Molecular weight dependence of the cloud-point curve of poly(dimethylsiloxane)/poly(methylethylsiloxane) mixtures

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Poly(dimethylsiloxane)s (PDMS) of molecular weight, M_w, $= 8 \times 10^4$–1.15×10^6 were found to be partially miscible with poly(methylethylsiloxane)s (PMES) of $M_w = 4 \times 10^3$–9×10^3, exhibiting the upper critical solution temperature. The extremum temperature, $T_{\mathrm{cl,ex}}$, of the cloud-point curve ranged from room temperature to 100°C, and the $T_{\mathrm{cl,ex}}$ of ternary blends consisting of PDMS and PMES having a bimodal molecular weight distribution could be controlled by changing the composition of the low and high molecular weight fractions in PMES. The temperature dependence of the interaction parameter χ between PDMS and PMES could be reasonably determined from the molecular weight dependence of $T_{\mathrm{cl,ex}}$. The result is expressed as χ (per PMES monomer unit)$=4.07/T(\mathrm{K}) - 2.00 \times 10^{-3}$, showing that the enthalpy term in χ is dominant. For a particular mixture with very narrow molecular weight distributions, the critical point was determined by measuring the volume ratio of two demixed phases and was found to shift from the extremum of the cloud point curve, indicating that the location of the critical point is very sensitive to the polydispersity.

(Keywords: poly(dimethylsiloxane); poly(methylethylsiloxane); blends; cloud point; χ parameter; miscibility)

INTRODUCTION

Compatibility and phase separation behaviour in polymer blends are of recent interest and have been studied extensively. However, experimental studies on their molecular weight dependence and influence of molecular weight distribution have not been extensively investigated considering their importance[1,2], although a large number of calculations for polydispersity effects on phase behaviour have been carried out using the Flory–Huggins type theory by Koningsveld[1]. One of the difficulties in such studies is to find a proper polymer blend system because polymer–polymer blends are generally incompatible, and the critical solution temperature usually changes dramatically with molecular weight. Recently we found that poly(dimethylsiloxane) (PDMS) and poly(methylethylsiloxane) (PMES) are partially miscible, having an upper critical solution temperature (*UCST*), and that the extremum of the cloud-point curve can be located at normal temperatures since it is in the region of room temperature[3]. It was also found that the temperature of the extremum of the cloud-point curve can be controlled using PMES of bimodal molecular weight distribution by changing the composition of the low and high molecular weight fractions. Molecular weights of PDMS were selected to be high (of the order of 10^5) while those of PMES were of the order of 10^3.

In this study, cloud-point curves were measured for binary mixtures of PDMS with PMES and ternary mixtures of PDMS with PMES of bimodal molecular weight distribution. An advantage of this blend system in phase diagram studies is that the glass transitions of both components are very low so that the viscosities of homogeneous mixtures and demixed phases are low enough to easily allow the determination of true cloud points and to obtain macroscopically separated phases even in higher molecular weight blends. In fact, for a particular binary blend with very narrow molecular weight distributions, the critical point could be determined on the cloud-point curve by measuring the volume ratio of demixed phases by using a centrifuge for macroscopic demixing. Using these data, we show that cloud points for different molecular weight mixtures enable us to reasonably determine the χ parameter between polymers in bulk as a function of temperature. A standard method of determining the χ parameter in polymer blends is based on the concentration fluctuation which can be observed by scattering techniques (neutron, X-ray and light)[4–6]. Another method is to determine the χ value as a function of temperature by fitting the theoretical coexistence curve to the experimental cloud-point curve[7]. Scattering measurements are not particularly easy or convenient for obtaining reliable and accurate data for calculating the χ value. The cloud-point profile method is very convenient but is totally based on the assumption of linear concentration dependence of χ, which is not always acceptable.

On the other hand, molecular weight dependence of the cloud-point temperature provides a more convenient and reliable method of determining the χ value as a function temperature[8]. In any method, molecular weight and polydispersity should be well characterized because miscibility and concentration fluctuations of blends are strongly dependent upon molecular weight.

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Table 1 Characterization of PDMS and PMES samples

Sample code	M_n[a]	M_w[b]	M_w/M_n[c]
PMES4	3190	(4340)[e]	1.36
PMES9	6190	(8790)[e]	1.42
PMES6N	4800[d]	(5710)[e]	1.19
PDMS80	–	79 000	1.32
PDMS200	–	193 000	1.39
PDMS1150	–	1 150 000[f]	1.25
PDMS250N	–	253 000	1.18

[a] Vapour pressure osmometry
[b] Light scattering in benzene at 30°C
[c] Gel permeation chromatography with PS standard
[d] Gel permeation chromatography with PMES standard
[e] Calculated from M_n and M_w/M_n values
[f] Gel permeation chromatography with PDMS standard

EXPERIMENTAL

Samples

Poly(dimethylsiloxane) samples were obtained from Shin-etsu Chemical Co. (KF-96H) with a nominal viscosity of 3×10^1 and 1×10^3 Pas. One of the PMES samples was supplied by Shin-etsu Chemical Co. and the other higher molecular weight sample was synthesized from poly(methylhydroxysiloxane) (PMHS) (KF-99) by addition of ethylene. The addition reaction was carried out in an autoclave at 50°C by using PMHS in toluene solution with more than two-fold excess ethylene gas with chlorinated platinaic acid as the catalyst. Completion of the reaction was checked by nuclear magnetic resonance spectroscopy.

The samples of PDMS and PMES were fractionated by molecular weight from their benzene solutions using methanol as precipitant. For selected fractions of PDMS and PMES, further fractionation was carried out using a preparative liquid chromatograph apparatus with a G5000 column (Toso Co. Ltd) to obain samples with narrower molecular weight distributions (sample codes PDMS250N and PMES6N). The weight-average molecular weight, M_w, values of PDMS were determined by light scattering from their toluene solutions and the number-average molecular weights, M_n, of PMES were determined using vapour pressure osmometry. The polydispersity index, M_w/M_n, was evaluated by gel permeation chromatography. Characteristics of the samples are listed in *Table 1*.

Blended samples were prepared by casting their benzene solutions. Residual solvent in the samples was completely removed by leaving the samples *in vacuo* at temperatures above the cloud point for more than 10 h.

Cloud-point measurements

The intensity of the scattered light from the samples under cooling was measured at the apparent scattering angle 10° to obtain the cloud point. The cloud point, T_{cl}, was defined as the temperature at which the scattered light intensity began to increase during cooling at a rate of $\sim 0.1°\mathrm{C\,min}^{-1}$. No dependence of T_{cl} on the cooling rate, R, was detected for R ranging from 0.067 to $1°\mathrm{C\,min}^{-1}$.

Volume ratio measurements

Blended sample was sealed in a glassy capillary tube (0.5 mm i.d.) and homogenized at a temperature in the one-phase region, and then cooled to a desired temperature in the two-phase region by placing in a centrifuge with the temperature being controlled to within ±0.1°C. It took several hours to complete the macroscopic phase separation. The volume ratio of the two phases was calculated from the length of the phase in the capillary tube. The volume ratio was measured for various compositions of PDMS/PMES at fixed temperatures, and the composition at which the volume ratio was 50/50 was determined by interpolation of the volume ratio *versus* composition relation obtained.

RESULTS AND DISCUSSION

Cloud-point curves and critical point

Table 2 gives the blend systems for which the cloud-point curve, i.e. the cloud point, T_{cl}, *versus* composition of PDMS, was measured. Here the compositions ϕ_w and θ_w are, respectively, defined by

$$\phi_w = w(\mathrm{PDMS})/[w(\mathrm{PDMS}) + w(\mathrm{PMES})]$$

$$\theta_w = w(\mathrm{PMES4})/[w(\mathrm{PMES4}) + w(\mathrm{PMES9})]$$

where w is the weight of each component indicated in parentheses, and w(PMES) is the total weight of PMES in the case of the ternary blend.

Figure 1 shows cloud-point curves for ternary blends of PMES4/PMES9 + PDMS. The extremal cloud points $T_{cl,ex}$ are listed in *Table 2*. The cloud-point curve shifts toward higher temperatures as the low molecular weight fraction θ_w in PMES decreases and/or the molecular weight of PDMS increases. The composition ϕ_w at the extremum of the cloud-point curve for a higher molecular weight PDMS (PDMS200) is smaller than that for PDMS80, while those for the same PDMS are almost the same irrespective of the PMES composition ϕ_w in the experimental range of θ_w.

Figure 2 shows the cloud-point curve for PDMS250N/PMES6N with narrower molecular weight distributions, together with the composition $\phi_{w1/2}$ at which the volume ratio of the demixed phases is 50/50. The intersection of the cloud-point curve and the $\phi_{w1/2}$ *versus* temperature curve should give the critical point. Location of the critical point shifts away from the extremum of the cloud-point curve towards lower concentrations of PDMS. Polydispersity effects on the phase diagram are still apparent even in the blend with narrow molecular weight distributions.

Table 2 Blend systems and their extremum temperatures of the cloud point, $T_{cl,ex}$

System	θ_w	$T_{cl,ex}$ (°C)
PMES4/PMES9/PDMS80	0.000	99
	0.101	88
	0.201	76
	0.302	64
	0.408	48
	0.506	36
PMES4/PMES9/PDMS200	0.408	89
	0.604	57
PMES6N/PDMS1150	–	95
PMES6N/PMES250N	–	60

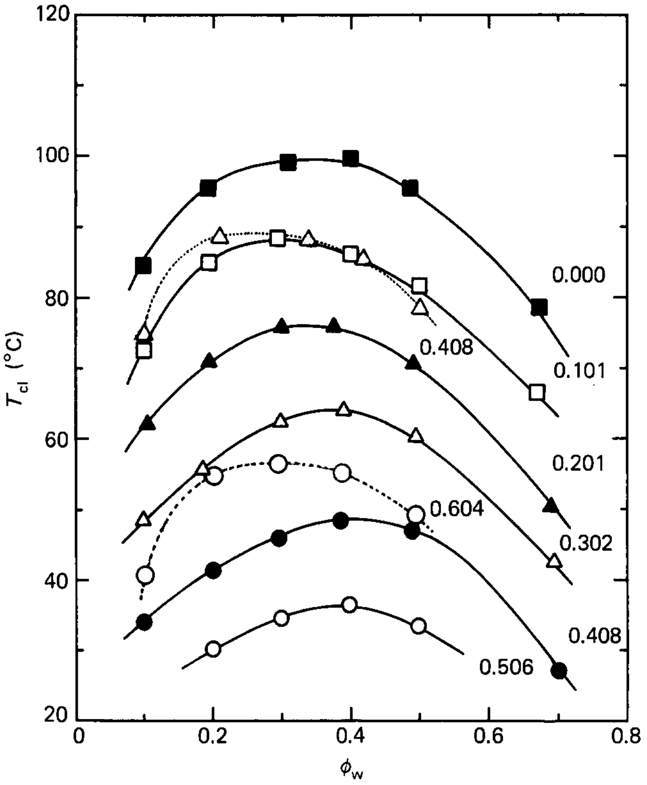

Figure 1 Cloud-point curves for ternary blends of PMES4/PMES9/PDMS. Open symbols, PDMS = PDMS80; closed symbols, PDMS = PDMS200. Numbers indicate values of θ_w. Solid and broken lines are guides for the eye only

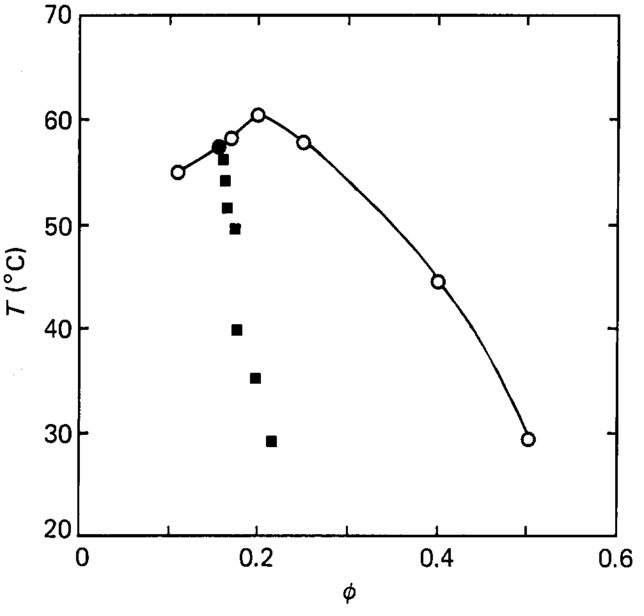

Figure 2 Cloud-point curve for PDMS250N/PMES6N. ○, Cloud-point curve; ●, critical point; ■, diameter at which the volume ratio of the demixed phases is 50/50. Solid line is a guide for the eye only

Effects of molecular weight distribution on the cloud-point curve

The above findings of the change in the cloud-point curve with molecular weight and its distribution can be understood, at least qualitatively, from the Flory–Huggins (F–H) theory. To show this we did numerical calculations of cloud-point curves, spinodal curves and critical points for a simple ternary system using F–H theory.

Consider a blend system consisting of polymer A with polymeric index, PI $= P_1$ and polymer B with bimodal molecular weight distribution of PI $= P_2$ and P_3, the compositions of each component being ϕ_1, ϕ_2 and ϕ_3 by volume fraction, respectively. The volume fraction θ of the P_2 fraction in polymer B is given by $\theta = \phi_2/(\phi_2 + \phi_3)$. The coexistence curve for the ternary system was computed as a function of χ for a set of given values of P_1, P_2 and P_3, where χ denoted the interaction parameter between polymers A and B, which was assumed to be independent of compositions ϕ_1 and θ (see Appendix). From the results, the cloud-point curve, spinodal curve and critical point for various fractions θ of polymer B were obtained to be plotted as χ *versus* ϕ_1 space. The minimum point (ϕ_m, χ_m) of the spinodal curve is given by

$$\phi_m = \frac{1}{1 + (P_1/P_w)^{1/2}} \tag{1}$$

and

$$\chi_m = \frac{1}{2}\left(\frac{1}{P_1^{1/2}} + \frac{1}{P_w^{1/2}}\right)^2 \tag{2}$$

where P_w is the weight-average PI of polymer B:

$$P_w = P_2\theta + P_3(1 - \theta)$$

On the other hand, the critical concentration ϕ_c is written as[1]

$$\phi_c = \frac{1}{1 + (P_1/P_w)^{1/2}(P_z/P_w)^{1/2}} \leqslant \phi_m \tag{3}$$

where P_z is the z-average PI given by $[P_2^2\theta + P_3^2(1 - \theta)]/P_w$.

Figure 3 represents change in phase diagram with composition θ for a set of $P_1 = 100$, $P_2 = 20$ and $P_3 = 40$, where $P_2 > P_3$, therefore, θ indicates the fraction of low molecular weight component in polymer B as in the present experimental cases. Although the degree of polymerization P_1 is lower than in the experiments, calculated phase behaviours must be qualitatively comparable with experimental values. As seen from the results in *Figure 3*, the extremum of the cloud-point curve $(\chi_{cl,ex}, \phi_{cl,ex})$, the minimum of the spinodal curve (ϕ_m, χ_m) and the critical point (χ_c, ϕ_c) are different from each other except for $\theta = 0$ due to polydispersity, as expected. With decreasing θ, i.e. as P_w increases, ϕ_c and ϕ_m decrease, but $\phi_{cl,ex}$ does not vary with θ so much if $\theta < 0.5$. This can explain the experimental finding for $\phi_{cl,ex}$.

It also follows from *Figure 3* that ϕ_c shifts from $\phi_{cl,ex}$ towards higher concentrations of bimodal-component polymer B, i.e. $\phi_c < \phi_{cl,ex}$ in agreeement with equations (2) and (3). This polydispersity effect in polymer blends has already been pointed out by Koningsveld[1], i.e. ϕ_c shifts away from ϕ_m and $\phi_{cl,ex}$ towards higher concentrations of the more polydisperse component. It was found experimentally, for example, in polystyrene (PS)/poly(methylphenylsiloxane) (PMPS), where M_w/M_n was 1.04–1.06 for PS and 1.43–1.57 for PMPS[9], respectively. Shift of the critical point away from the extremum of the cloud-point curve comes from the dissimilarity of polydispersity (M_z/M_w) between the components and/or from the combination of the concentration dependence of the χ parameter and polydispersity[1]. Even though the polydispersity index M_w/M_n is close to unity and similar

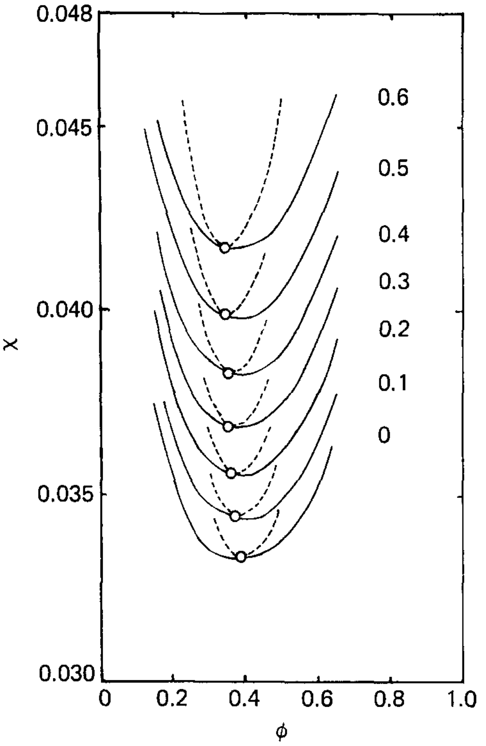

Figure 3 Cloud-point curves, spinodal curves and critical points computed by Flory–Huggins theory for ternary polymer mixtures consisting of polymer A ($P_1 = 100$), polymer B ($P_2 = 20$) and polymer B ($P_3 = 40$). $\phi =$ [Polymer A]/[total polymer A and B]; $\theta =$ [Polymer B(P_2)]/[total polymer B]. Numbers indicate values of θ

for both components, the PDMS250N/PMES6N blend exhibits $\phi_c < \phi_{cl,ex}$. This implies that PMES8N is a little more polydisperse than PDMS250N and/or the χ parameter is concentration dependent. It also shows that the profile of the cloud-point curve is quite sensitive to the polydispersity in polymer blends.

χ parameter as a function of temperature

As seen from *Figure 3*, the values of χ_c, χ_m and $\chi_{cl,ex}$ are not the same but $\chi_c > \chi_m > \chi_{cl,ex}$. However, the difference is not so great compared with the change in χ_m with θ. Therefore, we can reasonably approximate $\chi_{cl,ex}$ by χ_m for polymer mixtures with different θ in the present case, so that the χ parameter can be determined as a function of temperature by equation (2) with experimental values of $T_{cl,ex}$ for various combinations of molecular weight and composition θ. Namely, the value of χ_m calculated from equation (2) for given values of P_1 and P_w is approximately equal to the χ value at temperature $T = T_{cl,ex}$ of the blend with the given P_1 and P_w. This treatment is based on the assumption that the χ value is a function of temperature only, being independent of the molecular weights of PDMS and PMES. In *Figure 4*, the χ values thus obtained were plotted against the inverse of absolute temperature $1/T$. Here, PI was assumed to be proportional to the molar volume, and was evaluated by taking monomer unit of PMES (molecular weight M_0) as the monomer, i.e. $P_w = M_w/M_0$ for instance, so that the χ value is per monomer unit of PMES, i.e. per 91 ml volume. The following equation derived from equation (2) was used:

$$\chi_m = \frac{M_0}{2M_{wB}} \left\{ 1 + \sqrt{\frac{\rho_A M_{wB}}{\rho_B M_{wA}}} \right\}^2 \tag{4}$$

where subscripts A and B indicate PDMS and PMES, respectively, and the density ρ was 0.975 g ml^{-1} for PDMS and 0.965 g ml^{-1} for PMES[10]. In *Figure 4* the line with open circles indicates the results for a series of PDMS80/PMES4/PMES9 blends with various θ, while the closed symbols represent different blends. Considering experimental errors and the assumptions used in the analysis, one can say that the closed symbols fall roughly on the same line as the open circles. This implies the validity of equation (2) with $\chi_m \simeq \chi_{cl,ex}$ and the assumption of molecular weight independence of χ, and shows that the χ value can successfully be determined as a function of temperature from the molecular weight dependence of the cloud point, where the molecular weight can be substantially varied by changing the composition θ.

As seen from *Figure 4*, plots of χ values *versus* $1/T$ produce a straight line. The least-squares fitting for PDMS80/PMES4/PMES9 blends yields

$$\chi = 4.07/T(\text{K}) - 2.00 \times 10^{-3}$$

Therefore, separating the χ parameter into enthalpy (χ_H) and entropy (χ_S) terms, one has $\chi_H = 4.07/T$ and $\chi_S = -2.00 \times 10^{-3}$. Comparing the two terms at 50°C, one can see that the positive enthalpy term ($\chi_H = 0.0125$) dominates the entropy term. It turns out that χ decreases with increasing temperature and is always positive at normal temperatures. In other words, χ behaves as the originally defined χ parameter, which comes from the contact-energy change in mixing. Hence, the result suggests that the PDMS/PMES pair has no specific interaction and no appreciable effects of the equation of state. Partial miscibility of the present blend comes just from the similarity of the chemical structure of PDMS and PMES which results in a small value of χ. In fact, for a PS ($M_w = 2.4 \times 10^3$)/polybutadiene (PBD) ($M_w = 2.6 \times 10^4$) blend with a *UCST*-type phase diagram, Roe and Zim[7] have obtained the result of $\chi = 49.3/T - 0.081$ per 100 ml volume, which shows that both χ_H and χ_S for the PS/PBD blend are much larger than those for the

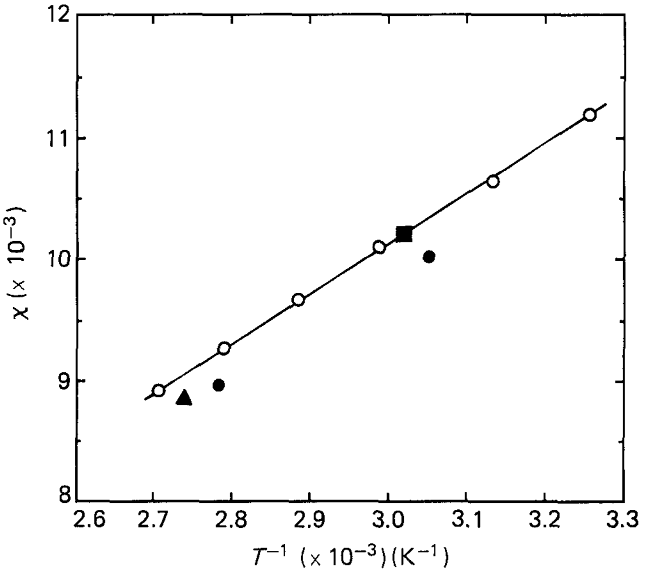

Figure 4 Temperature dependence of χ between PDMS and PMES calculated from the extremum temperature of cloud-point curves for various combinations of molecular weights and composition θ. ○, PMES4/PMES9/PDMS80; ●, PMES4/PMES9/PDMS200; ▲, PMES6N/PDMS1150; ■, PMES6N/PDMS250N. Solid line was obtained by least-squares fitting for PMES4/PMES9/PDMS80 blends

PDMS/PMES blend, probably because of dissimilarity in chemical structure and no specific interaction between PS and PBD. In contrast with these systems, PS/poly(vinylmethylether) (PVME) and PS/poly(2-chlorostyrene) (P2ClS), which have lower critical solution temperatures (*LCST*), exhibit a quite different χ behaviour. For PS/PVME of 50/50 wt%, $\chi = -35.6/T + 0.083$ per volume-average monomer (74.7 ml), obtained by small-angle neutron scattering[5,11]. For PS/P2ClS, the equation $\chi = -1.63/T + 7.8 \times 10^{-3}$ per PS monomer (103 ml) has been derived[8] from the molecular weight dependence of T_{cl}. Values of χ_H are very different for PS/PVME and PS/P2ClS. However, in both of these blends the magnitude of χ_S is comparable to that of χ_H which is negative in contrast with PS/PBD and the present blends. This contrast reflects the difference in the type of phase diagram, i.e. *UCST* and *LCST* types.

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APPENDIX

Phase diagram of a ternary blend

Consider a ternary system consisting of the following components:

component 1 (polymer A): PI $= P_1$; volume fraction, VF $= \phi_1$
component 2 (polymer B): PI $= P_2$; VF $= \phi_2$
component 3 (polymer B): PI $= P_3$; VF $= \phi_3$
Interaction parameter between polymer A and B: χ

Here, components 2 and 3 are assumed to be chemically identical, i.e. the interaction parameters χ_{ij} between components i and j are assumed to be $\chi_{23} = 0$; $\chi_{12} = \chi_{13} = \chi$. The chemical potentials $\Delta\mu_i$ are given by[12]

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + (1 - P_1/P_2)\phi_2 + (1 - P_1/P_3)\phi_3 + P_1(1 - \phi_1)^2\chi$$

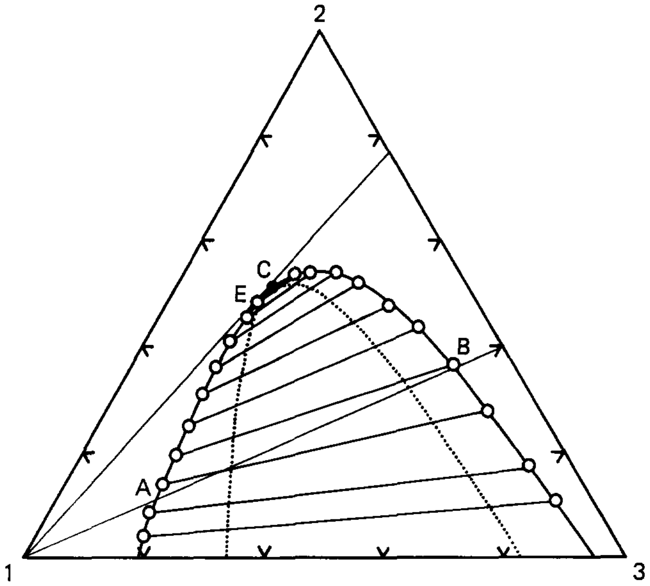

Figure 5 Phase diagram of a ternary polymer blend ($P_1 = 100$, $P_2 = 20$, $P_3 = 40$ and $\chi = 0.045$) computed by F–H theory. Details of the calculation are described in the Appendix. ▬▬, Coexistence curve; ——, tie lines; · · · ·, spinodal curve. A, B, Cloud points for $\theta = 0.6$; C, critical point; E, extremum of cloud point for $\theta = 0.6$

$$\frac{\Delta\mu_i}{RT} = \ln \phi_i + \sum_{j \neq i} (1 - P_i/P_j)\phi_j + P_i\phi_1^2\chi \qquad \text{for } i = 2 \text{ and } 3$$

under the assumption that χ is independent of ϕ_i ($i = 1$, 2 and 3). The coexistence curve with tie lines can be computed by solving the simultaneous equations of $\Delta\mu_1' = \Delta\mu_1''$, $\Delta\mu_2' = \Delta\mu_2''$ and $\Delta\mu_3' = \Delta\mu_3''$, where the prime and double prime denote each of the demixed phases, respectively. As an example, *Figure 5* shows the calculated coexistence curve for $P_1 = 100$, $P_2 = 20$, $P_3 = 40$ and $\chi = 0.045$, along with spinodal curve, which can be expressed by

$$\frac{1}{P_1\phi_1} + \frac{1}{P_w(1 - \phi_1)} - 2\chi = 0$$

This curve touches the coexistence curve at the critical point C. The cloud point for a given set of θ [$= \phi_2/(\phi_2 + \phi_3)$] and χ can be determined as the intersections of the coexistence curve and the line indicating $\theta =$ a given value, e.g. point A and B for $\theta = 0.6$ and $\chi = 0.045$ in *Figure 5*. The same procedure for various values of χ yields the cloud-point curve χ *versus* ϕ_1 for the given θ value. If the line of $\theta =$ constant touches the coexistence curve at a single point, for example, at the point E, this point E is the extremum of the cloud-point curve for this particular θ, which is generally different from the critical point C.