

Cross Fractionation of Styrene—Acrylonitrile Copolymer

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ABSTRACT: The most reliable method to determine the chemical-composition distribution of random copolymers may be cross fractionation. To carry out cross fractionation, it is necessary to find two different solvent—nonsolvent systems. The ethylene carbonate—ethylenecyanohydrin system together with the methyl ethyl ketone—cyclohexane system reported previously were found to be appropriate for cross fractionation of styrene—acrylonitrile copolymers. An example of chemical-composition distribution determination of commercial styrene—acrylonitrile random copolymers by cross fractionation using both systems is presented.

KEY WORDS Compositional Fractionation / Cross Fractionation /
Chemical-Composition Distribution / St—AN Copolymer /

Copolymers have distributions with respect to both molecular weight and chemical composition. The most reliable method to determine these distributions of random copolymers may be cross fractionation.¹⁻⁴ However, only a few experimental results of cross fractionation have so far been reported,³⁻⁵ because of the laborious experimental procedures required. To carry out cross fractionation, it is necessary to find two different solvent—nonsolvent systems which have different signs with respect to parameter K in the following equation^{6,7}

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

where $v'_{\gamma,\alpha}$ and $v_{\gamma,\alpha}$ are volume fractions of a component of polymerization degree γ and chemical composition α (volume fraction of A-monomer units in copolymer A—B) in precipitated and supernatant phases, respectively, and δ is a fractionation parameter. The sample is first fractionated into several intermediate fractions in one system, and then every intermediate fraction is further fractionated in the other system.

In a previous work,⁷ the chemical-composition distribution determination of styrene—acrylo-

nitrile random copolymer was carried out using the methyl ethyl ketone—cyclohexane system (I), which has positive K if α in eq 1 is expressed by acrylonitrile content. However, no system with negative K could be found to carry out a cross fractionation. In the present paper, it is reported that the ethylene carbonate—ethylenecyanohydrin system (II) has negative K and is appropriate for cross fractionation of styrene—acrylonitrile copolymers if combined with the former system. The purpose of this paper is to present an example of chemical-composition distribution determination of commercial styrene—acrylonitrile copolymers by cross fractionation using these two systems.

EXPERIMENTAL

Materials

The copolymer samples used in this work are industrial products of styrene—acrylonitrile random copolymer. Purification of the samples was carried out by dissolving pellets of the samples in methyl ethyl ketone (MEK), precipitating, washing with methanol, and drying *in vacuo* at room temperature. The acrylonitrile

contents of samples I and II thus purified are 31.2 and 29.8 wt%, respectively; these were determined by the micro-Kjeldahl method.

Purification of MEK was carried out by drying first-grade reagent with Na_2SO_4 and K_2CO_3 , followed by distillation over KMnO_4 . Practical-grade cyclohexane was washed several times with sulfuric acid and water and then distilled over sodium wire. Ethylene carbonate and ethylenecyanohydrin were purified by drying first-grade reagents with Na_2CO_3 and then by distillation under reduced nitrogen atmosphere.

Searching for Fractionation System

In the solvent—nonsolvent system, parameter K in eq 1 is given by

$$K = (v_1 - v_1')(\chi_{1A} - \chi_{1B}) + (v_2 - v_2')(\chi_{2A} - \chi_{2B}) \quad (2)$$

where χ_{iA} and χ_{iB} are interaction parameters of solvent i with A- and B-monomer units, respectively, and v_i and v_i' are volume fractions of solvent i in the supernatant and precipitated phases, respectively.⁷ To find a system with negative K , therefore, it may be necessary to select a solvent—nonsolvent system in which $\chi_{1A} < \chi_{1B}$ and $\chi_{2A} < \chi_{2B}$. [In general, two or more copolymer samples with different compositions and similar molecular weights are dissolved in good solvents which have $\chi_A < \chi_B$. Then the solutions are titrated with the solvents which have $\chi_A < \chi_B$, but are nonsolvents for the copolymers. The volume ratios of nonsolvent/solvent for the first phase-separation of those copolymer solutions are compared. The systems in which copolymer composition dependence of the volume ratio is most remarkable may be selected as the appropriate fractionation systems].

In the present work, some solvents which are nonsolvents for polystyrene but dissolve polyacrylonitrile were first chosen from published data.⁸ The solubilities of the both homopolymers in these solvents were then examined; ethylene carbonate, ethylenecyanohydrin, and malononitrile were found to be appropriate solvents. Among them, ethylenecyanohydrin and malononitrile cannot dissolve the copolymer samples, while ethylene carbonate can dissolve the copolymer samples at 40°C. Low conversion samples with AN contents of 26, 28, and 32 wt% and molecular weights of about 6×10^4

were dissolved in ethylene carbonate (polymer concentrations were about 1 wt%), and the solutions were titrated with each of the two nonsolvents at 35°C. It was found from the comparison of the volume ratios of nonsolvent/solvent for the first phase-separation of the three sample solutions that the ethylene carbonate—ethylenecyanohydrin system (II) is appropriate for the present purpose. That is, the volume ratios for this system were 0.065, 0.146, and 0.780 for the respective samples, whereas the volume ratios were very large and were not sensitive to copolymer composition when malononitrile was used as precipitant.

Fractionation Procedures

First, one-direction fractionation of sample I was carried out in system (I) and in system (II). In system (I), the sample of 2.084 g was fractionated from 2.0-wt% solution in MEK into 13 fractions by a successive precipitation method at $30.0^\circ \pm 0.01^\circ\text{C}$. The equilibration times were 5 days for the first fraction and one or a few days for the other fractions. Fractions thus separated were precipitated, washed with methanol, and dried *in vacuo* at room temperature. On the other hand, in system (II) in which the concentrated phase is the upper phase, the sample was fractionated into 12 fractions by an ordinary column-elution method at $35.0 \pm 0.01^\circ\text{C}$. The sample was deposited on glass beads having a size between 100 and 150 mesh, by evaporating the solvent, MEK, slowly. The glass beads coated by the polymer were dried out *in vacuo*, passed through a sieve of 50 mesh, and filled a glass column of 4-cm diameter and 80-cm height. The weight of the sample charged was thus 0.8273 g. Each fraction was eluted out with mixed solvent of 250 ml, which was almost equal to the hold-up volume of the glass beads. The mixing ratio of the solvents was varied. The equilibration times were about 4 hr for the respective fractions. Each fraction was concentrated by vacuum evaporation, precipitated with methanol, and dried *in vacuo*. Purifications of the fractions were repeated by the same method as for the original samples.

Unfortunately, sample I used in the above experiments was damaged and could not be used for cross fractionation. Instead, cross

fractionation of sample II was carried out using both systems (I) and (II). The sample of 15.00 g was first fractionated into 5 fractions in system (I) and then each intermediate fraction was fractionated into 5–7 fractions in system (II). Fractionation procedures in cross fractionation were the same as those in one-direction fractionation.

Table I. One-direction fractionation results of sample I in MEK–cyclohexane system^a

Fraction no.	AN content, wt%	Weight fraction
1	36.3	0.0550
2	33.9	0.0534
3	32.7	0.0914
4	31.9	0.1522
5	31.4	0.1330
6	31.5	0.0284
7	30.6	0.1348
8	31.0	0.0300
9	30.4	0.0422
10	30.1	0.1506
11	30.1	0.0152
12	30.5	0.0586
13	29.7	0.0552
Average	31.5	—

^a The recovery rate of the sample was 94.4%; AN content of the original sample was 31.2 wt%.

Table II. One-direction fractionation results of sample I in ethylene carbonate–ethylene cyanohydrin system^a

Fraction no.	AN content, wt%	Weight fraction
1	35.1	0.1677
2	33.6	0.0574
3	32.0	0.0622
4	31.8	0.0413
5	31.7	0.0452
6	31.3	0.0619
7	30.9	0.0732
8	30.8	0.0781
9	31.1	0.1417
10	30.4	0.1264
11	30.0	0.1156
12	28.6	0.0293
Average	31.7	—

^a The recovery rate of the sample was 98.8%; AN content of the original sample was 31.2 wt%.

Determinations of acrylonitrile contents of all fractions were carried out in the same manner as for the original samples.

EXPERIMENTAL RESULTS

Experimental data obtained by one-direction fractionation of sample I in systems (I) and (II) are shown in Tables I and II, respectively, while cross fractionation results of sample II are shown in Table III. The yields were 94.4%, 98.8%, and 94.0% of the original samples, respectively.

Table III. Cross fractionation results of sample II^a

Fraction no.	AN content, wt%	Weight fraction
1-1	29.8	0.0074
2	29.3	0.0131
3	30.5	0.0312
4	29.8	0.1710
5	29.9	0.1383
2-1	28.7	0.0051
2	30.2	0.0036
3	30.3	0.0070
4	29.9	0.0153
5	30.2	0.0436
6	29.6	0.0848
7	29.3	0.0056
3-1	30.7	0.0079
2	30.6	0.0094
3	30.4	0.0222
4	30.3	0.0405
5	29.8	0.0566
6	29.7	0.0640
7	28.0	0.0074
4-1	30.7	0.0032
2	30.4	0.0117
3	30.2	0.0258
4	30.0	0.0434
5	29.2	0.0350
6	27.4	0.0130
5-1	30.6	0.0249
2	29.1	0.0351
3	28.5	0.0362
4	26.4	0.0088
5	20.2	0.0155
6	19.7	0.0069
7	19.2	0.0065
Average	29.5	—

^a The recovery rate of the sample was 94.0%; AN content of the original sample was 29.8 wt%.

In all fractionation results, average acrylonitrile contents calculated from the fractionation data agreed with those of the original samples within experimental error. The chemical-composition distribution curves obtained from those fractionation data are shown in Figures 1, 2, and 3, respectively. The distribution curves for one-direction fractionations were obtained by plotting the experimental data in the order of fractionation step, while the curve due to cross fractionation was obtained by rearranging the experimental data in the order of acrylonitrile content.

The respective results obtained by one-direction fractionations in both systems are similar to one another, as shown in Figures 1 and 2. If the differential distribution curves are calculated from the results, the curves show the L-shaped feature, as shown by the dotted line in Figure 1.

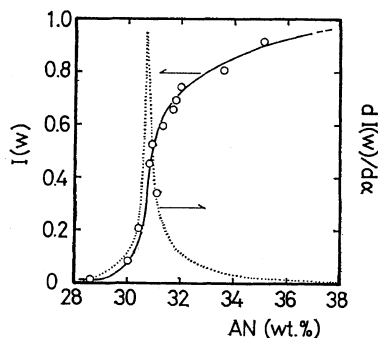


Fig. 1. Chemical-composition distribution curve of sample I obtained by one-direction fractionation with system (II). The dotted line shows the differential distribution curve.

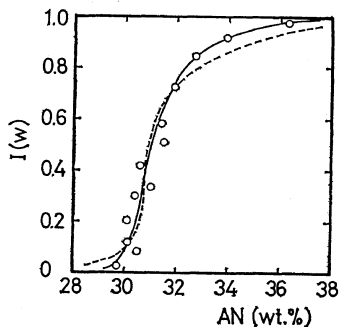


Fig. 2. Chemical-composition distribution curve of sample I obtained by one-direction fractionation with system (I). The dashed line shows the curve in Figure 1.

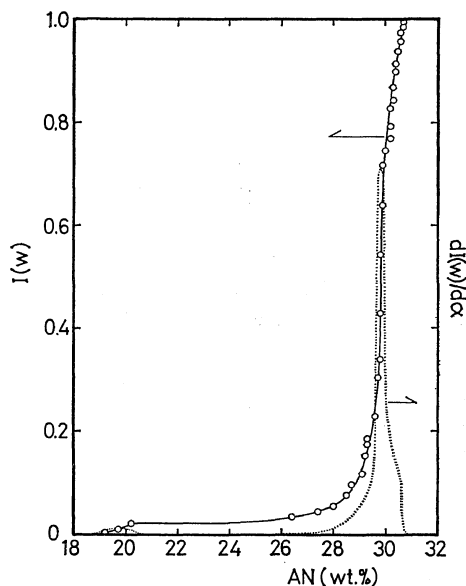


Fig. 3. Chemical-composition distribution curve of sample II obtained by cross fractionation. The dotted line shows the differential distribution curve.

The chemical-composition distribution curve of sample II determined by cross fractionation with systems (I) and (II) is shown in Figure 3. The curve shows two distinctly different peaks when the differential distribution curve is calculated from the results: One peak is the main peak, having acrylonitrile content of about 30 wt%, and the other peak is a small peak at about 20 wt%.

DISCUSSION

The shapes in Figures 1 and 2 are typical ones expected from the copolymerization theory⁹⁻¹¹ if the copolymerization of the sample was carried out in a batch. The main long tail of the curve at the right side of the peak (in the differential curve) may be caused by drift of the monomer mixture composition during the copolymerization process, while the short tail at the left side of the peak may be caused by the statistical distribution of chemical composition, as pointed out by Stockmayer.^{12,4}

According to a calculation of Litmanavich and Shtern,² the chemical-composition distribution curves should be different in shape, if the

curves are obtained by one-direction fractionation in two different systems with different signs of K . The shape of the curve is expected to be similar to the true distribution curve if the curve is obtained by precipitating the sample from the tail side to the peak side (with system (I) in this work). On the other hand, the curve obtained by precipitating from the peak side to the tail side using a system with an opposite K should show a different shape from the true one. In the present work, however, the results obtained in both systems (I) and (II) show almost the same shape, in contradiction to the predictions of Litmanovich and Shtern.² The reason may be that both fractionations were carried out from tail to peak since the fractionation with system (II) was carried out in a column, even though K in system (II) has the opposite sign from that in system (I). Thus, if a sample is fractionated from tail toward peak in any system, the shape of the distribution curve obtained would not be much different from the true one.

The width of the chemical-composition distribution curve obtained in system (II) is broader than that obtained in system (I), as shown in Figure 2. This may be caused either by the difference in the absolute value of K between systems (I) and (II), or by the difference of fractionation method in each system. That is, a successive precipitation method was used in system (I), while a column elution method was used in system (II).

In any case, the widths of the chemical-composition distribution curves are rather broad in both fractionation results, so that both absolute values of K may be rather large. The large values of K are an advantage for cross fractionation.

The chemical-composition distribution curve

of sample II determined by cross fractionation has two peaks, as shown in Figure 3. The cause for the appearance of such binomial chemical-composition distributions may be an interesting problem for discussion from the standpoint of polymerization mechanism. Unfortunately, however, the present authors do not know the polymerization procedure of this commercial sample, and hence cannot begin the discussion of the problem.

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