

Coexistence curve of a polydisperse polymer solution near the critical point

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The coexistence curve of well-characterized polydisperse polystyrene in cyclohexane ($M_w=23.9\times 10^4$, $M_w/M_n=2.8$) was measured near the critical point, where M_w and M_n are weight- and number-average molecular weights, respectively. The shape of the coexistence curve was expressed by the critical exponent $\beta_t=0.363\pm 0.005$, which agrees with the exponent of Fisher's renormalization for the Ising system with hidden variables. [S1063-651X(97)11903-1]

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I. INTRODUCTION

The coexistence curves of binary and ternary solutions near the critical point are expressed by Ising exponents and Fisher's renormalized exponents, respectively [1,2]. The difference in the exponents of ternary systems and those of binary systems results from the fluctuation in the density of the third component or impurity [3,4]. According to Fisher's theory, systems with more than two impurity components should give the same value of the renormalized exponent. Thus, it is interesting to study the critical behavior of multicomponent systems that contain a large number of components and closely examine critical exponents of the systems.

Because the critical point of a multicomponent system cannot be easily determined by experimental observations, theoretical analyses on the system using the Gibbs free energy are a prerequisite to experimental studies. To calculate the phase diagram of the multicomponent system it is necessary to specify all of the interaction energies for each pair of components and to solve the nonlinear simultaneous equations of phase equilibrium conditions. For conventional multicomponent systems this type of analytic study of the phase diagram is substantially unfeasible. However, the Gibbs free energy of homologous polymers in a solvent is expressed by a single interaction parameter for polymer segments and solvent. We can easily estimate the critical point of this system despite the multicomponent character due to different molecular weights of polymer homologs. The spinodal curve of the system depends on the weight-average molecular weight, whereas the critical concentration and temperature depend on the weight-average and the z -average molecular weight [5,6]. On a diagram of temperature versus total polymer volume fraction, the critical point is taken as the intersection of the

cloud point curve and the coexistence curve, which is obtained for the solution at the critical concentration. The system of homologous polymers in a solvent is the only multicomponent system that can be studied quantitatively [7-10]. Several experimental and theoretical works elucidated the three-component phase diagram for polymer systems [11-14]. In this work we studied the critical behavior of the multicomponent system of well-characterized polydisperse polystyrene in cyclohexane.

II. EXPERIMENT

We used the well-characterized [15] polydisperse polystyrene Styron 666 produced by Asahi Chemical Industry Co. Ltd. The weight-average molecular weight is $M_w=23.9\times 10^4$. The molecular-weight distribution is roughly represented by the Schulz-Zimm-type distribution, and the ratio of weight- to number-average molecular weight is $M_w/M_n=2.8$. The critical temperature and critical volume fraction of polystyrene were calculated as 26.11 °C and 0.0746, respectively, from an empirically determined Gibbs free energy [15]. Polystyrene F20 with very narrow molecular-weight distribution ($M_w=18.9\times 10^4$, $M_w/M_n<1.02$) purchased from Tosoh Co. Ltd., was used for a reference binary system. Reagent grade cyclohexane was twice distilled after slowly passing it through fine silica gel. No trace of impurities was observed from the results of gas chromatography. Hereafter, we designate the system of Styron 666 in cyclohexane as system *a* and F20 in cyclohexane as system *b*. An appropriate amount of the polystyrene sample was dissolved in cyclohexane to prepare a solution whose concentration is near the critical one predicted by analysis of the Gibbs free energy. The solution was transferred into a Brice-type cell under dry nitrogen gas and the cell was sealed tightly using a screw cap. The coexistence curve of the solution was measured by the refractive index

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TABLE I. Cloud point curve data for system *a*. T and ϕ denote the cloud point temperature and volume fraction of polystyrene, respectively.

T (°C)	ϕ
24.37	0.0006
25.08	0.0012
25.63	0.0020
26.35	0.0035
26.84	0.0054
27.01	0.0074
27.25	0.0101
27.41	0.0152
27.38	0.0177
27.29	0.0202
27.09	0.0296
26.85	0.0403
26.60	0.0502
26.48	0.0550
26.37	0.0603
26.30	0.0648
26.22	0.0701
26.10	0.0749
26.02	0.0803
25.83	0.0906
25.58	0.1008
25.34	0.1109
25.09	0.1211
24.81	0.1306
24.46	0.1410
24.07	0.1509

method [16]. The position of the laser beam refracted by the solution was detected using a position sensitive device (S1352, Hamamatsu). The photocurrent generated on the device was proportional to the distance of the position of the laser beam from a reference point. The volume fraction of total polystyrene ϕ in each phase was measured within a precision of <0.0004 . To determine cloud points, the increasing forward scattering and diminishing incident beam passing through the cloudy solution were carefully observed. We observed that the solutions used for the coexistence curve measurements separated into two phases of the same volume just below the cloud point. This implied that the concentration of the solutions was very close to the critical one. At each temperature two-phase equilibrium was reached more than 12 h after setting the temperature. The temperature of the water bath in which the solution cell was immersed was controlled within ± 0.003 K. All the data for the cloud point curve and coexistence curves are listed in Tables I and II.

III. RESULTS

Figure 1 shows the coexistence curve and the diameter (open circles) and the cloud point curve (solid circles) obtained for system *a*. The solid curves were fitted to the data points by eye. As expected from the numerical analysis of the Gibbs free energy, the three curves intersect at a point

TABLE II. Coexistence curve data for systems *a* and *b*. $T_c - T$, ϕ^+ , and ϕ^- denote the temperature difference from the critical temperature and volume fractions of concentrated phase and dilute phase, respectively.

$T_c - T$ (°C)	ϕ^+	ϕ^-
System <i>a</i>		
0.028	0.0825	0.0565
0.033	0.0847	0.0543
0.043	0.0857	0.0542
0.063	0.0879	0.0525
0.087	0.0906	0.0496
0.129	0.0947	0.0472
0.182	0.0977	0.0450
0.264	0.1023	0.0416
0.384	0.1077	0.0386
0.543	0.1145	0.0352
0.739	0.1218	0.0330
1.149	0.1344	0.0271
1.654	0.1474	0.0228
2.396	0.1643	0.0186
System <i>b</i>		
0.026	0.0863	0.0477
0.044	0.0886	0.0456
0.070	0.0932	0.0418
0.112	0.0981	0.0376
0.159	0.1020	0.0353
0.240	0.1095	0.0309
0.309	0.1128	0.0287
0.554	0.1249	0.0226
0.853	0.1374	0.0176
1.160	0.1477	0.0135
1.985	0.1705	0.0081

that yields the critical point as $T_c = 26.23$ °C and $\phi_c = 0.0694$. The critical point is on the inflection point of the cloud point curve in accordance with the numerical analysis [15]. For the coexistence curve measured for system *b* we obtained $T_c = 23.68$ °C and $\phi_c = 0.0669$.

A. Concentration difference of coexisting phases

Figure 2 shows log-log plots of the concentration difference $\Delta\phi$ versus reduced temperature $\varepsilon = (T_c - T)/T_c$. All of the curves for the concentration differences $\phi^+ - \phi^-$, $\phi^+ - \phi_c$, and $\phi_c - \phi^-$ appear to approach asymptotic straight lines with the same slope near the critical point. The difference $\phi^+ - \phi^-$ was analyzed by a least squares fit to simple scaling

$$\phi^+ - \phi^- = B\varepsilon^\beta. \quad (1)$$

Since the data points for the plot of $\phi^+ - \phi^-$ versus ε appear to give a line slightly curved at large ε , we analyzed the data by changing the range of ε . In the entire experimental range of $\varepsilon < 8 \times 10^{-3}$ (14 points), we obtained $\beta = 0.386 \pm 0.005$ and $B = 0.92 \pm 0.03$. However, an obvious systematic error was found for the fit with the large reduced chi square χ_ν^2 as 4.1. By reducing the range of ε we obtained $\beta = 0.363 \pm 0.005$ and $B = 0.78 \pm 0.03$ ($\chi_\nu^2 = 1.2$) for $\varepsilon < 2 \times 10^{-3}$ (11 points),

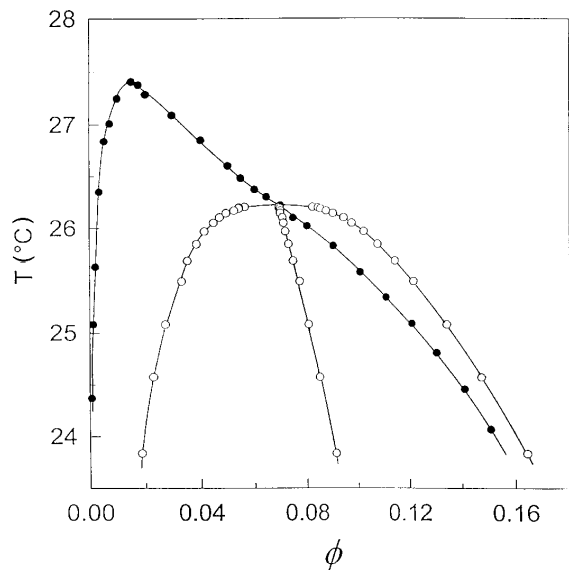


FIG. 1. Coexistence curve (\circ), diameter (\circ), and cloud point curve (\bullet) obtained for polydisperse polystyrene in cyclohexane (system *a*) on a diagram of temperature vs total polystyrene volume fraction ϕ .

$\beta=0.359\pm 0.010$, and $B=0.76\pm 0.06$ ($\chi^2=1.6$) for $\varepsilon < 9 \times 10^{-4}$ (8 points) and $\beta=0.357\pm 0.040$ and $B=0.74\pm 0.25$ ($\chi^2=3.7$) for $\varepsilon < 3 \times 10^{-4}$ (5 points). The values of β and B obtained by the analyses in the ranges $\varepsilon < 2 \times 10^{-3}$ and $\varepsilon < 9 \times 10^{-4}$ agree with reasonably small χ^2 and indicate the asymptotic behavior of the simple scaling as given by the straight line in Fig. 2. The deviation of the data points from the straight line at large ε may be explained by the Wegner expansion. However, it is difficult to determine the two parameters of the exponent and coefficient for the first correction term in addition to β and B with satisfactory accuracy. To discuss the correction term to scaling, we should obtain a large number of data points in a wide temperature range.

For system *b* the analysis by Eq. (1) yielded $\beta=0.344\pm 0.004$ and $B=0.90\pm 0.02$ ($\chi^2=2.5$) for $\varepsilon < 7 \times 10^{-3}$ (11

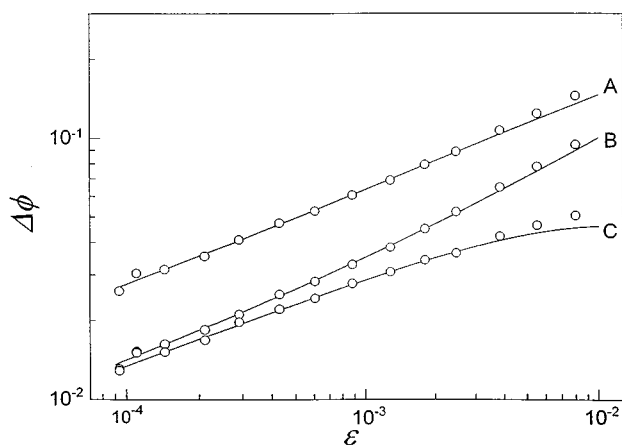


FIG. 2. log-log plots of concentration difference $\Delta\phi$ vs reduced temperature $\varepsilon=(T_c-T)/T_c$ for system *a*; $\Delta\phi=\phi^+-\phi^-$, $\phi^+-\phi_c$, and $\phi_c-\phi^-$ for the curves A, B, and C, respectively. Solid curves are calculated using Eqs. (1) and (2) with $\beta=0.363$, $B=0.78$, $\mu=0.93$, and $A=2.0$.

TABLE III. Critical exponents and coefficients in Eqs. (1) and (2) obtained for polydisperse polystyrene (*a*) and monodisperse polystyrene (*b*) in cyclohexane. The errors indicate the standard deviations.

System	β	B	μ	A
<i>a</i>	0.363 ± 0.005	0.78 ± 0.03	0.93 ± 0.02	2.0 ± 0.2
<i>b</i>	0.335 ± 0.005	0.85 ± 0.03	0.87 ± 0.02	1.8 ± 0.2

points) but showed a systematic deviation from the fit. By range variation analysis we obtained $\beta=0.335\pm 0.005$ and $B=0.85\pm 0.03$ ($\chi^2=1.8$) for $\varepsilon < 3 \times 10^{-3}$ (9 points), $\beta=0.330\pm 0.009$ and $B=0.82\pm 0.05$ ($\chi^2=2.1$) for $\varepsilon < 1 \times 10^{-3}$ (7 points), and $\beta=0.332\pm 0.012$ and $B=0.83\pm 0.08$ ($\chi^2=2.8$) for $\varepsilon < 8 \times 10^{-4}$ (6 points). In these analyses systematic deviation from the fits was not observed. The constant values of β and B independent of the ε range show asymptotic behavior. The value $\beta=0.335\pm 0.005$ agrees with the previous value $\beta=0.335\pm 0.004$ obtained in the range $\varepsilon < 3 \times 10^{-3}$ for polystyrene ($M_w=18.1 \times 10^4$) in methylcyclohexane [17]. This is also close to the values obtained from the fits to the equation $\phi^+-\phi^-=B\varepsilon^\beta(1+B'\varepsilon^\Delta)$ proposed by Wegner with Δ being a fixed value 0.5. This analysis yielded $\beta=0.320\pm 0.005$ in the range $\varepsilon < 1 \times 10^{-2}$ for polystyrene ($M_w=18.1 \times 10^4$) in methylcyclohexane [17] and $\beta=0.340\pm 0.005$ in the range $\varepsilon < 7 \times 10^{-3}$ for polystyrene ($M_w=20 \times 10^4$) in cyclohexane [18]. The values of β and B determined with the lowest χ^2 in the range variation analyses are listed in Table III.

B. Diameter

Figure 3 shows a log-log plot of diameter versus ε for system *a*. We made a least squares fit to the simple scaling

$$(\phi^+ + \phi^-)/2 - \phi_c = A\varepsilon^\mu. \quad (2)$$

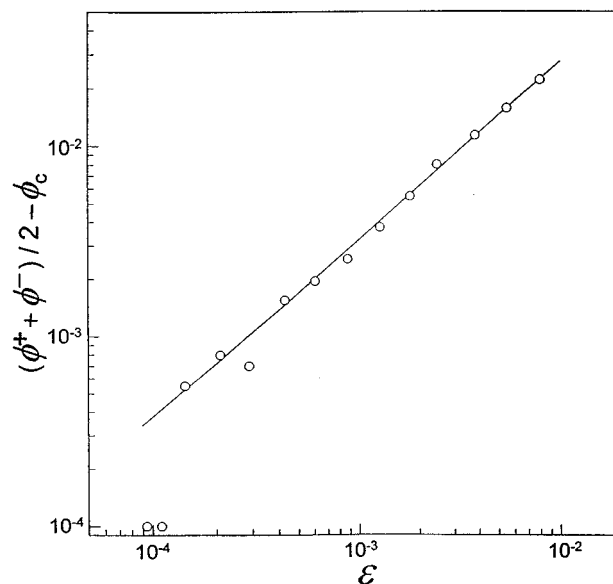


FIG. 3. log-log plot of diameter vs reduced temperature for system *a*. The solid line is calculated using Eq. (2) with $\mu=0.93$ and $A=2.0$.

Over the whole temperature range ($\varepsilon < 8 \times 10^{-3}$, 14 points) the analysis yielded the values $\mu = 0.93 \pm 0.02$ and $A = 2.0 \pm 0.2$ ($\chi^2_\nu = 0.5$), without indicating systematic deviation. The analysis regarding the diameter of system *b* also indicated no systematic deviation from the fit of Eq. (2) over the whole experimental temperature range ($\varepsilon < 7 \times 10^{-3}$, 11 points) and the values $\mu = 0.87 \pm 0.02$ and $A = 1.8 \pm 0.2$ ($\chi^2_\nu = 0.2$) were obtained. The range of simple scaling used with Eq. (2) is much wider than that used with Eq. (1). This was also the case for various binary polystyrene solutions with different molecular weights [16–18]. The obtained values of the exponent and coefficient are listed in Table III.

IV. DISCUSSION

The critical exponents $\beta = 0.335 \pm 0.005$ and $\mu = 0.87 \pm 0.02$ of system *b* agree with those of polymer solutions with narrow molecular-weight distribution, $\beta \sim 0.33$ and $\mu \sim 0.87$ [16–18], and also with typical theoretical values of $\beta = 0.326$ and $\mu = 1 - \alpha = 0.89$, where α is the exponent for specific heat, 0.110 [19]. It is known that the coexistence curve and the cloud point curve of a polymer solution coincide if the molecular-weight distribution of the polymer is sufficiently narrow [20]. System *b* in which polystyrene with a narrow molecular-weight distribution was used will have a cloud point curve that is not distinguishable from the coexistence curve under the present experimental accuracy. For system *a* in which polydisperse polystyrene was used, the cloud point curve is completely different from the coexistence curve. This difference in the cloud point curve and the coexistence curve demonstrates that system *a* should be taken as a multicomponent system. In each coexisting phase occurring in system *a*, the molecular-weight distributions of polystyrene are different. At the critical point the two coexisting phases have the same molecular-weight distribution. Therefore, the curves in Fig. 1 represent an aspect of phase behavior in a multidimensional space of temperature and polystyrene components. The critical exponents $\beta = 0.363 \pm 0.005$ and $\mu = 0.93 \pm 0.02$ are much larger than those for system *b* involving monodisperse polystyrene. This value of β agrees with the experimental value observed for ternary solutions [21–24] and bimodal polymer solutions [25,26], 0.36–0.38, and also with the theoretical value of Fisher's renormalization $\beta_r = \beta/(1 - \alpha) = 0.366$ obtained from the Ising values $\beta = 0.326$ and $\alpha = 0.110$ [19]. Furthermore, this agreement indicates that the total polymer volume fraction is a proper order parameter for the multicomponent system of polydisperse polymers.

For the system of two homologous polymers in a solvent, Broseta showed that Fisher's renormalization becomes visible at the critical value ε^* given by

$$\varepsilon^* < k^{1/\alpha}, \quad (3)$$

with $k = \xi_2 r (r - 1)^2$ [27]. Here, ξ_2 is the volume fraction of the larger molecular-weight polymer in two homologous polymers and r is the molecular-weight ratio of the polymer components. In a previous work [26], we showed that the crossover from the Ising exponent to Fisher's renormalized exponent could be observed for bimodal polystyrene solutions by varying the parameter k . The agreement of the observed value of β for system *a* and Fisher's renormalized

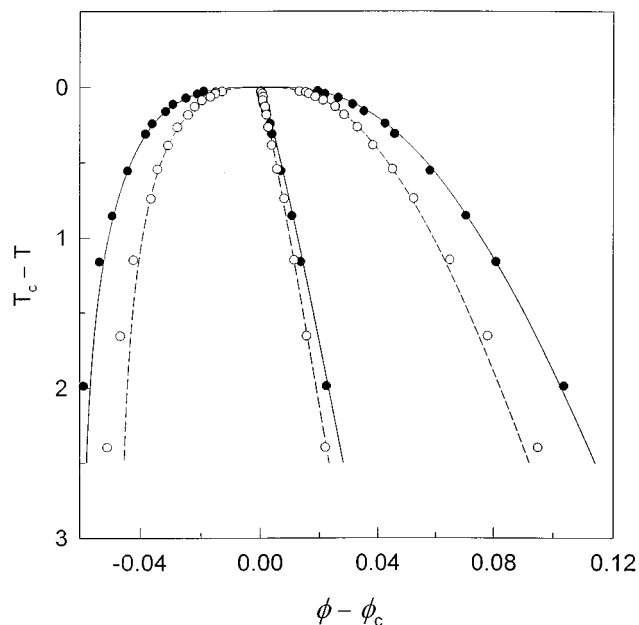


FIG. 4. Comparison of coexistence curves and diameters for system *a* (○) and system *b* (●). Solid curves and broken curves were calculated by Eqs. (1) and (2) with the values of the coefficient and exponent obtained for each system.

value suggests that the molecular weight distribution of the polystyrene is sufficiently wide to result in a large ε greater than ε^* ; the width of the molecular-weight distribution may correspond to the ratio r . To confirm this idea, it is interesting to study the critical behavior of the system of polydisperse polymer in a solvent by varying the shape of the molecular-weight distribution.

The molecular-weight distributions in the coexisting phases can be measured by gel permeation chromatography (GPC), although the precision of GPC is not sufficiently high to study the small change in molecular-weight distribution near the critical point. Using GPC measurements, Kamide carried out a rough investigation on the phase behavior of Schulz-Zimm-type polymers in solvent and showed that the molecular-weight distribution in the concentrated phase is much broader than that in the diluted phase [8]; the higher-molecular-weight components tend to cause phase separation more effectively than the lower-molecular-weight components. This experimental demonstration was compatible with the numerical analysis carried out using the Flory-Huggins Gibbs free energy with a phenomenological correction term [8].

The exponent μ obtained for system *a* is larger than those for system *b* and binary systems. Vause and Sak predicted that the exponent μ is unity for the Ising system with impurities [28]. The large value of $\mu = 0.93$ obtained in this study should not be overlooked in light of their theory. To clarify this point it is necessary to carry out further detailed experiments on polydisperse polymer systems as well as bimodal polymer systems.

Finally, Fig. 4 shows a comparison of the entire coexistence curves of systems *a* and *b*. Since the critical point of system *a* is very close to that of system *b*, the two coexistence curves can be compared with each other by plotting $T_c - T$ versus $\phi - \phi_c$. Obviously, system *a* has a smaller con-

centration difference $\phi^+ - \phi^-$ than system b , as reflected by the values of the coefficient B and the exponent β . It is remarkable that the two coexistence curves have similar symmetry features about the critical point with close behavior of the diameters when it is considered that ϕ is the total volume fraction of polydisperse polystyrene with numerous components for system a and the volume fraction of monodisperse polystyrene with a practically single component for system b . The solid and broken curves in Fig. 4 were calcu-

lated with the obtained values of B and β and A and μ to reproduce the data points. Each calculated coexistence curve deviates from the corresponding data points in a similar way.

In conclusion, the critical exponents β and μ were determined for a system with an extremely large degree of freedom. The values of the exponent β agree with those of ternary systems and theoretical values for the Ising model with impurities. This result indicates that the multicomponent system of polydisperse polymer solution also belongs to the same universality class as the three-dimensional Ising model.

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