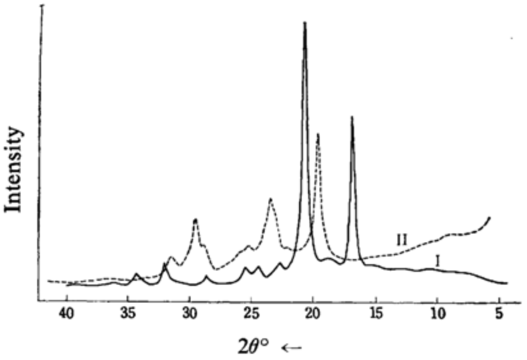


Fig. 2. X-ray diffraction spectra of the crystalline polymers.
I) Crystalline polypropylene oxide (full line).
II) Crystalline polyepichlorohydrin (dotted line).

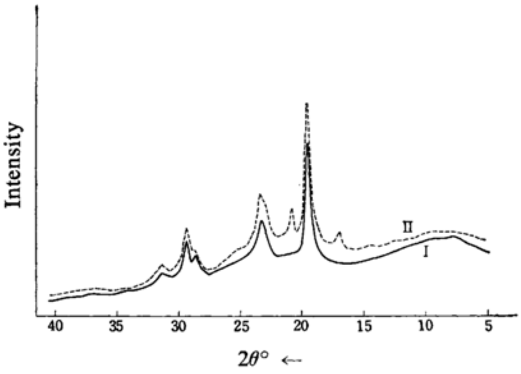


Fig. 3. X-ray diffraction spectra of the "copolymer" and "artificial mixture" of the homopolymers.
I) "Copolymer" (Found. EpCl mole % 67.2; full line).
II) "Artificial mixture" (poly-EpCl; 65 mole %, poly-PO; 35 mole %; dotted line).

of both the crystalline homopolymers which had the composition corresponding to that of the "copolymer", showed a superposed pattern of two crystalline homopolymers.

A comparison of a "copolymer" of 67.2 mole % of epichlorohydrin content with an artificial mixture of 65 mole % of crystalline polyepichlorohydrin and 35 mole % of crystalline polypropyleneoxide was shown Figs. 2 and 3, together with both crystalline homopolymers.

The experimental data were presented in Table III and the copolymer composition curve for this system together with the melting points of the "copolymers" by the capillary method were illustrated in Fig. 4.

TABLE III. COMPOSITIONS OF "COPOLYMERS" AND THEIR MELTING POINTS

No.	Comonomer EpCl mole %	"Copolymer" Cl %		
			EpCl mole %	m. p. °C
16	17.3	29.21	67.3	87
25	33.3	30.46	71.0	88
13	36.0	31.66	75.3	88
14	56.2	32.74	79.0	91
30	72.2	34.06	83.7	—
15	78.2	34.31	85.0	95
39	85.4	35.49	92.6	102
37	100	38.32	100	117

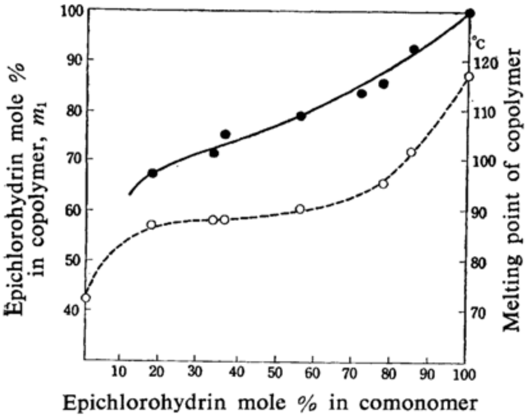


Fig. 4. Copolymer composition curve (● full line) for a system of epichlorohydrin and propylene oxide together with melting points of "copolymers" (○ dotted line).

From these data, the monomer reactivity ratios of epichlorohydrin and propylene oxide in copolymerization to crystalline "copolymer" were estimated by Mayo's method⁶⁾.

$$r_1(\text{epichlorohydrin}) = 1.8 \pm 0.3$$

$$r_2(\text{propylene oxide}) = 0.6 \pm 0.5$$

A soild non-tacky product which had been obtained by polymerization of equimolar mixture of propylene oxide and epifluorohydrin using $FeCl_3$–PO catalyst was purified by reprecipitation from an acetone solution with methanol-water. Then a fraction which was insoluble in methanol was separated from the acetone solution of the above product by adding a large excess of methanol. This fraction was a white non-tacky powder, and could not be further fractionated by reprecipitation using the same solvents and precipitants. It seemed to be possible that a crystalline polypropyleneoxide and a crystalline polyepifluorohydrin were contained in this fraction, as may be seen from the solubility data of both homopolymers in the preceding paper⁴⁾.

In fact, it was found by X-ray examination, that this fraction showed a superposed pattern of each specimen and so it might be a mixture of both the crystalline homopolymers. The attempted separation was unsuccessful because the author could not find a suitable solvent for the separation.

Attempts to copolymerize epichlorohydrin with 1, 1-dimethylethylene oxide by aluminum triethyl as catalyst did not give a copolymer but a mixture of each homopolymer.

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6) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).