Radical Copolymerization of Sulfur Dioxide and Styrene

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ABSTRACT: Radical copolymerization of sulfur dioxide and styrene was studied, especially as a function of total monomer concentration. The composition of poly(styrene sulfones) varies mainly with total monomer concentration and temperature but little with feed composition. However, at lower temperature (0°) it does not depend even on total monomer concentration. The overall rate of polymerization increases initially with $[SO_2]$ and then has a tendency to become a constant when $[SO_2]$ is increased. The existence of first-order depropagation of the growing sulfonyl radical, the loss of a sulfur dioxide unit forming a styryl ending, was confirmed by using the addition reaction of benzylsulfonyl chloride to styrene monomer as a model reaction for such depropagation. From these results it would seem possible to rule out both radical polymerization mechanisms, *i.e.*, the propagation process of separate monomers, explained by the Lewis–Mayo equation, and propagation processes involving a monomer charge-transfer complex. Thus, we propose a tentative propagation mechanism.

One of the most interesting features of free-radical polymerization is the tendency of many monomer pairs to form alternating copolymers, and quite distinct mechanisms have been proposed so far attempting to explain the alternating tendency: (1) self-propagation of an equimolar monomer complex and (2) activated complex formed between a growing electron-donating (or -accepting) radical and an electron-accepting (or -donating) monomer is stabilized by either electron transfer or electrostatic interaction. The participation of monomer complex was also proposed for the formation of poly(styrene sulfone), but, unlike the case of alternating copolymers, the composition of poly(styrene sulfone) varies mainly with polymerization temperature but little with feed composition. The first reference to the reaction of sulfur dioxide and styrene (St) was made in 1935 by Staudinger and Ritzenthaler,[1] who reported their product as an inseparable mixture of polystyrene and 1:1 poly(styrene sulfone). Subsequently Glavis, Ryden, and Marvel[2] reported the preparation of a 1:1 copolymer in the presence of aged paraldehyde as a catalyst. In 1952, Barb[3-5] studied the kinetics of radical copolymerization of sulfur dioxide and styrene with 2,2′-azobisisobutyronitrile (AIBN) as a thermal initiator. He found that it is impossible, within the temperature range 20–75°, to obtain a copolymer containing more than 1 mol of sulfur dioxide to 2 mol of styrene. He claimed that the composition of poly(styrene sulfone) prepared at 20° and above can be accounted for by a radical copolymerization of a 1:1 sulfur dioxide–styrene charge-transfer monomer complex and free styrene. Here, the complexyl radical ($\sim$C$\cdot$) was assumed to have the terminal structure $\sim SO_2$–St$\cdot$ and not $\sim$St–$SO_2\cdot$, and propagation between the complexyl radical and monomer complex was excluded in his scheme, since the copolymer compositions, n ($\equiv St/SO_2$), were always >2. He also considered depropagation, in which styrene and sulfur dioxide depropagate from growing complexyl and sulfonyl radicals, respectively. On the other hand, Walling[6] demonstrated that an equivalent equation can be derived without invoking complex participation by assuming that attack of a growing chain on sulfur dioxide is a rapidly reversible process at all temperatures, while at a higher temperature, addition of a chain ending with sulfur dioxide to styrene molecules becomes reversible as well. Tokura and Matsuda[7] also studied the radical copolymerization of sulfur dioxide with styrene or its derivatives,[8-10] but the polymerization conditions used were of a rather narrow range; *i.e.*, [St] was variable in the monomer mixtures under the condition $[SO_2] > [St]$ and the temperature range was only 40–60°. Since poly(styrene sulfone) containing two styrene units to one of sulfur dioxide ($n = 2$) was formed exclusively, it had been thought reasonable to assume the self-propagation of a monomer complex consisting of 2 mol of styrene monomer to 1 mol of sulfur dioxide. Recently, Matsuda and Iino[11] have returned to the study of the radical copolymerization of sulfur dioxide and styrene, especially as a function of total monomer concentration ($[SO_2] + [St]$), since if it is considered that the monomer complex is a real monomer species (*i.e.*, that the monomer complex is a more reactive species than the free monomers), both the composition of poly(styrene sulfone) and the rate of copolymerization should vary with a function of total monomer concentration.

The present work is concerned with further investigation of the dilution effect in the copolymerization, and from our experimental results it would seem possible to rule out both radical polymerization mechanisms, *i.e.*, a propagation process of separate monomers (sulfur dioxide and styrene), explained by the Lewis–Mayo equation, and propagation processes involving a monomer complex. Thus we would like to propose a tentative propagation mechanism.

Experimental Section

Radical copolymerization of sulfur dioxide and styrene was carried out with 2,2′-azobisisobutyronitrile (AIBN) as a thermal initiator, and diluents such as *o*-dichlorobenzene, sulfolane, dichloromethane, cyclohexane, and pyridine were used in order to investigate the polymerization as a function of total monomer concentration. Purifications of monomer, sulfur dioxide, and diluents were carried out essentially according to usual methods.

The polymerization reaction was carried out in a sealed glass vessel. The required quantities of AIBN, monomer, and diluent were pipetted into the vessel. The reaction vessel was provided

(1) H. Staudinger and B. Ritzenthaler, *Ber. Deutsch. Chem. Ges.*, **68**, 455 (1935).
(2) F. J. Glavis, L. L. Ryden, and C. S. Marvel, *J. Amer. Chem. Soc.*, **56**, 1815 (1934).
(3) W. G. Barb, *Proc. Roy. Soc., Ser. A*, **212**, 66 (1952).
(4) W. G. Barb, *ibid.*, **212**, 177 (1952).
(5) W. G. Barb, *J. Polym. Sci.*, **10**, 49 (1953).
(6) C. Walling, *ibid.*, **16**, 315 (1955).
(7) N. Tokura and M. Matsuda, *Kogyo Kagaku Zasshi*, **64**, 501 (1961).
(8) N. Tokura, M. Matsuda, and Y. Ogawa, *J. Polym. Sci., Part A-1*, 2965 (1963).
(9) N. Tokura, M. Matsuda, and K. Arakawa, *J. Polym. Sci., Part A-2*, 3355 (1964).
(10) M. Iino, I. Ohtsuka, and N. Tokura, *Kogyo Kagaku Zasshi*, **69**, 115 (1966).
(11) M. Matsuda and M. Iino, *Macromolecules*, **2**, 216 (1969).

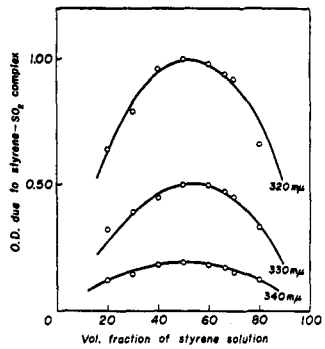


Figure 1. Continuous-variation data for obtaining the relationship between optical density (OD) due to monomer complex and mixing ratio of sulfur dioxide and styrene solutions. $[SO_2]$ = [styrene] = 1.8 M (solvent, chloroform; optical path length, 0.055 cm; temperature, 20°).

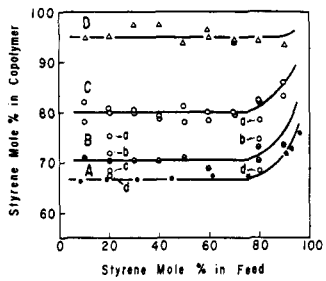


Figure 2. Relationship between feed and copolymer compositions. Capital letters cited in the figure are related to the total monomer concentrations shown in Table I, and small letters are also related to total concentrations: (a) $[SO_2]$ + [styrene] = 3.0 M, (b) 4.5 M, (c) 7.5 M, (d) 9.0 M (all in dichloromethane). Polymerization temperature, 50°.

with a ground-glass stopcock joint. The vessel, immersed in a cooled methanol bath (−78°), was attached to the liquid sulfur dioxide dropping apparatus. The oxygen in the reaction vessel was replaced as much as possible with purified dry nitrogen, the vacuum cock was closed, and liquid sulfur dioxide was fed into the reaction vessel. The polymerization proceeded in a homogeneous system except for the polymerization in cyclohexane solution. After allowing the reaction to proceed for a specified period, the reaction vessel was cooled in a cooled methanol bath (−78°), the stopcock was removed at the joint, and the copolymer was precipitated by addition of a large quantity of methanol. For all experiments the conversion was no more than 5 wt %. The polymer was collected on a sintered-glass filter and dried under reduced pressure to a constant weight to obtain the reaction rate. The copolymer obtained was dissolved with a small amount of dioxane, reprecipitated with methanol, and then dried under reduced pressure. The copolymer composition was determined from a microanalytical determination of the percentage of carbon.

The electronic spectrum of the complex of liquid sulfur dioxide and styrene was measured in chloroform with a Cary Model 14 spectrophotometer in a pressure-resistant quartz photocell (2-mm wide optical cell containing a 1.954-mm spacer).

The addition reaction of benzylsulfonyl chloride (BSC) to styrene monomer was designed as a model reaction to study the depropagation of growing sulfonyl radical. Synthesis of BSC was done according to the method described in the literature,[12,13] and the BSC synthesized was identified by ir, nmr, elementary analysis, and melting point. The addition reaction of BSC to styrene in dichloromethane was attempted by using a $CuCl_2$–$NH(C_2H_5)_3Cl$ initiator system which has been studied by Asscher and Vofsi.[14] Reaction products were identified by ir and nmr and quantitative measurement of them was done by nmr.

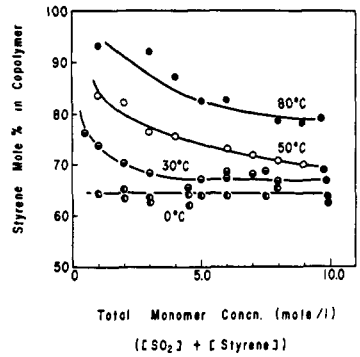


Figure 3. Relationship between total monomer concentration and copolymer composition obtained at various polymerization temperatures (diluent, dichloromethane). The styrene mole fraction in the feed is kept constant at 0.80.

TABLE I
POLYMERIZATION CONDITIONS OF CAPITAL LETTERS CITED IN FIGURE 2 AND COMPOSITION OF COPOLYMERS OBTAINED FROM FIGURE 2[a]

Symbol in Figure 2	Polymerization conditions: Added solvent	Total monomer concn, M	Molar ratio, St/SO_2 in copolymer
A	(Bulk polymerization)		2:1
B	Dichloromethane	6.0	7:3
C	Dichloromethane	2.0	4:1
D	Pyridine	2.0	19:1

[a] Polymerization temperature 50°.

Results

Charge-Transfer Complex Formed between Sulfur Dioxide and Styrene. The existence of a monomer complex of sulfur dioxide and styrene was detected spectrophotometrically, using the method of continuous variation. As shown in Figure 1, the maxima of the optical density (OD) due to the complex lie close to the region corresponding to 50 vol % styrene, suggesting the existence of an equimolar monomer complex. The association constant, K, was estimated to be about 0.05 l./mol at 20° in chloroform from Benesi–Hildebrand plots, and $\Delta H°$ was −3.0 ± 1.2 kcal/mol from the temperature variation of the optical density.

Copolymer Composition. The relationship between copolymer composition and feed is shown in Figure 2 for copolymers obtained under the different conditions shown in Table I; this is interesting in that copolymer composition does not appear to depend on the feed composition except at higher styrene concentrations.

The dilution effects and temperature effects on copolymer composition are shown in Figures 3 and 4, in which the tendency of sulfur dioxide to be incorporated into the copolymer decreases markedly with increasing temperature. The effect becomes more marked as the total monomer concentration is reduced by dilution with dichloromethane. At lower temperature (0°), however, this dilution effect is not

(12) J. Taylor, *J. Chem. Soc.*, **111**, 650 (1917).
(13) E. A. Werner, *ibid.*, **57**, 285 (1890).
(14) M. Asscher and D. Vofsi, *ibid.*, 4962 (1964).

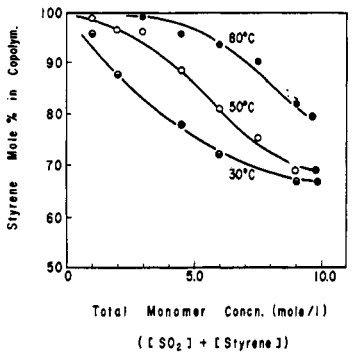


Figure 4. Relationship between total monomer concentration and copolymer composition obtained at various polymerization temperature (diluent, pyridine). The styrene mole fraction in the feed is kept constant at 0.80.

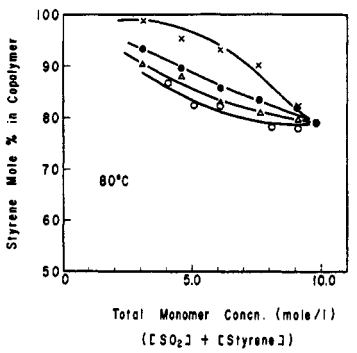


Figure 5. Relationship between total monomer concentration and copolymer composition (diluents, *o*-dichlorobenzene (○), sulfolane (△), dichloromethane (●), pyridine (×)). The styrene mole fraction in the feed is kept constant at 0.8.

TABLE II
ADDITION REACTION OF BENZYLSULFONYL CHLORIDE (BSC) TO STYRENE MONOMER IN DICHLOROMETHANE SOLVENT[a]

BSC, g	Styrene, ml	Temp, °C	Added solvent, ml	(I + II)/III (molar ratio)
8.28	5.0	100	3.0	9
8.28	5.0	100	18.0	29
8.28	5.0	100	38.0	106
8.28	5.0	100	18.0	29
8.28	5.0	50	18.0	3
8.28	5.0	30	18.0	1.6

[a] The numerical values of BSC and styrene shown in the table correspond to equimolar concentration (4.34×10^{-2} *M*), and conversion after 3 hr calculated on the basis of BSC reacted was around 100% except in the case of reaction at 30° (this was about 50%). Reaction was initiated by a $CuCl_2$ (0.16 g)–$NH(C_2H_5)_3Cl$ (0.27 g) system, but the reaction conducted at 30° was further activated by adding AIBN (0.20 g).

observed, as shown in Figure 3. The effect of the nature of the solvent is shown in Figures 5–8 at temperatures of 80, 50, and 30°, respectively.

Overall Rate of Polymerization. The relationship between the overall rate of polymerization, R_p, and the concentration of styrene monomer for constant concentration of sulfur dioxide is shown in Figure 9, and that of sulfur dioxide concentration for constant concentration of styrene monomer is shown in Figure 10.

Addition Reaction of Benzylsulfonyl Chloride (BSC) to Styrene. The addition reaction of BSC to styrene monomer proceeded in a homogeneous system and gave exclusively benzyl chloride (I), 1-chloro-1,3-diphenylpropane ($C_6H_5CH_2$-$CH_2CH(C_6H_5)Cl$, II), and β-chloro-β-phenethyl benzyl sulfone ($C_6H_5CH_2SO_2CH_2CH(C_6H_5)Cl$, III). The ease of elimination of sulfur dioxide molecule from benzylsulfonyl radical, which reaction corresponds to depropagation of a growing sulfonyl radical, could be given by a ratio of (I + II)/III shown in Table II. The results shown in table are still preliminary and details will be reported in the later paper, but it is clear that the ratio increases with decrease of reactant concentration (*i.e.*, with increasing dilution) and with increasing temperature. By analogy with Asscher and Vofsi's scheme,[14] Scheme I may be written.

SCHEME I

$$C_6H_5CH_2SO_2Cl + Cu^+ \longrightarrow C_6H_5CH_2SO_2\cdot + CuCl^+ \quad (1)$$

$$C_6H_5CH_2SO_2\cdot \longrightarrow C_6H_5CH_2\cdot + SO_2 \quad (2)$$

$$C_6H_5CH_2\cdot + CuCl^+ \longrightarrow \underset{\text{I}}{C_6H_5CH_2Cl} + Cu^+ \quad (3)$$

$$C_6H_5CH_2\cdot + CH_2{=}C(C_6H_5)H \longrightarrow C_6H_5CH_2CH_2C(C_6H_5)H\cdot \xrightarrow{CuCl^+} \underset{\text{II}}{C_6H_5CH_2CH_2C(C_6H_5)HCl} + Cu^+ \quad (4)$$

$$C_6H_5CH_2SO_2\cdot + CH_2{=}C(C_6H_5)H \longrightarrow C_6H_5CH_2SO_2CH_2C(C_6H_5)H\cdot \xrightarrow{CuCl^+} \underset{\text{III}}{C_6H_5CH_2SO_2CH_2C(C_6H_5)HCl} + Cu^+ \quad (5)$$

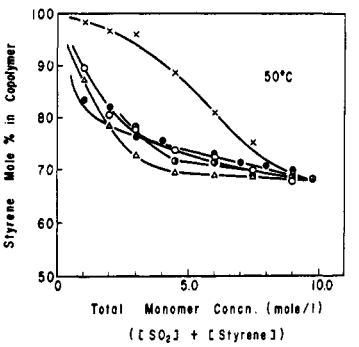


Figure 6. Relationship between total monomer concentration and copolymer composition (diluents, *o*-dichlorobenzene (○), sulfolane (△), dichloromethane (●), cyclohexane (◑), and pyridine (×)). The styrene mole fraction in the feed is kept constant at 0.80.

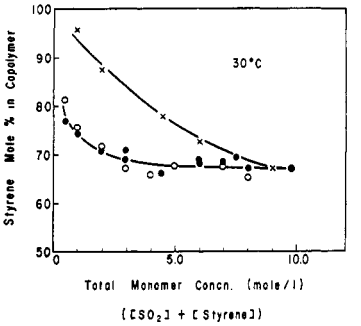


Figure 7. Relationship between total monomer concentration and copolymer composition (diluents, *o*-dichlorobenzene (○), dichloromethane (●), and pyridine (×)). The styrene mole fraction in the feed is kept constant at 0.80.

Discussion

On the Possibility of Monomer Complex Participation in the Propagation Process of the Poly(styrene sulfone) Formation Reaction. Dainton and Ivin[15–18] and Barb[3–5] independently proposed the participation of a monomer complex of sulfur dioxide and olefin. Recently, some investigators have been investigating the participation of charge-transfer complexes in synthetic processes, and from this point of view attention has been recalled to several alternating radical copolymerizations and to the formation of poly(olefin sulfones), which may also be associated with these complexes. In spite of a number of kinetic studies on polysulfone formation reactions, it remains uncertain that participation of a monomer complex in the alternating copolymerization actually takes place. We have investigated the copolymerization of sulfur dioxide and styrene from this point of view; thus, the composition of poly(styrene sulfone) and the overall rate of polymerization have been investigated as a function of total monomer concentration.

As shown in Figure 1, it is apparent that an equimolar monomer complex of sulfur dioxide and styrene exists in a mixture solution of sulfur dioxide and styrene, and lower values of the physical constant of complex formation suggest that a contact-type complex is predominant in the resonance structure of charge-transfer interaction between sulfur dioxide and styrene. In Figure 2 the differences in copolymer composition between the different series (*e.g.*, comparison of A with B or A with C, etc.) appear to provide evidence for the participation of a monomer complex in the propagation step, since the higher the total monomer concentration the higher the monomer complex concentration. It is then possible to consider that the differences in copolymer composition are due to the differences in monomer complex concentration. On the other hand, the composition of copolymers within each series (*i.e.*, within identical total monomer concentration; *e.g.*, within series A) does not depend on the feed composition except at higher styrene concentrations. Since total monomer concentration was kept constant in each series, the maximum concentration of monomer complex should lie at 50 mol % in the monomer mixtures. Thus, if the differences in copolymer composition between the different series are attributable to participation of a monomer complex, the copolymer composition should also depend on feed composition. The dilution effect shown in Figures 3 and 4 can also be regarded as evidence for complex participation in the cases where it was observed. However, copolymer composition should depend on total monomer concentration, even at lower temperatures, if monomer complex participates in the propagation step, and the absence of the dilution effect at 0° (Figure 3) indicates that in the case of poly(styrene sulfone) formation, monomer complex does not participate in the propagation step. This also suggests that, at this temperature, the depropagation shown in eq 10 is of little importance in comparison with the propagation step. This conclusion may be supported by the large difference between the activation energies of propagation and depropagation ($E_p - E_d \simeq 20$ kcal/mol), although this was observed during the copolymerization of aliphatic olefins and sulfur dioxide,[19]

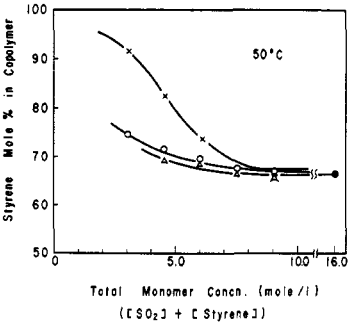


Figure 8. Relationship between total monomer concentration and copolymer composition (diluents, *o*-dichlorobenzene (○), sulfolane (△), and pyridine (×)). The styrene mole fraction in the feed is kept constant at 0.20.

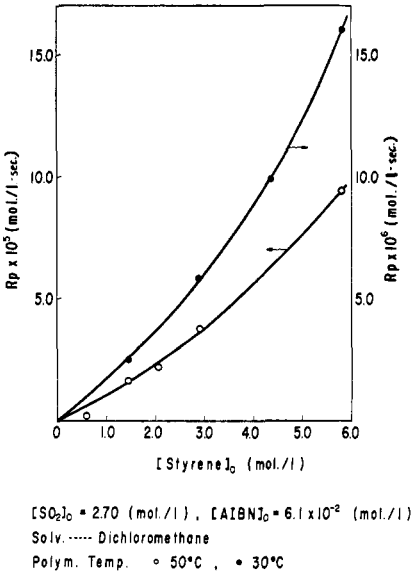


Figure 9. The relationship between the overall rate of polymerization and the concentration of styrene monomer for constant concentration of sulfur dioxide.

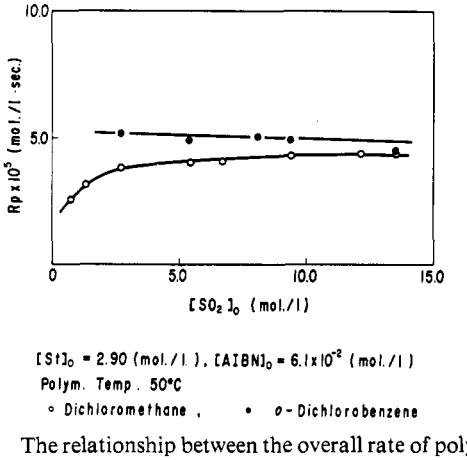


Figure 10. The relationship between the overall rate of polymerization and the concentration of sulfur dioxide for constant concentration of styrene monomer.

and the results shown in Table II, the molar ratio of (I + II)/III decrease with decreasing temperature, have suggested that in the case of the poly(styrene sulfone) formation reaction a rather large difference between activation energies may also exist.

As has been proposed by Barb,[3–5] depropagation reactions

(15) F. S. Dainton and K. J. Ivin, *Proc. Roy. Soc., Ser. A*, **212**, 96 (1952).
(16) F. S. Dainton and K. J. Ivin, *ibid.*, **212**, 207 (1952).
(17) G. M. Bristow and F. S. Dainton, *ibid.*, **212**, 509 (1952).
(18) G. M. Bristow and F. S. Dainton, *ibid.*, **212**, 525 (1952).
(19) F. S. Dainton and K. J. Ivin, *Quart. Rev., Chem. Soc.*, **12**, 61 (1958).

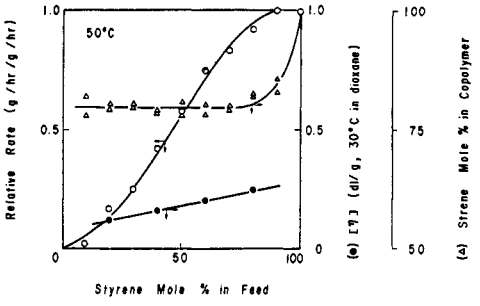


Figure 11. Relationships between feeds and relative rate (○), copolymer composition (△), and intrinsic viscosity (●). Total monomer concentration of $[SO_2]$ + [styrene] is being kept constant at 2.0 *M* and thus the mole fraction of styrene in feed was varied from 0.1 to 0.9 (diluent, dichloromethane; polymerization temperature, 50°).

during the formation of poly(styrene sulfone) can be divided into two types: (1) the loss of a sulfur dioxide unit from an ~St–SO_2· chain ending to form an ~St· ending and (2) the loss of a styrene unit, resulting in the formation of a sulfonyl or styryl radical ending. The temperature effects on polysulfone composition shown in Figures 3 and 4 and on the addition reaction of benzylsulfonyl chloride to styrene monomer shown in Table II suggest the existence of the former type of depropagation, but provide no evidence for the existence of the second sequence. As depropagation and propagation are first-order and second-order reactions, respectively, the decrease in the rate of depropagation on dilution is smaller than that for propagation, and this gives rise to the observed variability in copolymer composition. The increase in styrene content on dilution, shown in Figures 3–8, may thus be interpreted as a result of the increase in the depropagation rate relative to the propagation rate.

It appears from Figures 5–8 that the solvent effects, regardless of polarity (dielectric constants), can be classified into two groups, namely, pyridine and the remaining solvents. The interaction of the latter solvents, of which sulfolane is a representative example, with sulfur dioxide is rather small, and these solvents do not show a dilution effect at higher total monomer concentration. However, even in these solvents, at lower total monomer concentrations, the styrene mole fraction in the copolymer increases with increasing solvent volume fraction. The effect of pyridine on the depropagation process will be discussed later.

Our Tentative Propagation Mechanism in the Radical Copolymerization of Sulfur Dioxide and Styrene. From the experimental results described above, it would seem possible to rule out both radical polymerization mechanisms, *i.e.*, a propagation process of separate monomers (sulfur dioxide and styrene), explained by the Lewis–Mayo equation, and propagation processes involving a monomer complex. However, we cannot propose an exact mechanism to replace the above mechanisms, since there appear to be conflicting data, and in particular the relationship between copolymer composition and total monomer concentration shown in Figure 2 is quite difficult to correlate with a possible propagation mechanism. It is obvious that the variation of activity with total monomer concentration (on dilution) has no connection with the variation in copolymer composition in the light of the data presented by Ivin and O'Donnel,[20] who measured the activity of a sulfur dioxide–isobutylene system as a function of monomer concentration. Therefore, it seems likely that the dilution effect described in the preceding section is attributable to depropagation, but it is clear that the formation process of poly(styrene sulfone) is still more complicated in terms of the overall rate data. As shown in Figure 11, the relative rate of copolymerization increases almost linearly with increasing styrene concentration in the feed (relative rate was estimated on the basis of the rate obtained at 0.9 mol fraction of styrene), and the molecular weight of copolymers also increases, but to a lesser extent than the increase in rate. It has also been ascertained separately that the rate does not depend on the concentration of sulfur dioxide except at low concentrations of sulfur dioxide as shown in Figure 10.

Consequently, the most straightforward explanation for Figure 11 is that the number of polymer molecules of the same composition and of almost the same average molecular weight increases with increasing styrene monomer concentration. The increase in the number of polymer molecules is probably due to chain-transfer reactions of growing polymer radicals to styrene monomer (initiator (AIBN) concentration is kept constant for all feed compositions). We wish to propose the following tentative propagation mechanism with due regard to our experimental results described above.

The results obtained at lower polymerization temperature will be discussed first. As described in the preceding, at lower temperatures the copolymer composition is not affected by dilution; *i.e.*, it is independent of total monomer concentration (see Figure 3), and it is also clear that copolymer composition does not depend on feed composition (this is true also for data obtained at 50° (see Figure 2)). Data on the bulk copolymerization of sulfur dioxide and styrene obtained at 0° show that copolymer composition does not depend on feed composition,[21] but it has been shown that the composition changes on lowering the polymerization temperature below 0°, until finally, at −78°, the alternating poly(styrene sulfone) is obtained.[22] These compositions are also independent of both feed and dilution. These results strongly suggest that copolymer composition at temperatures below 0° can be accounted for by a term consisting solely of rate constants, and which, therefore, varies only with polymerization temperature. Consequently, copolymers having various compositions are obtainable simply by lowering the temperature. The composition of poly(styrene sulfone) prepared at lower temperatures can therefore be accounted for by a kinetic scheme involving the following elementary reactions.

$$\sim\!\mathrm{St}\text{–}\mathrm{SO_2}\cdot + \mathrm{St} \xrightarrow{k_{SM}} \sim\!\mathrm{SO_2}\text{–}\mathrm{St}\cdot \quad (6)$$

$$\sim\!\mathrm{St}\text{–}\mathrm{SO_2}\cdot + \mathrm{St} \xrightarrow{k_{d2}} \sim\!\mathrm{St}\text{–}\mathrm{St}\cdot + \mathrm{SO_2} \quad (7)$$

$$\sim\!\mathrm{St}\cdot + \mathrm{SO_2} \xrightarrow{k_{SM}} \sim\!\mathrm{St}\text{–}\mathrm{SO_2}\cdot \quad (8)$$

By assuming stationary concentration of growing polymer radicals, we have

$$n = \left(\frac{\mathrm{St}}{\mathrm{SO_2}}\right)_{\mathrm{copoly}} = 1 + \frac{k_{d2}}{k_{SM}} \quad (9)$$

and from Figure 3, the value of k_{d2}/k_{SM} is estimated to be 0.82 at 0°. Here, it is necessary to consider the validity of eq 7, which has been assumed by Huyser and Kim[23] in the reactions of trichloromethanesulfonyl radicals with cyclohexene, where

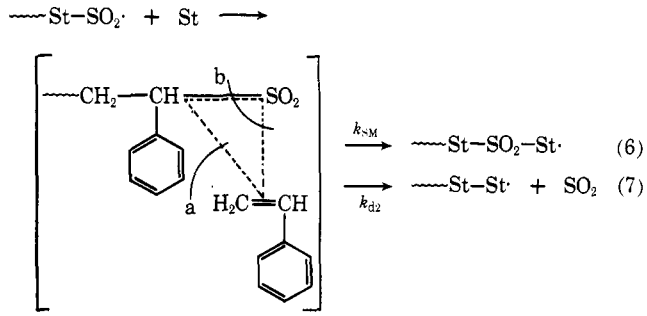
(20) K. J. Ivin and J. H. O'Donnel, *Trans. Faraday Soc.*, **61**, 1887 (1965).

(21) N. Tokura, M. Iino and H. Yoshimoto, unpublished data.

(22) J. Herz, D. Hummel and C. Schneider, *Makromol. Chem.*, **64**, 95 (1963).

(23) E. S. Huyser and L. Kim, *J. Org. Chem.*, **32**, 618 (1967).

the reaction products were sulfur dioxide and addition products. We regard eq 7 as a variety of depropagation, but it is a second-order depropagation differing from the usual first-order type. At low temperature, first-order depropagation may be negligible compared with other processes, since the difference between the activation energies of propagation and depropagation, $E_p - E_d$, was reported to be about 20 kcal/mol[19] and, as shown in Table II, the ease of elimination of sulfur dioxide from benzylsulfonyl radical decreases rapidly as the temperature goes down. A composition equation identical with eq 9 can also be derived by adding a first-order depropagation step to the proposed scheme, but for the above reasons this type of depropagation is unlikely to be significant at low temperature. The second-order depropagation proposed here is not affected in the same way, and eq 7 may represent a plausible process in view of the fact[24] that a sulfonyl radical attached to a carbon atom is originally unstable and may easily release a sulfur dioxide molecule, particularly when the donation of extra energy is expected by the addition of styrene. This situation can be illustrated by assuming the following intermediate in a second-order depropagation.



The intermediate shown above illustrates the nature of the second-order depropagation process proposed by us; the reaction of a styrene monomer and a sulfonyl radical forms the intermediate shown above and then is cleaved at either the a or b position, depending only on the polymerization temperature. According to the composition equation shown by eq 9, the value of the rate constant k_{SM} must be larger than that of k_{d2}, since the copolymer composition obtained at polymerization temperatures below 0° is always less than two ($n < 2$). It is a reasonable assumption that at lower temperatures the value of k_{MS} is much greater than both the values of k_{SM} and k_{d2} (*i.e.*, $k_{MS} \gg k_{SM} > k_{d2}$), since in a sulfur dioxide–aliphatic olefin system reacting at low temperature, only the sulfonyl radical is detectable by esr measurements, whereas at ambient temperature and above both carbon and sulfonyl radicals are detected.[25] Thus, the composition of copolymers obtained at low temperatures can be accounted for in terms of a second-order depropagation.

Secondly, the results obtained at ambient temperature and above are discussed. It has been shown that the styrene content of copolymers increases with decreasing total monomer concentration at these temperatures (*i.e.*, the dilution effect is operative), suggesting that a first-order depropagation is also operative here, as well as the second-order depropagation; the decrease in the rate of first-order depropagation due to dilution is smaller than that for second-order reaction, so the reaction would be expected to show a dilution effect.

(24) W. K. Busfield, K. J. Ivin, H. Mackel, and P. A. G. O'Hara, *Trans. Faraday Soc.*, 57, 1064 (1961).

(25) P. B. Ayscough, K. J. Ivin and J. H. O'Donnel, *Proc. Chem. Soc., London*, 71 (1961).

The difference between activation energies of propagation and depropagation is comparatively large, but at higher temperature a first-order depropagation is also worthy of consideration in the kinetic scheme. Furthermore, as copolymer composition is always greater than two, a propagation process between growing styryl radical and styrene monomer must also be considered in conjunction with the first-order depropagation. Adding both elementary processes onto the scheme proposed for low-temperature polymerization, a reaction scheme applicable at higher temperatures is obtained as follows.

$$\sim\!\sim St\text{–}SO_2\cdot + St \xrightarrow{k_{SM}} \sim\!\sim SO_2\text{–}St\cdot \quad (6)$$

$$\xrightarrow[k_{d2}]{} \sim\!\sim St\text{–}St\cdot + SO_2 \quad (7)$$

$$\sim\!\sim St\cdot + SO_2 \underset{k_{dMS}}{\overset{k_{MS}}{\rightleftharpoons}} \sim\!\sim St\text{–}SO_2\cdot \quad (8, 10)$$

$$\sim\!\sim St\cdot + St \xrightarrow{k_{MM}} \sim\!\sim St\text{–}St\cdot \quad (11)$$

By assuming stationary concentration of growing radicals, the composition equation can be derived as follows.

$$n = \left(\frac{St}{SO_2}\right)_{copoly} = 1 + \frac{k_{d2}}{k_{SM}} + \frac{k_{dMS}k_{MM}}{k_{SM}k_{MS}[SO_2]} + \frac{(k_{SM} + k_{d2})k_{MM}[St]}{k_{SM}k_{MS}[SO_2]} \quad (12)$$

The fourth term in eq 12 becomes significant for the composition of copolymers obtained at higher styrene monomer concentrations in the feed; as shown in Figure 2, the constancy of styrene content in the copolymers no longer applies above about 80 mol % styrene monomer. This may therefore be explained by the fourth term in eq 12. By analogy with the assumptions used for a rough comparison of the rate constants in the discussion of the low-temperature situation, we may take it that $k_{MS}, k_{dMS} \gg k_{SM}, k_{d2}, k_{MM}$, so that the fourth term becomes negligible at low styrene monomer concentration, compared to other terms. Equation 12 then reduces to

$$n = \left(\frac{St}{SO_2}\right)_{copoly} = 1 + \frac{k_{d2}}{k_{SM}} + \frac{k_{dMS}k_{MM}}{k_{SM}k_{MS}}\frac{1}{[SO_2]} \quad (13)$$

That the copolymer compositions obtained from any constant feed composition less than about 80 mol % styrene monomer (*e.g.*, the copolymer compositions A, B, and C obtained at 50 mol % styrene in the feed) are explicable by eq 13 is clear, since the sulfur dioxide concentration in the last term of the above equation is directly proportional to total monomer concentration for copolymer compositions obtained from a constant feed composition. However, each monomer composition is, of course, a function of sulfur dioxide concentration. Accordingly, the constant copolymer compositions obtained from all the feed compositions cannot be explained by eq 13. This seems logical, since in eq 13 a term containing total monomer concentration ($[SO_2] + [St]$) is not involved. However, it is impossible to derive an equation containing the sum of sulfur dioxide and styrene concentrations. Therefore, if the composition equation (eq 13) is to be valid, the rate constants involved in the last term should vary with the total monomer concentration. In other words, the reactivity of growing polymer radicals, either styryl or sulfonyl radical, or both, varies with total monomer concentration. The last term in eq 13 should involve total monomer concentration instead of sulfur dioxide concentra-

tion, and this term was derived in connection with the elementary reactions given in eq 8 and 10. By assuming that both k_{MS} and k_{dMS} have a large value (*i.e.*, by assuming that attack of growing styryl radical on sulfur dioxide is a rapidly reversible process), the ratio k_{dMS}/k_{MS} in the last term would depend on the difference of reactivities between sulfonyl and styryl radicals, and these reactivities are presumably affected by the change from bulk copolymerization to the more diluted systems.

As shown in Figure 11, relative rates increased almost linearly with increasing styrene monomer concentration in the feed, but the copolymer composition did not vary with feed containing less than about 80 mol % styrene monomer, and the molecular weight of the poly(styrene sulfone) did not increase significantly. It would seem possible to explain these findings in terms of a rapid addition process of sulfur dioxide to growing styryl radical and a rapid reverse process (eq 8 and 10). The apparent rate would then be controlled by the addition of styrene monomer to growing sulfonyl radical; a rapidly reversible process may be supported by the fact that the overall rate of polymerization does not depend on sulfur dioxide concentration except at low concentrations of sulfur dioxide. The dilution effects on composition of poly(hexene-1 sulfone) will be discussed in the later paper.[26]

The effects of pyridine (shown in Figures 9 to 13) are probably due to participation in the intermediate; pyridine may assist in the elimination of a sulfur dioxide molecule from the growing sulfonyl ending. In other words, the rate of second-order depropagation may be accelerated by the addition of pyridine.

It is necessary to compare our tentative scheme with Walling's scheme; he demonstrated that the formation of poly(styrene sulfone) can be explained without invoking monomer complex participation and assumed in his scheme that attack of a growing styryl radical on sulfur dioxide is a rapidly reversible process at all temperatures. This is the same assumption as in our scheme (eq 8 and 10), but we considered that this process (a first-order depropagation) could be excluded at lower temperatures because of the comparatively large difference in activation energy between propagation and first-order depropagation and because the dilution effect was not observed at low temperature. Walling also assumed k_{MS}, $k_{dMS} \gg k_{SM}$, as in our scheme. The contrast between the two schemes lies in the assumption of a second-order depropagation (eq 7) in our scheme and of depropagation of growing styryl ending by loss of a styrene unit (leaving a sulfonyl ending) in his scheme. Both schemes originated in attempts to use the experimental results to predict copolymer composition, but depropagation of a growing styryl ending, $\sim SO_2\text{–St}\cdot$, was unnecessary in our scheme. Walling also proposed the penultimate unit effect which has not been considered in our scheme. In any event, our results obtained at 0° cannot be explained according to Walling's scheme.

Finally, we will comment on alternating radical copolymerizations such as the styrene–maleic anhydride and *p*-dioxene–maleic anhydride systems. Some investigators have suggested monomer complex participation in the propagation stage of these copolymerizations. It is a long-standing research theme in the synthetic polymer field to determine which factor controls the alternating tendency, and it is still unresolved. If a monomer complex was shown to be the real propagating species, this would be of considerable importance. We have been investigating the copolymerization of sulfur dioxide and styrene from this point of view, but we have found no positive evidence for participation of monomer complex. Kokubo, Iwatsuki, and Yamashita[27] have postulated the participation of a monomer complex in alternating copolymerization systems and have estimated the reactivities of various types of monomer complex. However, in their data the relationship between terpolymer composition and dilution is too complex to indicate definitely the presence of monomer complex participation. It is possible to explain the alternating tendency without consideration of monomer complex participation by assuming that the styryl radical reacts exclusively with maleic anhydride monomer and that the homopolymerizability of maleic anhydride is negligibly small.

(26) M. Iino, K. Seki, and M. Matsuda, unpublished data.

(27) T. Kokubo, S. Iwatsuki, and Y. Yamashita, *Macromolecules*, 3, 518 (1970).