The Fractionation of Copolymers by Chemical Composition

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SUMMARY

Phase diagrams for the system of methyl ethyl ketone, cyclo-hexane, and styrene-acrylonitrile copolymer were determined. The phase diagrams indicate that the copolymer may be fractionated by chemical composition in this system. Discussions of the thermo-dynamics are also presented, to show that copolymers can effectively be fractionated into fractions of different compositions if a system can be found in which the difference between the Flory interaction parameters (χ parameters) of two constituents of the copolymer with solvent is sufficiently large. Theoretically, the fractionation of copolymer must always occur to a certain extent, depending both on chemical composition and molecular weight. The composition frac-tionation results of styrene-acrylonitrile copolymers are given to confirm the discussions.

INTRODUCTION

Random copolymers, in general, have distributions of molecular weight, chemical composition, and monomer sequence length. It is well known that the distribution of chemical composition greatly in-fluences the various properties of copolymers. For example, Molau [1] showed that the texture of blends of styrene-acrylonitrile co-polymers is often heterogeneous if the chemical compositions of the copolymers blended are slightly different. Scott [2] discussed the

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compatibility of copolymers using the thermodynamic theory of polymer mixtures and showed that a copolymeric mixture may separate into distinct phases if the sample does not have a sharp distribution in chemical composition.

To study the chemical composition distribution, there are several methods, such as density gradient sedimentation, fractionation, turbidity, light-scattering measurements in different solvents, and the NMR method. In case the densities of element monomers are different, density gradient sedimentation may be most promising, but, unfortunately, the method is not popular because of technical difficulties. The other methods, which may be easily carried out in practice, have some disadvantages. For example, light-scattering measurements in different solvents as well as the NMR method can give information concerning the broadness of chemical composition distribution but cannot give the distribution curve. The disadvantages in applying the turbidity method to the determination of chemical composition distribution may be the same as the disadvantages in using the method for the determination of molecular weight distribution; the method has not been used frequently recently. In contrast, the fractionation method has the following merits: The chemical composition distribution can be determined with a relatively simple technique, and fractions having different chemical compositions can be separately obtained by this method.

It is the purpose of this paper to study the phase-separation phenomena of copolymer solution and to discuss the principle of fractionation by chemical composition.

EXPERIMENTAL

Materials

The copolymers used in this experiment are styrene-acrylonitrile random copolymers. The samples were purified by dissolving pellets of the samples in N, N-dimethylformamide and precipitating them with methanol. The characteristics of the samples are shown in Table 1. The measurements of intrinsic viscosities were carried

Table 1

Sample	AN content (wt. %)	$M_n \times 10^{-4}$	$[\eta]$ (dl/g)
S-1	31. 2	8. 0	0.79_5
S-2	25. 9	7. 5	0.66_4
S-3	20. 8	9. 1	0.74_0

out in methyl ethyl ketone (MEK) at 35.00 ± 0.01°C with a visco-
meter of the Ubbelohde type, which was designed for the kinetic
energy correction to be negligible. The chemical compositions of
the samples were determined by the micro-Dumas method. The
number-average molecular weights were determined with a Mech-
rolab high-speed membrane osmometer in MEK at 25.0°C.

The acrylonitrile content of 24.0 wt.% corresponds to the azeo-
tropic composition for this copolymer, so that the chemical com-
position distributions are considered to be narrow for S-2 and S-3
and to be considerably broad for S-1. Shimura [3] showed the follow-
ing viscosity equations for the samples containing acrylonitrile of
24.0 and 46.3 wt.%;

$$[\eta] = 3.6 \times 10^{-4} \, Mw^{0.62} \tag{1}$$

$$[\eta] = 5.3 \times 10^{-4} \, Mw^{0.61} \tag{2}$$

in MEK at 30.0°C. From these equations the weight-average mole-
cular weights of the samples are estimated to be from 1.9 to
2.5×10^5. Therefore, molecular weight distributions of these
samples must be considerably broad.

MEK was purified by distillation from $KMnO_4$ after drying with
Na_2SO_4 and K_2CO_3. Cyclohexane was washed several times with
sulfuric acid and passed through a silica gel column to remove ben-
zene and then distilled from metalic sodium.

Fractionation

The fractionation was carried out by a successive precipitation
method. A mixture of the sample S-1 and S-3 was fractionated into
21 fractions from 5.0% solution in MEK using cyclohexane as the
precipitant at 35.00 ± 0.01°C.

Determination of Phase Diagram

The phase-boundary curves distinguishing a region of homogen-
eous phase from a region of heterogeneous phase were determined
by the titration method. The MEK solution of the sample was placed
in a glass tube kept at constant temperature (35.00 ± 0.01°C) and
titrated with cyclohexane. The volume of cyclohexane to cause the
first phase separation was determined visually. During the experi-
ment, the solution was continuously stirred by a magnetic stirrer.

Tie lines were determined from the data of phase separation. A
solution having a ternary composition, which was inside the phase-
boundary curve, was sealed into a glass tube and was immersed in
a constant-temperature bath for several days, until the phase separ-
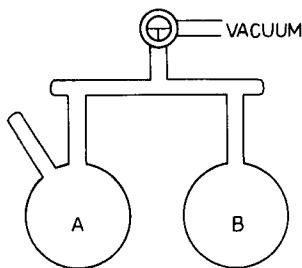ation was completed. The supernatant phase was weighed into a

Fig. 1. Vacuum distillation bulbs.

distillation bulb A in the vacuum line (Fig. 1). Polymer concentration was determined by weighing the residue after completing vacuum distillation. The rate of MEK and cyclohexane in the distillate was determined from the measured refractive index of the distillate and the calibration curve made in advance.
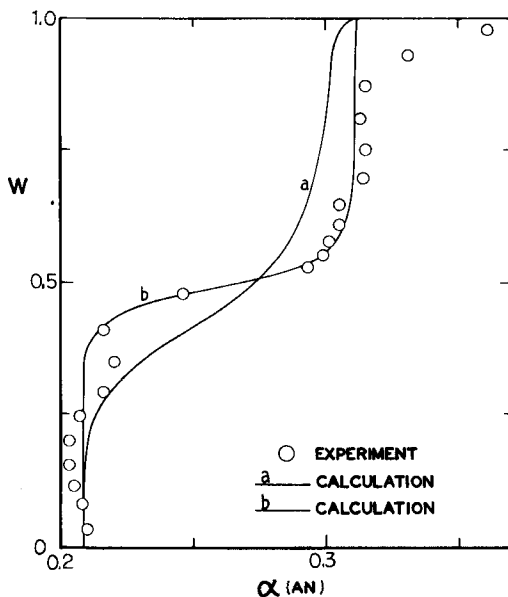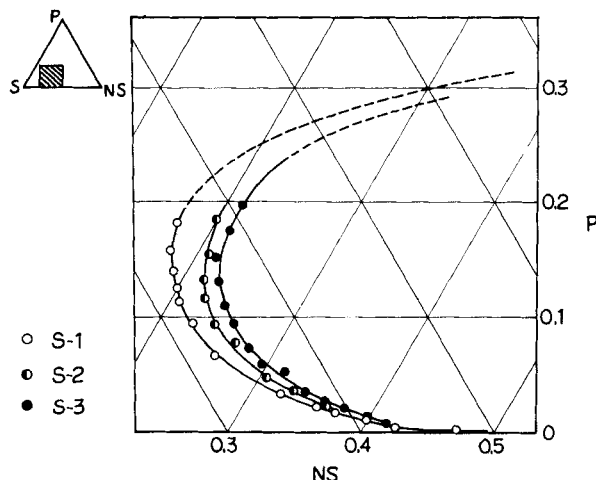

Fig. 2. Integral acrylonitrile content distributions of styrene-acrylonitrile copolymer obtained by experiment and calculations in conditions of (a) $K_n = 0.01, \sigma_n = 0$ and (b) $K_n = 0.02, \sigma_n = 0.003$. α, acrylonitrile content in weight fraction; W, cumulative weight fraction.

Fig. 3. Phase-boundary curves of the systems of styrene-acryloni-
trile copolymer (P), MEK (S), and cyclohexane (NS). Concentrations
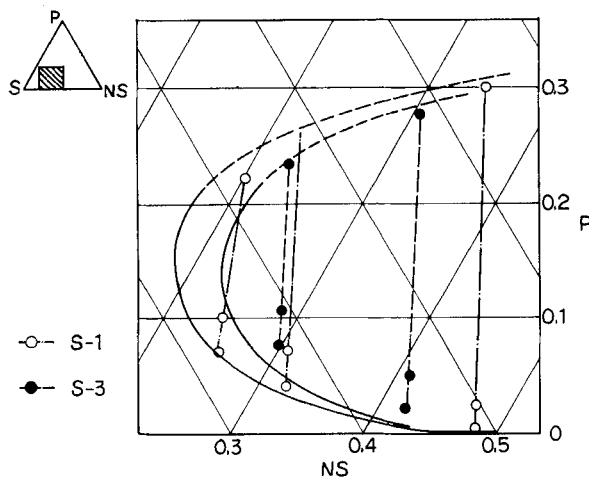are shown in weight fraction.

EXPERIMENTAL RESULTS

The result of the fractionation is shown in Fig. 2. The average
chemical composition of the fractions from Nos. 1 to 11 and of the
fractions from Nos. 12 to 21 are 31. 5 and 21. 5 wt. % of acrylonitrile,
respectively, which agree with the chemical compositions of the
original samples within the range of experimental error in nitrogen
analysis. Therefore, it may be concluded that the fractionation was
carried out effectively.

The phase-boundary curves for S-1, S-2, and S-3 and the tie
lines for S-1 and S-3 are shown in Figs. 3 and 4, respectively, as-
suming that the samples are monodisperse for chemical composi-
tion as well as for molecular weight. The phase separation points
shown in Fig. 3 are representatives of the experimental points.

DISCUSSION

The fractionation of copolymer by chemical composition is an
application of the phase-separation phenomenon of copolymer
solution. The following mixing free energy was given by Topchiev

Fig. 4. Tie lines of ths systems of styrene-acrylonitrile copolymer (P), MEK (S), and cyclohexane (NS). Concentrations are shown in weight fraction.

et al. [4] for the system of solvent (1) and heterogeneous copolymer A-B (2), applying the Flory-Huggins lattice model:

$$\Delta F_M = RT(n_1 \ln v_1 + \sum_{\gamma, \alpha} n_{\gamma, \alpha} \ln v_{\gamma, \alpha} + n_1 \sum_{\gamma, \alpha} v_{\gamma, \alpha} \chi_\alpha) \qquad (3)$$

where α denotes the mole fraction of A monomer in copolymer A-B; γ is the degree of polymerization; n_1, v_1 and $n_{\gamma, \alpha}$, $v_{\gamma, \alpha}$ are the numbers of molecules and the volume fractions of solvent (1) and copolymers (γ, α) denoted by suffix, respectively; and χ_α is the interaction parameter of a solvent molecule with copolymer A-B of composition α. χ_α may be expressed by the following approximate equation:

$$\chi_\alpha = \chi_A \alpha + \chi_B (1 - \alpha) \qquad (4)$$

if we express the interaction parameters of a solvent molecule with A monomer and B monomer by χ_A and χ_B, respectively. From Eq. (3), the chemical potential for component (γ, α) is given by

$$\mu_{\gamma, \alpha} - \mu_{\gamma, \alpha}^0 = RT[\ln v_{\gamma, \alpha} - (\gamma - 1) + v_2 \gamma (1 - 1/\bar{\gamma}_n)$$

$$+ (1 - v_2)\gamma \chi_\alpha] \qquad (5)$$

from which it follows that

$$\ln(v'_{\gamma,\alpha}/v_{\gamma,\alpha}) = \gamma(\sigma + K\alpha) \tag{6}$$

$$K = (v'_2 - v_2)(\chi_A - \chi_B) \qquad \chi_A > \chi_B \tag{7}$$

$$\sigma = [v_2(1 - 1/\bar{\gamma}_n) - v'_2(1 - 1/\bar{\gamma}'_n) - v_2(1 - v_2)\bar{\chi}_n$$
$$+ v'_2(1 - v'_2)\bar{\chi}'_n] + (v'_2 - v_2)\chi_B \tag{8}$$

at equilibrium between the supernatant phase and the precipitate phase, denoted by the prime. According to Eq. (6), in general, the fractionation of copolymer must occur depending upon both chemical composition and molecular weight.

If the system is composed of solvent (1), nonsolvent (2), and heterogeneous copolymer A-B (3) as in the present experiment, the calculation is more complicated but straightforward. Using the same assumptions [5] as used for Eq. (3), we have

$$\Delta F_M = kT[n_1 \ln v_1 + n_2 \ln v_2 + \sum_{\gamma,\alpha} n_{\gamma,\alpha} \ln v_{\gamma,\alpha}$$
$$+ n_1 v_2 \chi_{12} + n_1 \sum_{\gamma,\alpha} v_{\gamma,\alpha} \chi_{1\alpha} + n_2 \sum_{\gamma,\alpha} v_{\gamma,\alpha}\chi_{2\alpha}] \tag{9}$$

$$\chi_{1\alpha} = \chi_{1A}\alpha + \chi_{1B}(1 - \alpha) - \chi_{AB}\alpha(1 - \alpha)$$

$$\chi_{2\alpha} = \chi_{2A}\alpha + \chi_{2B}(1 - \alpha) - \chi_{AB}\alpha(1 - \alpha) \tag{10}$$

where χ_{iA} and χ_{iB} are the interaction parameters of solvent (i) with the A and B monomers, respectively. Even if all solvent and monomer molecules do not have the same volume, as is generally so, the above equations are still useful if we replace α by volume fractions. Then the chemical potential of component (γ, α) becomes

$$\mu_{\gamma,\alpha} - \mu^0_{\gamma,\alpha} = RT[\ln v_{\gamma,\alpha} - (\gamma - 1) + v_{3\gamma}(1 - 1/\bar{\gamma}_n) - v_1 v_{2\gamma}\chi_{12}$$
$$+ v_{1\gamma}\chi_{1\alpha} + v_{2\gamma}\chi_{2\alpha} - v_1 v_{3\gamma}\chi_{1n} - v_2 v_{3\gamma}\bar{\chi}_{2n}] \tag{11}$$

where $\bar{\chi}_{in} = \sum\limits_{\gamma,\alpha} n_{\gamma,\alpha} \gamma \chi_{i\alpha} / \sum\limits_{\gamma,\alpha} n_{\gamma,\alpha} \gamma$. Assuming $\chi_{iA} > \chi_{iB}$ and χ_{AB} to be negligible, as in the theory of Topchiev et al., the following equations are obtained:

$$\ln(v'_{\gamma,\alpha} / v_{\gamma,\alpha}) = \gamma(\sigma^* + K^*\alpha) \tag{12}$$

$$K^* = (v_1 - v'_1)(\chi_{1A} - \chi_{1B}) + (v_2 - v'_2)(\chi_{2A} - \chi_{2B}) \tag{13}$$

$$\sigma^* = [v_3(1 - 1/\bar{\gamma}_n) - v'_3(1 - 1/\bar{\gamma}'_n)$$
$$- (v_1 v_2 - v'_1 v'_2)\chi_{12} - v_1 v_3 \bar{\chi}_{1n} + v'_1 v'_3 \bar{\chi}'_{1n}$$
$$- v_2 v_3 \bar{\chi}_{2n} + v'_2 v'_3 \bar{\chi}'_{2n}] + [(v_1 - v'_1)\chi_{1B}$$
$$+ (v_2 - v'_2)\chi_{2B}] \tag{14}$$

which was the same form as Eq. (6) except K^* and σ^* are substituted for K and σ, respectively. Thus in a two-solvent system the same conclusions are obtained as in one-solvent system with regard to fractionating a copolymer by chemical composition.

If χ_{AB} is not negligible, Eq. (10) should be expressed by the following form:

$$\chi_\alpha = \chi_{AB}\alpha^2 + [(\chi_A - \chi_B) - \chi_{AB}]\alpha + \chi_B \tag{10'}$$

which means that χ_α is not always a monotonically increasing function in the overall range $0 \leqslant \alpha \leqslant 1$. Therefore, it is very difficult to speculate how the fractionation of copolymer by chemical composition should be carried out. Nevertheless, under the condition of $(\chi_A - \chi_B) \geqslant \chi_{AB}$, it is certain that the fractionation of copolymers must depend upon both molecular weight and chemical composition, and even if $(\chi_A - \chi_B) < \chi_{AB}$, the conclusion is the same in the range of $(\chi_{AB} + \chi_B - \chi_A)/2\chi_{AB} < \alpha < 1$.

Thus it is clear that the fractionation of a copolymer by chemical composition must be best carried out by the dual fractionation or "cross-fractionation method" of Rosenthal and White [6], as was discussed by Kudryavtseva and Litmanovich [7]. However, the difficulty in cross fractionation is so serious that the method is not considered very practicable. That is, to carry out the cross fractionation effectively, it is necessary to find two solvent-nonsolvent systems in which $\chi_A > \chi_B$ and $\chi_A < \chi_B$. For example, in the fractionation of vinyl chloride-vinyl acetate copolymer, we could find a system in which $\chi_{VCl} > \chi_{VAc}$ but could not find a system in which $\chi_{VCl} < \chi_{VAc}$ [8].

Therefore, it seems meaningful to study the effectiveness of the chemical composition fractionation by one-direction fractionation

carried out in one solvent-nonsolvent system. The method seems
promising if it is possible to find a system in which $(\chi_A - \chi_B)$ is
large. In practice, Fuchs [9], fairly successfully, fractionated vinyl
chloride-vinyl acetate copolymer having the average chlorine con-
tent 33.3% in several systems in which χ_{VCl} was always greater
than χ_{VAc}.

As is clear from the above discussion, the chemical composition
distribution curves may be calculated from the following equations
of Kudryavtseva and Litmanovich [7], which can be derived from Eq.
(6) as well as from Eq. (12), irrespective of whether the system is
binary or ternary. That is,

$$w_{\gamma,\alpha}^{\prime(n)} = w_{\gamma,\alpha}^{(n-1)} \frac{1}{1 + (1/R_n) \exp\{-\gamma(\sigma_n + K_n\alpha)\}} \tag{15}$$

$$W'^{(n)} = \int_0^\infty d\gamma \int_0^1 w_{\gamma,\alpha}^{\prime(n)} \, d\alpha$$

$$\bar{\alpha}'^{(n)} = \frac{1}{W'^{(n)}} \cdot \int_0^1 \alpha \, d\alpha \int_0^\infty w_{\gamma,\alpha}^{\prime(n)} \, d\gamma \tag{17}$$

where $w_{\gamma,\alpha}^{\prime(n)}$ and $w_{\gamma,\alpha}^{(n-1)}$ are the fractions of distribution in γ and α
for the nth fraction and for the sample remaining in solution after
the separation of the (n — 1)th fraction, respectively; $W'^{(n)}$ is the
weight of the nth fraction; $\alpha'^{(n)}$ the average chemical composition
of the nth fraction; and R_n the volume ratio of the precipitate phase
and the supernatant phase in the nth-phase separation. The appli-
cation of the theory on our fractionation data is shown in Fig. 2. The
calculated curves were obtained by assuming that the arbitrary con-
stants K_n and σ_n are (a) $K_n = 0.01$ and $\sigma_n = 0$, (b) $K_n = 0.02$ and
$\sigma_n = -0.003$, and also that the sample was fractionated into 10 frac-
tions. The model sample used in the calculation is a mixture of
two samples having the chemical composition $\alpha = 0.312$ and 0.208
but no molecular weight distribution ($\gamma = 2.5 \times 10^3$). Although in
our experiment the sample was fractionated into 21 fractions and
is believed to have a broad molecular weight distribution, the agree-
ment between the calculated result with the conditions of (b) and
the experimental result is satisfactory, at least qualitatively. From
the comparison it is clear that the fractionation can be carried out
effectively if K_n for the copolymer-solvent system is large enough.

The conclusions obtained above may be confirmed from the
phase diagram. It is found in Fig. 3 that the solution containing the
copolymer of the smaller acrylonitrile content requires a greater
amount of cyclohexane for the phase separation to occur. Although
the molecular weight of S-3 is larger than that of S-1 and S-2, the
system containing S-3 requires a greater amount of precipitant than
the systems containing the other two samples. This confirms that

the phase separation occurs mainly as a result of the effect of chemical composition in this system. Strictly speaking, however, the effect of molecular weight is not completely negligible, since it appears that the curve of S-2 is closer to curve of S-3 than to that of S-1.

Figure 4 shows $v_1 > v_1'$, $v_2 > v_2'$, and $v_2/v_1 \cong v_2'/v_1'$ in our system. In the system composed of solvent, nonsolvent, and homopolymer, v_2/v_1 is generally larger than v_2'/v_1' because good solvent is included in the precipitate phase more than poor solvent. Therefore, the present result may appear to be unreasonable, but it is understandable if we take into account that the chemical composition fractionation is possible in the case of large K^* and K^* becomes larger when $v_1 > v_1'$ and $v_2 > v_2'$, as can be understood from Eq. (13).

It appears that the polymer concentrations at the critical points (v_{3c}) are nearly 15% in Fig. 4. This means that the value of v_{3c} in these systems is remarkably larger than the value for ordinary polymers, including copolymers having homogeneous chemical composition, in which the value of v_{3c} is usually a few per cent or so, even if the polymers have broad molecular weight distribution. Therefore, the large v_{3c} may arise from the compositional heterogeneity of the copolymer. For the system composed of polymer (1) and polymer (2) and solvent (0), Scott [10] shown that the volume fraction of solvent at the critical point is obtained from the following equation:

$$v_{0c} \cong 1 - (1/2\chi_{12})[(1/x_1)^{1/2} + (1/x_2)^{1/2}]^2 \qquad (18)$$

assuming $|\chi_{10} - \chi_{20}| \ll 1$ and $x_1^{1/2} < x_2 < x_1^2$. Here the χ_{ij}'s are interaction parameters between i and j components, while $x_1 = V_1/V_0$, $x_2 = V_2/V_0$, and the V_i's are molal volumes of the i component, respectively. Since v_{3c} in our case is the same as $v_{1c} + v_{2c} = (1 - v_{0c})$ in Scott's case, we can calculate v_{3c} from Eq. (18), using x_1 and $x_2 = 2.5 \times 10^3$ and assuming several values for χ_{12}. Then we have $v_{3c} = 0.01, 0.08,$ and 0.16 for $\chi_{12} = 0.1, 0.01,$ and 0.005, respectively. Thus, from Scott's theory, too, it may be certain that the total polymer concentration at the critical point is considerably high in the solution containing two polymers having slightly different chemical properties. If this is true, the fractionation by chemical composition may be effectively carried out in solutions of considerably high concentration.

ACKNOWLEDGMENTS

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