

Polyethers. III. Polymerizations and Polymers of Some Substituted Ethylene Oxides*

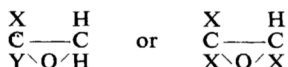
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A variety of polyethers has been prepared by ring-opening polymerization of cyclic ethers, for example from ethylene oxide¹⁾, propylene oxide²⁾, fluorine-containing olefine oxides³⁾, oxacyclobutanes⁴⁾ and from tetrahydrofuran⁵⁾.

A systematic survey in this field will offer an interesting new field for studies both on stereospecific polymerization and on structure of crystalline polyethers.

In the light of this consideration, polymerizations of some substituted ethylene oxides were tried with attempts to obtain crystalline polymers by a stereospecific polymerization for some oxides of the types.



The present paper is in the nature of a survey and a tentative report on some oxides involved.

Experimental

Materials.—*1-Chloro-2-methyl-2-propanol*.—It was prepared by Burgin's method⁶⁾. After the treatment of 90 g. of methallyl chloride with molar proportion of 80% sulfuric acid at 5–10°C for 2.5 hr. with vigorous stirring, the reaction mixture was hydrated on cracked ice. The chlorohydrin was distilled as a constant boiling mixture which, after being salted out, redistilled, b. p. 126–129°C. The yield was about 40–50% (63–66% reported).

1,1-Dimethyl Ethylene Oxide.—The preceding chlorohydrin (50 g.) was slowly added to powdered potassium hydroxide (120 g.) with stirring at such a rate that the temperature of the distillate did not exceed 55°C. When the reaction ceased the remaining volatile matter was distilled off under water pump vacuum at room temperature to a trap cooled at –70°C. The total condensate was dried with

potassium hydroxide and fractionated to yield the desired oxide; 25 g., 63% of theory, b. p. 50.2–50.5°C. n_D^{20} 1.3730 (reported b. p. 53°C, n_D^{20} 1.3730)⁷⁾.

2-Methyl-3-chloro-2-butanol.—It was prepared from 3-chlorobutanone-2 (b. p. 114°C) obtained by chlorination of methylethylketone in the presence of marbel and methyl magnesium bromide by Fournéau's method⁸⁾. 20% yield of light yellow liquid boiled at 140°C (reported b. p. 141–142°C). This chlorohydrin was also prepared by the action of hypochlorous acid on trimethyl ethylene in some runs but the yield and the purity were rather poor.

1,1,2-Trimethyl Ethylene Oxide.—It was prepared by dehydrochlorination of trimethyl ethylene chlorohydrin. Dehydrochlorination was carried out in all cases by adding the chlorohydrin slowly on to solid potassium hydroxide with stirring. The yield was about 30% based on the chlorohydrin.

Tetramethyl Ethylene Oxide.—Anhydrous pinacol (115 g.) obtained from acetone was treated with molar proportion of anhydrous hydrogen chloride (41 g.) at 35–45°C and the resulting chlorohydrin was recrystallized (melted at 63°C) and treated as above with solid potassium hydroxide to produce the epoxide (35 g.), b. p. 90–93°C, n_D^{20} 1.3985 (lit. b. p. as reported⁹⁾, n_D^{20} 1.3986). The yield was 13% based on anhydrous pinacol.

1-Methyl-1-phenyl-2-chloro Ethanol.—It was prepared by King's procedure¹⁰⁾ from monochloroacetone and phenylmagnesium bromide.

The reaction mixture was stirred at –10°C during the addition of Grignard reagent under the protection of dry nitrogen and then allowed to warm slowly to room temperature after being kept standing overnight. To the cold reaction mixture was then added dropwise with stirring a solution of ammonium chloride (100 g.) in water (400 ml.). The ether layer was separated and the aqueous layer was extracted with ether. The combined ether extracts were washed once with 250 ml. of water and dried over anhydrous sodium sulfate. Removal of the ether by distillation gave a crude residue (50 g.) which was fractionated under reduced pressure. Eighty grams (72.7%) of the product distilled at 109–112°C/12 mmHg were obtained (lit. b. p. 129–132°C/21 mmHg).

1-Methyl-1-phenyl Ethylene Oxide.—The chlorohydrin was decomposed with sodium ethoxide to give methylphenyl ethylene oxide. A colorless liquid

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1) H. Staudinger, "Hochmolekularen Organischen Verbindungen", Springer (1932), p. 287.

2) For example; C. C. Price et al., *J. Am. Chem. Soc.*, 78, 690, 4787 (1956).

3) D. D. Smith et al., *Ind. Eng. Chem.*, 49, 1241 (1957).

4) A. C. Farthing et al., *J. Chem. Soc.*, 1955, 3648.

5) K. Hamnan, *Angew. Chem.*, 63, 231 (1951).

6) J. Burgin and G. Hearne, *Ind. Eng. Chem.*, 33, 385 (1941).

7) W. T. Somerville, *J. Am. Chem. Soc.*, 72, 737, 2185 (1950).

8) M. M. Fournéau and M. Tiffeneau, *Compt. rend.*, 145, 437 (1907).

9) F. H. Norton, *J. Am. Chem. Soc.*, 58, 2147 (1936).

10) L. F. King, *ibid.*, 61, 2383 (1939); W. J. Hickinbottom et al., *J. Chem. Soc.*, 1954, 4200.

b. p. 75~76°C/12 mmHg (lit.¹⁰) b. p. 72~75°C/11 mmHg).

1,1-Diphenyl-2-chloroethanol.—To a stirred solution of ethyl chloroacetate (84 g.) in dry ether (300 ml.) was added dropwise over a period of 4.5 hr. a solution of phenylmagnesium bromide previously prepared from magnesium (36.5 g.) and bromobenzene (252 g.) in dry ether (650 ml.). The reaction mixture was maintained at 0 to -5°C and then treated according to the procedure similar to the synthesis of 1-methyl-1-phenyl-2-chloroethanol. The product was isolated by distillation under reduced pressure and purified by recrystallization from ligroin. A yield 46 g. (26%), m. p. 53~56°C (lit. m. p. 52~57°C).

1,1-Diphenyl Ethylene Oxide.—A yield of an almost quantitative amount of crude oxide (m. p. 42~45°C) was obtained by action of the chlorohydrin on the aqueous solution of sodium hydroxide by Zaugg's method¹¹). Twice recrystallization from absolute ethanol gave a pure oxide, m. p. 55~56°C (reported m. p. 56~57°C).

1,1-Diethyl-2-chloroethanol.—It was prepared by the same procedure used in the synthesis of 1,1-diphenyl-2-chloroethanol. To a stirred solution of ethylchloroacetate (65 g.) in dry ether (300 ml.) was added a solution of ethylmagnesium bromide previously prepared from magnesium (24 g.) and ethyl bromide (109 g.) in dry ether (200 ml.). Resulting chlorohydrin was obtained in a yield of 44%, b. p. 66~67°C/16~18 mmHg (lit.¹²) b. p. 70°C/20 mmHg).

1,1-Diethyl Ethylene Oxide.—It was prepared by the conversion of the chlorohydrin by the same procedure as in the synthesis of 1,1-dimethyl ethylene oxide mentioned above. Thirty grams of the chlorohydrin gave 15 g. of the raw epoxide, which gave by the fractional distillation a distillate boiling at 105~106°C (lit. b. p. 107°C).

General Procedure of Polymerization.—A catalyst was added to a monomer or a monomer solution in a glass tube which was flashed by nitrogen

previously and then cooled in dry ice-acetone.

The tube was sealed and placed in a constant temperature bath. At the end of the reaction time, the tube was recooled and opened. To the reaction mixture, a small quantity of methanol or some appropriate agents for stopping the reaction were added and the resulting polymer was washed thoroughly with methanol so as to remove the catalyst residue. In the case when the reaction product was an oil it was dissolved in acetone and precipitated with a large volume of methanol.

Results and Discussion

1, 1-Dimethyl Ethylene Oxide (D. M. E. O.).—1,1-Dimethyl ethylene oxide was attempted to polymerize by different catalysts and some details were given in Table I. The polymer was found to consist of two fractions; fraction I was insoluble in acetone, benzene, methanol and ether and soluble in hot tetrahydrofuran, dioxane and dimethylformamide, except in some cases, where a small quantity of the insoluble part in these solvents was contained. Fraction II was soluble in acetone but insoluble in methanol.

Fraction I, a white and nontacky powder, was shown by X-ray examination to be crystalline. The melting points of these materials obtained from the different catalysts varied from 127 to 155°C. Fraction II was usually a white solid, melting at about 90~100°C, but in the case, where diethyl zinc and FeCl₃-PO was used as catalyst, it was a tacky semi-solid or a pasty mass.

As may be seen in Table I, the polymerization with the catalysts borontrifluoride etherate (BF₃-Et₂O) and triethyl aluminum (AlEt₃) and diethyl zinc (ZnEt₂) respectively proceeded very rapidly at low temperatures;

TABLE I. POLYMERIZATION OF 1,1-DIMETHYL ETHYLENE OXIDE WITH DIFFERENT CATALYSTS

Catalyst	wt. %	Reaction temp. °C	Time hr.	Yield, %	Fraction, %		m. p. of I, °C
					I	II	
FeCl ₃ -PO	5	70	64	15.0	42	58	—
FeCl ₃ ^{a)}	5	80	20	15.6	major	minor	—
BF ₃ Et ₂ O	5	r. t.	24	considerable	major	minor	159~160
TiCl ₄	3.5	-78-r. t.	48	28.5	68.0	32.0	—
TiCl ₄	3.0	r. t.	3 days	25.9	83.0	17.0	127
AIP ^{b)}	2	80	20 days	nil	—	—	—
AIP-ZnCl ₂ ^{c)}	2	80	6 days	nil	—	—	—
AlEt ₃ ^{d)}	3.5	-78-r. t.	6 days	57.2	91.4	8.6	155
AlEt ₃	5	r. t.	5	—	27.2	—	152
ZnEt ₂ ^{e)}	5	r. t.	4 days	46.8	83.4	16.6	151~152
ZnEt ₂ -Al ₂ O ₃ ^{f)}	2	r. t.	20 days	nil	—	—	—

a) anhydrous ferric chloride, b) aluminum isopropoxide, c) aluminum isopropoxide-zinc chloride, d) trimethyl aluminum in *n*-hexane, e) diethyl zinc in diethyl ether, f) diethyl zinc on alumina.

11) H. E. Zaugg et al., *J. Am. Chem. Soc.*, **80**, 2770 (1958).

12) R. Dalebroux and H. Wuyts, *Chem. Zentr.*, 1906 II, 1179.

TABLE II. COPOLYMERIZATION OF 1,1-DIMETHYL ETHYLENE OXIDE (M_1) WITH EPICHLOROHYDRIN (M_2) USING $AlEt_3$ AS CATALYST IN *n*-HEXANE AT LOW TEMPERATURE

M_1 in comonomer		Total conversion %	Fraction, %		Chlorine content in I, %	m. p. of I °C	X-ray pattern of I
wt. %	mol. %		I	II			
100	100	57.2	91.0	9.0	—	155	DMEO
68.0	74.0	22.6	36.6	63.4	8.66	125	DMEO
41.3	47.0	34.3	8.5	91.5	37.37	117	EpCl
19.0	23.0	39.1	84.9	15.1	—	—	EpCl
0	0	72.7	73.7	26.3	—	117	EpCl

Fraction I: methanol-insoluble part, Fraction II: methanol-soluble part

TABLE III. COPOLYMERIZATION OF 1,1-DIMETHYL ETHYLENE OXIDE (M_1) WITH EPICHLOROHYDRIN (M_2) BY 4% OF $AlEt_3$ IN *n*-HEXANE AT $80 \pm 0.5^\circ C$

M_1 in comonomer		Total conversion %	Fraction			Chlorine content in I, %	m. p. of I °C	X-ray pattern of I
wt. %	mol. %		I	II	III			
86.4	89.8	80.8	16.7	83.3		2.44	140	DMEO
68.0	74.0	47.0	13.4	54.3	32.3	2.22	140	DMEO
41.3	47.0	76.6	4.3	3.2	92.5	36.45	117	EpCl
19.0	23.0	83.8	9.5	11.5	79.0	32.07	117	EpCl

the reaction mixture was solidified as soon as the catalyst was added. Aluminum isopropoxide (AIP) and the one in conjunction with zinc chloride ($AIP-ZnCl_2$)¹³⁾ as well as diethyl zinc-alumina system¹⁴⁾ were completely inactive for this monomer in contrast to the fact of their being active for propylene oxide.

Copolymerizations of 1,1-dimethyl ethylene oxide with epichlorohydrin (EpCl) were also studied. Epichlorohydrin was chosen for the convenience of its analysis and $AlEt_3$ was used as catalyst because of the feasibility of its purification from resulting polymer compared with those from $FeCl_3-PO$ catalyst. Some runs of polymerization were carried out at a low temperature. (The catalyst was added to the monomer solution in a glass tube cooled in dry ice-acetone, the reaction started and the reaction mixture was solidified immediately, and then the glass ampoule was placed in a water bath and kept at room temperature for further promotion of polymerization.) The other runs were done in an oil bath at $80^\circ C$ from the beginning. The resulting products were in both cases fractionated by the precipitation method. In the case at low temperature, the products were divided into two fractions; methanol-insoluble fraction (I) and methanol-soluble fraction (II). In the latter case at the higher temperature, the product was separated into three fractions; acetone-soluble fraction (I'), acetone-soluble but methanol-insoluble fraction (II') and methanol-soluble fraction

(III). These results were shown in Tables II and III.

In both the cases, there existed a minimum of conversion versus monomer composition fed in the range of monomer composition of about 70% of 1,1-dimethyl ethylene oxide (M_1) in comonomer, and this corresponded also with a minimum yield of fractions I, I' and II' at about 40% of M_1 . Of these fractions, fractions I and I' were white powders and these two were examined in some details. Melting points, chlorine contents and X-ray patterns of these fractions showed that these fractions were either homopolymer of D. M. E. O. or that of EpCl depending upon the preference of one monomer in the monomer composition.

The critical monomer composition coincided with the composition corresponding to a minimum percent of fraction I and I'.

From the results mentioned above, it may be seen, in this comonomer system, that a crystalline copolymer had not been obtained and fractions I and I' are both of the pure homopolymers.

1,1,2-Trimethyl Ethylene Oxide (tri-M.E.O.).

—This oxide was polymerized neither with $FeCl_3-PO$ nor with $AIP-ZnCl_2$ as catalyst but with BF_3Et_2O it was rapidly polymerized at low temperature to a viscous liquid (Table IV). A tacky solid or an elastic mass could be obtained only with $AlEt_3$ at room temperature. The polymer was soluble in ether and acetone but insoluble in methanol.

1,1,2,2-Tetramethyl Ethylene Oxide (tetra-M.E.O.). —Both the catalysts $AlEt_3$ and $AIP-ZnCl_2$ were inactive for the polymerization

13) M. Osgan and C. Price, *J. Polymer Sci.*, **34**, 153 (1959).

14) J. Furukawa et al., *ibid.*, **36**, 541 (1959).

TABLE IV. POLYMERIZATION OF 1,1,2-TRIMETHYL ETHYLENE OXIDE

Catalyst	%	Temp., °C	Time, hr.	Conversion, %	Remarks
BF ₃ Et ₂ O	0.5	-68-r. t.	24	ca. 98	viscous liquid
FeCl ₃ -PO	ca. 2	80	20 days	none	
AIP-ZnCl ₂	2	80	1 month	none	
AlEt ₃	2	r. t.	68	57.0	tacky solid

TABLE V. POLYMERIZATION OF TETRAMETHYL ETHYLENE OXIDE

Catalyst	wt. %	Solvent	Temp., °C	Time, hr.	Conversion, %
BF ₃ Et ₂ O	2	CH ₂ Cl ₂	r. t.	72	51.3
AIP-ZnCl ₂	2	benzene	80	5 days	none
AlEt ₃	5	benzene	r. t.	"	trace
"	5	none	r. t.	"	trace

of this monomer but BF₃Et₂O gave a crystalline polymer (Table V). The polymer neither melted nor decomposed even at 300°C. No usual organic solvents could be found for this polymer but the polymer was swollen by decalin or tetralin at 80~90°C. An attempt to copolymerize this monomer with 1,1-dimethyl ethylene oxide by BF₃Et₂O was failed and gave only polymer of tetra-M. E. O. which was proved by X-ray examination, melting point and solubility (Table VI).

TABLE VI. ATTEMPTED COPOLYMERIZATION OF TETRAMETHYL ETHYLENE OXIDE (M₁) with 1,1-dimethyl ethylene oxide
catalyst: BF₃-Et₂O 2% wt.,
solvent: methylene chloride,
temp.: r. t., reaction time: 4 days

M ₁ in comonomer mol. %	Total conversion wt %	Remarks
100	51.3	Poly-tetra-M. E. O.
90	20.6	"
75	5.9	"
50	3.9	"
25	trace	"
10	1.8	"
0	36.7	Poly-D.M.E.O.

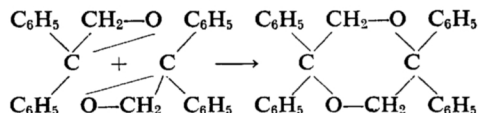
1-Methyl-1-phenyl Ethylene Oxide (M.P.E.O.)—BF₃Et₂O, AlEt₃ and ZnEt₂ were active to polymerize this epoxide which was converted into viscous liquid polymers which were insoluble in methanol. BF₃Et₂O gave a reddish brown oily polymer, while the others gave colorless polymers.

No polymer could be obtained with AIP-ZnCl₂ system even after prolonged heating at 80°C for two days. FeCl₃-PO catalyst gave a colored oily product accompanied by a small quantity of needle crystals whose structure has not yet been determined in this work.

1,1-Diphenyl Ethylene Oxide (D.P.E.O.).—AlEt₃ and AIP-ZnCl₂ were inactive for this

monomer while both BF₃Et₂O and TiCl₄ were active catalysts. To a cooled solution of the oxide in methylene dichloride, the catalyst, for instance BF₃Et₂O 3% by weight was added slowly and the reaction mixture was sealed and placed in a dry ice-acetone bath for two days. The glass ampoule was then opened and an ammoniacal methanol was poured into the ampule and the product was washed thoroughly with methanol.

The product (38.5% yield) was needle crystals and did not melt at 300°C but was found to sublime slightly. This material was believed to be a ring dimer of the epoxide



and was shown from the elemental analysis and the molecular weight determination, both of which were demonstrated in good accordance with a calculated value for the ring dimer (Table VII).

TABLE VII. SOME ANALYSIS OF THE REACTION PRODUCT

	C	H	O	Mol. wt*
Obs.	87.75	6.24	8.01	383
Calc. for ring dimer	85.68	6.16	8.15	392.3

* by cryoscopic method using camphor

Infrared spectra of the product showed the absence of the characteristic absorption band of hydroxyl group at near 3500 cm⁻¹ and disappearance of bands of epoxy ring observed in the monomer at 825 and 925 cm⁻¹. Bands associated with an epoxy ring of monomer epoxide were estimated to be at 825 and 925 cm⁻¹ by comparative method of spectra of 1,1-diphenyl ethylene, its polymer¹⁵⁾ and 1,4-

15) K. Kuwata et al., *J. Chem. Soc. Japan, Pure Chem. Section (Nippon Kagaku Zasshi)*, **80**, 25 (1959).

TABLE VIII. INFRARED SPECTRA OF THE POLYMERS FROM FOUR METHYL-SUBSTITUTED ETHYLENE OXIDES

Propylene oxide (cryst.)		D.M.E.O.		Tri-M.E.O.		Tetra-M.E.O.	
cm ⁻¹	Relative intensity	cm ⁻¹	Relative intensity	cm ⁻¹	Relative intensity	cm ⁻¹	Relative intensity
2980	7	2970	6	2975	8	2990	6
2910	sh 8	2920	5	2940	7	2960	sh 6
2880	sh 8	2880	4.5	2885	sh 5	2880	sh 2
1480	8 cr	1465	3.5	1465	4.5	1477	3.5
1453	9						
1375	10	1386	4	1370	6.5	1377	6
1342	8	1354	6	1360	6.5	1361	6
1330	8 cr						
1293	9	1266	2				
1240	8 cr	1245	b 2	1235	b 1		
1140	8 cr	1163	8.5	1160	7.5	1163	9
1105	9	1115	8	1105	9	1120	10
				1090	9		
1038	8.5 cr			1044			
1010	8	1013	3.5	1020	b 4		
				993	4	985	b 5
				970	b 2	975	4.5
932	9 cr			930	b 2	944	b 2
917	8.5	890	5.5			905	b 2
905	sh 6						
866	4.5					714	1
831	6						

sh : shoulder absorption band, b : broad band, cr : crystalline sensitive band*.

TABLE IX. SOME PHYSICAL PROPERTIES OF POLYMERS OF SUBSTITUTED ETHYLENE OXIDES

	$\begin{array}{c} R_1 \quad R_3 \\ \diagdown \quad \diagup \\ C-C \\ \diagup \quad \diagdown \\ R_2 \quad O \quad R_4 \end{array}$				m. p., °C	Remarks
PO	R ₁	R ₂	R ₃	R ₄	72	crystalline
D.M.E.O.	CH ₃	H	H	H	155	crystalline
Tri-M.E.O.	CH ₃	CH ₃	H	H	—	amorphous, pasty
Tetra-M.E.O.	CH ₃	CH ₃	CH ₃	CH ₃	<300	crystalline
M.P.E.O.	CH ₃	C ₆ H ₅	H	H	—	amorphous, liquid
D.P.E.O.	C ₆ H ₅	C ₆ H ₅	H	H	—	ring dimer

TABLE X. X-RAY DIFFRACTION SPECTRA OF CRYSTALLINE POLYMER

Propylene oxide		D.M.E.O.		tetra-M.E.O.	
Spacing, Å	Relative intensity	Spacing, Å	Relative intensity	Spacing, Å	Relative intensity
5.17	s	5.20	vs	6.04	vs
		4.58	w	4.61	w
4.23	s	4.12	s		
4.05	w	3.53	m	3.43	s
3.63	w	3.03	s	2.96	vw
3.46	w	2.79	m	2.68	w
3.10	w	2.54	m	2.31	m
2.78	w	2.23	w		
2.61	w	2.12	m		
		1.96	w		

* Part I. This Bulletin, 33, 727 (1960).

dioxane and these bands were in agreement with 877 ($11.40\ \mu$), 812 ($12.3\ \mu$) cm^{-1} of styrene oxide and 863 ($11.85\ \mu$), 786 ($12.72\ \mu$) cm^{-1} of α -methyl styrene oxide observed by Patterson¹⁶) (Fig. 1).

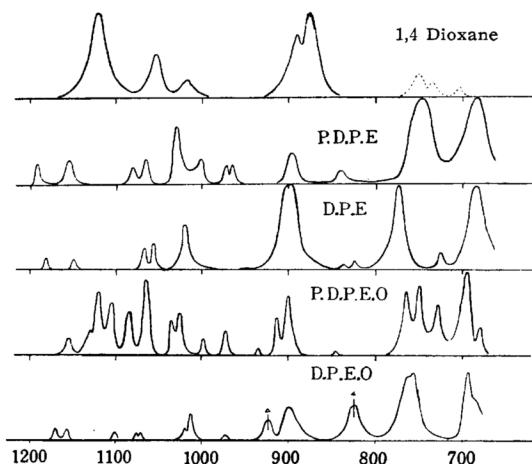


Fig. 1. Infrared spectra of diphenyl ethylene oxide and related compounds; D.P.E.O.; diphenyl ethylene oxide P.D.P.E.O.; polymer of D.P.E.O., D.P.E.: diphenyl ethylene, P.D.P.E.: polymer of D.P.E. Epoxy bands were marked by triangle.

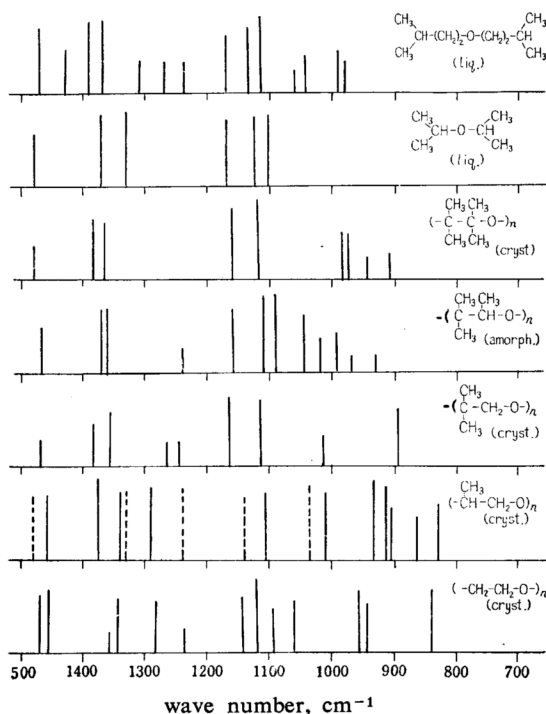


Fig. 2. Infrared spectra of polymers of methyl-substituted ethylene oxides and some related ethers (dotted line: crystalline sensitive bands).

Since absorption bands characteristic of 6-membered carbon oxygen ring had been noted to occur at near $11\ \mu$ and in the range $1124\sim 1030\ \text{cm}^{-1}$ by Shreve¹⁷), bands at near $1100\ \text{cm}^{-1}$ and $912\ \text{cm}^{-1}$ which appeared in the spectra of the dimer, would be bands characteristic of ring ether.

1,1-Diethyl Ethylene Oxide.—Using both $\text{BF}_3\text{Et}_2\text{O}$ and TiCl_4 as catalyst, no polymer-like substance could be obtained while a resin-like material was produced by AlEt_3 as catalyst. But no further experiments could proceed because of paucity of the material.

Infrared spectra of polymers from four methyl-substituted ethylene oxides together with some related ethers for comparison were shown in Fig. 2 and their characteristic bands were tabulated for comparison in Table VIII.

Some properties of polymers were summarized in Table IX and X-ray spectra of crystalline polymers were shown in Table X and Figs. 3 and 4.

The action of AlEt_3 as polymerization catalyst for epoxides used in this experiment might well be compared with those of cationic

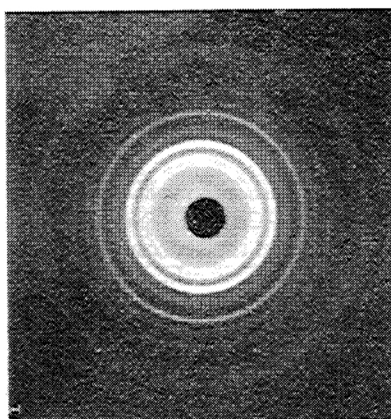


Fig. 3. X-ray pattern of the polymer of 1,1-dimethyl ethylene oxide.

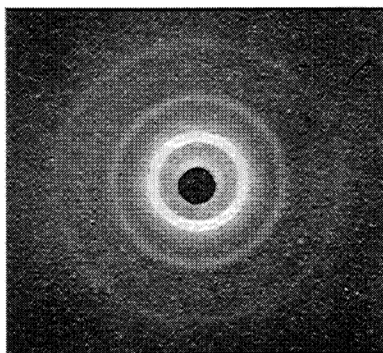


Fig. 4. X-ray pattern of the polymer of tetramethyl ethylene oxide.

16) W. A. Patterson, *Anal. Chem.*, **26**, 823 (1954).

17) O. D. Shreve et al., *Anal. Chem.*, **23**, 382 (1951).

catalysts. These epoxides were polymerized by AlEt_3 as well as $\text{BF}_3\text{Et}_2\text{O}$ and TiCl_4 at low temperature. The similar feature was illustrated in the case of four and five membered cyclic oxides¹⁸⁾, that is, ring ethers such as oxacyclobutanes, tetrahydrofuran were polymerized by AlEt_3 as well as $\text{BF}_3\text{Et}_2\text{O}$. While catalyst ZnEt_2 seemed to act in a manner unlike that of AlEt_3 .

"Coordinated complex catalyst" such as $\text{FeCl}_3\text{-PO}$ and AIP-ZnCl_2 could be applied to polymerization of limited kinds of epoxides and the polymerization by these catalysts proceeded much slower in the rate than that both by some cationic catalysts and some

organometallic compounds such as AlEt_3 and EnEt_2 .

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18) S. Kambara et al., *J. Polymer Sci.*, **27**, 586 (1958).