# The Cationic Copolymerization of Styrene and α-Methylstyrene in Liquid Sulfur Dioxide*

By Masashi IINO and Niichiro TOKURA

(Received October 12, 1964)

When liquid sulfur dioxide has been used as a solvent in the cationic polymerization of styrene, several characteristic features have been observed;[1] (1) the rate of the polymerization is exceedingly fast, (2) the polymer produced is of a high degree of polymerization and of a nearly mono-disperse distribution, and (3) even alkyl, aralkyl or acyl halide can initiate the poymerization in this solvent.[2]

This behavior of liquid sulfur dioxide may adequately be explained by its protophobic nature or by the inertness of this solvent toward the cationic species. In this cationic polymerization, monomer- and solvent-transfer reactions may be considered to be very small and the solvation of this solvent to anionic species may be very strong.

The present article will describe a study of the cationic copolymerization of styrene and α-methylstyrene, since the study of a copolymerization in a solvent can often provide many instructive suggestions on the nature of the solvent used and on the interactions among the cationic polymerizing species and the solvent.

The cationic copolymerizations in liquid sulfur dioxide of some pairs of copolymers, such as styrene-*p*-bromostyrene,[1c] styrene-isobutene,[3] and styrene-methylacrylate,[4] have already been studied, and a number of papers have been published elsewhere.

It has also been recognized that α-methylstyrene polymerizes readily in liquid sulfur dioxide without any catalyst,[5] as do *p*-methyl- and *p*-isopropyl-styrenes.[6]

In the study of the copolymerization of styrene and α-methylstyrene, NMR spectrometry has been adopted for the identification of the monomer units in the copolymer chain, according to the method of Bovey et al.[8a] The copolymerization in liquid sulfur dioxide is compared with that in methylene dichloride.

## Experimental

**Materials.** — Commercially-available styrene was distilled twice in a nitrogen atmosphere under reduced pressure. α-Methylstyrene was washed with a 10 per cent sodium hydroxide solution and water successively, dried with potassium carbonate, and distilled twice under reduced pressure in a nitrogen stream just before use.

Boron trifluoride etherate was used after repeated distillation in vacuo in a dry nitrogen stream and after having been stored in a glass ampule. Liquid sulfur dioxide was dehydrated with phosphorus pentoxide and distilled.

**Polymerization.** — The cationic copolymerization has been carried out at −40°C in liquid sulfur dioxide, since α-methylstyrene polymerizes spontaneously even at −20°C, while it does not undergo such spontaneous polymerization at −40°C. For a comparative study, a similar cationic copolymerization in methylene chloride was also carried out at −20°C, using the same procedure and the same apparatus.

The procedure of the polymerization was the same as in the case of the copolymerization of styrene and *p*-bromostyrene,[1c] using boron trifluoride etherate as a catalyst.

**Analyses of the Copolymer.**—The monomer composition of the copolymer was determined by NMR spectrophotometry, employing a Varian V-4300 B, 60 MC instrument, at 22—23°C. As the solvent for the spectrometry, carbon tetrachloride was used, dioxane being used as an internal reference. Figure 1 presents the NMR spectra in the carbon tetrachloride solutions (0.06 g. polymer in 1 ml. carbon tetrachloride) of polystyrene, poly-α-methyl styrene, a nearly equimolar mixture of the two homopolymers (polystyrene 54.3 mol. %), and a copolymer of styrene and α-methylstyrene (styrene in feed 82.0 mol. %, polymerized in liquid sulfur dioxide) respectively.

The assignment of the proton absorptions in the spectra of polystyrene and poly-α-methylstyrene has already been made.[8] The peak positions of the protons of the respective functional groups of the polymer or the copolymer are tabulated in Table I. As may be seen in Table I, the positions of the respective proton absorptions do not vary, even if

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* Polymerization in Liquid Sulfur Dioxide. Part XXIII. Part XXII: M. Matsuda and N. Tokura, *J. Polymer Sci.*, in press.

[1] a) R. Asami and N. Tokura, ibid., **42**, 545 (1960); b) N. Tokura, M. Matsuda and I. Shirai, This Bulletin, **35**, 371 (1962); c) N. Tokura, M. Matsuda and M. Iino, ibid., **36**, 278 (1953).

[2] a) N. Tokura and T. Kawahara, ibid., **35**, 1902 (1962); b) N. Tokura, T. Kawahara and T. Watanabe, ibid., **36**, 760 (1963).

[3] N. Tokura and M. Iino, ibid., **37**, 23 (1964).

[4] M. Matsuda, K. Oshima and N. Tokura, *J. Polymer Sci.*, in press.

[5] N. Tokura, M. Matsuda, I. Shirai, K. Shiina and Y. Kondo, This Bulletin, **35**, 1043 (1962).

[6] a) N. Tokura, M. Matsuda and Y. Ogawa, *J. Polymer Sci.*, **A1**, 2965 (1963); b) N. Tokura, M. Matsuda and K. Arakawa, ibid., **A2**, 3355 (1964).

TABLE I. THE NMR SPECTRA OF HOMOPOLYMERS, COPOLYMER AND A MIXTURES OF POLYSTYRENE AND POLY-α-METHYLSTYRENE

| Polymer | Peak position (τ value) | | | |
|---|---|---|---|---|
| | -$C_6H_5$ | | $CH_2$ and CH | -$CH_3$ |
| Polystyrene (liq. $SO_2$) | 3.01 | 3.50 | 8.49 | — |
| Polystyrene ($CH_2Cl_2$) | 2.92 | 3.37 | 8.27 | — |
| Poly-α-methylstyrene (liq. $SO_2$) | 2.97 | — | 8.51 | 9.87 |
| Poly-α-methylstyrene ($CH_2Cl_2$) | 2.97 | — | 8.46 | 9.81 |
| Mixture of homopolymers (polystyrene 91.5%)* | 3.01 | 3.50 | 8.51 | 9.88 |
| Mixture of homopolymers (polystyrene 33.7%)* | 3.00 | 3.47 | 8.51 | 9.88 |
| Copolymer (styrene feed 53.2%)* | 2.99 | — | 8.51 | 9.89 |
| Copolymer (styrene feed 22.2%)* | 2.99 | — | 8.51 | 9.89 |

* Mole per cent

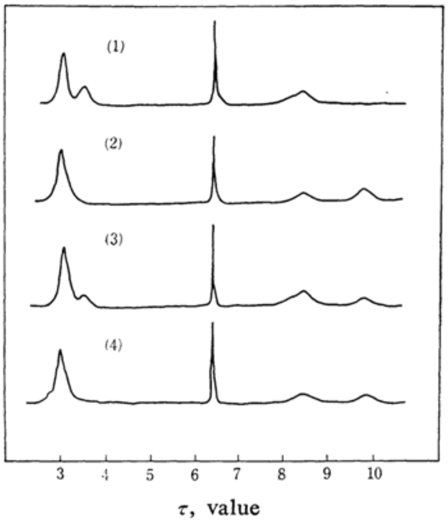

Fig. 1. NMR spectra of polystyrene, poly-α-methylstyrene, a mixture of the homopolymers and a copolymer, in $CCl_4$ (0.06 g. in 1 ml.).

(1) Polystyrene
(2) Poly-α-methylstyrene
(3) Mixture of polystyrene (54.3 mol. %) and poly-α-methylstyrene
(4) Copolymer of styrene (82.0 mol. % in feed) and α-methylstyrene

the polymer is a homopolymer, a mixture of homopolymers or copolymers is not affected by the kind of the solvent (liquid sulfur dioxide or methylene dichloride) used in the polymerization.

Tau (τ) values were calculated from the spectra of the protons, dioxane ($\tau=6.43$) or cyclohexane ($\tau=8.56$ p.p.m.) being used as an internal reference. No specific interaction between the samples and the reference was confirmed in the spectra. The content of each monomer in the copolymer chain of styrene and α-methylstyrene can be estimated either by the dimensional ratio of the proton absorption spectra of the phenyl- to the methyl protons, or by the dimensional ratio of the methyl protons to the methylene and methine protons. The latter method of estimation was chosen, because the estimation was simpler and subject to less error, as will be discussed later.

For the convenience of the experimental performance, a calibration line was prepared (Fig. 2), in which $(A_{CH_3}/A_{CH_2})_{obs}$, (the ratio of methyl- to methylene- and methine-protons) values in various mixtures of polystyrene and poly-α-methylstyrene were examined; the calculated values $(A_{CH_3}/A_{CH_2})_{calcd}$ (from the mixed ratios of the two homopolymers) were then plotted against the observed values $(A_{CH_3}/A_{CH_2})_{obs}$ (from the NMR measurements) on the rectangular coordinates. The fair coincidence between the calculated and the observed values in Fig. 2 may well support the validity of this technique for the estimation of the proportion of the components in the copolymer, as long as the mixture of the homopolymers behaves in a manner similar to that of the copolymer of the same monomers in the NMR phenomena. The NMR measurement was carried out in the concentration range of the polymer, 0.3 to 0.4 g. per 1 ml. of carbon tetrachloride. The dimensions of each proton-absorption area were estimated by weighing the NMR spectrum cut out from the chart of the spectra. Four to six measurements of the spectra of a copolymer were averaged in calculating the value of $(A_{CH_3}/A_{CH_2})_{obs}$.

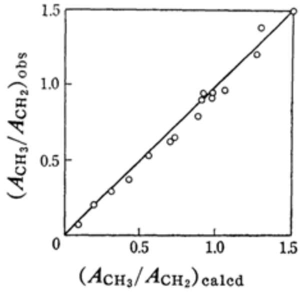

Fig. 2. Calibration line of calculated vs. observed values of $(A_{CH_3}/A_{CH_2})$.

$A_{CH_3}$ NMR absorption area of methyl protons.
$A_{CH_2}$ NMR absorption area of methylene and methine protons.

Harwood's method for the estimation of the comonomer proportion in the styrene-methylmethacrylate copolymer by NMR spectrometry⁷⁾ was modified and applied. The relationship between the molar fraction of styrene in the copolymer and the observed or calculated value of $(A_{CH_3}/A_{CH_2})$ is as follous:

$$x=\frac{3-(A_{CH_3}/A_{CH_2})\times 2}{3+(A_{CH_3}/A_{CH_2})}\times 100 \qquad (1)$$

or

$$(A_{CH_3}/A_{CH_2})=(100-x)\times 3/(100\times 2+x) \qquad (2)$$

where $x$ is the styrene mol.% in the copolymer.

**The Sequences of the Copolymer.** — The mole per cent in the copolymer of the sandwiched styrene ($S$), in the form of the -M-St-M- triad, where St and M are styrene and $\alpha$-methylstyrene units respectively, was estimated by using the following procedure;

$$(b/a)_{\text{calcd}}=\frac{2x}{5(100-x)+3x} \qquad (3)$$

where $a$ and $b$ are the areas of the meta and para protons, and of ortho protons, respectively.

$$(b/a)_{\text{obs}}=2(x-S)/3(x-S)+5S+5(100-x) \qquad (4)$$

or

$$S=\frac{x(2-x(b/a)_{\text{obs}})-5(b/a)_{\text{obs}}(100-x)}{x(2+2(b/a)_{\text{obs}})} \qquad (5)$$

The derivation and the meaning of these formulae will be discussed later.

## Results and Discussion

**The Reactivity Ratio.**—Figures 3 and 4 show the feed-copolymer composition curves in liquid sulfur dioxide and methylene dichloride respectively. The monomer reactivity ratios, $r_1$ and $r_2$, were estimated by the trial and error method. The results is listed in Table II. In order to suppress the reaction rate, a lower temperature (−40°) was used in liquid sulfur dioxide. On the other hand, in methylene dichloride −20°C was needed to assure good solubility for monomers, though it has been reported that in liquid sulfur dioxide the M.R.R.'s are almost independent of the temperature of the copolymerization.¹ᶜ⁾ However, some scattered results in Figs. 3 and 4 are perhaps due to such experimental difficulties as the fast reaction rates, the lesser solubilities of the monomers, and unavoidable error in the NMR determinations.

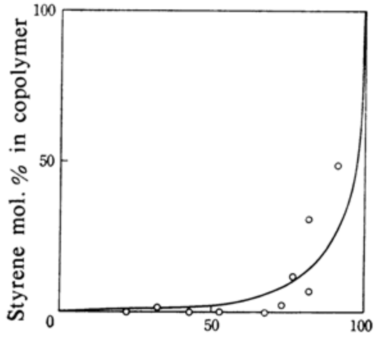

Fig. 3. Copolymer composition curve.
Copolymerization in liquid sulfur dioxide.
BF₃ etherate: $7.3\times 10^{-5}$ mol./l.
Temperature: −40°C

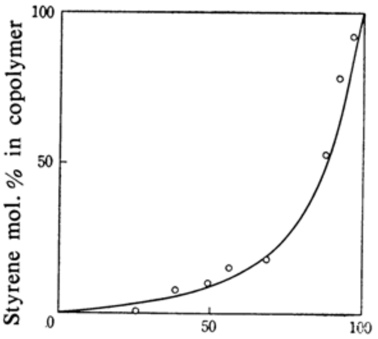

Fig. 4. Copolymer composition curve.
Copolymerization in methylene dichloride.
BF₃ etherate: $6.6\times 10^{-3}$ mol./l.
Temperature: −20°C

TABLE II. THE MONOMER REACTIVITY RATIOS OF THE COPOLYMERIZATION OF STYRENE AND α-METHYLSTYRENE IN TWO SOLVENTS

| Solvent | $r_1$ | $r_2$* |
|---|---|---|
| liq. SO₂ (−40°C) | 0—0.1 | over 20 |
| Methylene dichloride (−20°C) | 0.2—0.5 | 12±2 |

* M₁: Styrene, M₂: α-Methylstyrene

It has been confirmed, in spite of the above-discussed defect, that a non-alternating tendency prevails between styrene and $\alpha$-methylstyrene in both the solvents, the tendency being far more conspicuous in liquid sulfur dioxide. In view of the behavior of this solvent hitherto experienced by the present authors, the results are not unexpected.

**The Identification of the Sequence of the Monomer Unit in the Copolymer.**—The NMR spectra of phenyl groups of polystyrene, poly-$\alpha$-methylstyrene, the mixture of homopolymers and the copolymer can be recognized in the lower fields of the respective spectra, 1, 2, 3 and 4, of Fig. 1, where two peaks are observed as these of phenyl protons. These were assigned as the para- and the meta protons (lower field) and the ortho protons (higher field) by Bovey

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7) H. J. Harwood and W. M. Ritchey, *A. C. S. Polymer Reprints*, 5, No. 1, Philadelphia Meeting (April, 1964), p. 299.

TABLE III. VALUES OF $b/a$ AND $S$ MOL.% OF STYRENE-$\alpha$-METHYLSTYRENE-COPOLYMERS

| Styrene in copolymer mol. % | $\alpha$-Methylstyrene in copolymer mol. % | $(b/a)_{obs}$ | $(b/a)_{calcd}$ | $S_{mol\ \%}$ |
|---|---|---|---|---|
| Liquid sulfur dioxide as solvent | | | | |
| 0.0 | 100 | −0.01 | 0 | 0 |
| 0.0 | 100 | −0.02 | 0 | 0 |
| 1.8 | 98.2 | −0.03 | 0.01 | |
| 11.8 | 98.2 | 0.09 | 0.05 | |
| 30.8 | 69.2 | 0.33 | 0.14 | |
| 49.3 | 50.7 | 0.27 | 0.25 | |
| Methylene dichloride as solvent | | | | |
| 8.3 | 91.7 | 0 | 0.02 | 100 |
| 10.3 | 89.7 | 0 | 0.04 | 100 |
| 15.3 | 84.7 | 0.02 | 0.07 | 68.0 |
| 52.8 | 47.2 | 0.15 | 0.27 | 38.3 |
| 65.5 | 34.5 | 0.20 | 0.36 | 36.3 |
| 78.6 | 21.4 | 0.31 | 0.46 | 24.7 |
| 82.1 | 17.9 | 0.33 | 0.49 | 24.5 |
| 86.6 | 18.4 | 0.31 | 0.53 | 31.6 |
| 92.2 | 7.8 | 0.35 | 0.58 | 29.7 |

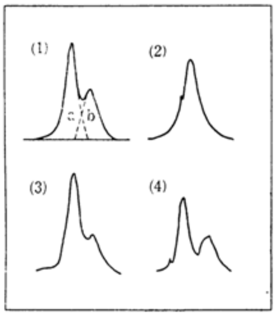

Fig. 5. NMR spectra of phenyl proton in polymers. (Solvent : $CCl_4$)
(1) Polystyrene
(2) Poly-$\alpha$-methylstyrene
(3) Styrene-$\alpha$-methylstyrene
Copolymer (styrene in feed, 91.1 mol.%)
(4) Styrene polysulfone

et al,[8a)] since the ratio of the respective areas is approximately 3 to 2 (Fig. 5).

The phenyl proton spectra afford two peaks because of the difference in the magnetic shielding effected by the adjacent benzene nucleus on the ortho protons and on the para- and meta protons.[8a)] However, the spectra of $\alpha$-methylstyrene do not afford the two peaks, but only one peak, because of the decrease in the interaction of the neighboring phenyl group because of the presence of the $\alpha$-methyl group.[8a)] In the mixture of the two homo-polymers or in the copolymer, the positions of the two peaks due to the phenyl protons are always the same (Table I) ; such a observation allows us to analyze the monomer sequences in the copolymer.

The dimensional ratios of the two peaks, $b/a$, were calculated (Fig. 5), where $a$ and $b$ are the area of the peak in the lower field and that in the higher one respectively. Therefore, in poly-$\alpha$-methylstyrene, $b/a$ was 0, while in polystyrene $b/a$ was 2/3. The relation of the styrene mole per cent in the mixed homopolymers or that in the copolymer to the $b/a$ value is presented in Table III.

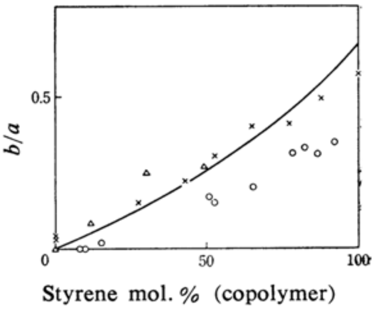

Fig. 6. Relations between styrene content vs. $b/a$ ratio in copolymers.

× Polystyrene, poly-$\alpha$-methylstyrene-mixture
△ Copolymer in liquid sulfur dioxide
○ Copolymer in methylene dichloride

Figure 6 also demonstrates the relation of the styrene mole per cent in the polymer and the $b/a$ value, where the full line (the calculated plot) agrees well with the crossed dots (the observed values of the mixture of homopolymers). However, the plot of the copolymer (circle dots) is not like this, the points

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8) a) F. A. Bovey, G. V. Tiers and G. Fieipovich, *J. Polymer Sci.*, **38**, 73 (1959) ; ibid., **62**, 197 (1962) ; b) A. Nishioka, ibid., **62**, 10 (1962) ; c) S. Brownstein, S. Bywater and D. J. Worsfold, *Makromol. Chem.*, 127 (1961).

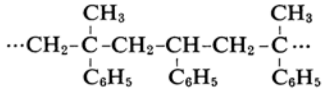
here being somewhat below the theoretical curve and this being supposed beyond the range of experimental error.

Such a deviation may be accounted for by the difference in the sequence of the styrene unit in the copolymer, where some styrene units did not demonstrate the two separated peaks in the NMR spectra. The NMR spectrum of the phenyl group in styrene-polysulfone is also shown in Fig. 5 as a reference. Styrene-polysulfone is obtained by a radical polymerization of styrene in liquid sulfur dioxide.[9] The molar ratio of the styrene unit to the sulfur dioxide unit in the copolymer is said to be strictly 2 to 1, the arrangement of the monomer sequence in the chain being believed to be:

$$-SO_2-St-St-SO_2-St-St-$$

where St is the styrene and $SO_2$ is the sulfur dioxide monomer.

From the considerations mentioned above and from the NMR spectrum of the styrene-homopolymer, it may be anticipated that the polymer chain consisting of two and more succssive styrene units will exhibit two separated peaks in the NMR absorption. Therefore, the styrene unit in the copolymer which presents only one peak is likely to have the structure of a styrene unit sandwiched between the two $\alpha$-methylstyrene units, such as:



$$\cdots CH_2-\underset{C_6H_5}{\overset{CH_3}{C}}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{\overset{CH_3}{C}}\cdots \qquad (S)$$

If this assumption is reasonable, the proportion of the sandwiched styrene (S) may be calculated by Eq. 5 from the observed curves in Fig. 6. The S value denotes the proportion of the sequences (S). The results are listed in Table III. As may be seen in Table III, the copolymer (equimolarly feed) afforded in methylene dichloride has as much as about 38.3% fragments (S). On the other hand, the copolymer produced in liquid sulfur dioxide seems to be a non-alternate copolymer, where $(b/a)_{\text{obs}} \fallingdotseq (b/a)_{\text{calcd}}$, and (S) is approximately zero. Such results agree well with the large value of $r_2$. The reaction in liquid sulfur dioxide favors the activity of cationic species remarkably. At a higher temperature, $\alpha$-methylstyrene can be polymerized spontaneously in liquid sulfur dioxide.[5],[**] This phenomenon is to be attributed to the low $e$ value (of the $Q$, $e$ scheme) of $\alpha$-methylstyrene. Thus, in the mixture of styrene and $\alpha$-methylstyrene, the latter monomer initiates the cationic polymerization faster than does styrene. In addition, styrene in liquid sulfur dioxide may be solvated by sulfur dioxide molecules more strongly than $\alpha$-methylstyrene in the same solvent, whereas the difference in the solvation between the two monomers is supposed to be not as distinguished as in methylene dichloride.

Secondly, in liquid sulfur dioxide, the $\alpha$-methylstyrene would be more reactive toward the growing carbonium ion end than styrene, since the electron density on the vinyl group in the former may be larger than that of styrene due to the $\alpha$-methyl inductive effect and the lesser solvation by a sulfur dioxide solvent on $\alpha$-methylstyrene. The non-alternative nature of such a polymerization is well elucidated by the above discussion.

## Summary

The copolymerizations of styrene and $\alpha$-methylstyrene in liquid sulfur dioxide have been carried out at $-40$°C using boron trifluoride etherate as a catalyst, and the results compared with the same copolymerizations in methylene dichloride at $-20$°C. The $r_1$ and $r_2$ values have been estimated by NMR spectrometry as 0—0.1 and over 20 in liquid sulfur dioxide, and 0.2—0.3 and $12\pm2$ in methylene chloride. The styrene unit sandwiched between two $\alpha$-methylstyrene units has been calculated by a comparison of the phenyl doublet with phenyl singlet absorptions. The (S) per cent (S is the sandwiched styrene sequence, M-St-M, in the copolymer, where St is the styrene unit and M is the $\alpha$-methylstyrene unit) has been estimated. In liquid sulfur dioxide, S is approximately zero. This fact agrees well with the large $r_2$ value. The reason for such a non-alternative nature of the copolymerization in liquid sulfur dioxide had also been discussed.

The present authors are grateful to the Seitetsu Kagaku K. K. for the donation of liquid sulfur dixide.

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

*Department of Applied Chemistry*
*Faculty of Engineering*
*Osaka University*
*Miyakojima-ku, Osaka*

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[9] W. G. Barb, *Proc. Roy. Soc.*, **A212**, 66, 177 (1952).

[**] The present authors are inclined to believe in the initiation of the cationic polymerization without the Lewis acid catalyst, as the $H^+$ is derived from the trace of water in liquid sulfur dioxide as.

$$SO_2 + H_2O = H^+ + HSO_3^-$$