Thermoresponsive Nanoassemblies: Layer-by-Layer Assembly of Hydrophilic−Hydrophobic Alternating Copolymers

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ABSTRACT: Multilayer films were assembled using the sequential alternate adsorption of a hydrophilic−hydrophobic copolymer, poly(styrene-*alt*-maleic acid) (PSMA), and poly(ethylene oxide) (PEO). The film buildup was followed using quartz crystal microgravimetry, and it was demonstrated that the incorporation of 0.2 M sodium chloride into the adsorption solution increased the adsorbed amount by a factor of approximately 2. Ten bilayer films of PSMA/PEO were shown to have a thickness of approximately 200−500 nm, depending on the specific adsorption conditions used. The surface roughness of the films was examined using scanning force microscopy and shown to be dependent on both the adsorption conditions used and the terminal layer of the assembly. Films prepared at higher ionic strength had a rougher surface, and films terminated with PSMA were rougher than those terminated with PEO. The films were shown to have a strong affinity for Rhodamine B, with the dye concentration in the film exceeding that in the adjacent solution by a factor of approximately 7.3×10^4. The absorbed dye was then released by elevating the temperature of the film, with the release rate dependent on the temperature of the release solution. The inclusion of the hydrophobic domains was shown to have a strong influence on the thermoresponsive behavior of the assemblies.

Introduction

Layer-by-layer (LbL) assembly is widely used as a versatile method for preparing thin films of various materials.[1,2] The technique exploits the sequential adsorption of complementary species to construct films in a stepwise fashion. In early work, oppositely charged polymers (such as poly(styrenesulfonate) and poly(allylamine hydrochloride)) were used to prepare these multilayer assemblies,[3−7] but more recently it has been demonstrated that secondary interactions, such as hydrogen bonding,[8−10] charge-transfer complexation,[11] and hydrophobic interactions,[12] can be used. In particular, hydrogen bonding has been used to assemble a variety of different materials into LbL thin films. Stockton and Rubner first reported hydrogen-bonded LbL assembly of polyaniline with a number of different alternating species: poly(vinyl alcohol) (PVA), poly(acrylamide) (PAAm), poly(vinylpyrrolidone) (PVPON), and poly(ethylene oxide) (PEO).[8] Almost simultaneously, Zhang and co-workers demonstrated the use of hydrogen bonding to assemble multilayers comprising poly(vinylpyridine) (PVP) and poly(acrylic acid) (PAA).[9,10] Since these reports, a number of other systems have also been examined: PAA/PEO,[13,14] PAA/PVPON,[13,14] poly(methacrylic acid) (PMAA)/PEO,[13,14] PMAA/PVPON,[13,14] PAA/PAAm,[15] PVP/poly(vinylphenol) (PVPh),[16] and PAA/poly(*N*-isopropylacrylamide) (PNIPAAm).[17] Further, hydrogen-bonded thin films have also been transferred to three-dimensional substrates, with studies showing that PAA/PAAm,[18] PEO/PMAA,[19] and PVPON/PMAA[19] multilayers can be constructed on colloidal particles. Hydrogen-bonded films show promise due to their response to variations in pH[13] and temperature[17] and because they are more likely to resist protein and other biomolecule deposition.

A number of studies have detailed the release of guest molecules from within both electrostatic and hydrogen-bonded multilayer assemblies. Chung and Rubner demonstrated the triggered release of methylene blue from multilayer assemblies initiated by changing pH,[20] while Sukhishvili et al. demonstrated that a dye molecule (Rhodamine 6G) could be released from a multilayer assembly on erasure of the multilayer (by pH change)[13] or by adsorption of another layer.[21] Adsorption-triggered release has also been reported for the case of pyrenetetrasulfonic acid embedded in multilayer films upon exposure to poly(styrenesulfonate).[22] We recently demonstrated that multilayers containing the commonly utilized thermoresponsive polymer, PNIPAAm, could be reversibly loaded with dye and emptied by varying the temperature of the surrounding solution. Lyon and co-workers reported similar results, although using nanocomposite films constructed from microgel particles assembled in alternation with PAH.[23] Other work has also focused on the release of guest materials from within multilayer capsules, triggered by a change in the solution pH[24] or ionic strength.[25] One novel approach recently reported has been to use multilayer assemblies incorporating metal nanoparticles which absorb radiation in the near-infrared region. Subsequent dissemination of absorbed energy leads to capsule destruction and release of the capsule contents.[26]

While PNIPAAm/PAA multilayer films show some promise as carriers for guest molecules, significant leakage from the film was observed at ambient temperature.[17] As such, we examined alternative building blocks for the construction of thermoresponsive thin films. Yin and Stöver recently reported the preparation of a thermoresponsive polymer by grafting PEO side chains onto a poly(styrene-*alt*-maleic acid) (PSMA) backbone.[27] The resulting graft copolymers exhibit lower critical solubility temperature (LCST) behavior, with the transition temperature tailorable by varying the length

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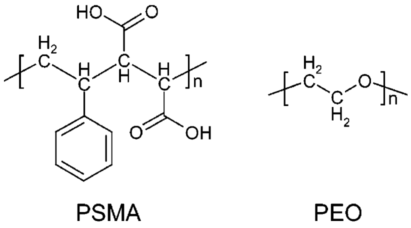
Chart 1. Molecular Structures of Poly(styrene-*alt*-maleic acid) (PSMA) and Poly(ethylene oxide) (PEO)



of the PEO side chains. Importantly, these graft copolymers include functional groups which have previously been used in LbL assembly (carboxylic acid and oxyethylene groups).[13,14] Herein, we investigate the possibility of preparing thin film analogues of these polymers by assembling PSMA in alternation with PEO (Chart 1) via hydrogen bonding. The resulting films can be loaded with a guest molecule, which can be released upon heating. Film thickness and morphology can be tailored by varying the assembly conditions, layer number, and the final layer adsorbed. The films were shown to have a high affinity for Rhodamine B, with loadings of greater than 40 wt % achieved. A much higher dye concentration was observed within the film than in the surrounding solution. The films were shown to be stable to changes in temperature and to release the dye when "instructed" by a change in temperature. Significantly, the amount of leakage from the film when exposed to temperatures close to 21 °C was significantly less than previously observed with the PNIPAAm/PAA system (10% over 1 h compared with 30% over 40 min). These films may find application in controlled release, drug delivery, or high functionality coatings.

Experimental Section

Materials. Poly(styrene-*alt*-maleic acid) (PSMA, M_w = 120 000 g mol^{-1}, 30 wt % solution in water), poly(ethylene oxide) (PEO, M_v = 100 000 g mol^{-1}), poly(ethylenimine) (PEI, M_w = 25 000 g mol^{-1}), poly(allylamine hydrochloride) (PAH, M_w = 70 000 g mol^{-1}), poly(acrylic acid, sodium salt) (PAA, M_w = 30 000 g mol^{-1}), and Rhodamine B were obtained from Sigma-Aldrich and used as received. Hydrochloric acid (HCl) was obtained from BDH and used as obtained. High-purity water with a resistivity greater than 18 MΩ cm was obtained from an in-line Millipore RiOs/Origin system. Quartz substrates were purchased from H.A. Groisse and Co. (Melbourne, Australia), silicon wafers (monocrystalline prime grade) from MMRC Pty Ltd. (Melbourne, Australia), and quartz crystal microbalance (QCM) electrodes (F_0 = 9 MHz, gold-coated AT-cut quartz) from Kyushu Dentsu Co. Ltd. (Nagasaki, Japan).

Quartz slides were cleaned via treatment with Pirahna solution (70/30 v/v % sulfuric acid:hydrogen peroxide) *Caution! Piranha solution is highly corrosive. Extreme care should be taken when handling Piranha solution, and only small quantities should be prepared.* Silicon wafers were cleaned by dipping in 2-propanol for 10 min. Both quartz slides and silicon wafers were further cleaned and hydrophilized by treatment with RCA solution (5:1:1 water:ammonia:hydrogen peroxide) at 60 °C. This treatment imparts a negative charge on the substrate, allowing subsequent adsorption of polyelectrolyte.

The PEI deposition solution was prepared to a polymer concentration of 1 mg mL^{-1} in 0.5 M sodium chloride. PSMA, PEO, and PAA deposition solutions were also 1 mg mL^{-1} with respect to polymer and had their pH adjusted to 3.0 using 1 M HCl (to ensure that carboxylic acid groups were largely in the protonated state).

Methods. *Preparation of Multilayer Thin Films.* Quartz slides, QCM electrodes, and silicon wafers were initially exposed to a PEI solution for 15 min (followed by three 1 min rinses in water) to yield surfaces with hydrogen-bonding sites. The substrates were then exposed to PSMA solution for 15 min, followed by three 1 min rinses in dilute HCl (pH = 3.0). Each substrate was then dried under a gentle stream of nitrogen, and the process was repeated, replacing PSMA with PEO. Alternate depositions of PSMA and PEO were performed until 10 bilayers were adsorbed, (PSMA/PEO)$_{10}$. The deposition process was repeated from polymer solutions at three different supporting electrolyte concentrations (0, 0.02, and 0.2 M NaCl).

Quartz Crystal Microgravimetry (QCM). QCM measurements were taken after deposition of each layer. The resonance frequency of the QCM electrodes was approximately 9 MHz. Assuming the film density is 1.2 × 10^6 g m^{-3}, the average polyelectrolyte layer thickness, d, was calculated from the change in QCM frequency, ΔF, according to the equation d (nm) = $-0.017\Delta F$ (Hz).[28,29] Applicability of the Sauerbrey relationship was verified by additionally measuring the dissipation of the films using a Q-Sense QCM-D300 (Q-Sense AB, Västra Frölunda, Sweden). The measured dissipation was less than 1 × 10^{-6} per 5 Hz frequency change, allowing use of the Sauerbrey relationship.

Scanning Force Microscopy (SFM). SFM images were taken using a Nanoscope IIIA atomic force microscope in tapping mode on air-dried films. The scan area was 1 μm × 1 μm or 10 μm × 10 μm.

Loading and Release Studies. (PSMA/PEO)$_{10}$ films on quartz substrates were exposed to Rhodamine B (0.005 mg mL^{-1}, pH = 3.0, 3.0 mL) at a variety of temperatures. After a prescribed time (2.5, 5, 10, 15, 20, 30, 40, 50, or 60 min) the sample was removed, washed by three dips (approximately 1 s each) in dilute HCl (pH = 3.0), and dried under a gentle stream of nitrogen. The UV−vis spectrum was then collected using an Agilent 8453 UV−vis spectrophotometer. An air blank was used for all measurements. The absorbance at 567 nm was recorded to monitor the amount of Rhodamine B within the film. The measured absorbances were corrected using a single reference wavelength (700 nm). Release experiments were conducted in the same way, by suspending a dye-loaded film in dilute HCl (pH = 3.0, 100 mL) with gentle stirring. The film was removed and absorbance recorded after the same time intervals as in the loading experiments. For equilibrium experiments, the film was left in contact with the dye until there was no further increase in the absorbance of the film with additional exposure to the loading solution. Blank experiments were also performed using multilayers of PAA and PEO.

Results and Discussion

Multilayer thin films were prepared by assembling PSMA in alternation with PEO at pH = 3.0. Figure 1a shows QCM data for the assembly of the films under three different ionic strength conditions. The 10-bilayer films had a thickness of approximately 200 nm when prepared at either 0 or 0.02 M NaCl and close to 500 nm when prepared at 0.2 M NaCl. Such a dramatic increase in the film thickness is likely to originate from the well-documented conformational variations which are evident in maleic acid copolymers with varying pH and ionic strength.[30−35] The film buildup is nonlinear, which has been described as "exponential" by other authors.[36] Two possible reasons have been invoked for this buildup profile. First, as the multilayer grows, an increase in the surface roughness may lead to more available surface area for adsorption and therefore allow for a greater adsorbed mass.[14] Second, diffusion of one (or both) of the polyelectrolytes into the multilayer assembly, and release of this uncomplexed material during subsequent adsorption, may lead to an adsorbed mass proportional to the increasing film thickness.[36] As exponential behavior is observed in this case even when the film surface is relatively smooth (see below), it is more likely that the second reason is responsible.

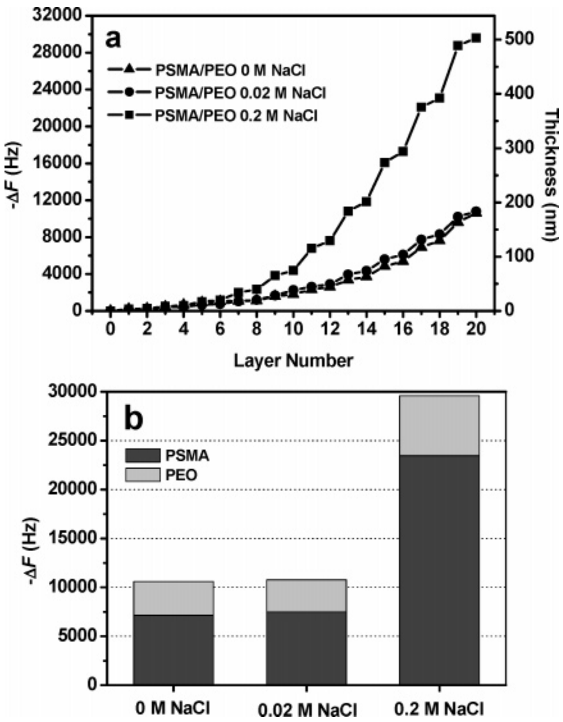


Figure 1. Growth of PSMA/PEO multilayer films followed using QCM. [PSMA] = [PEO] = 1 mg mL^{-1}, pH = 3.0. (a) Frequency change and film thickness vs layer number. Odd layer numbers correspond to PSMA and even layer numbers to PEO. (b) Average frequency change per 20 layers, including the proportion contributed by adsorption of each species.

The total frequency change for 20 layers, and fraction of the change corresponding to PSMA and PEO adsorption, is shown in Figure 1b. Under each ionic strength condition, there is a greater amount of mass added to the film for the PSMA adsorption than for the PEO step. The mismatch between the fractions is greatest when the polymers are adsorbed from solutions containing 0.2 M NaCl. This can be rationalized by the higher Na^+ concentration leading to deprotonation of some of the carboxylic acid groups and therefore a reduction in the number of carboxylic acid groups available to hydrogen bond. This would result in a greater mass of PSMA being adsorbed to "compensate" the available H-bonding groups on the underlying PEO layer. Such increased carboxylic acid dissociation has been observed in studies on the dissociation of PSMA in solution. At pH = 3.0 the percentage of ionized groups increases from ca. 5 to 10% when 0.1 M NaCl is added to the solution,[37] and we observed the same increase when a titration of PSMA in 0.2 M NaCl was performed (data not shown). Additionally, binding of sodium ions to oxyethylene sites may cause a similar reduction in hydrogen-bonding sites on the PEO chains. Importantly, salt effects on the construction of hydrogen-bonded multilayers are not unprecedented. Hammond and DeLongchamp have also observed a dependence of film thickness on salt concentration in PAA/PEO multilayer films assembled via hydrogen bonding,[38] though in that case the effect is considerably less than that observed here.

The morphology of the films was examined using scanning force microscopy. Figure 2a shows a 1 μm^2 section of a $(PSMA/PEO)_{10}$ film prepared at 0 M NaCl. The film is quite smooth, with a surface roughness of approximately 1.5 nm. Films prepared from solutions containing 0.2 M NaCl are also smooth (Figure 2b, root-mean-squared roughness ~2.5 nm), and examination of a larger 100 μm^2 region (Figure 2c) reveals that there are no larger features. However, the adsorption of a

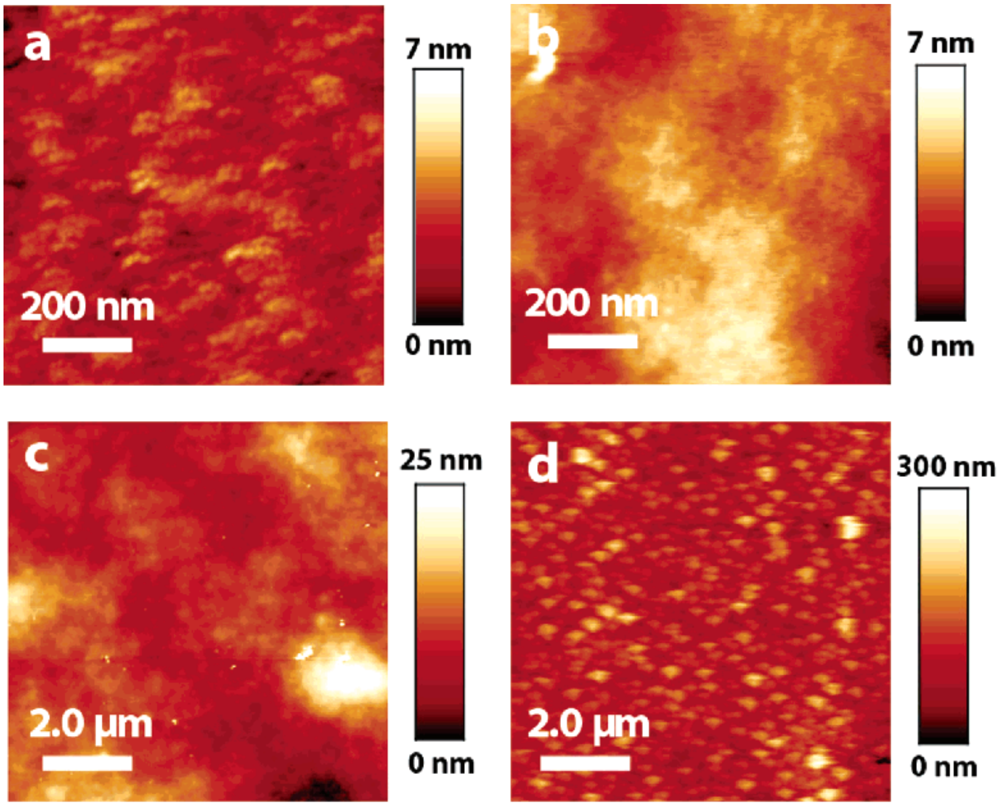


Figure 2. SFM images of $(PSMA/PEO)_{10}$ multilayer thin films prepared under different conditions: (a) 0 M NaCl; (b, c) 0.2 M NaCl; (d) $(PSMA/PEO)_{10}$/PSMA prepared from solutions containing 0.2 M NaCl. Scan area = 1 μm × 1 μm (a, b) or 10 μm × 10 μm (c, d).

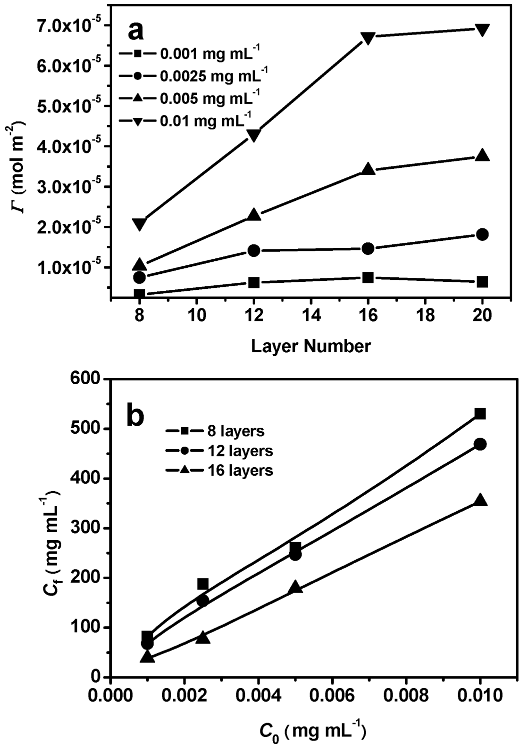


Figure 3. Equilibrium dye loading studies for PSMA/PEO multilayer films of varying layer number (prepared from adsorption solutions containing 0 M NaCl and pH = 3.0). (a) Dye loading vs layer number. (b) Dye concentration in film vs initial dye concentration in solution. The concentration of Rhodamine B in the film was determined from the decrease of Rhodamine B concentration in the solution. All studies were performed at 21 °C and pH = 3.0.

terminal PSMA layer at 0.2 M NaCl led to a drastic change in the surface morphology of the film. The film roughness increased from 2.5 to 30 nm, and inspection of the image reveals small, regular nodules (Figure 2d). Interestingly, analysis of the film roughness during construction (i.e., after 1, 2, 5, 6, 10, and 11 layers) showed that rougher surfaces corresponded to films in which the outer layer was PSMA. Further, the roughness increased with increasing layer number. This suggests that the increasing surface roughness is due to macroscopic rearrangement of the film after adsorption rather than the morphology of the single adsorbed outer layer.

To examine the utility of PSMA/PEO films as potential carriers for guest molecules, experiments were performed to determine the loading of the film with Rhodamine B. Films of varying thickness (i.e., layer number) were constructed on quartz substrates (without added salt in the deposition solution), and these films were exposed to Rhodamine B solutions of varying concentration. It is anticipated that Rhodamine B will be retained within the film by a variety of interactions, including hydrogen bonding (between the carboxylate groups on the Rhodamine B and oxyethylene groups in the film), electrostatic interactions (between the protonated amine groups in the Rhodamine B and carboxylate groups in the film), and $\pi-\pi$ interactions (between the phenyl groups in both the dye and film). The film was left in contact with the dye solution until equilibrium was reached between the dye concentration in the film and the solution. Figure 3a shows the amount of dye absorbed into the film as a function of layer number. As expected, thicker films absorb a greater amount of dye for a given dye concentration in the surrounding solution. Importantly, $(\mathrm{PSMA/PEO})_{10}$ films do not absorb significantly more dye than do $(\mathrm{PSMA/PEO})_8$ films, suggesting that there is a certain film thickness beyond which the loading amount plateaus. This may be indicative of only a constant outer region of the film successfully retaining the dye. This phenomenon has also been observed in studies of probe diffusion into electrostatically bound multilayer thin films.[22]

To quantify the equilibrium between free dye in solution and dye absorbed by the film, the following relationship was used:

$$K = \frac{C_f}{C_s} \tag{1}$$

where K is the partition coefficient, C_f the concentration of the dye molecule within the film, and C_s the concentration of the dye in the solution. Since a constant amount of dye remains in the system throughout the experiment, we can rearrange this equation in terms of C_f and C_0, the initial dye concentration in the solution. This yields the equation

$$C_f = \left[\frac{KV_s}{V_s + KV_f}\right]C_0 \tag{2}$$

where V_s and V_f are the volumes of the solution and film, respectively. Using this equation, a plot of C_f vs C_0 (Figure 3b) can be used to extract the partition coefficient via the gradient. Averaging the partition coefficients obtained for films of varying thickness (excluding the 20-layer film where dye loading limits become effective), a partition coefficient of $(7.3 \pm 2.0) \times 10^4$ was obtained, indicating that these films have a very strong affinity for Rhodamine B. Importantly, the data remain linear over the range of initial dye concentrations studied, suggesting that saturation of the films with dye did not occur in any of these cases. High loadings were achieved, with up to 40 wt % dye being incorporated into the film. This demonstrates that PSMA/PEO films are effective carriers for small organic molecules such as Rhodamine B and that the film loading can be carefully tuned by varying the dye solution concentration.

To examine the applicability of these films in thermoresponsive release, the dye-loaded films were exposed to release solutions at various temperatures, and the absorbance of the film was studied as a function of time (Figure 4a). The amount of dye released from the film was strongly dependent on the temperature of the release solution, with only 10% of the dye released after 60 min at 21 °C. Upon elevation of the temperature, the amount of dye released was considerably higher, with 35% released at 35 °C and 60% at 50 °C. PSMA/PEO films represent a considerable improvement on PNIPAAm/PAA films, from which there was leakage of approximately 30% in the first 40 min at 21 °C. In the current system, leakage is markedly reduced, while the films retain their thermoresponsive behavior.

To probe the origin of the thermoresponsive behavior, films were also assembled from PAA and PEO. These polymers were chosen as they contain similar functional groups to PSMA/PEO (carboxylic acid and oxyethylene groups), but without the hydrophobic styrene pendants. The PAA/PEO films were loaded with Rhodamine B (to a similar loading as the PSMA/PEO films) and then

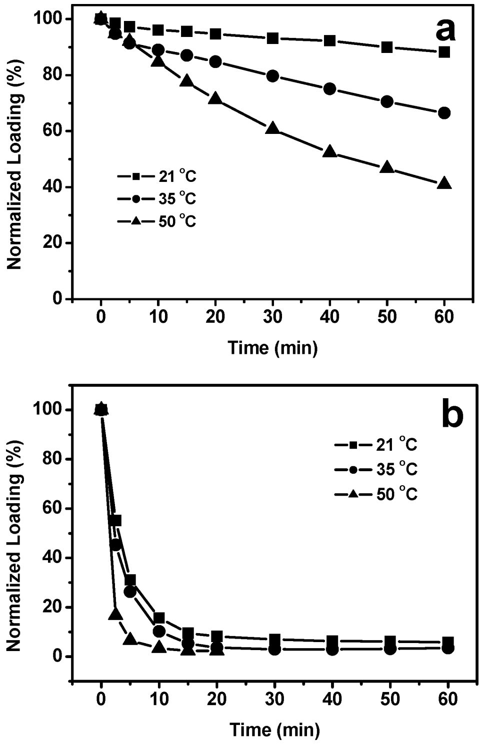


Figure 4. Release profiles for (a) $(PSMA/PEO)_{10}$ and (b) $(PAA/PEO)_{10}$ multilayer thin films loaded with Rhodamine B upon exposure to dilute HCl (pH = 3.0) at various temperatures. The films were prepared from adsorption solutions containing 0 M NaCl and pH = 3.0. Data were obtained using UV−vis spectrophotometry of thin films on quartz slides. The ratio of film volume to release volume was constant between the two film types to account for differences in film thickness.

exposed to release solutions at various temperatures. To account for thickness differences between $(PSMA/PEO)_{10}$ and $(PAA/PEO)_{10}$ films, the ratio of release volume to film volume was kept constant between the two experiments. Figure 4b demonstrates that the performance of PSMA/PEO films is superior to that of the PAA/PEO films. PAA/PEO films show little propensity to retain the dye, which is effectively released within the first 20 min at all three temperatures. As such, it is evident that the addition of large hydrophobic pendants to the polymer chains increases the retention of Rhodamine B (possibly due to $\pi-\pi$ interactions between the aromatic groups of the PSMA and Rhodamine B) as well as enhancing the thermoresponsive performance of the films. Therefore, the current system represents proof-of-principle for the use of hydrophilic/hydrophobic copolymers in the preparation of enhanced thermoresponsive thin films.

Conclusion

Multilayer thin films were prepared based on hydrogen-bonding interactions between PSMA and PEO. The films were shown to grow nonlinearly, and the film thickness was able to be varied by changing the total number of layers and the ionic strength of the adsorption solution (up to 500 nm for 10 bilayers, [NaCl] = 0.2 M). The film morphology was shown to depend on the specific adsorption conditions, with films prepared at [NaCl] = 0.2 M and with a terminal PSMA layer having a significantly rougher surface than films prepared without added salt and with a terminal PEO layer. The films showed a strong affinity for Rhodamine B, with the concentration of dye in the film approximately 7.3×10^4 times larger than in the surrounding solution. The films were shown to release the dye in response to changing temperature, with approximately 60% of the film loading released over 60 min at 50 °C, in comparison to only 10% release at 21 °C. The use of a hydrophilic−hydrophobic copolymer was shown to significantly influence the utility of these films as thermoresponsive materials by comparing the films to those assembled without a hydrophobic moiety. These results indicate that thermoresponsive materials can be prepared from polymers that are themselves not intrinsically thermoresponsive, by exploiting the interplay of functional groups within the total film assembly.

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References and Notes

(1) Decher, G., Schlenoff, J. B., Eds.; *Multilayer Thin Films*; Wiley-VCH: Weinheim, 2003.
(2) Decher, G. *Science* **1997**, *277*, 1232.
(3) Decher, G.; Hong, J.-D.; Schmitt, J. *Macromol. Chem., Macromol. Symp.* **1991**, *46*, 321.
(4) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.
(5) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32*, 8153.
(6) Picart, C.; Lavalle, P.; Hubert, P.; F.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J.-C. *Langmuir* **2001**, *17*, 7414.
(7) Lvov, Y.; Decher, G.; Sukhorukhov, G. B. *Macromolecules* **1993**, *26*, 5396.
(8) Stockton, W. B.; Rubner, M. F. *Macromolecules* **1997**, *30*, 2717.
(9) Wang, L.; Wang, Z. Q.; Zhang, X.; Shen, J. C.; Chi, L. F.; Fuchs, H. *Macromol. Rapid Commun.* **1997**, *18*, 509.
(10) Wang, L.; Fu, Y.; Wang, Z.; Fan, Y.; Zhang, X. *Langmuir* **1999**, *15*, 1360.
(11) Shimazaki, Y.; Ito, S.; Tsutsumi, N. *Langmuir* **2000**, *16*, 9478.
(12) Serizawa, T.; Hashaguchi, S.; Akashi, M. *Langmuir* **1999**, *15*, 5363.
(13) Sukhishvili, S. A.; Granick, S. *J. Am. Chem. Soc.* **2000**, *122*, 9550.
(14) Sukhishvili, S. A.; Granick, S. *Macromolecules* **2002**, *35*, 301.
(15) Yang, S. Y.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 2100.
(16) Zhang, H. Y.; Wang, Z. Q.; Zhang, Y. Q.; Zhang, X. *Langmuir* **2004**, *20*, 9366.
(17) Quinn, J. F.; Caruso, F. *Langmuir* **2004**, *20*, 20.
(18) Yang, S. Y.; Lee, D.; Cohen, R. E.; Rubner, M. F. *Langmuir* **2004**, *20*, 5978.
(19) Kozlovskaya, V.; Ok, S.; Sousa, A.; Libera, M.; Sukhishvili, S. A. *Macromolecules* **2003**, *36*, 8590.
(20) Chung, A. J.; Rubner, M. F. *Langmuir* **2002**, *18*, 1176.
(21) Kharlampieva, E.; Sukhishvili, S. A. *Langmuir* **2004**, *20*, 9677.
(22) Caruso, F.; Lichtenfeld, H.; Donath, E.; Möhwald, H. *Macromolecules* **1999**, *32*, 2317.
(23) Nolan, C. M.; Serpe, M. J.; Lyon, L. A. *Biomacromolecules* **2004**, *5*, 1940.
(24) Antipov, A. A.; Sukhorukov, G. B.; Möhwald, H. *Langmuir* **2003**, *19*, 2444.
(25) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Möhwald, H. *Macromol. Rapid Commun.* **2001**, *22*, 44.
(26) Radt, B.; Smith, T. A.; Caruso, F. *Adv. Mater.* **2004**, *16*, 2184.
(27) Yin, X. C.; Stöver, H. D. H. *Macromolecules* **2002**, *35*, 10178.
(28) Schoeler, B.; Kumaraswamy, G.; Caruso, F. *Macromolecules* **2002**, *35*, 889.
(29) Cho, J.; Caruso, F. *Macromolecules* **2003**, *36*, 2845.
(30) Sugai, S.; Ohno, N.; Nitta, K. *Macromolecules* **1974**, *6*, 916.
(31) Ohno, N.; Nitta, K.; Makino, S.; Sugai, S. *J. Polym. Sci., Part A-2* **1973**, *11*, 413.
(32) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1967**, *71*, 2757.
(33) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842.
(34) Olea, A. F.; Acevedo, B.; Martinez, F. *J. Phys. Chem. B* **1999**, *103*, 9306.

(35) Hirvonen, S. P.; Aseyev, V.; Chitanu, G. C.; Tenhu, H. *Polym. Adv. Technol.* **2004**, *15*, 260.

(36) Lavalle, P.; Picart, C.; Mutterer, J.; Gergely, C.; Reiss, H.; Voegel, J. C.; Senger, B.; Schaaf, P. *J. Phys. Chem. B* **2004**, *108*, 635.

(37) Ferry, J. D.; Udy, D. C.; Wu, F. C.; Heckler, G. E.; Fordyce, D. B. J. *Colloid Sci.* **1951**, *6*, 429.

(38) DeLongchamp, D. M.; Hammond, P. T. *Langmuir* **2004**, *20*, 5403.

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