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Table V) for the two systems is explained. Remaining deviations from theory are the findings that slopes are generally smaller than expected and that the binodal for the PAN-containing system falls below that for the X-500 system.

The foregoing analysis has failed to provide an explanation for the remaining discrepancies between theory and experiment. The study of additional systems exhibiting even greater differences in chemical constitution and conformation (as noted above) might help in clarifying said discrepancies. It is, in any case, important to appreciate that the differences exhibited by the two systems, both with respect to each other and with respect to theory, are relatively minor ones. The theory appears to be on a very sound basis.

Registry No. PBA, 24991-08-0; PAN, 25014-41-9; DMAc, 127-19-5; 4-aminobenzoic acid homopolymer, 25136-77-0.

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Effect of Block Copolymers at a Demixed Homopolymer Interface

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ABSTRACT: A statistical thermodynamic theory is used to derive the mean-field equations for the fundamental probability distribution functions characterizing a system of two immiscible homopolymers (A and B), diluted with solvent, in the presence of a diblock copolymer (AB). The equations are solved numerically in a "*computer experiment*" and the various contributions to the free energy and interfacial tension are evaluated to determine their relative importance. For a symmetric diblock copolymer and homopolymers of infinite molecular weight (as well as a symmetric solvent), we find that the reduction in interfacial tension, $\Delta\gamma$, with increasing copolymer molecular weight and concentration arises mainly from the energetically preferred orientation of the blocks at the interface into their respective compatible homopolymers. The main counterbalancing term in the expression for $\Delta\gamma$ is the entropy loss of the copolymer which localizes at the interface. The loss of conformational or "*turning-back*" entropy of both copolymers and homopolymers at the interface is shown to contribute little to $\Delta\gamma$. Keeping only the two main terms in $\Delta\gamma$, we find an exponential dependence on the parameter $Z_C\chi\varphi_P$, where Z_C is the degree of polymerization of the symmetric copolymer, χ is the interaction parameter between A and B, and φ_P is the volume fraction of homopolymer.

1. Introduction

The use of block copolymers has led to the design of polymer blends with remarkably versatile mechanical properties.[1-5] In particular, when added in small amounts to immiscible homopolymers, the block copolymers are found to behave as classical surfactants, similar to soap molecules at an oil–water interface.[6-8] The additive facilitates mixing by dramatically lowering the interfacial tension between the two normally immiscible phases.

Although there is now a great deal of experimental information available,[9-12] our theoretical understanding has not kept up with the latest practical developments. The purpose of this series of papers is to apply our recently developed general theory of polymeric alloys to study the emulsifying behavior of block copolymers in immiscible homopolymer blends.

In an earlier paper[13] we set up and solved numerically the mean-field equations for a quaternary system consisting of two highly incompatible homopolymers, along with the associated diblock copolymer, and diluted with a good solvent. In the absence of detailed microscopic information about the modified interphase region between the homopolymers, we performed what was essentially a computer experiment, in which the interfacial polymer

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density profiles were calculated, along with the interfacial tension. The block copolymer was found to be localized at the interface, as expected, and the homopolymer profiles were broadened with increasing copolymer concentration and molecular weight. In the present paper we have carefully analyzed the importance of the different terms in the free energy of the system and identified two main effects that account for most of the change in the interfacial tension. Our finding is that the loss of entropy due to the localization of the block copolymer at the interface is more than offset by the associated reduction in interaction energy resulting from the confinement of the blocks of the copolymer to their respective homopolymer phases.

In section 2 we review our previously developed mean-field equations for multicomponent systems,[14] and we cast the theory in a form that separates out the conformational (or "turning-back") entropy of the homopolymers and copolymers at the interface from the strictly combinatorial terms associated with the inhomogeneous system. Section 3 is concerned with a simplification of the equations for the most transparent case of a completely symmetric system, with degrees of polymerization (DP) of the homopolymer taken to be infinite (in order to simplify the combinatorial entropy expression for the homopolymers), and equal DP for the blocks of the copolymer. The system is characterized by a single χ parameter, with the corresponding parameters for the polymer–solvent interaction set equal to zero for a symmetric solvent. A simple scaling law for the reduction in the interfacial tension is derived, and plots of the polymer profiles, interfacial lengths, and interfacial tension are given for the case $\chi\varphi_P Z_C \leq 2$ (φ_P is the volume fraction of homopolymer and Z_C is the DP of the block copolymer). The discussion and conclusions are given in sections 4 and 5, respectively.

2. Mean-Field Theory

In an earlier paper we have discussed in great detail the derivation of the mean-field equations for a multicomponent system.[13] Here we review some of the main results and nomenclature required for an understanding of the present problem.

Previously, the free energy functional was minimized with respect to the density of monomer units $\rho_\kappa(r)$ of each component (or alternatively the volume fraction $\varphi_\kappa(r) = \rho_\kappa(r)/\rho_{0\kappa}$, $\rho_{0\kappa}$ being the density of the pure material) and the associated mean field $\omega_\kappa(r)$, subject to the usual constraints of no volume change upon mixing, i.e.

$$\sum\varphi_\kappa(r) = 1 \tag{2-1}$$

and a constant number of particles

$$\int \mathrm{d}^3r\ \rho_\kappa(r) = N_\kappa \tag{2-2}$$

In the following, in order to simplify the results as much as possible, we will assume that the densities of all pure components are the same, denoted by ρ_0. Generalization of these results is straightforward. The (reduced) free energy of mixing of the multicomponent system is then given by

$$\mathcal{F}/\rho_0 = {}^1\!/_2\sum_{\kappa,\kappa'}\chi_{\kappa\kappa'}\int \mathrm{d}^3r\ \varphi_\kappa(r)\varphi_{\kappa'}(r) - \sum_\kappa\int \mathrm{d}^3r\ \varphi_\kappa(r)\omega_\kappa(r) - \sum_\kappa^{\mathrm{C}}\frac{N_\kappa}{Z_\kappa\rho_0}\ln\left(\mathcal{Q}_\kappa\rho_0/N_\kappa\right) \tag{2-3}$$

Here the summation over κ with a "C" means that the block copolymer is to be treated as a single component, and no "C" over the summation sign indicates that the A and B blocks of the copolymer are to be treated as independent components. In the latter case the index κ runs over HA (homopolymer A), CA (block A of copolymer), HB (homopolymer B), CB (block B of copolymer), and S (solvent). $\chi_{\kappa\kappa'}$ is the Flory–Huggins interaction parameter, N_κ is the total number of monomer units of component κ, and Z_κ is the corresponding degree of polymerization ($Z_S = 1$).

The quantity $\mathcal{Q}_\kappa$ for the homopolymers is defined as the integral of the fundamental probability distribution function $Q_\kappa(r,t|r_0)$ for a chain of t repeat units to start at r_0 and end at r

$$\begin{aligned}\mathcal{Q}_\kappa &= \int \mathrm{d}^3r \int \mathrm{d}^3r_0\ Q_\kappa(r,t|r_0)\\ &= \int \mathrm{d}^3r\ q_\kappa(r,t)\end{aligned} \tag{2-4}$$

and Q_κ itself satisfies a modified diffusion equation,[15]

$$\frac{\partial Q_\kappa}{\partial t} = \frac{b_\kappa^{\,2}}{6}\nabla^2 Q_\kappa - \omega_\kappa Q_\kappa \tag{2-5}$$

where b_κ is the Kuhn statistical length of a single segment of the polymer. In what follows we will assume that all the Kuhn lengths for the polymers are equal, denoted by b. The quantity $\mathcal{Q}_S$ for the solvent is defined by

$$\mathcal{Q}_S = \int \mathrm{d}^3r\ e^{-\omega_S(r)} \tag{2-6}$$

The minimization of the free energy functional also gives the following key relations between q_κ, the integral of the probability distribution function, and the volume fractions of the various components. In particular, for κ = P (homopolymers HA or HB) we have

$$\varphi_P(r) = \frac{N_P}{\mathcal{Q}_P\rho_0}\int_0^1 \mathrm{d}t\ q_P q^\dagger{}_P \tag{2-7}$$

where $q^\dagger{}_P(r,t) = q_P(r, 1 - t)$, and for κ = CA and CB (blocks A and B of copolymer)

$$\varphi_{CA}(r) = \frac{f_{CA}N_C}{\mathcal{Q}_C\rho_0}\int_0^1 \mathrm{d}t\ q_{CA}q^\dagger{}_{CA,CB} \tag{2-8}$$

$$\varphi_{CB}(r) = \frac{f_{CB}N_C}{\mathcal{Q}_C\rho_0}\int_0^1 \mathrm{d}t\ q_{CB}q^\dagger{}_{CB,CA} \tag{2-9}$$

where $f_{CA} = Z_{CA}/Z_C$, $f_{CB} = Z_{CB}/Z_C$, and the block copolymer distribution functions $q_{CA,CB}$ and $q_{CB,CA}$ have been defined in an earlier paper[13] (where they were denoted by q_{AB} and q_{BA}). In addition for κ = S (solvent) we have

$$\varphi_S(r) = \frac{N_S}{\mathcal{Q}_S\rho_0}e^{-\omega_S(r)} \tag{2-10}$$

At this point we are ready to discuss the physical significance of the different contributions to the free energy, eq 2-3. The first term includes the Flory–Huggins interaction parameter $\chi_{\kappa\kappa'}$ and represents the interaction energy between the different polymers. The approximations involved in the use of the χ parameter are well-known and require no further elaboration here. The last two terms together represent the combinatorial entropy of the polymers (and solvent), as well as the "turning-back" entropy of the polymer chains at interfaces. The "turning-back" entropy plays an important role in determining the width of an interface. In general, the broader the interphase region, the smaller the entropy loss associated with the return of a part of a polymer chain to its compatible domain. Of course other limitations such as the interaction energy and the requirement of uniform domain densities favor segregation and restrict the wanderings of incompatible polymers.

The intermixing of the conformational and combinatorial entropies in each of the last two terms of the free energy expression, eq 2-3, makes it difficult to assess the importance of the various contributions for a specific system such as block copolymers localized at a homopolymer interface. Fortunately it is possible to surmount this difficulty and to simplify the free energy expression further by making use of a degree of freedom in the definition of the mean fields $\omega_\kappa(r)$.

As shown in an earlier paper, each mean-field function is defined only up to an additive constant. We now choose this constant so that ω_κ in one of the bulk phases (which phase is chosen is immaterial) is given by

$$\omega_\kappa{}^{\mathrm{b}} = -\frac{1}{Z_\kappa} \ln \varphi_\kappa{}^{\mathrm{b}} \tag{2-11}$$

for the homopolymers and solvent and by

$$f_{\mathrm{CA}}\omega_{\mathrm{CA}}{}^{\mathrm{b}} + f_{\mathrm{CB}}\omega_{\mathrm{CB}}{}^{\mathrm{b}} = -\frac{1}{Z_{\mathrm{C}}} \ln \varphi_{\mathrm{C}}{}^{\mathrm{b}} \tag{2-12}$$

for the blocks of the copolymer. In fact eq 2-12 does not completely specify the mean fields for the blocks since we may still choose one arbitrary constant, but this indeterminancy is not important since $\omega_{\mathrm{CA}}{}^{\mathrm{b}}$ and $\omega_{\mathrm{CB}}{}^{\mathrm{b}}$ always occur together in the above combination. Using the equations of motion for the appropriate q functions, we have for all components

$$q_\kappa{}^{\mathrm{b}} = e^{-tZ_\kappa \omega_\kappa{}^{\mathrm{b}}} \tag{2-13}$$

and for the blocks

$$q_{\mathrm{CA,CB}}{}^{\mathrm{b}} = e^{-(tZ_{\mathrm{CA}}\omega_{\mathrm{CA}}{}^{\mathrm{b}} + Z_{\mathrm{CB}}\omega_{\mathrm{CB}}{}^{\mathrm{b}})} \tag{2-14}$$

Combining eq 2-11 and 2-12 with eq 2-13 and 2-14 and substituting into eq (2-7) to (2-10), we find

$$N_\kappa/(Q_\kappa \rho_0) = 1 \tag{2-15}$$

for all components, and hence the last term in eq 2-3 vanishes. The expression for the total (reduced) free energy is now simply

$$\mathcal{F}/\rho_0 = {}^1\!/_2 \sum_{\kappa,\kappa'} \chi_{\kappa\kappa'} \int \mathrm{d}^3r\; \varphi_\kappa(r)\varphi_{\kappa'}(r) - \sum_\kappa \int \mathrm{d}^3r\; \varphi_\kappa(r)\omega_\kappa(r) \tag{2-16}$$

We are finally in a position to "open up" the last term in eq 2-16 and to look at the relative importance of the various contributions. For the solvent we have, using eq 2-7,

$$\omega_{\mathrm{S}}\varphi_{\mathrm{S}} = -\varphi_{\mathrm{S}} \ln \varphi_{\mathrm{S}} \tag{2-17}$$

and the modified diffusion equation for the homopolymers gives

$$\omega_{\mathrm{P}}\varphi_{\mathrm{P}} = \int_0^1 \mathrm{d}t \left\{ \frac{b^2}{6} \nabla^2 q_{\mathrm{P}} q^\dagger{}_{\mathrm{P}} - \frac{1}{Z_{\mathrm{P}}} \frac{\partial q_{\mathrm{P}}}{\partial t} q^\dagger{}_{\mathrm{P}} \right\} \tag{2-18}$$

while

$$\omega_{\mathrm{CA}}\varphi_{\mathrm{CA}} = f_{\mathrm{CA}} \int_0^1 \mathrm{d}t \left\{ \frac{b^2}{6} \nabla^2 q_{\mathrm{CA}} q^\dagger{}_{\mathrm{AB}} - \frac{1}{Z_{\mathrm{CA}}} \frac{\partial q_{\mathrm{CA}}}{\partial t} q^\dagger{}_{\mathrm{AB}} \right\} \tag{2-19}$$

with a similar expression for $\omega_{\mathrm{CB}}\varphi_{\mathrm{CB}}$.

Using the above relations in eq 2-16, we get

$$\begin{aligned}\mathcal{F}/\rho_0 = \int \mathrm{d}^3r\, \{ {}^1\!/_2 \sum_{\kappa,\kappa'} \chi_{\kappa\kappa'}\varphi_\kappa\varphi_{\kappa'} + \sum_\kappa^{\mathrm{C}} \frac{\varphi_\kappa}{Z_\kappa} \ln \varphi_\kappa &+ \\ \sum_{\mathrm{P=HA,HB}} \int_0^1 \mathrm{d}t\, \frac{b^2}{6} \nabla q_{\mathrm{P}} \nabla q^\dagger{}_{\mathrm{P}} &+ \\ \sum_{\kappa,\kappa'=\mathrm{CA,CB}} \int_0^1 \mathrm{d}t\, \frac{b^2}{6} \nabla q_\kappa \nabla q^\dagger{}_{\kappa\kappa'} &+ \\ \sum_{\mathrm{P=HA,HB}} \frac{1}{Z_{\mathrm{P}}} \left(\int_0^1 \mathrm{d}t\, \frac{\partial q_{\mathrm{P}}}{\partial t} q^\dagger{}_{\mathrm{P}} - \varphi_{\mathrm{P}} \ln \varphi_{\mathrm{P}} \right) &+ \\ \frac{1}{Z_{\mathrm{C}}} \left(\sum_{\kappa,\kappa'=\mathrm{CA,CB}} \int_0^1 \mathrm{d}t\, \frac{\partial q_{\mathrm{P}}}{\partial t} q^\dagger{}_{\kappa\kappa'} - \varphi_{\mathrm{C}} \ln \varphi_{\mathrm{C}} \right)&\end{aligned} \tag{2-20}$$

where $q_{\kappa\kappa} = 0$ by definition. The first two terms have the same functional form as the Flory–Huggins free energy of mixing for a uniform system. The third and fourth terms represent the "turning-back" conformational entropy of the homopolymers and block copolymers, respectively, and the last two terms arise from the decrease in the combinatorial entropy of the inhomogeneous polymers from the corresponding value for a homogeneous system. For a homogeneous system, only the first two terms of the expression are nonvanishing. Finally, the interfacial tension is obtained by subtracting off the bulk contribution to the free energy, and specializing to a one-dimensional geometry for the interface, we have

$$\gamma = \int \mathrm{d}x\, \{\Delta f(x) + \text{terms same as in eq 2-20}\} \tag{2-21}$$

where

$$\Delta f(x) = f(x)_{\text{Flory–Huggins}} - \sum_\kappa^{\mathrm{C}} \varphi_\kappa(x)\mu_\kappa \tag{2-22}$$

Since the chemical potential is given by

$$\mu_\kappa = \left\{ \frac{\partial f_{\mathrm{FH}}}{\partial \varphi_\kappa} + f_{\mathrm{FH}} - \sum_\kappa^{\mathrm{C}} \varphi_\kappa \frac{\partial f_{\mathrm{FH}}}{\partial \varphi_\kappa} \right\}^{\mathrm{bulk}} \tag{2-23}$$

the "inhomogeneous" Flory–Huggins free energy relative to the bulk free energy may be written

$$\Delta f = {}^1\!/_2 \sum_{\kappa,\kappa'} \chi_{\kappa\kappa'} (\varphi_\kappa - \varphi_\kappa{}^{\mathrm{b}})(\varphi_{\kappa'} - \varphi_{\kappa'}{}^{\mathrm{b}}) + \sum_\kappa^{\mathrm{C}} \frac{\varphi_\kappa}{Z_\kappa} \ln (\varphi_\kappa/\varphi_\kappa{}^{\mathrm{b}}) - \sum_\kappa^{\mathrm{C}} \frac{\varphi_\kappa - \varphi_\kappa{}^{\mathrm{b}}}{Z_\kappa} \tag{2-24}$$

In the next section we will discuss the relative importance of the different terms in eq 2-21 for γ.

3. Interfacial Tension and Width of a Symmetric System

In order to obtain some insight into the mechanism governing the reduction in interfacial tension, we consider a completely symmetric system with $Z_{\mathrm{HA}} = Z_{\mathrm{HB}} = \infty$, $Z_{\mathrm{CA}} = Z_{\mathrm{CB}}$, and $\chi_{\mathrm{AB}} = \chi$ (see Figure 1). Similar calculations may be carried out for homopolymers of finite molecular weight, but we expect the trends to be predictable from our present analysis. We choose $\chi_{\mathrm{AS}} = \chi_{\mathrm{BS}} = 0$ because for a completely symmetric solvent there is very little dependence of the interfacial tension on the actual values of these interaction parameters, the main effect of the solvent being a reduction in the volume fraction of polymer. The two variables of interest to use are therefore the molecular weight and volume fraction (or concentration) of block copolymer.

We denote the bulk values of the copolymer volume fraction by $\varphi_{\mathrm{C}}(\infty) = \varphi_{\mathrm{C}}(-\infty) = \varphi_{\mathrm{C}}$ for a symmetric system. This quantity is very close to the nominal amount of block

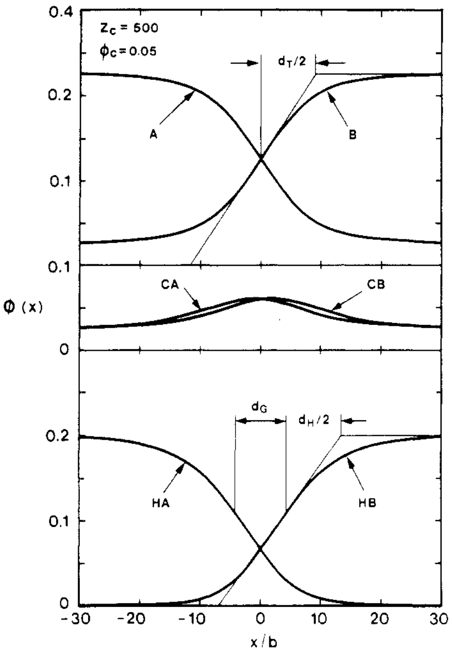

Figure 1. Interfacial profiles of total A and B segments of two immiscible homopolymers with localized AB diblock copolymer (top panel). $\varphi(x)$ is the volume fraction, and the distance through the interface is measured in units of the Kuhn length, b. The middle panel shows the volume fractions of the CA and CB blocks and the bottom panel displays the homopolymer profiles. The profiles in the top panel are obtained by adding the corresponding contributions from the lower two panels. The complete set of parameters for this symmetric system is shown in Figure 2. The various lengths characterizing the interphase region are discussed in section 3.

copolymer present (e.g., $\varphi_C = 0.05$ in Figures 1 and 3) since the amount of material collecting at the interface is negligible compared to the total amount for a large system. In addition, $\varphi_{HA}(\infty) = \varphi_{HB}(-\infty) = \varphi_P$, and introducing $\varphi_A(x)$ and $\varphi_B(x)$ as the volume fractions of *total* A and B units (blocks and homopolymers), the expression for the interfacial tension derived in the previous section becomes

$$\gamma = \int \mathrm{d}x \left\{ \Delta f + \sum_{P=HA,HB} \frac{b^2}{6} \left(\frac{\partial q_P}{\partial x} \right)^2 + \sum_{\kappa,\kappa'=CA,CB} \frac{b^2}{6} \int_0^1 \mathrm{d}t \, \frac{\partial q_\kappa}{\partial x} \frac{\partial q^\dagger{}_{\kappa\kappa'}}{\partial x} + \frac{1}{Z_C} \left(\sum_{\kappa,\kappa'=CA,CB} \int_0^1 \mathrm{d}t \, \frac{\partial q_\kappa}{\partial t} q^\dagger{}_{\kappa\kappa'} - \varphi_C(x) \ln \varphi_C(x) \right) \right\} \tag{3-1}$$

where

$$\Delta f = \chi \left(\varphi_A(x) - \varphi_P - \frac{\varphi_C}{2} \right) \left(\varphi_B(x) - \varphi_P - \frac{\varphi_C}{2} \right) + \chi\varphi_P(\varphi_A(x) + \varphi_B(x) - \varphi_P - \varphi_C) - \tfrac{1}{2}\chi\varphi_P(\varphi_C(x) - \varphi_C) + \frac{1}{Z_C}\{\varphi_C(x) \ln (\varphi_C(x)/\varphi_C(\infty)) - (\varphi_C(x) - \varphi_C(\infty))\} + \text{solvent terms} \tag{3-2}$$

In deriving eq 3-2 it is important to notice that combinatorial entropy terms for the homopolymers survive, in spite of the fact that $Z_{HA} = Z_{HB} = \infty$; for example

$$\lim_{Z_{HB}\to\infty} \frac{1}{Z_{HB}} \ln \varphi_{HB}(\infty) = -\chi\varphi_P \tag{3-3}$$

which may be easily shown by using the constancy of the chemical potential for homopolymer B. We also neglect the terms in eq 3-2 that depend only on the solvent volume fraction. The expression for the interfacial tension can then be considered as the sum of three main terms.

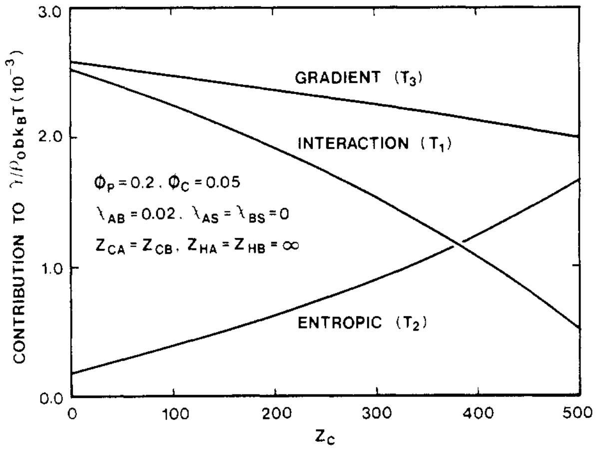

Figure 2. Various contributions to the reduced interfacial tension $\gamma/\rho_0 b k_B T$, according to the decomposition given by eq 3-4 in the text.

$$\gamma = \int \mathrm{d}x \, (T_1 + T_2 + T_3) \tag{3-4}$$

where the interaction term T_1 is given by

$$T_1 = \chi \left(\varphi_A(x) - \varphi_P - \frac{\varphi_C}{2} \right) \left(\varphi_B(x) - \varphi_P - \frac{\varphi_C}{2} \right) + \chi\varphi_P(\varphi_A(x) + \varphi_B(x) - \varphi_P - \varphi_C) - \tfrac{1}{2}\chi\varphi_P(\varphi_C(x) - \varphi_C) \tag{3-5}$$

Figure 2 shows the variation of T_1 with block copolymer molecular weight. We have found that the last term in T_1, which represents the gain in the interaction energy obtained by moving the diblock copolymer from the bulk to the interface (and orienting the blocks so that block A is in homopolymer A, etc.), is primarily responsible for the reduction of γ.

T_2 is related to the combinatorial entropy of the block copolymers

$$T_2 = \frac{1}{Z_C} \left\{ \sum_{\kappa,\kappa'=CA,CB} \int_0^1 \mathrm{d}t \, \frac{\partial q_\kappa}{\partial t} q^\dagger{}_{\kappa\kappa'} - \varphi_C(x) \ln \varphi_C(x) \right\} + \frac{1}{Z_C}\{\varphi_C(x) \ln (\varphi_C(x)/\varphi_C) - (\varphi_C(x) - \varphi_C)\} \tag{3-6}$$

and in Figure 2 we show the variation of this expression with Z_C. The last term in eq 3-6, representing the entropy loss arising from copolymer localization at the interface, gives the main positive contribution to the change in γ.

Finally, T_3 represents the "turning-back" entropy (or loss of conformational entropy) of the copolymers and homopolymers

$$T_3 = \sum_P \frac{b^2}{6} \left(\frac{\partial q_P}{\partial x} \right)^2 + \sum_{\kappa,\kappa'} \frac{b^2}{6} \int_0^1 \mathrm{d}t \, \frac{\partial q_\kappa}{\partial x} \frac{\partial q^\dagger{}_{\kappa\kappa'}}{\partial x} \tag{3-7}$$

and as shown in Figure 2 the variation in this term (which vanishes for a homogeneous system) is negligible compared to the changes in the entropic and interaction terms discussed earlier.

The reduction in the interfacial tension, $\Delta\gamma$, may therefore be well approximated by

$$\Delta\gamma \simeq \int \mathrm{d}x \left\{ \frac{\varphi_C(x)}{Z_C} \ln (\varphi_C(x)/\varphi_C) - \frac{\varphi_C(x) - \varphi_C}{Z_C} - \tfrac{1}{2}\chi\varphi_P(\varphi_C(x) - \varphi_C) \right\} \tag{3-8}$$

Calculations of the copolymer profiles (Figure 3) show that

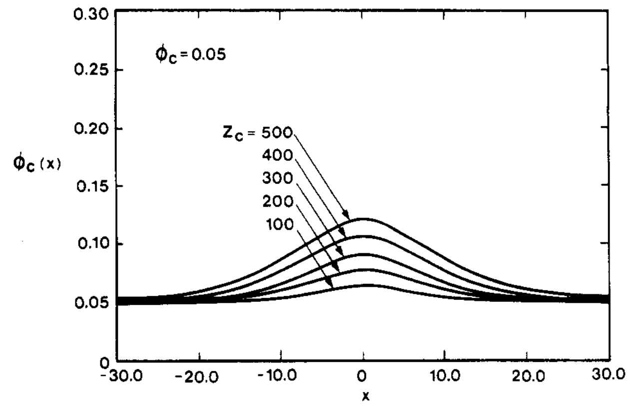

Figure 3. Block copolymer profiles through the interphase region for different copolymer molecular weights. The width at half-height (*d*) is almost constant for the different curves.

the width at half-height (*d*) is almost constant for varying copolymer molecular weight. Using this result we approximate the integral in eq 3-8 by

$$\Delta\gamma \simeq d\left\{\frac{\varphi_C(0)}{Z_C}\ln\left(\frac{\varphi_C(0)}{\varphi_C}\right) - \frac{\varphi_C(0)-\varphi_C}{Z_C} - \tfrac{1}{2}\chi\varphi_P(\varphi_C(0)-\varphi_C)\right\} \tag{3-9}$$

For constant *d* we minimize this expression with respect to $\varphi_C(0)$ to obtain

$$\varphi_C(0) \simeq \varphi_C e^{Z_C\chi\varphi_P/2} \tag{3-10}$$

and hence

$$\Delta\gamma \simeq d\varphi_C\left\{\left(\tfrac{1}{2}\chi\varphi_P + \frac{1}{Z_C}\right) - \frac{1}{Z_C}e^{Z_C\chi\varphi_P/2}\right\} \tag{3-11}$$

For $Z_C\chi\varphi_P \ll 1$, this result reduces to

$$\Delta\gamma \simeq -\frac{d}{8}Z_C\varphi_C\chi^2\varphi_P^2 \tag{3-12}$$

In the above treatment, *d* is just a parameter and is not determined by the theory. The numerical solution of the complete set of mean-field equations of course gives *d*, and as mentioned earlier, it turns out to be almost independent of the copolymer molecular weight. Apparently the loss of entropy associated with this effect is small or offset by the associated gain in interaction energy.

Several interesting features of the results eq 3-10 and 3-11 deserve comment. First, the exponential dependence on the block copolymer molecular weight, as well as the homopolymer volume fraction, explains the remarkable effectiveness of using large molecular weight diblocks as surfactants for concentrated mixtures of immiscible homopolymers. By comparison with the "exact" numerical calculation, shown in Figure 4, we see that eq 3-11, which predicts a linear dependence of $\Delta\gamma$ on Z_C (for small Z_C), represents a good approximation. Second, Figure 5 again shows the results of the numerical work, in which the linear dependence of the interfacial tension on block copolymer volume fraction can be seen, in agreement with eq 3-11.

Finally, referring back to Figure 1, it is interesting to plot some of the lengths associated with the interphase region. The distance between the midpoints of the homopolymer profiles (lower panel of Figure 1), also called the gap distance d_G, is shown in Figures 6 and 7 for varying copolymer molecular weight and concentration. For small Z_C and φ_C, the gap separation follows closely the copolymer concentration profile

$$d_G \simeq d(\varphi_C(0) - \varphi_C) \tag{3-13}$$

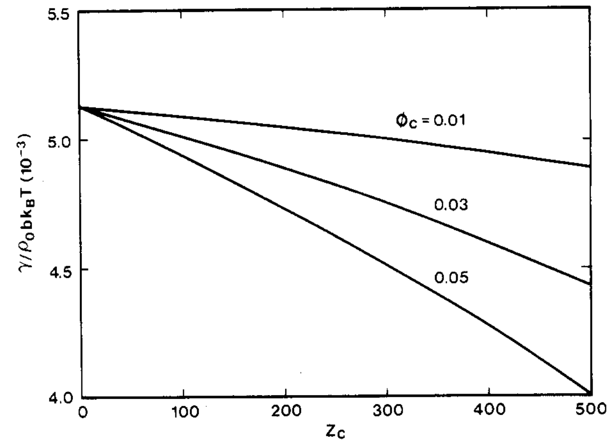

Figure 4. Variation of reduced interfacial tension with copolymer molecular weight for different overall copolymer volume fractions.

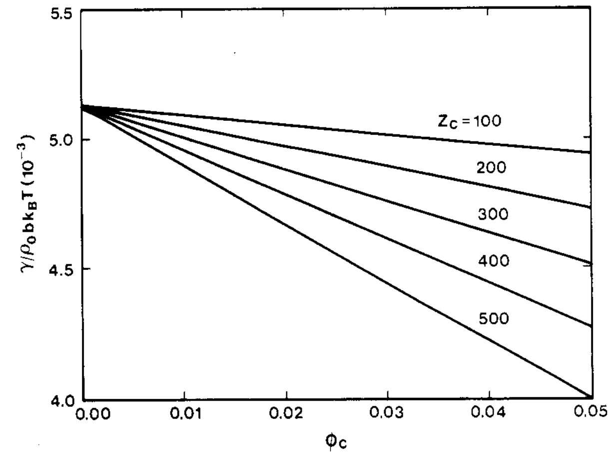

Figure 5. Variation of reduced interfacial tension with overall copolymer volume fraction for different copolymer molecular weights.

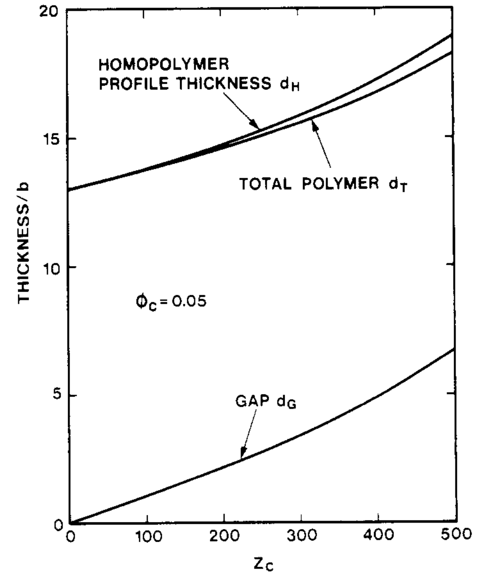

Figure 6. Thickness parameters (in units of the Kuhn length *b*) as a function of the copolymer molecular weight of the symmetric system shown in Figure 1.

As expected, the gap separation goes to zero for a symmetric system in the limit of decreasing copolymer concentration.

As shown in Figure 6, the profile thickness d_H increases exponentially with copolymer molecular weight and correlates well with the corresponding increase in d_G. The

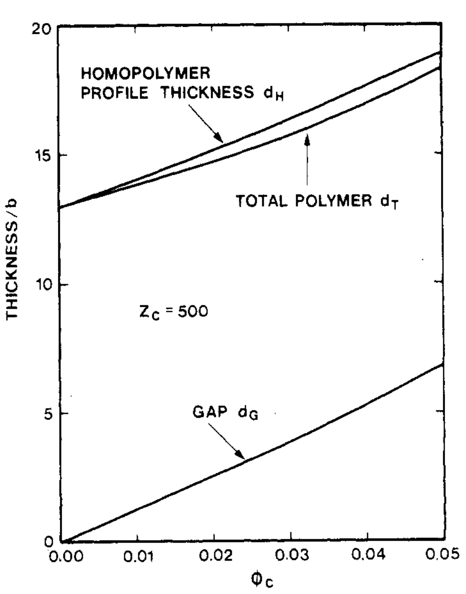

Figure 7. Thickness parameters (in units of the Kuhn length *b*) as a function of the overall copolymer volume fraction for the symmetric system shown in Figure 1.

increasing width (or decreasing slope) of the homopolymer profiles, compared to the total polymer profiles, reflects the necessity to accommodate the exponentially growing (with molecular weight) amount of copolymer at the interface. For increasing φ_C (and fixed Z_C), d_G in Figure 7 shows a linear dependence, as expected from eq 3-10 and 3-13. In this case the homopolymer profiles are pushed apart gradually by the intrusion of the copolymer, and d_H, the homopolymer profile thickness, also increases linearly with φ_C. As in Figure 6, the total polymer profiles are seen to be steeper than the homopolymer profiles, because of the need to accommodate block copolymer at the interface.

4. Discussion

A major problem with our analysis is to develop a criterion for the formation of a third phase in the system. We have analyzed the effect of solubilizing small amounts of block copolymer in a two-phase system consisting of immiscible homopolymers diluted with a solvent. However, it is well-known that under certain conditions the block copolymer will form an ordered mesophase.[11,19] Here we will show that the condition $\chi Z_C \varphi_P \leq 2$ certainly ensures no mesophase formation, although this criterion is probably too strong. A more detailed discussion of the phase diagram for $\chi Z_C \varphi_P > 2$ is outside the scope of this paper.[20]

Starting with the well-known formula for the critical value of the interaction parameter for phase separation as applied to the copolymer and one of the homopolymers ($Z_{HA} = Z_{HB} = Z_H$)

$$\chi_{\text{crit}} = \frac{1}{2}\left(\frac{1}{Z_C^{1/2}} + \frac{1}{Z_H^{1/2}}\right)^2 \tag{4-1}$$

and letting $Z_H \rightarrow \infty$, we get

$$\chi_{\text{crit}} = \frac{1}{2}\frac{1}{Z_C} \tag{4-2}$$

On the other hand, from the composition rules for the effective interaction between a symmetric diblock copolymer and a homopolymer we have[13]

$$\chi^{\text{eff}}{}_{\text{cop-hom}} = (\chi/4)\varphi_P \tag{4-3}$$

which must be less than χ_{crit} for no phase separation, giving

$$\chi \varphi_P Z_C \leq 2 \tag{4-4}$$

For larger values of this parameter, the effects shown in the figures are accentuated but they have to be interpreted with care because of the possibility of third-phase formation.

We find no evidence that choosing the degree of polymerization (DP) of the blocks of the copolymer equal to the DP of the corresponding homopolymers has any singular effect on the interfacial tension. With Z_{HA} and Z_{HB} finite, the interfacial tension and its decrease with increasing copolymer concentration or molecular weight simply scale down monotonically, as already noted in our earlier publication. Recently, we have found that Dr. Dale Meier has come to the same conclusions working with the ratio of block copolymer to homopolymer molecular weight.[21] The sometimes quoted "rule of thumb" that matching the DP of the copolymer to the DP of the homopolymer gives the greatest reduction in interfacial tension may be simply due to the fact that larger blocks have very much longer equilibration times, thus appearing to render the longer blocks ineffective. In any case, both copolymer concentration and molecular weight are equally important in reducing the interfacial tension, as is evident from the figures. It should be noted, however, that the interfacial tension *surface* (γ plotted against Z_C and φ_C) is bounded by a cmc (critical micelle concentration) line, since blocks of large molecular weight tend to form micelles in the bulk of the homopolymer, rather than congregating at the interface. Using our previous rough estimates for the cmc,[13] we have verified that our system is well inside the cmc boundary. In a practical sense, using shorter blocks for the copolymers means avoiding micelle formation along with better mixing due to shorter reptation times and lower cost of manufacture. The length of the blocks is, of course, a matter of choice for the practical application involved.

Finally, we comment on a recent work by Leibler,[22] dealing with a system of a nearly compatible mixture of two homopolymers with added block copolymer. Since the interface is very broad in this case, a gradient expansion can be carried out, giving a generalization of the Cahn–Hilliard theory.[23] We have also carried out the gradient expansion starting from our expression for the free energy and find results similar to Leibler's, with a minor difference in one of the coefficients arising from his different definition of the random phase approximation. The physically important point however is that with the gradient expansion the block copolymer is effectively treated as a small-molecule solvent compared to the large width of the interface region, and the structure of the copolymer becomes irrelevant. The system thus behaves as a mixture of two homopolymers driven to the consolute point by the addition of an excess of solvent. The lowering of the interfacial tension in this case has nothing to do with the surfactant activity of the block copolymer molecules and is qualitatively different from the mechanism described in this paper.

5. Conclusions

Starting with the functional integral representation of the partition function, we have derived the mean-field equations for a ternary system consisting of two immiscible homopolymers, diluted with a solvent and with added diblock copolymer. We solved these equations numerically and found that the reduction in interfacial tension with increasing copolymer concentration and molecular weight could be accounted for by the reduction in interaction energy of the block copolymers at the interface, taking into account the associated entropy loss of the localized chains. The simplified expression for the interfacial tension showed an exponential dependence on the copolymer molecular weight, as well as the interaction parameter and homopolymer volume fraction, thus explaining the dramatic effect of block copolymers as emulsifiers for immiscible homopolymers.

In the end, our simplified model bears a striking resemblance to phenomenological descriptions of hydrocarbon–water–surfactant systems, which postulate surfactant molecule–interface interactions and include the entropy loss due to localization in the expression for the free energy.[24] However, it was not obvious a priori that polymeric systems could be described in the same way since there is considerable rearrangement of the polymer density profiles at the interface when the surfactant is added. Moreover, our model gives a specific form for the surfactant molecule–interface interaction and allows us to predict the dependence of the interfacial tension on important parameters such as the block copolymer molecular weight.

Finally, we end with an appeal for new experiments to determine the interfacial tension and microstructure of polymeric interfaces with added block copolymer surfactants. While traditional surface tension measurements leave a lot to be desired[25] and mechanical surface wave methods[26] are difficult to apply to these systems, we believe that the use of scattering techniques may have some useful potential.

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Supplementary Material Available: Program A to calculate asymptotic volume fractions of all components, program B to calculate interfacial density profiles (using input from program A), and a general description of both programs (14 pages). Ordering information is given on any current masthead page.

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Dynamic Motions of Rodlike Polymers in Semiconcentrated Solution: Poly(*n*-butyl isocyanate) in Carbon Tetrachloride[†]

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ABSTRACT: Dynamic motions of a rodlike polymer, poly(*n*-butyl isocyanate) ($M = 7.5 \times 10^4$, $M_w/M_n \lesssim 1.2$), in carbon tetrachloride were studied by quasi-elastic laser light scattering. The Edwards and Evans model predicts that, in semiconcentrated solution, the rods should exhibit two translational motions, a free translational motion and a cooperative translational motion. Both motions have been observed. However, the cooperative motions do not appear to follow the predicted behavior exactly. The rotational motions follow the Doi and Edwards model where free translational diffusion is a determining factor.

Introduction

The equation describing the Brownian motions of a rodlike particle in an infinitely dilute solution is given by[1]

$$\partial F/\partial t = \{D_{t0\parallel}(\vec{u}\cdot\vec{\nabla}_r)^2 + D_{t0\perp}[\nabla_r{}^2 - (\vec{u}\cdot\vec{\nabla}_r)^2] - D_{r0}\hat{I}^2\}F \quad (1)$$

where F $(=F(\vec{r},\vec{u};t))$ is the probability of finding a rod specified by a position vector $\vec{r}$ and an orientation vector $\vec{u}$ at time t, and $\hat{I}^2$ $[=-(\sin^{-1}\theta\ \partial/\partial\theta \sin\theta\ \partial/\partial\theta + \sin^{-2}\theta\ \partial^2/\partial\phi^2)]$ is a dimensionless orbital angular momentum operator. The "free" diffusion coefficients (at infinite dilution), $D_{t0\parallel}$, $D_{t0\perp}$, and D_{r0} are given by[2]

$$D_{t0\parallel} = k_B T \ln (L/d)(2\pi\eta_s L)^{-1} \quad (2a)$$

$$D_{t0\perp} = {}^1\!/_2 D_{t0\parallel} \quad (2b)$$

$$D_{r0} = {}^2\!/_3 D_{t0\parallel} L^{-2} \quad (2c)$$

where L is the length of the rod, d is the diameter, η_s is the solvent viscosity, k_B is the Boltzmann constant, and T is the absolute temperature (K).

In "semidilute" solution, defined within the limits

$$L^{-3} \ll c \ll (dL^2)^{-1} \quad (3)$$

where c is the rod number concentration per unit volume. Doi and Edwards[2] have considered rod–rod encounters which affect mainly the lateral $(D_{t\perp})$ and rotational (D_r) diffusion. They constructed a model in which the rod was

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