

Effect of Film Thickness on the Validity of the Sauerbrey Equation for Hydrated Polyelectrolyte Films

Bryan D. Vogt,^{*,†} Eric K. Lin,[†] Wen-li Wu,[†] and Christopher C. White[‡]

Polymers and Building Materials Divisions, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8541

Received: May 3, 2004; In Final Form: June 15, 2004

The frequency and energy dissipation change of a quartz crystal microbalance during moisture absorption was measured for films with thickness ranging from 3 to 205 nm. Evidence of the viscoelastic nature of the films was observed for films thicker than 90 nm through the frequency and energy dissipation changes. For sufficiently thin films ($t < 40$ nm), the frequency change could be effectively modeled as a simple increase in mass, as predicted by the Sauerbrey equation. The viscosity of the swollen films was independent of initial polymer film thickness (93–205 nm). The equilibrium swelling ratio was independent of film thickness for all films examined (3–205 nm). The transition between the observation of a rigid film and a film showing viscoelastic character was found to be at $\beta_1 D = 0.26 \pm 0.10$, where $\beta_1 = 2\pi/\lambda_s$, λ_s is the shear wavelength, and D is the film thickness. This transition agrees with the predictions of White and Schrag (*J. Chem. Phys.* 1999, 111, 11192).

Introduction

Quartz crystal resonators have seen wide application in the measurement of small masses due to their stability, simplicity of measurement, high precision, high sensitivity, and ease of analysis. Sauerbrey^{1,2} provided a description and experimental verification of the mass/frequency relationship between rigid foreign layers firmly attached to the quartz crystal resonators. The frequency change is directly proportional to the added mass as long as the added mass behaves elastically similar to the quartz itself as shown in eq 1

$$\Delta f = \left[\frac{-2f_{ro}^2}{A\sqrt{\rho_q G_q}} \right] \Delta m_q \quad (1)$$

where Δf is the change in the resonance frequency due to the added mass, f_{ro} is the resonance frequency of the unloaded resonator, ρ_q and G_q are the density and shear modulus of the quartz, and A is the surface area of the resonator.

In the 1980s, improvements led to the operation of the oscillators in damping liquids.³ The change in the resonance frequency of the crystal due to the presence of the liquid is given by⁴

$$\Delta f = \frac{-\sqrt{f_{ro}\rho_l\eta_{lm}}}{\rho_q h\sqrt{2\pi}} \sin [\pi/4 - \phi_l/2] \quad (2)$$

where h is the thickness of the quartz crystal and ρ_l , η_{lm} , and ϕ_l are the density, magnitude of the complex viscosity, and relative phase angle of the liquid medium, respectively. The complex viscosity is given by $\eta^* = \eta' - i\eta'' = \eta_m e^{-i\phi}$, where η' describes the energy dissipation and η'' describes the energy storage.⁵

There has been increasing interest in using the quartz crystal microbalance (QCM) technique for aqueous-based biological applications.⁶ It is common to assume that the combination of eqs 1 and 2 can describe the behavior. At some applied layer thickness, the viscoelastic nature of the layer will become a significant part of the response of the quartz crystal, thereby requiring a more complete model. Recently, several techniques have been developed to measure the viscoelastic nature of the applied layer by monitoring the energy loss during oscillation.^{8–10} The validity of this technique has been shown for micrometer thick films of polyisobutylene with order of magnitude agreement with bulk measurements.^{10,11} White and Schrag⁷ proposed that when the applied layer has a value of $\beta_1 D > 0.28$ and $\beta_1/\beta_2 > 0.2$ (assuming an elastic applied layer, where β_1 is the applied layer and β_2 is the surrounding medium), deviations from eqs 1 and 2 should be observed. (Note: β is related to the shear wavelength of the medium, λ_s , and can be easily calculated from $\beta = 2\pi/\lambda_s = \sqrt{\omega\rho/\eta_M} \cos [\pi/4 - \phi/2]$). To date, these predictions have not been verified experimentally, but the energy loss measurement provides a simple test of onset predictions for QCM detection of viscoelastic effects.

Recently, we reported confinement effects on moisture absorption in thin polymer films.¹² In the course of these measurements, an increase in the dampening of a quartz resonator, as determined by an increase in the dissipation factor, was found as the film thickness was increased. In the previous work,¹² the measured frequencies where the dissipation exceeded a critical value (2×10^{-6}) were not used in the calculation of mass change during the absorption as the applicability of the Sauerbrey analysis was questionable. Here, we re-examine these data in terms of both the Sauerbrey analysis and more complete expressions for the viscoelastic behavior of the films. A comparison between theoretical and experimental results on the performance of the Sauerbrey expression is reported for these films.

* Corresponding author: bryan.vogt@nist.gov.

† Polymers Division, NIST.

‡ Building Materials Division, NIST.

Experimental Section

Poly(4-ammonium styrenesulfonic acid) with a relative molecular mass of approximately 200 000 g/mol was purchased from Aldrich. Films were prepared by spin coating from dilute aqueous solution. Prior to preparing the solutions, the polymer was dried in vacuo under dry magnesium sulfate (Aldrich) for more than 12 h. The solutions were filtered (1 μm) prior to spinning. Films were prepared by spinning onto SiO_x sputtered gold electrode quartz crystals (Q-Sense). Prior to measurement, the films were dried under vacuum at 120 $^\circ\text{C}$ for 2 h.

The mass uptake of moisture into the films was measured using a quartz crystal microbalance (Q-Sense) with dissipation (QCM-D). The QCM-D technique has been described previously in the literature.^{13,14} The QCM-D is a transient mode resonator that measures the frequency and the dissipation of the crystal simultaneously. The dissipation factor, D , is the reciprocal of the Q factor and defined as

$$D = \frac{1}{Q} = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}} \quad (3)$$

where $E_{\text{dissipated}}$ is the energy dissipated during one oscillation period and E_{stored} is the energy stored during oscillation. The crystals were 5.0 MHz AT-cut quartz resonators with silica-coated gold electrodes. The dissipation for a typical crystal is on the order of 10^{-6} . The crystals were washed in methanol 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 approximately two seconds. Since the films are hydrophilic, a significant amount of water (equilibrated film is $>50\%$ water by mass) is absorbed. All measurements were done at 25 ± 0.5 $^\circ\text{C}$. The data throughout the manuscript and the tables and figures are presented along with the standard uncertainty (\pm) involved in the measurement based on one standard deviation. The moisture was introduced to the sample in a flow system using dry air as a carrier gas, bubbled through distilled water. Typically, the relation between the frequency shift, Δf , and the added mass per unit area, Δm , is linear, obeying the Sauerbrey equation:²

$$\Delta m = -C\Delta f \quad (4)$$

where C is a proportionality constant that depends only on the intrinsic properties of the quartz. However, there are several assumptions necessary for this expression to hold. First, the added mass must be evenly distributed over the electrode. Second, the added mass must be much less than the mass of the quartz crystal itself. Finally, the mass is rigidly attached with no deformation from oscillatory motion of the crystal. It is in this last assumption where the direct proportionality begins to break down, as will be demonstrated shortly. The frequency and dissipation resolution for the instrument is 0.01 Hz and 10^{-9} , respectively.

Results

Figure 1 shows the frequency and dissipation shift for moisture absorption in an initially 28 nm thick film of poly(4-ammonium styrenesulfonic acid). The frequency shifts have been normalized with the resonance number ($n = 1, 3, 5, \text{ or } 7$), $\Delta f/n$. In this case, the dissipation shift is relatively small and all the normalized frequency shifts are nearly identical. The film appears to obey the Sauerbrey equation, which states

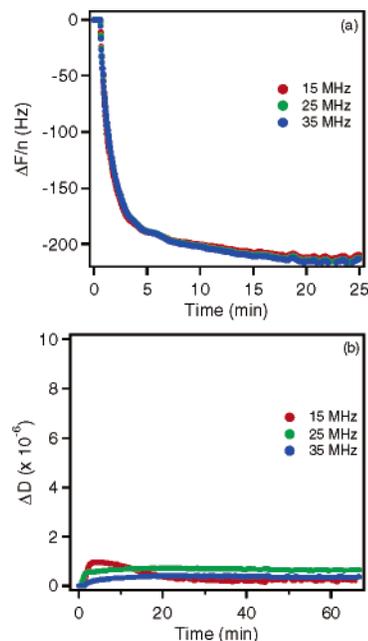


Figure 1. QCM response of a 28 nm thick poly(4-ammonium styrene sulfonic acid) film when exposed to saturated water vapor. The frequency response (a) for the 15 (red), 25 (green), and 35 (blue) MHz resonances has been normalized by the resonance number. The dissipation change for the film is shown in (b).

that the frequency shift is directly proportional to the added mass, because the dissipation does not change appreciably over the course of the absorption. The lack of an increase in the energy loss of the crystal implies that the film behaves rigidly. Additionally, the collapse of the normalized frequency shifts validates the Sauerbrey expression for this film.

As the initial thickness of the applied polymer film is increased above 90 nm, the dissipation increases tremendously as shown in Figure 2. Additionally, the dissipation is dependent upon the measured frequency, with higher frequencies leading to larger dissipation factors. As the initial film thickness is increased from 44 to 205 nm, the dissipation shift during the absorption process increases from only 2×10^{-6} to nearly 150×10^{-6} . Previously, a threshold of 2×10^{-6} was used to assign the validity of the Sauerbrey equation.¹² By examining the normalized frequency shifts, the rationale for this threshold can be determined. In Figure 2a, the normalized frequency shifts are nearly independent of frequency (apparent validity of Sauerbrey expression), corresponding to a maximum dissipation change of $\approx 5 \times 10^{-6}$. There is a small spike in the dissipation for this film when the air flow is changed from dry to saturated vapor. The spike appears to be a result of the change in the pressure exerted on the crystal when closing and opening valves to introduce water to the system. This artifact can be avoided by carefully and simultaneously opening and closing the different valves. In this way, no deviations in the dissipation are observed, such as in Figure 1b. From the increase in the dissipation shift and deviations in the normalized frequency shifts, it is clear that the Sauerbrey equation is not valid for the thickest films. Determining what the nonideal frequency shift means physically is a more difficult proposition. However, several models have been proposed to account for nonideal behavior in QCMs.^{8,9,15}

The frequency and energy dissipation changes can be related to the film density, viscoelastic properties, and thickness using

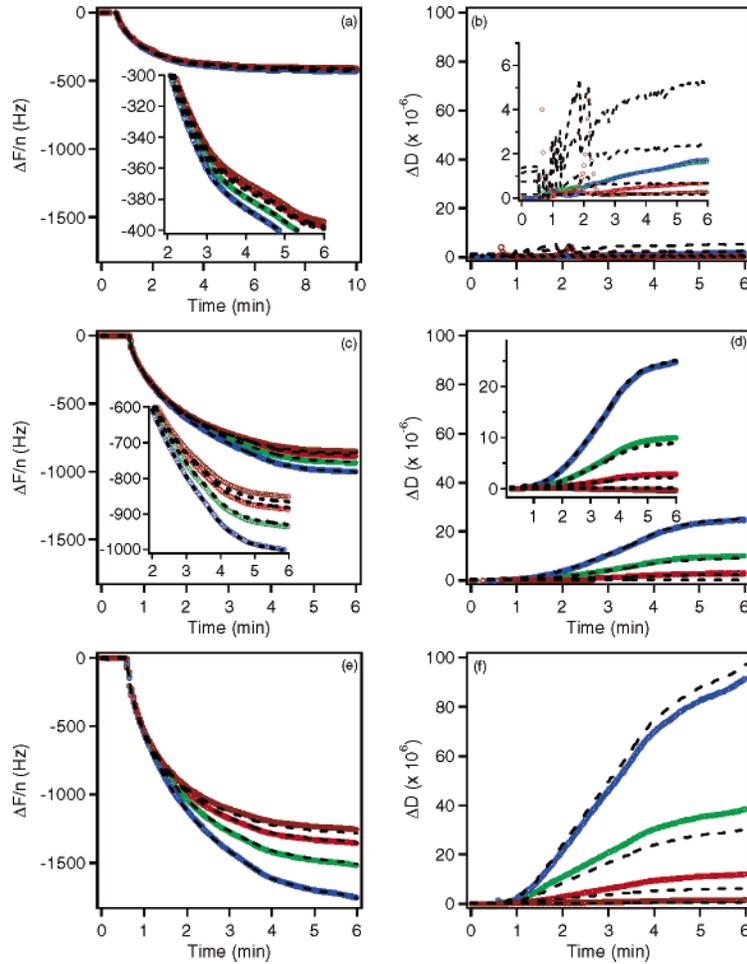


Figure 2. Deviations from ideal behavior is observed in the QCM response of (a,b) 44, (c,d) 96, and (e,f) 127 nm thick films (initial thickness) upon exposure to water vapor. The frequency response for the 15 (red), 25 (green), and 35 (blue) MHz resonances has been normalized by the resonance number and is shown along with the frequency change for the fundamental frequency (brown). The insets better illustrate the deviations in the frequency responses to frequency and dissipation shifts. Fits are shown by black dashed lines.

the derivation of Voinova and co-workers in terms of a Taylor expansion.¹⁶

$$\Delta f \approx \frac{1}{2\pi\rho_q h_q} h \rho f \left(1 + \frac{2h^2\chi}{3\delta^2(1+\chi^2)} \right) \quad (5)$$

$$\Delta D \approx \frac{2h^3\rho f}{3\pi f_{r0}\rho_q h_q} \frac{1}{\delta^2(1+\chi^2)} \quad (6)$$

$$\chi = \frac{\mu}{\eta f} \quad (7)$$

$$\delta = \sqrt{\frac{2\eta}{\rho f}} \quad (8)$$

where ρ_q and ρ are the density of the quartz and film respectively, h_q and h are the thickness of the quartz and film respectively, f is the measured frequency, χ is the ratio of the storage modulus (μ) and the loss modulus (η), f_{r0} is the resonance frequency of the crystal, and δ is the viscous penetration depth. The frequency and dissipation of the crystal is measured at the resonance frequency ($n = 1$), as well as at several overtones ($n = 3, 5, 7$), with the relationship $f = n f_{r0}$ for the uncoated resonator. The frequency and energy dissipation changes can be fit assuming the film behaves according to the Voigt model as shown by the dashed lines in Figure 2. The Voigt element is a mechanical element analogy for a viscoelastic system that

consists of a spring and dashpot. In this model, the spring corresponds to the shear rigidity ($G_i = 1/J_i$) and the dashpot to the viscosity (η_i); the retardation time is defined as their ratio ($\tau_i = \eta_i/G_i$). The governing viscoelastic functions for the Voigt element are defined using these three variables.⁵ As can be seen in Figure 2, the model accurately captures the frequency and dissipation shifts despite the differences in shape between the different thicknesses. There are four measured frequencies and four dissipation measurements at each time step. Through eqs 5 and 6, the changes in the frequency and dissipation are fit to the film viscosity (η), shear modulus (μ), thickness (h), and density (ρ). This model, although rigorously derived, has the problem of neglecting the longitudinal waves from the oscillator. Additionally, the viscosity is assumed to be frequency independent in the model. The data suggest that the films are shear-thinning, as can be observed from the model fits of the thicker film (see Figure 2e and f). The high-frequency (35 MHz, $n = 7$) fit overestimates the actual dissipation, whereas at 25 MHz ($n = 5$), the dissipation is underestimated in the fit. A shear-rate-dependent viscosity could account for these deviations but is not currently present in the model. As independent verification, the equilibrium moisture absorption determined by this model is compared to that determined previously from X-ray reflectivity for identical films.¹² The agreement between the absorption determined by fitting the frequency and dissipation and the X-ray reflectivity is reasonable as seen in Table 1. Good agreement was also found when only using frequencies with

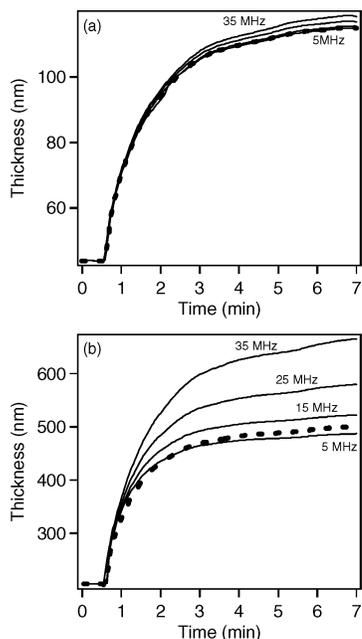


Figure 3. Film thickness as determined from the Sauerbrey equation for (a) 44 and (b) 205 nm thick poly(4-ammonium styrenesulfonic acid) films using the fundamental frequency and three overtones. The film thickness, as determined by fitting all the frequency and dissipation data, is shown by the thick dashed line.

TABLE 1. Comparison of X-ray Reflectivity (XR) and QCM Determination (from Model Fit (m) or Sauerbrey Expression (s)) of Swollen Poly(4-ammonium styrenesulfonic acid) Film Thickness

initial thickness (nm)	final thickness (nm) (XR)	final thickness (nm) (QCM)	swelling ratio (QCM)
2.7	6.0	6.4 (s)	2.3
12.7	26.8	29.1 (s)	2.3
27.6	62.8	65.1 (s)	2.4
44	129	116 (m)	2.5
96	245	271 (m)	2.8
127	438	372 (m)	2.9
205	490	520 (m)	2.5

dissipation shifts less than 2×10^{-6} and then applying the Sauerbrey expression.¹²

Figure 3 shows indiscriminate application of the Sauerbrey expression to two of the different film thicknesses (solid lines) for the resonant and overtone frequencies. These are compared to the fit obtained using eqs 5 and 6 applied simultaneously to the resonant and overtone frequencies ($n = 1, 3, 5,$ and 7). For the thin film (Figure 3a), the Sauerbrey expression and the fit agree for all measured frequencies, as expected from the lack of dissipation and the collapse of the normalized frequency shifts (Figure 2a and b). However, for the thick film (Figure 3b), the fundamental frequency agrees well with the model fit, but significant deviations occur if the Sauerbrey equation is used for any of the resonance frequencies. Further increase in the film thickness would result in deviations even for the fundamental frequency. From fitting the frequency and dissipation changes, viscosity of the swollen films is determined (Table 2). No conclusions can be made on the film-thickness dependence of the viscoelastic properties due to significant scatter in the data, but there does not appear to be any significant deviations in this thickness range. It is difficult to extract information about the thinner films in the frequency range studied; the films behave rigidly when the thickness is less than 40 nm.

TABLE 2. Mechanical Properties of Swollen Poly(4-ammonium styrenesulfonic acid) Films

initial thickness (nm)	final thickness (nm)	viscosity (kg/ms)	shear modulus (MPa)
44	116	0.013 ± 0.003	3.5 ± 0.6
96	271	0.020 ± 0.004	12.9 ± 5.9
127	372	0.017 ± 0.004	10.1 ± 2.5
205	520	0.027 ± 0.002	18.9 ± 1.5

The determination of film viscosity from QCM experiments is not a new idea; however, to date no film-thickness-dependent studies have been undertaken using this method. One of the main impediments in film-thickness-dependent viscosity measurements using QCM is the ability of the resonator to probe the inelastic properties of ultrathin films. This point can best be illustrated by the data in Figure 1. Although the polymeric material is identical to that used to extract the viscosity from thicker films, there are no significant deviations from the Sauerbrey equation nor is the dissipation a strong function of the frequency for the thinnest films. Inspection of the data in Figure 2 shows several features that give some insight into this phenomenon. First, the normalized frequencies are initially identical and then diverge (from that of the fundamental frequency) as moisture is absorbed. This divergence occurs in an order with the highest frequency diverging first. Second, the time required for the normalized frequencies to diverge is dependent upon the film thickness: the thicker the film, the sooner the frequency diverges. Finally, similar relations are also observed with the dissipation shifts. Thus, three factors contribute to the ability to extract viscoelastic properties from QCM measurements: film thickness, measured frequency, and film viscosity. These are also the same properties that were used to determine the validity of the Sauerbrey equation for viscoelastic films.⁷ From first principles, deviations from the Sauerbrey equation should be observed when $\beta_1 D > 0.28$, where β_1 is $2\pi/\lambda_s$, and D is the film thickness. To clearly observe viscoelastic effects using QCM, deviations from the Sauerbrey equation are extremely useful, if not necessary. From the fit of the QCM data using eqs 5 and 6, the film viscosity, thickness, and density are determined. All the parameters required to calculate β are known, except the angle of the complex viscosity. Thus, the average of the extremes (perfectly viscous, $\phi = 0$, and perfectly elastic, $\phi = \pi/2$) was used to calculate the value for β . The location of the deviation is determined by comparison of the fit thickness (as calculated with eqs 5 and 6) to the film thickness determined by the application of the Sauerbrey expression for the resonant and overtone frequencies. Examination of Figure 3 shows two examples of this procedure. The location of the deviations is frequency dependent as expected from the functional form of β . For the specific case of the moisture absorption examined here, the higher frequency always deviates sooner in the experiment than the resonant frequency. This is due to a higher viscosity threshold as the oscillatory frequency is increased, which is a general conclusion for quartz resonators. Although the film viscosity at which deviations from the Sauerbrey expression are observed is dependent upon the film thickness and viscosity, the deviation is expected to be reduced to a single parameter through use of βD . For the four films shown in Figure 2, the location of the deviations is $\beta_1 D = 0.26 \pm 0.10$, which agrees with the theoretical predictions ($\beta_1 D > 0.28$). The location of the deviation from the Sauerbrey expression in terms of βD as a function of initial film thickness is shown in Figure 4. Thus, for the poly(4-ammonium styrenesulfonic acid) films swollen with water, a thickness of at least 178 ± 55 nm should be required to observe deviations from

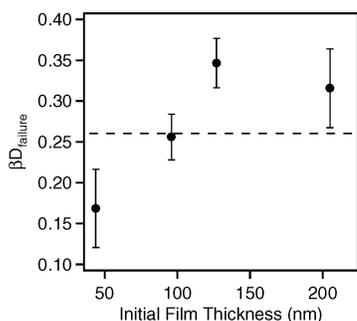


Figure 4. Experimentally determined deviations from the Sauerbrey expression for various film thickness. The dashed line is the theoretical prediction from White and Schrag.⁷

the Sauerbrey equation for a frequency of 35 MHz. For the film that shows only minor deviations (initial thickness = 44 nm), the film thickness in the swollen state is 117 nm, almost at the predicted limit (within the uncertainty) for the deviations, as would be expected given the small differences between the frequencies. For the thinnest film discussed here (Figure 1), the thickness in the swollen state only reaches 65 nm, and no deviations are observed. Attempts to fit these data using the same model as that used for the thicker films (Figure 2) result in underestimation of the viscosity by greater than one order of magnitude using the least-squares of the error. Additionally, the quality of the fit is relatively insensitive to the calculated viscosity, with uncertainty an order of magnitude greater than the fit viscosity itself. Thus, there appears to be a limit to extracting viscoelastic properties from QCM measurements, which is also the limit where the Sauerbrey equation begins to be less valid ($\beta D > 0.28$).

To predict the failure of the Sauerbrey expression, knowledge of the viscosity, density, and thickness of the film is required. This prediction would be useful for QCM systems that only measure a single frequency as an output. Typically, reasonable estimates for the density and thickness can be determined from other means, but estimates for the film viscosity are more ambiguous. For complex fluids, the viscosity is shear-rate dependent, thus, the relevant frequency for QCM measurements is on the order of megahertz, whereas most conventional rheometers are only capable of measuring responses at several hundred hertz. Thus, it is possible that the measured viscosity from a rheometer at low frequencies ($<10^2$ Hz) may be irrelevant for the QCM measurements ($>10^6$ Hz). To investigate this possibility, the rheology of an equivalent aqueous polymer solution (38% poly(4-ammonium styrenesulfonic acid) by volume) was measured with a stress rheometer in the frequency range from 1 to 100 Hz (the film, when exposed to saturated water vapor, swells to this concentration). The complex viscosity (η^*) for the solution over this frequency range is relatively constant, 2.3 ± 1 Pa s. This is several orders of magnitude larger than the viscosity determined from fitting the QCM data. This difference may be due to shear-thinning of the polymer solution, which would make predictions regarding the applicability of the Sauerbrey equation quite difficult.

Shear-thinning behavior at high frequencies was previously observed for polyacrylamide solutions using the same QCM system.¹⁷ For these polyacrylamide solutions, deviations of several orders of magnitude in the viscosity between the bulk solution rheology and QCM measurements were observed. However, the bulk rheology measurements extended to higher frequencies where shear-thinning was observed. Thus, it is probable that the frequency range for our measurements was too low to observe shear-thinning. However, due to the

multicomponent nature of the solution, there exists the potential for segregation near the interface. Due to the low pK_a of the silicon oxide surface and the polymer being in salt form, the substrate surface will be negatively charged upon adsorption of water. Electrostatic repulsion with the negatively charged polymer could result in a low-viscosity water-rich layer near the silicon oxide substrate. Accumulation of water at the buried interface during moisture absorption in supported polymer films has been observed for many systems.^{18–20} The segregation of a thin water-rich layer near the quartz resonator surface would tend to greatly shift the apparent viscosity toward that for pure water. This is what is observed for the apparent viscosity of the polymer film. Previously, Forrest and co-workers demonstrated that addition of rigid particles to a polymer surface increases the surface viscoelastic contributions to the QCM signal.²¹ A similar effect appears to be present here, with the polymer film being relatively rigid on top of a water-rich layer. This possibility is of particular interest as it potentially allows for an understanding of some of the anomalous QCM results found for certain biological systems.⁶ However, this is unlikely as the apparent viscosity should be thickness dependent for the case of a water-rich layer, but the viscosity for the hydrated films was found to be consistent between different thicknesses. Most importantly, the location of the frequency deviation is consistent with the predictions of White and Schrag.⁷

Conclusions

The frequency and dissipation behavior of quartz resonators coated with poly(4-ammonium styrenesulfonic acid) films was measured during exposure to saturated water vapor. As moisture is absorbed into the films, the film becomes less rigid, allowing for deviations from the well-known Sauerbrey expression. However, not all films exhibit a deviation from ideal behavior despite equal water content in the films. The deviation is governed by three parameters: the film viscosity, the film thickness, and the resonator frequency. A critical term, $\beta_1 D$, can be used to determine where deviations from ideal behavior will occur. These deviations were observed for $\beta_1 D > 0.26 \pm 0.10$. This value is in agreement with the theoretical limit of 0.28.⁷ Thus, even for nonrigid films, the Sauerbrey equation can be successfully applied as long as the film is thin enough. This also potentially has implications for using quartz resonators to extract viscoelastic characteristics of ultrathin films. If βD is too small, only ideal (rigid) behavior is observed. For these thin films, we found that the viscoelastic character of the film cannot be accurately determined.

Acknowledgment. The authors are grateful to Michael Rodahl, Patrik Dahlquist, and Patrik Björn of Q-Sense for providing assistance with the data fits and helpful discussions. The authors acknowledge Jai Pathak for the bulk rheological measurements. B.D.V. acknowledges financial support from the NIST/NRC postdoctoral program. Disclaimer: 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.

References and Notes

- (1) Sauerbrey, G. *Phys. Verh.* **1957**, *8*, 113–114.
- (2) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206–222.

- (3) Nomura, T.; Okuhara, M. *Anal. Chim. Acta* **1982**, *142*, 281–284.
- (4) Kanazawa, K. K.; Gordon, J. G. *Anal. Chim. Acta* **1985**, *175*, 99–105.
- (5) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley and Sons: New York, 1980.
- (6) Marx, K. A. *Biomacromolecules* **2003**, *4*, 1099–1120.
- (7) White, C. C.; Schrag, J. L. *J. Chem. Phys.* **1999**, *111*, 11192–11206.
- (8) Reed, C. E.; Kanazawa, K. K.; Kaufman, J. H. *J. Appl. Phys.* **1990**, *68*, 1993–2001.
- (9) Kanazawa, K. K. *Faraday Discuss.* **1997**, *107*, 77–90.
- (10) Lucklum, R.; Hauptmann, P. *Faraday Discuss.* **1997**, *107*, 123–140.
- (11) Wolff, O.; Seydel, E.; Johannsmann, D. *Faraday Discuss.* **1997**, *107*, 91–104.
- (12) Vogt, B. D.; Soles, C. L.; Lee, H.-J.; Lin, E. K.; Wu, W. L. *Langmuir* **2004**, *20*, 1453–1458.
- (13) Rodahl, M.; Hook, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. *Rev. Sci. Instrum.* **1995**, *66*, 3924–3930.
- (14) Rodahl, M.; Kasemo, B. *Rev. Sci. Instrum.* **1996**, *67*, 3238–3241.
- (15) Martin, S. J.; Bandey, H. L.; Cernosek, R. W.; Hillman, A. R.; Brown, M. J. *Anal. Chem.* **2000**, *72*, 141–149.
- (16) Voinova, M. V.; Rodahl, M.; Jonson, M.; Kasemo, B. *Phys. Scr.* **1999**, *59*, 391–396.
- (17) Munro, J. C.; Frank, C. W. *Macromolecules* **2004**, *37*, 925–938.
- (18) Kent, M. S.; Smith, G. S.; Baker, S. M.; Nyitray, A.; Browning, J.; Moore, G. *J. Mater. Sci.* **1996**, *31*, 927–937.
- (19) Kent, M. S.; McNamara, W. F.; Fein, D. B.; Domeier, L. A.; Wong, A. P. Y. *J. Adhes.* **1999**, *69*, 121–138.
- (20) Vogt, B. D.; Soles, C. L.; Jones, R. L.; Wang, C.-Y.; Lin, E. K.; Wu, W.; Satija, S. K.; Goldfarb, D. L.; Angelopoulos, M. *Langmuir* **2004**, *20*, 5285–5290.
- (21) Forrest, J. A.; Mattsson, J.; Borjesson, L. *E. Phys. J. E* **2002**, *8*, 129–136.