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# Cross Fractionation of Styrene-Butadiene Copolymer

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## SUMMARY

A sample of styrene-butadiene copolymer was fractionated by successive precipitation (one-direction fractionation) in cyclohexane/isooctane and benzene/methyl ethyl ketone systems. The chemical composition and molecular weight distributions of the sample were constructed from the fractionation data. The results obtained in both systems were nearly identical for the chemical composition distribution, but were different for the molecular weight distribution. The same sample was fractionated by cross fractionation using both solvent/nonsolvent systems. Comparing the results of cross fractionation with the results of one-direction fractionation, the first gave broader molecular weight and chemical composition distribution curves than the second. However, only cross fractionation showed that the chemical composition distribution curve has a long tail not only at the right side but also at the left side of the distribution maximum.

The superiority of cross fractionation over one-direction fractionation seems clear from the present work. It is also clear that even if the chemical composition distribution curves obtained by one-direction fractionation in different systems are identical with one another, the curves do not always show the true distribution.

## INTRODUCTION

Copolymers have distributions with respect to both molecular weight and chemical composition. It is important to determine the distribution of chemical composition, since it markedly influences various physical properties of copolymers. To determine the chemical composition distribution, several methods, such as fractionation, turbidity measurement, thin layer chromatography, light-scattering measurements in different solvents, density gradient sedimentation, and NMR, have been proposed. The fractionation method discussed in this paper is one of the most fundamental methods.

Distribution of copolymer of polymerization degree $\gamma$ and chemical composition $\alpha$ between two phases was given by Topchiev et al. [1] as follows;

$$v'_{\gamma,\alpha}/v_{\gamma,\alpha} = \exp \gamma\,(\sigma + K\alpha) \tag{1}$$

where $v'_{\gamma,\alpha}$ and $v_{\gamma,\alpha}$ are volume fraction of a component $(\gamma, \alpha)$ in precipitated and supernatant phases, $\sigma$ is a fractionation parameter, and the chemical composition $\alpha$ is taken as the volume fraction of A-monomer units in copolymer A-B. In the case of a one-solvent system, K is given by

$$K = (v'_3 - v_3)(\chi_A - \chi_B) \tag{2}$$

while in the case of a two-solvent system as in our previous work [2];

$$K = (v_1 - v'_1)(\chi_{1A} - \chi_{1B}) + (v_2 - v'_2)(\chi_{2A} - \chi_{2B}) \tag{3}$$

where $v_1$, $v_2$, and $v_3$ are volume fractions of solvent (1), solvent (2), and copolymer. The prime is used to denote the precipitated phase and $\chi_{iA}$ and $\chi_{iB}$ are the interaction parameters of solvent (i) with A- and B-monomer units.

We know that the true molecular weight distribution is obtained by successive fractionation in a system of $K = 0$, because the distribution of copolymer molecules between two phases is not affected by chemical composition. However, the true chemical composition distribution cannot be obtained by one-direction fractionation (i.e., successive precipitation fractionation). Equation (1) shows that the fractionation of copolymer must be determined by both chemical composition and molecular weight even if a system of large K is chosen.

Based on the above theory, Litmanovich and Shtern [3] showed that the chemical composition distribution determined by so-called cross fractionation is closer to the true distribution than that obtained by one-direction fractionation.

In cross fractionation, two solvent/nonsolvent systems are employed which have different signs with respect to parameter K. The sample is first fractionated into intermediate fractions in one system, and then every intermediate fraction is further fractionated in the other system. In principle, the chemical composition distribution curve obtained by this cross fractionation approaches the true distribution as the number of fractions increases.

Although a few experimental results of cross fractionation have been reported [4, 5], no comparison between cross fractionation and one-direction fractionation using the same sample have been reported. In the present work, a sample of styrene-butadiene copolymer is fractionated by cross fractionation in mixtures of cyclohexane/isooctane and benzene/methyl ethyl ketone and compared with the results obtained by one-direction fractionation in each system. If $\alpha$ is expressed by styrene content, the first system has a positive K, while the second has a negative K.

## EXPERIMENTAL

### Materials

The copolymer sample used in this work is an industrial product of styrene-butadiene copolymer which was polymerized to abut 100% conversion with n-buthyl lithium. A monomer mixture of constant composition (about 18 mole % styrene) is supplied to a polymerization chamber continuously. The polymerization proceeds essentially the same as in a batch process. Unfortunately we cannot calculate an expected distribution of chemical composition from monomer reactivity ratio because the copolymerization is carried out with a randomizer added. Purification of the sample was carried out by precipitating the sample from benzene with methanol. A number-average molecular weight of $12.2 \times 10^4$ was determined with a Mechrolab high-speed membrane osmometer in toluene at 25.0°C. The styrene content equaling 19.8 mole % was determined by measuring the refractive index of the sample with an Abbe refractmeter [6].

First grade toluene and benzene of Katayama Chem. Co., Ltd., were purified by shaking with concentrated $H_2SO_4$, drying with $CaCl_2$, and distilling over sodium wire. First grade methyl ethyl ketone was purified by drying over $Na_2SO_4$ and $K_2CO_3$ and then distilling over $KMnO_4$ in a stream of nitrogen gas. Practical grade cyclohexane was passed through silica gel to remove aromatic impurities and then fractionally distilled over sodium wire. Neither ultraviolet spectroscopy nor gas chromatography showed any impurity (especially benzene) in cyclohexane thus purified. First grade isooctane was purified by fractional distillation over sodium wire.

### Fractionation Procedure

To carry out cross fractionation, it is necessary to find two different solvent/nonsolvent systems in which $\chi_{St}$ is larger than $\chi_{Bu}$ and vice versa, so that K in Eq. (1) is positive in one system and negative in the other. The two copolymer samples were dissolved in several solvents. Each solution was titrated with several nonsolvents at 25.0°C and then the first phase separation point was determined visually. The systems which showed the greatest difference in volume ratios for the two samples were selected. Cyclohexane/isooctane system (I) and benzene/methyl ethyl ketone system (II) were thus found to be appropriate for the present fractionation experiments. If $\alpha$ is given with respect to styrene content, K is positive in the first and negative in the second.

Successive precipitation fractionation was carried out at 25.0 ± 0.01°C in both systems. Since the polymer concentration becomes too dilute as the fractionation is repeated, the solutions were concentrated by evaporation. The polymer concentration at which the first fraction was separated was about 0.45 g/100 ml in System I and about 0.70 g/100 ml in System II.

In cross fractionation the sample was first fractionated into 4 intermediate fractions in System II and then each intermediate fraction was fractionated into 5 fractions in System I. The concentration of polymer at the first phase separation in each system is almost equal to that employed in the corresponding successive precipitation fractionation. The characterization of each fraction was carried out in the same manner as that of the original sample.

## EXPERIMENTAL RESULTS

Experimental data from one-direction fractionation in System I and II are shown in Tables 1 and 2 while those from cross fractionation are shown

**Table 1.** Fractionation Results in Cyclohexane/Isooctane System (I)

| Fraction No. | Weight fraction ($w_i$) | Styrene content (mole %) | Molecular weight ($\overline{M}_n$) |
|---|---|---|---|
| 1 | 0.1003 | 24.1 | $43.6 \times 10^4$ |
| 2 | 0.0825 | 23.4 | 32.0 |
| 3 | 0.1030 | 21.8 | 23.9 |
| 4 | 0.1063 | 20.5 | 17.6 |
| 5 | 0.1108 | 19.3 | 20.6 |
| 6 | 0.0926 | 18.4 | 11.9 |
| 7 | 0.0803 | 17.9 | 15.2 |
| 8 | 0.0544 | 17.9 | 13.3 |
| 9 | 0.0626 | 17.9 | 10.5 |
| 10 | 0.0538 | 17.8 | 8.7 |
| 11 | 0.0327 | 17.8 | 7.7 |
| 12 | 0.0367 | 17.6 | 6.3 |
| 13 | 0.0840 | 17.2 | 4.1 |
| Mean value | | 19.8 | 12.4 |

Recovery per cent 96.7%.

**Table 2.** Fractionation Results in Benzene/Methyl Ethyl Ketone System (II)

| Fraction No. | Weight fraction ($w_i$) | Styrene content (mole %) | Molecular weight ($\overline{M}_n$) |
|---|---|---|---|
| 1 | 0.0424 | 16.9 | $43.6 \times 10^4$ |
| 2 | 0.1661 | 17.8 | 39.5 |
| 3 | 0.1522 | 17.8 | 23.9 |
| 4 | 0.1516 | 18.0 | 21.6 |
| 5 | 0.0776 | 19.0 | 18.7 |
| 6 | 0.0766 | 20.0 | 12.7 |
| 7 | 0.0674 | 20.9 | 10.4 |
| 8 | 0.1037 | 21.7 | 8.5 |
| 9 | 0.0469 | 22.9 | 5.4 |
| 10 | 0.1155 | 25.5 | 3.3 |
| Mean value | | 19.8 | 11.0 |

Recovery per cent 96.4%.

in Table 3. The chemical composition and molecular weight distributions calculated from those data are shown in Figs. 1 and 2. The distribution curves for one-direction fractionations can be obtained by plotting the experimental data in the order of fractionation step. The curves due to cross fractionation were obtained by re-arranging the experimental data in the order of chemical composition and molecular weight.

Cross fractionation gave broader distribution curves than one-direction fractionation with respect to both molecular weight and chemical composition. It is important to note that the components with low styrene contents (lower than about 17 mole %) could only be found by cross fractionation and not by one-direction fractionation.

The average chemical composition and molecular weight calculated from the fractionation results agree with the values for the original sample within experimental error (Table 4), except for the average molecular weight calculated from the results of one-direction fractionation in System II. The number-average molecular weight was calculated by

$$\bar{M}_n = 1/\Sigma_i(w_i/M_{n_i}) \qquad (4)$$

where $w_i$ is the weight fraction of fraction i.

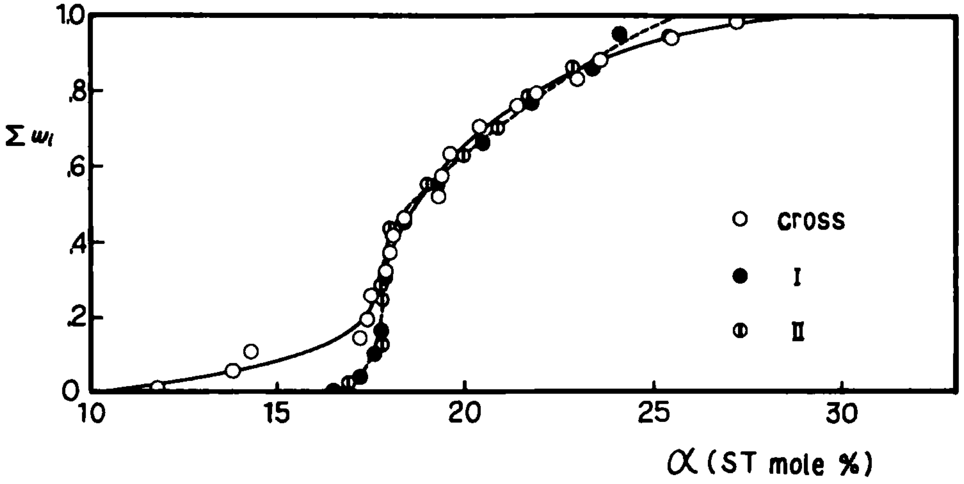

Fig. 1. Integral chemical composition distribution curves obtained by one-direction fractionations in Systems I and II and by cross fractionation in both systems.

**Table 3.** Results of Cross Fractionation in Systems I and II

| Fraction No. | Weight fraction ($w_i$) | Styrene content (mole %) | Molecular weight ($\bar{M}_n$) |
|---|---|---|---|
| 1-1 | 0.0467 | 18.1 | $43.6 \times 10^4$ |
| 2 | 0.0454 | 18.0 | 60.2 |
| 3 | 0.0545 | 17.9 | 55.0 |
| 4 | 0.0426 | 17.2 | 36.7 |
| 5 | 0.0700 | 13.8 | 15.7 |
| 2-1 | 0.0298 | 21.9 | 29.8 |
| 2 | 0.0590 | 19.6 | 34.2 |
| 3 | 0.0624 | 19.3 | 29.4 |
| 4 | 0.0747 | 17.5 | 21.6 |
| 5 | 0.0304 | 14.3 | 10.5 |
| 3-1 | 0.0624 | 23.6 | 18.5 |
| 2 | 0.0849 | 20.4 | 16.6 |
| 3 | 0.0474 | 19.4 | 17.8 |
| 4 | 0.0526 | 17.4 | 10.7 |
| 5 | 0.0251 | 11.8 | 6.39 |
| 4-1 | 0.0330 | 27.2 | 9.77 |
| 2 | 0.0531 | 25.5 | 8.27 |
| 3 | 0.0419 | 23.0 | 6.66 |
| 4 | 0.0362 | 21.4 | 4.87 |
| 5 | 0.0476 | 18.4 | 2.48 |
| Mean value | | 19.3 | 12.1 |

Recovery per cent 92.5%.

## DISCUSSION

Chemical composition distribution of a binary copolymer formed during copolymerization is given by [7-9]

$$M/M^\circ = (f_1/f_1^\circ)^\alpha (f_2/f_2^\circ)^\beta (f_1^\circ - \delta/f_1 - \delta)^\gamma \qquad (5)$$

where $1 - M/M^\circ$ is the mole conversion, $f_1 = 1 - f_2$ is the instantaneous mole fraction of monomer 1 in the course of copolymerization, $f_1^\circ = 1 - f_2^\circ$ is the mole fraction of monomer 1 in the original monomer mixture,

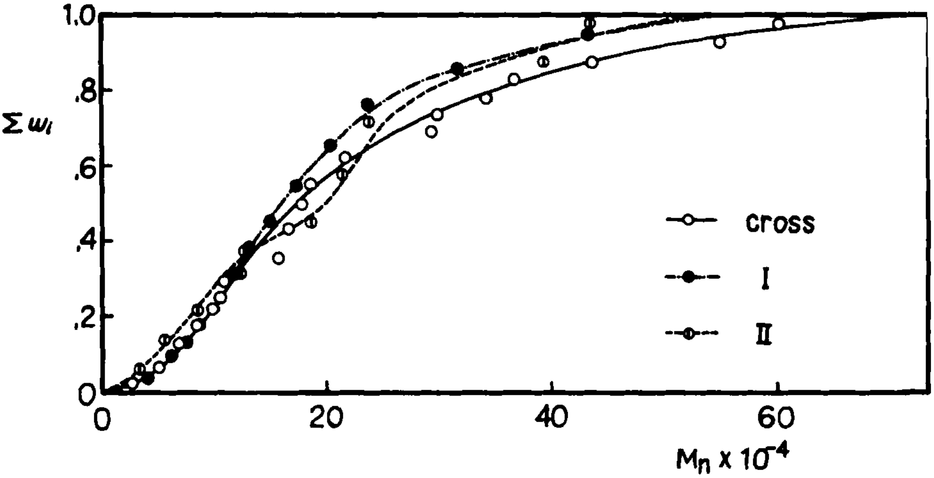

Fig. 2. Integral molecular weight distribution curves obtained by one-direction fractionations in Systems I and II and by cross fractionation in both systems.

Table 4

| | | Styrene content (mole %) | Molecular weight ($\overline{M}_n$) |
|---|---|---|---|
| Average | I | 19.8 | $12.4 \times 10^4$ |
| | II | 19.8 | 11.0 |
| | Cross | 19.3 | 12.1 |
| Original sample | | 19.8 | 12.2 |

$\alpha = r_2/(1 - r_1)$, $\beta = r_1/(1 - r_2)$, $\gamma = (1 - r_1r_2)/(1 - r_1)(1 - r_2)$, and $\delta = (1 - r_2)/(2 - r_1 - r_2)$. According to Eq. (5), many binary copolymers that are obtained by batch polymerization have a typical chemical composition distribution. That is, the differential distribution curve has a long tail on one side of the peak maximum and no tail but a cliff is found on the other side. The differential distribution curve is thus an L-shaped curve. If we convert such a typical differential distribution curve to an integral distribution curve, it will also show a correspondingly long tail to one side and a sharp drop to zero on the other side.

The distribution curve of our sample shown in Fig. 1 appears to show the L-shape feature. However, the chemical composition distribution curve resulting from cross fractionation has a long tail not only at the right side but also at the left side of the peak.

The reason for the long tail at the left side of the peak is not very clear at present but our speculation is as follows: In Eq. (5) it is assumed that only a copolymer of uniform composition is derived from a monomer mixture at a certain composition. That is, there exists no distribution in chemical composition in the copolymer formed at any instant. However, it was theoretically [10, 11] pointed out that even in the copolymer formed during an infinitesimal time interval, there must exist distributions in both chemical composition and molecular weight. According to Stockmayer [10], chemical composition distribution of copolymer radicals formed during an infinitesimal time interval is given by the following equation;

$$\langle w(y)\rangle dy = \frac{3dz}{4(1 + z^2)^{5/2}} \tag{6}$$

with

$$z^2 = \lambda y^2/2p_0q_0\kappa \tag{7}$$

$$y = p - p_0 = q_0 - q \tag{8}$$

$$\kappa = [1 - 4p_0q_0(1 - r_1r_2)]^{1/2} \tag{9}$$

where $\lambda$ is the number-average length (polymerization degree) of the chain radicals, $p = 1 - q$ is the chemical composition of an individual chain, $p_0 = 1 - q_0$ is the over-all chemical composition, and $r_1$ and $r_2$ are monomer reactivity ratios. Equation (6) describes the chemical composition distribution of chain radicals. We may safely assume that Eq. (6) gives the chemical composition distribution of stable polymers formed at an instant, since no combination between active centers should occur in anionic polymerization.

The chemical composition distribution curve was calculated by using Eqs. (5) and (6). Although $r_1 = 0.05$ and $r_2 = 20$ are reported for the copolymerization of styrene and butadiene initiated with n-buthyllithium [14], the calculated curve using these values differs greatly from the experimental curve, probably because of the addition of a randomizer. Therefore, monomer reactivity ratios are assumed to be 0.95 ($r_1$; styrene) and 1.25 ($r_2$; butadiene). These values give the best agreement between the right side part of the experimental curve and the calculated curve. The styrene content of the copolymer formed at the initial time of copolymerization is assumed to be 17.8 mole % and corresponds to the styrene content of the peak of the experimental curve. $\lambda$ is assumed to be $2.0 \times 10^3$, corresponding to the number-average degree of polymerization of the original sample and to remain constant throughout the polymerization. In general, $\lambda$ would change with reaction degree.

The distribution curve is first calculated using Eq. (5). Then, assuming that the curve is made of 10 fractions, the distribution of each fraction is calculated from Eq. (6). If we integrate the chemical composition distributions of these fractions graphically, we can obtain over-all distribution of the sample. This procedure thus takes into account the distribution of polymers formed at any instant, as suggested by Stockmayer. The dashed line in Fig. 3 was calculated by this method. The dotted line was calculated from Eq. (5).

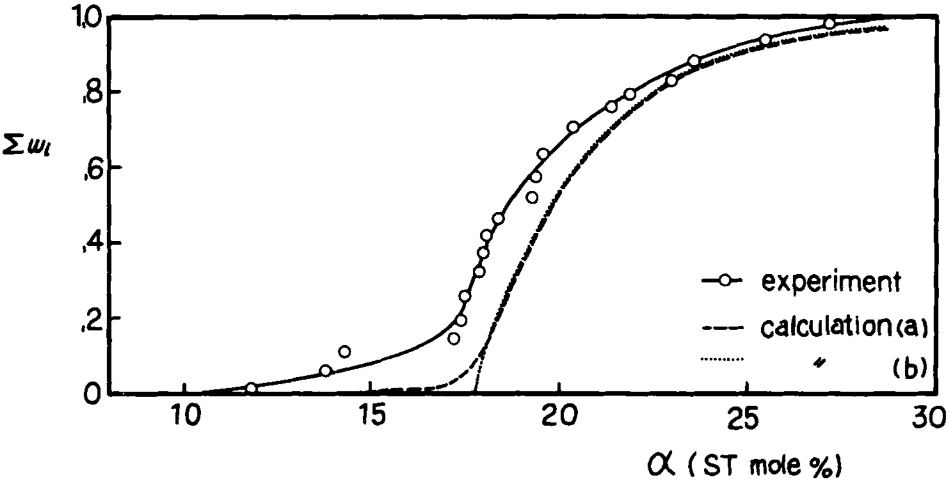

Fig. 3. Comparison of the calculated integral distribution curves of chemical composition with that obtained by cross fractionation. Curve a was calculated from Eqs. (5) and (6). Curve b was calculated from Eq. (5) only.

Although the calculated curve does not agree perfectly with the experimental curve, its shape probably results from the mechanism proposed by Stockmayer. We agree that the experimental test of Stockmayer's theory should be conducted on samples prepared under well-defined conditions (e.g., for azeotropic copolymers at low conversion). Until we have such unambiguous data, we would like to present Fig. 3 to support Stockmayer's theory.

In addition, the superiority of cross fractionation over one-direction fractionation appears to be clear from the present results. It is important that the tail at the left side of the distribution curve was found only by cross fractionation.

It is also clear from Fig. 1 that even if the chemical composition distribution curves obtained by one-direction fractionation in different systems are identical, the curves do not always show the true distribution.

Concerning molecular weight distribution, the results obtained by one-direction fractionation in both systems give nearly the same width but different shapes of distribution curves. The distribution curve obtained in System II seems to have a splitting at the peak or a shoulder. According to a calculation of Litmanovich and Topchiev [12], if the sample is precipitated from the cliff side to the tail side of the chemical composition distribution curve and if the K value is large, the molecular weight distribution curves of some fractions may show double peaks. Consequently, the molecular weight distribution curve constructed from the fractionation results may show a splitting at the peak of a clear shoulder. The conclusion they reached from their model calculation appears to agree with our experimental results. Similar experimental results were reported in a paper of Kudryavtseva et al. [13].

The difference between the number-average molecular weight calculated from the fractionation data in System II and that of the original sample, as seen in Table 4, may arise from this extreme heterogeneity of molecular weight in some fractions.

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## REFERENCES

[1] A. V. Topchiev, A. D. Litmanovich, and V. Ya. Shtern, *Dokl. Akad. Nauk SSSR,* **147**, 1389 (1962).

[2] S. Teramachi and M. Nagasawa, *J. Macromol. Sci.–Chem.,* **A2**, 1169 (1968).

[3] A. D. Litmanovich and V. Ya. Shtern, *J. Polym. Sci., Part C,* **16**, 1375 (1967).

[4] A. J. Rosenthal and B. B. White, *Ind. Eng. Chem.*, **44**. 2693 (1952).

[5] V. A. Agasandyan, L. G. Kudryavtseva, A. D. Litmanovich, and V. Ya. Shtern, *Vysokomol. Soedin.*, **A9**, 2634 (1967).

[6] A. Arnold, I. Modorsky, and L. A. Wood, *Anal. Chem.*, **23**, 1656 (1951). Japanese Industrial Standard, K 6383-(1961).

[7] I. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1946).

[8] V. E. Meyer and G. G. Lowry, *J. Polym. Sci., Part A*, **3**, 2843 (1965).

[9] I. H. Spinner, C.-Y. Cu, and W. F. Graydon, *J. Amer. Chem. Soc.*, **77**, 2198 (1955).

[10] W. H. Stockmayer, *J. Chem. Phys.*, **13**, 199 (1945).

[11] R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944).

[12] A. D. Litmanovich and A. V. Topchiev, *Neftekhimiya*, **3**, 336 (1963).

[13] L. G. Kudryavtseva, A. D. Litmanovich, A. V. Topchiev, and V. Ya. Shtern, *Neftekhimiya*, **3**, 343 (1963).

[14] A. A. Korotkov and N. N. Chesnokova, *Vysokomol. Soedin.*, **2**, 365 (1960).

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