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Phase-Separation Phenomena of Random Copolymer Solution: Styrene-Acrylonitrile Random Copolymer-Toluene Systems

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ABSTRACT

To clarify the basis of fractionation of copolymers by chemical composition, the effects of chemical composition and molecular weight on the phase-separation phenomena of random copolymer solutions were studied. Two copolymer samples of styrene-acrylonitrile of different chemical composition were prepared and fractionated by molecular weight in the chloroform-methanol system. Precipitation temperature-polymer concentration diagrams for toluene solutions of these copolymer fractions were determined. Using the theory of Flory for ordinary homopolymer solution, θ-temperatures and ψ_1-parameters for respective samples were determined from the phase diagrams. The critical interaction parameter of each fraction was calculated from the critical temperature by using the values of θ and ψ_1 plotted against the value of $(1/X^{1/2} + 1/2X)$, where X is the ratio of the molar volumes of polymer and solvent. All data for both copolymer samples fall on a single straight line. From the results it is concluded that the interaction parameter, χ_1, at a certain temperature in a certain solvent depends on chemical composition of the copolymer sample, but the value of χ_1 at the phase-separation point is, essentially, determined by molecular weight only. Moreover, it is also concluded that phase-separation phenomena of random copolymer solutions can be treated within the framework of the Flory theory if the copolymer samples have sharp chemical composition distributions.

INTRODUCTION

Fractionation of copolymer is an application of the phase-separation phenomena of copolymer solution, and the fractionation of copolymer is governed by both chemical composition and molecular weight [1]. Therefore, it is important for progress in the fractionation of copolymers by chemical composition to study the effects of chemical composition and molecular weight on the phase-separation phenomena of copolymer solution.

Applying the Flory-Huggins lattice model, the free energy of mixing of a random copolymer homogeneous in chemical composition and molecular weight with a monomeric solvent is given by

$$\Delta F_M = kT\,[n_1 \ln V_1 + n_2 \ln V_2 + n_1 V_2\,\chi_{1\alpha}] \tag{1}$$

which is identical with that for ordinary homopolymers. Then the chemical potential of the solvent is expressed as:

$$\mu_1 - \mu_1^0 = RT\,[\ln(1 - V_2) + (1 - 1/X)V_2 + \chi_{1\alpha} V_2^2] \tag{2}$$

where n_1, v_1 and n_2, v_2 are the numbers of molecules and the volume fractions of solvent (1) and polymer (2), respectively, and $\chi_{1\alpha}$ is the interaction parameter of a solvent molecule with a copolymer molecule of chemical composition α, and X is equal to the ratio of the molar volume of the polymer to that of the solvent. Therefore, if the copolymer has no distribution in chemical composition, the statistical thermodynamic theory, well-established for ordinary homopolymer solutions, may be applicable to random copolymer solutions.

According to the theory of Flory [3], the temperature dependence of the interaction parameter χ_1 in two-component systems is given by

$$\chi_1 = (1/2 - \psi_1) + \psi_1 \theta / T \tag{3}$$

where ψ_1 is the entropy parameter and θ is the Flory temperature.

The critical interaction parameter, $(\chi_1)_c$, and the polymer concentration, $(v_2)_c$, are obtained by equating the first and second derivatives of Eq. (2) with respect to the concentration to zero:

$$(\chi_1)_c = 1/2 + (1/X^{1/2} + 1/2X) \tag{4}$$

$$(V_2)_c = 1/(1 + X^{1/2}) \tag{5}$$

From Eqs. (3) and (4), the relationship between the critical temperature and the chain length is

$$1/T_c = (1/\theta)\{1 + (1/\psi_1)(1/X^{1/2} + 1/2X)\} \tag{6}$$

The quantitative agreement between experimental data and Eqs. (4) and (6) has been extensively demonstrated, whereas discrepancies have often been found between $(v_2)_c$ values determined by experiments and theoretical values.

On the other hand, it is confirmed [4] that the concepts of the θ condition are valid for solutions of random copolymers, from the molecular weight dependence of intrinsic viscosity, under the conditions of the zero osmotic second virial coefficient $A_2 = 0$. From this fact it is expected that the thermodynamic relationships for homopolymer solutions mentioned above will also be valid for random copolymer solutions if there is no distribution in chemical composition. In the present work, based on the theory of Flory, we study the phase-separation phenomena in toluene solutions of styrene-acrylonitrile random copolymers and discuss the effects of chemical composition and molecular weight on phase-separation phenomena.

It has been reported elsewhere [5] that the precipitation temperature of the copolymer in toluene is very sensitive to the chemical composition, and a mixture of the two copolymer samples different in chemical composition is effectively fractionated in toluene. Therefore, the system composed of styrene-acrylonitrile random copolymer and toluene is suitable for the present purpose.

EXPERIMENTAL

Copolymerization

The styrene and acrylonitrile monomers used in the copolymerization were washed several times with dilute sodium hydroxide solution, followed by repeated water washing, and then dried over calcium chloride. The monomers were distilled under reduced nitrogen atmosphere just before use. The copolymer samples were prepared by bulk polymerization of mixtures at 60° C under nitrogen atmosphere in the ratios shown in Table 1. To obtain samples whose chemical composition distributions are sharp, the copolymerizations were stopped at low conversion by pouring the reaction mixtures into an excess amount of methanol. The copolymers obtained were dissolved in methyl ethyl ketone, precipitated, washed with methanol, and dried in vacuo at room temperature. This procedure was repeated twice. The chemical compositions of the copolymer samples were determined by the micro-Kjeldahl method, as shown in Table 1.

TABLE 1

	Monomer mixture			Copolymer	
Sample	St (g)	AN (g)	BPO (g)	Conversion (%)	AN content (wt%)
B-21	161.88	38.40	0.310	4.5	21.1
B-23	156.53	43.98	0.303	5.0	23.2

Fractionation

The copolymer samples thus obtained were fractionated using chloroform and methanol as solvent and precipitant, respectively, at 30.0 ± 0.01°C by a successive precipitation method. Copolymer sample B-21 and B-23 were fractionated into 7 and 8 fractions, respectively. All the fractions were again purified and their chemical compositions were determined by the same method as for the whole polymers. The chemical compositions of the respective fractions agreed with those of the whole polymers within the experimental error of nitrogen analysis. The number-average molecular weights of the fractions were determined with a high-speed membrane osmometer (Hewlett-Packard 502) in methyl ethyl ketone at 25° C.

Solvents

Toluene, used as the solvent for the determination of phase diagrams, was purified as follows: First-grade toluene was shaken with concentrated sulfuric acid until no color remained in the acid layer. It was further shaken with dilute sodium hydroxide and then with water, dried by shaking with calcium chloride, followed by fractional distillation over sodium wire in a dried nitrogen gas stream. Methyl ethyl ketone was purified by distillation with potasium permanganate in a dried nitrogen gas stream after drying with anhydrous sodium sulfate and potassium carbonate. Chloroform was purified by distillation after drying over calcium chloride. Methanol was distilled after drying with calcium chloride.

Determination of Phase Diagram

The precipitation temperatures, T_p, of the several fractions of B-21 and B-23 in toluene were visually determined in a test-tube which had a short cooling column on its wall to prevent evaporation of the solvent. The test-tube containing a sample solution was immersed in a well-stirred bath whose temperature could be slowly varied. During measurement of T_p, the test-tube solutions were stirred with a magnetic stirrer. The difference between T_p's, determined by decreasing and increasing the solution temperature, was within 0.2°C. The concentration of the copolymer at various points was determined from the weight of the sample dissolved.

RESULTS AND DISCUSSION

The copolymerizations were stopped at low conversion and the chemical compositions of these samples were chosen to be close to the azeotropic point (acrylonitrile content of 24 wt%). Each sample thus prepared was further fractionated into 7 or 8 fractions. Therefore, the copolymer fractions used in the phase-separation measurements are considered to have relatively sharp distributions of chemical composition and molecular weight, so that their toluene solutions may be treated, approximately, as two-components systems. Binary phase-diagrams were constructed from the data of phase-separation measurements by plotting precipitation temperature, T_p, against weight concentration of the copolymer fraction in the solution, C_p, as shown in Fig. 1. The shapes of the phase boundary curves in Fig. 1 are almost the same as those of ordinary homopolymers. Therefore, assuming the temperature above which coexistence of two phases in the solution is impossible to be the critical temperature, T_c, for copolymer solutions, too, the reciprocal of the critical temperature, $1/T_c$, observed for each

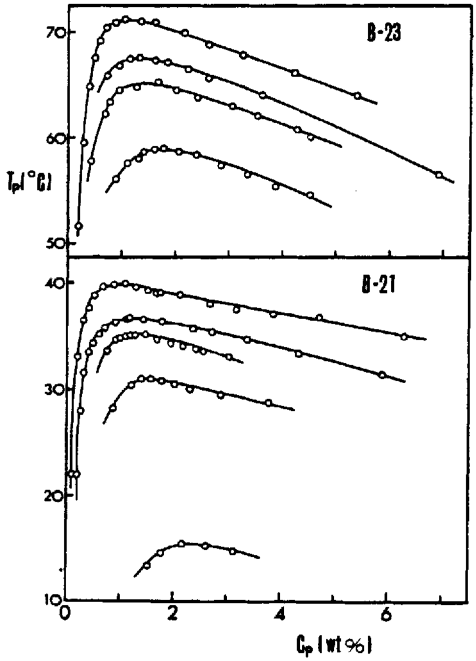

FIG. 1. Phase diagrams of St-AN copolymer-toluene solutions.

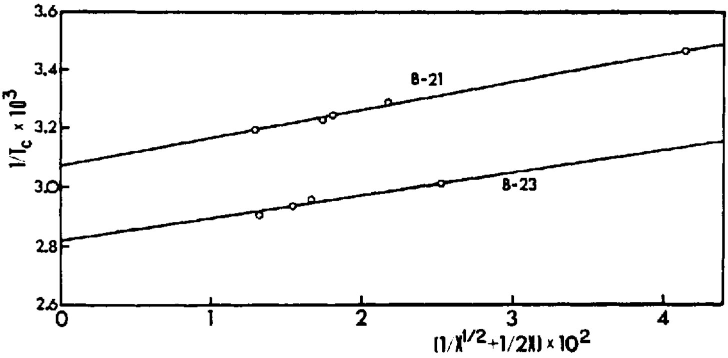

FIG. 2. The relationship between the reciprocal of the critical temperature, $1/T_c$, and $(1/X^{1/2} + 1/2X)$.

fraction of the two copolymer samples was plotted against $(1/X^{1/2} + 1/2X)$, in Fig. 2. The value of X for each fraction was calculated from the number-average molecular weight, using the densities [7] of polystyrene and polyacrylonitrile, 1.05 and 1.17, respectively, and the molar volume of toluene, 106.8_5 at 25°C. The plots thus obtained gave two straight lines for the respective samples, as predicted from Eq. (6). The values of θ, ψ_1, and κ_1 obtained from the intercepts and slopes of the lines are shown in Table 2.

Using these values of θ and ψ_1, the precipitation temperature, T_p, can be converted to χ_1 through Eq. (3). Using this interaction parameter, χ_1, phase boundary curves for some fractions were plotted against polymer volume fraction in solution, v_2, together with the theoretical ones calculated from the values of X in the same manner as by Flory [3] in Fig. 3. The volume fractions, v_2, were calculated from the weight concentration, using the densities of copolymer samples calculated from those of the two parent homopolymers and the density of toluene, 0.8636 at 25°C. The critical interaction parameters of all

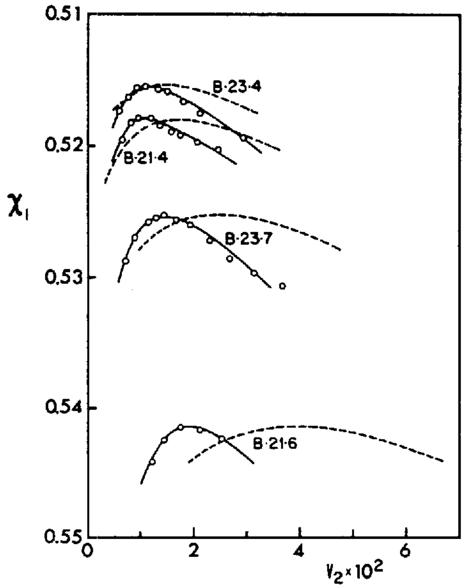

FIG. 3. Phase diagrams of St-AN copolymer-toluene solutions plotted as interaction parameter, χ_1, against volume fraction of copolymer in solution. Open circles are the experimental results. Dashed lines are the curves calculated from theory.

fractions obtained by experiments agreed with those obtained by calculation, as shown in Fig. 3, just as in the cases of ordinary homopolymers. Moreover, the values of $(\chi_1)_c$ of all the fractions converted from the respective values of T_c through Eq. (3) by using the values of θ and ψ_1 for the respective samples were plotted against the values of $(1/X^{1/2} + 1/2X)$ in Fig. 4. All data fall on a single straight line.

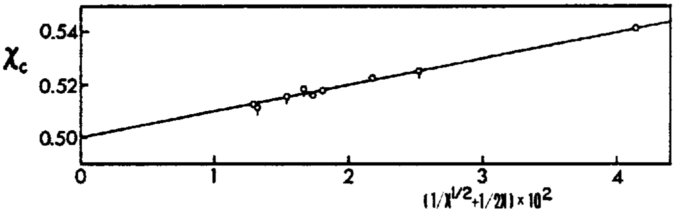

FIG. 4. The relationship between critical interaction parameter, χ_c, and $(1/X^{1/2} + 1/2X)$. (O) For sample B-21. (Ϙ) For sample B-23.

These facts show that, also in the case of copolymer, the critical interaction parameter, $(\chi_1)_c$, is determined only by X. The value of X is defined mainly by molecular weight, so that $(\chi_1)_c$ is essentially determined by molecular weight even in the case of copolymers. On the other hand, the value of interaction parameter, χ_1, for each sample at a certain temperature is determined from the values of θ and ψ_1 through Eq. (3), and the values of these parameters in a certain solvent depend upon the chemical compositions of the copolymer samples. Therefore, χ_1-parameters should also depend upon chemical composition of the copolymer samples. The relationship between χ_1-parameter and chemical composition is expressed as [8]

$$\chi_{1\alpha} = \chi_{1A}\alpha + \chi_{1B}(1 - \alpha) - \chi_{AB}\alpha(1 - \alpha) \tag{7}$$

where χ_{ij} is an interaction parameter characterizing first neighbor interactions between i and j units, and α is chemical composition expressed by the volume fraction of A-monomer units in copolymer A-B. It has been confirmed [8, 9] that this relationship can approximately explain the experimental results.

Thus we can speculate, in short, how phase-separation phenomena of copolymer solutions depend upon both chemical composition and molecular weight: χ_1 at a certain temperature in a certain solvent is determined by the chemical composition of the copolymer sample, but the value of χ_1 at the first phase-separation point is essentially determined by molecular weight.

As shown in Table 2, the entropy parameter, ψ_1, for both samples are smaller than 1/2. Since $R(\psi_1 - 1/2)v_2^2$ is considered to be the deviation from the ideal entropy of dilution, the fact that the value of ψ_1 is smaller than 1/2 shows that there must be a gain in local order of the solution relative to that of the pure components.. It is understandable that a certain degree of orientation of toluene around the copolymer molecules occurs in the solution, and the solution of sample B-21, having a larger content of styrene units, gives a larger value of $(1/2 - \psi_1)$, i.e., larger gain in local order, than that of B-23 which has a smaller content of styrene units because toluene has a favorable interaction with styrene units but not with acrylonitrile units. From the same reasoning the κ_1-parameter of the sample B-21, characterizing the excess partial molar enthalpy, is smaller than that of B-23.

TABLE 2

Sample	θ (°K)	ψ_1	κ_1
B-21	325.4	0.324_9	$105._7/T$
B-23	355.1	0.365_7	$129._9/T$

It is interesting to see that, as shown in Fig. 3, phase boundary curves obtained by experiments are appreciably narrower, and the critical points observed occur at a lower polymer concentration than those calculated from the theory. In contrast to the case of copolymer, with ordinary homopolymers [10] the observed curves are markedly broader and the observed critical points occur at higher polymer concentrations than those calculated. The cause of these opposite discrepancies from theoretical calculations is not clear. However, although the present copolymer samples do not have chemical composition distributions due to drifts of monomer mixture compositions during polymerization, they may have the statistical distributions of chemical composition pointed out by Stockmayer [11, 12]. It is our speculation that these chemical composition distributions may be a cause of the discrepancies.

In spite of this unclear point, we may conclude that phase-separation phenomena of random copolymer solutions can be treated within the framework of the Flory theory for ordinary homopolymer solutions if the copolymer samples have sharp chemical composition distributions.

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