*The Cationic Copolymerization of Styrene and p-Bromostyrene in Liquid Sulfur Dioxide**

By Niichiro TOKURA, Minoru MATSUDA and Masashi IINO

(Received August 11, 1962)

The effect of a solvent on the monomer reactivity ratios in cationic polymerization has been the subject of recent study. Overberger et al., carrying out the cationic copolymerization of styrene and *p*-chlorostyrene in carbon tetrachloride and nitrobenzene respectively, found no appreciable difference in r_1's and r_2's[1a,b]. However, in the cationic polymerization of *p*-chlorostyrene with isobutene, r_1 and r_2 varied as the solvent used was changed[1c]. They therefore suggested that the independence of r_1 and r_2 in the former case was due to the similarity of the structure of the comonomers applied[1b].

Marvel and Dunphy[2] have shown that the cationic copolymerization of 2-chloroethyl vinyl ether with α-methylstyrene and its derivatives resulted in a marked difference in the monomer reactivity ratios according to the solvents applied. Pepper[3] first found that the rate of cationic polymerization is largely dependent on the dielectric constants of the solvents applied. However, other examples have also been shown in which anomalies in the relationship between the dielectric constants of the solvents and the rates have been observed[4,5].

This paper aims at the elucidation of the effect of liquid sulfur dioxide on the cationic polymerization. A cationic copolymerization of styrene and *p*-bromostyrene in liquid sulfur dioxide has been undertaken; the results will be described below. The cationic polymerization in liquid sulfur dioxide differs from that in any other solvent; viz., in liquid sulfur dioxide, (1) the polymerization is much faster than that which would be expected from the dielectric constant of the solvent (liquid sulfur dioxide)[6a], (2) the reaction is assisted by a number of sulfur dioxide molecules in the transition state[6b], and (3) the chain transfers, both to the monomer and the solvent, are very small[6a]. Accordingly, somewhat different results have been expected in this copolymerization.

Experimental

Materials.—Styrene (U.C.C. product) was distilled twice in vacuo in a nitrogen atmosphere. *p*-Bromostyrene was prepared by a known method[7]; b. p., 89°C/13 mmHg, n_D^{20}, 1.5931. Boron trifluoride etherate was distilled twice in a nitrogen atmosphere. Liquid sulfur dioxide was dried over phosphorus pentoxide and distilled. Carbon tetrachloride was refluxed with sodium hydroxide and distilled. Benzene was purified by the ordinary method. Nitrobenzene was washed with a sodium hydroxide solution and with water, dried with phosphorus pentoxide, and distilled in vacuo. Ethylene dichloride was washed with sodium hydroxide and then with water, dehydrated with phosphorus pentoxide, and distilled. *p*-Cymene was washed with concentrated sulfuric acid, an aqueous sodium hydroxide solution, and water successively, dehydrated with calcium chloride, and distilled in vacuo in a nitrogen atmosphere. Cyclohexane was shaken with a mixture of ten per cent of concentrated sulfuric acid and one per cent of fuming sulfuric acid for 24 hr., washed with water, a sodium hydroxide solution, a potassium permanganate solution and water successively, dehydrated with calcium chloride, and distilled over sodium wire.

Method of Polymerization.—Styrene, *p*-bromostyrene and solvent were pipetted into a glass pressure vessel of 20 ml. capacity. The mixture was then, with the catalyst (borontrifluoride etherate), added to liquid sulfur dioxide. The polymerization was started in a constant temperature bath. The reaction was stopped by mixing in a large quantity of methanol. The precipitate was washed with methanol and dried in vacuo. From the weight of the copolymer produced, the rate of the polymerization was calculated. The composition of the copolymer was calculated from the elementary analysis.

---

* Polymerization in Liquid Sulfur Dioxide, Part XVI.

[1] a) C. G. Overberger, L. H. Arond and J. J. Taylor, *J. Am. Chem. Soc.*, **73**, 554 (1951); b) C. G. Overberger, R. J. Ehrig and D. Tanner, ibid., **76**, 772 (1954); c) C. G. Overberger and V. G. Kamath, ibid., **81**, 2910 (1959).

[2] C. S. Marvel and J. F. Dunphy, *J. Org. Chem.*, **25**, 2209 (1960).

[3] D. C. Pepper, *Nature*, **158**, 789 (1940); *Trans. Faraday Soc.*, **45**, 397 (1949).

[4] Y. Imanishi, T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **17**, 236 (1960).

[5] D. C. Pepper and P. J. Reilly, *Proc. Chem. Soc.*, **1960**, 200.

[6] a) R. Asami and N. Tokura, *J. Polymer Sci.*, **42**, 545 (1960). b) N. Tokura, M. Matsuda and Y. Watanabe, ibid., **62**, 135 (1962).

[7] R. H. Boundy and R. Boyer, "Styrene. Its Polymers, Copolymers and Derivatives", Reinhold Pub. Co., New York (1952), p. 788.

Results and Discussion

The Overall Rate of Copolymerization.—To a system consisting of styrene $(St)_0$ (3.0 ml.), *p*-bromostyrene $(BSt)_0$, and liquid sulfur dioxide $(SO_2)_0$ (3.0 ml.) with a catalyst $(BF_3Et_2O)_0$, was added 3.0 ml. of solvent of various dielectric constants. The reaction mixture then consisted of, $(St)_0$ 2.2, $(BSt)_0$ 1.9 and $(BF_3Et_2O)_0$ 5.7×10^{-3} mol./l., respectively. The added solvents were nitrobenzene (dielectric constant at 20°C $D=34.8$), ethylene dichloride ($D=10.4$), carbon tetrachloride ($D=2.3$) and benzene ($D=2.3$). The polymerization was conducted at −15°C.

The relationship between the mixed solvents and the rates of the copolymerization at −15°C is visualized in Fig. 1. As is seen in the figure, the copolymerization in pure liquid sulfur dioxide is the fastest among those in the solvent mixtures. This result is also consistent with the previous finding from the cationic polymerization in liquid sulfur dioxide[6a]. In Fig. 2, similar experiments with added solvents of small dielectric constants are compared: ($(St)_0$, 3.0 ml. (1.9 mol./l.), $(BSt)_0$, 3.0 ml. (1.6 mol./l.), $(BF_3Et_2O)_0$, 3.0×10^{-3} mol./l., $(SO_2)_0$, 3.0 ml., added solvent 5.0 ml., respectively, at −10°C). Although the dielectric constants of the added solvents were very close to each other, it is to be noted that a marked difference among the rates is to be found.

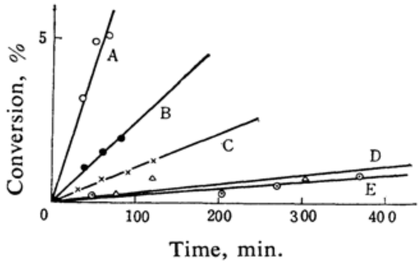

Fig. 1. Conversion vs. time plots.
A liq. SO_2
B Nitrobenzene with liq. SO_2
C Ethylene dichloride with liq. SO_2
D Carbon tetrachloride with liq. SO_2
E Benzene with liq. SO_2

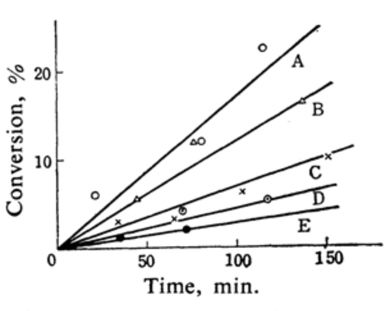

Fig. 2. Conversion vs. time plots.
A Cyclohexane with liq. SO_2
B Carbon tetrachloride with liq. SO_2
C *p*-Cymene with liq. SO_2
D Benzene with liq. SO_2
E Ethylene dichloride with liq. SO_2

The rate of copolymerization may be varied as the interaction of the solvent in this system changes. By the addition of cyclohexane to this system the rate is hardly affected. The order of rate is:

cyclohexane ($D=2.0$) > carbon tetrachloride ($D=2.3$) > *p*-cymene ($D=2.2$) > benzene ($D=2.3$)

and the largest rate drop is brought about by the addition of benzene. Despite the larger dielectric constant of ethylene dichloride ($D=10.4$), its rate ranks among the smallest, as may be seen in Fig. 2. The action of the added solvent on the rate of the cationic polymerization in liquid sulfur dioxide has already been shown and discussed in a previous article[6b], in which aromatic hydrocarbons in the liquid sulfur dioxide-polymerizing system also has a rate retarding effect.

Monomer Reactivity Ratio. — The monomer reactivity ratios were calculated according to

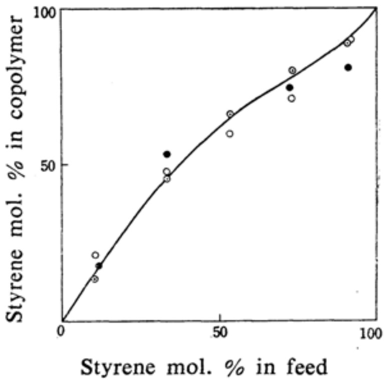

Fig. 3. Feed vs. copolymer composition plots.
○ −20°C ⊙ −15°C ● +10°C

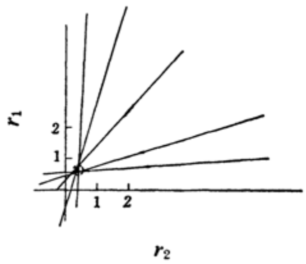

Fig. 4. MRR, r_1-r_2 plots for −20°C copolymerization in liquid sulfur dioxide.

TABLE I

Solvent	Catalyst, ×10^3 mol./l.	Temp., °C	r_1	r_2
liq. SO_2	1.5	10	0.8±0.3	0.4±0.1
liq. SO_2	1.5	−20	0.8±0.3	0.4±0.1
liq. SO_2	5.7	−15	0.8±0.3	0.4±0.1
$C_6H_5NO_2$−liq. SO_2	5.7	−15	0.7±0.3	0.3±0.1[a)]
C_6H_6−liq. SO_2	5.7	−15	0.9±0.4	0.4±0.2[a)]
CCl_4−liq. SO_2	5.7	−15	1.0±0.5	0.5±0.2[a)]
$C_6H_5NO_2$	10[c)]	10	1.8±0.3	0.3±0.1[b)]
C_6H_6	30	10	1.4±0.4	0.5±0.1[b)]
CCl_4	30	10	1.8±0.4	0.3±0.2[b)]
$CH_2CH_2Cl_2$	30	10	1.8±0.6	0.3±0.2[b)]

a) liq. SO_2 5.0 ml., St-BSt 10.0 ml., solvent 5.0 ml.

b) St-BSt 8.0 ml., solvent 8.0 ml.

c) As the rate of the copolymerization (without liquid sulfur dioxide) was very slow, the catalyst content was increased.

the intersection method of Mayo and Lewis[8)]. A typical example is shown in Figs. 3 and 4. In Fig. 3, feed vs. copolymer composition plots for the copolymerization in pure liquid sulfur dioxide at the temperatures of −20, −15 and 10°C with BF_3Et_2O are visualized. In Fig. 4, r_1 and r_2 are plotted to obtain the most suitable value of the monomer reactivity ratio for the result in Fig. 3 (−20°C). The MRR's (monomer reactivity ratios) of styrene (r_1) and *p*-bromostyrene (r_2) in liquid sulfur dioxide were found to be 0.8 and 0.4, respectively. As is shown in Fig. 3, the MRR's in liquid sulfur dioxide were independent both of the temperature of the reaction and of the quantity of the catalyst (BF_3Et_2O) used in the copolymerization.

The r_1's and r_2's were also calculated, by the same method, in the binary mixtures of solvent and liquid sulfur dioxide and in pure solvents. The results are summarized in Table I. Figures 5 and 6 are the summarized plots of the feed vs. copolymer composition diagram in various solvents.

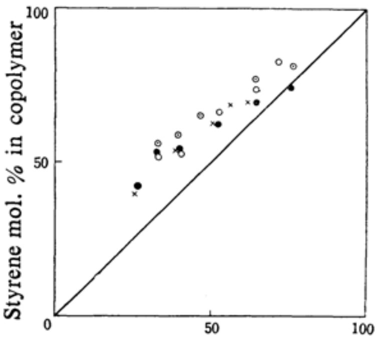

Fig. 6. Feed vs. copolymer composition plots in various solvents.
● Benzene ⊙ Nitrobenzene
○ CCl_4 × Ethylene dichloride

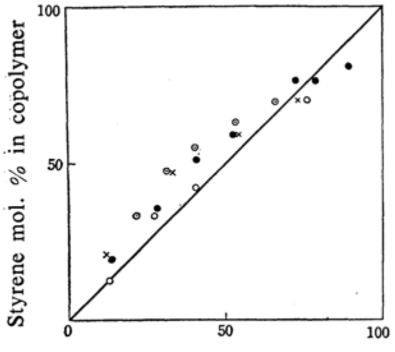

Fig. 5. Feed vs. copolymer composition plots in mixed solvents.
● Benzene+liq. SO_2
⊙ Nitrobenzene+liq. SO_2
○ CCl_4+liq. SO_2
× Liq. SO_2 (alone)

The MRR's were measured in equi-volume mixtures of liquid sulfur dioxide and the added solvents at −15°C. In system without liquid sulfur dioxide, since the rate of the copolymerization is too slow to permit the adequate performance of the experiment, the catalyst was increased to 10×10^{-3} in nitrobenzene and to 30×10^{-3} mol./l. in the other solvents respectively, as is described in Table I. The MRR's in the mixture of liquid sulfur dioxide with equi-volumes of *p*-cymene, *p*-xylene and cyclohexane were each also estimated by the same procedures; 0.9 and 0.4 were the values found for r_1, and r_2 respectively, which figures were similar to those of benzene.

The copolymerization in liquid sulfur dioxide is very fast. This fact is consistent with the previous finding that cationic polymerization

---

8) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

is the fastest in liquid sulfur dioxide[6a] and with the fact that the Beckmann rearrangement in liquid sulfur dioxide is instantaneous[9].

In liquid sulfur dioxide, the monomer reactivity ratios are independent both of the temperatures and of the concentration of the catalyst in the reaction.

It is a very interesting finding that the MRR's in the respective solvents are very similar ($r_1=1.6$ and $r_2=0.3$), whereas by adding liquid sulfur dioxide the MRR's of r_1 drop to $1\sim0.7$, while in liquid sulfur dioxide r_1 is 0.8 in spite of the similarity in the comonomer structure. When sulfur dioxide is added to the system the chain end of the styryl carbonium ion may lose its selectivity to styrene, the reactivity for *p*-bromostyrene being increased. The product of $r_1 \times r_2$ in liquid sulfur dioxide is 0.32, and the composition of the copolymer approaches that of the alternative copolymer. This finding is also in good accordance with the explanation above mentioned.

Summary

1) The cationic copolymerization of styrene and *p*-bromostyrene in liquid sulfur dioxide using boron trifluoride etherate as a catalyst has been carried out; the monomer reactivity ratios (MRR) have been found to be $r_1=0.8$ and $r_2=0.4$. The MRR value was independent of the temperature and of the quantity of the catalyst in the copolymerization.

2) The effect of added solvents in liquid sulfur dioxide has also been examined. However, the MRR's have been little affected by the added solvents, the rates of the copolymerization have largely been depressed, and the rates were not dependent on the dielectric constants of the added solvents, the rate in pure liquid sulfur dioxide being the fastest.

3) The same cationic copolymerization has been conducted in benzene, carbon tetrachloride, nitrobenzene and ethylene dichloride.

The MRR's were almost equal in all ($r_1=1.8$ and $r_2=0.3$).

The authors are indebted to the Seitetsu Kagaku K.K., Ltd., for its donation of liquid sulfur dioxide. A part of the expense for this project has been defrayed by a grant-in-aid by the Ministry of Education.

The Chemical Research Institute
of Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai

---

[9] N. Tokura, K. Shiina and T. Terashima, This Bulletin, 35, 1986 (1962).