Polyelectrolyte Desorption and Exchange Dynamics near the Sharp Adsorption Transition: Weakly Charged Chains

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ABSTRACT: This paper examines the desorption and self-exchange dynamics of polyelectrolyte chains on an oppositely charged surface, in the limit of weak charge, such that the polymer is readily displaced by added ions. The model system adhering to this physically limiting behavior is poly[(dimethylamino)-ethyl methacrylate] [PDMAEMA] adsorbing on silica from aqueous solution at elevated pH. Desorption kinetics follow expectations: a single-exponential decay consistent with a first-order desorption model, with an activation energy for chain removal that adheres reasonably to the Muthukumar treatment and quantitatively to the Dobrynin−Rubinstein model. Self-exchange kinetics, however, present a surprise: They are quantitatively identical to desorption, with the exchange process being completely controlled by chain release from the surface. The single-exponential form for self-exchange is atypical, and the quantitative similarity with desorption suggests that, with weakly charged chains, approximately 3−5 segment−surface contacts make up a minimum dynamic unit for adhesion.

Introduction

Polyelectrolytes have found importance over the years as colloidal stabilizers, flocculants, and rheological modifiers, while a recent renewed interest in their interfacial behavior has been sparked by their potential in biomedical technologies and their role in DNA fingerprinting. In both conventional and novel applications, the appropriate interfacial dynamics of charged chains is key to process success. Undesirable interfacial chain dynamics, either relaxations that occur too quickly or very sluggish chain movement, can lead to product and process failures.

Scientists are just beginning to truly understand polyelectrolyte adsorption. Banks of data chart static features in terms of charge density and ionic strength,[1−7] but theory only predicts scaling trends[8] and quantitative means to anticipate coverage are imperfect.[9−11] The dynamic features of polyelectrolytes present an even greater challenge: For the case of charged polymers adsorbing to an oppositely charged surface, a handful of studies confirm transport-limited adsorption,[12,13] following expectations. The dynamics of established polyelectrolyte layers has gone virtually unexplored. To be sure, the experimental space over which one might probe dynamics is huge, and so the observations from some groups[14−16] may not translate directly to the studies with different systems.[17,18] The conceptual regimes for static polyelectrolyte adsorption therefore provide an initial road map for our dynamic studies.

While little is known about dynamics within adsorbed polyelectrolyte layers, the literature does present limited information on adsorbed nonionic polymer dynamics, as a starting point. Indeed, one might learn the most by identifying situations where adsorbed polyelectrolytes behave similarly or differently from adsorbed nonionics. The two most-often studied dynamic features of nonionics are desorption[19] and self-exchange.[20−23] Desorption applies to a process in which chains leave an interface and are carried away by gently flowing solvent. Self-exchange pertains to the case where the chains that leave the interface are replaced by new ones from solution, while the bulk solution concentration is fixed by gentle flow. In self-exchange the invading and originally adsorbed chains are identical with the exception of a label. Desorption typically occurs more slowly than self-exchange since, with exchange, the invading chains may facilitate the removal of the originally adsorbed chains, swapping a few segments at a time on a crowded surface. This segment swapping between invading and adsorbed chains should have a lower energy barrier than desorption of an entire chain, making self-exchange occur faster than desorption.[24]

This paper compares desorption and self-exchange kinetics for a model polyelectrolyte system (poly((dimethylamino)ethyl methacrylate) [PDMAEMA] on silica) which constitutes a relatively simple case: a positively charged polymer adsorbed to a negative surface, where adsorption is driven exclusively by electrostatics without additional chemical or hydrophobic attractions between the polymer and the surface.[25,26] Further, the polymer remains soluble in water even without charge, so there are no hydrophobic segmental attractions. This model system therefore captures the basic physics of a string of charge attracted to an oppositely charged plane.

The PDMAEMA−silica system is particularly attractive because the variables fundamental to polyelectrolyte adsorption are experimentally accessible.[25−27] Since PDMAEMA is a weak polycation, its backbone charge increases as the solution pH is lowered. Likewise, the charge spacing on the silica surface is increased at elevated pH. Hence, the relative charge spacing on the polymer and surface can be tuned precisely.[26] Furthermore, the range of electrostatic interactions can be tuned through ionic strength.[28]

In this work we focus on the dynamic behavior for the situation where the chain is sparsely charged, and the surface charge is in relative excess. Here the polymer binding is relatively weak, and addition of a modest amount of salt can inhibit adsorption altogether, a feature we refer to as the "sharp adsorption transition".[28] As a point of comparison with other works (addressing static features such as coverage), it is worth

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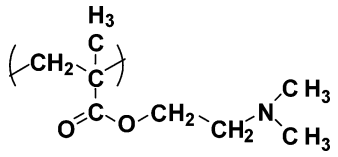

Figure 1. Chemical structure of PDMAEMA.

noting that several groups have focused on a low charge limit and the fact that added salt reduces coverage.[12,29−32] The "sharp adsorption transition" in the current work occurs at polymer charge fractions of less than 2%, which is below the charge densities in most of these other "low polymer charge" works. The distinction is noteworthy only because with 5 or 10% backbone charge, one might find still different dynamic behavior, a subject of a future paper.[33]

In this paper, we compare the adsorbed layer dynamics for sparsely charged PDMAEMA chains near the sharp adsorption transition with the dynamics seen in PDMAEMA layers of much greater charge. Self-exchange and desorption kinetics are interpreted in terms of activation energies, and these in turn are interpreted in the context of existing models for polyelectrolyte adsorption. From this we develop the concept of a minimum dynamic unit: the number of charges along the backbone which must desorb together, to define the activation energy for chain removal from the interface.

Experimental Section

Poly[(dimethylamino)ethyl methacrylate] (PDMAEMA) was a gift from DuPont. Its structure is illustrated in Figure 1. The sample had a molecular weight of 31 300 and a polydispersity of 1.1 as a result of the group transfer polymerization method used for its synthesis. It was supplied in a THF solution. Replacement of THF by water was accomplished through rotary evaporation. Sample purity and complete removal of unwanted organics were confirmed via proton NMR spectroscopy.

The planar silica substrates were the surfaces of microscope slides (Fisher Scientific, Pittsburgh, PA) which had been treated with sulfuric acid and rinsed in-situ in a sealed flow cell to avoid exposure to airborne contaminants. Previous XPS studies confirmed the removal of sodium, calcium, and other salts from the region near the surface, leaving a silica layer exposed.[34,35] This silica layer was characterized optically with scanning Brewster angle reflectometry, as previously described,[36] to determine its thickness (9 nm) and refractive index, 1.49.[37]

Buffer solutions were made with salts purchased from Fisher Scientific. At pH 7.2, 0.008 M Na_2HPO_4 and 0.002 M KH_2PO_4 were used. At pH 9.6 a borate buffer (0.006 M Borax with 0.009 M NaOH) was employed. NaCl was added to solutions as needed to further increase the ionic strength.

To facilitate self-exchange experiments, a rhodamine B isothiocyanate label (Aldrich, Milwaukee, WI) was attached to some of the PDMAEMA at extremely low levels: one label per every 100 000 mass of PDMAEMA (one label/3 chains). Attachment was accomplished in the original PDMAEMA solvent for 11 days at 55 °C. Proof of attachment of the rhodamine B to the PDMAEMA was achieved using chromatographic separation and TIRF runs.[37] Purification of the reaction solution in a gel column (P-6, BioRad, CA) revealed separate peaks from free dye and labeled polymer. With only 1 label per 3 chains, IR and NMR spectroscopies could not distinguish the isothiocyanate reactive groups, though the ultimate fluorescence was obvious.[37] A number of additional control chromatographic and TIRF studies were conducted to ensure labeling: Free dye was found not to substantially adsorb to silica at these conditions, and mixtures of free dye and unlabeled polymer did not give signal because the free dye was not retained. Throughout this paper, "R-PDMAEMA" is used to describe the labeled polymer when it is necessary to distinguish labeled chains from unlabeled ones.

Rhodamine B was chosen as a label because it was noninvasive in the aqueous PDMAEMA−silica system. We applied two of our standard tests for label invasiveness:[37] First, rhodamine B labeling did not affect the overall coverage of PDMAEMA on silica, for a variety of pH's and ionic strengths tested, over the full range of the current study. Second, we could not discern, in studies with mixtures of labeled and unlabeled PDMAEMA chains, a surface selectivity for labeled or unlabeled chains. We previously showed such a surface selectivity effect for different labels on PEO when it adsorbs to silica and note that the effect is substantially diminished above polymer molecular weights of 30 000, where these other labels contribute less than 1 kT of binding energy per chain.[22,38] As a final proof that the presence of dye did not affect the physics studied here, we reproduced a limited number of runs with a fluorescein tagged version of the polymer, using 488 nm light. Kinetics were quantitatively identical with the two different labeled versions of the same polymer.

All self-exchange studies and most desorption studies reported here were conducted on a home-built TIRF (total internal reflectance fluorescence) instrument,[39] which requires fluorescently labeled samples. While desorption experiments were also sometimes conducted using near-Brewster reflectometry with unlabeled PDMAEMA, the long experiments in the current study required stable baselines which were often difficult to achieve with reflectometry due to the substantial influence of slight thermal drift on the refractive indices of the polymer, solvent, and substrate. In TIRF, excitation light at 556 nm was totally internally reflected inside the microscope slide substrate, with the help of a dove prism to which the microscope slide was coupled. The resulting evanescent wave with a decay length near 100 nm excited labels on chains near the glass−water interface. Most of these resided on chains in the adsorbed layer though there was a small contribution from free chains near the surface, which was eliminated when the bulk solution was replaced with pure buffer.

In the current investigation, we employed a TIRF setup built inside a Spex Fluorolog II fluorescence spectrometer. The main differences with this and our laser-based instrument[39] are that here (1) a xenon lamp with a monochromator provides excitation light at a chosen wavelength, (2) a double monochromator sorts the emissions, and (3) the flow cell is mounted with vertical flow. In the current investigation, emissions were measured in real time at 576 nm.

The flow cell followed that of our previous studies:[39] A 1 × 10 × 40 mm slit was machined into a black Teflon block and sealed against the microscope slide substrate using an O-ring. Continuous gentle flow through this slit (with wall shear rates in the range 1−50 s^{-1}) maintained a constant bulk solution concentration and defined the mass-transport conditions, without being strong enough to perturb the configurations of the adsorbing chains. All runs in this paper were conducted at 14 s^{-1}.

Results

Influence of pH and Ionic Strength on Coverage: A Road Map. Figure 2A presents the PDMAEMA coverage as a function of ionic strength for 2 pH's relevant to our study, 7.2 and 9.6, providing a road map for the dynamic phase of this investigation. These data were obtained for a bulk solution concentration of 80 ppm, near the isotherm plateau. The related adsorption isotherms are shown in Figure 2B. These isotherms demonstrate a moderate coverage of PDMAEMA on silica at the low ionic strength of 0.026 M and substantially reduced coverage at a higher ionic strength of 0.08 M for pH 9.6. At the low ionic strength of 0.026 M, the isotherm for pH 7.2 is relatively flat; however, that for pH 9.6 has a less well-defined plateau. This is likely a result of the sparse polymer charging at pH 9.6 which gives weaker binding and substantial tails and loops.[27]

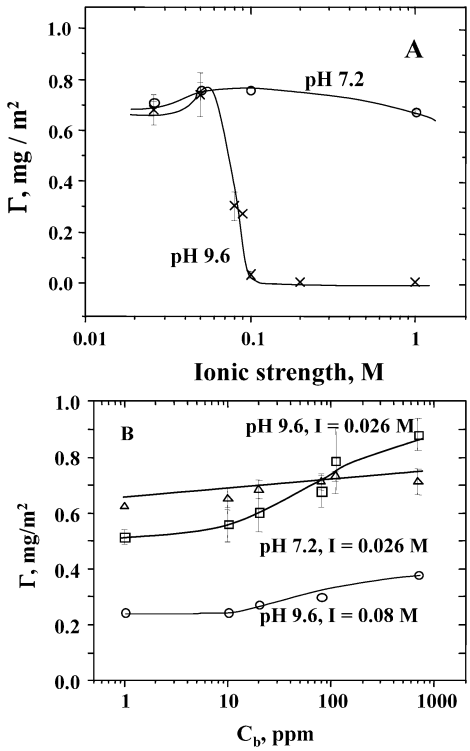

Figure 2. PDMAEMA coverage, from a bulk solution concentration of 80 ppm, on silica as a function of added NaCl, for two different pH's. The ionic strength axis includes the buffering ions plus any added NaCl. (B) Adsorption isotherms.

In Figure 2A, ionic strength has a very slight effect on the adsorbed amount of PDMAEMA at pH 7.2, where the polymer charge is substantial, about 83/chain (every ~2nd segment is protonated). Conversely, in the limit that the chain is weakly charged, at pH 9.6, a small increase (from 0.06 to 0.1 M) in ionic strength completely eliminates adsorption. We call this the *sharp adsorption cutoff*, and this regime is the focal point for the current dynamic studies. As discussed in greater detail in a previous paper, this cutoff occurs because with very little charge on the chain (3−5/chain at a pH of 9.6[26,40]), salt ions compete effectively for adsorption sites.[28] Similar trends, including the displacement of PDMAEMA by salt, were observed in a previous study employing titania.[12] Of course, the competition between charged polymer segments and salt ions is not the only means by which salt can complicate adsorption. In systems where the surface charge is overcompensated by that of the polymer, salt screens segmental repulsions to increase adsorption.[41] In Figure 2A at salt concentrations corresponding to 0.04−0.05 M ionic strength, increases in the salt concentration slightly promote adsorption. This secondary effect may result from the screening of repulsive charges between neighboring adsorbing chains.

Parenthetically, it may be of interest to note that in the low salt limit the coverages converge approximately to the same level, for different pH's, i.e., different backbone charge densities. This is because the pH range in this paper is relatively narrow. Figure 2 of ref 28 demonstrates that, in the limit of low and high pHs, the coverage is lower. At low pH's, the silica presents reduced negative charge to drive adsorption, and in the high pH limit, the polymer is uncharged. In the pH range of the current paper, the backbone charge varies dramatically, but at low salt concentrations, the coverage lies near the maximum observed in studies with pH variations. Even in the low salt limit, the coverage drops sharply to zero slightly above pH 10, the expected effect.

Table 1. Properties of the DMAEMA−Silica System at pH 9.6 and 7.2

	pH 7.2	pH 9.6
DMAEMA charge (no./chain)	83	3−5
bare silica charge (no./nm²)	−0.3	−1
total charge of DMAEMA layer + underlying silica (no./nm²)	+0.1	−0.6 to −0.8

The PDMAEMA−silica system has been previously characterized by titrations and electrophoretic mobility using colloidal silicas over a full range of pH's.[25−27] The features relevant to the current study are summarized in Table 1. Several findings are worth reiterating here. First, for pH's of 8 and above, PDMAEMA adsorption did not further increase silica surface charge. Also, the charge on the polymer backbone was unaffected by adsorption at pH 8 and below.[26,40] At pH 9.6 where adsorption-enhanced backbone charging is more likely, the effect could not be quantified within experimental error.

Some additional facts compliment Figure 2. First, at pH 9.6, even with coverages around 0.7 mg/m², the adsorbed polymer does not contain sufficient charge to compensate the underlying silica charge.[26] In other words, the electrophoretic mobility of silica particles with their adsorbed polymer layer at pH 9.6 is negative, the same sign as the bare silica particles. This should also occur for our microscope slide substrates. By contrast, at pH 7.2, the adsorbing PDMAEMA is highly charged, and a fully saturated PDMAEMA layer reverses the underlying surface charge.[26] At pH 7.2, this substantial positive charge in the layer will repel positively charged chains approaching from free solution, hindering self-exchange. At pH 9.6, the smaller positive charge within the adsorbed layer would present less of an electrosteric barrier to approaching chains.

A few other important points relating to Figure 2 are worth mentioning: At both pH 7.2 and 9.6, counterion condensation on the polymer backbone is minimal because the underlying charges are substantially far apart on the chain.[26] Only below pH 7 does conterion condensation occur. Also, at pH 7 and below, the PDMAEMA chains tend to lie flat on the surface, with most of each chain in contact with the silica, i.e., in "trains".[27] At elevated pH's there are greater numbers of loops and tails and fewer trains. The train fraction of PDMAEMA on colloidal silica drops rapidly to zero near pH 10 as the isotherm plateau coverage also approaches zero. In the case of our planar silica surfaces, this effect happens between pH 10 and 11. The observation that PDMAEMA no longer adsorbs when the chain becomes uncharged is strong evidence that the sole driving force for adsorption is electrostatic.

Dynamic Behavior: The Many Contact Limit. We first examined the dynamic behavior of PDMAEMA on silica at pH 7.2, where the polymer chain carries a substantial positive charge: Figure 3 compares desorption and self-exchange data at an ionic strength of 1.0 M. In either run, flowing buffered saline was initially pumped through the flow cell, and at time zero, an 80 ppm R-PDMAEMA solution at the same ionic conditions was injected and adsorbed in continuous flow. After 10 min, the original buffer was restored. In the desorption run, the buffer flowed through the cell for the next ~46 h, while in the self-exchange run, it flowed only for 5

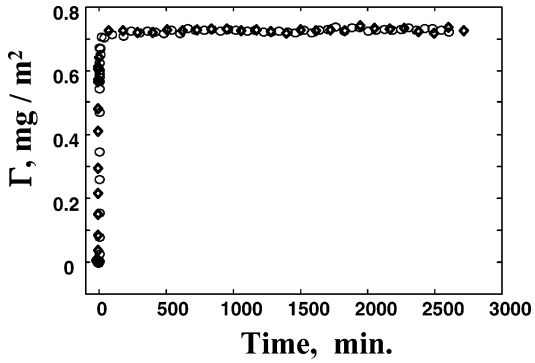

Figure 3. Self-exchange (○) and desorption (diamonds) traces at pH 7.2 and an overall ionic strength of 1.0 M. Polymer solution concentrations are 80 ppm.

min, after which time a solution of unlabeled 80 ppm PDMAEMA was injected and flowed continuously. Were self-exchange to have occurred, the fluorescence signal would have decreased, indicating displacement of labeled chains by unlabeled ones.

Figure 3 demonstrates that with many potential segment−surface contacts per chain (approaching 100 here) chains are tightly bound to the substrate: After initial adsorption, exposure to flowing solvent of the same ionic strength does not facilitate desorption, though, the chains are only physisorbed. (Elevating the pH above 8.5 facilitates slow pH-dependent desorption.) Also, at pH 7.2 and an ionic strength of 1.0 M, the layer was equally resistant to self-exchange.

We attempted self-exchange and desorption experiments at pH 7.2 for a variety of ionic strengths, from 0.026 to 1.0 M, and found kinetics identical to those shown in Figure 3. Salt had no observable influence on dynamics in this limit of many segment−surface contacts, and the layer was immobile to desorption and self-exchange on our experimental time scales.

The Limit of Low Contact Number: Salt Effects. In contrast with the immobility of moderately charged PDMAEMA chains at pH 7.2, interesting dynamics are found at pH 9.6, where there are only about 3−5 charges per PDMAEMA chain. At pH 9.6 added salt diminishes PDMAEMA adsorption as seen previously in Figure 2. The reduced adsorption energy in this regime is manifest in the layer dynamics, as revealed in Figure 4, for a number of points on the pH 9.6 curve of Figure 2.

In Figure 4, desorption data are shown for four different ionic strengths at pH 9.6. Figure 4A presents the raw data for the full experimental duration, including the initial adsorption, which appears oddly compressed on this time scale. Figure 4B magnifies the time axis for the same runs, and it is easier to see how adsorption was conducted for 10 min to give a saturated layer with a well-established coverage, and then desorption was initiated, at the same ionic conditions as the adsorption process. We comment in an appendix on the implications of this particular adsorption and layer aging history. In Figure 4B, the initial decrease in signal upon reintroduction of pH 9.6 buffer is caused by removal of some free chains from the interfacial region (where their labels were excited by the evanescent wave) and the removal of loosely bound chains from the surface. This initial signal drop was sensitive to flow rate, suggesting rapid interfacial processes and influence of mass transport on the kinetics. (We will later show that the dominant long-term portion of the signal decay is not influenced by transport.)

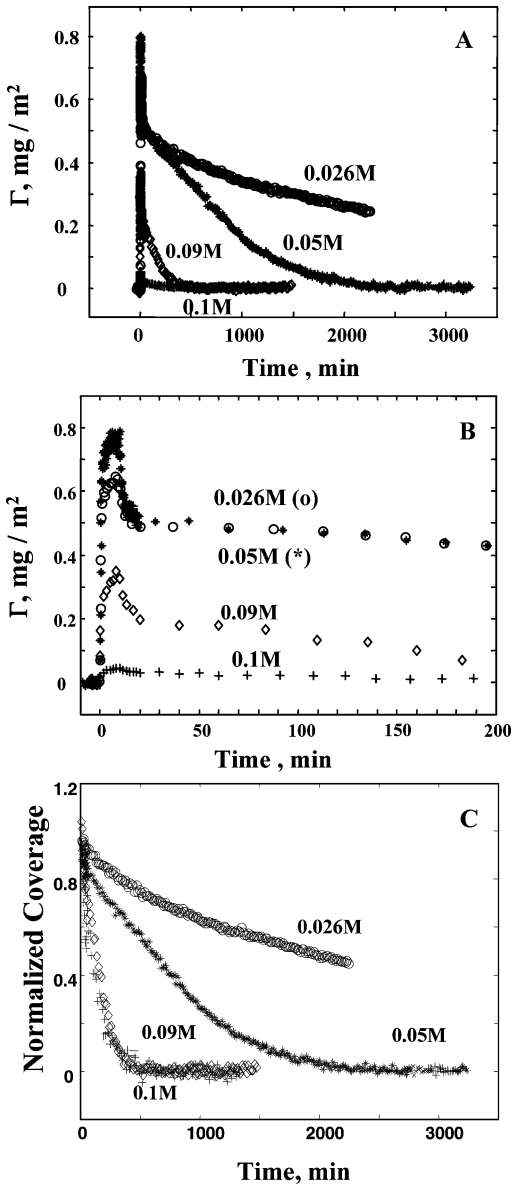

Figure 4. (A) Raw desorption data at pH 9.6 and different ionic strengths. (B) The first 200 min of the same runs in (A). (C) The desorption portions of the runs normalized on coverage. In (B) the 0.026 and 0.05 M runs ultimately cross because slower desorption kinetics occur at lower ionic strengths; however, the 0.05 M run has the higher initial coverage, per the maximum in Figure 2. All polymer solution concentrations are 80 ppm.

In Figure 4C, the data for the desorption portions of the runs are renormalized, facilitating the kinetic analysis. It is worth noting that if only Figure 4C were shown, it would be difficult to appreciate the substantially different levels of coverage occurring in the initial states prior to desorption, seen in Figure 4A. By contrast, Figure 4C suggests that in the limit of relatively large amounts of added salt the data converge to a single kinetic form, despite these differences in initial coverage. Also, of note in Figure 4C, time zero starts 5 min after the reinjection of pH 9.6 buffers to facilitate comparison with self-exchange runs, below in semilog form. (In the self-exchange runs, 5 min of flowing buffer followed adsorption but preceded introduction of unlabeled chains and the self-exchange process. Therefore, time zero in these desorption runs matches that for the start of self-exchange in later

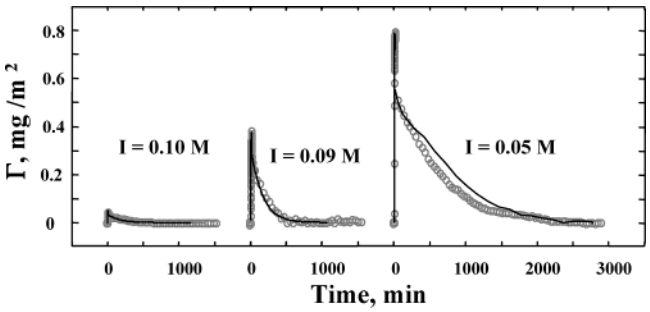

Figure 5. Comparing three self-exchange (○) and three desorption (lines) runs at pH 9.6. All polymer solution concentrations are 80 ppm.

experiments. The elimination of the first minutes of the desorption is small compared with the 40+ hours to follow.)

Figure 5 compares raw self-exchange data with those of desorption for three ionic strengths from 0.05 to 0.1 M. In the self-exchange experiments, after a 10 min adsorption period for the PDMAEMA, pH 9.6 buffer is reintroduced for 5 min, and then unlabeled PDMAEMA is injected at the same ionic conditions. The signal decrease tracks the removal of tagged chains from the surface, but because of the PDMAEMA in bulk solution, the overall surface mass is constant. (In contrast, the surface mass decreases with time in a desorption run.) For the runs presented here, we conducted complementary reflectometry experiments to confirm constant surface mass in the self-exchange experiments.

The self-exchange kinetics in Figure 5 are quantitatively identical to those of desorption with the exception of a small reproducible shoulder in the desorption run at 0.05 M, which was absent during self-exchange. Identical kinetics for self-exchange and desorption were also found at 0.026 M,[37] but not shown here. The observation that self-exchange does not proceed more rapidly than desorption for this system is remarkable and has not been seen for any other polymer systems to our knowledge.

Figure 6 presents data from Figure 5, including runs at 0.026 M, on a semilog scale to demonstrate that both self-exchange and desorption proceed with a single-exponential decay. It is worth remembering that in this plot time zero corresponds to the beginning of the slow self-exchange process. If we had set time zero to correspond to the reintroduction of pH 9.6 buffer, there would be a short-time upward curling lip on the data, which we interpret to correspond to a loosely bound population of chains. Rajagopalan reported a similar small lip on simulations where polymer chains were removed from a surface.[42] It was shown that the loosely bound chains were responsible, while the rest of the "sample" exhibited a single-exponential self-exchange. For the desorption run at 0.05 M ionic strength, the shoulder in the raw data translates to an intermediate slope region, before the terminal decay is approached. We emphasize here that this shoulder is a reproducible feature of desorption runs in this ionic regime, where the coverage in Figure 2A goes through a small maximum. Both the dynamic shoulder and the static maximum of Figure 2A likely result from competing interfacial forces: segment−surface attractions and segment−segment repulsions.

The characteristic decay time as a function of ionic strength is shown in Figure 7. Added ions give rise to

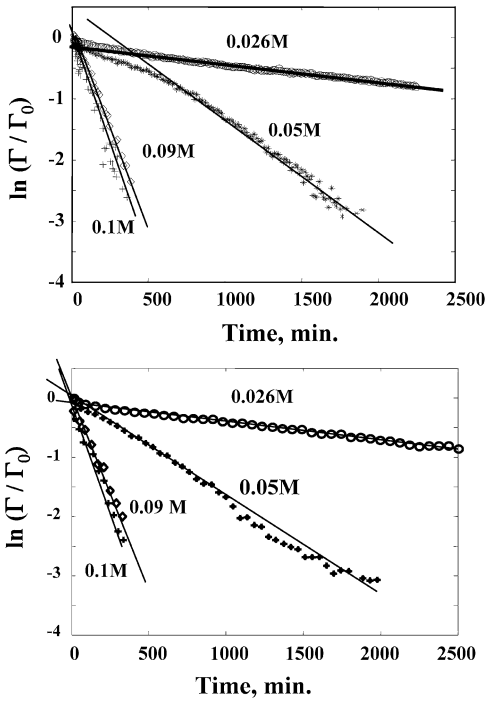

Figure 6. Desorption (above) and self-exchange (below) are nearly single exponential, with the exception of desorption at intermediate ionic strengths.

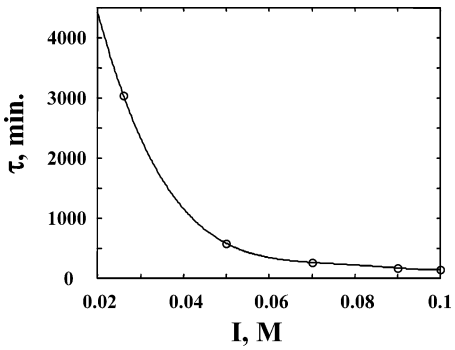

Figure 7. Summary of time constants for desorption and exchange processes, as a function of ionic strength. The curve guides the eye.

faster interfacial dynamics, with the dynamic features converging at ionic strengths near 0.1 M.

The Dynamic Mechanism at pH 9.6. For some polymeric systems such as poly(ethylene oxide) on silica, there are documented reports that desorption[19] and, to some extent, exchange[22] occur at the mass transport limited rate or at least are strongly influenced by transport from the bulk. In other systems, data suggest that slow desorption and exchange kinetics reflect interfacially trapped states or surface-controlled chain release.[43,44]

One way to test for mass-transport-limited or -influenced desorption (or self-exchange) is to change factors affecting the driving force for mass transfer: solution flow rate and the bulk concentration of challenging species in solution, in Figure 8A,B. Here we find no influence of bulk solution concentration from 0 to 500 ppm on the rate of removal of the initially adsorbed chains from the surface. Likewise, flow rate had no observable affect after the first few minutes of buffer reintroduction. Hence, at pH 9.6 for the ionic strength shown (0.09 M) and the others tested but not shown (0.026−0.1 M), desorption is not influenced by mass

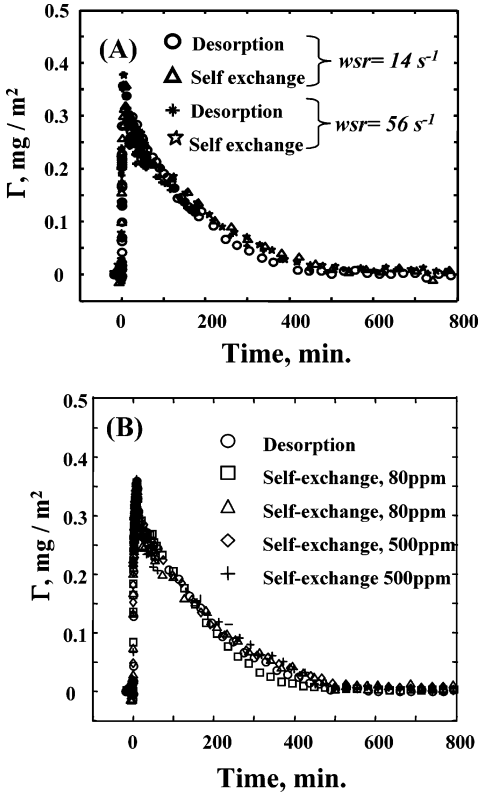

Figure 8. (A) Showing that wall shear rate (wsr) does not affect desorption or self-exchange.The adsorption portions of runs were conducted at using 80 ppm PDMAEMA and wsr = 14 s^{-1}. The desorption and exchange parts of runs were done with variable flow. (B) Showing that concentration of unlabeled chain during self-exchange does not affect kinetics. Repeat runs are shown to establish limits of reproducibility. All adsorption portions of runs were done using 80 ppm R-PDMAEMA. For all runs, pH = 9.6 and I = 0.09 M.

transfer to the bulk. Unlike the previously observed behavior of PEO on silica,[20−22] PDMAEMA desorption is controlled exclusively by the kinetics of chain release from the surface. Furthermore, the similarity of desorption and self-exchange traces in Figure 5 tells us that self-exchange is kinetically controlled by the release of chains from the surface, without help from free chains nearby.

While it was previously observed with other systems that the concentration or molecular weight of invading chains did not influence exchange rates,[45] we believe ours to be the first study exhibiting complete domination by surface chains. In those other works which involved potentially greater train fractions than in the current study, self-exchange was faster than desorption,[15,43−45] so that the free chains had some influence on the exchange process. In the current work, the equality of self-exchange and desorption kinetics defines the extreme regime of domination by surface dynamics.

The next issue is to understand how the chain release rate (which controls desorption and self-exchange equally) is influenced by ionic strength, as summarized in Figure 7. Simple desorption kinetics are such that the desorption rate, $-d\Gamma/dt$, should be proportional to the instantaneous adsorbed amount, Γ

$$-\frac{d\Gamma}{dt} = k_{off}\Gamma \tag{1}$$

giving rise to the single-exponential behavior of Figure

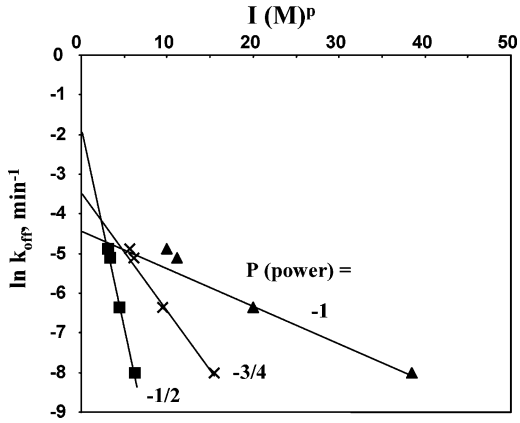

Figure 9. Analysis of k_{off} for ionic strength dependence. All three data sets contain the same data, but plotted with a different exponent for ionic strength, on the x-axis. Squares: $I^{-1/2}$; ×'s: $I^{-3/4}$; triangles: I^{-1}.

6, with the characteristic time $\tau = 1/k_{off}$. Kinetic theory dictates the following form for the desorption constant:

$$k_{off} = \omega \exp\left(-\frac{E_a}{k_B T}\right) \tag{2}$$

Here E_a is the activation energy, k_B is Boltzmann's constant, T is temperature, and ω is a prefactor typically interpreted as an attempt frequency. For gas-phase reactions, the prefactor is related to Planck's constant, but for condensed systems, it is left as an unknown frequency, perhaps related to a condensed phase diffusivity or segmental hopping frequency. The ionic strength should affect E_a through the coil interaction with the surface. It is not obvious that ionic strength should affect ω substantially.

The observed rate constants from the slopes in Figure 6 are plotted in Figure 9, in a form motivated by eq 2, assuming an ionic strength-independent attempt frequency. ln k_{off} on the y-axis is plotted as a function of different powers of the ionic strength. Only inverse powers of ionic strength are considered because increasing the ionic strength increases the desorption rate and therefore decreases the activation energy. Of the forms considered ($I^{-1/2}$, $I^{-3/4}$, I^{-1}), $I^{-1/2}$ best fits the data suggesting scaling for E_a/k_BT:

$$\frac{E_a}{k_B T} \sim I^{-1/2} \tag{3}$$

For the experiments in Figures 5 and 6, measured E_a values range from 3 to 6 k_BT. Also, the attempt frequency from the y-intercept of Figure 9 turns out to be 2.25×10^{-3} s^{-1}, which appears very sluggish at first inspection. If one chooses a diffusion length on the order of 5 nm, one obtains a diffusivity of 7×10^{-16} cm^2/s, 6 orders of magnitude slower than the surface diffusivity of albumin on a hydrophobic surface.[46] Hence, the attempt frequency from our analysis is slower than diffusive time scales. One potential explanation is that these longer time scales correspond to constrained or glassy segmental motions.

The observed ionic strength scaling of the activation energy for chain release from the surface is consistent with the desorption (or adsorption) energies of polymer chains, though different interpretations apply. Here we

examine two theories: that of Dobrynin−Rubinstein[8,47] and that of Muthukumar.[9]

The Dobrynin−Rubinstein model[8,47] for polyelectrolyte adhesion to a surface proposes the following form for the binding energy, W_{ads}, per electrostatic persistence unit having length l_p:

$$\frac{W_{ads}}{k_B T} = \frac{l_b f \sigma}{\kappa^3 l^2} \tag{4a}$$

Here σ is the surface charge density and f is the fraction of charged polymer segments (fN is the number of charges per chain). The electrostatic persistence length itself goes as $\kappa^{-2} D_e^{-1}$. κ is the inverse Debye length (which is proportional to $I^{1/2}$), and D_e is the size of an electrostatic blob, which depends only on the polymer charge, Kuhn step size, l, and Bjerrum length ($l_b = 0.7$ nm), and therefore is independent of I. To obtain the adsorption energy of an entire chain, the result in eq 4a must be multiplied by the number of electrostatic persistence units per chain ($\sim Nl^2/\kappa^{-2}$), which leaves a $\kappa^{-1}(I^{-1/2})$ dependence for the adsorption on a per chain basis.

$$\frac{W_{ads}}{k_B T} = \frac{l_b f N \sigma}{\kappa} \quad \text{per chain} \tag{4b}$$

One can also compare the slope measured for the $I^{-1/2}$ line in Figure 9 with eq 4b to the magnitude of the prefactor for the $E_a/k_B T \sim I^{-1/2}$ scaling. We observe a slope of −1. With the number of charges per chain, $Nf = 4$, the group $l_b f N \sigma$ takes a value of 3.1 nm^{-1}, while $\kappa = 3.29 I^{1/2}$ nm^{-1} (for a monovalent electrolyte), giving a total predicted prefactor of −0.94. Therefore, within experimental error, there is very good quantitative agreement between theory and experiment for the observed prefactor. Perfect quantitative agreement would be obtained if we assumed a charge/chain (fN) of 4.5 rather than the value of 3 we estimated from solution titrations.

Another well-known model for single-chain polyelectrolyte adsorption is that of Muthukumar,[9] which predicts that increased ionic strength reduces adsorption energy and therefore that added ions ultimately prevent adsorption. The form for the adsorption energy per chain in this single-chain treatment is

$$\frac{W_{ads}}{k_B T} = \frac{48\pi |q\sigma|}{{j_{0,1}}^2 \epsilon \kappa^3 l l_1} \tag{5}$$

q is the charge per Kuhn segment, $j_{0,1}$ is the first root of the zeroth-order Bessel function of the first kind, ϵ is the dielectric constant of water, and l_1 is a renormalized Kuhn step size, accounting for electrostatics. Solution of an expression[9] for l_1 at the ionic conditions corresponding to the adsorption cutoff reveals it is quantitatively identical to the Kuhn step size because at pH 9.6 the polymer charge density is so low. l_1 does, however, exhibit an ionic strength dependence, such that the overall influence of ionic strength, through the combined effects of κ and l_1 in eq 5, yields $W_{ads} \sim I^{-11/10}$, stronger than what we observe in Figure 9.

Equation 5 predicts a sharp adsorption cutoff for ionic strengths that reduce the adsorption energy in eq 5 to about 1 $k_B T$. Our observed activation energies fall within this range as the ionic strength of 0.1 M is approached. We previously demonstrated that eq 5 quantitatively anticipates diminished adsorption in the ionic strength range of 0.06−0.09 M at pH 9.6 in Figure 2.[28] Therefore, its application for desorption dynamics is particularly interesting, despite the $I^{-11/10}$ scaling of W_{ads}.

One potentially complicating factor in the analysis above for the interpretation of desorption rate constants and ionic strength is the fact that surface charge densities typically increase with added salt, which has been shown to be the case for silica.[26] In the current experiments, the range of ionic strengths from 0.026 to 0.1 M is relatively small because the adsorption cutoff is sharp. Indeed, titrations reveal nearly constant surface charge density in the range from 0.026 to 0.07 M added salt, but at higher salt concentrations, the surface charge does indeed increase slightly. We feel, however, that because σ is nearly constant for three of the four data points in Figure 9, a $\sigma(I)$ dependence should not be included in our interpretation of E_a.

Despite the potentially complicating effect of surface charge on interpreting the scaling dependence of ionic strength on the activation energy, it is clear that the dynamic mechanism for desorption and self-exchange alike is release of all segment−surface contacts between PDMAEMA and silica. The order of the activation energy is in reasonable quantitative agreement with both treatments for W_{ads}.

Noncooperativity and the Minimum Dynamic Unit. Adsorbed polymers are almost always slow to desorb, since breaking a large number of segment−surface contacts might cost 50−100 $k_B T$. Self-exchange might occur more rapidly if trains or groups of adsorbed segments can swap places, bringing the energy barrier down to 5−10 $k_B T$.[24] The PDMAEMA−silica system defies this concept. In the many-contact limit (near pH 7.2), desorption is slow, as expected, but self-exchange is equally slow. Perhaps with an interface whose net charge is positive at pH 7.2, incoming chains cannot effectively approach the interface. At pH 9.6 where such an electrostatic energy barrier is absent, however, self-exchange and desorption still defy expectations: They are quantitatively identical. Indeed, the data presented here are the only polymer dynamic data of which we know displaying this anomaly.

At pH 9.6 both desorption and self-exchange are kinetically dominated by release of chains from the surface, and in the case of self-exchange, approaching chains do not facilitate removal of chains on the surface. Our explanation for control of desorption and exchange by the same surface release process is that with only 3−5 contacts per chain, once the leaving chains lose enough contact for an approaching chain to get a foothold on the surface, the leaving chain is already gone. That is, there is no way for a chain with only 3−5 adsorbable groups to be partly adsorbed, to make room for an incoming chain. With only 3−5 contacts, chains "lose their grip" if they release one or two contacts. From this, we arrive at the concept of a critical or minimum number of contacts needed for chains to "hang on". If chains have fewer than the minimum contacts, then they would be washed away in solvent or replaced by chains from solution. The conditions at pH 9.6 therefore provide an estimate of the minimum contacts needed for adsorption.

For the kinds of experiments presented here, this minimum or critical contact number could translate to a minimum dynamic unit. In the case of desorption, if

chains have a greater number of contacts, corresponding to 2 or 3 or 4 times the minimum dynamic unit, when one unit desorbs, the chain is still attached and there is a substantial probability that the desorbed units could reattach to the surface. Also, in the case of desorption, at lower pH's with substantially larger numbers of charged groups per chain, some of the charge may reside in loops and tails. When a dynamic unit desorbs from the trains within one chain, charged loops or tails may replace the desorbed segments, in a sort of intramolecular self-exchange, which may give the appearance of cooperativity. Also for chains possessing more contacts than the minimum dynamic unit, we might expect self-exchange to occur more quickly than desorption: There would be a competition between charged segments on approaching chains and charged segments in loops and tails of the existing layer for empty surface created when a dynamic unit releases. With only one dynamic unit per chain, however, there can be no cooperativity or competition between approaching and originally adsorbed chains.

The concept of the minimum dynamic unit, as one of the referees points out, has implications for adsorption processes, as well as the exchange and desorption kinetics presented here. One can imagine that while adsorption onto a bare or partially covered surface will proceed at the transport limited rate, near saturation, the surface offers few open areas for further chain deposition. Therefore, as the surface saturates, the number of adhered segments per chain (at short times before interfacial relaxations allow adsorbed chains to share the surface with newcomers) could drop below the critical number, preventing further adsorption.

This concept of the minimum dynamic unit suggests a crossover behavior in the dynamics as the number of charges per chain is increased: Ultimately, at lower pH's, one would expect to see a separation of desorption and exchange kinetics, as long as the relevant desorption and exchange time scales can be accessed experimentally. The dependence of the dynamics on the number of contacts per chain is the subject of ongoing work and a future paper.

Summary and Conclusions

This work compared self-exchange and desorption kinetics of a weak polyelectrolyte on a surface where adsorption was driven exclusively by electrostatics. The two regimes of high and extremely low backbone charge were compared. In the first case, self-exchange and desorption were both too slow to be detected. In the opposing limit of just a few charges per chain, desorption and self-exchange were quantitatively identical, adhering to single-exponential kinetics dominated by an energy barrier equal to the ionic strength-dependent adsorption energy. Oddly, chains from free solution in no way influenced self-exchange. While previous works have claimed a similar observation, those same works documented differences between self-exchange and desorption kinetics which demonstrates that invading chains did in fact influence interfacial chain release. In the current work, the complete domination of kinetics by chain release from the surface points toward a minimum dynamic unit, which, if partially compromised, would cause the entire chain to desorb.

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Appendix

A few fine points concerning the chosen adsorption history are worth mentioning as an aside. Notably, the adsorption time in these studies in only 10 min, with a 5 min rinsing time in buffer before the initiation of self-exchange. There are subtle implications here.

First of these is the issue of polydispersity. In all samples, even research grade materials such as ours with a polydispersity of 1.1, there can exist fractions that differ substantially in molecular weight. For example with polydispersity of 1.1, the sample can include 10% chains whose length is double that elsewhere in the sample. In general, for homopolymer adsorption, long chains are preferred on the surface over short ones,[48] and in dynamic studies, long chains will displace short ones eventually producing an interfaces with a higher average molecular weight than the bulk solution.[49,50] (We have confirmed the very slow displacement of oligomers by the 31K chains studied here, if such exchange is allowed.[37])

We avoid this upward drift in average interfacial molecular weight through our experimental design: By maintaining a short adsorption period of 10 min, only slightly longer than needed to saturate the surface, we lock in the average molecular weight of the adsorbed layer. Thus, at the initiation of desorption or self-exchange, the molecular weight in the adsorbed layer closely corresponds to that for the free solution, giving a reasonable measure of self-exchange. We have confirmed, with a different system, that overincubation of the surface in the adsorbing polymer solution can lead to retarded self-exchange kinetics, an artifact of an increased interfacial molecular weight and a reduced driving force for displacement of adsorbed chains by free ones.[51]

While the 10 min adsorption period and short aging period in buffer prior to self-exchange are good from the standpoint of avoiding polydispersity artifacts, they raise the question as to whether the layer is equilibrated or relaxed at the onset of desorption or self-exchange. We feel that with weak adsorption and a limited number of segment surface contacts per chain, at pH 9.6, there is a greater chance for equilibration, relative to conditions with large numbers of segment−surface contacts, for instance at pH 7.2.

One other comment on layer age is worth making since an obvious question comes to mind: If the layer cannot be aged in polymer solution because of potential polydispersity artifacts, why cannot it be aged in pure buffer? Aging in pure buffer is equivalent to a desorption experiment. During long "aging" periods, the PDMAEMA desorbs in the single-exponential fashion that was one of the major results of this work. For the situation at pH 9.6 with few segment−surface contacts per chain and self-exchange kinetics equal to those of desorption, one obtains the same exponential decay, independent of when one switches from the buffer aging solution to that of the unlabeled polymer for self-exchange. So in fact, the 5 min buffer rinse is irrelevant. The same kinetic traces are obtained for buffer rinses of 1 h: the release of chains from the surface completely controls the dynamics.

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