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Theory of Homopolymer–Block Copolymer Blends. The Search for a Universal Compatibilizer

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ABSTRACT: We discuss by means of a statistical theory the thermodynamic behavior of a blend containing homopolymer A, homopolymer B, an arbitrary block copolymer CXY, and solvent. The behavior of the diblock copolymer near the interface is studied in detail. When CXY is added, the interfacial tension decreases and the width of the interface increases if special relationships between the χ parameters, χ_{XA}, χ_{XY}, χ_{YB}, etc., are chosen. Under such circumstances, CXY can be considered as a universal compatibilizer, if the concentration is below the critical micelle concentration.

1. Introduction

The modified behavior of a blend of two homopolymers with the addition of a few percent of a diblock copolymer is of great practical importance.[1-5] The use of diblock copolymers as surfactants or emulsifying agents in blends or alloys of incompatible homopolymers can dramatically improve the mechanical and morphological properties. However, the molecular weight of the diblock must be adjusted to the specific blend to get maximum improvement of desired properties. We denote the homopolymers by A and B. A widely used diblock copolymer is of the form AB so that each of the blocks is composed of the same type of monomer as the homopolymer and the molecular weights are the only variable parameters. For the A–AB–B system theoretical results have been given in detail in earlier papers[6-10] and it has been shown experimentally and theoretically that quite satisfactory improvement can be achieved.

The quantities of interest are the local interfacial properties which are influenced by the diblock copolymer. To study the use of the diblock copolymers as compatibilizing agents, we focus on properties such as the interfacial tension or the width of the interface. Other quantities of interest are the amount of the copolymer at the interface, the concentration profiles, and the critical micelle concentration.[11,12]

In this paper we generalize our earlier study to an arbitrary A–XY–B blend where the block copolymer is made out of totally different blocks (Figure 1). This seems to be a very unpromising situation at first glance, but one can imagine that if, for example, X is very incompatible with B but is less incompatible with A,[13] then locally we have a thermodynamic driving force that will orient the block copolymer at the interface and lead to compatibilizing effects. Clearly this system will only be in local thermodynamic equilibrium, as the lowest free energy state would consist of the block copolymers macroscopically phase separated from the homopolymer blend. The relevance of the calculations presented here to real systems therefore depends very much on the preparation of the multicomponent system in such a way as to promote the interfacial activity of the block copolymer. Nevertheless, there is some evidence that blends with incompatible block copolymers as interfacial agents do exist as shown by the work by Paul and collaborators,[3] on poly(ethyleneterephthalate) and high-density polyethylene with poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) as compatibilizer. The problem we discuss is the most general one, since all cases A–AB–B or any combination A–XB–B, etc., can be derived from the general case.

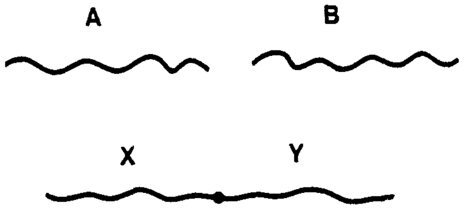

Figure 1. Block copolymer XY as a surfactant between homopolymers A and B.

We assume our multicomponent system is composed of $\tilde{N}_A$ polymers of type A, $\tilde{N}_B$ of type B, $\tilde{N}_S$ solvent molecules, and $\tilde{N}_C$ of the copolymers (the notation will be clarified later). First we suppose that the total concentration of the polymers is well in the semiconcentrated regime and we may neglect self-interactions of the type $V_{\kappa\kappa}$ where the index κ runs over all polymer components. Similarly, we choose ϕ_A or ϕ_B not too close to unity in order to justify the mean-field approximation, since concentration fluctuations can then be neglected. With these assumptions the general partition function

$$Z = (\text{kinetic part}) \int \prod d^3 r_{si} \int \prod \delta \mathbf{r}_{pj} \times \exp\left\{ -\frac{3}{2b^2} \int dt\, r_p^{\,2}(t) - \int \beta V \right\} \quad (1.1)$$

can be calculated by the method of steepest descent,[6] which is the mean-field approximation. Here the functional integral is over all space curves $\mathbf{r}_{pj}$, which represent possible configurations of the jth type of macromolecule p, r_{si} is the spatial variable corresponding to the ith type of solvent, and t is the curvilinear coordinate.

2. Outline of the Theory and Basic Equations

The theory has been developed in refs 6 and 7, and here we use the general results derived previously. The main result of interest to us is the free energy functional

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$$\mathcal{F} = \frac{F}{\rho_0} = \int \mathrm{d}^3 r \left\{ f_\mathrm{h} - \sum_\kappa \phi_\kappa \left[\omega_\kappa + \frac{1}{r_\kappa} \log \phi_\kappa \right] - \frac{1}{12} \sum_{\kappa\kappa'} \chi_{\kappa\kappa'} \sigma_{\kappa\kappa'}{}^2 \nabla\phi_\kappa \nabla\phi_{\kappa'} \right\} - \frac{1}{\rho_0} \sum_\kappa \tilde{N}_\kappa \log \left(\frac{\rho_0}{r_\kappa z_\kappa e} \right) + \frac{1}{\rho_0} \sum_\kappa^{C} \tilde{N}_\kappa \log \left(\frac{\tilde{N}_\kappa}{z_\kappa Q_\kappa e} \right) \quad (2.1)$$

The notation is as follows. The index κ runs over all components in the system. $\tilde{N}_\kappa$ denotes the number of polymer chains of type κ; i.e., if κ belongs to a polymer ($\kappa = p$), $\tilde{N}_p$ is then $\tilde{N}_p = N_p/Z_p$, where N_p is the number of monomer units of type p and Z_p is the degree of polymerization. If κ refers to the solvent, we have $N_s = \tilde{N}_s$ solvent molecules, since the degree of polymerization for the solvent molecules is unity. When $\kappa = \mathrm{X}$ and $\kappa = \mathrm{Y}$ are linked together to form a copolymer XY, we have $\tilde{N}_\mathrm{XY} = N_\mathrm{CX}/Z_\mathrm{CX} = N_\mathrm{CY}/Z_\mathrm{CY}$. In general, we must use reduced quantities in terms of $\rho_{\mathrm{o}\kappa}$ as the density of the pure material and ρ_o as a reference density. We define then

$$\hat{\omega}_\kappa = (\rho_{\mathrm{o}\kappa}/\rho_\mathrm{o})\omega_\kappa \qquad \hat{b}_\kappa{}^2 = (\rho_{\mathrm{o}\kappa}/\rho_\mathrm{o}) b_\kappa{}^2$$
$$r_\kappa = (\rho_\mathrm{o}/\rho_{\mathrm{o}\kappa}) Z_\kappa \qquad \hat{\mu}_\kappa = (\rho_{\mathrm{o}\kappa}/\rho_\mathrm{o})\mu_\kappa \quad (2.2)$$

where ω_κ is the mean field (or effective potential) acting on component κ in the presence of all other components. However, for the calculations in this paper we assume $\rho_{\mathrm{o}\kappa} = \rho_\mathrm{o}$ for all κ and we use the reduced and normal quantities interchangeably. ω_κ is a function of all the components in the system. The $\chi_{\kappa\kappa'}$ parameters are the Flory–Huggins interaction parameters and are related to the potentials $V_{\kappa\kappa'}$ if $V_{\kappa\kappa'}$ is short-ranged. The range of the potential is denoted by a parameter $\sigma_{\kappa\kappa'}$, which is of the order of the Kuhn length, b_κ. The volume fractions ϕ_κ are given by

$$\phi_\kappa = \rho_\kappa/\rho_{\mathrm{o}\kappa} \quad (2.3)$$

z_κ is the kinetic contribution to the partition function and will not be of interest in this paper. All information about the chain distribution, i.e., the shape of the chain, is contained in the Q_κ's, which are a multiple integrals over the corresponding chain distribution functions. $\sum_\kappa^C$ means the diblock is treated as a single component while $\sum_\kappa$ means the blocks are treated separately. Finally, f_h is the rescaled Flory–Huggins free energy given by

$$f_\mathrm{h} = \sum_\kappa \phi_\kappa \mu_{\mathrm{o}\kappa} + \frac{1}{2} \sum_{\kappa\kappa'} \chi_{\kappa\kappa'} \phi_\kappa \phi_{\kappa'} + \sum_\kappa \frac{\phi_\kappa}{r_\kappa} \log \phi_\kappa \quad (2.4)$$

where the chemical potentials are given by

$$\mu_\kappa = Df_\mathrm{h}/D\phi_\kappa + \phi_\mathrm{C}/r_\mathrm{C} \qquad \forall\ \kappa \neq C \quad (2.5)$$

and the derivative is given by the Gibbs–Duhem rule

$$Df_\mathrm{h}/D\phi_\kappa = \partial f_\mathrm{h}/\partial\phi_\kappa - (f_\mathrm{h} - \sum_\gamma \phi_\gamma (\partial f_\mathrm{h}/\partial\phi_\gamma)) \quad (2.6)$$

In general, we find for the chemical potential

$$\mu_\gamma = \mu_{\mathrm{o}\gamma} + \frac{1}{r_\gamma} + \frac{1}{r_\gamma} \log \phi_\gamma + \sum_\kappa \chi_{\gamma\kappa} \phi_\kappa - \sum_{a,\kappa} \chi_{a\kappa} \phi_a \phi_\kappa - \sum_a \frac{\phi_a}{r_a} + \frac{\phi_\mathrm{C}}{\gamma_\mathrm{C}} \quad (2.7)$$

In the phase-separated polymer blend the bulk values of the chemical potential have to be equal. Thus

$$\mu_\kappa(\infty) = \mu_\kappa(-\infty) \quad (2.8)$$

giving a general condition for determining the asymptotic bulk volume fractions of all the components.

The most general expressions for the mean fields, ω_γ, have been given previously[7,8] and we quote the result

$$\omega_\gamma = \omega_\gamma{}^b + \left(\frac{Df_\mathrm{h}}{D\phi_\gamma} + \frac{\phi_\mathrm{C}}{r_\mathrm{C}} \right) - \left(\frac{Df_\mathrm{h}}{D\phi_\gamma} + \frac{\phi_\mathrm{C}}{r_\mathrm{C}} \right)^b - \frac{1}{r_\gamma} \log \frac{\phi_\gamma}{\phi_\gamma{}^b} - \frac{1}{6} \sum_\kappa \chi_{\gamma\kappa} \sigma_{\gamma\kappa}{}^2 \nabla^2 \phi_\kappa + \frac{\Delta\zeta}{\zeta_\mathrm{o}} \quad (2.9)$$

The index b refers always to the corresponding bulk values at $x = \pm\infty$. The term $\Delta\zeta/\zeta_\mathrm{o}$ can be calculated from the effective potential for the solvent; i.e.

$$\phi_\mathrm{S} = \phi_\mathrm{S}{}^b \exp\{(\omega^b - \omega_\mathrm{s})\} \quad (2.10)$$

which leads to

$$\frac{\Delta\zeta}{\zeta_\mathrm{o}} = \left(\frac{Df_\mathrm{h}}{D\phi_\mathrm{S}} + \frac{\phi_\mathrm{C}}{r_\mathrm{C}} \right)^b - \left(\frac{Df_\mathrm{h}}{D\phi_\mathrm{S}} + \frac{\phi_\mathrm{C}}{r_\mathrm{C}} \right) + \frac{1}{6} \sum_\kappa \chi_{\kappa\mathrm{s}} \sigma_{\kappa\mathrm{s}}{}^2 \nabla^2 \phi_\kappa \quad (2.11)$$

When no solvent is present, this quantity is determined by the self-consistent solution of the mean field equations for the distribution functions.

3. A–XY–B System

We now set up the equations for the distribution functions determining the concentration properties of the A–XY–B system with solvent. We suppose that the homopolymers are demixed. We find from condition 2.8 the four relations

$$F_\gamma(\infty) = F_\gamma(-\infty) \quad (3.1)$$

where F_γ is given by

$$F_\gamma = \sum_\kappa \chi_{\gamma\kappa} + \frac{1}{r_\gamma} \log \phi_\gamma - \sum_\kappa \frac{\phi_\kappa}{r_\kappa} - \sum_{\gamma<\kappa} \chi_{\gamma\kappa} \phi_\gamma \phi_\kappa \qquad \forall\ \gamma \neq \mathrm{C} \quad (3.2)$$

The special case for the copolymer ($\gamma = \mathrm{C}$) can be written in the same form if $\sum$ becomes $\sum^C$. In (3.2) the constant terms have been dropped since they cancel out in (2.8).

For homopolymer A, we obtain, for example

$$F_\mathrm{A}(x) = \chi_\mathrm{AS} \phi_\mathrm{S}(x) + \chi_\mathrm{AB} \phi_\mathrm{B}(x) + \chi_\mathrm{AX} \phi_\mathrm{CX}(x) + \chi_\mathrm{AY} \phi_\mathrm{CY}(x) + \frac{1}{r_\mathrm{A}} \log \phi_\mathrm{A}(x) - \left[\frac{\phi_\mathrm{A}(x)}{r_\mathrm{A}} + \frac{\phi_\mathrm{B}(x)}{r_\mathrm{B}} + \frac{\phi_\mathrm{C}(x)}{r_\mathrm{C}} + \frac{\phi_\mathrm{S}(x)}{r_\mathrm{S}} \right] + \chi_\mathrm{AB} \phi_\mathrm{A}(x)\, \phi_\mathrm{B}(x) + \text{all other paired terms} \quad (3.3)$$

where we have assumed for simplicity a one-dimensional spatial dependence, regarding this problem as rotationally invariant.

Now we turn to the effective potentials, ω_γ, given by (2.9) and (2.11). Consider ω_A first:

$$\omega_\mathrm{A} = -\frac{1}{r_\mathrm{S}} \log (\phi_\mathrm{S}(x)/\phi_\mathrm{S}{}^b) + \chi_\mathrm{AS}[\phi_\mathrm{S}(x) - \phi_\mathrm{S}{}^b] + (\chi_\mathrm{AB} - \chi_\mathrm{SB})[\phi_\mathrm{B}(x) - \phi_\mathrm{B}{}^b] + (\chi_\mathrm{AX} - \chi_\mathrm{SX})[\phi_\mathrm{CX}(x) - \phi_\mathrm{CX}{}^b] + (\chi_\mathrm{AY} - \chi_\mathrm{SY})[\phi_\mathrm{CY}(x) - \phi_\mathrm{CY}{}^b] - \chi_\mathrm{AS}[\phi_\mathrm{A}(x) - \phi_\mathrm{A}{}^b] + \text{gradient terms} \quad (3.4)$$

We now discuss some special cases. In the context of compatibilization, a widely studied case is X = A and Y

= B, and it is straightforward to show that (3.4) reduces to

$$\omega_A = \chi_{AB}[\phi_B(x) + \phi_{CB}(x)] - \log(\phi_S(x)/\phi_S{}^b) - \text{bulk terms} + \text{gradient terms} \quad (3.5)$$

if we assume a "symmetric solvent", $\chi_{\kappa S} = 0$.

Another case is if one of the blocks has the same chemical composition as one of the homopolymers, i.e., X = A and Y is arbitrary, and we get

$$\omega_A = -\log(\phi_S(x)/\phi_S{}^b) + \chi_{AB}[\phi_B(x) - \phi_B{}^b] + \chi_{AY}[\phi_{CY}(x) - \phi_{CY}{}^b] + \text{gradient terms} \quad (3.6)$$

Yet another case is given by the relations

$$\chi_{AS} = \chi_{BS} = \chi_{SH} \qquad \chi_{XS} = \chi_{YS} = \chi_{SC} \quad (3.7)$$

and the effective potential becomes

$$\omega_A = (\chi_{SH} - \chi_{SC})[(\phi_{CX} + \phi_{CY}) - (\phi_{CX}{}^b + \phi_{CY}{}^b)] + \chi_{AB}(\phi_B - \phi_B{}^b) + \chi_{AX}(\phi_{CX} - \phi_{CX}{}^b) + \chi_{AB}(\phi_{CY} - \phi_{CY}{}^b) - \log(\phi_S/\phi_S{}^b) + \text{gradient terms} \quad (3.8)$$

and further if we assume

$$\chi_{AY} = \chi_{AX} + \chi_0 \quad (3.9)$$

we find

$$\omega_A = (\chi_{SH} - \chi_{SC} + \chi_{AX})\Delta\phi_C + \chi_{AB}\Delta\phi_B + \chi_0\Delta\phi_{CY} - \log\left(\frac{\phi_S}{\phi_S{}^b}\right) + \text{gradient terms} \quad (3.10)$$

where

$$\Delta\phi_\kappa = \phi_\kappa - \phi_\kappa{}^b$$

The above demonstrates that in principle one can look at many different possibilities for the choice of an interfacial agent between incompatible homopolymers. The potential $\omega_\kappa[\{\phi_\gamma\}]$ enters in the equation for the distribution of the polymer chains, i.e., for homopolymer A.

$$\frac{1}{r_A}\frac{\partial q_A}{\partial t} = \frac{b_A{}^2}{6}\frac{\partial^2 q_A}{\partial x^2} - \omega_A q_A \quad (3.11)$$

where t is the curvilinear variable and b the Kuhn segment. The initial condition for (3.11) is given by

$$q_A(x,0) = 1 \quad (3.12)$$

and the boundary conditions by

$$q_A(\infty,t) = 1$$

$$q_A(-\infty,t) = e^{-r_A\omega_A(-\infty)t} \quad (3.13)$$

Similarly the distribution function for homopolymer B is given by

$$\frac{1}{r_B}\frac{\partial q_B}{\partial t} = \frac{b_B{}^2}{6}\frac{\partial^2}{\partial x^2}q_B - \omega_B q_B \quad (3.14)$$

with the appropriate initial condition and boundary conditions.

$$q_B(x,0) = 1$$

$$q_B(\infty,t) = e^{-r_B\omega_B(\infty)t}$$

$$q_B(-\infty,t) = 1 \quad (3.15)$$

The volume fractions are related to the distribution function by

$$\phi_A(x) = \phi_A(\infty)\int_0^1 \mathrm{d}t\, q_A(x,t)\, q_A(x,1-t) \quad (3.16)$$

and

$$\phi_B(x) = \phi_B(-\infty)\int_0^1 \mathrm{d}t\, q_B(x,t)\, q_B(x,1-t) \quad (3.17)$$

Similar equations hold for the copolymers and in previous work it is shown in detail how the distribution functions can be generalized for the block copolymers.[7,8]

We give first the effective potential acting on the block CX:

$$\omega_{CX} = -\frac{1}{r_S}\log\frac{\phi_S(x)}{\phi_S(\infty)} + (\chi_{XA} - \chi_{SA})\Delta\phi_A + (\chi_{XB} - \chi_{SB})\Delta\phi_B + (\chi_{XY} - \chi_{SY})\Delta\phi_{CY} + \chi_{SX}\Delta\phi_S - \chi_{SX}\Delta\phi_{CX} + \text{gradient terms} \quad (3.18)$$

with the corresponding differential equation

$$\frac{1}{r_{CX}}\frac{\partial q_{CX}}{\partial t} = \frac{b_{CX}{}^2}{6}\frac{\partial^2}{\partial x^2}q_{CX} - \omega_{CX}q_{CX} \quad (3.19)$$

with the supplementary conditions

$$q_{CX}(x,0) = 1 \qquad q_{CX}(\infty,t) = 1$$

$$q_{CX}(-\infty,t) = e^{-r_{CX}\omega_{CX}(-\infty)t} \quad (3.20)$$

Similarly for the Y block

$$\frac{1}{r_{CY}}\frac{\partial q_{CY}}{\partial t} = \frac{b_{CY}{}^2}{6}\frac{\partial^2}{\partial x^2}q_{CY} - \omega_{CY}q_{CY} \quad (3.21)$$

with

$$\omega_{CY} = -(1/r_S)\log(\phi_S(x)/\phi_S{}^b) + (\chi_{YA} - \chi_{SA})\Delta\phi_A + (\chi_{YB} - \chi_{SB})\Delta\phi_B + (\chi_{YX} - \chi_{SX})\Delta\phi_{CX} + \chi_{YS}\Delta\phi_S - \chi_{SY}\Delta\phi_{CY} + \text{gradient terms} \quad (3.22)$$

and the boundary conditions

$$q_{CY}(x,0) = 1 \qquad q_{CY}(-\infty,t) = 1 \quad (3.23)$$

$$q_{CY}(\infty,t) = e^{-r_{CY}\omega_{CY}(\infty)t}$$

The calculation of the volume fraction for the copolymer involves a similar relationship as for the homopolymers (3.16, 3.17). From previous work we have[7,8]

$$\phi_{CX}(x) = \phi_{CX}(\infty)e^{r_{CY}\omega_{CY}(\infty)}\int_0^1 \mathrm{d}t\, q_{CX}(x,t)\, q_{XY}(x,1-t) \quad (3.24)$$

and

$$\phi_{CY}(x) = \phi_{CY}(\infty)e^{r_{CY}\omega_{CX}(\infty)}\int_0^1 \mathrm{d}t\, q_{CY}(x,t)\, q_{YX}(x,1-t) \quad (3.25)$$

where q_{XY} and q_{YX} account for the connectivity of the two blocks at a point x_0, i.e.

$$q_{XY}(x,1-t) = \int_0^1 \mathrm{d}x_0\, Q_{CX}(x,1-t|x_0)\, q_{CY}(x_0,t) \quad (3.26)$$

and similarly

$$q_{YX}(x,1-t) = \int_0^1 \mathrm{d}x_0\, Q_{CY}(x,1-t|x_0)\, q_{CX}(x_0,t) \quad (3.27)$$

and the functions Q_{Ca} are the usual distribution functions of a polymer a, i.e., the solutions of

$$\left\{\frac{\partial}{\partial t} - \frac{b_a{}^2}{6}\frac{\partial^2}{\partial x^2} + \omega_a\right\}Q_a(x,t|x_0) = \delta(x - x_0)\,\delta(t) \quad (3.28)$$

The integration over x_0 comes from the fact that the junction point can be located anywhere in space though the polymer blocks are connected.

The corresponding equations for q_{XY}'s are given by

$$\frac{1}{r_{CX}}\frac{\partial q_{XY}}{\partial t} = \frac{b_{CX}^2}{6}\frac{\partial^2}{\partial x^2}q_{XY} - \omega_{CX}q_{XY} \tag{3.29}$$

with

$$q_{XY}(x,0) = 1$$

$$q_{XY}(\infty,t) = e^{-r_{CY}\omega_{CY}(\infty)t}$$

$$q_{XY}(-\infty,t) = e^{-r_{CX}\omega_{CX}(-\infty)t} \tag{3.30}$$

and q_{YX} obeys the same differential equation, but with the boundary conditions

$$q_{YX}(x,0) = q_{CX}(x,1) \tag{3.31}$$

$$q_{YX}(x,0) = q_{CY}(x,1)$$

Thus, one has to solve a system of eight coupled differential equations simultaneously, which is done numerically using the computer codes described previously.[7]

4. Results for the A–XY–B System

Our main goal is to investigate the use of block copolymers as surfactants or emulsifying agents in incompatible polymer blends. Therefore we chose a one-dimensional geometry for the A–XY–B system and calculated the dependence of the interfacial tension on the block length for a given interaction of the blocks with the homopolymers.

If we consider our system, A–XY–B, we have in principle many ways to realize a low interfacial tension. First, we have the freedom to optimize the different Flory–Huggins interaction parameters, χ_{AB}, χ_{AX}, χ_{AY}, χ_{BX}, χ_{BY}, and χ_{XY}, as well as all solvent interactions, $\chi_{\kappa S}$, where κ runs over all A, X, Y, and B's.

Second, we may adjust the block lengths of the copolymer for a given molecular weight distribution of the homopolymers. This is, of course, a multidimensional problem, with many variations to be considered. We restrict ourselves to a few examples to show the range of possibilities.

To understand the basic physics, consider the A–AB–B case or similarly the case where $\chi_{AX} = \chi_{BY} = 0$ and $\chi_{XY} = \chi_{AB}$ in a nonselective solvent $\chi_{\kappa S} = 0$ for all κ's. The copolymer localizes at the interface between A and B, and some configurational entropy is lost. However, this loss is compensated by the gain of energy (or enthalpy) by the placement of the compatible blocks in the appropriate homopolymer phases, and the interfacial free energy is lowered.[7,8]

What happens now if we have further interaction of the blocks with the homopolymer and we have in principle all the χ's available? In order to reduce the problem to a manageable number of parameters, we again choose a nonselective solvent, i.e., $\chi_{\kappa S} = 0$, for all the polymeric components and equal interaction parameters for all the other components, i.e., $\chi_{AB} = \chi_{AX} = \chi_{BY} = \chi_{XY} = \chi_1$, with the crucial distinction that $\chi_{AY} = \chi_{BX} = \chi_2 > \chi_1$. We also vary the block length $Z_{CX} = Z_{CY}$ for a fixed degree of polymerization of A and B.

The results are summarized in Figures 2 and 3. Parts A–D of Figure 2 show the concentration profiles of the AB mixture and the blocks X and Y for the case $\chi_1 = 0.05$ and $\chi_2 = 0.1$ with the lengths of the (equal) blocks of the copolymer increasing from 100 to 500 (in terms of the Kuhn length). The lengths of the homopolymers are $Z_A = Z_B = 400$. From this series of figures we see that the longer copolymers localize more strongly at the interface.

In parts A–C of Figure 3, we maintain the block length and increase the interaction parameter χ_2, while keeping χ_1 the same value, $\chi_1 = 0.1$. As for the case where the degree of polymerization of the block copolymer was increased, the concentration of surfactant at the interface increases with increasing χ_2.

By increasing the block length the interfacial tension is lowered by a factor of 2 over the range of block molecular weights considered. The width of the interface also increases with decreasing interfacial tension.

In all the cases above we see that interfacial activity of the block copolymer is promoted if the interaction of the X block with homopolymer B is more repulsive than the interaction of the X block with homopolymer A and similarly if the interaction of the Y block is more repulsive with homopolymer A than with homopolymer B.[13]

5. Interfacial Tension

The block copolymers XY between two homopolymers A and B act as a surfactant with a strong emulsifying effect if the interactions between all the components are properly chosen. This feature agrees well with the better known A–AB–A system. The longer the blocks are, the better the compatibilization effect, i.e., longer blocks lead to a larger reduction in the interfacial tension.

However, there is a practical limit for a useful "window" of lengths, beyond which the diblock copolymer prefers to associate into micelles in the bulk of the blend, and a limited emulsifying effect will be expected for this case. The best compatibilizer has to be long enough to decrease the interfacial tension significantly and to form entanglements with the homopolymers, but is still short enough to avoid appreciable micelle formation. The prediction of the best molecular weight requires an estimation of the cmc (critical micelle concentration) for a given block length and given χ's in the system. We have investigated the variation of the cmc with block copolymer molecular weight using a simplified version of an earlier model,[14] in which only the interfacial tension, copolymer joint entropy, "elastic" stretching energy of the blocks, and the interaction energy of the blocks were included. We found that although micelles form at smaller Z_C for the A–XY–B system, there is still a range of block copolymer sizes where useful surfactant activity can occur. The results of the calculation are shown in Figure 4. The homopolymer A–block copolymer AB calculation was carried out to test the accuracy of the simplified model. In this paper, however, we do not discuss the details of the micelle calculation.

An interesting question is, what is the specific origin of the strong reduction in the interfacial tension of the interface? We have seen that the free energy is minimized if the copolymer localizes in the interface between the homopolymers A and B. Despite the different nature of the blocks, in comparison with the homopolymers, interfacial activity can still take place. Clearly the preferential interactions (repulsions) between all components favor orientation of the copolymer blocks into the appropriate homopolymer phases.

The calculation of the interfacial tension and its reduction, due to the interfacial activity of block copolymers, is difficult and cannot be solved analytically. Nevertheless, we are able to derive approximate analytical expressions for a completely symmetric system, where the block

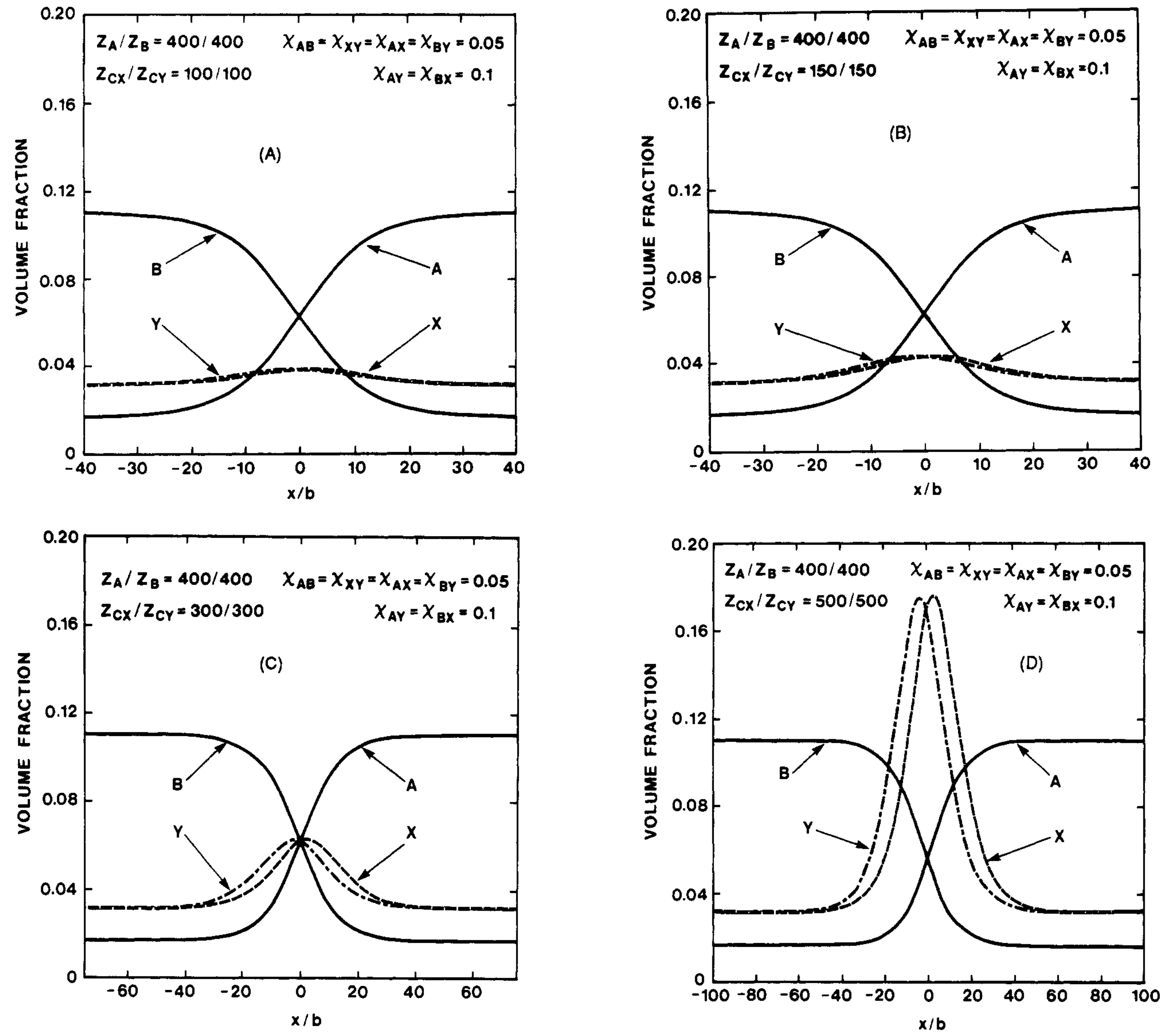

Figure 2. (A) Polymer density profiles for block copolymer XY localized at the interface between homopolymers A and B. The copolymer concentrations here and in the following figures have been arbitrarily scaled up to highlight the localization effect. The distance from the center of the interface is denoted by x, and b is the Kuhn segment length. (B) Polymer density profile for block copolymer XY localized at the interface between homopolymers A and B. The block lengths are longer than in Figure 2A. (C) Polymer density profiles for block copolymer XY localized at the interface between homopolymers A and B. The block lengths are larger than in Figure 2B. (D) Polymer density profiles for block copolymer XY localized at the interface between homopolymers A and B. The block lengths are larger than in Figure 2C.

lengths of the copolymer are equal, $Z_{CX} = Z_{CY}$, and the lengths of the homopolymers are equal and large so that we may assume $Z_A = Z_B = \infty$.

For the totally symmetric system, we have $\phi_A(\infty) = \phi_B(-\infty) = \phi_H$ and $\phi_{CX}(-\infty) = \phi_{CY}(\infty) = \phi_C$ for the volume fractions in the bulk. The approximate expression for the reduction in the interfacial tension appropriate to the system chosen above, i.e., $\chi_{\kappa S} = 0$, $\chi_{AB} = \chi_{AX} = \chi_{BY} = \chi_{XY} = \chi_{AX} = \chi_1$, $\chi_{AY} = \chi_{BX} = \chi_2 > \chi_1$, is given by

$$\Delta_Y \simeq d\left\{\frac{\phi_C(0)}{Z_C}\log\frac{\phi_C(0)}{\phi_C} - \frac{\phi_C(0)-\phi_C}{Z_C} - \left(\frac{\chi_1}{2}+\chi_2\right)\phi_H(\phi_C(0)-\phi_C)\right\} \quad (5.1)$$

where d is the width of the interface, which is treated as parameter in this expression. The approximations given in the derivation of this result are similar to earlier work;[7,8] i.e., all gradient terms are neglected and only the copolymer terms have been retained.

Minimizing $\Delta\gamma$ with respect to $\phi_C(0)$, we find

$$\phi_C(0) \simeq \phi_C \exp\{Z_C(\chi_1/2 + \chi_2)\phi_H\} \quad (5.2)$$

for the concentration of copolymer in the middle of the interface. The corresponding reduction of the interfacial tension is then given by

$$\Delta\gamma \simeq -(1/Z_C)\exp\{Z_C(\chi_1/2 + \chi_2)\phi_H\} \quad (5.3)$$

This formula, showing an exponential dependence on the key variables, shows the extraordinary effectiveness of the block copolymer on the reduction of the interfacial tension.

The interfacial tension as a function of copolymer block length is shown in Figure 5 for the χ parameters used in the calculations of parts A–D of Figure 2.

6. Conclusion

We have generalized the theory for the interfacial properties of polymeric blends of immiscible homopolymers in the presence of a diblock copolymer. Instead of using copolymers with blocks chemically identical with the

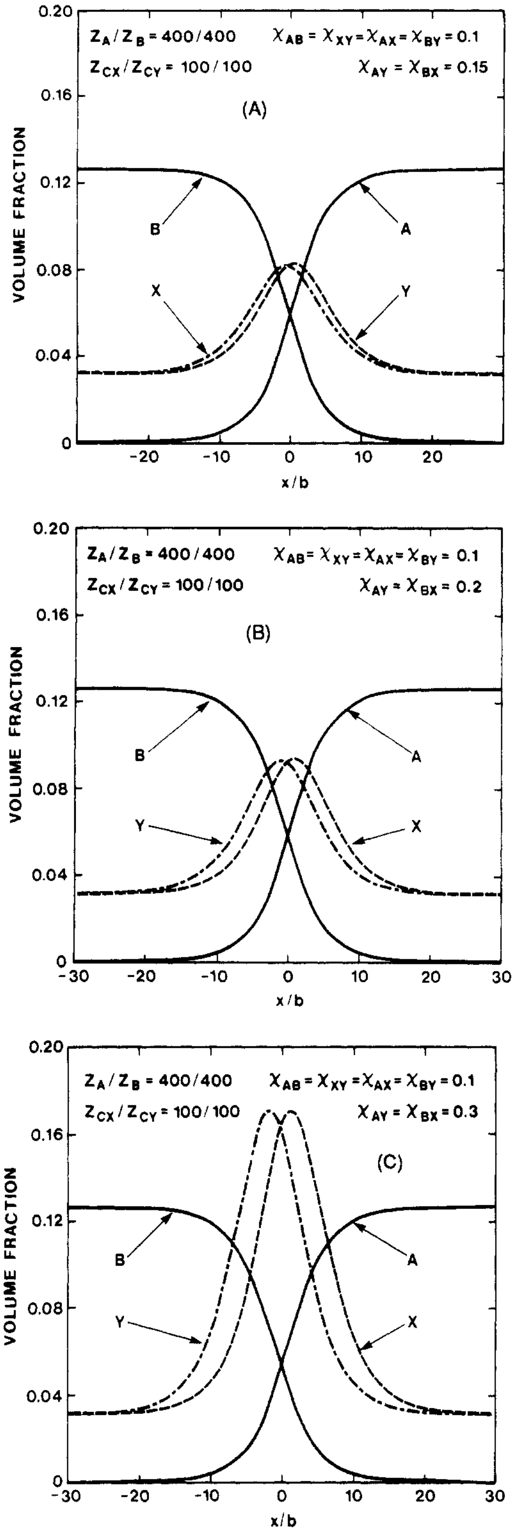

Figure 3. (A) Polymer density profiles for block copolymer XY localized at the interface between homopolymers A and B. The block lengths are the same in Figure 2A, but the preferential repulsive interactions between blocks and homopolymers have been increased. (B) Polymer density profiles for block copolymer XY localized at the interface between homopolymers A and B. The repulsive interaction parameters of the blocks and homopolymers have been increased from Figure 3A. (C) Polymer density profiles for block copolymer XY localized at the interface between homopolymers A and B. The repulsive interaction parameters of the blocks and homopolymers have been increased from Figure 3B.

homopolymers, we introduced arbitrary blocks into the system.

The diffusion equations for the polymer density profiles were solved numerically. In this paper, we restricted ourselves to only one concentration of copolymer (5%). Despite the use of chemically different blocks, we have shown a reduction of the interfacial tension with increasing block molecular weight. A strong localization effect of the emulsifier was also observed if the interaction of the blocks with the homopolymers was increased. Thus the competitive interactions of the blocks with the different homopolymers was shown to promote strong interfacial activity. As a result, we expect to find selective orientation of the blocks in the homopolymers in the same way as for the A–AB–B system.

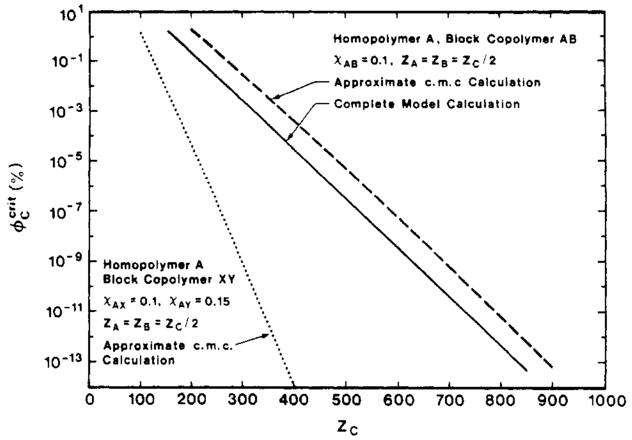

Figure 4. Critical micelle concentration as a function of the degree of polymerization of diblocks with equal block lengths. The approximate calculation follows ref 7, whereas the complete model calculation is discussed in ref 14. The homopolymer A–block copolymer XY case was treated only with the approximate model, whereas the homopolymer A–block copolymer AB case was investigated with both methods in order to test the accuracy of the approximate model.

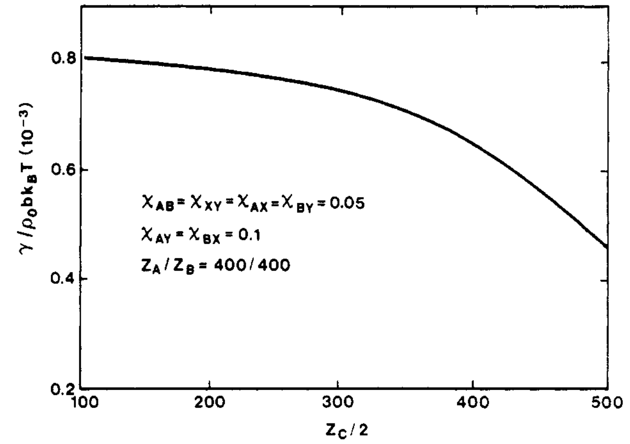

Figure 5. Interfacial tension as a function of copolymer block length. ρ_0 is the reference density.

A simplified analytical calculation led to a result predicting the reduction of the interfacial tension in terms of the block length and the *sum* of both interaction parameters. The level of approximation in this case was similar to the earlier calculation where the A–AB–B system was discussed.[7,8] The result for the A–AB–B system was also similar

$$\Delta\gamma \simeq \exp\{(1/2)Z_C\chi_{AB}\phi_H\} \qquad (6.1)$$

Finally, our work suggests the design of a universal compatibilizer, which makes use of preferential repulsive interactions between the homopolymers and the different blocks of the copolymer.

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Effects of Long-Range Polymer–Pore Interactions on the Partitioning of Linear Polymers

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ABSTRACT: A "diffusion–reaction" equation is used to describe the effects of long-range polymer–pore interactions on equilibrium partition coefficients for linear polymers between dilute bulk solution and cylindrical or slit-like pores. Results are presented for square-well potentials, electrostatic double-layer potentials, and van der Waals potentials. Intramolecular potentials were neglected in these calculations. In general, a weak potential acting over a large fraction of the pore cross section was found to have a greater effect on partitioning than a stronger but shorter ranged potential. In other words, the partition coefficient did not correlate very well with the average potential, a result of steric exclusion of polymer chains by the pore wall. For attractive polymer–pore interactions, conditions are identified which correspond to a transition from free to weakly adsorbed polymer.

Introduction

The partitioning of macromolecular solutes between small pores and bulk solution underlies various chromatographic and membrane separation processes and is important also in heterogeneous catalysis. This phenomenon is characterized by the partition coefficient, Φ, which is the pore-to-bulk concentration ratio at equilibrium. For rigid solutes, the theoretical results available for Φ encompass "neutral" molecules having a wide variety of shapes and pore geometries ranging from cylinders to the interstices in an array of randomly oriented fibers.[1-3] Whereas the studies just cited focus on purely steric exclusion for very dilute solutions, additional results are available for other solute–pore potentials[4,5] and/or for finite solute concentration,[6-9] in the case of rigid, spherical molecules.

Fewer quantitative predictions of Φ are available for flexible macromolecules, such as long-chain linear polymers. Casassa[10] and Casassa and Tagami[11] exploited the well-known analogy between the random motion of a Brownian particle and the conformation of a freely jointed polymer chain. This enabled them to calculate Φ for neutral polymers (linear or star shaped) by solving an analogue to a transient diffusion equation. For a chain consisting of N mass points connected by rectilinear segments of length l, this continuum approach requires that N be very large and that l be much smaller than the characteristic pore dimension (e.g., the pore radius r_p). Davidson et al.[12] used Monte Carlo simulations to calculate Φ for freely jointed chains, enabling them to obtain results for moderate values of N and l/r_p.

Theoretical results for linear polymers with long-range polymer–pore interactions are even more limited. Davidson et al.[12] reported a few values of Φ from Monte Carlo simulations which included attractive potentials, and Davidson and Deen[13] have recently performed the analogous continuum, "diffusion equation" calculation. Both studies considered only attractive potentials of a particular form, a square well of width comparable to the segment length, l. Zhulina et al.[14] and Gorbunov et al.[15] used lattice models to examine the effects of polymer–pore interactions on the partitioning of long chains in slit-like pores and pores of square cross section, respectively. Pouchlý[16] used the diffusion equation approach to describe partitioning in pores with permeable walls, including surface forces near the walls.

The objective of the present study was to estimate Φ for long chains experiencing various attractive or repulsive polymer–pore potentials. To do this, we have extended the diffusion equation method of Casassa to account for long-range interactions. Our approach was to add a source or sink term to the diffusion equation, as has been done in modeling the excluded volume of linear polymers[17,18]

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