separately provided. For our CPC calculations S is minimized with respect to $\{\tilde{T}, \sigma_1, \sigma_2, ..., \sigma_{R*}\}$, where

$$\sigma_i \equiv \ln (\phi_i''/\phi_i')/m_i \tag{A4-2}$$

and $\tilde{T} = \tilde{T}/T^*$, where T^* is a constant scale factor chosen so that $\tilde{T}$ has about the same magnitude as σ. The algorithm NAG:C05NAF, which has to evaluate elements of the Jacobian matrix of $(\Delta\mu' - \Delta\mu'')^2$, performs best when its arguments are of similar magnitude.

For B–W plot and phase volume ratio calculations S is minimized with respect to $\{\sigma_1, \sigma_2, ..., \sigma_R^*\}$, since here T is fixed.

Before NAG:C05NAF is called a preliminary search is performed with respect to σ (or σ and $\tilde{T}$) to locate a minimum in S, using $\sigma_i = \sigma'$ for all i. This condition on the σ_i is, in fact, the case for ΔG function GI (eq 26) for which σ depends only on ϕ, though not for GII (eq 27), where $\sigma_i = \sigma_i(m_i)$. Once this approximate solution $(\sigma', \tilde{T}')$ is found, artificial bounds $\Delta\sigma$ and ΔT are placed on the arguments, viz.: $(\sigma' - \Delta\sigma) < \sigma_i < (\sigma' + \Delta\sigma)$ and $(\tilde{T}' - \Delta T) < \tilde{T} < (\tilde{T} + \Delta T)$ so that the program is confined to work over a limited range in σ/T space, with S being set to a very large value if an iteration results in a root being "out of bounds".

For the calculations presented in this paper true roots were usually obtained with $S < 10^{-16}$, with cloud point temperatures accurate to $\pm 5 \times 10^{-4}$ K and with phase compositions accurate to $\pm 10^{-4}$.

A tricky feature of these calculations is to avoid the trivial roots $\sigma_i = 0$. This problem becomes more pronounced near a critical point, where the two phases become identical. We did not pursue these calculations, but one possibility is to divide out the trivial root and minimize $S = \sum_i(\Delta\mu_i' - \Delta\mu_i'')^2/\sigma_i$; but now the convergence criteria must be chosen with care since when σ is small, S may become rather large.

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Interfacial Properties of Immiscible Homopolymer Blends in the Presence of Block Copolymers

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ABSTRACT: The emulsifying effect of block copolymers in immiscible homopolymer blends is studied theoretically, using a general formalism for inhomogeneous multicomponent polymer systems developed earlier by the authors. The reduction in interfacial tension with increasing block copolymer concentration is calculated for a range of copolymer and homopolymer molecular weights, and comparison is made with the experimental results of Riess and co-workers on the polystyrene–polybutadiene–copolymer–styrene system. The calculated interfacial density profiles clearly show greater exclusion of the homopolymers from the interphase region as the molecular weight of the block copolymer is increased. We also estimate the critical concentration of block copolymer required for micellar aggregation in the bulk of the homopolymer.

1. Introduction

An interesting property of diblock copolymers in incompatible homopolymer blends is their behavior as emulsifying agents, similar to soap molecules at an oil–water interface. The practical importance of this observation is that outstanding mechanical properties may be obtained by properly choosing the type and molecular weight of the block copolymer to maximally lower the interfacial tension of highly incompatible homopolymers, thereby facilitating phase separation into uniformly dispersed microdomains. Early work in this area has been carried out by Riess and co-workers[1–4] and Kawai et al.[5,6] for ternary blends of polystyrene–polyisoprene with the associated block copolymer. Recently, Cohen and Ramos[7,8] have studied the influence of diblock copolymers on the structure and properties of polybutadiene–polyisoprene

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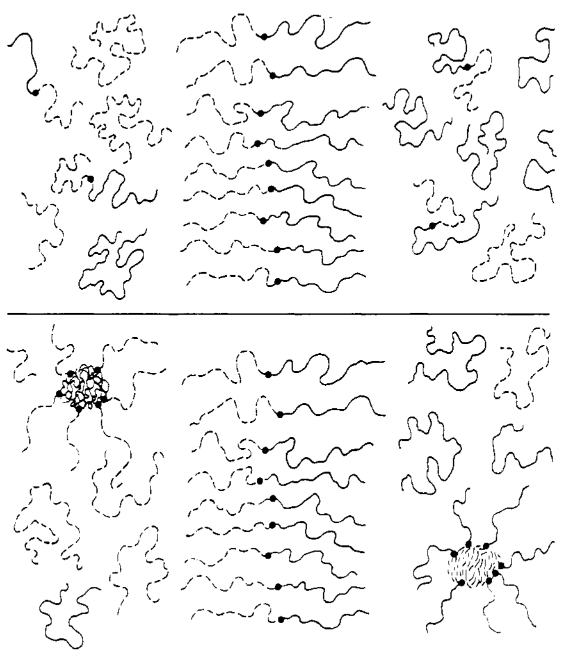

Figure 1. Schematic diagram of interphase between the immiscible homopolymers containing corresponding diblock copolymers. Some of the block copolymers settle in the interphase region, while those in the bulk are either randomly distributed (upper panel) or aggregate to form micelles (lower panel), depending on the copolymer concentration. The entanglements between polymers are not shown in the interest of clarity.

blends, and Riess et al.[9] have carried out measurements of the interfacial tension in the quaternary system polystyrene–polybutadiene–styrene–copolymer.

In this paper we make use of a general theory of inhomogeneous multicomponent polymer system, developed by us earlier,[10,11] to study the interfacial properties of diblock copolymers in immiscible homopolymer blends. As a specific example, we consider the system studied by Riess et al.[9] and we compare our theory with their measurements of the interfacial tension.

There are a number of factors which determine the state of the block copolymers in a phase-separated homopolymer system. First, the entropy of mixing of the block copolymers with the homopolymers favors a random distribution of the copolymers. On the other hand, localization of the block copolymers at the interface displaces the homopolymers away from each other and lowers the homopolymer enthalpy of mixing. In addition, each block of the copolymer will prefer to extend into its compatible homopolymer to lower the block copolymer–homopolymer enthalpy of mixing. This situation is illustrated schematically in the upper panel of Figure 1. Besides suffering an entropy loss as a whole because of confinement to the interphase, there is a further entropy loss for the blocks of the copolymer arising from the restriction of the blocks to their respective homopolymer regions. Finally, extension or compression of the copolymer chains, as well as the effect of the excluded volume at the interphase for the homopolymers, leads to further loss of entropy. In the theoretical development we include the contributions to the free energy from all these effects, and we obtain the concentration of block copolymers at the interface, as well as the associated reduction in the interfacial tension.

Referring to the lower panel in Figure 1, it is clear that similar considerations for the enthalpy and entropy of mixing of the block copolymers could favor micellar aggregation[5] rather than random distribution in the bulk of the homopolymers. In this case the micelles could compete with the interfacial region for copolymer chains, and the amount in each state would depend on the relative reduction in the free energy, as well as the surface area. In this paper we do not give a complete treatment of this complicated case but restrict ourselves to a simple estimate of the critical micelle concentration (CMC) for the formation of a regular array of noninteracting micelles in the bulk. We also ignore the possibility of micellar adsorption to the interface.[12]

In section 2 we review some of the general theory of inhomogeneous polymer systems applicable to this problem, and we derive expressions for the mean fields acting on the block copolymers and homopolymers. The equations for the polymer distribution functions are solved numerically using the same techniques as described in the earlier paper[10] (hereafter referred to as I), and section 3 presents the results of the calculations for the interfacial tension and the corresponding interfacial polymer density profiles. Section 4 deals with the estimate of the CMC, and a general discussion of the results is given in section 5.

2. Theory

In this section we rely heavily on the results obtained in I, in particular section 4, entitled "Extension to Block Copolymers". To review our notation, we denote the number of polymer chains of type p by $\tilde{N}_p = N_p/Z_p$, where N_p is the number of monomer units and Z_p the degree of polymerization. N_s is the number of solvent molecules and $\tilde{N}_s = N_s$, since $Z_s = 1$. When polymers A and B are linked together to form a block copolymer AB, we have $\tilde{N}_{\mathrm{AB}} = N_{\mathrm{CA}}/Z_{\mathrm{CA}} = N_{\mathrm{CB}}/Z_{\mathrm{CB}}$. In general, we will use the subscript κ to label homopolymers, solvent molecules, or block copolymers. Furthermore if $\rho_{0\kappa}$ is the density of the pure material, and ρ_0 is some reference density, we define the scaled quantities

$$\hat{\omega}_\kappa = \frac{\rho_{0\kappa}}{\rho_0}\omega_\kappa \qquad \hat{b}_\kappa{}^2 = \frac{\rho_{0\kappa}}{\rho_0}b_\kappa{}^2$$
$$r_\kappa = \frac{\rho_0}{\rho_{0\kappa}}Z_\kappa \qquad \hat{\mu}_\kappa = \frac{\rho_{0\kappa}}{\rho_0}\mu_\kappa \tag{2-1}$$

where ω_κ is the mean field acting on component κ, b_κ is the Kuhn length, μ_κ is the chemical potential, and we work with volume fractions

$$\phi_\kappa = \rho_\kappa/\rho_{0\kappa} \tag{2-2}$$

which are equal to the reduced densities since we assume no volume change upon mixing.

First we derive expressions for the chemical potentials and utilize them to obtain the mean field equations for our system, which consists of two homopolymers, the corresponding block copolymer, and a solvent. The free energy $\mathcal{F}$ (in units of $k_{\mathrm{B}}T$) for this inhomogeneous mixture is given by eq 4-2 of I, which may be written in the reduced form

$$\hat{\mathcal{F}} \equiv \mathcal{F}/\rho_0 = \int \mathrm{d}^3r \left\{\hat{f}_{\mathrm{h}} - \sum_\kappa \phi_\kappa \left[\hat{\omega}_\kappa + \frac{1}{r_\kappa}\ln \phi_\kappa\right] - \frac{1}{12}\sum_{\kappa,\kappa'} \chi_{\kappa\kappa'}\sigma_{\kappa\kappa'}{}^2 \vec{\nabla}\phi_\kappa \cdot \vec{\nabla}\phi_{\kappa'}\right\} - \frac{1}{\rho_0}\sum_\kappa \tilde{N}_\kappa \ln\left(\frac{\rho_0}{r_\kappa Z_\kappa e}\right) + \frac{1}{\rho_0}\sum_\kappa^C \tilde{N}_\kappa \ln\left(\frac{\tilde{N}_\kappa}{Z_\kappa Q_\kappa e}\right) \tag{2-3}$$

where $\chi_{\kappa\kappa'}$ is the Flory–Huggins interaction parameter[13] and $\sigma_{\kappa\kappa'}$ is a short-range parameter (of order $\hat{b}_\kappa$). Z_κ is the kinetic contribution to the partition function, and for the block copolymer $Z_{AB} = Z_A Z_B$. $\mathcal{Q}_\kappa$ is defined as a multiple integral over the fundamental chain distribution function, and for the block copolymer this definition is modified to reflect the linkage of the two blocks. The summation over κ with a "C" over the summation sign means that the block copolymer is to be treated as a single component. No "C" over the summation sign indicates that the A and B blocks of the copolymer are treated as independent components. The part of the free energy density of the inhomogeneous system which has the same functional form as the Flory–Huggins free energy for a uniform system is denoted by $\hat{f}_h$

$$\hat{f}_h = \sum_\kappa \phi_\kappa \hat{\mu}_{0\kappa} + \frac{1}{2}\sum_{\kappa,\kappa'} \chi_{\kappa\kappa'}\phi_\kappa\phi_{\kappa'} + \sum_\kappa \frac{\phi_\kappa}{r_\kappa} \ln \phi_\kappa \tag{2-4}$$

Now for a bulk, homogeneous phase ϕ_κ and $\hat{\omega}_\kappa$ are constant and, as shown in I, are related by

$$\frac{\rho_0\phi_\kappa}{r_\kappa} = \frac{\tilde{N}_\kappa}{\mathcal{Q}_\kappa} e^{-r_\kappa\hat{\omega}_\kappa} \tag{2-5}$$

for homopolymers or solvents. Equation 2-5 follows from eq 2-31 of I, using the relation $\mathcal{Q}_\kappa = N_\kappa/\rho_{0\kappa}$, which is also discussed in the earlier paper. Denoting the blocks of the copolymer C by CA and CB, we also have the relations

$$\frac{\rho_0\phi_C}{r_C} = \frac{\tilde{N}_C}{\mathcal{Q}_C} e^{-(r_{CA}\hat{\omega}_{CA} + r_{CB}\hat{\omega}_{CB})} \tag{2-6}$$

where $r_C = r_{CA} + r_{CB}$, $\rho_{0C}^{-1} = (Z_{CA} + Z_{CB})^{-1}(Z_{CA}\rho_{0A}^{-1} + Z_{CB}\rho_{0B}^{-1})$, $r_{CA}\hat{\omega}_{CA} + r_{CB}\hat{\omega}_{CB}$ is the total mean field acting on the copolymer, and

$$\frac{\rho_0\phi_{CA}}{r_{CA}} = \frac{\rho_0\phi_{CB}}{r_{CB}} = \frac{\rho_0\phi_C}{r_C} \tag{2-7}$$

for a random distribution of block copolymers in a homogeneous homopolymer–solvent phase. The free energy per unit volume for the uniform phase then becomes, from eq 2-3,

$$\hat{f} \equiv \hat{\mathfrak{F}}/V = \hat{f}_h - \frac{\phi_C}{r_C} \ln \left(\frac{\rho_0\phi_C}{r_C e} \right) \tag{2-8}$$

which can be rewritten in the standard Flory–Huggins form, treating the block copolymer as a single component,

$$\hat{f} = \sum_\kappa^{C} \phi_\kappa \hat{\mu}_{0\kappa} + \frac{1}{2}\sum_{\kappa,\kappa'}^{C} \chi_{\kappa\kappa'}\phi_\kappa\phi_{\kappa'} + \sum_\kappa^{C} \frac{\phi_\kappa}{r_\kappa} \ln \phi_\kappa \tag{2-9}$$

with the copolymer chemical potential and interaction parameters now given by

$$\hat{\mu}_{0C} = \frac{1}{r_C}(r_{CA}\hat{\mu}_{0A} + r_{CB}\hat{\mu}_{0B}) + \chi_{AB}\frac{r_{CA}r_{CB}}{r_C^2} - \frac{1}{r_C} \ln \left(\frac{\rho_0 r_C}{r_{CA}r_{CB}} \right) \tag{2-10}$$

and

$$\chi_{C\kappa} = \frac{1}{r_C}(r_{CA}\chi_{A\kappa} + r_{CB}\chi_{B\kappa}) - \chi_{AB}\frac{r_{CA}r_{CB}}{r_C^2} \tag{2-11}$$

As expected, the copolymer self-interaction parameter χ_{CC} vanishes. The combination formulas eq 2-11 for the interaction parameters between a block copolymer and the corresponding homopolymers have been discussed earlier by Scott[14] and by Roe and Zin.[15]

The chemical potential is obtained in the usual way from the free energy per unit volume in the homogeneous phase, taking into account variation of the volume with particle number,

$$\hat{\mu}_\kappa = \frac{\partial \hat{f}}{\partial \phi_\kappa} + \hat{f} - \sum_\kappa^{C} \phi_\kappa \frac{\partial \hat{f}}{\partial \phi_\kappa} \tag{2-12}$$

as before (see eq 2-37 of I). For $\kappa \neq$ C, using eq 2-8 this result reduces to

$$\hat{\mu}_\kappa = \frac{D\hat{f}_h}{D\phi_\kappa} + \frac{\phi_C}{r_C} \tag{2-13}$$

where

$$\frac{D\hat{f}_h}{D\phi_\kappa} \equiv \frac{\partial \hat{f}_h}{\partial \phi_\kappa} + \left(\hat{f}_h - \sum_\kappa \phi_\kappa \frac{\partial \hat{f}_h}{\partial \phi_\kappa} \right) \tag{2-14}$$

and in the last expression the CA and CB blocks of the copolymer are treated as independent. For the copolymer, we note that $\phi_{CA} + \phi_{CB} = \phi_C$, and the result for the chemical potential is slightly more complicated

$$\hat{\mu}_C = \frac{1}{r_C}\left(r_{CA}\frac{D\hat{f}_h}{D\phi_{CA}} + r_{CB}\frac{D\hat{f}_h}{D\phi_{CB}} \right) + \frac{\phi_C}{r_C} - \frac{1}{r_C} \ln \left(\frac{\rho_0\phi_C}{r_C} \right) \tag{2-15}$$

Assuming that our block copolymer–homopolymer–solvent mixture separates into two homogeneous phases with an inhomogeneous interphase region, the asymptotic concentrations of the components may be calculated by equating the chemical potentials in the two phases, giving four relations

$$F_\kappa(\infty) = F_\kappa(-\infty) \tag{2-16}$$

where κ refers to homopolymer A (HA), homopolymer B (HB), block copolymer AB (C), or solvent (S). For example, F_{HA} is given by

$$\begin{aligned} F_{HA}(x) = {} & \chi_{AB}\phi_{HB}(x) + \chi_{AC}\phi_C(x) + \chi_{AS}\phi_S(x) + \frac{1}{r_{HA}} \ln \phi_{HA}(x) - \\ & [\chi_{AB}\phi_{HA}(x)\phi_{HB}(x) + \chi_{AC}\phi_{HA}(x)\phi_C(x) + \chi_{AS}\phi_{HA}(x)\phi_S(x) + \\ & \chi_{BC}\phi_{HB}(x)\phi_C(x) + \chi_{BS}\phi_{HB}(x)\phi_S(x) + \chi_{CS}\phi_C(x)\phi_S(x)] - \\ & \left[\frac{\phi_{HA}(x)}{r_{HA}} + \frac{\phi_{HB}(x)}{r_{HB}} + \frac{\phi_C(x)}{r_C} + \frac{\phi_S(x)}{r_S} \right] \end{aligned} \tag{2-17}$$

where constant terms have been dropped. Similar expressions may be obtained for the other F functions. The four equations given above are, of course, not sufficient to obtain the eight unknown quantities $\phi_\kappa(\pm\infty)$. We also have the relations

$$\sum_\kappa \phi_\kappa(\pm\infty) = 1 \tag{2-18}$$

as well as

$$V\phi_\kappa(\infty) + V'\phi_\kappa(-\infty) = W_\kappa/(\rho_{0\kappa}M_\kappa) \tag{2-19}$$

where V and V' are the macroscopic volumes of the two homogeneous phases and W_κ and M_κ are the weight and molecular weight of component κ, respectively. The quantities V and V' will not be required in our calculations. The case when the system does not separate into two homogeneous phases but instead forms micelles[5] is discussed in section 4.

Having outlined the procedure for obtaining the concentrations of the components in the bulk phases, we now turn to the interphase region. Following the same procedure as in section 3 of I, we obtain for the mean field equations

$$\hat{\omega}_\kappa = \hat{\omega}_\kappa{}^{\mathrm{b}} + \left(\frac{\mathrm{D}\hat{f}_{\mathrm{h}}}{\mathrm{D}\phi_\kappa} + \frac{\phi_{\mathrm{C}}}{r_{\mathrm{C}}}\right) - \left(\frac{\mathrm{D}\hat{f}_{\mathrm{h}}}{\mathrm{D}\phi_\kappa} + \frac{\phi_{\mathrm{C}}}{r_{\mathrm{C}}}\right)_{\mathrm{b}} - \frac{1}{r_\kappa}\ln\left(\frac{\phi_\kappa}{\phi_\kappa{}^{\mathrm{b}}}\right) + \frac{1}{6}\sum_{\kappa'}\chi_{\kappa\kappa'}\sigma_{\kappa\kappa'}{}^2\nabla^2\phi_{\kappa'} + \frac{\Delta\zeta}{\rho_0} \tag{2-20}$$

where "b" refers to one of the bulk homogeneous phases and κ denotes HA, HB, CA, CB, or S. Now eq 2-25 of I for the solvent molecules can be written

$$\phi_{\mathrm{S}} = \frac{N_{\mathrm{S}}}{\rho_0 Q_{\mathrm{S}}} e^{-\hat{\omega}_{\mathrm{S}}} = \phi_{\mathrm{S}}{}^{\mathrm{b}} \exp(\hat{\omega}_{\mathrm{S}}{}^{\mathrm{b}} - \hat{\omega}_{\mathrm{S}}) \tag{2-21}$$

for both homogeneous and inhomogeneous regions. Using eq 2-21 in eq 2-20, we find immediately

$$-\frac{\Delta\zeta}{\rho_0} = \left(\frac{\mathrm{D}\hat{f}_{\mathrm{h}}}{\mathrm{D}\phi_{\mathrm{S}}} + \frac{\phi_{\mathrm{C}}}{r_{\mathrm{C}}}\right) - \left(\frac{\mathrm{D}\hat{f}_{\mathrm{h}}}{\mathrm{D}\phi_{\mathrm{S}}} + \frac{\phi_{\mathrm{C}}}{r_{\mathrm{C}}}\right)_{\mathrm{b}} + \frac{1}{6}\sum_{\kappa}\chi_{\kappa\mathrm{S}}\sigma_{\kappa\mathrm{S}}{}^2\nabla^2\phi_\kappa \tag{2-22}$$

Equations 2-20 and 2-22 together completely determine the mean field acting on the homopolymers and on the blocks of the copolymer. We also note that the second quantity on the right-hand side of eq 2-22 is the chemical potential of the solvent molecules, which is independent of b, and hence $\Delta\zeta = 0$ in both phases.

The first conclusion to be drawn from the mean field equations is that $\hat{\omega}_{\mathrm{CA}} = \hat{\omega}_{\mathrm{HA}}$, if $\hat{\omega}_{\mathrm{CA}}{}^{\mathrm{b}}$ and $\hat{\omega}_{\mathrm{HA}}{}^{\mathrm{b}}$ are chosen equal, since $\chi_{\kappa,\mathrm{CA}} = \chi_{\kappa\mathrm{A}}$ and $\sigma_{\kappa,\mathrm{CA}} = \sigma_{\kappa\mathrm{A}}$, and similarly $\hat{\omega}_{\mathrm{CB}} = \hat{\omega}_{\mathrm{HB}}$. Second, both of the corresponding homopolymer and block copolymer volume fractions can be lumped together

$$\phi_{\mathrm{A}}(x) = \phi_{\mathrm{HA}}(x) + \phi_{\mathrm{CA}}(x)$$

$$\phi_{\mathrm{B}}(x) = \phi_{\mathrm{HB}}(x) + \phi_{\mathrm{CB}}(x) \tag{2-23}$$

and the mean field expressions can be written entirely in terms of these quantities, *as if we were dealing with a three-component homopolymer A–homopolymer B–solvent system.*[16] The final expressions for the mean fields are

$$\hat{\omega}_{\mathrm{A}}(x) = (\chi_{\mathrm{AB}} - \chi_{\mathrm{AS}} - \chi_{\mathrm{BS}})(\phi_{\mathrm{B}}(x) - \phi_{\mathrm{B}}(\infty)) - 2\chi_{\mathrm{AS}}(\phi_{\mathrm{A}}(x) - \phi_{\mathrm{A}}(\infty)) - \ln(\phi_{\mathrm{S}}(x)/\phi_{\mathrm{S}}(\infty)) + \frac{1}{6}\left\{(\chi_{\mathrm{AB}}\sigma_{\mathrm{AB}}{}^2 - \chi_{\mathrm{AS}}\sigma_{\mathrm{AS}}{}^2 - \chi_{\mathrm{BS}}\sigma_{\mathrm{BS}}{}^2)\frac{\mathrm{d}^2\phi_{\mathrm{B}}}{\mathrm{d}x^2} - 2\chi_{\mathrm{AS}}\sigma_{\mathrm{AS}}{}^2\frac{\mathrm{d}^2\phi_{\mathrm{A}}}{\mathrm{d}x^2}\right\} \tag{2-24}$$

and

$$\hat{\omega}_{\mathrm{B}}(x) = (\chi_{\mathrm{AB}} - \chi_{\mathrm{AS}} - \chi_{\mathrm{BS}})(\phi_{\mathrm{A}}(x) - \phi_{\mathrm{A}}(-\infty)) - 2\chi_{\mathrm{BS}}(\phi_{\mathrm{B}}(x) - \phi_{\mathrm{B}}(-\infty)) - \ln(\phi_{\mathrm{S}}(x)/\phi_{\mathrm{S}}(-\infty)) + \frac{1}{6}\left\{(\chi_{\mathrm{AB}}\sigma_{\mathrm{AB}}{}^2 - \chi_{\mathrm{AS}}\sigma_{\mathrm{AS}}{}^2 - \chi_{\mathrm{BS}}\sigma_{\mathrm{BS}}{}^2)\frac{\mathrm{d}^2\phi_{\mathrm{B}}}{\mathrm{d}x^2} - 2\chi_{\mathrm{BS}}\sigma_{\mathrm{BS}}{}^2\frac{\mathrm{d}^2\phi_{\mathrm{B}}}{\mathrm{d}x^2}\right\} \tag{2-25}$$

The equation for the homopolymer A distribution function

$$\frac{1}{r_{\mathrm{HA}}}\frac{\partial q_{\mathrm{HA}}}{\partial t} = \frac{\hat{b}_{\mathrm{A}}{}^2}{6}\frac{\partial^2 q_{\mathrm{HA}}}{\partial x^2} - \hat{\omega}_{\mathrm{A}} q_{\mathrm{HA}} \tag{2-26}$$

with the initial condition

$$q_{\mathrm{HA}}(x,0) = 1 \tag{2-27}$$

and the boundary conditions

$$q_{\mathrm{HA}}(\infty,t) = 1$$

$$q_{\mathrm{HA}}(-\infty,t) = e^{-r_{\mathrm{HA}}\hat{\omega}_{\mathrm{A}}(-\infty)t} \tag{2-28}$$

The boundary conditions follow immediately from the asymptotic values of $\hat{\omega}_{\mathrm{A}}(x)$. Similarly the equation for homopolymer B is

$$\frac{1}{r_{\mathrm{HB}}}\frac{\partial q_{\mathrm{HB}}}{\partial t} = \frac{\hat{b}_{\mathrm{B}}{}^2}{6}\frac{\partial^2 q_{\mathrm{HB}}}{\partial x^2} - \hat{\omega}_{\mathrm{B}} q_{\mathrm{HB}} \tag{2-29}$$

with the initial condition

$$q_{\mathrm{HB}}(x,0) = 1 \tag{2-30}$$

and the boundary conditions

$$q_{\mathrm{HB}}(\infty,t) = e^{-r_{\mathrm{HB}}\hat{\omega}_{\mathrm{B}}(\infty)t}$$

$$q_{\mathrm{HB}}(-\infty,t) = 1 \tag{2-31}$$

The volume fractions are related to the distribution functions by

$$\phi_{\mathrm{HA}}(x) = \phi_{\mathrm{HA}}(\infty)\int_0^1 \mathrm{d}t\; q_{\mathrm{HA}}(x,t)q_{\mathrm{HA}}(x, 1 - t) \tag{2-32}$$

and

$$\phi_{\mathrm{HB}}(x) = \phi_{\mathrm{HB}}(-\infty)\int_0^1 \mathrm{d}t\; q_{\mathrm{HB}}(x,t)q_{\mathrm{HB}}(x, 1 - t) \tag{2-33}$$

Next we need the equations for the copolymer distribution functions. Before proceeding with this problem, we rewrite eq 4-3 of I for the block copolymer components

$$\phi_{\mathrm{CA}}(x) = \phi_{\mathrm{CA}}(\infty)e^{r_{\mathrm{CA}}\hat{\omega}_{\mathrm{B}}(\infty)}\int_0^1 \mathrm{d}t\; q_{\mathrm{CA}}(x,t)q_{\mathrm{AB}}(x, 1 - t) \tag{2-34}$$

$$\phi_{\mathrm{CB}}(x) = \phi_{\mathrm{CB}}(\infty)e^{r_{\mathrm{CA}}\hat{\omega}_{\mathrm{A}}(-\infty)}\int_0^1 \mathrm{d}t\; q_{\mathrm{CB}}(x,t)q_{\mathrm{BA}}(x, 1 - t) \tag{2-35}$$

where

$$q_{\mathrm{AB}}(x, 1 - t) = \int \mathrm{d}x_0\; Q_{\mathrm{A}}(x, 1 - t|x_0)q_{\mathrm{CB}}(x_0,1) \tag{2-36}$$

$$q_{\mathrm{BA}}(x, 1 - t) = \int \mathrm{d}x_0\; Q_{\mathrm{B}}(x, 1 - t|x_0)q_{\mathrm{CA}}(x_0,1) \tag{2-37}$$

and $Q_{\mathrm{P}}(x,t|x_0)$ is the fundamental distribution function for a chain of t repeat units to start at x_0 and end at x. The factors in front of the integrals in eq 2-34 and 2-35 can be sorted out later from the boundary conditions. For the time being we note that *four* distribution functions are required to completely specify the block copolymer. The equation for $q_{\mathrm{CA}}(x,t)$ is

$$\frac{1}{r_{\mathrm{CA}}}\frac{\partial q_{\mathrm{CA}}(x,t)}{\partial t} = \frac{\hat{b}_{\mathrm{A}}{}^2}{6}\frac{\partial^2 q_{\mathrm{CA}}}{\partial x^2} - \hat{\omega}_{\mathrm{A}} q_{\mathrm{CA}} \tag{2-38}$$

with the initial condition

$$q_{\mathrm{CA}}(x,0) = 1 \tag{2-39}$$

and the boundary conditions

$$q_{\mathrm{CA}}(\infty,t) = 1$$

$$q_{\mathrm{CA}}(-\infty,t) = e^{-r_{\mathrm{CA}}\hat{\omega}_{\mathrm{A}}(-\infty)t} \tag{2-40}$$

Similarly, the equation for $q_{\mathrm{CB}}(x,t)$ is

$$\frac{1}{r_{\mathrm{CB}}} \frac{\partial q_{\mathrm{CB}}(x,t)}{\partial t} = \frac{\hat{b}_{\mathrm{B}}^{2}}{6} \frac{\partial^2 q_{\mathrm{CB}}}{\partial x^2} - \hat{\omega}_{\mathrm{B}} q_{\mathrm{CB}} \qquad (2\text{-}41)$$

with the initial condition

$$q_{\mathrm{CB}}(x,0) = 1 \qquad (2\text{-}42)$$

and the boundary conditions

$$q_{\mathrm{CB}}(\infty,t) = e^{-r_{\mathrm{CB}}\hat{\omega}_{\mathrm{B}}(\infty)t}$$

$$q_{\mathrm{CB}}(-\infty,t) = 1 \qquad (2\text{-}43)$$

The equation for $q_{\mathrm{AB}}(x,t)$ is the same as that for $q_{\mathrm{CA}}(x,t)$ (eq 2-38). However, the initial condition now becomes

$$q_{\mathrm{AB}}(x,0) = q_{\mathrm{CB}}(x,1) \qquad (2\text{-}44)$$

which follows from eq 2-36, since $Q_{\mathrm{A}}(x,0|x_0)$ is a delta function. The boundary conditions consistent with eq 2-44 are

$$q_{\mathrm{AB}}(\infty,t) = e^{-r_{\mathrm{CB}}\hat{\omega}_{\mathrm{B}}(\infty)}$$

$$q_{\mathrm{AB}}(-\infty,t) = e^{-r_{\mathrm{CA}}\hat{\omega}_{\mathrm{A}}(-\infty)t} \qquad (2\text{-}45)$$

The equation for $q_{\mathrm{BA}}(x,t)$ is the same as for $q_{\mathrm{CB}}(x,t)$, eq 2-41, but the initial condition is

$$q_{\mathrm{BA}}(x,0) = q_{\mathrm{CA}}(x,1) \qquad (2\text{-}46)$$

while the boundary conditions are now

$$q_{\mathrm{BA}}(\infty,t) = e^{-r_{\mathrm{CB}}\hat{\omega}_{\mathrm{B}}(\infty)t}$$

$$q_{\mathrm{BA}}(-\infty,t) = e^{-r_{\mathrm{CA}}\hat{\omega}_{\mathrm{A}}(-\infty)t} \qquad (2\text{-}47)$$

This completes the enumeration of all the distribution functions and their associated equations of motion. For the interphase region we need to determine four volume fractions, $\phi_{\mathrm{HA}}(x)$, $\phi_{\mathrm{HB}}(x)$, $\phi_{\mathrm{CA}}(x)$, and $\phi_{\mathrm{CB}}(x)$. The amount of solvent is given by the remaining volume fraction after all polymer components have been accounted for

$$\phi_{\mathrm{S}}(x) = 1 - \phi_{\mathrm{A}}(x) - \phi_{\mathrm{B}}(x) \qquad (2\text{-}48)$$

In this paper we also present plots of the copolymer end and joint distributions. From eq 2-34 and 2-35, these quantities are given by

$$\rho_{\mathrm{CA}}{}^{\mathrm{end}}(x) = \frac{\rho_{0\mathrm{A}}}{Z_{\mathrm{CA}}} \phi_{\mathrm{CA}}(\infty) e^{r_{\mathrm{CB}}\hat{\omega}_{\mathrm{B}}(\infty)} q_{\mathrm{AB}}(x,1) \qquad (2\text{-}49)$$

$$\rho_{\mathrm{CB}}{}^{\mathrm{end}}(x) = \frac{\rho_{0\mathrm{B}}}{Z_{\mathrm{CB}}} \phi_{\mathrm{CB}}(-\infty) e^{r_{\mathrm{CA}}\hat{\omega}_{\mathrm{A}}(-\infty)} q_{\mathrm{BA}}(x,1) \qquad (2\text{-}50)$$

and for the joints

$$\begin{aligned} \rho^{\mathrm{joint}}(x) &= \frac{\rho_{0\mathrm{A}}}{Z_{\mathrm{CA}}} \phi_{\mathrm{CA}}(\infty) e^{r_{\mathrm{CB}}\hat{\omega}_{\mathrm{B}}(\infty)} q_{\mathrm{CA}}(x,1) q_{\mathrm{CB}}(x,1) \\ &= \frac{\rho_{0\mathrm{B}}}{Z_{\mathrm{CB}}} \phi_{\mathrm{CB}}(\infty) e^{r_{\mathrm{CA}}\hat{\omega}_{\mathrm{A}}(-\infty)} q_{\mathrm{CA}}(x,1) q_{\mathrm{CB}}(x,1) \end{aligned} \qquad (2\text{-}51)$$

Finally, we need an expression for another important quantity, the interfacial tension γ. This can be easily obtained by substituting the result for $\hat{\omega}_\kappa$ (eq 2-20) into the expression for the free energy $\hat{\mathcal{F}}$ (eq 2-3), to give, after some algebra,

$$\mathcal{F} \equiv \rho_0 \hat{\mathcal{F}} = \sum_{\kappa}^{\mathrm{C}} N_\kappa \mu_\kappa + \gamma A \qquad (2\text{-}52)$$

with

$$\gamma A = \rho_0 \int \mathrm{d}^3 r \left\{ \frac{1}{12} \sum_{\kappa,\kappa'} \chi_{\kappa\kappa'} \sigma_{\kappa\kappa'}{}^2 \vec{\nabla}\phi_\kappa \cdot \vec{\nabla}\phi_{\kappa'} - \frac{\Delta\zeta}{\rho_0} \right\} \qquad (2\text{-}53)$$

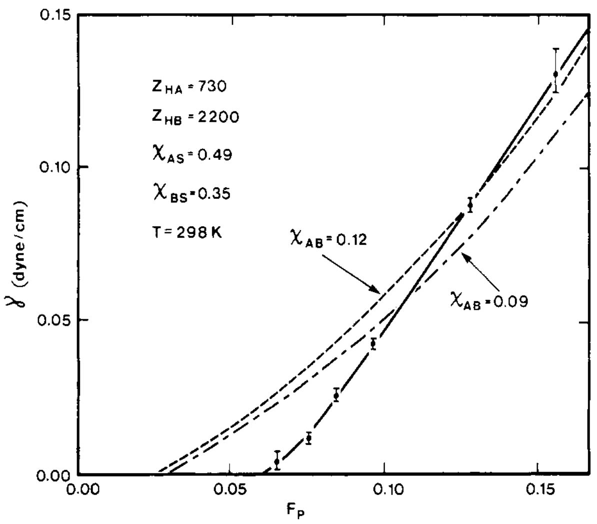

Figure 2. Interfacial tension for the ternary PS–PBD–S system as a function of the weight fraction of homopolymer (F_{P}), with equal weights of polystyrene (HA) and polybutadiene (HB) homopolymers. The experimental values (solid line) have been measured by Riess and co-workers[9] using the spinning drop technique. Note that in this experiment no block copolymer is present. Z_{HA} and Z_{HB} refer to the degrees of polymerization of PS and PBD homopolymers, respectively, and the two theoretical curves (dashed lines) correspond to different values of χ_{AB}. In this paper we choose $\chi_{\mathrm{AB}} = 0.12$, to give agreement with the experimental value of γ for $F_{\mathrm{P}} = 0.128$ (see Figure 3).

The expression for $\Delta\zeta/\rho_0$ has been given earlier (eq 2-22). For our four-component system the interfacial tension is explicitly given by

$$\begin{aligned} \gamma/\rho_0 = \int \mathrm{d}x \Bigg\{ &(F_{\mathrm{S}}'(x) - F_{\mathrm{S}}'(\infty)) + \frac{1}{6}\Bigg(\chi_{\mathrm{AS}}\sigma_{\mathrm{AS}}{}^2 \frac{\mathrm{d}\phi_{\mathrm{A}}}{\mathrm{d}x} \frac{\mathrm{d}\phi_{\mathrm{S}}}{\mathrm{d}x} \\ &+ \chi_{\mathrm{BS}}\sigma_{\mathrm{BS}}{}^2 \frac{\mathrm{d}\phi_{\mathrm{B}}}{\mathrm{d}x} \frac{\mathrm{d}\phi_{\mathrm{S}}}{\mathrm{d}x} + \chi_{\mathrm{AB}}\sigma_{\mathrm{AB}}{}^2 \frac{\mathrm{d}\phi_{\mathrm{A}}}{\mathrm{d}x} \frac{\mathrm{d}\phi_{\mathrm{B}}}{\mathrm{d}x} \Bigg) \Bigg\} \end{aligned} \qquad (2\text{-}54)$$

where

$$\begin{aligned} F_{\mathrm{S}}'(x) = {} & \chi_{\mathrm{AS}}\phi_{\mathrm{A}}(x) + \chi_{\mathrm{BS}}\phi_{\mathrm{B}}(x) + \ln \phi_{\mathrm{S}}(x) - \\ & \{\chi_{\mathrm{AS}}\phi_{\mathrm{A}}(x)\phi_{\mathrm{S}}(x) + \chi_{\mathrm{BS}}\phi_{\mathrm{B}}(x)\phi_{\mathrm{S}}(x) + \chi_{\mathrm{AB}}\phi_{\mathrm{A}}(x)\phi_{\mathrm{B}}(x)\} - \\ & \left\{ \phi_{\mathrm{S}}(x) + \frac{\phi_{\mathrm{CA}}(x)}{r_{\mathrm{C}}} + \frac{\phi_{\mathrm{CB}}(x)}{r_{\mathrm{C}}} + \frac{\phi_{\mathrm{HA}}(x)}{r_{\mathrm{HA}}} + \frac{\phi_{\mathrm{HB}}(x)}{r_{\mathrm{HB}}} \right\} \end{aligned} \qquad (2\text{-}55)$$

The quantity $F_{\mathrm{S}}'(x)$ introduced here for the inhomogeneous interphase region is more general than the corresponding $F_{\mathrm{S}}(x)$ referred to earlier (eq 2-23), and recalling that in the homogeneous phase ϕ_{CA} and ϕ_{CB} are simply proportional to ϕ_{C}, we recover the $F_{\mathrm{S}}(x)$ function introduced earlier. In the region of the interphase, however, there is no simple relation between $\phi_{\mathrm{CA}}(x)$, $\phi_{\mathrm{CB}}(x)$, and $\phi_{\mathrm{C}}(x)$, and these quantities have to be determined self-consistently by solving the mean field equations.

3. Results of Calculations

With the density of styrene monomer as the reference density ($\rho_{\mathrm{S}} = 0.00872$ mol cm^{-3}, $\rho_{\mathrm{PS}} = 0.0103$ mol cm^{-3})[17,18] and $\chi_{\mathrm{AS}} = 0.49$ for polystyrene–styrene and $\chi_{\mathrm{BS}} = 0.35$ for polybutadiene–styrene (obtained using volume fractions),[19] the calculated interfacial tension γ for the ternary PS–PBD–S system is shown in Figure 2 as a function of the weight fraction of total homopolymer. The dashed lines show the results for two assumed values of the polymer–polymer interaction parameter χ_{AB}, and the solid line represents the experimental values of Riess and co-work-

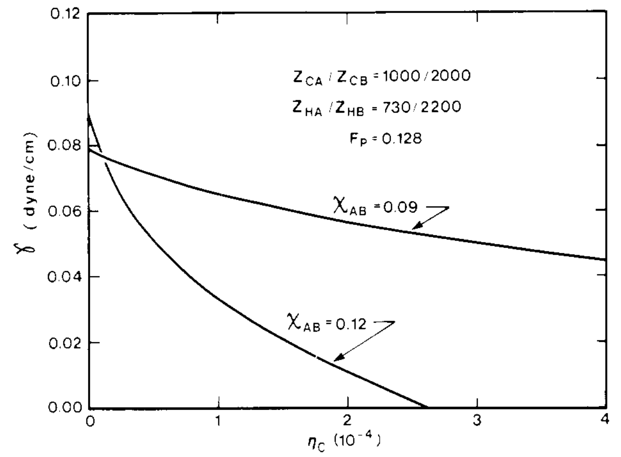

Figure 3. Calculated interfacial tension for the phase-separated quaternary PS-PBD-CopSBD-S system with varying weight fraction η_C of block copolymer (with respect to one of the two homopolymers, of equal weight in this case) and two different values of χ_{AB}. F_P gives the initial weight fraction of homopolymer, and Z_{CA} and Z_{CB} refer to the degrees of polymerization of the polystyrene and polybutadiene blocks of the copolymer, respectively. For $\chi_{AB} = 0.12$ and $\eta_C = 0$ the theoretical value of γ agrees with Riess' measurement.[9]

ers[9] obtained by the spinning drop method.[20] For $\chi_{AB} = 0.12$ the theoretical curve passes through the experimental point for $F_P = 0.128$, which corresponds to the initial value of the homopolymer weight fraction before the addition of block copolymer to the polybutadiene-rich phase. Although a 25% variation in χ_{AB} gives little change in the values of γ for the ternary system (Figure 2), the effect on the calculated value of the interfacial tension when block copolymer is added is more dramatic (Figure 3). The experimental results for Figure 3 are practically flat over the small range of block copolymer weight fraction η_C shown and are not indicated on the diagram. Possible reasons for the difference between the experimental and theoretical values in this case are discussed in detail in section 5. Other estimates of χ_{AB} for polystyrene-polybutadiene obtained by using a light scattering technique[15] to measure the phase separation temperatures give values in the range 0.17–0.18 for $T = 298$ K. The value $\chi_{PS-PBD} = 0.024$ estimated by Kruse[19] using solubility parameters and quoted by us earlier is probably too low. The numerical technique used to solve the differential equations for the polymer distribution functions in these calculations is discussed briefly in Appendix A and outlined in greater detail in I.

An interesting feature of the theoretical results is that the interfacial tension for the quaternary system is predicted to vanish for some concentration of block copolymer. This, of course, is related to the assumption that some of the block copolymer finds it energetically favorable to settle at the interface, while the remainder is randomly dispersed in the bulk phases (top panel of Figure 1). In reality, for a certain concentration of block copolymer, micelles will form away from the interphase region (bottom panel of Figure 1), and the assumption of homogeneous bulk phases, with randomly dispersed block copolymers, will no longer be valid. In section 4 we estimate the critical micelle concentration (CMC) as a function of molecular weight for polystyrene-polybutadiene. When the concentration of the block copolymer becomes sufficiently high, micelle formation becomes energetically favorable, and we expect the concentration of block copolymer *in the interphase region* to remain approximately constant, with the interfacial tension correspondingly unchanged.[12] The results of the calculations discussed in this section are therefore to be considered together with the estimates of the CMC given in section 4 to obtain a complete picture of the variation of interfacial tension with block copolymer concentration.

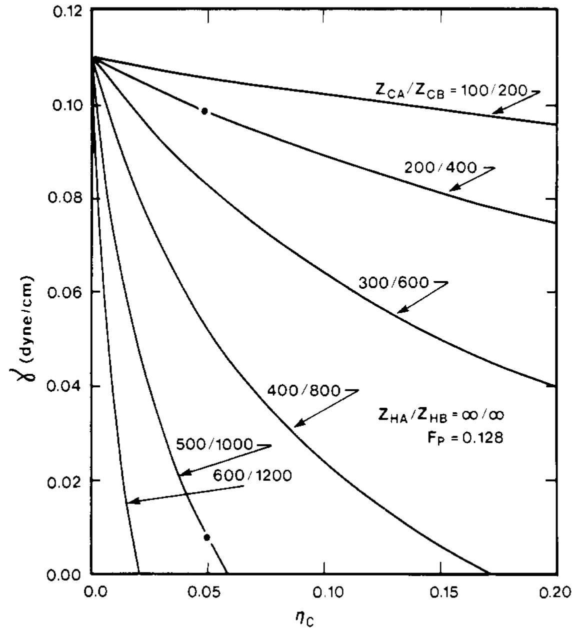

Figure 4. Variation of calculated interfacial tension as a function of block copolymer weight fraction η_C (with respect to the weight of PS) for PS-PBD-CopSBD-S with different degrees of polymerization of the polystyrene (CA) and polybutadiene (CB) blocks of CopSBD. The initial weight fraction of homopolymer is $F_P = 0.128$, and we have assumed infinite molecular weight for the homopolymers. The interfacial profiles displayed in Figures 8 and 9 correspond to the dots marked on this graph.

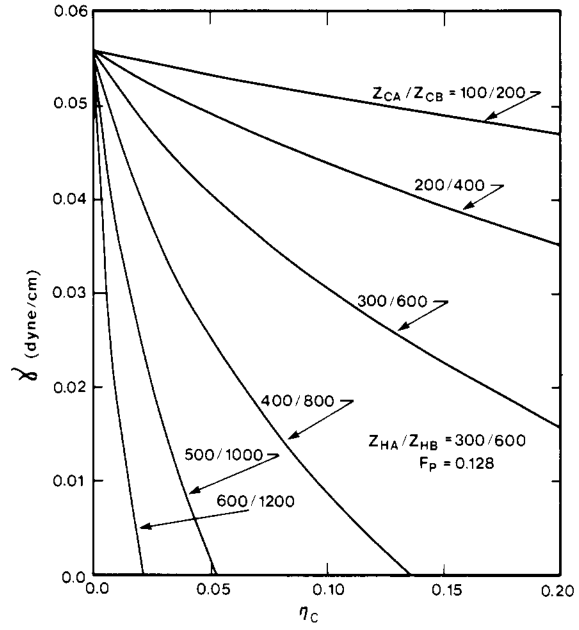

Figure 5. Calculations of interfacial tension for the PS-PBD-CopSBD-S system under the same conditions as in Figure 4 except for the finite degrees of polymerization of the polystyrene (HA) and polybutadiene (HB) homopolymers.

Figure 4 shows the calculated decrease in γ with increasing weight fraction of the block copolymer (with respect to one of the equal-weight homopolymers) for various values of the copolymer molecular weight. In this calculation the molecular weights of the homopolymers are taken to be infinite. For polystyrene-polybutadiene blocks the ratio $Z_{CA}:Z_{CB} = 1:2$ corresponds to approximately 50%

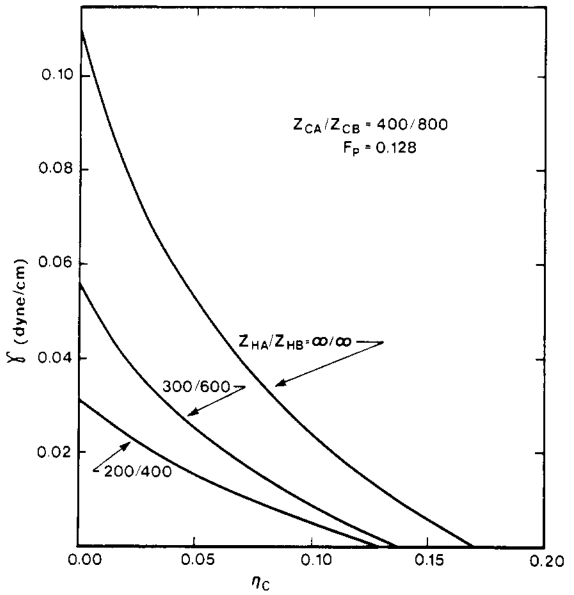

Figure 6. Interfacial tension for PS-PBD-CopSBD-S, calculated assuming fixed Z_{CA} and Z_{CB} for the polystyrene and polybutadiene blocks of the copolymer, respectively, with varying degrees of polymerization for the polystyrene (HA) and polybutadiene (HB) homopolymers. η_C is the weight fraction of copolymer with respect to one of the (equal weight) homopolymers, and F_P is the initial weight fraction of homopolymer present.

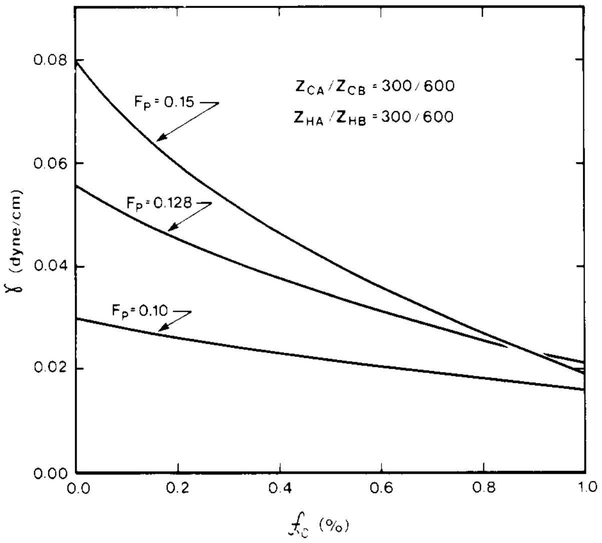

Figure 7. Variation of calculated interfacial tension, for fixed degrees of polymerization of both the homopolymers and the blocks of the copolymer, with different amounts of styrene monomer in the PS-PBD-CopSBD-S system, as measured by the initial weight fraction of homopolymer, F_P. Here f_C denotes the weight fraction (in percent) of copolymer with respect to the total weight of the system.

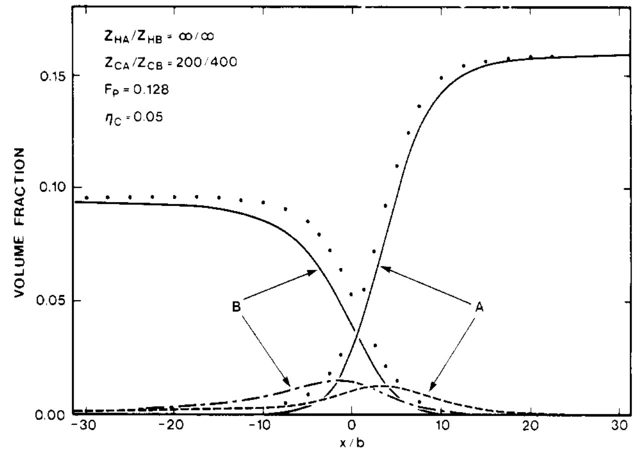

Figure 8. Interfacial density profiles of styrene homopolymer (A, solid line), styrene blocks of copolymer (A, dashed line), butadiene homopolymer (B, solid line), and butadiene blocks of copolymer (B, dashed line). The dots correspond to the total volume fractions of the A and B components, respectively, and the length through the interphase is measured in units of the average Kuhn length (6.95 Å).[17]

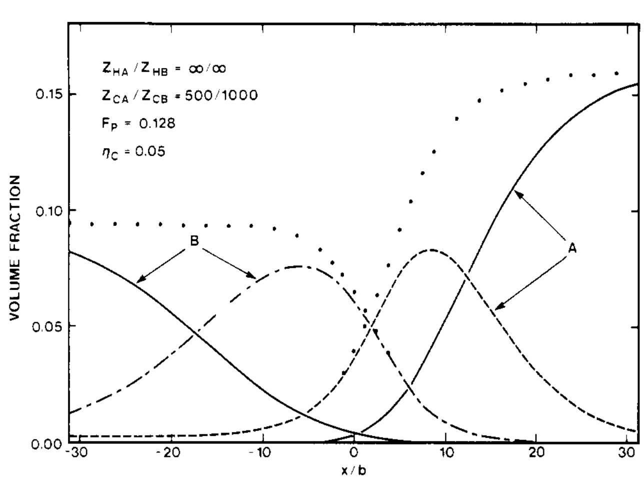

Figure 9. Same interfacial density profiles as in Figure 8, with increased degrees of polymerization of the polystyrene (CA) and polybutadiene (CB) blocks of the copolymer.

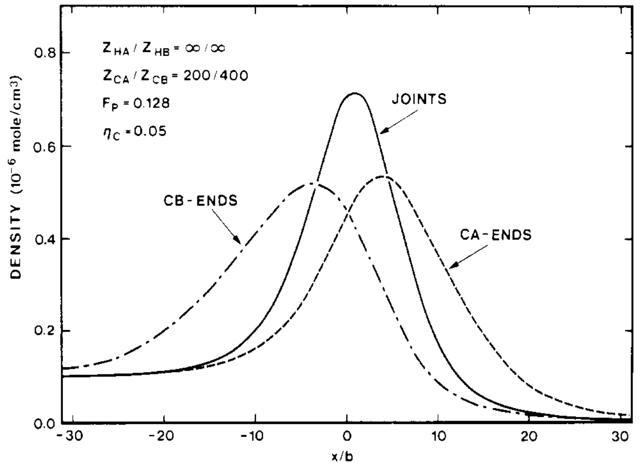

Figure 10. Copolymer end and joint distribution functions for the interfacial profiles shown in Figure 8.

by weight of each component, as in Riess' experiments. When the molecular weights of the polystyrene and polybutadiene homopolymers are finite, as in Figure 5, the rate of decrease in γ *relative* to the infinite molecular weight curves (Figure 4) is smaller, depending on the values of Z_{CA} and Z_{CB}. This is clearly evident in Figure 6, where we have fixed Z_{CA}, Z_{CB}, and the initial weight fraction of total homopolymer, F_P, and varied Z_{HA} and Z_{HB}. Although increasing the copolymer molecular weight in general leads to lower values of γ for any Z_{HA}, Z_{HB}, according to section 4 lower critical values of η_C also make micelle formation more favorable. In Figure 7 we see the decrease of the interfacial tension with increasing weight fraction of copolymer (with respect to the total weight of the system in this case) for different values of the initial weight fraction of homopolymer. As expected, the effect is more marked for a greater concentration of homopolymer in the system. For $F_P = 0.10$ we are approaching the critical point of the ternary system, and the effect of increasing the block co-

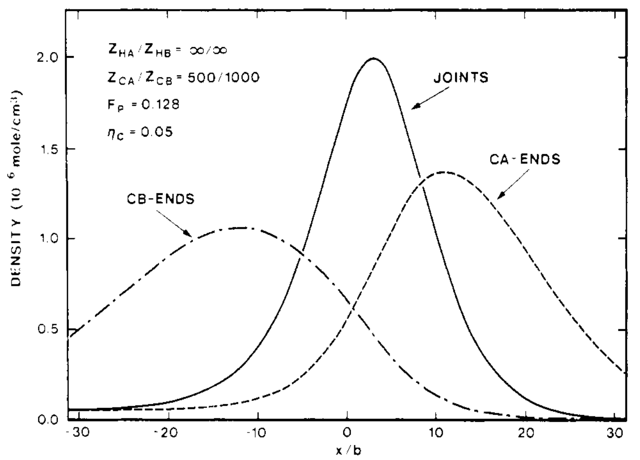

Figure 11. Copolymer end and joint distribution functions for the interfacial profiles shown in Figure 9.

polymer concentration is much less, probably because the interphase region is very broad.

Figures 8–11 show interfacial profiles for different points on the calculated curves we have just discussed. Figure 8 refers to the upper point in Figure 4, with $\eta_C = 0.05$ and $Z_{CA}/Z_{CB} = 200/400$. The lines labeled A and B indicate the volume fractions of the polystyrene blocks of the copolymer with the polystyrene homopolymer, and the polybutadiene blocks with the polybutadiene homopolymer, respectively. The dots mark the total volume fractions of polymers A and B. The interfacial tension for the profile shown in Figure 8 is relatively high, with considerable mixing of A and B homopolymers in the interphase region. It is interesting to compare this profile with the one shown in Figure 9, which corresponds to a low value of the interfacial tension. Here the block copolymers, with a larger molecular weight, occupy most of the interphase region, and the homopolymers have been displaced away from the interphase. As a result, there is less mixing of the homopolymers, and since the interaction energy of the A and B blocks of the copolymer is approximately the same in the bulk or at the interphase, the overall interfacial tension is smaller.

Figures 10 and 11 give the distribution of copolymer ends and joints for the profiles shown in Figures 8 and 9. The end distribution functions are quite broad and are shifted slightly toward the bulk from the corresponding interfacial density profiles, but are otherwise similar. Figure 10 also shows the larger degree of solubility of the low molecular weight block copolymer in homopolymer B than in homopolymer A, as expected from the larger degree of polymerization of the B blocks of the copolymer relative to the A blocks. Besides providing some insight into the complicated structure of the interphase, the distribution functions for the copolymer ends and joints may be helpful in interpreting experiments designed to probe the interfacial region with block copolymers labeled for NMR studies or with attached fluorescent groups.

4. Estimate of Critical Micelle Concentration (CMC)

Instead of the block copolymers distributing themselves randomly in the bulk homogeneous phases, as shown in the top panel of Figure 1, it is likely that at some copolymer concentration micelle formation will take place, as depicted schematically in the lower panel of the same figure. In this section we will give a rough estimate of the critical micelle concentration (CMC).[5] A more accurate calculation of the CMC will be presented in a future publication.

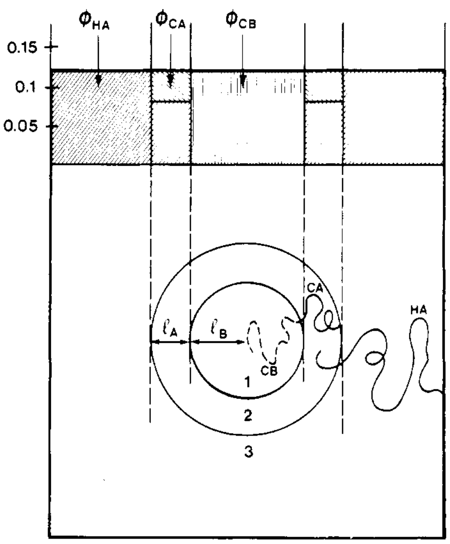

Figure 12. Schematic diagram of spherical micelle structure assumed in calculation of critical micelle concentration (CMC) in section 4. Polybutadiene blocks (CB) of CopSBD are contained in region 1, and region 2 is composed of polystyrene blocks (CA) of CopSBD as well as polystyrene homopolymer (HA). A narrow interphase (not shown) separates regions 1 and 2. Region 3 contains polystyrene homopolymer (HA). Styrene monomer is present in all three regions in varying amounts. The upper panel shows the results of the calculations for the volume fractions of the components in the three regions, assuming $Z_{CA} = Z_{CB} = 700$, with $\phi^0{}_{HA} = 0.12$ and the other parameters as indicated in Figure 13.

Referring to Figure 12, we assume the existence of three uniform regions for a spherical micelle with $Z_{CA} \simeq Z_{CB}$. The central region 1 is filled up with B blocks of the copolymer and a solvent. The end-to-end distance of the B blocks, l_B, is taken to be a parameter of the model. Region 2 consists of A blocks of the copolymer, homopolymer A, and solvent. The end-to-end distance of the A blocks is another parameter, l_A. The third region consists of homopolymers A and solvent. The small width of the interphase between the A and B blocks of the copolymer is estimated from our previous microscopic calculations and is not a parameter. The overall volume fractions of the homopolymer, $\phi^0{}_{HA}$, copolymer, $\phi^0{}_C$, and solvent, $\phi^0{}_S$, will be assumed to be given, and we will determine the equilibrium number of chains per micelle and hence the number of micelles per unit volume at the CMC. The distance between micelles, or equivalently the volume of the unit cell occupied by regions 1, 2, and 3, is therefore an important parameter. Finally, other quantities which will appear in the calculation are the fractions of solvent appearing in regions 1, 2, and 3, denoted by $F_1{}^S$, $F_2{}^S$, and $F_3{}^S$, respectively, and the fractions of the total volume of the three regions, denoted by $G_1{}^v$, $G_2{}^v$, and $G_3{}^v$. $P_3{}^{HA}$ is the fraction of homopolymer A found in region 3 and $P_2{}^{HA} = 1 - P_3{}^{HA}$ is the corresponding fraction in region 2. As before, the degrees of polymerization of the copolymer blocks are given by Z_{CA} and Z_{CB}, with $Z_C = Z_{CA} + Z_{CB}$, and for simplicity the degree of polymerization of the homopolymer is assumed to be infinite.

For micelle formation the free energy per unit volume of the ordered state must be lower than the corresponding free energy of the random state; i.e.

$$\Delta g = \frac{G_{\text{micelle}} - G_{\text{random}}}{\rho_0 V k_B T} \tag{4-1}$$

must be negative. The contribution of the interaction energy of the polymers to Δg (exclusive of the interfacial tension, which is included later) is

$$\Delta g_{\mathrm{int}} = -\chi_{\mathrm{AB}}(\phi^0{}_{\mathrm{HA}} + Z_{\mathrm{A}}\phi^0{}_{\mathrm{C}}/Z_{\mathrm{C}})(Z_{\mathrm{B}}\phi^0{}_{\mathrm{C}}/Z_{\mathrm{C}}) - \chi_{\mathrm{AS}}(P_2{}^{\mathrm{HA}}\phi^0{}_{\mathrm{HA}} + Z_{\mathrm{A}}\phi^0{}_{\mathrm{C}}/Z_{\mathrm{C}})\phi^0{}_{\mathrm{S}}(1 - F_2{}^{\mathrm{S}}/G_2{}^{v}) - \chi_{\mathrm{AS}}P_3{}^{\mathrm{HA}}\phi^0{}_{\mathrm{HA}}\phi^0{}_{\mathrm{S}}(1 - F_3{}^{\mathrm{S}}/G_3{}^{v}) - \chi_{\mathrm{BS}}(Z_{\mathrm{B}}\phi^0{}_{\mathrm{C}}/Z_{\mathrm{C}})\phi^0{}_{\mathrm{S}}(1 - F_1{}^{\mathrm{S}}/G_1{}^{v}) \quad (4\text{-}2)$$

where the AB interaction term in the micellar state is taken to be zero in Δg_{int}. The combinational term of the solvent molecules can easily be seen to contribute

$$\Delta g_{\mathrm{S}} = \phi^0{}_{\mathrm{S}}\{F_1{}^{\mathrm{S}} \ln (F_1{}^{\mathrm{S}}/G_1{}^{v}) + F_2{}^{\mathrm{S}} \ln (F_2{}^{\mathrm{S}}/G_2{}^{v}) + F_3{}^{\mathrm{S}} \ln (F_3{}^{\mathrm{S}}/G_3{}^{v})\} \quad (4\text{-}3)$$

Now the decrease in entropy of the block copolymers from that of the random state will be lumped into three terms, the first arising from the localization of joints[21]

$$g_{\mathrm{J}} = -(\phi^0{}_{\mathrm{C}}/Z_{\mathrm{C}}) \ln (3l_{\mathrm{B}}{}^2 d_{\mathrm{I}}/R^3) \quad (4\text{-}4)$$

where d_{I} is the width of the interphase and the cubic unit cell has been replaced by a sphere, radius R, of the same volume. The second term is the interfacial tension

$$g_{\mathrm{I}} = (\gamma/\rho_0 k_{\mathrm{B}}T)(3l_{\mathrm{B}}{}^2/R^3) \quad (4\text{-}5)$$

which is partly due to the interaction of the A and B blocks but also includes the change in the copolymer entropy arising from the turning back of the A and B chains at the interface and confinement in their respective regions. The last term, the so-called "elastic energy", accounts for the decrease in entropy arising from a stretching or compression of the copolymer chains along the radial direction, given by[13]

$$g_{\mathrm{el}} = (\phi^0{}_{\mathrm{C}}/Z_{\mathrm{C}})\frac{1}{2}\left(\alpha_{\mathrm{A}}{}^2 + \alpha_{\mathrm{B}}{}^2 + \frac{2}{\alpha_{\mathrm{A}}} + \frac{2}{\alpha_{\mathrm{B}}} - 6\right) \quad (4\text{-}6)$$

where

$$\alpha_{\mathrm{A}} = \left(\frac{3}{Z_{\mathrm{CA}}}\right)^{1/2}\frac{l_{\mathrm{A}}}{b} \qquad \alpha_{\mathrm{B}} = \left(\frac{3}{Z_{\mathrm{CB}}}\right)^{1/2}\frac{l_{\mathrm{B}}}{b} \quad (4\text{-}7)$$

and b is an average Kuhn length for the copolymer. The sum of all the contributions to Δg is then

$$\Delta g = \Delta g_{\mathrm{int}} + \Delta g_{\mathrm{S}} + g_{\mathrm{J}} + g_{\mathrm{I}} + g_{\mathrm{el}} \quad (4\text{-}8)$$

For simplicity we take $\chi_{\mathrm{AS}} = \chi_{\mathrm{BS}}$ and $Z_{\mathrm{CA}} = Z_{\mathrm{CB}}$. From earlier work[16,22] we then have for large Z_{CA}

$$(\gamma/\rho_0 b k_{\mathrm{B}}T) \simeq (\chi_{\mathrm{AB}}/6)^{1/2}(1 - \phi_{\mathrm{S}})^{3/2} \quad (4\text{-}9)$$

and

$$d_{\mathrm{I}}/b \simeq (2/3\chi_{\mathrm{AB}})^{1/2}(1 - \phi_{\mathrm{S}})^{-1/2} \quad (4\text{-}10)$$

Although the F^{S} and G^{v} quantities are unknown, as well as l_{A}, l_{B}, $P_2{}^{\mathrm{HA}}$, and R, we have the following relations between these parameters:

$$G_1{}^{v} = (Z_{\mathrm{B}}/Z_{\mathrm{C}})\phi^0{}_{\mathrm{C}} + F_1{}^{\mathrm{S}}\phi^0{}_{\mathrm{S}}$$

$$G_2{}^{v} = (Z_{\mathrm{A}}/Z_{\mathrm{C}})\phi^0{}_{\mathrm{C}} + P_2{}^{\mathrm{HA}}\phi^0{}_{\mathrm{HA}} + F_2{}^{\mathrm{S}}\phi^0{}_{\mathrm{S}}$$

$$G_3{}^{v} = P_3{}^{\mathrm{HA}}\phi^0{}_{\mathrm{HA}} + F_3{}^{\mathrm{S}}\phi^0{}_{\mathrm{S}} \quad (4\text{-}11)$$

and

$$G_1{}^{v} = (l_{\mathrm{B}}/R)^3$$

$$G_2{}^{v} = \left(\frac{l_{\mathrm{A}} + l_{\mathrm{B}}}{R}\right)^3 - \left(\frac{l_{\mathrm{B}}}{R}\right)^3$$

$$G_3{}^{v} = 1 - \left(\frac{l_{\mathrm{A}} + l_{\mathrm{B}}}{R}\right)^3 \quad (4\text{-}12)$$

so that the total number of unknowns is four. These parameters were determined numerically by calculating the absolute minimum of Δg, and the CMC was obtained by changing the input data until $\Delta g_{\mathrm{minimum}} = 0$. Figure 13 shows a plot of the CMC obtained in this way as a function of the total degree of polymerization of the copolymer, with $\phi^0{}_{\mathrm{A}} = 0.12$. The polymer–solvent interaction parameter was chosen by averaging the interaction parameters for styrene–polystyrene and styrene–polybutadiene.

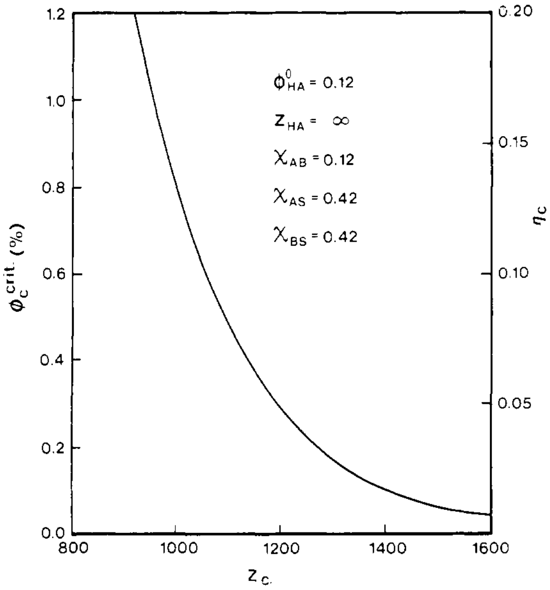

Figure 13. Critical micelle volume fraction (in percent) as a function of degree of polymerization of the block copolymer, $Z_{\mathrm{C}} = Z_{\mathrm{CA}} + Z_{\mathrm{CB}}$ (with $Z_{\mathrm{CA}} = Z_{\mathrm{CB}}$), for polystyrene homopolymer volume fraction $\phi^0{}_{\mathrm{HA}} = 0.12$. The polymer–solvent interaction parameters have been assumed equal (the average of the parameters shown in Figure 2) for this approximate calculation, and $\eta_{\mathrm{C}} = 2\phi^0{}_{\mathrm{C}}/\phi^0{}_{\mathrm{HA}}$ as well, ignoring the difference in molecular weights of the A and B components.

The parameters α_{A} and α_{B}, which give a measure of the stretching of the blocks of the copolymer, do not change appreciably with Z_{C}, and for $Z_{\mathrm{CA}} = Z_{\mathrm{CB}} = 450$ we have $\alpha_{\mathrm{A}} = 1.00$ and $\alpha_{\mathrm{B}} = 1.65$. It is interesting that the B blocks of the copolymer are stretched to maintain a constant volume fraction of polymer through the micelle (Figure 12). This effect has been noted earlier by Meier[23] in his calculations on block copolymer structures. In general, the CMC falls rapidly with increasing molecular weight of the block copolymer, indicating that for very long copolymer chains a micellar structure is preferred in the bulk of the homopolymer. This result is easily understood by noting that one block of a long copolymer chain in a random configuration has a large enthalpy of mixing in the incompatible homopolymer, and for long chains the contribution to the free energy is much smaller in the spherical micellar configuration, easily outweighing the associated loss of entropy. The results shown in Figure 13 are complementary to the curves displayed in Figures 3–7 since they establish the range of validity of our earlier calculations assuming a random distribution of block copolymers in the bulk of the homopolymers.

5. Discussion

The main area of disagreement between our theory and experiment is illustrated in Figure 3, where the calculated interfacial tension falls rapidly to zero for $\eta_{\mathrm{C}} \sim 10^{-4}$, while measurements indicate that γ decreases much more slowly with increasing block copolymer concentration[9] and reaches a constant value for $\eta_{\mathrm{C}} \sim 5$. One possible reason for this discrepancy is that the amount of block copolymer at the interface of the spinning drop, used to determine the interfacial tension, is much less than we have calculated theoretically assuming complete thermodynamic equilibrium. The phase diagram of the quaternary system is quite complicated, and it is not absolutely clear experimentally when thermodynamic equilibrium is achieved. In addition, it is not known whether the rapid spinning of the drop (50–250 rev/s)[9] can cause a slight shift in the position of the block copolymers at the interphase. As the calculations show (see Figures 8 and 9) the decrease in γ is very sensitive to the distance that the two immiscible homopolymers are pushed apart by the intrusion of the block copolymers at the interphase, and a small change in the location of the block copolymers can lead to an increase in the interfacial tension. Bearing in mind these difficulties in the interpretation of the experimental results, the discrepancy between Figure 3 of this paper and Figure 2 of ref 9 should not be considered a major failure of the theory. Further experimental and theoretical work will undoubtedly clarify the understanding of this point.

The constant value of the interfacial tension observed for large block copolymer concentrations has been seen in other systems[12] and may be attributed to micelle formation in the bulk, away from the interphase, or to saturation of the interphase region with block copolymer. In section 4 we have given a rough estimate of the critical volume fraction of block copolymer required for micelle formation. In this calculation we assumed that each micelle is centrally located in a unit cell and that all the micelles are the same size. In reality, the micelles will be randomly distributed, and there will be a distribution of sizes, since the gain in free energy from size fluctuations will be compensated by an increase in entropy resulting from the freedom of allowing the block copolymers to associate with different micelles. We have also assumed a spherical micelle, and, of course different shapes are possible.[24] It is easy to think of many ways that our estimate of the free energy of a micelle could be improved, and a more complete calculation deserves a separate treatment. Nevertheless we have attempted to discuss micelle formation in this paper because the state of the block copolymers away from the interphase has an important effect on the calculation of the interfacial tension. For low concentrations of block copolymer, the picture shown in the upper panel of Figure 1 is probably correct, whereas for high concentrations (before the interfacial tensions vanishes with a random distribution of block copolymers in the bulk) the situation depicted in the lower panel undoubtedly exists. Our mean-field calculation cannot adequately describe the critical crossover regime from a random copolymer distribution to aggregation (micelle formation) and thus, as emphasized earlier, we only give a rough estimate of the CMC. However, for low copolymer concentrations our mean-field calculations of γ should be reliable.

Another possible mechanism for the observed constant value of the interfacial tension for high block copolymer concentration may be the formation of a copolymer multilayer structure in the interphase. Thus, instead of going into a single layer at the interface, resulting in a higher volume fraction, the additional copolymer may simply form additional lamellae.[25] The effective interfacial tension will then remain more or less constant. However, such a structure is admittedly rather speculative and is not considered in this paper.

It is worth noting that in our derivation of the mean-field equations the condition of zero volume change upon mixing, which constrains the sum of all the reduced densities to remain constant throughout the system, automatically includes excluded volume effects. In fact for a single polymer chain in a solvent the effective polymer interaction potential in our theory reduces to that given earlier by other authors.[26,27] In the present calculations this effect is evident in Figures 8 and 9, where the exclusion of the homopolymer by different amounts of block copolymer at the interphase takes place in such a way as to maintain the same overall reduced density profiles of A and B polymers. The same result is obtained from the reduced density profiles through the micelle as shown in Figure 12.

In summary, we have evaluated the sum of the various contributions to the interfacial free energy of an immiscible homopolymer blend with the corresponding block copolymer at the interphase. The block copolymer was assumed to have a random configuration in the bulk of the homopolymer, and an estimate of the CMC was given. Out of a large number of possible molecular weight combinations, we chose the conditions closest to the experiments of Riess et al.[9] for the quaternary polystyrene–polybutadiene–copolymer–styrene system. The calculated values of the interfacial tension γ were found to decrease too rapidly compared to experiment with increasing copolymer concentration, and reasons for this discrepancy were explored.

Acknowledgment. We thank Professor Gérard Riess for many stimulating discussions and correspondence concerning his measurements of the interfacial tension in the quaternary PS–PBD–CopSBD–S system. We also thank L. M. Marks for developing the computer programs used to evaluate the interfacial density profiles and surface tensions and for general assistance with the numerical calculations. Finally, we are grateful to Dr. R. H. Marchessault and Professor K. F. O'Driscoll for comments regarding the calculation of the critical micelle concentration.

Appendix A

The procedure for solving numerically the equations for the polymer distribution functions follows closely the method outlined in Appendix B of I. Initial guesses are made for $\phi_A(x) = \phi_{HA}(x) + \phi_{CA}(x)$ and $\phi_B(x) = \phi_{HB}(x) + \phi_{CB}(x)$ which interpolate between $\phi_A(\pm\infty)$ and $\phi_B(\pm\infty)$, respectively. From these estimates we obtain the initial guesses for $\hat{\omega}_A(x)$ and $\hat{\omega}_B(x)$. The discretized versions of eq 2-26 and 2-29 are then solved for $q_{HA}(x,t)$ and $q_{HB}(x,t)$, from which we obtain new values of $\phi_{HA}(x)$ and $\phi_{HB}(x)$. Also, eq 2-38 and 2-41 are solved for $q_{CA}(x,t)$ and $q_{CB}(x,t)$, and then with $q_{CB}(x,1)$ and $q_{CA}(x,1)$ as initial conditions the same equations are solved for $q_{AB}(x,t)$ and $q_{BA}(x,t)$, respectively. From these quantities new sets of $\phi_{CA}(x)$ and $\phi_{CB}(x)$, and hence $\phi_A(x)$, $\phi_B(x)$, $\hat{\omega}_A(x)$, and $\hat{\omega}_B(x)$, are obtained. The iteration is then repeated using the relaxation and modified secant methods outlined in I until convergence is obtained.

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Polymers at an Interface. 2. Interaction between Two Plates Carrying Adsorbed Polymer Layers

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ABSTRACT: We analyze the concentration profiles and the interaction energy for flexible polymer chains, plus a solvent, inside a narrow gap (thickness $2h$) between two weakly adsorbing plates. (1) For complete equilibrium (i.e., when the chains can exchange reversibly with a bulk solution), we prove that the interaction between plates is *always attractive*: this holds in good or bad solvents. (2) A more practical case corresponds to a constrained equilibrium, where the total number of chains between the two plates is fixed. This case is more delicate, and we restrict it here to *good solvents*. (a) The simplest mean field calculation gives an exact cancellation (no force for any h). (b) We have constructed a more sophisticated approach, incorporating the scaling exponents but allowing for precise numerical calculations. The result is a *repulsive* interaction, decreasing like h^{-2} at large h and like $h^{-5/4}$ at small h.

I. Introduction

Colloidal suspensions, where the grains are coated with an adsorbed polymer, are often "protected" or "sterically stabilized".[1-8] Direct measurements of the repulsions between two plates coated with a block copolymer [poly(vinyl acetate) + poly(vinyl alcohol)] have been carried out in Bristol.[9] More recently, the interactions between mica plates covered with adsorbed polystyrene have been studied.[10] Unfortunately, for technical reasons, the choice of solvent was limited, and the data of ref 10 are restricted to a bad solvent (cyclohexane at ~21 °C). They do show forces of range comparable to the coil size, which are in this case repulsive at short distances and attractive at long distances.

On the theoretical side, the situation is somewhat complex.[11-17] Consider, for instance, the more common case where the solvent is good. Each plate is assumed to carry a diffuse adsorption layer of thickness much larger than the monomer size. When we bring the two plates close together, as shown in Figure 1, the two adsorption layers begin to overlap. Because the chains repel each other in good solvent conditions, we can immediately think of a repulsive effect. But we should also keep in mind the fact that each plate attracts the chains: thus an increase in the local monomer concentration near the plates tends to lower the energy; this gives an attractive component to the force.

Thus the overall interaction between plates is the result of a delicate balance between opposite effects. There is a rough qualitative analogy between this situation and the problem of *chemical binding*, where the overlap between electron clouds from two molecules may or may not lower the energy. The analogy is not very deep because the polymer problem does not display any analogue of the Pauli principle. But the relation with quantum effects does exist when we work at the mean field level[18-20] describing the concentration profiles in terms of a field ψ rather than in terms of a monomer concentration $\Phi \sim |\psi|^2$.

We shall show, however, that the mean field approach is *completely inadequate* to discuss the plate–plate interactions in good solvents.[31] Indeed this is one case where a correct scaling description of the concentration profiles is absolutely required to predict even the sign of the forces. In a recent paper[21] (hereafter referred to as I), we constructed the adsorption profile near a single plate, including all scaling exponents. We restricted our attention to *weak coupling*, i.e., to situations where the adsorbing sites are not saturated with polymer. But we pointed out that this weak coupling remains compatible with strong adsorption, i.e., with a free energy of sticking *per chain* which is many times kT. The aim of the present paper is to apply the methods of I to the discussion of interactions between two plates. We are faced with two possible situations:

(1) *Ideal equilibrium*, where the adsorbed layers (in the gap between the two plates) can exchange polymer with an ambient solution of prescribed concentration. Of course, this assumption of complete reversibility is bad for strong adsorption, but we must discuss it first to understand the basic facts (section III).

(2) *Restricted equilibrium*, where we assume that the adsorbed layers have been prepared by contact with a solution (for widely separated plates). Then the solution is washed out and replaced by pure solvent. Each plate keeps an adsorbed layer with a certain number Γ of monomers per cm^2. We then bring the interplate gap down to a prescribed value $2h$ and assume that during this "squeezing" operation no chain leaves the gap region: Γ is fixed. From refractive index measurements, Klein was led to suggest a condition of this sort for his experiments on PS + mica.[10] We further assume that the concentration

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