(29) Oppenheim, I., Shuler, K. E., Weiss, G. H., Eds. *Stochastic Processes in Chemical Physics*: *The Master Equation*: MIT Press: Cambridge, MA, 1977.
(30) Casati, G., Ed. *Chaotic Behavior in Quantum Systems, Theory and Applications*; Plenum: New York, 1985.
(31) Lichtenberg, A. J.; Lieberman, M. A. *Regular and Stochastic Motion*; Springer-Verlag: New York, 1983.
(32) Rendell, R. W.; Ngai, K. L., to be published.
(33) Ngai, K. L.; Fytas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1683.
(34) Ngai, K. L.; Rendell, R. W. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1982**, *23*, 46.
(35) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys.* Ed. **1985**, *23*, 2159.
(36) McKenna, G. B.; Ngai, K. L.; Plazek, D. J. *Polymer* **1985**, *26*, 1651.
(37) Rendell, R. W.; Ngai, K. L.; McKenna, G. B., to be published.
(38) Bendler, J. T.; Ngai, K. L. *Macromolecules* **1984**, *17*, 1174.
(39) Kovacs, A. J.; Stratton, R. A.; Ferry, J. D. *J. Phys. Chem.* **1963**, *67*, 152.
(40) Plazek, D. J.; Ngai, K. L.; Rendell, R. W. *Polym. Eng. Sci.* **1984**, *24*, 1111.
(41) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci. Part B*: **1986**, *24*, 619.
(42) Mashimo, S.; Nozaki, R.; Yagihara, S.; Takeishi, S. *J. Chem. Phys.* **1982**, *77*, 6259.
(43) Williams, M. L.; Ferry, J. D. *J. Colloid Sci.* **1954**, *9*, 479.

Three-Phase Separation in Cyclohexane Solutions of Binary Polystyrene Mixtures

Yoshiyuki Einaga,* Yo Nakamura, and Hiroshi Fujita

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan.

Received August 12, 1986

ABSTRACT: Three-phase separation was observed in solutions of cyclohexane and two narrow distribution samples of polystyrene with $M_w = 4.36 \times 10^4$ and 1.26×10^6 at temperatures near 14.0 °C. The phase diagram constructed from the composition data for the three phases was compared with the theoretical predictions derived from our recently proposed empirical expression for the apparent second virial coefficient Γ. A fairly good agreement was found between experiment and theory, crediting a high accuracy of our Γ function. It was also confirmed by the present calculation that three-phase separation proceeds via the heterogeneous double plait point mechanism as originally pointed out by Tompa and recently discussed in detail by Šolc and Dobashi and Nakata.

Koningsveld and co-workers[1–4] early observed three-phase separation to occur in (quasi-binary) ternary solutions consisting of diphenyl ether and two polyethylenes or cyclohexane (CH) and two polystyrenes (PS) as predicted by Tompa's theory.[5] Very recently, Dobashi and Nakata[6] published a more extensive and precise study of this phenomenon in the system of methylcyclohexane (MCH) and two narrow distribution PS. Actually, they determined the three-phase line (coexistence curve) on the temperature vs. total polymer concentration plane and compared it with the prediction from the *g* function (defined originally by Koningsveld and Staverman[7]) similar to that proposed by Koningsveld and Kleintjens.[8] The agreement was only moderate; the calculated curve was much narrower than the observed one and appeared 2 K below the latter. This finding is not surprising because it was already known that Koningsveld and Kleintjens' *g* does not take into account the dilute solution effect and the chain length dependence in the concentrated regime, as was pointed out by Nies et al.[9]

As in previous work, Dobashi and Nakata did not take direct measurements of the compositions of the three separated phases. However, experimental data of these compositions are necessary to determine the triangular phase diagram of a system containing three phases in equilibrium. They also can be used for a stringent test of a theoretical or empirical expression of the Gibbs free energy *G* (or the *g* function) of the system, since the pattern of three-phase equilibrium should be very sensitive to the form of *G* as a function of temperature and composition.

Motivated by these considerations we undertook an experimental study as reported in this paper. Thus, we allowed a ternary solution of cyclohexane and two narrow distribution PS to be separated into two or three phases by a suitable choice of experimental conditions and tried to measure the composition of each phase by gel permeation chromatography (GPC). Further, the results were compared with predictions from the empirical expression of *G* recently proposed by Einaga et al.[10] for an arbitrary mixture of monodisperse PS homologues in cyclohexane.

Proposed Expression for the Γ Function

For the ternary system considered here we designate solvent cyclohexane as component 0, shorter chain PS as component 1, and longer chain PS as component 2. We express the chemical potential μ_0 of component 0 as[10]

$$\mu_0/RT = \mu_0{}^\circ/RT - \phi/P_n - \Gamma(T,\phi_1,\phi_2;P_1,P_2)\phi^2 \quad (1)$$

where $\mu_0{}^\circ$ is the value of μ_0 in the pure state of component 0, R the gas constant, T the absolute temperature, ϕ_i the volume fraction of component i, P_i the relative chain length of component i ($P_0 = 1$), and ϕ the total polymer volume fraction. The number-average relative chain length P_n of the polymer mixture is expressed by

$$P_n{}^{-1} = \sum_{i=1}^{2} \xi_i P_i{}^{-1} \quad (2)$$

with $\xi_i = \phi_i/\phi$, which is the weight fraction of component i in the polymer mixture subject to the usually valid assumption that the specific volume of a polymer is independent of its chain length.

From eq 1 and the Gibbs–Duhem relation it follows[10] that the chemical potential μ_i of component i ($i = 1, 2$) is given by

$$\mu_i/RT = \mu_i{}^\infty/RT + \ln \phi_i - \phi + (1 - P_i/P_n)\phi + \phi(1 - \phi)P_i\Gamma + P_i\int_0^\phi [\Gamma + (1 - \xi_i)(\partial\Gamma/\partial\xi_i)]\, d\phi \quad (3)$$

where $\mu_i{}^\infty$ defined by

$$\mu_i{}^\infty = \lim_{\phi\to 0} (\mu_i - RT \ln \phi_i) \quad (4)$$

0024-9297/87/2220-1083$01.50/0

is independent of ϕ and ξ_i.

The above expressions can be adapted to the binary system consisting of CH and a single PS with relative chain length P if we set $\phi_2 = 0$ and $P_1 = P$. Einaga et al.[10] derived an empirical expression of Γ for this system from light scattering measurements made down to the cloud point. It reads

$$\Gamma = \Gamma_{c0} + (1/2)\Gamma_{c1}\phi^2 + 2(\Gamma_{d0} - \Gamma_{c0})[1 - e^{-\phi/\phi^*}(1 + \phi/\phi^*)](\phi^*/\phi)^2 \quad (5)$$

where

$$\Gamma_{d0} = -0.26(\theta/T - 1) - 4.6(\Theta/T - 1)^2 \quad (6)$$

$$\Gamma_{c0} = 0.03P^{-1/3} - 0.23(\Theta/T - 1) \quad (7)$$

$$\Gamma_{c1} = 0.47 - 3.5(\Theta/T - 1) \quad (8)$$

$$\phi^* = P^{-1/2} \quad (9)$$

with Θ being the Θ temperature for PS in CH. Einaga et al.[10] took a bold step to infer Γ for the ternary system concerned in this work. It was simply assuming eq 5 as it stands, with Γ_{c0} and ϕ^* replaced by

$$\Gamma_{c0} = \sum_{i=1}^{2} \xi_i \Gamma_{c0i} \quad (10)$$

$$\phi^* = \sum_{i=1}^{2} \xi_i \phi_i^* \quad (11)$$

where Γ_{c0i} and ϕ_i^* are given by replacing P in eq 7 and 9 respectively by P_i.

It was found that the expression of Γ so obtained for the system of CH and a binary mixture of PS yields predictions, with no free adjustment of parameters, that are in close agreement with the cloud-point and binodal curves measured in our laboratory.[10,11] As mentioned above, the present work purported to subject this expression to a more stringent test by examining how correctly it can reproduce observed three-phase separations.

Experimental Section

Polymer Solutions. Two narrow distribution polystyrene samples F4 and F128 were supplied by Dr. M. Fukuda of Toyo Soda Co. The weight-average molecular weight M_w was 4.36 × 10^4 for F4 and 126 × 10^4 for F128, and the polymolecularity index M_w/M_n (M_n is the number-average molecular weight) was 1.01 for the former and 1.05 for the latter (the values by GPC). After thorough drying these two PS samples were mixed at a desired weight fraction ξ_2, with F128 taken as component 2. Each mixture was homogenized by dissolving in benzene and then freeze dried.

Test solutions for phase separation experiments were prepared by weight with thoroughly dried PS mixtures and CH distilled immediately before use. This operation was carried out in a drybag filled with dry nitrogen to prevent contamination due to moisture. The polymer volume fraction ϕ was computed from the measured polymer weight fraction w by

$$\phi = [1 + (v_0/v_p)(w^{-1} - 1)]^{-1} \quad (12)$$

where v_0 and v_p are the specific volumes of the solvent and the polymer, respectively. The values of 1.2924 and 0.9343 cm^3/g were used for the former and the latter, respectively, at any temperature studied; note that these refer to 25 °C.

Measurement of Phase Properties. The cloud point of a given solution was determined by the same method as described previously.[11] Actual measurements were made on a series of solutions with $\xi_2 = 0.05$.

On the basis of the theoretical calculations described below phase separation experiments were carried out at 13.80 and 13.90 °C for solutions with suitably chosen ϕ and ξ_2. Phase equilibrium was attained in a period of time from 3 days to 1 week, in which the solution was maintained within ±0.01 °C. As expected, the test solutions were separated into two or three phases, depending on their ϕ and ξ_2. Each phase was taken out of the vessel by a syringe, and its w and ξ_2 were determined by the dry weight method and by GPC.[11,12]

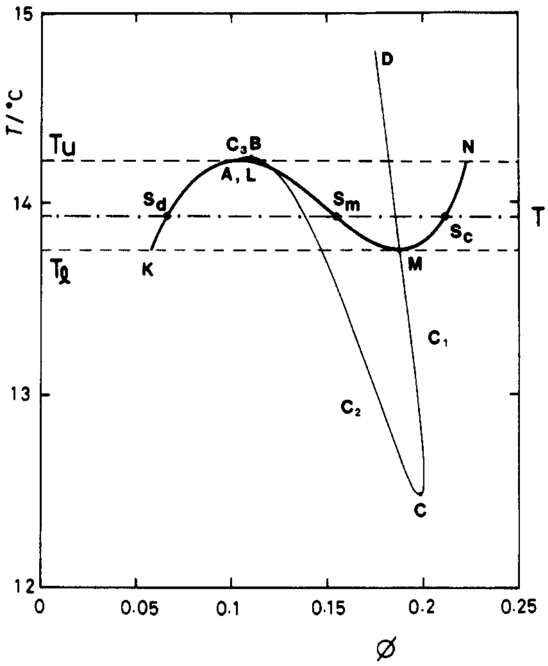

Figure 1. Calculated three-phase line (thick line) and locus of critical points (thin line) for the ternary system F4 + F128 + CH on the T–ϕ plane.

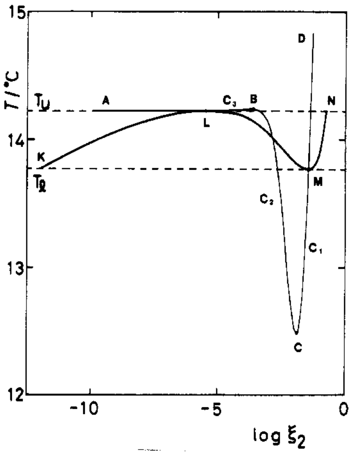

Figure 2. Calculated three-phase line (thick line) and locus of critical points (thin line) for the ternary system F4 + F128 + CH on the T–ξ_2 plane.

Realization of the state of three-phase separation is very sensitively affected by a slight change in temperature as well as by experimental operations. Thus, in our study, the solution sometimes remained in the state of two phases, with one phase being highly turbid, though three-phase separation had been anticipated. This seemed to be due to a high viscosity of the solution and to the density of the turbid phase being very close to that of a third phase which would have separated out of it after a long standing. In another case, the solution first separated into two phases and then into three phases during the course of cooling to a desired phase separation temperature, and the situation remained essentially unchanged afterward. In such a solution, the boundary between concentrated and medium phases was not sharp and easily disturbed by slight shaking. The data on such solutions were discarded, since three phases in them were considered to be at a false equilibrium.

One or sometimes two of the three separated phases were more or less turbid, as observed by previous authors.[4,6] In most cases, the dilute phase was turbid and never became transparent until it was taken out for composition analysis. The cause of this phenomenon is not yet clear to us. In some cases, one of the

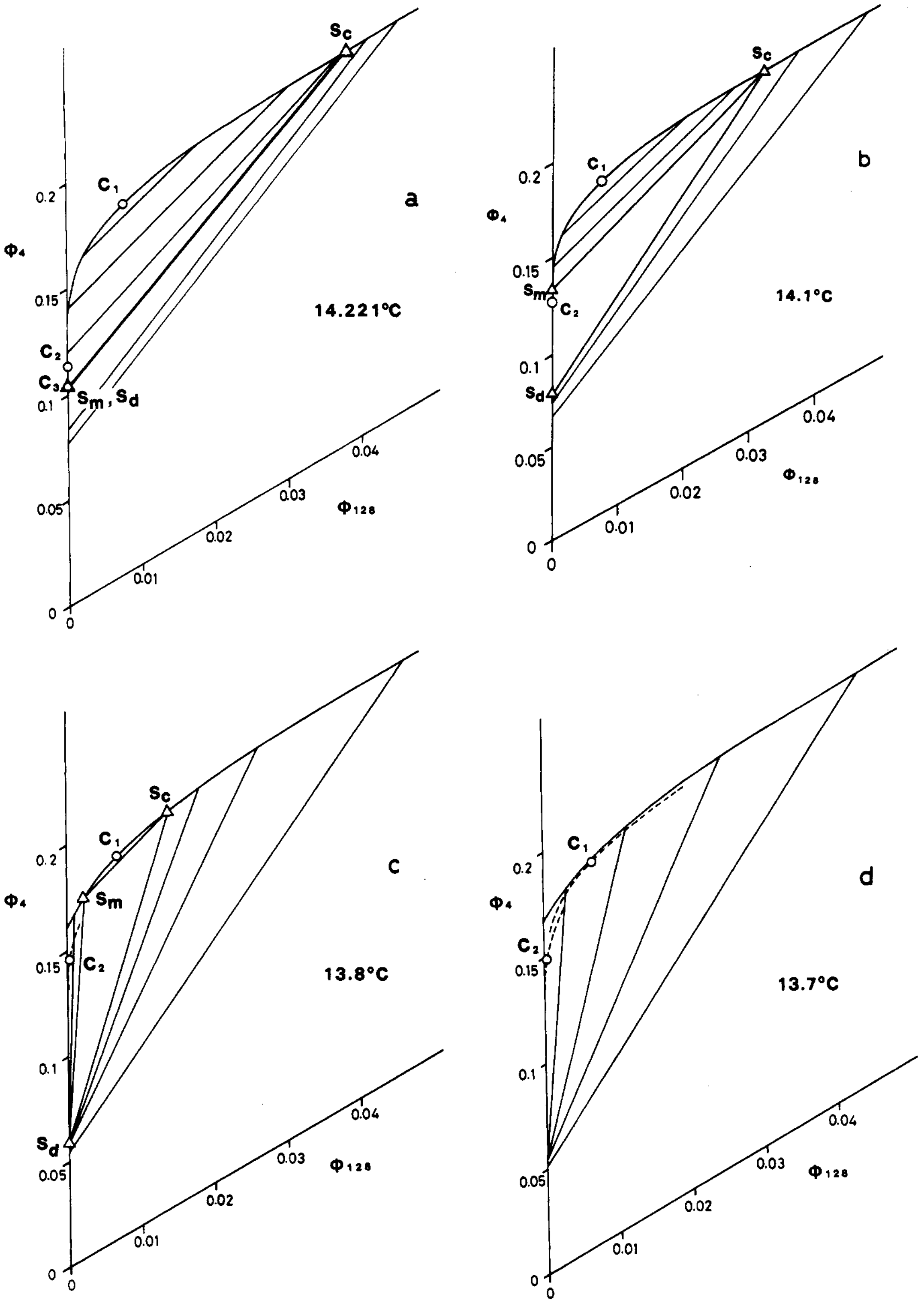

Figure 3. Theoretical evolution of the phase diagram with temperature for the ternary system F4 + F128 + CH: (a) 14.221 °C; (b) 14.1 °C; (c) 13.8 °C; (d) 13.7 °C. Solid curves, stable binodals; dashed curves, unstable binodals; straight lines, tie lines; circles, critical points; triangles, three-phase points.

separated phases was too small in volume for its composition to be measured by our method.

Results and Discussion

Calculated Results. Critical Points and Three-Phase Lines. For the ternary system subjected to the present experiment we solved the phase equilibrium relations $\mu_i' = \mu_i''$ (i = 0, 1, 2; single and double primes indicate different phases) at a number of temperatures, using the empirical expression of Einaga et al.[10] for Γ mentioned in a previous section. The results showed that three-phase separation takes place in a very narrow range of temperature from T_u = 14.221 to T_l = 13.765 °C, in agreement with our experiment, which found it to occur in this temperature range.

The thick solid curves in Figures 1 and 2, which are referred to as three-phase lines, show ϕ and ξ_2, respectively, of the three phases plotted against temperature T (in degrees Celsius). Thus, points S_d, S_m, and S_c in Figure 1 give the ϕ values in the dilute, medium, and concentrated phases at temperature T'. It can be seen that three-phase separation appears in the range ϕ = 0.058–0.233 and ξ_2 =

Table I
Phase Composition Data for the System F4 and F128 in Cyclohexane[a]

ϕ_4*	ϕ_{128}*	ϕ_4^d	ϕ_{128}^d	ϕ_4^m	ϕ_{128}^m	ϕ_4^c	ϕ_{128}^c
			13.8 °C Two-Phase Separation				
0.0736	0.0071	0.06846					
0.1800	0.0102					0.1923	0.0114
0.1825	0.0159	0.0517				0.2067	0.0183
0.1277	0.0056	0.0800				0.1879	0.0139
0.1256	0.0158	0.0671				0.1978	0.0331
0.0914	0.0120	0.0728				0.1813	0.0717
0.0845	0.0157	0.0608				0.1791	0.0781
0.1279	0.0039	0.0687				0.1965	0.0077
			13.8 °C Three-Phase Separation				
0.1665	0.0081			0.1618	0.0025	0.1848	0.0184
0.1572	0.0052	0.1291	0.0015	0.1678	0.0039	0.1665	0.0115
0.1648	0.0074	0.1162	0.0008	0.1724	0.0039	0.1844	0.0131
			13.9 °C Two-Phase Separation				
0.1535	0.0134	0.0777				0.1964	0.0197
			13.9 °C Three-Phase Separation				
0.1647	0.0074			0.1575	0.0022	0.1891	0.0178

[a] ϕ* represents the solution composition before phase separation. The superscripts d, m, and c represent dilute, medium, and concentrated phases, respectively.

0–0.17 and that the portions KL, LM, and MN of the three-phase lines define the ranges of ϕ and ξ_2 covered by the dilute, medium, and concentrated phases, respectively. At T_u the solution is separated into two phases represented by points L and N. On cooling further, the dilute phase L is separated into dilute and medium phases, while the concentration of the concentrated phase N decreases. Thus, the solution contains three phases until it is cooled to T_l, at which temperature the medium and concentrated phases merge to one phase and the solution returns to the state of two phases.

In Figures 1 and 2 the thin solid curve, which is referred to as the critical line, illustrates the locus of critical points. One, two, or three critical points appear depending on the temperature of the solution. The critical points associated with the portions DC, CB, and BA of the critical line are denoted C_1, C_2, and C_3, respectively. The extrema B and C are double plait points, at which two critical points merge to one. Point B is above T_u, while point C is significantly below T_l, in agreement with the finding from Šolc's model calculations.[13,14] Critical point C_1 is stable and metastable above and below T_l. Critical point C_2 is unstable wherever it is located. Critical point C_3 is metastable in the range between B and L and becomes stable at T_u.

Phase Diagram. Figure 3 shows the evolution of the phase diagram on the composition triangle with a change in temperature. Unfilled circles C_1, C_2, and C_3 are the critical points defining the critical line in Figure 1 or 2, and unfilled triangles S_d, S_m, and S_c correspond to the three-phase points S_d, S_m, and S_c in Figure 1, respectively.

At 14.221 °C (T_u), at which temperature three-phase separation starts appearing, the triangle $S_dS_mS_c$ reduces to the bold tie line, with S_d and S_m merged to one phase, and the three critical points exist inside the composition triangle, though C_2 and C_3 are virtually on the ϕ_4 axis (ϕ_4 and ϕ_{128} are hereafter used for ϕ_1 and ϕ_2 defined before for a more concrete understanding of the phase diagram). At 14.1 °C, S_m and S_d are apart, though still found virtually on the ϕ_4 axis, S_d moves toward a lower polymer concentration, and C_3 disappears, having moved out the composition triangle. A solution with any composition inside the triangle $S_dS_mS_c$ separates into three phases at S_d, S_m, and S_c. At 13.8 °C, C_2 moves inside the stable binodal, S_m leaves the ϕ_4 axis, and it comes closer to S_c than to S_d. On further cooling, S_m and S_c eventually merge, and the triangle $S_dS_mS_c$ again reduces to a tie line. This is the situation at temperature T_l. At 13.7 °C, no three-phase region is seen, but C_1 as well as C_2 are found inside the stable binodal. This phase diagram indicates that the three-phase region disappears owing not to the merging of two critical points C_1 and C_2 but to that of two phases S_m and S_c.

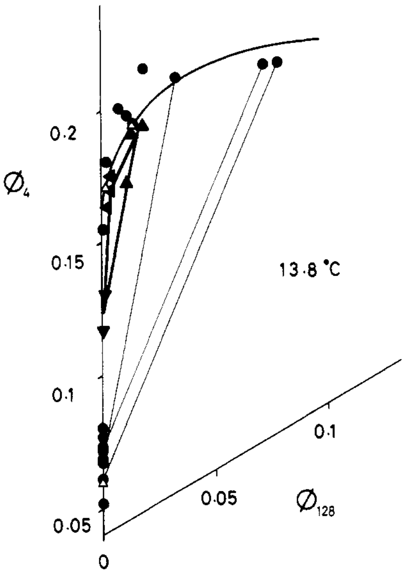

Figure 4. Comparison between calculated and experimental phase diagrams for the ternary system F4 + F128 + CH at 13.8 °C. Thick curve, calculated binodal; unfilled triangles, calculated three-phase points; filled triangles, observed three-phase points; (▲) S_c; (◀) S_m; (▼) S_d; filled circles, composition data for two phase separation; straight lines, tie lines (tie lines near the three-phase triangle are omitted).

Comparison of Experimental and Calculated Results. All the composition data obtained in the present experiment are summarized in Table I, and the phase diagram constructed from the data at 13.8 °C is shown in Figure 4. Here, the filled circles and triangles indicate the results from two- and three-phase separation, respectively, while the unfilled triangles are the theoretically predicted positions of three separated phases.

Because of their considerable scatter the filled triangles do not make the three-phase triangle determined unambiguously, but undoubtedly it occupies a small region in the vicinity of the ϕ_4 axis. As for the concentrated and

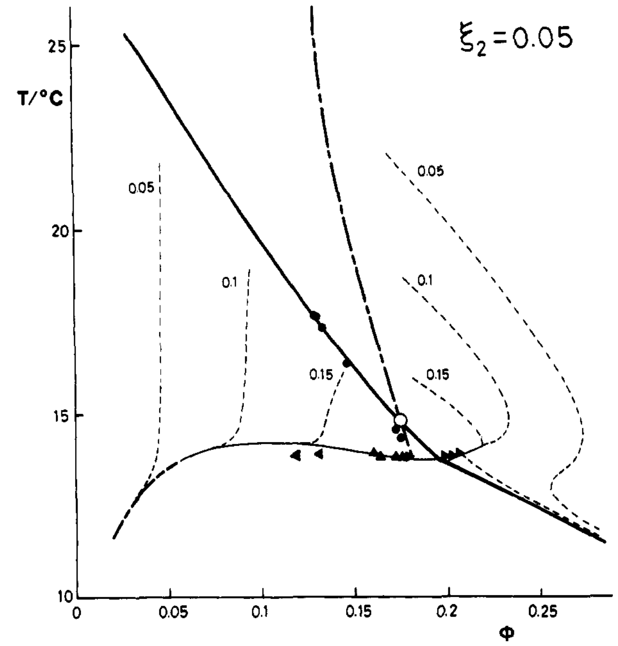

Figure 5. Observed and calculated phase diagrams for the ternary system F4 + F128 + CH on the T–ϕ plane. Filled circles, observed cloud points for $\xi_2 = 0.05$; filled triangles, observed three-phase points. Thick solid line, calculated cloud-point curve for $\xi_2 = 0.05$; dot–dash line, calculated shadow curve; thin solid line, calculated three-phase line; dashed curves, coexistence curves calculated for the indicated total polymer volume fractions and $\xi_2 = 0.05$; unfilled circle, calculated critical point for $\xi_2 = 0.05$.

medium phases, the agreement of experimental and calculated points is not as bad. However, this is not the case for the dilute phase, the calculated polymer volume fraction being about half the measured ones. As has been mentioned above, the dilute phases in most three-phase separations had remained turbid, for reasons yet unknown to us, until they were taken out for composition analysis. Such a phase may not have yet reached a true equilibrium state, retaining some polymer fraction that eventually should move to either the medium or concentrated phase. Thus, its measured concentration might be too high compared with the true value. Tentatively we consider that this was responsible for the disagreement of the measured and calculated results for the dilute phase.

In Figure 4 it can be seen that the calculated binodal (the bold curve) descibes fairly accurately the data points for the concentrated phase (filled circles) in two-phase solutions. Filled circles for the conjugated dilute phase crowd in a narrow range virtually on the ϕ_4 axis and are close to the dilute phase of the calculated three-phase triangle. This observed result is very consistent with the theoretical prediction depicted in Figure 3c.

The thick solid line in Figure 5 shows the calculated cloud-point curve for $\xi_2 = 0.05$ and fits the data points (filled circles) closely. This graph also compares the calculated three-phase line (thin solid line) with the measured concentrations of the three separated phases (filled triangles). Its agreement with the data points is satisfactory except for two points.

Conclusions

The present calculations based on the empirical expression of Einaga et al. for Γ of the system CH and two PS have led to phase relationships that are essentially similar to those predicted by Šolc[13] and by Dobashi and Nakata[6] using the Koningsveld–Staverman g functions which do not depend on the variable ξ_2. They have confirmed, among others, the conclusion of Tompa[5] and Šolc[13,14] that the heterogeneous double plait point mechanism is responsible for three-phase separation.

What seemed more significant to us was that the calculated results agreed fairly well with the observed ones in the temperature region where three-phase separation occurs. This fact gives a more credit to the accuracy of the Γ function of Einaga et al., since three-phase separation is very sensitively affected by the Gibbs free energy of the solution as a function of composition and temperature.

In practice, an extremely careful experiment is needed to bring a quasi-binary polymer solution to the state of true three phases and to determine the composition of each phase with high accuracy. The bad scatter of data points as can be seen in Figure 4 indicates that our efforts were not always sufficient. It is hoped that further work will be attempted to obtain more accurate data on three-phase separation.

Registry No. Cyclohexane, 110-82-7; polystyrene, 9003-53-6.

References and Notes

(1) Koningsveld, R.; Staverman, A. J. *Kolloid Z. Z. Polym.* **1966**, *210*, 151.
(2) Koningsveld, R.; Staverman, A. J. *Kolloid Z. Z. Polym.* **1967**, *220*, 31.
(3) Koningsveld, R.; Kleintjens, L. A.; Shultz, A. R. *J. Polym. Sci., Part A-2* **1970**, *8*, 1261.
(4) Kleintjens, L. A.; Schoffeleers, H. M.; Domingo, L. *Br. Polym. J.* **1976**, *8*, 29.
(5) Tompa, H. *Trans. Faraday Soc.* **1949**, *45*, 1142.
(6) Dobashi, T.; Nakata, M. *J. Chem. Phys.* **1986**, *84*, 5775.
(7) Koningsveld, R.; Staverman, A. J. *J. Polym. Sci., Part A-2* **1968**, *6*, 305.
(8) Koningsveld, R.; Kleintjens, L. A. *Macromolecules* **1971**, *4*, 637.
(9) Nies, R.; Koningsveld, R.; Kleintjens, L. A., unpublished (private communication from Dr. Koningsveld).
(10) Einaga, Y.; Tong, Z.; Fujita, H. *Macromolecules* **1985**, *18*, 2258.
(11) Tsuyumoto, M.; Einaga, Y.; Fujita, H. *Polym. J.* (*Tokyo*) **1984**, *16*, 229.
(12) Tong, Z.; Einaga, Y.; Fujita, H. *Macromolecules* **1985**, *18*, 2264.
(13) Šolc, K. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1947.
(14) Šolc, K. *Macromolecules* **1983**, *16*, 236.