*The Cationic Copolymerization of Styrene and Isobutene in Liquid Sulfur Dioxide**

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Recently, there have been published many investigations of the solvent effect on the monomer reactivity ratios as a means of examining the reaction mechanism operating during a cationic polymerization.[1a-g]

A study of the cationic copolymerization of styrene and *p*-bromostyrene presented in a previous paper[3] by the present authors has demonstrated that:

(1) The monomer reactivity ratios in liquid sulfur dioxide are $r_1=0.8$ and $r_2=0.4$ respectively, where r_1 is the ratio of styrene and r_2 is that of *p*-bromostyrene.

(2) In nitrobenzene, $r_1=1.8$ and $r_2=0.3$.

(3) The values of the reactivity ratios in the mixed solvent systems (equivolume) of liquid sulfur dioxide-benzene, liquid sulfur dioxide-nitrobenzene and liquid sulfur dioxide-carbon tetrachloride are almost the same within the range of experimental error as those in liquid sulfur dioxide itself (in case 1).

The absence of any distinct difference in monomer reactivity ratios, *r*'s, among these solvent systems is due perhaps to the similarity of the reactivities of styrene and *p*-bromostyrene. The purpose of the present investigation is to make clearer the behavior of liquid sulfur dioxide in the cationic copolymerization of styrene and isobutene, which are different from each other in monomer structure and in reactivity.

Lately, Higashimura and his coworkers[1g] have reported, of the cationic copolymerizations of styrene-isobutene in various organic solvents, that the isobutene monomer, which is usually more reactive than styrene in cationic polymerization, gets less reactive as the dielectric constants of the systems become lower.

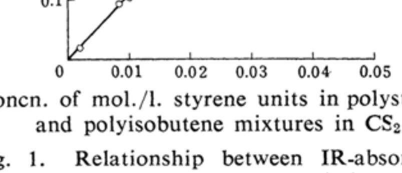
Overberger et al.[1c] have found the same relation between dielectric constant and monomer reactivity ratios in the copolymerization of *p*-chlorostyrene and isobutene.

However, it is doubtful whether the reactivity of the monomer will be explained only by the differences in the dielectric constants of the solvent, since in liquid sulfur dioxide behavior considerably different from that of usual organic solvents have been seen in cationic polymerization.[2a,b]

Experimental

Materials. — The purification of styrene, liquid sulfur dioxide, benzene, nitrobenzene and ethylene dichloride was carried out according to the procedures described in a previous paper.[3] Isobutene used was fractionated after the removal of water with sodium-wire. It was confirmed by gas chromatography that its purity was 99%; it contained about one per cent propane. Stannic chloride was distilled under reduced pressure in a nitrogen stream and sealed into an ampoule. Nitromethane was dehydrated over the phosphorus pentoxide and distilled.

Polymerization. — The charge of isobutene into the reaction tube was carried out according to the same procedure as that employed previously (using a pressure buret), and the other details of the polymerization employed here were the same as those employed in the previous paper[3] with the exception that stannic chloride was used as an



Concn. of mol./l. styrene units in polystyrene and polyisobutene mixtures in CS_2

Fig. 1. Relationship between IR-absorbancy and concentration of styrene unit in mixture.

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* Polymerization in Liquid Sulfur Dioxide, Part XX.

[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); d) C. G. Overbegrer and V. G. Kamath, ibid., **85**, 446 (1963); e) C. S. Marvel and J. F. Dunphy, *J. Org. Chem.*, **25**, 2209 (1960); f) R. E. Florin, *J. Am. Chem. Soc.*, **73**, 4468 (1951); g) T. Higashimura, *Kagaku*, Special Issue No. 7, "Syntheses of High Polymers" (1960), p. 46.

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

[3] N. Tokura, M. Matsuda and M. Iino, This Bulletin, **35**, 278 (1963).

initiator. Moreover, this polymerization resulted in a heterogeneous system, a polyisobutene or isobutene-rich copolymer being insoluble in liquid sulfur dioxide.

Analyses of Copolymers.—The quantity of styrene in the copolymer was determined on the basis of infrared spectrometry using a Hitachi EPI-S infrared spectrometer, with ν_{max}, 700 cm^{-1}, as the key band. Carbon disulfide was used as the solvent; the thickness of the sodium chloride cell was 0.516 or 0.525 mm. The copolymer used for the measurement was purified by precipitation from carbon disulfide. Beer's law held strictly, as may be seen in Fig. 1.

Results

The r_1 and r_2 Values on Using Liquid Sulfur Dioxide as the Solvent. — The experimental conditions were as follows; total volume of styrene and isobutene, 10.0 ml.; liquid sulfur dioxide, 10.0 ml.; polymerization temperature, −78°C (dry ice-methanol bath); concentration of stannic chloride, 2.1×10^{-3} mol./l.

Figures 2 and 5a show the feed-copolymer composition curve and the results obtained

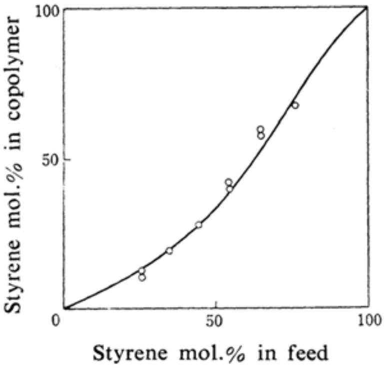


Fig. 2. Copolymerization in liquid sulfur dioxide.

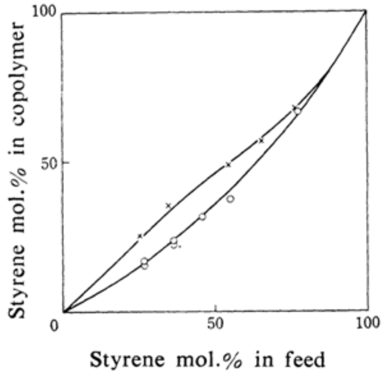


Fig. 3. Copolymerization in liq. SO_2+nitrobenzene and in liq. SO_2+benzene.

× Liq. SO_2+nitrobenzene

○ Liq. SO_2+benzene

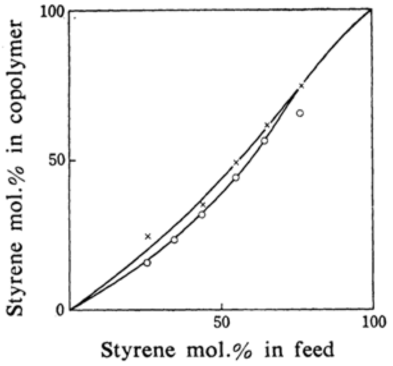


Fig. 4. Copolymerization in liq. SO_2+ethylene dichloride and in liq. SO_2+nitromethane.

× Liq. SO_2+ethylene dichloride

○ Liq. SO_2+nitromethane

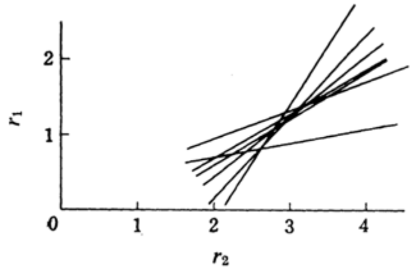


Fig. 5a. MRR of copolymerization in liq. SO_2. r_1, Styrene, r_2, Isobutene

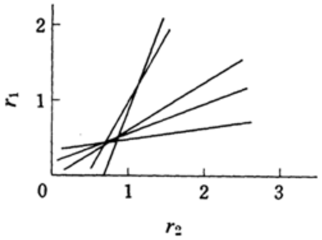


Fig. 5b. MRR of copolymerization in liq. SO_2+nitrobenzene. r_1, Styrene, r_2, Isobutene

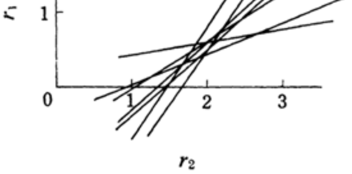


Fig. 5c. MRR of copolymerization in liq. SO_2+benzene. r_1, Styrene, r_2, Isobutene

TABLE I. MONOMER REACTIVITY RATIOS OF THE COPOLYMERIZATION OF STYRENE (M_1) AND ISOBUTENE (M_2) IN LIQUID SULFUR DIOXIDE

Solvent.	r_1	r_2	$r_1 \times r_2$	SO_2 $\times 10$ mol./l.	$SnCl_4$ $\times 10^{-3}$ mol./l.	Poly. temp., °C
Liq.SO_2 a)	1.1	3.1	3.4	1.1	2.1	−78
Liq.$SO_2+CH_3NO_2$ b)	1.1	2.2	2.4	1.0	4.2	−78
Liq.$SO_2+C_2H_4Cl_2$ b)	1.0	1.5	1.5	1.0	4.2	−78
Liq.$SO_2+C_6H_5NO_2$ b)	0.5	0.8	0.4	1.0	4.2	−78
Liq.$SO_2+C_6H_6$ b)	0.6	1.9	1.1	1.0	7.4	−78

a) Liq.SO_2, 10.0 ml. styrene+isobutene, 10.0 ml.

b) Liq.SO_2, 11.5 ml. added solvent, 4.0 ml. styrene+isobutene, 10.0 ml.

TABLE II.

Monomer, ml.	Liq. SO_2, ml.	$SnCl_4$ $\times 10^{-3}$ mol./l.	Conversion %	$\bar{P} \times 10^{-2}$	α, %
Styrene 10.0	10.0	1.2	5.3	63	3.2
Isobutene 10.0	10.0	1.2	5.2	5.7	43

α = (Total numbers of polymers/Total numbers of catalysts) × 100

from the intersection method respectively.

The reactivity ratios of $r_1=1.1$ and $r_2=3.1$, where styrene and isobutene are M_1 and M_2 respectively, were obtained from Fig. 5a.

The r_1 and r_2 Values in the Mixed Solvent Systems of Liquid Sulfur Dioxide-Benzene, Liquid Sulfur Dioxide-Nitrobenzene, Liquid Sulfur Dioxide-Nitromethane and Liquid Sulfur Dioxide-Ethylene Dichloride. — In each solvent system, the composition in feed was as follows: total volume of styrene and isobutene, 10.0 ml.; liquid sulfur dioxide, 11.5 ml.; and the added solvent, 4.0 ml.

Figures 3 and 4 show the composition curve and r_1 and r_2 were obtained by the intersection method respectively. Figure 5 illustrates the results obtained by the intersection method in each solvent system of liquid sulfur dioxide, liquid sulfur dioxide-benzene, and liquid sulfur dioxide-nitrobenzene.

Discussion

The results described above are summarized in Table I.

In liquid sulfur dioxide, the rate of the polymerization of isobutene is far larger than that of styrene. A comparison of the two monomers is shown in Table II.

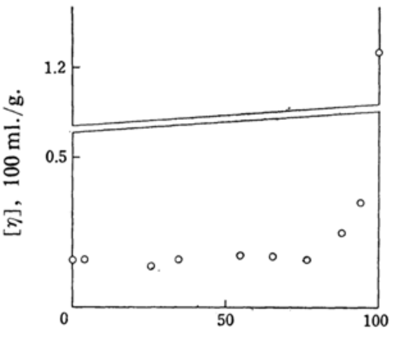
In the case of styrene polymerization, $\alpha=3.2$, and only 3% of the catalyst at the maximum (without transfer) was used, whereas the α value of isobutene is 43%, suggesting that the initiation rate of the latter was very fast in liquid sulfur dioxide when stannic chloride was used as the catalyst.

As has been mentioned before, in the usual cationic copolymerization,[1g] the value of r_2 decreases but r_1 increases as the dielectric constant of the system is reduced, and the product, $r_1 \times r_2$, is approximately unity. A similar tendency was also observed in the cationic copolymerization of *p*-chlorostyrene and isobutene.[1c] On the contrary, as may be seen in Table I, the results obtained here have proved there to be no definite relation between *r* values and the dielectric constants of the systems, the order of the dielectric constants of the solvents being: liq. SO_2+nitromethane>liq. SO_2+nitrobenzene>liq. SO_2>liq. SO_2+ethylene dichloride > liq. SO_2+benzene, whereas, r_2 values vary in the order liq. SO_2> liq. SO_2+nitromethane > liq. SO_2+benzene > liq. SO_2+ethylene dichloride > liq. SO_2+nitrobenzene; r_1 values are classified in two groups, one being $r_1 \fallingdotseq 1$ in liq. SO_2, liq. SO_2+nitromethane and liq. SO_2+ethylene dichloride and the other being $r_1 \fallingdotseq 0.5$ in liq. SO_2+nitrobenzene and liq. SO_2+benzene.

The differences in r_1 values in the two groups may be ascribed to the differences in the monomer reactivities in these two sets of solvent systems. The values of the products, $r_1 \times r_2$ cover a wide range from 0.4 in liquid sulfur dioxide-nitrobenzene to 3.4 in liquid sulfur dioxide.

The r_1 values show no difference in the series of solvent mixtures, liquid sulfur dioxide, liquid sulfur dioxide+nitromethane and liquid sulfur dioxide+ethylene dichloride, wherein $r \fallingdotseq 1$, while r_2 values differ as the solvents are varied. Obviously the differences in reactivities of the carbonium ions derived from the isobutene moiety of the growing end in each solvent may be responsible for these phenomena.

In liquid sulfur dioxide, styrene can give a high molecular weight polymer, whereas isobutene can not. Figure 6 illustrates the correlation between the composition of the feed and the intrinsic viscosity of the copolymer in the copolymerization. That the η values here can give the measurement of the degrees of polymerization for polymers of styrene, isobutene, and the copolymers of the two on the same basis has been demonstrated elsewhere.[4] Isobutene polymerizes heterogeneously in liquid sulfur dioxide, and the solubility of the polyisobutene is extremely meager.



Styrene mol.% in feed

Fig. 6. Relationship between styrene concentration in feed and the intrinsic viscosity* of the copolymer.

* Viscosity was measured in toluene at 30°C.

Though the molar per cent of styrene in feed is about 70%, the η values of the copolymers are as small as in the case of polyisobutene, which suggests that though isobutene is a more reactive monomer than styrene, the growing of the isobutene carbonium ion end is likely to be easily terminated in liquid sulfur dioxide. A controlled polymerization of isobutene in liquid sulfur dioxide (an experiment to be reported on in the near future) also proved the formation of a very low molecular weight polymer. Polyisobutene cannot remain in the solution and separates out on the surface of liquid sulfur dioxide, the polymerization being terminated by keeping away monomers in the solution and eliminating any catalyst fragments. The present authors would like to recall the fact that the classical Edeleanu process for petroleum refining by using liquid sulfur dioxide is based on the scarce solubility of paraffins in liquid sulfur dioxide. At the experimental temperature (−78°C), the higher polymers of isobutene may be insoluble. This means that if the copolymer's propagating end consists of two or more sequences of isobutene units, the copolymer may be separated out and a heterogeneous copolymerization may occur. In mixed solvent systems, the sequence length of isobutene units may also be affected by the added solvents. It should be also noticed that styrene has a stronger solvation than isobutene with liquid sulfur dioxide because the former has a benzene nucleus. However, the present authors have not yet examined precisely the correlation between the reactivities and the solubilities of the monomers and the carbonium ions in each mixed solvent; further study is called for.

Summary

The copolymerizations of styrene and isobutene in liquid sulfur dioxide and in mixtures of liquid sulfur dioxide with nitromethane, ethylene dichloride, nitrobenzene and benzene have been carried out at −78°C. The r_1 and r_2 values have been estimated by the intersection method. When M_1 stands for styrene and M_2 for isobutene, r_1 and r_2 are 1.1 and 3.1 in liquid sulfur dioxide. The r_2 values vary, as the added solvent is changed. Two sets of r_1 values, approximately unity and 0.5, have been found. The meager solubility of polyisobutene and isobutene sequence in the copolymer may be responsible for the findings.

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[4] S. Okamura, T. Higashimura and K. Takeda, *Kobunshi Kagaku*, **18**, 389 (1961).