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Surface Segregation in Binary Polymer Mixtures: A Lattice Model

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ABSTRACT: In this work, the influence of energetic effects on the structure and properties of a binary polymer–melt/surface interface has been investigated. Our interest is in the modeling of the behavior of binary, isotopic polymer blends near surfaces from a fundamental viewpoint, and to this end polymer–surface and polymer–polymer interaction energies were taken into account in the development of the model. The results of the calculations show that the component with the lower surface energy segregates to the surface, and the driving force for this partitioning was shown to arise even from very small differences in energetic effects. Detailed investigations of the predicted concentration profiles show that the segregation can be high enough to cause complete wetting of the surface by one of the components. In general, the extent of this segregation was found to depend strongly on the molecular weights, the energetic interactions with the surface, and the bulk volume fractions of the components in the melt. In addition, the interfacial tension was calculated in order to highlight some of the consequences of the segregation. Finally, calculations were performed to provide insight into the orientation of the chain segments and the behavior of chain ends in the interface.

1. Introduction

Polymeric materials in the vicinity of surfaces have been the focus of recent research, and a variety of analytical,[1-12] computational,[13] and experimental techniques[14-18] have been used to study these problems. The motivation for studying the polymer–melt/solid interface arises from its relevance in practical applications such as in the design of composite materials based on macromolecules. A fundamental understanding of the interfacial structure and properties, and the factors that affect them, allows, in principle, for the controlled modification of the microstructure and composition of the interface by the appropriate choice of the different factors that affect them (i.e., chain architecture, molecular weights, and bulk compositions).

Although a good understanding exists on the behavior of model, monodisperse polymer melts in the vicinity of hard surfaces,[1-12] there are relatively few results on the behavior of "real" polymers near surfaces. To probe this issue, we have examined[19] the behavior of an athermal, polydisperse melt in the vicinity of a hard, energetically neutral surface. The results of these calculations suggest that the shorter chains partition preferentially to the hard surface due to entropic considerations. It was found in the case of truly macromolecular systems, however, that the surface composition of the short chains were different from their bulk values by only ca. 1% or less. The conclusion of these results thus stressed that polydispersity effects in the absence of energetic interactions do not cause significant changes in the structure of a polymer interface.

In contrast, the inclusion of even small differences in the chemical structure between the components of a binary polymer blend in the vicinity of a surface has been shown to affect the surface segregation of the two components dramatically.[20] For example, Jones and co-workers[20] have considered isotopic blends of polystyrene of essentially equal chain lengths (ca. 10 000) and show that the segments of the deuterated PS are strongly segregated to the air surface. Since these experiments deal with isotopic systems that experience small differences in energetic interactions, these experiments reiterate that even small energetic differences can play a dominant role in determining the surface behavior of a polymer blend.

In this paper we present the results of a self-consistent investigation of the modification of the interfacial properties of a binary polymer blend due to the differences in the energetic effects between the two components in a polymer sample and the surface. A compatible binary polymer blend in the vicinity of a plane, homogeneous surface was studied in the framework of the Scheutjens and Fleer formalism,[12] taking account of polymer–surface and polymer–polymer nearest-neighbor energetic interactions. The concentration profiles of the chain segments of the two species normal to the surface were obtained as a function of molecular weights, bulk concentrations, and all energetic interactions. Calculations of the interfacial tension have also been performed. In addition, the density of chain ends and the orientation of the chain segments at the interface have been studied in detail.

2. Theoretical Development

2.1. Definition of the Model. The development of the model presented here closely parallels the derivation given in ref 19, and the interested reader is referred to this publication for more details. Consider a binary polymer melt comprised of N chains distributed on a fully filled lattice containing M layers having L lattice sites each, in which layers 1 and M denote the solid surfaces. If n_α chains each of length r_α constitute component α in the melt, then the population balance dictating complete filling

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of the lattice is

$$\sum_{\alpha} r_{\alpha} n_{\alpha} = ML \qquad (\alpha = 1,2) \tag{1}$$

There are several possible arrangements of segments comprising chains of type α in any given conformation c_{α} (in this context, a conformation specifies the sequence of layer numbers in which the segments of a chain are found).[19] The number of arrangements in any conformation c_{α} can be enumerated as

$$L(z\delta_{j-i})(z\delta_{k-j})(z\delta_{l-k})...(z\delta_{m-p}) \equiv Lz^{r-1}w_{c_{\alpha}} \tag{2}$$

where z denotes the lattice coordination number and δ_{j-i} is defined to be the fraction of nearest neighbors in layer j available to any site in layer i. The possible values that δ_{j-i} can assume are therefore

$$\begin{aligned} \delta_{j-i} &= \delta_0, \quad j = i \\ &= \delta_1, \quad j = i \pm 1 \\ &= 0, \quad \text{otherwise} \end{aligned} \tag{3}$$

Correspondingly, the following normalization conditions must be fulfilled.

$$\sum_{i} \delta_{j-i} = 1 \qquad 1 < i < M \tag{4a}$$

$$= 1 - \delta_1 \qquad i = 1, M \tag{4b}$$

In the above normalization conditions, eq 4a arises naturally for any bulk lattice system, while eq 4b is a restatement of the boundary condition that determines the impenetrability of the surfaces.

If the number of segments of component α in layer i is given by $n_{\alpha,i}$, then its corresponding volume fraction in that layer is given by

$$\Phi_{\alpha,i} = n_{\alpha,i}/L \qquad (\alpha = 1, 2) \tag{5}$$

2.2. Partition Function. The grand canonical partition function for this system is formally defined relative to appropriate reference states as

$$G = \sum Q(\{n_{c_{\alpha}}\},M,L,T) \exp(\sum_{\alpha} \mu_{\alpha} n_{c_{\alpha}}/k_{B}T) \qquad (\alpha = 1, 2) \tag{6a}$$

where the summation $\sum$ is over all possible conformational states, μ_{α} is the chemical potential of the component α with respect to its reference state, $n_{c_{\alpha}}$ is defined to be the number of molecules of type α in conformation c_{α} at a temperature T, and k_B is Boltzmann's constant. The reference states for this model have been chosen to be the pure components comprising the system in their unconstrained, bulk states. For a mean-field theory the canonical partition function, Q, is defined relative to these reference states as

$$Q(\{n_{c_{\alpha}}\},M,L,T) = (\Omega/\prod_{\alpha} \Omega_{\alpha}) \exp(-U/k_{B}T) \qquad (\alpha = 1, 2) \tag{6b}$$

Ω is the number of ways of arranging the N molecules of the bimodal melt on an interfacial lattice with ML sites. Ω_{α} pertains to the entropic contribution of the reference states and is the number of ways of arranging n_{α} molecules of length r_{α} on an unconstrained lattice of $n_{\alpha}r_{\alpha}$ sites. These combinatorial terms (Ω,Ω_{α}), which have already been calculated in a previous publication,[19] will not be repeated in this paper. However, the form of U, the potential energy of the system relative to the reference states, is derived below.

2.2.1. Potential Energy. The potential energy of the interfacial system relative to the pure-component reference states has been calculated by accounting for the nearest-neighbor interactions alone in the spirit of the Bragg–Williams approximation.[21] From eq 3, any site in layer i has $z(\delta_{j-i})$ contacts in layer j. Therefore, a site in layer i will have $z(\delta_{j-i}\Phi_{\alpha,j})$ contacts in layer j with segments belonging to component α. The total number of contacts that any site has, with segments of component α, is thus

$$z(\sum_{j} \delta_{j-i}\Phi_{\alpha,j}) \equiv z\langle \Phi_{\alpha,i} \rangle \qquad (i, j = 1, M) \tag{7}$$

Let us define $w_{\alpha\alpha}$ and $w_{\alpha\beta}$ to be the intracomponent and intercomponent interaction energies per segment, respectively, and $w_{\alpha s}$ to be the surface interaction energy per segment of component α. According to these definitions and approximations, the potential energy of the interfacial system will therefore be

$$\begin{aligned} U_{\text{int}} = z\sum_{i} \{n_{1,i}\langle \Phi_{1,i} \rangle (w_{11}/2) + n_{2,i}\langle \Phi_{2,i} \rangle (w_{22}/2) + \\ n_{1,i}\langle \Phi_{2,i} \rangle (w_{12})\} + z\delta_1(n_{1,1}w_{1s} + n_{2,1}w_{2s}) \qquad (i, j = 1, M) \end{aligned} \tag{8}$$

Similarly, the potential energy of the reference states will be

$$U_{\text{ref}} = (\sum_{\alpha} n_{\alpha} r_{\alpha} w_{\alpha\alpha})/2 \qquad (\alpha = 1, 2) \tag{9}$$

The required potential energy U in eq 6b is thus given by

$$\begin{aligned} U = U_{\text{int}} - U_{\text{ref}} = k_{B}T[\chi \sum_{i} n_{1,i}\langle \Phi_{2,i} \rangle] + \\ [n_{1,1}u_1 + n_{2,1}u_2] \qquad (i = 1, M) \end{aligned} \tag{10}$$

where

$$k_{B}T\chi \equiv z[w_{12} - (w_{11} + w_{22})/2] \tag{11a}$$

is the conventional definition of the Flory interchange energy parameter[21] and

$$u_{\alpha} \equiv w_{\alpha s} - (w_{\alpha\alpha}/2) \tag{11b}$$

is defined to be the adsorption energy of component α to the surface relative to its bulk interaction.

2.3. Minimization of the Grand Potential. Since the grand potential is given by $-k_{B}T \ln G$, the condition for the system to be in equilibrium is that $\ln G$ be maximized, subject to the constraint of full occupancy in each layer. This amounts to maximizing the function f given below

$$f = \ln G - \sum_{i} m_i[(\sum_{c_{\alpha}} r_{\alpha,i_{c\alpha}} n_{c_{\alpha}}) - L] \tag{12}$$

where m_i is a Lagrange multiplier that incorporates the constraints corresponding to the full occupancy of layer i into the expression for the grand potential, and $r_{\alpha,i_{c\alpha}}$ is defined to be the number of segments in layer i of component α having a conformation c_{α}. Extremization of the function f with respect to the number of molecules in any conformation $n_{c_{\alpha}}$ yields the unnormalized conformational probabilities of this species at equilibrium

$$(n_{c_{\alpha}}/L) = k_{\alpha} w_{c_{\alpha}} \prod_{i} \{P_{\alpha,i}\}^{r_{\alpha},i_{c\alpha}} \qquad (\alpha, \beta = 1, 2; \alpha \neq \beta) \tag{13}$$

where

$$P_{\alpha,i} = \exp(m_i + [\delta_{1i} + \delta_{Mi}]U_{S_{\alpha}} + \chi\langle \Phi_{\beta,i} \rangle) \qquad (\alpha, \beta = 1, 2; \alpha \neq \beta) \tag{14}$$

and

$$k_\alpha = (1/r_\alpha e)L^{\{1-[r_\alpha/r_\beta]\}}{r_\beta}^{r_\alpha/r_\beta}e^{(1/k_BT)(\mu_\alpha-[r_\alpha\mu_\beta/r_\beta])} \qquad (\alpha, \beta = 1, 2; \alpha \neq \beta) \quad (15)$$

$P_{\alpha i}$ is defined to be the free-segment probability[2,19] of component α in layer i. k_α is a constant depending upon chain length, lattice parameters, and the chemical potentials of the chains. $\delta_{1i}(\delta_{Mi})$ is the Kronecker delta.

Let us define $p_{\alpha,i}$ to be the free-segment probability, $P_{\alpha,i}$, normalized with respect to its bulk value, $P_{\alpha b}$

$$p_{\alpha,i} = P_{\alpha,i}/P_{\alpha b} = \exp\{[m_i - m_b] + [\delta_{1i} + \delta_{Mi}]U_\alpha + \chi[\langle\Phi_{\beta,i}\rangle - \Phi_{\beta b}]\} \qquad (\alpha, \beta = 1, 2; \alpha \neq \beta) \quad (16a)$$

where the subscript "b" denotes bulk values and

$$U_\alpha = u_\alpha/k_BT \quad (16b)$$

is the adsorption energy of a segment of component α, in units of k_BT. $p_{\alpha,i}$, by definition, will assume a value of 1 far away from the surface. Eliminating the Lagrange multiplier from eq 16a then yields

$$p_{1,i} = p_{2,i} \exp\{\chi([\Phi_{2b} - \langle\Phi_{2,i}\rangle] - [\Phi_{1b} - \langle\Phi_{1,i}\rangle]) - [\delta_{1i} + \delta_{Mi}]\chi_s\} \qquad (i = 1, M) \quad (17a)$$

where

$$\chi_s \equiv U_1 - U_2 \equiv (1/k_BT)[(w_{1s} - w_{2s}) - 0.5(w_{11} - w_{22})] \quad (17b)$$

χ_s thus defines the adsorption energy difference between the segments of the two constituent chains and is a measure of the preference of any segment of one component for the surface over that of the segments of the other. Note is made of the fact that χ_s assumes a nonzero value $[=(w_{22} - w_{11})/2k_BT]$ even in the case where the segments of the two chains experience identical interactions with the surface $[w_{1s} = w_{2s}]$. This factor arises from the absence of nearest neighbors for the segments that are in the immediate vicinity of the surface and emphasizes that the system will preferentially partition to the surface those segments that experience less favorable intersegment interactions in the bulk even in the absence of specific interactions with the surface. The consequences of such a situation have been addressed elsewhere with reference to isotopic blends in the vicinity of a surface.[22,23]

The volume fractions of the two species can be obtained following the Scheutjens and Fleer formalism[12] to be

$$\Phi_{\alpha,i} = [\Phi_{\alpha b}/r_\alpha](1/p_{\alpha,i})\sum_{s_\alpha=1}^{r_\alpha} p(i,s_\alpha)\, p(i,r_\alpha - s_\alpha + 1) \qquad (\alpha = 1, 2) \quad (18)$$

where Φ_{1b} and Φ_{2b} are the volume fractions of the two components in the bulk. Equation 18 can be understood by realizing that each term in the summation represents the contribution of a particular chain segment in layer i to the volume fraction of species α. The average volume fraction of the chains belonging to one of the components is thus evaluated by summing over all chain segments sequentially. $p(i,s_\alpha)$ is the normalized end-segment probability[12,19] and is equal to the free-segment probability, $p_{\alpha,i}$, for $s_\alpha = 1$. For other values of s_α it can be calculated from the recurrence relation[12]

$$p(i,r_\alpha) = \sum_j \delta_{j-i} p_i p(j,r_\alpha - 1) \qquad (\alpha = 1, 2) \quad (19)$$

Since the system under consideration has a bimodal distribution

$$\sum_\alpha \Phi_{\alpha,i} = \sum_\alpha [\Phi_{\alpha b}/r_\alpha](1/p_{\alpha,i}) \sum_{s_\alpha=1}^{r_\alpha} p(i,s_\alpha)\, p(i,r_\alpha - s_\alpha + 1) = 1 \qquad (\alpha = 1, 2) \quad (20)$$

Based on the relationship between the free-segment probabilities (given by eq 17) and the recursive relation (eq 19), eq 20 can then be solved simultaneously for $\Phi_{\alpha,i}$.

3. Results and Discussion

The theory derived here is a mean-field lattice calculation to delineate the surface behavior of a binary polymer blend interacting through short-range, dispersive forces. In this section we will investigate both the structural and thermodynamic aspects of the chains at the interface by calculating the concentration of the two species as a function of the distance from the surface. Further, the interfacial tensions and the conformational properties of the chains in the vicinity of the surface will be studied through the calculation of segment orientations and end-segment densities as a function of the distance from the surface. In the past this problem has been addressed by Schmidt and Binder, on a phenomenological basis.[11] The advantages and disadvantages of employing either one of these two theories will therefore be examined in the Discussion section.

3.1. Segment Density Distributions. We begin by examining the volume fractions of the segments of the two chains in each of the lattice layers as a function of the variables in the system, i.e., the chain lengths of the two polymers (r_1 and r_2), the bulk volume fractions (Φ_{1b} and Φ_{2b}), and the interaction energy parameters (χ and χ_s). The motivation for this analysis arises from the fact that the experimental characterization of interfaces is most often performed by measurements of their concentration profiles. It must be noted that the calculations presented in this paper neglect any dependence of χ or χ_s on the molecular weights or the concentration of the two species in the specimen, and the incorporation of such dependences is left to future work.

3.1.1. Dependence on the Surface Interaction Parameter. We begin by discussing the sensitivity of the segment density distributions on χ_s. The rationale for expecting variations in χ_s is clear by examining its definition

$$\chi_s \equiv (1/k_BT)[(w_{1s} - w_{2s}) - 0.5(w_{11} - w_{22})] \quad (17b)$$

which suggests that any changes in polymer or surface structure will manifest itself as a change in χ_s.

For a blend containing two components with equal chain lengths ($r_1 = r_2$) and compositions in the bulk ($\Phi_{1b} = \Phi_{2b} = 0.5$), the component with the lower adsorption energy was always found to segregate to the surface. Positive values of χ_s, as defined by eq 17b, thus led to the partitioning of component 2 to the surface. As expected, the extent of the segregation was found to increase with the magnitude of χ_s. For example, for systems comprised of chains of length 100 with $\chi = 0.0005$, $\chi_s = 0.02$, and $\Phi_{1b} = \Phi_{2b} = 0.5$, the volume fraction of the component that partitioned preferentially to the surface ($\Phi_{2,i}$) was found to be the highest (ca. 0.64) at the surface as shown in Figure 1. The volume fraction decreased continuously in subsequent layers and reached its bulk value asymptotically as one proceeded to ca. 10 lattice layers from the surface. Increasing the value of χ_s, while keeping all other pa-

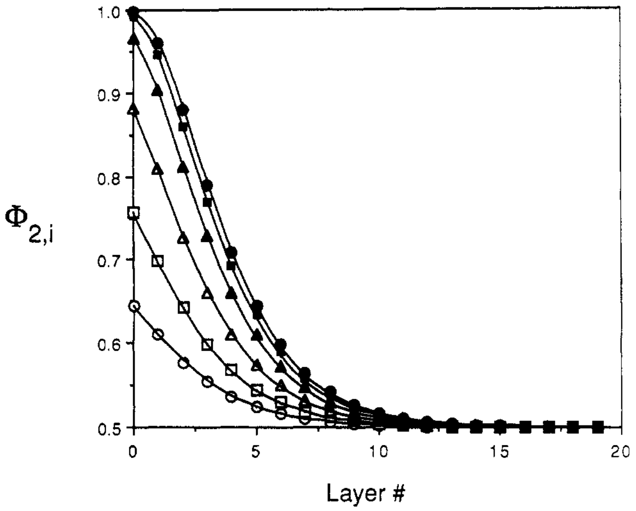

Figure 1. Concentration profiles of the component that partitions preferentially to the surface, for different values of χ_s. The system is characterized by $r_1 = r_2 = 100$, $\chi = 0.0002$, and $\Phi_{2b} = 0.5$. The solid lines correspond to the profile defined by eq 21 while the labels represent the lattice model predictions. χ_s values used were 0.02 (○), 0.04 (□), 0.08 (△), 0.18 (▲), 0.4 (■), 0.8 (●).

rameters in the system constant, caused the surface enhancement to increase. As shown in Figure 1, increasing χ_s from 0.02 to 0.8 caused the volume fraction of species 2 on the surface to increase from a value of 0.64 to almost complete saturation, with a concomitant increase in the volume fraction of this species in subsequent layers. One can also observe that this causes a significant change in the shape of the concentration profile of this species.

Numerous functions can be used to describe the depth dependence of the concentration shown in Figure 1. However, a hyperbolic tangent function, of the form given below, was found to best describe the results.

$$A_{2,i} = A_{2,1}(1 - \{\tanh[(i-1)/\tau]\}^{\epsilon}) \qquad (21)$$

where $A_{\alpha,i} = \Phi_{\alpha,i} - \Phi_{\alpha,b}$ is the excess volume fraction of component α in layer i relative to the bulk and is defined to be the absolute enhancement of component α in layer i. τ is a correlation length, which describes the rate of decay of the profile to its bulk value, and ϵ is an exponent, which assumed values in the range $\epsilon \geq 1$.

One can see in Figure 1 that the suggested profile (eq 21) reproduces the results from theory quite accurately. The correlation lengths τ for all the profiles shown in Figure 1 was 4.2 lattice layers, a number that is approximately equal to the unperturbed radius of gyration of the chains in the melt. The change in the shape of the profile observed at high levels of enhancement manifested itself as an ϵ value greater than 1 (for example, for $\chi_s = 0.8$, $\epsilon = 1.85$), while ϵ always took a value of 1 for lower values of χ_s (corresponding to a hyperbolic tangent profile). It is thus clear that ϵ defines the shape of the concentration profile and assumes values different from 1 for high levels of surface enhancements. In such situations the concentration profile assumes a flat shape near the surface.

3.1.2. Dependence on Molecular Weights. The effect of increasing the chain lengths of the two components while maintaining them equal to each other ($r_1 = r_2$) is shown in Figure 2, where concentration profiles for segments of species 2 are shown for $\chi = 0.0002$, $\chi_s = 0.005$, and $\Phi_{\alpha b} = 0.5$. Clearly, increasing the molecular weights causes an increase in the enrichment at the surface. This is illustrated in the inset of the Figure 2 where the surface volume fraction, $\Phi_{2,1}$, is plotted as a function of the inverse chain length. One can see that $\Phi_{2,1}$ increases rapidly with chain length. The conclusion of this analysis is that one can achieve dramatic increases in the surface enhancement by increasing the degrees of polymerization of the chains in the blend even for systems characterized by small values of χ_s.

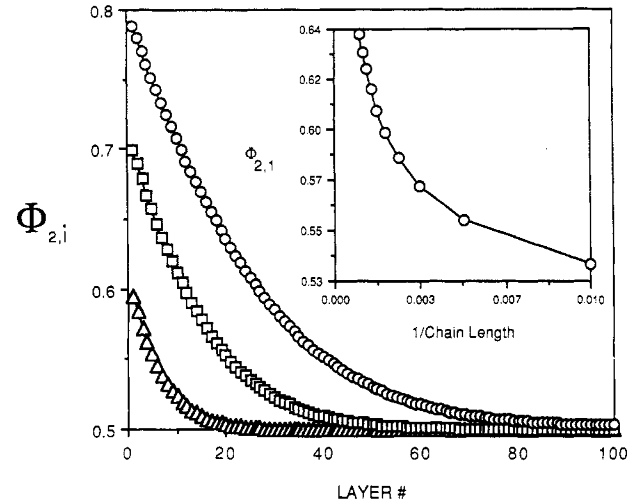

Figure 2. Concentration profiles for systems with equal chain lengths with $\chi = 0.0002$, $\chi_s = 0.005$, and $\Phi_{2b} = 0.5$. The curves represent the different chain lengths that were used. $r_1 = r_2 = 500$ (△), 4000 (□), 6000 (○). The inset shows a plot of inverse chain length versus the surface composition of component 2.

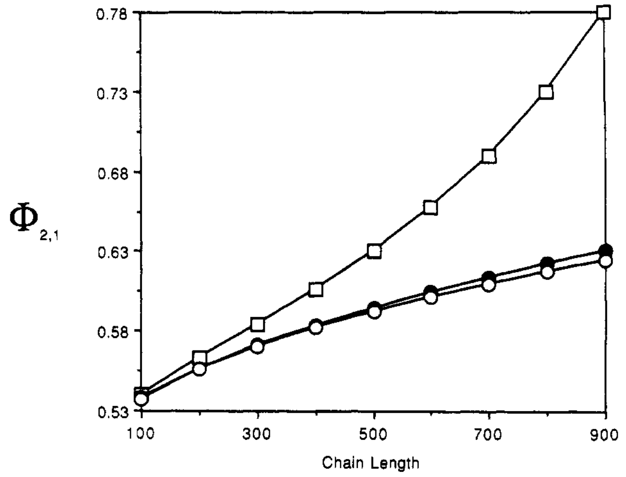

Figure 3. Surface volume fraction of the component that partitions preferentially to the surface plotted as a function of chain length for three different values of χ: 2×10^{-3} (□), 2×10^{-4} (●), 2×10^{-5} (○). Here, $\chi_s = 0.005$ and $\Phi_{2b} = 0.5$.

Another factor to be noted in Figure 2 is that the interface width increases with increasing chain length. For example, for chain lengths of 500 the profile has a correlation length, τ, of bulk value ca. 9 lattice layers, while for chains of length 4000, it is ca. 41 lattice layers ($\epsilon = 1$, in both of these cases). The results of this analysis suggest that increasing the chain lengths ($r_1 = r_2$) has a 2-fold effect on surface behavior; i.e., both the enhancement on the surface ($\Phi_{2,1}$) and the correlation length (τ) increase with increasing degrees of polymerization.

To analyze this effect in more detail, we consider blends with a bulk composition of 0.5 and $\chi_s = 0.005$, for three different values of χ (2×10^{-3}, 2×10^{-4}, and 2×10^{-5}, respectively). These systems are expected to phase separate in the bulk when the chain lengths of the two polymers in the systems are ca. 1×10^3, 1×10^4, and 1×10^5, respectively.[21] In Figure 3, the surface composition $\Phi_{2,1}$ is plotted as a function of the chain lengths ($r_1 = r_2$) of the constituent polymers for chain lengths ranging from

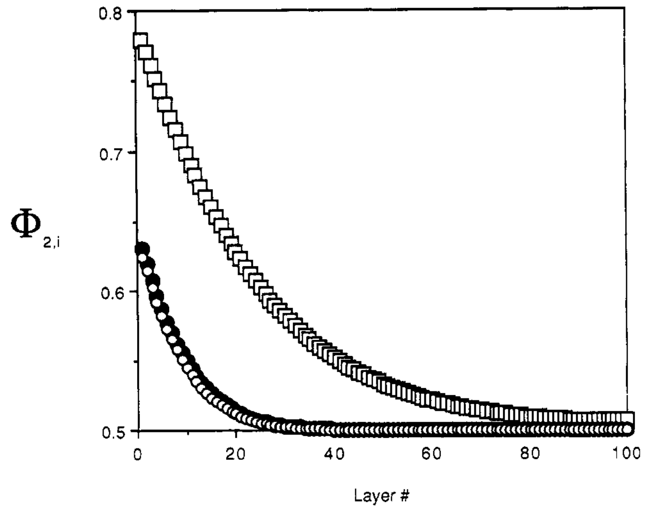

Figure 4. Concentration profiles of the component that partitions preferentially to the surface plotted for the three different values of χ: 2×10^{-3} (□), 2×10^{-4} (●), 2×10^{-5} (○) that were used in Figure 3. Here, $\chi_s = 0.005$ and $\Phi_{2b} = 0.5$ and $r_1 = r_2 = 900$.

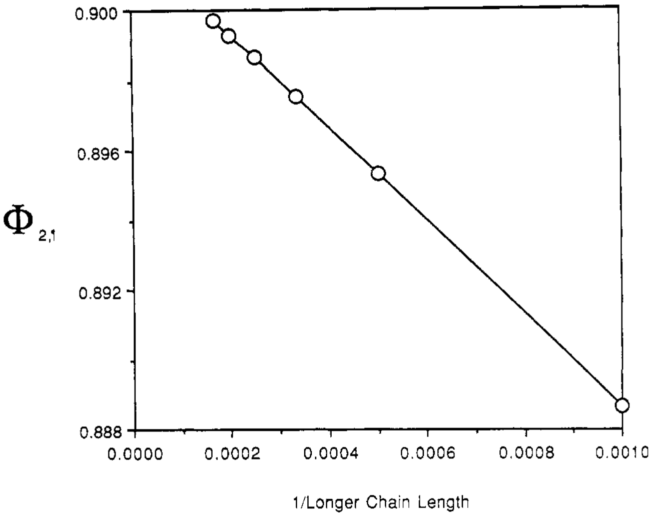

Figure 5. Surface volume fraction $\Phi_{2,1}$ of the shorter chain of length 100 plotted as a function of the reciprocal of the long chain length. The system was characterized by χ_s, $\chi = 0.0002$, and $\Phi_{2b} = 0.5$.

100 to 900. It is clear that the surface enhancements $\Phi_{2,1}$ for the systems characterized by the two lower values of χ are almost equal to each other over the range of molecular weights considered. However, for the system with $\chi = 2 \times 10^{-3}$, $\Phi_{2,1}$ increases rapidly from a value that is equal to the surface enhancements corresponding to the other two values of χ at low chain lengths, and the curve is seen to diverge from the other two as one approaches the critical point of this system ($r_1 = r_2 = 1000$).

In Figure 4, the concentration profiles of the systems corresponding to the highest molecular weight ($r_1 = r_2 = 900$) considered in (Figure 3) are plotted to highlight additional details about the interface. It is obvious from the profiles that the one corresponding to $\chi = 2 \times 10^{-3}$ shows not only a high surface segregation but also a much broader interface compared to the other two. The profiles corresponding to the two smaller χ values, however, are almost identical with each other even though the values of χ that characterize them differ by 1 order of magnitude. We thus arrive at two important conclusions based on this analysis:

(a) The surface segregation is driven mainly by the surface energy difference, χ_s, when systems are far from their bulk critical points (or UCST).[21] In such situations the value of χ is relatively unimportant in determining surface behavior.

(b) However, χ plays an active role in determining the interfacial composition when one approaches the critical point of the binary polymer mixture.[21]

It must be reemphasized that these results are based on the assumption that χ_s and χ are independent of molecular weight, a result that is not normally valid for real systems.[22,23,28,29] In spite of this simplification, it is clear from this analysis that one can tailor the interface through an appropriate choice of the molecular weights of the chains in the system.

If one now considered a bimodal blend comprised of shorter chains of length 100, at a bulk composition of 50% and characterized by $\chi = 0.0002$ and $\chi_s = 0.05$, and varied the length of the longer chain from 1000 to 6000, a plot of $\Phi_{2,1}$, i.e., the volume fraction of the shorter chain at the surface as a function of the inverse chain length (Figure 5), suggests that $\Phi_{2,1}$ increases as the longer chain length is increased. The magnitude of χ that has been chosen for this calculation is well below the critical value ($\chi_c = 0.005$) at which the blend will phase separate if the long chain is of infinite length. It is evident in this situation that $\Phi_{2,1}$ is proceeding toward an asymptotic value corresponding to an infinite length of the long chain. Similar behavior (not shown) was observed in the opposite case where the shorter chain was made to energetically dislike the surface (i.e., $\chi_s < 0$). It is therefore clear that the lower surface energy component from the blend is always partitioned preferentially to the surface, emphasizing that entropic effects do not play a strong role in the context of such macromolecular systems near surfaces.

3.1.3. Effect of Varying Bulk Composition.

In practical situations a quantity that can be varied with sufficient ease is the bulk composition of the melt that is in contact with the surface. To study the effect of bulk compositions on the surface segregation, we define the relative enhancement $R_{\alpha,i}$ of component α in layer i.

$$R_{\alpha,i} = A_{\alpha,i}/\Phi_{\alpha b} \qquad (22)$$

We have chosen this form to examine the data since $A_{\alpha,i} \rightarrow 0$ in the limit $\Phi_{2b} \rightarrow 0$, and the form chosen here, which is similar to Henry's constant, gives us a measure of the fractional enrichment of species 2 at the surface. In Figure 6 the relative surface enhancement $R_{2,1}$ in the case $\chi_s > 0$ has been plotted as a function of the bulk volume fraction of component 2, for different values of χ_s. The systems represented in the figure are comprised of chains that have a degree of polymerization of 100 ($r_1 = r_2 = 100$), and χ assumed a value of 0.0005 (identical with the systems that were used in Figure 1). Again this analysis is based on the assumption that χ_s is constant over the composition range.

For all the cases, $R_{2,1}$ increased from a value of 0 in limit $\Phi_{2b} \rightarrow 1$ to a value that is characteristic of each of the values of χ_s as $\Phi_{2b} \rightarrow 0$. As one now increased the value of χ_s, $R_{2,1}$ was found to increase, with changes being most dramatic at low concentrations of component 2. In general, therefore, one concludes that the most dramatic relative segregations occur when one has an infinitesimal quantity of the species attracted to the surface.

It should be emphasized, however, that although the relative enhancements show dramatic behavior in the limit of $\Phi_{2b} \rightarrow 0$, the maximum segregation in absolute terms (i.e., $\Phi_{21} - \Phi_{2b}$) occurs at finite values of Φ_{2b}. This is due to the fact that the absolute segregation, $A_{2,1}$, can be

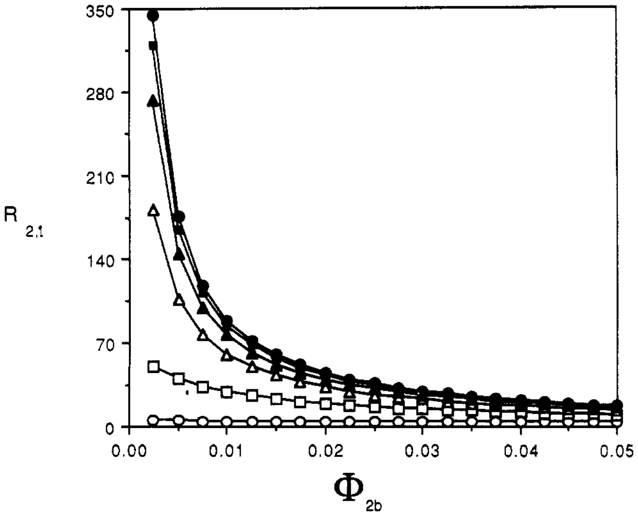

Figure 6. Relative surface enhancement $R_{2,1}$ of component 2 plotted as a function of the bulk volume fraction Φ_{2b} for various values of χ_s. The systems used (and the corresponding data labels) are identical with those in Figure 1.

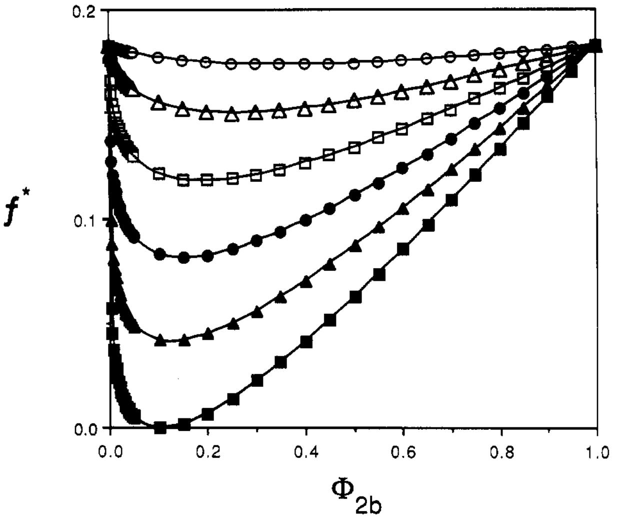

Figure 7. Variation of surface tension with bulk volume fraction of the segments of component 2, for various values of χ_s. The systems used (and the corresponding data labels) are identical with those in Figures 1 and 6.

obtained from the equation

$$A_{\alpha,1} = R_{\alpha,1}\Phi_{\alpha b} \quad (22)$$

which involves scaling a decreasing function ($R_{2,1}$; Figure 6) with an increasing function, Φ_{2b}, and hence results in a maximum when one examines $A_{2,1}$ as a function of Φ_{2b}. In all cases examined in Figure 6 it was found that the maximum for $A_{2,1}$ occurred at Φ_{2b} values between 0.1 and 0.5, with the maxima at smaller values of $\Phi_{2,b}$ occurring for larger values of χ_s.

3.2. Interfacial Tension. To understand the thermodynamic implications of the preferential segregation of a mixture component to the surface, a quantity of interest is the surface tension, which is also a measure of the extent of the adhesion of the polymer to the substrate. The grand potential of the interfacial system at equilibrium, relative to the reference states, can be calculated from the grand canonical partition function (eq 6a) and directly yields the interfacial tension of the system.

$$fa/k_BT = -1/L(\ln Q + n_1\mu_1 + n_2\mu_2) \quad (23)$$

Here, f is the interfacial tension and a is the area per site on the surface. The chemical potentials μ_α of component α in the bulk can be derived from the appropriate grand canonical partition function (eq 6a), with the boundary condition specified by eq 4b being removed. The resulting expression is the Flory result for the chemical potential of one component in a binary polymer blend[21]

$$\mu_\alpha = \Phi_{\beta b} + \ln \Phi_{\alpha b} - (r_\alpha/r_\beta)\Phi_{\beta b} + \chi({\Phi_{\beta b}}^2 r_\alpha) \qquad (\alpha, \beta = 1, 2; \alpha \neq \beta) \quad (24)$$

Substituting the expressions for the chemical potentials (eq 24) and the conformational probabilities at equilibrium (eq 13) into eq 23 yields

$$fa/k_BT = \sum_i \{(\Phi_{1,i} \ln p_{1,i} + \Phi_{2,i} \ln p_{2,i}) + (\Phi_{2,i} - \Phi_{2b})({r_1}^{-1} - {r_2}^{-1}) + \chi(\Phi_{1,i}[\langle\Phi_{2i}\rangle - \Phi_{2,b}] - \Phi_{1b}[\Phi_{2,i} - \Phi_{2b}]) + (\Phi_{1,i}U_1 + \Phi_{2,i}U_2)\delta_{1i}\} \quad (25)$$

The expression for the interfacial tension (eq 25) consists of four terms. The first is a term that is dependent only on the free-segment probabilities of each of the components in the layer. The second term is simply the surface excess Γ_2 ($=\sum_i A_{2,i}$) multiplied by a factor representing the disparity in the molecular sizes and becomes equal to 0 for systems comprised of equal chain length polymers ($r_1 = r_2$). The third and the fourth terms are the energetic contributions to the surface tension. Setting $\chi = \chi_s = 0$ in the above equation reduces it to the expression that was obtained for athermal bimodal melts.[19]

In Figure 7 f^* is shown as a function of the bulk volume fraction, Φ_{2b}, of the component with the lower surface energy, where

$$f^* = (fa/k_BT) - \Phi_{1b}U_1 - \Phi_{2b}U_2 \quad (26)$$

The interfacial tension was plotted in the form that is defined by eq 26 for the sake of symmetry with respect to the two components in the system, so that it converged to the correct entropic limit[19] when $\chi = \chi_s = 0$.

The different curves shown in Figure 7 correspond to the same systems shown in Figure 6, and one can see that, at any given value of χ_s, f^* reaches the correct limit corresponding to single-component systems.[25] At intermediate compositions, f^* goes through a minimum. It is also clear that this minimum is located at the lower end of the composition range ($\Phi_{2b} \rightarrow 0$) and that increasing the value of χ_s causes this minimum to shift to even lower values of Φ_{2b}. Clearly there is a lowering of the surface tension at small values of Φ_{2b}, and it is over this range where the component with the lower surface energy shows the greatest tendency for segregation, a feature that was reflected clearly in our earlier discussion on the relative enhancement $R_{2,1}$. Physically, this can explained by considering the addition of trace amounts of a lower adsorption energy component (labeled 2) to a thin film comprised of a component with the higher adsorption energy (component 1). Then, the chains comprising component 2 are strongly partitioned to the surface (as reflected in the behavior of $R_{2,1}$) and thus cause a lowering of the surface tension. At the other end of the composition range no dramatic changes occur since component 1, the higher adsorption energy component, does not partition preferentially to the surface.

3.3. Bond Orientation Characteristics. We now proceed to explore the arrangement of the segments of the two components at the interface. The order parameter $S_{\alpha,i}$ (α = 1, 2), defining the average orientation of the segments in the interface, was calculated for both the components in the system. Here

$$S_{\alpha,i} = 0.5(3\langle\cos^2\Theta\rangle - 1) = 1 - 1.5q_{\alpha,i} \qquad (\alpha = 1, 2) \qquad (27)$$

where, $q_{\alpha,i}$ is the average side-stepping probability and Θ is the average angle between a segment in layer i and the normal to the surface. $S_{\alpha,i}$ assumes a value of 1 (−0.5) if the segments are absolutely perpendicular (parallel) to the surface and 0 if the segments are randomly oriented. From ref 25

$$q_{\alpha,i} = \frac{\delta_0 p_{\alpha,i} \sum_{s_\alpha=1}^{r_\alpha-1} p(i,s_\alpha)\, p(i,r_\alpha-s_\alpha)}{\sum_{s_\alpha=1}^{r_\alpha-1} p(i,s_\alpha)\, p(i,r_\alpha-s_\alpha+1)} \qquad (28)$$

The order parameter of the component that partitioned preferentially to the surface (i.e., component 2 when $\chi_s > 0$) was similar to that observed in the case of a homopolymer melt[23] and a bimodal athermal melt.[19] In these cases there is a tendency for the segments to lie parallel to the surface as evidenced by a negative value of $S_{2,1}$, and the order parameter reached its bulk value of 0 in ca. three lattice layers. One can see this behavior in Figure 8a, which shows the order parameter profiles for the same systems that were depicted in Figure 1. It was also observed that the order parameter for the component that partitioned to the surface was insensitive to changes in molecular weights, the surface interaction parameter, χ_s, and the bulk composition. The insensitivity to χ_s, for example, is obvious in Figure 8a, which shows different curves representing a range of χ_s (0.02–0.8), lying on top of each other.

In contrast, the order parameter of the component that is depleted from the surface behaves in a very different fashion. The value of $S_{1,i}$ on the surface goes from a negative value through 0 to a positive value as χ_s is increased. In other words, the segments exhibit an inclination to lie perpendicular to the surface at high values of χ_s compared to the tendency to lie parallel to it when χ_s assumes a smaller value. This can be seen on Figure 8b, which shows the order parameter profile of the component that is depleted from the surface for the systems that were described in Figure 1.

3.3.1. End-Segment Density. In this section, we will calculate the relative end-segment density $\Phi_{\alpha,i}^{re}$, which is defined to be the ratio of the absolute end-segment density $\Phi_{\alpha,i}^{e}$ of component α to the volume fraction of that component, in any given layer i. According to this definition $\Phi_{\alpha,i}^{re}$ will assume a value of 0 if layer i is completely devoid of any end segments and a value of 1 if it contains only end segments. Therefore, for all other cases, $\Phi_{\alpha,i}^{re}$ will assume values that are between these two extremes. Also, if one considers the ideal case when the surface ($i = 1$) is comprised only of end segments, then the segment immediately following the end segment is constrained to lie on the layer adjacent to the surface ($i = 2$). Hence, in this extreme situation all bonds in contact with the surface will be completely perpendicular to it, and the other parameter $S_{\alpha,1}$ of that component will assume an ideal positive value of 1. $\Phi_{\alpha,i}^{re}$ is therefore expected to provide insight into the observed behavior of the bond orientation characteristics of the segments of the two components shown in Figure 8.

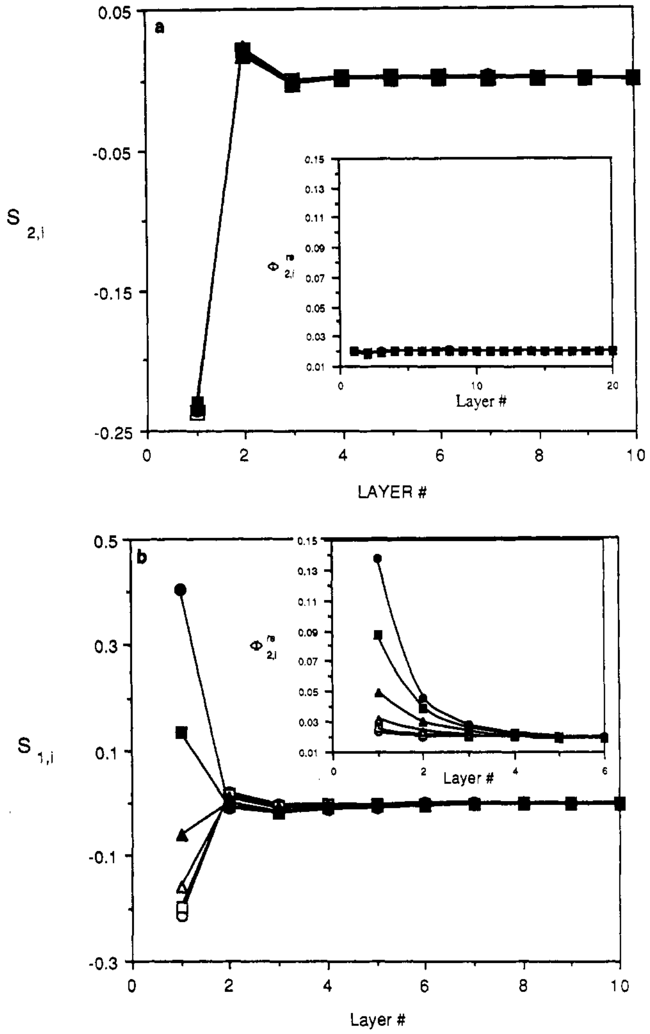

Figure 8. (a) Order parameter profile of the component that is partitioned preferentially to the surface, for the systems identical with those depicted in Figure 1. The inset shows the corresponding relative end-segment density profiles for the same component. (b) Order parameter profile of the component being depleted from the surface for the systems identical with those depicted in Figure 1. The inset shows the corresponding relative end-segment density profiles for the same component.

The absolute end-segment density $\Phi_{\alpha,i}^{e}$ for component α in any layer i is given by (section 2.3)

$$\Phi_{\alpha,i}^{e} = [\Phi_{ab}/r_\alpha](1/p_{\alpha,i}) \sum_{s_\alpha} p(i,s_\alpha)\, p(i,r_\alpha-s_\alpha+1) \qquad (\alpha = 1, 2;\ s_\alpha = 1, r_\alpha) \qquad (29a)$$

$$= 2\Phi_{ab} p(i,r_\alpha)/r_\alpha \qquad (29b)$$

In the insets of parts a and b of Figure 8, the relative end-segment density profiles of the two components are plotted for χ_s values ranging from 0.02 to 0.8. The systems corresponding to the curves are those represented in their respective figures (and in Figure 1). It is clear from all the curves shown in the inset that $\Phi_{\alpha,i}^{re}$ attains the correct value of $2/r_\alpha$ ($r_1 = r_2 = 100$) corresponding to the unconstrained bulk far away from the surface.

If one considered the behavior of $\Phi_{1,i}^{re}$ (the component that is being depleted) on the surface (see inset of Figure 8b), it is clear that for the case $\chi_s = 0.02$, $\Phi_{1,1}^{re}$ (≈ 0.02) $\approx 2/r_\alpha$. However, when $\chi_s = 0.8$, $\Phi_{1,1}^{re}$ (≈ 0.15) $\gg 2/r_\alpha$. For component 1, it is therefore clear that when χ_s is increased from 0.02 to 0.8, the volume fraction of ends on the surface increases from a value of about 2% to about 15%, relative to the volume fraction of the component itself on the surface. In comparison, the behavior of $\Phi_{2,1}{}^{re}$ is considerably different. One can see in the inset of Figure 8a that, for all the values of χ_s that were used, $\Phi_{2,1}{}^{re}$ (≈ 0.02) $\approx 2/r_\alpha$, suggesting that even large changes in χ_s (0.02 to 0.8) do not cause any perceptible changes to $\Phi_{\alpha,i}{}^{re}$ from its bulk value.

On the basis of the argument presented in the beginning of this section, it is clear that, as χ_s is increased by 1 order of magnitude, the drastic change in the bond orientation on the surface of the component being depleted from the surface is explained by the concurrent order of magnitude increase in the relative end-segment density of that component. By the same argument, the relatively smaller and constant value of $\Phi_{2,i}{}^{re}$ ($\approx 2\%$) apparently explains the tendency of $S_{2,i}$ to be unchanged over large changes in χ_s.

3.4. Discussion. The model that has been developed in this paper was shown to predict the structure and properties of the interface formed due to the presence of energetic interactions when one places a binary polymer blend in contact with a hard, homogenous surface. In the past, this problem has been addressed on a phenomenological basis by Schmidt and Binder (SB).[11] While the SB theory does successfully predict the surface segregation that occurs in the vicinity of the surface, the model uses phenomenological parameters to interpret the results. In our model, the parameters that are used are the Flory χ parameter of the polymer blend and the difference in the adsorption energies per segment between the two components in the system (χ_s). In addition, the construction of the model and the employment of the Scheutjens and Fleer formalism[12] result in a description of the polymer chain that starts from one end segment and proceeds sequentially along its length to the other end. While this aspect of the model directly enables the study of the modification of the conformational properties of the polymer in the interface in considerable detail, phenomenological theories cannot be used for this purpose. In our model, for example, one can distinguish an end segment from a middle one and hence study the effect of the variation of chain architecture on the properties of the interface. In a forthcoming publication,[26] we discuss the implications of having end groups tailored to the polymer chains making up the blend that is placed in contact with a surface.

An apparently ideal means of studying the surface behavior of polymer blends is to label one component with deuterium since the perturbation induced by this labeling as quantified by a χ parameter has been shown to be relatively small.[24] Therefore, if one can measure the concentration profiles from the surface for such systems (which are located well below the upper critical solution temperature[21] in the bulk state), the proposed model can be used to quantify the adsorption energy difference (χ_s) between the segments making up the two components.

Neutron reflectivity experiments conducted on thin films of deuterated/protonated polystyrene have shown that the deuterated component segregates to the air surface and is thus the lower adsorption energy component,[27] when the molecular weights of the two components are essentially *equal*. If one were to extract χ_s from a given system by using this model and use it to predict the concentration profiles of others, it can be shown that a deuterated component always segregates to the surface, irrespective of the chain lengths of the two components in the system. However, more recent experiments have shown χ_s to be a function of the chain lengths of the constituent polymers.[22] One of the limitations of this theory is that it does not predict the value of χ or χ_s, nor does it take into account this chain-length dependence that was observed.

5. Conclusions

In this paper, a binary polymer mixture in contact with a hard surface has been modeled on a quasi-crystalline lattice in the mean-field approximation of Scheutjens and Fleer.[12] The treatment, in general, involved the construction of a partition function into which the entropic and energetic factors were incorporated. While the entropic factor was derived from the description of the polymer chains near the surface as biased random walks, the energetic contribution came from intracomponent, intercomponent, and surface interactions, which were accounted for in the Bragg–Williams approximation. The important conclusions of the paper can be briefly summarized as follows.

(a) For the case of equal chain lengths, the existence of a distinct interface formed due to the segregation of the component with the lower adsorption energy was shown. This segregation was found to be thermodynamically driven by the adsorption energy difference between the two components as quantified by χ_s, in a situation when the value of χ characterizing the segmental interactions was well below its bulk critical value.[21] The molecular weights of the polymers in the blend were found to play an important role in determining the magnitude of the segregation, with the surface excess increasing as the molecular weights were increased. However, in the vicinity of the critical point (of the bulk system), the segregation at the surface and the interfacial size was found to be dramatically dependent on χ.

(b) A detailed investigation of the concentration profiles also showed that the segregation depended strongly on bulk concentrations of the components, with the segregation of the component that energetically prefers the surface being dramatic when the system is dilute in that component. This phenomenon was also reflected in the calculation of the interfacial tensions of the corresponding systems.

(c) An analysis of the conformational details of the chains on the surface in the region of complete phase mixing showed that the two components behaved very differently. Both the components in the blend displayed a tendency to lie parallel to the surface at small values of χ_s. This was shown by quantifying the bond orientation of component α in terms of a bond order parameter, $S_{\alpha,i}$. However, when χ_s was increased, the component that was being depleted showed a drastic change in bond orientation by displaying a tendency to order perpendicular to the surface. In addition, the order parameter of the component that partitioned preferentially to the surface was found to be insensitive to the changes in the parameters affecting the system (i.e., the adsorption energies, molecular weights, and the bulk volume fractions).

(d) Finally, the end-segment densities of the two components were calculated in an effort to explain the behavior of the bond order parameter. The component that disliked the surface energetically was found to preferentially partition its end segments to the surface, relative to its middle ones. The extent of the enrichment of ends was found to increase dramatically with increasing χ_s, thus causing the chains to align perpendicular to the surface on the average, at relatively high values χ_s. It was also shown that the fractional end-segment density of the component that preferentially partitioned to the surface was not significantly different from its value in the bulk, and changes in the χ_s did not affect it at all.

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Notation

a	area per segment
b	denotes bulk properties
$A_{\alpha,i}$	absolute enhancement of segments of chain of type α in layer i
c_α	any conformation of a chain of type α
G	grand canonical partition function
i, j, k	layer numbers
k_B	Boltzmann's constant
L	no. of lattice sites in a lattice layer
m_i	Lagrange multiplier in layer i
M	no. of lattice layers
n_α	no. of chains of type α
$n_{\alpha,i}$	no. of segments of type α in layer i
n_{c_α}	no. of chains in conformation c_α
N	total no. of chains
$p_{\alpha,i}$	normalized free-segment probability of component α in layer i
$p(i,r_\alpha)$	normalized end-segment probability of a chain of length r_α
$P_{\alpha,i}$	unnormalized free-segment probability of component α in layer i
Q	canonical partition function
r_α	no. of segments in single chain of type α
r_{α,i,c_α}	no. of segments of the chain of type α in layer i in conformation c_α
R_g	radius of gyration of a chain of DP r_α
S_α	conformation of a chain of type α
T	temperature
U	potential energy of the interfacial system with respect to the reference states
U_{ref}	potential energy of the reference states
U_{int}	potential energy of the interfacial system
u_α	adsorption energy per segment of component α
z	lattice coordination number (=6)
f	interfacial tension

Greek

α, β	components
δ_{j-i}	fraction of nearest neighbors for any site in layer i in layer j
δ_{1i}	Kronecker delta
μ_i	chemical potential of species i relative to the reference state
τ	correlation length of the concentration profiles of the two species
$\Phi_{\alpha,i}$	volume fraction of species α in layer i
Ω	combinatorial factor for the interfacial system
Ω_α	combinatorial factor for the reference system containing chains of type α

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