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Coexistence curve near the tricritical point in ternary polymer solutions

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Two-phase coexistence curves were measured for ternary solutions of bimodal polystyrene in methylcyclohexane with the molecular weight ratio near the tricritical value 23. Coexistence curves were determined by the refractive index method on a diagram of temperature versus volume fraction of total polystyrene. The diameter was strongly curved near the top. The double logarithmic plots of volume fraction difference between two coexisting phases versus reduced temperature yielded the critical exponent $\beta = 0.250 \pm 0.005$ for the tricritical solution and, 0.412 ± 0.005 and 0.383 ± 0.016 for solutions not far from the tricritical one. The former value could be compared with the classical tricritical exponent $\beta = \frac{1}{4}$ and the latter values near 0.40 could be explained by a crossover between the ordinary critical exponent 0.32 or the tricritical exponents $\frac{1}{4}$ and the classical exponent $\frac{1}{2}$.

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INTRODUCTION

The ternary system of two polymer homologs with the molecular weights M_1 and $M_2(>M_1)$ in a solvent exhibits a tricritical point, at which the three coexisting phases simultaneously become identical. According to the analysis due to the Flory-Huggins equation for the free energy, the tricritical point appears for the molecular weight ratio $M_2/M_1 \sim 10$, above which three-phase separation occurs [1–3]. For the ternary solution of bimodal polystyrene (PS) in methylcyclohexane with $M_2/M_1 = 42$, the three-phase coexistence curve was determined in a diagram of temperature versus overall volume fraction of PS [4]. Although the ratio was much larger than the predicted one, the observed three-phase coexistence curve exhibited an s-shaped symmetry and parallel diameters for the critical end points. These features were considered to be a sign for the tricritical phenomena [5,6]. For characteristic bimodal PS solutions, the three-phase coexistence curve was measured as a function of M_2/M_1 to locate the tricritical point. The size of the three-phase region was analyzed by a classical equation and was found to vanish near $M_2/M_1 = 23$, which was taken as a tricritical ratio [7–9].

A tricritical solution has been argued to undergo a transition from a two-phase state to a one-phase state at the tricritical point with increasing temperature [6,10,11]. In a previous paper we calculated two-phase coexistence curves of critical solutions at the tricritical ratio M_2/M_1 with $M_1 = 1.7 \times 10^4$ by using an empirical free energy obtained for the bimodal polystyrene in methylcyclohexane [12]. In the range of the reduced temperature as $\varepsilon \equiv (T - T_c)/T_c > 10^{-6}$, the coexistence curves showed a common feature in asymptotic behavior and volume ratio of the two coexisting phases. With decreasing ε, the critical exponent β approached $\frac{1}{2}$ and the volume ratio approached unity. For the tricritical solution, however, the exponent β decreased slowly with decreasing ε and was roughly estimated as 0.33. The volume ratio of the dilute phase to the concentrated one decreased in the range of an order of 10^{-2} with decreasing ε. The small value of the volume ratio, which corresponded to an extremely asymmetric two-phase coexistence curve about the tricritical point, has been predicted by analyses based on the Landau-type classical theory [10,11]. However, since the coexistence curve near the tricritical point reflects a subtle behavior of the free energy function, the calculated coexistence curve may exhibit artificial behavior due to an approximate nature of the empirical free energy function. At this situation, only a direct measurement could reveal the characteristic feature of the two-phase coexistence curve of the tricritical solution. Fortunately, Shen *et al.* determined the tricritical point for the ternary system of bimodal polystyrene in methylcyclohexane with $M_2 = 9.29 \times 10^5$ by extensive experiments to be $M_2/M_1 = 23$, $w_1 = 0.22$, $w_2 = 0.0046$, and $T_t = 36.2\,^\circ\mathrm{C}$ [9]. Here, w_1 and w_2 are the weight fractions of the lower- and higher-molecular-weight polystyrenes, respectively, and can be converted to the volume fractions as $\phi_1 = 0.169$ and $\phi_2 = 0.0033$ by using the density 1.0711 for polystyrene and 0.7694 for methylcyclohexane at 35 °C. In this study, we were able to determine the two-phase coexistence curve for the tricritical solution taking advantage of this tricritical data determined by Shen *et al.* The observed coexistence curve was represented by the critical exponent $\beta = 0.250 \pm 0.005$ with the volume fraction $\phi = \phi_1 + \phi_2$ of total polystyrene as an order parameter.

EXPERIMENT

Lower-molecular-weight polystyrene (PSI) and higher-molecular-weight polystyrene (PSII) were purchased from Tosoh Co. Tokyo and Scientific Polymer Products Connecticut, respectively. These samples were used for measurements without further purification. Reagent grade methylcyclohexane was passed through silica gel and distilled twice before use. For the coexistence curve measurements we prepared three solutions near the tricritical one. The preparation was

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TABLE I. Coexistence curve data.

$T_c - T$ (°C)	ϕ^+	ϕ^-
	System *A*	
0.0380	0.2146	0.1444
0.0470	0.2154	0.1418
0.0580	0.2164	0.1394
0.0680	0.2173	0.1383
0.0280	0.2143	0.1436
0.0840	0.2186	0.1344
0.0980	0.2197	0.1325
0.1480	0.2226	0.1255
0.2990	0.2310	0.1144
0.2030	0.2258	0.1214
0.4030	0.2360	0.1089
0.5070	0.2406	0.1043
0.6120	0.2447	0.1010
0.6990	0.2475	0.0981
0.8460	0.2530	0.0937
0.9900	0.2576	0.0910
1.2600	0.2660	0.0862
1.4740	0.2719	0.0832
	System *B*	
0.0270	0.1573	0.1241
0.0280	0.1579	0.1215
0.0380	0.1593	0.1200
0.0450	0.1595	0.1197
0.0710	0.1626	0.1143
0.0780	0.1632	0.1141
0.0930	0.1644	0.1117
0.1340	0.1686	0.1058
0.1930	0.1736	0.0986
0.2540	0.1765	0.0930
0.3080	0.1801	0.0900
0.4210	0.1867	0.0824
0.5020	0.1903	0.0779
0.7180	0.2000	0.0693
0.8080	0.2033	0.0665
0.9070	0.2077	0.0634
1.0030	0.2099	0.0616
1.2080	0.2167	0.0574
1.3000	0.2191	0.0544
1.6590	0.2297	0.0488
1.9660	0.2377	0.0445
	System C	
0.0910	0.1831	0.1426
0.1400	0.1860	0.1179
0.1970	0.1896	0.1050
0.2400	0.1911	0.1004
0.3020	0.1931	0.0964
0.3360	0.1953	0.0909
0.4010	0.1988	0.0848
0.5950	0.2049	0.0755
0.6840	0.2074	0.0728
0.9860	0.2171	0.0637

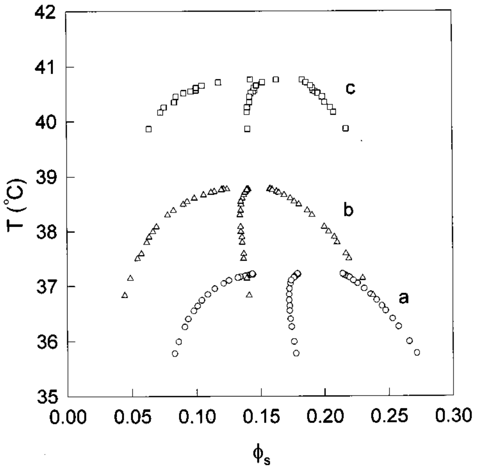

FIG. 1. Coexistence curves for systems *A* (curve *a*), *B* (curve *b*), and *C* (curve *c*). The curves *b* and *c* were shifted +2 and +4 K to avoid the overlap of the data points.

made under dry nitrogen gas to avoid moisture in air. The molecular weights and the overall volume fractions of PSI and PSII for the solutions are summarized in Table I. The solution *A* was prepared to meet the tricritical solution obtained by Shen *et al.* The solutions *B* and *C* are appreciably different from the tricritical one in the molecular weight ratio and in overall volume fractions. The coexistence curve measurements were carried out with a differential refractometer, which gave the volume fraction ϕ of total polystyrene in two coexisting phases [13]. The coexistence curves were determined with the precision of 3 mK in the temperature and 0.1% in the volume fraction. The laser beam passing through the solutions exhibited a spinodal ring just below the cloud point temperature, which demonstrated that the cloud point was very close to the critical point. However, we could not observe the equal volumes for two coexisting phases just below the critical temperature, because the top of the coexistence curve was markedly asymmetrical and the diameter was considerably curved. Especially, for the solution *A* the

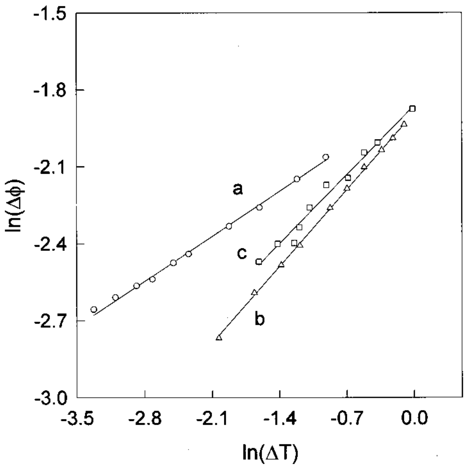

FIG. 2. Double logarithmic plot for systems *A* (curve *a*), *B* (curve *b*), and *C* (curve *c*).

TABLE II. Characteristics of ternary solutions. M_1 and M_2 are the weight-average molecular weights of PSI and PSII, respectively, ϕ_1 and ϕ_2 the overall volume fractions of PSI and PSII, respectively and T_c the critical temperature. β and B are critical exponent and the coefficient, respectively, in Eq. (1) determined by a least squares method. The errors are the standard deviations.

System	M_1	M_2	ϕ_1	ϕ_2	T_c (C)	β	B
A	3.79×10^4	9.29×10^5	0.1693	0.0036	37.25	0.250 ± 0.005	0.158 ± 0.002
B	3.45×10^4	8.69×10^5	0.1522	0.0012	36.80	0.412 ± 0.005	0.148 ± 0.001
C	2.93×10^4	9.29×10^5	0.1707	0.0049	36.85	0.383 ± 0.016	0.155 ± 0.002

volume of the dilute phase was much smaller than that of the concentrated one near the critical point, as predicted by the analysis with the empirical free energy function [12,14]. Moreover, an attainment of the two-phase equilibrium required a very long time period, e.g., a few days, which prevented a precise determination of the coexistence curve just below the critical point.

RESULTS AND DISCUSSION

Figure 1 shows the observed coexistence curves and diameters in a plot of temperature (in °C) versus volume fraction ϕ. The curves *a*, *b*, and *c* were obtained for the solutions *A*, *B*, and *C*, respectively. The curves *b* and *c* are shifted by 2 and 4 K to avoid the overlap of the data points. The obtained critical temperatures are listed in Table I.

Figure 2 shows the double logarithmic plot of the volume fraction difference $\Delta\phi$ between two coexisting phases versus temperature difference $\Delta T = T_c - T$ (°C). The data points are well represented by the straight lines and can be fitted to the equation.

$$\Delta\phi = B\varepsilon^{\beta}. \tag{1}$$

The critical exponent β and the coefficient *B*, which were determined by a least squares method, are listed in Table I. The coefficient *B* has nearly the same values, while the critical exponent depends largely on the solution. It has been predicted that the tricritical behavior can be described by the phenomenological Landau theory of phase transitions except for logarithmic correction factors [15–18]. The symmetric tricritical phenomena of He^3-He^4 mixtures have been represented by the classical theory [19]. Lang and Widom, and Bocko, determined three-phase coexistence curves near the tricritical point for quaternary liquid mixtures [20,21]. As the temperature approached the tricritical one, the characteristic dimensions of the three-phase region vanished according to the Landau type classical theory [10]. In light of the above experiments, the tricritical behavior of the ternary solution of bimodal polymer in a solvent could be represented by the classical theory. Moreover, the two- and three-phase coexistence curves for polystyrene solutions have been analyzed properly with the volume fraction of total polystyrene as an order parameter. Accordingly, the volume fraction difference $\Delta\phi$ in Eq. (1) would also give an order parameter. Thus, the value of $\beta = 0.250\pm0.005$ obtained for the solution *A* could be taken as the classical tricritical exponent for the order parameter. The value of β obtained for the solution *B* (see Table II) is considerably larger than the ordinary critical exponent $\beta\sim0.32$ or renormalized critical exponent $\beta/(1-\alpha)\sim0.37$ [22,23]. It should be mentioned that in the previous paper we have also obtained large critical exponents, such as, $\beta\sim0.4$ for ternary solutions of bimodal polystyrene in methylcyclohexane with $M_2/M_1 = 22$ [12]. Since the solutions were prepared not far from the tricritical condition, the large values of β may exhibit the crossover between the ordinary critical exponent 0.32 or the tricritical exponent $\frac{1}{4}$ and the classical exponent $\frac{1}{2}$.

The data points could also be discussed by using the functional form of Landau type for ϕ^6 model as

$$F(\Delta\phi) = F(0) + r\Delta\phi^2 + u\Delta\phi^4 + c\Delta\phi^6, \tag{2}$$

where $\Delta\phi$ is the concentration difference between the concentrated and dilute phases, and the parameters *r* and *u* are simultaneously zero at the tricritical point (TCP). The solution of the condition for the minimum free energy at the equilibrium state is given by

$$x = \frac{-2u + \sqrt{4u^2 - 12rc}}{6c} = -\frac{u}{3c} + \left\{ \left(\frac{u^2}{9c^2} \right) - \left(\frac{r}{3c} \right) \right\}^{1/2}, \tag{3}$$

TABLE III. Parameters used in Eqs. (3) and (4) determined by a least squares method. The errors are the standard deviations.

System	A_0	ΔA	C	ΔC	$a = \Delta C/C$ (K)	$b = \Delta A/A_0$ (K)
A	7.7×10^{-3} $\pm2.7\times10^{-3}$	1.2×10^{-3} $\pm1.8\times10^{-3}$	3.1×10^{-4} $\pm2.0\times10^{-4}$	-1.5×10^{-6} $\pm1.2\times10^{-5}$	-4.7×10^{-3}	1.6×10^{-2}
B	1.7×10^{-3} $\pm3.1\times10^{-3}$	-2.6×10^{-2} $\pm1.4\times10^{-2}$	1.6×10^{-3} $\pm7.3\times10^{-4}$	1.9×10^{-5} $\pm1.5\times10^{-5}$	83.4	-15.6
C	6.9×10^{-3} $\pm2.6\times10^{-3}$	-3.4×10^{-4} $\pm1.9\times10^{-3}$	2.8×10^{-4} $\pm2.1\times10^{-4}$	-2.4×10^{-5} $\pm1.3\times10^{-5}$	-11.5	-4.9×10^{-2}

where $x=\Delta\phi^2$. Putting $r(T)=r'(T-T_c+a)$ and $u(T)=u'(T-T_c+b)$ with $r'>0$ and $u'>0$, we obtain

$$x=-\frac{u'}{3c}(\Delta T+b)+\left[\frac{u'^2}{9c^2}(\Delta T+b)^2-\frac{r'}{3c}(\Delta T+a)\right]^{1/2}, \tag{4}$$

where $\Delta T=T-T_c$, and a and b denote deviations in temperature from TCP. If we substitute new parameters defined by $A_0=u'/3c$, $\Delta A=bu'/3c$, $C_0=r'/3c$, and $\Delta C=ar'/3c$ in Eq. (4), we have

$$x=-A_0\Delta T-\Delta A+\sqrt{(A_0\Delta T+\Delta A)^2-C_0\Delta T-\Delta C}. \tag{5}$$

Fitting experimental data to Eq. (5) and determining the parameters a, b, r'/c, and u'/c or another set of the parameters A_0, ΔA, C_0, and ΔC, we can estimate the deviation from TCP for each observed coexistence curve (see Table III). The condition $a=\Delta A/A_0=0$ and $b=\Delta C/C_0=0$ should be simultaneously satisfied at TCP.

The data points were well fitted to Eq. (5) (not shown) and the values of a and b obtained by a least squares fit as -4.7×10^{-3} and 1.6×10^{-2} K for system *A*, 83.4 and -15.6 K for system *B*, and -11.5 and -4.9×10^{-2} K for system *C*. The values of a and b for system *A* are in the order of the experimental error, indicating the tricritical solution. On the other hand, those for systems *B* and *C* are very large, which shows the coefficient u in Eq. (2) could not be negligible compared with the term $c\Delta\phi^6$ and Eq. (2) reduces to ϕ^4 model. Therefore, the above discussion based on the Landau free energy supports the idea that $\beta=0.250\pm0.005$ for system *A* is the tricritical one and, 0.412 ± 0.005 and 0.383 ± 0.016 for systems *B* and *C* are the crossover between the ordinary critical exponent 0.32 or the tricritical exponents $\frac{1}{4}$ and the classical exponent $\frac{1}{2}$.

The experiment made by Shen *et al.* located the tricritical point correctly [9]. The present observation of the classical tricritical exponents disclosed that the tricritical region is much wider than the predicted one [12] from the calculation by using the free energy function determined from the molecular weight dependence of the critical point for the binary system PS in methylcyclohexane [24]. The crossover exponents observed in the present and the previous study [12] also indicate a wide region of the tricritical phenomena. It is interesting to study further the phenomena characteristic to the tricritical point to be observed in, such as, correlation length and turbidity, based on the tricritical point data by Shen *et al.* and our coexistence curves.

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