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An Extended Universal Coexistence Curve for Polymer Solutions

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ABSTRACT: The symmetrized universal coexistence (COEX) curve for binary polymer/solvent solutions, as proposed by Sanchez (*J. Appl. Phys.* 1985, *58*, 2871), has been extended based on the Wegner expansion. Together with empirical relationships between the polymer molecular weight (M) and the critical volume fraction (ϕ_C) as well as between M and the critical solution temperature (T_C), all the high-precision COEX curve data for polystyrene (PS) in methylcyclohexane (MCH) and in cyclohexane (CH) can be represented by an expression of the form $|\psi - \psi_C| = AX^\beta + BX^{\beta+\Delta}$ where $X = \epsilon N^{0.31}$, $\epsilon = (T_C - T)/T_C$, N is the degree of polymerization, ψ is a dimensionless variable which symmetrizes the COEX curve, and the values of β and Δ are fixed at 0.327 and 0.50, respectively. Results of the extended universal COEX curve permit us to distinguish phase-separation behavior from polymer coil-to-globule transition.

I. Introduction

In binary fluid mixtures, the coexistence (COEX) curves are fairly symmetric in a $T - \phi$ plot where T and ϕ are the phase-separation temperature and the volume fraction, respectively. In binary polymer/solvent solutions the COEX curves are asymmetric with $(\phi_{SD} - \phi_C) > (\phi_C - \phi_D)$ except possibly for values of $\epsilon \leq 10^{-5}$; SD and D subscripts denote polymer-rich semidilute and polymer-poor dilute phases, respectively, and $\epsilon \equiv (T_C - T)/T_C$. Sanchez[1] proposed a dimensionless variable ψ $(=\phi/[\phi + R(1 - \phi)])$ and symmetrized the polymer solution COEX curve with the expression

$$|\psi - \psi_C| = \psi_0(\epsilon N^b)^\beta \tag{1}$$

in which N is the degree of polymerization; the parameters R and b, the amplitude ψ_0, the critical concentration ψ_C, and the critical exponent β could be determined experimentally. He then carried out a nonlinear least-squares fit to eq 1 using ten COEX curve data sets for the polystyrene (PS)/methylcyclohexane (MCH) system[2,3] and obtained values of $\psi_0 = 0.564 \pm 0.004$, $\psi_C = 0.307 \pm 0.001$, $b = 0.313 \pm 0.004$, and $\beta = 0.327 \pm 0.002$.

The simple scaling relation of eq 1 is valid up to a maximum value of ϵ, denoted as ϵ_{max}, which satisfies the condition $\epsilon_{max}N^{0.3} \leq 0.075$. For polystyrene, $N = M/104$, and the ϵ_{max} values are of the order of 10^{-3} for $M \sim 10^6$ g/mol and 10^{-2} for $M \sim 5 \times 10^4$ g/mol.

In an experimental study of polymer interactions in a bad solvent, Perzynski, Delsanti, and Adam[4] found that for PS in cyclohexane (CH)

$$c_C = 6.8M_w^{-0.38\pm0.01} \tag{2}$$

$$\frac{10^3}{T_C(\mathrm{K})} = 3.256\left(1 + \frac{14.6 \pm 0.2}{M_w^{1/2}}\right) \tag{3}$$

where c_C is the critical solution concentration in grams per centimeter cubed and M_w is the weight-average molecular weight in grams per mole. By combining the concepts of eq 1–3 and by taking into account the asymmetry in the symmetrized universal COEX curve according to the Wegner expansion,[5] we derive an extended universal COEX curve (section II) which can fit all the high-precision COEX data for each binary polymer/solvent system, i.e., PS in MCH (section III.a) and PS in CH (section III.b). The resultant extended universal COEX curve can then be used to distinguish phase-separation behavior from measurements of polymer coil-to-globule transition (section IV).

II. Extended Universal Coexistence Curve

By extending the simple scaling relation of eq 1 with correction terms according to the Wegner expansion,[5] the extended universal COEX curve has the form

$$|\psi - \psi_C| = AX^\beta + BX^{\beta+\Delta} + B_2X^{\beta+2\Delta} + \ldots \tag{4}$$

where $X = \epsilon N^{0.31}$, β is a critical exponent, and Δ is fixed at 0.50.[6,7] Over the accessible temperature ranges of PS/MCH[2,3] and PS/CH,[8,9] we can set $B_2 = 0$ and write down explicitly for the polymer-poor side and the polymer-rich side of the COEX curve the following:

$$\psi_C - \psi_D = A_DX^{0.327} + B_DX^{0.827} \tag{5}$$

$$\psi_{SD} - \psi_C = A_{SD}X^{0.327} + B_{SD}X^{0.827} \tag{6}$$

where we have taken an experimentally determined value of 0.327 for β.[1,9] The quality of fitting should remain unchanged if we were to use a theoretical β value of 0.3265 ± 0.0011 based on the renormalization group calculations[9] for the Ising model, the two β values, i.e., 0.327 ± 0.004 versus 0.3265 ± 0.0011, being virtually identical. We shall also set $A_D = A_{SD}$ since Sanchez has shown that eq 1 is symmetric for small values of ϵ.

From eq 2 and 3, we retain the forms

$$\phi_C = HM_w^{-\alpha_c} \tag{7}$$

$$10^3/T_C(\mathrm{K}) = P\left(1 + \frac{Q}{M_w^{0.5}}\right) \tag{8}$$

where $c_C = \phi_C\rho_{polymer}$ with $\rho_{polymer}$ being the polymer density and the parameters α_c, H, P, and Q are constants to be determined experimentally by using the high-precision data for PS/MCH (and PS/CH) which are available in the literature.

III. Results

From the literature, we first took experimentally measured values of N (or M_w), T_c, ϕ_C, and the COEX curve data, i.e., $\{T,\phi_D\}$ pairs for each polymer molecular weight/solvent set, and used the nonlinear (IMSL) least-squares fitting of eq 5 in the form

$$\frac{\phi_D}{\phi_D + R(1 - \phi_D)} = \frac{\phi_C}{\phi_C + R(1 - \phi_C)} - A_DX^{0.327} - B_DX^{0.827} \tag{9}$$

to determine the three fitting parameters R $(=(1 - 1/\psi_C)/(1 - 1/\phi_C))$, A_D, and B_D for each polymer molecular weight. The details of the curve-fitting procedure are presented in the Appendix. The values of A_D and B_D, as

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Table I
Critical Point Data for PS/MCH[2,3] and Best-Fit Parameters (A_D, B_D, B_{Sd}, and R) for Equations 11 and 12

	experimental data			parameters[a]						
PS/MCH	M_w	ϕ_C	T_c, K	A_D	B_D	R	B_{SD}	ψ_C	RSQ[b]	χ^2 [c]
A[d]	1.02×10^4	0.1954	285.71	0.3373	−0.1868	1.365	0.1500		0.9964	6.5×10^{-6}
B	1.61×10^4	0.1691	295.98	0.4285	−0.2744	0.8811	0.1507	0.191	0.9996	5.1×10^{-7}
C	1.72×10^4	0.1658	296.75	0.4201	−0.2495	0.8326	0.1501	0.193	0.9995	9.2×10^{-7}
D	2.02×10^4	0.1564	298.95	0.4250	−0.2520	0.6210	0.1502	0.193	0.9993	8.7×10^{-7}
E	3.49×10^4	0.1266	309.00	0.4250	−0.2520	0.7900	0.1500	0.193	0.9986	2.1×10^{-6}
F	4.64×10^4	0.1148	312.61	0.420	−0.2521	0.5540	0.1498	0.193	0.9990	8.5×10^{-7}
G	10.9×10^4	0.0816	322.71	0.4250	−0.2521	0.3840	0.1500	0.193	0.9991	6.3×10^{-7}
H	18.1×10^4	0.0685	327.00	0.420	−0.2522	0.3150	0.1498	0.193	0.9993	2.7×10^{-7}
I	71.9×10^4	0.0393	334.82	0.4251	−0.2518	0.1770	0.1503	0.193	0.9765	3.4×10^{-6}

[a] Average fitting parameters: $\bar{A}_D$, 0.425 ± 0.002; $\bar{B}_D$, −0.252 ± 0.001; $\bar{B}_{SD}$, 0.150 ± 0.001; $\bar{\psi}_C$, 0.193 ± 0.001. [b] RSQ, see definition in Table II. [c] χ^2 is the reduced χ-squared statistic parameter used as a measure of the goodness of fit. See definition in Table II. [d] Data set A shows larger than expected deviation in the fitting parameters. The A_D, B_D, and χ_C values from data set A were not used in computing $\bar{A}_D$, $\bar{B}_D$, and $\bar{\psi}_C$.

Table II
Critical Point Data for PS/CH and Best-Fit Parameters (A_D, B_D, B_{SD}, R)[a] for Equations 16 and 17

	M_w	ϕ_C	T_c	A_D	B_D	B_{SD}	R	ψ_C	RSQ[b]	χ^2 [b]
X	1.56×10^6	0.0317	303.65	0.5950	−0.4251	0.0200	0.09819	0.2500	0.9970	1.9×10^{-7}
Y	1.56×10^6	0.0317	303.65	0.5950	−0.4250	0.0203	0.09820	0.2500	0.9946	3.6×10^{-7}
A	0.2×10^6	0.0688	296.99	0.5951	−0.4500	0.0124	0.2278	0.2449	0.9984	4.1×10^{-7}
B	0.2×10^6	0.0688	296.99	0.5950	−0.4244	0.0178	0.2216	0.2500	0.9945	1.4×10^{-6}

[a] Average fitting parameters: $\bar{A}_D$, 0.595 ± 0.001; $\bar{B}_D$, −0.425 ± 0.001; $\bar{B}_{SD}$, 0.018 ± 0.004; $\bar{\psi}_C$, 0.250 ± 0.003. [b] Defined, RSQ and χ^2: $\chi^2 = (\sum_{i=1}^{N}(Y_i - Y_{i,\text{calcd}})^2)/(N - M)$; RSQ $= 1 - \sum_{i=1}^{N}(Y_i - Y_{i,\text{calcd}})^2/[\sum_{i=1}^{N}Y_i^2 - \sum_{i=1}^{N}Y_i\sum_{i=1}^{N}Y_i/N]$; where N is the number of data points used in the fitting procedure, M is the number of fitting parameters, Y_i ($\equiv\phi_i$) denotes data point i, and $Y_{i,\text{calcd}}$ ($\equiv\phi_{i,\text{calcd}}$) is the calculated value.

listed in Tables I and II, were remarkably constant. Thus, we have shown that eq 5 (or eq 9) represents the dilute side of the COEX curve extremely well, and there is no need to recompute a generalized A_D, B_D, and R for the polymer/solvent system by using all the data sets simultaneously. By setting $A_D = A_{SD}$, we then determine B_{SD} according to the expression

$$\frac{\phi_{SD}}{\phi_{SD} + R(1 - \phi_{SD})} = \frac{\phi_C}{\phi_C + R(1 - \phi_C)} + A_D X^{0.327} + B_{SD} X^{0.827} \quad (10)$$

In eq 9 and 10, we have also taken the same critical exponent values for both PS/MCH and PS/CH. Specific values for the PS/MCH and PS/CH systems are presented as follows.

III.a. PS/MCH COEX Curve. For the PS/MCH COEX curve, we get

$$\psi_C - \psi_D = (0.425 \pm 0.002)X^{0.327} - (0.252 \pm 0.001)X^{0.827} \quad (11)$$

$$\psi_{SD} - \psi_C = (0.425 \pm 0.002)X^{0.327} + (0.150 \pm 0.001)X^{0.827} \quad (12)$$

where we have set $A_D = A_{SD}$ and $\psi_C = 0.193 \pm 0.001$. The deviation from the law of rectilinear diameter in the symmetrized COEX curve can be represented by

$$\frac{\psi_{SD} + \psi_D}{2} = \psi_C + (0.201 \pm 0.002)X^{0.827} \quad (13)$$

Equations 11–13 are valid for $X \leq 0.29$ (instead of 0.075) and $\psi_D \gtrsim 6 \times 10^{-6}$. From the critical point data, we also determined the constants in eq 7 and 8 with

$$10^3/T_C(\text{K}) = (2.921 \pm 0.004)[1 + (20.2 \pm 0.2)/M_w^{1/2}] \quad (14)$$

$$\phi_C = (6.68 \pm 0.02)M_w^{-(0.38 \pm 0.01)} \quad (15)$$

and M_w expressed in grams per mole. Thus, $R \simeq 32.9M_w^{-0.38} \sim 5\phi_C$. It should be noted that if we were to fit the semidilute side using eq 10 but without setting $A_{SD} = A_D$, we would obtain A_{SD} = 0.4250, 0.4251, 0.4250, 0.4251,

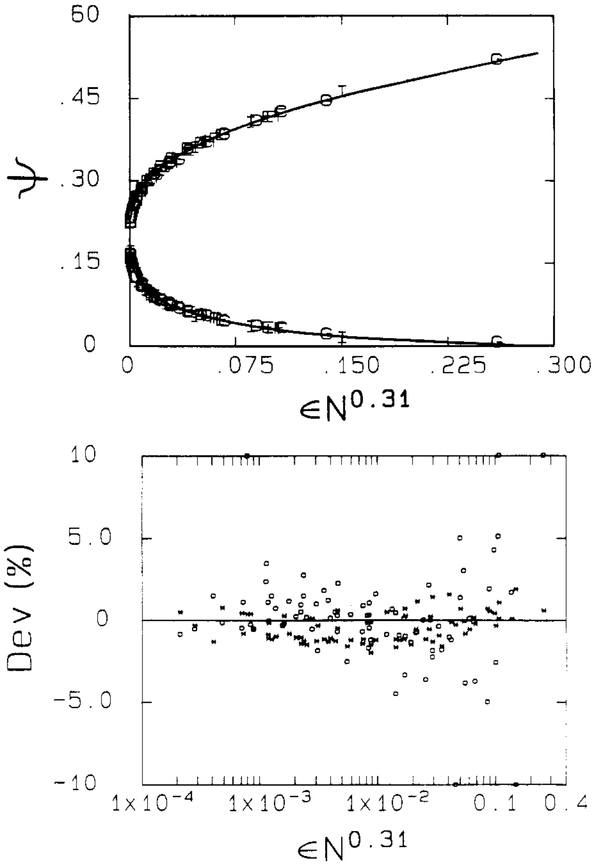

Figure 1. (a, top) Extended universal COEX curve, eq 11 and 12 and data[2,3] corresponding to the symbols (A–I) listed in Table I, for polystyrene in methyl cyclohexane. (b, bottom) Deviation plot shows excellent agreement between the calculated values and the measured data. Dev (%) = $[(\psi_{\text{meas}} - \psi_{\text{calcd}})/\psi_{\text{meas}}] \times 100$. Hollow squares denote the dilute side; * denotes the semidilute side.

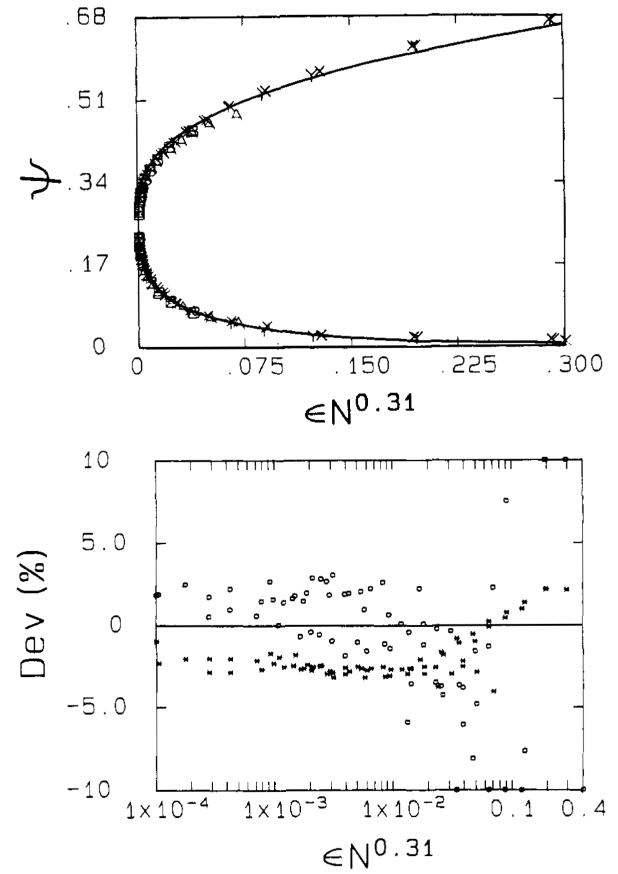

Figure 2. (a, top) Extended universal COEX curve, eq 16 and 17 and data[8,9] corresponding to the symbols (A, B, X, Y) listed in Table II, for polystyrene in cyclohexane. (b, bottom) Deviation plot shows very good agreement between calculated values and measured data.

0.4250, 0.4249, 0.4250, 0.4249, and 0.4250 for data sets A–I in Table I. Thus, we show independently that $\tilde{A}_D = \tilde{A}_{SD} = 0.425$.

III.b. PS/CH COEX Curve. For the PS/CH COEX curve, we get

$$\psi_C - \psi_D = (0.595 \pm 0.001)X^{0.327} - (0.425 \pm 0.001)X^{0.827} \tag{16}$$

$$\psi_{SD} - \psi_C = (0.595 \pm 0.001)X^{0.327} + (0.018 \pm 0.004)X^{0.827} \tag{17}$$

where we have set $A_D = A_{SD}$ and $\psi_C = 0.250 \pm 0.003$. The deviation from the law of rectilinear diameter in the symmetrized COEX curve can be expressed by

$$\frac{\psi_{SD} + \psi_D}{2} = \psi_C + (0.222 \pm 0.005)X^{0.827} \tag{18}$$

Equations 16–18 are valid for $X \leq 0.306$ and $\psi_D \gtrsim 5.65 \times 10^{-3}$. From critical-point data, we recall the relations from ref 4

$$10^3/T_C(\mathrm{K}) = 3.256(1 + 14.6/M_w^{1/2}) \tag{3}$$

$$\phi_C = (7.13 \pm 0.02)M_w^{-0.38} \tag{2'}$$

resulting in $R \simeq 22.7M_w^{-0.38} \sim 3\phi_C$. We did not try to establish better values for the constants in eq 2 and 3 for lack of data in the PS/CH system.

IV. Discussion

The extended universal COEX curve can fit all molecular weights of each binary polymer/solvent system over the entire accessible temperature range, as shown in Figures 1 and 2 for PS in MCH and PS in CH, respectively.

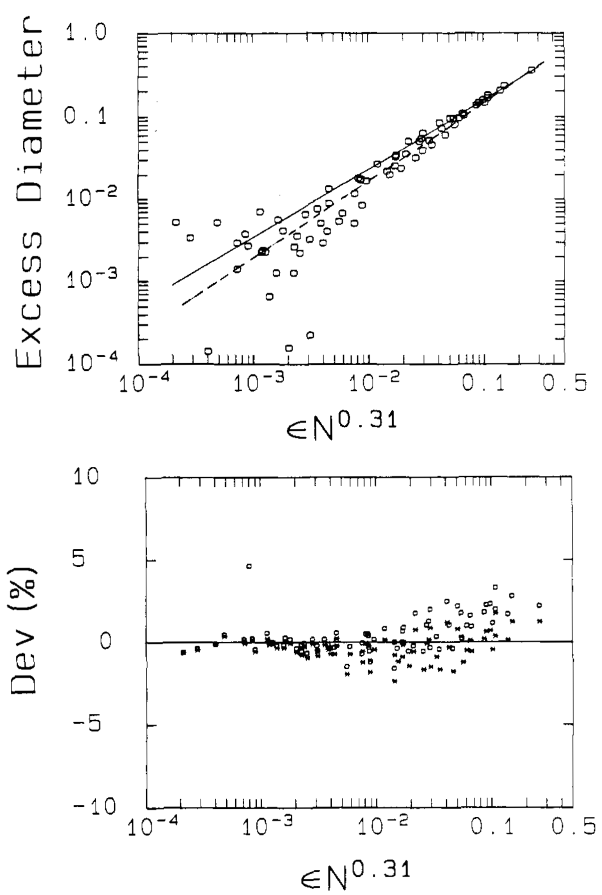

Figure 3. (a, top) log–log plot of excess diameter $(\psi_D + \psi_{SD})/2\psi_C - 1$ versus X ($=\epsilon N^{0.31}$) for PS in MCH. Solid line represents a slope of 0.827. A least-squares fitting of the data gives $(\psi_D + \psi_{SD})/2\psi_C = 1 + 1.14X^{0.92\pm0.05}$ (eq 20), as denoted by the dashed line. (b, bottom) Deviation plot of eq 20 with measured data. □ and * denote deviations of dashed and solid lines with measured data, respectively.

For PS/MCH, deviation plots in Figure 1b show fairly good agreement on both sides of the coexistence curve (□, dilute; *, semidilute) up to $\epsilon N^{0.31} \lesssim 0.3$. For PS/CH, deviations occur on both sides of the coexistence, as shown in Figure 2b, with $\psi_{SD,meas} < \psi_{SD,calcd}$ and $\psi_{D,meas} > \psi_{D,calcd}$ at $\epsilon N^{0.31} \gtrsim 2 \times 10^{-2}$. We can rewrite eq 5 and 6, yielding

$$\frac{\psi_D + \psi_{SD}}{2\psi_C} - 1 = \frac{(B_{SD} - B_D)X^{\beta+\Delta}}{2\psi_C} \tag{19}$$

Thus, in a log–log plot of $((\psi_D + \psi_{SD})/2\psi_C - 1)$ versus X, we should expect a slope of $\beta + \Delta = 0.827$. Figure 3a shows a log–log plot of $(\psi_{SD} + \psi_D)/2\psi_C - 1$ versus X yielding

$$\frac{\psi_D + \psi_{SD}}{2\psi_C} = 1 + 1.14X^{0.92\pm0.05} \tag{20}$$

An exponent of 0.92 ± 0.05 is slightly larger than 0.827. The scattered data, however, suggest that our assumed value of 0.827 is quite reasonable. Figure 3b shows deviation plots of eq 20 (dashed line in Figure 3a) and eq 13 (solid line in Figure 3a) with measured data. It will be difficult to distinguish the two expressions. Nevertheless, we have succeeded in representing the COEX curve of PS in MCH and that of PS in CH with the best available COEX curve data from the literature.

The extended universal COEX curve for polystyrene in cyclohexane can now be used to predict the phase-separation behavior. Many experiments have been performed in polymer coil-to-globule transition studies.[11] With the extended universal COEX curve, we can predict whether

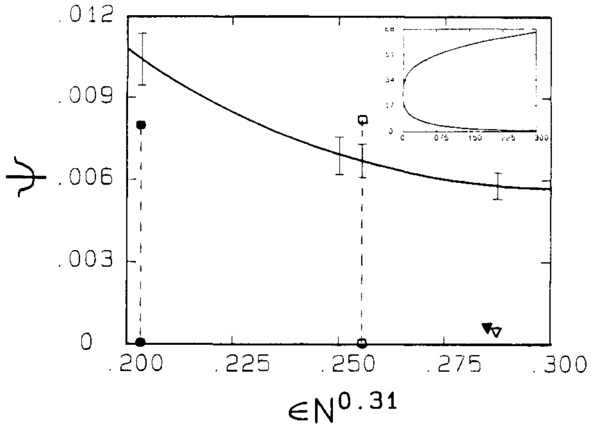

Figure 4. Thermodynamic states of some typical measurements on polymer coil-to-globule transition studies for the PS/CH system: (▼) M_w = 20.6 × 10^6 g/mol, (▽) 8.42 × 10^6 g/mol, ref 12; (□) M_w = 3.84 × 10^6 g/mol; (■) M_w = 6.77 × 10^6 g/mol, ref 13. Inset denotes the overall COEX curve. The vertical dashed lines and the squares □-----□ and ■-----■ denote the experimental ranges in ref 13. Uncertainties in the universal curve of Figure 4 are about ±10% (maximum dev (%) as defined in the caption to Figure 1). The symbol "I" denotes the uncertainty at different values of $\epsilon N^{0.31}$.

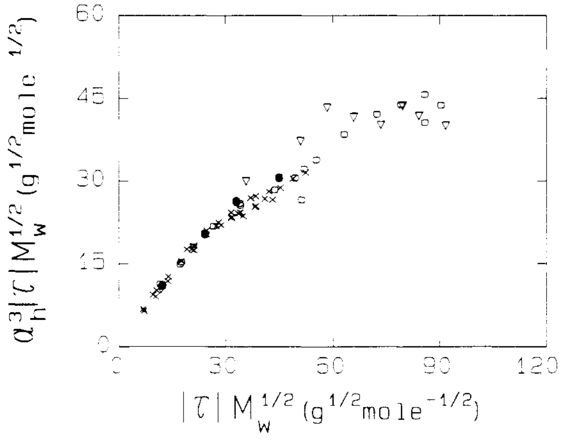

Figure 5. Variation of scaled expansion factor of hydrodynamic size $\alpha_h^3|\tau|M_w^{1/2}$ versus scaled reduced temperature $|\tau|M_w^{1/2}$ where $|\tau| = |T - \Theta|/\Theta$, $\alpha_h = R_h(T)/R_h(\Theta)$, with R_h being the hydrodynamic radius. Crosses denote data from ref 11. Hollow circles denote data from ref 14. Filled circles denote data from ref 15. Inverted triangles denote data from ref 12. All data are for the PS/CH system.

any of the reported measurements could have been performed in the metastable region. Figure 4 shows some typical comparisons on the thermodynamic states of reported polymer (PS) coil-to-globule studies, e.g., data by Vidakovic and Rondelez should be acceptable while those by Perzynski et al. should be examined with caution. We have collected those sets of data which passed our phase-separation test and plotted them in Figure 5. It is interesting to note that Vidakovic and Rondelez (triangle data points for the PS/CH system) appeared to have reached the collapsed state based on hydrodynamic size in 1984 using the sedimentation technique. The plateau values of $\alpha_h^3|\tau|M_w^{1/2}$ by the two different methods, i.e., sedimentation versus dynamic light scattering, are the same, even though there is a possible difference, perhaps beyond the experimental error limits, in the crossover regime between the two experiments.

In conclusion, we have extended the universal COEX curve of Sanchez to fit the binary polymer/solvent solutions over a very broad temperature and molecular weight range. The coexistence curve can be used to test the thermodynamic state of polymer coil-to-globule experiments. By excluding those data which show possibilities of phase-separation behavior, we can come to a very reasonable conclusion on the findings in the collapsed regime.

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Appendix. Curve Fitting Procedure

Step 1. Starting from eq 9

$$\frac{\phi_D}{\phi_D + R(1-\phi_D)}(=\psi_D) = \frac{\phi_C}{\phi_C + R(1-\phi_C)} - A_D X^{0.327} - B_D X^{0.827}$$

we used the three parameters $\{R, A_D, B_D\}$ and K experimental data sets $\{M_w, \phi_C, (X,\phi_D)\}$.

Step 2. For the ith set of data points $\{M_w, \phi_C, (X,\phi_D)\}_i$, the nonlinear least-squares fitting program yields three parameters $\{R, A_D, B_D\}_i$. The results are listed in Tables I and II. By repeating the K data sets, K sets parameters of $\{R, A_D, B_D\}$ are obtained.

Step 3. R has a molecular weight dependence. With $\psi_C = \phi_C/(\phi_C + \mathrm{R}(1 - \phi_C))$, K sets of parameters $\{\psi_C, A_D, B_D\}$, as listed in Tables I and II, are obtained.

Step 4. As values of A_D, B_D, and ψ_C are constant for the K data sets, average values of $\{A_D, B_D, \psi_C\}$, defined as $\bar{A}_D$, $\bar{B}_D$, and $\bar{\psi}_C$, are computed and listed in Tables I and II. Equations 11 and 16 are obtained.

Step 5. By setting $\bar{A}_D = A_{SD}$ and the value of $\bar{\psi}_C$ from step 4, together with the K experimental data sets (X, ϕ_{SD}), a nonlinear least-squares fitting of eq 10 yields eq 12 and 17.

Registry No. PS, 9003-53-6.

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