φ_C^{crit}, $\varphi_C^{(3)} = \varphi_C^{\text{crit}}$, and all excess copolymer molecules aggregate into micelles. For the case of large Z_{CA}, there is a range of φ_C^0 just below φ_C^{crit} for which micelles exist, but addition of more copolymer results in a slight increase in $\varphi_C^{(3)}$. However, this corresponds to a small range of φ_C^0, and the transition becomes sharper with decreasing Z_{CA}.

5. Conclusions

The experimental measurements by Selb. et al.[1] of the core radius were analyzed and found to be consistently described by a scaling relationship $l_B \propto Z_{CA}^{\mu} Z_{CB}^{\nu}$, with $-0.19 \leq \mu \leq -0.14$ and $0.75 \leq \nu \leq 0.81$. This behavior was well reproduced by the model, except that the magnitude of each of the exponents was slightly smaller, with $-0.10 \leq \mu \leq -0.07$ and $0.68 \leq \nu \leq 0.70$. The small variations in both the experimental and theoretical exponents exhibited the same trends with respect to changes in homopolymer and copolymer molecular weights. It was emphasized that the dominant dependence of l_B is on the core block dp Z_{CB}, not the total Z_C, and in fact l_B tends to *decrease* if the CA block molecular weight increases, rather than increase as it does when the CB block molecular weight increases. More generally, l_B is not a single-valued function of only the total molecular weight.

This behavior was evident throughout calculations over large ranges of molecular weight, with Z_{CB} and Z_{CA} varying up to 2000. Physically, the core radius is primarily determined by a balance between the stretching energy of the core and the interfacial free energy. In the corona, different mechanisms are important. For $Z_{HA} \gg Z_{CA}$, there is little stretching of the blocks in the corona, so that $l_A \simeq (Z_{CA}/3)^{1/2} b_A$. However, for smaller Z_{HA} or larger Z_{CA}, the homopolymer penetrates more into the corona, stretching the A blocks with the result that l_A increases faster than $Z_{CA}^{1/2}$. This also has the effect of shrinking the core radius, $l_B \sim Z_{CA}^{\mu}$, where μ is small and negative.

In all cases, there was almost no homopolymer in the core of the micelle, and far from the critical concentration relatively little copolymer remaining in the region between micelles. The critical concentration itself was found to have primarily an exponential dependence on $\chi_{AB} Z_{CB}$, and a simple expression for φ_C^{crit} was exhibited. Physically, the Z_{CB} dependence arises from the enthalpic interaction of the CB block of the copolymer with the homopolymer. By contrast, φ_C^{crit} *increases* as Z_{CA} increases. This reflects primarily the dependence of overall copolymer volume fraction φ_C^0 with Z_{CA} for a given φ_{CB}^0.

Throughout, the composition of the copolymer, not just the total molecular weight, has been found to be important. Analyses which make specific assumptions, such as $Z_{CA} = Z_{CB}$, must be considered incomplete.

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Registry No. Polybutadiene (homopolymer), 9003-17-2; (butadiene)·(styrene) (copolymer), 9003-55-8.

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Thermodynamics of Phase Separation in Polymer Mixtures

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ABSTRACT: Phase equilibria and spinodal decomposition of polystyrene/polybutadiene blends are investigated by using the Flory–Huggins approximation and the Landau expansion of the free energy. Experimental cloud point curves extrapolated to infinitely slow heating and cooling rates are adequately explained by assuming a suitable power law dependence of the effective interaction parameter $\bar{\chi}$ on temperature. Theoretical arguments stressing the configurational effects of a concentration gradient yield an expression for the gradient term that is substantially different from the de Gennes–Pincus formula. According to our calculations, the gradient term is a homogeneous quadratic form of the three interaction parameters of the binary mixture and has a much stronger molecular weight dependence. Finally, the interphase thickness and surface tension are evaluated near the critical point. In this limit, provided $\bar{\chi}$ has a power law dependence on temperature, the surface tension is found to be proportional to $[(T_c - T)/T_c]^{3/2} M^{-1/2} g(M)$, where $g(M)$ is a constant only if all of the interaction parameters have the same temperature dependence.

Introduction

The spontaneous phase separation of amorphous glass and metal mixtures via a spinodal mechanism has been extensively studied. Since the initial work of Cahn and Hilliard,[1] there have been numerous experimental and theoretical treatments of this problem. As is evidenced by the substantial amount of current research in this field, it is apparent that even for these small-molecule mixtures a complete description of the kinetics of phase separation is still not available.

In contrast polymer/polymer mixtures have received relatively little attention. This is due in part to the small number of systems accessible to experimental observation. Investigations on the phase separation kinetics in some high[2-4] and low[5-8] molecular weight polymer mixtures have recently appeared in the literature. Joanny,[9] de Gennes,[10] and, later, Pincus[11] attempted to treat spinodal phase separation in polymers theoretically. Using scaling and reptation arguments they obtained a modified Cahn–Hilliard expression for the fluctuation wavelength amplification factor describing both the thermodynamics and kinetics of phase separation. Their treatments predict the dominant features of the process; however, agreement between theory and experiment is not quantitative.

Recent experimental studies on the spinodal decomposition of some low[8] and high[12] molecular weight polymer

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mixtures showed the existence of a critical fluctuation wavelength beyond which the amplitude of the fluctuations increased with time. The magnitude of this critical wavelength, being directly related to the thermodynamics of the mixture, can be investigated without considering the dynamics. This provides an opportunity to understand one aspect of this problem before addressing the more complicated issue of kinetics.

In this paper some of the thermodynamic characteristics of a phase-separating polymer mixture are considered. For simplification the interaction parameter was assumed to depend only on temperature, which is shown to adequately describe the experimentally observed binodal. Utilizing this result, the excess free energy associated with the presence of a concentration gradient is evaluated by using a Gaussian bead/spring model for the polymer chain. Comparison of the derived results with experiment are discussed. Finally, the interfacial tension for this model is evaluated in the vicinity of the consolute point where the size of the interface is assumed to be much larger than the coil size.

Phase Equilibria

Thermodynamic equilibria of polymer blends have been investigated by several authors using the lattice model.[13,14] The lattice analysis leads to an expression of the free energy whose entropic part is

$$-\Delta S/k = n_A \ln \phi + n_B \ln (1 - \phi) \tag{1}$$

where n_A and n_B are the numbers of molecules of types A and B, respectively, and ϕ is the volume fraction of polymer A. Equation 1, deduced by condensing the step segments of both polymers in cells of equal volume, does not depend on details of the lattice model and has, therefore, general validity for highly flexible polymers. The energetic part of the free energy at the high concentrations of interest in polymer mixtures is better evaluated in terms of simple mean field ideas, counting the three kinds of interaction (AA, BB, and AB) on the basis of the volume fractions. The total free energy, apart from configurational factors that are not affected by mixing, is given by

$$\Delta G/kT = n_A \ln \phi + n_B \ln (1 - \phi) + \chi_{AA} n_A N_A \phi/2 + \chi_{BB} n_B N_B (1 - \phi)/2 + \chi_{AB} n_A N_A (1 - \phi) \tag{2}$$

where N_A and N_B are the respective monomer numbers per chain, χ_{AA} and χ_{BB} are the energetic parameters associated with the interaction between monomers belonging to different chains of the same kind, and χ_{AB} characterizes the interaction of monomers A with monomers B. Equation 2 is identical with that used by de Gennes[15] with the exception that the volumes of the monomer units were not assumed equal in this work. The cross term of eq 2 is written considering chains of type A dispersed in a medium partially filled by molecules of the other kind. Alternatively, this term can be written as $\chi_{BA} n_B N_B \phi$ when B is dispersed in A. Equivalence of the two formulations requires that

$$\chi_{AB}/v_A = \chi_{BA}/v_B$$

where v_A and v_B are the volumes of the corresponding monomer units. Despite the appearance of the three independent quantities χ_{AA}, χ_{BB}, and χ_{AB}, phase equilibria are governed by only one reduced parameter, given by a suitable combination of the three χ's. Derivation of the chemical potentials shows this fortunate feature directly. As we will see, the derivation of the gradient term leads to less compact results. It is also important to observe that the above conclusion concerning phase equilibria holds only if the χ's are concentration independent. Previous treatments[13,14] generally allow for a concentration dependence, in which case reduction to a single effective interaction parameter is unwarranted. The chemical potentials of components A and B are defined as

$$\mu_A = (\partial \Delta G/\partial n_A)_{T,n_B} \tag{3}$$

$$\mu_B = (\partial \Delta G/\partial n_B)_{Tn_A} \tag{4}$$

For a two phase system thermodynamic equilibrium requires that the chemical potential of each component has the same value in both phases. Assuming that the volumes of the monomer units are independent of ϕ, which corresponds to ideal mixing, and defining ϕ as

$$\phi = \frac{n_A N_A v_A}{n_A N_A v_A + n_B N_B v_B} \tag{5}$$

eq 3 yields

$$\frac{\mu_A}{kT} = \ln \phi + (1 - \phi)\left[1 - \frac{N_A v_A}{N_B v_B}\right] + \bar{\chi} N_A (1 - \phi)^2 + \chi_{AA} N_A/2 \tag{6}$$

$$\frac{\mu_B}{kT} = \ln (1 - \phi) + \phi\left[1 - \frac{N_B v_B}{N_A v_A}\right] + \frac{v_B}{v_A}\bar{\chi} N_B \phi^2 + \chi_{BB} N_B/2 \tag{7}$$

where $\bar{\chi} = \chi_{AB} - (\chi_{AA} + \chi_{BB}(v_A/v_B))/2$ is the only effective parameter characterizing the energetics of phase equilibria, the terms $\chi_{BB}N_B$ and $\chi_{AA}N_A$ being immaterial.

For a given ϕ, the volume fraction ϕ' of A in the coexisting phase and the value of $\bar{\chi}$ are found by solving the equations

$$\mu_A(\phi,\bar{\chi}) = \mu_A(\phi',\bar{\chi}) \tag{8a}$$

$$\mu_B(\phi,\bar{\chi}) = \mu_B(\phi',\bar{\chi}) \tag{8b}$$

The spinodal, defining the limit of local stability for a homogeneous mixture, can be obtained by solving the equation $(\partial^2 \Delta G/\partial \phi^2)_v = 0$ at constant volume. Therefore, from eq 2

$$\frac{\bar{\chi}^s}{v_A} = \frac{1}{2N_A v_A \phi} + \frac{1}{2N_B v_B (1 - \phi)} \tag{9}$$

where the superscript s denotes the value of $\bar{\chi}$ at the spinodal temperature. The spinodal and binodal are tangent to each other at the plait or consolute point, where

$$\phi_c = \frac{1}{1 + \left(\dfrac{N_A v_A}{N_B v_B}\right)^{1/2}} \tag{10}$$

and

$$\bar{\chi}^c = \frac{1}{2N_A}\left[1 + \left(\frac{N_A v_A}{N_B v_B}\right)^{1/2}\right]^2 \tag{11}$$

The particular mixtures of interest in this study were two polystyrene/polybutadiene (PS/PBD) blends where the molecular weight of PS was kept constant ($M_w = 2000$ (2K), $M_w/M_n = 1.3$) and that of PBD was varied ($M_w = 1000$ (1K), $M_w/M_n = 1.2$ and $M_w = 2500$ (2.5K), $M_w/M_n = 1.15$). All the mixtures were prepared in the melt without the use of solvents. The PS used in this study contains ca. 19.2 monomers per chain, with a monomer volume of 178.04 Å^3 (assuming a density of 0.97 g/cm^3 over

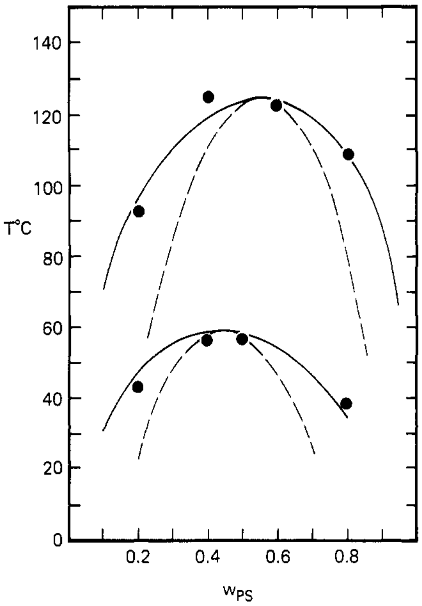

Figure 1. Experimental cloud points (●) determined from optical density measurements[8] compared to the theoretical binodals (—) calculated from the free energy formula using eq 11, which optimizes the temperature dependence of $\bar{\chi}$. The spinodal lines (---), also shown, were calculated from eq 8 and 11.

the temperature range of interest[16]). With an average density of 0.9 g/cm^3,[16] the monomer volume of PBD is 99.63 Å^3 and the number of monomers per chain is 18.5 for 1K PBD and 46.3 for 2.5K PBD. Substitution of these values into eq 9 yields $\phi_c = 0.423$ and 0.537 for the 1K and 2.5K PBD mixtures, respectively. Experimental cloud point curves[8] determined from optical density measurements extrapolated to infinitely slow heating and cooling rates are shown for both mixtures in Figure 1 as a function of the weight fraction of PS. The interpolated maxima in these curves are consistent with the calculated values of ϕ_c. Using eq 6–8 for each of the experimentally determined cloud points, we find that calculated values of $\bar{\chi}$, although obtained for different concentrations and molecular weights, correlate smoothly with the temperature (K), as shown in Figure 2. Linear least-squares analysis of these data yields

$$\bar{\chi} = 6.96 \times 10^5 / T^{2.65} \tag{12}$$

over the temperature range of $313 \leq T \leq 403$ K. The solid lines in Figure 1 depict the binodals calculated from eq 6 and 11 whereas the dashed lines are the spinodals calculated from eq 8 and 11. This result differs from the approach previously used by Roe and Zin,[17] where $\bar{\chi}$ was assumed to depend both on temperature and composition. However, for the results obtained here, calculated phase diagrams agree with their experimental results for those mixtures where the molecular weight is well defined and where the chemical composition of the PBD is similar to that used in this study. The consolute temperatures calculated from eq 10 and 11 are 59 and 125 °C for the 1K and 2.5K PBD mixtures with 2K PS, respectively.

It should be noted that, due to kinetic effects, the experimental cloud point curve does not necessarily correspond to the binodal line. Consequently, for these low molecular weight systems where the viscosities are low, extrapolation to infinitely slow heating and cooling rates was used to minimize effects associated with this problem. In addition, while the polydispersity in these systems is low, it is not insignificant. As shown by Koningsveld,[18] this may dramatically alter the shape of the binodal. We are currently in the process of examining the effects of polydispersity on our calculations. Therefore, due to the factors outlined above, the cloud points in Figure 1 may not correspond to the coexistence curves.

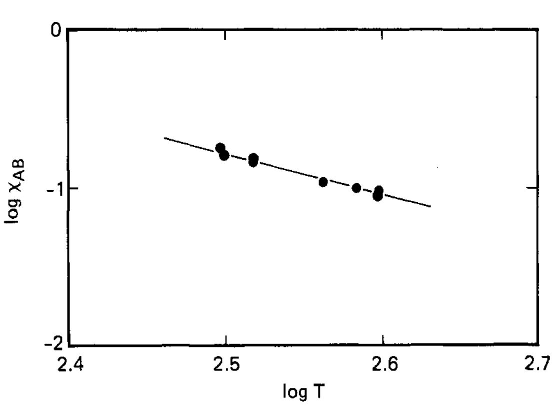

Figure 2. Effective interaction parameter $\bar{\chi}$ evaluated from the free energy formula and the experimentally observed cloud point curves as a function of temperature. Results of this correlation are shown in eq 12.

Spinodal Decomposition: Evaluation of the Gradient Term

Sudden quenching below the spinodal line (see Figure 1) forces polymer mixtures to develop unstable fluctuations leading to phase separation. In the presence of long-range inhomogeneities of the concentration, spatial variations of the free energy of mixing per unit volume can be taken into account by assuming that the concentration ϕ appearing in eq 2 is a function of position. However, an additional *positive* contribution to the free energy is expected to arise from local gradients of concentration.[1] In the simplest formulation, this extra term takes the form

$$\Delta G_f / kT = [\alpha(\phi) n_A' + \beta(\phi) n_B'](\nabla\phi)^2 \tag{13}$$

where ΔG_f, n_A', and n_B' refer to a region of space large enough to contain many molecules but considerably smaller than the characteristic fluctuation wavelength. The two functions $\alpha(\phi)$ and $\beta(\phi)$ have been evaluated[9-11] by applying linear response theory combined with single-chain approximations to the calculation of the scattering function, $S(q)$, defined as the Fourier transform of the concentration correlation function $\langle[\phi(\mathbf{0}) - \langle\phi\rangle][\phi(\mathbf{r}) - \langle\phi\rangle]\rangle$.[15] Extension to the case where $N_A \neq N_B$ yields

$$\alpha(\phi) = \langle r_A^2 \rangle / 36\phi^2 \tag{14a}$$

$$\beta(\phi) = \langle r_B^2 \rangle / 36(1 - \phi)^2 \tag{14b}$$

where $\langle r_i^2 \rangle$ is the mean square end-to-end distance of chain i. From eq 2, 13, and 14 the complete expression for the local free energy density is given by

$$\Delta G / kT\Omega = g(\phi,\nabla\phi) = \frac{\phi}{N_A v_A} \ln \phi + \frac{1-\phi}{N_B v_B} \ln (1-\phi) + \frac{\chi_{AA}}{2v_A}\phi^2 + \frac{\chi_{BB}}{2v_B}(1-\phi)^2 + \frac{\chi_{AB}}{v_A}\phi(1-\phi) + Q(A,B,\phi)(\nabla\phi)^2 \tag{15}$$

where

$$Q(A,B,\phi) = \frac{\langle r_A^2 \rangle}{36\phi v_A N_A} + \frac{\langle r_B^2 \rangle}{36(1-\phi) v_B N_B} \tag{16}$$

and Ω is a convenient reference volume.

At equilibrium, the partition function of a macroscopic system of volume V is

$$Z(\phi_0,T) = \int \exp\left[-\int_V g(\phi,\nabla\phi)\, d^3\mathbf{r}\right] \{d\phi\} \tag{17}$$

where $\phi(\mathbf{r})$ is a constrained random field satisfying the requirement

$$\int \phi \, \mathrm{d}^3\mathbf{r} = \phi_0 V \tag{18}$$

ϕ_0 being the average value of the concentration. At equilibrium in the mixed phase or during the initial stages of spinodal decomposition, concentration fluctuations must be small compared to ϕ_0. Therefore, we can write $\phi = \phi_0 + \Phi(\mathbf{r})$ and expand $g(\phi,\nabla\phi)$ in powers of Φ. Because of eq 18, the linear terms of the expansion vanish. Neglecting terms higher than quadratic and expressing $\Phi(\mathbf{r})$ as a Fourier cosine series with the exclusion of the constant term as required by eq 18, we obtain the partition function in factorized form:

$$Z(\phi_0,T) = Z_{\mathrm{mf}}(\phi_0,T) \prod_{0<|q|<\lambda^{-1}} \left\{ \int_{-\infty}^{\infty} \exp[-m(\mathbf{q},\phi_0)\Phi^2(\mathbf{q})] \, \mathrm{d}\Phi_{\mathrm{c}}(\mathbf{q}) \right\} \tag{19}$$

where

$$m(q,\phi_0) = \frac{V}{8}\left[q^2 Q(A,B,\phi_0) - \frac{\bar{\chi}}{\upsilon_{\mathrm{A}}} + \frac{1}{2N_{\mathrm{A}}\upsilon_{\mathrm{A}}\phi_0} + \frac{1}{2N_{\mathrm{B}}\upsilon_{\mathrm{B}}(1-\phi_0)} \right]$$

$\Phi_{\mathrm{c}}(q)$ is the Fourier cosine transform of the fluctuation field Φ. The mean field contribution $Z_{\mathrm{mf}}(\phi_0,T)$ corresponds to the classical mixing term. The other factors, obtained by integrating over the Fourier amplitudes, are associated with harmonic fluctuations of different wavelength. The cutoff at $|q| = \lambda^{-1}$, with $\lambda \sim (\langle r_{\mathrm{AB}}^2 \rangle)$,$^{1/2}$ must be introduced for physical consistency. After sudden quenching below the spinodal temperature some of the integrals do not converge since $m(q,\phi_0) < 0$ when $q < q_{\mathrm{c}}$, where q_{c} is defined by the equation

$$q_{\mathrm{c}}^2 Q(A,B,\phi_0) - \frac{\bar{\chi}(T)}{\upsilon_{\mathrm{A}}} + \frac{1}{2N_{\mathrm{A}}\upsilon_{\mathrm{A}}\phi_0} + \frac{1}{2N_{\mathrm{B}}\upsilon_{\mathrm{B}}(1-\phi_0)} = 0 \tag{20}$$

All fluctuations with $q < q_{\mathrm{c}}$ are unstable and can initiate decomposition. A dynamical extension of this analysis allows the evaluation of the scattering function during the initial stages of phase separation. Accurate prediction of the time scale poses a nontrivial problem. However, q_{c} can be related to measurable quantities provided $\bar{\chi}$ is known.

The operational derivation of eq 16 is basically an extrapolation of *single-chain* concepts, like the Debye scattering function. The highly cooperative nature of polymer blends may require more direct physical justifications of the assumed form of the gradient term. In polymer mixtures long-range fluctuations of the concentration affect both the translational freedom of the chains and the energetics of their repulsive interactions. However, these effects are already taken into account by assuming that ϕ is a function of position. Extra terms due to concentration gradients can only be associated with nonlocal variables, such as the configurational free energy of the whole chain. For bulk mixtures of polymers with comparable molecular weights, concentration fluctuations do not introduce substantial alterations to the "steric field" surrounding each molecule but redistribute the local intensity of repulsive interactions, modifying the spatial distribution of its chain segments. We assume that the long-range fluctuations are slow in comparison to the statistical equilibration time of the general chain. In the presence of a slowly varying concentration gradient, the extra configurational contribution to the mixing free energy must be evaluated for each chain by subtracting the ideal value from the calculated configurational part.

Since only *differences* between configurational terms are required, simplified chain models can be used. Gaussian units can be defined by grouping together sets of r consecutive monomers, with $r \gg 1$. We assume r to be the same for molecules of both kinds. By scaling requirements, the quantities $\chi_{\mathrm{AB}}{}^{\mathrm{G}}$, $\chi_{\mathrm{AA}}{}^{\mathrm{G}}$, $\chi_{\mathrm{BB}}{}^{\mathrm{G}}$, $\upsilon_{\mathrm{A}}{}^{\mathrm{G}}$, and $\upsilon_{\mathrm{B}}{}^{\mathrm{G}}$, redefined for the general Gaussian strand, are r times larger than their monomer values, whereas the numbers of Gaussian segments per chain $N_{\mathrm{A}}{}^{\mathrm{G}}$ and $N_{\mathrm{B}}{}^{\mathrm{G}}$ are r times smaller than N_{A} and N_{B}. We represent the general A molecule as a sequence of $N_{\mathrm{A}}{}^{\mathrm{G}} + 1$ beads linked by $N_{\mathrm{A}}{}^{\mathrm{G}}$ springs. Up to first gradient terms, the expansion of the density ϕ is $\phi = \phi_0 + \Delta\cdot(\mathbf{r} - \mathbf{r}_0)$, where $\phi_0 = \phi(\mathbf{r}_0)$. The partition function of a Gaussian molecule immersed in a concentration gradient reduces to the product of three independent factors. For a chain of type A contained in a representative cube defined by $0 < X_i$ ($i = 1, 2, 3$) $< L$, the general factor Z_x can be written as

$$Z_x = \int_0^L \mathrm{d}X \int \{\mathrm{d}x_n\} \exp\left\{ -\frac{C}{2kT}\sum_{m=1}^{N_{\mathrm{A}}{}^{\mathrm{G}}} x_m{}^2 + \chi_{\mathrm{AA}}{}^{\mathrm{G}} N_{\mathrm{A}}{}^{\mathrm{G}} \phi_0 + \chi_{\mathrm{AB}}{}^{\mathrm{G}} N_{\mathrm{B}}{}^{\mathrm{G}} (1-\phi_0) + (\chi_{\mathrm{AA}}{}^{\mathrm{G}} - \chi_{\mathrm{AB}}{}^{\mathrm{G}})\Delta \sum_{i=1}^{N_{\mathrm{A}}{}^{\mathrm{G}}} [X + \sum_{m=1}^{i} x_m] \right\} \tag{21}$$

where C is the spring rigidity, X the general coordinate of the first bead, Δ the gradient component in the X direction, and ϕ_0 the concentration at $X_1 = X_2 = X_3 = 0$. The $\{x_n\}$ are the components of the $N_{\mathrm{A}}{}^{\mathrm{G}}$ Gaussian bond vectors. Omitting irrelevant constants, evaluation of the integral yields

$$Z_x = Z_0 Z_{\mathrm{int}} \tag{22}$$

where

$$Z_0 = \int_0^L \mathrm{d}X \exp[N_{\mathrm{A}}{}^{\mathrm{G}}(\chi_{\mathrm{AA}}{}^{\mathrm{G}} - \chi_{\mathrm{AB}}{}^{\mathrm{G}})X\Delta] \tag{23}$$

refers to the motion of the molecule as a whole and

$$Z_{\mathrm{int}} = \left(\frac{2\pi kT}{C}\right)^{N_{\mathrm{A}}{}^{\mathrm{G}}/2} \exp\left\{ \frac{kT(\chi_{\mathrm{AA}}{}^{\mathrm{G}} - \chi_{\mathrm{AB}}{}^{\mathrm{G}})^2\Delta^2}{2C} \sum_{m=1}^{N_{\mathrm{A}}{}^{\mathrm{G}}} (N_{\mathrm{A}}{}^{\mathrm{G}} - m + 1)^2 \right\} \tag{24}$$

results from inhomogeneities of the energetic interaction with the external medium as well as from purely configurational effects. Translational degrees of freedom are already taken into account in eq 21 and 22, which also allow for inhomogeneities of the energetic interaction, assuming that ϕ is a function of position. The only nonlocal contribution due to gradient effects is purely configurational. The corresponding free energy $-kT \ln Z_{\mathrm{conf}}$ is calculated by subtracting from $-kT \ln Z_{\mathrm{int}}$ the energy of interaction with the surrounding medium due only to the gradient component considered.

$$-kT \ln Z_{\mathrm{conf}} = -kT \ln Z_{\mathrm{int}} + kT(\chi_{\mathrm{AA}}{}^{\mathrm{G}} - \chi_{\mathrm{AB}}{}^{\mathrm{G}})\Delta \langle \sum_{i=1}^{N_{\mathrm{A}}{}^{\mathrm{G}}} \sum_{m=1}^{i} x_m \rangle \tag{25}$$

yielding for $N_{\mathrm{A}}{}^{\mathrm{G}} \gg 1$

$$-kT \ln Z_{\mathrm{conf}} \simeq \frac{k^2T^2(\chi_{\mathrm{AA}}{}^{\mathrm{G}} - \chi_{\mathrm{AB}}{}^{\mathrm{G}})^2\Delta^2(N_{\mathrm{A}}{}^{\mathrm{G}})^3}{6C} - \frac{kTN_{\mathrm{A}}{}^{\mathrm{G}}}{2} \ln\left(\frac{2kT\pi}{C}\right) \tag{26}$$

where the logarithmic term expressing the ideal contribution has to be dropped.

Summing over the three directions and returning to monomer variables, we obtain in this way the extra free energy of the general A chain immersed in a concentration gradient. Applying the same procedure to the B molecules and summing over both contributions, we finally calculate the gradient term. With the nomenclature of eq 16

$$Q(A,B,\phi) = \frac{1}{18 v_A}(\chi_{AB} - \chi_{AA})^2 \phi \langle r_A{}^2 \rangle N_A + \frac{1}{18 v_B}\left(\frac{v_B}{v_A}\chi_{AB} - \chi_{BB}\right)^2 (1 - \phi)\langle r_B{}^2\rangle N_B \quad (27)$$

Compared to eq 16, eq 27 predicts a stronger dependence of $Q(A,B,\phi)$ and, consequently, q_c on molecular weight. This strong dependence of q_c on molecular weight is found experimentally. A dramatic decrease in q_c is observed in going from low molecular weight mixtures of polystyrene and polybutadiene[8] to high molecular weight mixtures of polystyrene and poly(vinyl methyl ether).[12] Previous theories predict values of q_c inconsistent with these experimental findings. It should be noted that the Gaussian approximation becomes problematic for low molecular weight polymers whose number of Gaussian chain segments is small. It is important to note that even with the assumption that the interaction parameter is not a function of concentration, the dynamics of spinodal decomposition depends upon three independent parameters. Our evaluation of the gradient term has also neglected the requirement of constant overall density. However, this inaccuracy is not serious as long as the characteristic fluctuation wavelength is much larger than the coil size. From all experiments on polymer mixtures to date, this latter condition is always observed.

Demixed Phases: Interphase Thickness and Surface Tension near the Consolute Point

Slightly below the critical point, even after decomposition, fluctuations may contribute to the total value of the free energy in an important way. Following previous treatments,[1] in this section we evaluate the surface tension by neglecting fluctuations. Our results are therefore only indicative. A more complete analysis, possibly based on the modern developments of field theory, is required. For simplicity, we assume that the polymer mixture has an overall concentration corresponding to the consolute value ϕ_c.

Up to the fourth order in $(\phi - \phi_c)$, the expansion of the local part of the free energy density in the vicinity of the consolute point, where $\phi = \phi_c$ and $\bar{\chi} = \bar{\chi}_c(T = T_c)$, is

$$\frac{\Delta G}{kT\Omega} = \frac{\Delta G(\phi_c)}{kT\Omega} + \frac{\partial}{\partial\phi}\left(\frac{\Delta G}{kT\Omega}\right)_{\phi=\phi_c}(\phi - \phi_c) - \frac{(\bar{\chi} - \bar{\chi}_c)}{v_A}(\phi - \phi_c)^2 + \frac{1}{12 N_A v_A}\left(\frac{N_B v_B}{N_A v_A}\right)^{1/2}\left[1 + \left(\frac{N_A v_A}{N_B v_B}\right)^{1/2}\right]^4 (\phi - \phi_c)^4 \quad (28)$$

By analogous expansion of the chemical potentials, the coexisting concentrations become in this limit

$$\phi_\pm = \phi_c \pm \frac{\left[6 N_A \left(\frac{N_A v_A}{N_B v_B}\right)^{1/2} (\bar{\chi} - \bar{\chi}_c)\right]^{1/2}}{\left[1 + \left(\frac{N_A v_A}{N_B v_B}\right)^{1/2}\right]^2} \quad (29)$$

At $T < T_c$, we consider a polymer mixture of concentration varying smoothly along the x coordinate. Let ϕ_+ and ϕ_- be the limiting concentrations at $x = \pm\infty$, respectively. The concentration profile can be calculated by minimizing the total free energy, obtained by adding the gradient term to eq 28. The constraint of a fixed average concentration can be incorporated by adding to the free energy functional a suitable Lagrange multiplier. This corresponds to leaving the coefficient of the linear term of the expansion (28) free to take arbitrary values. In keeping with our approximation scheme, $Q(A,B,\phi)$ has to be taken with $\phi = \phi_c$, $\chi_{AA} = \chi^c{}_{AA}$, $\chi_{AB} = \chi^c{}_{AB}$, and $\chi_{BB} = \chi^c{}_{BB}$, where $\chi^c{}_{AA}$, $\chi^c{}_{AB}$, and $\chi^c{}_{BB}$ are the consolute values of the separate interaction parameters. Introducing the quantity $\Phi = \phi - \phi_c$ and the variable $\alpha = (N_A v_A / N_B v_B)^{1/2}$, we may write the reduced free energy functional $\mathcal{G}$ per infinite strip of unit area by subtracting the consolute value.

$$\frac{\mathcal{G}[\Phi(x)]}{kT} = \int_{-\infty}^{\infty}\left\{\lambda\Phi - \frac{\bar{\chi} - \bar{\chi}_c}{v_A}\Phi^2 + \frac{f(\alpha)}{12 N_A v_A}\Phi^4 + Q(\phi_c, T_c) \times \left(\frac{\mathrm{d}\Phi}{\mathrm{d}x}\right)^2\right\}\mathrm{d}x \quad (30)$$

where λ is the Lagrange multiplier and $f(\alpha) = (1 + \alpha)^4/\alpha$. Minimization of the functional (30) yields the associated Euler–Lagrange equation

$$\frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} = \frac{\lambda}{2Q} - \frac{\bar{\chi} - \bar{\chi}_c}{v_A Q}\Phi + \frac{f(\alpha)}{6 N_A v_A Q}\Phi^3 \quad (31)$$

According to eq 29, the boundary conditions at $x = \pm\infty$ are

$$\Phi(\pm\infty) = \pm\Phi_\infty = \pm\left(\frac{6 N_A(\bar{\chi} - \bar{\chi}_c)}{f(\alpha)}\right)^{1/2} \quad (32)$$

At $x = \pm\infty$ all derivatives of $\Phi(x)$ must vanish. This latter condition is satisfied by taking $\lambda = 0$ in eq 31. Assuming that $\Phi(x)$ is monotonic, we introduce $u = \mathrm{d}\Phi/\mathrm{d}x$ and rewrite eq 31 in the form

$$\frac{\mathrm{d}u^2}{\mathrm{d}\Phi} = \frac{f(\alpha)}{3 N_A v_A Q}\Phi^3 - \frac{2(\bar{\chi} - \bar{\chi}_c)}{v_A Q}\Phi \quad (33)$$

which solved in the range $-\Phi_\infty < \Phi < \Phi_\infty$ with the condition $u(\pm\Phi_\infty) = 0$, gives

$$\frac{\mathrm{d}\Phi}{\mathrm{d}x} = \left(\frac{f(\alpha)}{12 N_A v_A Q}\right)^{1/2}[\Phi_\infty{}^2 - \Phi^2] \quad (34)$$

Shifting the origin to the point where Φ vanishes, final integration yields

$$\Phi = \left(\frac{6 N_A(\bar{\chi} - \bar{\chi}_c)}{f(\alpha)}\right)^{1/2}\tanh\left[x\left(\frac{(\bar{\chi} - \bar{\chi}_c)}{2 v_A Q}\right)^{1/2}\right] \quad (35)$$

From eq 27, at constant ratio of the molecular weights, $Q \propto N^2 f(\chi_{AA}, \chi_{BB}, \chi_{AB})$, where f is a homogeneous quadratic form and N is the number of monomers per chain. If eq 12 is valid, from eq 35 we find that the width of the interface is proportional to $((T_c - T)/T_c)^{-1/2} N^{1/2}[Q(N,T_c)]^{1/2}$, where Q is globally independent of N only if the three interaction parameters have the same temperature dependence. The derivation of eq 28–35, in the vicinity of the consolute point, is formally similar to that developed by Joanny and Leibler[22] but differs in an important way. Terms of first order in the expansion of the free energy do not vanish. Their relevance becomes negligible only with the Lagrange multiplier at coexistence. Experimental conditions can be conceived in which either λ does not vanish or its introduction is physically unjustified.

We adopt a Joanny–Leibler procedure for the calculation of the interfacial free energy. In the absence of the gradient term, we could place an ideal separation surface at $x = 0$, such that $\Phi = +\Phi_\infty$ for $x > 0$ and $-\Phi_\infty$ for $x < 0$. In reality, nonlocal effects force the profile to be continuous. Therefore, the correct definition of the interfacial free energy is

$$\frac{\sigma}{kT} = \int_{-\infty}^{\infty} \{g(\Phi(x)) - g(\pm\Phi_\infty)\}\, \mathrm{d}x \tag{36}$$

where the + sign has to be taken in $x > 0$ and $g(\Phi(x))$ is the local free energy density given in eq 15. Expansion of the integrand in powers of $\Phi(x)$ gives, to the first nonvanishing terms, the approximation

$$\frac{\sigma}{kT} = \int_{-\infty}^{\infty} \left\{ Q\left(\frac{\mathrm{d}\Phi}{\mathrm{d}x}\right)^2 + \frac{1}{2kT}\left(\frac{\partial^2 g}{\partial \phi^2}\right)_{\phi=\phi_c} [\Phi^2(x) - \Phi_\infty^{\ 2}] + \frac{1}{24kT}\left(\frac{\partial^4 g}{\partial \phi^4}\right)_{\phi=\phi_c} [\Phi^4(x) - \Phi_\infty^{\ 4}] \right\} \mathrm{d}x \tag{37}$$

In the expansion of the integrand, linear terms give a rigorously vanishing contribution because of the requirement of fixed overall composition. Using eq 35, we finally obtain

$$\frac{\sigma}{kT} = \frac{16(\bar{\chi} - \bar{\chi}_c)^{3/2} N_A}{f(\alpha)} \left(\frac{Q}{2v_A}\right)^{1/2} \tag{38}$$

At constant ratio of the molecular weights and assuming a power law dependence of $\bar{\chi}$ on temperature, we obtain

$$\frac{\sigma}{kT} \propto \left[\frac{T_c - T}{T_c}\right]^{3/2} N^{-1/2}[Q(N,T_c)]^{1/2} \tag{39}$$

where N is the molecular weight of one component. In the work of Joanny[9] and de Gennes,[10] $Q(N,T_c)$ does not depend on N at fixed ratio of the molecular weights, in which case eq 39 reduces to the Joanny and Leibler[22] result. The same conclusion applies to our expression of Q only if all the three interaction parameters χ_{AA}, χ_{AB}, and χ_{BB} have the same temperature dependence, which at the moment, does not seem very likely.

At 10 K below the critical temperature, assuming tentative values of the interaction parameters, application of eq 38 to the PS/PBD system yields values of σ of ~0.1 erg/cm^2 with an interphase thickness on the order of 100 Å, not much larger than the coil size (~30 Å). Much below the consolute temperature, σ would approach higher values with an interfacial thickness of a few angstroms, consistent with previous theoretical work.[20,21] With a chain size of ~30 Å, our derivation of the gradient term becomes inaccurate in this limit.

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Registry No. PS (homopolymer), 9003-53-6; PBD (homopolymer), 9003-17-2.

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