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Semiempirical Determination of Solution Structure in Polymer Solution Based on the Clustering Theory. 2. Noncritical and Critical Regions

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ABSTRACT: The solution structure of the polymer solutions polystyrene (PS)–cyclohexane and PS–methylcyclohexane, in both the noncritical and critical regions, has been determined by using the experimental data of the coexistence curves by Koningsveld et al. and by Dobashi et al. based on the clustering function of Zimm and of Kirkwood and Buff. This is expressed by $G_{00}/\bar{v}_0 = -\phi_1\{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} - 1$ for systems of negligible compressibility, where G_{00} is the clustering function of the solvent, $\bar{v}_0$ is the partial molecular volume of solvent, a_0 is the activity of solvent, and ϕ_0 and ϕ_1 are the volume fractions of solvent and polymer, respectively. The solvent activity a_0 is expressed by using the clustering theory by $\ln a_0 \sim X^{1+\alpha}\phi_{1,c}/\phi_{0,c}$ near the critical point and $\ln a_0 = (1 - r^{-n})^{-1} \ln \phi_0 - \beta_0 \ln (1 - \phi_1/\beta_0)$ for the noncritical region, where $\phi_{i,c}$ is the critical concentration of component i; α, n, and β_0 are constants; and $X = (\phi_0 - \phi_{0,c})/\phi_0$. The value of n in PS–cyclohexane and PS–methylcyclohexane determined in this work is about 0.84, while β_0 is dependent on temperature and approaches 1.0 at the critical solution temperature, T_c, for the infinite molecular weight or Θ temperature. The value of α is estimated to be equal to 4.0, which leads to the critical exponent for the coexistence curve to be 0.33 and $(\phi_{1,c} - \phi_1)/\phi_{1,c} \sim r^{0.21}(T_c - T)^{0.33}$, where r is the ratio of molar volume of the polymer to that of the solvent.

Introduction

A quantitative and critical test for the theories of polymer solution thermodynamics became easier by the extensive studies of the critical phenomena in polymer solutions. The cloud point and coexistence curves for the polystyrene solutions have been measured by many authors.[1–4] The isothermal osmotic compressibility and correlation length near the critical temperature were measured by using the laser-light-scattering technique by Kuwahara et al.[5–10] and Shinozaki et al.,[11] while the light-scattering studies in the noncritical region have been done by Wolf et al.,[12–14] Einaga et al.,[15–17] and other many authors. Investigations of the liquid–liquid phase separation and concentration, temperature, and molecular weight dependence of the χ parameter were made extensively by Koningsveld et al.[18–24] It has been recognized theoretically that the coexistence curve near the critical point predicted by the Flory–Huggins theory is given by[25,26]

$$|\phi_1 - \phi_{1,c}|/\phi_{1,c} \sim r^{1/4}\epsilon^{1/2} \tag{1}$$

$$\phi_{1,c} \sim r^{-1/2} \tag{2}$$

where ϕ_1 is the coexistent polymer volume fraction, $\phi_{1,c}$ is the critical concentration, r is the ratio of molar volume of the polymer to that of the solvent, $\epsilon = |T - T_c|/T_c$, and T_c is the critical solution temperature. The experimental coexistent curve for polymer solution is characterized by[27]

$$|\phi_1 - \phi_{1,c}|/\phi_{1,c} \sim N^{0.102}\epsilon^{0.327} \tag{3}$$

where N is the degree of polymerization of the polymer.

In the previous work[28] we derived a simple equation of the chemical potential of solvent in a polymer solution based on the clustering function of Zimm[29] and Kirkwood and Buff,[30] which predicts the experimental data over a wide concentration range at temperatures higher than the phase-separation temperature. It is very important to determine the solution structure in the critical and noncritical region semiempirically in understanding peculiar behavior at the critical point. In this work we have derived an equation of the chemical potential for the noncritical and critical regions based on the clustering theory, without using complicated calculations.

Derivation of the Equation of the Activity Coefficient in the Noncritical and Critical Regions

According to Zimm's extension of the Kirkwood–Buff theory,[29,30] the activity coefficient of a solvent (a_0/ϕ_0), neglecting terms from compressibility, is given by

$$G_{00}/\bar{v}_0 = -\phi_1\{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} - 1 \tag{4}$$

We use an assumption that $G_{00}/\bar{v}_0$ increases very rapidly in the vicinity of the critical point. The other assumption is that $(G_{00}/\bar{v}_0)\phi_0$ approaches a value independent of temperature at $\phi_0 \rightarrow 0$. The first assumption means that the concentration in the vicinity of the critical point fluctuates greatly from the mean, overall concentration. The second one is based on the assumption made by Fixman[31] that the properties of a random distribution of segments at high concentration are explained by the fact that the nonrandom distribution of segments belonging to a single polymer molecule is precisely compensated for by a deficiency of segments belonging to the other molecules. This deficiency approaches a constant value as the concentration is increased. We take the constant deficiency at the limit of $\phi_0 = 0$ to be a decreasing function of molecular weight of polymer. In the Kurata theory of chain polymer solutions,[32] the clustering function $G_{00}/\bar{v}_0$ is expressed by a function of the coiling probability g, which consists of the short-range mode of coiling and the long-range one, which is proportional to $r^{-1/2}$. By using the two assumptions mentioned above, we express the clustering function by

$$\phi_1\{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} = K_0 + r^{-n}\phi_0^{-1} + K_1\{\phi_0/(\phi_0 - \phi_{0,c})\}^{\alpha} \tag{5}$$

where n and α are constants and K_0 and K_1 are values independent of concentration. The following equation is derived from eq 5:

$$(1/a_0)(\partial a_0/\partial\phi_0)_{P,T} = 1/\{\phi_0(1 - r^{-n})\} + (K_1X^{-\alpha} + K_0 + r^{-n})/[(1 - r^{-n})\{1 - r^{-n} - \phi_0(1 + K_1X^{-\alpha} + K_0)\}] \tag{6}$$

where X is defined by

$$X = (\phi_0 - \phi_{0,c})/\phi_0 \tag{7}$$

Integration of eq 6 with respect to ϕ_0 from ϕ_0 to $\phi_{0,c}$ gives

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$$\ln (a_{0,c}/a_0) = (1 - r^{-n})^{-1} \ln (\phi_{0,c}/\phi_0) + (1 - r^{-n})^{-1} \int_{\phi_0}^{\phi_{0,c}} (K_1 X^{-\alpha} + K_0 + r^{-n}) / \{1 - r^{-n} - \phi_0(1 + K_1 X^{-\alpha} + K_0)\} \mathrm{d}\phi_0 \quad (8)$$

where $a_{0,c}$ is a value of a_0 at the critical point. Over the temperature region near the critical point where the $X^{-\alpha}$ term in eq 8 is dominant, eq 8 is given by

$$\ln a_0 = \ln a_{0,c} + K_1^{-1}\left\{\int_0^X X^\alpha/(1 - X)\,\mathrm{d}X - \int_0^X X^\alpha/\phi_{0,c}\,\mathrm{d}X\right\} + C(P,T)$$
$$= \ln a_{0,c} - K_1^{-1}\{X^{1+\alpha}/(1 + \alpha)\}(\phi_{1,c}/\phi_{0,c}) + C(P,T) \quad (9)$$

where $C(P,T)$ is an integration constant and a function of temperature and pressure. It is evident that the $\ln \phi_0$ term derived from random distribution of solvent molecules disappears in eq 9 due to the effect of the $X^{-\alpha}$ term and since $\ln a_0$ is proportional to $X^{1+\alpha}$ in the vicinity of the critical point.

It is interesting to derive an equation of a_0 far from the critical point where the $\{\phi_0/(\phi_0 - \phi_{0,c})\}^\alpha$ term in eq 5 is negligible. The equation for the clustering function far from the critical point is expressed by

$$\phi_1\{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} = K_0 + r^{-n}\phi_0^{-1} \quad (10)$$

The following equation is derived from a procedure similar to that for the critical point:

$$\ln a_0 = (1 - r^{-n})^{-1} \ln \phi_0 - \beta_0 \ln (\beta_0 - 1 + \phi_0) + \beta_0 \ln \beta_0 \quad (11)$$

where β_0 is defined by

$$\beta_0 = K_0/(K_0 + 1) \quad (12)$$

and the assumption that $K_0 \gg r^{-n}\phi_0^{-1}$ is used.

Relations at the Critical Point

It is important to derive the $\phi_{1,c} - r$ relation at the critical point. We use eq 11 to derive the $\phi_{1,c} - r$ relations, although eq 11 is assumed to be valid over the temperature range far from the critical point. The spinodal and critical conditions are given by using $(\mu_0 - \mu_0{}^0)/RT = \ln a_0$ by

$$\partial \ln a_0/\partial \phi_1 = 0 \quad (13)$$

for the spinodal condition and

$$\partial^2 \ln a_0/\partial \phi_1{}^2 = 0 \quad (14)$$

for the critical condition with eq 13. Equation 11 is expressed by using a series expansion of $\beta_0 \ln (\beta_0 - 1 + \phi_0) - \beta_0 \ln \beta_0 = \beta_0 \ln (1 - \phi_1/\beta_0)$:

$$\ln a_0 = (1 - r^{-n})^{-1} \ln \phi_0 + \phi_1 + \phi_1{}^2/2\beta_0 \quad (15)$$

From eq 13 and 15, it obtains that

$$(1 - r^{-n})^{-1}/\phi_0 = 1 + \phi_1/\beta_0 \quad (16)$$

and from eq 14 and 15

$$(1 - r^{-n})^{-1}/\phi_0{}^2 = 1/\beta_0 \quad (17)$$

The critical concentration and critical value of $\beta_{0,c}$ are calculated and are given as a function of r by

$$\phi_{1,c} = 1/(r^{n/2} + 1) \quad (18)$$

$$\beta_{0,c} = (r^{n/2} - 1)/(r^{n/2} + 1) \quad (19)$$

$$\phi_{1,c} = (1 - \beta_{0,c})/2 \quad (20)$$

Determination of the Exponents *n* and *α* in Eq 5

It is very important to determine the exponents n and α in eq 5 empirically. The following is derived from eq 18:

$$\ln (\phi_{0,c}/\phi_{1,c})^2 = n \ln r \quad (21)$$

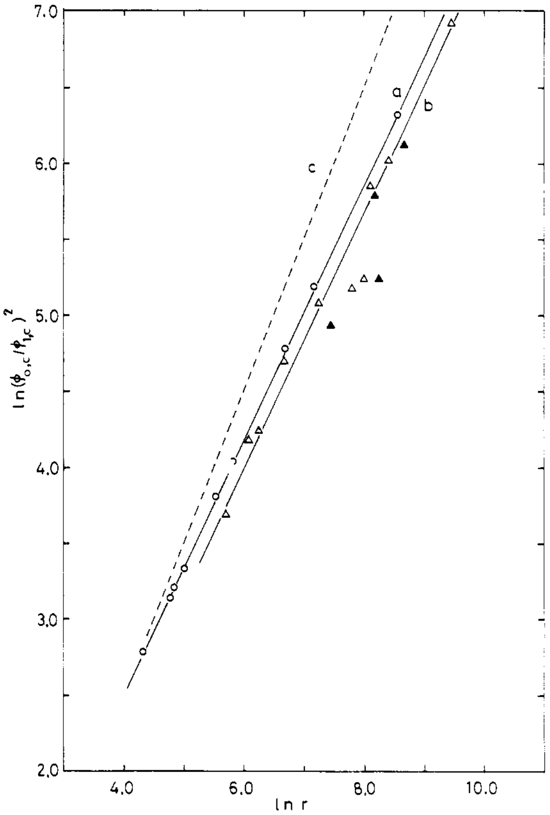

Figure 1. ln $(\phi_{0,c}/\phi_{1,c})^2$ versus ln r plot in (a) polystyrene (PS)–methylcyclohexane (MCH) (○[4]) and (b) PS–cyclohexane (CH) (△;[20] ▲[33]). Values of r are calculated by using v_{sp}(PS) = 0.9336 cm^3/g, v_{sp}(MCH) = 1.299 cm^3/g, and v_{sp}(CH) = 1.292 cm^3/g. The dotted line c is for slope = 1.0 or n = 1.0 in eq 18, while the value of n for PS–MCH and PS–CH is about 0.84.

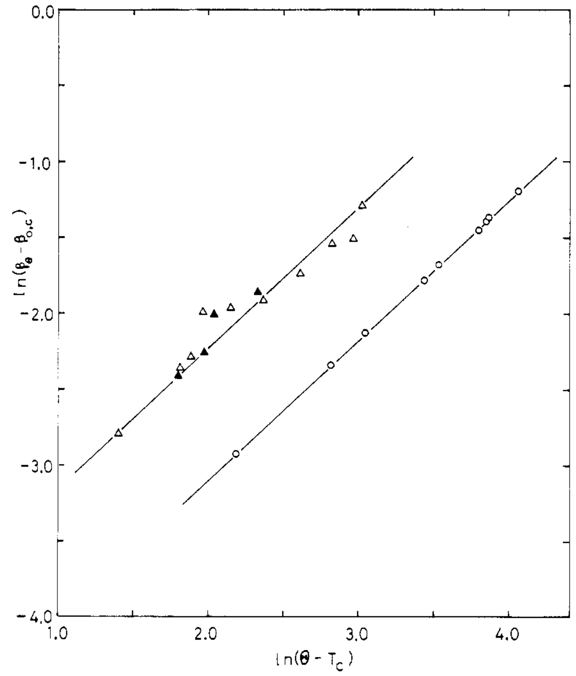

Figure 2. ln $(\beta_\Theta - \beta_{0,c})$ versus ln $(T_\Theta - T_c)$ plot for PS–MCH (○[4]) and PS–CH (△[20]; ▲[33]). Vaues of $\beta_{0,c}$ are calculated from the critical concentration $\phi_{1,c}$ by using eq 20 and β_Θ = 1.0. The Θ temperatures are 34.1 °C for PS–CH[20] and 70.5 °C[34] for PS–MCH.

The plot of eq 21 for the polystyrene (PS)–cyclohexane[20,33] and PS–methylcyclohexane[4] systems is shown in Figure 1, where a linearity is observed and n is about 0.84. The exponent α is estimated from eq 9 and the experimental data of coexistence curves in polymer solutions. The condition for the coexistence curve is given thermodynamically by using the relation $(\mu_i - \mu_i^0)/RT = \ln a_i$ by

$$\ln a_0 = \ln a_0' \qquad (22)$$

$$\ln a_1 = \ln a_1' \qquad (23)$$

where the prime indicates one of two phases and a_1 is the activity of polymer in solution. From eq 9 multiplied by ϕ_0 and eq 22 one can derive

$$C(P,T) = \ln (a_0/a_{0,c}) + \{K_1(1+\alpha)\}^{-1}(\phi_{1,c}/\phi_{0,c})\{X^{1+\alpha} - (X')^{1+\alpha}\}/(X - X') \qquad (24)$$

$$C(P,T) = \ln (a_0/a_{0,c}) + \{K_1(1+\alpha)\}^{-1}(\phi_{1,c}/\phi_{0,c})X^{\alpha} \qquad (25)$$

where X' is defined by $(\phi_0' - \phi_{0,c})/\phi_0'$ and is negative due to $\phi_0' < \phi_{0,c} < \phi_0$. Approximations that $X \ll 1$ and $|X'| \ll 1$ are used in deriving eq 24, which are valid in the vicinity of the critical point T_c, while assumptions that $X = -X'$ and that $1 + \alpha$ is an odd number are used in obtaining eq 25. The function $C(P,T)$ must be 0 at the critical point because $a_0 \rightarrow a_{0,c}$ and $X \rightarrow 0$ at $T \rightarrow T_c$. In this work we assume that $C(P,T)$ is a function of temperature only and is expressed by

$$C(T) = (\beta_{0,c} - \beta_0)^{\gamma} \qquad (26)$$

where γ is a constant and $\beta_{0,c}$ is a value of β_0 at T_c. The coexistence curve in the vicinity of the critical point is expressed by using eq 25 and 26 by

$$(\phi_{1,c}/\phi_{0,c})X^{\alpha} \sim (\beta_{0,c} - \beta_0)^{\gamma} \qquad (27)$$

or

$$(\phi_0 - \phi_{0,c})/\phi_{0,c} \sim \{r^{n/2}(\beta_{0,c} - \beta_0)^{\gamma}\}^{1/\alpha} \qquad (28)$$

where $(\phi_0 - \phi_{0,c})/\phi_0 \sim (\phi_0 - \phi_{0,c})/\phi_{0,c}$ and eq 18, where $\phi_{1,c} \sim r^{-n/2}$, are used. The determination of β_0 as a function of temperature is given below. It is shown in Figure 2 that $\ln (\beta_\Theta - \beta_{0,c})$ calculated from eq 20 is a linear function of $\ln (T_\Theta - T_c)$ with a slope $\sim$0.93, where β_Θ is a value of β at Θ and is equal to 1.0 from eq 19 at the limit of $r \rightarrow \infty$. The Θ temperatures are obtained from the experimental data of 34.1 °C for PS–cyclohexane[20] and 70.5 °C for PS–methylcyclohexane.[34] The result suggests that

$$\beta_{0,c} - \beta_0 \sim (T_c - T)^{\delta} \qquad (29)$$

and $\delta = 0.93$. Therefore eq 28 is given by using eq 29 by

$$(\phi_0 - \phi_{0,c})/\phi_{0,c} \sim \{r^{n/2}(T_c - T)^{\gamma\delta}\}^{1/\alpha} \qquad (30)$$

Values of $\alpha = 4.0$ and $\gamma = 1.43$ are speculated from the experimental data of the coexistence curve, and eq 30 is expressed by using $n = 0.84$ and $\delta = 0.93$ by

$$(\phi_0 - \phi_{0,c})/\phi_{0,c} \sim \{r^{0.105}(T_c - T)^{0.33}\} \qquad (31)$$

Although we derived eq 31 in terms of $(\phi_0 - \phi_{0,c})/\phi_{0,c}$, the similar equation for $(\phi_{1,c} - \phi_1)/\phi_{1,c}$ as eq 31 can be obtained by replacing $\phi_0/(\phi_0 - \phi_{0,c})$ by $\phi_1/(\phi_{1,c} - \phi_1)$ in eq 5, which is expressed from use of the same procedure as that for eq 31 by

$$(\phi_{1,c} - \phi_1)/\phi_{1,c} \sim \{r^{n}(T_c - T)^{\gamma\delta}\}^{1/\alpha} \sim r^{0.21}(T_c - T)^{0.33} \qquad (32)$$

Muthukumar[35] found by a consideration of the monomer fluctuation and three-body interaction in the free energy of a polymer solution that the critical volume fractions of polymer $\phi_{1,c}$ and $(\phi_1 - \phi_{1,c})/\phi_{1,c}$ are proportional to $N^{-1/3}$ and $N^{1/9}$, respectively. Experimental data show that $\phi_1^+ - \phi_1^- \sim N^{-0.23}$ (Dobashi et al.[4]), while Shinozaki et al.[11] concluded that $\phi_1^+ - \phi_1^- \sim N^{-0.34}$ and $\phi_{1,c} \sim N^{-0.40}$, where ϕ_1^+ and ϕ_1^- are concentrations of the polymer in two phases and N is the degree of polymerization. According to the above results, the exponent of r in eq 32 is in the range 0.06–0.17,[27] where it is assumed that $(\phi_1^+ - \phi_1^-)/\phi_{1,c} = 2(\phi_1^+ - \phi_{1,c})/\phi_{1,c}$ due to the symmetry of the coexistence curve in the vicinity of the critical point.[3]

Discussion

It is useful to examine the clustering function in understanding the solution structure of polymer solution, which is given from use of eq 4 and 5 by

$$G_{00}/\bar{v}_0 = -(K_0 + 1) - r^{-n}\phi_0^{-1} - K_1\{\phi_0/(\phi_0 - \phi_{0,c})\}^{\alpha} \qquad |T - T_c| \approx 0 \qquad (33)$$

$$G_{00}/\bar{v}_0 = -(K_0 + 1) - r^{-n}\phi_0^{-1} \qquad |T - T_c| \gg 0 \qquad (34)$$

Experimental data show that $G_{00}/\bar{v}_0$ in a good solvent system is positive and very small, for example, 0.54 for PS–toluene, while it is much larger than 1.0 for a poor solvent system, for example, 10.0 for PS–cyclohexane at 34 °C.[28] The mean number of solvent molecules in excess of the mean concentration in the neighborhood of a given solvent molecule is characterized by $\phi_0 G_{00}/\bar{v}_0$. Values of $\phi_0 G_{00}/\bar{v}_0$ are positive in both poor and good solvent systems, decrease with increasing polymer concentration, and become nearly zero at the limit of zero solvent concentration, suggesting that the system is in a state of random mixing at $\phi_0 \rightarrow 0$.[28]

The osmotic pressure π is derived by using the relation $\pi = -(RT/V_0) \ln a_0$ and eq 9, 32, and 11 by

$$\pi V_0/RT = K_1^{-1}\{Y^{1+\alpha}/(1+\alpha)\}r^{-n} - (T_c - T)^{\gamma\delta} - \ln a_{0,c} \qquad (35)$$

for the critical region, Y being defined by $Y = (\phi_{1,c} - \phi_1)/\phi_1$ and

$$\pi V_0/RT = -(1 - r^{-n})^{-1} \ln \phi_0 + \beta_0 \ln (1 - \phi_1/\beta_0) \qquad (36)$$

for the noncritical region where V_0 is the molar volume of the solvent and R is the gas constant. From eq 35 and $\alpha = 4.0$ is obtained $\pi \sim (\phi_{1,c} - \phi_1)^{5.0}$, which can compare with $\pi \sim |\phi_1 - \phi_{1,c}|^{4.5}$ determined by the light-scattering method.[6,8] The second virial coefficient A_2 in the noncritical region is derived from eq 36 by

$$A_2 = (V_0/2m^2)\{(1 - r^{-n})^{-1} - \beta_0^{-1}\} \qquad (37)$$

where m is the molecular weight per segment, $m = M/r$. Since values of $\beta_{0,c}$ below the Θ temperature are given by eq 19, A_2 below Θ is expressed by using eq 37 by

$$A_2 \sim -(2r^{-n/2} - r^{-n})/2 \qquad (38)$$

or

$$A_2 \sim -(2r^{-0.42} - r^{-0.84})/2 \qquad T < \Theta \qquad (39)$$

where $n = 0.84$ is used. It is also possible to determine A_2 above the Θ temperature if β_0 is evaluated above Θ. It is estimated that β_0 approaches 1.0 at the limit $r \rightarrow \infty$ and is larger than 1.0 above Θ. One of the simplest expressions for β_0 satisfying the above conditions may be given as

$$\beta_0 = (r^m + 1)/(r^m - 1) \qquad T > \Theta \qquad (40)$$

where m (>0) is a constant. If the eq 40 is valid, A_2 is given by using eq 37 and the approximation $r \gg 1$ by

$$A_2 \sim (2r^{-m} + r^{-n})/2 \qquad T > \Theta \qquad (41)$$

which is essentially the same as eq 38 or 39 except for the sign if m is equal to $n/2$. Sotobayashi and Ueberreiter[36] proposed that the molecular weight (M) dependence of the second virial coefficient A_2 is described by the equation $A_2 = (a/M^{1/2}) + b$ through the cryoscopic measurements in solution of polystyrene in naphthalene, where a and b are constants, and they tested the equation with various systems and confirmed its validity.[36,37] Wolf et al.[12,13] proposed the A_2–M relation on the basis of the experimental data from light-scattering measurements, which is expressed by $A_2 = A_2^{\infty} + b_xM^{-(a-0.5)}$ for $A_2 > 0$ and $A_2 = A'_2{}^{\infty} + b'_xM^{a-0.5}$ for $A_2 < 0$, where a is the exponent of the viscosity–molecular weight relationship $[\eta] = KM^a$ and A_2^{∞} and b_x are constants.[14] Huber and Stockmayer found that A_2 at low M does not vanish and decreases with $M^{-1.1}$ at the Θ temperature in solutions of polystyrene in cyclohexane.[38] Bellemans and Janssens evaluated A_2 of athermal solutions by a Monte Carlo technique and concluded that $A_2(n) \sim 0.58n^{-0.28}$ for large n, where each polymer molecule is a linear chain occupying n sites (n-mer) of a regular lattice.[39] Sanchez and Lohse[40] derived $A_2 \sim M^{-0.2}$ in a good solvent and $A_2 \sim M^{-0.5}$ in a poor solvent from the cell model theory of polymer solution in which concentration inhomogeneities are taken into account. It is shown from comparisons between our results of $A_2(r)$ in eq 38 and 41 and those mentioned above that our equations of $A_2(r)$ are consistent with the experimental results qualitatively.

It is instructive to compare the results obtained in this work with those of the Flory–Huggins theory,[41] which is given by

$$\ln (a_0/\phi_0) = (1 - r^{-1})\phi_1 + \chi_1\phi_1^2 \qquad (42)$$

where χ_1 is the polymer–solvent interaction parameter depending on temperature. On the other hand, eq 15 is expressed by using an approximation that $\ln \phi_0 \sim -\phi_1 - \phi_1^2/2$ and $(1 - r^{-n})^{-1} \sim 1 + r^{-n}$ by

$$\ln (a_0/\phi_0) = (1 - r^{-n})\phi_1 + (\beta_0^{-1} - r^{-n})\phi_1^2/2 \qquad (43)$$

In this work we obtained $n = 0.84$ based on the experimental data of the critical concentrations in polymer solutions of various molecular weights of polymers, which is the essential difference between the Flory–Huggins theory with $n = 1.0$. The critical exponent of coexistence curve in the Flory–Huggins theory is estimated by using eq 42 by

$$\ln (a_0/a_0') = \ln (\phi_0/\phi_0') + (1 - r^{-1})(\phi_1 - \phi_1') + \chi_1(\phi_1^2 - \phi_1'^2) = 0 \qquad (44)$$

or

$$\chi_1 = \{\Delta\phi_1/\phi_{0,c} + (\Delta\phi_1/\phi_{0,c})^3/3 - (1 - r^{-1})\Delta\phi_1\}/\{2(\Delta\phi_1)\phi_{1,c}\} \sim (\Delta\phi_1)^2/\phi_{1,c} \qquad (45)$$

where $\Delta\phi_1 = \phi_{1,c} - \phi_1$, $-\Delta\phi_1' = \phi_{1,c} - \phi_1'$, and $\Delta\phi_1 = \Delta\phi_1'$ are used. From eq 45 one can show that

$$|\phi_1 - \phi_{1,c}|/\phi_{1,c} \sim \{|T_c - T|/T_c\}^{1/2}r^{1/4} \qquad (46)$$

where $\chi_1 \propto T^{-1}$, $\phi_{1,c} \sim r^{-1/2}$, and $\phi_{0,c} \sim 1$ are used. Note that eq 46 is determined by the term $\ln (\phi_0/\phi_0') = 2\{\Delta\phi_1/\phi_{0,c} + (\Delta\phi_1/\phi_{0,c})^3/3 + \ldots\}$, which comes from a random distribution of solvent molecules in solution. As is shown in eq 9, the random distribution of solvent collapses in the vicinity of T_c due to the cluster formation of solvent molecules. According to eq 33, the clustering function diverges in the critical region as $G_{00}/\bar{v}_0 \sim (\phi_0 - \phi_{0,c})^{-\alpha} \sim (\phi_{1,c} - \phi_1)^{-\alpha}$, which can compare with that of the osmotic compressibility $(\partial\pi/\partial\phi_1)^{-1} \sim (\phi_{1,c} - \phi_1)^{-\alpha}$ obtained from eq 35.

It is essentially important to discuss α in eq 5. As is shown in eq 24, α must be even number such as 2.0, 4.0, and so on. This means from eq 33 that the clustering function $G_{00}/\bar{v}_0$ of one phase of X is the same as that of the other coexistent phase corresponding to X' in the vicinity of the critical point. The selection of $\alpha = 4.0$ is made based on the results of theoretical calculations from many models,[42] which are in the range 3.0–5.2, and the experimental results of 4.5 from the light scattering measurements.[8] If $\alpha = 4.5$ is used in eq 24, the equation contains a complex number due to $X = -X'$ and the symmetry of the clustering function at X and X' in the vicinity of T_c breaks down.

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