Reversible Molecular Memory and pH-Switchable Swelling Transitions in Polyelectrolyte Multilayers

Jeri'Ann Hiller and Michael F. Rubner*

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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ABSTRACT: The systematic design of materials that alter their macroscopic properties in response to environmental stimuli continues to provide a basis for stimuli-responsive applications in biomaterials and microelectronics. We report discrete volume phase transitions in ultrathin polyelectrolyte multilayers (PEMs) driven by changes in environmental pH of the post-assembled film. These films exhibit a history-dependent swelling behavior and molecular conformational memory. We illustrate that the same two polymers—poly(allylamine hydrochloride)/poly(styrenesulfonic acid) (PAH/SPS)—can be incorporated into a multilayer film with specifically designed molecular architectures (by virtue of assembly pH conditions) that enable them to be either virtually insensitive or highly responsive to small changes in post-assembly pH. We thus provide a general design strategy for PEMs that exhibit multiple conformational states and related phenomena. We further demonstrate the ability to spatially regulate the affinity of molecular species to PEMS—specifically, by virtue of pH-triggered conformational changes in the PEM. Finally, we show the potential of these materials for sustained molecular release.

Introduction

It is now well established that certain chemically cross-linked polymer gels can undergo discontinuous volume-phase transitions, swelling by many times their original volume, in response to subtle changes in environmental temperature, pH,[1] ionic strength,[2] and light,[3] among other stimuli. Acrylamide-based gels, for example, have been extensively studied due to their propensity to exhibit multiple conformational states, expressed by different degrees of swelling in solution, in response to changes in their environment.[4] In these materials, the resultant molecular conformations, often reversibly accessed, may exhibit distinct optical and physical properties and are thus macroscopically distinguishable "states" of the material. This presents intriguing possibilities for novel designs of molecular sensing and actuation devices.[5]

Materials capable of reversibly expressing various molecular states often exhibit the desirable attribute of history-dependent memory effects. For example, a hysteretic response to a stimulus enables different states to be exhibited at a given environmental condition depending on the stimulus history.[4] Consequently, molecular information storage and retrieval are viable design options. The expression of multiple molecular conformational phases and memory effects has gathered considerable interest in recent years and, until now, has only been observed in copolymers and homopolymers of chemically cross-linked gels.[1,4] More recently, there has been interest in developing stimuli-responsive gels with confined dimensions such as substrate-supported thin films[6] and end-supported cylindrical gels.[7] By restricting the swelling transitions of these materials to fewer dimensions, it is possible to create stimuli-responsive surfaces and interfaces to modulate cell attachment[8] as well as enable new approaches to cell harvesting[9] and coculturing.[10]

Polyelectrolyte multilayers (PEMs),[11] typically formed as dimensionally constrained thin films (fixed at a surface), represent an intriguing new material's platform for exploring such effects. PEMs are created by the alternative adsorption of oppositely charged polyelectrolytes or hydrogen-bonding polymers onto substrates. This versatile thin-film fabrication technique offers the benefit of solvent-free processing as well as the ability to conformally coat all available surfaces of virtually any material, irrespective of shape or size, with uniform ultrathin films of precisely controlled thickness. In contrast to the typical process of synthesizing polymer gels which involves the polymerization and chemical cross-linking of monomers and no control over the spatial arrangement of the resultant polymer chains, this technique provides a rather simple aqueous-based means of varying film composition while providing enormous design flexibility, including the ability to create complex multilayer heterostructures.[12,13] Thus, by controlling the number, sequence, and type of polymer layers incorporated in the film, it is possible to create a wide variety of chemically and structurally diverse materials. Of particular note is the possibility of incorporating polymers with temperature- and pH-responsive functional groups, hydrophobic moieties, and hydrogen-bonding groups,[14,15] the key elements of many stimuli-responsive gels.

The swelling response of PEMs to stimuli such as ionic strength and pH has been investigated in past years. Reversible swelling (∼18%)[16] induced by ionic strength changes and swelling due to humidity changes (∼26%) have been reported.[17] In addition, reversible pH-induced swelling[18] and pH-gated nanoporosity[19] as well as ionic strength and pH-induced swelling associated with the deconstruction and desorption of PEMs[20] have been observed in weak polyelectrolyte multilayers. Recent work has also investigated temperature-responsive chemically cross-linked acrylamide-based PEMs that swell by a factor of 2 and undergo a phase transition (upon heating).[21] However, despite important

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* To whom correspondence should be addressed: e-mail rubner@mit.edu.

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studies in this field, to our knowledge, no work has demonstrated discontinuous volume-phase transitions or the expression of multiple coexisting phases in PEMs.

In this paper, we demonstrate the first example of a polyelectrolyte multilayer thin film fabricated with a molecular architecture and composition that undergoes discontinuous volume-phase transitions that enable the expression of conformational memory. We further demonstrate that this type of molecular organization is well-suited for regulating and even selectively directing the affinity of molecular species to a PEM, by a process involving the pH-driven switching of conformational states. In addition, we discuss the potential of these systems for sustained delivery of small molecules in the useful physiological pH range as well as in physiological buffered environments. While this report describes a specific multilayer system poly(allylamine hydrochloride)/poly(styrenesulfonic acid) (PAH/SPS), our experimental findings, in conjunction with the prior work of others with copolymer hydrogels, suggest a general design strategy for creating PEMs that exhibit tunable discontinuous phase transitions, multiple coexisting phases, and memory capabilities.

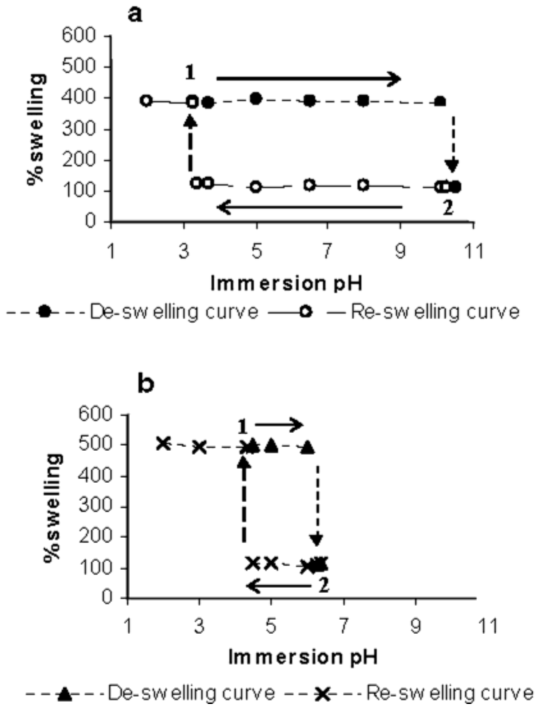

Figure 1. (a) Room temperature instantaneous (45 s) swelling hysteresis pH-loop for the 9.5/9.5 system: (closed symbols) deswelling data generated from samples previously swollen at pH 3.25; (open symbols) reswelling curve generated from samples previously deswollen at pH 10.3. (b) 45 °C instantaneous (45 s) swelling hysteresis: (triangles), deswelling data generated from samples swollen at pH 4.4; (cross-hatches) reswelling curve generated from samples shrunk at pH 6.25. The numbers 1 and 2 indicated in Figures 1a,b and 2a are used as described in the text.

Experimental Section

Materials and Sample Preparation. PAH ($M_w \sim 70\,000$) (Aldrich) and SPS ($M_w \sim 70\,000$) (Aldrich) were used as received and prepared as 10^{-2} M solutions (based on the repeat unit molecular weight) in ultrapure 18 MΩ·cm Millipore water. The pH of both polyelectrolyte solutions was adjusted, typically in the range of pH 2.0−9.5. PAH/SPS multilayer thin films were assembled at room temperature by an automated HMS programmable slide stainer (Zeiss, Inc.) using a previously described procedure.[22] For PAH/SPS 9.5/9.5 multilayer assembly, the pH of the rinse water was adjusted to pH 9.5 but used unadjusted at pH 5.5−6 for other multilayer systems. Multilayer films were assembled onto polished ⟨100⟩ silicon wafers and tissue culture polystyrene (TCPS) substrates. All experiments were carried out on samples with dry thickness ~ 65 nm with PAH as the outermost layer. Rose bengal (Aldrich) was used as received and prepared in a 10^{-3} M concentration, which was then pH adjusted to pH 5. After the initial multilayer fabrication, the films were exposed to pH-adjusted water. These adjustments were made with 1 M HCl for pH values 2−5 and 1 M NaOH for pH values >5.5. For temperature studies, the films were exposed to the pH-adjusted aqueous solutions equilibrated at 45 °C in a water bath.

Swelling Studies. The transition points, optical thickness, physical thickness, and index of refraction were determined by the use of UV−vis reflectivity, fluid cell contact mode AFM step-height analysis, ex- and in-situ ellipsometry, and profilometry. To evaluate the transition points, UV−vis−NIR reflectivity (in conjunction with visual observations of the interference reflection color of the film on silicon) was performed on the swollen films to determine the change in optical thickness of the film. This method is well-suited for identifying the range of pH immersions over which films exhibit the same optical thickness (within experimental error) and hence the transition points. The optical thickness of the dry film on a Si substrate was first recorded, and the physical thickness and index of refraction were verified by ellipsometry and profilometry as previously described.[18,19] Some dry film thickness measurements were determined by step-height analysis by AFM in tapping mode (in air) with Si cantilevers. These AFM measurements were within 10% of thickness data obtained from ellipsometry and UV−vis−NIR reflectivity. Since the reflectivity measurements of the swollen films were taken in air from a hydrated sample, the error in measurement was reduced by first scanning the appropriate spectral range to locate the minimum in reflectivity of the film. The film was then fully rehydrated and the reflectivity spectrum taken (acquired in seconds) before significant drying of the films occurred. In some cases, the reflectivity data were modeled using the matrix theory method as previously described.[19] The physical thickness measurements obtained by fluid cell AFM were generally within 15−20% of estimates obtained by modeling UV−vis−NIR reflectivity data.

The equilibration swelling times for samples were determined to be on the order of hours. Thus, for instantaneous-response studies, the films were exposed to the specified pH for 45 s and then dried in compressed air. For generation of the swelling curves (Figure 1a,b), multiple samples, identically prepared, were swollen at pH 3.25 (the swelling trigger point), dried, and then briefly exposed to a solution of higher pH. The film thickness was then measured in an AFM fluid cell containing fluid at the pH the film last experienced. For the reswelling curve, samples swollen at pH 3.25 were then shrunk at pH 10.25 (the instantaneous trigger point determined) followed by reimmersion in lower pH solution. (Again, each point shown corresponds to a unique sample.) On average, the film experienced the last pH ~ minutes.

The film thickness was then obtained via contact mode AFM (atomic force microscopy) (Digital Instruments Dimension 3000 scanning probe microscope) characterization in a fluid cell using $SiNi_3$ cantilevers. The film was scratched to the bare silicon surface, and the height of the effective step was measured in fluid of the same pH as the 45 s treatment. For equilibration studies, the films were immersed in the specified pH for at least 6−8 h and then measured in a fluid cell as described above. For studies at 45 °C, all thickness measurements were obtained at room temperature, in fluid of the same pH as the high temperature treatment. The inference that the high-temperature phase was stable at room temperature for short times in the same pH was deduced by visually monitoring the interference reflection color of the film on the Si or TCPS substrate to verify that the equivalent degree of swelling observed at the high temperature persisted in the same pH solution at room temperature. We recognize that some error may have been introduced by this approach.

In-situ ellipsometry measurements were carried out in self-built fluid cells as described in the literature.[18,23] As was the case for ex-situ measurements, a Gaertner ellipsometery equipped with a He−Ne at 633 nm (70° angle of incidence) was used. Fluid cells were constructed from glass slides bonded together by commercially available epoxy. The tilt angle of the entrance and exit windows for the incident beam was designed at 70° with the base window of the cell. For a given measurement, the laser was first aligned on the sample in air and the fluid was subsequently added to the cell. Measurements of the thickness of a spin-cast polystyrene film were taken in the fluid cell both in air and in water to verify the accuracy of the cell design. The error in thickness measurements was determined to be within ±3%.

Uptake and Release of Anionic Dye Molecules. For the uptake of dye, the films were either used as assembled or swollen in pH 2.0−4.2 solutions for 5 min−4 h and then dried in air. For all dye-uptake experiments, films were immersed in rose bengal 10^{-3} M solution at pH 5.0 for 5−200 min followed by a 60 s rinse in deionized water pH adjusted to 4.0−5.0. For the release of dye, the film was immersed in pH 6.5−12 water or buffered solution at pH 7.5 for times in the range of minutes to weeks. UV/vis measurements were taken with an Oriel UV−vis spectrophotometer, and the spectra of films assembled on polystyrene substrates were analyzed to monitor the absorption of rose bengal. To direct the adsorption of the dye to specified regions of a film, a pH 2−4 solution was applied directly only to those regions, prior to the film being immersed in the dye solution.

Results and Discussion

Multilayer films assembled from SPS and PAH contain two unique design features: a weak polyelectrolyte with a pH-tunable charge density (PAH) and a strong polyelectrolyte with hydrophobic aromatic units (SPS). We have found that multilayer films fabricated with the dipping solutions of both polymers at pH 9.5 undergo a discontinuous swelling transition when exposed to a low-pH solution and a subsequent shrinking transition upon exposure to a solution of higher pH. In addition, the degree of swelling of the film at, for example, neutral pH depends on whether it has previously been activated to its most or least swollen state. The nonequilibrium state of swelling of films immersed in aqueous solutions of different pH for 45 s is shown in Figure 1. After a brief immersion in a pH 3.25 aqueous solution, the as-assembled film swells by a factor of ∼3.9× its original *dry* film thickness. The closed symbols in Figure 1a show the short-time swelling response at room temperature of a series of 9.5/9.5 PAH/SPS multilayer films previously swollen at pH 3.25 (starting point indicated by the number 1) and subsequently exposed to higher pH solutions. As is illustrated, a film first swollen at pH 3.25 retains its swollen thickness within 10% for brief immersions in solutions up to pH ∼ 10.25 but at pH ∼10.3 *shrinks* from 3.9× to ∼1.15× its original *dry* thickness. The short-time reswelling behavior (Figure 1a (open symbols)) depicts the swelling response of a series of films deswollen at pH 10.3 (starting point indicated by the number 2) for 45 s followed by immersions in solutions of lower pH. In this case, the film thickness remains unchanged (at ∼1.15× the original dry thickness) down to pH 3.25, at which point it swells once again to ∼3.9× its original thickness. This swelling/deswelling behavior is repeatable and reversible when the film is cyclically immersed into pH 3.25 and then pH 10.3.

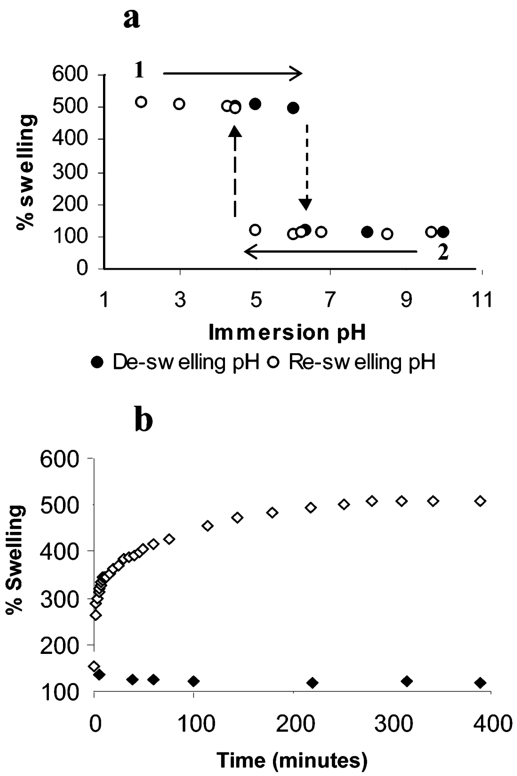

Figure 2. (a) Room temperature steady-state swelling hysteresis pH loop: (closed symbols) deswelling data generated from samples previously swollen at pH 2; (open symbols) reswelling curve generated from samples previously shrunk at pH 10.3. Data generated from measurements taken on a single sample cycled through pH 2−7 matched data shown within 10%. The accuracy of the transition points shown is to ±0.15 pH units. (b) Ellipsometrically determined time-dependent swelling of samples immersed into pH 4 water (open symbols) and pH 6 water (closed symbols) at 25 °C.

If the above swelling experiments are conducted at 45 °C instead of at room temperature, the swelling transition occurs at pH 4.25 and the film swells by ∼5× its original thickness. The shrinking transition, on the other hand, occurs at pH 6.25, at which point the film shrinks to ∼1.15× (Figure 1b). These results suggest that the swelling−deswelling pH-trigger points observed at room temperature for the short immersion times are influenced by swelling and shrinking kinetics. Consistent with this notion, the room temperature pH-swelling curves shown in Figure 2a reveal that, if the system is permitted to reach steady state (5−8 h), the swelling transition occurs at pH 4.4 while the shrinking transition occurs at pH ∼ 6.1. Thus, higher temperatures simply drive the molecules to their steady-state swelling at a faster rate. It should be noted that the instantaneous transition points at room temperature depend on film thickness, consistent with the idea that kinetic effects play a role in the observed swelling behavior. The time-dependent swelling response of 9.5/9.5 films immersed in pH 4.0 water (open symbols) and pH 6.0 water (closed symbols) is shown in Figure 2b. As is illustrated, a 9.5/9.5 film undergoes a swelling transition when immersed in pH 4 but does not swell appreciably when immersed in pH 6, for immersion times > 5 h.

The existence of an equilibrium pH−hysteresis loop suggests a memory effect such that in the pH range of ∼4.4−6 the PEM can attain either of two states (hereafter referred to as 5× and 1.15× for the phases swollen 5× and 1.15× their original dry thickness, respectively) depending on its pH history which is stored as molecular information. The important feature is that the expressed state is determined by whether the film was last introduced to pH < 4.4 or pH > 6 prior to immersion in a new solution of different pH. An additional feature of this system, similar to the phenomenon observed in chemically cross-linked PE gels,[4] is that the low-pH conformational state can be reversibly stored at low pH and then erased at high pH. The inherent reversible history dependence, characteristic of this system, could in principle be useful in devices such as threshold sensors.

The onset of swelling and shrinking is visually detected by a change in the film's optical interference reflection color. This change in the optical properties of the film as it undergoes a molecular transition may serve as a useful response function in a sensing application. A further potential benefit of this material is that the memory of the conformational state (in solution) is stored once the film is dried and in the solid state. Upon rehydration in a solution with a pH in the "two-state" pH range, the film essentially remembers the stored conformation and swells to either the 5× or the 1.15× state. The storage of molecular information in the solid state may become useful for materials handling, storage, and even facilitating potential applications. In the dry state, regardless of prior pH history, all films collapse back to essentially the same thickness of the as-assembled film.

The origin of discontinuous phase transitions as well as multiple-phase capabilities in polymer gels is believed to result from competition between attractive and repulsive interactions.[4] The effective frustration of the system gives rise to multiple minima in the free energy of the system and therefore several possible conformations that the chains can attain.[24] In the context of our PEM system, the critical points occur when the system is able to overcome the energy barriers between these minima. It has also been proposed that such swelling transitions in PE gels are driven by conformational changes in the polymer backbone triggered by variations in the electrostatic nature of the system.[25] In the PAH/SPS multilayers, the degree of ionization of the PAH chains is low during the multilayer assembly process (pH 9.5) but increases with decreasing pH. Thus, the origin of the trigger point at low pH (swelling transition) is likely linked to the increased ionization of the PAH chains relative to the high-pH environment in which they were constructed. However, this trigger point seems slightly low if one considers that the pK_a of PAH in solution is pH ~ 9, which means that the polymer would be expected to be ~90% ionized by pH 6.5.[26,27] It has been shown in hydrophobic copolymer gels that the effective pK_a of a weakly basic polymeric component (such as PAH in this case) can be reduced in the presence of hydrophobic groups (such as SPS, in this case).[28,29] Similarly, large shifts in the pK_a's of weak polyacids contained within polyelectrolyte multilayers have also been reported.[18,30,31] Thus, it is reasonable to conclude that the low-pH swelling transition is driven by changes in the degree of ionization of PAH and that a critical increase in the degree of ionization is needed to overcome hydrophobic interactions presented by the SPS chains.

As inferred above, hydrophobic interactions in SPS also appear to be important in controlling the trigger points. Assuming a model of competing attractive and repulsive interactions, at pH > 6 the hydrophobic interactions in SPS dominate the swelling-response and conformational state, while at pH < 4.4, electrostatic interactions dominate and determine the expressed phase. Consistent with the idea of an effectively frustrated system, both conformational states appear to be stable states in the pH range 4.4−6. In essence, the presence of associating aromatic rings acts to increase the effective cross-link density of the gel and thereby restrict the level of swelling possible. When the degree of ionization of the PAH chains is increased sufficiently to overcome these hydrophobic interactions, the multilayer swells to a higher level. Hydrophobic interactions may also explain an irreversibility which is introduced in these films after immersions for longer than ~10 h in the pH range 6−10, ~5 h at pH > 11, and within tens of minutes if heated to 45 °C at pH > 6.5. If deswollen outside the prescribed scope of reversibility, the reswelling of the film at low pH is markedly reduced. This may be due to more extensive hydrophobic interactions that form under these conditions and irreversibly change the nature of the film. However, the possibility that the film enters a different hysteresis loop[1] has not been ruled out.

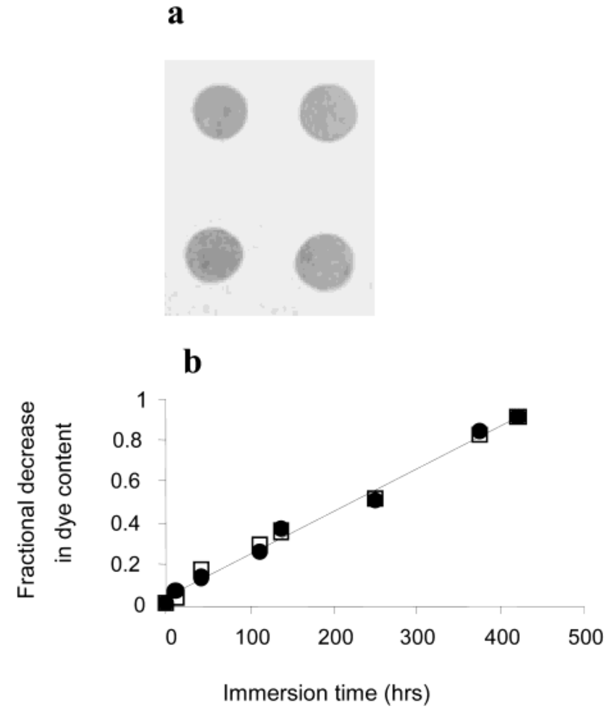

Figure 3. (a) Photograph illustrating the directed adsorption of rose bengal dye to low-pH preswollen regions (dots) of a 9.5/9.5 film. Droplets of pH 2 water were applied to 1 side of the film after which the film was then immersed in the dye solution that preferentially adsorbed to the 5× phase (dots) relative to the 1.15× phase (background). (b) Release profiles of rose bengal dye from the 5× phase of PAH/SPS films at pH (open symbols) 6.5 and (closed symbols) pH 8.

As mentioned previously, the coexistence of two distinct molecular states of the same material under the same conditions raises the prospect of molecular switching. We illustrate this principle by effectively switching the affinity that the PEM has for dye molecules on or off by switching the conformational state of the PEM. In the PAH/SPS system, since the two molecular organizations have different environments, structurally as well as electronically, their interaction with dye molecules is expected to differ drastically. Figure 3a shows the adsorption behavior of rose bengal, an anionic dye, with respect to the 5× and 1.15× phases. The 5×

phase is seen to adsorb ∼8 times as much dye as the 1.15× state, even at adsorption saturation. The dye molecules have a significantly higher affinity for the 5× phase, and this high contrast in dye adsorption between the two phases can be approximated as an on/off response (Figure 3a).

The incorporation of anionic dye molecules in the highly swollen, positively charged PEM is not surprising given the strong electrostatic attraction between the PEM and the dye. This is similar to what we have previously reported for the loading of cationic dyes into multilayer films containing many free anionic carboxylic acid groups.[32] In sharp contrast, however, in the present case, we find that the dye molecules can be loaded quickly at a low pH but are only slowly released at pH levels useful for drug delivery systems (buffered pH 7.4 solutions). For example, it takes about 15 min to completely load the dye into the multilayer film at pH 5.0, but the release process takes on the order of days to weeks in the pH 6−11 range in physiologically relevant buffered solutions (results to be published). Only at a higher pH of 12 is the dye released on the time scale of minutes. It is also interesting to note that preliminary results indicate that the release process is essentially linear in time in the useful pH range of 6.5−8 (Figure 3b), making this system potentially useful for sustained drug delivery. This system overcomes the problem of fast release (∼ minutes) of captured molecules in PEMs immersed in physiological buffered solution. For example, in PEMs based on weak polyacids, it has been observed that the pH conditions needed to achieve fast loading of a small molecule are the same as those utilized for drug release.[32]

In the PAH/SPS (9.5/9.5) multilayer system, the loading and release of a small anionic dye molecule appears to be directly linked to its phase transitions. Consistent with the mechanism suggested earlier, it seems reasonable to conclude that the anionic dye binds preferentially to the highly swollen, low-pH phase (5×) since the free amine groups are essentially fully ionized (positively charged) in this phase and readily accessible to the dye. One would expect that at a higher pH the charge density of the PAH chains would decrease and the dye would be released quickly: this is what was observed when cationic dyes were released by the acid groups of poly(acrylic acid)/PAH multilayer films at low pH (in this case, the charge density of the polyacid decreases with decreasing pH).[32] In a pH 7.4 buffered solution, however, the rose bengal molecules are released over a period of weeks rather than minutes, as might be expected for a anionic dye electrostatically bound to the functional groups of a weak polybase. It is therefore reasonable to infer that the release of the dye is linked to the increased hydrophobic interactions and concomitant shrinking transition that occurs in the deswelling pH range. This may be the result of a shifting pK_a effect due to the increasing hydrophobicity of the multilayer film, slower diffusion kinetics in this state, or some combination thereof. More work is needed to fully understand the mechanism of release. Possibly related molecular adsorption phenomena associated with conformational changes of PE gels[33] as well as molecular imprinting schemes[34] have been previously reported.

The key elements for creating multilayers with pH-switchable properties are low levels of ionic cross-linking, tunable levels of charge density, and competing attractive (hydrogen-bonding and/or hydrophobic interactions) and repulsive forces (electrostatic interactions).[4] We believe that assembling the PAH/SPS film with a relatively low degree of ionic cross-linking and a high extent of chain loopiness creates sufficient “flexibility” for the system to access various conformational states. Indeed, in direct contrast to the 9.5/9.5 system, PAH/SPS multilayers assembled at 6.5/6.5 or 2.0/2.0 (data not shown) exhibit relatively pH-insensitive swelling behavior (swelling by ∼110−130% irrespective of pH). This is likely due to the relatively high degree of ionic cross-linking and interpenetration afforded by their molecular designs. More intriguing, perhaps, is the fact that the PAH/SPS multilayers can be tuned to be pH-responsive (9.5/9.5) or pH-insensitive (6.5/6.5) by simple adjustments in the polyelectrolyte assembly pH.

In conclusion, we have demonstrated that polyelectrolyte multilayers based on PAH/SPS can exhibit pH-dependent properties with stored molecular memory capabilities. The demonstration of these phenomena in PEMs suggests that these materials could provide an ideal vehicle for studying the origin of volume phase transitions and multiple coexisting swollen phases in ultrathin films. The enormous design capability of PEMs further suggests that these novel thin film architectures could lead to new phenomena that may eventually be applied to applications ranging from biological sensing and actuation to artificial muscles.

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