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Phase-Separation Phenomena of Copolymer Solutions and Fractionation of Copolymers by Chemical Composition

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SUMMARY

Precipitation temperature-total polymer concentration diagrams for toluene solutions of two styrene-acrylonitrile copolymers different in chemical composition and their mixtures were determined and then triangular phase diagrams of this system were constructed from these diagrams. It is speculated from the triangular phase diagrams and experimentally shown that the copolymer may be effectively fractionated by chemical composition in this system.

INTRODUCTION

Fractionation of copolymers by chemical composition is an application of the phase-separation phenomena of copolymer solution.

The ternary system consisting of a solvent and two copolymer samples which differ in chemical composition provides a simplified prototype of a fractionation system for copolymers which are heterogeneous in chemical composition.

However, only a few studies of phase-separation phenomena of such ternary systems have been reported [1, 2]. No phase diagram of ternary system has so far been reported. It is the purpose of this work to study the phase-separation phenomena of the ternary system consisting of a solvent and two copolymer samples which differ in chemical composition, and then to discuss the principles of the fractionation of the copolymer by chemical composition.

EXPERIMENTAL

Materials

The copolymer samples used in the present work are styrene-acrylonitrile random copolymers. The samples were prepared by bulk polymerization of mixtures of two monomers, at 60°C under nitrogen gas stream, in the ratios shown in Table 1. The polymerizations were stopped at low conversion by pouring the reaction mixture into methanol, so that the samples are considered to have sharp distributions in chemical composition. The copolymers obtained were dissolved in methyl ethyl ketone, precipitated and washed with methanol, and dried in vacuo. The chemical compositions of samples determined by the micro-Kjeldahl method [3], and the number-avarage molecular weights determined with a high-speed membrane osmometer of Hewlett-Packard 502 in methyl ethyl ketone at 25°C are shown in Table 1.

TABLE 1. Samples of Styrene-Acrylonitrile Copolymer

	Copolymer			Reaction mixture		
Sample	AN (wt-%)	$\overline{M}_n \times 10^{-4}$	Conversion (%)	St (g)	AN (g)	BPO (g)
A-23	23.3	16.2	6.5	276.1	76.4	1.472
A-21	21.2	17.9	6.0	289.8	64.2	1.913

Toluene was washed several times with concd H_2SO_4 and then with water, dried by $CaCl_2$, and distilled over sodium wire in nitrogen gas. Methyl ethyl ketone was purified by distillation with $KMnO_4$ in nitrogen gas after drying with Na_2SO_4 and K_2CO_3. Methanol was distilled after drying with $CaCl_2$.

Determination of Phase Diagram

Precipitation temperatures (T_p) of two copolymers A-23 and A-21 and their mixtures in toluene were visually determined [4] in a test tube. To mix the two copolymers, both copolymers were thoroughly dissolved in methyl ethyl ketone and then precipitated with methanol. The copolymer mixtures obtained were washed with methanol and dried in vacuo. The mixing ratios of the samples are shown in Table 2. The test tube used to observe the precipitation temperature has a short cooling column on its wall to prevent evaporation of solvent. The test tube containing a sample solution was immersed in a well-stirred bath whose temperature could be varied slowly. The difference between T_p's determined by decreasing and increasing the solution temperature was within 0.2°C

TABLE 2. Copolymer Mixtures Used in Determination of Phase Diagrams

Mixture	Wt-% of A-23 in mixtures
0.50	49.9
0.24	24.3
0.19	19.0
0.05	4.6_9

Toluene solutions of mixed samples whose compositions are in the two-phase region at 60°C were sealed in glass tubes and immersed in a thermostat for several days until the phase separation was completed. A portion of the supernatant phase was quickly transferred into a weighing bottle by using a preheated pipet, and then the total polymer concentration in the solution was determined. The total polymer concentration of the precipitated phase was determined by the same method. The mixing ratios of two copolymers in the sample thus separated were determined by measuring the nitrogen content of the samples.

Fractionation Procedure

Fractionation was carried out by a successive precipitation method. A mixture of the sample A-23 (3.9999 g) and A-21 (4.0000 g) was fractionated into 17 fractions in a toluene solution by decreasing the temperature stepwise from 66.0 to 2.5°C. Since the polymer concentration becomes too dilute if the fractionation is repeated, the solutions were concentrated by evaporation. The total polymer concentration at which the first fraction was separated was about 0.667 g/100 ml and the concentrations in other cases were lower than this concentration. The characteristics of the fractions were determined by the same method as those of the original samples.

RESULTS

Precipitation temperature-total polymer concentration diagrams for toluene solutions of the two samples A-23 and A-21 and their mixtures are shown in Fig. 1. The profiles of the diagrams for solutions of the copolymer mixtures are appreciably different from those for mixtures of homopolymer fractions [4], whereas the profiles of the pure copolymers, which have fairly sharp distributions of chemical composition, are similar to those of homopolymer fractions.

The phase boundary curves in the triangular phase diagram at several temperatures, constructed from Fig. 1, are shown in Fig. 2. A triangular phase diagram for the system consisting of samples A-23, A-21, and toluene at 60°C is shown in Fig. 3, where the tie lines are shown by chainlike lines.

Fractionation results are summarized in Table 3 and Fig. 4. The yield was 95.9% of the original sample mixture. Average acrylonitrile content calculated from fractionation data agree with the value of the original sample mixture within experimental error. It may be concluded from Fig. 4 that the two copolymer samples can be separated effectively by fractionation in toluene.

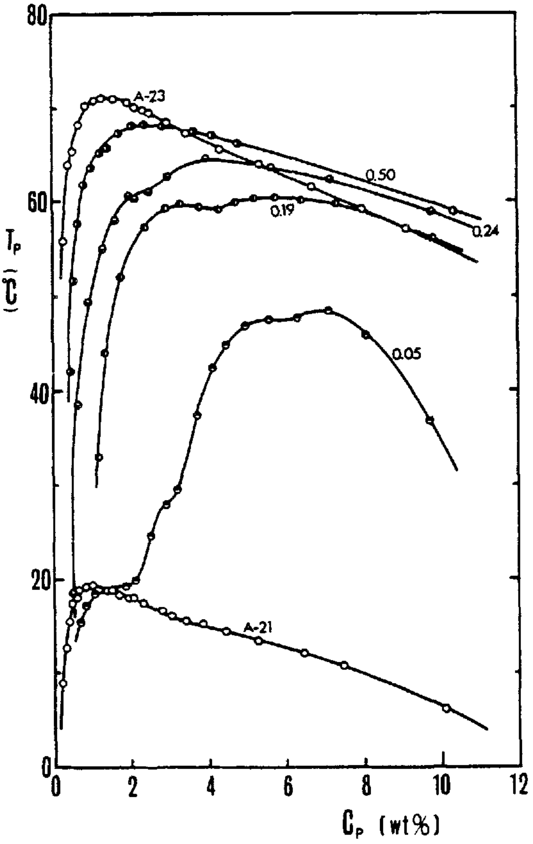

FIG. 1. Precipitation temperature (T_p) plotted against total polymer concentration expressed by wt-% (C_p) for the mixed St-AN copolymer samples (A-23 and A-21)—toluene system (see Table 2 for the polymer mixture composition).

DISCUSSION

If phase separation occurs in a copolymer solution, distribution of a copolymer component of polymerization degree γ and chemical composition α between two phases is given by [5, 6]

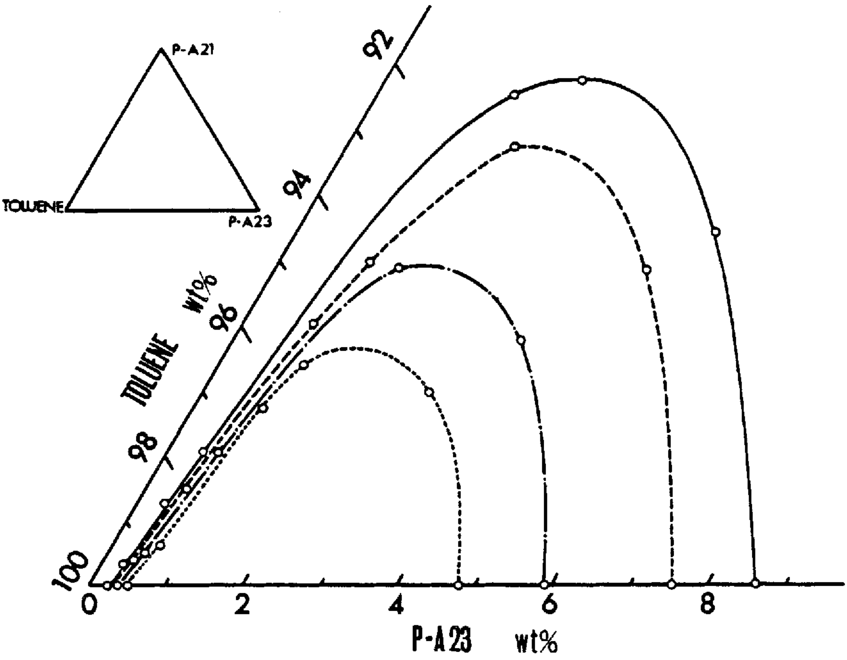

FIG. 2. Phase boundary curves for the system of A-23—A-21—toluene at 65°C (...), 63°C (— · —), 60°C (- -) and 58°C (——).

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

where $v'_{\gamma,\alpha}$ and $v_{\gamma,\alpha}$ are volume fractions of a component (γ,α) in the precipitated and supernatant phases, and σ is a fractionation parameter. In the case of a one-solvent system, K is given by

$$K = (v'_p - v_p)(\chi_A - \chi_B) \tag{2}$$

where v'_p and v_p are volume fractions of total copolymer in the respective phases, and χ_A and χ_B are the interaction parameters

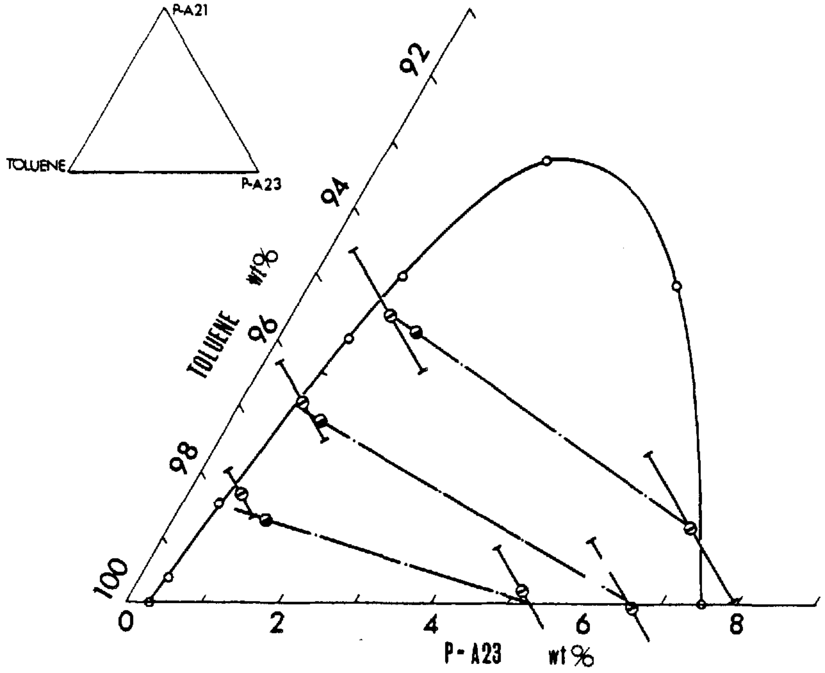

FIG. 3. Phase equilibria diagram for the system of A-23—A-21—toluene at 60°C. (— . —) Tie lines.

of the solvent with A- and B-monomer units. If K = 0, the partition of copolymer species between the two phases is controlled by molecular weight with no effect from chemical composition. If the absolute value of K is not so small, the two copolymer species which differ in chemical composition are distributed between the two phases in a different ratio, so that the choice of solvent has a large effect on the distribution of copolymers between phases.

Toluene is a good solvent for polystyrene but a nonsolvent for polyacrylonitrile, so that the difference between the interaction parameters of toluene with both monomer units A and B, $(\chi_A - \chi_B)$ may be considerably large. Therefore, the phase-separation temperature of the copolymer in toluene is sensitive to the change in chemical composition. In practice, as shown in Fig. 1, precipitation

TABLE 3. Fractionation Results

Fraction No.	w_i	AN (wt-%)	$\overline{M}_n \times 10^{-4}$
1	0.051	23.3	41.7
2	0.066	23.5	-
3	0.072	23.5	34.2
4	0.063	23.3	28.6
5	0.032	23.4	-
6	0.042	23.2	20.2
7	0.051	23.1	21.7
8	0.024	22.6	-
9	0.033	22.4	-
10	0.043	22.4	24.3
11	0.022	21.9	-
12	0.069	21.3	35.8
13	0.056	21.4	-
14	0.054	21.6	-
15	0.072	21.4	18.7
16	0.069	21.5	-
17	0.181	21.2	5.3
Mean		22.2	

temperatures of the two samples having almost equal molecular weights are very different, as much as 52°C, in spite of as small a difference as 2% in acrylonitrile content.

In the ternary phase diagram, Fig. 2, the two-phase region expands increasingly with decreasing temperature. Thus Fig. 2 implies that successive precipitation fractionation may be possible in this system if we decrease the solution temperature stepwise.

From the phase diagram shown in Fig. 3 it may be concluded that the precipitated phase separated from the master solution, in which the total polymer concentration is lower than about 4%,

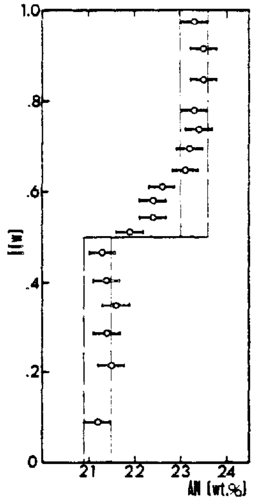

FIG. 4. Integral chemical composition distribution curve of the mixture of A-23 and A-21 constructed from fractionation data (see Table 3).

contains only A-23, though the experimental ambiguities in the nitrogen analysis are fairly high. Figure 4 shows a fractionation result of a mixture of the two copolymer samples in toluene. That is, this appears to support the conclusion obtained from Eq. (1) that copolymers heterogeneous in chemical composition can be effectively fractionated by chemical composition in the solvent having a large value of $(\chi_A - \chi_B)$.

The fractionation result is affected by molecular weight, too, as is expected from Eq. (1). That is, in the range from Fraction Nos. 1 to 6 and from 12 to 17, where every fraction consists of pure copolymer sample A-23 or A-21, molecular weight decreases in the order of fraction number, while in the range from Fraction Nos. 6 to 12, where every fraction is a mixture of the two samples, inversion of molecular weight is observed. This inversion of molecular weight can be explained from Eq. (1) which shows that no practical difference should be observed between distributions of two molecular species if their values of $\gamma(\sigma + K\alpha)$ in Eq. (1) are equal.

When phase separation occurs in solution of copolymer mixture, there may be two cases. One is the phase separation due to incompatibility of polymer mixtures and the other is the ordinary phase separation in a poor solvent. The phase-separation phenomena in ternary systems of two different species of homopolymers and a solvent have been studied theoretically and experimentally [1, 7-12]. It may be pointed out from those researches that two polymers of different chemical species are generally immiscible in the absence of a solvent unless their heat of mixing is virtually zero or negative. However, these two homopolymers may be mixed if they are dissolved in a common solvent and if the concentrations are very dilute. In this case the nature of the solvent is insignificant; those homopolymers are miscible simply because the solvent decreases the heat of interaction by dilution. Therefore, even if the samples are copolymers which differ only in chemical composition, there is a possibility that the two copolymers are separated due to incompatibility. However, this kind of phase separation is realized only if the difference between the chemical compositions of the two copolymer samples is appreciably large. Even if the chemical properties of the two monomer constituents are very different, the heat of interaction between two copolymer samples having similar compositions is generally so small that the copolymers cannot be separated due to incompatibility. For the samples in this work, examination of the data of Molau [2] and an equation of Scott on the condition for single-phase stability (Eq. 29 in Ref. 13) show that mixtures of samples A-23 and A-21 are compatible, so that phase separation due to incompatibility cannot occur in the system of A-23, A-21, and any common good solvent.

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