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Liquid–Liquid Phase Separation in Multicomponent Polymer Systems. 22. Thermodynamics of Statistical Copolymers[†]

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ABSTRACT: Limits of thermodynamic stability (spinodals) and critical points in liquid systems containing statistical copolymers are investigated numerically on the basis of the classic lattice model. The calculated phase behavior reproduces the scarce experimental data in the literature in a qualitatively correct manner, provided the model is extended to allow for the various constitutional repeat units (CRUs) to differ in number of nearest-neighbor contacts. In particular, the sensitivity of phase relations toward small changes in chemical composition and/or chain length is reproduced. Multiplicity of critical points may be expected to arise easily and, with it, separations into three phases. The latter is in accordance with observations reported several years ago by Molau. Whether or not a third copolymer compatibilizes a mixture of two (co)polymers seems to depend subtly on the molecular characteristics mentioned and on the pair interactions between the various CRUs.

Compared with homopolymers statistical copolymers have so far not received the attention in the thermodynamic literature one would expect on account of their practical importance. Their complex molecular structure may explain this apparent negligence, studies of homopolymers already being up against formidable difficulties.

In this paper we focus on liquid–liquid phase relationships in mixtures containing statistical copolymers. We exclude dilute-solution properties from the discussion which thus covers systems in which the segment density can to a good approximation be considered uniform. The molecular model used is based on the rigid lattice treatment of Flory, Huggins, and others, amended to deal with the situation in hand.[1-6]

Among the systems of interest we have solutions of copolymers in a single solvent where the influences of chemical composition and chain length could be explored theoretically. Another system of practical importance is a partially miscible blend of two chemically different homopolymers in which a statistical copolymer might have a compatibilizing effect. The copolymer may or may not consist of the monomers in the two homopolymers. The first case has recently been studied theoretically by Leibler.[7] The investigation of the systems mentioned is complicated by the fact that two statistical copolymers, having the same chain length but differing in monomer content, are not necessarily miscible in all proportions. This conclusion came out of a theoretical analysis by Scott,[6] and it was subsequently experimentally verified by Molau[8] and by Locatelli and Riess,[9] for copolymers of styrene and acrylonitrile (SAN). With the molar masses Molau used, a difference in AN content of only 4 mol % already sufficed to bring about partial miscibility. This effect, caused by the decrease the entropy of mixing per unit volume undergoes upon stringing the two types of repeat units together, is also present if the copolymers are dissolved in a common solvent. The tolerable difference in chemical composition is then (understandably) found to become larger when the dilution is increased.

A similar investigation of solvent-free copolymer mixtures was carried out by Kollinsky and Markert,[10,11] who used various acrylic monomers. The tolerable composition difference proved to depend on the chemical structure and this finding could later be analyzed thermodynamically on the basis of Scott's treatment, if properly amended for the relative sizes of the monomer units.[12]

Whereas solvent-free systems only call for a single parameter for the interaction between the two types of repeat units, addition of a solvent (which leads to at least a binary solution) brings two additional parameters, one for each of the solvent–segment interactions. It has been tried to circumvent the complication by the introduction of a single "effective" interaction parameter which represents a linear interpolation between the two solvent–homopolymer parameters, i.e.

$$g = g_{o\alpha}\phi_\alpha + g_{o\beta}\phi_\beta \qquad (1)$$

where g is the effective interaction parameter, $g_{o\alpha}$ and $g_{o\beta}$ are the solvent–homopolymer interaction parameters (α and β refer to the two types of repeat units), and ϕ_α (=1 − ϕ_β) is the α content of the copolymer. This approach has been followed inter alia by Lautout-Magat,[13,14] Topchiev et al.,[15] and Teramachi et al.[16,17]

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It has been shown long ago by Simha and Branson[18] and later by Stockmayer et al.[19] that eq 1 is too simple an approximation which, in ignoring the α–β interaction $g_{\alpha\beta}$, throws away essential information regarding compatibilization. Within the rigid lattice model the effective interaction parameter should read

$$g = g_{o\alpha}\phi_\alpha + g_{o\beta}\phi_\beta - g_{\alpha\beta}\phi_\alpha\phi_\beta \tag{2}$$

Shibuya et al.,[20] Glöckner and Lohmann,[21] and Paul et al.[22,23] have shown experimentally that eq 1 is inadequate and that eq 2 may serve as a better, albeit first, approximation.[20,21]

In the following sections we first discuss a suitable model and subsequently apply it to various systems, some of which were mentioned above. In most systems one encounters a critical miscibility behavior which is particularly sensitive to variations in the chemical composition of the copolymer constituent(s). Miscibility gaps may show one critical point as usual, but it is not at all rare for a small change in copolymer composition to give rise to either disappearance of this single critical point or the appearance of one or two others in addition to the first one. Whatever the nature of the system, in the latter case we know that separations into three liquid phases then occur, and (quasi) binary cloud-point curves will reveal this showing a shoulder or, more pronounced, two extrema. Also, multiplicity of critical points is closely related to these phenomena,[24] which have not seldom been observed experimentally.[16,25,26]

Model

The rigid-lattice treatment of solutions of an n-component statistical copolymer, $P_{\alpha\beta}$, expresses ΔG, the free enthalpy (Gibbs free energy) of mixing, as[6,12]

$$\begin{aligned}\Delta G/N_\phi RT = {} & (\phi_o/m_o)\ln\phi_o + \sum_{i=1}^{n}(\phi_i/m_i)\ln\phi_i + \\ & Q^{-1}\phi_o\{g_{o\alpha}\textstyle\sum\phi_{\alpha i}\phi_i + g_{o\beta}\sum\phi_{\beta i}\phi_i - s_\alpha s_\beta g_{\alpha\beta}\sum(\phi_{\alpha i}\phi_{\beta i}\phi_i/\delta_i)\} + \\ & s_\alpha{}^2 s_\beta{}^2 Q^{-1} g_{\alpha\beta}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\{d_{ij}{}^2\phi_i\phi_j(\delta_i\delta_j)^{-1}\}\end{aligned} \tag{3}$$

where ϕ_o and ϕ_i are the volume fractions of solvent molecules o and copolymer molecules i, each occupying m_o and m_i lattice sites, respectively, $\phi_{\alpha i}$ and $\phi_{\beta i}$ are the volume fractions of repeat groups α and β in copolymer chain i, $s_\alpha = \sigma_\alpha/\sigma_o$ and $s_\beta = \sigma_\beta/\sigma_o$ are the ratio of interacting surface areas of repeat units and solvent, $\delta_i = s_\alpha\phi_{\alpha i} + s_\beta\phi_{\beta i}$, $Q = \phi_o + \sum\delta_i\phi_i$, $d_{ij} = \phi_{\alpha i} - \phi_{\alpha j}$, $g_{o\alpha} = \sigma_\alpha\Delta w_{o\alpha}/RT$, $g_{o\beta} = \sigma_\beta\Delta w_{o\beta}/RT$, $g_{\alpha\beta} = \sigma_o\Delta w_{\alpha\beta}/RT$, Δw_{kl} is the interchange (free) energy per contact, RT has its usual meaning, and N_ϕ stands for $(n_o m_o + \sum n_i m_i)$, where n_o and n_i are the numbers of moles of solvent and polymer i, respectively.

In the derivation of eq 3 repeat units and solvent molecules (or segments) have been assigned one lattice site each, a natural assumption in the original version of the model. However, size and shape will usually differ between the various comonomers. We follow Staverman[27] and Kanig[28] and others and account for such differences by the introduction of interacting surface areas to which the number of nearest-neighbor contacts is assumed to be proportional. The model thus becomes an abstraction but, qualitative descriptions and comparisons being aimed at here, we ignore this artificiality and proceed along the well-known lines of regular-solution theory.[29] This results in eq 3 which, for a strictly binary solution, reduces to equations derived earlier by Simha andd Branson[18] and Stockmayer et al.[19] upon setting $\sigma_\alpha = \sigma_o$ and $\sigma_\beta = \sigma_o$. Equation 3 covers copolymer solutions in a small-molecule solvent ($m_o = 1$) as well as mixtures of a copolymer and a (monodisperse) homopolymer with relative chain length m_o. Incidentally, multiplication of both sides of eq 3 by m_o shows such polymeric mixtures to represent a special case of copolymer solutions ($m_o = 1$) where g parameters and relative chain lengths m_i are rescaled by a factor m_o.

Analysis of spinodal curves and critical points provides a relatively simple way of investigating miscibility behavior.[25,26] Every miscibility gap encompasses a spinodal curve which separates the metastable and unstable regions within the gap.[30,31] The spinodal is defined by

$$J_s = \|\partial^2(\Delta G/N_\phi RT)/\partial\phi_i\partial\phi_j\|_{p,T} = 0 \tag{4}$$

where ϕ_i and ϕ_j are the independent concentration variables (all ϕ_i in eq 3). Spinodals carry one or more critical points which are determined by eq 5 in conjunction with eq 4

$$J_c = 0 \tag{5}$$

where J_c is the determinant formed from J_s upon replacement of the elements in any line by $\partial J_s/\partial\phi_1$, $\partial J_s/\partial\phi_2$, etc.[30]

Simple equations arise in this way only for binary systems; with more complicated mixtures we shall not work out spinodal and critical expressions explicitly but rather let the computer deal with them. For instance, for a solution of a binary copolymer

$$J_s = G_{11}G_{22} - G_{12}{}^2 = 0 \tag{6}$$

where $G_{kl} = \partial^2(\Delta G/N_\phi RT)/\partial\phi_k\partial\phi_l$, we would use numerical iterations to find solutions, feeding the appropriate expressions for G_{kl} into the computer.

Binary and Ternary Copolymer Mixtures

Setting $\phi_o = 0$ in eq 3 we retain

$$\Delta G/N_\phi RT = \sum_{i=1}^{n}(\phi_i/m_i)\ln\phi_i + s_\alpha{}^2 s_\beta{}^2 Q^{-1} g_{\alpha\beta}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\{d_{ij}{}^2\phi_i\phi_j(\delta_i\delta_j)^{-1}\} \tag{7}$$

for an n-component statistical copolymer composed of repeat units α and β. If we further assume the interacting surface areas to be identical ($s_\alpha = s_\beta = 1$; $Q = 1$; $\delta_i = \delta_j = 1$) we recover in the present formulation an expression derived earlier by Scott[6]

$$\Delta G/N_\phi RT = \sum_{i=1}^{n}(\phi_i/m_i)\ln\phi_i + g_{\alpha\beta}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}(d_{ij}{}^2\phi_i\phi_j) \tag{8}$$

1. Binary Copolymers. Further simplification to $n = 2$ turns eq 7 into

$$\Delta G/N_\phi RT = (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + s_\alpha{}^2 s_\beta{}^2 g_{\alpha\beta} d_{12}{}^2\phi_1\phi_2(\delta_1\delta_2 Q)^{-1} \tag{9}$$

and the spinodal condition 4 yields

$$(1/m_1\phi_1) + (1/m_2\phi_2) - 2s_\alpha{}^2 s_\beta{}^2 g_{\alpha\beta} d_{12}{}^2 Q^{-3} = 0 \tag{10}$$

The critical point (eq 5) is given by

$$(1/m_1\phi_1{}^2) - (1/m_2\phi_2{}^2) - 6s_\alpha{}^2 s_\beta{}^2 g_{\alpha\beta} d_{12}{}^2(\delta_2 - \delta_1)Q^{-4} = 0 \tag{11}$$

The surface area σ_o of the solvent (absent here) cancels in eq 9–11, and $g_{\alpha\beta}$ now scales to $\Delta w_{\alpha\beta}$ by σ_α. For identical surface-area ratios ($\sigma_\alpha = \sigma_\beta$) eq 10 and 11 reduce to

$$(1/m_1\phi_1) + (1/m_2\phi_2) - 2g_{\alpha\beta}d_{12}{}^2 = 0 \quad \text{(spinodal)} \tag{12}$$

$$(1/m_1\phi_1{}^2) - (1/m_2\phi_2{}^2) = 0 \quad \text{(critical point)} \tag{13}$$

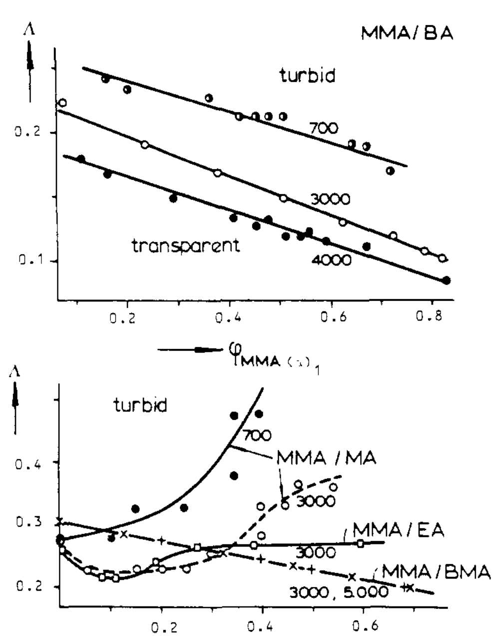


Figure 1. Tolerable composition difference Λ in 1:1 mixtures of acrylic copolymers as a function of $\phi_{\alpha 1}$, the α content in the first of the two copolymers: α = MMA (methyl methacrylate); β = BA (butyl acrylate), MA (methyl acrylate), EA (ethyl acrylate), or BMA (butyl methacrylate). The mass-average degree of polymerization in the mixture is indicated. Data by Kollinsky and Markert.[10,11]

Equation 12 shows that, within its framework, spinodals (and hence, limits of phase stability) must be expected to depend on the difference in chemical composition between the two copolymer components. At given $g_{\alpha\beta}$, m_1, m_2, and ϕ_2 it depends entirely on d_{12} whether the system is homogeneous or not. Scott[6] therefore predicted that binary copolymer mixtures would be characterized by a maximum tolerable value of d_{12} (difference in chemical composition, in the following denoted by Λ) beyond which they are only partially miscible. This prediction has found experimental verification in Molau's work on mixtures of styrene/acrylonitrile copolymers.[8] Molau found Λ in that system to be about 0.04 for molar masses around 10^5.

Kollinsky and Markert carried out a detailed study of this effect in acrylic copolymers.[10,11] They combined methyl methacrylate (MMA, α) with diverse second constitutional repeat units (CRUs β), methacrylate (MA), butyl acrylate (BA), butyl methacrylate (BMA), and ethyl acrylate (EA). Their work substantiated Scott's and Molau's findings but also revealed Λ to depend on the chemical composition $\phi_{\alpha 1}$ of the first copolymer in the mixture (Figure 1). This feature is not included in Scott's eq 12, but it can be dealt with in a qualitatively correct manner if the various acrylic CRUs are given different interacting surface areas.[12] For instance, if the second CRU (β) can make more nearest-neighbor contacts per site than the first (α) Λ decreases with increasing $\phi_{\alpha 1}$, and the reverse behavior is found if CRUs α make more contacts than β. It would not seem too farfetched to assume this molecular picture to be valid for the acrylic CRUs on hand, if only qualitatively. Figure 2 gives some examples showing that sets of $\sigma_\alpha/\sigma_\beta$ and $g_{\alpha\beta}$ values can be found for eq 10 to represent the trend of the experimental data. Quantitative agreement was not sought because Kollinsky and Markert's data refer to cloud points and eq 10 and 12 represent spinodal points.

Molar mass (or relative chain length m) has an effect in that the thermodynamic stability increases with decreasing chain length. The combinatory entropy of mixing per unit volume increases and, consequently, larger values of Λ are possible.

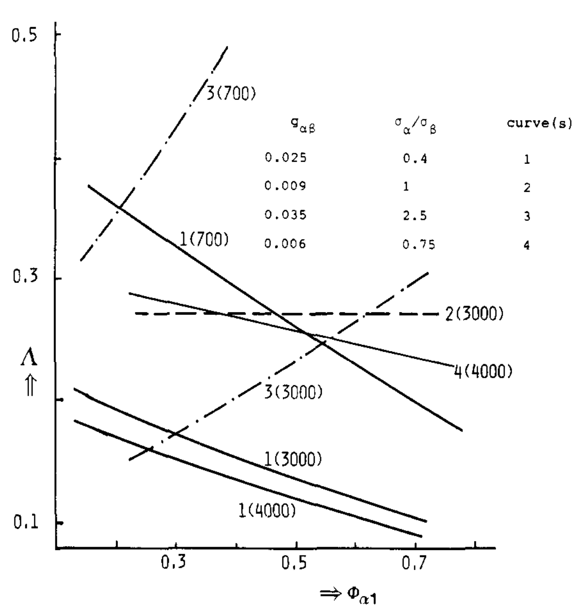


Figure 2. Tolerable composition difference Λ calculated with eq 10 for strictly binary copolymer mixtures as a function of $\phi_{\alpha 1}$, the chemical composition of the first copolymer, for indicated values of relative chain length m_1 (=m_2).

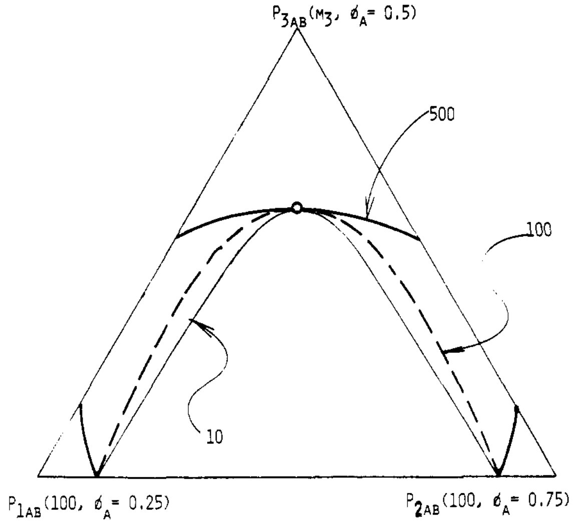


Figure 3. Ternary copolymer mixture ($P_{i\alpha\beta}$, m_i, $\phi_{\alpha i}$) at $g_{\alpha\beta}$ = 0.2 (A and B ≡ α and β) for indicated values of m_3. Curves and circle(s) represent spinodals and critical point(s) calculated with eq 5–7. $\sigma_\alpha/\sigma_\beta = 1$.

2. Ternary Copolymers. With n = 3 eq 7 represents ternary copolymer mixtures for which thermodynamic stability (spinodal) and critical conditions can be derived with eq 6 and 5. We have calculated ternary diagrams for a few cases to explore what features may be anticipated (Figures 3–9).

It has been observed[8,10,11] that miscibility in a binary copolymer ($P_{\alpha\beta 1}/P_{\alpha\beta 2}$) mixture is hardly if at all improved by the addition of a third copolymer ($P_{\alpha\beta 3}$) with an intermediate chemical composition. In such studies one normally investigates the effect addition of $P_{\alpha\beta 3}$ has on a 1:1 mixture of $P_{\alpha\beta 1}$ and $P_{\alpha\beta 2}$. The examples in Figure 3 fall into line with such information. It is to be noted that those examples are wholly symmetrical in chemical composition and chain length, and refer to equal numbers of contacts on CRUs α and β. In these cases the amount of $P_{\alpha\beta 3}$ needed to bring about homogeneity is so large that

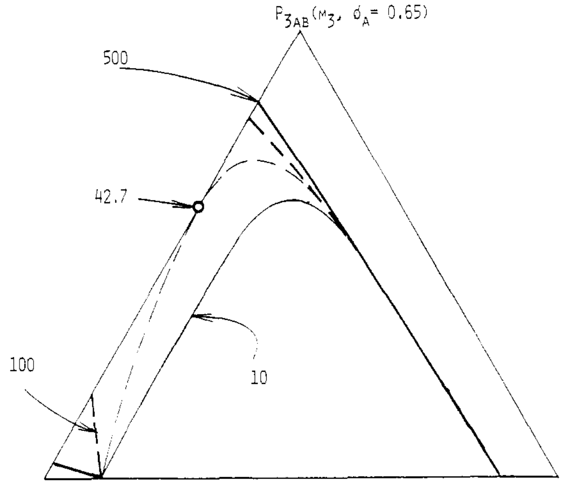


Figure 4. See caption to Figure 3.

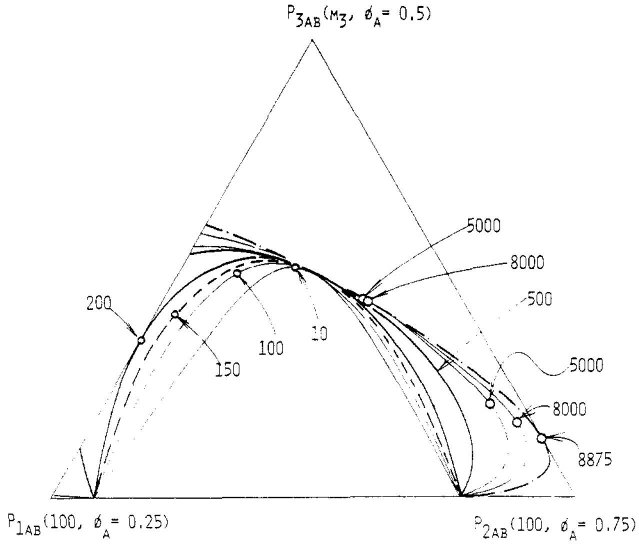


Figure 5. See caption to Figure 3, $\sigma_\alpha/\sigma_\beta = 9/4$.

it would be more practical to use the intermediate copolymer itself.

As we noted before,[32] some of the diagrams have the peculiar feature that the molar mass of the third copolymer does not make any difference, except close to the 1/3 and 2/3 binary edges. In particular, the location of the critical point is independent of m_3. Figure 4 demonstrates that such behavior cannot be expected to be general, it has to do with the symmetry of the system; if we change $\phi_{\alpha 3}$ from 0.5 to 0.65, keeping the other parameters constant, a noticeable sensitivity toward m_3 exists for 1:1 mixtures of $P_{\alpha\beta 1}$ and $P_{\alpha\beta 2}$. Returning to the original situation we might change the surface areas of α and β, which distorts the spinodals but retains the insensitivity of Figure 3, albeit not at a critical point. Now the spinodals share a common tangent which does not necessarily mean that also the cloud-point curves do so (Figure 5). This point is currently being studied.

Another interesting feature may show up, viz., the appearance of more than one critical point. The calculations indicate that such a behavior would be very sensitive for changes in chain length m_3 in $P_{\alpha\beta 3}$. An appropriate change may even induce the critical point(s) to disappear altogether (at $m_3 = 500$). It is demonstrated below that such features also relate to the chemical compositions involved, and small variations therein may also change the picture drastically.

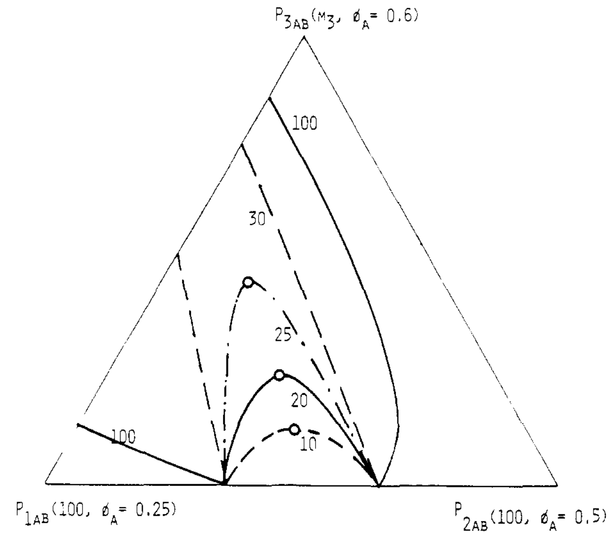


Figure 6. See caption to Figure 3, $\sigma_\alpha/\sigma_\beta = 1$; $g_{\alpha\beta} = 0.35$.

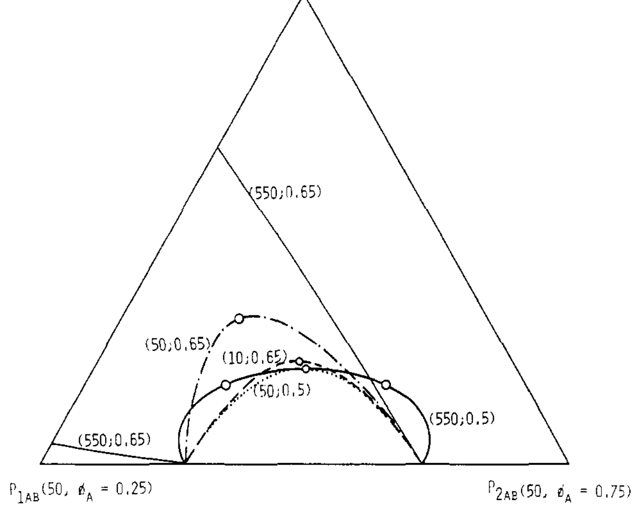


Figure 7. See caption to Figure 3.

If a third copolymer with an intermediate chemical composition does not improve miscibility one might out of curiosity explore the effect of a chemical composition outside the range of the first two copolymers. Surprisingly, calculations suggest that possibilities for improved miscibility then exist, albeit at not too large chain length m_3 (Figure 6). Contrary to the preceding examples we now have a considerable sensitivity to m_3.

Situations are conceivable where compatibilization does take place in symmetrical as well as asymmetric systems. Figure 7 illustrates this; the original binary 1/2 already shows better miscibility than that in Figure 3 and the amount of $P_{\alpha\beta 3}$ needed is about 20% for a 1:1 mixture of $P_{\alpha\beta 1}$ and $P_{\alpha\beta 2}$. Better miscibility can also be achieved by a decrease of $g_{\alpha\beta}$, i.e., a change in temperature. The observations mentioned above would, in the light of these calculations, not seem to be quite general. Compatibilization appears to depend very much on the particulars of the system in hand.

In Figure 8 we show the spinodal in Figure 7 which carries three critical points. The nature of these becomes clearer if we add the binodal and enlarge the relevant part of the diagram (Figure 9). It is seen how the three critical points, two of which are stable, relate to the three-phase triangle. The nature of the critical behavior in these systems is currently being studied. For homopolymeric systems an extensive analysis has appeared recently.[24]

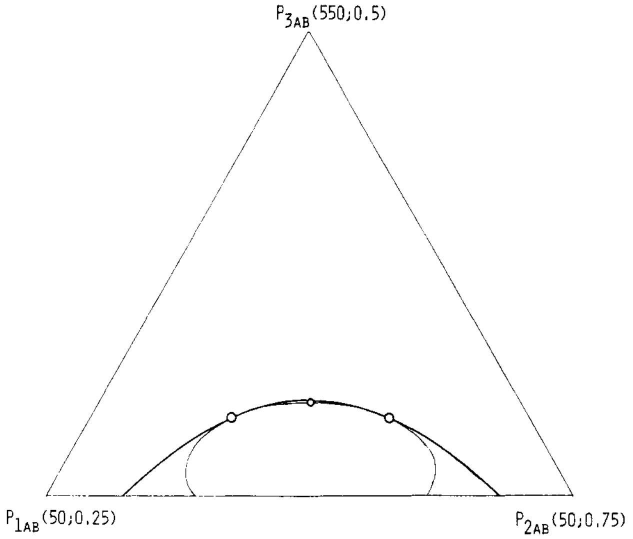


Figure 8. See caption to Figure 3, $\sigma_\alpha/\sigma_\beta = 1$; $g_{\alpha\beta} = 0.2$. Heavy curve: binodal, light curve: spinodal, circles: critical points.

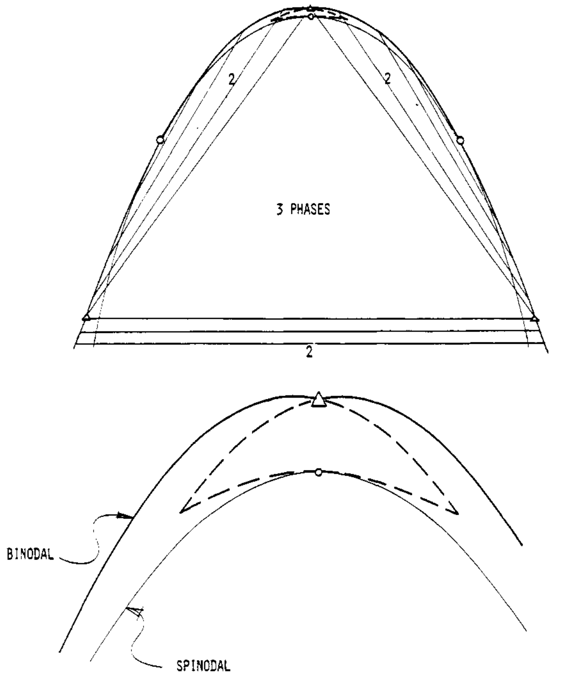


Figure 9. Enlarged details from Figure 8. Triangles, corners of three-phase region; dashed curves, metastable and unstable branches of the binodal.

We do not know of any experimental evidence for these subtleties, except the qualitative study by Molau.[8] Yet the phenomena described could be useful in the establishment of accurate free-enthalpy functions for systems containing copolymers. Methods for the determination of spinodals and critical- and cloud-points in highly viscous systems having been developed,[33-37] instrumental problems would not seem to exist at present.

Indirect experimental evidence, however, has been reported. It can be shown that the occurrence of three-phase regions is revealed by cloud-point curves deviating from the familiar dome shape.[24-26,32,38] Curves with a shoulder or even with two extrema have been found, not infrequently in connection with the presence of copolymers.[16,39]

Copolymer Solutions

1. Small-Molecule Solvents. Setting $m_o = 1$ in eq 3 we obtain the free enthalpy of mixing for solutions of doubly polydisperse copolymers in a single small-molecule solvent. The chains may differ on two points, length and chemical composition. For binary solutions the last term on the right-hand side vanishes. The third term is retained and represents the expression derived by Simha and Branson[18] and Stockmayer et al.[19] (eq 2), extended here to account for differences in interacting surface areas.

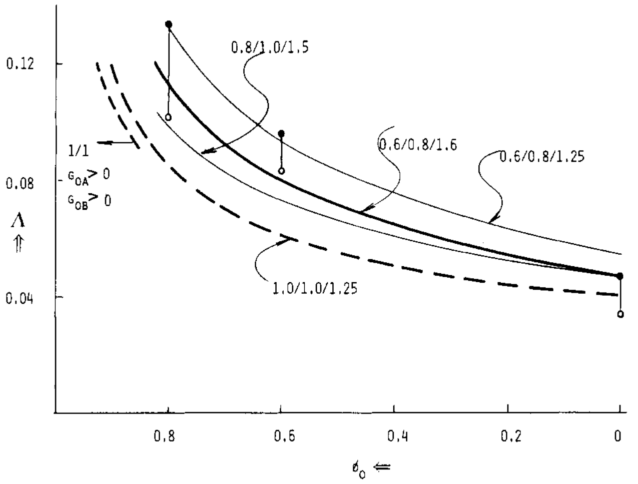


Figure 10. Spinodal curves calculated with eq 3 and 4 for indicated sets of $(\sigma_\alpha/\sigma_o; \sigma_\beta/\sigma_o; g_{\alpha\beta})$ values. Tolerable composition difference Λ as a function of solvent concentration ϕ_o. Data for poly(acrylonitrile (α)-*co*-styrene (β)) in methyl ethyl ketone (○) by Molau.[8] Filled circles, phase separated; open circles, homogeneous systems.

An alternative extension for binary solutions has been advanced by Shibuya et al.[20] who applied the quasi-chemical approach[29] to the problem. Their data and the later more elaborate work by Glöckner and Lohmann[21] strongly indicate that even eq 2 is not good enough. Equation 3 is being tested in this respect. Shibuya et al.'s equation for the effective interaction parameter g reads

$$g = g_{o\alpha}\phi_\alpha + g_{o\beta}\phi_\beta - g_{\alpha\beta}\phi_\alpha\phi_\beta(1 - C\phi_\alpha\phi_\beta) \tag{14}$$

where C, describing departures from random mixing, can be used as an adaptable parameter to fit data to eq 14.

The binary version of our eq 3 leads to

$$g = g_{o\alpha}\phi_\alpha + g_{o\beta}\phi_\beta - g_{\alpha\beta}\phi_\alpha\phi_\beta s_\alpha s_\beta/(s_\alpha\phi_\alpha + s_\beta\phi_\beta) \tag{15}$$

Equation 2 is seen to be included in eq 14 for $C = 0$ (random mixing) and in eq 15 for $s_\alpha = 1$ and $s_\beta = 1$.

Molau[8] did not only investigate mixtures of styrene/acrylonitrile copolymers as such but also studied the influence of solvent (methyl ethyl ketone, (MEK)). Figure 10, based on his data, illustrates that the addition of solvent (increasing ϕ_o) widens the chemical composition range of miscibility and pushes the tolerable difference Λ up. The small solvent molecules substantially increase the entropy of mixing per unit volume. Spinodal curves calculated with eq 3 and 4 (binary case) are shown in Figure 10. If the interacting surface-area ratios are set equal to 1, the calculated curves cannot be made to agree with the experiments unless quite unrealistic (negative) values are assigned to $g_{o\alpha}$ and $g_{o\beta}$ (the MEK/AN and MEK/S interactions, see ref 21). The assumption that the CRUs styrene and acrylonitrile have smaller interacting surface areas than the solvent MEK allows the calculated spinodal to follow the measurements quite closely. Admittedly, Molau measured cloud-point ranges and not spinodal points, but the comparison again strongly suggests surface areas to play an important role in copolymer mixture stability.

Molau's significant paper further contains information about phase behavior of solutions containing three co-

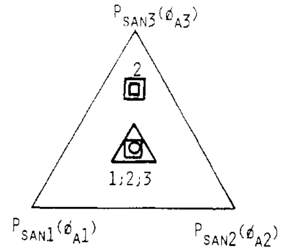


Figure 11. Liquid–liquid phase separation in quasi-quaternary 25% solutions of blends of acrylonitrile–styrene copolymers in methyl ethyl ketone with various ($\phi_{\alpha 1}/\phi_{\alpha 2}/\phi_{\alpha 3}$) combinations ($\phi_\alpha$ = AN content). Circle, one-phase system (0.255/0.387/0.323); top and bottom square, two-phase systems (0.046/0.291/0.206); top square and bottom triangle, (0.046/0.291/0.142). Molar masses around 10^5 (Molau[8]). Symbols indicate overall compositions. The triangle indicates three-phase separation.

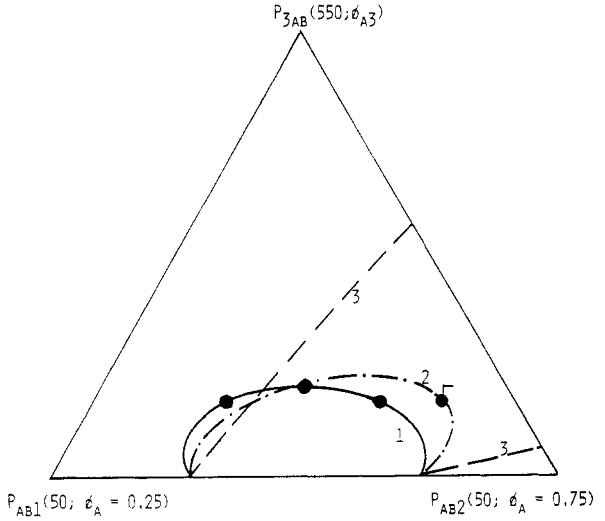


Figure 12. Spinodal curves and critical points calculated with eq 3 and 4 for $\phi_0 = 0.5$, $g_{\alpha\beta} = 0.4$, $g_{o\alpha} = 0$, $g_{o\beta} = 0$, $s_\alpha = 1$, $s_\beta = 1$, $\phi_{\alpha 1} = 0.25$, $\phi_{\alpha 2} = 0.75$. Curve 1, $\phi_{\alpha 3} = 0.5$; curve 2, $\phi_{\alpha 3} = 0.475$; curve 3, $\phi_{\alpha 3} = 0.4$, $m_1 = m_2 = 50$, $m_3 = 550$.

polymers, roughly equal in molar mass but differing in chemical composition. Depending on the latter, a 25% solution of a 1:1:1 mixture could show one, two, or three phases; Figure 11 summarizes the experimental data. Figure 12, calculated with eq 3–5, illustrates that extreme sensitivity for chemical composition variations is to be expected, very small differences already leading to appearance or disappearance of critical points and, thereby, to changes in the number of phases under seemingly analogous conditions.

It thus appears that the simple model can reproduce experimental phase relations quite well which encourages some further exploration. The consolute temperature T_c as a function of copolymer composition, $T(\phi_\alpha)$, for instance, may be expected to yield useful information. We have two limiting solvent S/homopolymer systems, S/$P_{\alpha\alpha}$ ($\phi_\alpha = 1$) and S/$P_{\beta\beta}$ ($\phi_\alpha = 0$), with their respective Flory temperatures $\Theta_{o\alpha}$ and $\Theta_{o\beta}$. The $g_{o\alpha}(T)$ and $g_{o\beta}(T)$ functions are assumed here to have the usual form

$$g_{oi}(T) = k_{oi} + h_{oi}/T \qquad (16)$$

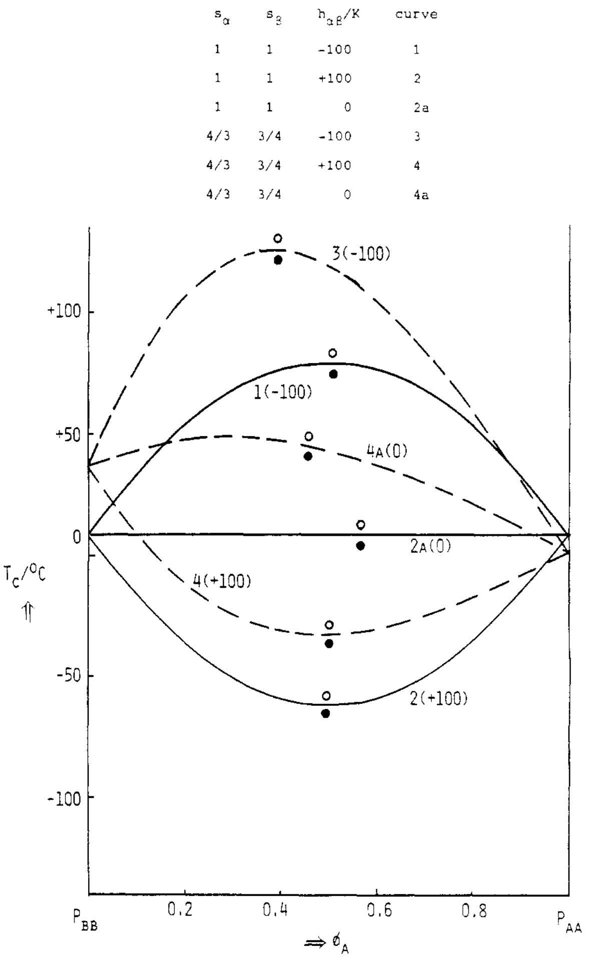
and the two Θ values serve to define the k_{oi} by

$$k_{oi} = (1/2m_o s_i) - (h_{oi}/\Theta_{oi}) \qquad (17)$$

We ignore entropic contributions to $g_{\alpha\beta}$ and let

$$g_{\alpha\beta} = h_{\alpha\beta}/T \qquad (18)$$

Figure 13 gives T_c (ϕ_α) curves for some cases where the limiting homopolymer solutions S/$P_{\alpha\alpha}$ and S/$P_{\beta\beta}$ are of



s_α	s_β	$h_{\alpha\beta}$/K	curve
1	1	-100	1
1	1	+100	2
1	1	0	2a
4/3	3/4	-100	3
4/3	3/4	+100	4
4/3	3/4	0	4a

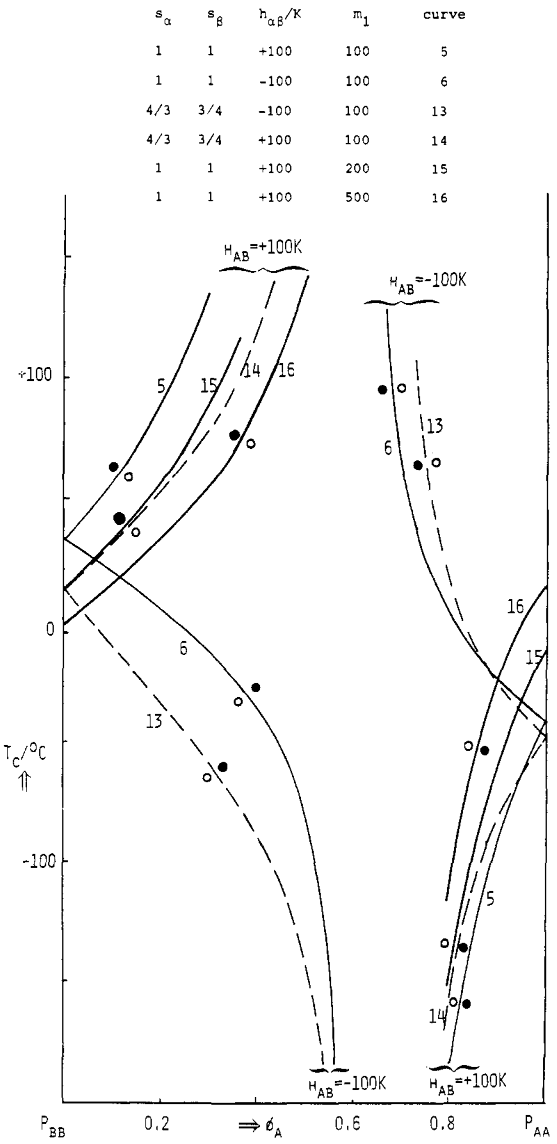
Figure 13. Critical temperature of a copolymer solution as a function of the chemical composition ϕ_α. Open circle, (meta)stable side; closed circle, unstable side, $m_o = 1$, $m_1 = 100$, $\Theta_{o\alpha} = 400$ K, $\Theta_{o\beta} = 400$ K, $h_{o\alpha} = 100$ K, $h_{o\beta} = 100$ K.

the upper consolute type. This means the enthalpic contributions to g_{oi} ($h_{o\alpha}$ and $h_{o\beta}$) are both positive. The sign and magnitude of $h_{\alpha\beta}$ can then be expected to be determinative for phase behavior in the intermediate ϕ_α range. If $h_{\alpha\beta} > 0$ the CRUs α and β repel each other and have a preference for making contacts with solvent molecules. As a result miscibility is enlarged and the critical curve shows a minimum. One-phase systems are found above, demixed systems under, the curve.

If the CRUs attract each other ($h_{\alpha\beta} < 0$) we have the opposite effect and miscibility is diminished. Setting $h_{\alpha\beta} = 0$ reduces the effective interaction function g to the simple interpolation (eq 1) and, clearly, essential information is lost. Stockmayer et al.[19] have already drawn attention to this aspect. The difference in surface area between the CRUs distorts the critical curves and its introduction might prove necessary when it comes to quantitative descriptions.

If the two homopolymer solutions are of the lower consolute type ($h_{o\alpha} < 0$, $h_{o\beta} < 0$) we have a quite similar behavior but for the two-phase states now being above the critical curves. A positive $h_{\alpha\beta}$ then moves the critical points upwards and so enlarges the one-phase region of miscibility. Like those in Figure 13 the calculated curves suggest that such effects might be quite noticeable.

An interesting case is presented by a system in which the two homopolymer solutions exhibit opposite consolute behavior. Figure 14 illustrates that the influence of copolymerizing α and β can be very large. If the copolymer CRUs repel each other, extensive areas of miscibility may



s_α	s_β	$h_{\alpha\beta}/K$	m_1	curve
1	1	+100	100	5
1	1	-100	100	6
4/3	3/4	-100	100	13
4/3	3/4	+100	100	14
1	1	+100	200	15
1	1	+100	500	16

Figure 14. See caption to Figure 13, $m_o = 1$, $\Theta_{o\alpha} = 400$ K, $\Theta_{o\beta} = 300$ K, $h_{o\alpha} = +100$ K, $h_{o\beta} = -200$ K.

be expected to occur stretching far beyond the two Θ temperatures. Reversely, little miscibility remains if the CRUs have a preference for each other. It follows that the measurement of spinodals and critical curves would supply deep-probing information about the thermodynamic properties of copolymeric systems of any of the three types discussed here. We are not aware of such experimental information having been published.

2. Polymeric Solvents. For $m_o > 1$ eq 3 represents solutions of copolymers in chain-molecule solvents, a type of system that has received quite some attention in the last few years.[7,39-49] If the CRUs in the "solvent" polymer are identical with one of those in the copolymer we have a rather simple situation in that only one interaction parameter is needed in the present framework. Leibler[7] has reported a theoretical study of such systems and Roe and Zin[41] have demonstrated their potential usefulness for the detn. of interaction functions in situations where two homopolymers cannot be handled. The latter authors studied mixtures of polystyrene and polybutadiene and found the interaction function to agree with that determined on mixtures of polystyrene and copolymers of styrene and butadiene. This is a significant result, not only for the practical reason mentioned but also from a theoretical viewpoint. For example, all calculations in this paper are based on the tacit assumption that the copolymer composition does not affect the interaction parameters.

The extensive systematic work by Karasz and MacKnight et al.[42-49] provides some striking examples of miscibility attenuation by CRU interactions. These authors studied blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with various series of copolymers based on styrene. Specially noteworthy in the present context are copolymers of *o*-chlorostyrene (PoCS) and *p*-chlorostyrene (PpCS) and their fluorine analogues (PoFS and PpFS). Figure 15 collects some of the data in the form of diagrams similar to those in Figures 13 and 14. It is seen that compatibility goes through a maximum and the phase-separated systems are found at temperatures higher than those for clear transparent blends at a given ϕ_α. The latter feature points to PPO/PoFS and PPO/PpFS blends and their chlorine analogues to exhibit lower consolute demixing. The authors report the immiscibility of such blends.

Figure 15 also shows that it is possible to find sets of parameters that allow eq 3 to pass spinodal curves (by eq 4) through the regions where the spinodal may be expected to be located. Since its exact position is not known, we do not pursue the analysis at this moment and we refrain therefore from a statement of the actual parameter values used. However, it seems clear that the present model

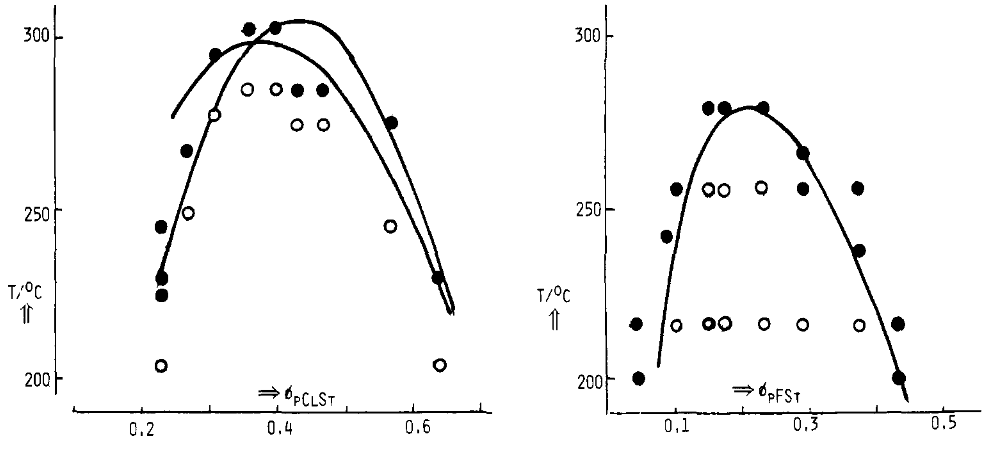


Figure 15. Compatibility–incompatibility transition for PPO/copolymer blends as a function of copolymer composition. Open circles, miscible systems; closed circles, phase-separated systems. Data by Karasz and MacKnight et al.[42,49] Left, PPO/poly(pCS/oCS); right, PPO/poly(pFS/oFS). Curves calculated with eq 3 and 4 with parameter values chosen so as to roughly fit in with the data. In all three cases $h_{\alpha\beta} > 0$.

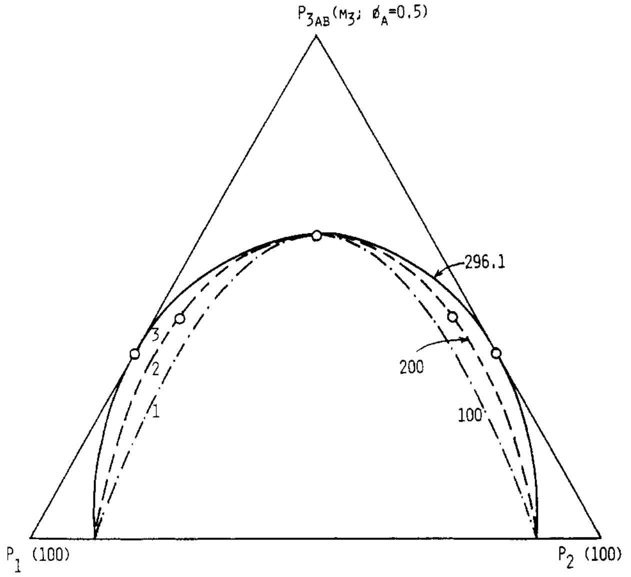


Figure 16. Compatibilization of a homopolymer blend (P_1/P_2) by a statistical copolymer ($P_{3\alpha\beta}$). Spinodal curves and critical points (○) calculated with eq 4, 5, and 19. $m_1 = 100$, $m_2 = 100$, $g_{1\alpha} = 0$, $g_{2\beta} = 0$, $g_{2\alpha} = g_{1\beta} = g_{\alpha\beta} = g_{12} = 0.05$. Curve 1, $m_3 = 100$; curve 2, $m_3 = 200$; curve 3, $m_3 = 296.1$, $s_\alpha = 1$, $s_\beta = 1$.

requires the α–β interaction to be repulsive. The negative values needed for $h_{o\alpha}$ and $h_{o\beta}$ point to free volume treatments being applicable. The latter's relevance to the compatibility problem has been amply illustrated[41,50–55] and will be the subject of a subsequent paper on copolymer thermodynamics.

Compatibilization of Homopolymer Blends

A further extension of eq 3 to include mixtures of two homopolymers (binary polymeric solvent) and a statistical copolymer leads to

$$\Delta G/N_\phi RT = (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + (\phi_3/m_3)\ln\phi_3 + \phi_1\phi_2 s_1 s_2 g_{12}/Q + \phi_1\phi_3 Q^{-1}\{s_1(\phi_\alpha g_{1\alpha} + \phi_\beta g_{1\beta}) - s_\alpha s_\beta \phi_\alpha \phi_\beta g_{\alpha\beta}/\delta_3\} + \phi_2\phi_3 Q^{-1}\{s_2(\phi_\alpha g_{2\alpha} + \phi_\beta g_{2\beta}) - s_\alpha s_\beta \phi_\alpha \phi_\beta g_{\alpha\beta}/\delta_3\} \quad (19)$$

where the subscripts 1, 2, and 3 refer to homopolymers P_1 and P_2, and copolymer $P_{3\alpha\beta}$, respectively. The surface-area ratios s_1, s_2, s_α, and s_β are scaled to σ_o, the area of here absent solvent molecules, e.g., $s_1 = \sigma_1/\sigma_o$ (see also eq 10 and 11). Further, $g_{12} = \sigma_o \Delta w_{12}/RT$, $g_{1\alpha} = \sigma_\alpha \Delta w_{1\alpha}/RT$, $g_{\alpha\beta} = \sigma_o \Delta w_{\alpha\beta}/RT$, etc., $N_\phi = n_1 m_1 + n_2 m_2 + n_3 m_3$ (n_i = number of moles of component i), $\delta_3 = s_\alpha \phi_\alpha + s_\beta \phi_\beta$, and $Q = s_1\phi_1 + s_2\phi_2 + \delta_3\phi_3$.

Mixtures of a homopolymer and a copolymer sharing one of its CRUs with the homopolymer, mentioned above (e.g., $P_{1\alpha\alpha}/P_{3\alpha\beta}$), as well as similar ternary blends $P_{1\alpha\alpha}/P_{2\beta\beta}/P_{3\alpha\beta}$ are included in eq 19 as special cases for which $g_{1\alpha} = 0$, $g_{2\beta} = 0$, and $g_{2\alpha} = g_{1\beta} = g_{\alpha\beta} = g_{12}$.

Starting from eq 19 and applying eq 4 and 5 we have calculated diagrams that illustrate the compatibilizing effect a statistical copolymer can be expected to have. Figure 16 gives a fully symmetrical case, also representative for $P_{1\alpha\alpha}/P_{2\beta\beta}/P_{3\alpha\beta}$ mixtures. Leibler[7] made similar calculations for such symmetric systems and reported the possible occurrence of three-phase separations. Indeed, it is seen in Figure 16 that, in addition to the single critical point at $m_3 = 100$, two new consolute states may develop upon an increase of m_3. With m_3 having increased to 296.1 the additional critical points have just reached the 1/3 and 2/3 edges of the ternary diagram and a further rise of m_3 moves them into physically meaningless concentration ranges.

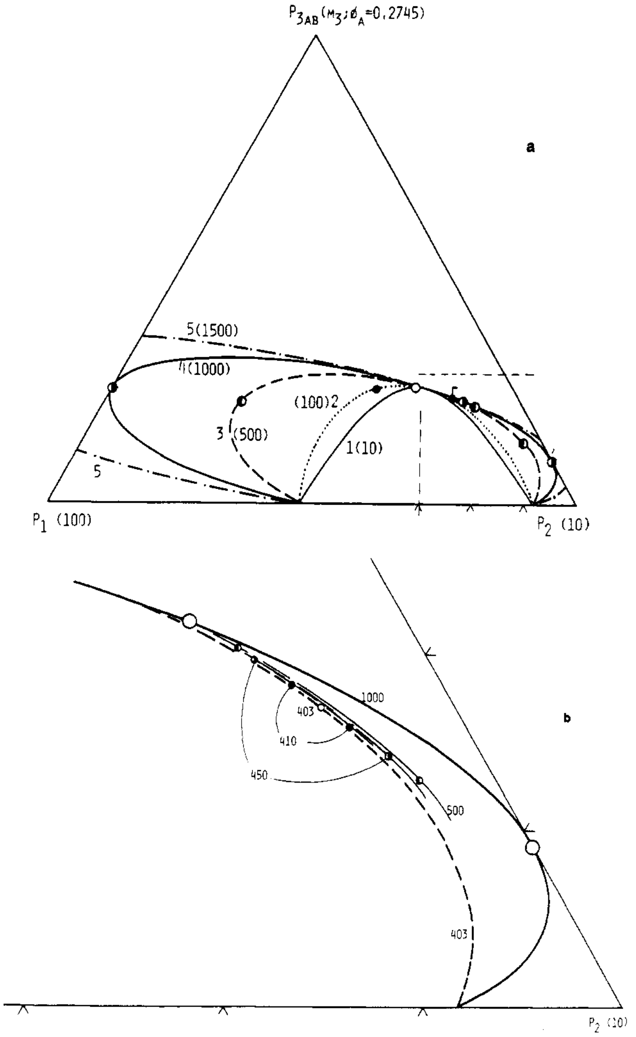


Figure 17. (a) Compatibilization of a homopolymer blend (P_1/P_2) with a statistical copolymer ($P_{3\alpha\beta}$). Spinodal curves and critical points (●, ◕, ◑, ◐, ○) calculated with eq 4, 5, and 19. $m_1 = 100$, $m_2 = 10$, $g_{1\alpha} = 0$, $g_{2\beta} = 0$, $g_{2\alpha} = g_{1\beta} = g_{\alpha\beta} = g_{12} = 0.11495$. Curves 1–5, $m_3 = 10$, 100, 500, 1000, and 1500, respectively; $s_\alpha = 1$, $s_\beta = 1$. (b) Enlarged detail from (a). Spinodal curves and critical points for various values of m_3: 403 (○), 410 (●), 450 (◑), 500 (◐), and 1000 (◯).

This phenomenon is further exemplified in Figure 17a,b which demonstrate that multiplicity of critical points, once started (at $m_3 = 403$), needs little change in m_3 for the two evolving consolute points to move away, the relevant spinodal then carrying three critical points until an m_3 value of 1000 is reached. The $g_{\alpha\beta}$ value was so chosen as to let the 1/3 and 2/3 binaries be critical at $m_3 = 1000$. Below $m_3 = 403$ there is only one critical point on the spinodal.

Figure 16, like Figure 3, suggests that no spectacular compatibilizing effects may be expected from addition of $P_{3\alpha\beta}$, and its chain length again does not seem to make any difference. Dropping the symmetry, i.e., setting $\phi_{\alpha 3} \neq 1/2$, does not help, like it did not in Figure 4. This is in line with experimental findings by Riess.[56] Figure 17a however, suggests that possibilities ought to exist at a lower level of chain length in the two homopolymers. Figure 18 indicates that relatively long $P_{3\alpha\beta}$ chains could be active compatibilizers in short-chain homopolymer blends.

Walsh et al.[57–59] advanced the idea that effective compatibilization might rather be anticipated if specific attractive interactions occur in the system. These cannot

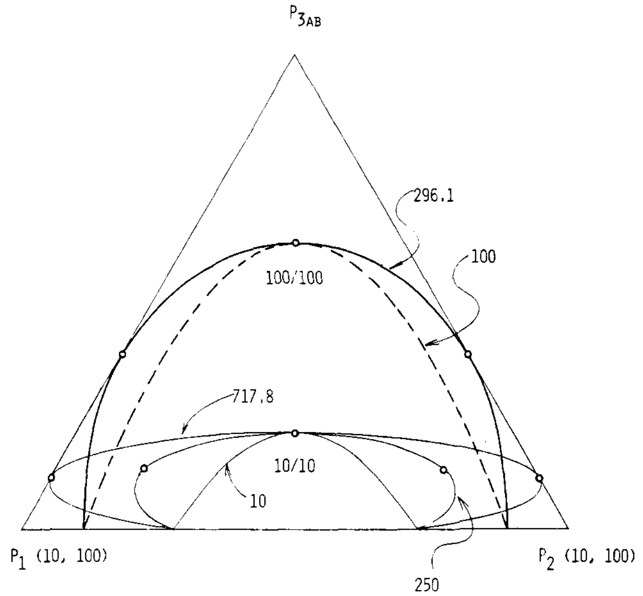


Figure 18. Spinodals and critical points (○) calculated with eq 4, 5, and 19 for $P_1/P_2/P_{3\alpha\beta}$ systems with two sets of m_1/m_2 values (10/10 and 100/100), m_3 values indicated. $s_\alpha = 1$, $s_\beta = 1$; $g_{12} = 0.05$, $g_{1\alpha} = 0$, $g_{1\beta} = 0.05$, $g_{\alpha\beta} = 0.05$, $g_{2\alpha} = 0.05$, $g_{2\beta} = 0$; in $P_{\alpha\beta3}$, $\phi_\alpha = 0.5$.

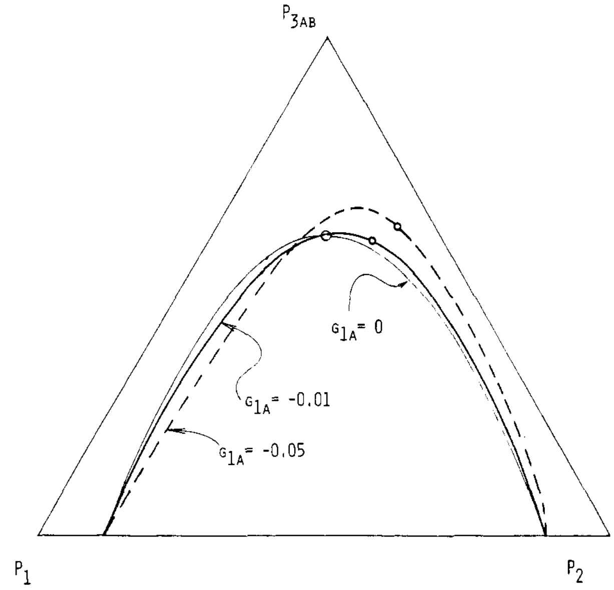


Figure 19. Spinodals and critical points (○) calculated with eq 4, 5, and 19 for $P_1/P_2/P_{\alpha\beta3}$ systems ($m_1 = m_2 = m_3 = 100$). Same g values as Figure 18 except $g_{1\alpha}$ (values indicated). In $P_{\alpha\beta3}$: $\phi_\alpha = 0.5$; $s_\alpha = s_\beta = 1$.

refer to interactions within the copolymer ($g_{\alpha\beta}$) because these would diminish compatibility, as we have seen above. Walsh et al. substantiated the principle with a series of well-chosen experiments. In terms of the model used here, negative values for some of the other g parameters can be looked upon as representative for such specific interactions. Figure 19 provides an example showing the distortion of the unstable region upon an increasing preference of the CRUs in polymer P_1 for one of the CRUs in the copolymer (α). A channel of compatibility remains along the 1/3 edge. If a similar effect occurs in the $2/\beta$ combination, the spinodal is forced away from both edges, whatever the chain length of $P_{3\alpha\beta}$ (Figure 20). Finally, Figure 21 indicates that differences in interacting surface ratios bring distortions in the phase diagram going with complications in critical behavior.

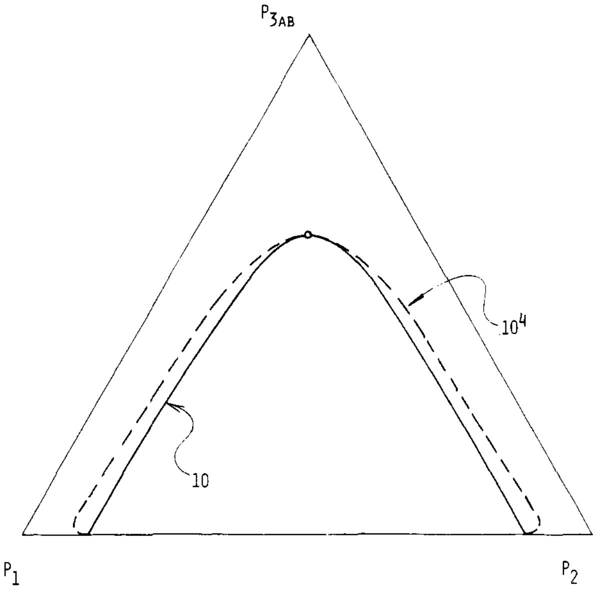


Figure 20. Spinodals and critical point (○) calculated with eq 4, 5, and 19 for a $P_1/P_2/P_{\alpha\beta3}$ system; $m_1 = m_2 = 100$, m_3 values indicated; in P_3, $\phi_\alpha = 0.5$. $g_{12} = 0.05$, $g_{1\alpha} = -0.05$, $g_{1\beta} = +0.05$, $g_{\alpha\beta} = +0.05$, $g_{2\alpha} = +0.05$, $g_{2\beta} = -0.05$, $s_\alpha = s_\beta = 1$.

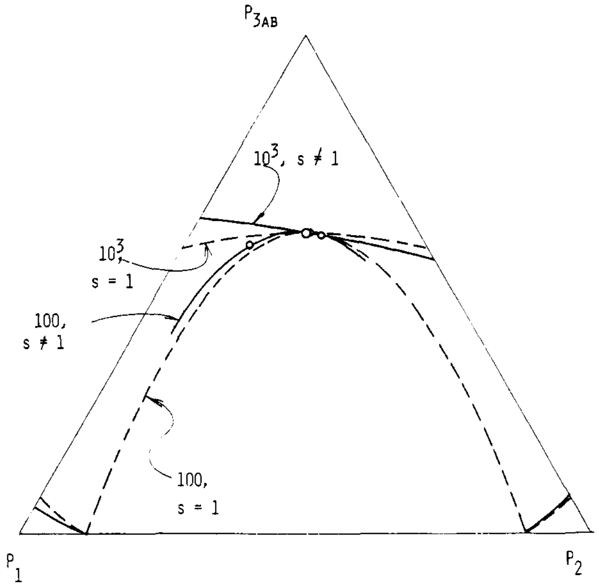


Figure 21. Same as Figure 20, except $g_{\alpha\beta} = -0.05$; curves marked $s \neq 1$, $s_\alpha = 1.2$, $s_\beta = 0.08$; $s = 1$, $s_\alpha = s_\beta = 1$.

Conclusions

The present numerical study suggests that miscibility relations in systems containing statistical copolymers will usually be complex and extremely sensitive to small variations in molecular parameters such as chemical composition, chain length, and repulsive or attractive interactions between the constitutional repeat units. Some of the subtleties described have been verified by experiment, albeit in a quite qualitative manner as yet. The sensitivity might come in useful as a means to discover the factors responsible for miscibility behavior and, subsequently, its influencing.

Spinodals and critical points present themselves as useful tools for the purpose. Since the recent development of the pulse-induced critical scattering[33-35] and centrifugal homogenization techniques[36,37] by Gordon et al. even relatively highly viscous systems can be handled. The second and third derivatives of the free enthalpy of mixing with respect to concentration thus having become measurable molecular models can be deeply probed into.

The interesting multiplicity of critical points, that seems to occur so easily in the systems on hand, would warrant a theoretical analysis which is currently being carried out.

Note added during the reviewing procedure: After completion of the manuscript we learned that ten Brinke, Karasz, and MacKnight have also concluded that miscibility enhancement in blends of homopolymers and statistical copolymers is to be ascribed to repulsion between the CRUs in the copolymer.[60]

Registry No. (Acrylonitrile)·(styrene) (copolymer), 9003-54-7; poly(2,6-dimethylphenylene oxide) (SRU), 24938-67-8; poly(2,6-dimethylphenol) (homopolymer), 25134-01-4; (*o*-chlorostyrene)·(*p*-chlorostyrene) (copolymer), 27755-63-1; (*o*-fluorostyrene)·(*p*-fluorostyrene) (copolymer), 74108-70-6; (butyl acrylate)·(methyl methacrylate) (copolymer), 25852-37-3; (methyl acrylate)·(methyl methacrylate) (copolymer), 9011-87-4; (ethyl acrylate)·(methyl methacrylate) (copolymer), 9010-88-2; (butyl methacrylate)·(methyl methacrylate) (copolymer), 25608-33-7.

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