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Spinoidal and Critical Points in Polydisperse Random Copolymer Blends

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SPINOIDAL AND CRITICAL POINTS IN POLYDISPERSE RANDOM COPOLYMER BLENDS

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ABSTRACT

Spinoidal and critical points of the liquid–liquid equilibrium in random copolymer blends are calculated by application of continuous thermodynamics. Blends are composed of two copolymers, each consisting of two different monomer units. Both copolymers are characterized by divariate distribution functions with respect to molecular weight and to chemical composition. Based on a model for the excess Gibbs free energy of mixing, the necessary relations are derived for the calculation of spinoidal and critical points. The influences of the polydispersities of molecular weight and/or chemical composition on the instability limit are discussed. Miscibility maps are calculated on the basis of the critical point. Cloud-point curves are shown to be most sensitive to polydispersities if the excess Gibbs free energy of mixing exceeds only slightly the lowest value necessary for demixing.

INTRODUCTION

The problem of compatibility in copolymer blends has been a subject of interest for many years, mainly from the practical viewpoint of materials science. Copolymer blends may exhibit interesting properties which

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are not shown by single copolymers or by homopolymers. Tailor-made polymeric materials can be composed of copolymer blends in many ways. Their properties depend, to a certain extent, on whether the blends are thermodynamically stable or not. The thermodynamic stability of a blend means the location in a homogeneous region of the phase diagram.

Thermodynamic considerations in the literature are usually restricted to a qualitative analysis of the negative or positive sign of the Gibbs free energy of mixing, e.g., Refs. 1 and 2, or to a calculation of the spinoidal and/or critical state criterion, e.g., Refs. 3–7. In most cases, polydispersity effects are neglected or are only roughly taken into account. The chemical polydispersity, in particular, is included within the calculations only in a very few papers [8, 9].

In our preceding paper [10], continuous thermodynamics was applied to random copolymer blends to calculate the phase diagram in the liquid–liquid demixing region. We could demonstrated some special polydispersity effects on the cloud-point curve, on the shadow curve, and on the true boundary curves in the phase diagram of a polydisperse mixture.

We continue this work in the present paper, where continuous thermodynamics is applied to the calculation of the correct relations for the spinoidal curve and the critical point in blends of two copolymers, each consisting of two different monomer units and both characterized by divariate distribution functions. The influence of both chemical and molecular weight distributions on the location of spinoidal and critical points are discussed. The calculation of miscibility maps based on the critical point allows some special features of the cloud-point curve to be investigated when the Gibbs free energy of mixing slightly exceeds the lowest value necessary for demixing.

DIVARIATE DISTRIBUTION FUNCTIONS

We consider two copolymers B and C (the symbol A is reserved for solvents [11]), each consisting of two kinds of monomer units, α and β, γ and δ in C. Choosing a standard segment, we introduce the segment numbers $r_\alpha, \ldots, r_\delta$. A given species of the copolymer B is characterized by the segment number r_B and the segment fraction Y_B:

$$r_B = r_\alpha + r_\beta \tag{1}$$

$$Y_B = r_\alpha/r_B \tag{2}$$

where r_B corresponds to the molecular weight and Y_B describes the chemical composition. Analogously, a species of copolymer C is characterized by r_C and Y_C.

The polydisperse copolymers B and C may be described by divariate distribution functions $W_B(r_B, Y_B)$ and $W_C(r_C, Y_C)$, respectively, which have to fulfill the normalization condition

$$\int_{r_K}\int_{Y_K} W_K(r_K, Y_K)dY_K dr_K = 1; \qquad \int_{r_K} = \int_{r_0}^{r^0}; \qquad \int_{y_K} = \int_0^1 \qquad (3)$$

$K = B, C.$

The number average, $\bar{r}_K$, and the weight averages, $\tilde{r}_K$ and $\bar{Y}_K$, are defined by

$$1/\bar{r}_K = \int_{r_K}\int_{Y_K} W_K(r_K, Y_K)r_K^{-1}dY_K dr_K \qquad (4a)$$

$$\tilde{r}_K = \int_{r_K}\int_{Y_K} W_K(r_K, Y_K)r_K dY_K dr_K \qquad (4b)$$

$$\bar{Y}_K = \int_{r_K}\int_{Y_K} W_K(r_K, Y_K)Y_K dY_K dr_K \qquad (4c)$$

$K = B, C.$

Copolymers B and C are assumed to obey the generalized Stockmayer distribution.

$$W_K(r_K, Y_K) = \left\{ \frac{\int_{k_K}^{k_K+1}}{\bar{r}_K\Gamma(k_K + 1)} \left(\frac{r_K}{\bar{r}_K}\right)^{k_K} \exp\left(-k_K \frac{r_K}{\bar{r}_K}\right) \right\} \qquad (5)$$

$$\left\{ \sqrt{\frac{r_K}{2\pi\epsilon_K}} \exp\left(-\frac{r_K(Y_K - \tilde{Y}_K)^2}{2\epsilon_K}\right) \right\}, \quad K = B, C$$

where Γ is the gamma function, and k_K and ϵ_K are given by

$$k_K = 1/(\tilde{r}_K/r_K - 1) \qquad (6a)$$

$$\epsilon_K \approx \tilde{Y}_K(1 - \tilde{Y}_K) \tag{6b}$$

$$K = B, C.$$

GENERAL EXPRESSION FOR THE SPINOIDAL

If the stability theory in the framework of continuous thermodynamics [12–16] is applied to the copolymer blends B + C, the spinoidal curve is the solution of the equation

$$\det Q_S = 0 \tag{7}$$

where $\det Q_S$ means the determinant of the matrix Q_S. This matrix is defined by

$$Q_S = \begin{pmatrix} q_{22}^{BB} & q_{21}^{BC} & q_{22}^{BC} \\ q_{12}^{CB} & q_{11}^{CC} & q_{12}^{CC} \\ q_{22}^{CB} & q_{21}^{CC} & q_{22}^{CC} \end{pmatrix} \tag{8a}$$

where the elements are given by

$$q_{21}^{BC} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_B \overline{Y}_B^{(1)} \partial\psi_C \overline{Y}_C^{(0)}} - r_{21}^B; \qquad q_{22}^{BC} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_B \overline{Y}_B^{(1)} \partial\psi_C \overline{Y}_C^{(1)}}$$

$$q_{12}^{CB} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_C \overline{Y}_C^{(0)} \partial\psi_B \overline{Y}_B^{(1)}} - r_{12}^B; \qquad q_{22}^{CB} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_C \overline{Y}_C^{(1)} \partial\psi_B \overline{Y}_B^{(1)}}$$

$$q_{22}^{BB} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_B \overline{Y}_B^{(1)} \partial\psi_B \overline{Y}_B^{(1)}} + r_{22}^B$$

$$q_{11}^{CC} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_C \overline{Y}_C^{(0)} \partial\psi_C \overline{Y}_C^{(0)}} + r_{11}^B + r_{11}^C; \qquad q_{12}^{CC} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_C \overline{Y}_C^{(0)} \partial\psi_C \overline{Y}_C^{(1)}} + r_{12}^C$$

$$q_{21}^{CC} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_C \overline{Y}_C^{(1)} \partial\psi_C \overline{Y}_C^{(0)}} + r_{21}^C; \qquad q_{22}^{CC} = \frac{\partial^2 \overline{\overline{G}}^E/RT}{\partial\psi_C \overline{Y}_C^{(1)} \partial\psi_C \overline{Y}_C^{(1)}} + r_{22}^C \tag{8b}$$

Here $\overline{\overline{G}}^E$ is the segment molar excess Gibbs free energy of the mixture B + C, R is the universal gas constant, and T is the absolute temperature. All differentiations in Eqs. (8) have to be performed with respect to the four moments of the non-normalized distribution functions $\psi_K W_K(r_K, Y_K)$. These moments are defined by

$$\psi_K \overline{Y_K^{(i)}} = \int_{r_K} \int_{Y_K} \psi_K W_K(r_K, Y_K) Y_K^i dY_K dr_K; \qquad K = \mathrm{B, C} \qquad (9)$$

The zeroth moment, ψ_K, is the overall segment fraction of copolymers B and C, respectively, in the blend.

The quantities r_{ij}^K are the elements of the matrix inverse to the matrix

$$R^K = \begin{pmatrix} R_{11}^K & R_{12}^K \\ R_{21}^K & R_{22}^K \end{pmatrix} \qquad (10)$$

i.e.,

$$r_{11}^K = R_{22}^K/\det R^K; \qquad r_{22}^K = R_{11}^K/\det R^K$$
$$r_{12}^K = r_{21}^K = -R_{21}^K/\det R^K = -R_{21}^K/\det R^K \qquad (11)$$

with [15]

$$R_{ij}^K = \int_{r_K} r_K \int_{Y_K} Y_K^{i+j-2} \psi_K W_K(r_K, Y_K) dY_K dr_K; \qquad K = \mathrm{B, C} \qquad (12)$$

Further calculations depend on the $\overline{\overline{G}}^E$ model chosen and can be performed straightforward by applying the general differentiation rules.

FREE ENERGY MODEL AND PHASE EQUILIBRIUM

We use the model for the segment molar excess Gibbs free energy $\overline{\overline{G}}^E$ derived in Ref. 10, which is based on the assumption of random mixing for all copolymer segments in the blend.

$$\frac{\overline{\overline{G}}^E}{RT} = \frac{L(\psi_B)}{Q} \beta(T)g \tag{13}$$

with

$$L(\psi_B) = \psi_B(1 - \psi_B)(1 + c\psi_B + d\psi_B^2 + \cdots) \tag{14}$$

$$\beta(T) = a + b/T \tag{15}$$

$$Q = \psi_B\eta_1 + \psi_C\eta_2 \tag{16}$$

$$\eta_1 = s_\alpha\tilde{Y}_B + s_\beta(1 - \tilde{Y}_B); \quad \eta_2 = s_\gamma\tilde{Y}_C + s_\delta(1 - \tilde{Y}_C) \tag{17}$$

$$g = -s_\alpha s_\beta\tilde{Y}_B)(1 - \tilde{Y}_B)(\eta_2/\eta_1)g_{\alpha\beta} + s_\alpha s_\gamma\tilde{Y}_B\tilde{Y}_C g_{\alpha\beta} + s_\alpha s_\delta\tilde{Y}_B(1$$
$$- \tilde{Y}_C)g_{\alpha\beta} + s_\beta s_\gamma(1 - \tilde{Y}_B)\tilde{Y}_C g_{\beta\gamma} + s_\beta s_\delta(1 - \tilde{Y}_B)(1$$
$$- \tilde{Y}_C)g_{\beta\delta}s_\gamma s_\delta\tilde{Y}_C(1 - \tilde{Y}_C)(\eta_1/\eta_2)g_{\gamma\delta} \tag{18}$$

The function $L(\psi_B)$ contains two empirical parameters, c and d, taking into account that $\overline{\overline{G}}^E$ usually is a more complicated function of the concentration than in the classic Flory–Huggins relation. The function $\beta(T)$ describes (to a first approximation) the influence of temperature at a given pressure. The parameters $s_\alpha, \ldots, s_\delta$ account for different surface contact areas of the segments. The function g describes the effects (depending on chemical composition) that are concerned with the empirical interaction parameters g_{ij} between the four monomer units α to δ, in a random mixing approach.

The phase equilibrium conditions in continuous thermodynamics lead to [10, 11]

$$\psi_K^{II}W_K^{II}(r_K, Y_K) = \psi^I W_K^I(r_K, Y_K) \exp[r_K\rho_K(r_K, Y_K)] \tag{19}$$

where

$$\rho_K(r_K, Y_K) = \ln(\bar{f}_K^I/\bar{f}_K^{II}) + 1/\bar{r}^{II} - 1/\bar{r}^I; \quad K = B, C \tag{20}$$

and

$$1/r' = \psi_B'/r_B' + \psi_C'/r_C'; \quad ' = I, II \tag{21}$$

$\bar{r}_B$ and $\bar{r}_C$ have to be calculated for both phases in equilibrium by applying Eq. (4a). The quantities $\bar{\bar{f}}_B$ and $\bar{\bar{f}}_C$ are the so-called segment molar activity coefficients containing all deviations from the Flory–Huggins mixture (with $\chi = 0$). The logarithms of $\bar{\bar{f}}_B$ and $\bar{\bar{f}}_C$ are the partial segment molar quantities with respect to $\overline{\overline{G}}^E/RT$.

An explicit expression of the general relation given by Eq. (19) was derived in Ref. 10 by applying the generalized Stockmayer distribution, Eq. (5), and the $\overline{\overline{G}}^E$ model summarized above. This expression reads (Eq. 27 in Ref. 10):

$$FU = 0 = \psi_K^{II} - \psi_K^I/[1 - (\tilde{r}_K^I/k_K)(A_K + B_K \tilde{Y}_K^I + \epsilon_K B_K^2/2)]^{k_K+1} \qquad (22)$$

where

$$A_K = \frac{1}{\bar{r}^{II}} - \frac{1}{\bar{r}^I} + \frac{\overline{\overline{G}}^{E^I}}{RT} - \frac{\overline{\overline{G}}^{E^{II}}}{RT} + (1 - \psi_K^I)\frac{\partial \overline{\overline{G}}^{E^I}/RT}{\partial \psi_K^I}$$

$$- (1 - \psi_K^{II})\frac{\partial \overline{\overline{G}}^{E^{II}}/RT}{\partial \psi_K^{II}} + \frac{\tilde{Y}_K^{II}}{\psi_K^{II}}\frac{\partial \overline{\overline{G}}^{E^{II}}/RT}{\partial \tilde{Y}_K^{II}} - \frac{\tilde{Y}_K^I}{\psi_K^I}\frac{\partial \overline{\overline{G}}^{E^{II}}/RT}{\partial \tilde{Y}_K^I} \qquad (23)$$

$$B_K = \frac{1}{\psi_K^I}\frac{\partial \overline{\overline{G}}^{E^I}/RT}{\partial \tilde{Y}_K^I} - \frac{1}{\psi_K^{II}}\frac{\partial \overline{\overline{G}}^{E^{II}}/RT}{\partial \tilde{Y}_K^{II}}; \qquad K = B, C. \qquad (24)$$

The derivations in Eqs. (23) and (24) are given elsewhere (Eqs. 20–24 in Ref. 10). Equations (22)–(24) are the solution for the problem of the cloud-point curve and the shadow curve, i.e., the boundary curves of phase separation in polydisperse mixtures.

SPINOIDAL AND CRITICAL POINTS BY POWER SERIES EXPANSION METHOD

A general expression is given above for the spinoidal curve derived from the stability theory of continuous thermodynamics. Equation (7) is valid independent of the $\overline{\overline{G}}^E$ model and of the distribution function chosen.

In many cases it appears to be more convenient to calculate the spinoi-

dal curve and the critical point for a special case where the $\overline{\overline{G}}^E$ model and the distribution functions are fixed from the first. Such a special case is given by Eqs. (22)–(24). It was shown earlier [17–20] that the expansion of the phase equilibrium relations, Eqs. (19), in powers of ψ_B^{II} or ψ_C^{II} or T, respectively, at the critical point provides the necessary and sufficient conditions for the instability limit, i.e., the spinoidal curve, and also for multiple critical points. Starting from the result given by Eq. (22), the spinoidal curve is the solution of the equation

$$\partial FU/\partial \psi_B^{II} = 0 \tag{25}$$

and the additionally necessary equations for a stable single critical point read

$$\frac{\partial^2 FU}{\partial (\psi_B^{II})^2} = 0; \qquad \frac{\partial^3 FU}{\partial (\psi_B^{II})^3} > 0 \tag{26}$$

Differentiation of Eq. (22) leads to

$$\frac{\partial FU}{\partial \psi_B^{II}} = \frac{1}{\bar{r}_B^I \psi_B^I} - \frac{\partial A_B}{\partial \psi_B^{II}} - \bar{Y}_B^I \frac{\partial B_B}{\partial \psi_B^{II}} \tag{27}$$

$$\frac{\partial^2 FU}{\partial (\psi_B^{II})^2} = -\frac{(k_B + 2)\bar{r}_B^I}{\bar{r}_B^I k_B \psi_B^{I2}} - \frac{\partial^2 A_B}{\partial (\psi_B^{II})^2} - \bar{Y}_B^I \frac{\partial^2 B_B}{\partial (\psi_B^{II})^2} - \epsilon_B \left(\frac{\partial B_B}{\partial \psi_B^{II}}\right)^2 \tag{28}$$

All differentiations have to be performed according to the chain rule, taking into consideration that $\bar{r}_B^{II}$, $\bar{r}_B^{II}$, and $\bar{Y}_B^{II}$ are functions of ψ_B^{II}, too.

The resulting equations are omitted here because of the large number of terms included [21]. The critical point is not equivalent to the extremum of the spinoidal curve, due to polydispersity effects, as can be deduced directly from Eqs. (25)–(28).

The general result given by Eqs. (7)–(12) and the special result obtained by Eqs. (25)–(28) agree if the special $\overline{\overline{G}}^E$ model and the Stockmayer distribution are introduced into Eqs. (7)–(12).

APPLICATIONS

As we are mainly interested in a discussion of the influence of both polydispersities, calculations are performed mainly by using model mixtures for the copolymer system B + C.

1. Model Blends of the Type B($\alpha\beta$) + C($\alpha\beta$)

Casper and Morbitzer [22] gave a detailed study of the stability limits of such mixtures by using the spinoidal equation and the critical point condition for the monodisperse case. Koningsveld and Kleintjens [9] discussed the behavior of such blends for the polydisperse case. The relationship for the spinoidal and the critical point given in the present paper reduce to those given in Ref. 9 for the special type of blends considered in this section. Thus, we restrict ourselves to some illustrating examples.

Model calculations are carried out in analogy to our preceding paper [10] for the following conditions:

(a) $\bar{r}_B = 50$, $k_B = 1$, $\bar{r}_C = 50$, $k_C = 1$, all $s_i = 1$, $c = d = 0$, $g_{\alpha\beta} = 1$, $\Delta = \tilde{Y}_C - \tilde{Y}_B = 0.1 = $ constant; Fig. 1(a).

(b) Parameters as for (a), but $\tilde{Y}_B = 0.1$ and Δ increases; Fig. 1(b).

(c) Parameters as for (a), but s_α/s_β increases; Fig. 1(c).

(d) Parameters as for (a), but $\tilde{Y}_B = 0.5$, $\tilde{Y}_C = 0.7$, and ϵ_C increases (not using Eq. 6b); Fig. 1(d).

(e) Parameters as for (d), but $\epsilon_C = 0.21$ and k_C increases; Fig. 1(e).

(f) Parameters as for (d), but $\epsilon_C = 0.21$ and $c \neq 0$, $d \neq 0$; Fig. 1(f).

As the critical point is a special point on the cloud-point curve (the point where spinoidal and cloud-point curve have a common tangent), there is agreement between the results presented in Fig. 1 and the corresponding results discussed in Ref. 10. But due to polydispersity, the critical point and the threshold of demixing do not coincide. Again, we observe that the main effect on the stability limit is caused by $\Delta = \tilde{Y}_C - \tilde{Y}_B$, which was already pointed out in principle by Scott [23]. Polydispersity, as well as the molecular weight, Fig. 1(e), and the chemical composition, Figs. 1(a) and 1(d), leads to shifts in the location of the critical point. This effect becomes larger if more than two monomer units are present in the mixture (see below). Influences caused by different contact surface areas, Fig. 1(c), or by parameters of the $\overline{G}^E$ model, Fig. 1(f), can partially compensate or amplify the polydispersity effects.

2. Miscibility Maps in Blends of the Type B($\alpha\beta$) + C($\gamma\delta$)

The discussion about compatibility in copolymer blends is often performed on the basis of miscibility maps, i.e., diagrams with two axes indicating $\tilde{Y}_C$ and $\tilde{Y}_B$. The areas of such miscibility maps correspond to
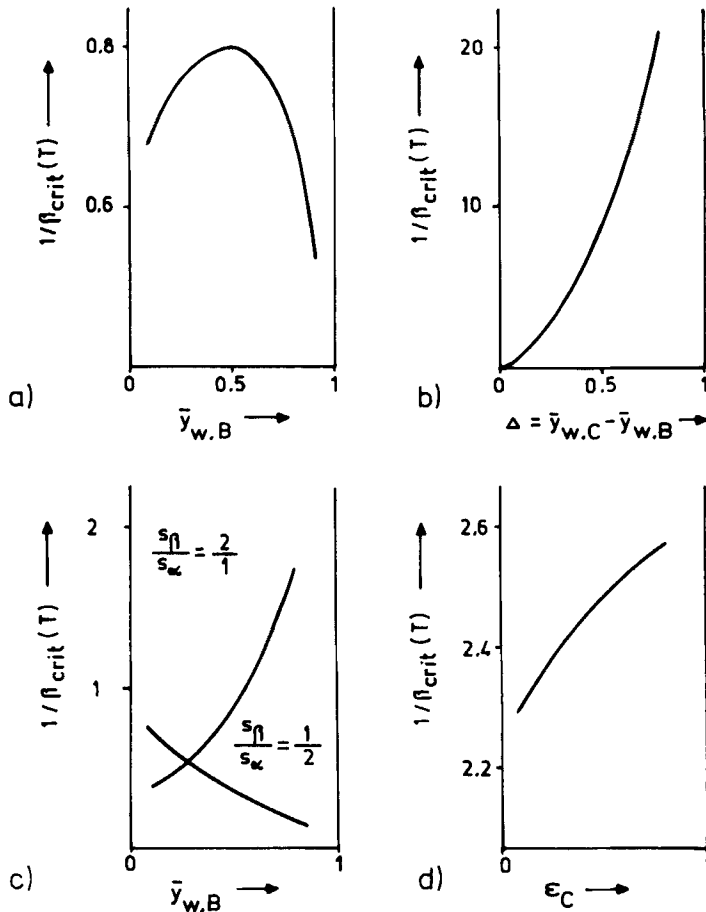
FIG. 1. Calculated critical points for copolymer blends of the type $B(\alpha\beta)$ + $C(\alpha\beta)$ as functions of (a) The weight averages $\tilde{Y}_B$, $\tilde{Y}_C$ at constant $\Delta = \tilde{Y}_C - \tilde{Y}_B$ = 0.1. For the other parameters, see text. (b) The value of Δ with constant $\tilde{Y}_B$ = 0.1. Other parameters as in (a). (c) The surface ratio s_β/s_α. Other parameters as in (a). (d) The width of the chemical distribution ϵ_C (not using Eq. 6b with $\tilde{Y}_B$ = 0.5 and $\tilde{Y}_C$ = 0.7. Other parameters as in (a). (e) The width of the molecular weight distribution as expressed by k_C. Other parameters as in (d) with ϵ_C = 0.21. (f) The $\overline{\overline{G}}^E$ parameters c and d. Other parameters as in (d) with ϵ_C = 0.21.
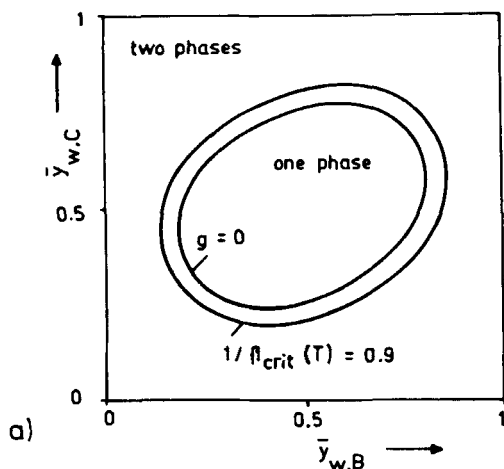
(e)

(f)
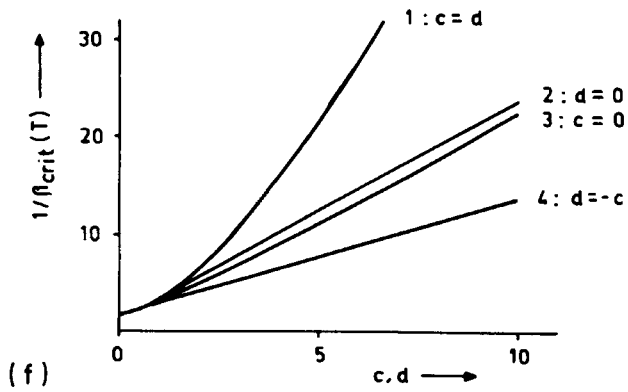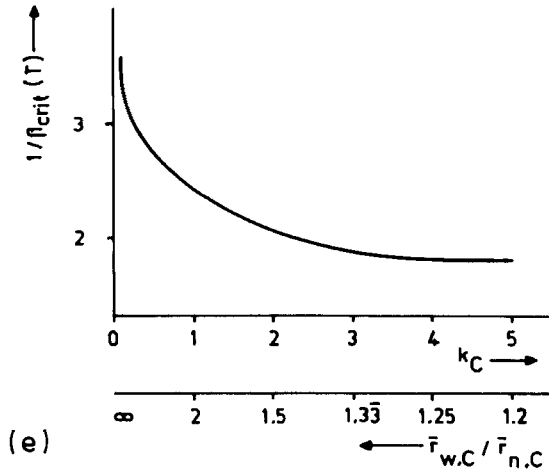
FIG. 2. Calculated miscibility maps for copolymer blends of the type $B(\alpha\beta)$ + $C(\gamma\delta)$. For the parameters, see text. (a) Case with repulsive interactions only and closed miscibility region. (b) Case as in (a) but with a miscibility window in the system $B(\beta)$ + $C(\gamma\delta)$. (c) Case with attractive interactions between the units α and γ or β and δ, respectively, i.e., miscibility of the corresponding homopolymer mixtures.

one-phase regions, i.e., complete miscibility, and two-phase regions. Such miscibility maps are usually constructed by application of the criterion $\overline{\overline{G}}^E \leq 0$, e.g., Ref. 2. This criterion is satisfied here for Eqs. (13)–(18) if $g \leq 0$, because $L(\psi_B)$ is positive in common cases. However, this approach somewhat underestimates the real miscibility region (it also implies that $\bar{r}_B$ and $\bar{r}_C$ are infinitely large). The necessary and sufficient criterion of thermodynamic stability in polydisperse copolymer blends, as considered here, is given by Eq. (7) or (25) which have to be solved for a given blend composition ψ_B at fixed parameters for the distribution functions chosen.

To calculate the miscibility map, the most reasonable choice for ψ_B is the value at the stable critical point. However, one has to keep in mind that the critical temperature and the threshold temperature do not coincide. Thus, the miscibility map based on the critical point somewhat overestimates the region of complete miscibility. The differences are shown in Fig. 2.

To calculate some miscibility maps, we apply the g_{ij} parameter sets given by Karasz and MacKnight [2] who calculated the miscibility maps

b)

c)
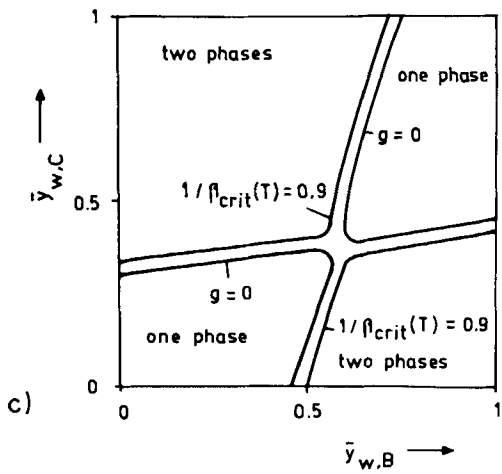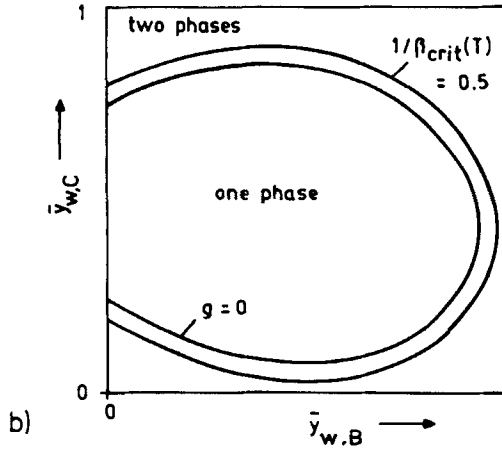
on the basis of $g \leq 0$ (with all $s_i = 1$ in our $\overline{\overline{G}}_E$ model). The following conditions are chosen for the model calculations: $\bar{r}_B = 50$, $k_B = 1$, $\bar{r}_C = 50$, $k_C = 1$, all $s_i = 1$, $\overline{\overline{G}}^E$ parameters $c = d = 0$. As g_{ij} parameter sets we apply:

(a) $g_{\alpha\beta}$ = 0.3, $g_{\alpha\gamma}$ = 0.1, $g_{\alpha\delta} = 0.2$, $g_{\beta\gamma}$ = 0.2,

   $g_{\beta\delta}$ = 0.1, $g_{\gamma\delta}$ = 0.4; Fig. 2(a)

(b) $g_{\alpha\beta}$ = 0.3, $g_{\alpha\gamma}$ = 0.2, $g_{\alpha\delta} = 0.1$, $g_{\beta\gamma}$ = 0.1,

   $g_{\beta\delta}$ = 0.1, $g_{\gamma\delta}$ = 0.5; Fig. 2(b)

(c) $g_{\alpha\beta}$ = 0.1, $g_{\delta\gamma}$ = −0.1, $g_{\alpha\delta} = 0.17$, $g_{\beta\gamma}$ = 0.37,

   $g_{\beta\delta}$ = −0.1, $g_{\beta\delta}$ = 0.2; Fig. 2(c)

The model calculations by Karasz and MacKnight indicate that the region of complete miscibility is independent of the molecular weight ($\bar{r}_B = \bar{r}_C = \infty$), i.e., the smallest possible region of miscibility. Therefore, the miscibility region calculated in this paper for given distribution functions with rather low molecular weight averages has to be enlarged. Due to the symmetric choice for copolymers B and C, there is no large difference in these maps between the critical point criterion and the threshold criterion.

However, there is an interesting effect in the phase diagram regarding the region of limited compatibility of the blend. We observe a drastic change in the shape of the cloud-point curve and the location of the critical point on it if special conditions are chosen for $\tilde{Y}_B$ and $\tilde{Y}_C$. In cases where $\tilde{Y}_B$ and/or $\tilde{Y}_C$ come close to the region of complete miscibility, i.e., where g is very close to zero, the polydispersity effects are strongly amplified. This is demonstrated in Fig. 3. The cloud-point curve, spinoidal, and critical point are calculated for the g_{ij} parameter set (c), given above, with $\tilde{Y}_B = 0.1$ = constant and $\tilde{Y}_C$ changed from $\tilde{Y}_C = 0.6$ to $\tilde{Y}_C = 0.35$. We do not know whether experiments can be performed with enough precision to substantiate these calculated findings. However, we suggest that near to miscibility windows or areas, polydispersity effects should be taken into consideration.

3. Blends of Copolymers Composed of Styrenic, Acrylonitrilic, and Methyl Methacrylic Units

Compatibility in such blends was recently investigated by Kammer et al. [24-27] and by Cowie and Lath [3]. We apply their χ_{ij} parameter sets which lead to the following g_{ij} parameter sets (after some recalculation and normalization to $g_{\alpha\beta} = 1$):
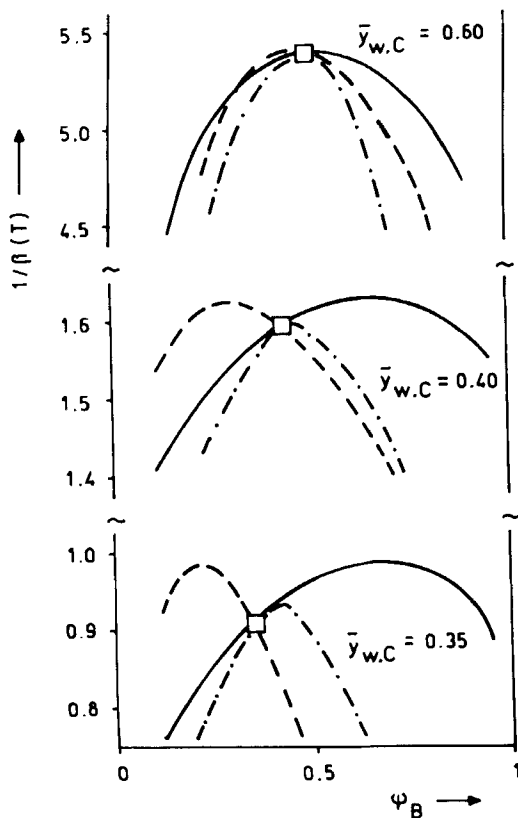
FIG. 3. Illustration of the amplification of polydispersity effects in the phase diagram if the copolymer blend comes close to the region of complete miscibility. Parameters as in Fig. 2(c). Cloud-point curve (——), shadow curve (- - -), spinoidal curve (- · -), and critical point (□).

(1) $g_{\alpha\beta} = g_{\beta\gamma} = 1$, $g_{\alpha\delta} = g_{\gamma\delta} = 0.0833$, $g_{\beta\delta} = 0.461$

(2) $g_{\alpha\beta} = g_{\beta\gamma} = 1$, $g_{\alpha\delta} = g_{\gamma\delta} = 0.0362$, $g_{\beta\delta} = 0.556$

and $g_{\alpha\gamma} = 0$, where α and γ indicate styrenic, β indicates acrylonitrilic, and δ indicates methyl methacrylic units. Surface parameters are obtained on the basis of van-der-Waals surfaces [28] to $s_\beta/s_\alpha = 0.89$ and $s_\gamma/s_\alpha = 1.15$.
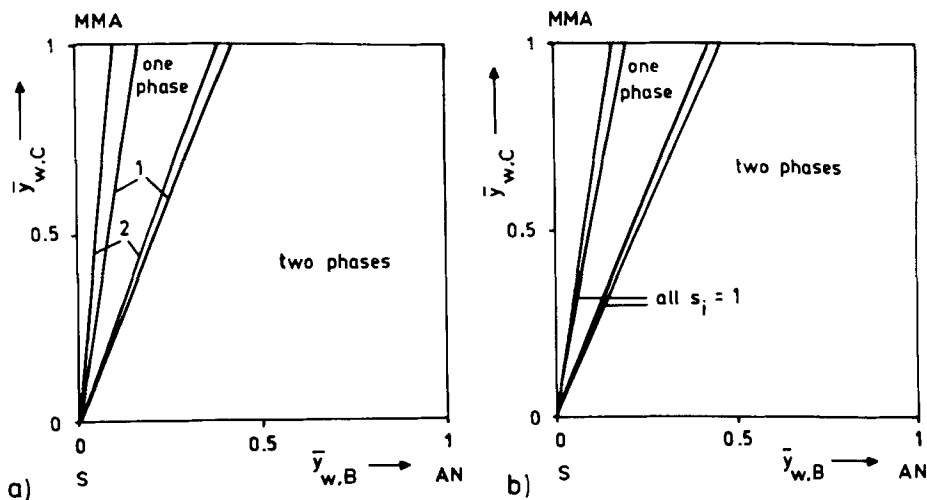
FIG. 4. Calculated miscibility maps for the copolymer blend poly(styrene-*co*-acrylonitrile) + poly(styrene-*co*-methyl methacrylate). (a) Parameter sets (1) and (2), see text, and all $s_i = 1$. (b) Parameter set (1) and s_i varied, see text.

Figure 4 shows the miscibility maps calculated on the basis of the critical point with $\tilde{r}_K$ and $\tilde{r}_K$, chosen as above. There is an observable difference between the cases $s_i = 1$ and $s_i \neq 1$. The miscibility region changes somewhat due to weighing the interacting units with the surface factors. Neglect of the surface factors leads to a certain overestimation of the miscibility region with respect to $\tilde{Y}_B$. Again, we observe an amplifying effect of polydispersity if we calculate the cloud-point curve, spinoidal, and critical point close to the border where g equals zero. This is demonstrated by Fig. 5 for the parameter set (1) with all $s_i = 1$, for which g equals zero at $\tilde{Y}_B$ near 0.58.

CONCLUDING REMARKS

The aim of this paper is to provide the relationships for the spinoidal and the critical point in blends of random copolymers which are polydisperse both in molecular weight and in chemical composition. The neglect of both polydispersities, which often occurs in the literature, leads to a distinct loss of accuracy in calculating the instability limit of such blends
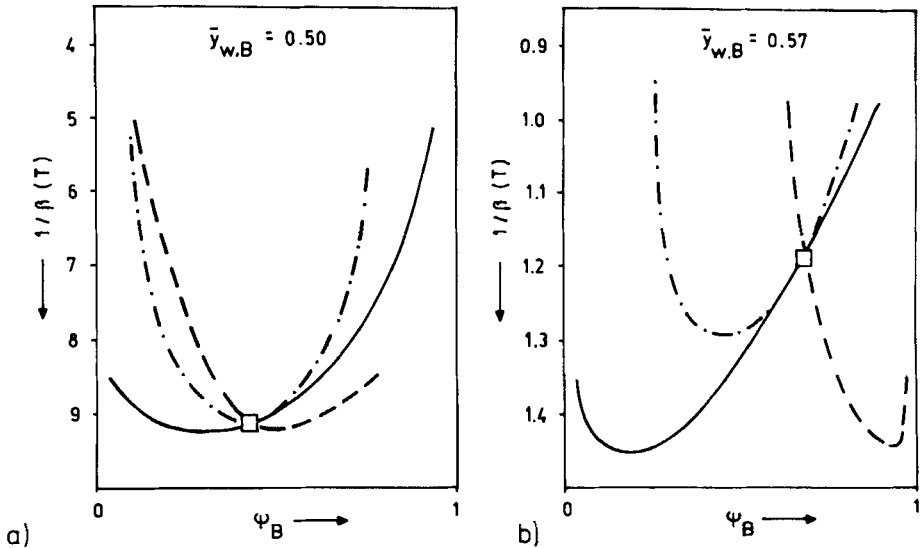
FIG. 5. Calculated phase diagrams for the same blend as in Fig. 4. Cloud-point curve (——), shadow curve (- - -), spinoidal curve (- · -), and critical point (□). For the parameters, see text.

(in addition to the effect of some assumptions with respect to the model parameters necessary for practical calculations).

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