3438 *Macromolecules* 1993, *26*, 3438-3443

Phase Behavior of Binary Mixtures Containing a Self-Associating Polymer

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Received February 2, 1993; Revised Manuscript Received March 22, 1993

ABSTRACT: A simple association model has been developed and used to calculate the phase diagrams of a self-associating block copolymer/inert homopolymer mixture. It is shown that in this type of system a closed immiscibility regime can be observed, even in mixtures without strong specific interactions. A comparison of the model phase diagrams with the known phase diagram of a mixture of the block copolymer poly(styrene-*co*-butadiene) and polystyrene is satisfactory and leads to the suggestion that in this system a closed immiscibility regime is possible at higher temperatures and a noncritical–critical "sideways coalescence" of two miscibility gaps can occur.

Introduction

A strong concentration and temperature dependence in segmental interaction parameters can lead to complex phase diagrams for a polymer mixture, as has been shown by calculations of Šolc and Koningsveld.[1] Such a strong concentration dependence of the interaction parameter can be expected in polymer mixtures in which some form of association takes place as a result of specific interactions.[2] Another possible case is in mixtures containing a block copolymer (self-associating polymer) A and an inert polymer B, because a repulsive interaction between dissimilar blocks in a copolymer leading to a microphase separation and formation of ordered structures (aggregation)[3,4] also leads to conditions for a strong concentration dependence of the effective interaction parameter. The phase behavior of block copolymer/homopolymer mixtures has been studied both theoretically[4] and experimentally.[5,6] Roe and Zin[5] obtained phase diagrams with interesting features for the mixture of block copolymer poly(styrene-*co*-butadiene) and polystyrene. Kang and Zin[7] based their theoretical calculation of this phase diagram on the model of copolymer lamellar structure with localized homopolymer solubility within the structure. This model might be especially appropriate at high concentrations of the homopolymer.

In this contribution a simple association model for a generalized mixture of a self-associating polymer A and an inert polymer B is developed. The resulting phase diagrams are discussed, and a qualitative comparison with Roe's experimental phase diagram[5] is made.

Association Model and the Condition of Phase Stability. We consider a generalized self-associating polymer, species A; the reasons for self-association can vary and can include, for example, an appropriate specific interaction or, as in the case of block copolymers, repulsive interactions between chemically different blocks in the chain. For simplicity, we allow the aggregates to contain a fixed number of A macromolecules. In this case the self-association is described by a quasi-chemical equation

$$nA \rightleftarrows A_n, \quad n = \text{constant} \tag{1}$$

where n is the association number. In a mixture of polymer A with a second, nonassociating (hereafter called inert) polymer, B, there are then three types of species present: unassociated polymer A (component 1, which we will call a unimer),[8] aggregates of polymer A (component 2, hereafter A_n), and molecules of the inert polymer B (component 3). Interactions between these species will be characterized by three generalized interaction parameters χ_i: χ_1 for interactions of the unimer with polymer B, χ_2 for interactions of A_n with polymer B, χ_{12} for interactions between the unimer and A_n. Using Flory's method,[9] we can express the Gibbs free energy of mixing per unit volume for the quasi-ternary system as

$$\frac{\Delta G_M}{RT} = \frac{\phi_3}{r_3}\ln\phi_3 + \frac{1}{r_1}\left[\phi_1\ln\phi_1 + \frac{\phi_2}{n}\left(\frac{\Delta G_2{}^\circ}{RT} + \ln\phi_2\right)\right] + (\chi_1\phi_1 + \chi_2\phi_2)\phi_3 + \chi_{12}\phi_1\phi_2 \tag{2}$$

where r_i and ϕ_i are respectively the degree of polymerization of component i and its volume fraction; $\Delta G_2{}^\circ$ is the standard Gibbs free energy of association for the reaction described by eq 1. Volume fractions ϕ_1 and ϕ_2 are constrained by the relation

$$\phi_1 + \phi_2 = \phi_A \tag{3}$$

where ϕ_A is the total volume fraction of self-associating polymer A. At equilibrium, the condition

$$\left(\frac{\partial\Delta G_M}{\partial\phi_1}\right)_{T,P} = \left(\frac{\partial\Delta G_M}{\partial\phi_2}\right)_{T,P} \tag{4}$$

must be fulfilled.[10] The application of this condition to eq 2 yields the relation between the equilibrium concentrations of unimers, ϕ_1, and aggregates, ϕ_2:

$$\phi_2 = \phi_1{}^n K \exp(-r_1 n \chi_{eff}) \tag{5}$$

$$K = \exp[(n-1) - \Delta G_2{}^\circ/RT] \tag{5a}$$

$$\chi_{eff} = (\chi_2 - \chi_1)\phi_3 + \chi_{12}(\phi_1 - \phi_2) \tag{5b}$$

where K is the equilibrium association constant.

Gibbs[11] defines the condition for phase stability of a multicomponent system in the well-known form

$$|G_{sp}| = \left|\frac{\partial^2\Delta G_M}{\partial\phi_i\partial\phi_j}\right|_{T,P} = 0 \tag{6}$$

where in this case $i, j = 1, 2, 3$ and $|G_{sp}|$ is the spinodal determinant. Pouchlý and Sikora[10] showed, using a general thermodynamic procedure, that the spinodal condition for a binary system in which one component is aggregated is the same as the spinodal condition of a polydisperse mixture with a distribution of species determined by an association equilibrium and that the

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conditions of the association equilibrium can simply be substituted into the former expression. Thus, the application of condition (6) to eq 2 leads to the spinodal equation for the system:

$$\frac{1}{r_3\phi_3} + \frac{1}{r_1(\phi_1 + n\phi_2)} - \frac{2}{(\phi_1 + n\phi_2)}\left(\phi_1\chi_1 + \phi_2\chi_2 + \frac{r_1 n\phi_1\phi_2\chi_{12}}{r_3\phi_3}\right) + r_1 n\phi_1\phi_2\frac{4\chi_1\chi_2 - (\chi_1 + \chi_2 - \chi_{12})^2}{\phi_1 + n\phi_2} = 0 \quad (7)$$

where ϕ_1 and ϕ_2 are bounded by eqs 3 and 5. Simultaneous solution of eqs 3, 5, and 7 thus yields the spinodals and phase diagram of a mixture containing a self-associating copolymer and an inert polymer.

Discussion

The basic system for our model calculations is a mixture of two polymers, A and B, with the same degree of polymerization, $r_1 = r_3 = 100$. The self-association of polymer A is characterized by the association number n and the association constant K, the temperature dependence of which has the usual form

$$\ln K = \alpha + \beta/T \quad (8)$$

In the numerical calculations below, the constants α and β have been chosen so that the transition between the unassociated and aggregated forms of polymer A take place in the temperature range 350–430 K. Leibler et al.[3] analyzed the formation of block copolymer micelles in a mixture with a homopolymer and showed that the association number n was weakly dependent on temperature. Therefore, we will consider, in addition to the case for a constant $n = 10$, the situation in which n is dependent on temperature:

$$n = 25.5 - 5655/T \quad (9)$$

In these calculations, we do not need to assume any special structure for the aggregates.

The three χ_i's are defined above; their magnitudes were chosen so that $\chi_1 > \chi_{12} > \chi_2$ and so that all χ's would lie in the range typical for interactions between two nonpolar polymers. The temperature dependence of all three χ_i's has the form

$$\chi = C + D/T \quad (10)$$

with the constants C and D lying in an appropriate range for polymers.[5]

Association Equilibria. The transition from an unaggregated state to an aggregated one is gradual, and its sharpness depends on the parameters influencing the association.[3,8,12] This causes some problems with the definition of a critical concentration or a critical temperature characterizing this transition as is known from studies of low molecular weight micellar systems.[13] For this reason we arbitrarily defined the transition temperature T_t in the homogeneous mixture containing unimer A and the aggregates A_n as the temperature at which 5% of polymer A is in the form of aggregates, i.e., the fraction of unaggregated unimer $w_1 = \phi_1/\phi_A = 0.95$.

Using eq 5, we first calculated the association curves, i.e., the dependence of the transition temperature T_t on the composition of the system. The influence of the interaction parameter set on the association equilibrium is shown in Figure 1. Curve 1 is the association curve for the ideal case in which there are no interactions between any species. The negative slope of the curve is related simply to the decreasing total concentration of polymer A. The decrease of the unimer fraction with decreasing temperature is in the ideal case very slow (Figure 2, curve 1).

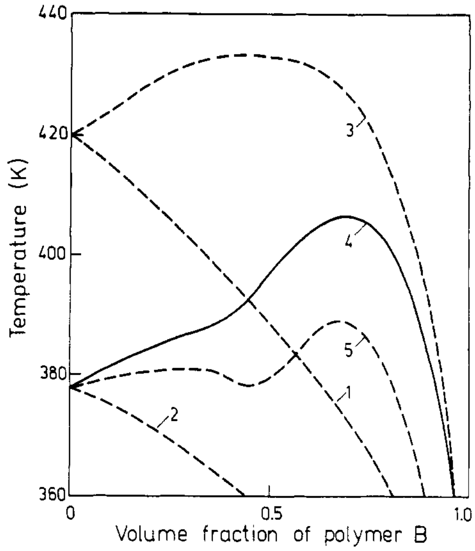

Figure 1. Influence of the interaction parameters χ_i on the association equilibrium of a mixture of a self-associating polymer A and an inert polymer B. $r_1 = r_3 = 100$; $\ln K = -85.71 + 35000/T$; $n = 25.5 - 5655/T$. Curve 1: $\chi_1 = \chi_2 = \chi_{12} = 0$. Curve 2: $\chi_1 = \chi_2 = 0$; $\chi_{12} = -0.0646 + 31.58/T$. Curve 3: $\chi_1 = -0.0546 + 31.58/T$, $\chi_2 = -0.0718 + 31.58/T$, $\chi_{12} = 0$. Curve 4: $\chi_1 = -0.0546 + 31.58/T$, $\chi_2 = -0.0718 + 31.5/T$, $\chi_{12} = -0.0646 + 31.58/T$. Curve 5: $\chi_1 = -0.0618 + 31.58/T$, $\chi_2 = -0.0734 + 31.58/T$, $\chi_{12} = -0.0646 + 31.58/T$.

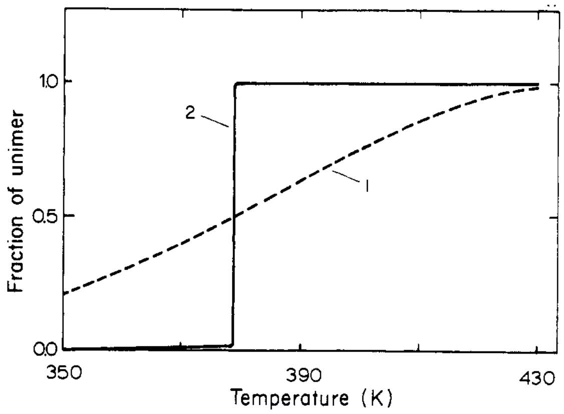

Figure 2. Dependence of the unimer fraction w_1 on temperature in a pure self-associating polymer A. The parameters for curves 1 and 2 are the same as for curves 1 and 2 in Figure 1.

A repulsive interaction between the unimer and the aggregates shifts the association curve on the temperature scale to a lower temperature (Figure 1, curve 2), and causes a sharpening of the dependence of the unimer fraction on temperature in pure polymer A (Figure 2, curve 2).

From the spinodal equation for a pure self-associating polymer,

$$\frac{1}{r_1\phi_1} + \frac{1}{r_1 n\phi_2} - 2\chi_{12} = 0 \quad (11)$$

the critical value of χ_{12} can be calculated. If $\chi_{12} > {}^1/_2(1 + 1/n)$, the sharp transition from unimer to aggregates in pure polymer A is, in a very narrow temperature range, accompanied by a macroscopic phase separation.

A more favorable interaction between aggregates A_n and the inert polymer B than between unimer A and the inert polymer B (i.e., $\chi_2 < \chi_1$) shifts the association equilibrium toward higher temperatures as the concentration of B

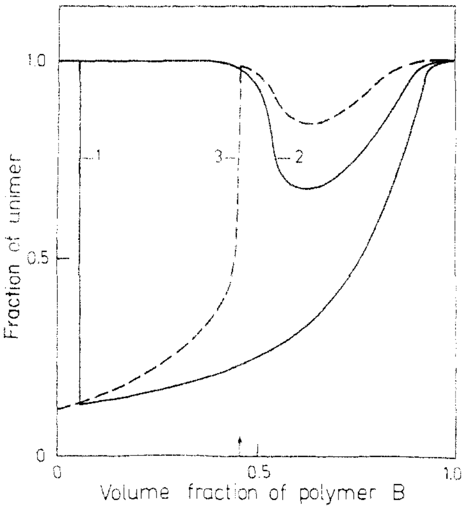

Figure 3. Influence of temperature and composition of the mixture on the unimer fraction in a mixture of a self-associating polymer A and an inert polymer B. $r_1 = r_3 = 100$, $n = 10$, $\ln K = -85.7 + 35000/T$. Curves 1 and 2: χ parameters as in curve 4, Figure 1. Curve 3: χ parameters as in curve 5, Figure 1. Curve 1: $T = 380$ K. Curve 2: $T = 395$ K. Curve 3: $T = 378$ K. Arrow denotes minimum in association curve 5, Figure 1.

increases (Figure 1, curve 3). Curve 4 shows the situation in which all three interaction parameters vary with temperature.

Curves 1 and 2 in Figure 3 show the respective concentration dependences of the unimer fraction at temperature $T = 380$ and 395 K for association curve 4 in Figure 1. There are no aggregates in pure polymer A at the given temperatures. However, addition of polymer B, the amount depending on the temperature, induces aggregation of polymer A. This has been observed experimentally[3,5,6] and, in fact, theoretically predicted.[4] The aggregates again vanish at higher concentration of polymer B. The sharpness of the unimer–aggregate transition depends on polymer B concentration and the temperature. The higher the concentration of polymer B or the temperature, the more diffuse the transition (Figure 3).

If the difference $(\chi_2 - \chi_1)$ is smaller than for the case represented by curve 4 in Figure 1, the calculated association curve has *two* maxima (curve 5, Figure 1). In this case, a decreasing content of aggregates is observed near the minimum of the association curve (curve 3, Figure 3).

Macroscopic Phase Separation. Solving eqs 3, 5, and 7, we obtain the spinodal curve of the binary mixture. In the following discussion of representative phase diagrams, we will use the symbols L, L_1, and L_2 to denote various mixtures of unimer A and polymer B and M, M_1, and M_2 to denote mesophases formed by unimer A, aggregates A_n, and the inert polymer B.

First we shall examine the influence of the self-association of polymer A on the shape of the spinodal curve. Figure 4 shows, for reference, the spinodal phase boundary of a mixture of two nonassociating polymers A and B (curve 1), with a critical point CP at 423 K. The interaction parameter for this polymer pair is the same as the interaction parameter χ_1 for the unimer A–polymer B pair in our association model. When self-association of polymer A takes place in this mixture, the phase diagram changes to include a number of new features. Polymer A forms aggregates over the whole concentration range with the exception of narrow regimes at both ends of the composition (curve 3, Figure 4). With the given set of parameters (see captions), a small closed immiscibility regime appears at higher temperatures and high concentrations of polymer A; and at lower temperatures and high concentrations of polymer B, there is phase separation with an upper critical solution temperature (UCST) (Figure 4, curve 2). In this case, the critical point of the reference polymer pair lies below the association curve. Therefore, the equilibrium phases contain aggregates in both regions of partial miscibility, but the fractions of aggregates present in them are different, as can be seen in Figure 5. The latter shows the changes in the unimer fraction w_1 along the spinodal curve 2 in Figure 4.

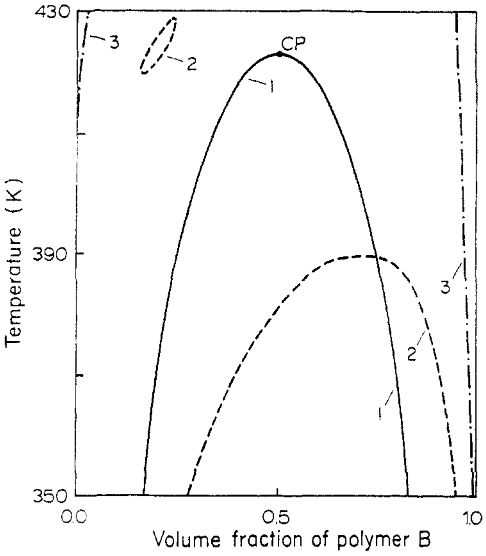

Figure 4. Spinodal and association curves of a mixture of a self-associating polymer A and an inert polymer B. $r_1 = r_3 = 100$. Curve 1: mixture of two nonassociating polymers, $\chi = -0.0546 + 31.58/T$. Curve 2: spinodal curve, $n = 10$, $\ln K = -78.71 + 35000/T$; $\chi_1 = -0.0546 + 31.58/T$, $\chi_2 = -0.0718 + 31.58/T$, $\chi_{12} = -0.0646 + 31.58/T$. Curve 3: association curve, parameters the same as for curve 2. CP, critical point.

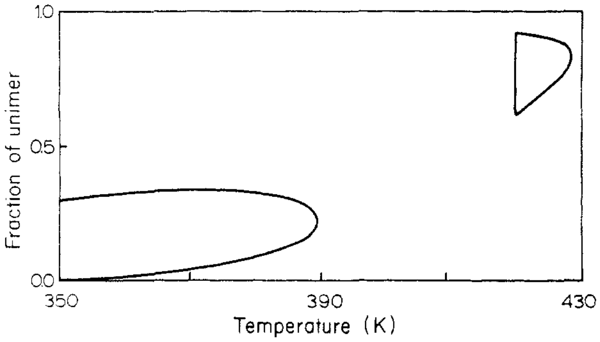

Figure 5. Temperature dependence of the unimer fraction w_1 along the spinodal (curve 2 in Figure 4).

When the association curve falls (which happens as the association constant K decreases) below the critical temperature of a mixture of nonassociating polymers, we obtain the even more complex spinodal curves shown in Figure 6. For the constant value of $n = 10$, the boundary between L and M is given by the association curve 1A. Below the critical temperature for the nonassociating polymer mixture, T_{c1}, the system is separated into two disordered phases L_1 and L_2. At the temperature T_1, when the association curve 1A intersects the spinodal curve 1S at the point D, the formation of aggregates extends into the equilibrium phase L_2 and this phase changes into the ordered mesophase M_2. Below T_1, the two phases L_1 and M_2 are in equilibrium. At the lower critical temperature T_{c2} (point B), the immiscibility loop is closed; at tem-

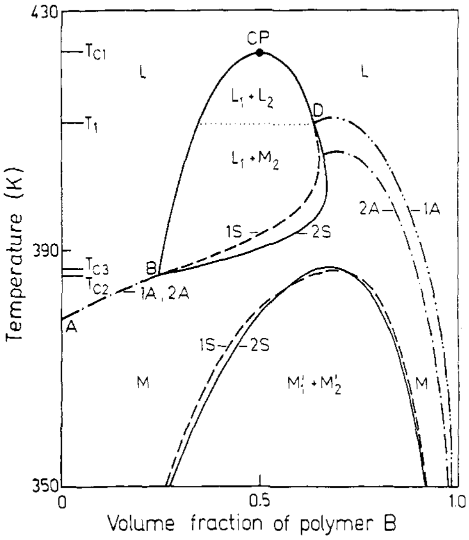

Figure 6. Spinodal and association curves of a mixture of a self-associating polymer A and an inert polymer B. Parameters the same as in curve 4, Figure 1. S, spinodal curve; A, association curve. Curve 1: $n = 10$. Curve 2: $n = 25.5 - 5655/T$. For a description of phases, see the discussion.

peratures lower than T_{c2}, a macroscopically homogeneous ordered mesophase M exists.

The presence of a closed immiscibility regime is one of the characteristics of systems containing an associating component[14] and is dependent on the existence of a UCST for a mixture of the respective nonassociating components. The closure of the immiscibility regime takes place if the enthalpic gain connected with the formation of aggregates is greater than the entropic loss for this process. In our case the enthalpic gain is due to the fact that interaction between the aggregates and the molecules of the inert polymer is more favorable than that between the unimer and the inert polymer. The entropy loss is caused by the drop in the combinatorial entropy of mixing due to the association of polymer A. In the region of higher concentrations of polymer B, a decrease in temperature leads again to a macrophase separation at a UCST T_{c3}. In this case we have two further equilibrium mesophases, M_1' and M_2'. The effect of a change in n with temperature (as has been postulated above) on the phase and the association equilibria is moderate and is illustrated by the curves 2S and 2A in Figure 6.

When the chain length of one or both of the components of a polymer mixture decreases, miscibility in the system generally increases. The same effect is observed in systems containing a self-associating polymer, as can be seen in Figure 7. A shortening of the inert polymer chain (to $r_3 = 75$) leads to a decrease and shift of the critical temperatures for both regimes of immiscibility to higher concentrations of the shorter component, as can be seen by comparing Figure 7 with Figure 6. The association equilibrium is not affected by the reduced chain length of the inert polymer.

Comparison of Model with Experimental Phase Diagrams. Roe and Zin[5] have obtained a complex phase diagram for the block copolymer poly(styrene-*co*-butadiene)/polystyrene mixture. Figure 8 presents schematically the Roe phase diagram for subsequent comparisons with our model phase diagrams. In Figure 8, L denotes a liquid homogeneous phase formed by the disordered block copolymer and homopolymer. L_1 and L_2 are equilibrium disordered phases. M_1 denotes a mesophase in which the ordered block copolymer is the major component, and M_2 is a mesophase in which the homopolymer is the major component.

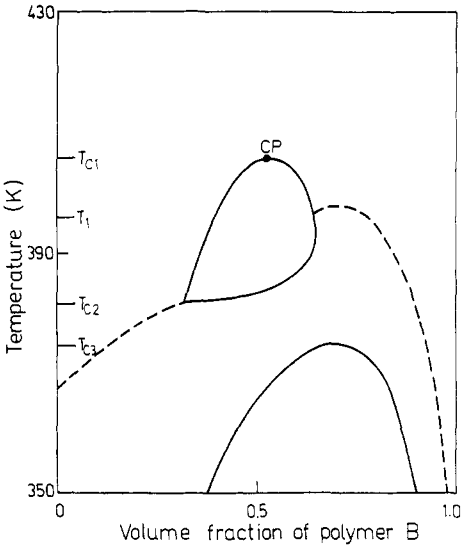

Figure 7. Spinodal curves (solid lines) and association curves (dashed lines) of a mixture of a self-associating polymer A and an inert polymer B. $r_1 = 100$, $r_3 = 75$, $n = 10$, $\ln K = -87.7 + 35000/T$, χ parameters as in curve 4, Figure 1. Compare with Figure 6.

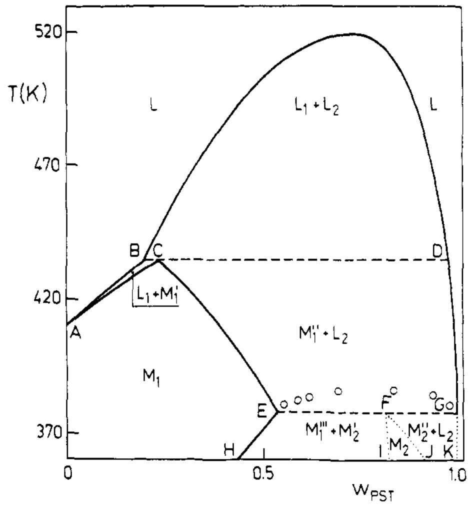

Figure 8. Schematic phase diagram of a mixture of the block copolymer poly(styrene-*co*-butadiene)/polystyrene.[5]

There are at least three phenomena of interest shown in this experimental phase diagram: (1) appearance of a third phase at the peritectic point (C, Figure 8); (2) decrease of polystyrene miscibility with the mesophase accompanied by a decreasing content of the mesophase as the temperature and copolymer concentration increase (curves C–E, Figure 8); (3) complex phase behavior at low temperature and high concentration of polystyrene, namely, the macroscopic phase separation into mesophases M_1''' and M_2'.

In our association model the unimer is formally equivalent to the disordered block copolymer and the aggregates to the ordered mesophase. For the model calculations, we have again chosen relatively short, 100-segment polymer chains. The interaction parameters and association constant used (see caption) resulted in a phase diagram having several common characteristics with the experimental one. Figure 9 shows the spinodal (solid line) and association (dashed line) curves of the model system. The dependence of the unimer fraction (i.e., fraction of disordered block copolymer) on the temperature along the spinodal curve from Figure 9 is shown in Figure 10.

The mixture of the self-associating polymer A and an inert polymer B is macroscopically homogeneous (L) at

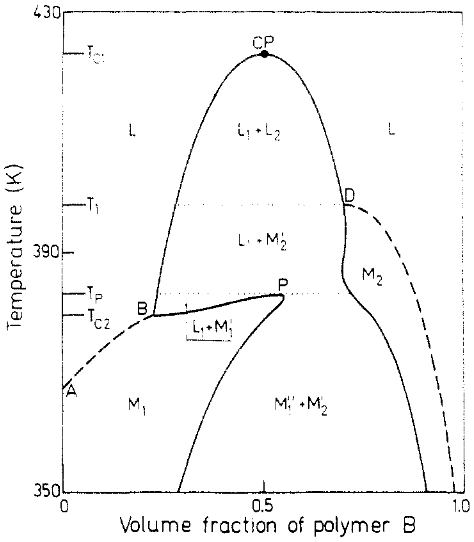

Figure 9. Spinodal curves (solid lines) and association curve (dashed lines) of a mixture of a self-associating polymer A and an inert polymer B. $r_1 = r_3 = 100$, $\ln K = -87.7 + 35000/T$, $n = 10$, χ parameters as in curve 4, Figure 1. Dotted lines have been inserted to guide the eye at T_1 and T_P.

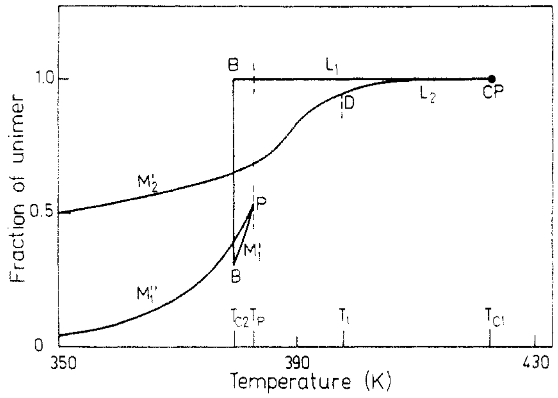

Figure 10. Temperature dependence of the unimer fraction w_1 along the spinodal curve in Figure 8.

temperatures higher than T_{c1} in the whole concentration range, and polymer A is in a nonaggregated state. Below the temperature T_{c1}, phase separation occurs. Outside the miscibility gap, the mixture is homogeneous; at temperatures above the association curve, polymer A remains in the unimer state (L). Inside the miscibility gap, two macroscopic phases are in equilibrium. Polymer A is in a nonaggregated state in both phases L_1 and L_2 in the temperature interval $T_1 < T < T_{c1}$, as can be seen in Figure 10, curve CP–D. At temperatures near T_1, the formation of polymer A aggregates starts in the phase L_2, and it is transformed into the mesophase M_2'. As the temperature decreases, the content of aggregates in the mesophase M_2' increases (curve M_2' starting from the point D, Figure 10). The phase L_1 contains no aggregates until the temperature T_{c2} is reached (line CP–B, Figure 10). At the peritectic temperature T_P, the third macroscopic phase appears—the mesophase M_1 (point P, Figures 9 and 10). The spinodal curves for mesophases M_1' and M_2'' start at this point. The content of polymer A aggregates in both mesophases is different, as we can see in Figure 10 (curves M_1' and M_1'', starting at point P). A peritectic point has been experimentally found by Roe and Zin[5] (point C, Figure 8). In the temperature interval $T_{c2} < T < T_P$, there is a range of concentrations in which the mesophase M_1 coexists with liquid phase L_1. If the temperature decreases below T_P, a macroscopic separation of two mesophases M_1'' and M_2' occurs. The equilibrium mesophases contain different amounts of aggregates (curves M_1'' and M_2', Figure 10). The coalescence of the two miscibility gaps (shown in Figure 9) can be characterized, using the nomenclature of Šolc and Koningsveld,[1] as a noncritical–critical (n–c) "sideways coalescence".

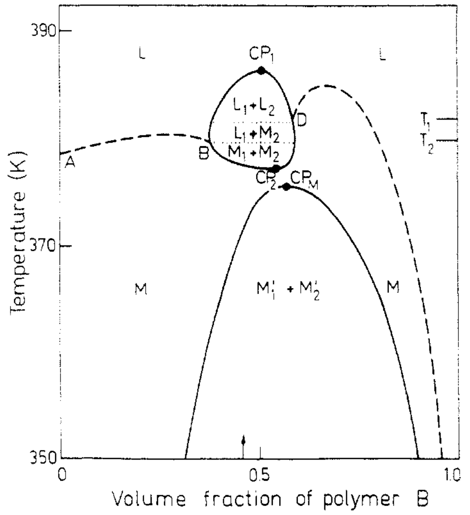

Figure 11. Spinodal (solid lines) and association curves (dashed lines) of a mixture of a self-associating polymer A and an inert polymer B. The set of parameters is the same as that for curve 5 in Figure 3.

Lowering the interaction parameters difference ($\chi_2 - \chi_1$) not only causes a change of the character of the association curve (Figure 1, curve 5) but also changes the nature of the phase diagram. In the phase diagram in Figure 11 (based on the parameters used to calculate curve 5, Figure 1), the peritectic point P vanishes and a separated closed miscibility regime developed. In this region the equilibrium phases are changing from liquid disordered phases L_1 and L_2 into ordered mesophases M_1 and M_2 as the temperature decreases. The misicibility of polymers A and B decreases along part of the spinodal curve B–CP_2 as the content of B in the mixture increases. The effect is caused by a decreasing content of aggregates A_n in this concentration and temperature range, as can be seen in Figure 3, curve 3. Roe and Zin[5] have used the same argument—a diminution of the ordered phase—in explaining their experimental findings (curve C–E, Figure 8).

Below the critical point CP_2 (Figure 11), we have a macroscopically homogeneous mesophase M, which again separates into two mesophases M_1' and M_2' as the temperature declines.

A change of sample turbidity is typically used as an indicator of phase instability of a mixture. The turbidity changes occur when a cloud-point curve (macroscopic phase separation) or an association curve (transition of the unimer $\rightleftharpoons$ aggregates) are crossed. On this basis, the nonlinear experimentally observed boundary (circles between points E and G, Figure 8) can be interpreted in terms of part of the demixing curve near the upper critical solution temperature CP_M in Figure 11. These results lead us to the conclusion that the experimentally obtained phase diagram for the block copolymer poly(styrene-*co*-butadiene)/polystyrene mixture obtained by Roe and Zin[5] can be interpreted by the simple association model.

Conclusions

A thermodynamic model for the self-association of polymer A in a mixture with an inert polymer B can be relatively straightforward if the structure of the aggregates does not need to be taken into consideration. The calculations of the spinodal curves of the model binary mixtures containing the self-associating polymer have shown that the existence of a closed immiscibility regime is possible even without specific interactions if the general requirement that an entropic loss connected with the association is compensated by an enthalpic gain[14] is fulfilled. The LCST caused by the association always lies below the UCST of the respective nonassociating components. In polymer systems, it is necessary to distinguish between an LCST due to compressibility of the polymers[15] and an LCST due to association. Unlike the association-driven LCST, the compressibility-driven LCST may lie above the UCST of the polymer mixture, in which case the phase diagram can have two regimes of partial miscibility.[15] There is a further theoretical possibility that both types of LCST occur and consequently that a phase diagram with both low- and high-temperature regions of partial miscibility and a closed immiscibility regime between them can exist. This type of phase diagram was shown in calculations by Qian et al.[16]

The complex phase diagram of the system poly(styrene-*co*-butadiene)/polystyrene[5] can be qualitatively explained by the simple association model. Comparison of Figure 8 with the model phase diagrams leads to the conclusion that in this experimental system there probably are two regions of immiscibility. One is the closed immiscibility regime at higher temperature, and the second one is the region of partial miscibility of the mesophases at lower temperatures. The LCST of the closed immiscibility regime and the UCST of a low-temperature region of partial miscibility lie close to each other. The richness of the phase diagram is conditioned by a weak association of the block copolymer and the resulting comparable concentrations of the unimer and aggregates in certain temperature regions. In the case of a strong association, the equilibrium between the unimer and the aggregates is markedly shifted toward aggregate formation. This shift removes the closed immiscibility regime, and only the region of partial miscibility of the mesophases remains. We find that the spinodal and association curves of such systems are very sensitive to changes in the interaction parameters χ_i.

Acknowledgment. We gratefully acknowledge the support of the Air Force Office of Scientific Research through Grant No. 92-003.

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