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Behavior of Polyacid Chains Tethered to an Elastic Substrate

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ABSTRACT: We use scaling arguments and an analytical self-consistent field theory to investigate the behavior of polyacid chains that are grafted onto an elastic surface and immersed in an aqueous solution. The surface is assumed to be neutral, while the polyacid groups can dissociate and become negatively charged at elevated pH. We determine how the elasticity of the substrate affects the response of the tethered chains to variations in pH and the concentration of salt in the solution. Under these conditions, we find that the surface elasticity, γ, affects both the area per chain, σ, and the height of the brush, h, and we derive specific scaling relationships correlating σ and h to γ. The results provide guidelines for coupling γ, pH, and the salt concentration to tailor the structure of the polyacid brush and thereby adapt the system for specific applications.

Introduction

The properties of polyacid polymers are dependent on the local pH: at low pH, the chains are effectively neutral, but at high pH, the acid groups dissociate and the chains become negatively charged. Due to the mutual repulsion of the negative species, the chains change their conformation. This behavior can be exploited in a variety of applications. In particular, polyacid gels can be made to expand and contract by variations in the local pH and can be made to perform mechanical work[1,2] or even convert mechanical work into chemical energy.[3] Vesicles containing polyacid chains can be made to burst at a relatively high pH and thereby release their contents.[4] This system constitutes an effective drug carrier or controlled-release device. By tethering such polyacid polymers to a surface, their properties can be harnessed for other applications. Grafted to the surface of a membrane or porous substrate, the chains can be made to act like a gate,[5] permitting molecules to enter the membrane for one range of pH values but prohibiting the diffusion at another pH.[6] The tethered chains can also be used to cover up a reactive surface molecule, such as a catalyst, at one pH and expose the reactive center at another pH level.[7] In this way, the extent of reaction can be carefully controlled.

One can further modulate the response of the polyacid chains by introducing a finite concentration of salt[8−11] or varying the solvent quality.[5] With such a large number of variables, theoretical models can play an active role in providing guidelines for tailoring the system for specific applications. Existing studies on the behavior of grafted polyacids, or polyacid brushes, have already revealed novel behavior. In particular, the height of the brush initially increases and then decreases with increasing salt concentration.[8−11] These results revealed a new "handle" for making the system expand and contract. In this and other prior theoretical studies[8−17] on charged brushes, the substrate is always assumed to be a flat, rigid surface. Incorporating characteristics of the substrate into a description of the system may reveal new behaviors, which can in turn lead to new applications.

In this paper, we consider the behavior of an ionizable or polyacid brush grafted onto a flat, but elastic surface (for example, a polymer network). Specifically, we determine how the elasticity of the substrate affects the response of the brush to variations in pH and salt concentration. To carry out this investigation, we introduce a factor that characterizes the elasticity of the surface. We then use two theoretical techniques to analyze the behavior of this system. First, we utilize a simple method based on scaling arguments, which allows us to obtain power-law dependencies for the average characteristics of the brush. The second model is an analytical self-consistent-field method that allows one to take into account the vertical inhomogeneities within the grafted layer and thus provides additional information about the inner structure of the brush.

Below, we describe how we calculated the free energy for the system and thereby obtained simple scaling laws. The details of the analytical self-consistent-field method are given in Appendix 1. The findings from models are presented in the Results section.

Model

We consider chains of length N that are grafted by one end onto a flat surface. The grafting density is sufficiently high that the chains form a polymer brush. Here, σ, the area per chain is $\ll R_G^2$, where R_G is the radius of gyration of the unperturbed chain.[18] The monomers are assumed to be spherically symmetric, and all lengths are expressed in the units of a monomer length. When the brush is immersed in a good solvent, the chains stretch or extend into the favorable solvent, and the brush becomes swollen. If the surface is rigid, the chains can only stretch in the direction normal to the surface. The energetic loss associated with this stretching is $\sim h^2/N$, where h is the height of the brush. The balance between this energetic loss and the favorable polymer−solvent interactions determines the equilibrium value for the brush height.

When the surface is elastic, favorable polymer−solvent interactions can also lead to an increase in the area per chain, σ. We characterize the elasticity of the surface by the parameter γ, so that $\gamma\sigma$ gives the loss in free energy associated with the stretching of the surface in the lateral direction. Note that this term is valid only for materials that display rubber elasticity or a rubber surface under the assumption that the surface dilates by a very large amount. (One could also view this term as a surface tension.) Low values of γ correspond to a flexible surface, whereas high values of γ correspond to a rigid surface. Now, the balance between the polymer−

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solvent interactions and the losses associated with the stretching of the chains andthe surface yields the equilibrium values of area per chain, σ, and the height of the brush, h.

When the brush is charged, an additional term associated with the translational entropy of the charged groups should be included in the expression for the free energy. In this case, the full expression for the free energy per chain has the form

$$\Delta F = h^2/N + \gamma\sigma + \chi N(1 - \varphi) + f(\varphi)\sigma h \tag{1}$$

where the first two terms correspond to the loss in free energy due to stretching of the chains and the surface, respectively. The third term, $\chi N(1 - \varphi)$, corresponds to the interactions between the polymer and solvent, where χ is the Flory–Huggins interaction parameter, and φ is the volume fraction of polymer units in the brush. Below, we only consider the good solvent case and set $\chi = 0$. Note that eq 1 is written in terms of the average characteristics of the brush and thus describes a brush that is homogeneous in both the lateral and vertical directions.

The fourth term, $f(\varphi)$, is associated with the translational entropy of the solvent (and charged groups along the chain in the case of a polyacid brush). Note that electrostatic interactions are not explicitly formulated in the expression for the free energy, eq 1; nevertheless, they will be taken into account by introducing the relative distribution of the charged groups, as discussed below. This approach is valid when the polymer chains are sufficiently long to maintain a cloud of counterions inside the brush.[11,14,15]

The normalization condition establishes a relationship between h, σ, and φ:

$$h = N/(\sigma\varphi) \tag{2}$$

and at a fixed N, makes ΔF a function of only two variables: φ and σ. Equation 1 is valid for all types of brushes: neutral ($f(\varphi) = (1 - \varphi)\ln(1 - \varphi)$) and charged ($f(\varphi)$ depends on the distribution of charged groups inside the brush), grafted onto a rigid (σ = constant) or a flexible (σ = variable) surface. Minimization of ΔF with respect to φ yields the equilibrium value of φ for a rigid surface (σ = constant). When the surface is elastic (σ = variable), it is necessary to minimize the free energy with respect to both variables, σ and φ.

In this study, the surface is neutral, and the grafted polymer is a weak polyacid, $(HA)_N$. The surface, covered with the layer of grafted polyacids, is immersed in an aqueous solution of fixed pH and fixed salt concentration, Φ_S. We consider Φ_S to be the volume fraction of positive ions from the dissociated salt. For example, if NaCl is chosen to be the salt, then $\Phi_S = \Phi_{Na^+}$. The complete set of species in the bulk is now the following: Na^+, Cl^-, H^+, OH^-, H_2O.

When a polyacid brush is in contact with the bulk (solvent), each of the above species penetrates into the grafted layer and, hence, contributes to swelling the brush. We consider all the species from the bulk to be a good “solvent” for the polyacid chains. That is, $\chi = 0$ between all the solute species and the monomers in the brush. The volume fraction of polymer units in the brush that is swollen in this way is $\varphi \ll 1$.

The brush dissociates and produces an electric potential ψ that is attractive to positive ions and repulsive to negative ones. This leads to a distribution of ions inside the brush that is different from that in the bulk. The degree of dissociation for the polyacid, α, is controlled by the pH, or the amount of H^+ groups in the brush, φ_{H^+}:

$$\frac{\alpha}{1 - \alpha}\varphi_{H^+} = K_{HA} \tag{3}$$

where $K_{HA} = \exp(\mu^\circ_{HA} - \mu^\circ_{H^+} - \mu^\circ_{A^-})$ is the dissociation of the polyacid, and the μ°_i are the standard chemical potentials of the species of type i. Here and below, the symbols φ_i correspond to the volume fractions of the species of type i inside the brush, and the Φ_i represent the corresponding volume fractions in the bulk. Note that in general $\varphi_i \neq \Phi_i$. When $\varphi_{H^+} = \Phi_{H^+}$, α reaches the value α_b, the characteristic degree of dissociation of the polyacid in the solvent:

$$\frac{\alpha_b}{1 - \alpha_b}\Phi_{H^+} = K_{HA} \tag{4}$$

or

$$\alpha_b = 1/(1 + \exp(pK_a - pH)) \tag{5}$$

where $pK_a = -\log K_{HA}$ and $pH = -\log \Phi_{H^+}$.

The parameter α_b can be considered as an indicator of the pH: an increase (decrease) in the pH results in an increase (decrease) in α_b. Thus, one can easily relate the effect of the pH to the effect of α_b. Below, it will be more convenient to use α_b instead of pH.

To utilize eq 1 for a charged brush, we must know an expression for $f(\varphi)$. The expression for the translational entropy of the charged groups inside the brush, $f^{brush}(\varphi)$, was previously derived in refs 9 and 11 and is given as

$$f^{brush}(\varphi) = \varphi(\alpha \ln \alpha + (1 - \alpha)\ln(1 - \alpha) + \alpha\mu^\circ_{A^-} - \alpha\mu^\circ_{AH}) + \sum_i \varphi_i\mu_i^{in} \tag{6}$$

Here, the bracketed term pertains to the polymer, with the first two terms describing the respective translational entropies of the charged and uncharged groups along the chain. The terms factored by μ°_i represent the energy of dissociation for the polyacid groups. The sum $\sum_i\varphi_i\mu_i^{in}$ describes the translational entropy of the mobile ions inside the brush. When the brush is in equilibrium with the bulk, the total loss in the free energy of the system due to the translational entropy of mobile species and charges on the chains is given by

$$f(\varphi) = f^{brush}(\varphi) - \sum_i \varphi_i\mu_i^{out} + \alpha\varphi\mu_{H^+}^{out} \tag{7}$$

The sum $\sum_i\varphi_i\mu_i^{out}$ accounts for the change in the free energy of the bulk when an amount φ_i (per unit volume) of the species of type i penetrates into the brush. The last term is a correction due to the fact that an amount $\alpha\varphi$ of H^+ ions appears within the brush due to the dissociation of the acid groups and, hence, does not influence the free energy of the bulk. In the above, $\mu_i^{in} = \ln \varphi_i + \mu^\circ_i$, $\mu_i^{out} = \ln \Phi_i + \mu^\circ_i$, and μ°_i is the standard chemical potential of the species of type i.

It follows from eq 7 that $f(\varphi)$ and, consequently, ΔF are functions not only of φ but also of α and of all the φ_i, i = Na^+, Cl^-, H^+, OH^-, H_2O. To reduce the number of independent variables, we implement the following assumptions:

1. The distribution of ions in the electric field of a charged brush is considered to obey Boltzmann's law:

$$\frac{\varphi_{i+}}{\Phi_{i+}} = \frac{\Phi i_{-}}{\varphi_{i-}} = e^{-\psi e/kT} \equiv y \qquad (8)$$

where e is the elementary charge and kT is the thermal energy. Below, all energy values will be expressed in units of kT. Equation 8 relates all volume fractions of charged ions in the brush to only one unknown variable, y. This assumption also leads to the equality $\varphi_{H_2O} = \Phi_{H_2O}$, and reduces the number of unknown characteristics of the brush to y, α, and φ.

2. The condition of electroneutrality is obeyed:

$$\varphi_{Na^+} + \varphi_{H^+} = \varphi_{Cl^-} + \varphi_{OH^-} + \alpha\varphi \qquad (9)$$

3. The mass conservation law is obeyed:

$$\varphi_{Na^+} + \varphi_{H^+} + \varphi_{Cl^-} + \varphi_{OH^-} + \varphi_{H_2O} + \varphi = 1 \qquad (10)$$

With these assumptions, $f(\varphi)$ has a very simple form:

$$f(\varphi) = \varphi \ln(1 - \alpha) \qquad (11)$$

where α is related to the variable φ in the following way:[9,11]

$$\varphi = \Phi_+\left[\frac{1-\alpha}{\alpha^2}\,\frac{\alpha_b}{1-\alpha_b} - \frac{1}{1-\alpha}\,\frac{1-\alpha_b}{\alpha_b}\right] \qquad (12)$$

and $\Phi_+ = \Phi_S + \Phi_{H^+}$. In most cases of interest, $\Phi_{H^+} \ll \Phi_S$ and $\Phi_+ \approx \Phi_S$. Assumptions 8–10 and eq 12 were also discussed in refs 9 and 11, and we refer the reader to these papers for further details.

In this way, $f(\varphi)$ is a function of only one variable, φ, and the full expression for the free energy of a polyacid brush is now

$$\Delta F = h^2/N + N \ln(1 - \alpha) + \gamma\sigma \qquad (13)$$

The terms in eq 13 reflect the contributions from the stretching of the chains, the osmotic pressure of an ion gas (which is the translational entropy of the mobile ions), and the stretching of the surface. Below, we minimize eq 13 (with eqs 2 and 12 taken into account) to obtain the equilibrium values of h and σ.

Results

We begin by comparing our results to previous findings for a neutral brush grafted onto a rigid surface (σ = constant).[18] This comparison will facilitate further discussion below. We then describe earlier findings for charged polyacid polymers grafted onto a rigid surface[9,11] and compare this result with our findings for polyacids tethered to an elastic substrate.

In the case of a neutral brush on a rigid surface (σ = constant), the brush height scales as[18]

$$h \sim N v^{1/3} \sigma^{-1/3} \qquad (14)$$

where $v = (0.5 - \chi)$ is the second virial coefficient. To determine how the elasticity of the surface alters this behavior, we return to eq 1 and set $f(\varphi) = (1 - \varphi) \ln(1 - \varphi)$. We then minimize ΔF with respect to both h and σ to find

$$h \sim N^{4/5} v^{1/5} \gamma^{1/5}$$

$$\sigma \sim N^{3/5} v^{2/5} \gamma^{-3/5} \qquad (15)$$

Even in the case of a neutral brush, the elasticity of the substrate affects the characteristics of the grafted layer. As may be expected, the height of the brush increases with the rigidity of the surface, while the area per chain decreases with increasing rigidity. The effect, however, is more complicated in the case of polyacid chains and is discussed below.

In order to determine analytical expressions for $\varphi(\Phi_S,N,\gamma,\alpha_b)$ and $\sigma(\Phi_S,N,\gamma,\alpha_b)$ for a charged brush, it is convenient to consider two limits: (1) when the salt concentration Φ_S is relatively low, $\Phi_S \ll \alpha\varphi$, and (2) when the salt concentration Φ_S is relatively high, $\Phi_S \gg \alpha\varphi$. In these limits, α can be obtained as a direct function of φ:[9,11]

$$\alpha \sim ((\Phi_S/\varphi)(\alpha_b/(1-\alpha_b)))^{1/2}, \qquad \text{low } \Phi_S$$

$$\alpha \sim \alpha_b(1 - (\alpha_b\varphi)/(2\Phi_S)), \qquad \text{high } \Phi_S \qquad (16)$$

Using the approximation $N \ln(1 - \alpha) \approx \alpha N$ in eq 13, we can now obtain the asymptotic behavior of $h(\Phi_S)$ and $\sigma(\Phi_S)$. We will also calculate the complete behavior of $h(\Phi_S)$ and $\sigma(\Phi_S)$ by taking into account the vertical inhomogeneity of the brush. This approach is outlined in Appendix 1.

Minimizing the free energy, ΔF, with respect to φ under the assumption that σ = constant yields the dependence of h on the properties of the polyacid brush grafted onto the rigid surface in the limits of low and high Φ_S:

$$h \sim N(\Phi_S\sigma\alpha_b/(1-\alpha_b))^{1/3}, \qquad \text{low } \Phi_S$$

$$h \sim N(\alpha_b^2/(\Phi_S\sigma))^{1/3}, \qquad \text{high } \Phi_S \qquad (17)$$

These results are the same as those obtained in refs 9 and 11, where a different formulation was used. As noted before and can be seen from eq 17, $h(\Phi_S)$ displays rather unusual behavior: h is an increasing function of Φ_S at low Φ_S and is a decreasing function of Φ_S at high Φ_S. At high salt concentrations, the salt ions effectively screen the charges on the chain, and the brush behaves like a neutral layer, with an effective virial coefficient $v_{eff} = \alpha^2/\Phi_S$ (compares eqs 17 and 14). At low salt concentrations, screening does not occur; rather, an increase in Φ_S increases the exchange between H^+ groups inside the brush and NA^+ groups in the solvent. This in turn causes a higher dissociation of the polyacids and, consequently, a swelling of the brush.

In the case of an elastic surface, or variable σ, minimization of the free energy, eq 13, with respect to two variables, h and σ, gives the equilibrium values of these variables. Again, we only consider the behavior in the limits of high and low Φ_S. The full curves for $h(\Phi_S)$ and $\sigma(\Phi_S)$ will be calculated with the help of the equations in Appendix 1, and the results will be compared below. From minimizing eq 13, the asymptotes for h and σ in the limits of high ($\Phi_S \gg \alpha\varphi$) and low ($\Phi_S \ll \alpha\varphi$) salt concentrations, Φ_S, are

$$h \sim (\Phi_S\alpha_b/(1-\alpha_b))N(N/\gamma), \qquad \text{low } \Phi_S$$

$$h \sim (\alpha_b^2/\Phi_S)^{1/5} N(\gamma/N)^{1/5}, \qquad \text{high } \Phi_S \qquad (18)$$

$$\sigma \sim (\Phi_S\alpha_b/(1-\alpha_b))^2 (N/\gamma)^3, \qquad \text{low } \Phi_S$$

$$\sigma \sim (\alpha_b^2/\Phi_S)^{2/5} (N/\gamma)^{3/5}, \qquad \text{high } \Phi_S \qquad (19)$$

Equations 18 and 19 provide a full description of the swelling of the brush. Here, we highlight several

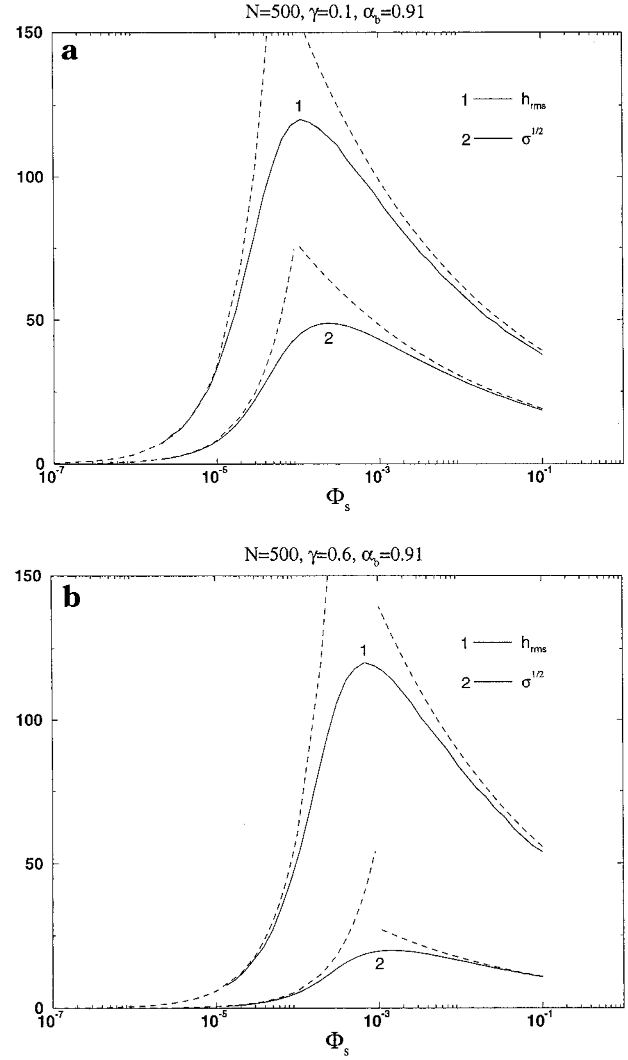

Figure 1. Dependence of the root-mean-squared height of the brush, h_{rms}, and the distance between chains, $\sigma^{1/2}$, as a function of the salt concentration, Φ_S. The full curves were calculated through eq 38, and the dashed curves correspond to the asymptotic behavior given by eq 23. Scaling arguments neglect numerical coefficients; thus, the dashed curves can be arbitrarily shifted up or down. Here, we plotted the dashed curves close to the solid lines to clearly demonstrate the similarity in behavior. The plot in (a) is for a flexible surface, or $\gamma = 0.1$. In (b), the surface is relatively rigid and $\gamma = 0.6$. In both curves, $N = 500$ and $\alpha_b = 0.91$.

interesting features, which will be discussed in greater depth below.

1. h is a nonmonotonic function of Φ_S: These results are qualitatively the same as those for σ = constant; however, the exponents are different.
2. σ is also a nonmonotonic function of Φ_S, increasing at low Φ_S and decreasing at high Φ_S.
3. Comparing h with the linear, lateral dimension $\sigma^{1/2}$ shows that the swelling of the brush is isotropic with respect to an increase in Φ_S.
4. At high and low Φ_S, h and σ have different dependencies not only on Φ_S and α_b but also on N and γ.
5. At high Φ_S, a polyacid brush behaves in the same way as a neutral brush. This can be seen by comparing eqs 18, 19, and 15.

Below, we detail each of these characteristics.

Dependence on Φ_S. As in the case of a polyacid brush grafted onto a rigid surface (σ = constant),[9,11] the dependence of h on Φ_S in the case of an elastic substrate is nonmonotonic. As can be seen from eq 18, h is an increasing function of Φ_S at low Φ_S, $h \sim \Phi_S$ (instead of $h \sim \Phi_S^{1/3}$ for σ = constant), and h is a decreasing function of Φ_S at high Φ_S, $h \sim \Phi_S^{-1/5}$ (instead of $h \sim \Phi_S^{-1/3}$ for σ = constant). Although the exponents are different, the qualitative behavior is the same in both cases. In the case of an elastic surface, an increase in h with Φ_S (at low Φ_S) is slower and a decrease (at high Φ_S) is more rapid than that in the case of a rigid surface.

Figures 1a and 1b show the dependencies of $h(\Phi_S)$ and $\sigma(\Phi_S)$ at low and high salt concentrations. The transition from one regime to the other occurs at the value of Φ_S that is the intersection of the two asymptotes for $h(\Phi_S)$ (or $\sigma(\Phi_S)$) (see eqs 18 and 19). This gives

$$\Phi_S \sim \frac{\gamma(1-\alpha_b)^{5/6}}{N\alpha_b^{1/2}} \qquad (20)$$

Note that this transition point is the same for both h and σ. The values of h and σ corresponding to the maximum of the curves for $h(\Phi_S)$ and $\sigma(\Phi_S)$ are

$$h^{\max} \sim N\alpha_b^{1/2}/(1-\alpha_b)^{1/6} \qquad (21)$$

$$\sigma^{\max} \sim N\gamma^{-1}\alpha_b/(1-\alpha_b)^{1/3} \qquad (22)$$

It follows from eq 19 that the dependence of σ on Φ_S is also nonmonotonic; i.e., it is an increasing function of Φ_S at low Φ_S and a decreasing function of Φ_S at high Φ_S, displaying qualitatively the same behavior as $h(\Phi_S)$.

When we compare the perpendicular (normal) dimension $d_\perp = h$ to the linear, lateral dimension, $d_\parallel = \sigma^{1/2}$, it appears that both h and $\sigma^{1/2}$ have the same power-law dependence on Φ_S:

$$d_\perp = h = k_\perp^{l}\Phi_S, \qquad \text{low } \Phi_S$$

$$d_\parallel = \sigma^{1/2} = k_\parallel^{l}\Phi_S, \qquad \text{low } \Phi_S \qquad (23a)$$

$$d_\perp = h = k_\perp^{h}\Phi_S^{-1/5}, \qquad \text{high } \Phi_S$$

$$d_\parallel = \sigma^{1/2} = k_\parallel^{h}\Phi_S^{-1/5}, \qquad \text{high } \Phi_S \qquad (23b)$$

where

$$k_\perp^{l} \sim N^2\gamma^{-1}\,\alpha_b/(1-\alpha_b), \qquad \text{low } \Phi_S$$

$$k_\parallel^{l} \sim N^{3/5}\gamma^{-3/2}\alpha_b/(1-\alpha_b), \qquad \text{low } \Phi_S \qquad (24a)$$

$$k_\perp^{h} \sim \alpha_b^{2/5}N^{4/5}\gamma^{1/5}, \qquad \text{high } \Phi_S$$

$$k_\parallel^{h} \sim \alpha_b^{2/5}N^{3/10}\gamma^{-3/10}, \qquad \text{high } \Phi_S \qquad (24b)$$

Thus, both the sizes h and $\sigma^{1/2}$ change with Φ_S according to the same power law but with different coefficients ($k_\parallel$, $k_\perp$). Figures 1a and 1b show the behavior of $h(\Phi_S)$ and $\sigma^{1/2}(\Phi_S)$ for $\gamma = 0.1$ and $\gamma = 0.6$, $\alpha_b = 0.91$. The full curves were calculated according to Appendix 1, and the dashed curves were calculated according to eqs 18 and 19. The plots reveal good agreement between the asymptotes and full curves. As can be seen, h and $\sigma^{1/2}$ indeed follow the same power-law dependence.

The isotropic dependence of the sizes h and $\sigma^{1/2}$ on Φ_S is the result of the isotropy of the osmotic pressure, which is the leading force swelling the polyacid brush.

Since the osmotic pressure is isotropic, the system's response should also be isotropic. In particular, the stretching energy of the brush in the lateral and normal directions should be equal:

$$h^2/N \sim \gamma\sigma \tag{25}$$

This readily gives

$$h/\sigma^{1/2} \sim (\gamma N)^{1/2} \tag{26}$$

Equation 26 shows, indeed, that h and $\sigma^{1/2}$ have different dependences only on γ and N and that they should have the same dependences on Φ_S and α_b. Note that this result should be the same for brushes with any isotropic interactions, such as the osmotic pressure of an ion gas or polymer−solvent interactions.

Although the brush swells isotropically with respect to salt concentration, Φ_S, the absolute changes in h and $\sigma^{1/2}$ are different depending on the elasticity of the surface, γ, and molecular weight of the chains, N (see eq 26). This result becomes clear if we recall that γ and $1/N$ are essentially the spring constants for the brush stretching in the normal and lateral directions, respectively.

Dependence on γ and N. As shown in eq 26, the ratio $h/\sigma^{1/2}$ is a function of γN only and does not depend on the salt concentration, Φ_S, or on the pH (α_b). Here, we can consider two limits: $\gamma N \gg 1$ and $\gamma N \ll 1$. The first limit, $\gamma N \gg 1$, corresponds to a surface that is much less flexible than the chains. In other words, the spring constant of the surface, γ, is much higher than that of the chains, $1/N$. In this situation, changes in h are more pronounced than in $\sigma^{1/2}$ (see eqs 23 and 24 and Figure 1a). Here, the height of the brush increases (or decreases) whereas the distance between the chains stays approximately the same.

The other limiting case of $\gamma N \ll 1$ corresponds to a surface that is much more flexible than the chains. In particular, the spring constant of the surface, γ, is much lower than that of the chains, $1/N$. This leads to more pronounced changes in $\sigma^{1/2}$ than in h (see eqs 23 and 24 and Figure 1b). Here, only the lateral dimension of the brush increases, whereas the height of the brush does not experience pronounced changes. However, when the surface is highly flexible and sufficiently stretched, the chains no longer overlap and the system no longer behaves as a polymer brush. For the chains to overlap, σ must be less than R_g^2. For Gaussian chains, this implies that $\sigma < N$. Coupling this restriction with eq 22, we have that $\sigma^{\max} \sim N\gamma^{-1}\alpha_b/(1 - \alpha_b)^{1/3} < N$, which implies that $\alpha_b/(1 - \alpha_b)^{1/3}$ should be less than γ. In the limit that $\gamma N \ll 1$, this stipulation becomes $\alpha_b/(1 - \alpha_b)^{1/3} \ll 1/N$. Hence, only at very low values of α_b will chains tethered to a highly flexible surface overlap and retain their brushlike structure. At relatively high values of α_b ($> 1/N$), the polyacid chains will only overlap at very low and high salt concentration, far from the maximum in the curve for $\sigma^{1/2}(\Phi_S)$. At intermediate salt concentrations, the polymers will behave as single chains under the corresponding conditions.

There is another interesting dependence on γ: it follows from eq 18 that h is an increasing function of γ at low Φ_S and a decreasing function of γ at high Φ_S. This allows one to control the brush height by changing γ, which can be altered, for example, by varying temperature.

Dependence on pH. Here we introduce pH through the variable, $\alpha_b = 1/(1 + \exp(\mathrm{p}K_a - \mathrm{pH}))$. As a reminder, an increase in α_b corresponds to an increase in the pH. It follows from eqs 18 and 19 that both sizes h and $\sigma^{1/2}$ are increasing functions of α_b. Nevertheless, the power laws are different for high and low Φ_S: at low Φ_S, both sizes increase rapidly, $h \sim \sigma^{1/2} \sim \alpha_b/(1 - \alpha_b)$, and at high Φ_S, they increase slowly, $h \sim \sigma^{1/2} \sim \alpha_b^{2/5}$.

Conclusions

In various controlled-release devices, polyacids are grafted to the surface of membranes or porous substrates.[6] Such substrates are relatively flexible and their pliability will affect the conformation of the tethered chains. This, in turn, will affect the permeability and effectiveness of the polymer-coated device. To characterize this effect, we incorporated the elasticity of the surface and a lateral stretching energy into our expression for the free energy of the system. The findings show that the surface elasticity, γ, affects not only the lateral spacing between the chains but also the height of the brush. Thus, the results demonstrate that the flexibility of the substrate should be considered in designing polyacid-coated assemblies for controlled release. The results also show how variations in pH and salt concentration couple with γ to control the equilibrium properties of the grafted layer. In effect, the equations relating h and σ to these variables provide a prescription for tailoring the structure and the permeability of the system.

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Appendix 1. Vertical Inhomogeneity

Up to this point, we assumed that all the ends of the chains are located at the same height; i.e., we described the brush by its average characteristics. Here, we consider the vertical inhomogeneity of the brush. This means that we allow chains to be stretched nonuniformly and we take into account the distribution of chain ends $g(z)$ in the direction normal to the surface, z.[19] In this case, all intrinsic characteristics of the brush, such as α, φ, etc., become dependent on z. In particular, the general form of eqs 1−11 remains the same, but the variables are expressed as functions of z. For example, the dependence of $\varphi(z)$ on $\alpha(z)$ is now written as

$$\varphi(z) = \frac{1 - \alpha(z)}{\alpha^2(z)} \frac{\alpha_b}{1 - \alpha_b} - \frac{1}{1 - \alpha(z)} \frac{1 - \alpha_b}{\alpha_b} \tag{27}$$

In this approach, the full expression for the free energy per chain should be written in the integral form:

$$F = F_{\mathrm{str}} + \sigma\int_0^h f(z)\,\mathrm{d}z + \gamma\sigma \tag{28}$$

where

$$f(z) = \varphi(z)\ln(1 - \alpha(z)) \tag{29}$$

and σ can be obtained from the normalization condition:

$$\int_0^h \varphi(z)\,\mathrm{d}z = N/\sigma \tag{30}$$

The stretching energy term in eq 28 can be written according to ref 19 in the form

$$F_{\mathrm{str}} = (3/2\sigma)\int_0^h g(z)\,\mathrm{d}z\int_0^z E(x,z)\,\mathrm{d}x \qquad (31)$$

where $E(x,z)$ relates the local stretching of the chain at height x, assuming that the chain end is located at a height z:[19]

$$E(x,z) = (\pi/2N)\,(z^2 - x^2)^{1/2} \qquad (32)$$

The relationship between $g(z)$, $E(x,z)$, and $\varphi(x)$ is given by

$$\varphi(x) = \sigma\int_x^h g(z)/(E(x,z))\,\mathrm{d}z \qquad (33)$$

When this expression is taken into account, the stretching energy, eq 31, has the form

$$F_{\mathrm{str}} = \sigma\int_0^h k^2x^2\varphi\,(x)\,\mathrm{d}x \qquad (34)$$

where

$$k^2 = 3\pi^2/8N^2 \qquad (35)$$

In this way, the free energy, eq 28, is a functional of $\varphi(x)$, which in turn is a function of $\alpha(x)$, as given by eq 27. The variation of the functional ΔF with respect to unknown volume fraction $\varphi(x)$ gives (see ref 11)

$$\alpha(x) = 1 - (1 - \alpha_{\mathrm{b}})\exp(k^2(h^2 - x^2)) \qquad (36)$$

Equations 28−30, 34, and 36 allow one to write ΔF in the form

$$\Delta F = N(\ln(1 - \alpha_{\mathrm{b}}) + k^2h^2) + \gamma N/(\int_0^h\varphi(x,H)\,\mathrm{d}x)^2 \qquad (37)$$

Minimizing ΔF with respect to h, with eqs 27 and 36 taken into account, gives

$$(\int_0^h\varphi(x,h)\,\mathrm{d}x)^2 = \gamma\int_0^h((\alpha(x) - 1)(\delta\varphi)/(\delta\alpha))\,\mathrm{d}x \qquad (38)$$

We solve this equation numerically and introduce the results in the form of the plots of $h(\Phi_{\mathrm{S}})$ and $\sigma^{1/2}(\Phi_{\mathrm{S}})$ (see Figures 1a and 1b).

It is interesting to note that eq 34 for the stretching energy can be written in the form

$$F_{\mathrm{str}} = k^2h_{\mathrm{rms}}^2/N \qquad (39)$$

where h_{rms}^2 is the root-mean-square height of the brush:

$$h_{\mathrm{rms}}^2 = \int_0^h z^2\varphi(z)\,\mathrm{d}z/\int_0^h\varphi(z)\,\mathrm{d}z \qquad (40)$$

In this way, the total free energy ΔF is given by the expression

$$\Delta F = k^2h_{\mathrm{rms}}^2/N + N\,\overline{\ln\,(1 - \alpha)} + \gamma\sigma \qquad (41)$$

and is identical to the scaling expression, eq 13, with the only difference being in the coefficient k^2. This means that both approaches should yield qualitatively the same behavior for the average characteristics. Nevertheless, eq 38 can be solved for all values of the salt concentration, while we can use the scaling approach only in the limiting cases of low and high salt concentrations. We use eq 38 to calculate the full curves for $h(\Phi_{\mathrm{S}})$ and $\sigma^{1/2}(\Phi_{\mathrm{S}})$ in Figures 1a and 1b.

References and Notes

(1) Urry, D. W. *Angew. Chem.* **1993**, *105*, 859.
(2) Urry, D. W. *Prog. Biophys. Mol. Biol.* **1992**, *57*, 23.
(3) Urry, D. W.; Shao, Q. P. *J. Am. Chem. Soc.* **1995**, *117*, 8478.
(4) Thomas, J. L.; You, H.; Tirrell, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 2949.
(5) Israels, R.; Gersappe, D.; Fasolka, M.; Roberts, V. A.; Balazs, A. C. *Macromolecules* **1994**, *27*, 6679.
(6) Errede, L. A. *J. Colloid Interface Sci.* **1984**, *100*, 414. Errede, L. A. *J. Membr. Sci.* **1984**, *20*, 45. Barbucci, R.; Casolaro, M.; Magnani, A. *J. Controlled Release* **1991**, *17*, 79. Hirotsu, T. *Ind. Eng. Chem. Res.* **1987**, *26*, 1287. Ito, Y.; Inaba, M.; Chung, D.-J.; Imanishi, Y. *Macromolecules* **1992**, *25*, 7313. Ito, Y.; Kotera, S.; Inaba, M.; Kono, K.; Imanishi, Y. *Polymer* **1990**, *31*, 2157. Niwa, M.; Mukai, A.; Higashi, N. *Langmuir* **1990**, *6*, 1432.
(7) Bergbreiter, R., private communications. Dagani, R. *Chem. Eng. News* **1995**, *18*, 30.
(8) Israels, R.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B. *Macromolecules* **1994**, *27*, 3249.
(9) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491.
(10) Misra, S.; Varanasi, S. *J. Colloid Interface Sci.* **1991**, *146*, 251.
(11) Lyatskaya, Yu. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562.
(12) Miklavic, S. J.; Marselja, S. J. *J. Phys. Chem.* **1988**, *92*, 6718.
(13) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 4173.
(14) Pincus, P. *Macromolecules* **1991**, *24*, 2912.
(15) Borisov, O. V.; Birshtein, T. M.; Zhulina, E. B. *J. Phys. II Fr.* **1991**, *1*, 521.
(16) Zhulina, E. B.; Borisov, O. V.; Birshtein, T. M. *J. Phys. II Fr.* **1992**, *2*, 63.
(17) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1994**, *27*, 4795.
(18) Alexander, S. *J. Phys.* **1977**, *38*, 983. De Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069. Birshtein, T. M.; Zhulina, E. B. *Polym. Sci. USSR (Engl. Transl.)* **1983**, *25*, 2165. Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453. Skvortsov, A. M.; Gorbunov, A. A.; Pavlushkov, I. V.; Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A. *Polym. Sci. USSR (Engl. Transl.)* **1988**, *30*, 1706. Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A.; Birshtein, T. M. *Macromolecules* **1991**, *24*, 140. Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413. Milner, S. T. *Europhys. Lett.* **1988**, *7*, 695. Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(19) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733.

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