Comparison between Successive Precipitation and Column Elution Methods in Compositional Fractionation of Copolymers

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ABSTRACT

In order to compare the efficiencies of successive precipitation and column elution methods in compositional fractionation, mixtures of two styrene–acrylonitrile random copolymers with different chemical compositions were fractionated by the two methods by using the methyl ethyl ketone–cyclohexane system. The compositional distribution curve determined by each method was compared with the curve calculated from a theory on compositional fractionation. The value of a parameter K, which shows the efficiency of compositional fractionation, was determined to have the best agreement between the experimental and calculated curves. It was found that the column elution method is more effective than the successive precipitation method.

INTRODUCTION

Copolymers have, in general, distributions with respect to both chemical composition and molecular weight. Therefore, the fractionation of copolymers is governed by chemical composition as well as by molecular weight, as shown by the following equation;

$$v_{X,\alpha}'/v_{X,\alpha} = \exp\{X(\sigma + K\alpha)\} \qquad (1)$$

where $v_{X,\alpha}'$ and $v_{X,\alpha}$ are volume fractions of a component of polymerization degree X and chemical composition α (mole or volume fraction of monomer A units in copolymer A-B) in the concentrate and dilute phases, respectively, and σ is a fractionation parameter [1, 2]. In the case of two-solvent systems, K is given by

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

where v_1 and v_2 are the volume fractions of solvents 1 and 2, respectively. χ_{iA} and χ_{iB} are the interaction parameters of solvent i with A and B monomer units, respectively.

It is clear from Eq. (1) that the efficiency of compositional fractionation is determined by a parameter K. If a system with a larger value of K is employed, the fractionation is expected to be carried out more effectively. The value of K depends, first of all, on the solvents used through the values of $(\chi_{1A} - \chi_{1B})$ and $(\chi_{2A} - \chi_{2B})$. Since the values of K depend on $(v_1 - v_1')$ and $(v_2 - v_2')$, moreover, the efficiency of fractionation may depend on the operational method of fractionation, such as fractional precipitation or fractional solution method. In the fractionation of homopolymers by molecular weight, the fractional solution method is recommended, in general. It has not as yet, however, been concluded which method is more effective in compositional fractionation, though a few studies concerning the problem have been reported [3, 4].

In the present work, mixtures of styrene—acrylonitrile random copolymers with different chemical compositions were fractionated by two methods, i.e., successive precipitation (SP) and column elution (CE) methods. In addition to the fractionation results by the two methods, the values of K in those methods are compared to determine

which method is more effective in the compositional fractionation. That is, the values of K in both methods are determined to have the best agreement between the experimental distribution curve of chemical composition and the curve calculated from Eq. (1). The values of K chosen for the two fractionation methods are compared.

EXPERIMENTAL

Materials

The copolymer samples used in the present work are styrene–acrylonitrile random copolymers prepared by bulk polymerization at 60°C under a nitrogen atmosphere with the use of benzoyl peroxide as initiator. The monomers were distilled under reduced nitrogen atmosphere just before use. The polymerizations were stopped at low conversion by pouring the reaction mixtures into methanol, so that the samples have narrow distributions of chemical composition. The copolymers obtained were dissolved in methyl ethyl ketone (MEK), precipitated and washed with methanol, and dried in vacuo. The acrylonitrile (AN) contents and the limiting viscosity indexes $[\eta]$ of the samples were determined by a micro-Kjeldahl method and viscometry with an Ubbelohde-type instrument in MEK at $25.0 \pm 0.01°C$, respectively. The values thus determined are shown in Table 1, together with the degree of conversion in polymerization. Purification of MEK was carried out by drying commercial reagent of the first grade with K_2CO_3 and Na_2SO_4 and then distilling over $KMnO_4$ under nitrogen atmosphere. Cyclohexane of the first grade was washed several times with sulfuric acid and water, dried with $CaCl_2$, and then distilled. Methanol was simply distilled.

Fractionation Procedure by the SP Method

MEK and cyclohexane were used as solvent and precipitant, respectively, in both methods.
A mixture of 2.000 g of sample A-19 and 2.000 g of A-28 was dissolved in 200 ml MEK. Phase separations were caused by adding cyclohexane at 25.0°C. The total polymer concentration at which the first fraction was separated was about 0.98 g/dl. The equilibration time was 1-3 days for each fractionation. The fractions separated were diluted with MEK and then precipitated by pouring them into methanol. The last fraction was recovered by concentrating the

TABLE 1. Samples

	AN content (mole %)	$[\eta]$ (dl/g)	Conversion (%)
A-28	42.6	1.39_4	22.2
A-19	33.3	1.26_1	8.2

supernatant phase at the 12th fractionation. All of the fractions were washed with methanol and dried in vacuo at 70°C. The characteristics of the fractions were determined by the same manner as those of the original samples.

Fractionation Procedure by the CE Method

A glass column with water jacket was used for column elution fractionation. The effective length and the inner diameter of the column were 105 and 3.7 cm, respectively. The size of the glass beads used as the support for the concentrate phase was between 150 and 170 mesh. The glass beads were purified with HCl and concentrated HNO$_3$, and washed with water and acetone, successively.

A mixture of 0.751 g of sample A-19 and of 0.750 g of A-28 was dissolved in a beaker with 264 ml MEK, which was equal to the hold-up volume of the glass beads in the column. The mixed sample was deposited on the glass beads by evaporating the solvent slowly at room temperature, and then the glass beads coated with the sample were dried in vacuo, passed through a sieve of 70 mesh and filled into the column as a slurry with cyclohexane. The weight of the mixed sample charged in the column was 1.190 g, because of the loss of the sample adhered onto the wall of the beaker. Each fraction was eluted out with 264 ml of a mixture of MEK and cyclohexane. The mixing ratio of the solvents was varied stepwise. The equilibration time was about 3 hr for each fraction, and the flow rate each elution was adjusted by a stopcock at the bottom of the column at about 500 ml/hr. The temperature of the column was maintained at 25.0°C by circulating a constant temperature water through the jacket. The fractions eluted from the column were collected in flasks, concentrated by evaporating the solvents, and then recovered and characterized by the same manner as those of the SP method.

CALCULATION

With respect to the SP method, the distribution function of X and α, $w_{X,\alpha}{}^{'(n)}$, weight fraction $W^{'(n)}$, and average chemical composition $\alpha^{'(n)}$ of the n-th fraction were given by Eqs. (3)-(5), which were obtained from Eq. (1) by Litmanovich and Shtern [5].

$$w_{X,\alpha}{}^{'(n)} = w_{X,\alpha}{}^{(n-1)} \frac{1}{1 + (1/R_n) \exp\{-X(\sigma_n + K_n\alpha)\}} \qquad (3)$$

$$W^{'(n)} = \int_0^\infty dX \int_0^1 w_{X,\alpha}{}^{'(n)} d\alpha \qquad (4)$$

$$\alpha^{'(n)} = (1/W^{'(n)}) \int_0^1 \alpha \, d\alpha \int_0^\infty w_{X,\alpha}{}^{'(n)} dX \qquad (5)$$

where $w_{X,\alpha}{}^{(n-1)}$ is the distribution function of copolymer remaining in the dilute phase after separating the (n-1)th fraction and $R_n = (V'/V)_n$ is the ratio of the volumes of the two phases. With respect to the CE method, the Eqs. (6)-(8) are derived from Eq. (1).

$$w_{X,\alpha}{}^{(n)} = w'_{X,\alpha}{}^{(n-1)} \frac{1}{1 + R_n \exp\{X(\sigma_n + K_n\alpha)\}} \qquad (6)$$

$$W^{(n)} = \int_0^\infty dX \int_0^1 w_{X,\alpha}{}^{(n)} d\alpha \qquad (7)$$

$$\bar{\alpha}^{(n)} = (1/W^{(n)}) \int_0^1 \alpha d\alpha \int_0^\infty w_{X,\alpha}{}^{(n)} dX \qquad (8)$$

The sample of copolymer is an equal weight mixture of two com-
ponents. Both components were assumed to be homogeneous in
chemical composition and to have the most probable distribution of
polymerization degree X, i.e.,

$$w_X = (X/\overline{X}_n^2) \exp \{-X/\overline{X}_n\} \tag{9}$$

where $\overline{X}_n$ is the number-average degree of polymerization. The
chemical compositions of two components α_1 and α_2 are 0.333 and
0.426, respectively, and $\overline{X}_n = 2.5 \times 10^3$ if estimated from the limit-
ing viscosity index [6].

In the calculations, it was assumed that K_n is constant throughout
the series of fractionations and R_n has a value from 4.4×10^{-3} to
0.6×10^{-3} in the SP method and from 1.0×10^{-2} to 0.6×10^{-3} in the
CE method. The values of R_n were evaluated from the experimental
results. To choose a value for σ_n, $w_{X,\alpha}^{'(n)}$ and $w_{X,\alpha}^{(n)}$ were calcu-
lated from Eqs. (3) and (6), respectively. Then $W^{'(n)}$ and $W^{(n)}$ were
calculated from Eqs. (4) and (7), respectively. The value of σ_n is
determined so that the values of $W^{'(n)}$ and $W^{(n)}$ may become 1/11,
since the sample was fractionated into 11 fractions. On using the
values of σ_n thus obtained, the average values of AN content,
$\overline{\alpha}^{'(n)}$ and $\overline{\alpha}^{(n)}$ were calculated from Eqs. (5) and (8) for the respec-
tive methods. An integral distribution curve of chemical composition
of the sample can be obtained by plotting $(1/2)W^{(n)} + \sum W^{(n-1)}$
against $\overline{\alpha}^{(n)}$. The curve obtained depends on the value of K used.
The curve obtained depends on the value of K used. The value of
K is varied to have the best agreement between the calculated
integral distribution curve and the experimental data. The calcula-
tions were carried out by use of an NEAC 2200 computer, model 300
with memory size of 65 KC.

RESULTS

The experimental results of fractionation by the SP method and
CE method are shown in Tables 2 and 3, respectively, and also plotted
in Figs. 1 and 2. The yields were 99.6% and 97.8%, respectively.

TABLE 2. Fractionation Results by the SP Method

Fraction no.	Weight fraction	AN content (mole %)	$[\eta]$ (dl/g)
1	0.0555	42.8	2.21_5
2	0.1097	42.6	1.83_0
3	0.0748	42.7	1.57_1
4	0.1073	42.7	1.28_6
5	0.0151	42.3	0.99_8
6	0.0408	41.7	0.93_1
7	0.0170	41.4	0.84_5
8	0.2450	35.2	1.52_5
9	0.1741	34.6	1.11_4
10	0.0826	33.7	0.84_7
11	0.0549	33.1	0.59_7
12	0.0139	32.2	0.50_0
13	0.0092	–	0.38_6
	Average	37.6	

Both values of the average AN content calculated from two series of fractionation results are in good agreement with the value of the original mixed sample, 37.9_5 mole %. In Fig. 1, it is found that the distribution curve obtained by the CE method is more clearly separated into two peaks, corresponding to two components in original sample, than that by the SP method. In the distribution curves of Fig. 2, the difference between $[\eta]$ values of fractions 6 and 7 obtained by the CE method is larger than the difference between $[\eta]$ values of fractions 7 and 8 by the SP method.

The calculated integral distribution curves of chemical composition depend on the value of K. The values of K chosen to have the best agreement between the calculated curves and the experimental data are 0.06 in the CE method and 0.04 in the SP method, respectively. The curves of AN content calculated with these values of K are shown in Fig. 1. Here, it is to be noted that the value of K used in the CE method is larger than that in the SP method.

TABLE 3. Fractionation Results by the CE Method

Fraction no.	Weight fraction	AN content (mole %)	$[\eta]$ (dl/g)
1	0.018_1	30.1	0.24_2
2	0.014_1	33.1	0.38_7
3	0.045_6	33.3	0.54_1
4	0.176_3	33.7	0.95_7
5	0.216_1	34.2	1.47_4
6	0.030_8	34.2	1.49_9
7	0.016_1	39.0	0.79_8
8	0.043_0	41.2	0.72_7
9	0.262_1	42.1	1.25_2
10	0.173_4	42.9	1.82_3
11	0.004_4	42.6	–
	Average	38.0	

From these comparisons, it may be concluded that the CE method is more effective than the SP method in the compositional fractionation of copolymer.

DISCUSSION

The physical meaning of K is given in Eq. (2). The values of $(x_{1A} - x_{1B})$ and $(x_{2A} - x_{2B})$ are the same in both SP and CE methods. It was shown elsewhere [2] that $v_1 - v_1' > 0$, $v_2 - v_2' > 0$ and also that the values of $(v_1 - v_1')$ and $(v_2 - v_2')$ are larger if the AN content of the copolymer is larger. Moreover, in general, phase separation in the system containing a component with higher molecular weight occurs in broader region of the phase diagram than that in the system containing a component with lower molecular weight. Therefore, the values of $(v_1 - v_1')$ and $(v_2 - v_2')$ should become larger as either the molecular weight or the AN content of the copolymer or both increase.
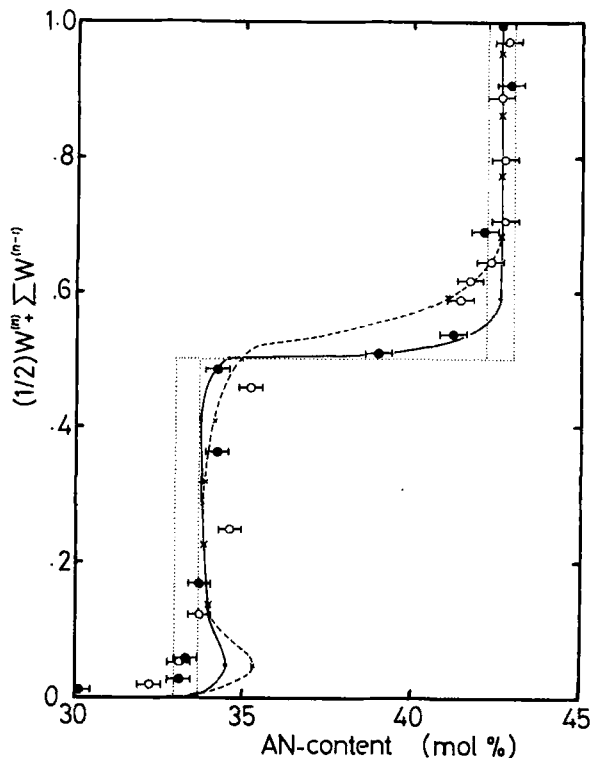
FIG. 1. Integral distribution curves of AN content: (●) experimental data by the CE method; (○) experimental data by the SP method; (– · –) calculated data for the CE method; (-- ×) calculated data for the SP method.

In the CE method, the component with higher AN content and higher molecular weight remains in the fractionation system for all steps of fractionation. In the SP method, on the other hand, the component with higher AN-content and higher molecular weight is contained in the fractionation system on the early stage of the fractionation, but, as the fractionation proceeds, the component is gradually removed from the system. Thus, the values of $(v_1 - v_1')$ and $(v_2 - v_2')$ in the CE method are generally larger than the values in the SP method. Therefore, it may be clear that the higher efficiency of the CE method than the SP method results from the difference in $(v_1 - v_1')$ and $(v_2 - v_2')$.
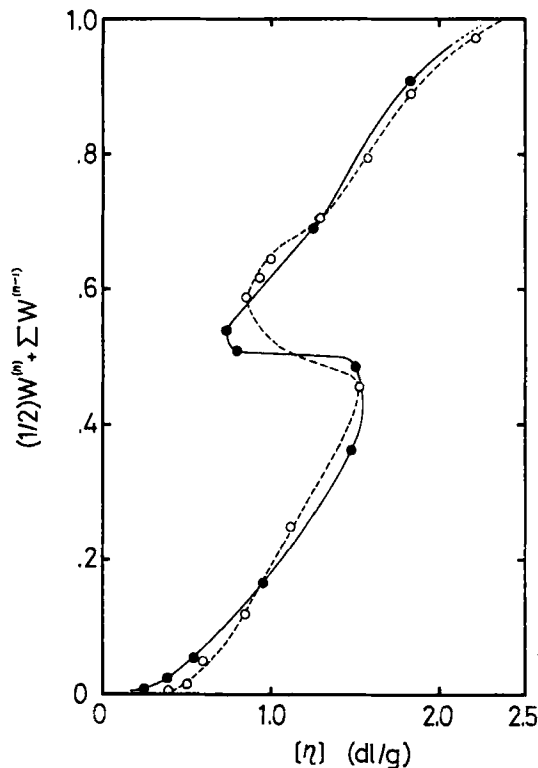
FIG. 2. Integral distribution curves of limiting viscosity index:
(—●) data by the CE method; (--o) data by the SP method.

In the calculated curves of Fig. 1, reversals of AN content are
observed in the region of low AN content. This may result from the
lower efficiency of compositional fractionation in the region of lower
molecular weight. That is, Eq. (1) shows that if the polymerization
degree X is small, the efficiency of fractionation by α (AN content in
the present work) becomes low. Since Eq. (9) is assumed for the
distribution of polymerization degree in the calculation of chemical
composition distribution, the sample is assumed to contain an amount
of low molecular weight components. Therefore, it is understandable

that the reversal of AN content is observed in the calculated curves in Fig. 1.

In practice, however, the reversals were not found in the experimental results. This may be due to the fact that the samples used in the actual experiments did not contain molecular species of low molecular weights because of the repeated purification of the samples. Strictly speaking, moreover, the two components in the sample must · have statistical distributions of chemical composition as pointed out by Stockmayer [7-9], but the distribution was not assumed in the present calculations. Considering these simplified assumptions, the disagreement between the calculated curves and experimental data in the region of low AN content in Fig. 1 should not be taken seriously.

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