P H Y S I C A L   R E V I E W   L E T T E R S

*p*H-Induced Release of Polyanions from Multilayer Films

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We discovered *p*H-induced selective desorption and readsorption of weakly acidic polymers from polyacid or polybase layer-by-layer films. *In situ* attenuated total reflection Fourier transform infrared spectroscopy confirms the selectivity of polyacid release and shows that film response is caused by *p*H-induced charge imbalance. Experimentally the characteristic time of chain release τ scales with molar mass M as $M^{1.1\pm0.1}$. A new theoretical model of "sticky gel electrophoresis" of entangled polyacids agrees with experiments and predicts $\tau \sim MH$, where H is film thickness. Neutron reflectivity shows that polyacid release results in disordering of the film structure.

Polyelectrolyte multilayers (PEMs) represent a new class of nanostructured materials obtained through alternating self-assembly of water-soluble polymers carrying positive and negative charges at solid-liquid interfaces. The use of weakly acidic or weakly basic polyelectrolytes (termed below as "weak polyelectrolytes") as film constituents [1,2] allows one to produce films that are responsive to variations of the external *p*H [3]. The mechanism of response of weak polyelectrolyte multilayers (WPEMs) to *p*H variation involves *p*H-induced accumulation of excess charge within WPEMs, when the *p*H changes are in the region close to the apparent pK_a of a weak polyelectrolyte. This charge can then be used, for example, to bind and release dyes or drugs [4,5], to fabricate novel metal-containing inorganic nanocomposite materials [6,7], or to control electro-osmotic flow in microchannels [8]. As a result of *p*H-induced electrostatic stress within the film, WPEMs swell and change their morphology [9,10]. Porous films have been produced from WPEMs as a result of ionic strength, *p*H, or solvent variations [11–13], and have been recently suggested to be used as antireflection coatings [14].

However, designing WPEM films with predictable response properties is not yet possible, largely due to insufficient understanding of the fundamental mechanisms of their environmental response. While the majority of other studies consider layer-by-layer films which remain compositionally stable after *p*H variations, here we present a different scenario where films can respond to *p*H variations by changing their composition.

Chain expulsion from PEM films was observed for hydrogen-bonded systems as a result of complete disruption of hydrogen bonds in a selective solvent [13,15,16]. With electrostatically assembled PEMs, diffusion of polyelectrolyte chains in and out of a film during the deposition cycle at a constant *p*H has been reported [17], while *p*H-triggered polyelecrolyte charge extrusion to the surface of WPEM films has been considered by Sui and

Schlenoff [18]. Here we study the truly reversible and tunable compositional changes within WPEM films in response to *p*H variations. We present the first direct observation as well as theoretical analysis of the *p*H-induced expulsion and readsorption of one of the polymer components from the electrostatically stabilized film. Of specific interest is the mechanism, kinetics, and molecular-weight dependence of selective polymer release and readsorption.

The polymers used in these studies include poly(methacrylic acid) (PMAA) with weight average molecular weights $M_w = 6$, 22, 72, and 350 kDa with narrow molecular-weight distributions (polydispersity indices 1.07, 1.05, 1.04, and 1.01, respectively) and a polycation with 20% of charged units ($Q20$), which was synthesized by partial quaternization of poly-4-vinylpyridine (PVP) ($M_w = 200$ kDa) with ethyl bromide to produce quaternized PVP (QPVP) as described elsewhere [19]. The polycation was then self-assembled with PMAA onto the surface of an oxidized Si crystal at *p*H 5 from 0.01 M phosphate buffer solutions. Si crystal was first primed with $Q20$, which adsorbed at the amount ~1.5 mg/m^2. This layer was not counted towards total number of polymer layers in the film. Further growth of PMAA/$Q20$ films (which were always topped with $Q20$) was linear, with individual layer coverages of 1.7 mg/m^2 and 3.3 mg/m^2 and thicknesses of 1.7 and 3.3 nm (for density of 1 g/cm^3) for PMAA and $Q20$, respectively [20]. The *p*H-induced compositional changes within the film were quantified using *in situ* attenuated total reflection Fourier transform infrared spectroscopy (ATRFTIR) as described elsewhere [20]. The salient feature of this technique is its ability to selectively detect individual chemical components of multilayers as well as being sensitive to the ionization of functional groups.

Figure 1(a) illustrates that a (PMAA/$Q20$)$_5$ multilayer deposited at *p*H 5 and exposed to *p*H 7.2 releases PMAA, while no mass loss is observed for $Q20$. The applied *in situ* ATRFTIR technique allows quantification of the
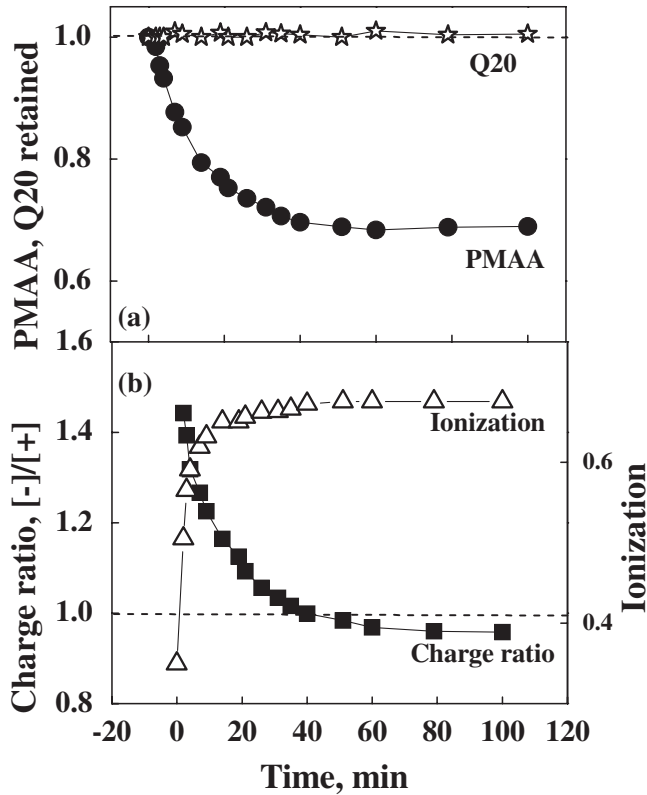
FIG. 1. (a) pH-triggered time evolution of $Q20$ (stars) and PMAA with $M_w = 72$ kDa (circles) in a 5-bilayer PMAA/$Q20$ film deposited at pH 5 and exposed to pH 7.2 as measured by *in situ* ATRFTIR. (b) Time evolution of PMAA ionization for the PMAA/$Q20$ film (triangles) and of the charge ratio within the film (squares) at pH 7.2. Here and in Figs. 2 and 3, experimental error is within the symbol size.

pH-induced imbalance of negative to positive charges in the film, which is the driving force for chain release. Figure 1(b) shows the evolution of the charge ratio within the PMAA/$Q20$ film. Significantly, the charge imbalance correlates with a rapid increase in ionization of self-assembled PMAA upon pH variation. When negative charges accumulate within the film, PMAA chains with excess charge are released into solution to bring the ratio of "$-$" to "$+$" polymer charges back to its original value close to unity [21]. ATRFTIR experiments showed that $\sim 90\%$ of the polyacid released at high pH is readsorbed by the film upon lowering the pH to its initial value. Note that a similar response of the QPVP/PMAA film to pH variation was observed for the polycations with other degrees of quaternization (Q) from 12 to 28.

We then focused on the PMAA molecular-weight dependence of pH-triggered selective release. We kept the driving force for chain release, i.e., the pH-induced imbalance of charges within the film, constant by exposing the films to either pH 7.2 or pH 7. At the same time, the molecular weight of the polyacid was varied from 6 to 350 kDa. Using *in situ* ATRFTIR, we found that at pH 7.2,

the same fraction of PMAA of 0.3–0.35 was released from the film regardless of PMAA molecular weight. However, the molecular weight of PMAA significantly affected release kinetics. Figure 2 shows that a significantly longer time was required for the release of longer PMAA chains. The characteristic time $\tau_{0.5}$ is defined as the time at which the fraction of released PMAA is half of that reached upon system equilibration. At a constant external pH, $\tau_{0.5}$ depends strongly on the molecular weight of PMAA: the inset of Fig. 2 shows that this dependence is approximately linear, i.e., $\tau_{0.5} \sim M^{1.1 \pm 0.1}$.

We next present the effect of film thickness on PMAA release. These experiments were performed with PMAA of $M_w = 22$ kDa at pH 7 rather than at pH 7.2, since the longer time scale of release was convenient for studying the film-thickness dependence. Square symbols in Fig. 3 show $\tau_{0.5}$ of PMAA release as a function of the number of PMAA/$Q20$ bilayers. The plot shows a distinct kink at 4–5 bilayers, with a linear dependence of $\tau_{0.5}$ on the film thickness at larger bilayer numbers. Circles in Fig. 3 represent the fraction of released PMAA, which increases with film thickness for films with fewer than 5 bilayers, and saturates, approaching 0.35 for thicker films. The first PMAA layer, closest to the substrate, does not release its PMAA due to "pinning" of polymer chains to a solid surface. The amount of polymers deposited within the first 2–3 polymer bilayers of PEMs has earlier been shown to differ from that deposited within the "bulk" of the film [22]. Here, we show that the proximity of the substrate also significantly suppresses the pH-triggered release of polymer chains.

We observe that the desorption time of PMAA for films with bilayer number larger than 4–5 scales as $\tau_{0.5} \sim M_w^{1.1 \pm 0.1} H$, where H is the film thickness. Below, we present a theoretical model which predicts $\tau_{0.5} \sim MH$, in
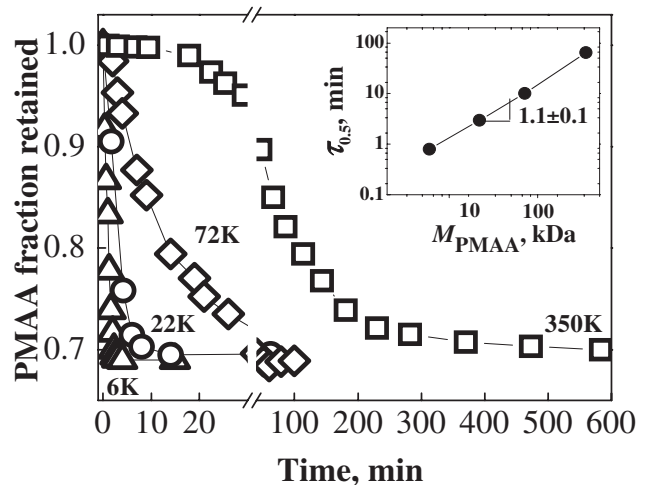

FIG. 2. Release rates of PMAA with different molecular weights from a 5-bilayer PMAA/$Q20$ film at pH 7.2. Inset shows characteristic time as a function of molecular weight for PMAA release.
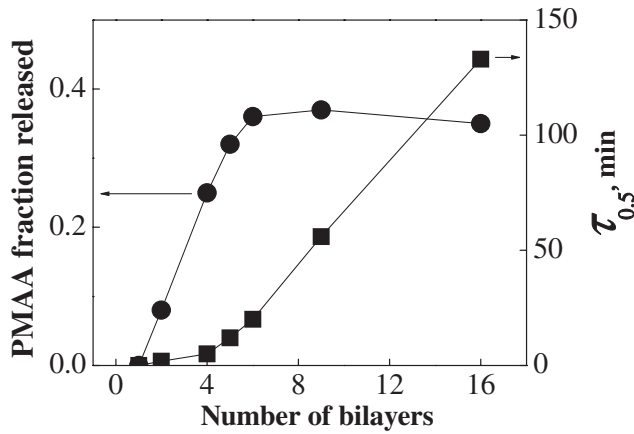
FIG. 3. Polyacid fraction released (circles, left axis) and characteristic half-time (squares, right axis) for 22 kDa PMAA release from PMAA/$Q$20 films of different thicknesses deposited at pH 5 and exposed to 0.01 M phosphate buffer solutions at pH 7.

good agreement with experimental results. The model is based on our claim that the driving force for the release of polyanions from the film is the electric field created by the counterions [23]. Specifically, pH-triggered increase of the polyacid charge causes a corresponding release of counterions. Although the escape of counterions from the film is favored entropically, such an escape leaves a negatively charged film behind. Therefore the counterions can sample only a volume slightly larger than the film, balancing their increased entropy with the energy of the resulting electric field (Fig. 4, left). This electric field imposes a force on polyanions directed out of the film that causes them to drift towards the free surface.

However, unlike the counterions, the polyanions cannot freely move out of the film, since they are bound to poly-
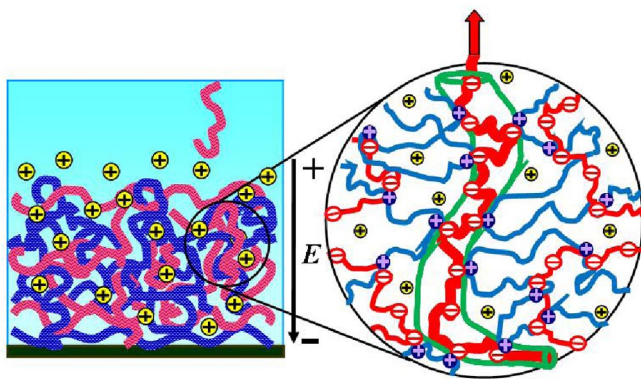

FIG. 4 (color online). Left: Polycation-polyanion multilayer film with excess charge on polyanions under high pH conditions. The counterions (circles with "+") occupy larger volume than the film, creating a net electric field **E**. Right: "Sticky gel electrophoresis." "Sticky" reptation of a polyanion (bold line) in electric field occurs through dissociation and association of ionic bonds.

cations by reversible ionic bonds (pairs of circles with "−" and "+"), forming a polyanion-polycation network. The electric field induced by counterion release drives the polyanions through this network in a way similar to that in gel electrophoresis [24]. As in gel electrophoresis, the polyanions in the multilayer film are entangled within the network and thus can only move along their confining tubes. One such confining tube for a typical polyanion (bold line) is shown in the right-hand part of Fig. 4. In contrast to gel electrophoresis, the polyanions can only move by breaking and reforming ionic bonds with polycations. Since reptation of macromolecules through reversible network occurring via dissociation or association of ionic pairs ("stickers") has been termed "sticky reptation" [25], the movement of entangled polyanions through the film in electric field might be called "sticky gel electrophoresis." As in the conventional gel electrophoresis of entangled polymers [24], the electrophoretic mobility in the "sticky gel electrophoresis" model is inversely proportional to the molecular weight M of moving chains (in this case, to the number of stickers per chain). Therefore the polyanion release time is proportional to M, as well as the distance the polyanions have to move (i.e., the film thickness H). Both predictions agree with our experimental
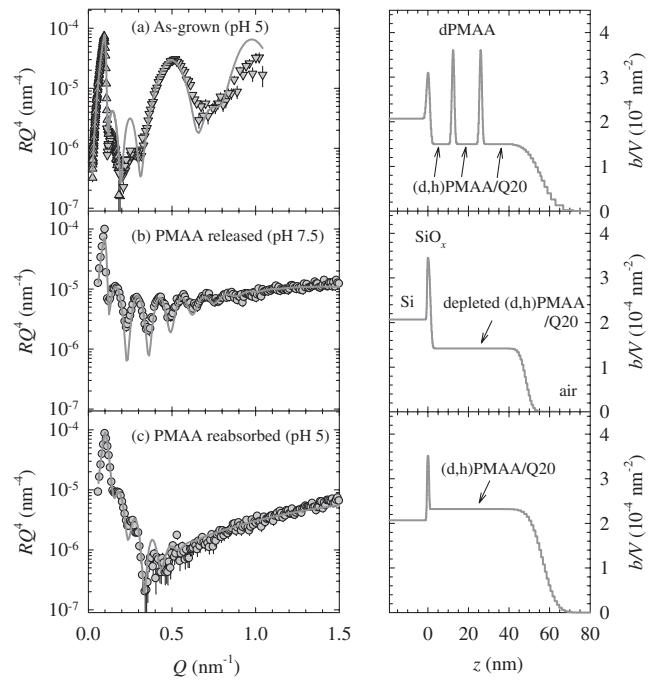

FIG. 5. Neutron reflectivity data (left) and fitted scattering-length-density profiles (right) obtained experimentally for air-dried $[(\text{PMAA}/Q20)_4/(\text{dPMAA}/Q20)]_4$ films—every fifth PMAA ($M_w = 22$ kDa) layer is deuterated to enhance neutron contrast. (a) Deposited at pH 5, data collected at the Spallation Neutron Source Liquids Reflectometer. (b) After exposure to pH 7.5, collected at NIST NG-7 reflectometer at fixed wavelength $\lambda = 0.475$ nm. (c) After solution pH was reduced back to pH 5, collected at NIST.

results. We also suggest that polyanions move through the film in a plug-flow-like fashion similar to the reverse process of polyions entering oppositely charged gels [26]. Note that as polyions migrate through the film, its multilayer structure is destroyed, as verified by neutron reflectivity (see below). Therefore our model considers a simpler case of polyion motion through spatially homogeneous reversible network of polyanions and polycations.

Finally, we asked whether the pH-triggered release and readsorption of polymer chains affected multilayer film structure. Figure 5 shows neutron reflectivity data of a 20-bilayer PMAA/$Q$20 film, where each fifth PMAA layer was deuturated, collected with as-deposited film at pH 5 [Fig. 5(a)], after exposure of the film to pH 7.5 [Fig. 5(b)], and subsequent readsorption of deuterated PMAA (dPMAA) at pH 5 [Fig. 5(c)]. As-assembled films (pH 5) show Bragg peaks characteristic of substrate-mediated layering within the film, with typical ''fussiness'' found earlier for different electrostatically self-assembled films [27,28]. Strikingly, the multilayer structure completely disappears after pH-induced release of PMAA [Fig. 5(b)]. The absence of periodic Bragg peaks in the reflectivity profile reveals complete mixing of the $Q$20 and PMAA layers, and the reduction of the total polymer layer thickness from 56 to 47 nm is consistent with release into solution of 35%–38% of the PMAA originally present in the film. Upon reduction of pH back to its deposition value (pH 5), and exposure to dPMAA solution, film recovered $95 \pm 5\%$ of its original thickness, implying complete reabsorption of dPMAA by the film [Fig. 5(c)]. The constant scattering-length-density profile of the film after reabsorption suggests a uniform distribution of this material throughout the film.

In conclusion, we have reported a novel phenomenon of selective release of weak polyacid from the polyanion or polycation multilayers in response to increase of external pH. Molecular weight M and thickness H dependence of chain release time $\tau_{0.5} \sim MH$ predicted by our ''sticky gel electrophoresis'' model agrees with our experimental results. Neutron reflectivity studies show that chain diffusion and pH-triggered release results in disordering of the film structure, as expected from the theoretical model. The obtained results might be used to rationally design WPEMs with desired characteristics for release of macromolecular components.

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