Cloud Point Curve and Critical Point of Multicomponent Polymer/Single Solvent System

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ABSTRACT: An attempt was made to establish a theoretical method for calculating the cloud point curve (CPC) and critical point of solutions of polydisperse polymers in a single solvent (*i.e.*, quasi-binary system) on the basis of the polydispersity of the polymer and concentration- and molecular weight-dependences of the polymer-solvent thermodynamic interaction parameter χ . Expressions giving the cloud point curve were derived and a computer simulation technique, based on the theory, was developed. The effects of the average molecular weight, polydispersity of polymer and concentration dependence of χ -parameter on CPC, threshold cloud point and critical point were clarified. In order to represent accurately the CPC for the entire concentration range from the molecular characteristics of the original polymer and operating conditions, such as polymer-volume fraction and χ -parameter, the concentration dependence parameters p_1 and p_2 , in the relation $\chi = \chi_0(1 + p_1 v_p + p_2 v_p^2)$ (χ_0 ; concentration-independent parameter, v_p , polymer volume fraction) should be adequately taken into account. Very delicate changes in p_1 and p_2 cause significant variation in CPC and none of the literature data on p_1 and p_2 for polystyrene/cyclohexane adequately represent the experimental CPC. From an actual CPC experiment, $p_1 = 0.643$ and $p_2 = 0.200$ were evaluated. The effective role of the molecular weight dependence of χ in CPC was shown in the lower v_p region.

KEY WORDS Cloud Point Curve / Polydispersity / Concentration Dependence / Molecular Weight Dependence / χ Parameter / Polystyrene / Computer Simulation / Threshold Cloud Point / Critical Point / Quasi-Binary System /

The cloud point curve (CPC) of polymer/single solvent system is experimentally known to be highly unsymmetrical with respect to polymer concentration, regardless of the polymericity of the polymer.^{1,2} This high degree of dissymmetry in CPC for monodisperse polymer/solvent system can be explained theoretically in terms of the large molar volume ratio X of the polymer to the solvent. For the strictly monodisperse polymer solution (if available) the coexistence curve (CC) should be in excellent agreement with CPC. As early

as 1952, Shultz and Flory³ determined experimentally the CPC for polydisperse polyisobutylene/diisobutyl ketone and polystyrene/cyclohexane systems, comparing CC instead of CPC for these systems, using the Flory-Huggins type thermodynamic theory for polymer solutions and assuming a monodisperse polymer/single solvent system and a constant thermodynamic interaction parameter χ over a wide range of concentration (see Figures 2 and 3 of ref 3). They noticed that the shapes of the calculated CPC agreed only

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quantitatively with those observed and the latter was markedly broader and the observed critical points occurred at higher polymer concentrations than those predicted. The significant divergence of the observed CPC from the simple thermodynamic theory may be due to (1) the polymolecularity of the polymers and (2) the concentration dependence of the thermodynamic interaction parameter χ , because an important role of χ -parameter in the phase equilibrium of polymer solutions as shown by Kamide *et al.*⁴⁻¹² Unfortunately, the effect of the polymolecularity of the polymer and concentration dependence of the χ -parameter on CPC and CC could not be correctly estimated in 1952 due to the lack of theoretical background of phase equilibrium of multicomponent polymer solutions. Shultz and Flory determined also experimentally the CPC for a mixture of two polystyrene fractions (the relative molar volume ratio of the polymer to the solvent $X = 768$ and 1.095×10^4) dissolved in cyclohexane, pointing out that the CPC of this quasi-ternary system is depressed in a higher concentration range than the precipitation threshold point.

Rehage *et al.*¹³ estimated the cloud point as the cross point of a CC, obtained for a multicomponent polystyrene-cyclohexane system with a given initial polymer volume fraction v_p^0 , and the v_p^0 axis. Kuwahara *et al.*¹⁴ measured directly the CPC of five polystyrenes dissolved in cyclohexane near their critical points, showing experimentally that the polymer volume fractions at the precipitation threshold point ($v_{p,tc}$) are significantly smaller than those at the critical point (v_p^c) even for a solution of "monodisperse" polystyrene characterized by the ratio of the weight- to the number-average molecular weight $M_w/M_n < 1.03$. Koningsveld and Staverman¹⁵⁻¹⁷ applied Rehage *et al.*'s procedure for estimating the cloud point to their calculations using log-normal, bimodal, and exponential type molecular weight distributions for the original polymer.

At the present, spinodal and coexistence

curves can be calculated for multicomponent polymer/single solvent systems,^{4,9,15,17-21} But, there is no example of a direct theoretical calculation of CPC. The indirect method originally proposed by Rehage *et al.* is strongly limited and applicable to an extremely limited range. Rehage *et al.*'s procedure, as expected, very tedious and time consuming, because a single coexistence curve yields only a single point in a CPC. Systematic study on CPC has not been pursued very much.

This article attempts to establish a theoretical method for directly evaluating CPC without reliance on a coexistence curve and carry out the computer experiment to clarify the effects of the molecular characteristics of the original polymer and of concentration- and molecular weight-dependence of the χ -parameter on CPC and compare the observed CPC for a multicomponent polystyrene-cyclohexane system with that theoretically determined.

The critical solution point of the polydisperse polymer solution in a single solvent was first studied by Stockmayer who did not consider the concentration dependence of the χ -parameter. The most rigorous expressions for critical points were derived by Koningsveld and Staverman,²² who considered the concentration dependence of the χ -parameter along with the polymolecularity of the polymer. Koningsveld *et al.*^{23,34} applied their theory to estimate the concentration dependence of the χ -parameter. Unfortunately, no systematic treatment has been given for critical solution points. In this paper, we also extend the theory to the case in which the polymolecularity of a polymer and the concentration- and molecular weight-dependence of χ -parameter exist for a quasibinary mixture and show the effects of these factors on the critical points in some detail.

THEORETICAL BACKGROUND

Since 1968, computer experiments based on

the rigorous theory have been energetically carried out on multicomponent polymer/single solvent systems by Kamide and his coworkers^{4,9,11,20,21} and Koningsveld *et al.*¹⁵⁻¹⁹ Kamide *et al.*¹¹ expressed, in a purely phenomenological sense, the thermodynamic interaction parameter χ_i of the i -th polymer component in the form

$$\chi_i = \chi_{00}(1 + k'/X_i)(1 + pv_p) \quad (i = 1, 2, \dots, m) \quad (1)$$

where χ_{00} is a parameter independent of the polymer volume fraction v_p and the molar volume ratio of the i -th component to the solvent X . k' and p are molecular weight- and the concentration-independent parameters. χ_{00} and k' are functions of temperature and probably of pressure. m is the total number of components. They confirmed experimentally that eq 1 is accurate enough to represent the two-phase equilibrium of a multicomponent polymer-single solvent system and disclose the effects of the k' and p parameters on the characteristics of coexistence curve in detail. In other words, although a higher term containing v_p^2 can be observed in the χ -parameter by membrane osmometry and vapor pressure measurements, the term does not significantly contribute to the phase separation characteristics including coexistence curve, within experimental certainty.

In this article, we express χ_i in the generalized form of eq 1,

$$\chi_i = \chi_{00}(1 + k'/X_i) \left(1 + \sum_{j=1}^n p_j v_p^j \right) \quad (i = 1, \dots, m) \quad (2)$$

Assuming that (1) the enthalpy change results from contact of solvent and solute and not from contact of solutes with different X_i and (2) the Bragg-Williams approximation is applicable to the solution, we can write the heat of dilution ΔH of the solution consisting multicomponent polymers (total number of the component m) and a single solvent by

$$\Delta H = \tilde{R}T \left\{ \chi_{00}(1 + k'/X_n) \left(1 + \sum_{j=1}^n p_j v_p^j \right) \right\} v_0 v_p \quad (3)$$

where $\tilde{R}$ is the gas constant, T , temperature (K), X_n , the number average X , and v_0 , the solvent volume fraction ($= 1 - v_p$). From eq 3 the partial molar heat of dilution ΔH_0 can be directly derived.

Using eq 3, the chemical potential of the solvent $\Delta\mu_0$ can be rewritten as

$$\Delta\mu_0 = \tilde{R}T \left\{ \ln(1 - v_p) + \left(1 - \frac{1}{X_n} \right) v_p + \chi_{00} \left(1 + \frac{k'}{X_n} \right) \left(1 + \sum_{j=1}^n p_j v_p^j \right) v_p^2 \right\} \quad (4)$$

The chemical potential of X_i -mer $\Delta\mu_i$ is derived from eq 4 when these potentials satisfy the Gibbs-Duhem equation. The results are

$$\begin{aligned} \Delta\mu_i = \tilde{R}T \left[\ln v_i - (X_i - 1) + X_i \left(1 - \frac{1}{X_n} \right) v_p \right. \\ \left. + X_i(1 - v_p)^2 \chi_{00} \left[\left(1 + \frac{k'}{X_n} \right) \right. \right. \\ \left. \times \left\{ 1 + \sum_{j=1}^n \frac{p_j}{j+1} \left(\sum_{q=0}^j (q+1) v_p^q \right) \right\} \right. \right. \\ \left. \left. + k' \left(\frac{1}{X_i} - \frac{1}{X_n} \right) \right. \right. \\ \left. \left. \times \left\{ \frac{1}{1 - v_p} + \sum_{j=1}^n \frac{p_j}{j+1} \left(\sum_{q=0}^j \frac{v_p^q}{1 - v_p} \right) \right\} \right] \right] \quad (5) \end{aligned}$$

A detailed derivation of eq 5 is given in Appendix A. Note that the applicability of eq 5 is not restricted only to the lattice model used originally in the Flory-Huggins theory.

The well-known Gibbs's conditions for the phase equilibrium of a quasi-binary solution at constant temperature and pressure are

$$\Delta\mu_{0(1)} = \Delta\mu_{0(2)} \quad (6)$$

$$\Delta\mu_{i(1)} = \Delta\mu_{i(2)} \quad (i = 1, \dots, m) \quad (7)$$

Here, the suffixes (1) and (2) denote the polymer-lean and the rich phases, respectively.

Combining eq 4—7 yields

$$\chi_{00} = \left\{ \ln \frac{1 - v_{p(1)}}{1 - v_{p(2)}} + (v_{p(1)} - v_{p(2)}) - \left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}} \right) \right\} / \left\{ (v_{p(2)}^2 - v_{p(1)}^2) + k' \left(\frac{v_{p(2)}^2}{X_{n(2)}} - \frac{v_{p(1)}^2}{X_{n(2)}} \right) + \sum_{j=1}^n p_j (v_{p(2)}^{j+2} - v_{p(1)}^{j+2}) + k' \left(\frac{v_{p(2)}^{j+2}}{X_{n(2)}} - \frac{v_{p(1)}^{j+2}}{X_{n(1)}} \right) \right\} \quad (7)$$

and

$$\sigma_i \equiv \frac{1}{X_i} \ln \frac{v_{i(2)}}{v_{i(1)}} = \sigma_0 + \sigma_{01}/X_i \quad (8)$$

with

$$\begin{aligned} \sigma_0 &= (v_{p(1)} - v_{p(2)}) - \left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}} \right) \\ &+ \chi_{00} \left[2(v_{p(1)} - v_{p(2)}) - (v_{p(1)}^2 - v_{p(2)}^2) \right. \\ &+ \left. \sum_{j=1}^n p_j \left\{ \frac{j+2}{j+1} (v_{p(1)}^{j+1} - v_{p(2)}^{j+1}) - (v_{p(1)}^{j+2} - v_{p(2)}^{j+2}) \right\} \right] \\ &- \chi_{00} k' \left[\left(\frac{v_{p(1)}}{X_{n(1)}} - \frac{v_{p(2)}}{X_{n(2)}} \right) - \left(\frac{v_{p(1)}^2}{X_{n(1)}} - \frac{v_{p(2)}^2}{X_{n(2)}} \right) \right. \\ &- \left. \sum_{j=1}^n p_j \left\{ \left(\frac{v_{p(1)}^{j+1}}{X_{n(1)}} - \frac{v_{p(2)}^{j+1}}{X_{n(2)}} \right) - \left(\frac{v_{p(1)}^{j+2}}{X_{n(1)}} - \frac{v_{p(2)}^{j+2}}{X_{n(2)}} \right) \right\} \right] \quad (9) \end{aligned}$$

and

$$\sigma_{01} = k' \left\{ (v_{p(1)} - v_{p(2)}) + \sum_{j=1}^n \frac{p_j}{j+1} (v_{p(1)}^{j+2} - v_{p(2)}^{j+2}) \right\} \quad (10)$$

When $k' = 0$, eq 2 reduces to

$$\chi = \chi_0 \left(1 + \sum_{j=1}^n p_j v_p^j \right) \quad (11)$$

The polymer-solvent interaction parameter g , introduced in Koningsveld *et al.*'s theory,²² can be expressed as a power function of v_p ,

$$g = \sum_{i=0}^n g_i v_p^i \quad (12)$$

where g_i is a function of temperature and independent of concentration.

If both χ and g have only concentration dependence and no molecular weight dependence, χ is related to g through

$$\chi = g - (1 - v_p) \frac{\partial g}{\partial v_p} \quad (13)$$

From eq 11—13, we obtain

$$\chi_0 = g_0 - g_1 \quad (14)$$

$$p_i = (i+1)(g_i - g_{i+1})/(g_0 - g_1) \quad (i=1, \dots, n-1) \quad (15)$$

$$p_n = (n+1)g_n/(g_0 - g_1) \quad (16)$$

Koningsveld and Kleintjens²³ expressed g in the closed form of v_p , given by

$$g = \alpha + \beta/(1 - \gamma v_p) \quad (17)$$

where α , β , and γ are parameters. In the range $0 < \gamma < 1$, the relation $0 < \gamma v_p < 1$ is valid and the second term in the right-hand side of eq 17 can be expanded in infinite series so that eq 17 may be rewritten as,

$$\begin{aligned} g &= \alpha + \beta + \sum_{i=1}^{\infty} \beta(\gamma v_p)^i \\ &\simeq \alpha + \beta + \sum_{i=1}^n \beta(\gamma v_p)^i \quad (18) \end{aligned}$$

By putting $\alpha + \beta = g_0$ and $\beta\gamma^i = g_i$ ($i = 1, \dots, n$) eq 18 is reduced to eq 12. Parameters χ_0 , p_i , and p_n can be expressed in terms of α , β , and γ as follows.

$$\chi_0 = \alpha + \beta(1 - \gamma) \quad (19)$$

$$p_i = (i+1)\beta\gamma^i(1 - \gamma)/\{\alpha + \beta(1 - \gamma)\} \quad (i=1, \dots, n-1) \quad (20)$$

$$p_n = (n+1)\beta\gamma^n/\{\alpha + \beta(1 - \gamma)\} \quad (21)$$

The spinodal is determined by

$$|\Delta G'| \equiv \begin{vmatrix} \overline{\Delta G}'_{11} & \overline{\Delta G}'_{12} & \cdots & \overline{\Delta G}'_{1m} \\ \overline{\Delta G}'_{21} & \overline{\Delta G}'_{22} & \cdots & \overline{\Delta G}'_{2m} \\ \vdots & & & \\ \overline{\Delta G}'_{m1} & \overline{\Delta G}'_{m2} & \cdots & \overline{\Delta G}'_{mm} \end{vmatrix} = 0 \quad (22)$$

and this can be combined with

$$|G''| \equiv \begin{vmatrix} \frac{\partial |\Delta G'|}{\partial v_1} & \frac{\partial |\Delta G'|}{\partial v_2} & \cdots & \frac{\partial |\Delta G'|}{\partial v_m} \\ \overline{\Delta G}'_{21} & \overline{\Delta G}'_{22} & \cdots & \overline{\Delta G}'_{2m} \\ \vdots & & & \\ \overline{\Delta G}'_{m1} & \overline{\Delta G}'_{m2} & \cdots & \overline{\Delta G}'_{mm} \end{vmatrix} = 0 \quad (23)$$

to obtain the critical solution point for multicomponent polymer/single solvent systems.¹⁸ In eq 22 and 23, $\Delta G'$ is the Gibbs free energy change of mixing per unit volume, given by

$$\Delta G' = v_0 \left(\frac{\Delta \mu_0}{V_0} \right) + \sum_{i=1}^m v_i \left(\frac{\Delta \mu_i}{X_i V_0} \right) \quad (24)$$

and $\overline{\Delta G}'_{ij}$ is defined by eq 25

$$\overline{\Delta G}'_{ij} = \left(\frac{\partial^2 \Delta G'}{\partial v_i \partial v_j} \right)_{T,p} \quad (i, j = 1, \cdots, m) \quad (25)$$

where V_0 is the molar volume of solvent, and v_i , the volume fraction of X_i -mer. The differentiation is carried out at constant temperature and pressure.

We attempted to solve eq 22 and 23 in a case where χ depends on molecular weight as well as concentration, as expressed by eq 1.

Substituting eq 4 and 5 into eq 24, we obtain

$$\begin{aligned} \Delta G' = & \frac{\tilde{R}T}{V_0} \left[(1-v_p) \ln(1-v_p) + \sum_{i=1}^m \frac{v_i \ln v_i}{X_i} \right. \\ & + \chi_{00} \left\{ 1 + \frac{k'}{X_n} (1 + X_n - X_w) \right\} \\ & \times \left. \left\{ 1 + \sum_{j=1}^n \frac{p_j}{j+1} \left(\sum_{q=0}^j v_p^q \right) \right\} v_p (1-v_p) \right] \end{aligned} \quad (26)$$

Here, X_w is the weight-average X_i .

Considering eq 25 and combining eq 26 with

eq 22 and 23, we finally obtain eq 27 and 28. (Appendix B) to give the composition of a critical solution point.

$$\begin{aligned} \frac{1}{X_w v_p} + \frac{1}{1-v_p} - \chi_{00} \left\{ 1 + k' \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right\} \\ \times \left\{ 2 + \sum_{j=1}^n p_j (j+2) v_p^j \right\} = 0 \end{aligned} \quad (27)$$

$$\begin{aligned} \frac{1}{(1-v_p)^2} - \frac{X_z}{(X_w v_p)^2} - \chi_{00} \left\{ 1 + k' \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right\} \\ \times \left\{ \sum_{j=1}^n p_j j (j+2) v_p^{j-1} \right\} = 0 \end{aligned} \quad (28)$$

where X_z is the z -average X . Both v_p and χ_{00} at critical points, are referred to as v_p^c and χ_{00}^c , and can be calculated by application of eq 27 and 28 from X_w , X_z , of the original polymer (X_w^0 and X_z^0) k' and p_j ($j=1, \cdots, n$).

The temperature dependence of k' and χ_{00} can be empirically expressed as

$$k' = k_0 (1 - \theta/T) \quad (29)$$

and

$$\chi_{00} = a + b/T \quad (30)$$

where k_0 , a , and b are constants independent of temperature and θ , the Flory temperature.¹² The concentration and temperature dependence of the χ -parameter are thus given by

$$\begin{aligned} \chi = & (a' + b'/T + c'/T^2) \\ & \times (1 + p_1 v_p + p_2 v_p^2) \end{aligned} \quad (31)$$

with

$$\begin{aligned} a' = & a(1 + k_0/X_n) \\ b' = & b + (k_0/X_n)(b - a\theta) \\ c' = & -(k_0 b \theta / X_n) \end{aligned} \quad (32)$$

Equation 31 is readily derived by comparing eq 11, 29, and 30. When $k_0=0$, a' reduces to a , b' to b and c' to zero.

COMPUTER SIMULATION OF CPC

The volume fractions of the X_i -mer in both phases, $v_{(1)}(X_i)$ and $v_{(2)}(X_i)$, are given by

$$v_{(1)}(X_i) = \frac{R+1}{R + \exp(\sigma_i X_i)} v_0(X_i) \quad (33)$$

$$v_{(2)}(X_i) = \frac{(R+1) \exp(\sigma_i X_i)}{R + \exp(\sigma_i X_i)} v_0(X_i) \quad (34)$$

where R is the ratio of the volume of the polymer-lean phase $V_{(1)}$ to that of the polymer-rich phase $V_{(2)}$ and $v_0(X_i)$ is the volume fraction of X_i -mer in the starting solution. The $v_{(1)}(X_i)$ and $v_{(2)}(X_i)$ at the cloud point, (referred to as $v_{(1)}^{cp}(X_i)$, $v_{(2)}^{cp}(X_i)$), are given from eq 33 and 34 as limiting cases of $R \rightarrow \infty$ when the polymer volume fraction of the starting solution v_p^0 is lower than v_p^c (i.e., $v_p^0 < v_p^c$) and $R \rightarrow 0$ for $v_p^0 > v_p^c$ in the form:

$$(1) \quad v_{(1)}^{cp}(X_i) = v_0(X_i)$$

$$v_{(2)}^{cp}(X_i) = v_0(X_i) \exp(\sigma_i X_i)$$

$$\text{for } v_p^0 < v_p^c \quad (i=1, \dots, m) \quad (35)$$

$$(2) \quad v_{(1)}^{cp}(X_i) = v_0(X_i) \exp(-\sigma_i X_i)$$

$$v_{(2)}^{cp}(X_i) = v_0(X_i)$$

$$\text{for } v_p^0 > v_p^c \quad (i=1, \dots, m) \quad (36)$$

Thus, on the basis of eq 8–10, 35, and 36, χ_{00} at cloud point (χ_{00}^{cp}), σ , $v_{(1)}(X_i)$ and $v_{(2)}(X_i)$, $v_{p(1)}$ and $v_{p(2)}$ can be directly calculated for a given v_p^0 solution. A brief flow chart presentation of the computer simulation is shown in Figure 1. The prerequisites for this simulation are,

(a) molecular weight distribution and accordingly the weight- and the number-average X of the original polymer (X_w^0 and X_n^0/X_w^0)

(b) polymer volume fraction of the starting solution v_p^0

(c) parameters k_0 and θ in eq 29

(d) concentration dependence parameters p_j ($j=1, \dots, n$) in eq 1.

We can obtain v_p^c and χ_{00}^c by resolving the simultaneous equations (eq 27 and 28) using Newton's procedure. In this calculation, as the initial value of v_p^c , the critical value given by the Stockmayer equation,²⁵

$$v_p^c = \frac{1}{1 + X_w(X_z)^{-1/2}} \quad (37)$$

was taken.

Computer Experiment 1

To clarify the effects of X_w^0 , X_w^0/X_n^0 , p_1 , and p_2 on CPC, a series of computer experiments was carried out. The original polymers were assumed to have the Schulz–Zimm (SZ) type molecular weight distribution with X_w^0 in the range of 300 to 5000 and with X_w^0/X_n^0 ranging from 1.03 to 4, having polymer components of 1500 to 6000, differing in X . The following parameters were employed for the calculation: $v_p^0 = 0.0005 - 0.15$, $k' = 0$, $a = 0.0481$ and $b = 137.2$, $p_1 = 0 - 0.8$, and $p_2 = 0 - 0.6$.

Computer Experiment 2

For a comparison with the actual experiment on a polystyrene/cyclohexane system, CPC was calculated under the same conditions as those in the actual experiment. The polymer had the Schulz–Zimm type distribution with $X_w^0 = 2117$, $X_w^0/X_n^0 = 2.8$ for cyclohexane.

DETERMINATION OF PARAMETERS a , b , AND p_j

Parameters a , b , and p_j ($j=1, \dots, n$) can be unambiguously determined when the cloud point temperature $T_{cp,e}$, experimentally determined, coincides with that calculated by computer simulation, $T_{cp,c}$, for any solution. In this study the following procedure was used to evaluate these parameters:

(1) Determine the relations between ρ_p (ρ_p is the weight fraction of the polymer partitioned into the polymer-rich phase to the polymer dissolved in the initial solution), and T from the two-phase equilibrium experi-

Figure 1. Flow chart for calculating the cloud point of a multicomponent polymer/single solvent system.

ments,

(2) Carry out computer simulation assuming arbitrarily chosen values of p_j ($j=1, \dots, n$) to obtain the relations between x_{00} and ρ_p .

(3) Construct the relations between x_{00} and $1/T$ using ρ_p vs. T relations obtained in step (1) and x_{00} vs. ρ_p relations obtained in step (2) and determined a and b as the intercept and slope of x_{00} vs. T plot, respectively,

(4) Calculate CPC ($T_{cp,c}$ vs. v_p relations)

using a and b obtained in step (3),

(5) Compute $\delta \equiv \sum_N (T_{cp,c} - T_{cp,e})^2 / N$ (N is the total number of the solutions, for which the cloud point was determined) and determine a set of p_j ($j=1, \dots, n$) to minimize δ , (where $N \gg n$),

(6) Repeat steps 2—5 and evaluate a , b , and p_j where δ is below the permissible limit.

EXPERIMENTAL

Polymer

The polystyrene (PS) sample of our study was Styron 666 (Asahi-Dow (now, Asahi Chemical Industry Co., Ltd.)) and also used in the previous papers.^{9,10,12,26} It was again characterized as follows: the weight-average molecular weight M_w was 23.9×10^4 by gel-permeation chromatography (GPC) in tetrahydrofuran (THF) and 23.2×10^4 by light scattering in benzene at 25°C; the number-average molecular weight M_n was 8.6×10^4 by GPC in THF and 8.9×10^4 by membrane osmometry in toluene at 25°C.

Solvent

Reagent grade cyclohexane (CH) was dried over anhydrous calcium chloride before use.

Cloud Point Determination

Cloud point temperature T_{cp} was determined visually (for dilute solutions) or with a He-Ne laser beam (for concentrated solutions) or both (for an intermediate concentration

range) within an accuracy of $\pm 0.03^\circ\text{C}$ in a sealed capillary glass tube with inner diameter of 0.4 cm and filled nitrogen gas. The initial polymer volume fraction v_p^0 was chosen from 6×10^{-4} to 0.1509. The detailed procedure is described elsewhere.^{27,28}

Determination of ρ_p vs. T relation

The relationships between ρ_p and the temperature T were determined for three PS/CH systems with $v_p^0 = 0.6, 1.184$, and 1.737% to an accuracy of ± 0.001 in ρ_p and $\pm 0.01^\circ\text{C}$ in T . The detailed experimental procedure for evaluating ρ_p and have already been described.¹⁴

RESULTS AND DISCUSSION

Figure 2 shows the effect of X_w^0 on CPC, calculated from the solutions of four polymers (SZ, $X_w^0/X_n^0 = 1, 1.1, 2$, and 4) in a single solvent ($p_1 = 0.6, p_2 = 0$, and $k_0 = 0$). The unfilled circle in the figure is the critical point and the filled circle, the threshold cloud point. The critical point, independently calculated by a

Figure 2. Effect of weight-average molar volume ratio X_w^0 of the polymer in a single solvent on cloud point curve ($p_1 = 0.5, p_2 = 0$, and $k_0 = 0$): $X_w^0/X_n^0 = 1$ (a), 1.1 (b), 2 (c), and 4 (d); ○, critical point; ●, precipitation threshold point; number on curve denotes X_w^0 .

different procedure from CPC, lies just on the CPC. This verifies the reliability of the CPC calculation procedure used here.

A monodisperse polymer solution with low X_w^0 shows CPC having approximate symmetry, which disappears with increasing X_w^0 and X_w^0/X_n^0 . As X_w^0 increases, CPC shifts to lower v_p and higher T regions, showing a skewness in the former. The critical points (T_c and v_p^c) coincides very well as expected from the threshold points (T_{tcp} and $v_{p,tcp}$) for solutions of strictly monodisperse polymers. As the polydispersity of the polymer increases, the critical point moves to higher v_p region, but the threshold cloud point shifts to lower v_p region causing them to differ significantly. The deviation in the critical point from threshold cloud point increases remarkably with an increase in X_w^0/X_n^0 and slightly with a decrease in X_w^0 . Note that this difference is significant even for a polymer with $X_w^0/X_n^0 = 1.1$, which is often regarded as "monodisperse polymer." Very careful attention should be given to this point in the case of a low X_w^0 polymer.

Figure 3 shows correlations between the difference, $v_{p,tcp} - v_p^c$ ($\equiv \Delta v_p$) or $T_{tcp} - T_c$ ($\equiv \Delta T$), X_w^0 and X_w^0/X_n^0 . The contour lines mean ΔT or Δv_p . For polymers having sharp molecular weight distributions, both Δv_p and ΔT are predominantly controlled by the polymolecularity of the polymers. In contrast to this, Δv_p as well as ΔT are independent of X_w^0 .

Figure 4 shows the effect of the polymolecularity of the original polymer dissolved is a single solvent on CPC. In the rather concentrated v_p region (*i.e.*, $v_p > v_p^c$), CPC is very insensitive to X_w^0/X_n^0 and in the range of v_p smaller than v_p^c , it shifts to higher temperature possibly as a result to the precipitation of higher molecular weight components contained in polymers having large polymolecularity. Evidently, T_{tcp} is much more sensitive than T_c to X_w^0/X_n^0 . Effect of X_w^0/X_n^0 on CPC becomes less remarkable for larger X_w^0 polymer solutions.

Figure 5 shows the effects of X_w^0 and X_w^0/X_n^0

Figure 3. Relationships between the weight-average molar volume ratio X_w^0 , ratio of X_w^0 to the number-average molar volume ratio X_n^0 (X_w^0/X_n^0) of the polymer and the difference in the polymer volume fraction Δv_p (a) in temperature ΔT (b) between the critical and precipitation threshold points.

Figure 4. Effect of polydispersity expressed by X_w^0/X_n^0 of the polymer on the cloud point curves of polymers ($X_w^0 = 500$ (a), 1000 (b), 2000 (c), and 5000 (d)) in a single solvent ($p_1 = 0.5$, $p_2 = 0$, and $k_0 = 0$); $\circ$, critical point; number on each curve denotes X_w^0/X_n^0 .

Figure 7. Effect of the concentration dependence parameter p_2 on the cloud point curve of the polymer-solvent system ($p_1 = 0.6$ and $k = 0$); broken line, monodisperse polymer ($X_w^0/X_n^0 = 1$); full line, $X_w^0/X_n^0 = 2$; $X_w^0 = 300$ (a), 500 (b), 1000 (c), and 2000 (d); number on curve denotes p_2 ; ○, critical point; ●, precipitation threshold point.

tem consisting of multicomponent polymers, solvent 1 and solvent 2, can be reasonably approximated by those of a quasi-binary system having negative p_1 . Figure 8 suggests strongly that, for a quasi-ternary system, the concentration dependence of the χ -parameter plays only a minor role in the two-phase equilibrium, in contrast to the quasi-ternary system. The conclusions obtained for the case of $k' = 0$, as shown in Figures 2–8 are expected to be valid even when $k' \neq 0$, although the calculation of CPC with $k' \neq 0$ is not always possible at present due to mathematical difficulty.

Figure 9 shows CPC calculated assuming various p_1 values and p_i ($i \geq 2$) = 0 for a PS/CH system. In the figure, the unfilled circle is the

Figure 8. Dependence of the critical concentration v_p^c and its temperature T_c of the polymer/single solvent system ($k = 0$) on p_1 and p_2 : broken line, $X_w^0/X_n^0 = 1$; full line $X_w^0/X_n^0 = 2$; $p_2 = 0$ (a) and (c) or $p_1 = 0.6$ (b) and (d)); number on curve denotes X_w^0 .

Figure 9. Cloud point curves of a polystyrene ($X_w = 2117$, $X_w^0/X_n^0 = 2.8$)/cyclohexane system: Full line, theoretical curve calculated using the value of p_1 shown on the curve and assuming $p_2 = 0$; circle, experimental data point.

Figure 10. Plot of δ ($\equiv \sum (T_{cp,c} - T_{cp,e})^2/N$) vs. p_1 for polystyrene/cyclohexane system: In this case, p_2 was assumed zero. Black point gives the optimum p_1 and its relative error δ ($p_1 = 0.65$, $\delta = 0.332$).

Figure 11. The concentration dependence of the χ parameter for a polystyrene/cyclohexane system: ○, osmotic pressure by Krigbaum-Geymer; ●, isothermal distillation by Krigbaum-Geymer; □, ultracentrifuge by Scholte; lines a—f are calculated using p_1 and p_2 , obtained by experiments; a, Krigbaum-Geymer; b, Scholte; c, Koningsveld *et al.* (1970); d, Koningsveld *et al.* (1971); e, Kuwahara *et al.*; f, this work.

Figure 12. Cloud point curves of polystyrene/cyclohexane system: Full line, theoretical curve calculated using the values of a' , b' , p_1 and p_2 summarized in Table I. Lines a—f have the same meaning as those in Fig. 11. Unfilled circle, experimental data points.

experimental data point. Evidently, using a single p_1 we can never calculate CPC adequately for this system over a wide range of v_p . In other words, p_1 , which is suitable for representing the experimental CPC in a lower v_p region, overestimates T_{cp} in a higher v_p region and visa versa. δ was calculated from the figure and plotted against p_1 in Figure 10. δ attains a minimum (0.333) at $p_1 = 0.65$, but, the agreement between the theoretical and experimental CPC is not satisfactory. This suggests strongly that, in contrast to the characteristics of the coexistence curve, CPC cannot be explained by a single p_1 alone.

The concentration dependence of χ -parameter, evaluated for a PS/CH system by many investigators, is plotted in Figure 11. In the figure, the curves have been calculated from the p_1 and p_2 values evaluated from the critical points. The experimental data points can be reasonably represented by eq 31, in which terms higher than v_p^2 are neglected. That is, in the v_p range of 0—0.15, both p_2 and

Table I. Parameters a' , b' , p_1 and p_2 in eq 31 for a polystyrene–cyclohexane system ($T=299$ K)

Author(s)	a'	b'	p_1	p_2	References
Krigbaum, Geymer (1959)	0.2496	76.67	0.630 ₄	0.480 ₈	32
Scholte (1970)	0.2631	74.31	0.534 ₄	0.430 ₄	33
Koningsveld <i>et al.</i> (1970)	0.2035	90.50	0.610 ₆	0.920 ₇	34
Koningsveld <i>et al.</i> (1971)	0.2211	85.313	0.622 ₂	0.289 ₁	23
Kuwahara <i>et al.</i> (1973)	0.2798	67.50	0.607 ₃	0.512 ₁	28
This work	-0.0242 ₄	158.79	0.643	0.200	—

p_1 are necessary to represent the concentration dependence of χ and in a comparatively dilute range, there is no sharp distinction in χ between the investigators.

Figure 12 shows the CPC of a PS/CH system. The unfilled circle is the actual experimental data and the full lines, theoretical curves calculated using the p_1 and p_2 parameters in the literature given in Table I. The curve calculated from χ value obtained by Krigbaum and Geymer³² can express experimental points in a lower v_p region, but overestimate them at a higher v_p region. The theoretical curve based on the χ of Scholte³³ overestimates these points very much at $v_p < 0.12$ and under estimates them at $v_p > 0.12$. The total shape of CPC, calculated by p_1 and p_2 obtained by Koningsveld *et al.*³⁴ and Kuwahara *et al.*,²⁸ using the critical point data of Koningsveld *et al.*'s method,³⁴ is similar to the actual experimental points, but their CPCs are underestimated throughout the entire range of v_p by *ca.* 1–1.5°C. It is of interest that a very slight change in p_1 and p_2 cause remarkable variation in CPC. p_1 and p_2 should thus be estimated from CPC.

Figure 13 shows the relations between ρ_p and T , obtained by an actual phase separation experiment of PS/CH system. The relations can be roughly approximated by a part of a circular arc with ρ_p approaching zero at specific temperature T_{cp} (*i.e.*, the cloud point). As v_p increases, the ρ_p vs. T curve shifts to lower T axis concurrently.

We carried out a computer experiment on

Figure 13. Experimental relations between ρ_p and T for polystyrene ($X_w^0=2117$, $X_w^0/X_n^0=2.8$) in cyclohexane. The polymer volume fractions of the starting solution v_p^0 are 0.6×10^{-2} (∇), 1.184×10^{-2} ($\square$) and 1.737×10^{-2} ($\circ$), respectively. **Figure 14.** Temperature dependence of χ_{00} in eq 30 for polystyrene ($X_w^0=2117$, $X_w^0/X_n^0=2.8$) in cyclohexane: $v_p^0 \times 10^2 = 0.60$ (∇), 1.184 ($\square$) and 1.737 ($\circ$); full line, theoretical curve calculated by assuming $p_1 = 0.62$, $p_2 = 0.20$ and $k_0 = 0$.

two-phase equilibrium assuming variable p_1 and p_2 to obtain the relations between χ_{00} and ρ_p , and converted them to those between χ_{00}

Figure 15. Relations among p_1 , p_2 and δ for polystyrene/cyclohexane system: number denotes δ and the full line is the contour line of the same δ .

Figure 16. Cloud point curve of polystyrene ($X_w^0 = 2117$, $X_w^0/X_n^0 = 2.8$) in cyclohexane: ○, experimental data; full line, theoretical curve calculated using $p_1 = 0.643$, $p_2 = 0.200$, $k_0 = 0$; broken line, theoretical curve calculated using $p_1 = 0.643$, $p_2 = 0.200$, $\theta = 307$ and $k_0 = 108$.

and T by a comparison with the ρ_p - T relations in Figure 14, from which a' and b' were found for a given combination of p_1 and p_2 .

Figure 15 shows the relations among p_1 , p_2 , and δ , defined in the previous section, for the PS/CH system. The most appropriate set of p_1 and p_2 , giving the minimum δ (≈ 0.1), could be determined as $p_1 = 0.643$ and $p_2 = 0.200$. These values are very near to the corresponding values evaluated by Kamide and Matsuda³⁵ from the critical point data. The cloud point curve, calculated using these values of a' , b' , p_1 , and p_2 can express accurately the exper-

imental data except the threshold point region ($v_p \approx 0.07$) as shown as full line in Figure 16. The maximum deviation of the theoretical T_c from the experiment is about 1°C . In the figure the molecular weight dependence of χ -parameter was not taken into account. The cloud point curve at lower v_p region is expected to be significantly influenced by the large molecular weight components and the above inconsistency at lower v_p region may be due to the neglect of the molecular weight dependence on χ -parameter.

Kamide *et al.*¹² evaluated for PS/CH system $k_0 = 108$ and $\theta = 307$ K. We calculated the cloud point curve using these values together with α , β , p_1 , and p_2 values determined before and shown as broken line in Figure 16. Inspection of Figure 16 leads us to the conclusion that the experimental cloud point data of the polydisperse polymer in a single solvent can be reasonably represented by the theory, in which the polydispersity of the polymer and the concentration- and the molecular weight-dependence of the χ -parameter are taken into consideration.

APPENDIX A

Derivation of Eq 5

The chemical potentials of the solvent and X -mer, $\Delta\mu_0$ and $\Delta\mu_i$ ($i = 1, \dots, m$) for a multicomponent polymer-single solvent system are given by³⁶

$$\Delta\mu_0 = RT \left\{ \ln(1 - v_p) + \left(1 - \frac{1}{X_n} \right) v_p + \chi v_p^2 \right\} \quad (\text{A-1})$$

and

$$\Delta\mu_i = RT \left\{ \ln v_i + (X_i - 1) + X_i \left(1 - \frac{1}{X_n} \right) v_p \right\} + \frac{\partial \Delta H}{\partial N_i} \quad (\text{A-2})$$

where N_i is the number of X_i -mer moles. Substituting eq 2 into eq A-1, we obtain eq 4.

In eq A-1, χv_p^2 must be of the form

$$RT\chi v_p^2 = \frac{\partial \Delta H}{\partial N_0} \quad (\text{A-3})$$

where N_0 is the number of solvent moles. The necessary and sufficient 'condition' under which $\Delta\mu_0$ and $\Delta\mu_i$ satisfy the Gibbs-Duhem relation

$$N_0 d(\Delta\mu_0) + \sum_{i=1}^m N_i d(\Delta\mu_i) = 0 \quad (\text{A-4})$$

is

$$\frac{\partial \Delta H}{\partial N_i} = \frac{\partial}{\partial N_i} \left\{ \int_0^{N_0} \left(\frac{\partial \Delta H}{\partial N_0} \right) dN_0 \right\} \quad (\text{A-5})$$

On substituting eq 2 into eq A-5 we obtain

$$\begin{aligned} \frac{1}{RT} \cdot \frac{\partial \Delta H}{\partial N_i} = & \chi_{00} X_i \left(1 + \frac{k'}{X_n} \right) \left\{ (1 - v_p)^2 \right. \\ & + \sum_{j=1}^m p_j \left(\frac{1}{j+1} - \frac{j+2}{j+1} v_p^{j+1} + v_p^{j+2} \right) \left. \right\} \\ & + \chi_{00} k' X_i \left(\frac{1}{X_i} - \frac{1}{X_n} \right) \left\{ (1 - v_p) \right. \\ & + \sum_{j=1}^m \frac{p_j}{j+1} (1 - v_p^{j+1}) \left. \right\} \quad (\text{A-6}) \end{aligned}$$

Combining eq A-6 with eq A-2 leads to eq 5.

APPENDIX B

Deviation of Eq 27 and 28

Substitution of eq 26 into 25 leads to

$$\begin{aligned} \frac{V_0}{RT} \overline{\Delta G'_{ij}} = & \frac{1}{1 - v_p} - \chi_{00} \left\{ 1 + k' \left(1 + \frac{1}{X_n} - \frac{X_w}{X_n} \right) \right\} \\ & \left\{ 2 + \sum_{q=1}^n p_q (q+2) v_p^q \right\} \equiv M \\ & \text{for } i \neq j \quad (\text{B-1}) \end{aligned}$$

or

$$\frac{V_0}{RT} \overline{\Delta G'_{ii}} = M + \frac{1}{X_i v_i} \equiv M + M_i \quad \text{for } i=j \quad (\text{B-2})$$

From eq B-1, B-2, and eq 22, we obtain

$$\begin{aligned} |\Delta G'| = & \left(\frac{RT}{V_0} \right)^m \begin{vmatrix} M+M_1 & M & \cdots & M \\ M & M+M_2 & \cdots & M \\ \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix} \\ = & \left(\frac{RT}{V_0} \right)^m \left(\prod_{i=1}^m M_i \right) \left(1 + M \sum_{i=1}^m \frac{1}{M_i} \right) = 0 \quad (\text{B-3}) \end{aligned}$$

Then, we have

$$1 + M \sum_{i=1}^m \frac{1}{M_i} = 0 \quad (\text{B-4})$$

for the spinodal. Rearrangement of eq B-4 with the aid of eq B-1 and B-2 gives eq 27. In deriving eq B-3, we employed the relation

$$|D| = \begin{vmatrix} x_1 & a & \cdots & a \\ a & x_2 & \cdots & a \\ \vdots & \vdots & & \vdots \\ a & a & \cdots & x_m \end{vmatrix} = f(a) - a \frac{df(X)}{dX} \Big|_{x=a} \quad (\text{B-5})$$

where

$$f(x) = \sum_{i=1}^m (x_i - x) \quad (\text{B-6})$$

Differentiating eq B-3 by v_i , we obtain

$$\begin{aligned} \frac{\partial |\Delta G'|}{\partial v_i} = & \left(\frac{RT}{V_0} \right)^m \left(\prod_{i=1}^m M_i \right) \left(\frac{\partial M}{\partial v_p} v_p X_w - \frac{X_i}{X_w v_p} \right) \equiv W_i \quad (\text{B-7}) \end{aligned}$$

Then, from eq B-1, B-2, B-7, and 23 and using eq B-5 and B-6 we obtain

$$|\Delta G''| = (-1)^2 W_1 \begin{vmatrix} M+M_2 & M & \cdots & M \\ M & M+M_3 & \cdots & M \\ \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix}$$

$$\begin{aligned}
& + \sum_{j=2}^m W_j (-1)^{j+1} (-1)^j \begin{vmatrix} M & M & & \cdots & & M \\ M & M+M_2 & & & & \\ \vdots & \vdots & \ddots & & & \\ M & M & & M+M_{j-1} & & M \\ M & M & & M & & M+M_{j+1} \\ \vdots & \vdots & & & \ddots & \\ M & M & & \cdots & & M+M_m \end{vmatrix} \\
& = - \left(\prod_{i=1}^m M_i \right) \left(\frac{M}{M_i} \right) \left(\sum_{i=1}^m \frac{W_i}{M_i} \right) = 0
\end{aligned} \tag{B-8}$$

Equation B-8 can be rewritten, using eq B-1 and B-2, as eq 28.

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