Phase Behavior and Charge Regulation of Weak Polyelectrolyte Grafted Layers

Peng Gong,1 Jan Genzer,2 and I. Szleifer1,*

1Department of Chemistry, 560 Oval Dr., Purdue University, West Lafayette, Indiana 47907-1393, USA
2Department of Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, USA
(Received 14 April 2006; published 5 January 2007)

The stability of weak polyelectrolytes end grafted to a planar surface has been studied with a molecular theory. The effective quality of the solvent is found to depend on the interplay between polymer grafting density, acid-base equilibrium, and salt concentration. Our results reveal that increasing salt concentration results in a thermodynamically more stable layer. This reverse salt effect is due to the competition between the solvent quality and the dual role of the ionic strength in screening the electrostatic interactions (reducing stability with increasing salt concentration), and regulating the charge on the polymer (increasing charge with increasing salt concentration). Grafted weak polyelectrolyte layers are found to be thermodynamically unstable at intermediate surface coverages. Additionally, it is established that the increased solubility of the layer at low surface coverage is due to the relatively large charge of the grafted polymers. The range of stability of the film with regard to polymer surface coverage, temperature, bulk pH and salt concentration is demonstrated.

DOI: 10.1103/PhysRevLett.98.018302 PACS numbers: 82.35.Jk, 68.47.Pe, 82.35.Gh, 82.35.Rs

So-called smart polymer layers have the ability to change their properties in a reversible way as a response to changes in the surrounding environment [1]. Typical examples include polyelectrolyte layers grafted to surfaces where variations in the ionic strength of the solution result in changes on the structure of the layer and a coil-to-globule transition of grafted polymer layers upon changes in temperature [2,3]. Weak polyelectrolytes, in particular, are intriguing because they can change their degree of charge depending upon the pH and solution ionic strength [4–7]. A major issue in controlling the properties of responsive polymer layers made of weak polyelectrolytes involves understanding the ability of the chargeable segments to adjust their charge in response to variations of pH, concentration of external salt, solvent quality, and the local polymer density on the surface.

In this Letter we present theoretical predictions for the phase behavior of weak polyelectrolytes grafted at one of their ends to a flat surface and the role that ionic strength, pH and solvent quality play in controlling the solubility of the layer. We show that increasing the salt concentration in solution, and thus decreasing the range and strength of the electrostatic interactions, results in increased solubility of the polymer layer. This behavior is exactly opposite to that found for strong polyelectrolytes [8]. As it will be detailed below, this behavior results from coupling between the chemical equilibrium among the charged and uncharged polymer segments (charge regulation), the salt concentration, the pH, the quality of the solvent and the local density of each of the species. In particular, we find in agreement with earlier work [5–7], that increasing salt concentration plays two opposite roles of screening electrostatic interactions while increasing the charge on the polymer. However, here we show for the first time that the coupling of this effect with the large local concentration of polymer segments due to their grafting on the surface (lack of translational mobility), and the collapsing effect of the poor solvent quality, results in increased stability of the polymer layer with increasing salt concentration.

We apply a molecular theory that explicitly accounts for the size, shape, charge distribution, and conformations of all molecular species, incorporating the molecular interactions and chemical equilibrium necessary for the proper treatment of weak polyelectrolytes [9]. The theory has been shown to predict structural and thermodynamic properties of grafted polymer layers in excellent quantitative agreement with experimental observations and full scale simulations [10]. Consider an uncharged surface with \( \sigma \) polymers grafted per unit area. The chain molecules are composed of \( n \) segments, each having volume \( \nu_s \), that can be in two possible states, charged (\( BH^+ \)) or uncharged (\( B \)), related by the chemical reaction \( B + H^+ = BH^+ \), e.g., \( B = NH_2 \). The surface is in contact with aqueous solution (buffer) containing dissociated monovalent salt at bulk concentration \( c_{salt} \) and bulk \( pH_{bulk} \). The free energy of the system is given by
\[ W_A = \alpha \sum_{\gamma} P(\gamma) \ln P(\gamma) + \sigma \left[ \langle n_\gamma(z) \rangle f(z) \ln f(z) + \beta \mu_{H^+} \right] dz + \sigma \left[ \langle n_\gamma(z) \rangle [1 - f(z)] \ln [1 - f(z)] + \beta \mu_B^0 \right] dz \]

+ \beta \int \left[ (\rho_\gamma(z)) \Psi(z) - \frac{1}{2} e \left( \frac{\partial \Psi(z)}{\partial z} \right)^2 \right] dz + \int \rho_{H^+}(z) \ln [\rho_{H^+}(z)v_{w} - 1 + \beta \mu_{H^+}^0] dz

+ \int \rho_{OH^-}(z) \ln [\rho_{OH^-}(z)v_{w} - 1] dz + \int \rho_w(z) \ln [\rho_w(z)v_{w} - 1] dz + \int \rho_{Na^+}(z) \ln [\rho_{Na^+}(z)v_{w} - 1] dz

+ \int \rho_{Cl^-}(z) \ln [\rho_{Cl^-}(z)v_{w} - 1] dz + \sigma \int \chi(|z - z'|) \langle n_\gamma(z) \rangle \langle \phi_\gamma(z') \rangle dz dz'. \tag{1}

where \( \beta = 1/k_B T \) is the inverse temperature. The first term in Eq. (1) represents the conformational entropy of the polymer chains, with \( P(\gamma) \) being the probability (pdf) of finding the polymer in conformation \( \gamma \). The next two terms correspond to the entropy of mixing between the charged and uncharged states of the polymer segments, \( f(z) \) is the fraction of charged polymer segments at a distance \( z \) from the surface and \( \langle n_\gamma(z) \rangle \) represents the average number of polymer segments at \( z \), \( \mu_B^0 \) denotes the standard chemical potential of species \( B \). In bulk solution the equilibrium constant between the charged and uncharged states is given by \( K_B = \exp[-\beta(\mu_{H^+}^0 - \mu_{H^+}^0 - \mu_B^0)] = C[BH^+] / [H^+] [B] \), where \( C \) is a constant and \( [ ] \) denotes molar concentration.

The third integral in Eq. (1) represents the electrostatic contribution. \( \epsilon \) is the dielectric constant of the solution, \( \Psi(z) \) is the electrostatic potential at \( z \), and \( \langle \rho_\gamma(z) \rangle \) is the total average charge density at \( z \) given by

\[ \langle \rho_\gamma(z) \rangle = \sigma \sum_{\gamma} P(\gamma) f(z) n_\gamma(z) e + \rho_{Na^+}(z) e - \rho_{Cl^-}(z) e \]

with the first term representing the average charge that the grafted polymers contribute to \( z \). Note that the charge is obtained by multiplying the number of polymer segments at \( z \) by the fraction of the charged segments, \( f(z) \). The last four terms in Eq. (2) correspond to the charge arising from cations, anions, protons, and hydroxyl, respectively, with \( e \) being the elementary charge.

The fourth to eighth integrals in the free energy expression, Eq. (1), represent the \( z \)-dependent translational (mixing) entropy of the protons, hydroxyl, water, chloride, and sodium, respectively. The last term in the free energy is the van der Waals (vdW) attractive energy of the polymers, with \( \chi(|z - z'|) \) measuring the quality of the solvent \( [11] \) and \( \langle \phi_\gamma(z') \rangle \) being the average volume fraction of grafted polymers at \( z \). The repulsions among all the molecular species are modeled using excluded volume interactions and are accounted for through packing constraints that read

\[ 1 = \alpha \sum_{\gamma} P(\gamma) n_\gamma(z) v_k + \rho_{Na^+}(z) v_{Na^+} + \rho_{H^+}(z) v_{H^+} \]

+ \rho_{Cl^-}(z) v_{Cl^-} + \rho_{OH^-}(z) v_{OH^-} + \rho_w v_w. \tag{3}

The chain conformations probability, the density profile of each of the molecular species, the electrostatic potential, and the \( z \)-dependent fraction of charged groups are determined by finding the saddle point of the free energy functional, Eq. (1), subject to the packing constraints Eq. (3). For example, the pdf of chain conformations is

\[ P(\gamma) = \frac{1}{q} \exp \left[ -\beta \int \pi(z) v_{g(\gamma,z)} dz \right. \]

\[ - \beta \int \left[ \ln f(z) - \Psi(z) \right] n_\gamma(z) v_{g(\gamma,z)} dz \]

\[ - \int \chi(|z - z'|) n_\gamma(z) \langle \phi_\gamma(z') \rangle dz dz', \tag{4} \]

where \( \pi(z) \) is the lateral pressure field, representing the free energy cost of packing a unit volume at \( z \). Thus, the three terms in the Boltzmann exponent represent the repulsive, electrostatic, and vdw interactions, respectively, that a grafted polymer in conformation \( \gamma \) experiences. Note that the effective electrostatic potential for the polymer in conformation \( \gamma \) is modulated by the charged fraction, i.e., an entropic term, see Ref. [9]. The density profile of the ions of type \( i \) is of the form

\[ \rho_i(z) = \exp[\beta \mu_i - \beta \pi(z) v_i - \beta \Psi(z) q_i], \tag{5} \]

where \( q_i \) is the charge of ion \( i \) and \( \mu_i \) is the chemical potential of \( i \) in the bulk solution. For the electrostatic potential we get a generalized Poisson-Boltzmann equation

\[ \frac{\partial^2 \Psi(z)}{\partial z^2} = -\frac{1}{\epsilon} \langle \rho_\gamma(z) \rangle, \tag{6} \]

where \( \langle \rho_\gamma(z) \rangle \) is given by Eq. (2) and the densities and pdf depend on the strongly coupled electrostatic and pressure fields, \( \Psi(z) \) and \( \pi(z) \). The expression for the fraction of charged polymer segments at \( z \) is

\[ f(z) = \frac{\rho_{H^+}v_{H^+} - \rho_{H^+}v_{H^+}}{1 - f(z)} K_B \]

with the \( K_B \) as defined above.

The electrostatic and repulsive fields, \( \Psi(z) \) and \( \pi(z) \), are determined by solving the constraint and generalized Poisson-Boltzmann equations by introducing the explicit form of the pdf, Eq. (4), density profiles, Eq. (5), and the fraction of charged groups, Eq. (7), into the constraint equation, Eq. (3), and in the charge density, Eq. (2). The resulting set of coupled integro-differential equations for the fields \( \Psi(z) \) and \( \pi(z) \) is discretized and solved by
standard numerical methods. The input necessary to solve the equations includes: the bulk pH, the bulk salt concentration \( c_{\text{salt}} \), the set of polymer conformations (a set of \( 10^6 \) independent conformations generated by simple sampling), the \( \chi \) parameter, the polymer surface coverage, the equilibrium constant, \( K_B \), and the size of all the ions. For details on the numerical methodology, the generation of the chains and the discretization of the equations see Refs. [9,11].

The thermodynamic properties of the polymer layer are obtained by taking the appropriate derivatives of the free energy. For example, the chemical potential of the grafted polymers is given by \( \mu_g = \partial (W/A) / \partial \sigma \). Figure 1 depicts the dependence of \( \mu_g \) on the surface coverage of the grafted polymer layer for various solution salt concentrations. The isotherms are at a temperature below the theta temperature of the uncharged polymer. The isotherm for the uncharged polymers exhibits a minimum. At surface coverages below the minimum the isothermal compressibility is negative, corresponding to an unstable homogeneous system. The lack of translational degrees of freedom forces the collapsed layer to microphase separate [11], thus forming domains of high density and domains of very low density. The other three isotherms shown in Fig. 1 correspond to the weak polyelectrolyte at different bulk salt concentrations. For the two lowest salt concentrations the polymer chemical potential isotherms exhibit a loop. This, however, is not a van der Waals loop since the grafted polymers do not have translational degrees of freedom. Instead, the loop indicates that at intermediate surface coverage the collapsed polymer layer is unstable and microphase separates; at high and low surface coverages the layer is stable. The isotherm for the weak polyelectrolyte layer at the highest salt concentration reveals that the layer is stable for all surface coverages. Note that the theory does not provide detailed structural information about the microphase separated domains. Rather, it predicts the regions where homogeneous layers will not be thermodynamically stable (negative isothermal compressibility) and thus, due to the lack of translational degrees of freedom, the system will microphase separate.

Figs. 2 depict the temperature-surface coverage “phase diagrams”, stability regions, for the same four cases as Fig. 1 at two different bulk pH’s. The uncharged polymer exhibits a temperature-surface coverage line below which the layer microphase separates under all conditions. For the weak polyelectrolyte the range of stable homogeneous layer is in all cases for temperatures lower than the equivalent uncharged polymer. This is a direct consequence of the increased solubility upon charging the polymers. The range of stable layers increases as the salt concentration increases. Furthermore, as the pH is reduced the range of stability also increases, at the same ionic strength.

In order to understand the reentrant stability of the films at a fixed temperature and the effect of salt, it is useful to examine the fraction of charges along the stability line. The data in Fig. 3 reveal that at \( pH = 7 \) the polymers are highly charged at low surface coverages: this increases their stability at all salt concentrations. However, there is a sharp decrease in the polymer charge that depends both on surface coverage and salt concentration. The stability at high surface coverage is due to the gain in van der Waals attractions. The average fraction of charge per polymer segment monotonically decreases with increasing polymer surface coverage. However, the overall charge on the layer increases monotonically with increasing surface coverage, as shown in the inset of Fig. 3.

The data plotted in Fig. 3 reveal that the fraction of charged groups increases with increasing bulk salt concentration. The reason is that as the concentration of salt decreases the \( \text{OH}^- \) units play a more important role as counter ions of the charged polymers. Concurrently, as \( \text{OH}^- \) increases the chemical equilibrium is shifted towards the uncharged polymer species. The effect of ionic strength and surface coverage can be explained in terms of a (local) Le Chatellier principle where the chemical equilibrium is shifted to outset the effect of changing the conditions.

The increase in polymer surface coverage and the decrease in salt concentration result in a decrease of the charge of the polymer. Therefore, the salt has two opposite effects on the electrostatic interactions. While decreasing the salt concentration increases the range and strength of
the electrostatic interactions, concurrently, it also decreases the number of charged groups in the polymer. This dual salt effect is similar to that predicted in the good solvent regime [5–7]. Under all conditions studied here, which correspond to experimentally realistic values of pH, pK_h, ionic strength, and polymer surface coverage [12,13], the charge regulation plays a more dominant role resulting in the observed salt reversal effect.

A more detailed picture of the dramatic effect that the charge regulation has on the polymer layer can be seen in Fig. 4, where the volume fraction and the charge density profiles are shown for two isothermal points along the stability line of the pH = 7, pK_h = 7, c_salt = 0.001M, and T/θ = 0.7. The inset in (b) shows the local fraction of charge as a function of distance from the surface.

To summarize, we have shown that the thermodynamic stability of weak polyelectrolytes grafted on surfaces shows a reentrant behavior and exhibits a reverse salt effect. Salt plays an important role in screening electrostatic interactions and in charge regulation. The degree of charge of the polymer depends upon the bulk pH, the pK_h of the groups, the local density of polymer, the solvent quality and the number of counterions. Because of the inhomogeneous density profiles, the local degree of dissociation is very different from that of a bulk solution under equivalent conditions. Furthermore, the coupling between local charge, pH and polymer concentration is enhanced in grafted polymer layers due to the very large local densities of polymers that can be reached, due to the lack of translational degrees of freedom of the polymers and the poor solvent quality. The calculations presented here provide guidelines for the conditions necessary to form stable layers. Moreover, the ability to manipulate the local charge, local pH, and the structure of the grafted layer by the proper choice of bulk solution conditions, pH, salt and temperature, makes these grafted layers potential candidates for sensors whose range of application can be reversible changed [1].

This work is supported by the National Science Foundation, under Grants No. CTS-0338377, No. CTS-0403535, and No. NIRT-0403903.

*Corresponding author.
Electronic address: igal@purdue.edu


FIG. 3 (color online). The average fraction of charged polymer segments along the stability lines for pH = 7. Lines and symbols are as in Fig. 2. The average fraction of charge per polymer is defined by $f = \langle \phi(z) \rangle = \langle \phi(z) \rangle dz/ \langle \phi(z) \rangle dz$. The inset shows the total charge on the polymer layer as a function of surface coverage. The total charge is the product of the average fraction of charged polymer segments multiplied by the polymer surface coverage.

FIG. 4 (color online). (a) Polymer volume fraction profiles and (b) the polymer charge density profiles for two points along the stability curve for pH = 7, pK_h = 7, c_salt = 0.001M, and T/θ = 0.7. The inset in (b) shows the local fraction of charge as a function of distance from the surface.