Radical Polymerization of Styrene in Liquid Sulfur Dioxide

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Synopsis

Polymerization reaction of styrene in liquid sulfur dioxide was carried out with α,α'-azo-bis(isobutyronitrile) as the initiator. Polymerization temperatures selected were 40°, 50°, and 60°C. The polymer thereby obtained were analyzed as styrene polysulfone but it was found that, irrespective of the polymerization temperature or polymerization rate, the polymers had a unit composition consisting of 2 moles of styrene and 1 mole of sulfur dioxide. From such an experimental fact, it was considered better to assume that a complex consisting of 2 moles of styrene and 1 mole of sulfur dioxide had formed prior to the initiation of polymerization, rather than treating this as the copolymerization of styrene and sulfur dioxide, and a kinetic treatment was made of the radical polymerization reation of this complex. As a result, the velocity of total polymerization reaction, Rp, was given as constant $\times$ $[\text{initiator}]_0^{1/2}[\text{styrene}+1/2SO_2]_0$. Activation energy of the total reaction calculated on the basis of such hypothesis was 14.7 kcal/mole.

I. Introduction

Reaction between liquid sulfur dioxide and olefin compounds has been studied in the past and it is known that polysulfone is formed in the presence of light or radical initiator, while polyolefin is formed in the presence of cationic reagents. Studies on polysulfone was instituted by Staudinger and others[1], and numerous interesting results have been reported to date by a number of investigators. The phenomenon of ceiling temperature discovered by Snow and Frey[2] was during copolymerization of olefin and sulfur dioxide and, as is well known, detailed studies on this phenomenon have since been made by Dainton and Ivin, using 1-butene and 2-butene.

The first report on styrene polysulfone made by Staudinger and Ritzenthaler[1] who stated that a mixture of polysulfone and polystyrene, in which the ratio of sulfur dioxide to styrene was 1 : 1, had been obtained and that their separation was impossible. Glavis and others[3] made detailed studies on this polymerization using para-aldehyde catalyst and, more recently, Barb[4] reported the result of this studies.

In the present series of work, polymerization of styrene in liquid sulfur dioxide was carried out using α,α'-azo-bis(isobutyronitrile) as the initiator.

* This paper was read before the Symposium of Polymer Chemistry in Tokyo on Nov. 23, 1959.
(1) H. Staudinger and B. Ritzenthaler, Ber., **68** (1935), 455.
(2) R. D. Snow and F. E. Frey, Ind. Eng. Chem., **30** (1938), 176 ; J. Am. Chem. Soc., **71** (1949), 1582.
(3) F. J. Glavis, L. L. Ryden and C. S. Marvel, J. Am. Chem. Soc., **59** (1937), 707.
(4) W. G. Barb, Proc. Roy. Soc., **A212**, (1952) 66, 177; J. Polymer Sci., **10** (1953), 49.

Polymerization temperatures were 40°, 50°, and 60°C. One of the objects of this work was to see if the composition of styrene polysulfone would vary according to polymerization conditions or not and the other was, if the composition were constant, if it would be possible to make a kinetic treatment as a single polymerization by using unit composition of the polymer as a monomer, rather than treating the reaction as a copolymerization. According to the experiment of Doak,[5] the composition of polysulfone is almost constant, irrespective of polymerization conditions and, even in the present case, composition of the polysulfone formed was always in molar ratio of 1 : 2 of sulfur dioxide to styrene in spite of variation in molar ratio of sulfur dioxide to styrene in the mixture from 17.67 : 1.69 to 5.89 : 6.20. The result was the same when the polymerization temperature was varied. This fact is very interesting and suggests the formation of such a complex before the initiation. It was also found in the kinetic treatment that, if the concentration consisting of 2 moles of styrene and 1 mole of sulfur dioxide is taken as the initial concentration of a monomer, the velocity of total reaction, Rp, becomes proportional to the multiple of such unit concentration and agrees with the velocity formula of polymerization reaction of ordinary single monomer.

Consideration of the present experiments will be made in comparison with kinetic results of Barb and others.

II. Experimental

II. 1. *Purification of Reagents*

Crude styrene (product of U.C.C.) was distilled twice in nitrogen atmosphere
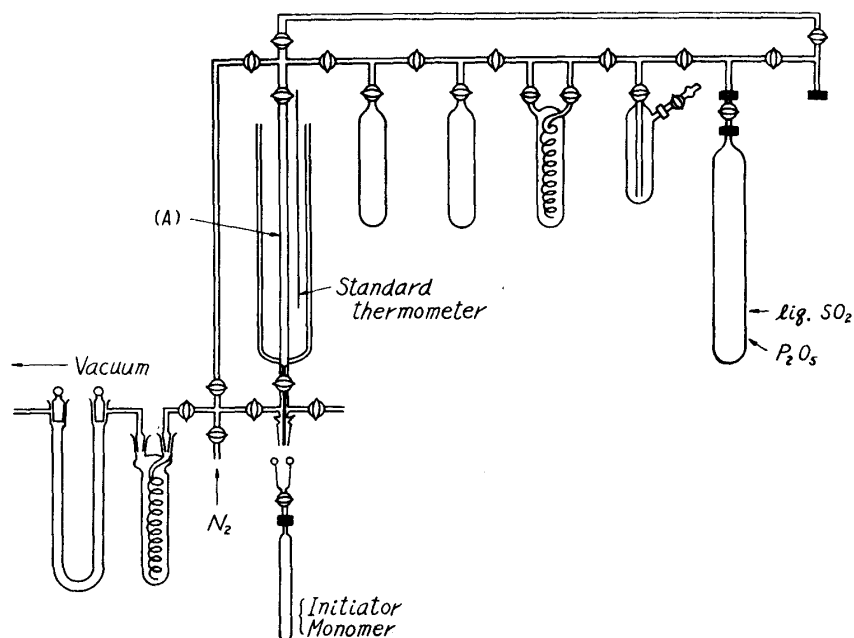

Fig. 1. The liquid sulfur dioxide dropping apparatus (capable of treating in N_2 atmosphere).

(5) K. W. Doak, private communication as cited in the work of Barb (cf. Footnote 4).

at a reduced pressure, b.p.$_{20}$ 46°C. The purity was checked by gas chromatography before use. There was a possibility the styrene might have formed a polystyrene during storage and, therefore, a small amount was dropped into methanol before use to confirm that no polymer had formed.

Liquid sulfur dioxide was collected in a pressure-resistant glass vessel (ca. 250 cc capactiy) containing about 60 g of phosphorus pentoxide, allowed to stand at room temperature for at least 24 hours, and attached to the apparatus for liquid sulfur dioxide (Fig. 1) to be led into a glass bomb (capacity, ca. 250cc) in the form of distillation for storage. Liquid sulfur dioxide dehydrated in this way contains about 50 p.p.m. of water.[6] Physical constants of liquid sulfur dioxide are as follows[7] : m.p. $-72.7°$, b.p. $-10.2°$; sp. gr., 1.4090 (10°), 1.4339 (0°), 1.4579 ($-10°$). α,α'-azo-bis(isobutyronitrile) used as the polymerization initiator was recrystallized from chloroform and ethanol, and dried in vacuum.

II. 2. *Preparation of Polymerization Tube and Determination of the Polymerization Velocity*

Polymerization reaction was carried out in a sealed pressure glass vessel, indicated in Fig. 2. A definite quantity of styrene solution containing α,α'-azobis(isobutyronitril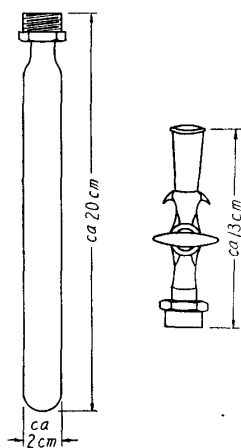e) of known concentration was pipetted into the vessel. The reaction vessel was provided with a cock by a joint and immersed into a methanol-dry ice bath. The vessel, in this state, was attached to the liquid sulfur dioxide dropping apparatus capable of treating in nitrogen atmosphere. The oxygen in the reaction vessel, containing chilled styrene, was replaced as much as possible with purified nitrogen (passed through pyrogallol-sodium hydroxide solution, sulfuric acid, and reduced copper), vacuum line cock was closed and liquid sulfur dioxide was led into the reaction vessel. Liquid sulfur dioxide, dehydrated as described above, was introduced from the storage bottle through a burette set in a windowed Dewar bottle (A in Fig. 1) and dropped onto styrene after evacuation as mentioned above. Specific gravity of liquid sulfur dioxide varies greatly according to temperature so that the burette readings should be made after adjusting the temperature to exactly 10°C, using a standard thermometer. After dropwise addition, the cock above the reaction vessel was closed, a catch was placed on the cock so as to stand the pressure formed during the reaction, and the reaction vessel was removed from the dropping apparatus.

Fig. 2. The reaction tube.

Each of the reaction vessels so obtained was allowed to stand in a thermostatic bath to effect polymerization reaction. Concentration of each reaction system was corrected by the specific gravity (1.3280, 1.2950, and 1.2629) of the correspond-

(6) N. Tokura and D. Murakami, Bull. Chem. Soc. Japan, 31 (1958), 431.
(7) L. F. Audrieth, 'Non-aqueous Solvents', John Wiley and Sons, Inc., New York (1953).

ing liquid sulfur dioxid at 40°, 50°, and 60°C, respectively. Polymerization proceeds in a homogeneous system. After allowing the reaction to proceed for a specified period, the reaction vessel was cooled in a methanol-dry ice bath, the cock was removed at the joint, and the polymer was precipitated by addition of a large quantity of methanol. The polymer was collected on a sintered glass filter and dried under a reduced pressure to a constant weight to obtain the reaction velocity. The rate of change in polymerization, used for calculation of the velocity, will be described in detail in the following section.

II. 3. *Composition of the Polymer*

Composition of styrene polysulfone was determined by microanalyses of carbon and hydrogen since there was some doubt on the accuracy of sulfur analysis.

III. Results and discussion

III. 1. *Determination of Polymerization Velocity* (Rp)

III. 1. 1. *With variation in initial concentration,* $[ABIN]_0$, *of the initiator*

Initial concentration, $[M]_0$, of styrene was made constant at 3.77 mole/l and that of liquid sulfur dioxide, $[SO_2]_0$, at 11.23 mole/l, while varying $[ABIN]_0$ from 8.39×10^{-4} to 1.75×10^{-1} mole/l, to obtain order of $[ABIN]_0$. Polymerization temperature was 50°C. The polymerization rate-polymerization time curve are shown in
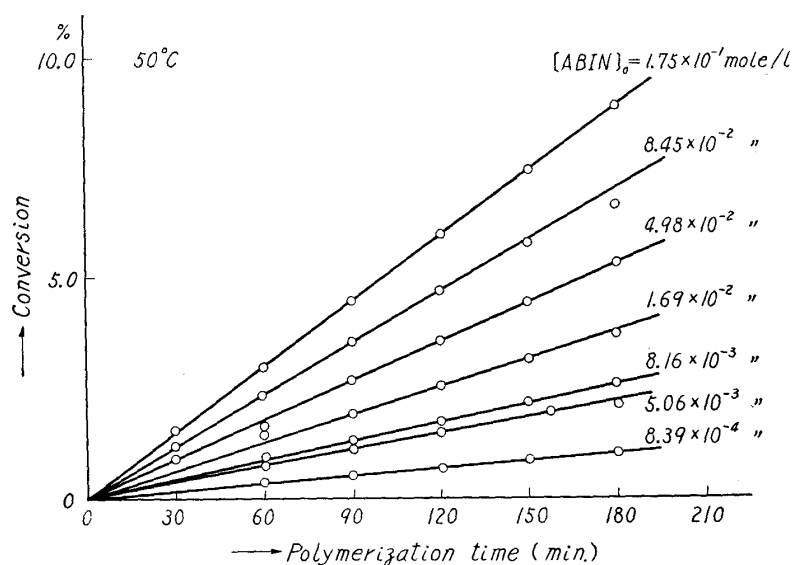

Fig. 3. Time-conversion curve (conversion *vs.* polymerization time).
$[Styrene]_0 = 3.77$ mole/l
$[ABIN]_0 = 1.75 \times 10^{-1} \sim 8.39 \times 10^{-4}$ mole/l

Fig. 3 and logarithmic plot of polymerization velocity, Rp and $[ABIN]_0$ in Fig. 4. (The rate of polymerization used here is the value obtained by dividing the total weight of styrene and sulfur dioxide before reaction with the yield of polymer. This is different from the polymerization rate described in III.1.2. but the order obtained with this value is not different.). The resultant Rp was expressed as constant $\times [ABIN]_0^{1/2}$.

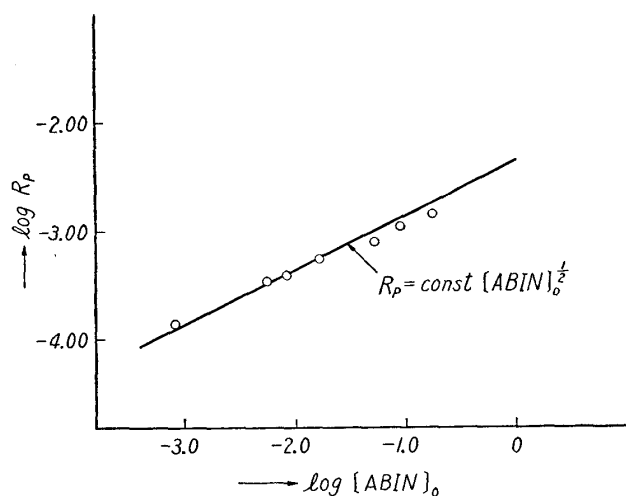Fig. 4. Over-all polymerization velocity $vs.$
initiator concentration. (50°C)
$[Styrene]_0 = 3.77$ mole/1
$[ABIN]_0 = 1.75 \times 10^{-1} \sim 8.39 \times 10^{-4}$mole/1

III. 1. 2. *With variation in the initial concentration of the monomer*

Polymerization was carried out at the temperatures of 40°, 50°, and 60°C. Initial concetration of the initiator was calculated so as to make it constant at 1.69×10^{-2} mole/1 at any of these temperatures and placed in each reaction vessel. Reproducible data were obtained in any of these temperatures. The polymerization rate-reaction time curve obtained at the polymerization temperature of 50°C is shown in Fig. 5. De-
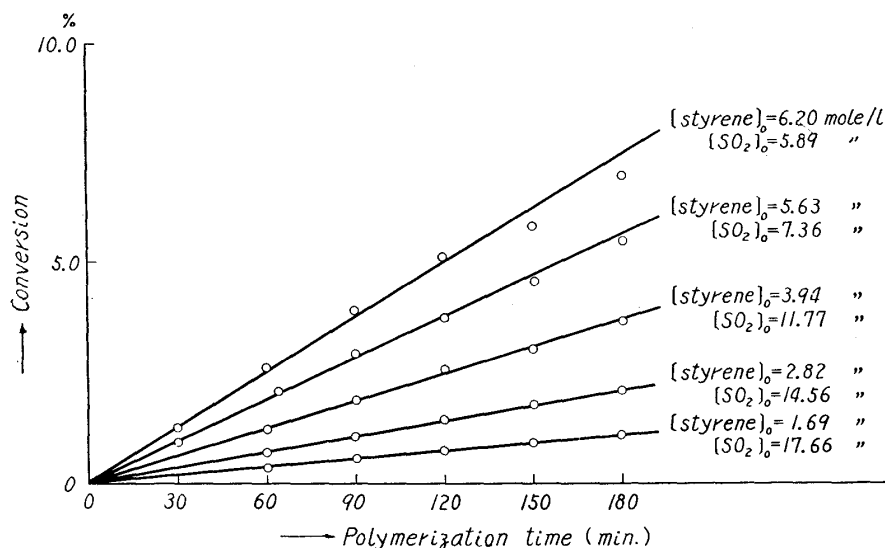

Fig. 5. The polymerization time-conversion curve.
$[ABIN]_0 = 1.69 \times 10^2$mole/1. temp. 50°C

pendability of the initial concentration of monomer on Rp at each of polymeri-zation temperatures is to be calculated. The polymerization rate used in Fig. 5 was calculated by dividing the sum of weight of styrene and sulfur dioxide, taken as the weight of monomer, with the polymer weight. In other words, the polymerization rate calculated by considering sulfur dioxide as a monomer was used in Fig. 5. Calculation of polymerization velocity from this correlation curve re-quires treatment as copolymerization reaction. However, under the polymerization conditions used in the present series of experiments, composition of the copolymer obtained was invariably in 2 : 1 ratio of styrene to sulfur dioxide (cf. Table 1 in section III.2). In copolymerization reaction in general, composition of the copolymer varies with changes in the mixing ratio of the two monomers before the poly-

merization reaction and in such a case, velocity formula for copolymerization should be used. In the present series of experiments, polymerization temperature was varied and mixing ratio before the reaction was also varied over a comparatively wide range (although it was more desirable to bring molar ratio of sulfur dioxide to styrene to a smaller range but this was impossible under the conditions used without causing experimental error), yet the copolymers obtained were invariably a polymer possessing unit structure shown below:

$$-\left[-CH_2-CH-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_2-CH-\right]_n-$$
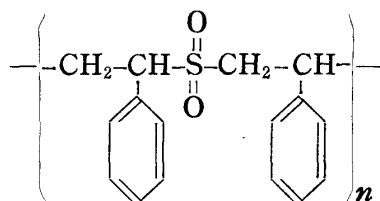
Therefore, it seemed more appropriate to treat this as a solution polymerization of a single monomer rather than copolymerization reaction.

Analytical results indicated that the sulfur dioxide present in the polymer is always in one-half the molar number of styrene in the polymer and, therefore, it was decided to treat sulfur dioxide before the reacaion in the following manner. Sulfur dioxide corresponding to one-half the molar number of styrene monomer was taken as a monomer and the remainder of sulfur dioxide was considered as a polymerization solvent. In other words, a part of sulfur dioxide is considered to take a monomeric behavior even before the polymerization reaction begins. As a matter of fact, sulfur dioxide is known to form a complex with numerous organic compounds and Barb has pointed out that sulfur dioxide and styrene forms a complex. Dropwise addition of colorless liquid sulfur dioxide into a colorless solution of styrene monomer results in immediate yellow coloration of the mixed solution, indicating the formation of a complex (even in the absence of a initiator). Barb,[4] in explaining the formation of styrene polysulfone, had already considered the formation of a complex consisting of 1 mole each of styrene and sulfur dioxide, and he suggested the formation of styrene polysufone by copolymerization of this 1 : 1-complex and styrene. According to this idea, formation of a polymer chain in 2 : 1 molar ratio of styrene to sulfur dioxide will require copolymerization of the 1 : 1-complex and styrene in 1 : 1 ratio. Otherwise, the fact will not agree with the present experimental results.

In this case, sole polymerization of 1 : 1-complex alone or styrene alone is denied. In copolymerization reaction in general, difference in molar ratio of the two monomers before the reaction should result in different composition of the copolymer thereby obtained and 1 : 1-copolymerization of 1 : 1-complex and styrene is not an appropriate assumption.

On the other hand, C. Walling[8] said that such considerations are not necessary and that it could be explained by the effect of the terminal active group of a growing polymer chain and a penultimate unit.

(8) C. Walling, J. Polymer Sci., **16** (1955), 315.

In the present work, it was assumed that a complex in 2 : 1 molar ratio of styrene to sulfur dioxide had been formed prior to polymerization. Considering the facile δ- charge of the vinyl group in styrene monomer and facile cationic charge of sulfur dioxide, formation of 2 : 1-complex seems quite possible. Consequently, a model like the following was considered, in which a complex is formed by coordination of one mole each of styrene molecule on either side of one mole

(Limit formula of SO_2)
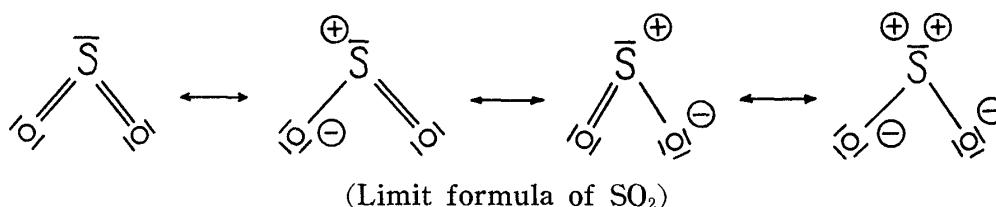
of sulfur dioxide. Such 2 : 1-complex is bound by a considerably strong mutual action and the equilibrium constant, K, between 2 : 1-complex and styrene, and sulfur dioxide is thought to be extremely small. It is also possible to consider a case of an olefinic compound in which the double bond of the vinyl group is in $\delta+$, reverse of that in styrene, is reacted in sulfur dioxide. For example, in the reaction with acrylonitrile, there is no formation of a complex as a result of repulsion between cationic action of SO_2 and $\delta+$ of the vinyl double bond in acrylonitrile. Consequently, the polymer formed is only polyacrylonitrile alone.[9] This agrees well with the result of heterogeneous polymerization of acrylonitrile in other solvents reported to date.

If it is assumed that sulfur dioxide which takes part in complex formation with styrene behaves like a conjugated monomer and the remainder of excess sulfur dioxide serves only as a polymerization solvent, the polymerization would take place by the chain reaction of 2 : 1-complex by the initiator radical. Consequently, the polysulfone formed would possess copolymer composition in which the ratio of styrene to sulfur dioxide would be 2 : 1.

As the monomer concentration, the sum of the styrene monomer and sulfur dioxide corresponding to one-half the moles of styrene monomer will be used which will hereinafter be written as [styrene + 1/2 SO_2]$_0$. (For the monomer concentration, [2 : 1-complex]$_0$ could also be used out it would be hard to consider that all the styrene monomers in the styrene-sulfur dioxide mixed system are taking part in this 2 : 1-complex and the recent report of Dainton and others[10] also seems to endorse this fact. Dainton and his collaborators examined the concentration of a complex of cyclopentene and isobutene in sulfur dioxide, and state that 40% of cyclopentene and 75% of isobutene are forming the complex. These complexes are 1 : 1 complex and the polysuflones formed also have 1 : 1 ratio of the olefin to sulfur dioxide). Polymerization rate-polymerization time curves, with the monomer concentration as [styrene + 1/2 SO_2]$_0$, are shown in Fig. 6 (at 60°), Fig. 7 (at 50°C), and Fig. 8 (at 40°C). Polymerization velocity calculated from these

(9) N. Tokura, M. Matsuda and F. Yazaki, unpublished data.

(10) D. Booth, F. S. Dainton and K. J. Ivin, Trans. Faraday Soc., 55 (1955), 1293.

curves and plotted on logarithmic axes with $[\text{styrene}+1/2\ SO_2]_0$ give the curves shown in Fig. 9, 10, and 11. From these plots, in any of the cases, Rp is represented by the formula constant × $[\text{styrene}+1/2SO_2]_0$ which, combined with the initiator concentration described earlier, would give equation (1).

Rp = constant ×

$$[\text{ABIN}]_0^{1/2}[\text{styrene}+1/2SO_2]_0 \qquad (1)$$

Equation (1) is exactly the same as the formula of radical polymerization of a solution of single monomer progressing in a uniform system. In the present case, presence of a complex in the term used here was assumed and equation (1) was obtained by assuming that
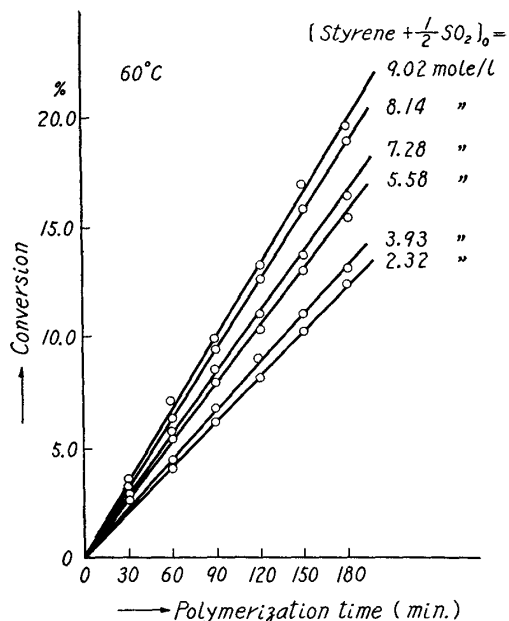

Fig. 6. Time-conversion curve, $[\text{styrene}+\frac{1}{2}SO_2]_0$ as monomer.
$[\text{ABIN}]_0=1.69\times10^{-2}$ mole/l. temp. 60°C
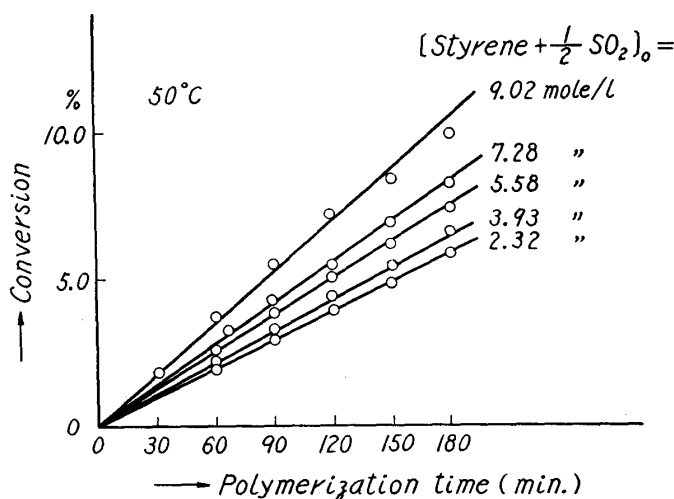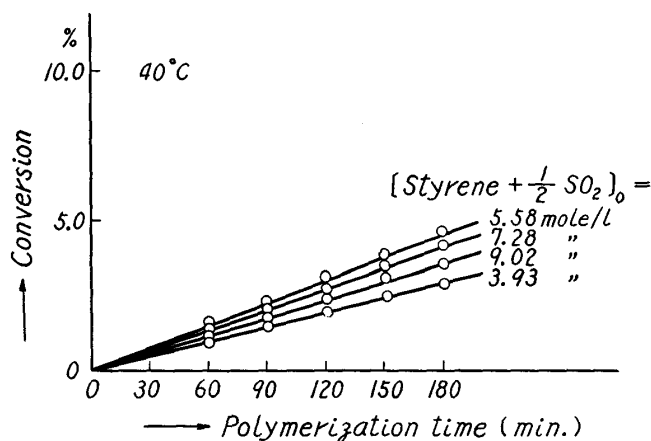

Fig. 7. Time-conversion curve. temp. 50°C

Fig. 8. Time-conversion curve. temp. 40°C
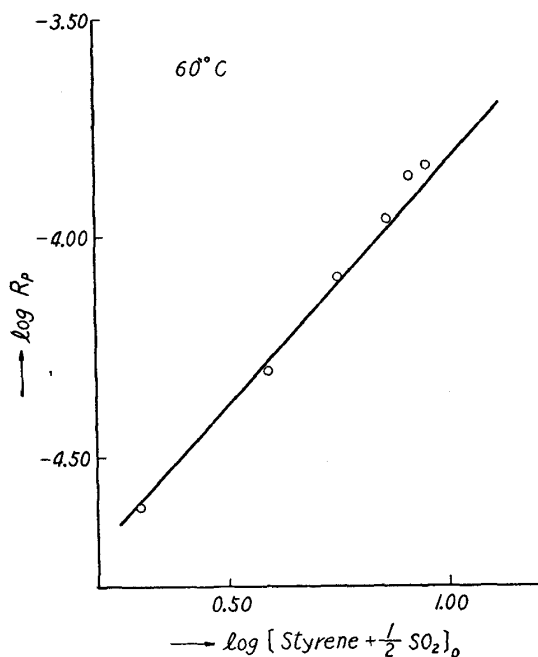
Fig. 9. Log. overall rate- log. monomer
conc. plot.
[Styrene + $\frac{1}{2}SO_2$]$_0$ = 9.02~2.32mole/l
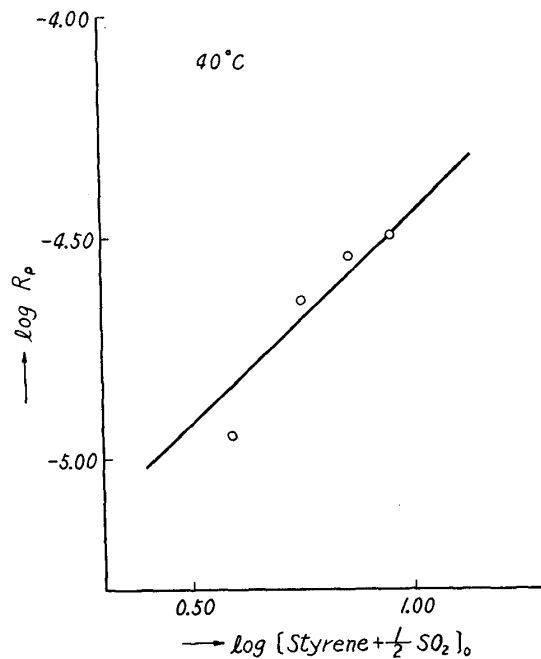[AIBN]$_0$ = 1.69 × 10^{-2}mole/l. temp. 60°C

Fig. 10. Log. overall rate-log. monomer
conc. plot. temp. 40°C
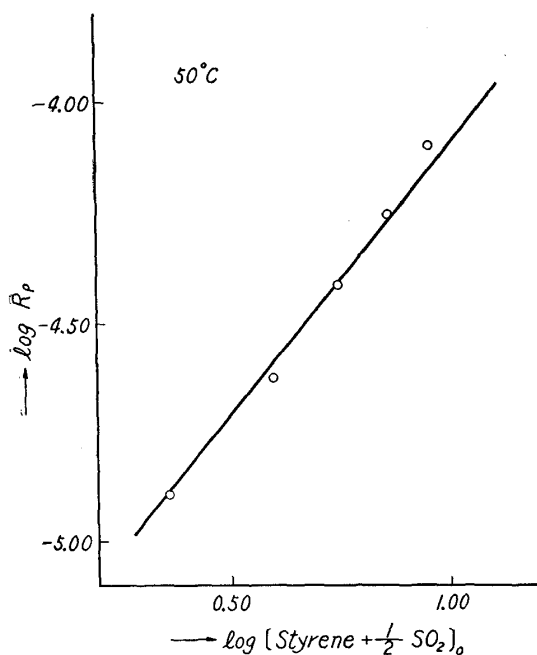

Fig. 11. Log. overall rate-log. monomer
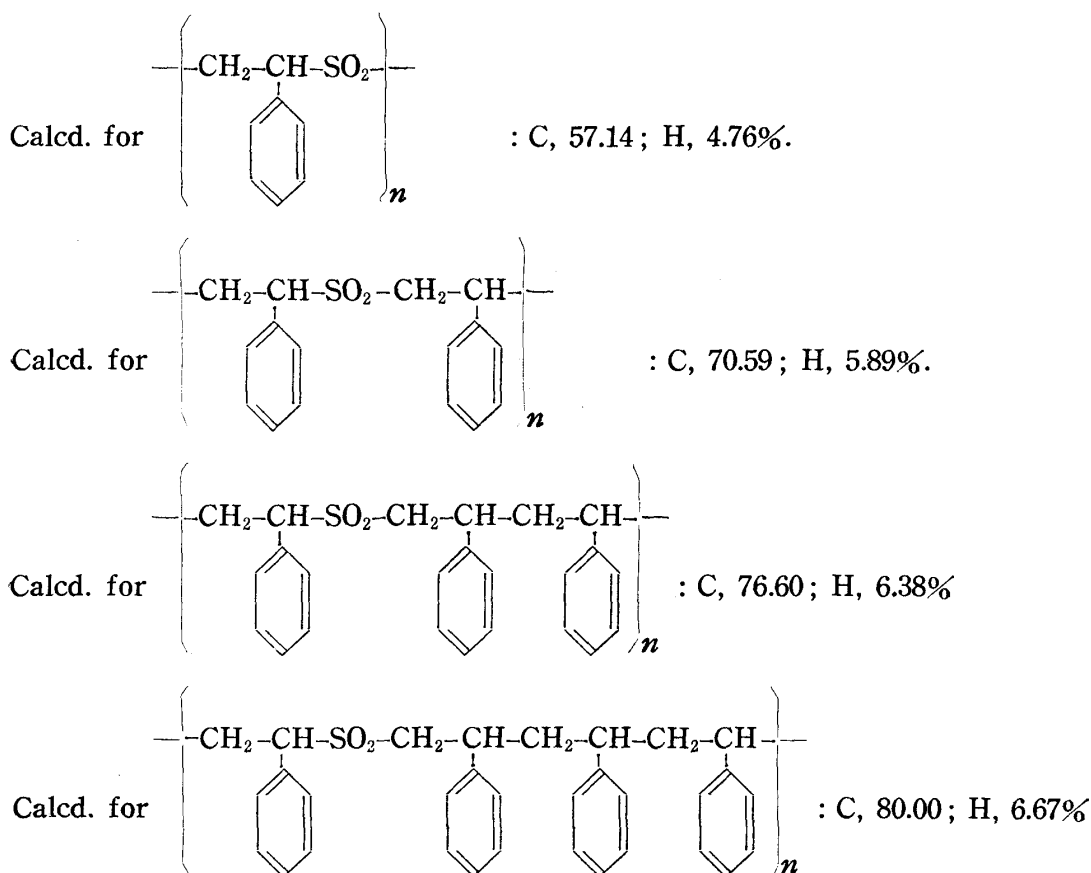conc. plot. temp. 50°C

polymerization occurred by growth of that complex. The presence of the complex could be proved by ultraviolet absorption spectrum and others but it may be impossible to ascertain whether such a complex is formed from 2 moles of styrene and 1 mole of sulfur dioxide. Further, equilibrium constant of the complex was taken as being extremely small but this point is still uncertain. The formation of a styrene polysulfone possessing a regular structure was explained by a hypothesis of a complex formation. Copolymerization of vinyl chloride and sulfur dioxide has also been reported to form a 2 : 1 polysulfone, as in the case of styrene.[11]

No considerations have been made on chain transfer reaction and the matter will be considered in the future, together with chain transfer reaction in the case of radical polymerization of monomers other than styrene and sulfur dioxide.

(11) C. S. Marvel and L. H. Dunlop, J. Am. Chem. Soc., 61 (1939), 2709.
      C. S. Marvel and F. G. Glavis, J. Am. Chem. Soc., 60 (1938), 2622.

III. 2. *Composition of Styrene Polysulfone*

In determination of a polymer composition, analysis of sulfur would be the best method but precision of this method was rather uncertain so that the determination was made through analyses of carbon and hydrogen. Theoretical values of carbon and hydrogen calculated for the assumed structure of the polymer would be as follows:

Calcd. for $-\left[-CH_2-CH(C_6H_5)-SO_2-\right]_n-$: C, 57.14; H, 4.76%.

Calcd. for $-\left[-CH_2-CH(C_6H_5)-SO_2-CH_2-CH(C_6H_5)-\right]_n-$: C, 70.59; H, 5.89%.

Calcd. for $-\left[-CH_2-CH(C_6H_5)-SO_2-CH_2-CH(C_6H_5)-CH_2-CH(C_6H_5)-\right]_n-$: C, 76.60; H, 6.38%

Calcd. for $-\left[-CH_2-CH(C_6H_5)-SO_2-CH_2-CH(C_6H_5)-CH_2-CH(C_6H_5)-CH_2-CH(C_6H_5)-\right]_n-$: C, 80.00; H, 6.67%

Analytical results obtained with the styrene polysulfones formed under the present experimental conditions are presented in Table 1. Comparison of elemental analyses given in Table 1 and theoretical values obtained by assuming various polymer compositions shows that almost all the polymers have a single unit consisting of two moles of styrene and one mole of sulfur dioxide. Based on such a fact, a 2 : 1-complex was assumed and $[styrene+1/2SO_2]_0$ was used as the monomer concentration. Variation in the composition with increased polymerization rate is presented in Table 2. The polymerization in this table is the percentage rate calculated with sulfur dioxide corresponding to one-half of styrene monomer.

Even when polymerization rate is considerably high, polymer composition retains the unit structure consisting of two moles of styrene and one mole of sulfur dioxide. This fact seems to support the assumptions iterated above. Contamination of styrene polymer in the styrene polysulfone was confirmed by extraction of polysulfone with benzene in a Soxhlet extractor for 10 hours from which

Table 1. Elemental analysis of the polymer.

Polymerization temperature (°C)	Polymerization condition[1]	Conversion[2] (wt.%)	Analyses (%) C	H
40	A	2.23	70.25	5.76
	A	0.97	68.68	5.97
	B	2.68	68.96	6.16
	D	2.85	69.73	5.79
50	A	0.98	70.36	6.01
	A	2.13	66.57	5.82
	A	2.47	69.12	5.93
	A	3.51	68.35	5.88
	A	5.19	68.91	6.09
	B	5.31	69.86	6.20
	C	4.43	70.59	5.78
	D	6.46	69.96	5.95
60	A	6.30	70.96	5.87
	A	7.34	70.44	5.94
	A	11.57	70.50	6.05
	B	7.22	71.11	6.18
	B	8.83	71.11	6.12

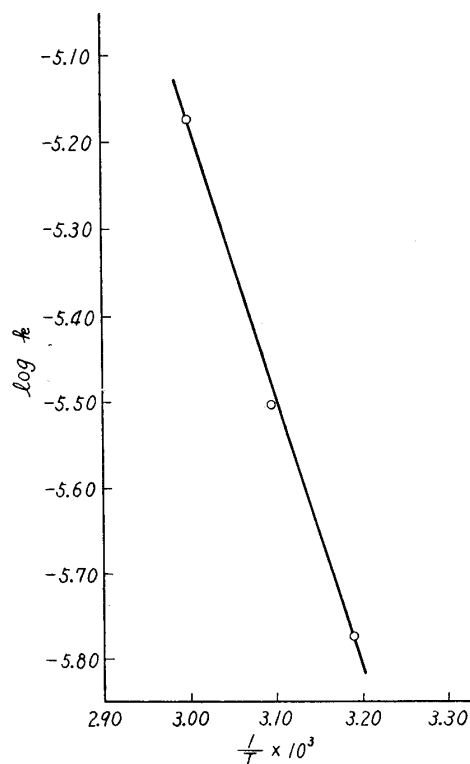(1) Polymerization conditions :

     A : $[styrene]_0 = 3.94$ mole/l, $[SO_2]_0 = 11.77$ mole/l
     B : $[styrene]_0 = 5.07$ mole/l, $[SO_2]_0 = 8.48$ mole/l
     C : $[styrene]_0 = 5.63$ mole/l, $[SO_2]_0 = 7.36$ mole/l
     D : $[styrene]_0 = 6.20$ mole/l, $[SO_2]_0 = 5.89$ mole/l

(2) Polymerization rate used here is the percentage in weight calculated with total SO_2 as a monomer.

Fig. 12. Arrhenius plot of the polymerization reaction.

Table 2. Polymerization time and polymer composition* (Polymerization temperature : 50°C).

Polymerization period (hr.)	Conversion (wt.%)	Analyses (%) C	H
5	13.51	68.82	5.77
6.5	17.74	70.10	6.19
8	21.02	69.90	5.83
20	42.08	68.89	5.88

* Polymerization conditions were the same as C in Table 1.

none was recovered. It follows, therefore, that the polymer obtained under the present experimental conditions is a polysulfone with 2 : 1 composition of styrene to sulfur dioxide.

III. 3. *The Activation Energy of the Over-all Reaction*

For the activation energy of the overall reaction, 14.7 Kcal/mole was obtained.