Polyethers. I. Stereospecific Polymerization of Epihalohydrins†

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Recenctly a number of publications have appeared which describe the polymerization of propylene oxide with different catalysts to give a product which contains crystalline polypropyleneoxide[1-5]. On the contrary, there has been no publication on stereospecific polymerization of epihalohydrins. In the earlier work[6] or epihalohydrin, using Friedel-Crafts catalysts such as stannic chloride, it was reported to produce only viscous liquid or pasty resins of low molecular weight.

In the present paper, the author wishes to report on the synthesis of crystalline polymers of epichlorohydrin and epifluorohydrin.

The attempted stereospecific polymerization of epiiodohydrin was unsuccessful.

Experimentals

Epichlorohydrin and Propylene Oxide. — Commercial materials were dried over a molecular sieve and fractionally distilled before use.

Epifluorohydrin.—It was prepared from epichlorohydrin and anhydrous potassium fluoride by Gryszkiewicz-Trochimowsky's method[7]. The yield was lower than that reported; only 7 g. of the product boiling at 85~86°C was obtained from 100 g. of epichlorohydrin and 100 g. of anhydrous potassium fluoride.

Epiiodohydrin.—It was prepared according to the direction given by E. Wedekind.[8] Epichlorohydrin (48.5 g.) was mixed with a solution of dry sodium iodide (78.5 g.) in acetone (530 ml.) and this mixture was refluxed for 30 hr. The yield of the product boiling at 62°C (24 mmHg) was 40% (37 g.). n_D^{20} 1.5418.

Ferric Chloride Complex Catalyst.—A complex of ferric chloride with propyleneoxide was prepared immediately before use according to the procedure of Price[1]. Analogous complexes of ferric chloride with epichlorohydrin and with epifluorohydrin were prepared in a similar manner. A pasty complex catalyst was weighed and dissolved into anhydrous acetone. (about 10% by weight.)

Polymerization by Ferric Chloride Complex

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1) C. C. Price and M. Osgan, *J. Am. Chem. Soc.* **78**, 4787 (1956).

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6) "Epichlorohydrin", Shell Chem. Corp. Technical Booklet (1949).

7) MM. E. Gryszkiewicz-Trochimowski, A. Spoizynski and J. Wnuk, *Rec. trav. chim.*, **66**, 413 (1947).

8) E. Wedekind and E. Bruch, *Ann.*, **471**, 97 (1929).

TABLE I. POLYMERIZATION OF EPICHLOROHYDRIN AND PROPYLENEOXIDE BY THE $FeCl_3$ COMPLEXES AT 80°C WITHOUT SOLVENT

No.	Catalyst	wt. %	Time hr.	Total conversion %	Fraction, % I	II	III	m. p. of of I, °C
Epichlorohydrin								
Ep-9	$FeCl_3$-PO	5	41	78.5	60.7	12.2	27.1	115
Ep-27	$FeCl_3$PO	5	48	61.0	55.0	10.7	34.3	108
Ep-101	$FeCl_3$-EpCl	10	68	46.0	38.0	nil*	62.0	104
Ep-104	$FeCl_3$-EpCl	5	68	31.7	41.3	nil*	58.7	111
Propyleneoxide								
Fp-22	$FeCl_3$-PO	5	68	34.6	28.2	nil†	71.8	—
PO-10	$FeCl_3$-PO	2.5	96	81.8	44.7	nil†	55.3	59
Ep-105	$FeCl_3$-EpCl	5	68	29.0	18.0	nil†	82.0	61

* No case of the complex with epichlorohydrin has been obtained fraction II.

† In the case of propylene oxide, there was found no fraction II.

Catalyst.—The general procedures were as follows: A catalyst solution of known concentration was injected into a glass tube and then the solvent was evaporated in vacuo at room temperature. In cooling, monomer was poured into tubes. The tubes were flushed with nitrogen and sealed and then placed in a constant temperature bath at 80±0.5°C.

Polymer Purification.—At the end of the reaction time the tube was cooled and opened. The polymer produced was fractionated into three parts by the following procedure.

Fraction I.—To the reaction mixture was added acidified (HCl) acetone. The insoluble material was collected, washed with dilute HCl-acetone and methanol successively, and then reprecipitated from tetrahydrofuran solution by adding methanol as precipitant.

Fraction II.—Acetone solution separated from fraction I was added dropwise with stirring to a large volume of methanol. A white powder, in some cases a pasty mass, separated out of the solution. The precipitate was further fractionated by washing with methanol in which it was partly soluble. The insoluble residue (Fraction II) was reprecipitated from acetone solution with metanol.

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

Polymerization by Organometallic Compounds.—In all cases, the catalyst was added to the monomer or the solution of monomer in *n*-hexane or benzene, which was placed in the glass tube cooling in Dry-Ice acetone under nitrogen atmosphere, and then the tube was sealed and placed in a constant temperature bath. The polymers were isolated by an appropriate reprecipitation procedure.

Results and Discussion

Epichlorohydrin was polymerized using a complex catalyst of ferric chloride and propylene oxide ($FeCl_3$–PO) or an analogous complex catalyst of ferric chloride and epichlorohydrin ($FeCl_3$–EpCl) without solvent at 80±0.5°C. Some results were shown in Table I, in which the results of polymerization of propylene oxide by the same catalysts were compared.

The product was fractionated to three fractions, an acetone-insoluble (at room temperature) fraction (I), an acetone-soluble and methanol-insoluble fraction (II) and a methanol-soluble fraction (III).

Fraction I, a white and non-tacky solid, was insoluble in boiling methanol, ethanol, and diethyl ether and cold acetone, but soluble in boiling acetone, tetrahydrofuran and benzene. This fraction was shown by X-ray diagram to be crystalline. The melting point of the fraction I obtained from the different conditions varied from 109 to 115°C, but a purified sample showed the melting point of 119°C by capillary method. The molten polymer could be formed into a strong fiber and a tough film which showed a high degree of orientation after drawing. The drawn fiber had an identity period of 7.05±0.1 Å.

This value is nearly equal to the period of 7.16 Å on polypropyleneoxide[9].

Fraction II was a white solid, melting at

TABLE II. ELEMENTAL ANALYSIS OF THREE FRACTIONS AND LIQUID POLYMERS OBTAINED BY BF_3-ETHERATE

Fraction	C	H	Cl
I	38.85	5.44	38.06
II	38.39	5.13	37.35
III	40.17	5.86	36.54
liquid polymer	38.85	5.62	38.76
calcd. for $(-CH_2-\underset{\displaystyle CH_2Cl}{\underset{\vert}{CH}}-O-)$	38.94	5.45	38.32

9) G. Natta, *Angew. Chem.*, **68**, 393 (1956).

about 75°C, or in some case, a tacky semi-solid from which a strong film or fiber could not be obtained. Usually, it was possible to obtain an additional crystalline polymer from this fraction by redissolving it in acetone and chilling the solution to −30°C. The amorphous polymer was recovered by evaporation of the filtrate to dryness.

Fraction III was a viscous liquid or a paste and was not found to be crystalline.

All these fractions mentioned above were confirmed to be polyepichlorohydrin by the elemental analysis (Table II).

The infrared spectra of fraction I differ from those of fractions II and III and also from an amorphous liquid polymer which was obtained by a polymerization using BF_3-etherate as a catalyst, and the differences might well be attributed to the presence of crystalline-sensitive bands. As may be seen in Fig. 1, the spectral difference between the amorphous and crystalline polymers is striking, several bands at 1472(w), 1336(sh.w), 1277(s), 1232(s), 1173(s), 1036(m), 972(s) and 900(s) cm^{-1} were observed only in spectra of the crystalline fraction. A similar feature was found in the case of polypropylene-oxide: bands at 1480(s), 1330(m), 1240(s), 1140(s), 1039(m) and 931(m) cm^{-1} were observed only

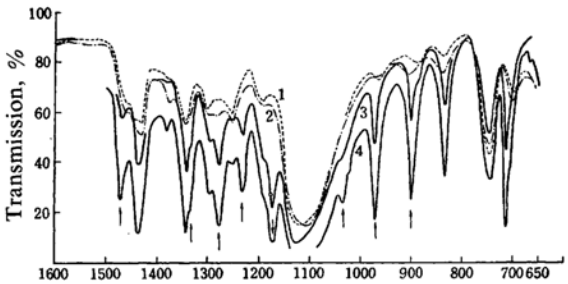

Fig. 1. Infrared spectra of the polymers of epichlorohydrin. Curve 1 ------: liquid polymer by BF_3-etherate, curve 2 -·-·-: fraction III, curve 3 ——: fraction I (KBr disk), curve 4 ——: fraction I (film). The curve of fraction II (pasty) was almost identical to that of fraction III.

TABLE III. POLYMERIZATION OF EPICHLOROHYDRIN BY SOME ORGANOMETALLIC COMPOUNDS

No.	Catalyst	%	Time, hr.	Temp., °C	Solvent	Total conv., % wt.	Fraction %		
							I	II	III
50	AIP-$ZnCl_2$	2	96	80	—	37.2	8.6	9.2	82.2
401	$AlEt_3$	2	20	r.t.	—	41.3	nil	100	nil
410	$AlEt_3$	2	6 days*	−78∼r.t.	*n*-hexane	72.7	56.2	17.5	26.3
403	$AlEt_3$-$ZnCl_2$	2	4 days*	80	benzene	ca.100	2.2	11.1	86.7
405	$AlEt_3$-$FeCl_3$	2	4 days*	80	benzene	50.9	10.5	17.0	72.5
13	$ZnEt_2$	2	8	r.t.	—	81.8	nil	0.5	99.5
14	$ZnEt_2$-Alumina		18 days	r.t.	—	none	—	—	—
40	$ZnEt_2$-$ZnCl_2$	2	8 days*	r.t.	benzene	29.2	nil	4.6	95.6

* After solidification of reaction mixture (two days), these had been kept standing with catalytic systems.

TABLE IV. X-RAY PATTERNS OF CRYSTALLINE POLYMERS

Propylene oxide		Epifluorohydrin		Epichlorohydrin	
Spacing (in Å)	Relative intensity	Spacing (in Å)	Relative intensity	Spacing (in Å)	Relative intensity
5.17	s	5.44	m		
		4.35	w	4.56	s
4.23	s	4.33	s		
4.05	w			3.83	m
3.63	w	3.67	m		
3.46	w	3.21	w		
3.10	w				
		2.85	m	3.09	w
2.78	w	2.69	m		
		2.49	w		
		2.35	w		
		2.20	w		
		1.87	w		
		1.81	w		
		1.75	w		

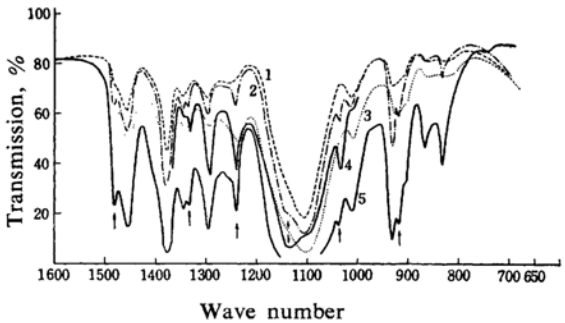

Fig. 2. Infrared spectra of the polymers of propylene oxide. Curve 1 ------ : fraction III (viscous liquid), curve 2 -·-·- : fraction II (pasty), curve 3 ····· : fraction III (pasty), curve 4 —— : fraction I (KBr disk), curves —— : fraction I (film).

in the crystalline fraction (Fig. 2).

Among organometallic compounds, some, such as aluminum triethyl, zinc diethyl and aluminum isopropoxide in conjunction with zinc chloride were found to be effective catalysts in converting epichlorohydrin to its polymer. The details were given in Table III. The polymerization proceeded rapidly at room temperature with the first two catalysts and went on fairly below room temperature, while with the last catalyst it was necessary to operate at higher temperatures. But in all cases, it was found that the amount of the crystalline fraction (fraction I) of the polymer obtained by these three catalysts was less than that of the $FeCl_3$-PO catalyst.

In the case of epifluorohydrin, ferric chloride complex catalyst was used. The polymer obtained was a solid powder which was soluble in acetone, and was insoluble in methanol, carbon tetrachloride and carbon disulfide. The polymer melted at about 68°C and was highly crystalline, a feature confirmed by X-ray examination. The molten polymer could be formed into a fiber and a film.

Table IV records the data from the X-ray

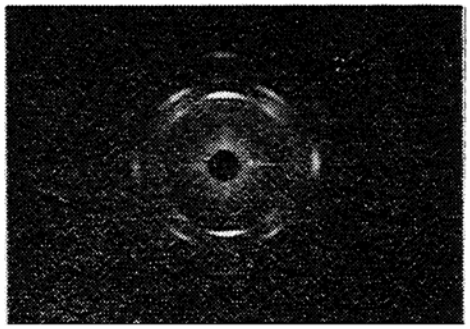

Fig. 3. X-ray pattern of a drawn fiber of polyepichlorohydrin. (fraction I).

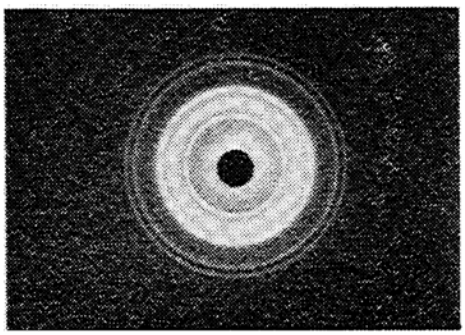

Fig. 4. X-ray pattern of polyepifluorohydrin.

patterns of the crystalline polymers of epichlorohydrin and epifluorohydrin together with that of crystalline polymer of propylene oxide for reference. X-ray diffraction patterns of the former two are shown in Figs. 3 and 4.

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