Interactions between Polymer-Coated Surfaces in Poor Solvents.
2. Surfaces Coated with AB Diblock Copolymers

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ABSTRACT: Using a two-dimensional self-consistent field theory, we investigate the interaction between two planar surfaces that are sparsely coated with AB diblock copolymers and immersed in solution. The B chains are assumed to be solvophobic. We vary χ_{AS} (the A-solvent interaction) and χ_{AB} (the interaction between the comonomers) and determine the morphology of the layers and the energy of interaction as the surfaces are brought closer together. If the chain is tethered by the end of the B block, the interactions are particularly sensitive to variations in χ_{AS} and χ_{AB}, and altering these parameters provides a means of "tuning" the repulsion or attraction between the surfaces. On the other hand, tethering chains by the A end increases the range of the attractive interaction between the layers. These guidelines are especially useful for controlling the behavior of colloidal particles in solution.

Introduction

The nature of the solvent plays a crucial role in mediating the interactions between polymer-coated substrates. Consider two surfaces that are covered with end-grafted homopolymers. In a good solvent, the surfaces exhibit a repulsive interaction when the layers come into contact.[1−6] In a poor solvent, however, the surfaces will experience an attractive interaction.[7−9] In part 1 of this study, we used a two-dimensional self-consistent field (SCF) model to examine how this interaction could be tailored by tethering a relatively low density of both solvophilic (A) and solvophobic (B) homopolymers onto the surfaces.[10] The results revealed that the shape of the force profile, or the range and strength of the attractive interaction, could be controlled by varying the A-solvent and A−B interaction energies, as well as the relative lengths of the two chains.

It may, however, be experimentally more feasible to tether one type of polymeric species onto the surface, rather than grafting a uniform distribution of both A and B chains. In this paper, we investigate whether effects similar to those observed with the two distinct homopolymers can be achieved by grafting copolymers that contain both solvophilic and solvophobic blocks. Specifically, we use our 2D SCF theory to examine the interactions between two surfaces that are sparsely coated with end-grafted AB diblock copolymers.

Our recent studies of diblock copolymers tethered onto a single surface in poor[11,12] and selective[13] solvents suggest that bringing two such layers into contact could lead to the formation of complex layers and unique energies of interaction. In particular, the studies revealed that at relatively sparse grafting densities and in poor solvents, the diblocks self-assemble into an ordered layer of "pinned micelles" on the surface[14−17] and that the micelles resemble "onion"-, "garlic"-, or "dumbbell"-like structures.[11,12] In the onion-like micelles, the less solvophobic blocks form an outer layer that encircles the more solvophobic segments. In the garlics, the highly solvophobic core splits into multiple, smaller cores, which are encapsulated in an outer layer. The dumbbells consist of two distinct cores, with one being atop the other. In selective solvents, the diblocks form a "flower"-like structure that has a dense solvophobic core and an extended solvophilic corona.[13]

Below, we provide a brief description of the SCF model that we use to investigate the effects of compressing two surfaces that are coated with such AB diblocks. We then describe our findings for chains that are grafted by the end of the less soluble B blocks and subsequently relate the results for the chains that are attached by the end of the more soluble A components. Finally, we examine the interactions between a layer of grafted diblocks and a hard wall.

The Model

The advantage of the SCF method is that the results provide a description of the system at thermodynamic equilibrium. One-dimensional SCF theory, however, is insufficient for describing the structure of the pinned micelles. We therefore use a two-dimensional SCF theory, which is a generalization of the 1D model developed by Scheutjens and Fleer.[18] In the Scheutjens and Fleer theory, the phase behavior of polymer systems is modeled by combining Markov chain statistics with a mean field approximation. Since the method is thoroughly described in ref 18, we simply provide the basic equations and refer the reader to that text for a more detailed discussion.

To start, the free energy per site in the mean field approximation is given by

$$f(r) = \sum_{i,c} n_{i,c}(r) \ln n_{i,c}(r) + (1/2) \sum_{j,k} \chi_{j,k} \int \eta(r-r')\, \phi_j(r)\, \phi_k(r')\, \mathrm{d}r' \quad (1)$$

where the first term on the right-hand side represents the entropy of mixing and the second term is the enthalpic contribution. The parameter $n_{i,c}(r)$ is the number density at r of molecules of type i in conformation c. In the enthalpic term, the indices j and k run over all the different types of segments and $\phi_j(r)$ represents the average density of monomers j at r. The $\chi_{j,k}$ term is the Flory−Huggins interaction parameter and $\eta(r-r')$ is the short-range interaction function, which is replaced by a summation over nearest neighbors.

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To calculate the segment density distribution $\phi_j(r)$ that minimizes the free energy, we exploit the analogy between the trajectory followed by a diffusing particle and the conformation of a chain.[18] We define Green's functions of the type $G(r_1,N'|r_2,N'')$ as the combined statistical weight of all conformations of a subchain starting with segment N' at r_1 and ending with segment N'' at r_2. For the homopolymer, the set of Green's functions for $N' < N''$ and $N' > N''$ are identical and obey the recursion relation

$$G(r,N'|r_1,1) = \exp[-U_i(r)]\int G(r',N'-1|r_1,1)\,\eta(r-r')\,\mathrm{d}r' \quad (2)$$

along with the boundary condition

$$G(r,1|r',1) = \exp[-U_i(r)]\,\delta(r-r') \quad (3)$$

where $\delta(r-r')$ is the Kronecker delta, and r and r' are the variables that denote the beginning and end of the chain, respectively. The parameter $U_i(r)$ is the potential of mean force acting on segment i at point r and is given by

$$U_i(r) = \alpha(r) + \sum_k \chi_{i,k}\int \phi_k(r')\,\eta(r-r')\,\mathrm{d}r' \quad (4)$$

where $\alpha(r)$ is a hard-core potential that ensures incompressibility. (We note that eq 4 is obtained by applying the saddle point approximation to the free energy expression in eq 1. The saddle point approximation involves taking the value of the free energy at its minimum value.) The segment density distribution can be calculated from the Green's functions as

$$\phi_j(r) = \sum_i C_i \exp[-U_j(r)] \sum_{N'\in j}\int G(r,N'|r_1,1) \times G(r,N'|r_2,N_i)\,\mathrm{d}r_1\,\mathrm{d}r_2 \quad (5)$$

where N_i is the length of molecule i and C_i is the normalization constant, which can be obtained from the total number of molecules n_i:

$$C_i = n_i/[\sum_{N'}\int G(r_1,N'|r_2,1)\,\mathrm{d}r_1\,\mathrm{d}r_2] \quad (6)$$

From eqs 2–6, the self-consistent density distribution for the different types of segments can be calculated by discretizing the equations and solving them numerically.[18]

We note that the expression for the excess free energy in terms of segment density distribution is given by

$$F(r) = \sum_j \phi_j(r)\ln G_j(r) + (1/2)\sum_{jk}\chi_{j,k}\int \eta(r-r') \times \phi_j(r)\,\phi_k(r')\,\mathrm{d}r' \quad (7)$$

For two grafted layers, the free energy of interaction as a function of surface separation, L, can be obtained by taking the difference between the free energies when the layers are infinitely apart and when they are separated by a distance L.

In the two-dimensional SCF theory, the above equations are written explicitly in terms of Y and Z, rather than r, and the mean field approximation is applied along the X direction. (In other words, we assume translational invariance along the X direction. Nonetheless, the probability of having a neighbor in the X direction is included in the calculation of the Green's functions.)

In the present 2D calculations, we consider two planar surfaces that lie parallel to each other in the XY plane and investigate the effect of bringing the surfaces closer together in the Z direction. We apply periodic boundary conditions along Y. Each surface is covered with end-grafted diblocks, which are assumed to be monodisperse. The ends of the chains are grafted to the $Z = 1$ and $Z = Z_n$ planes, which represent the two impenetrable surfaces.[19]

The grafted polymers are characterized by three parameters: grafting density, chain length, and the relevant χ parameters. We fix the grafting density per line along the Y direction at 0.5 for all calculations; i.e., the polymers are grafted on alternate lattice sites. The grafting density per line along the X direction is denoted by ρ and is fixed at $\rho = 0.025$ for all of the results presented below. (This implies that the average spacing between points along a line in X is $1/\rho$.) We focus on a relatively low grafting density since this is the regime where the formation of pinned micelles is most pronounced[17] and, consequently, where we expect novel self-assembled structures to appear when the layers are compressed.

The chains are symmetric diblocks and the respective block lengths are given by $N_A = N_B = 40$. As to the χ parameters, we let χ_{AS} and χ_{BS} represent the polymer–solvent interactions for the A and B components, respectively, and χ_{AB} is the interaction parameter for the two different monomers. The strength of interaction between the polymers and the planar, impenetrable surface is assumed to be the same as that between the polymer and the solvent. We fix the polymer–solvent interaction for the more solvophobic B chains at $\chi_{BS} = 2$, while gradually varying χ_{AS} from 0 to 1. We also set $\chi_{AB} = 0$ and subsequently determine the effect of increasing $\chi_{AB} > 0$.

Diblock Copolymers Grafted by the Ends of the Less Soluble B Blocks

Effect of Varying χ_{AS}; $\chi_{BS} = 2$, $\chi_{AB} = 0$. Each surface is coated with symmetric AB diblocks, which are grafted by the ends of the B blocks. We fix $\chi_{BS} = 2$ and $\chi_{AB} = 0$. When the layers are far apart and the A blocks are in a good or Θ solvent ($\chi_{AS} = 0$ or 0.5), the chains form "flower"-like structures on each of the surfaces.[13] Figure 1a shows this structure for $\chi_{AS} = 0$; the solvophobic B blocks form a dense core and the A chains form a broad corona around this B region. In this way, the B segments are shielded from the unfavorable solvent and the surface tensions within the system are minimized.

Note, however, that the solvent-compatible A's also extend into the solution; thus, the density of A sites around the B domain is relatively low and the B core is not completely covered. As a consequence, when the surfaces are compressed (Figure 1b), the solvophobic cores are driven to aggregate and thereby provide a more effective, mutual shielding from the surrounding fluid. The A blocks from both sides now form a layer that surrounds the central B core. In effect, the "flowers" from the two surfaces have merged to yield a larger flower that is located halfway between the substrates. The merging of the micelles happens at a distance that is significantly greater than the vertical extent of the isolated micelles. This is due to the fact that there is

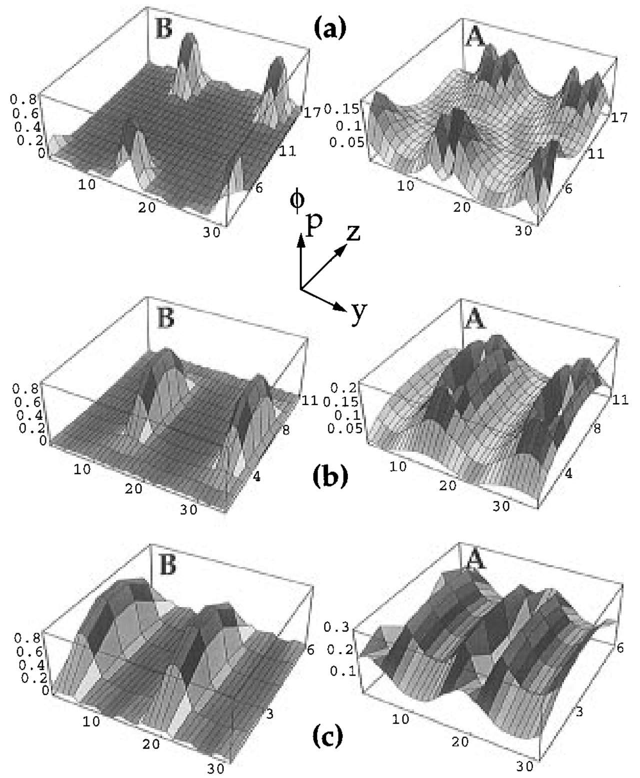

Figure 1. Three-dimensional plots showing the effect of decreasing the surface separation, L, for symmetric diblocks grafted by the end of the less soluble B blocks. The block lengths are $N_A = N_B = 40$. The grafting density per line ρ is 0.025, $\chi_{BS} = 2$, $\chi_{AS} = 0$, and $\chi_{AB} = 0$. The figures are for the following surface separations: (a) $L = 16$, (b) $L = 10$, and (c) $L = 5$. Y refers to the grafting direction and ϕ_p denotes the polymer density. The plots marked “B” show the polymer density of the B blocks, while the plots marked “A” show the density of the A blocks.

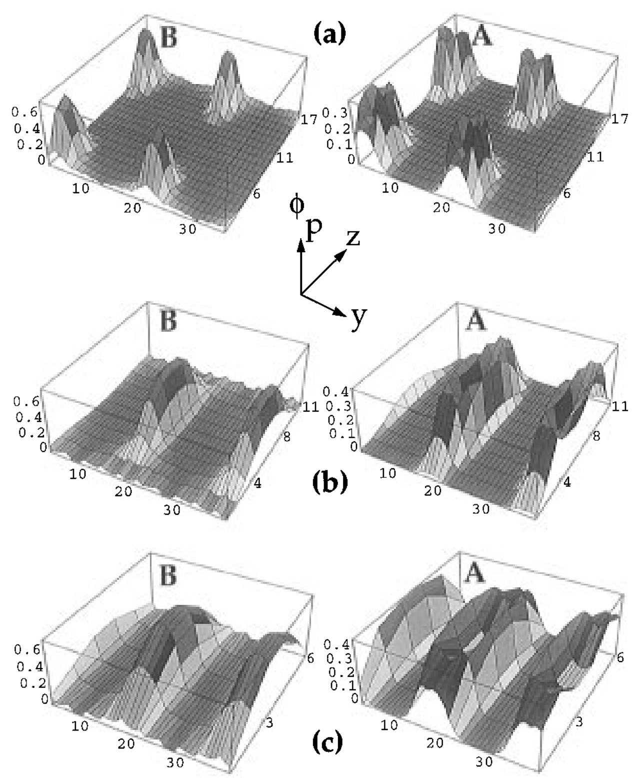

Figure 2. Three-dimensional plots showing the effect of decreasing the surface separation, L, for symmetric diblock copolymers grafted by the end of the less soluble B component. The block lengths are $N_A = N_B = 40$. The grafting density per line ρ is 0.025, $\chi_{BS} = 2$, $\chi_{AS} = 1$, and $\chi_{AB} = 0$. The figures are for the following surface separations: (a) $L = 16$, (b) $L = 10$, and (c) $L = 5$. Y refers to the grafting direction and ϕ_p denotes the polymer density. The plots marked “B” show the polymer density of the B blocks, while the plots marked “A” show the density of the A blocks.

an enthalpic driving force for the B cores to self-assemble.

Further compression of the layers results in the expulsion of solvent and a monotonic increase in the density of the A blocks around the B domains (Figure 1c). This arrangement reduces the unfavorable B−solvent contacts.

For the case where both components are solvophobic ($\chi_{AS} = 1$) and the layers are far apart, the diblocks associate into “onion”-like micelles (see Figure 2a).[12] Here, the B blocks form a dense core and the A blocks form an outer shell that encircles the B region. Since $\chi_{AS} < X_{BS}$, the polymer density in the A layer is lower than the density of the highly solvophobic B core. However, since the A blocks are also solvent-incompatible, they do not stretch into the surrounding solution and the A layer is more localized around the B domain than in the $X_{AS} = 0$ or 0.5 case.

When these layers are compressed, the B cores merge into a large B region in the center and the A blocks now encircle this central core (Figure 2b). (Again, the merging of the micelles happens at a distance that is greater than the vertical extent of the isolated micelles.) Upon further compression (Figure 2c), the density of both components remains relatively unchanged until the separation between the surfaces becomes equal to the size of the central onions.

Figure 3 shows the free energy of interaction as a function of surface separation. Figure 3a shows that for $\chi_{AS} = 0$ the free energy of interaction has a small repulsive part ($F_{int} > 0$), which arises from contact between the stretched, solvophilic A coronas as the flowers are compressed. With the merging of the micelles, the curve exhibits a wide attractive region ($F_{int} < 0$). The attraction at a given surface separation is greatest when both components are solvophobic (Figure 3c). Here, the solvophobic A’s are also driven to mutually associate and thereby shield themselves from the unfavorable solvent. The additional attraction between the A’s results in a greater attraction between the surfaces. For all three cases, the entropic losses dominate at small surface separations and the interaction eventually becomes repulsive.

Effect of Increasing χ_{AB}; $\chi_{BS} = 2$. When the A component is in a good or Θ solvent and χ_{AB} is increased to 0.5 or 1.5, the ability of the A blocks to shield the B domains is diminished. Nonetheless, the qualitative features of the system are similar to those for $\chi_{AB} = 0$. There are, however, major changes in the polymer self-assembly if both components are in a poor solvent ($\chi_{AS} = 1$) and $\chi_{AB} = 1.5$. The conformations of the layers as a function of surface separation are shown in Figure 4. If the surfaces are far apart, the B blocks form micelles close to the surface. The A blocks form separate micelles that are located atop the B’s and thus, the assembly resembles a dumbbell (see Figure 4a).[12] Since $\chi_{AS} < \chi_{BS}$, the density of the A core is smaller and is more extended in the Z direction.

As the layers are compressed, the A micelles from the two surfaces merge, forming a single A micelle. The B micelles, which are closer to the grafting surface,

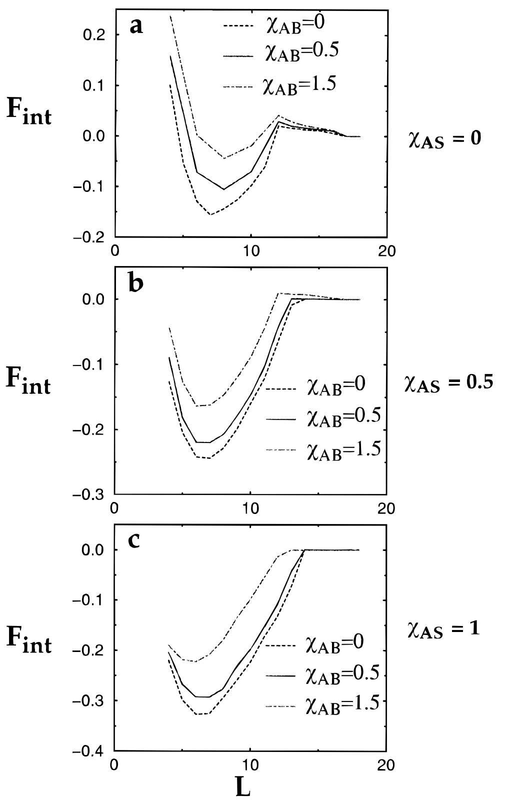

Figure 3. Free energy of interaction, $F_{\rm int}$, as a function of surface separation, L, for symmetric diblock copolymers grafted by the end of the B blocks. The length of each of the blocks is 40, the grafting density per line ρ is 0.025, and $\chi_{\rm BS} = 2$. The A-solvent interaction is (a) $\chi_{\rm AS} = 0$, (b) $\chi_{\rm AS} = 0.5$, and (c) $\chi_{\rm AS} = 1$. Each of the figures shows results for three different $\chi_{\rm AB}$, which are shown with different types of lines.

maintain their separate structures (Figure 4b). With a further decrease in the surface separation, the B micelles from the two surfaces merge, forming a single micelle halfway between the substrates. The A micelles now split into two and are located on either side of the B domains (Figure 4c). Further compression of the surfaces does not change the core density of the micelles unless the distance between the surfaces becomes less than or equal to the size of the micelles. We note that this series of conformations (4a−c) is not observed when the surfaces are covered with alternately grafted A and B homopolymers.[10] The formation of dumbbells and the subsequent structures are only feasible if the A and B blocks are chemically attached.

The free energy of interaction as a function of surface separation for $\chi_{\rm AB} = 0.5$ and 1.5 are shown in Figure 3, along with $\chi_{\rm AB} = 0$. The qualitative features in the cases of $\chi_{\rm AB} > 0$ are very similar to those for $\chi_{\rm AB} = 0$, including the presence of an attractive region. However, the strength of attraction decreases as $\chi_{\rm AB}$ is increased. This is due to the extra enthalpic losses that arise from the A−B repulsion.

If both the components are in poor solvents and the length of the more soluble A component is much longer than the B component, the chains form “garlic”-like structures.[12] In this structure, multiple B cores are shielded by a single A shell. While we did not investigate the effect of bringing such surfaces together, we anticipate that the results for this case will be qualitatively similar to those described above in that there will be an attractive regime in the free energy of interaction. This would correspond to the merging of the micelles that form the cores of the “garlic”.

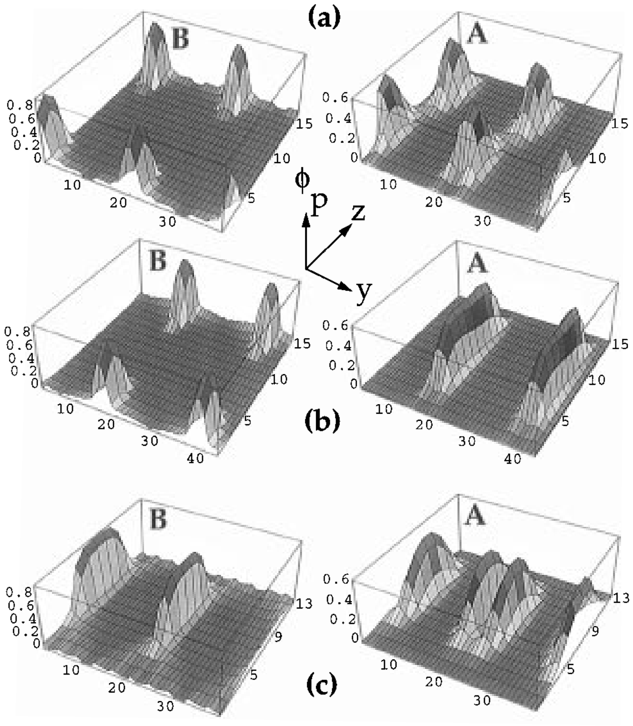

Figure 4. Three-dimensional plots showing the effect of decreasing the surface separation, L, for symmetric diblock copolymers grafted by the B ends. The length of each of the blocks is 40, the grafting density per line ρ is 0.025, $\chi_{\rm BS} = 2$, $\chi_{\rm AS} = 1$, and $\chi_{\rm AB} = 1.5$. The figures are for the following surface separations: (a) $L = 15$, (b) $L = 14$, and (c) $L = 12$. Y refers to the grafting direction and $\phi_{\rm p}$ denotes the polymer density. The plots marked “B” show the polymer density of the B blocks, while the plots marked “A” show the density of the A blocks.

Diblock Copolymers Grafted by the Ends of the More Soluble A Blocks

Effect of Varying $\chi_{\rm AS}$; $\chi_{\rm BS} = 2$, $\chi_{\rm AB} = 0$. We now explore the effect of bringing together surfaces where the symmetric diblocks are grafted by the ends of the A blocks. Depending upon the A−solvent interactions, the chains form “flowers” (good or Θ solvent) or “onions” (poor solvent) when the surfaces are far apart. However, since the chains are grafted by the A blocks, the corona or “petals” of the flowers are not as extended as in the case where the chains are tethered by the B blocks.

To facilitate the discussion, we first consider that case where $\chi_{\rm AS} = 1$ and thus, both blocks are solvophobic. When the layers are brought together, the B micelles from the two surfaces merge into a larger, common micelle. Figure 5a shows the structure of the layer for this example. For the sake of comparison, Figure 5b reveals the morphology for the corresponding case where the chains are grafted by the ends of the B blocks (and $\chi_{\rm AS} = 1$, $\chi_{\rm BS} = 2$). In the case where the chains are attached by A sites, the B blocks lie further from the surface. Consequently, these segments undergo less stretching and the merging of the micelles happens at greater surface separations than in the previous example ($L = 19$ in Figure 5a, while $L = 12$ in Figure 5b). Note that with the B blocks in the upper half of each chain, the central micelles are highly localized; with the B blocks at the bottom of the chain, the central micelles are rather elongated since the individual micelles must extend from the grafting surface. The density at the core of the extended micelles is somewhat less than the core density of the more localized structures. We

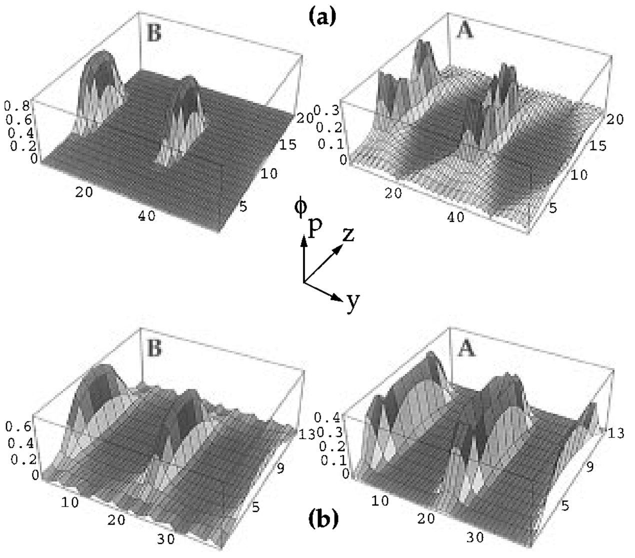

Figure 5. Three-dimensional plots comparing the self-assemblies of the symmetric diblock copolymers immediately after the micelles from the two surfaces merge for (a) diblocks grafted by the A ends ($L = 19$) and (b) diblocks tethered by the B ends ($L = 12$). The length of each of the blocks is 40, the grafting density per line ρ is 0.025, $\chi_{BS} = 2$, $\chi_{AS} = 1$, and $\chi_{AB} = 0$. Y refers to the grafting direction and ϕ_p denotes the polymer density. The plots marked "B" show the polymer density of the B blocks, while the plots marked "A" show the density of the A blocks.

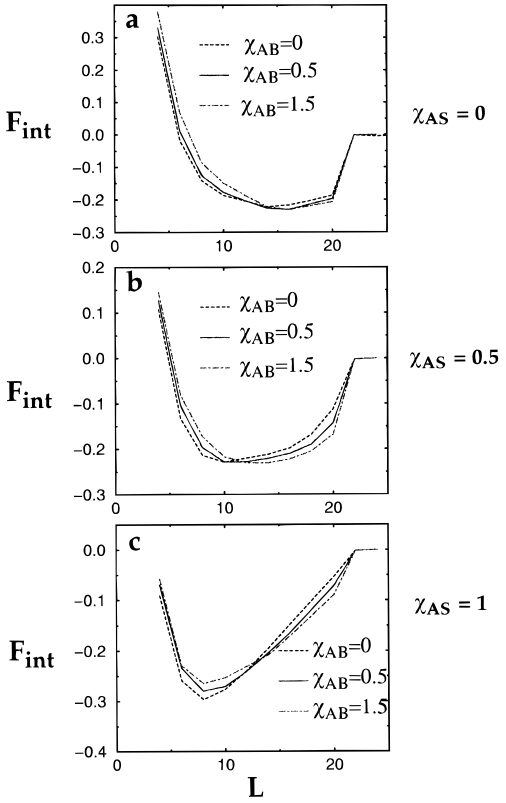

Figure 6. Free energy of interaction, F_{int}, as a function of surface separation, L, for symmetric diblock copolymers grafted by the end of the more soluble A component. The length of each of the blocks is 40, the grafting density per line ρ is 0.025, and $\chi_{BS} = 2$. The A-solvent interaction is (a) $\chi_{AS} = 0$, (b) $\chi_{AS} = 0.5$, and (c) $\chi_{AS} = 1$. Each of the figures shows results for three different χ_{AB}, which are shown with different types of lines.

further note that the distance between these localized micelles is greater than the distance between the more delocalized ones.

As in the previous cases, the A blocks form a common shell around the merged B micelles. However, since the chains are tethered by the A's, these blocks must stretch farther in order to shield the B cores. Thus, the density of A is somewhat larger near the edges of the core (which are closer to the surfaces) than at the center (see Figure 5a). The density of A near the core increases gradually with an increase in the surface compression and provides better shielding of the B's. Finally, if the surface separation becomes equal to or smaller than the size of the merged micelles, the overall morphology of the layers for the two cases becomes very similar.

The effect of systematically decreasing χ_{AS} from 1 to 0 on the structure of the layers is qualitatively similar to that described above for diblocks grafted by the B blocks, but the free energy of interaction shows unique features. The free energy of interaction as a function of surface separation for $\chi_{AS} = 0$, 0.5, and 1 are shown in Figures 6a, b, and c, respectively. Comparison of curves a, b, and c for $\chi_{AB} = 0$ shows that in the attractive regime between $L \approx 14$ and $L \approx 22$, the surfaces are most attractive for $\chi_{AS} = 0$ and least attractive for $\chi_{AS} = 1$. This is in contrast to the previous case where the interaction is most attractive for $\chi_{AS} = 1$ for all the surface separations. In the present case, the A blocks must stretch from the grafting surface to the center to minimize the B−solvent contacts. This results in an increase in A−solvent contacts. If $\chi_{AS} = 0$, there is no penalty for increased A−solvent contacts. For $\chi_{AS} = 1$, however, the increased A−solvent contacts lead to enthalpic losses. While the self-assembly of the A blocks contributed to an attractive interaction between the layers in the previous example, with the A blocks near the surface, the ability of these chains to associate is diminished (compare Figures 5a and b). Thus, the net effect for chains tethered by the A block is that the total free energy of interaction is more attractive for $\chi_{AS} = 0$.

If the compression of the surfaces is continued, more and more solvent is expelled from the system and the entropic losses start to dominate. A crossover takes place below a separation of $L \approx 14$ where the entropic penalty for confining the chains with $\chi_{AS} = 0$ exceeds that for $\chi_{AS} = 1$ and the free energy of interaction becomes most attractive for $\chi_{AS} = 1$. Moreover, the minima in the free energy of interaction shift to smaller surface separations as χ_{AS} increases (i.e., as the solvent quality gets worse) because the cost of confining the chains at a separation L is more severe in good solvents than in poor solvents.

A direct comparison of Figures 3 and 6 also reveals that for all values of χ_{AS}, the attractive regions ($F_{int} < 0$) are broader in Figure 6. As noted above, with the solvophobic B blocks at the top of the chains, the surfaces experience an attractive interaction at greater surface separations.

Effect of Increasing χ_{AB}; $\chi_{BS} = 2$. If the two blocks are relatively incompatible, but the A block is in a good or Θ solvent, the self-assembly of the polymers is qualitatively similar to the corresponding case for diblocks grafted by the B block. For these cases, an increase in χ_{AB} decreases the ability of the soluble A component to shield the B blocks, but the other features of the self-assembly remain similar to those for $\chi_{AB} = 0$.

Interesting morphologies do, however, appear if both blocks are in poor solvents ($\chi_{AS} = 1$) and $\chi_{AB} = 1.5$. As shown in Figure 7a, when the surfaces are far apart, the B blocks form micelles close to the surface, which

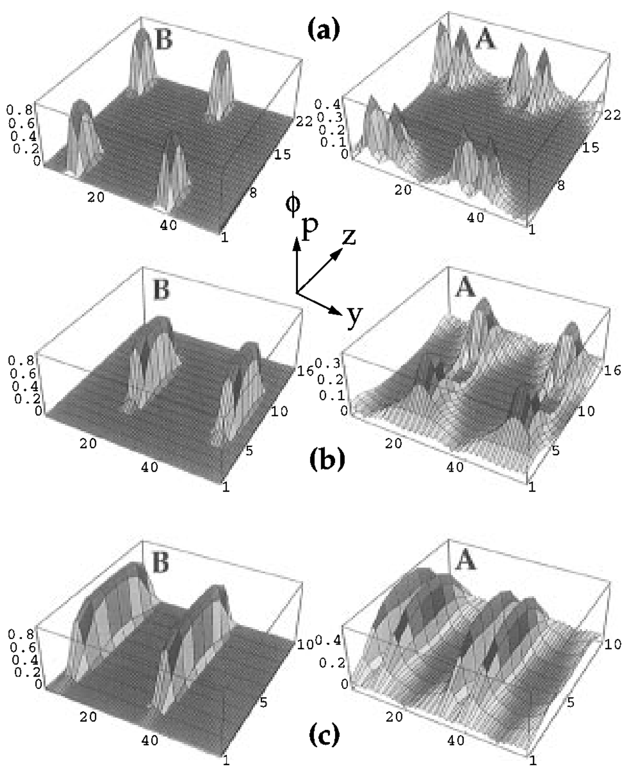

Figure 7. Three-dimensional plots showing the effect of decreasing the surface separation, L, for symmetric diblock copolymers grafted by the end of the A blocks. The length of each of the blocks is 40, the grafting density per line ρ is 0.025, $\chi_{BS} = 2$, $\chi_{AS} = 1$, and $\chi_{AB} = 1.5$. The figures are for the following surface separations: (a) $L = 21$, (b) $L = 15$, and (c) $L = 9$. Y refers to the grafting direction and ϕ_p denotes the polymer density. The plots marked "B" show the polymer density of the B blocks, while the plots marked "A" show the density of the A blocks.

are shielded on both sides by the A micelles. The density of the A core is lower than that of the less soluble B core. As the layers come together (see Figure 7b), the B micelles from the two surfaces merge to form a single micelle situated halfway between the substrates. On the other hand, the tethered A micelles do not merge because this would require considerable stretching energy. Instead, they shield only those parts of the B micelles that are closer to the grafting surfaces; furthermore, the A domains are no longer split like they were at large surface separations.

A gradual decrease in the surface separation increases the density of the A cores in the region halfway between the surfaces so that the center of the B micelle is more effectively shielded. The increase in A can occur because the decrease in the surface separation reduces the cost of stretching the grafted chains. With further compression of the surfaces, the A blocks from opposite sides can more effectively overlap and these blocks now associate into two micelles, with one on either side of a B micelle (Figure 7c). If the surface separation is made smaller than the size of the micelles, the micelle density increases monotonically as in the previous cases.

The free energy of interaction as a function of surface separation for $\chi_{AB} = 0.5$ and 1.5 is shown in Figure 6, along with $\chi_{AB} = 0$. Immediately after the merging of the micelles ($L \approx 22$), the free energy of interaction shows that the interaction is most attractive for $\chi_{AB} = 1.5$ and is least attractive for $\chi_{AB} = 0$ for the same surface separation. This trend is different from that described above for diblocks that are grafted by the B blocks. In general, the density of the A blocks around the B micelle is higher for smaller values of χ_{AB} and thus, the shielding is more effective for smaller χ_{AB}'s. When B micelles from the opposing surfaces merge, the A blocks must stretch all the way from the grafting surface to the center. The stretching cost is obviously higher for smaller χ_{AB} since the density of the A's around the central B micelle is higher for that case. Therefore, the total gain in free energy due to the merging of the micelles is not as high for $\chi_{AB} = 0$ as for larger χ_{AB}.

However, as the surface separation decreases, the cost of stretching the grafted A blocks all the way to the center decreases and the enthalpic losses due to the unfavorable AB contacts become more important. For L smaller than this separation, the free energy of interaction is most attractive for smaller χ_{AB}. This crossover is shown in Figure 6. Below this value of L, the qualitative trends as a function of χ_{AB} become similar to those described above for diblocks that are grafted by B's.

A broad-scale comparison of Figures 3 and 6 shows the chains grafted by the ends of the B blocks are significantly more affected by variations in the value of χ_{AB}. This is attributable to the fact that there is more A–B overlap in the case where the chains are tethered by the B blocks, as can be seen, for example, by comparing Figures 5a and b.

We note that if we increase the length of the more soluble component we still get "onion"- or "flower"-like structures (but not the "garlic" morphology).[12] Although we did not calculate the free energy of interaction as a function of surface separation for this case, we anticipate an attractive regime similar to the previous cases. However, if the more soluble component is in a good or Θ solvent, a repulsive region much larger than that for the symmetric diblocks will be observed before the attraction due to the merging of the micelles has an effect.

Grafted Diblock Copolymers Compressed with Hard Wall

Effect of Varying χ_{AS}; $\chi_{BS} = 2$, $\chi_{AB} = 0$. We also investigate the effect of compressing a surface coated with diblock copolymers against a hard wall. The chains are tethered by the ends of the solvophobic B blocks. The self-assembled structures for a compressed state (surface separation $L = 3$) are shown in Figure 8 for $\chi_{BS} = 2$ and the following values of χ_{AS}: (a) 0, (b) 0.5, and (c) 1. The hard wall is located at $Z = 4$. The figure shows that at a fixed surface separation, the shielding of the B component becomes more effective as the A block becomes more solvophobic. Moreover, when both components are in poor solvents ($\chi_{AS} = 1$), the density of the B core is lower than in the other two cases. This is due to the intermixing of the two relatively solvophobic blocks.

Figure 9 shows that the free energy of interaction as a function of surface separation is monotonically repulsive for all cases. Here, the entropic losses associated with compressing the polymer layer constitute the dominant contribution to the free energy. For the same surface separation, the repulsive force is largest for $\chi_{AS} = 0$. For this value of χ_{AS}, the solvophilic A's extend further into solvent (and along the Z direction) than in the cases where the A blocks are less solvent-compatible, $\chi_{AS} = 0.5$ and 1.0.

Effect of Increasing χ_{AB}; $\chi_{BS} = 2$. When $\chi_{AB} > 0$, the shielding ability of the more soluble A component

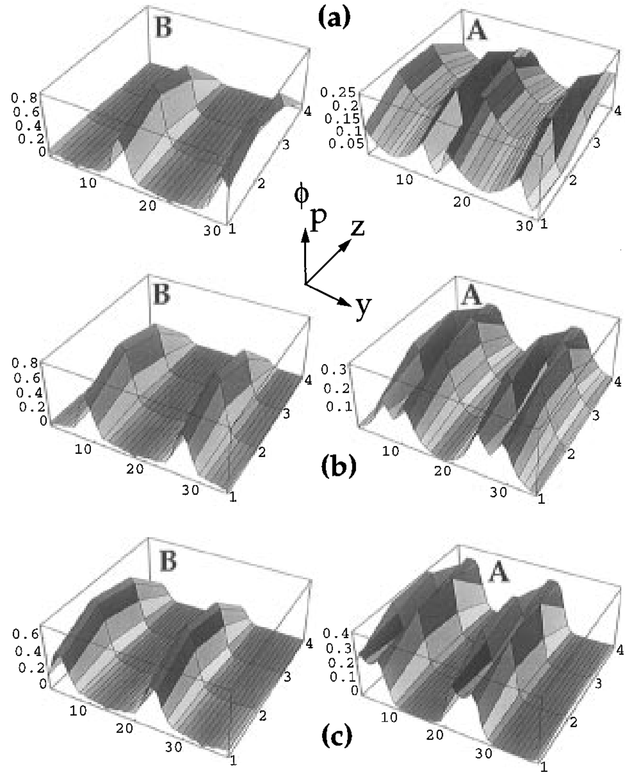

Figure 8. Three-dimensional plots showing the effect of changing χ_{AS} for a fixed surface separation $L = 3$ for grafted diblock copolymers compressed with a hard wall: (a) $\chi_{AS} = 0$, (b) $\chi_{AS} = 0.5$, and (c) $\chi_{AS} = 1$. The chains are grafted by the end of the B blocks and the length of each of the blocks is 40. The grafting density per line ρ is 0.025, $\chi_{BS} = 2$, and $\chi_{AB} = 0$. Y refers to the grafting direction and ϕ_p denotes the polymer density. The plots marked "B" show the polymer density of the B blocks, while the plots marked "A" show the density of the A blocks.

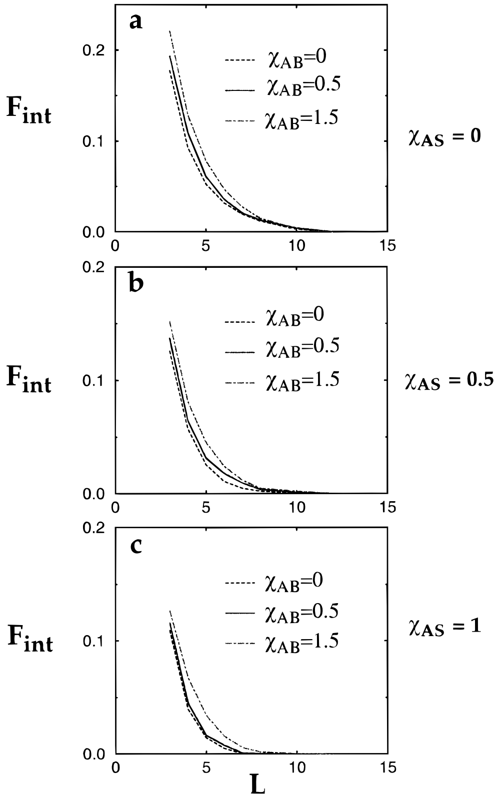

Figure 9. Free energy of interaction, F_{int}, as a function of surface separation, L, for grafted diblock copolymers compressed with a hard wall. The chains are grafted by the end of the B blocks and the length of each of the blocks is 40. The grafting density per line ρ is 0.025 and $\chi_{BS} = 2$. The A-solvent interaction is (a) $\chi_{AS} = 0$, (b) $\chi_{AS} = 0.5$, and (c) $\chi_{AS} = 1$. Each of the figures shows results for three different χ_{AB}, which are shown with different types of lines.

decreases. As in the previous cases, if the A block is in a good or Θ solvent, there are no dramatic changes in the self-assembly of the chains, even if $\chi_{AB} = 1.5$. However, if both components are in poor solvents ($\chi_{AS} = 1$) and $\chi_{AB} = 1.5$, the tendency of the A blocks to shield the B domains decreases significantly. In this case, the A component forms its own micelles, which sit atop the B micelles (as in Figure 4a) and provides very little shielding of the B region. The A micelles have a lower core density and extend farther in the Z direction than the more solvophobic micelles.

As the polymer-coated surface is compressed against the wall, the A micelles stretch from one surface to another. The B micelles now form adjacent to the A, so that there is a common boundary between the micelles. (Recall that both micelles are formed by the same diblock copolymers.) Further compression causes both types of micelles to extend from one surface to another. The interaction profiles for $\chi_{AB} = 0.5$ and 1.5 are shown in Figure 9, along with $\chi_{AB} = 0$. The interactions are more repulsive for larger χ_{AB}; this is due to the extra enthalpic losses that arise from the incompatibility of the A−B monomers.

Conclusions

We examined the interactions between two surfaces that are covered with end-grafted AB diblocks. The B block was assumed to be highly solvophobic. We considered both cases: (1) when the chains are tethered by the B end and (2) when they are grafted by the A end. In a previous study, we investigated the interactions between substrates that are coated with alternately grafted A and B homopolymers.[10] If the A blocks are in a good or Θ solvent, all three cases show qualitatively similar features (for the same χ values). This was observed even for $\chi_{AB} > 0$.

If the A block is solvophobic and $\chi_{AB} = 0$, we observed differences between cases 1 and 2 for the diblock copolymers. This is illustrated in Figure 5. However, at these χ values, case 1 and the alternately grafted homopolymers yielded similar behavior.

The self-assembly of the polymers in the three cases is significantly different when the A component is solvophobic and $\chi_{AB} > 0$. Here, the morphology of the layers is sensitive to whether or not the different components are chemically tethered. For example, for the same χ values, the structures seen in Figures 4 and 7 with diblocks are not observed for the alternatively grafted homopolymers.[10] Furthermore, the system is now sensitive to the chemical nature (A or B) of the tethered block, as can be seen by comparing Figures 4a,b and 7a,b.

Overall, the results show that by grafting a low density of AB diblocks (where B is solvophobic), one can tailor the nature of the interaction between the substrates. If the chains are tethered by the end of the solvophobic B blocks, the interactions are particularly sensitive to variations in χ_{AS} and χ_{AB}, and altering these parameters provides a means of "tuning" the repulsion or attraction between the surfaces. While chains tethered by the A end are less sensitive to variations in these χ's,[20] grafting the chains by the solvophilic block increases the range of the attractive interaction between the layers. These guidelines are especially useful for controlling the behavior of colloidal particles in solution or designing effective polymeric lubricants.

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(19) The two surfaces are located in a "larger box", or a bulk concentration of solvent. As the surfaces are compressed, the solvent is expelled from the region between the layers and becomes redistributed throughout the bulk.
(20) As noted above, tethering the chains by the A end diminishes both the stretching of the A blocks and the extent of A−B contact; thus, the chains are less affected by changes in χ_{AS} and χ_{AB}.

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