3488 *Macromolecules* **2000,** *33,* 3488−3491

Static Forces in Confined Polyelectrolyte Layers

E. B. Zhulina,*,[†] O. V. Borisov,[†,‡] and T. M. Birshtein[†]

Institute of Macromolecular Compounds of the Russian Academy of Sciences, 199004 St. Petersburg, Russia, and BASF AG, ZDP, D-67056 Ludwigshafen, Germany

Received April 13, 1999
Revised Manuscript Received November 29, 1999

Adsorption of polymers at the solid−liquid interfaces provides an efficient way to modify the interfaces and to control the aggregative and rheological properties of colloidal dispersions.[1,2] When two colloidal particles approach each other, the steric repulsion between polymer coatings opposes the van der Waals attraction between the particles and provides the aggregational stability of such a dispersion. Polymer layers serve also as “lubricants”, which reduce the friction force between two surfaces brought into a grazing contact and sliding with respect to each other.[3]

The protective properties of polymer coatings are determined by the elastic restoring force arising in response to the normal deformation of the layer. An important feature of such forces is that they act on the mesoscopic scales, that is when the polymer-modified surfaces approach each other at the distance on the order of macromolecule size. Recently, the normal forces between surfaces covered by end-grafted or irreversibly adsorbed polymer layers have become experimentally measurable in a surface force apparatus (SFA)[2−8] or by atomic force microscopy (AMF).[7,9]

Compression of the adsorbed layer leads to an increase in the concentration of polymer and the corresponding increase in the osmotic pressure inside the layer. At relatively strong confinement, the excess osmotic pressure gives the dominant contribution to the restoring force. Although below we focus on polymer brushes (monolayers formed by end-anchored chains), our findings, nonetheless, are applicable to other types of confined polymeric layers where the restoring force is governed by the excess osmotic pressure.

The shape of the normal force versus deformation (f-D) profile is determined by the dependence of the osmotic pressure on the polymer concentration inside the layer. For neutral polymers under good solvent conditions, the interaction between monomers has a character of short-range repulsion. Two brushes facing each other get confined when the distance $2D$ between the two polymer-coated surfaces becomes smaller than twice the brush thickness, $2H$.

In compressed brushes, the osmotic pressure π scales with the concentration c of monomers as

$$\pi/k_{\mathrm{B}}T \cong vc^2 + wc^3 \tag{1}$$

where v and w are respectively the normalized second and third virial coefficients of the monomer−monomer interaction and the numerical coefficients are omitted. (Both v and w are positive under good solvent conditions, while in a Θ solvent, $v = 0$.) At $D \le H$ the concentration of monomers is related to the distance between the surfaces $2D$ and to the amount of polymer adsorbed per unit area of each surface Γ as $c = \Gamma/D$; the repulsive force per unit area $f \sim \pi$ scales at distances $D \ll H$ as $f \sim D^{-2}$ or $f \sim D^{-3}$ under good and Θ solvent conditions, respectively.

The goal of this paper is to quantify the force f, which arises upon compression of the brushes formed by weakly charged (in particular, weakly dissociating) polyelectrolytes. Charged polymers (polyelectrolytes) become increasingly important because of industrial applications and environmental concerns. The long-range Coulomb forces dominate in the interactions between polyelectrolytes both in the bulk solutions and at the interfaces.

If the density of grafting of polyelectrolytes to the surface is sufficiently large, then most of counterions are localized inside the brush even when it is in contact with a salt-free solution.[10−12] The brush is swollen (the chains are extended normally to the grafting surface) because of the excess osmotic pressure of the counterions. The onset of interaction of two polyelectrolyte brushes facing each other corresponds to the beginning of the overlap of their ionic atmospheres which extend in the solution above the brush edge. The characteristic thickness of the ionic atmosphere is determined by the Debye screening length in a salt-added solution or by the renormalized Gouy−Chapman length in a salt-free solution. The latter length is determined by uncompensated charge per unit area of the brush and weakly decreases with increasing grafting density.[13] At $D \ge H$ the contraction of the brushes compressed against each other occurs without a grazing contact due to redistribution of counterions which leads to enhancing screening of the inter- and intrachain Coulomb repulsion. In this range of deformations, the shape of the f−D profiles can be derived on the basis of the solution of the Poisson−Boltzmann equation with account of increasing conformational entropy of the chains which progressively lose their extension upon compression.[13] The initial slope of the f−D profiles is very sensitive to the intrinsic structure of the brush, e.g., to polydispersity, possible formation of loops due to attraction of uncharged monomers to hydrophobic surface, etc. In contrast, under strong confinement, i.e., at $H \ll D$, which is considered below the excess osmotic pressure of mobile ions gives the dominant contribution to the disjoining force which can be derived on the basis of the osmotic balance agruments.

The distribution of mobile ions between the interior of the brush and the bulk of the solution can be obtained by employing the local electroneutrality condition inside the brush

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

where α is the fraction of elementary (negatively) charged monomers, and the Donnan rule for the distribution of all species of co- and counterions

$$c_{i-}/c_{\mathrm{b}i-} = c_{\mathrm{b}j+}/c_{j+} \tag{3}$$

where c_{j+}, $c_{\mathrm{b}j+}$ and c_{i-}, $c_{\mathrm{b}i-}$ are the concentrations of

---

[†] Institute of Macromolecular Compounds of the Russian Academy of Sciences.
[‡] BASF AG, ZDP.

10.1021/ma990579p CCC: $19.00

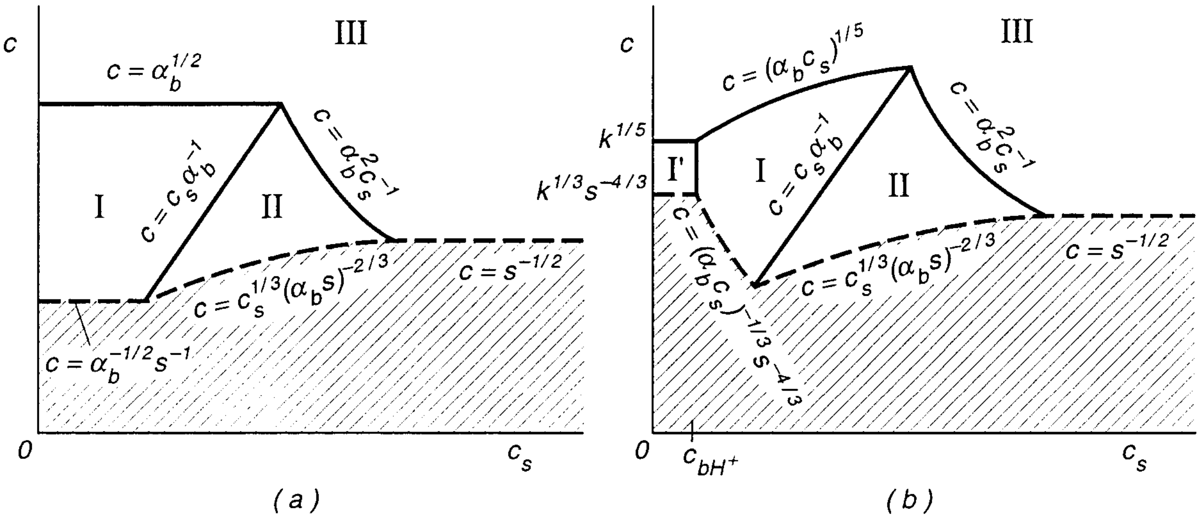

Figure 1. Diagrams of compression of the quenched (a) and annealed (b) polyelectrolyte brushes in (c, c_s) coordinates.

different types of cations (counterions) $j+$ and anions (co-ions) $i-$ inside the brush and in the bulk of the solution (subscript b), respectively. Here all of the valences of mobile ions and that of charged monomers are equal to unity; i.e., the solution contains 1:1 salt and hydrogen H^+ and hydroxyl OH^- ions due to dissociation of water. $c_+ = \sum_{j+}c_{j+}$ and $c- = \sum_{i-}c_{i-}$ are the total concentrations of counterions and co-ions inside the brush, respectively. The total concentrations of co-ions and counterions in the bulk of the solution are equal, i.e., $\sum_{i-}c_{bi-} = \sum_{j+}c_{bj+} = (1/2)\sum_j c_{bj}$, because of the electroneutrality condition, and the last summation is performed over all of the ion species present in the solution. The restoring force is then proportional to the differential osmotic pressure of the ions and is given by

$$\Delta\pi_{el}/kT = \sum_j (c_j - c_{bj}) \cong \begin{cases} \alpha c & \alpha c \gg \sum_j c_{bj} \\ \alpha^2 c^2/\sum_j c_{bj} & \alpha c \ll \sum_j c_{bj} \end{cases} \tag{4}$$

In the case of a neutral (pH $\cong$ 7) solution and 1:1 added electrolyte, $\sum_j c_{bj} \cong 2c_s$. To reflect the nonrepulsive nature of binary interaction between the noncharged monomer units in water-soluble polyelectrolytes, we focus on the case of a Θ solvent ($v = 0$ and $w = 1$). Here, the total restoring force is given by

$$f/k_BT \cong \Delta\pi_{el}/k_BT + c^3 \tag{5}$$

At this point we distinguish between two types of weakly charged polyelectrolytes: quenched and annealing.

Quenched Polyelectrolytes. For quenched polyelectrolytes, the fraction of charged monomers α_b is constant and does not depend on the local concentration of counterions. This is the case if the polymer chains contain a small fraction of strongly dissociating ionogenic groups, while the majority of monomers are neutral. Poly(styrene sulfonate) (PSS) at a low degree of sulfonation is a typical example of weakly charged quenched polyelectrolytes. Depending on the range of compression, D, and the amount of added salt, c_s, we find different scaling laws for the disjoining force, f.

Figure 1a demonstrates the diagram of the brush compression in the ($c = \Gamma/D$, c_s) coordinates. The dashed line indicates the equilibrium polymer concentration $c_0 \cong \Gamma/H_0$ in an undeformed brush. This concentration is determined by the balance of the excess osmotic pressure inside the brush given by eq 5 and the elastic tension arising in the extended chains due to conformational entropy losses. The corresponding elastic force (per unit area) scales as $f_{elastic}(c)/k_BT \cong c^{-1}s^{-2}$ if the chains obey Gaussian elasticity (s is the surface area per one grafted chain). The scaling dependences for c_0 were derived in ref 12. At small concentrations of salt, $c_s < \alpha_b^{1/2}s^{-1}$, the brush is found in the "osmotic" regime and $c_0 \cong \alpha_b^{-1/2}s^{-1}$. At $c_s > \alpha_b^{1/2}s^{-1}$, the undeformed brush is found in the "salt dominance" regime, and here $c_0 \cong c_s^{1/3}\alpha_b^{-2/3}s^{-2/3}$. Finally, at high salt concentrations, $c_s > \alpha_b^2 s^{1/2}$, the electrostatic interactions are essentially screened off and the brush is found in the quasi-neutral (Θ) regime where $c_0 \cong s^{-1/2}$. Above the boundary $c \cong c_0$, the layer is compressed. We distinguish the three different regimes of the brush compression. These regimes corresponding to different regions in the diagram (Figure 1a) are characterized by different scaling laws for the disjoining force. In region I (the osmotic regime, $\alpha_b c > c_s$), the disjoining force is determined by the osmotic pressure of counterions confined inside the brush

$$f/k_BT \cong \alpha_b c \sim 1/D \tag{6}$$

In region II (the salt dominance regime, $\alpha_b c < c_s$), both counterions and co-ions of added salt contribute significantly to the differential osmotic pressure and we find with the account of eq 4

$$f/k_BT \cong \alpha_b^2 c^2/c_s \sim 1/D^2 \tag{7}$$

while in region III (the quasi-neutral regime), the Coulomb interactions are essentially screened off and the force is determined by the ternary contacts between the uncharged monomers to give

$$f/k_BT \cong c^3 \sim 1/D^3 \tag{8}$$

The boundaries between the regions are found from crossover of the corresponding expressions for the force. As follows from the diagram in Figure 1a, compression of the brush (an increase in c) at a fixed value of c_s can lead to different patterns in the $f-D$ profiles. For example, compression of the brush in the salt dominance regime can transfer the system into the quasi-neutral regime passing through the intermediate osmotic regime. As a result, the $f-D$ profile will exhibit different slopes ($\sim D^{-2}$, $\sim D^{-1}$, and finally $\sim D^{-3}$) with progressively decreasing D. We emphasize that for other types of quenched polyelectrolyte coatings, e.g., for irreversibly adsorbed polyelectrolyte layers, the equilibrium polymer concentration c_0 will scale differently, and the boundary $c \cong c_0$ on the diagram will shift. However, upon compression of such layers (that is, at $c \gg c_0$) we expect the same power laws (eqs 6 and 7) for the disjoining force.

Annealing Polyelectrolytes. In the annealing polyelectrolytes, the ionization equilibrium gets shifted toward a recombination of charges with increasing concentration of counterions in the solution. Typical examples of such polyelectrolytes are weak polyacids, such as poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMA). We assume that the grafted chains constitute weak polyacids. That is, the dissociation constant k for hydrogen ions H^+ is rather small, while the dissociation constants for other types of cations are sufficiently large.

Then, the degree of ionization α is not constant anymore but depends on the concentration of hydrogen ions, c_{H^+}, inside the brush as

$$\frac{\alpha}{1-\alpha} = \frac{k}{c_{H^+}} \tag{9}$$

c_{H^+} is coupled to the concentrations of all other types of ions and to that of charged monomers via eqs 2 and 3. Therefore, eqs 2, 3, and 9 form a close set of equations to determine the concentrations of all of the ion species inside the brush as a function of their bulk concentrations and of the polymer concentration c. After simple algebra, one gets for $\alpha \ll 1$

$$\alpha \cong \begin{cases} (\alpha_b \sum_j c_{bj}/c)^{1/2} & \alpha c \gg \sum_j c_{bj} \\ \alpha_b & \alpha c \ll \sum_j c_{bj} \end{cases} \tag{10}$$

where $\alpha_b \cong k/c_{bH^+}$ is the average degree of ionization of an isolated acidic monomer in the bulk solution. At very small concentrations of the added ions, the major contribution to the sums in eq 10 is given by the hydrogen ions with bulk concentration c_{bH^+}. Correspondingly, at $c_s \ll c_{bH^+}$, the degree of ionization is given by $\alpha \cong (\alpha_b c_{bH^+}/c)^{1/2}$.

Figure 1b demonstrates the diagram of compression for annealing polyelectrolyte brush in the (c,c_s) coordinates. As before, the dashed boundary indicates the equilibrium polymer concentration c_0 in an undeformed annealing brush. In contrast to the quenched polyelectrolytes (Figure 1a), c_0 is now a nonmonotonic function of the bulk salt concentration. At low concentrations of the salt, $c_s < \alpha_b^{1/2} s^{-1}$, c_0 *decreases* as $c_0 \cong \alpha_b^{-1/3} c_s^{-1/3} s^{-4/3}$ with increases in c_s due to enhancing ionization of the chains forming the brush. At $c_s > \alpha_b^{1/2} s^{-1}$, the brush is found in the salt-dominance regime, and here the degree of ionization remains virtually constant, $\alpha \cong \alpha_b$. The behavior of c_0 is therefore the same as that for quenched polyelectrolytes. Namely, $c_0 \cong c_s^{1/3} \alpha_b^{-2/3} s^{-2/3}$ at $c_s < \alpha_b^2 s^{1/2}$ and $c_0 \cong s^{-1/2}$ at $c_s > \alpha_b^2 s^{1/2}$ (see ref 14 for details). Recent experiments by Currie and Cohen-Stuart[15] clearly demonstrated that such a nonmonotonic behavior of c_0 as a function of c_s is indeed found for the annealing brushes. By using ellipsometry, they measured the thickness of the tethered PAA layer at different ionic strengths on the bulk solution. At low pH = 3, no effect of the salt was detected. However, increases in pH up to pH = 4 and 5.8 lead to the swelling of the layer at small ionic strengths that was then followed by a decrease in the layer thickness H_0 (increase in c_0) at high ionic strengths. The estimated values of the exponents in $H_0 \simeq c_0^{-1}$ vs c_s dependences were higher than those predicted by the theory.[14] This can be attributed to the effect of the nonelectrostatic interactions between PAA chains. The nonmonotonic dependence of the undeformed brush thickness H_0 on the grafting density has also been observed by Prinz et al.[9] in AFM measurements performed on tethered poly(vinyl-2-pyridine) (P2VP) layers (weak polybase). The observed slope of the ln H_0 vs ln s dependence is close to $^1/_3$ as predicted by the theory.[14]

Similarly to the case of quenched polyelectrolytes, we distinguish three regimes of the brush compression with different scaling laws for the disjoining force. These regimes correspond to regions I–III in the diagram (Figure 1b). In regions II (salt-dominance regime) and III (quasi-neutral regime), the degree of ionization $\alpha \cong \alpha_b$, and we therefore get expressions (7) and (8) for the force, respectively. The effect of annealing manifests itself in region I (osmotic regime), which has noticeably decreased in size in comparison to the quenched case (see Figure 1a,b). The major part of region I is located at $c_s < c_{bH^+}$ because c_{bH^+} is normally negligibly small. Here, we find with the account of eq 10

$$f/k_B T \cong \alpha c \cong (\alpha_b c_s c)^{1/2} \tag{11}$$

(In the subregion I′, c_s is substituted by c_{bH^+}.) We thus find that the disjoining force grows with deformation as $\sim D^{-1/2}$ and increases with increasing bulk salt concentration c_s as $\sim c_s^{1/2}$. Both, the softness of the potential and an enhancement in repulsion with increases in the salt concentration are explained by the variable degree of ionization of chains in the brush. Namely, the confinement of the brush increases the concentration of charged monomers and, therefore, enhances also the concentration of counterions inside the brush. This induces recombination of H^+ ions with the charged monomers, i.e., a decrease in α. As a result, the osmotic pressure and the restoring force grow weaker with deformation than in the quenched brush with the fixed degree of ionization ($\alpha = \alpha_b$).

An increase in the bulk salt concentration results in an opposite effect: the concentration of H^+ ions in the brush (at given polymer concentration c) decreases. This induces additional ionization of monomers, the corresponding increase in the concentration of counterions, and the growth of an excess osmotic pressure inside the brush. We thus predict that, at moderate salt contents, the slope of the $f-D$ profile will decrease with addition of salt due to the shift in the ionization–recombination balance. At higher salt concentration, the screening effects become important and therefore the $f-D$ profile gets steeper (eqs 7 and 8 are recovered).

It is instructive to analyze the effect of added base on the compressibility of the weak polyacid brush. Because $c_{H^+} c_{OH^-}$ = const, the addition of base (e.g., NaOH) results not only in an increase of the ionic strength of the solution, $\sum_i c_{ib}$ but also in an increase of the bulk degree of ionization $\alpha_b \sim c_{OH^-}$. As a result at low salt concentration the degree of ionization of chains in the brush and the osmotic pressure grows with the base concentration as $\sim c_{OH}^{-4/3}$. A similar effect is expected for weak polybase brushes upon added acid.

Our theoretical findings are in qualitative agreement with the results of the SFA study of the $f-D$ profiles between PMA brushes performed by Kurihara et al.[6] at diferent pH and salt concentrations. As demonstrated in ref 6, an increase in pH leads to (i) increasing brush thickness manifested in an increasing interbrush separation at which the repulsive force is detected, (ii) increasing magnitude of the repulsion at given separation, and (iii) decreasing slope of the $f-D$ profiles (at low salt concentration). All of these trends are explained by increasing ionization of the chains. At low salt concentration and small pH, the chains are not ionized and the $f-D$ profile follows roughly the dependence given by eq 8 for neutral chains. At large pH, when the chains are strongly ionized, the range and magnitude of the force get larger while the slope of the $f-D$ curves is much smaller, in accordance to eq 11. An addition of salt (NaBr) results in two opposite effects: (i) an increase of the ionization of polyelectrolytes and (ii) enhancement of the screening of Coulomb interactions. The first effect is dominant and leads to an increasing disjoining force at small pH and/or strong compression. In contrast, for high pH (when the chains are strongly ionized even in the absence of salt) and weak compression, the screening effect is dominant and the disjoining force decreases with increasing c_s. In the intermediate range of pH, the effect of added salt is clearly nonmonotonic: At small c_s the $f-D$ profiles get shifted to higher values of f with increasing c_s without changing their shape (annealing osmotic regime I). However, at larger c_s this trend in $f-D$ profiles is observed only at strong compression while the force arising in a weakly compressed, $H \leq D$, brush decreases with increasing c_s and the $f-D$ profile gets steeper (salt-dominance regime II); the inflection point appears on the $f-D$ profiles corresponding to the crossing of the boundary between regimes I and II upon confinement. We remark that experimentally measured in ref 6 $f-D$ profiles are systematically steeper than the theory predicts. This can be attributed to the high polydispersity ($M_w/M_n = 1.98$) of the PMA chains used in preparation of the brushes.

The experiments of Schorr et al.[8] also demonstrated that these trends are indeed seen in the $f-D$ profiles for the annealing PAA brushes. Increases in the bulk concentration of the salt (NaCl) at approximately constant values of pH = 6−7 caused a nonmonotonic shift in the theshold of the force detection. The distance at which the force started to be detected, initially increased with increases in the salt concentration and then decreased at high ionic strengths. By relating this threshold distance to the characteristic thickness of the PAA layer, one finds the same type of behavior as that found by Currie and Cohen-Stuart.[15] The measurements of Schorr et al. also demonstrated that increases in the salt concentration changed the slope of the $f-D$ profiles. At low bulk contents of the salt, the profiles were less steep than those at high concentrations of the salt. This trend is also in agreement with our predictions. According to eqs 7 and 11, the force profiles in the salt-dominance regime (where $f \sim D^{-2}$) should be noticeably steeper than those in the annealing osmotic regime where $f \sim D^{-1/2}$.

Conclusions. The restoring force arising in the deformed (confined) polyelectrolyte brushes grows weaker with deformation than that in neutral brushes. Brushes formed by weak (annealing) polyelectrolytes exhibit even weaker elastic response with respect to normal deformation because the confinement results in the recombination of charged monomers with counterions that reduces the osmotic pressure inside the brush. Small amounts of added salt lead to an increase in the restoring force in annealed brushes. An even stronger effect of the same sign results from the addition of base or acid in cases of weak polyacid or polybase brushes, respectively.

Acknowledgment. We are thankful to C. Prinz, P. Schorr, M. Tirrell, E. Currie, and M. Cohen-Stuart for discussions of their experimental results before publication. This work was partially supported by the Dutch−Russian NWO project "Polyelectrolytes in Complex Fluids" and Russian Fund for Fundamental Research (RFFR), Grant 99-03-33319.

References and Notes

(1) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1985.
(2) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1985.
(3) Klein, J.; Kamiyama, Y.; Yoshizawa, H.; Israelachvili, J. N.; Fredrickson, G. H.; Pincus, P.; Fetters, L. *Macromolecules* **1993**, *26*, 5552.
(4) Patel, S. S.; Tirrell, M. *Annu. Rev. Phys. Chem.* **1989**, *40*, 579.
(5) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.
(6) Kurihara, K.; Kunitake, T.; Higashi, N.; Niwa, M. *Langmuir* **1992**, *8*, 2087.
(7) Kelley, T. W.; Schorr, P. A.; Johnson, K. D.; Tirrell, M.; Frisbie, C. D. *Macromolecules* **1998**, *31*, 4297.
(8) Schorr, P.; Toomey, R.; Tirrell, M.; Cook, D.; Mays, J. W. In *Proceedings of Yamada Conference L "Polyelectrolytes"*, Yamada, Japan, 1999, Noda, I., Kokofuta, E., Eds.; 1999; p 393.
(9) Prinz, C.; Muller, P.; Maaloum, M., in press.
(10) Borisov, O. V.; Birshtein, T. M.; Zhulina, E. B. *J. Phys. II* **1991**, *1*, 521.
(11) Pincus, P. *Macromolecules* **1991**, *24*, 2912.
(12) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1994**, *27*, 4795.
(13) (a) Zhulina, E. B.; Borisov, O. V. *J. Chem. Phys.* **1997**, *107*, 5952. (b) Zhulina, E. B.; Klein Wolterink, J.; Borisov, O. V. *Macromolecules* **1999**, submitted for publication.
(14) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491.
(15) Currie, E. P. K.; Cohen-Stuart, M. A. *Langmuir* **1999**, submitted.

MA990579P