

Controlling the physicochemical properties of weak polyelectrolyte multilayer films through acid/base equilibria*

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Abstract: Multilayer thin films prepared from weak polyelectrolytes can exhibit a rich suite of anomalous physicochemical properties. One of the major factors that influence the properties of such films is the acid/base chemistry of the weak functional groups of the polyelectrolytes. In fact, the apparent dissociation constants of weak polyelectrolytes can shift by as much as 1–4 pH units upon incorporation into multilayer films from that in dilute solution. Here, we discuss this variability in the dissociation behavior of polyelectrolytes in multilayer films, and how it relates to understanding the diversity in the physicochemical properties observed for films assembled from the same polyelectrolytes, but under different pH conditions. In turn, we review some of the recent research that attempts to take advantage of the pH-tunable properties of multilayer films for a variety of applications.

INTRODUCTION

In the rapidly advancing field of materials science, there is a continual demand for materials that are progressively smaller, on the order of nanometers to microns, are multicomposite, have easily tailored properties, and that are cheap, easy, and clean to prepare [1]. Although this is quite a daunting task, much progress has been made recently in this area. Just over a decade ago, Decher and Hong introduced a method of preparing polymer-based materials with such characteristics [2,3]. Their so-called layer-by-layer self-assembly technique involves the sequential deposition of oppositely charged polymers onto a charged substrate from dilute aqueous solutions. The resulting polyelectrolyte multilayer (PEM) thin films are stable and uniform, but have highly interpenetrated architectures [4]. The success of the multilayer growth is achieved only when the addition of a new layer results in charge over-compensation on the film surface. Multilayer films are most commonly prepared from aqueous solutions, making this technique environmentally and economically appealing. Multilayering has been done on a variety of different substrates differing in size, composition, and geometry [5]. In addition, the simplicity of the layer-by-layer concept allows for the preparation of multicomposite materials. Recent advances have yielded more complex hybrid materials that incorporate such things as nanoparticles, enzymes, cells, and carbon nanotubes into the film structure [6–9]. More importantly, however, multilayering is achieved using relatively inexpensive experimental techniques.

Traditionally, layer-by-layer assembly on planar substrates is carried out using a solution dipping method [1,2]. In this case, the substrate is dipped into a solution of the polyelectrolyte to be deposited. This is followed by a series of wash steps to remove unadsorbed polymer. The next layer is deposited by immersion of the substrate containing the first layer into a solution of the oppositely charged poly-

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mer. The new layer is then washed. This cyclic process is carried out until the desired number of layers is achieved. The solution dip method has been automated using a variety of commercially available instruments. The two other experimental methods that have been used to assemble multilayer films include spray and spin-coating techniques. Schlenoff et al. reported the successful assembly of polyelectrolyte multilayer thin films using a rudimentary spray device [10]. They found that the film thickness, morphology, uniformity, chemical composition, and membrane selectivity properties were quite similar for films prepared using the spray method in comparison to those assembled using solution dipping. Spin assembly using a commercially available spin-coater has also been employed to prepare multilayer films [11,12]. The reported protocols are very similar to those used for solution dipping, a cyclic process whereby a layer of polymer is deposited and then washed. However, in this case, the substrate is spun during each step of the assembly process. The spray and spin assembly techniques have the advantage that they require less sample and are less time-consuming than the solution dipping procedure.

By simply varying either the total number of layers deposited or the conditions used during the assembly process, the films can range from nanometers to microns in thickness [13,14]. In fact, it has been well documented that variation in such parameters as the concentration of polymers [14], their molecular weight [15], the concentration of salt used in the adsorption and wash baths [14,16], and the time allowed for polymer adsorption [17], among other film properties, greatly influence the film thickness. However, the possibility of controlling the film properties by varying the charge density of the polymer chains has only recently been explored [13,18]. Typically, multilayer films are prepared from strong polyelectrolytes that remain fully charged over the entire pH range, but multilayer films of weak polyelectrolytes are found to exhibit a rich suite of properties because of their pH-responsive behavior [13,18–24]. Some examples of weak polyelectrolytes are shown in Fig. 1. The charge density of weak polyelectrolytes is dependent on the solution pH. This affects the solution behavior of the chains and in turn influences their conformation upon adsorption onto a surface.

This short review article is intended to summarize the work that has been devoted to the study of multilayer thin films composed of weak polyelectrolytes. First, a discussion of the acid/base equilibria of the polyelectrolytes in the films is presented as a basis to explain the origin of the pH-responsive properties of these films. This is followed by a more detailed description of the vast array of diverse physicochemical properties observed in weak polyelectrolyte multilayer systems that can be controlled

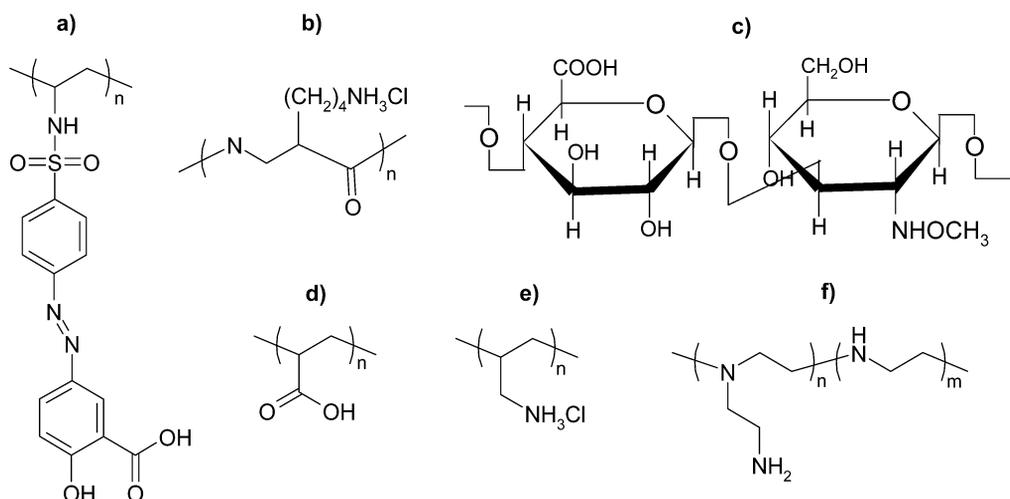


Fig. 1 Some examples of weak polyelectrolytes (a) poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediy] (PAZO), (b) poly(L-lysine hydrochloride) (PLL), (c) hyaluronic acid (HA), (d) poly(acrylic acid) (PAA), (e) polyallylamine hydrochloride (PAH), (f) poly(ethylenimine) (PEI).

with pH. The final section describes some of the applications that have been proposed for weak polyelectrolyte multilayer thin films.

ACID/BASE EQUILIBRIA

One of the major benefits of working with weak polyelectrolytes for multilayer film applications is the ability to prepare films from the same two polymers that have dramatically different physicochemical properties. This is largely a result of the fact that the charge density of the polymer chains in solution influences how they adsorb onto a surface, which in turn dictates the overall properties of the films [13]. For weak polyelectrolytes, the charge density is a function of their acid/base equilibria. In the case of polyacids and polybases, the dissociation behavior of each functional group along the chain is affected by the dissociation behavior of its nearest neighbors [25]. Intuitively, the apparent acidity of the weak polyacid decreases with progressive ionization of the polymer because of the difficulty of removing protons from polyions with increasing charge. Hence, the acid/base equilibrium of the chains is described by a modified version of the Henderson–Haselbalch equation, which takes this multifaceted relationship into account [25].

$$\text{pH} = \text{p}K_{\text{a}(\text{app})} - n \log\left(\frac{1-\alpha}{\alpha}\right) \quad (1)$$

The $\text{p}K_{\text{a}(\text{app})}$ is an apparent dissociation constant that reflects the overall acid/base equilibrium of the polyelectrolyte chains, and α is the degree of dissociation. The parameter n is related to the extension of the polymer chains, which is related to their charge density. Despite the fact that the acid/base equilibria of weak polyelectrolytes has been a topic of investigation for many decades [25–28], the affect of chain adsorption on the acid/base dissociation is not well understood, not to mention the influence of multiple polyelectrolyte under-layers. Recent studies have attempted to address such issues in multilayer thin films [24,29,30].

Rmaile and Schlenoff recently suggested unusual dissociation behavior of the chromophore-containing weak polyelectrolyte poly{1-[(4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl} (PAZO), incorporated into multilayer films with strong polyelectrolytes using UV-visible spectroscopy [29]. They found that the adsorption of the PAZO chains and the presence of strong, oppositely charged polymers in the film resulted in an increase in the acid strength of PAZO in comparison to its dilute solution behavior. However, when the films were exposed to a NaCl solution the $\text{p}K_{\text{a}(\text{app})}$ of the adsorbed PAZO chains shifted more toward the dilute solution $\text{p}K_{\text{a}(\text{app})}$. They hypothesized that as more salt is added to the solution, more segments are charge-compensated for by salt counterions, resulting in decrease in the population of polyelectrolyte ion pairs and consequently a reduction in the acidity of PAZO.

Our group has provided the first detailed study on the acid/base equilibria in multilayer thin films that contain both a weak polyacid and a weak polybase [24,30]. The first report dealt with multilayer films composed of the simple polyelectrolytes poly(acrylic acid) and poly(allylamine hydrochloride) [30]. We chose this system because several studies reported unusual physicochemical behavior observed for these films that is produced simply by varying the solution pH used during the film assembly process. It was speculated that such physicochemical anomalies stemmed from shifts in the acid/base equilibria of the polyelectrolytes. We evaluated the influence of the total number of polymer layers in the film, the assembly solution pH, and the salt concentration in the polymer solutions on the $\text{p}K_{\text{a}(\text{app})}$ of each polymer. In all cases, the polyacid becomes a stronger acid and the polybase a stronger base upon incorporation into multilayer films. In fact, the $\text{p}K_{\text{a}(\text{app})}$ values shift by as much as 1–4 pH units from their dilute solution values. The $\text{p}K_{\text{a}(\text{app})}$ value for both polyallylamine hydrochloride (PAH) and poly(acrylic acid) (PAA) varies with the layer number until 5 to 6 layers have been deposited. It is believed that the plateau in the dissociation constants is reached when the film reaches a stage of full

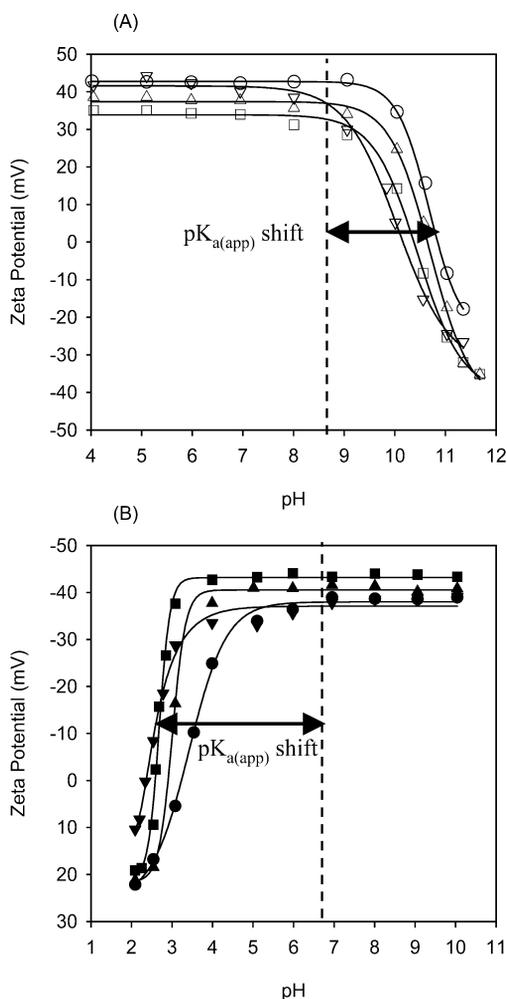


Fig. 2 Acid/base titration curves for PAH/PAA multilayer films assembled at different pH values; (A) 7-layer film assembled at pH = 3.0 (▽), pH = 5.0 (□), pH = 7.0 (△), pH = 9.0 (○); (B) 8-layer film assembled at pH = 3.0 (▼), pH = 5.0 (■), pH = 7.0 (▲), pH = 9.0 (●). The dotted lines indicate the dilute solution $pK_{a(app)}$ of PAH and PAA respectively [30].

homogeneous coverage. The trends in the $pK_{a(app)}$ values also indicate that the strength of the PAA increases as the assembly solution pH is reduced with the opposite trend being observed for the base strength of PAH (Fig. 2). However, there is only a slight variation in the $pK_{a(app)}$ values with a change in the salt concentration in the polyelectrolyte solutions used in the assembly process.

Acid/base equilibria studies were also carried out for a more complex polyelectrolyte multilayer system. Multilayer films were prepared from the biopolymer combination hyaluronic acid (HA) and poly(L-lysine) (PLL) [24]. Both of these polymers have the ability to adopt secondary conformational order, which can strongly impact their dissociation behavior in solution [31,32]. One of the most startling finds in this case is that in contrast to the other studies HA becomes a weaker acid and PLL a weaker base when they are assembled in a multilayer film. The strength of the polyacid and polybase becomes weaker as the number of layers in the film is increased. However, as was found in the study of PAH/PAA films, the acid strength of HA increases with a decrease in the assembly pH, with the opposite being true for the base strength of PLL. The inability to generalize the acid/base equilibria trends is attributed largely to the increased complexity of the polyelectrolyte systems, whose chains experi-

ence an increase in their degree of secondary conformational ordering when incorporated into multilayer films. Table 1 summarizes the $pK_{a(\text{app})}$ shifts we observed for polyelectrolytes in multilayer films. The key note is that the $pK_{a(\text{app})}$ trends in multilayer films are reflected in their physicochemical behavior [18,24]. Hence, such studies provide a chemical bases for understanding how to successfully control weak PEM films to obtained desired properties.

Table 1 Maximum shift in the $pK_{a(\text{app})}$ from dilute solution to multilayer film (+ or – indicates increase or decrease in $pK_{a(\text{app})}$ from dilute solution value).

Multilayer combination	Polyelectrolyte on surface	$pK_{a(\text{app})}$ Shift
PAH/PAA	PAH	+2
PAH/PAA	PAA	–4
PLL/HA	PLL	–3
PLL/HA	HA	+2

PHYSICOCHEMICAL PROPERTIES

This section is meant to highlight some of the work that has been done on investigating the host of diverse physicochemical properties that have been observed for weak polyelectrolyte multilayer films and how they relate to the acid/base equilibria within the films. These properties begin to be shaped and molded during the assembly process with the choice of solution pH and ionic strength. By taking advantage of the pH-sensitivity of weak polyelectrolytes, Rubner and coworkers were able to demonstrate that they could easily manipulate the chemical composition of the films [13,18]. The films can be made to be rich in one polymer over the other by working in a pH-regime where one of the polymers is weakly charged while the other is strongly charged. As the charge density of the polymer chains is reduced, they tend to adsorb in larger quantities on a surface and in a globular structure with many loops and tails [33,34]. Such films are highly populated with unbound functional groups from the weakly charged polymer, which can be taken advantage of for many applications. Thus, by varying the assembly pH for weak systems, the films can be prepared to be rich in the polycation, the polyanion, or to be relatively equivalent in both. This property is exclusive to weak systems because strong polyelectrolytes tend to adsorb in flat conformations with very few unbound functional groups [35]. Notably, the rate of polymer adsorption is also found to be orders of magnitude faster when the charge density is low, which allows for efficient preparation of the films and more precise control over their composition, as well as their bulk and surface properties [36].

The very nature of this unprecedented control that can be exercised over the composition of weak PEM films consequently influences the range of accessible film thicknesses (Fig. 3). When the polymers are highly charged, unfavorable segment–segment interactions lead to extended chain conformations in solution and in the adsorbed state, hence the resulting films are relatively thin [35]. However, slight variations in the charge density of the polyelectrolyte chains result in an energetically favorable transformation to globular conformations [33,34]. The chains adsorb on the surface in this fashion producing thick, loopy, and coiled layers. In fact, it is possible to vary the thickness of a single layer from 5 to 80 Å by adjusting the pH of the polyelectrolyte baths [18]. A model to account for such behavior was developed by Park and coworkers [22]. Even larger differences have been observed in film thickness values when a linear weak polyelectrolyte is multilayered with a multigenerational dendimer containing weakly basic functional groups [37]. In this case, the bilayer thickness can be tuned from 10 to 4000 Å. In addition, although electrostatic screening from salt ions can be used to vary the thickness of strongly charged PEM films to a limited extent, it can have a profound affect on the thickness of films

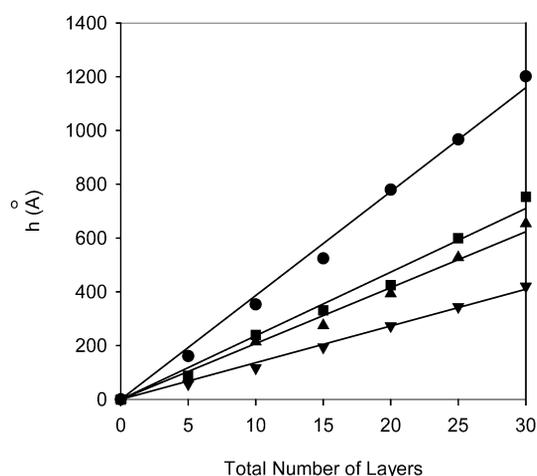


Fig. 3 Thickness of PAH/HA films assembled using different pH values. Assembly pH = 4.0 (●), 6.0 (▲), 8.0 (▼), 10.0 (■).

containing weak polyelectrolytes [38]. The ion pairs formed with the functional groups tend to be more easily disrupted, resulting in segmental rearrangement and hence thicker films.

Some weak polyelectrolytes, mainly biopolymers such as polyisopeptides and proteins, have an additional pH-sensitive feature that influences the internal structure and resulting thickness of the PEM films in which they are present. This feature is the ability of the chains to adopt complex secondary conformational ordering (i.e., helix, β -sheets), which is sensitive to local pH changes because this ordering depends heavily on secondary interactions such as hydrogen bonding [39]. There has been precedence established in the literature regarding the ability of such biopolymer chains to retain their secondary ordering upon incorporation into PEM films [40]. However, in other cases, rearrangement occurs when the chains adsorb resulting in a different composition of secondary conformational structures [41,42]. It has also been found that the multilayering process leads to the formation of secondary ordering of the chains that normally is not exhibited in solution under such pH conditions [43,44].

This variability in the conformational arrangement of polymer chains in weak PEM films not only has profound effects on their overall thickness in the dry state, but is primarily responsible for the unusually large variation in the degree of swelling that these films experience when exposed to solutions of different pH values [19,24,45,46]. When a film is assembled under highly charged conditions, the layers are stitched together tightly with many ionic cross-links. Thus, when exposed to a solution environment, these films experience a limited degree of swelling. This has been documented by Mendelsohn et al., who have reported only a 10 % increase in film thickness of PAA/PAH multilayer films assembled under pH conditions where both polymers are highly charged in solution [19]. However, as previously mentioned, by reducing the charge density of one or both of the adsorbing polymers many loops and tails are incorporated into the structure of the films. Upon exposure to solution, these films can undergo an extraordinary degree of swelling by as much as 8 times their original dry thickness, because the local pH and ionic strength environment leads to unfavorable interactions causing an increase in the extension of the unadsorbed segments in conjunction with the increase in hydration of the chains [24,46]. An example of this extraordinary ability of weak PEM films to swell is shown in Fig. 4. In most cases, the pH-induced swelling behavior of PEM films is reversible in nature, however, exposure to extreme solution conditions, such as high salt concentration, can lead to swelling to the point of deconstruction of the films due to breaking of the ionic cross-links that hold the layers together [38]. In addition, a recent report on the swelling of PAH/PSS films shows that such films undergo discontinuous swelling, which is linked to the expression of conformational memory [46]. The films go through a swelling loop where they are triggered to swell at low pH values, retain this state of swelling until trig-

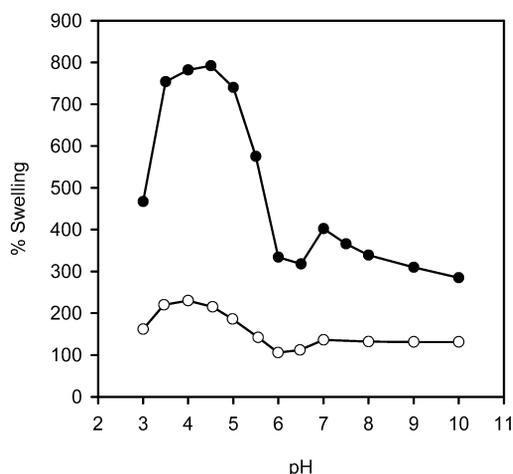


Fig. 4 Dependence of the equilibrium degree of swelling (relative to initial thickness) for (PLL/HA)₇₅ films assembled at pH = 5.0 (○) and pH = 9.0 (●) [24].

gered to compress their structure at high pH, and will then remain compressed over the same pH range until they are triggered to swell again at the trigger pH value. They have the unique ability to adopt either a stretched or collapsed conformation in the solution pH range of ~3.5 to 10.0.

For weak PEM films, pH not only influences their bulk properties, but can be used to tune their surface characteristics as well. As discussed above, the ability to change the conformation of the adsorbing weak polyelectrolyte chains with solution pH strongly affects the bulk properties of the films. However, the properties of the surface layer of the films are also dependent on the conformation of the absorbed chains. Dramatic variations in the film morphology and surface roughness have been observed in weak PEM films assembled under different pH conditions [13,18,19,47]. For example, the assembly pH and ionic strength conditions can be varied to produce PAH/PAA films that are homogeneous and nearly featureless, have a vermiculate pattern, or contain a series of nanopores [19,47]. In addition, nanopores can be reversibly or irreversibly created in such films by post-assembly exposure to extreme acid conditions [19,48]. These changes in the surface morphology are naturally accompanied by an alteration in the surface roughness of the films [13,47]. In fact, the surface roughness for PAH/PAA multilayer films can be varied by an order of magnitude from ~5 to 55 Å [13].

Such variability in the film morphology and surface roughness is also reflected in the surface physicochemical properties such as wettability and surface friction. Yoo et al. reported remarkable control over the contact angle of a droplet of water from essentially zero to as high as 50° for films containing the same polyelectrolyte combination, but assembled using different pH values [13]. In addition, the surface chemistry of weak PEM films is sensitive to the pH of the droplet of water, experiencing variations in the hydrophilic/hydrophobic nature of the surface with protonation and deprotonation of the functional groups. In the case of films prepared from hyaluronic acid and poly(L-lysine), the contact angle of a water droplet can be varied by as much as 25° for the same film by changing the droplet pH [24]. Additionally, film morphology and surface roughness are important parameters in determining the surface friction of the films. Lateral force microscopy studies reveal that the surface friction of a HA/PLL multilayer film can vary by as much as an order of magnitude depending on the assembly pH conditions, and the local pH environment at the surface (Fig. 5) [24]. This phenomenon indicates that polyelectrolytes can be assembled from solution under highly charged, “sticky” pH conditions and the resulting films can be stable with slick surfaces in the same pH environment because of the variation in the acid/base equilibria of the polyelectrolytes in the films.

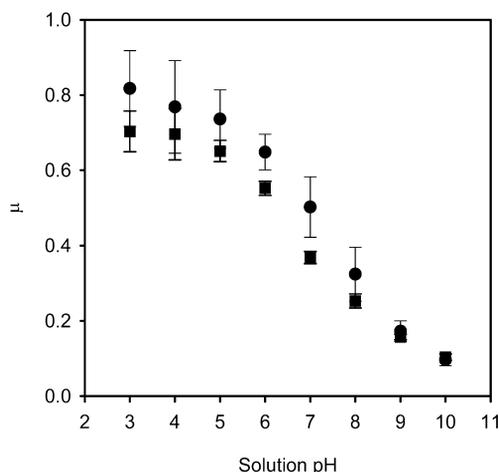


Fig. 5 Influence of solution pH on the coefficient of friction of a $(\text{PLL}/\text{HA})_{25}$ film assembled at pH = 5.0 (■) and 9.0 (●) [24].

APPLICATION OF WEAK PEM FILMS

This final section is devoted to discussing the host of applied research that attempts to take advantage of the rich suite of properties of pH-responsive PEM films. The versatility of these films has led to their application in such areas as sensors, coatings, drug delivery, biomaterials, and electrooptics. One of the simplest proposed applications is the use of such films as sensor materials. Lee et al. assembled multilayer films using PAH and PAA containing a covalently attached fluorophore whose peak position and intensity are sensitive to changes in the local pH environment [49]. Additionally, the fluorescence quenching for this fluorophore is strongly dependent on the concentration of metal ions and as such, the PEM films become metal ion sensors. Mermut and Barrett also demonstrated this pH-sensing principle using PEM films that were cleverly embedded with a chromophore-containing polyacid PAZO, whose *cis-trans*-isomerization rate is sensitive to changes in the local pH environment as shown in Fig. 6 [23].

A number of studies have found uses for weak PEM films in a variety of other optical applications. For example, the preparation of surface relief gratings for light-guiding applications was found to be successful only when the chromophore-containing polyelectrolyte was weakly charged, as opposed to fully dissociated, because the light-driven mass transport used to create the gratings is highly dependent on the ionic cross-link density in the films [50]. Rubner and coworkers have also illustrated that chromophore-containing polycations can be incorporated into multilayer films for the fabrication of devices with controllable light-emitting properties, the efficiency of which depends on the pH conditions used during the assembly process [51–53]. This group showed that they could also harness the optical properties of pH-sensitive PEM films to create antireflection coatings [48]. They found that by exposing the films to low pH salt solutions, they could induce reversible nanopore formation in the film structure leading to films with a controllable refractive index variable from 1.5 to ~1.15. The resulting films had reflective losses as low as 0.01 %.

The concept of using controllable weak polyelectrolyte multilayer films in optical and electronic applications has been recently extended to the areas of electroless plating [54] and the soft lithography technique of polymer-on-polymer micro-contact printing [55]. The electroless plating technique involves using the weakly acidic or basic functional groups in PAA/PAH multilayer films to selectively bind palladium catalysts that promote the deposition of metals such as nickel on the surface of the film. The plating process is dependent on the density of available functional groups in the films, which is controlled in the assembly process with solution pH. In micro-contact printing, pH is used to control the

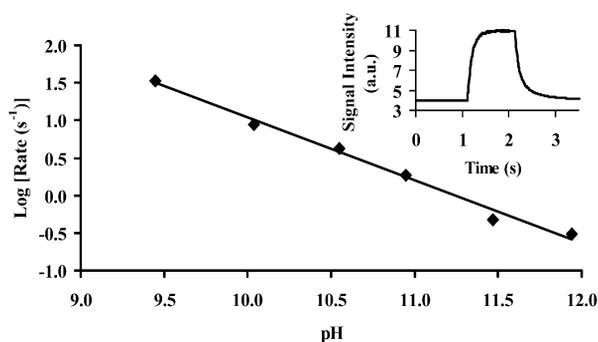


Fig. 6 Optical transmission during photoisomerization (inset) and the resulting *cis-trans* thermal isomerization rate constant as a function of pH for ER azobenzene chromophores [23].

patterning of the film through the thickness of the deposited layers and the density of functional groups in the patterned regions for further chemical processes.

The porosity of multilayer thin films is another property that has been exploited for creating tunable permeable coatings and membranes for separations. A number of groups have studied the transport of simple salts and redox-active species through PEM films in which one or both of the polyelectrolytes is weak [56–60]. Other studies report the use of pH-sensitive PEM films for selective separation of such species as ethanol/water and myoglobin/methyl orange mixtures [61,62]. The take-home message for all of this research is that the permeability through the PEM films is strongly dependent on their morphology, charge density, number of layers, cross-link density, and the ambient ionic strength. Hence, by manipulating the weak functional groups along the polymer chains, they were able to engineer the films to be completely impermeable, selectively permeable, or completely permeable.

This principle of permeability of PEM films has also formed the basis for using such films for the pH-stimulated loading and release of small molecules and drugs. The concept of using PEM films for drug and small molecule delivery technology was first introduced by Möhwald and coworkers [63–65]. They developed core-shell nanoparticles by multilayering on solid colloidal particles and then removing the core to leave the multilayer shell intact. They have successfully demonstrated the ability to load the hollow core with small molecules at one pH and then release them at various rates depending on a change in the solution pH and/or ionic strength. In addition, this group also showed they could multilayer on crystals of the drug ibuprofen and then use a pH-trigger to dissolve the crystal and control the release of the drug into solution with the surrounding multilayer membrane [66]. Other studies have utilized ionic cross-links between the small molecules and the functional groups of the pH-sensitive polymer in the films in combination with the bulk swelling properties to control the uptake and release of these molecules in a controlled way [46,67].

The use of pH to control drug delivery from PEM films is not the only biomaterials applications for such systems. Many recent studies have been devoted to exploring the possibility of creating multilayer films that can be controlled to promote or resist the adsorption of proteins or cells [68–71]. Others have focused on incorporating such things as enzymes and hormones that retain their activity allowing the films to function as novel bioreactors [72–74]. In addition, a recent study has shown that multilayer films of hyaluronic acid and chitosan could be layered on damaged arteries, creating an effective protective coating that can also be used to promote the healing process by incorporating therapeutic molecules into the film structure [75].

CONCLUSION

Polyelectrolyte multilayer thin films prepared from weak polyacids and polybases are emerging as viable new materials because of the ability to tune their properties in dramatic ways by simply changing the pH used to assemble them. The charge density of the polymer chains is sensitive to the local pH environment. It is the charge density that dictates their conformation in solution, which in turn affects how the chains adsorb onto a surface. This parameter is fundamental to the ability to control the overall properties of the films. Hence, understanding the acid/base chemistry of the polymers in the films is key to learning how to prepare films with desired properties. Many groups have started to take advantage of this phenomenon for a variety of applications and as such, weak polyelectrolyte multilayer films have a promising future.

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