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# The Copolymerization of the Vinyl Monomer with a Cyclic Compound. III. The Cationic Copolymerization of Styrene with Substituted Ethylene Oxides*

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The copolymerization of styrene with substituted ethylene oxides catalyzed by boron trifluoride - diethyl ether has been investigated. In all cases, rather low-molecular-weight copolymers were obtained. The copolymerization reactivity of the substituted ethylene oxides with styrene varied with the substituents, in the order of: isobutene oxide>propylene oxide>styrene oxide>epichlorohydrin. This has been explained in terms of cross-propagation or the reaction of the growing oxide cation with styrene.

The styrene unit content of the copolymer of styrene and epichlorohydrin increases with an increase in the solvent polarity and with an increase in the temperature. It has been concluded from the experimental results that the copolymerizability of alkylene oxide toward styrene is increased by the introduction of electron-releasing substituents into the oxide and by the use of a polar solvent at a moderate temperature.

Recently the investigations of the cationic copolymerizations of some vinyl monomers with 3, 3-bis(chloromethyl)oxetane[1] and with β-propiolactone[2] have been reported. During the course of these investigations, it has been suggested that the structure of a growing terminal cation arising from the cyclic compound in its copolymerization reactivity is significant.

This work was undertaken in order to obtain information regarding the effect of the substituents in cyclic ethers on their cationic copolymerizations with styrene. Styrene (St) was copolymerized with substituted ethylene oxides, such as epichlorohydrin (ECH), propylene oxide (PO), isobutene oxide (IBO) and styrene oxide (StO), in the presence of a boron trifluoride - diethyl ether catalyst. The effects of the solvent and the temperature were also investigated.

## Experimental

**Materials.**—Isobutene oxide was prepared from methallyl chloride through the corresponding chlorohydrin by the method described by Ishida.[3] B. p. 52°C, $n_D^{20}$ 1.3732; lit.[3] b. p. 50.2—50.5°C, $n_D^{20}$ 1.3730.

Styrene oxide was prepared from styrene through the corresponding iodohydrin, following the procedure used by Golumbic and Cottle.[4] B. p. 87°C/23 mmHg, $n_D^{25}$ 1.5329; lit.[4] b. p. 87—88°C/23 mmHg, $n_D^{25}$ 1.5331.

Epichlorohydrin, propylene oxide and styrene were obtained commercially. All of the monomers were distilled over calcium hydride before use.

The purifications of boron trifluoride - diethyl ether and methylene chloride were carried out as has been described in a previous paper.[1] Toluene and nitromethane were also purified by the usual methods.

**Copolymerization Procedure.**—The copolymerization was carried out in a glass stoppered-test tube. The initial concentrations of the total monomers and the catalyst in the copolymerization were kept constant at 3.0 and 0.07 mol./l. respectively. The reaction was stopped at a given time by the addition of ammoniacal methanol. Then the mixture was washed by pure water in order to remove the residual catalyst, and the volatile substances were evaporated under reduced pressure at a somewhat elevated temperature until the weight of residue became constant. The other procedures were the same as in a previous paper.[1]

**The Analysis of the Resulting Polymer.**—The copolymer composition was determined from the ele-

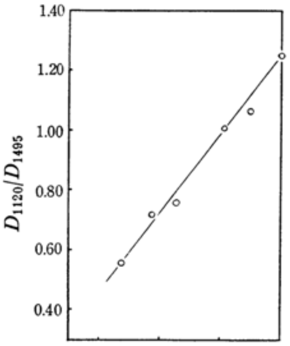

Fig. 1. Calibration curve for the composition of the styrene-styrene oxide copolymer.

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* Vinyl Polymerization. CXXXII.

[1] S. Aoki, Y. Harita, T. Otsu and M. Imoto, This Bulletin, **38**, 1922 (1965).

[2] S. Aoki, Y. Harita, T. Otsu and M. Imoto, ibid., **38**, 1928 (1965).

[3] S. Ishida, ibid., **33**, 924 (1960).

[4] C. Golumbic and D. L. Cottle, *J. Am. Chem. Soc.*, **61**, 996 (1939).

Table I. Copolymerization of styrene with substituted ethylene oxides*

| Substituted ethylene oxide | Reaction time min. | Conversion % | Polymer obtained | | | | Hot methanol-insoluble fraction | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Anal. % | St mole fraction | Mol. wt. | Appearance | Wt. % | Anal. % | St mole fraction | Mol. wt. | Appearance |
| ECH | 5 | 5.5 | Cl: 28.34 | 0.25 | 590 | Viscous liquid | 17.0 | Cl: 13.24 | 0.63 | 3240 | Glassy solid |
| PO | 5 | 5.1 | C: 83.71 | 0.64 | 1270 | Resinous solid | 84.2 | C: 87.41 | 0.78 | 2340 | Colorless powder |
| IBO | 7 | 4.9 | C: 88.75 | 0.81 | 3760 | Resinous solid | 93.2 | C: 89.49 | 0.85 | 4210 | Colorless powder |
| StO | 1 | 18.9 | $\frac{D_{1120}}{D_{1495}}$: 0.668 | 0.44 | 420 | Waxy solid | 24.5 | $\frac{D_{1120}}{D_{1495}}$: 0.485 | 0.57 | 1060 | Glassy solid |

* Initial mole ratio of styrene and substituted ethylene oxide was 9/1, in methylene chloride at 0°C.

Table IV. Effects of solvents and temperature on the composition of styrene-epichlorohydrin copolymer*

| Solvent** | Reaction temp. °C | Reaction time min. | Conversion % | Polymer obtained | | | Hot methanol-insoluble fraction | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Cl content % | St mole fraction | Appearance | Wt. % | Cl content % | St mole fraction | Mol. wt. | Appearance |
| Toluene (2.38) | −30 | 3.3 | 3.0 | 33.60 | 0.11 | Viscous liquid | 11.6 | | | | Rubbery substance |
| | 0 | 2.2 | 5.1 | 32.66 | 0.13 | | 3.4 | | | | |
| | 30 | 1.3 | 7.4 | 31.21 | 0.17 | | 2.0 | | | | |
| Methylene chloride (9.08) | −30 | 4.0 | 4.1 | 30.18 | 0.19 | Viscous liquid | 21.0 | 21.03 | 0.42 | | Rubbery substance |
| | 0 | 5.0 | 5.5 | 28.34 | 0.25 | | 17.0 | 13.24 | 0.63 | 3240 | |
| | 30 | 2.2 | 6.4 | 24.68 | 0.38 | | 33.0 | 12.23 | 0.66 | 1380 | Glassy solid |
| Nitromethane (35.87) | −30 | 2.0 | 1.8 | 15.45 | 0.57 | Resinous solid | 43.2 | 5.70 | 0.84 | 2040 | Glassy solid |
| | 0 | 1.3 | 3.3 | 11.41 | 0.68 | | 44.5 | 4.84 | 0.86 | 1780 | |
| | 30 | 0.8 | 5.2 | 8.42 | 0.76 | | 70.5 | 4.87 | 0.86 | 1300 | |

* $[\text{Styrene}]_0/[\text{Epichlorohydrin}]_0=9/1$.

** Figures in parentheses are the dielectric constant.

mentary analysis of the resulting polymer, except in the case of the styrene oxide copolymer. The composition of the styrene - styrene oxide copolymer was determined from its infrared spectrum, using the ratio of the optical densities at 1120 and 1495 cm$^{-1}$, which are the characteristic frequencies of the ether linkage and the benzene nucleus respectively. The calibration curve is shown in Fig. 1.

The copolymer formation was confirmed by the fractional extraction of the resulting polymer with hot methanol, in which the homopolyethers were soluble, while polystyrene was insoluble.

The molecular weight of the resulting polymer was determined with a Mechrolab. vapor pressure osmometer Model 301-A.

## Results and Discussion

**The Effect of the Substituents of the Oxides.** —Styrene was copolymerized with the substituted ethylene oxides in the initial monomer mole ratio of 9/1 in methylene chloride at 0°C. The results are given in Table I, while the infrared spectra of the resulting polymers are shown in Fig. 2.

The polymers obtained above were separated by fractional extraction with hot methanol into soluble and insoluble fractions in order to confirm the copolymer formation. The data on hot methanol-insoluble fractions are also given in Table I.

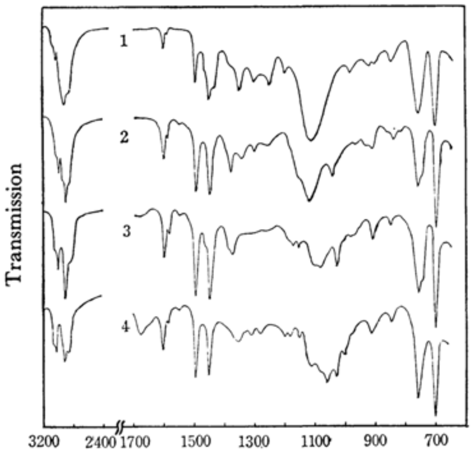


Fig. 2. Infrared spectra of the copolymer of styrene and substituted ethylene oxides.
1: St-ECH; 2: St-PO; 3: St-IBO; 4: St-StO

Furthermore, the copolymerizations of styrene with epichlorohydrin and with styrene oxide were carried out at different monomer mole ratios in methylene chloride at 0°C. The results are given in Tables II and III, while the monomer-copolymer composition curves are shown in Fig. 3.

Table II. Copolymerization of styrene with epichlorohydrin*

| St mole fraction in monomer mixture | Reaction time min. | Conversion % | Cl in copolymer % | St mole fraction in copolymer |
|---|---|---|---|---|
| 0.90 | 3 | 5.4 | 29.57 | 0.20 |
| 0.80 | 1 | 8.2 | 34.76 | 0.07 |
| 0.70 | 5 | 13.8 | 36.33 | 0.03 |
| 0.60 | 5 | 18.6 | 36.49 | 0.03 |
| 0.50 | 5 | 23.7 | — | — |
| 0.00 | 1 | 54.4 | 37.75** | 0.00 |

* In methylene chloride at 0°C.
** Calculated value for $C_3H_5OCl$ is 38.32.

Table III. Copolymerization of styrene with styrene oxide*

| St mole fraction in monomer mixture | Reaction time sec. | Conversion % | $\frac{D_{1120}}{D_{1495}}$ | St mole fraction in monomer mixture |
|---|---|---|---|---|
| 0.90 | 60 | 18.9 | 0.668 | 0.44 |
| 0.80 | 45 | 25.6 | 0.739 | 0.39 |
| 0.70 | 45 | 30.9 | 0.889 | 0.27 |
| 0.60 | 45 | 29.9 | 0.923 | 0.24 |
| 0.50 | 30 | 30.8 | 1.091 | 0.12 |
| 0.40 | 30 | 35.5 | 1.074 | 0.13 |
| 0.00 | 15 | 33.3 | 1.250 | 0.00 |

* In methylene chloride at 0°C.

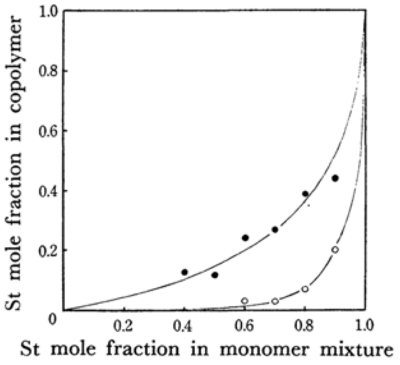


Fig. 3. Monomer-copolymer composition curves.
-○-: St-ECH; -●-: St-StO

From the infrared spectra (Fig. 2) and the elementary analyses (Table I), it was found that the polymers obtained in the systems of styrene-substituted ethylene oxides contained both monomer units. The hot methanol-insoluble fractions of the resulting polymers also contained both monomer units (Table I). This indicates that the copolymers were obtained under the present conditions in every case.

Table I makes it clear that the cationic copolymerizability of the substituted ethylene oxides by styrene varied with their substituents, in the order of:

isobutene oxide>propylene oxide>styrene oxide
>epichlorohydrin

The contents of the methanol-insoluble fraction in these copolymers and of styrene units in this fraction were also found to increase in the order given above (Table I).

The real values of the monomer reactivity ratios could not be evaluated in this work, because the molecular weights of the resulting copolymers were low. However, the following propagation reactions may reasonably be the most significant in determining the resulting copolymer composition, even though the initiation and the termination reactions have an influence on them:

$$\text{-St}^+ + \text{St} \xrightarrow{k_{11}} \text{-St·St}^+ \quad (1)$$

$$\text{-St}^+ + \text{Oxide} \xrightarrow{k_{12}} \text{-St·Oxide}^+ \quad (2)$$

$$\text{-Oxide}^+ + \text{Oxide} \xrightarrow{k_{22}} \text{-Oxide·Oxide}^+ \quad (3)$$

$$\text{-Oxide}^+ + \text{St} \xrightarrow{k_{21}} \text{-Oxide·St}^+ \quad (4)$$

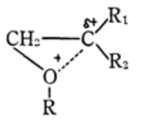
The $k_{11}$ value is essentially constant as compared with the other constants. When both $k_{12}$ and $k_{22}$ decrease and $k_{21}$ increases, the formation of a copolymer containing a large quantity of styrene units is encouraged. The values of $k_{12}$ and also probably of $k_{22}$ depend on the nucleophilicity of the oxides, which is to be expected from their basicity.5) Thus the reactivity in their reaction is:

propylene oxide > styrene oxide > epichlorohydrin

This order is the reverse of that used to explain the experimental results given above. Therefore, the results should be explained by an increase in the value of the residual $k_{21}$.

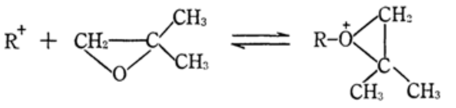
It has been discussed in the previous papers1,2) how, in the cationic copolymerization of vinyl monomers with cyclic compounds, the structure of the growing terminal cation arising from the cyclic compound has a significant effect on the copolymer formation; a growing carbonium ion could react with a vinyl monomer, but an oxonium ion could not. Therefore, it is assumed that the substituted ethylene oxides which copolymerize with styrene give a carbonium ion in the propagation reaction, and that hence the cross-propagation becomes favorable.

In the cationic copolymerization of the substituted ethylene oxides and 3, 3-bis(chloromethyl)oxetane,6) we proposed an intermediate structure (I) of both carbonium and oxonium ions for the growing oxide cation in the transition state. A similar structure:

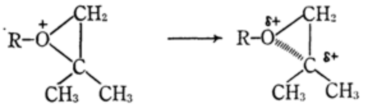


(I)

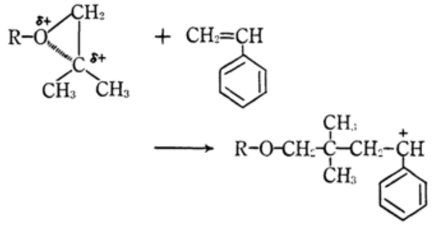
was postulated for the β-propiolactone growing cation.2) The carbonium ion character of the ion I may be increased by the electron-releasing substituents and the ring strain. Thus, it may be assumed that, in this work, the oxides copolymerized with styrene in the order mentioned above, according to the following scheme:



(5)



(6)



(7)

Pritchard and Long7) have reported on the hydrolysis of the substituted ethylene oxides in aqueous perchloric acid. The rate constant of this reaction, which proceeds through an $S_N1$-type mechanism, varied with the substituents, in the order of:

isobutene oxide > propylene oxide > epichlorohydrin

This order agrees with that of their copolymerization reactivities given above; it indicates the enhanced significance of carbonium ion participation in their propagations in the cationic copolymerization with styrene.

**The Effects of the Solvent and the Temperature.**—It may be expected that the extent of the partial charge distribution in the growing ion of the oxide I may be affected by both the solvent polarity and the temperature. The copolymerization of styrene and epichlorohydrin was carried out in the monomer mole ratio of 9/1 in toluene, methylene chloride and nitromethane at −30, 0 and 30°C. The results are given in Table IV.

The styrene unit content of the resulting polymer increased with an increase in the polarity of the solvent and with an increase in the temperature. This can be explained from the enhanced carbonium

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5) S. Iwatsuki, N. Takigawa, M. Okada, Y. Yamashita and Y. Ishii, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **67**, 1236 (1964).

6) S. Aoki, K. Fujisawa, T. Otsu and M. Imoto, ibid., **69**, 131 (1966).

7) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **78**, 2667 (1956).

ion character of the growing oxide cation I. However, if the $k_{11}$ in Eq. 1 increases in a polar solvent and at a higher temperature more than the $k_{22}$ in Eq. 3, this also affects the copolymer composition.

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