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A Theory of Interface between Polymer and Polymer Mixture

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We present a theoretical study of the non-symmetrical A/BC polymeric system. The polymer blends consist of two phases, a pure polymeric phase A on one side and a mixture of polymers B as a compatibilizer and C on the other. The adsorption of homopolymer B to the interface improves the interfacial adhesion between two phases. By employing the functional integral techniques, we derive the mean-field equations and solve them numerically to obtain the interfacial properties including the concentration profiles in the limit of infinite molecular weight for the polymers. The calculations of the interfacial properties are performed for typical values of the Flory χ parameters and the volume fraction of polymer B in the asymptotic mixture phase. The interfacial adsorption of polymer B and the degrees of the specific interaction between the polymers play an important role in modification of the interfacial properties.

Introduction

For most polymers it is thermodynamically unfavorable to form the homogeneous mixtures with each other. This is so because the combinatorial entropy of mixing of two polymers is dramatically smaller than that for the low molecular weight components. The enthalpy of mixing, on the other hand, is often a small positive quantity or, at best, zero. In such cases immiscibility results when polymers are mixed. For that reason, it is worthwhile and interesting that the understanding and adjusting of the interfacial properties between the phases in the immiscible polymeric systems.

There has been a great deal of interest in experimental¹⁻⁵ and theoretical⁶⁻²⁰ studies of the interfacial properties of inhomogeneous multicomponent polymeric systems. Helfand and co-workers⁸⁻¹⁰ developed a mean-field theory for predic-

ting the interfacial properties between two immiscible polymers, and Noolandi and co-workers¹³⁻¹⁵ also presented fully self-consistent calculations of the polymer density profiles and resulting interfacial tension at polymer/polymer interfaces in the presence of a solvent and the effects of copolymers at these interfaces. However, relatively little work has been done to extend the immiscible polymer-polymer systems to include the effects of third homopolymers as compatibilizers, which polymeric systems usually show the intrinsic non-symmetrical interfaces. Recently Helfand¹⁶ extended the theory of the A/B interface to the specific one of A/BC for the interfacial tension via equations of motion.^{8-10,21}

In this work the A/BC interface between two phases is considered, which is the same model as recent Helfand's work,¹⁶ a pure polymeric phase A on one side and a mixture of polymer B as a compatibilizer and polymer C on the other

hand. Our theoretical formulation constitutes an extension of some work by Noolandi.¹³ By employing the functional integral techniques,^{9,13,22-24} the mean-field equations are derived and numerically solved by a self-consistent procedure in the limit of infinite molecular weight for the polymers and a vanishing compressibility. This work may be easily extended to the system including the effect of solvent.

We will assume that the interface between two phases is planar. However, there seems to be no sharply defined boundary in the actual interfacial region, so it is convenient to choose the mathematical dividing surface. We will select it as the Gibbs dividing surface^{16,25} for polymer A. The calculations of interfacial properties are performed for typical values of the Flory χ parameters,^{26,27} χ_{AC} and χ_{BC} as negative value and the volume fraction of polymer B in the asymptotic mixture phase, $\phi_B(\infty)$. As the results, we obtain the concentration profiles, the interfacial tension, the width of polymer B, the amount of polymer B adsorbed to the interface, and the overlap lengths between the polymers.

The next section contains the general theory for the polymeric systems on the basis of the mean-field approximation, the case of infinite molecular weight for the polymers as a good approximation, and the numerical method used to solve the mean-field equations. We discuss the results of the calculation of the physical properties of the interface in the third section, and remark the conclusions in the last section.

Theory

Partition Function. The polymer chains will be looked upon as space curves with τ varying from 0 to Z_K , the degree of polymerization (hereafter, we use the letter K to symbolize the polymers A, B, and C). The space curves $\{r_{K\tau}(\bullet)\}$, which are Gaussianly distributed and represent possible configurations of the polymers, are continuous with the rate of extension at each point $dr_{K\tau}/d\tau$. The probability density functional for a given space curve is

$$P[\{r_{K\tau}(\bullet)\}] \propto \exp\left\{-\frac{3}{2b_K^2} \int_0^{Z_K} d\tau \left[\frac{dr_{K\tau}(\tau)}{d\tau}\right]^2\right\} \quad (1)$$

where b_K is the Kuhn statistical length.

Assuming the A/BC system to be incompressible, the partition function can be written as a functional integral of the probability density functional with the incompressibility constraint over all possible configurations of the polymers in the field of intermolecular potential, $\hat{W}[\{r_{K\tau}(\bullet)\}]$, in units of $k_B T$; viz.

$$Z = \left(\prod_K \frac{1}{N_K!}\right) \int \prod_K \prod_{\tau} d[\{r_{K\tau}(\bullet)\}] P[\{r_{K\tau}(\bullet)\}] \times \delta\left[1 - \sum_K \frac{\rho_K(\bullet)}{\rho_{0K}}\right] \exp\{-\hat{W}[\{r_{K\tau}(\bullet)\}]\} \quad (2)$$

Here $\tilde{N}_K = N_K/Z_K$ is the number of polymer chains, where N_K is the total number of monomer units of polymer K. The δ -function ensures an incompressibility, and ρ_{0K} is the density of pure polymer K in monomer segments per unit volume. Using the three microscopic densities of monomer units which are given by

$$\hat{\rho}_K(r) = \hat{\rho}_K(r; \{r_{K\tau}(\bullet)\}) = \sum_{\tau}^{\tilde{N}_K} d\tau \delta[r - r_{K\tau}(\tau)] \quad (3)$$

the intermolecular potential related to the interaction between monomer units can be conveniently expressed via two-body interactions, $W_{KK'}(r-r')$, as

$$\hat{W}_K[\{r_{K\tau}(\bullet)\}] = \frac{1}{2} \sum_{KK'} \int dr' d\tau' \hat{\rho}_K(r) W_{KK'}(r-r') \hat{\rho}_{K'}(r') \quad (4)$$

By introducing the integral representation over a Dirac δ -function which fixes the density pattern, we have

$$\delta\left[1 - \sum_K \frac{\hat{\rho}_K(\bullet)}{\rho_{0K}}\right] e^{-\hat{W}} = \int \left[\prod_K d\rho_K(\bullet) \delta[\rho_K(\bullet) - \hat{\rho}_K(\bullet)] \right] \times \delta\left[1 - \sum_{K'} \frac{\rho_{K'}(\bullet)}{\rho_{0K'}}\right] e^{-W} \quad (5)$$

and two δ -functions in Eq. (5) can be parameterized as

$$\delta[\rho_K(\bullet) - \hat{\rho}_K(\bullet)] \propto \int d\omega_K(\bullet) \exp\left\{\int d\omega_K(r) [\rho_K(r) - \hat{\rho}_K(r)]\right\} \quad (6)$$

$$\delta\left[1 - \sum_K \frac{\rho_K(\bullet)}{\rho_{0K}}\right] \propto \int d\eta(\bullet) \exp\left\{\int d\eta(r) \left[1 - \sum_K \frac{\rho_K(r)}{\rho_{0K}}\right]\right\} \quad (7)$$

In these ways the dependence of the densities on all possible configurations can be expressed by the local values which are only coupled by the fields $\omega_K(\bullet)$ and $\eta(\bullet)$ defined in Eq. (6) and Eq. (7), respectively. Therefore, the integration over all possible configurations of a given chain can be done independently of the other chains. Here $\omega_K(r)$ is the mean field acting on the polymer, and the field $\eta(r)$ is the Lagrangian multiplier corresponding to the constraint of no volume change locally upon mixing. By substituting the integral representations of δ -functions, Eqs. (5)-(7), into the δ -function appearing in Eq. (2), we obtain the final expression for the partition function

$$Z = N_0 \left(\prod_K \frac{J_K^{\tilde{N}_K}}{N_K!}\right) \int \left[\prod_K d\rho_K(\bullet) d\omega_K(\bullet) \right] d\eta(\bullet) \times \exp\left\{\int d\eta(r) \left[1 - \sum_K \frac{\rho_K(r)}{\rho_{0K}}\right] + \sum_K \int d\omega_K(r) \rho_K(r) - W\right\} \quad (8)$$

Here N_0 is an appropriate normalization constant, and the quantity J_K is given by

$$J_K = \int d[\{r(\bullet)\}] P[\{r(\bullet)\}] \exp\left\{-\int_0^{Z_K} d\tau \omega_K[r(\tau)]\right\} \quad (9)$$

This J_K can be expressed in terms of the distribution function, $Q_K(r, \tau | r_0)$ for a chain of τ repeat units to start at r_0 and end at r , which can be interpreted as the propagator of the inhomogeneous differential equation^{9,13,24}

$$\left[\frac{1}{Z_K} \frac{\partial}{\partial \tau} - \frac{b_K^2}{6} \nabla^2 + \omega_K(r)\right] Q_K(r, \tau | r_0) = \delta(r - r_0) \delta(\tau) \quad (10)$$

The function $q_K(r, \tau)$ can be expressed as the integral of $Q_K(r, \tau | r_0)$ over all the starting positions r_0 , and in this case the function $q_K(r, \tau)$ also can be solved from the modified diffusion equation; viz.

$$\left[\frac{1}{Z_K} \frac{\partial}{\partial \tau} - \frac{b_K^2}{6} \nabla^2 + \omega_K(r)\right] q_K(r, \tau) = \delta(\tau) \quad (11)$$

In polymer chains with the length Z_K , any segment of length

$Z_K\tau$ may be regarded as the origin of two walks, one of length $Z_K\tau$ and one of length $Z_K(1-\tau)$. Thus $q_K(\mathbf{r}, Z_K)$ can be written as two distribution functions, i.e., one is $q_K(\mathbf{r}, Z_K\tau)$, and the other $q_K[\mathbf{r}, Z_K(1-\tau)]$:

$$J_K = \int d\mathbf{r} \int d\mathbf{r}_0 Q_K(\mathbf{r}, Z_K | \mathbf{r}_0) = \int d\mathbf{r} q_K(\mathbf{r}, Z_K) = \int d\mathbf{r} q_K(\mathbf{r}, Z_K\tau) q_K[\mathbf{r}, Z_K(1-\tau)] \quad (12)$$

Free Energy Functional. For large \tilde{N}_K , the partition function can be written as

$$Z = N_0 \left[\prod_K \int d\rho_K(\cdot) d\omega_K(\cdot) d\eta(\cdot) \exp\{-F_T[\{\rho_K(\cdot)\}, \{\omega_K(\cdot)\}, \eta(\cdot)]\} \right] \quad (13)$$

where F_T is the total free energy functional in units of $k_B T$, given by two terms

$$F_T[\{\rho_K(\cdot)\}, \{\omega_K(\cdot)\}, \eta(\cdot)] = F[\{\rho_K(\cdot)\}, \{\omega_K(\cdot)\}] + H[\{\rho_K(\cdot)\}, \eta(\cdot)] \quad (14)$$

with

$$F[\{\rho_K(\cdot)\}, \{\omega_K(\cdot)\}] = W(\{\rho_K(\cdot)\}) - \sum_K \int d\mathbf{r} \omega_K(\mathbf{r}) \rho_K(\mathbf{r}) + \sum_K \tilde{N}_K \left[\ln\left(\frac{\tilde{N}_K}{J_K}\right) - 1 \right] \quad (15)$$

and

$$H[\{\rho_K(\cdot)\}, \eta(\cdot)] = \int d\mathbf{r} \eta(\mathbf{r}) \left[\sum_K \frac{\rho_K(\mathbf{r})}{\rho_{0K}} - 1 \right] \quad (16)$$

When the free energy H , associated with the volume change locally upon mixing, is subjected to zero, an approximate free energy is given by F only, Eq. (15).

Introducing the symmetric form of the potential energy, $U_{KK'}(\mathbf{r})$, which we can obtain by subtracting the interactions between like polymers from $W_{KK'}(\mathbf{r}-\mathbf{r}')$ in Eq. (4), the intermolecular potential in Eq. (15) is given by

$$W = \frac{1}{2} \sum_K \rho_{0K} W_{KK} N_K + \frac{1}{2} \sum_{KK'} \int d\mathbf{r} \int d\mathbf{r}' \rho_K(\mathbf{r}) U_{KK'}(\mathbf{r}-\mathbf{r}') \rho_{K'}(\mathbf{r}') \quad (17)$$

where

$$N_K = \int d\mathbf{r} \rho_K(\mathbf{r}) \quad (18)$$

$$W_{KK} = \int d\mathbf{r} W_{KK}(\mathbf{r}) \quad (19)$$

When the polymeric system is uniform all over, from Eqs. (15) and (17) the local homogeneous free energy density is given by

$$f_h = \frac{1}{2} \sum_K \rho_{0K} W_{KK} \rho_K + \frac{1}{2} \sum_{KK'} \rho_K(\mathbf{r}) U_{KK'}(\mathbf{r}) \rho_{K'}(\mathbf{r}) + \sum_K \frac{\rho_K(\mathbf{r})}{Z_K} \left[\ln\left(\frac{\rho_K(\mathbf{r})}{Z_K}\right) - 1 \right] \quad (20)$$

where

$$U_{KK'} = \int d\mathbf{r} U_{KK'}(\mathbf{r}) \quad (21)$$

In terms of the chemical potential of the pure polymer, Eq. (20) can be rewritten as

$$f_h = \sum_K \mu_{0K} \rho_K(\mathbf{r}) + \frac{1}{2} \sum_{KK'} \rho_K(\mathbf{r}) U_{KK'} \rho_{K'}(\mathbf{r}) + \sum_K \frac{\rho_K(\mathbf{r})}{Z_K} \ln\left(\frac{\rho_K(\mathbf{r})}{\rho_{0K}}\right) \quad (22)$$

where

$$\mu_{0K} = \frac{1}{2} \rho_{0K} W_{KK} + \frac{1}{Z_K} \left[\ln\left(\frac{\rho_K(\mathbf{r})}{Z_K}\right) - 1 \right] \quad (23)$$

In terms of the local homogeneous free energy density, Eq. (17) becomes

$$W = \int d\mathbf{r} \left\{ f_h - \sum_K \frac{\rho_K(\mathbf{r})}{Z_K} \left[\ln\left(\frac{\rho_K(\mathbf{r})}{Z_K}\right) - 1 \right] \right\} \quad (24)$$

where the nonlocal terms that are generally negligible¹⁰ are excluded. Eqs. (14)-(16) and (24) give the free energy functional set that will be minimized by the saddle-point method in the next part.

Mean-Field Approximation. Using the saddle-point method,^{9,13} we can obtain the mean-field equations, given by the minimization of the functional, Eq. (14), with respect to each $\omega_K(\mathbf{r})$, $\rho_K(\mathbf{r})$, and $\eta(\mathbf{r})$, subject to the constraint of a constant number of monomers, Eq. (18). The minimization equation for $\omega_K(\mathbf{r})$ is given by

$$\rho_K(\mathbf{r}) + \frac{\tilde{N}_K}{J_K} \frac{\delta J_K}{\delta \omega_K(\mathbf{r})} = 0 \quad (25)$$

From Eqs. (9) and (12), in terms of the distribution functions, Eq. (25) becomes

$$\rho_K(\mathbf{r}) = \frac{N_K}{J_K} \int_0^1 d\tau q_K(\mathbf{r}, \tau) q_K(\mathbf{r}, 1-\tau) \quad (26)$$

where J_K satisfies the relation $N_K/J_K = \rho_{0K}$.^{13,14} Minimization for $\rho_K(\mathbf{r})$ yields the following equation:

$$\frac{\partial f_h}{\partial \rho_K(\mathbf{r})} - \frac{1}{Z_K} \ln\left(\frac{\rho_K(\mathbf{r})}{Z_K}\right) - \omega_K(\mathbf{r}) + \frac{\eta(\mathbf{r})}{\rho_{0K}} - \lambda_K = 0 \quad (27)$$

where λ_K is the Lagrangian multiplier corresponding to, Eq. (18), the constraint of a constant number of monomers, and the first term is the chemical potential of the polymer K. In the two asymptotic bulk phases, Eq. (27) becomes

$$\left[\frac{\partial f_h}{\partial \rho_K(\mathbf{r})} \right]^b - \frac{1}{Z_K} \ln\left(\frac{\rho_{0K}}{Z_K}\right) + \frac{\eta^b}{\rho_{0K}} - \lambda_K = 0 \quad (28)$$

then the mean field potential in terms of the chemical potential is given by

$$\omega_K(\mathbf{r}) = \Delta\mu_K - \frac{1}{Z_K} \ln\left(\frac{\rho_K(\mathbf{r})}{\rho_{0K}}\right) + g(\mathbf{r}) \quad (29)$$

The minimization equation for the $\eta(\mathbf{r})$ is

$$\sum_K \frac{\rho_K(\mathbf{r})}{\rho_{0K}} = 1 \quad (30)$$

which makes $H=0$, Eq. (16), at the saddle point, then F only contributes to the free energy of the system. In Eq. (29) $g(\mathbf{r}) = [\eta(\mathbf{r}) - \eta^b]/\rho_{0K}$, which is associated with an incompressibility, is a function which must be chosen such that Eq. (30) is satisfied for all the local points.

The local homogeneous free energy density relative to the asymptotic phases is given by

$$\Delta f = f_h - \sum_K \rho_K(r) \mu_K^b \quad (31)$$

From Eq. (22), Eq. (31) is rewritten as

$$\begin{aligned} \Delta f / \rho_0 = & \sum_K \frac{\rho_{0K}}{\rho_0} \phi_K(r) [\mu_{0K} - \mu_K^b] + \frac{1}{2} \sum_{KK'} \chi_{KK'} \phi_K(r) \phi_{K'}(r) \\ & + \sum_K \frac{\rho_{0K}}{\rho_0} \frac{\phi_K(r)}{Z_K} \ln \phi_K(r) \end{aligned} \quad (32)$$

where ρ_0 is the reference density, $\phi_K(r) = \rho_K(r) / \rho_{0K}$ is the volume fraction as the reduced density for no volume change upon mixing, and $\chi_{KK'} = U_{KK'} \rho_{0K} \rho_{0K'} / \rho_0$ is the usual Flory interaction parameter with $k_B T$ as the unit of energy.

The interfacial tension which characterizes the interface is given by

$$\gamma_A = F - \sum_K N_K \mu_K^b \quad (33)$$

where A is the interfacial area, and from Eqs. (15) and (24) the free energy is written as

$$F / \rho_0 = \int dr \left\{ f_h / \rho_0 - \sum_K \frac{\rho_{0K}}{\rho_0} \left[\omega_K(r) \phi_K(r) + \frac{\phi_K(r)}{Z_K} \ln \phi_K(r) \right] \right\} \quad (34)$$

where the second term from Eqs. (11) and (26) is given by

$$\begin{aligned} \omega_K(r) \rho_K(r) = & \int_0^1 d\tau \left[\frac{b_K^2}{6} \nabla^2 q_K(r, \tau) q_K(r, 1-\tau) \right. \\ & \left. - \frac{1}{Z_K} \frac{\partial q_K(r, \tau)}{\partial \tau} q_K(r, 1-\tau) \right] \end{aligned} \quad (35)$$

The interfacial tension is then obtained in terms of the free energy density of the polymeric system, the conformational entropy, and the combinatorial entropy which has relation with the degree of polymerization:

$$\begin{aligned} \gamma_A / \rho_0 = & \int dr \left\{ \Delta f / \rho_0 - \sum_K \frac{\rho_{0K}}{\rho_0} \int_0^1 d\tau \frac{b_K^2}{6} \nabla^2 q_K(r, \tau) q_K(r, 1-\tau) \right\} \\ & + \int dr \left\{ \sum_K \frac{\rho_{0K}}{\rho_0} \frac{1}{Z_K} \int_0^1 d\tau \frac{\partial q_K(r, \tau)}{\partial \tau} q_K(r, 1-\tau) \right. \\ & \left. - \phi_K(r) \ln \phi_K(r) \right\} \end{aligned} \quad (36)$$

Infinite Molecular Weight. For most polymeric systems the physical properties, in reality, depend on the degree of polymerization.^{3,18} In here we assume the high molecular weights of all the polymers as a good approximation. For simplicity, we take $\rho_{0K} = \rho_0$, $b_K = b$ for all the polymers and consider the one-dimensional nature for the interfacial problem. With these assumptions,^{8,10,11} all segments take on the same density distribution excluding the effects of the chain ends, because there is a loss of correlation between segments of the polymer chain. As consequence, the distribution function $q_K(x, \tau)$ becomes $q_K(x)$. Then volume fraction is given by

$$\phi_K(x) = q_K^2(x) \quad (37)$$

and $q_K(x)$ also satisfies the following differential equation

$$\frac{b^2}{6} \frac{d^2 q_K(x)}{dx^2} - \omega_K(x) q_K(x) = 0 \quad (38)$$

Centering around the interface, $x=0$, the Gibbs dividing sur-

face for polymer A, the negative x region is polymer A rich, and the positive x one is polymers B and C rich.

$$\begin{aligned} \phi_A(-\infty) = 1, \quad \phi_B(-\infty) = \phi_C(-\infty) = 0 \\ \phi_A(+\infty) = 0, \quad \phi_B(+\infty) + \phi_C(+\infty) = 1 \end{aligned} \quad (39)$$

The boundary conditions of distribution functions are then given in terms of the concentration boundary conditions

$$\begin{aligned} q_A(-\infty) = 1, \quad q_B(-\infty) = q_C(-\infty) = 0 \\ q_A(+\infty) = 0, \quad q_B(+\infty) = [\phi_B(+\infty)]^{1/2}, \quad q_C(+\infty) = [\phi_C(+\infty)]^{1/2} \end{aligned} \quad (40)$$

The surface excess Γ_A in monomers per unit area is usually defined as

$$\Gamma_A / \rho_0 = - \int_{-\infty}^{+\infty} dx [\phi_A(x) - \phi_A(-\infty) H(x)] \quad (41)$$

where $H(x)$ is a Heaviside function, $H(x) = 1$ for $x \geq 0$ and $H(x) = 0$ otherwise, and the mathematical Gibbs dividing surface, $x=0$, is justly at $\Gamma_A = 0$.

Equation (29), the expression for the polymer mean field becomes

$$\omega_K(x) = \Delta \mu_K + g(x) \quad (42)$$

Using the fact that $\Delta f = 0$ in the asymptotic phases, we can obtain the change of chemical potential. The free energy density of the A/BC system from Eq. (32) is

$$\begin{aligned} \Delta f / \rho_0 = & \sum_K (\mu_{0K} - \mu_K^b) \phi_K(x) \\ & + \chi_{AB} \phi_A(x) \phi_B(x) + \chi_{AC} \phi_A(x) \phi_C(x) + \chi_{BC} \phi_B(x) \phi_C(x) \end{aligned} \quad (43)$$

Using the concentration boundary conditions, the polymer mean field for polymer A becomes

$$\begin{aligned} \omega_A(x) = & [\chi_{AB} \phi_B(x) + \chi_{AC} \phi_C(x)] [1 - \phi_A(x)] \\ & - \chi_{BC} \phi_B(x) \phi_C(x) + g(x) \end{aligned} \quad (44)$$

and the boundary conditions in two asymptotic phases are

$$\begin{aligned} \omega_A(-\infty) = 0 \\ \omega_A(\infty) = \chi_{AB} \phi_B(\infty) + \chi_{AC} \phi_C(\infty) - \chi_{BC} \phi_B(\infty) \phi_C(\infty) \end{aligned} \quad (45)$$

For polymer B, the mean field potential is given by

$$\begin{aligned} \omega_B(x) = & [\chi_{AB} \phi_A(x) - \chi_{BC} \phi_C(x)] [1 - \phi_B(x)] - \chi_{AC} \phi_A(x) \phi_C(x) \\ & - \chi_{BC} \phi_C^2(x) + g(x) \end{aligned} \quad (46)$$

with

$$\begin{aligned} \omega_B(-\infty) = \chi_{AB} - \chi_{BC} \phi_C^2(\infty) \\ \omega_B(\infty) = 0 \end{aligned} \quad (47)$$

and we can also obtain the similar expressions for polymer C by interchanging B and C in Eqs. (46) and (47).

Calculation of Physical Properties. Assuming the infinite molecular weight for the polymers, the third term including Z_K in Eq. (36) does not contribute to the interfacial tension. We then have

$$\gamma / \rho_0 = \int dx \left\{ \Delta f / \rho_0 + \sum_K \frac{b^2}{6} \left(\frac{dq_K(x)}{dx} \right)^2 \right\} \quad (48)$$

The following equivalent expression^{10,11,16} is more convenient.

$$\gamma / \rho_0 = 2 \int dx \Delta f / \rho_0 \quad (49)$$

where the free energy density of the A/BC polymeric system, Eq. (43), in terms of the asymptotic volume fractions, is rewritten as

$$\begin{aligned} \Delta f/\rho_0 = & \chi_{AB}\phi_A(x)\phi_B(x) + \chi_{AC}\phi_A(x)\phi_C(x) + \chi_{BC}\phi_B(x)\phi_C(x) \\ & - \chi_{BC}\phi_B(x)\phi_C^2(\infty) - \chi_{BC}\phi_C(x)\phi_B^2(\infty) \end{aligned} \quad (50)$$

The amount of polymer B (as a compatibilizer) in monomers per unit area, which is the differential adsorption to the interface, is given as like Eq. (41) by

$$\Gamma_B/\rho_0 = \int_{-\infty}^{+\infty} dx [\phi_B(x) - \phi_B(\infty)H(x)] \quad (51)$$

As a measure of the thickness of the diffuse interface, we define the widths of the polymers as

$$D_{K=A,C} = \frac{\mp[\phi_K(\pm\infty) - \phi_K(x)]}{[d\phi_K(x)/dx]} \Big|_{\Gamma_K=0} \quad (52)$$

where $[d\phi_K(x)/dx]$ denotes the value of the derivative evaluated at the Gibbs dividing surface for polymer A, and at $\Gamma_C=0$ for polymer C. In the case of polymer B, $D_B=x|_{\Gamma_C=0}$ is evaluated at $\Gamma_C=0$ relative to the Gibbs dividing surface.

A measure of the overlap between the polymers is defined as follows

$$L_{AK(K=B,C)} = 2 \int_{-\infty}^{+\infty} dx \phi_A(x)\phi_K(x) \quad (53)$$

Numerical Method. For the numerical solutions of Eq. (38), first, we discretize the variable x and the mean-field equation by using the Numerov's method²⁸

$$\tilde{x} = (i-N)\Delta\tilde{x}, \quad i=1, \dots, 2N-1 \quad (54)$$

where $\tilde{x}=x/b$ (in reduced unit of length), the equal discrete thickness $\Delta\tilde{x}$ is a constant, and we write $q_K(x)$ as $q_K(i)$. In our numerical calculations we used $N=160$ and chose $\Delta\tilde{x} \sim 0.1$. For the calculation of the concentration profiles, $q_K(0)$ and $q_K(320)$ in Eq. (38) are the boundary conditions of the distribution function. The discretized mean-field equation has the following tridiagonal form in i :

$$q_K(i-1) + B_K(i)q_K(i) + C_K(i)q_K(i+1) = 0 \quad (55)$$

where

$$B_K(i) = -2 \frac{\left[1 + \frac{5}{2}(\Delta\tilde{x})^2\omega_K(i)\right]}{\left[1 - \frac{1}{2}(\Delta\tilde{x})^2\omega_K(i-1)\right]}, \quad C_K(i) = \frac{\left[1 + \frac{1}{2}(\Delta\tilde{x})^2\omega_K(i+1)\right]}{\left[1 - \frac{1}{2}(\Delta\tilde{x})^2\omega_K(i-1)\right]} \quad (56)$$

Solving this equation for $q_K(i)$ and $q_K(i\pm 1)$ then provides a recursion relation for integrating either forward or backward in i , with a local error $O[(\Delta\tilde{x})^6]$.

We begin with the guess for $\phi_K(i)$ which is chosen as a trial function, $\phi_K(i) \sim \arctan[\exp(i)]$, and we use Eqs. (44)-(47) to obtain the initial guess for $\omega_K(i)$. We then refer $\omega_K(i)$ to $\omega_K^{old}(i)$. This determines the coefficient $B_K(i)$ and $C_K(i)$ in Eq. (56). The square matrix of dimension $(2N-1)$ is easily solved by a subroutine TRIDAG²⁹ with the help of the boundary conditions, Eq. (40). We then obtain a set of $q_K(i)$.

From this set of $q_K(i)$, we get the new concentration profile $\phi_K^{new}(i)$ by using Eq. (37). This $\phi_K^{new}(i)$ is controlled such that sum of the local volume fractions to be unity. The new mean

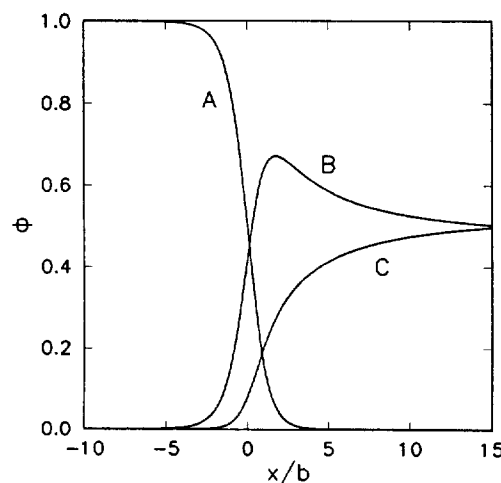


Figure 1. Concentration profiles of polymers A, B, and C with $\chi_{AB}=0.03$, $\chi_{AC}=0.1$, $\chi_{BC}=-0.001$, and $\phi_B(\infty)=0.5$ for the A/BC interface as a reference system. The plane, $x/b=0$, shows the Gibbs dividing surface for polymer A.

field potential $\omega_K^{new}(i)$ is calculated by using $\phi_K^{new}(i)$ and Eqs. (44)-(47) again. Here we take the new guess for $\omega_K(i)$:

$$\omega_K(i) = \omega_K^{old}(i) + \lambda[\omega_K^{new}(i) - \omega_K^{old}(i)] \quad (57)$$

where λ is some relaxation parameter, in our calculations this is taken to be in the range 0.3 to 1.2. We refer $\omega_K(i)$ to $\omega_K^{old}(i)$ again, and obtain a set of $q_K(i)$. This iteration process is continued until the following condition is satisfied

$$\max_{i=1, \dots, 2N-1} |\omega_K^{old}(i) - \omega_K^{old}(i)| \leq \epsilon (\sim 10^{-6}) \quad (58)$$

After convergence, we finally obtain the concentration profile $\phi_K(i)$.

Results and Discussion

Three parameters used in this A/BC polymeric system are as follows: χ_{AC} , χ_{BC} (it must be negative such that allows for mixing of B and C), and the volume fraction of polymer B in the asymptotic mixture phase, $\phi_B(\infty)$. We begin with the selection for the reference polymeric system with a reasonable particular set of parameters. Figure 1 shows the concentration profiles of polymers (A, B, and C) for an A/BC interface as a reference: $\chi_{AB}=0.03$ (we will fix $\chi_{AB}=0.03$), $\chi_{AC}=0.1$, $\chi_{BC}=-0.001$, and $\phi_B(\infty)=0.5$. The repulsive interaction between A and C usually drives C away from the interface, and therefore B is easily located in the interfacial region. When the attractive interaction between B and C is not large, in the same way the polymers A and B mainly remain near the interface. In Figure 1 we can see the preferential adsorption of B in the interfacial region in spite of the same quantities of B and C in the asymptotic mixture phase. This adsorption may improve the interfacial adhesion between two polymers A and C.

Effects of Varying χ_{AC} . Figures 2-5 show how the repulsion between polymers A and C can modify the physical properties of the A/BC interface. In Figure 2 we can see the preferential adsorption of B as increasing χ_{AC} because of the strong repulsive interaction of A and C. As the intera-

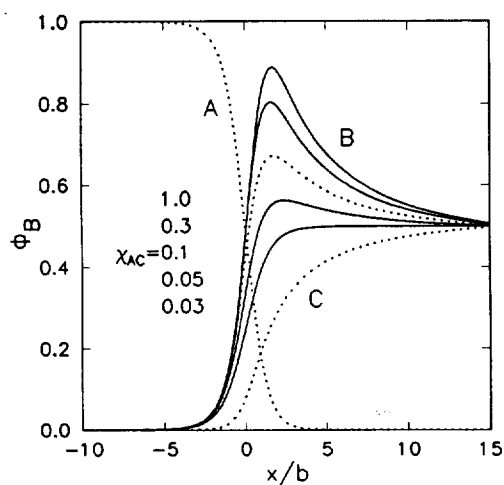


Figure 2. Concentration profiles of polymer B for varying χ_{AC} with $\chi_{BC} = -0.001$ and $\phi_B(\infty) = 0.5$. The dotted lines indicate a reference as in Figure 1.

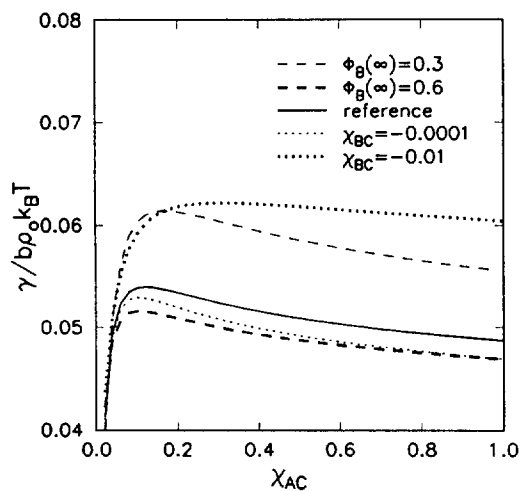


Figure 3. Variation of the interfacial tension, in units of $b\rho_0 k_B T$, with χ_{AC} for different values of the parameters, χ_{BC} and $\phi_B(\infty)$. The solid lines in Figures 3-5 indicate a reference: $\chi_{BC} = -0.001$ and $\phi_B(\infty) = 0.5$

ction parameter χ_{AC} approaches to χ_{AB} , A feels the same degree of the interaction against B and C, therefore the concentration profiles of B and C nearly remain constant, and there is no excess B in the interfacial region regardless of χ_{BC} and $\phi_B(\infty)$, as shown in Figure 4. As increasing χ_{AC} , C is driven away from the overlap with A in the interfacial region, then the interfacial tension increases, as shown in Figure 3. In the case of large χ_{AC} (above around 0.1~0.2), C is strongly repelled from the overlap with A, but on the other hand this effect can lead to a preferential adsorption of B to the interface. Consequently, the interfacial tension levels off or decreases in small, and these curves have the maximum points through χ_{AC} . Then B competes with C against A for varying χ_{AC} and χ_{BC} . This picture may be seen in such non-symmetrical A/BC polymeric systems. Figure 4 shows the dependence of the excess B on χ_{AC} . For any sets of the parameters, the excess B increases throughout, but eventually the curves level off at some values. In small $\chi_{BC} = -0.01$

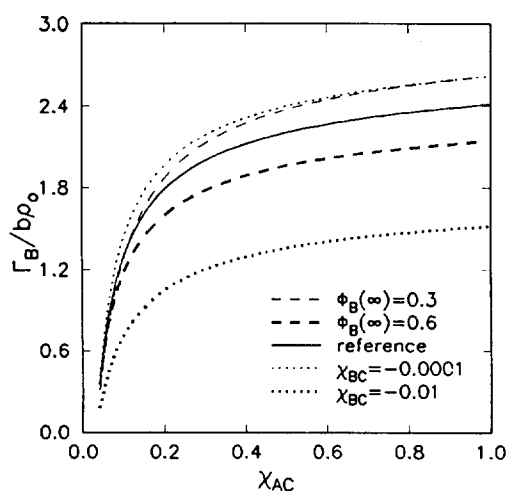


Figure 4. Variation of the excess polymer B per unit area, in units of $b\rho_0$, with χ_{AC} for the same conditions as in Figure 3.

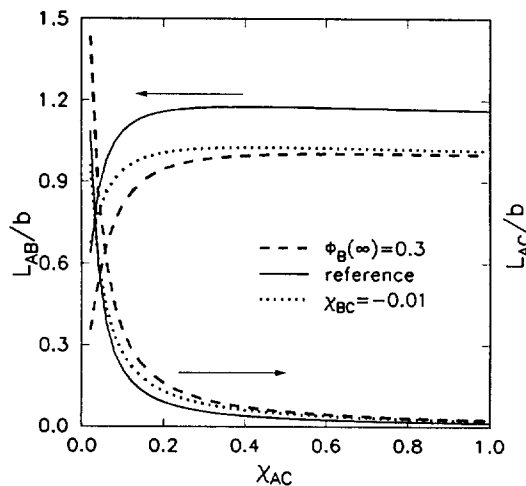


Figure 5. Variation of the overlap lengths between the polymers, in units of b , with χ_{AC} for the same conditions as in Figure 3.

we can see that the separation of B from C is energetically unfavorable. It is interesting that the adsorption of B in $\phi_B(\infty) = 0.3$ exceeds the case of $\phi_B(\infty) = 0.6$. We will discuss more about the behavior at small and large $\phi_B(\infty)$ below. Figure 5 shows the measure of the overlaps between the polymers. L_{AB} increases more rapidly at large $\phi_B(\infty)$ and χ_{BC} , and then L_{AC} naturally decreases. In large χ_{AC} , the overlap lengths nearly remain constant through above around 0.15 because of the increasing B adsorption, as the interfacial tension levels off in Figure 3.

Effects of Varying $\phi_B(\infty)$. In the interfaces between two immiscible polymers, the role of compatibilizers is exceedingly important. Figures 6-10 show how the polymer B as a compatibilizer can modify the interfacial properties of the A/BC system. Figure 6 shows that even if the amount of B in the BC mixture is small, that can lead to a considerable adsorption of B to the interface and consequent modification of the interfacial properties. In large $\phi_B(\infty)$, the concentration profiles in the right of the interface become flat gradually and the interfacial region becomes thick, and on the contrary the excess B decreases. In Figure 7 the interfacial

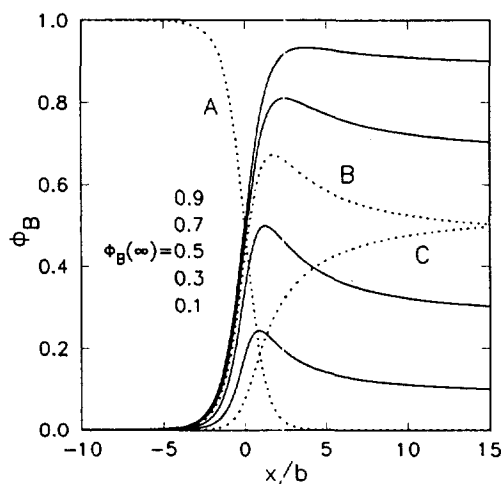


Figure 6. Concentration profiles of polymer B for varying $\phi_B(\infty)$ with $\chi_{AC}=0.1$ and $\chi_{BC}=-0.001$. The dotted lines indicate a reference as in Figure 1.

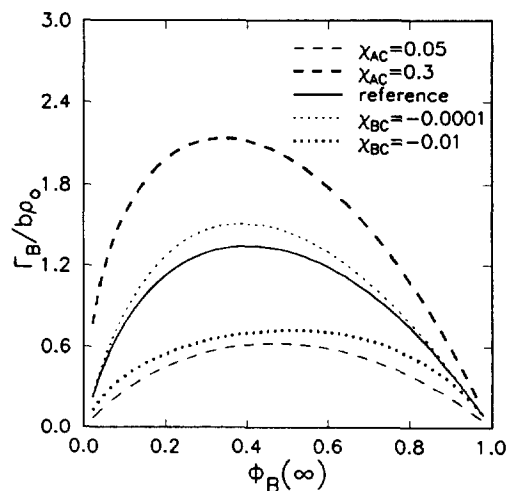


Figure 8. Variation of the excess polymer B per unit area, in units of $b\rho_0$, with $\phi_B(\infty)$ for the same conditions as in Figure 7.

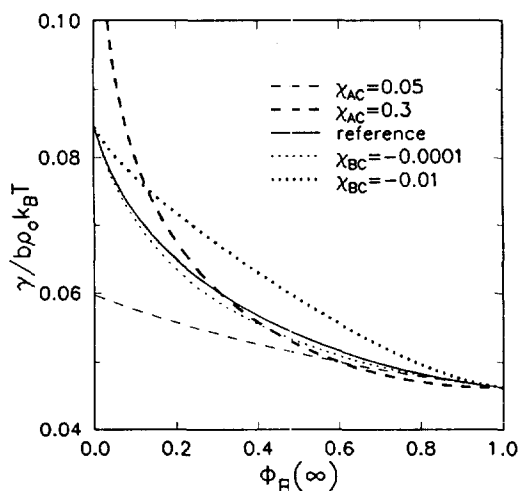


Figure 7. Variation of the interfacial tension, in units of $b\rho_0 k_B T$, with $\phi_B(\infty)$ for different values of the parameters, χ_{AC} and χ_{BC} . The solid lines in Figures 8-10 indicate a reference: $\chi_{AC}=0.1$ and $\chi_{BC}=-0.001$.

tension rapidly decreases for all sets of parameters. The decreasing effect of the interfacial tension by the adsorption of B improves the interfacial adhesion between two phases, and then slows the demixing process of the polymeric phases. For very small $\phi_B(\infty)$ [nearly zero] all curves approach to the values for the A/C binary system, and $\phi_B(\infty)$ goes to one all curves also approach to the binary A/B. In the case of a solid line, $\gamma/b\rho_0 k_B T=0.0845$ and 0.0463 for the A/C and A/B binary systems, respectively. Figure 8 shows the dependence of the excess B upon $\phi_B(\infty)$. At the limits of $\phi_B(\infty)\rightarrow 0$ and 1, the excess B is very small but not zero, the maximum points appear in the range of 0.3 and 0.7. This result is because the amount of B adsorbed to the interface is estimated by the amount of B in the interfacial region and the relative one for polymer B in the asymptotic mixture phase, as in Figure 6 and Eq. (51). Figure 9 shows the width of B plotted against ϕ_B . In $\phi_B(\infty)\rightarrow 1$ limit (nearly pure B), i.e., in the absence of polymer C we can not compare the

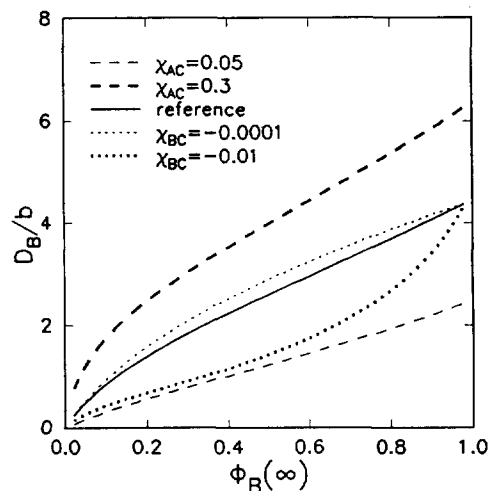


Figure 9. Variation of the width of polymer B, in units of b , with $\phi_B(\infty)$ for the same conditions as in Figure 7.

width of B in the A/BC with the one in the A/B system. There is no meaning in this case, then we can only deal with the overlap between A and B or A and C, as in Figure 10. When χ_{AC} is large and $|\chi_{BC}|$ small, the overlap length between A and B is large, and consequently this affects the interfacial tension. At the limit of $\phi_B(\infty)\rightarrow 1$ or 0, the overlap between the polymers becomes that of the A/B or A/C binary polymeric system.

Concluding Remarks

In this paper by solving the mean-field equations numerically for the A/BC system in the limit of infinite molecular weight for the polymers, we obtained the concentration profiles, the interfacial tension, the width of polymer B, the amount of polymer B adsorbed to the interface, and the overlap lengths between the polymers for various typical values of two Flory interaction parameters, χ_{AC} and χ_{BC} , and the volume fraction of B in the asymptotic phase, $\phi_B(\infty)$.

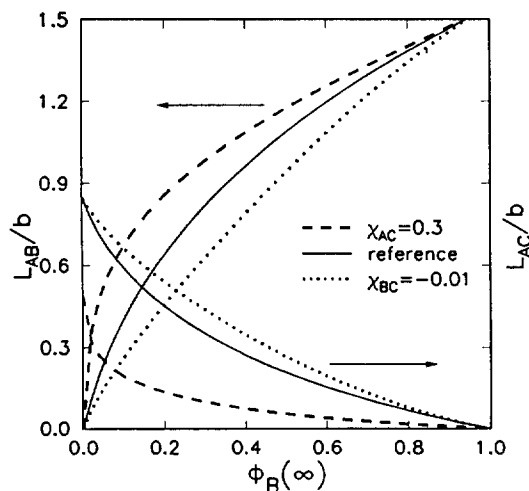


Figure 10. Variation of the overlap lengths between the polymers, in units of b , with $\phi_B(\infty)$ for the same conditions as in Figure 7.

Increasing χ_{AC} repels the polymer C from the interfacial region, consequently it leads to the preferential adsorption of B to the interface, the increasing of the overlap between A and B, and the interfacial tension (in the case of large χ_{AC} , the interfacial tension levels off or decreases in small). Increasing $|\chi_{BC}|$ has the opposite effect to χ_{AC} in the excess polymer B and the overlap between A and B, however the interfacial tension increases through $|\chi_{BC}|$ over all, even if not shown in this paper.

Even small amounts of polymer B as a compatibilizer in the asymptotic mixture phase can modify the physical properties of the interface. As increasing $\phi_B(\infty)$, the interfacial tension reduces, the overlap of the polymers A and B increases, and the width of polymer B increases. However, the adsorption of polymer B to the interface first increases and then decreases through $\phi_B(\infty)$. When $\phi_B(\infty) \rightarrow 0$ the system goes to the binary A/C, and $\phi_B(\infty) \rightarrow 1$ the A/B binary polymeric system.

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