Moisture Absorption and Absorption Kinetics in Polyelectrolyte Films: Influence of Film Thickness

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Specular X-ray reflectivity (XR) and quartz crystal microbalance (QCM) measurements were used to determine the absorption of water into thin poly(4-ammonium styrenesulfonic acid) films from saturated vapor at 25 °C. The effect of film thickness on the absorption kinetics and overall absorption was investigated in the range of thickness from (3 to 200) nm. The equilibrium swelling of all the films irrespective of film thickness was (0.57 ± 0.03) volume fraction. Although the equilibrium absorption is independent of thickness, the absorption rate substantially decreases for film thickness < 100 nm. For the thinnest film (3 nm), there is a 5 orders of magnitude decrease in the diffusion coefficient for water.

Introduction

Thin polymeric films have technological importance for numerous applications including in fuel cells,[1] sensors,[2] and coatings.[3] One area of recent significant research on thin films has been the production and properties of layer-by-layer assembled multilayers.[4−6] These polyelectrolyte films have shown promise as biosensors,[7] electrochromic devices,[8] and electroluminescent devices[9] among many other applications. One limitation in these devices is their switching time. Understanding film thickness and interface effects on the dynamics of these films is key to their application in future technology. In this work, we present the influence of film thickness on absorption and absorption kinetics of a good solvent (water) in thin poly(4-ammonium styrenesulfonic acid) films. The absorption behavior is studied using specular X-ray reflectivity (XR) and quartz crystal microbalance (QCM) measurements, while the kinetics of the absorption process are determined from the QCM measurements.

Background

The properties of uncharged thin polymeric films have been studied quite extensively. It is well understood that confinement of polymers in thin films can lead to changes in the chain dynamics,[10] physical properties, and film morphology.[11] These confinement effects occur when the film thickness approaches the radius of gyration (R_g). However, the Gaussian nature of the chain has not been affected by confinement even for films with thickness < R_g.[12−14] The most studied phenomenological change in the thin polymeric film has been the glass transition temperature (T_g). It has been found that the glass transition can increase,[15−20] decrease,[17,20−24] or remain constant[17,25] upon confinement. This change in T_g can be tuned by varying the interfacial interactions.[17,22] Not ony are the thermal properties of these thin films shifted by the difference in T_g with respect to the bulk, but the thermal expansion coefficients are themselves functions of film thickness and influenced by interfacial interactions.[26,27] Confinement can also cause an increase or decrease in the chain diffusivity depending upon the interfacial interactions.[18,28,29,32]

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(1) Paddison, S. J. *J. New Mater. Electrochem. Syst.* **2001**, *4*, 207.

(2) Eaton, K. *Sens. Actuators, B* **2002**, *85*, 42−51.

(3) van der Wel, G. K.; Adan, O. C. G. *Prog. Org. Coat.* **1999**, *37*, 1−14.

(4) Cheung, J. H.; Fou, A. F.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 985−989.

(5) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210/211*, 831−835.

(6) Ferreira, M.; Cheung, J. H.; Rubner, M. F. *Thin Solid Films* **1994**, *244*, 806−809.

(7) Wang, J. *Biosens. Bioelectron.* **2003**, *13*, 757−762.

(8) DeLongchamp, D.; Hammond, P. T. *Adv. Mater.* **2001**, *13*, 1455−1459.

(9) Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, *254*, 1485−1487.

(10) Soles, C. L.; Douglas, J. F.; Wu, W. L.; Dimeo, R. M. *Macromolecules* **2003**, *36*, 373−379.

(11) Frank, C. W.; Rao, V.; Despotopoulou, M. M.; Pease, R. F. W.; Hinsberg, W. D.; Miller, R. D.; Rabolt, J. F. *Science* **1996**, *273*, 912−915.

(12) Jones, R. L.; Kumar, S. K.; Ho, D. L.; Briber, R. M.; Russell, T. P. *Nature* **1999**, *400*, 146−149.

(13) Jones, R. L.; Kumar, S. K.; Ho, D. L.; Briber, R. M.; Russell, T. P. *Macromolecules* **2001**, *34*, 559−567.

(14) Jones, R. L.; Soles, C. L.; Starr, F. W.; Lin, E. K.; Lenhart, J. L.; Wu, W. L.; Goldfarb, D. L.; Angelopoulos, M. *Proc. SPIE* **2002**, *4690*, 342−350.

(15) Fryer, D. S.; Nealey, P. F.; de Pablo, J. J. *J. Vac. Sci. Technol., B* **2000**, *18*, 3376−3380.

(16) Fryer, D. S.; Peters, R. D.; Kim, E. J.; Tomaszewski, J. E.; de Pablo, J. J.; Nealey, P. F.; White, C. C.; Wu, W. L. *Macromolecules* **2001**, *34*, 5627−5634.

(17) Jiang, X. Q.; Yang, C. Z.; Tanaka, K.; Takahara, A.; Kajiyama, T. *Phys. Lett. A* **2001**, *281*, 363−367.

(18) Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. *Macromolecules* **1996**, *29*, 6531−6534.

(19) Wallace, W. E.; Vanzanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, R3329−R3332.

(20) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, 219−230.

(21) Kim, J. H.; Jang, J.; Zin, W. C. *Langmuir* **2000**, *16*, 4064−4067.

(22) Tsui, O. K. C.; Russell, T. P.; Hawker, C. J. *Macromolecules* **2001**, *34*, 5535−5539.

(23) Forrest, J. A.; DalnokiVeress, K.; Dutcher, J. R. *Phys. Rev. E* **1997**, *56*, 5705−5716.

(24) DeMaggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1997**, *78*, 1524−1527.

(25) White, C. C.; Migler, K. B.; Wu, W. L. *Polym. Eng. Sci.* **2001**, *41*, 1497−1505.

(26) Lenhart, J. L.; Wu, W. L. *Macromolecules* **2002**, *35*, 5145−5152.

(27) Soles, C. L.; Lin, E. K.; Lenhart, J. L.; Jones, R. L.; Wu, W. L.; Goldfarb, D. L.; Angelopoulos, M. *J. Vac. Sci. Technol., B* **2001**, *19*, 2690−2693.

(28) Tseng, K. C.; Turro, N. J.; Durning, C. J. *Phys. Rev. E* **2000**, *61*, 1800−1811.

For many practical thin film applications, more complex systems are necessary. One common example is polymer multilayers that consist of charged polymers.[30] The transport of ions through these polyelectrolyte multilayers has been found to be enhanced for films with fewer than 10 layers.[31] This suggests that the film confinement tends to increase the mobility of small species, in agreement with diffusivities calculated for dye molecules within a polymer film.[28] However, incoherent neutron scattering experiments have shown that polymer chain motion is retarded by film confinement.[10] Most related to the results presented here is a nuclear magnetic resonance (NMR) spectroscopy study on the dynamics of water absorbed in polyelectrolyte multilayers.[33] The water mobility is enhanced as the number of layers is increased. Additionally, NMR has been used to compare the properties of polyelectrolyte multilayers with those of their analogous bulk polyelectrolyte complex where water absorption is found to increase the polymer mobility only in the multilayer system.[34] Although film confinement has been studied in a variety of different systems, it is uncertain if confinement can cause these observed changes in water mobility.

The kinetics of the absorption process of small molecules into polymer matrixes have been studied for approximately half of a century.[35,36] However, there is little work on how film confinement affects the absorption kinetics, but it has been suggested that film thickness may influence the absorption.[37] Previously, it has been shown for polyimide films that the moisture absorption is slightly dependent upon film thickness.[38] In this case, there is an excess of water that accumulates at the polymer/substrate interface. The degree of excess can be controlled by changing the substrate surface energy. Here, the influence of film thickness on absorption and absorption kinetics of a good solvent (water) in thin poly(4-ammonium styrenesulfonic acid) films is examined. The absorption of a good solvent into thin films has not been studied previously systematically to determine any confinement effects. Additionally, salts of poly(styrenesulfonic acid) are regularly used in layer-by-layer deposited films where the mobility of water has been found to be dependent upon the number of deposited layers.[33] The absorption behavior in poly(4-ammonium styrenesulfonic acid) is studied using XR and QCM measurements, while the kinetics of the absorption process are determined from the QCM measurements.

Experimental Section

Poly(4-ammonium styrenesulfonic acid) with a relative molecular mass of approximately 200 000 g/mol was purchased from Aldrich.[39] Films were prepared by spin coating from a dilute solution of either water or cyclopentanone. Prior to preparation of the solutions, the polymer was dried in vacuo under dry magnesium sulfate (Aldrich) for more than 12 h. It is important to note that the solubility in cyclopentanone is quite low (<0.002

mass fraction) but it can be used to prepare thinner films due to its lower volatility than that of water. The solutions were filtered (1 μm) prior to spinning. Films were prepared by spinning onto 76.2 mm silicon wafers or SiO_x sputtered gold electrode quartz crystals (Q-Sense). For the thickest films, reasonable agreement was found between the thickness from the crystal frequency shift and that measured on the silicon wafers using X-ray reflectivity. The crystal frequency is dependent upon mounting, which can lead to substantial errors for the thinnest films. Thus, the film thickness was assumed to be identical between the quartz crystals and silicon wafers; this assumption will be confirmed later in the text. Prior to measurement, the films were dried under vacuum at 25 °C (XR) or 120 °C (QCM). No difference was found in the film swelling between these two drying temperatures. For the thinnest film from cyclopentanone (3 nm), a conditioning step over saturated KCl solution was needed to obtain a consistent dry film thickness.

The film thickness, for both dry and hydrated films, was determined by specular X-ray reflectivity. For thin films (<120 nm), the reflectivity measurements were made in θ/θ mode with Cu Kα radiation ($\lambda = 1.54$ Å) using two sets of collimation slits. The humidity was controlled using an aluminum chamber with beryllium windows either under vacuum or closed with an excess of liquid water in the chamber to produce nearly saturated vapor. Each sample measurement was allowed at least 6 h to equilibrate, after which time the film thickness remained constant (± 0.1 nm). For thicker films (>120 nm), reflectivity measurements were made in $\theta/2\theta$ mode with a finely focused Cu Kα beam of radiation using a focusing mirror and a 4 bounce Ge (220) crystal monochromator. The reflected beam then passes through a 3 bounce channel cut Ge (220) crystal into a proportional gas detector.

The mass uptake of moisture into the films was measured using a quartz crystal microbalance (Q-Sense) with dissipation (QCM-D). The crystals were 5.0 MHz AT-cut quartz resonators with silica coated gold electrodes. The crystals were washed in methanol and then acetone and cleaned with UV ozone for 2 min prior to use. During the course of the swelling experiment, the fundamental and three resonance frequencies (1:3:5:7) were measured at intervals of ~2 s. Since the films are hydrophilic, a significant (>50%) amount of water is absorbed. The degree of hydration should plasticize the films from the glassy ($T_g \approx 165$ °C) to rubbery state. At this point, the rigidity of the film is questionable, as is the applicability of the Sauerbrey equation. The valid region for the Sauerbrey equation has been derived for viscoelastic films on a quartz crystal resonator by White and Schrag.[40] In the limiting case where the film viscosity is that of water (this is a significant underestimation in the true viscosity), a thickness of ~100 nm is required for significant deviations from the Sauerbrey equation for the 5 MHz crystal resonance. For the hydrated polymer films, the minimum thickness at which to observe deviations from the Sauerbrey expression will be larger as the film viscosity is larger. Additionally, the crystal dissipation, which is related to the film viscosity, is measured simultaneously with the frequency. In almost all cases, the film thickness is small enough that the film behaves rigidly, as the dissipation shift during the course of the experiment is less than 2×10^{-6}. The dissipation sensitivity is ~4×10^{-8}. For the thickest films (those greater than 100 nm), the dissipation shift for some of the higher resonance frequencies is larger than 2×10^{-6} and consequently the mass gain calculated by the Sauerbrey equation shows a frequency dependence. In these cases, the higher frequencies with large dissipation are not used to determine the mass gain. Under these prescribed conditions, the mass absorbed in the film can be determined from the change in the resonance frequency using the Sauerbrey equation, relating the frequency shift, Δf, to the change in mass, Δm.

(29) Lin, E. K.; Wu, W. I.; Satija, S. K. *Macromolecules* **1997**, *30*, 7224−7231.

(30) Decher, G. *Science* **1997**, *277*, 1232−1237.

(31) Farhat, T. R.; Schlenoff, J. B. *Langmuir* **2001**, *17*, 1192.

(32) Reiter, G. *Europhys. Lett.* **1993**, *23*, 579−584.

(33) Schwarz, B.; Schonhoff, M. *Langmuir* **2002**, *18*, 2964−2966.

(34) McCormick, M.; Smith, R. N.; Graf, R.; Barrett, C. J.; Reven, L.; Spiess, H. W. *Macromolecules* **2003**, *36*, 3616−3625.

(35) Barrie, J. A. Water in Polymers. In *Diffusion in Polymers*; Crank, J., Park, G. S., Eds.; Academic Press: London, 1968; pp 259−314.

(36) Crank, J.; Park, G. S. Methods of Measurement. In *Diffusion in Polymers*; Crank, J., Park, G. S., Eds.; Academic Press: London, 1968; pp 1−40.

(37) Vrentas, J. S.; Jarzebski, C. M.; Duda, J. L. *AIChE J.* **1975**, *21*, 894−901.

(38) Tan, N. C. B.; Wu, W. L.; Wallace, W. E.; Davis, G. T. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 155−162.

(39) Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

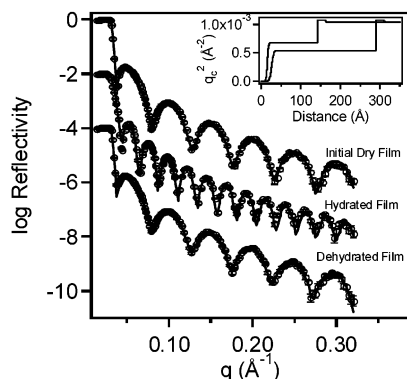(40) White, C. C.; Schrag, J. L. *J. Chem. Phys.* **1999**, *111*, 11192−11206.

Figure 1. Specular X-ray reflectivity of a thin poly(4-ammonium styrenesulfonic acid) film before hydration and after hydration and dehydration. The film doubles in thickness upon moisture exposure but returns to its original thickness under vacuum.

$$\Delta f = -\frac{2f_0^2 \Delta m}{nA(\mu_q \rho_q)^{0.5}} = -C_f \frac{\Delta m}{nA} \tag{1}$$

where f_0 is the measured resonant frequency or overtone, n is the number of the overtone, A is the electrode area (0.25 cm²), μ_q and ρ_q are the shear modulus (2.95×10^6 N cm⁻²) and the density (2.65 g cm⁻³), respectively, and C_f is the integral sensitivity constant (57 Hz cm² μg⁻¹). The mass of the dry film was not determined by comparison with the clean crystal, as the crystal is stressed by the drying of the glassy polymer during spin coating. This stress leads the frequency shifts for the different resonances to not be in the common ratios (1:3:5:7). For thick films, reasonable agreement between the frequency shifts in comparison to the cases of the clean crystal and the XR measurements was found. The agreement in mass uptake between the resonances is within ±5%, for frequencies with a dissipation shift < 2 × 10⁻⁶. All measurements were done at (25 ± 0.5) °C. The moisture was introduced to the sample in a flow system using dry air as a carrier gas, bubbled through distilled water. The sample chamber containing the QCM crystal is sealed except for two ports for the inlet and outlet of the humid air flow. Prior to measuring the water absorption, the films were dried for 2 h under vacuum at 120 °C. The elevated annealing temperature did not influence the mass uptake but decreased the drying time significantly over ambient temperatures (>6 h). After the crystals were mounted in the sample chamber, dry air was flowed over the sample to remove moisture that was absorbed from ambient air, as evidenced by a flat baseline prior to measurements.

Results and Discussion

Equilibrium Absorption. The reflectivity as a function of the momentum transfer vector, $q = 4\pi/\lambda \sin(\theta)$, collected on a poly(4-ammonium styrenesulfonic acid) film is shown in Figure 1,[41] where λ is the radiation wavelength (1.54 Å) and θ is the scattering angle. This profile was modeled using a nonlinear least-squares fitting using a recursive multilayer method.[42] The Figure 1 inset illustrates the scattering length density profile obtained from the model fit of the reflectivity where $q_c^2 = 16\pi\rho_m$ and ρ_m is the electron density. The density profile has an arbitrary zero distance in the atmosphere above the sample. The electron density increases from the vacuum/water vapor to a constant value that represents the polymer film and then further increases to the electron density of the silicon oxide and then decreases to the electron density of pure silicon. The density of the film

changes as water is absorbed. The change in the scattering length density can be used along with the change in film thickness to estimate the density of the absorbed material (water). As can be seen from Figure 1, there is a tremendous change in the reflectivity profile upon absorption of water vapor. The film swells from 12.6 to 26.3 nm. Importantly, the film thickness upon desorption returns to its original thickness. Assuming that the swelling is one-dimensional, a reasonable approximation due to the large surface area-to-volume ratio, the density of the absorbed water in the film can be estimated to be (0.98 ± 0.15) g cm⁻³. This is in good agreement with the expected water density (1.0 g cm⁻³). The film in hydrated form contains more than half water. For the thick film reflectivity measurements, the wafer is vertical during the measurement, and after water exposure these films return to their original thickness.

Additionally, the swelling is dependent upon the exposure history. For example, a greater than 50% decrease in the swelling can be observed when the film is initially exposed to unsaturated vapor followed by exposure to saturated vapor in comparison with the case of direct exposure to saturated vapor. This effect is reversible if the sample is evacuated prior to the next vapor exposure. This effect is similar to the molecular memory effects recently observed in polyelectrolyte multilayers[43] and is reminiscent of the unusual swelling behavior of polymer gels.[44] The similarity to polymer gels will be revisited shortly.

Since water is a good solvent for this polymer, one might expect the film to swell uncontrollably in the presence of excess saturated vapor until the reflectivity cannot be measured. It is possible to dissolve the polymer film from the substrate by immersion in liquid water. This state dependent behavior has been observed previously for an insoluble hydrophilic copolymer that absorbs 50% more water from the liquid state than from saturated vapor.[45] There are two potential explanations for this behavior. First, the film could form a gel phase, as discussed previously. The second explanation for the difference between liquid and vapor absorption is that the solvent quality is influenced by the entropic nature of the absorbate. Recently, for *n*-alkane systems, the state of the fluid was found to have a significant influence on the polymer solubility, with liquids being better solvents than supercritical fluids.[46]

The film swelling by water vapor absorption for various film thicknesses is summarized in Figure 2. The volume fraction of water was calculated from the XR data from the change in film thickness. The raw frequency shift data from the QCM are shown in Figure 3. As time increases, the frequency of the crystal decreases until a constant frequency is obtained, indicating that the absorption process has reached equilibrium. For the QCM data, the volume fraction of water was determined by assuming that the density of the absorbed water is 1.0 g cm⁻³ and the film thickness is identical to the one obtained from XR measurements. As can be observed from Figure 2, there is relatively good agreement between the volume fraction of water absorbed as calculated from the QCM or XR data. The fractional water absorption is independent of film

(41) The data throughout the manuscript and Figures 1, 2, and 4 are presented along with the standard uncertainty (±) involved in the measurement based on one standard deviation.

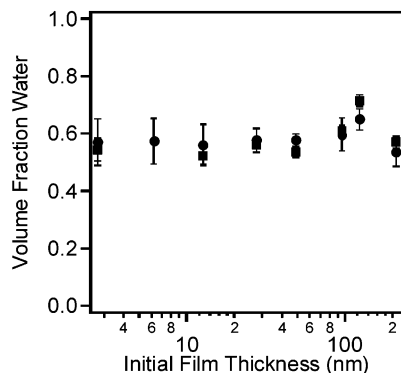(42) Ankner, J. F.; Maikrzak, C. F. *SPIE* **1992**, *1738*, 260.

(43) Hiller, J. A.; Rubner, M. F. *Macromolecules*, in press.

(44) Annaka, M.; Tokita, M.; Tanaka, T.; Tanaka, S.; Nakahira, T. *J. Chem. Phys.* **2000**, *112*, 471–477.

(45) Chen, W.-L.; Shull, K. R.; Papatheodorou, T.; Styrkas, D. A.; Keddie, J. L. *Macromolecules* **1999**, *32*, 136–144.

(46) DiNoia, T. P.; Kirby, C. F.; van Zanten, J. H.; McHugh, M. A. *Macromolecules* **2000**, *33*, 6321–6329.

Figure 2. Equilibrium water absorption in different thickness films as determined by (■) XR and (●) QCM measurements.
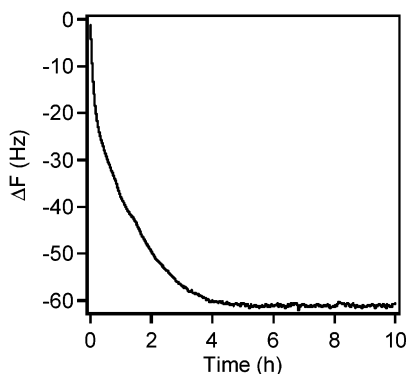

Figure 3. Response of the third harmonic frequency to a 3 nm thick film during exposure to saturated water vapor.

thickness. This is in contrast to the previous study on moisture absorption into thin films where an excess absorption was found in the thinnest films.[38] It is important to note that this excess fraction can be tuned by varying the substrate surface energy. For the current case, the water affinities for the substrate (SiO$_x$) and the polymer can be inferred to be comparable, as there is no film thickness influence on the equilibrium water absorption.

Kinetics of Absorption. The study of absorption into polymers involves both the equilibrium uptake as described above and the kinetics of the absorption process. The moisture absorption process has been studied for many diverse polymer systems.[35] However, typically, bulk (>1 μm) samples were examined. There have been various models proposed to describe the different absorption behaviors. The simplest case for water absorption is a Fickian process where the time-resolved mass increase for a thin film on an impermeable substrate can be written as[36]

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{h^2}\right)^{0.5}\left(\frac{1}{\pi^{0.5}} + 2\sum_{n=1}^{\infty}(-1)^n i\operatorname{erfc}\frac{nh}{2(Dt)^{0.5}}\right) \quad (2)$$

where M_t and M_∞ are the mass gains at any time, t, and at equilibrium, respectively, D is the diffusivity of the penetrant, and h is the film thickness. This assumes that the penetrant absorption is one-dimensional, which should be valid given the large surface area-to-volume ratio and the impermeable substrate. At short times, this expression can be simplified to

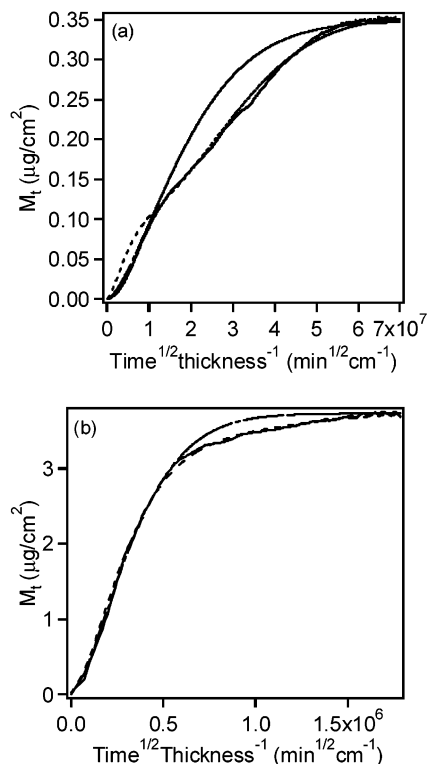$$\frac{M_t}{M_\infty} = \frac{2}{h}\sqrt{\frac{Dt}{\pi}} \quad (3)$$

Figure 4. Moisture absorption in (a) 3 nm thick and (b) 28 nm thick poly(4-ammonium styrenesulfonic acid) films (solid line). The absorption is fit to (- — -) Fickian and (- - -) two-stage absorption models.

which results in a simple expression for the diffusivity:

$$D = \frac{\pi}{4}\left(\frac{\dfrac{M_t}{M_\infty}}{\dfrac{\sqrt{t}}{h}}\right)^2 \quad (4)$$

The diffusion coefficient can be determined from the initial slope of the absorption curve plotted in the form of M_t/M_∞ versus $t^{1/2}/h$. However, there have been numerous examples of small molecule diffusion in polymers showing various non-Fickian behaviors, ranging from type II to two stage to sigmoidal.[3,47−49] Two-stage absorption has been observed in a poly(styrenesulfonic acid)/poly(4-vinyl-*N*-ethylpyridinium bromide) complex which is similar to the films studied here.[49,54] For the case of two-stage absorption processes, the first stage is Fickian in nature, followed by an anomalous stage which is not diffusion controlled.[35] Many explanations have been given for the anomalous behavior including time dependent solubility,[50] variable surface concentration,[48] polymeric relaxation,[51] and free volume.[52] Additionally, the diffusion coefficient could be thickness dependent near the interface. Figure 4 shows the mass uptake as measured by QCM measurements plotted in form of eq 4 for poly(4-ammonium styrenesulfonic acid) films. As can be seen in the figure,

(47) Blahnik, R. *Prog. Org. Coat.* **1983**, *11*, 353−392.
(48) Long, F. A.; Richman, D. *J. Am. Chem. Soc.* **1960**, *82*, 513−519.
(49) Neogi, P. *AIChE J.* **1983**, *29*, 833−839.
(50) Petropoulos, J. H. *J. Polym. Sci., Part B: Polym. Phys.* **1984**, *22*, 1885−1900.
(51) Berens, A. R.; Hopfenberg, H. B. *Polymer* **1978**, *19*, 489−496.
(52) Vrentas, J. S.; Duda, J. L.; Ling, H.-C. *Macromolecules* **1988**, *21*, 1470−1475.
(53) Bagley, E.; Long, F. A. *J. Am. Chem. Soc.* **1955**, *77*, 2172−2178.
(54) Hirai, Y.; Nakajima, T. *J. Macromol. Sci., Phys.* **1991**, *B30*, 141−153.

Table 1. Fit Parameters to the Two-Stage Absorption Model of Long and Richman for Different Film Thicknesses (Uncertainties are for 95% Confidence Intervals)

dry thickness (nm)	swollen thickness (nm)	D (cm^2/min)	ϕ	ψ	M_∞ (μg/cm^2)
2.7	6.4	$(3.06 \pm 1.16) \times 10^{-15}$	(0.29 ± 0.08)	(0.30 ± 0.09)	(0.39 ± 0.09)
6.2	14.5	$(2.56 \pm 0.65) \times 10^{-14}$	(0.76 ± 0.03)	(0.87 ± 0.29)	(0.89 ± 0.08)
12.7	29.1	$(2.04 \pm 0.46) \times 10^{-13}$	(0.77 ± 0.05)	(0.59 ± 0.32)	(2.29 ± 0.58)
27.6	65.1	$(5.58 \pm 0.69) \times 10^{-13}$	(0.89 ± 0.07)	(0.94 ± 0.20)	(4.02 ± 0.42)
48.9	116	$(2.14 \pm 1.08) \times 10^{-12}$	1.0	N/A	(7.15 ± 0.13)
95.9	238	$(4.79 \pm 0.46) \times 10^{-12}$	1.0	N/A	(16.78 ± 1.41)
124	353	$(6.17 \pm 1.06) \times 10^{-12}$	(0.99 ± 0.02)	(0.81 ± 0.06)	(24.53 ± 2.45)
210	452	$(2.74 \pm 0.58) \times 10^{-11}$	(0.98 ± 0.07)	(0.97 ± 0.43)	(39.0 ± 8.4)
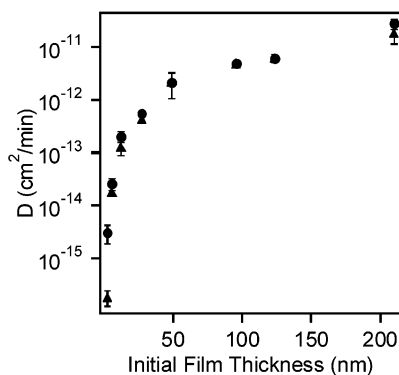
Figure 5. Water diffusion coefficients into thin films as a function of film thickness as determined by (▲) Fickian and (●) two-stage absorption models.

the absorption behavior is non-Fickian. There is an initial fast increase in the mass of the film, followed by a slower step that continues until the film equilibrates. However, there is no obvious inflection point, as is typically observed in two-stage absorption.[35,53] Two-stage absorption is usually observed in thicker films only. In general, the initial fast stage has been found to be Fickian and the initial slope can be used to calculate the diffusion coefficient for the penetrant.[35,53] Typically for two-stage absorption, the second stage is significantly slower than the first. In this case however, the second stage is only slightly slower than the first. Using the initial slope of the absorption and neglecting the non-Fickian behavior, the diffusion coefficient for the water in the films can be estimated. The fit of this diffusivity to eq 2 is shown in Figure 4. The diffusion coefficient as a function of film thickness is illustrated in Figure 5 using the initial slope method (eq 4). The diffusivity as determined from Fick's second law decreases when the film is <100 nm thick, and orders of magnitude deviations occur as the film thickness approaches a 10 nm thickness. However, since the observed absorption behavior is not completely Fickian, it is possible that deviations in the apparent diffusivity may be an artifact of the film thickness influence on the non-Fickian nature of the absorption. The anomalous behavior in the absorption is probably related to chain relaxations from swelling stress that allow an increased amount of water in the film.[49,55]

The first mechanistic model to describe two-stage sorption was proposed by Long and Richman using a variable surface concentration.[48] In this model, the surface concentration jumps to less than equilibrium upon vapor exposure (C_0) and then increases to equilibrium (C_∞) via a first-order relaxation process at a rate k. The normalized mass uptake in terms of dimensionless variable (using the notation of Sun[56]) is

$$\frac{M_t}{M_\infty} = \phi\left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\dfrac{-(2n+1)^2\pi^2\theta}{4}\right)}{(2n+1)^2}\right] +$$

$$(1-\phi)\left[1 - \frac{\tan\sqrt{\psi}\,\exp(-\psi\theta)}{\sqrt{\psi}} - \right.$$

$$\left. \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{\exp\left(\dfrac{-(2n+1)^2\pi\theta}{4}\right)}{(2n+1)^2\left(1 - \dfrac{(2n+1)^2\pi^2}{4\psi}\right)}\right] \quad (5)$$

where

$$\phi = \frac{C_0}{C_\infty} \qquad \theta = \frac{Dt}{h^2} \qquad \psi = \frac{kh^2}{D}$$

The dimensionless quantity ψ is the inverse of the diffusion Deborah number that characterizes the relative rate of the absorbate diffusion and the polymer relaxation.[37] An alternative diffusion-relaxation model was proposed by Berens and Hopfenberg;[51] however, this is only valid for $\psi \ll 1$,[57] which is not the case here. The model of Long and Richman is still quite simple with only three parameters, each with a physical significance. The absorption isotherm for each film thickness was fit to this model. The model fits are shown in Figure 4 for an extremely thin film and a thicker film. The model captures the absorption quite well in both cases, although there are deviations at short times. The deviation in the fit at short times occurs in all the samples and is attributed to initial moisture adsorption on the apparatus walls, leading to an initially lower humidity. The deviations are most severe for the thinnest films, as the x-axis is a function of the inverse of the film thickness. The fit model parameters are compared to the diffusivity as determined by the initial slope in Table 1. The trend in diffusion coefficients is similar between both fits with the water diffusivity decreasing as the film is confined, as can be seen in Figure 5. The diffusion coefficient decrease with confinement is seen if either Fickian or two-stage absorption processes are used, although the degree of deviation is model dependent. Using the Long−Richman model, the amount of relaxation controlled absorption increases in the thinnest films (as manifest by a decrease in ϕ). The diffusion coefficient decreases markedly for films thinner than 50 nm. The decrease in water mobility with film confinement is consistent with the observed change in water mobility in

(55) Sanopoulou, M.; Petropoulos, J. H. *Macromolecules* **2001**, *34*, 1400−1410.

(56) Sun, Y. M. *Polymer* **1996**, *37*, 3921−3928.

(57) Joshi, S.; Astarita, G. *Polymer* **1979**, *20*, 455−458.

polymer multilayers.[33] It is probable that the water diffusion is coupled to the chain motion. Thus, the decrease in the water diffusion coefficient could be a result of a decrease in the local polymer chain dynamics in thin films.[10]

Conclusions

Film thickness was found to have no influence on the equilibrium swelling of poly(4-ammonium styrenesulfonic acid) by water vapor. This is not unexpected, since both the substrate and polymer are highly hydrophilic. However, the absorption process itself is dependent upon the film thickness. Film confinement leads to a decrease in the water diffusion coefficient. A large drop in the diffusivity occurs when the film thickness becomes <50 nm. Additionally, there is a significant deviation from Fickian behavior for the thinnest films. The absorption in all the films was fit to either Fickian or two-stage absorption models. An over 3 orders of magnitude decrease in the diffusion coefficient has been observed upon confinement in the most conservative case.