

A Theoretical Investigation on the pH-induced Switching of Mixed Polyelectrolyte Brushes*

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Abstract A theoretical investigation on the pH-induced switching of mixed polyelectrolyte brushes was performed by using a molecular theory. The results indicate that the switching properties of mixed polyelectrolyte brushes are dependent on the pH values. At low pH, negatively charged chains adopt a compact conformation on the bottom of the brush while positively charged chains are highly stretched away from the surface. At high pH values, the inverse transformation takes place. The role of pH determining the polymer chains conformation and charge behavior of mixed polyelectrolyte brushes was analyzed. It is found that there exists a mechanism for reducing strong electrostatic repulsions: stretching of the chains. The H^+ and OH^- units play a more important role as counterions of the charged polymers do. The collapse of the polyelectrolyte chains for different pH values could be attributed to the screening of the electrostatic interactions and the counterion-mediated attractive interaction along the chains.

Keywords: Mixed polyelectrolyte brushes; Molecular theory; pH-induced switching.

INTRODUCTION

Mixed polyelectrolyte brushes composed of two oppositely charged homopolymers represent a special case of responding surfaces. Due to particular sensitivity to pH and ion concentration in aqueous environment, mixed polyelectrolyte brushes are especially promising for control of adsorption, adhesion, wetting and many biotechnological applications^[1–4]. Therefore, the properties of mixed polyelectrolyte brushes have been intensively investigated experimentally^[5–12].

Theoretical treatments of mixed polyelectrolyte brushes have employed mean-field arguments^[13], electrostatic free energy descriptions^[14] and self-consistent-field analysis^[15]. Shusharina and Linse^[13] discussed the influence of the charges of the blocks, the relative length of the oppositely charged blocks and the ionic strength of the solution on the brush inhomogeneity and structural differences between the two types of brushes. Biesheuvel and Cohen-Stuart^[14] presented a theory to describe the electrostatic free energy change when ionizable molecules form a macroscopic polyelectrolyte complex. Witte and Won^[15] presented a theoretical study of the phase behaviors of mixed brushes composed of charged and noncharged polymers that are mutually incompatible. They found that an increase in the effective charge on the polyelectrolyte favors the mixed state, while increasing the grafting density favors phase separation.

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Although a number of theoretical studies have focused on surface properties of a mixed polyelectrolyte brush controlled by composition and charge ratio, no theoretical investigation on the pH-induced switching of mixed polyelectrolyte brushes has been reported. Experimentally, a mixed polyelectrolyte brush consisting of two oppositely charged weak polyelectrolytes, poly(2-vinyl pyridine) (P2VP) and poly(acrylic acid) (PAA), was reported^[1, 5]. Such a mixed brush can provide new possibilities to control surface properties with a pH signal.

In this paper, we will investigate the pH-induced switching of mixed polyelectrolyte brushes using a molecular theory^[16–18]. Our aim is to explore the switching properties, and to explain the mechanism of switching that is responsive to pH in mixed polyelectrolyte brushes. The remainder of this paper is organized as follows: In Section 1, we describe the molecular theory; In Section 2, we present relevant results, focusing on the effect of pH in mixed polyelectrolyte brushes; In the last Section, we give discussions and draw conclusions about the switching behavior depending on pH in mixed polyelectrolyte brushes.

Model and Methods

In order to create a mixed polyelectrolyte brushes system, we assume two species are homogeneously grafted onto the substrate surface defined as the $x - y$ plane at $z = 0$. Our model system contains seven species, which are referred to as (A) positively charged polymer chains, (B) negatively charged polymer chains, cation, anion, H^+ , OH^- and (W) solvent. We write the free energy of the mixed polyelectrolyte brushes system containing equal amounts of species A and B chains exposed to solvent, which explicitly includes the size, shape, and conformation of every molecule. We assume the two components have identical chain length N_p and segment volume v_p . They are tethered onto the substrate surface, and can be allowed only in the $z \geq 0$ half-space. The number of tethered chains per unit area is $\sigma_A = \sigma_B = N_p/A_r$. We assume that the only inhomogeneous direction is the one perpendicular to the substrate surface, that is, the z direction. The free energy per unit area of mixed polyelectrolyte brushes in solution is given by

$$\begin{aligned}
 \frac{\beta F}{A_r} = & \sum_{i=A,B} \{ \sigma_i \sum_{\alpha} P_i(\alpha) \ln P_i(\alpha) + \int \langle \rho_{pi}(z) \rangle [f_i(z) (\ln f_i(z) + \beta \mu_{i,\pm}^0) \\
 & + (1 - f_i(z)) \ln(1 - f_i(z)) + \beta \mu_i^0] dz \} + \int \sum_{\gamma=W,+, -, H^+, OH^-} \rho_{\gamma}(z) [\ln(\rho_{\gamma}(z) v_{\gamma}) - 1] dz \\
 & + \sum_{i=A,B} \left\{ \frac{l_B}{2} \iint U(|z - z'|) f_i(z) f_i(z') \langle \phi_{pi}(z) \rangle \langle \phi_{pi}(z') \rangle dz dz' \right. \\
 & \left. - l_B \iint U(|z - z'|) f_i(z) \langle \phi_{pi}(z) \rangle \langle \phi_c(z') \rangle dz dz' \right\} \\
 & + \int \left[\langle \rho_q(z) \rangle \beta \psi(z) - \frac{1}{2} \beta \epsilon \left(\frac{\partial \psi}{\partial z} \right)^2 + \lambda \langle \rho_q(z) \rangle \right] dz \\
 & + \int \beta \pi(z) \left[\sum_{i=A,B} \langle \phi_{pi}(z) \rangle + \sum_{\gamma=W,+, -, H^+, OH^-} \rho_{\gamma}(z) v_{\gamma} \right] dz
 \end{aligned} \tag{1}$$

The first term in the above sum represents the conformational entropy of the charged polymer chains, where $P_i(\alpha)$ ($i = A, B$) is the probability distribution function (PDF) of finding a chain in conformation α . The polymer volume fraction profile is given by

$$\langle \phi_{pi}(z) \rangle dz = \sigma_i \sum_{\alpha} P_i(\alpha) v_p(z; \alpha) dz \tag{2}$$

where $v_p(z; \alpha)$ denotes the volume that a polymer chain in conformation α contributes in the layer between z and $z + dz$. The second and third terms together represent the chemical free energy of the acid-base equilibrium. The standard chemical potentials of charged and uncharged monomers are $\mu_{i,\pm}^0$ and μ_i^0 respectively. The fourth term in Eq. (1) represents the translational entropy of the different mobile species molecules, where $\rho_{\gamma}(z)$ ($\gamma = W, +, -, H^+, OH^-$) are the local number density of the corresponding free species, while v_{γ} is the volume of the corresponding molecule. The fifth term in the total free-energy expression of Eq. (1) represents the Coulombic

interactions between the monomers of the chain. The sixth term in Eq. (1) accounts for the Coulombic interactions between the counterions and the chain, where l_B is Bjerrum length, $U(|z-z'|)$ is the Coulomb potential^[19] and $\phi_c(z) = \rho_c(z)v_c$ is the counterions local volume fraction. In this paper, the H^+ and OH^- are considered as counterions, since we study the pH-responsive mixed polyelectrolyte brushes. The seventh term integral in Eq. (1) represents the electrostatic contribution^[20]. ϵ is the dielectric constant of the solution, $\psi(z)$ is the electrostatic potential at z , and $\langle \rho_q(z) \rangle$ is the total average charge density at z , given by

$$\langle \rho_q(z) \rangle = \sum_{i=A,B} f_i(z) \frac{\langle \phi_{pi}(z) \rangle}{v_p} q_{pi} + \sum_{\gamma=+, -, H^+, OH^-} \rho_\gamma(z) q_\gamma \quad (3)$$

where the quantity q_{pi} represents the electric charge of the protonated and deprotonated polymer chains, while $q_\gamma (\gamma = +, -, H^+, OH^-)$ denotes the electric charge of the various charged free species. The last term in Eq. (1) represents the repulsive interactions of the system, where $\pi(z)$ represents the position-dependent pressure fields. We now impose two physical constraints to the free energy in Eq. (1). First, the incompressibility constraint that accounts for the inter-molecular repulsions (excluded volume) in the system. Namely, at each distance from the surface, z , the total volume must be completely filled by some of the molecular species, *i.e.*,

$$\sum_{i=A,B} \langle \phi_{pi}(z) \rangle + \sum_{\gamma=W,+, -, H^+, OH^-} \rho_\gamma(z) v_\gamma = 1 \quad (4)$$

Secondly, we require the system to be globally electroneutral, *i.e.*

$$\int \langle \rho_q(z) \rangle dz = 0 \quad (5)$$

Minimization of the free energy with respect to $P_i(\alpha) (i = A, B)$ yields

$$\begin{aligned} P_i(\alpha) = & \frac{1}{Q_i} \exp \left[-\frac{l_B}{2} \iint U(|z-z'|) f_i(z) f_i(z') \langle \phi_{pi}(z') \rangle n_i(\alpha; z) dz dz' \right. \\ & + l_B \iint U(|z-z'|) f_i(z) n_i(\alpha; z) \langle \phi_c(z') \rangle dz dz' \\ & - \beta \int \psi(z) q_{pi} n_i(\alpha; z) dz - \int n_i(\alpha; z) \ln(1 - f_i(z)) dz \\ & \left. - \beta \int \pi(z) n_i(\alpha; z) v_p dz \right] \end{aligned} \quad (6)$$

Where Q_i is a normalization constant ensuring that $\sum_\alpha P_i(\alpha) = 1$. $n_i(\alpha; z) dz$ is the number of monomer units located at z when the chain is in conformation α .

Minimizing Eq. (1) yields the following equilibrium expressions for the density profiles of free species:

$$\rho_i(z) = \exp[-\beta \pi(z) v_i - \beta \psi(z) q_i - l_B \int U(|z-z'|) f_i(z) n_i(\alpha; z) v_i dz], \quad (7)$$

$$\phi_w(z) = \exp[-\beta \pi(z) v_w], \quad (8)$$

where $q_i = \pm e$ is the charge of ion i in the bulk solution. For the electrostatic potential, we get a generalized Poisson-Boltzmann equation:

$$\frac{\partial^2 \psi}{\partial z^2} = -\frac{1}{\epsilon} \langle \rho_q(z) \rangle \quad (9)$$

where $\langle \rho_q(z) \rangle$ is given by Eq. (3), and both densities and PDF depend on the strongly coupled electrostatic and pressure fields, $\psi(z)$ and $\pi(z)$. The expression for the fraction^[20] of charged polymer segments at z is

$$\frac{f_i(z)}{1 - f_i(z)} = -\frac{\phi_{H^+}(z)}{K_a^0 \phi_w(z)} \quad (10)$$

In the bulk solution the acid-base equilibrium is determined by the equilibrium constant, K_a^0 [20]. The unknowns in the above equations are the position dependent electrostatic and pressure fields. These quantities are determined by substituting Eqs. (6–10) into the packing constraints of Eqs. (4–5). Detailed numerical methodology can be found in Refs [16–18].

RESULTS AND DISCUSSION

In this section, we present some representative results for the pH responsive properties of mixed polyelectrolyte brushes.

First, we quantify the average fraction of charged polyelectrolyte monomers. It can be defined^[21, 22] by the polymer volume fraction, *i.e.*,

$$\langle f_i \rangle = \frac{\int \langle \phi_p(z) \rangle f_i(z) dz}{\int \langle \phi_p(z) \rangle dz} \quad (11)$$

The apparent pK_a of the polyelectrolyte *A* and *B*, pK_{ai} ($i = A, B$), is defined as the pH at which the average fraction of charged polyelectrolyte monomers is one-half, *i.e.*, $\langle f_i \rangle (pH = pK_{ai}) = \frac{1}{2}$ [21]. This means that half of the polyelectrolyte monomers are charged if the bulk pH is equal to pK_{ai} . Therefore, whether pH is increased or decreased, pK_{ai} always gives the transition.

By using $\langle f_i \rangle$ and pK_{ai} , we quantify the charging behavior of the mixed polyelectrolyte brushes in response to changes in external stimuli, as shown in Fig. 1. Figure 1(a) presents the average fraction of charged polymer monomers as a function of pH. More importantly, we find that the transition between the charged and uncharged polymer occurs over a broad range of pH. This is because the polyelectrolyte chains have more degrees of freedom to respond to varying pH, which can only change the fraction of charged polymer monomers as a consequence of a variation in pH. Figure 1(b) gives pK_{ai} versus the grafting density, σ_i , at different pH. In the case of a low grafting density, most polyelectrolyte B molecules are deprotonated if the solution pH is larger than the acid-base equilibrium constant of the monomer's acid groups, pK_{aB} . However, most polyelectrolyte A molecules are protonated if the solution pH is lower than the acid-base equilibrium constant of the monomer's acid groups, pK_{aA} . Increasing the grafting density would result in larger electrostatic attraction between polyelectrolyte A and B, which is favorable for many A and B monomers within the brushes to remain charged at the cost of the free energy of the acid-base reaction. In the case of a high grafting density, on the contrary, increasing the grafting density would result in very little free volume. Because of the limited available volume,

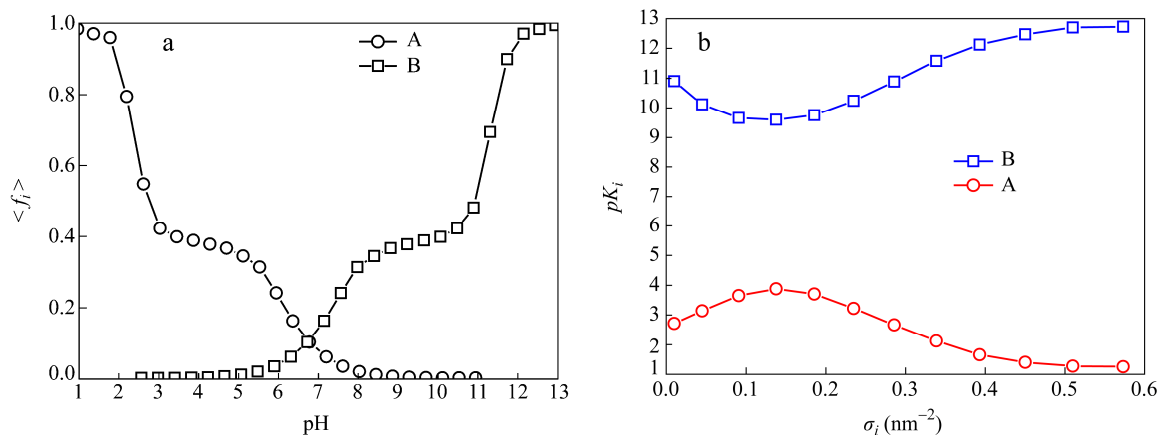


Fig. 1 Charging behavior of the mixed polyelectrolyte brushes: (a) the average fraction of charged polyelectrolyte A and B monomers as a function of bulk pH (The grafting density is $\sigma_i = 0.1 \text{ nm}^{-2}$) and (b) apparent pK_{ai} ($i = A, B$) of the polyelectrolyte A and B as a function of the grafting density

charged chains must extend from the surface due to repulsion with simultaneous loss of entropy of the counterions. To gain greater entropy and to reduce the energy cost from repulsion will be favorable for many monomers within the brushes remaining uncharged. Thus, in the case of a low grafting density, the more compressed the polyelectrolyte is, the more favorable to increase the number of charged monomers it becomes, while in the case of a high grafting density, the situation is quite the opposite. Thus, pK_{aB} and pK_{aA} present nonmonotonic change with increasing grafting density, as shown in Fig. 1(b). In this case, polyelectrolyte can only modify its charge as a response to the external stimulus. It has to be pointed out that the values of pK_{ai} of weak mixed polyelectrolyte brushes depend on many parameters. In addition to the pH and the grafting density, the salt concentration and thickness of the brushes also affect the values of pK_{ai} of mixed polyelectrolyte brushes^[22]. However, studying the relation between pK_{ai} and such parameters is beyond the scope of this work.

Now let us analyze the switching behavior of mixed polyelectrolyte brushes in terms of varying bulk pH.

The distributions of mixed-charge polymer segments at different pH can be shown in Fig. 2. From Fig. 2(a), it is easy to see that the free A-segment distribution is bimodal at pH = 3.0, displaying a rather broad distribution. The more pronounced bimodality displayed in system is attributed to the electrostatic attraction of the oppositely charged segments. The bimodal A-segment distribution shows that some of the A-chains form loops back to the surface, whereas the remaining ones are more stretched. Thus, most of the A-ends are far from the surface signaling stretched A-sequences. The distribution of B polymer chain segments follows a parabolic profile, which means that the B-sequences are coiled. From Fig. 2(b), it can be seen that the inverse switching are presented at pH = 10.5.

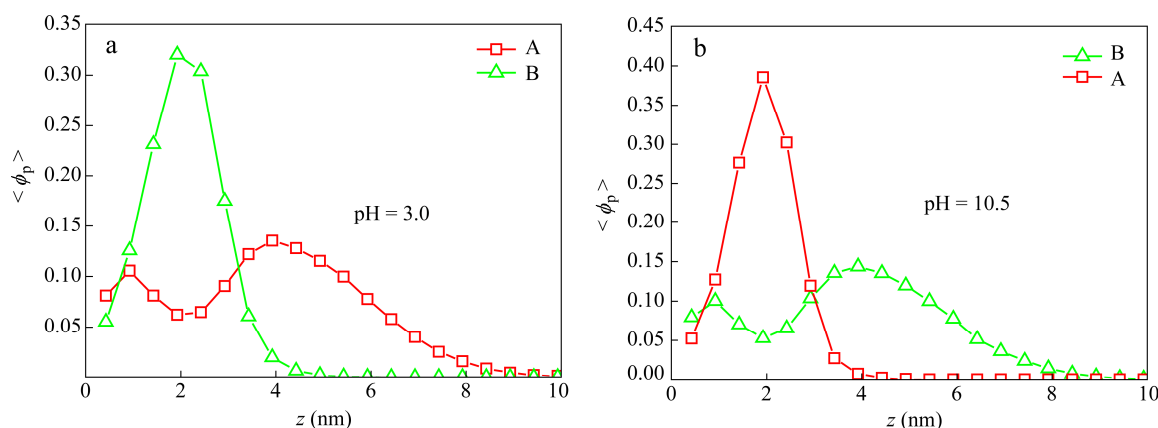


Fig. 2 The average volume fraction of the grafted chains as a function of the distance from the surface for the mixed polyelectrolyte brushes composed of polymer species A and B (The grafting density is $\sigma_i = 0.1 \text{ nm}^{-2}$.)

The shape of the A-segment and B-segment profiles implies the existence of two regions inside the brush: a thin and dense layer near the solid surface and a more extended and solvated one further out. In this case, the perpendicular segregation induced by pH in mixed polyelectrolyte brushes will be presented. Indeed, in the experiments previously reported^[5] the mixed poly(2-vinyl pyridine) (P2VP) and poly(acrylic acid) (PAA) brush demonstrated switching behavior where the top of the brush was occupied by the negatively charged PAA at pH > 6.7 or by the positively charged P2VP chains at pH < 3.2.

The unequal conformation of the A-and B-chains originates from their opposite charges. However, the charge density of the weak polyelectrolyte depends on pH. The positively charged polymer chains are protonated at low pH. The degree of protonation and the charge density of the positively charged polymer chains increase with a decrease of pH. A similar scenario can be applied to the negatively charged polymer chains, which are dissociated at high pH.

Figure 3 shows an average volume fraction of the charged chains at different pH. When pH < 7.0, chains of a polymer with a low pH are more stretched than the polymers with a high pH, while B polymers chains with a

low pH are more coiled, which can be shown in Figs. 3(a) and 3(b). When $\text{pH} > 7.0$, From Figs. 3(c) and 3(d), it is easy to see that B polymer chains with a high pH are more stretched than B polymer chains with a low pH, and A polymer chains with a high pH are more coiled.

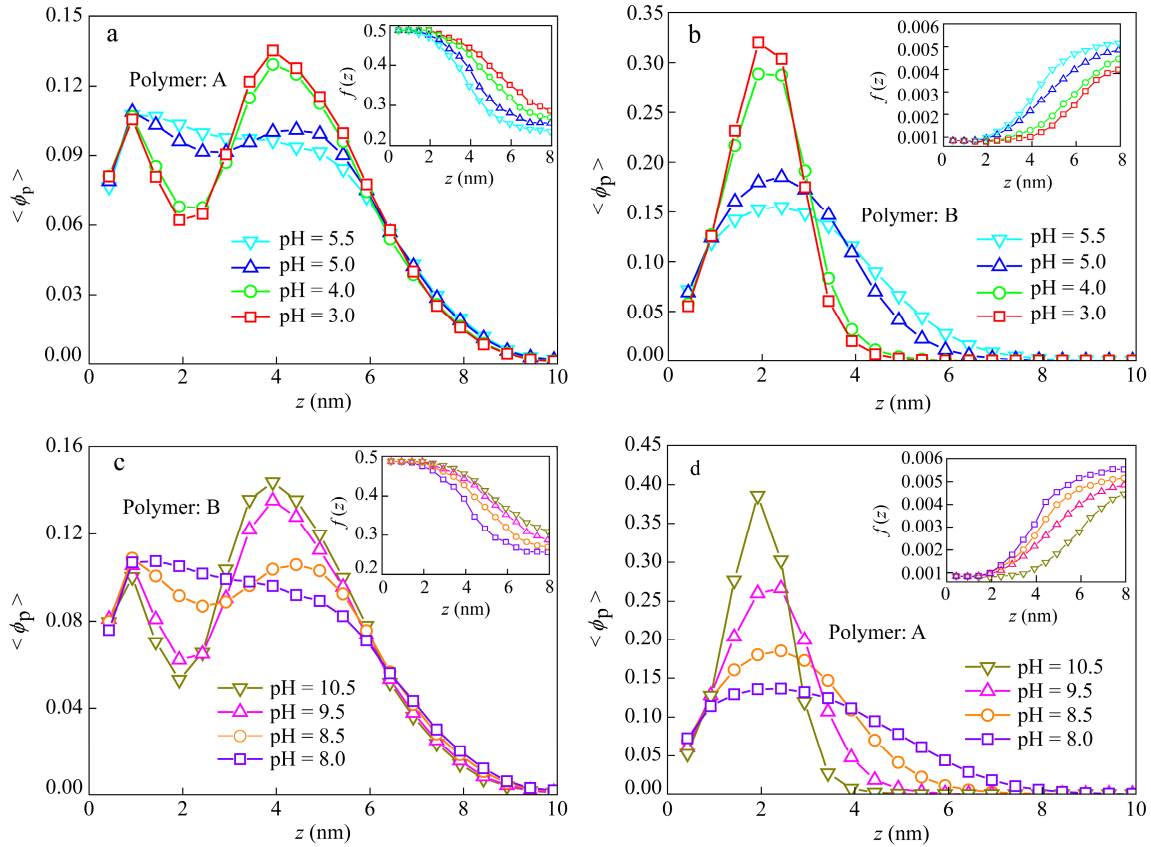


Fig. 3 The average volume fraction of the grafted chains in mixed polyelectrolyte brushes at different pH. The insets show the degree of protonation and dissociation as a function of the distance from the surface.

Insets in Fig. 3 show the degree of protonation and degree of dissociation as a function of the distance from the substrate surface. They show similar behavior: when $\text{pH} < 7.0$, higher degree of protonation for the inner layer of A polymer chains and lower degree of protonation for the outer layer. The degree of dissociation of B is lower in the inner layer. When $\text{pH} > 7.0$, the degree of dissociation of B polymer chains in the inner layer is higher, and the degree of protonation of A polymer chains in the inner layer is lower.

As explained in a theoretical discussion, insertion of charged monomers into a varying electrostatic potential is energetically unfavorable. With decreasing pH, the H^+ concentration thus increases, the acid-base equilibrium of the polymer A shifts towards the charged state, and the polymer A becomes more positively charged. With increasing pH, the OH^- concentration increases, the polymer B becomes more negatively charged. Since the electrostatic potential increases with increasing charge, the electrostatic repulsions will cause the polymer chain to stretch. Another interesting feature involves the collapse of the A and B polymer chains for $\text{pH} < 7.0$ and $\text{pH} > 7.0$. There exist two mechanisms to induce the collapse of the A and B polymer chains. One is due to the counterion condensation leading to the screening of electrostatic interactions, while another is due to the attractive interactions along chains. The screened Coulombic interactions give rise to a negative pressure which takes over chains, and counterions result in an entropic pressure, which can induce the polyelectrolyte collapse. The attractive interactions along a chain also can lead to a collapse of the whole chain into a very compact structure and an inhomogeneous distribution.

To account for the attractive interactions along chains, in particular, we found a similar distribution between the local concentration of H^+ , OH^- (as shown in Figs. 4a and 4b) and the average volume fraction of the grafted chains at different pH. The fact is in very close agreement with the Monte Carlo simulations^[23] and self-consistent-field analysis^[24]. Therefore, we expect that the attractive interactions along chains can be attributed to H^+ and OH^- mediated electrostatic attractions among polyelectrolyte chains. This effect leads to the ion-pair formation, which is associated with the appearance of dipole moments. Winkler *et al.*^[25] have found that dipoles are aligned preferentially antiparallel.

In order to clarify the charge behavior of the complex, the electrostatic potential has been calculated. Figure 5 shows the distribution of electrostatic potential inside the mixed polyelectrolyte brushes with different pH. It should be stressed that all the charged species in the solution contribute to electrostatic potential. The electrostatic potential of the complex displays negative values and positive values for $pH < 7.0$ and $pH > 7.0$, respectively. The negative and positive electrostatic potentials inside the mixed polyelectrolyte brushes show the privilege of adsorbing H^+ and OH^- , which leads to the formation of ion pairs.

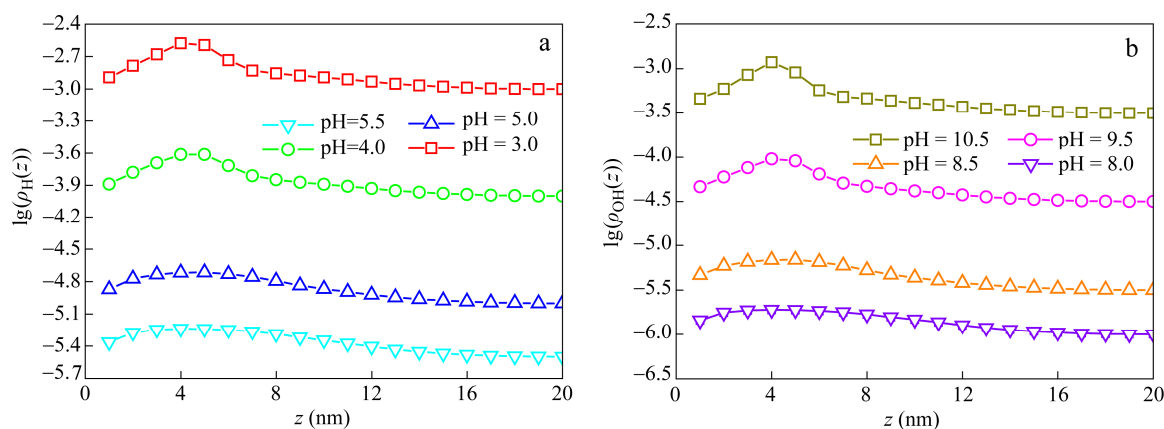


Fig. 4 Local concentration of H^+ and OH^- as a function of the distance from the surface for the mixed polyelectrolyte brushes in cases of (a) low pH values and (b) high pH values

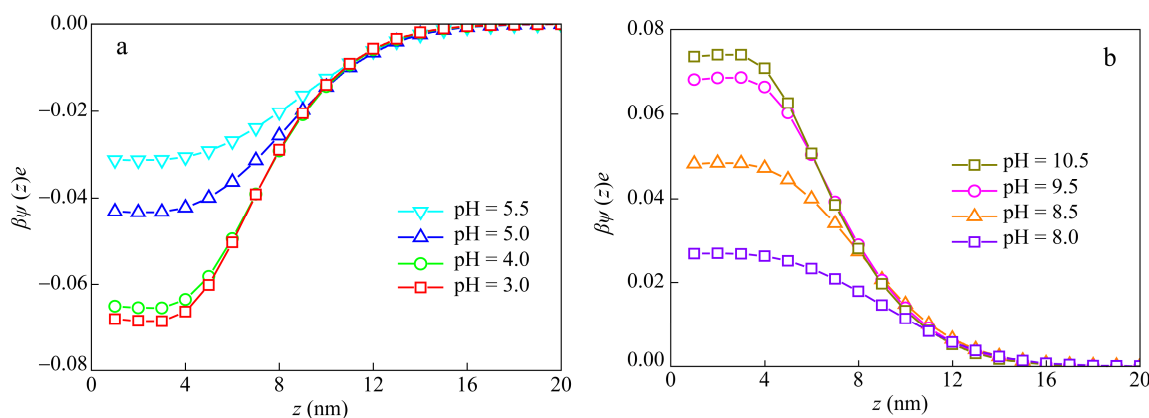


Fig. 5 Electrostatic potential as a function of distance from the surface for (a) $pH = 3.0, 4.0, 5.0$ and 5.5 , (b) $pH = 8.0, 8.5, 9.5$ and 10.5

In the condition of electrical neutrality, both polymers formed similar conformation, as shown in Fig. 6(a). This result is consistent with the experimental fact that both polymers formed a dense collapsed polyelectrolyte brushes complex at $pH = 7.0$, as reported by Ionov *et al.*^[5] The electrostatic potential inside the mixed polyelectrolyte brushes shows the electrical neutrality (Fig. 6b).

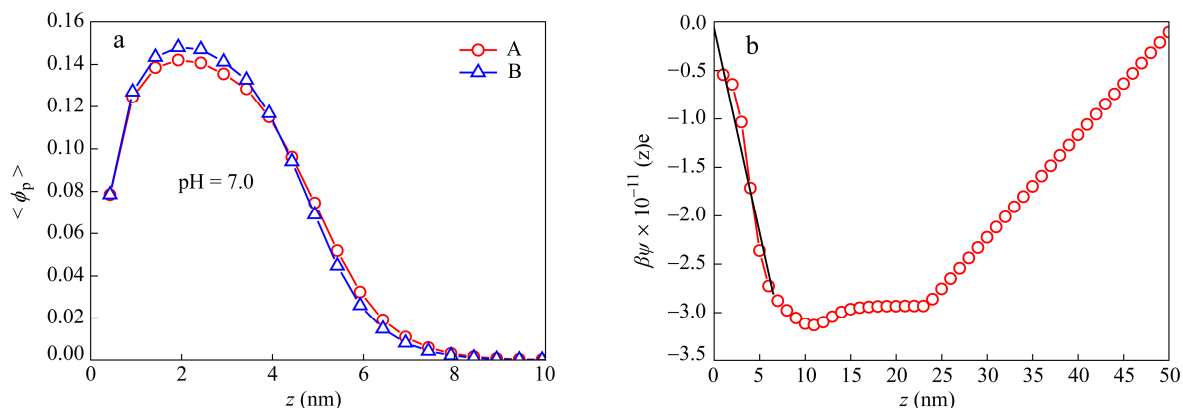


Fig. 6 The average volume fraction of the grafted chains and electrostatic potential as a function of distance from the surface for pH = 7.0

CONCLUSIONS

We have employed a molecular theory to study pH-induced switching of mixed polyelectrolyte brushes. At low pH, negatively charged chains adopt a compact conformation on the bottom of the brush while positively charged chains are highly stretched away from the surface. They preferentially occupy the top of the brush. At high pH values, the inverse transformation takes place. Positively charged chains are collapsed on the bottom, while negatively charged chains are on the top. In conditions of electrical neutrality, both polymers formed a similar polyelectrolyte brushes complex. This is in agreement with experiments of PAA-mix-P2VP brushes in an aqueous environment at different pH, which reveals the unique switching behavior of the PAA-mix-P2VP brushes^[1, 5].

We also systematically studied structural behavior of mixed polyelectrolyte brushes at different pH. In this case, we try to analyze the role of pH determining the polymer chains conformation. We found that there exists a mechanism for reducing strong electrostatic repulsions: stretching of the chains. The collapse of the polymer brush with very high and very low pH values can be attributed to the screening of electrostatic interactions and the counterion-mediated attractive interaction along the chain. The H^+ and OH^- units play a more important role as counterions of the charged polymers. The condensations of counterions lead to the screening of electrostatic interactions and formation of dipoles. Combined with the concept of the screening of electrostatic interactions, the counterion-mediated and dipole-dipole attractive interactions may help us to understand the collapse of mixed polyelectrolyte brushes. Kumar *et al.*^[26] have developed a field-theory to study charge regulation in planar polyelectrolyte brushes. Their theoretical investigations also reveal that the dipole moment of the ion-pairs can be formed as a result of counterion adsorption on the chain backbones.

It is important to mention that whether increasing or decreasing the pH requires the addition of NaOH and HCl to the bulk solution. The increase and decrease in pH are accompanied with increases of the Na^+ (cation) and Cl^- (anion) concentrations, which are not considered as counterions in the present work. However, we believe that the main pH-induced mixed polyelectrolyte brushes switching effects are captured. The theory results are consistent with experimental observations. The agreement with experiments suggests that pH is a key element of inducing the mixed polyelectrolyte brushes switching. Though other contributions (Na^+ and Cl^-) certainly play a role, they might not crucially change the mixed polyelectrolyte brushes switching effects.

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