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Theory of Ionizable Polymer Brushes

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ABSTRACT: The mean-field theory describing the conformation of an ionizable polymer chain (weak polyacid or polybase) grafted at one end onto an impermeable planar surface and immersed into a water–salt solution is presented. The dependences of the brush thickness and degree of chain ionization on grafting density and ionic strength of the solution are analyzed. It is shown that the annealing of the brush affects the brush structure mostly at low ionic strength of the solution and relatively sparse grafting. The nontrivial effect of an increase in the brush thickness with decreasing grafting density and/or increasing ionic strength is predicted.

1. Introduction

Due to the long-range character of electrostatic interactions, even weak charging of macromolecules can lead to qualitatively new features in the behavior of polymer systems. A typical example of such systems is polyelectrolyte gels.[1–2] Polyelectrolyte brushes and mesogels, which were considered rather recently,[3–7] also demonstrate new regularities of behavior with respect to the corresponding neutral systems.

Up to now theoretical analysis of polyelectrolyte brushes was restricted mainly to the so-called quenched case, when the degree of charging of the grafted chains was fixed and independent of external conditions. One can envision such a situation for a random or regular copolymer of a neutral component B and a strong electrolyte (for example, a strong acid) A. The composition $f = N_A/(N_A + N_B)$, where N_A and N_B are the total numbers of units A and B, respectively, determines then the degree of ionization of such a polyelectrolyte $\alpha = f$, provided that all electrolyte groups are charged. Grafting of such chains onto a surface does not change the degree of charging of a chain, and one obtains a polyelectrolyte brush with quenched charge.

One can envision, however, another situation when the degree of ionization of a chain can vary adjusting to the variation of the external conditions. A typical example of such a polyelectrolyte is a weak polyacid (polybase). The degree of ionization of a weak polyacid is determined by the concentration of protons and, thus, can be varied, for example, by the variation of pH of the solution. Moreover, α depends on the pH values inside the brush and hence will be rather sensitive also to the other parameters of the system (grafting density, ionic strength of solution, etc.). Equilibration of such a system needs, thus, the adjustment of the degree of ionization of polyelectrolyte chains in the brush to the external conditions, and we shall call such a brush an annealed brush. So far, only two papers with numerical investigations of the properties of annealed brushes are available. Reference 8 presents some numerical results of the analytical self-consistent field theory, whereas the analysis of ref 9 is based on the Scheutjens–Fleer numerical model. The effect of annealing for an individual polyion under poor solvent conditions was considered recently by Raphael and Joanny.[10]

In this paper we focus our attention on a planar brush formed by long homopolyacid chains with varying degrees of ionization (annealed brush) and analyze in scaling terms the dependences of the brush thickness (polyion stretching) and degree of chain ionization on the grafting density and ionic strength of the solution. As will be shown below, the annealed polyelectrolyte brush exhibits some qualitatively different features in behavior in comparison with the quenched one. The most spectacular effect consists of the nonmonotonic dependence of the brush thickness on the grafting density and the ionic strength of the solution.

After a brief description of our models of quenched and annealed polyelectrolyte brushes (section 2) and formulation of the basic charge and force balance equations (section 3), we compare the behavior of quenched and annealed brushes under the conditions of salt-free and salt-added solutions (section 4) and discuss our results in section 5.

2. Model

We consider a layer formed by long polyelectrolyte chains consisting of N symmetrical monomer units of the size a grafted at one end onto an impermeable planar surface with the grafting density $1/\sigma$ chains per unit area (Figure 1). The chains are assumed to be flexible, so that the Kuhn segment of a chain l is equal to a, $l = a$, and the Bjerrum length $l_B = e^2/(\epsilon T)$ is of the order of magnitude of a chain unit length $l_B/a \simeq 1$.

We will be interested only in the scaling type analysis of the polyelectrolyte brush characteristics. In this case, as in our previous analysis of a quenched brush,[6] it is sufficient to use a simple box model according to which all the chains in the brush are stretched homogeneously and their free ends are localized at the outer boundary of the brush (Alexander[11]–de Gennes[12] model).

In the quenched case, the fixed average degree of ionization α of the grafted chains was assumed. In our case of the annealing system, we assume that the grafted chains are weak homopolyacids $(HA)_N$. (The generalization for the case of a weak polybase is straightforward.) The dissociation of acid groups is governed by its dissociation constant K_D and by the concentration of H^+ ions in solution inside the brush (see below).

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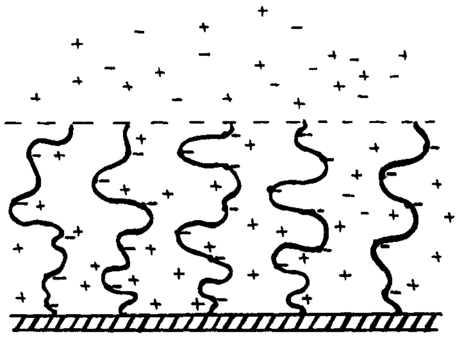


Figure 1. Charged brush in solution.

We assume that the brush is immersed in an infinite reservoir of water (dimensions of the water molecule are supposed to be a), which besides H^+ and OH^- ions contains also the fixed concentrations of monovalent ions of different chemical nature (Na^+, Cl^-, etc). We will not deal with the dimensions of these mobile ions, considering them as dimensionless charges. This approximation is usual in the theories of dilute electrolyte solutions. It takes into account only the electrostatic interactions between charges and neglects their steric interactions. We will use the molar concentrations C_i of ions (the number of ions in the unit volume; standard units, mol/L) as a characteristic of the system. The bulk solution can be characterized by the fixed concentration C_{H^+} of H^+ ions (or by pH = $-\log C_{H^+}$) and by the ionic strength

$$I = {}^1\!/_2 \sum_i C_i = {}^1\!/_2 (C_+ + C_-)$$

where $C_+ = \sum_i C_{i^+}$ and $C_- = \sum_i C_{i^-}$ are the total molar concentrations of positively and negatively charged ions in the bulk solution.

3. Brush Electroneutrality Condition

According to the theory[5,6,8] and modeling[13] of quenched polyelectrolyte brushes, the most generally presented regimes of brush behavior are characterized by brush electroneutrality.

In this case we have two electroneutral subsystems: the brush and the bulk solution, separated by the semipermeable membrane. These subsystems are in equilibrium; i.e., there are both charge and force balances.

A. Charge Balance. The average degree of ionization α of grafted polyacid chains inside the brush

$$HA = H^+ + A^-$$

is related to the value of the dissociation constant K_D according to the active mass law

$$\frac{\alpha}{1-\alpha} = \frac{K_D}{c_{H^+}} \tag{1}$$

where

$$\alpha = \frac{n_{A^-}}{n_{A^-} + n_{AH}}$$

is the fraction of charged groups, c_{H^+} is the concentration (activity) of protons inside the brush (we will use large C_i and small c_i for molar concentrations of ions in the bulk solution and inside the brush, respectively), and the dimensionality of K_D is equal to that of c_{H^+}. Let us ignore for simplicity the possible dependence of K_D on α (polyelectrolyte effect) and suppose that K_D is constant.

Let us suppose that c_p is the molar concentration of polymer units (charged and uncharged in the brush), $c_p = \varphi/a^3$, where φ is the polymer volume concentration. The brush electroneutrality provides the dependence of the total concentrations c_- and c_+ of negatively and positively charged mobile ions in the brush ($c_- = \sum_i c_{i^-}$, $c_+ = \sum_i c_{i^+}$; the different i correspond to chemically different ions) on the molar concentration of "immobilized" charge αc_p,

$$\alpha c_p + c_- = c_+ \tag{2}$$

Evidently, for bulk solution we have

$$C_- = C_+ \tag{3}$$

The conditions of electroneutrality (2) and (3) of the brush and of the solution indicate that mobile ions are redistributed in the brush with respect to the solution: $c_i \neq C_i$. This redistribution occurs due to the existence of the excess electrostatic potential Ψ in the brush with respect to the bulk of solution. The Boltzmann law then gives for the distribution of the ions

$$c_{i^-} = C_{i^-} \exp(e\Psi/kT) \tag{4}$$

$$c_i^{\,+} = C_{i^+} \exp(-e\Psi/kT) \tag{5}$$

Thus, the ratios of the concentrations of the different positively charged ions inside and outside the brush are equal to each other and are inverse to that for negatively charged ions (Donnan rule); i.e.

$$c_{i^+}/C_{i^+} = C_{j^-}/c_{j^-} > 1 \tag{6}$$

From the Donnan rule (eq 6) and the electroneutrality condition (eq 2), we have for the total concentration of mobile ions inside the brush

$$(c_+ + c_-)^2 = \alpha^2 c_p^{\,2} + 4C_+C_- \tag{7}$$

Note that eqs 2–7 are independent of the structure of subsystem with immobilized charges (we use the term "brush" in this section only for simplicity) and contain only the dependence on the concentration of these charges. They are valid also for both the "quenched" degree of ionization α and for the "annealed" α according to eq 1.

It is essential, however, that this annealed α not only affects the ion redistribution, eqs 2–7, but also depends on this redistribution via the c_{H^+} value (eq 1).

To analyze this effect let us restrict ourselves to the typical case, assuming that the bulk solution is pure or salted water at pH = 7, i.e., a solution of H^+ and OH^- ions, $C_{H^+} = C_{OH^-} = C_H{}^* = 10^{-7}$ mol/L, and salt ions $C_{S^+} = C_{S^-} = C_S$ (for example, Na^+ and Cl^- ions). In this case $C_+ = C_- = C_S + C_H{}^*$.

Taking into account the ionization equilibrium (eq 1) and the Donnan rule (eq 6), the electroneutrality condition inside the brush, immersed in pure or salted water is reduced to

$$\frac{K_D}{C_H{}^*}\frac{1-\alpha}{\alpha} - \frac{C_H{}^*}{K_D}\frac{\alpha}{1-\alpha} = \frac{\alpha c_p}{C_S + C_H{}^*} \tag{8}$$

or

$$\frac{\alpha_B}{1-\alpha_B}\frac{1-\alpha}{\alpha}-\frac{1-\alpha_B}{\alpha_B}\frac{\alpha}{1-\alpha}=\frac{\alpha c_p}{C_H{}^*+C_S} \qquad (8')$$

where $\alpha_B > \alpha$ is the degree of ionization of a single polymeric chain immersed in the bulk solution; $\alpha_B/(1-\alpha_B) = K_D/C_H{}^*$ (see eq 1). It can be seen from eq 8′ that the degree of ionization of the brush α is always smaller than that of an individual polyacid molecule in the bulk of the solution α_B. This is due to the effect of concentration of protons: their average concentration in the brush is higher than in the bulk of the solution and, correspondingly, the chains in the brush are less charged. The total concentration of mobile ions inside the brush, eq 7, is

$$(c_+ + c_-)^2 = \alpha^2 c_p{}^2 + 4(C_H{}^* + C_S)^2 \qquad (9)$$

Equations 8 and 9 give us the dependences of α, c_+, and c_- on the polymer characteristic K_D (or α_B), the brush characteristic c_p, and the external characteristic C_s. The dependence of α on these characteristics is especially pronounced in the limiting case $\alpha \ll 1$, $\alpha c_p \gg C_s$. For larger C_S and α the dependences $\alpha(\varphi)$ and $\alpha(C_S)$ vanish and $\alpha = \alpha_B$:

$$\alpha \cong \left(\frac{\alpha_B}{1-\alpha_B}\frac{C_H{}^*+C_S}{c_p}\right)^{1/2} \qquad \alpha c_p \gg C_S + C_H{}^*, \alpha \ll 1 \qquad (10a)$$

$$\alpha \cong \alpha_B \qquad \alpha c_p \ll C_S \qquad (10b)$$

It is interesting to note that in the bulk solution α_B does not depend on the salt concentration C_S. The increase in α with increasing C_S is related to the substitution of H^+ ions by Na^+ ions inside the brush. As a result c_{H^+} tends to $C_H{}^*$, and α tends to α_B.

B. Force Balance. To obtain the equilibrium value of the polymer molar c_p or volume $\varphi = c_p a^3$ concentration, we consider the balance of various forces applied to grafted chains: the elastic force f_{conf} arising in the stretched chains, the force f_{conc} due to the nonelectrostatic (volume) interactions between polymer units, and, finally, the electrostatic force f_{ion} due to the electrostatic interactions between charged units. The electrostatic force f_{ion} as well as the force f_{conc} tend to stretch the grafted chains in the direction normal to the surface, whereas the elastic force, f_{conf}, opposes this stretching. The force balance is given by

$$f_{conf} = f_{conc} + f_{ion} \qquad (11)$$

Assuming Gaussian elasticity for the grated chains, corresponding to the mean-field picture of a brush, one has

$$f_{conf}/kT \cong H/Na^2 = a/(\sigma\varphi) \qquad (12)$$

$$f_{conc}/kT \cong v\varphi^2\sigma/a^3 + w\varphi^3\sigma/a^3 \qquad (13)$$

where H is the average thickness of the brush, $\varphi = Na^3/(\sigma H)$ is the average concentration (volume fraction) of monomer units ($\varphi = \varphi_A + \varphi_{HA}$), and va^3 and wa^6 are the second and third virial coefficients of volume interaction between monomers. The electrostatic force f_{ion} is approximately equal to the difference in the osmotic pressure of mobile ions inside and outside the brush (see refs 5, 6, and 8 for details)

$$f_{ion}/kT \cong \sigma\Delta\pi_{ion} = \sigma(c_+ + c_- - C_+ - C_-) \qquad (14)$$

For the brush immersed in a salt–water solution, we have according to eq 9

$$f_{ion}/kT = \sigma\left\{\left[\left(\frac{\alpha\varphi}{a^3}\right)^2 + 4(C_H{}^* + C_S)^2\right]^{1/2} - 2(C_H{}^* + C_S)\right\} \qquad (15)$$

This formula for f_{ion} is valid for both the "quenched" α and the "annealed" α obtained from solution of eq 8.

In the polyelectrolyte regimes of the brush behavior the force f_{conc} due to the short-range volume interactions is weak compared to the electrostatic force f_{ion}, and, hence, the force balance (eq 11) has the form

$$f_{conf} \cong f_{ion} \qquad (16)$$

Using eqs 12, 15, and 16, we obtain the polymer concentration φ in a brush as a function of the brush characteristics α and σ and the bulk solution characteristic C_S

$$\varphi \cong a^2\sigma^{-1}\alpha^{-1/2} \qquad C_H{}^* + C_S \ll \alpha\varphi/a^3 \qquad (17a)$$

$$\varphi \cong a^{7/3}C_S{}^{1/3}\alpha^{-2/3}\sigma^{-2/3} \qquad C_S \gg \alpha\varphi/a^3, C_H{}^* \qquad (17b)$$

The brush height $H = (Na^3)/(\sigma\varphi)$ scales as

$$H \cong Na\alpha^{1/2} \qquad C_H{}^* + C_S \ll \alpha\varphi/a^3 \qquad (18a)$$

$$H \cong N(a^2\alpha^2\sigma^{-1}C_S{}^{-1})^{1/3} \qquad C_S \gg \alpha\varphi/a^3, C_H{}^* \qquad (18b)$$

These scaling type formulas characterize the brush properties in two different regimes. Equation 17a and 18a correspond to the so-called osmotic regime OsB[6] in which the concentration of salt in bulk solution is small and the concentration of counterions inside the brush is equal to that of the immobilized charge.

Equations 17b and 18b at $\alpha = \alpha_B$ correspond to the so-called salted brush regime SB,[6] in which salt ion charges dominate compared to the immobilized charges inside the brush due to the high concentration of salt in the bulk of solution.

Let us compare the brush behavior in these regimes for the quenched and annealed α cases.

4. Brushes with Quenched and Annealed Degree of Ionization

A. OsB, Os̃B, and SB Regimes. Formulas 17 and 18 are quite general and are applicable both for brushes with fixed α (quenched α) and for ionizable brushes (annealed α).

In the case of quenched α, these formulas provide the final result: the scaling dependences of φ and H on α.[5,6,8]

In the case of annealed α, the problem is more complicated, because not only φ depends on α, according to eq 17, but also α itself depends on φ, according to eqs 8 and 10. Therefore it is necessary to combine these dependences.

Substituting α from eq 10a into eq 17a, we find new scaling dependences for the polymer concentration φ and thickness H of the annealed polyelectrolyte brush at $\alpha\varphi/a^3 \gg C_H^* + C_S$

$$\varphi = a^{5/3}\sigma^{-4/3}\left(\frac{1-\alpha_B}{\alpha_B}\frac{1}{C_H^* + C_S}\right)^{1/3} \qquad (19)$$

$$H = Na^{4/3}\sigma^{1/3}\left(\frac{\alpha_B}{1-\alpha_B}(C_H^* + C_S)\right)^{1/3} \qquad (20)$$

(Note that the condition $\alpha \ll 1$ in eq 10a is equivalent to the condition $[\alpha_B/(1 - \alpha_B)]\,(C_H^* + C_S) \ll (a\sigma)^{-1}$). We will refer to this regime as the Os̃B regime to distinguish it from the corresponding OsB regime for quenched α. Although both the electrostatic force f_{ion} and the brush thickness H scale with α similarly to that in the quenched case, the dependence of α itself on C_S and φ provides the new features in the annealed brush behavior: H increases with both increasing σ and C_S. For a quenched brush in the OsB regime, H is independent (within scaling approximation) of both σ and C_S (eq 18a).

At high ionic strengths $C_S \gg \alpha\varphi/a^3$ (SB regime) when the degree of brush ionization becomes practically constant (and virtually coincides with that in the bulk solution, $\alpha \cong \alpha_B$, eq 10b), the difference between the annealed and quenched brushes disappears. Thus, in the SB regime the scaling behavior of the quenched and annealed brushes is similar (eqs 17b and 18b), and one can find the difference only on the level of nonpower dependences.

Note that in the SB regime we also have the dependence of H on σ and C_S: H increases with decreasing σ and/or C_S. In other words, the degree of brush expansion in solution increases with increasing grafting density $1/\sigma$ and decreasing ionic strength of solution. It is quite usual behavior. In contrast to this "normal" behavior is the "anomalous" behavior of the annealed brush in the Os̃B regime, where the degree of brush expansion decreases with increasing grafting density $1/\sigma$ and decreasing ionic strength. This "anomaly" is connected with the decrease of ionization degree α. From eqs 10a and 19 we have at $\alpha \ll 1$

$$\alpha \cong \left[\frac{\alpha_B}{1-\alpha_B}a\sigma(C_H^* + C_S)\right]^{2/3} \qquad (21)$$

B. Diagram of State. Salt-Free Case. So far, we have analyzed only the OsB and SB regimes of the brush behavior. Let us compare now the behavior of the quenched and annealed brushes in all other regimes of the total diagram of state.

Figure 2 shows the scaling-type diagram of state of the quenched polyelectrolyte brush in salt-free water (assumed to be a good solvent ($v = (T - \theta)/T > 0$) for uncharged chains[8,13]). In addition to the OsB regime in the central part of the diagram, it incorporates four other regimes, separated from each other by the crossover lines. In the right part of the diagram at large σ values (low grafting density) two regimes of isolated grafted chains are located. At small α where the intrachain electrostatic interactions are weak compared to the intrachain volume interactions $f_{ion} \ll f_{conc}$, the regime of grafted individual neutral coils (NC) (mushroom regime) is located. At higher α it is bordered by the region IS of isolated grafted polyions stretched due to intramolecular Coulomb repulsion. These polyions are oriented either in the part OrS of this region or in the entire region due to long-range intermolecular repulsion and polarization effects (see ref 8 and Appendix I for details). The thickness of the polymer layer in these two regimes scales as the end-to-end dimensions of individual chains

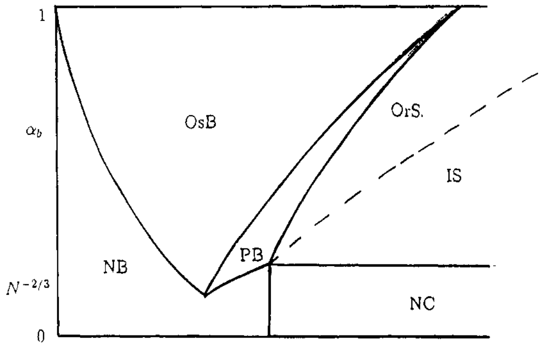


Figure 2. Scaling type diagram of state of a quenched polyelectrolyte brush in salt-free water in σ/a^2, $\alpha = \alpha_B$ coordinates. The OrS region is separated from the IS region (see Appendix I).

$$H_{NC} = aN^{3/5}v^{1/5} \qquad (22)$$

$$H_{IS} = aN\alpha^{2/3} \qquad (23)$$

In the left part of the diagram at low α or at high grafting density $1/\sigma$ the regime NB of the quasineutral brush is located, where the intermolecular electrostatic interactions are weak compared to the intermolecular volume interactions, $f_{ion} \ll f_{conc}$. The brush thickness in this regime scales as that of the uncharged brush

$$H_{NB} = aN(va^2/\sigma)^{1/3} \qquad (24)$$

Finally, in contrast to the boundary (crossover) line between the NC and NB regimes of quasineutral behavior (corresponding to the chain overlapping condition), the diagram of state contains the intermediate narrow region PB (Pincus regime[5]) in between the main region of the charged brush OsB and the region of individual polyions IS. In the PB regime as in the OsB regime, the chains are overlapped but the pictures of the mobile ion distribution in these regimes are different. Sufficiently large values of α and $1/\sigma$ in the OsB regime are responsible for the high electrostatic potential which confines the counterions inside the brush. Only a small fraction of all counterions $q \cong r_D/H \ll 1$ (where $r_D = a^{3/2}(l_B\alpha\varphi)^{-1/2}$ is the Debye–Hückel screening length determined by the concentration of counterions inside the brush) leaves the brush and is localized in the thin layer of the thickness r_D outside it. The brush, thus, is virtually electroneutral.

Under the condition of the PB regime (lower α and $1/\sigma$ values) the mobile counterions are distributed in space above the grafting surface so that the characteristic length scale of this distribution (Guoy–Chapman length)

$$\lambda = \frac{\sigma}{l_B N\alpha} \qquad (25)$$

is much higher than the brush thickness H, which in this regime scales as[5,8]

$$H_{PB} = a^2 l_B N^3\alpha^2\sigma^{-1} \qquad (26)$$

Let us consider now the change of this diagram due to brush annealing. As was already shown, the OsB regime for quenched α transforms into a new Os̃B regime for annealed α with the change in the character of the brush thickness dependence on the parameters (cf. eqs 18 and 20). The reason is that α itself is involved in the system equilibration.

The same reason can cause the transformation of all other regimes in the annealed α case. It is easy to see, however, that there is no change in scaling equations for the brush thickness for the cases of the quasineutral behavior, regimes NC and NB (because H scales as α^0). Thus, the effect of brush annealing remains to be investigated in the PB regime, $\lambda \gg H$. As a result of this investigation (see section 4D), we obtain for the degree of ionization in the PB regime in a salt-free solution (assuming $\alpha \ll 1$)

$$\alpha_{P\tilde{B}} = \left[\frac{\alpha_B}{1-\alpha_B}\sigma^2 C_H^*/N^2 l_B\right]^{1/3} \qquad (27)$$

Correspondingly, eq 26 is transformed into

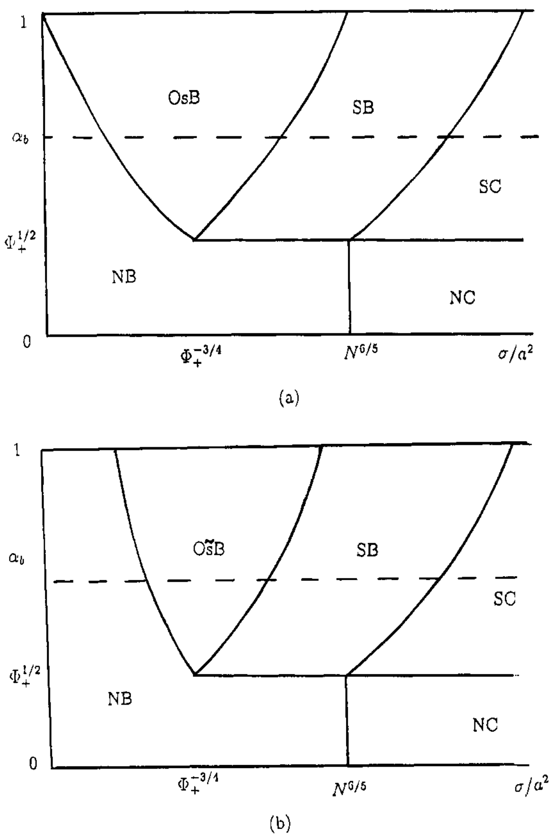
$$H_{P\tilde{B}} = a^2 N^{5/3}\left[\frac{\alpha_B}{1-\alpha_B}C_H^*\right]^{2/3}(l_B\sigma)^{1/3} \qquad (28)$$

It is seen from eqs 27 and 28 that in the annealed PB regime (PB̃ regime), as in the Os̃B regime, α (and H) are increasing functions of σ. Moreover, α scales with σ in a similar manner in these two regimes. The physical origin of this effect in the PB̃ regime is the same as in the Os̃B regime: in looser brushes the concentration of protons is smaller and, correspondingly, the degree of ionization and the brush thickness are higher. However, the scaling dependences of α and H on the other parameters are different in the Os̃B and PB̃ regimes, indicating the different physical pictures of a polyelectrolyte brush in these regimes.

The change in the scaling dependences of the brush characteristics in the ionizable brush (compared to the brush with quenched charges) leads to the change in the form of the different regions located on the diagram of state. The crossover lines between the regions are displaced and their orientations are changed. For example, due to the same scaling of H with σ in the Os̃B and PB̃ regimes, the boundary between these regimes (crossover line) became parallel to the σ axis.

The additionally strong deformation of the diagram is connected to the fact that, as distinct from the quenched case, where the α axis gives us the degree of ionization inside the brush, in the annealed case we can specify only the α_B values. As follows from the results obtained, in the Os̃B and PB̃ regimes we have $\alpha \ll \alpha_B$, and to satisfy the condition of the occurrence of the Os̃B and PB̃ regions, it is necessary to have sufficiently high ionization degree for the free chain, $1 - \alpha_B \ll 1$. Hence in the case of the ionizable brush in pure water, the regions of polyelectrolyte behavior Os̃B and PB̃ are small and are located in the upper part of the (σ,α_B) diagram. The main part of this diagram belongs to the regions of quasineutral behavior or/and individual chain behavior. It will be analyzed in detail elsewhere.

C. Salt-Added Solution. As was shown above, the degree of ionization α in a brush increases and tends to α_B when salt is added to the bulk solution. As a result, the difference between the diagrams of state of the ionizable and quenched brushes becomes smaller. Figure 3 presents the corresponding diagrams in the case of moderate salt content ($C_S > N^{-6/5}a^{-3}$). In both cases the PB/PB̃ region disappears and a broad SB region (salt dominance region) appears between the OsB/Os̃B regime and the regime of the isolated charged chain in salted water (SC). The brush annealing results in the substitution of the OsB regime partly by the Os̃B regime and partly by the NB regime. The localization of all other regimes (SB, NC, and SC) is retained.



(a)

(b)

Figure 3. Scaling-type diagrams of state of a quenched (a) and annealed (b) polyelectrolyte brush in the salt-added solution; $I \gg N^{-6/5}a^{-3}$. The designation Φ_+ on the axes signifies $\Phi_+ = (C_H^* + C_S)a^3$.

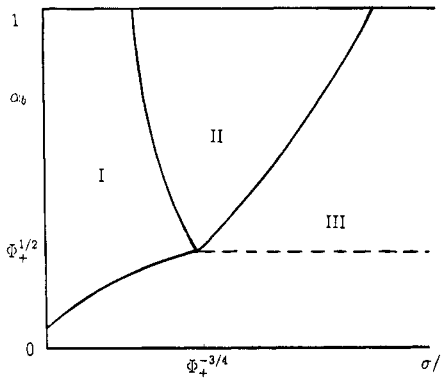


Figure 4. Scaling-type diagram of ionization of the annealed polyelectrolyte brush (see text). $\Phi_+ = (C_H^* + C_S)a^3$; $I \gg N^{-6/5}a^{-3}$.

Figure 4 demonstrates the scaling-type diagram of brush ionization at the same conditions ($C_S > N^{-6/5}a^{-3}$) as Figure 3 and with the same coordinates as Figures 2 and 3b. Three different regions are distinguishable. At high grafting densities $1/\sigma$ we have a quasineutral NB regime, where the nonelectrostatic interactions determine the brush structure. Nevertheless, the α value is not constant in this regime due to its dependence on polymer concentration via the c_H dependence

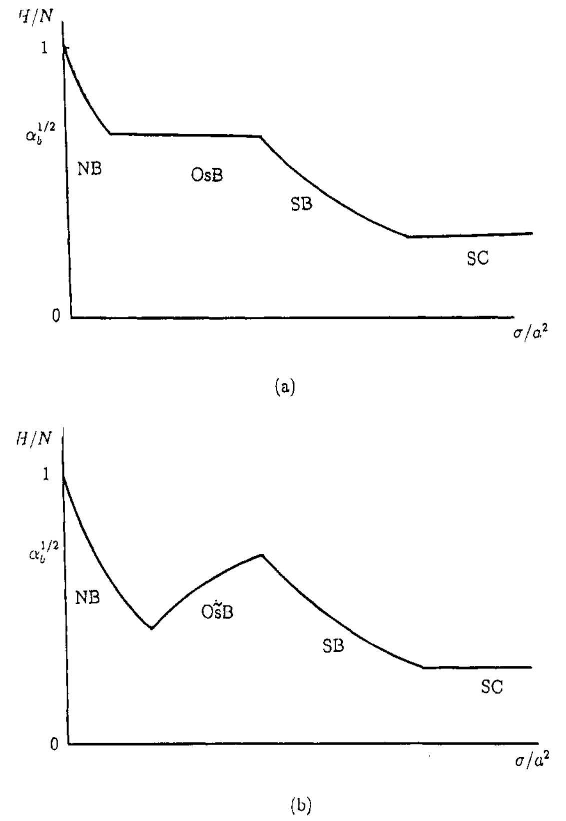


Figure 5. Schematic dependence of the polyelectrolyte brush thickness on the grafting density for quenched (a) and annealed (b) cases corresponding to the intersections of the diagrams of state at Figure 3.

on this concentration (see section 3). For the NB regime

$$\varphi \equiv c_p a^3 = (\sigma/a^2)^{-2/3} v^{-1/3} \qquad (29)$$

and according to eq 10a, we have in region I

$$\alpha = \left[\frac{\alpha_B}{1 - \alpha_B}(C_H{}^* + C_S)a^3\right]^{1/2} (\sigma/a^2)^{1/3} v^{1/6} \qquad (30)$$

With increasing σ and the transition to more sparse brushes, α increases. If $\alpha_B/(1 - \alpha_B) < (C_H{}^* + C_S)^{1/2}a^{3/2}$, the brush retains its quasineutral behavior up to $\alpha \cong \alpha_B$ (region III below the dashed line). If $\alpha_B/(1 - \alpha_B) > (C_H{}^* + C_S)^{1/2}a^{3/2}$, the increase in σ leads to the transition into the Os̃B regime (Figure 3b), where φ and α are given by eqs 19 and 21. WIth further increase in σ, α reaches its limiting bulk value α_B (upper part of region III).

Figure 5 demonstrates the differences in scaling dependences $H = H(\sigma)$ for annealed and quenched brushes corresponding to the intersections of the diagrams (shown by the dashed lines in Figure 3) at the same values of $C_H{}^* + C_S$ and α_B. As the quenched brush passes successively through the NB–OsB–SB–SC regimes, the brush thickness H either diminishes with σ (NB and SB regimes) or stays virtually constant (OsB and SC regimes). For an annealed brush passing through the NB–Os̃B–SB–SC regimes, the brush thickness H passes through a minimum and a maximum with increasing σ. Whereas H decreases with increasing σ in the NB and SB regimes (just as in the quenched brush case), in the Os̃B regime H increases with σ according to eq 18 and exhibits a maximum in the vicinity of the boundary between the Os̃B and SB regimes. Within the scaling approximation the value of this maximum, H_{max}, coincides with the quenched brush thickness in the OsB regime, $H_{max} = H_{OsB} = aN\alpha_B{}^{1/2}$. However, due to the general effect of weakening of the electrostatic interactions in the annealed brush, the value of the numerical coefficient, omitted in the scaling dependence, is expected to be somewhat smaller than in a quenched system.

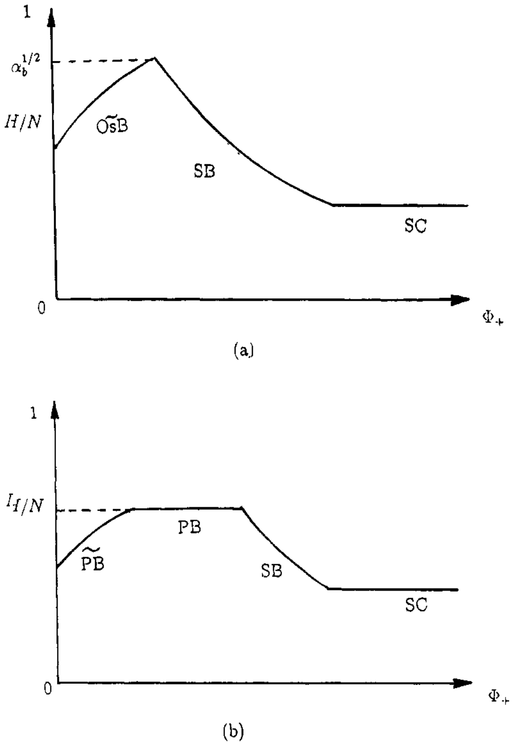


Figure 6. Schematic dependence of the annealed polyelectrolyte brush thickness on the ionic strength of the solution. The grafting density corresponds to the Os̃B regime (a) or to the P̃B regime (b) in the salt-free solution. $\Phi_+ = (C_H{}^* + C_S)a^3$.

Even more surprising appears to be the nonmonotonic dependence of the annealed brush thickness on the ionic strength of the solution I (Figure 6a): at high ionic strength conventional decrease in the brush thickness due to the screening of electrostatic interactions can be observed, while at low ionic strength (in the Os̃B and P̃B regimes) H increases with I. This is in pronounced contrast to the case of a quenched brush, where the brush thickness remains virtually independent of I at low salt concentration (dashed line in Figure 6a). The origin of the increase in the annealed brush thickness in the range of low ionic strength of the solution was shown above: the addition of salt ions into the solution leads to the substitution of H^+ ions in the brush by Na^+, reducing the local proton concentration in the brush and thus causing its additional ionization.

D. Annealed "Pincus" Brush Regime (P̃B). Let us consider the effect of brush annealing under the conditions of the PB regime corresponding to relatively small ionic strengths of the solution and $\lambda = \sigma/\alpha N l_B \gg H$, where λ is the characteristic length scale for the distribution of ions near the charged surface (the surface charge density is equal to $\varrho = N\alpha/\sigma$). In Appendix II we present the simple scaling-type estimation of this length in salt–water solution. According to eq A2.5 in the case when the salt concentration is not too large, λ does not approximately depend on C_S and is given by eq 25. The average concentration of counterions inside the λ layer is

$$c_+ \cong \frac{\alpha N}{\sigma \lambda} = \frac{\alpha^2 N^2 l_B}{\sigma^2} \tag{31}$$

and the concentration of H$^+$ ions is given by the Donnan rule

$$c_H = C_H{}^* \frac{c_+}{C_+} = \frac{\alpha^2 N^2 l_B}{\sigma^2} \frac{C_H{}^*}{C_H{}^* + C_S} \tag{32}$$

Taking into account that α is related to c_H via conventional dependence eq 1

$$\frac{\alpha}{1-\alpha} = \frac{K_D}{c_H} = \frac{C_H{}^*}{c_H} \frac{\alpha_B}{1-\alpha_B}$$

we obtain for the degree of ionization in the P$\tilde{B}$ regime (assuming $\alpha \ll 1$)

$$\alpha = \left[\frac{\alpha_B}{1-\alpha_B} \frac{\sigma^2 (C_H{}^* + C_S)}{N^2 l_B}\right]^{1/3} \quad (\mathrm{P\tilde{B}}) \tag{33}$$

Correspondingly, eq 26 transforms into

$$H_{\mathrm{P\tilde{B}}} = a^2 N^{5/3} \left[\frac{\alpha_B}{1-\alpha_B}(C_H{}^* + C_S)\right]^{2/3} [l_B \sigma]^{1/3} \tag{34}$$

As follows from eqs 25 and 33, the screening length

$$\lambda \cong \left[\frac{\sigma}{N l_B{}^2 (C_H{}^* + C_S)} \frac{1-\alpha_B}{\alpha_B}\right]^{1/3} \tag{35}$$

decreases with increase in C_S and, as follows from eq A2.5, tends to the Debye screening length r_{Db} in bulk solution $r_{Db} = (l_B(C_H{}^* + C_S))^{-1/2}$, which being larger than λ also decreases with increase in C_S. At $C_S = l_B N^2(\alpha_B/(1-\alpha_B))^4 \sigma^{-2}$ both screening lengths become of the same order of magnitude. Here the degree of brush ionization approaches its bulk value, $\alpha = \alpha_B$, and at higher values of C_S one finds the conventional PB regime where H scales according to eq 26. Further behavior of an annealed Pincus brush coincides with that of a quenched system. The PB regime of the brush holds in the range of C_S providing $H \ll r_D$. At $r_D \ll H$ the brush passes into the SB regime (eq 18). The dependence of H on C_S for an annealed Pincus brush is presented schematically in Figure 6b. Just as in the O$\tilde{s}$B regime this dependence exhibits a nonmonotonic behavior. However, in contrast to the latter case, a plateau at the $H(I)$ curves corresponding to the maximum value of the brush thickness can be observed.

5. Discussion

The above results indicate that annealing of a polyelectrolyte brush provides new surprising features of brush behavior. These features are most evident in sparse brushes at low ionic strengths. Due to the fact that under these conditions the average concentration of protons in the brush is sufficiently higher than in solution, the ionization process is suppressed and $\alpha \ll \alpha_B$. Correspondingly, in an annealed system the electrostatic stretching force is more weak and brush thickness H is smaller than in a quenched brush. The concentration of protons in the brush can be affected by the variation of both the ionic strength I of the outer solution and the grafting density $1/\sigma$. In the former case the addition of ions to the solution at a fixed value of pH leads to the redistribution of the corresponding ions and protons inside the brush, so that the concentration of protons in the brush diminishes and α increases. In the latter case when $C_S \simeq 0$ and σ increases, the average concentration of protons in the brush decreases following the decrease in concentration of polymer units $\varphi = Na^3/\sigma H$, and α also increases. An increase in α with increasing C_S and σ in the O$\tilde{s}$B and P$\tilde{B}$ regimes (eqs 21 and 27) provides the nonmonotonic dependence of H on C_S and σ (Figures 5 and 6). For the osmotic brush the maximum is localized at the boundary between the O$\tilde{s}$B and SB regimes, and its value corresponds to the thickness of a quenched brush,

$$H_{\max} = aN\alpha_B{}^{1/2} \tag{36}$$

Under the condition of the Pincus regime, this maximum is transformed into a plateau with the plateau value

$$H_{\mathrm{plateau}} = \alpha_B{}^2 N^3 a^2 l_B / \sigma \tag{37}$$

corresponding to the thickness of a quenched brush. This plateau is expected in the range of C_S providing the value of the Debye–Hückel radius $H \ll r_D \ll \lambda$.

At high ionic strengths of solution the concentrations of ions inside and outside the brush are virtually the same and the degree of brush ionization coincides with its bulk value, $\alpha = \alpha_B$. Under these conditions the behavior of quenched and annealed brushes is hardly distinguishable.

The existence of the maximum in the dependence of some inherent characteristic brush dimension on the salt concentration has been predicted also by a recent self-consistent field numerical calculation[8,9,14] incorporating the direct solution of the Poisson–Boltzmann equation for the distribution of free charges in the system and taking into account the intrinsic structure of the brush. The increase in brush thickness with decreasing grafting density at low ionic strengths was also reported in refs 9 and 14. The detailed analysis carried out in ref 16 demonstrated that the account of intrinsic brush structure does not affect the main conclusions of this work. The predicted effects—"anomalous" dependencies of brush dimensions on the grafting density and ionic strength in the range of small ionic strengths of solution (OsB regime)—are still rather noticeable. However, they refer not to the overall brush thickness, but certain averaged characteristics, for example, weight-averaged brush thickness, which is just the moment of inertia of units with respect to the grafting surface. More detailed discussion of these results will be presented elsewhere.[16]

Experimental verification of the predicted relationships of the annealed brush behavior could be performed by the variation of the ionic strength of the solution I. For given values of α_B and σ one expects to observe the manifestation of the O$\tilde{s}$B regime of the brush behavior in the range of I providing

$$H_{\mathrm{NB}} \ll H_{\mathrm{O\tilde{s}B}} \ll H_{\max}$$

which corresponds to

$$a^4 \alpha_B{}^{-1} \sigma^{-2} \ll Ia^3 \ll a^2 \alpha_B{}^{1/2} \sigma^{-1}$$

Thus, the nonmonotonic dependence of the brush thickness on the ionic strength is expected to be more pronounced for moderately dense brushes. For example, for $\alpha_B \cong 10^{-1}$ and $\sigma/a^2 \cong 10^4$ the range of I given by inequality 38 corresponds to $10^{-7} \leq Ia^3 \leq 3 \times 10^{-5}$, i.e., sufficiently wide for the realization of the asymptotic dependence (20).

Note that to estimate the ionic strength I in usual units (mole/liter) it is necessary to use an a^3 value in unusual units (liter/mole). It is easy to see that $a^3 = 6 \times 10^{-4}\, \tilde{a}^3$ (Å) L/mol, where $\tilde{a}$ is the dimension in angstroms of the chain segments and of the solvent molecules. At $a = 5-7$ Å, $a^3 \cong 0.1-0.2$ L/mol.

A certain experimental problem can arise in connection with the realization of the good or Θ solvent conditions for the polyelectrolyte chain. Typically, water is a poor solvent for the uncharged monomer units of a polyacid and the addition of salt can cause the collapse of the brush.[6] To avoid this difficulty, one can use the random copolymer of a weak acid and a neutral water-soluble polymer (for example, POE) which will ensure the solubility of the macromolecule over a wide range of ionic strength.

Finally, it is worth noting that the predicted effect of the nonmonotonic dependence of chain stretching on the ionic strength of the solution can be observed also for such systems as polyelectrolyte networks and mesogels with an ionizable central block.[9]

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Appendix I. Orientation of Individual Grafted Polyions in the IS Region (Salt-Free Solution)

Individual polyelectrolyte chains in salt-free solution are stretched due to long-range electrostatic repulsion and appear as sticks of blobs with end-to-end dimensions $H = N a \alpha^{2/3}$. If these sticks of blobs are attached at one end onto an impermeable planar surface, they retain this conformation in the IS regime but may be randomly oriented in half-space or strongly oriented perpendicular to the surface. Investigating the diagram of state of brushes with a quenced degree of ionization α, we analyzed the orientation of polyions caused by the electrostatic interactions between them.[8] In this case the IS region is subdivided into a region of randomly oriented sticks (IS region in Figure 2), where the chains are grafted so sparsely that the interaction between them is negligible, and a region of sticks oriented perpendicular to the surface (OrS region in Figure 2).

The conclusion about the random orientation of polyions in the IS subregime is valid only in the absence of electrostatic interactions between this polyion and the surface, providing the dielectric constant, ϵ_S, of the surface is equal to that of bulk solvent, $\epsilon_S = \epsilon$. In the opposite case the polarization of the environment, induced by the polyion, is not the same above and below the surface (interface). This is equivalent to the appearance of an image charge $Q' = Q(\epsilon - \epsilon_S)/(\epsilon + \epsilon_S)$ interacting with the polyion, where $Q = N\alpha$. If $\epsilon \gg \epsilon_S$ (the case of water solution), the image charge $Q' \cong Q$ repels the polyion with the force

$$f_{\mathrm{el},\perp}/T \cong \frac{Q'Q}{H_\perp^{\,2}} \cong \frac{Q^2}{H_\perp^{\,2}} \tag{A1.1}$$

which causes very strong polyion orientation perpendicular to the grafting surface in the whole IS region (see ref 15 for details).

Appendix II. Screening of a Charged Plane in a Salt–Water Solution

In the Pincus brush (PB) regime the brush thickness H is small compared to the surface screening length λ (the characteristic length of the mobile ion distribution near the charged plane surface). Let us investigate the simple scaling-type dependence of λ on the surface charge density ϱ (in our case as above we suppose that the immobilized charge is negative) $\varrho = N\alpha/\sigma$ and the characteristics of solution l_B, $C_H{}^*$, and C_S.

Let us formulate the simplest naive picture of a charged plane screening:

1. The charged layer exists near the surface which compensates the surface charge. The system surface + layer is electroneutral.
2. The layer is in equilibrium with the bulk solution. This defines the concentrations of mobile ions inside the layer.
3. The concentration of mobile ions inside the layer defines its thickness, which is equal to the Debye–Hückel screening length associated with this concentration.

Hence we have (cf. section 3A) the following:

1. The electroneutrality condition (cf. eq 2)

$$c_+ = c_- + \varrho/\lambda \tag{A2.1}$$

where λ is the layer thickness and c_+ and c_- are the "+" and "−" mobile ion concentrations inside the layer

2. The equilibrium condition (Donnan rule) (cf. eqs 7 and 9)

$$(c_+ + c_-)^2 = \frac{\varrho^2}{\lambda^2} + 4C_+C_- = \frac{\varrho^2}{\lambda^2} + 4(C_H{}^* + C_S)^2 \tag{A2.2}$$

where $C_+ = C_- = C_H{}^* + C_S$ are the concentrations of mobile ions in the bulk solution

3. The Debye–Hückel formula

$$\lambda = [l_B(c_+ + c_-)]^{-1/2} \tag{A2.3}$$

From (A2.1–A2.3) it follows that

$$l_B{}^2\lambda^4\left[4(C_H{}^* + C_S)^2 + \frac{\varrho^2}{\lambda^2}\right] = 1 \tag{A2.4}$$

and

$$\lambda \cong \frac{1}{\varrho l_B} = r_{\mathrm{Do}} \qquad \varrho/\lambda \gg C_H{}^* + C_S \tag{A2.5a}$$

$$\lambda \cong \frac{1}{[l_B(C_H{}^* + C_S)]^{1/2}} = r_{\mathrm{Db}} \qquad \varrho/\lambda \ll C_H{}^* + C_S \tag{A2.5b}$$

where $r_{\mathrm{Do}} = (\varrho l_B)^{-1}$ and r_{Db} are the Debye–Hückel radii associated with the counterions of the charged surface and with the salt ions in the bulk solution, respectively.

References and Notes

(1) Tanaka, T.; Fillmore, D.; Sun, S.; Nishio, I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636.
(2) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982**, *77*, 5725.
(3) Miklavic, S. J.; Marcelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.
(4) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 4173.
(5) Pincus, P. *Macromolecules* **1991**, *24*, 2912. Ross, R.; Pincus, P. *Macromolecules* **1992**, *25*, 1503.
(6) Borisov, O. V.; Birshtein, T. M.; Zhulina, E. B. *J. Phys. II*, **1991**, *1*, 521; **1992**, *2*, 63; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 1016; *Macromolecules* **1994**, *27*, 4795.
(7) Zhulina, E. B. *Macromolecules* **1993**, *26*, 6273.
(8) Misra, S., Varanasi, S. *J. Colloid Interface Sci.* **1991**, *146*, 251.
(9) Israels, R.; Leermakers, F.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3087.
(10) Raphael, E.; Joanny, J.-F. *Europhys. Lett.* **1990**, *N13*, 623.
(11) Alexander, S. *J. Phys.* **1977**, *38*, 983.
(12) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(13) Israels, R.; Fleer, G. J.; Leermakers, F. A. M.; Zhulina, E. B. *Macromolecules* **1994**, *27*, 3249.
(14) Israels, R. Adsorption of Charged Diblock Copolymers: Effect on Colloidal Stability. Thesis, Wageningen Agricultural University, 1993.
(15) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *J. Phys. II Fr.* **1994**, *4*, 913.
(16) Lyatskaya, Yu. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules*, submitted.

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