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Phase Separation of Mixed Solvents within Polymer Brushes

Yulia Lyatskaya* and Anna C. Balazs

Department of Chemical and Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania 15261

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ABSTRACT: Using numerical self-consistent-field (SCF) calculations and analytical theory, we investigate the behavior of polymer brushes immersed in a mixture of two immiscible solvents. When only a small amount of one of the solvents is present in the mixture, the fluids can phase separate within the brush. We find that the grafted polymers saturate the solvent−solvent interface, and we analyze this effect as a function of solvent composition and grafting density. Modifying the SCF method, we also examine the behavior of a weak polyacid brush immersed in a mixture of oil and water. Now, the polymer segments in water can become ionized; the segments in oil remain neutral. The results demonstrate that the brush height is readily controlled by varying the amount of water in the solution. The findings provide guidelines for tailoring the adhesion or lubrication between polymer-coated surfaces or the steric stabilization of colloidal particles.

I. Introduction

Polymer brushes[1] or end-grafted chains play a critical role in the stabilization of colloidal dispersions.[2] When polymers are anchored to the surface of a colloid, they form a thick corona around the particle. The repulsion between coronas on neighboring particles effectively prevents the colloids from aggregating and thereby stabilizes the suspension. In general, the thicker the corona, the greater the repulsion and the better the stabilization. Therefore, the thickness of the corona, or the height of the brush, H, is the crucial characteristic in this problem. The dependence of H on the molecular weight of the polymer layer and the solvent quality are well-known. In general, the longer polymer in the better solvent provides a higher value for H. When the brush is immersed in a mixed solvent,[3−6] however, the behavior of the system is much more complicated. Now, the height of the brush depends not only on the polymer−solvent interactions but also on the mutual compatibility of the solvents. It was shown[6] that a brush can collapse in a mixture of two good solvents if these liquids are relatively more compatible with each other than they are with the polymer. In the opposite limit, where the two solvents have a greater affinity for the polymer than for each other, the brush can swell, even in a mixture of two poor solvents.[6]

When the mixed solvents are highly immiscible, the mixture will undergo a phase separation. If the amount of one component is relatively low, the mixture will even phase separate inside a polymer brush. De Gennes considered this phenomenon for a polyacid brush in the presence of water and oil[7] and predicted that the demixing of the solvents could be exploited to control the brush height. In particular, for a polyacid layer in oil, the height can be tailored by adding a small amount of water. Such behavior can be mimicked by placing a polymer brush in a potential field that acts only in the vicinity of the surface.[8−10] It was shown that such a local potential can cause a dramatic change in the overall height of the tethered layer.

In this paper, we use a numerical self-consistent-field (SCF) model to determine the behavior of a polymer brush in a mixture of two immiscible solvents. We consider both neutral chains and weakly ionized polyacids. In the latter case, we modify the SCF model to allow the chains to become charged within the aqueous solution, where the acid groups are driven to dissociate but remain neutral within the oil phase.

In both cases, we show that, by varying the amount of the minority solvent, one can control not only the height of the brush but also the position of the chains' free ends. We also demonstrate that polymer segments within the tethered layer can saturate the solvent−solvent interface, and we develop an analytical theory to describe this effect. Finally, we provide guidelines for tailoring such brushes for specific applications, such as creating dense adhesive or lubricating bridges between two surfaces.

II. The System

We consider polymer chains that are grafted by one end onto a flat surface at a grafting density given by σ (which is the number of grafted chains per unit area). The degree of polymerization of the monodisperse chains is N, and the chains are assumed to be composed of spherically symmetric monomers. The diameter of a monomer, or a, is chosen as the unit of length.

The brush is immersed in a mixed solvent, which consists of two components. The interactions between the species in the system are characterized by three Flory−Huggins interaction parameters, χ_{12}, χ_{1p}, χ_{2p}, where p stands for the polymer and 1 and 2 denote the two solvent components. To model the fact that the solvents are mutually immiscible, we set $\chi_{12} = 3.5$ in all the ensuing calculations. For the solvents to phase separate inside the brush, one needs a high asymmetry in the composition of the mixture. Here, solvent 1 is chosen as the minor component and solvent 2 is the major constituent. We characterize the composition of the mixture by fixing the amount (per unit area) of solvent 1 in the system; this quantity is given by

$$\theta_1 = \int_0^L \phi_1(z)\,\mathrm{d}z \qquad (2.1)$$

where $\phi_1(z)$ is the volume fraction of solvent 1 at a distance z from the grafting surface, and L is the size of the system in the direction perpendicular to the surface (below, we set $L = 300$).

For phase-separated solvents, the value of θ_1 roughly indicates the position of the solvent−solvent interface,

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* To whom correspondence should be addressed.

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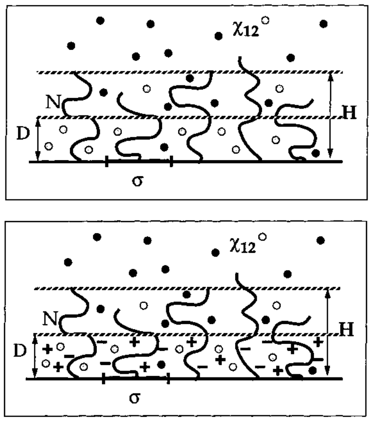

Figure 1. Schematic picture of a polymer brush in a phase-separated solvent: (a) neutral brush; (b) polyacid brush in a mixture of water and oil.

D (see Figure 1a). The deviation of D from θ_1 is due to the presence of polymer and solvent 2 in the region $z < D$. If $\phi_1(z) = 1$ at all values of $z < D$, then $D = \theta_1$. In order to relate the parameter θ_1 to the experimentally tractable volume fraction of solvent 1 in the bulk, ϕ_{bulk}, one needs to know the total surface area S and the volume V occupied by the mixed solvent. Then, the relationship between θ_1 and ϕ_{bulk} is given roughly by

$$\phi_{\text{bulk}} = \theta_1(S/V) \qquad (2.2)$$

As in the case of solvent 1, the volume fractions of the polymer, $\phi_p(z)$, and solvent 2, $\phi_2(z)$, only depend on the value of z. Here, we assume that the brush is homogeneous in the lateral direction and is characterized by the height of the layer, H.

In the examples we analyze below, the polymer chains can be either neutral or charged. In particular, we consider the following different situations:

1. The polymer is neutral and the two immiscible solutions are good solvents for the polymer, or $\chi_{1p} = \chi_{2p} = 0$. Through this example, we can isolate the effects on the brush that are solely due to the phase separation of the solvents.

2. The polymer is neutral, the minor solvent component is a θ solvent, or $\chi_{1p} = 0.5$, and the major solvent component is a good solvent, or $\chi_{2p} = 0$. This case illustrates the effect of adding a small amount of a θ solvent to a brush immersed in a good solvent.

3. The polymer is a weak polyacid, and the two solvents model a "water and oil" mixture. Both solvents are good, or $\chi_{1p} = \chi_{2p} = 0$, but their dielectric constants are different. Specifically, $\epsilon_{\text{water}} = 80$, and $\epsilon_{\text{oil}} = 1$. The latter difference gives rise to the unique behavior of the system. In oil, the polyacid brush stays effectively neutral. In water, however, the polyacid chains dissociate, producing negative charges on the polymers and hydrogens in the solution (see Figure 1b):

$$\text{HA} = \text{H}^+ + \text{A}^-$$

where A stands for an acid group.

The degree of dissociation, α, is controlled by the dissociation constant, K_a, the pH of the solution, and the salt concentration, ϕ_{salt}. In our study, we introduce a small amount of salt to the system, since it was previously shown that the degree of dissociation of a polyacid is higher when salt is added to water.[11-13] We set $K_a = 10^{-7}$, pH = 8, and $\phi_{\text{salt}} = 10^{-2}$. With respect to its neutral state, this set of parameters gives rise to a highly stretched polyacid brush in water.[11,13]

III. Model

To analyze the above system, we use a numerical self-consistent-field (SCF) model based on the approach of Scheutjens and Fleer[14] and applied by Israels et al.[11] to the case of a polyacid brush. In this lattice model, every site is occupied, either by a polymer segment or a solvent molecule. (The size of the lattice unit and the size of the solvent molecules are set equal to the monomer size a.) The brush is assumed to be homogeneous in the lateral direction; hence, the problem is one-dimensional, with the characteristic distance being given by z, the distance from the grafting surface. The local density of each component, $\phi_i(z)$, is calculated through the weighting function, $G_i(z)$,[14] which is the probability that the monomer of type i is localized in the layer z with respect to the bulk:

$$G_i(z) = \exp(-u_i(z)/kT) \qquad (3.1)$$

Here, the potential $u_i(z)$ for a segment of type i in layer z is given by

$$u_i(z) = u'(z) + kT\sum_{j\neq i}\chi_{ij}\phi_j(z) \qquad (3.2)$$

The parameter $u'(z)$ is a "hard-core potential", which ensures that every lattice layer is filled. The second term comes from the mixing interactions. When we consider charged systems, we must add an electrostatic potential, $\psi(z)$, to the right-hand side of eq 3.2. The potential $\psi(z)$ is calculated from the density of charges through Poisson's law. As in the original model,[11,14] we keep the condition of total electroneutrality of the system (which says that the total amount of negative charges in the system equals the total amount of positive charges in the system). However, all the ions except those on the polymer chains are free to leave the brush. An additional constraint on the system is that the lattice is fully occupied: for any layer in the lattice

$$\sum(\phi_i(z)) = 1 \qquad (3.3)$$

where the sum is over the different components in the system.

We refer the reader to the original publications[11,14] for details on the numerical procedure. Here, we describe how to adapt the model to the case of a polyacid brush immersed in solvents that have different dielectric constants. In this situation, different regions of a chain will display different degrees of dissociation. In the SCF model, the degree of dissociation of a polyacid, α(z), is calculated self-consistently from the weighting factors, $G_i(z)$, and the degree of dissociation of a polyacid chain in the bulk, α_b, which is given by

$$\alpha_b = K_a/(K_a + [\text{H}^+]) \qquad (3.4)$$

The value of α_b given by eq 3.4 is only valid for polyacid chains immersed in an aqueous solution. In our case, however, α_b must depend on ϵ, so that α_b will be low for polyacids immersed in a low ϵ solvent (for example, oil). Here, we assume that the effective degree of dissociation in the bulk, α_{eff}, is proportional to the average dielectric constant of the solvents in which polyacid is immersed. In the mixed solvent, we calculate the average dielectric constant, $\langle\epsilon\rangle$, at every layer z:

$$\langle\epsilon(z)\rangle = \sum_i \epsilon_i(z)\,\phi_i(z) \tag{3.5}$$

The effective degree of dissociation of the polyacid, $\alpha_{\mathrm{eff}}(z)$, becomes

$$\alpha_{\mathrm{eff}}(z) = \alpha_{\mathrm{b}}\langle\epsilon(z)\rangle/\epsilon_{\mathrm{water}} \tag{3.6}$$

This approximation is particularly appropriate in the limiting case where the dielectric constants for the two immiscible solvents are sufficiently different. A more precise expression may be needed in the case of a solvent mixture with comparable values of $\langle\epsilon\rangle$. In our situation, however, we are modeling an oil/water mixture; thus, the above expression is highly useful. In the self-consistent procedure, eq 3.6 is then used to recalculate the weighting factors $G_i(z)$, which in turn are used to obtain the volume fractions of the different components.

We note that, in calculating the volume fraction of the end-grafted polymer, the first segment of each chain is assumed to be fixed at the position $z = 1$. The height (along z) of our one-dimensional lattice is taken to 300 sites, which is greater than the height of the brush. We also note that the solvent molecules can leave the brush and, therefore, the solvent concentration inside the brush will be in equilibrium with the concentration in the outer solution.

Below, we first describe the SCF results on neutral brushes immersed in immiscible solvents. We then apply the above model to examine the behavior of polyacid brushes immersed in "oil" and "water".

IV. Results

In the subsequent calculations, we set $N = 500$ for the number of units in the polymer and, as noted above, $\chi_{12} = 3.5$ for the mutually immiscible solvents. We set $\chi_{1\mathrm{p}} = 0.0$ or 0.5 to model a good or θ solvent, respectively, and fix $\chi_{2\mathrm{p}} = 0.0$. All Flory–Huggins interaction parameters between the species in the system and the surface are set to zero except for $\chi_{2\text{-surface}}$, which is set to 1.5 in the Good and θ Solvents section. We vary the grafting density of the brush, σ, and the amount of solvent 1 in the system, or θ_1 (which roughly indicates the boundary between the phase-separated solvents at $D = \theta_1$).

A. Neutral Brush. *1. Two Good Solvents.* In this section, we consider a neutral brush immersed in a mixture of two good solvents, where $\chi_{1\mathrm{p}} = \chi_{2\mathrm{p}} = 0.0$. We first set the grafting density at $\sigma = 0.02$ and the amount of solvent 1 in the system at $\theta_1 = 50$. Figure 2 shows the SCF density profiles for this set of parameters. The dashed curves correspond to the density profiles of the solvents, and the solid curve corresponds to the density profile of the polymer. As can be seen from the figure, the solvents have phase separated: the density profile of solvent 1 abruptly decreases and the density profile of solvent 2 increases at $D \approx 50$. Since the polymer profile extends to $z = 100$, it is clear that this phase separation occurs inside the brush.

The density profile for the polymer resembles the general profile for a polymer immersed in a single good solvent. In particular, the profile has a parabolic shape, and the height of the brush obeys the expression $H = (8v/\pi^2)^{1/3}N\sigma^{1/3}$.[1] There is, however, a unique feature in the polymer profile in Figure 2: a well-defined peak at the solvent–solvent interface, which demonstrates that the polymers in the brush effectively saturate the boundary between the immiscible solvents. The effect can be readily understood. When the interface between the immiscible solvents is saturated by the polymeric species, the unfavorable contacts between the solvents are exchanged with the favorable contacts between the polymer and solvents. The height of the peak is controlled by a balance between the energetic gain due to the reduction in the interfacial tension at the solvent–solvent boundary and the entropic losses associated with localizing polymer and solvent molecules in the narrow interfacial region. Below, we analyze the dependence of the height of the peak on the grafting density, σ, and the amount of solvent 1 in the system, θ_1.

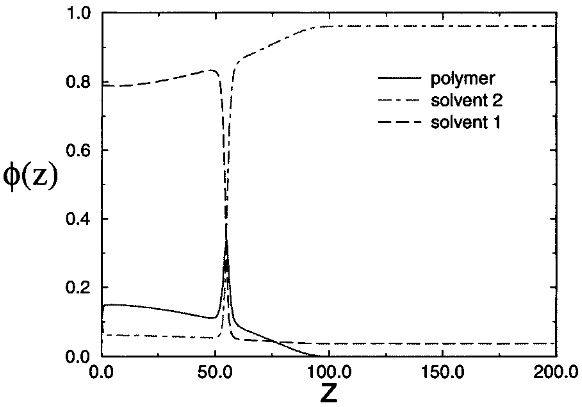

Figure 2. Density profiles for the polymer (solid curve) and solvents (dashed curves) at $\sigma = 0.02$ and $\theta_1 = 50$.

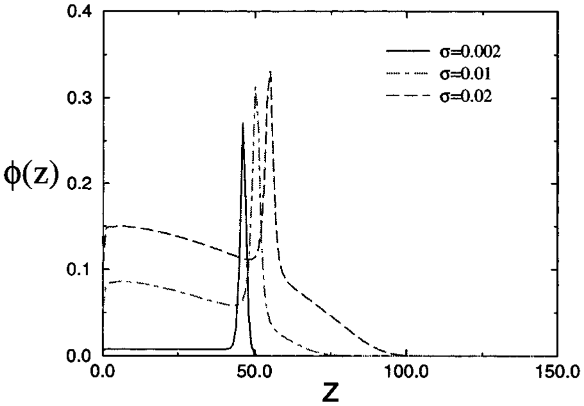

Figure 3. Polymer density profiles for variable σ at $\theta_1 = 50$.

Figure 3 shows the polymer density profiles for various values of σ and $\theta_1 = 50$. Although the height of the peak does not exhibit pronounced changes with variations in the grafting density, the structure of the brush does change rather dramatically. As expected, the total polymer density diminishes with a decrease in σ. At very low σ ($\sigma = 0.002$), however, the brush structure is completely destroyed. In the latter case, the energetic gain achieved by saturating the solvent–solvent interface is sufficiently high that the losses associated with stretching the chains from the grafting surface to the solvent–solvent interface are negligible.

Since the height of the peak is relatively independent of the grafting density, it is reasonable to expect the same peak height in the case where free homopolymers (of the same molecular weight, $N = 500$) are immersed in the same solvent mixture. Density profiles for this system, at a bulk concentration of polymer $\phi_{\mathrm{bulk}} = 10^{-3}$, are shown in Figure 4. It is indeed seen that the polymer saturates the interface between the immiscible

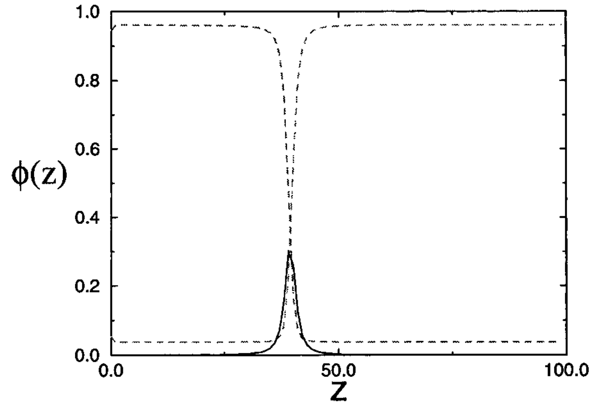

Figure 4. Density profiles of free homopolymer in the mixture of phase-separated solvents: the solid line corresponds to polymer, and dashed lines correspond to solvents. $N = 500$, $\chi_{1p} = \chi_{2p} = 0.0$, $\chi_{12} = 3.5$, and $\phi_{bulk} = 10^{-3}$.

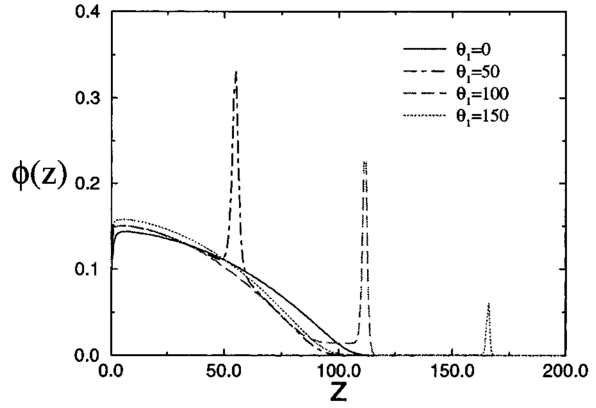

Figure 5. Polymer density profiles for variable θ_1 at $\sigma = 0.02$.

solvents to approximately the same volume fraction, $\phi_p = 0.36$, as in the case of the brush in Figures 2 and 3. Through additional SCF calculations, we also found that the value of the polymer volume fraction at the solvent–solvent interface is controlled mainly by the χ_{12} parameter and is effectively independent of the degree of polymerization and of the grafting density (or bulk concentration) of the polymer. It is also interesting to note that the width of the peak remained constant throughout all the calculations carried out for the chosen sets of parameters. Although we did not perform a systematic analysis to determine the width of the peak, we assume that this characteristic is mainly controlled by the χ_{ip} parameters. Similarly, the adsorption of a polymer chain from the solution onto a solid surface is controlled by the same parameters.[14]

To probe the behavior of the system further, we varied the amount of the minority component in the solvent mixture, θ_1. Figure 5 shows the density profiles of the brush at four different values of θ_1:0, 50, 100, and 150. Here, $\sigma = 0.02$. The majority of the polymer profile is unperturbed by changes in θ_1; the effect of varying θ_1 is seen only in the position and the height of the polymer peak at the solvent–solvent interface. With increasing amounts of solvent 1, the peak is pushed toward the outer edge of the brush and the height diminishes in size. Eventually, the peak will disappear. It is interesting to note, however, that at $\theta_1 = 100$ the peak is still quite high ($\phi_p = 0.25$) even at the edge of the brush, where the polymer concentration is normally close to zero. In fact, for $\theta_1 = 150$, there is a well-distinguished peak ($\phi_p = 0.06$) at $z = 170$, which is roughly twice the height of the brush.

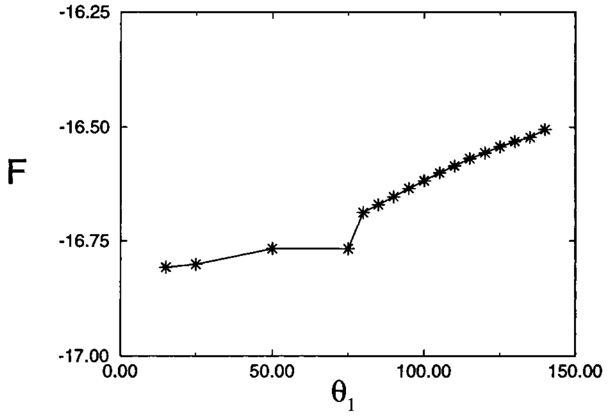

Figure 6. Free energy of the brush, F, in the mixed solvent as a function of the amount of solvent 1, θ_1. Here, $\sigma = 0.02$.

Another interesting result that emerges from Figure 5 is that the response of the brush to changes in θ_1 falls into two distinct regimes. As noted above, at small D or low amounts of solvent 1, the height of the peak is solely controlled by χ_{12} and does not depend on the grafting density. In this regime, the entropic losses associated with the stretching of the chains are negligible compared to the energetic gains arising from the exchange of solvent–solvent contacts with solvent–polymer contacts at the interface. Here, increases in θ_1 do not give rise to significant changes in the free energy of the system.

The second regime in the response of the brush is observed at relatively high amounts of solvent 1. In this case, the boundary between the two solvents is shifted far away from the grafting surface, and the chains must be highly stretched in order to saturate the interface. In this regime, the height of the peak is controlled by a balance between the stretching of the chains and the energetic gain at the interface. Increasing θ_1 causes a decrease in the amount of polymer at the solvent–solvent boundary. In addition, the free energy increases with an increase in θ_1 and ultimately approaches a value that equals the sum of free energy for an unperturbed brush in a good solvent and the interfacial tension between the solvents.

Figure 6 shows the free energy of the system (as calculated via the SCF model) as a function of the amount of solvent 1, or θ_1. As anticipated, the free energy exhibits two different regimes: it remains almost constant at low θ_1 and is an increasing function of θ_1 at high θ_1. In the Analytical Theory section, we introduce theoretical arguments to estimate the free energy of the system and subsequently analyze this term in more detail.

It is of particular interest to pinpoint which part of the polymer chain contributes to the saturation of the interface between the two solvents. Figure 7 shows plots of the end-point distribution function, which corresponds to the density of free ends in the brush at position z, for various values of θ_1. The large peaks in the end-point distribution functions reveal that the interface is primarily saturated by the ends of the chains. It is also apparent from this figure that variations in θ_1 do not affect the distribution of end points near the grafting surface; the main changes happen at the edge of the brush. Thus, the chains that were the most stretched in the one-component solvent contribute the most significantly to the saturation of the interface in the case where the two components phase separate.

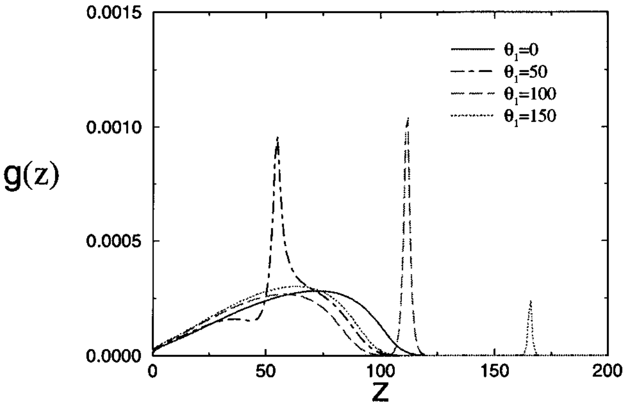

Figure 7. End-point distribution function for variable θ_1 at $\sigma = 0.02$.

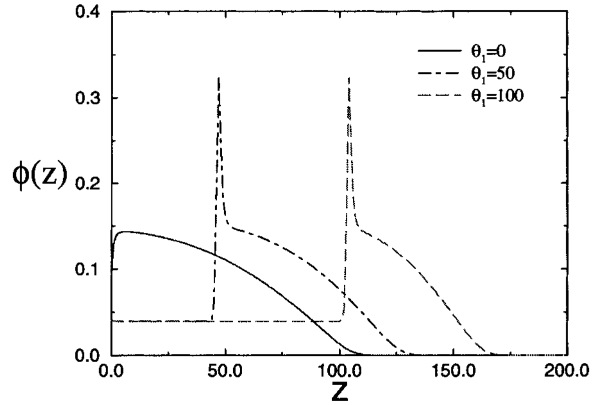

Figure 8. Polymer density profiles for variable θ_1 at $\sigma = 0.02$ and $\chi_{1p} = 0.5$.

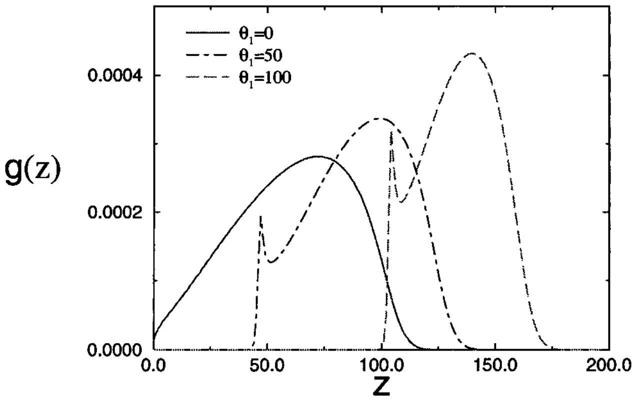

Figure 9. End-point distribution function for variable θ_1 at $\sigma = 0.02$ and $\chi_{1p} = 0.5$.

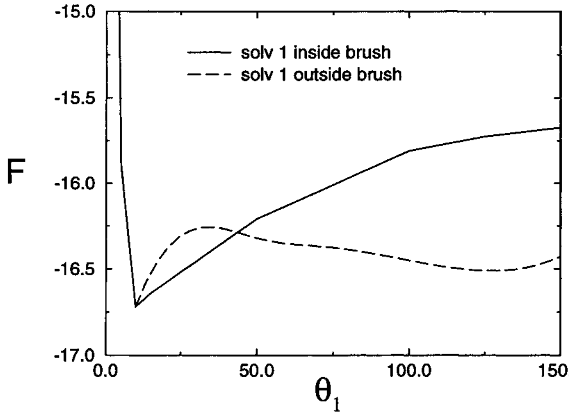

Figure 10. Free energy of the brush, F, in the mixed solvent as a function of the amount of solvent 1, θ_1. Here, $\chi_{1p} = 0.5$. The solid curve corresponds to the θ solvent trapped inside the brush, and the dashed curve corresponds to the θ solvent localized outside the brush. Here, $\sigma = 0.02$.

2. Good and θ Solvents. In this section, we analyze the situation where the two immiscible solvents have different affinities toward the polymer. We choose solvent 1 to be a θ solvent, with $\chi_{1p} = 0.5$, and solvent 2 to be a good solvent, with $\chi_{2p} = 0$. The grafting density is given by $\sigma = 0.02$. The other parameters are set at the values cited above. In order to localize an appreciable amount of the θ solvent inside the brush, we assume that the grafting surface is repulsive to the good solvent, or $\chi_{2-\text{surface}} = 1.5$, and is neutral to the θ solvent (and the polymer).

Figure 8 shows the polymer density profiles for this system at $\theta_1 = 0$, 50, and 100. We again see the pronounced peaks, which correspond to the chains saturating the solvent–solvent interface. The height of the peaks are somewhat lower than the heights in the previous section; this is due to the less favorable polymer–solvent 1 interaction in the θ solvent. Despite the similarity in the appearance of the peaks, the overall shapes of the profiles in Figure 8 are dramatically different from the profiles for a brush in two good solvents. While the polymer densities still have a parabolic form in the good-solvent phase, the profiles are effectively shifted from the grafting surface by the θ-solvent sublayer. In this sublayer, the polymer density is very low and remains constant up to the solvent–solvent interface. This profile indicates that the chains are highly stretched within the sublayer. In this system, the enthalpic cost associated with chain stretching in the θ solvent is compensated by energetic gains in the good-solvent environment.

The end-point distribution functions shown in Figure 9 also demonstrate that the chains are highly stretched in the θ-solvent sublayer. Here, one can see a total exclusion of free ends from the θ-solvent phase. Furthermore, the end-point distribution function becomes narrower when more of the θ solvent is added to the system. This result provides new guidelines for tailoring the location of the free ends of the grafted chains and makes the system highly attractive for applications that involve, for example, the formation of bridges between two surfaces.

A similar system was considered in refs. 8–10, where the influence of the minor component was introduced through an effective, local potential. Although the results of our study agree with the general predictions of refs. 8–10, our findings yield a more detailed description of the system. In particular, we predict a high saturation of the solvent–solvent interface by the grafted polymers, which was not predicted in the previous publications.[8–10] Furthermore, through our model, we can examine the possible expulsion of the θ solvent from inside the brush; we consider this scenario below.

Since the chains are highly stretched for even small amounts of θ solvent in the brush, the free energy of this system is expected to be an increasing function of θ_1. As seen from Figure 10 (solid curve), this is indeed the case. What is particularly important to note (and what makes the system different from the case of two good solvents) is the significant energetic penalty associated with the unfavorable polymer–θ solvent contacts. These interactions make it difficult to retain large amounts of the θ solvent within the brush. At a certain value of θ_1, this solvent will be expelled and the brush will be totally immersed in the good-solvent component. The free energy of the system in the latter state is marked in Figure 10 by the dashed curve. As Figure 10 shows, the two curves intersect at $\theta_1 = 45$; this behavior indicates that it is energetically unfavorable to keep solvent 1 in the brush for amounts higher than $\theta_1 = 45$. At smaller amounts of solvent 1, the free energy corresponds to a metastable state, and one can expect a coexistence of two phases, with a very small amount of solvent 1, or $\theta_1 = 5$, in the brush and a higher amount of solvent 1, or $\theta_1 = 130$, outside the polymer layer.

3. Analytical Theory. In this section, we develop a theoretical analysis for the behavior of a brush in a mixture of two immiscible solvents and compare our findings to the SCF calculations described above. On the basis of our SCF results, we assume that there are three different regions in this system: the first one is next to the grafting surface and is rich in solvent 1, the second is the narrow interfacial region between the two solvents, and the third is essentially pure solvent 2. We assume that all three regions are laterally homogeneous and the boundaries between them are flat. As in the previous sections, the length of the polymer chain is N and the grafting density is σ.

Since the solvents are phase-separated, the width of region 1, D, is approximately equal to the amount of solvent 1, θ_1. The width of region 2, d, should depend on the molecular weight of the polymer; an expression for d can be formulated by considering the conformational losses that arise from confining the polymer in the narrow interfacial region. Here, we do not derive such an expression; rather, we use d as an adjustable parameter, which we take from our SCF calculations to be approximately equal to 3 (in units of a). Since region 3 is primarily composed of solvent 2, it does not play an important role in our analysis and we neglect this region in further discussions.

Below, we minimize the total free energy of the system to find the equilibrium volume fraction of polymer in the interfacial region. Using the calculated polymer volume fractions, we can then evaluate the free energy. The expression for the total free energy can be written as a sum of the free energies in the two regions described above. We consider each of these contributions separately, starting with the terms for region 2. The free energy (per chain) for the interfacial region, f_2, can be expressed in the usual manner as a sum of enthalpic and entropic contributions:

$$f_2 = \sum_{i \le j} (\chi_{ij} n_{2i} \phi_{2j} + n_{2i} \ln \phi_{2i}) \qquad (4.1)$$

Here, n_{2i} represents the number of molecules of type i in the volume d/σ, and ϕ_{2i} denotes the volume fraction of the ith component in region 2.

The free energy for region 1 can be written in a similar manner, with additional contributions stemming from the stretching of the grafted chains to reach the interface. This term is essentially the same for both low grafting densities, where all the chains contribute to the saturation of the interface, and high grafting densities, where only a fraction q of the chains stretch in order to reach the interfacial region (and the remainder form an unperturbed brush). The only difference between the two cases will be in the effective grafting density, which equals σq in the second case. With this correction, the free energy (per chain) in region 1 for both cases has the following form:

$$f_1 = (\chi_{1p} n_1 \phi_p + n_1 \ln \phi_1) + (3/2)D^2/N_1 \qquad (4.2)$$

where n_i is the number of molecules of type i in the volume D/σ, and ϕ_i is the volume fraction of the ith component in region 1. In this expression, we assume that the polymer is immersed in pure solvent 1. We also take into account the fact that only part of the polymer chain, $N_1 = N - \phi_{2p}(d/\sigma)$, is stretched through a layer of thickness D, with the rest of the chain, $N_2 = N - N_1$, being localized in the interfacial region. Below, the *total* number of solvent 1 molecules will be kept constant.

To determine the unknown volume fractions in the interfacial region, ϕ_{2i}, and the distribution of polymer between regions 1 and 2, we minimize the total free energy, $f = f_1 + f_2$, with respect to the number of solvent 1 molecules in region 2, n_{21}. We then assume that, at $\chi_{1p} = \chi_{2p} = 0.0$, the volume fractions of the two solvents in region 2 are equal, or $\phi_{21} = \phi_{22} = (1-\phi_{2p})/2$, and obtain the following equation for $\phi = \phi_{2p}$:

$$A = B\phi^2 + (3/2)D^2/N_1^{\,2} - \mu_1 \qquad (4.3)$$

where $A = \chi_{12}/4 - \ln 2$, $B = \chi_{12}/4 + 1/2$, $N_1 = N - \phi(d/\sigma)$, and $\mu_1 = (\chi_{1p} - 1/2)\phi_p^{\,2}$. For $\chi_{12} = 3.5$, we obtain $A = 0.175$ and $B = 1.375$. Since $\phi_p \ll \phi$ (that is, the volume fraction of polymer in region 1 is less than the volume fraction of polymer in region 2), μ_1 is much smaller than the other terms in eq 4.3, and we can neglect this term in our analysis.

Although we cannot solve eq 4.3 for ϕ analytically, we can find solutions in two limiting cases. When D is small, the $B\phi^2$ term dominates over the $(3/2)D^2/N_1^{\,2}$ term, and the volume fraction of polymer in the interfacial region becomes a constant ϕ_0, which is given by

$$\phi_0 = \sqrt{A/B} \qquad (4.4)$$

For our set of parameters in the case of two good solvents, this equation yields $\phi_0 = 0.36$, which agrees with the results of the SCF analysis (see Figures 2 and 3).

In the opposite limit, where D is relatively large, the second term dominates over the first in eq 4.3 and then $N_1 = \sqrt{(3/2)}D$. Since N_1 cannot be greater than N, the maximum value of D equals $D_{\max} = \sqrt{(2A/3)}N$. For the case of two good solvents, at $\chi_{12} = 3.5$ and $N = 500$, this yields $D_{\max} = 170$, which is in good agreement with the results of the SCF calculations shown in Figure 5. The volume fraction of polymer in this regime is found as

$$\phi = (N - N_1)\sigma/d = (N\sigma/d)(1 - D/D_{\max}) \qquad (4.5)$$

Note that ϕ is a linear function of D and goes to 0 at $D = D_{\max}$. The maximum value of ϕ depends on the width of the interfacial region, d, which we set at $d = 3$.

The transition from the region of a constant ϕ (eq 4.4) to the regime where ϕ is described by eq 4.5 occurs at $D = D_*$. The value of D_* can be obtained through the equality $\phi(D_*) = \phi_0$:

$$D_* = D_{\max}(1 - \sqrt{(A/B)}(d/N\sigma)) \qquad (4.6)$$

It follows from eq 4.6 that at low grafting density, σ, the value of D_* may become negative. Thus, the regime of constant $\phi = \phi_0$ cannot be realized at low σ and, therefore, the value of ϕ in the peak is a decreasing function of D, as described by eq 4.5. We can then calculate the total free energy of the system from eqs 4.1 and 4.2. If the expression for the free energy is expanded with respect to ϕ, the dominant term in the expansion is one that is linear in ϕ. This results in a linear behavior for the free energy with respect to the parameter D. The free energy in this case is an increasing function of D.

When the grafting density is relatively high and the brush is rather dense, the value of D_* is always positive, and both regimes of ϕ, described by eqs 4.4 and 4.5 can be realized. At the amounts of solvent 1 for which $D < D_*$, the volume fraction ϕ is constant. This is because the amount of polymer is so high that there are no entropic losses associated with saturating the interface up to the maximum value of ϕ_0. Moreover, in this regime, not all the chains contribute to the saturation of the interface. We can estimate the fraction of chains at the interface, q, from the following condition: this fraction of chains saturates the interface up to the maximum value of ϕ_0 when the position of the solvent–solvent interface, D, coincides with the average height of the brush, $H = (8v/\pi^2)^{1/3}N\sigma^{1/3}$,[1] since there are no losses arising from chain stretching when the interface is localized inside the brush. From this condition, we get

$$q = \phi_0/(1 - H/D_{\max})(d/N\sigma) \tag{4.7}$$

The total free energy of the system can then be found from eqs 4.1 and 4.2 with the values of ϕ given by eqs 4.4 and 4.5 and with the value of σ replaced by σq, as was discussed above. At low amounts of solvent 1 in the system, which corresponds to small values of D ($D < D_*$), the volume fraction ϕ is constant; hence, the free energy is also constant. At high values of D ($D > D_*$), where the volume fraction ϕ is a linear function of D, the free energy is an increasing linear function of D. This behavior for the free energy was also obtained from the SCF calculations, as shown in Figure 6.

B. Polyacid Brush. We now consider the behavior of a polyacid brush immersed in a mixture of two solvents, water and oil, which have different dielectric constants. We assume that both water and oil are good solvents for the polymer chains. When immersed in water, the high dielectric solvent, the acid groups within the polymers dissociate in the manner described in The System section. We set the dielectric constant for water at $\epsilon_{\text{water}} = 80$. The polyacids, however, do not dissociate in solvents with low dielectric constants, such as oil. Here, we fix the dielectric constant for oil at $\epsilon_{\text{oil}} = 1$. We set the dissociation constant of the polyacid at $K_a = 10^{-7}$ and pH = 8. Since it was previously shown[11−13] that the addition of salt promotes the dissociation of the acid groups, we also introduce a finite salt concentration into the system, and we fix the bulk volume fraction of the salt at $\phi_{\text{salt}} = 0.01$. Using the modified SCF equations outlined above, we obtain the polymer density profiles in Figure 11a for $\theta_1 = 40$ and 70 and $\sigma = 0.01$. These profiles resemble those for a brush immersed in a mixture of θ and good solvents (see Figure 8). In particular, the chains are highly stretched through the inner (in this case, water) sublayer, forming a peak at the solvent–solvent interface. The remaining chain segments form a parabolic profile in the oil phase, as would be expected for a polymer in a good solvent. The height of the peak is somewhat lower than that for the neutral brush, possibly because it is more difficult to confine a charged chain within the narrow interfacial region than a neutral one. Figure 11b also shows the degree of ionization of the polymer chains in the brush, α, as a function of z. The polymer is highly charged in the inner (water) sublayer and stays effectively neutral in the outer (oil) layer. It is also seen that, in the interfacial region, the polymer is mostly uncharged.

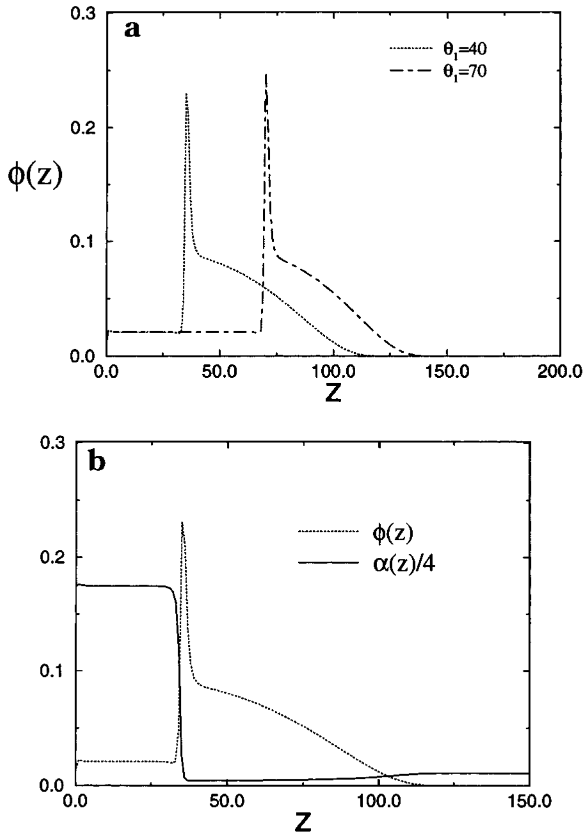

Figure 11. (a) Polymer density profiles of a polyacid brush in the mixture of water and oil for variable θ_1 at $\sigma = 0.01$. (b) Polymer density profile (dotted line) and the degree of ionization, α(z)/4 (solid line), of a polyacid brush in the mixture of water and oil at $\theta_1 = 40$ and $\sigma = 0.01$.

Despite the similarities in Figures 8 and 11, the specific driving forces that cause the chains to stretch through the sublayer are different in the two cases. In the case of a neutral brush in a mixture of θ and good solvents, the stretching of the chains minimizes the unfavorable polymer–θ solvent contacts and optimizes the number of favorable contacts with the good solvent. We note that the polymer fraction within the θ-solvent sublayer is much lower than the fraction of polymer (within the same volume) one would observe if the brush were immersed in a pure θ solvent. In the pure θ solvent, polymer–solvent contacts are exchanged by the more favorable polymer–polymer interactions; as a consequence, the chain collapses and the volume fraction near the surface is quite high. For a θ solvent in contact with a good solvent, polymer segments can escape the unfavorable interactions by extending into the good-solvent phase; as a consequence, the chain becomes stretched.

In the case of the polyacid brush in the water/oil mixture, the chains are stretched through the water phase *not* by energetically unfavorable contacts with the aqueous phase but rather by the osmotic pressure arising from the counterions. In fact, polyacid brushes in water are highly stretched with respect to their neutral state.[11−13] Since the location of water inside the brush is favorable, the profiles in Figure 11 correspond

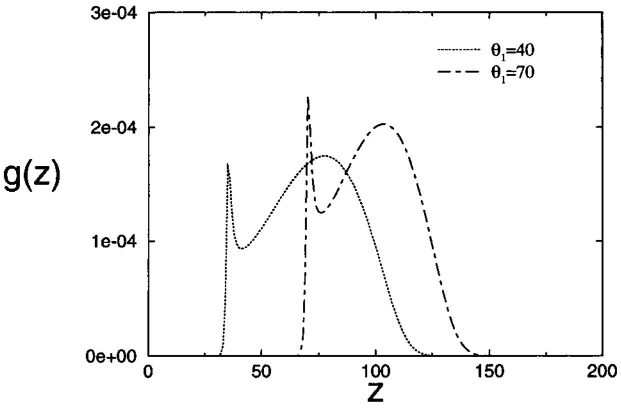

Figure 12. End-point distribution function of a polyacid brush in the mixture of water and oil for variable θ_1 at $\sigma = 0.01$.

to stable states. In this case, the height of the brush increases with an increase in the amount of water in the system. Figure 12 shows the end-point distribution functions for the polymer chains described above. The total exclusion of the chain ends from the water sublayer is observed in Figure 12. In addition, the figure reveals a certain saturation of the solvent−solvent interface by the chain ends, with the rest of the ends being localized in the oil phase. Again, these results provide useful guidelines for tailoring the location of the free ends of the chains.

The possibility of controlling the height of a polyacid brush immersed in oil by adding a small amount of water was suggested in ref 7. Here, we confirm the predictions of ref 7, furthermore, we characterize the solvent−solvent interface and pinpoint the location of the chain ends.

C. Conclusions. In this paper, we considered the behavior of a polymer brush immersed in a mixture of two immiscible solvents. When the amount of one of the solvents is relatively low, these fluids can phase separate inside the brush. The specific details of the polymer profiles depend on the quality of the solvents, but in all cases considered here, the polymers within the brush effectively saturate the solvent−solvent interface. A high peak at the solvent−solvent boundary is also observed in the end-point distribution function.

In the case of the polyacid brush immersed primarily in oil, the height of the brush can be dramatically increased by adding a small amount of water. The free ends of the chains are also shifted further from the grafting surface in this case.

The ability to readily tailor the location of the chain ends and the overall height of the brush makes these systems highly attractive in various applications. For example, by tailoring these quantities, one can vary and control the adhesion or lubrication between polymer-coated surfaces or the steric stabilization colloids.

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References and Notes

(1) Milner, S. T. *Science* **1991**, *251*, 845. Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *31*, 100.
(2) Napper, D. H. In *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1985.
(3) Auroy, P.; Auvray, L. *Macromolecules* **1992**, *25*, 4134.
(4) Marko, J. F. *Macromolecules* **1993**, *26*, 313.
(5) Lai, P.-Y.; Halperin, A. *Macromolecules* **1992**, *25*, 6693.
(6) Birshtein, T. M.; Lyatskaya, Yu. V. *Macromolecules* **1994**, *27*, 1256.
(7) De Gennes, P.-G. *C. R. Acad. Sci. Ser. II* **1996**, *322*, 819.
(8) Johner, A.; Marques, C. M. *Phys. Rev. Lett.* **1992**, *69*, 1827.
(9) Marko, J. F.; Johner, A.; Marques, C. M. *J. Chem. Phys.* **1993**, *99*, 10.
(10) Chakrabarti, A.; Nelson, P.; Toral, R. *Phys. Rev.* **1992**, *46*, 4930.
(11) Israels, R.; Leermakers, F. A. M.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3087.
(12) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491.
(13) Lyatskaya, Yu. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562.
(14) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. In *Polymers at Interfaces*; Chapman and Hall: London, 1993.

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