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Cationic Copolymerization of Styrene Oxide with Propylene Oxide

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ABSTRACT

Styrene oxide (SO) and propylene oxide (PO) were copolymerized at temperatures between -40 and +20°C using boron trifluoride etherate (BF_3) as catalyst, 1,3-propanediol (DIOL) as cocatalyst, and ethylene dichloride (EC) as solvent. The initial rates of consumption of SO and PO varied as follows with the initial catalyst, cocatalyst, and comonomer concentrations:

$$\frac{-d[SO]_0}{d\theta} \propto [BF_3]_0^{1.38 \text{ to } 1.0}[OH]_0^{0.27}[SO]_0^{-0.12}[PO]_0^{0.12}$$

$$\frac{-d[PO]_0}{d\theta} \propto [BF_3]_0^{0.75 \text{ to } 0.7}[OH]_0^{-0.03}[SO]_0^{-0.8}[PO]_0^{1.0}$$

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Computation of reactivity ratios yielded values of 0.1 for SO (M_1) and 0.4 for PO (M_2), indicating that the comonomers tend to alternate in the copolymer. SO yielded a cyclic dimer when homopolymerized with BF_3 in EC. In the presence of THF, copolymerization did not take place; instead, homopolymerization of SO into higher molecular weight polymers was observed. In the presence of PO, mixtures of SO and THF gave rise to terpolymers.

INTRODUCTION

The cationic polymerization of epoxides has received considerable attention in the past few years but limited information [1-3] is available on the homopolymerization and copolymerization of styrene oxide (SO). In 1967, Tabata [4] reported on the γ-ray-induced polymerization of propylene oxide (PO) in the presence of SO, where homopolymerization of SO was the only reaction found to take place. More recently, Spirin and Doroshenko [5] reported on the anionic polymerization of SO.

Some aspects of the cationic polymerization of SO and its copolymerization with PO were studied some time ago in this laboratory. This study gave rise to the publication of two reports [6, 7]. Further studies have been carried out on the subject and the results of this work, including earlier data [6] (some of which needed to be corrected), are interpreted in the light of recent developments in the field of cationic polymerizations. Some comparisions are made with results reported by others [4].

EXPERIMENTAL

Materials

The purification of the comonomers, PO from Eastman Organic and SO from Union Carbide, was carried out by stirring each with calcium hydride for a period of 4 to 6 hr under a dry nitrogen atmosphere. The mixtures were refluxed overnight then distilled on a column where the middle cuts with boiling ranges of 67 to 68°C (at 7 Torr) and 34 to 35°C (at 760 Torr) for SO and PO, respectively, were collected in brown glass bottles and stored in a dry box.

Tetrahydrofuran (THF), ethylene dichloride (EC), toluene, benzene, and n-hexane (all from Fisher Scientific) were purified in a similar manner and stored in the same dry box. Boron trifluoride etherate

(BF_3) and 1,3-propanediol (DIOL) (both from Eastman Organic) were used as such without further purification.

Experimental Procedure

The homopolymerization and the copolymerization of SO were carried out as described earlier [8, 9] for the copolymerization of PO and THF. In the present study the maximum initial water content (by Karl-Fisher technique) was 0.0055 moles/liter, while the concentration of DIOL was varied between 0.0205 and 0.205 moles/liter and that of BF_3 between 0.012 and 0.059 moles/liter. Reactions were carried out in the temperature range -40 to +20°C. The concentrations of PO, SO, and THF, as well as that of EC, were varied over a fairly wide range as will be seen in the next section (Results and Discussion). The initial rates of comonomer consumption reported in this study were computed on the basis of the concentrations of the comonomers left after a reaction time of 1 min. Molecular weights of the reaction products were determined by vapor pressure osmometry (VPO) [9].

RESULTS AND DISCUSSION

Figure 1 shows a plot of the concentration of SO with time for a homopolymerization carried out in EC at 0°C with 0.028 moles/liter

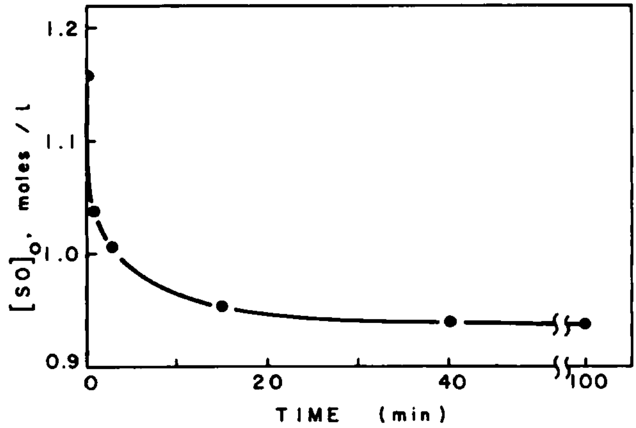


FIG. 1. Concentration vs time curves for the homopolymerization of SO at 0°C. $[SO]_0$ = 1.15 moles/liter; $[BF_3]_0$ = 0.028 moles/liter; $[water]_0$ = 0.0055 moles/liter (no DIOL was added).

of BF_3 and 0.0055 moles/liter of water. It is evident from the curve that the major part of the monomer conversion takes place during the initial 15 min of the reaction. This situation resembles the pattern followed by PO under similar reaction conditions [8]. The $\overline{M}_n$ (VPO) molecular weight of the poly(styrene oxide) thus prepared was very low (220). NMR spectra [7] revealed the presence of cyclic dimeric species. It is worth mentioning here that, when attempting to copolymerize SO with THF in EC, the products recovered were pure homopolymer of SO. THF did not homopolymerize nor did it copolymerize with SO. Furthermore, it was noted that when 31% of the SO had been converted to homopolymer, the $\overline{M}_n$ (VPO) value of the products was 490 and 1330 when 52% of the SO had been converted. The specific role of THF by which it enables poly(styrene oxide) of higher molecular weights to be formed is discussed later in the text.

Figure 2 shows plots of the concentrations of SO and PO with time for a copolymerization reaction carried out in EC at -20°C, with 0.012 moles/liter of BF_3 and 0.02 moles/liter of DIOL. It appears that the initial rates of disappearance of SO and PO are of approximately equal magnitude, indicating a high propensity for the comonomers to form alternate copolymers. If one were to base one's judgment on the nature of these copolymers solely from the results of PO and SO homopolymerizations, one would expect the copolymer mixtures to be rich in longer segments of PO-based chains.

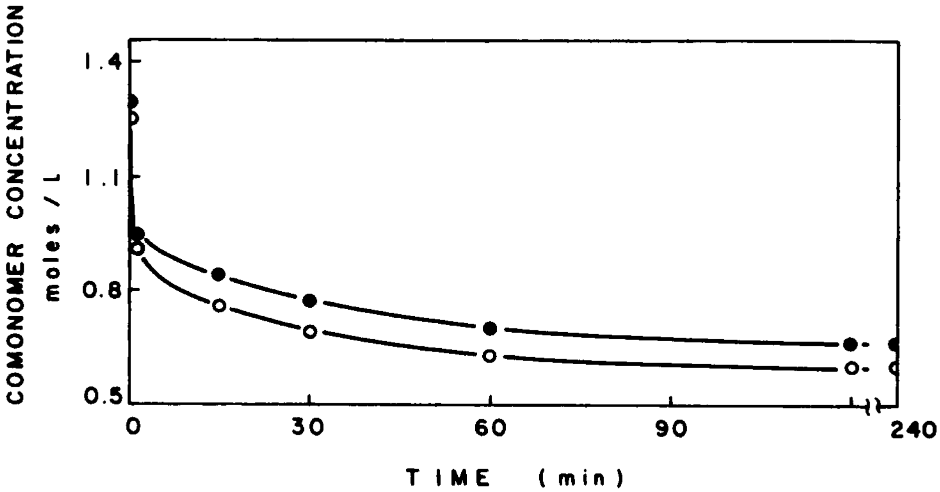


FIG. 2. Concentration vs time curves for the copolymerization of SO with PO. (●) SO and (○) PO. (See F-19 in Table 5.)

During the course of this work it was observed that with BF_3 as catalyst and water as cocatalyst, the solvent dichloroethane acts in the capacity of a transfer agent. In order to throw light on the role played by the solvent in the present study, two sets of experiments were carried out. In the first, PO and SO were copolymerized in two other solvents and the initial rates of comonomer consumption as well as the molecular weights of the final products were compared (see Table 1).

The data presented in Table 1 show that the copolymerization of SO and PO in n-hexane and in benzene leads exclusively to the homopolymerization of SO and that the $\overline{M}_n$ (VPO) values, 635 and 625 for n-hexane and benzene, respectively, are higher than the value obtained (220) with the products of the homopolymerization of SO in EC.

The copolymerization of SO and PO in EC yields a copolymer with a molecular weight of 345, a value situated between the molecular weights of poly(styrene oxide) (220) and poly(propylene oxide) (600). Furthermore, the initial rates of comonomer consumption are substantially higher in the EC medium than the corresponding values in n-hexane and in benzene.

In the second set of experiments with EC as a solvent for the copolymerization of SO and PO, the effect of the EC to comonomer molar ratio on the initial rates of comonomer consumption as well as on the molecular weights of the products of the reaction was studied. Table 2 summarizes the data obtained and, as was to be expected, the initial rates of comonomer consumption increased on lowering the EC to comonomer molar ratio of the reaction mixture. This is undoubtedly due to the associated increase in the comonomer concentrations.

With regards to the molecular weights, the $\overline{M}_n$ (VPO) values decreased with decreasing EC to comonomer ratio, contrary to expectations. This would indicate that EC does not take part in a chain "back-biting" process, if any, because, otherwise, one would expect less chain "back-biting" in the presence of a lower concentration of solvent and reaction products with correspondingly higher molecular weights. Because of the highest molecular weight (610) obtained with the copolymer products, an SO to PO to EC molar ratio of 1:1:10 was selected for the remainder of the study.

Based on the results reported in Table 3, log-log plots (see Fig. 3) of the initial rates of comonomer consumption as a function of the initial catalyst concentration were prepared.

The straight lines in Fig. 3(a) show that, with 0.0055 moles/liter of water in the reaction mixture (no DIOL having been added) the initial rates of comonomer consumption vary with the catalyst concentration raised to a certain but constant power. Under these

TABLE 1. Effect of Different Solvents on the Initial Rates of Comonomer Consumption and on the Molecular Weights of the Reaction Products[a]

No.	Solvent	Reaction time (hr)	$(-d[SO]_0/d\theta) \times 10^2$ (moles/liter/min)	$(-d[PO]_0/d\theta) \times 10^2$ (moles/liter/min)	$\overline{M}_n$ (VPO)
A-1	Ethylene dichloride	10	41.1	60.2	345
A-2	n-Hexane	4	26.5	0.0	635
A-3	Benzene	22	12.5	1.0	625

[a] Component molar proportions: [SO:PO:EC] = [1:1:10]. Component concentrations in moles/liter: $[DIOL]_0 = 2.05 \times 10^{-2}$; $[BF_3]_0 = 6.0 \times 10^{-2}$; $[SO]_0 = 1.277$; and $[PO]_0 = 1.248$. Temperature of reaction: 20°C.

TABLE 2. Effect of Solvent to Comonomer Molar Ratio on the Initial Rates of Comonomer Consumption and on the Molecular Weights of the Copolymer Products[a]

No.	Molar ratio of system SO:PO:EC	$(-d[SO]_0/d\theta) \times 10^2$ (moles/liter/min)	$(-d[PO]_0/d\theta) \times 10^2$ (moles/liter/min)	Maximum % conversion SO	Maximum % conversion PO	$\overline{M}_n$ (VPO)
B-4	1:1:10	19.0	24.2	42.7	35.1	610
B-5	1:1:5	29.0	26.8	39.1	37.6	414
B-6	1:1:1	41.6	31.8	54.2	22.8	403

[a] Component concentrations in moles/liter: $[BF_3]_0 = 1.2 \times 10^{-2}$; $[DIOL]_0 = 2.05 \times 10^{-2}$; $[water]_0 = 0.55 \times 10^{-2}$; $[SO]_0 = 1.278$; and $[PO]_0 = 1.248$. Temperature of reaction: 0°C.

TABLE 3. Effect of the Catalyst Concentration on the Initial Rates of Comonomer Consumption and on the Molecular Weights of the Copolymer Products[a]

No.	$[BF_3]_0 \times 10^2$ (moles/liter)	$(-d[SO]_0/d\theta) \times 10^2$ (moles/liter/min)	$(-d[PO]_0/d\theta) \times 10^2$ (moles/liter/min)	Maximum % conversion SO	Maximum % conversion PO	$\overline{M}_n$ (VPO)
	A: The case of a low (0.55×10^{-2}) hydroxyl concentration; water alone					
C-7	0.87	10.2	19.2	25.8	17.9	330
C-8	1.20	16.0	24.2	38.6	33.3	438
C-9	3.30	63.3	53.2	73.4	69.0	340
	B: The case of a high (4.65×10^{-2}) hydroxyl concentration; water + DIOL					
B-4	1.20	19.0	24.2	42.7	35.1	610
D-11	2.40	24.0	30.0	35.0	29.2	370
D-12	5.96	84.1	73.3	83.3	93.8	350

[a] Component molar proportions: [SO:PO:EC] = [1:1:10]. Component concentrations in moles/liter: $[\text{water}]_0 = 0.55 \times 10^{-2}$; $[\text{DIOL}]_0 = 2.05 \times 10^{-2}$; $[PO]_0 = 1.248$; and $[SO]_0 = 1.277$. Temperature of reaction: 0°C. Time of reaction: 8 hr.

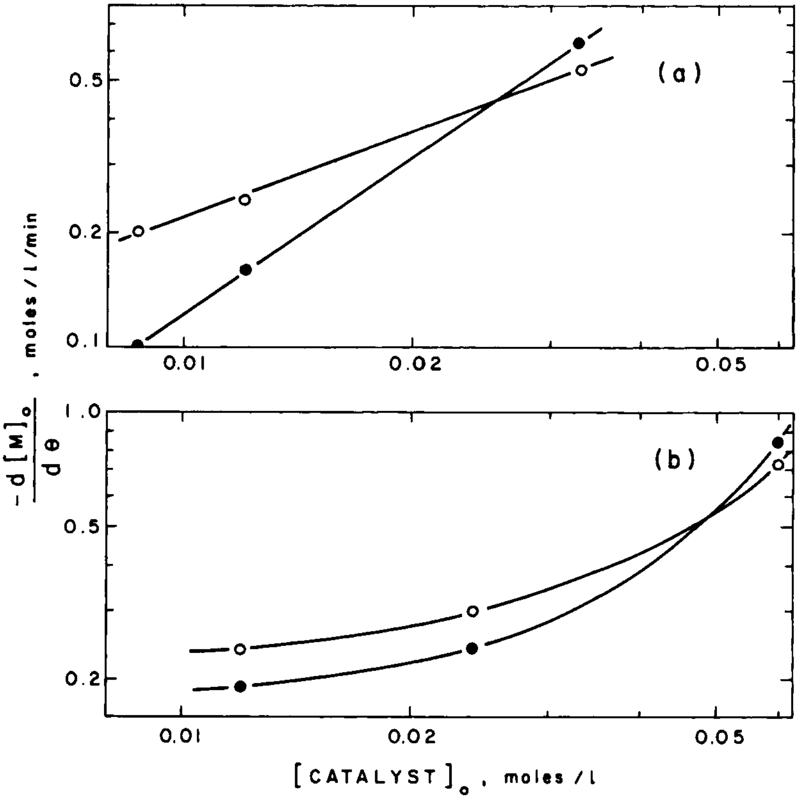


FIG. 3. Log-log plots of the initial rates of comonomer consumption as a function of the initial catalyst concentration (a) Water alone as cocatalyst. (b) Water in combination with DIOL as cocatalyst. (●) SO and (○) PO. (See data in Table 3.)

conditions, with increasing catalyst concentration one can expect an easily predictable increase in the number of reactive chain sites. This, however, is not the case when 0.0205 moles/liter of DIOL are added to the 0.0055 moles/liter of water already present in the same reaction system. Indeed, the two curves shown in Fig. 3(b) illustrate quite clearly that the initial rates of comonomer consumption vary with the catalyst concentration raised to a certain but no longer constant power. This would suggest that the increase in the number of reactive chain sites (or their nature) with the catalyst concentration is affected in a different manner. If the slopes of the lines in Fig. 3(a) are 1.38 for SO and 0.75 for PO, those of the lines in Fig. 3(b) are 1.0 for SO and 0.7 for PO. These values give rise to the following relationships:

(A) For reactions containing 0.0055 moles/liter of water:

$$-d[SO]_0/d\theta = 68.0[BF_3]_0^{1.38} \qquad (1a)$$

and

$$-d[PO]_0/d\theta = 6.8[BF_3]_0^{0.75} \qquad (2a)$$

(B) For reactions containing 0.0205 moles/liter of DIOL in addition to the 0.0055 moles/liter of water:

$$-d[SO]_0/d\theta = 12.8[BF_3]_0^{1.0} \qquad (1b)$$

and

$$-d[PO]_0/d\theta = 4.8[BF_3]_0^{0.7} \qquad (2b)$$

These equations show that, at different hydroxyl concentrations, the comonomer consumption rate laws, involving the catalyst concentration, vary over a certain range. The molecular weights of the products, however, show no similar trends.

Data showing the effect of the DIOL concentration on the initial rates of comonomer consumption are given in Table 4. Columns showing the total cocatalyst concentrations and the corresponding initial hydroxyl concentrations are given for comparison purposes only. Calculations of the initial hydroxyl concentrations are based on Eq. (3) obtained from results published earlier from this laboratory [6].

$$[OH]_0 = 2[DIOL]_0 + [water]_0 \qquad (3)$$

In Eq. (3) it has been assumed that 1 mole of 1,3-propanediol is equivalent to 2 moles of water insofar as the initial concentration of hydroxyl groups $[OH]_0$ is concerned. It is possible that, for steric or other reasons, only one of the two hydroxyl groups in the diol is active in the cocatalytic process. Thus 1 mole of DIOL would be equivalent to only 1 mole of water. With this in mind, the initial rates of comonomer consumption have been plotted on log-log scales as a function of the initial hydroxyl concentration (see Fig. 4a) and of the initial cocatalyst concentration (see Fig. 4b). All of the points shown in Fig. 4(a), which are based on the sum of the DIOL and water concentrations, fall on straight lines. Only those points which were obtained in the absence of DIOL fall away from the straight line. This would indicate that $[OH]_0$ alone does not control the nature or the number of

TABLE 4. Effect of the DIOL Concentration on the Initial Rates of Comonomer Consumption and on the Molecular Weights of the Copolymer Products[a]

No.	$[\text{DIOL}]_0 \times 10^2$ (moles/liter)	Total $[\text{Cocat}]_0 \times 10^2$ (moles/liter)	Total $[\text{OH}]_0 \times 10^2$ (moles/liter)	$(-d[\text{SO}]_0/d\theta) \times 10^2$ (moles/liter/min)	$(-d[\text{PO}]_0/d\theta) \times 10^2$ (moles/liter/min)	Maximum % conversion SO	Maximum % conversion PO	$\overline{M}_n$ (VPO)
C-8	0.0	0.55	0.55	16.0	24.2	38.6	33.3	438
B-4	2.05	2.60	4.65	19.0	24.2	42.7	35.1	610
E-13	10.25	10.80	21.05	29.8	23.1	57.1	37.4	520
E-14	20.50	21.05	41.55	35.5	22.4	86.3	44.8	480

[a] Component concentrations in moles/liter: $[\text{SO}]_0 = 1.277$; $[\text{PO}]_0 = 1.248$; $[\text{water}]_0 = 0.55 \times 10^{-2}$; and $[\text{BF}_3]_0 = 1.2 \times 10^{-2}$. Temperature of reaction: 0°C. Time of reaction: 8 hr.

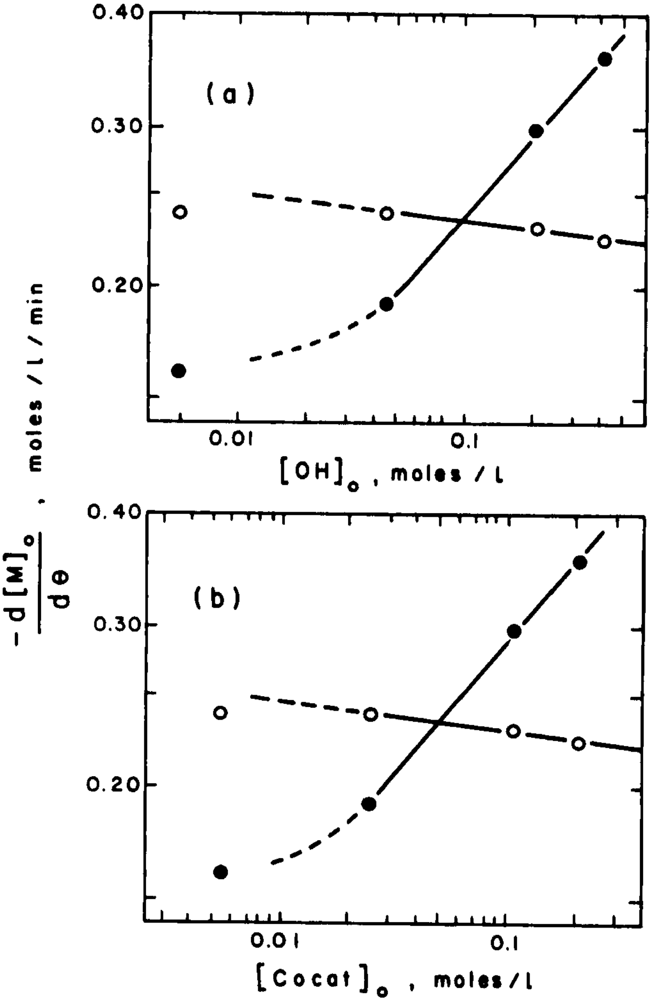


FIG. 4. Log-log plots of the initial rates of comonomer consumption of (a) the initial hydroxyl concentration and (b) the initial cocatalyst concentration. (●) SO and (○) PO. (See data in Table 4.)

reactive chain sites. On the other hand, the points plotted as a function of the initial equivalent total cocatalyst concentration $[\text{Cocat}]_0$ (Fig. 4b) show that equimolar quantities of water as well as 1,3-propanediol may play the same role as far as the cocatalytic reactivity is concerned. In this figure as in Fig. 4(a), the points obtained at zero DIOL concentration, i.e., where only water is present (0.0055 moles/liter), do not fall on the straight lines. From these observations the authors conclude that water has more influence on the initial rates of comonomer consumption than would a corresponding concentration of DIOL alone. This has led the authors to suggest the possibility that only one hydroxyl group in the DIOL is active at any one time in promoting the reactivity of potential chain sites.

The lines shown in Figs. 4(a) and 4(b) obey the following mathematical relationships:

$$-d[SO]_0/d\theta = 0.45[OH]_0^{0.27} \quad \text{or} \quad 0.54\,[Cocat]_0^{0.27} \tag{4}$$

$$-d[PO]_0/d\theta = 0.22\,[OH]_0^{-0.03} \quad \text{or} \quad 0.21\,[Cocat]_0^{-0.03} \tag{5}$$

These rate laws indicate that the initial rate of SO consumption is only slightly dependent on that of $[OH]_0$, whereas that of PO is, for all practical purposes, independent of it. The molecular weight values of the copolymer products (see Table 4) appear to have a maximum value at an $[OH]_0$ to $[BF_3]_0$ ratio of 2.0. Beyond that they are found to decrease.

In Table 5 are summarized the data obtained on the effects of the temperature and of the DIOL on the initial rates of comonomer consumption and on the molecular weights of the copolymer products. It is apparent that the initial rates of comonomer consumption, in the presence of a low (0.55×10^{-2} moles/liter) as well as a high (4.65×10^{-2} moles/liter) equivalent concentration of water, increase with temperature. The molecular weights of the copolymer products are, however, influenced little by temperature increases, the $\overline{M}_n$ values rising but slightly while the initial rates of comonomer consumption increase quite considerably. On the other hand, in the presence of DIOL with an $[OH]_0$ of 4.60×10^{-2} moles/liter, the molecular weights are slightly higher than when no DIOL is used ($[OH]_0 = 0.55 \times 10^{-2}$ moles/liter), the copolymers thus showing the specific effects of the DIOL. In the latter case, temperature changes likewise do not affect the molecular weight values.

In Fig. 5 are shown log-log plots of the initial rates of comonomer consumption as a function of the initial SO concentration. From the slopes of the lines, one may write the following rate laws:

$$-d[SO]_0/d\theta = 0.175[SO]_0^{-0.12} \tag{6}$$

and

$$-d[PO]_0/d\theta = 0.325[SO]_0^{-0.80} \tag{7}$$

TABLE 5. Effect of the Temperature and the Initial Hydroxyl Concentration on the Initial Rates of Comonomer Consumption and on the Molecular Weights of the Products[a]

No.	Temp (°C)	$[OH]_0 \times 10^2$ (moles/liter)	$(-d[SO]_0/d\theta) \times 10^2$ (moles/liter/min)	$(-d[PO]_0/d\theta) \times 10^2$ (moles/liter/min)	$\overline{M}_n$ (VPO)
F-15	20	0.50	16.2	16.7	436
C-8	0	0.50	16.0	24.2	438
F-16	-20	0.50	27.6	26.3	427
F-17	-40	0.50	43.6	53.7	478
F-18	20	4.60	13.9	17.6	604
B-4	0	4.60	19.0	24.2	610
F-19	-20	4.60	30.5	23.6	600
F-20	-40	4.60	51.5	29.0	602

[a] Component molar proportions: [SO:PO:EC] = [1:1:10]. Component concentrations in moles/liter: $[BF_3]_0 = 1.2 \times 10^{-2}$; $[\text{water}]_0 = 0.50 \times 10^{-2}$; $[\text{DIOL}]_0 = 2.05 \times 10^{-2}$; $[SO]_0 = 1.277$; and $[PO]_0 = 1.248$.

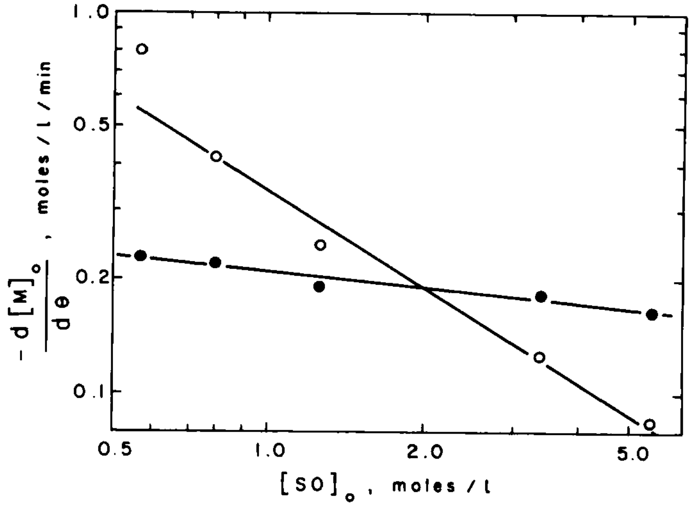


FIG. 5. Log-log plots of the initial rates of comonomer consumption as a function of the initial SO concentration. (●) $-d[SO]_0/d\theta$ and (○) $-d[PO]_0/d\theta$. (See data in Table 6.)

It is clear from these equations that on increasing the SO concentration, the rates of comonomer consumption will decrease.

In Fig. 6 are shown log-log plots of the initial rates of comonomer consumption as a function of the initial PO concentration. From the slopes of the lines, one may write the following rate laws:

$$-d[SO]_0/d\theta = 0.184[PO]_0^{0.12} \qquad (8)$$

and

$$-d[PO]_0/d\theta = 0.160[PO]_0^{1.00} \qquad (9)$$

These equations show that, on increasing the concentration of PO, the initial rates of comonomer consumption increase.

In both Figs. 5 and 6, one could draw two seemingly straight lines instead of the one shown for the initial rate of PO consumption. Two orders of reaction would then be obtained depending upon the comonomer concentration range involved. For instance, when the ratio of $[SO]_0/[PO]_0$ is less than 1, the order of the reaction, for the initial rate of PO consumption with respect to $[SO]_0$ (Fig. 5), is 1.45, the value of the constant k being 0.65. For ratios of $[SO]_0/[PO]_0$ between 1 and 10

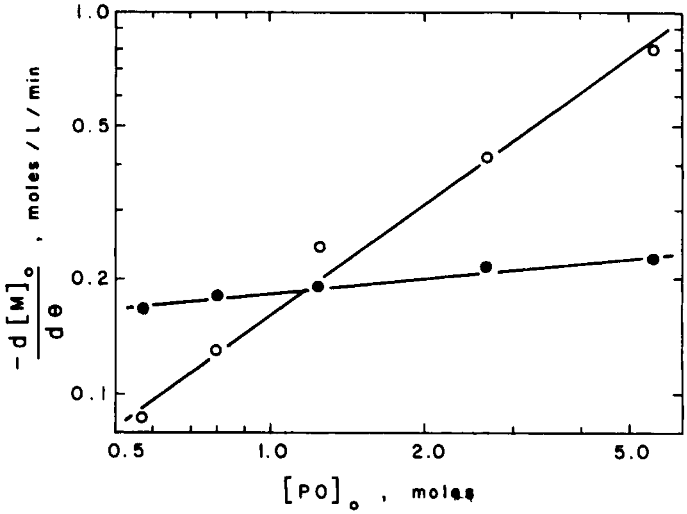


FIG. 6. Log-log plots of the initial rates of comonomer consumption as a function of the initial PO concentration. (●) -d$[SO]_0$/dθ and (○) -d$[PO]_0$/dθ. (See data in Table 6.)

(Fig. 5), the order of the reaction drops to 0.7 and the value of k changes to 0.305. For a ratio of $[SO]_0/[PO]_0$ of less than 1, the order of the reaction, for the initial rate of PO consumption with respect to $[PO]_0$ (Fig. 6), is 0.8 and k has a value of 0.19, whereas for $[SO]_0/[PO]_0$ between 1 and 10 (Fig. 6), the order of reaction is 1.28, and k has a value of 0.170. The order of the reaction, for the initial rate of SO consumption with respect to $[SO]_0$ or $[PO]_0$, however, does not change with the ratio of $[SO]_0/[PO]_0$. It is difficult to say whether the concept of different orders of reaction with changing initial comonomer concentration ratios is plausible or not.

The percent comonomer conversions and the molecular weights of the copolymer products as a function of $[SO]_0$ and $[PO]_0$ are given in Table 6. The data show clearly that the maximum percent conversion of styrene oxide is reached only when its own concentration in the solution is low. This is something quite different to the polymerization of styrene oxide in the presence of propylene oxide when initiated by γ-rays [4], where higher percent conversions of SO require higher initial concentrations of PO. Furthermore, in the present study, the initial rate of comonomer consumption increases with increasing mole fraction of PO. Tabata [4], in his work, observed the reverse, the initial rate of PO consumption decreasing with increasing PO mole

TABLE 6. Effect of the Initial Comonomer Ratio on the Rates of Comonomer Consumption, on the Percent Conversion, and on the Molecular Weights of Copolymer Products[a]

No.	$[SO]_0$ (moles/liter)	$[PO]_0$ (moles/liter)	$(-d[SO]_0/d\theta) \times 10^2$ (moles/liter/min)	$(-d[PO]_0/d\theta) \times 10^2$ (moles/liter/min)	Maximum % conversion SO	Maximum % conversion PO	$\overline{M}_n$ (VPO)
G-21	0.561	5.550	80.0	22.5	71.4	31.2	350
G-22	0.730	2.655	41.6	22.0	68.8	26.2	365
B-4	1.277	1.248	24.2	19.0	42.7	35.1	610
G-23	3.359	0.810	13.0	18.2	12.8	15.9	360
G-24	5.561	0.561	8.7	16.5	11.4	15.9	392

[a] Component concentrations in moles/liter: $[BF_3]_0 = 1.2 \times 10^{-2}$; $[DIOL]_0 = 2.05 \times 10^{-2}$; and $[water]_0 = 0.55 \times 10^{-2}$. Temperature of reaction: 0°C.

fraction. The differences observed may be attributed to the specific reaction mechanisms involved in each of the studies.

The molecular weights of the copolymer products obtained in the present study (see Table 6) show a maximum value for an SO to PO comonomer molar ratio of 1. Here, likewise, the percent conversions and the initial rates of comonomer consumption have, respectively, about the same values. For comonomer ratios of 1/3 and 1/10 the molecular weight values are considerably lower, due in all probability to the formation of a low molecular weight homopolymer of SO. For comonomer ratios of 4 and 10, the low molecular weight values are attributed to the relatively lower percent comonomer conversion.

Reactivity Ratios

The widely accepted equation of Mayo and Lewis [10]

$$\frac{-d[M_1]}{-d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \tag{10}$$

when used in the form:

$$\frac{-d[M_1]}{-d[M_2]} = K\left[\frac{[M_1]}{[M_2]}\right]^a \tag{11}$$

where K and a are constants whose values depend on the system, can yield, according to O'Driscoll and co-workers [11], valuable information regarding the nature of copolymerizations. For two monomer feed compositions, x_1 and x_2, the values of r_1 and r_2 can be determined from Eqs. (12) and (13) given in Ref. 11.

$$r_1 = -\frac{Kx_1^{a-2}x_2^{a-2}(x_1-x_2)}{x_1^{a-2} - x_2^{a-2}} - \frac{x_1^{a-1} - x_2^{a-1}}{x_1x_2(x_1^{a-2} - x_2^{a-2})} \tag{12}$$

and

$$r_2 = -\frac{x_1^{a-1} - x_2^{a-1}}{x_1^{a-2} - x_2^{a-2}} - \frac{x_1 - x_2}{K\, x_1x_2(x_1^{a-2} - x_2^{a-2})} \tag{13}$$

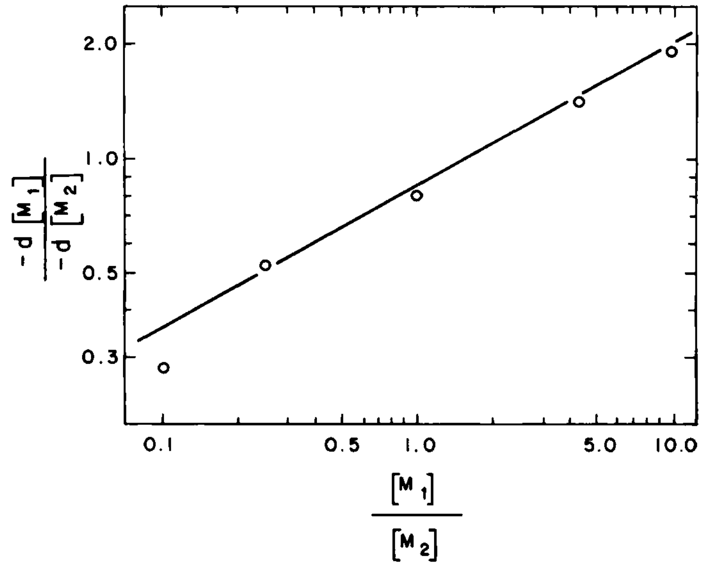


FIG. 7. Log-log plots of -d$[M_1]$/-d$[M_2]$ as a function of $[M_1]/[M_2]$ from which values of a and K are obtained for the system SO-PO-EC.

Plots of log (-d$[M_1]$/-d$[M_2]$) vs log ($[M_1]/[M_2]$) yield straight lines. From their slopes, values of a can be calculated and, at $[M_1]/[M_2] = 1$, one deduces the value of K which indicates the ratio of the reactivities of the monomers at equimolar feeds. Substituting in Eqs. (10) and (11) the value of 1 for $[M_1]/[M_2]$,

$$K = \frac{r_1 + 1}{r_2 + 1} \tag{14}$$

In Fig. 7 is shown a log-log plot of (-d$[M_1]$/[-d$[M_2]$]) as a function ($[M_1]/[M_2]$). The values of r_1, r_2, a, and K, as computed from the slope of the line in Fig. 7 and with the help of Eqs. (12) to (14), are as follows: $r_1 = 0.1$; $r_2 = 0.4$; $r_1r_2 = 0.04$; $a = 0.35$; and $K = 0.8$, where M_1 represents SO and M_2, PO. The value of 0.04 for r_1r_2 clearly demonstrates the strong tendency for the comonomers to alternate in the copolymer products.

The effect of different parameters, e.g., solvent, catalyst, and cocatalyst concentrations, on the initial rates of comonomer consumption was discussed earlier in the text and kinetic constants were evaluated. The rates can be related to the reactivity ratios of the comonomers by

TABLE 7. SO-PO Comonomer Reactivity Ratios Obtained under Different Reaction Conditions[a]

No.	a	K	r_1[SO]	r_2[PO]	$r_1 r_2$
B-4	0.35	0.80	0.10	0.40	0.040
B-5	0.46	1.01	0.25	0.16	0.040
B-6	0.52	1.30	0.42	0.10	0.042
C-7	0.40	0.53	0.04	1.00	0.040
C-8	0.35	0.66	0.065	0.61	0.042
C-9	0.50	1.17	0.33	0.13	0.043
B-4	0.35	0.80	0.10	0.40	0.040
D-11	0.35	0.80	0.10	0.39	0.039
D-12	0.46	1.14	0.30	0.14	0.042
C-8	0.35	0.67	0.07	0.60	0.042
B-4	0.35	0.80	0.10	0.40	0.040
E-13	0.51	1.28	0.41	0.10	0.041
E-14	0.65	1.57	0.66	0.06	0.040

[a] For the conditions used in series B, C, D, and E, refer to Tables 2, 3, and 4. Constants a and K and reactivity ratios r_1 and r_2 have the meanings implied in Eqs. (11) to (14).

making use of either the O'Driscoll equations [11-13] or the Mayo-Lewis equation [10]. In order to evaluate r_1 and r_2 with the O'Driscoll equations, one needs values of the initial rate of comonomer consumption for five or six different comonomer ratios. Alternatively, one may use the Mayo-Lewis equation but, with two unknowns, r_1 and r_2 in Eq. (10), one can only evaluate the relative values of the reactivity ratios. This is achieved by assigning a definite value to r_1 in Eq. (10) and calculating r_2. For each differing value of r_1, one obtains a corresponding value of r_2. Keeping in mind that the product of the reactivity ratios, $r_1 r_2$, for a given system is approximately constant, one can choose that set of values which best meets the requirement. Table 7 shows the changes in the reactivity ratio values with increasing concentrations of solvent, catalyst, and cocatalyst (1,3-propanediol) while assuming the value of the product of the reactivity ratios to be 0.04 as was calculated for the system. It can be seen from Table 7 that on decreasing the concentration of solvent and increasing the concentration of catalyst and cocatalyst, the reactivity ratio values for SO increase while those for PO decrease continuously. The values of the constants K and a computed from the values of r_1 and r_2 also show a corresponding increase under the same operating conditions. An increasing value of K in the present study, for a constant value of $([M_1]_0/[M_2]_0)^a$ suggests an increase in the number of SO based active centers, because, for fixed values of $[M_1]_0$ and $[M_2]_0$, K is a direct function of r_1 and r_2. On the other hand, an increase in K with a varying $([M_1]_0/[M_2]_0)^a$ but fixed values of $[M_1]_0$ and $[M_2]_0$ could also mean that there is a change in the nature of the active centers.

Terpolymerization of SO with PO and THF

It was mentioned earlier in the text that SO readily copolymerizes with PO but not with THF under corresponding operating conditions. When PO is added to a mixture of SO and THF in EC, as was the case for Experiment H-30 carried out at 0°C, the situation is quite different. Indeed, the three comonomers were consumed, as can be seen in Fig. 8, and converted into terpolymeric material at initial rates listed in Table 8. This table contains data obtained at several temperatures including that of Experiment H-30.

The results given in Table 8 indicate that, in the presence of 0.55×10^{-2} moles/liter of water, the initial rates of consumption of PO and THF are influenced substantially by temperature changes. Indeed, lowering of the temperature decreases their initial rates in a quite significant manner while that of SO is but little affected. When the hydroxyl content is raised to 2.85×10^{-2} moles/liter by the addition of 1.16 moles/liter of DIOL, the initial rate of consumption of SO varies in a pattern similar to that followed by PO and THF at the low hydroxyl concentration, but the magnitude of the decrease is slightly greater. As for the consumption of PO and THF, in the presence of the higher initial hydroxyl concentration, their initial rates of consumption do not show much variation with temperature except at -20°C where the change is attributed more to experimental discrepancy than to energetic changes. Earlier [6], it had been reported that overall activation energies for the terpolymerization process are lower with the higher $[OH]_0$ content, while in the copolymerization of SO and PO the activation energies are higher with the higher $[OH]_0$ content. Recent experiments have shown that these observations are true with the exception of SO which in a terpolymer system has an activation energy which increases with hydroxyl content. Table 9

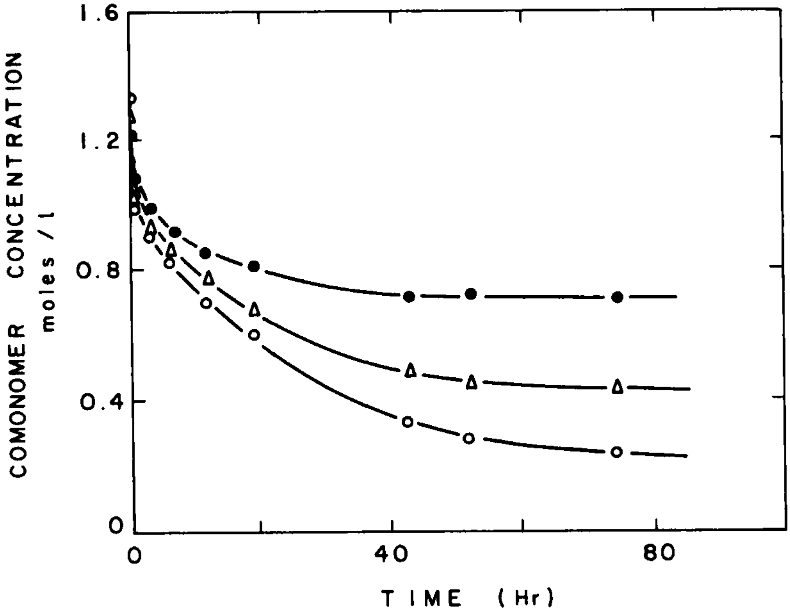


FIG. 8. Concentration vs time curves for the terpolymerization of SO, THF, and PO at 0°C. (●) SO, (○) PO, and (△) THF. (See H-30 in Table 8.)

summarizes the data on the overall activation energies. One notes in this table that the activation energies are negative in the copolymerization of SO with PO when computed from the slope of an ln R_p vs 1/T plot. If one attempts to explain the negative activation energy values obtained, one would immediately cast doubt on the validity of the data given for the initial rates of polymerization! The authors accept that activation energy values, such as -0.1 for THF in the terpolymerization process, are subject to experimental error; however, the higher negative values obtained for the copolymerization of SO with PO must have their origin in some other source. Similar results have been reported for the anionic polymerization of α-methylstyrene [12-16] as well as for the cationic polymerization of isobutene [17], indene [18], and cyclopentadiene [19], where negative activation energies are mentioned. These observations have been explained on the basis of a two-step propagation or a dual reaction mechanism, one operating actively at the lower temperatures, the other at the higher temperatures. The resulting initial rates of comonomer consumption, when

TABLE 8. Effect of the Reaction Temperature and the Initial Hydroxyl Concentration on the Initial Rates of Comonomer Consumption and on the Molecular Weights of the Terpolymer Products[a]

No.	Temp. (°C)	$[DIOL]_0 \times 10^2$ (moles/liter)	$[OH]_0 \times 10^2$ (moles/liter)	$-d[SO]_0/d\theta \times 10^2$ (moles/liter/min)	$-d[SO]_0/d\theta \times 10^2$ (moles/liter/min)	$-d[THF]_0/d\theta \times 10^2$ (moles/liter/min	$\overline{M}_n$ (VPO)
H-25	20	-	0.53	15.1	13.4	15.0	547
H-26	0	-	0.53	13.0	11.0	5.7	557
H-27	-20	-	0.53	12.0	4.2	4.0	531
H-28	-40	-	0.53	10.1	2.1	0.5	531
H-29	20	1.16	2.85	18.0	20.0	13.5	524
H-30	0	1.16	2.85	14.0	18.0	14.6	528
H-31	-20	1.16	2.85	8.5	6.0	6.0	576
H-32	-40	1.16	2.85	6.2	13.5	14.3	549

[a] Component molar proportions: [SO:PO:THF:CE] = [1:1:1:10]. Component concentrations in moles/liter: $[water]_0 = 0.53 \times 10^{-2}$; $[BF_3]_0 = 1.20 \times 10^{-2}$; $[SO]_0 = 1.234$; $[PO]_0 = 1.328$; and $[THF]_0 = 1.272$.

TABLE 9. Summary of Overall Activation Energies [E]

	E, terpolymer system (kcal/mole)				E, copolymer system (kcal/mole)	
$[OH]_0 \times 10^2$ (moles/liter)	SO	THF	PO	$[OH]_0 \times 10^2$ (moles/liter)	SO	PO
0.55	0.87	5.00	4.47	0.55	-1.8	-1.5
4.65	2.51	-0.10	0.95	4.65	-2.7	-1.4

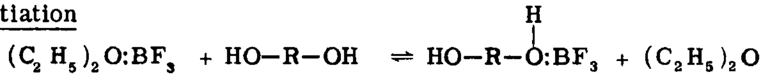
used to compute the activation energies with the usual Arrhenius equation, yield negative values. Thus, in reality, it is the procedure employed which requires modification when used in computing activation energy values for systems undergoing propagation via a dual or two-step mechanism. Binodal distributions obtained with GPC for the PO-THF copolymers [20, 21] support the concept of a dual mechanism in such polymerizations.

Mechanistic Considerations

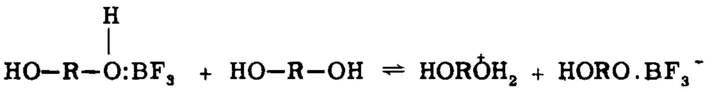
Homopolymerization of SO in the Presence of EC

In an earlier publication [22] originating from this laboratory it was suggested that two molecules of cocatalyst react with the catalyst to yield an oxonium ion $HO{-}R{-}\overset{+}{O}H_2$ (Eqs. 15 and 16) which initiate the polymerization reaction (Eq. 17). When a similar process of initiation is carried out with water [9] as cocatalyst to generate a hydronium ion H_3O^+, one would again require two molecules of cocatalyst (water). This means that the number of OH groups attached to the cocatalyst does not determine the number of molecules required to generate an initiating species. The results shown in Fig. 4(b) support this line of thought as the data plotted with the assumption that 1 mole of DIOL is equivalent to 1 mole of water, fit better than when 1 mole of the former is considered equivalent to 2 moles of the latter (Fig. 4a). The reason why the initial rates of comonomer consumption with water as cocatalyst are higher than those obtained with DIOL as cocatalyst may be due to the greater reactivity of the former. It has also been mentioned that the homopolymerization of SO yields dimeric material, and the NMR analyses of these products showed them to be cyclic in nature: 2,5-diphenyl-1,4-dioxane. A plausible mechanism leading to such cyclization is shown below.

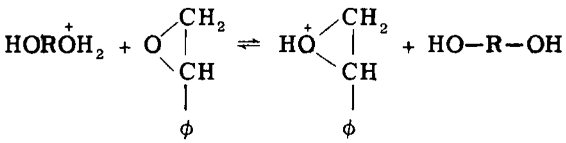
Initiation



$$(C_2H_5)_2O{:}BF_3 + HO{-}R{-}OH \rightleftharpoons HO{-}R{-}\overset{\displaystyle H}{\overset{|}{O}}{:}BF_3 + (C_2H_5)_2O \qquad (15)$$

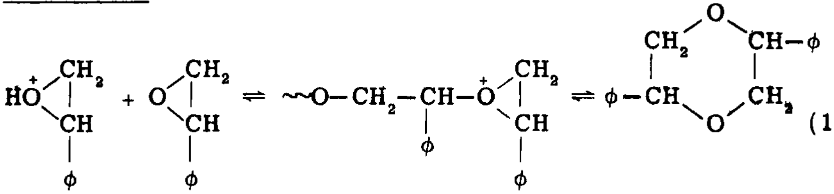


$$HO{-}R{-}\overset{\overset{\displaystyle H}{|}}{O}{:}BF_3 + HO{-}R{-}OH \rightleftharpoons HOR\overset{+}{O}H_2 + HORO.BF_3^- \qquad (16)$$



(17)

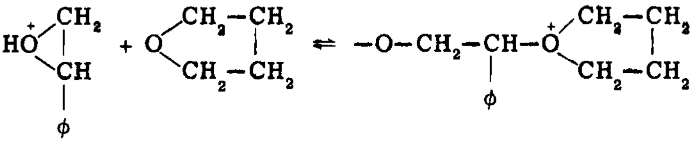
Propagation



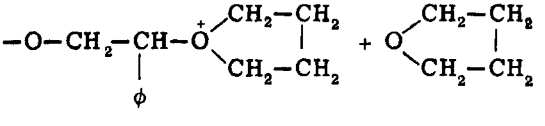
(18)

Homopolymerization of SO in the Presence of THF

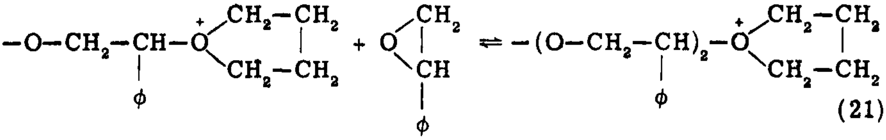
As was mentioned earlier, SO does not copolymerize with THF in the presence of EC, BF_3, and DIOL; however, the homopolymer of SO produced in this case is not a cyclized dimeric species but rather a higher molecular weight linear poly(styrene oxide). The role of THF in elevating the molecular weight of poly(styrene oxide) may be



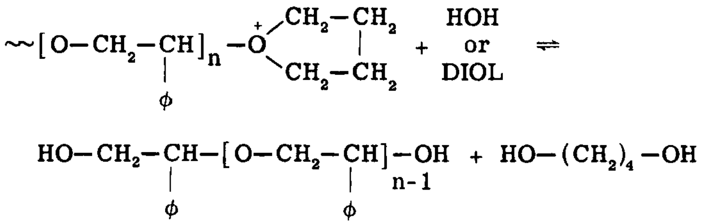
(19)



⇌ No reaction (20)

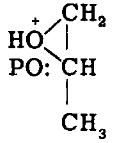


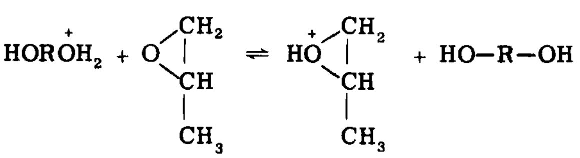
(21)



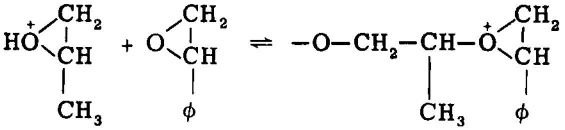
(22)

Copolymerization of SO with PO

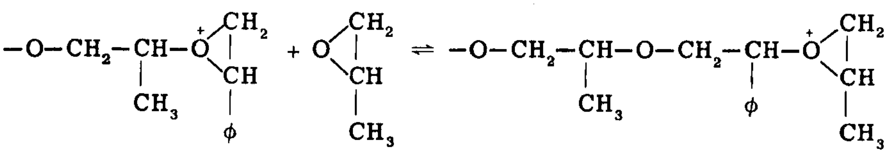
Due to the higher reactivity ratio value of PO, it has been assumed in Eq. (24) that the PO-based oxonium ion  initiates the propagation step in the copolymerization of SO with PO:



(23)



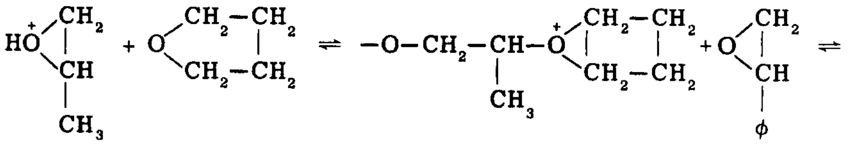
(24)

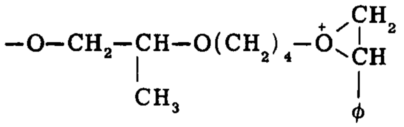


(25)

Terpolymerization of SO with THF and PO

Based on the experimental observation made during this study that THF polymerizes with SO only in the presence of PO, the mechanism of terpolymerization may be thought to follow a route such as





(26)

The suggestions given above on some aspects of the polymerization mechanism involved account for some of the experimental observations. Based on kinetic data alone, one can only speculate as to the types of reactions involved in the system under study; however, in other cases, e.g., the cyclization of SO where the reaction products have been clearly identified by NMR, the evidence is conclusive. Keeping this in mind, structural analyses of the reaction products have been undertaken and the results of these studies will be published at a later date.

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