Measurement of the Kinetics of Swelling and Deswelling Behavior of Poly(Methacrylic Acid) with Quartz Crystal Microbalance and Ellipsometry

Undergraduate Researcher
DivineJoy A. Akparanta
Essex County College, Newark, NJ

Faculty Mentor
Kenneth R. Shull
Department of Materials Science and Engineering
Northwestern University

Graduate Student Mentor
Yan Sun
Department of Materials Science and Engineering
Northwestern University

Abstract

The swelling and deswelling behavior of poly(methacrylic acid) (PMAA) thin films and the permeability of poly(styrene) (PS) membranes was investigated using quartz crystal microbalance and ellipsometry. The system consisted of either homopolymer PMAA film or diblock poly(methyl methacrylate)-poly(methacrylic acid) (PMMA-PMAA) brushes with a hydrophobic PS membrane capping layer. Results show that PMAA swells more under high pH values (pH 10) than under low pH values (pH 5 to 7). Additionally, the deswelling rate depends strongly on the film thickness as well as on the duration of the system's exposure to water. This result is significant for its mechanical application to hydrogels, which are used as synthetic alternatives to toughen biological materials (such as tissues) that can be used in tissue engineering, artificial cartilage, and filtration membranes.

Introduction

Polymer thin films have been the focus of scientific research for over a century. The structure of a polymer determines its reaction to different solvents. Polymers are either hydrophobic (lacking affinity for polar solvents) or hydrophilic (having great affinity for polar solvents such as water). Polymer films are thin layers of polymer with thicknesses in the nanometer range. Polymer brushes are also thin layers of polymer, but each chain of the polymer brush is individually attached to the substrate. Thin polymer films and brushes are used in a wide variety of applications, including integrated circuits,[1] dielectric layers, organic light-emitting devices, protective encapsulations, lubricant coatings,[2] surfactants, membranes,[3,4] adhesives, and photoresists.[5] Poly(methacrylic acid) (PMAA) is a hydrophilic polymer that increases in thickness when exposed to an aqueous environment. It is used in various applications such as retardation of tumor metastasis,[6] controlled drug release,[7] and biomaterials for the growth of artificial bones.[8]

This work uses ellipsometry to monitor the deswelling of both homopolymer PMAA and diblock after swelling in water. The sample thickness allows us to determine the rate at which the PMAA deswells. The quartz crystal microbalance (QCM), which can be operated in a liquid environment, was used to measure film thickness during swelling. The purpose of this research is to measure the amount of swelling and rate of deswelling of the PMAA and to determine the permeability of the polystyrene capping layer. This information will be used for future research on anionic crosslinking (ion distribution on PMAA brush). The distribution of ions (for example, Zn^{2+}) in an ionically crosslinked brush is very important for its implications in the mechanical properties of hydrogels, which are used as a synthetic alternative to toughen biological materials such as tissues and cartilage.

Background

In 1952 Morawetz and Hughes used PMAA for enzyme purification. They proved that bovine serum albumin could be precipitated with PMAA by interacting PMAA with protein. Their results also showed that the activity of liver esterase is preserved following precipitation with PMAA.[9] In 1997 Ito et al. used PMAA brushes to control the permeation of liquids through a porous membrane by changing the pH value of their solution.[10] More recent studies have focused on swelling and deswelling of PMAA. Biesalski et al. examined brushes of PMAA attached to a silicon wafer. The results indicate that the PMAA increased in thickness when exposed to water with different pH and ion concentrations.[11] The swelling and deswelling behavior of polymer thin films and brushes can be studied using techniques such as x-ray diffraction, neutron reflectivity, ellipsometry, and QCM. One advantage of the QCM is that it can be operated in a liquid environment.[12] Shull et al. used a QCM to measure the swelling properties of PMMA-PtBMA-PMMA films immersed in water.[13] Their results showed that the QCM is sensitive to small changes in the thickness of the polymer films. While it has been shown that polymer films exhibit swelling, there is still a lack of understanding of what controls the rate of the swelling and deswelling. Previous experiments conducted by the Shull group used a PMMA-PtBMA-PMMA acrylic triblock copolymer. This triblock copolymer consisted of a poly(tert-butyl methacrylate) midblock (PtBMA) and PMMA endblock. An acid-catalyzed hydrolysis was used to form PMAA from the PtBMA. Their results showed that the hydrogel containing PMAA swelled while the one containing PtBMA did not. Figure 1 shows a schematic of the PMAA preparation.

The ellipsometer measures the relative change in the polarization of waves after reflecting off a film/substrate system.[14] Figure 2 is a schematic of an ellipsometry experiment. Electromagnetic radiation is emitted by a light source, which passes through an optional

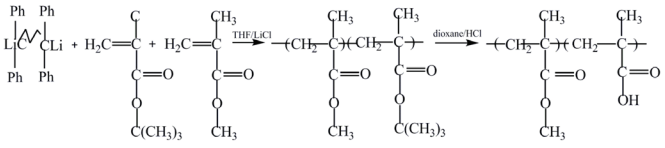


Figure 1. Anionic synthesis of the PMMA-PtBMA diblock copolymer, followed by hydrolysis of the PtBMA midblock to form PMAA.

compensator quarter-wave plate and reflects off the sample. After reflection, the radiation passes through the analyzer and into the detector.[15] The ellipsometer measures two parameters, (Ψ) and (Δ). The parameters are divided into *s* and *p* components, which refer to different polarizations of light reflecting from the surface. The s components are oscillating perpendicular to the plane of incidence but parallel to the sample surface, and the p component oscillates parallel to the incident direction. After reflection, their initial values are denoted by r_s and r_p and their ratios are calculated with the equation

$$\rho = \frac{r_p}{r_s} = \tan(\psi)\, e^{i\Delta}$$

where tan Ψ is the amplitude of reflection and Δ is the phase shift. The film thickness is calculated using this equation.

Quartz crystal resonators (QCRs) have been used extensively to study the mechanical properties of thin layers.[16] The QCM senses acoustic waves on the surface. It measures the mass per unit area by measuring the shift in the crystal's frequency (Δf) and dissipation (ΔΓ). This technique is highly efficient for measuring the affinity of molecules such as proteins to surfaces with recognition sites. The resonance frequency of oscillation of a QCM depends on the thickness of the crystal. A change in total thickness is proportional to a change in frequency.[17] As the load increases on the surface of the crystal, the thickness increases and the resonant frequency decreases. For thin films, the frequency shift is a function of the mass alone; its acoustic properties can be ignored.[18] The reflectivity of an acoustic wave at the crystal surface depends on the impedence ratio; the measurement of films in a liquid environment requires more care because liquids have small shear-acoustic impedence.

Approach

The ellipsometer has the capability to measure thin films with thicknesses ranging from less than a nanometer to several micrometers. The homopolymer and diblock films used here are in the nanometer range.

Technique 1: Measuring the Deswelling of PMAA by Ellipsometry

Solutions of homopolymers PMAA (242 kg/mol) and PS (131 kg/mol) (Aldrich) were prepared. PMAA solutions, 5% and 1% by weight, were prepared in ethanol. PS solutions, 5% and 10% by weight, were prepared in toluene. Silicon substrates were cleaned and oxidized by sequential dipping into water, acetone, and methanol. The substrate was exposed to UV/ozone for 10 min. The substrates were spin coated by PMAA, followed by PS, for 40 sec at 3000 rpm. The thickness of the film was adjusted by the rotation speed, solution concentration, and time of rotation. Figure 3 illustrates the spin-coating process, and Figure 4 shows the complete sample.

The homopolymer sample has hydrophobic PS as the top layer and hydrophilic PMAA as the middle layer. The sample was exposed to aqueous solutions of different pH at different times, from 10 min to 15 hrs. As the solution was removed, the sample was placed on the ellipsometer and the drying thickness was measured. The ellipsometer was expected to measure the amount of swelling and the rate of deswelling of these samples after their exposure to water, but the limitations of the ellipsometer precluded making these measurements; data could not be collected when the PMAA swelled to more than twice the dry thickness or, due to lack of signal intensity, when there was a top layer of water on the sample. To complete this project, another method was used to measure the swelling of PMAA.

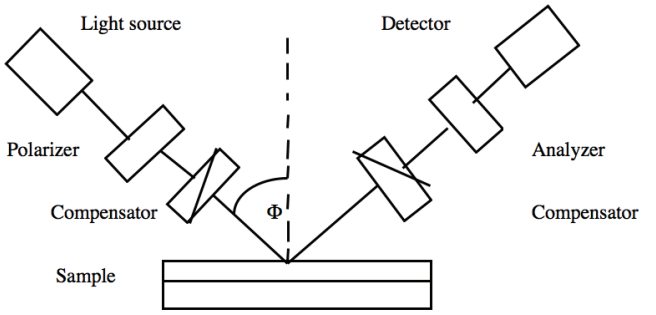


Figure 2. The schematic setup of an ellipsometer.

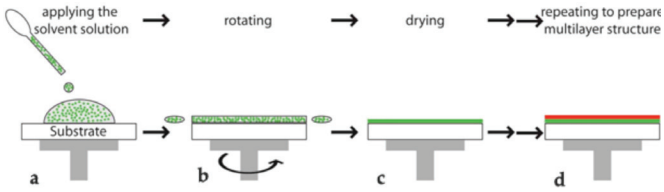


Figure 3. Depiction of (a) drops of PMAA on the top of the substrate, (b) the spin-coated time of 40 sec with a speed of 3000 rpm, (c) PMAA on a SiO_2 substrate, and (d) PMAA and PS on the substrate.[19]

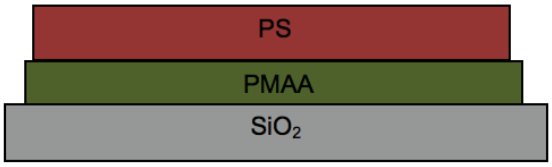


Figure 4. Illustration of the complete spin-coated sample of PMAA and PS on a silicon substrate.

Technique 2: Measuring the Swelling of PMAA by QCM

The sample measured with the QCM was a diblock copolymer (PMMA-PMAA) film. This sample contains a gold substrate, PMMA-PMAA as a middle layer, and PS as the top layer. The sample was prepared according to Guvendiren and Shull.[15] Their method explained how to make triblock compolymers, but it can also be used to make a diblock copolymer. Anionic polymerization of tBMA and MMA was carried out in a nitrogen atmosphere using a difunctional initiator. The PMMA-PMAA diblocks were dissolved in N, N-dimethylformamide (DMF). The diblock copolymer was spin coated onto a gold substrate to form a homogeneous layer for the QCM measurement. As an alternating voltage from the gold electrodes causes the quartz to oscillate, a shear wave propagates from the surface of the material, which causes a shift in frequency. The frequency increases as well as the dissipation. The QCM measured the frequency and dissipation shift as the layers of film and

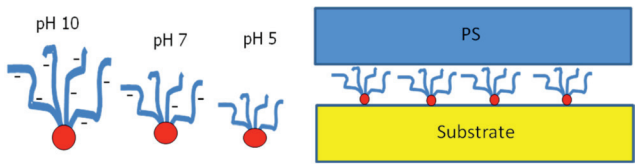


Figure 5. Schematic drawing of the structure of PMMA-PMAA diblock at pH values of 5, 7, and 10.

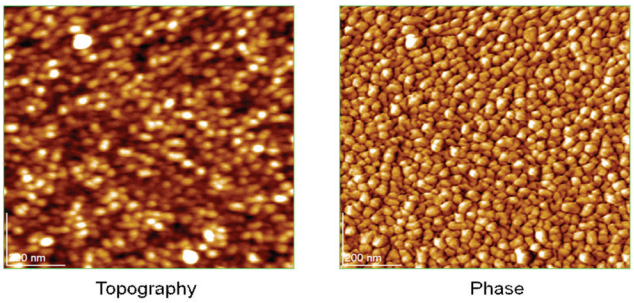


Figure 6. AFM topography and phase images of spin-coated 1% PMMA-PMAA film from DMF (1 x 1 um^2).

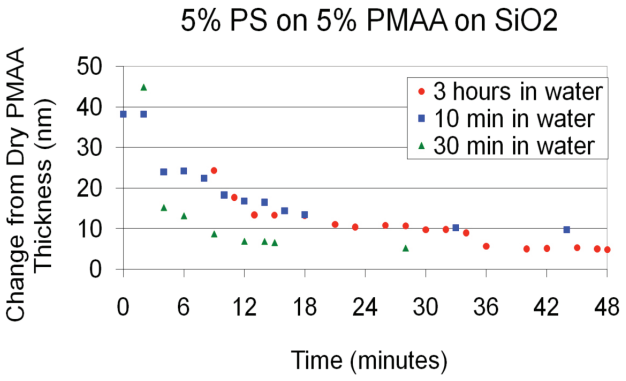


Figure 7. Decreasing thickness of the PMAA film as a function of time; the dry thickness was 471 nm, and after exposure to aqueous solution, the thickness increased to 509 nm. Optical constants: An: 1.5245, Bn: 0.0069003, Cn: -0.0002065.

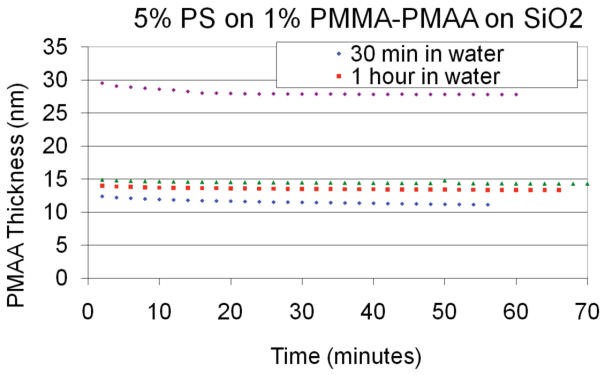


Figure 8. Deswelling graph of diblock copolymer PMAA for different lengths of time; the dry thickness was 12.4 nm, and after exposure for some hours, the PMAA swelled to 29.5 nm, showing 138% swelling.

water of pH 5, 7, and 10 were added to the top of the crystal. Figure 5 shows the complete spin-coated diblock sample and the diblock in different pH, while Figure 6 shows the AFM pictures of the spin-coated diblocks.

Formation of Micelles

When the diblock is spin coated, a micelle is formed, because the hydrophobic tail of the PMMA collapses to form clusters that adhere to the silicon substrate, while the hydrophilic head of PMAA extends outward to form brushes. Both the homopolymer PMAA and diblock PMMA-PMAA were spin coated with a PS capping layer that limits and controls the rate of aqueous solution slowly diffusing in the PMAA layer. After spin coating, these samples were exposed to water for different lengths of time and of different pH, with different concentrations.

Results

Technique 1

The data taken by ellipsometry within a one-hour time interval show that the thickness of PMAA decreases with the time constant. Table 1 lists the time constants of PMAA homopolymer and diblock copolymer exposed to aqueous solution for various lengths of time. Figures 7 and 8 show the thickness of the PMAA homopolymer and diblock samples, respectively, as a function of time.

Time Exposed to a Solution	Deswelling Time Constant
30 min	27.08 min
1 hour	22.77 min
3 hours	22.91 min
15 hours	8.88 min

5% PS on 5% PMAA on SiO_2

Time Exposed to Water	Deswelling Time Constant
10 min	8.46 min
30 min	1.52 min
3 hours	15.22 min
17 hours, 25 min	23.01 min

5% PS on 1% PMAA on SiO_2

Time Exposed to Water	Deswelling Time Constant
1 hour	18.79 min
5 hours	16.41 min

10% PS on 5% PMAA on SiO_2

Time Exposed to Water	Deswelling Time Constant
3 hours	37.67 min

Table 1. Time constant of the homopolymer and diblock samples measured by ellipsometry and calculated with exponential decay equation, $h = m_1 + m_2\, e^{-m3t}$

The pH played a vital role in the swelling process of PMAA. A pH 10 solution increased the thickness of the polymer more than 95%, while pH 7 increased the thickness 20%, and pH 5 caused very little swelling. The higher pH swelled the sample because of the lost hydrogen of the carboxyl group. The carboxyl group has an uncharged hydroxide that loses the hydrogen when exposed to a solution of higher pH. The pH 10 solution makes the acidic PMAA film become basic. This causes a donation of electrons to the surrounding water molecules, leaving the sample with almost all of its particles charged.

Technique 2

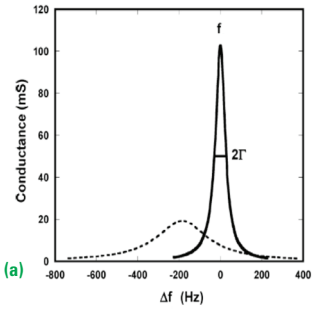
The diagram in Figure 9 shows a typical electrical conductance plot. The presence of a gel layer causes a change in both the resonance frequency and half-band–half-width value in the graph. The frequency shifts as the sample swells and is related to the thickness of the sample. For pH 10, the sample showed a higher frequency shift because the sample swells more as the frequency — measured in megahertz (MHz) — increases. As the sample swells, there is an increase in dissipation. Figure 10 shows the QCM measurements of 5% PS on 1% PMMA-PMAA with pH 5, 7, and 10 solutions. These show a normal frequency shift for loading of the resonator by a triple layer that is measured with 25 MHz frequency. Figure 11 shows the QCM measurements of 5% PS on 1% PMMA-PMAA with pH 5, 7, and 10 solutions showing the change in gamma (Γ = bandwidth/2). The increase in frequency is directly related to the increase in gamma.

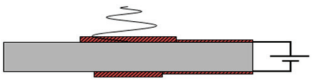
Discussion

The ellipsometry measured the rate of deswelling of the sample after its exposure to water by measuring the sample thickness as it decreases back to the dry thickness. The QCM measures the frequency and dissipation shift as the layers of PMMA-PMAA, PS, and an aqueous solution are added to the top of the crystal resonator. These values are used to determine relative changes in the sample thickness. The results from the ellipsometry data show that the PMAA thickness decreases in a regular manner depending on the length of time in water. The limitations of this method mean that the homopolymer cannot be exposed to water for a long period of time, as it is too thick for the ellipsometer to measure. PMAA dissolves after several hours, causing the thickness of the dry sample to be greater than the thickness of the sample exposed to water. The QCM is better at measuring thick films, but the limitation is that a complicated fitting procedure is required to extract physical variables such as film thickness. Therefore, while the shift in frequency and gamma indicates different swelling behavior in different pH, the change in thickness could not be quantified at this time. However, when a model taking into account the properties of both the swollen and capping layers in this system was used, the parameters could be determined.

Conclusions

The two topics studied in this research were the hydrophilic behavior of PMAA and the permeability property of the PS capping layer. Two techniques were used: ellipsometry and QCM. Ellipsometry measures deswelling of sample thickness by monitoring light reflecting off the sample surface. The QCM measures the swelling through shifts in the resonant frequency and dissipation of acoustic waves passing through the sample. The homopolymer PMAA and PMMA-PMAA diblock copolymers that were used in this study had a PS top layer that acted as a barrier membrane by limiting diffusion and allowing the rate at which the PMAA absorbed water to be studied. The results show that the PMAA thickness increased when exposed to solutions of different pH.





(b) Alternating voltage from gold electrodes causes quartz to oscillate. Shear wave propagates into material on the surface.

Figure 9. (a) Impedance analysis that is based on the electrical conductance curve; the central parameters of measurement are the resonance frequency (f) and half-band–half-width (2Γ). (b) Schematic of the quartz crystal resonator.

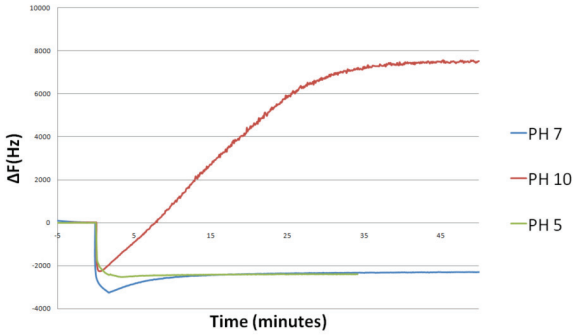


Figure 10. QCM measurement of 5% PS on 1% PMMA-PMAA with pH 5, 7, and 10 solutions measured with 25 MHz frequency.

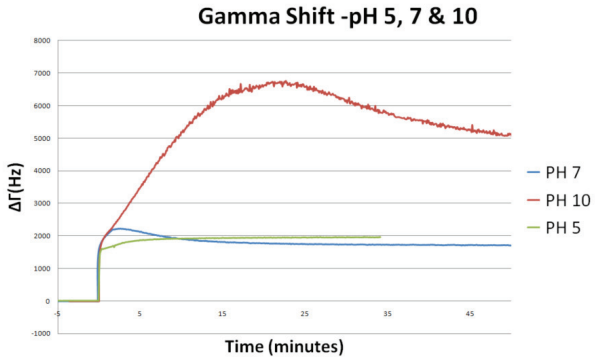


Figure 11. QCM measurement of 5% PS on 1% PMMA-PMAA with pH 5, 7, and 10 solutions showing the change in gamma (Γ = bandwidth/2).

At pH 10 the PMAA thickness increased more than 138% because of the polymer's loss of hydrogen to water molecules. At pH 7 the sample swelled 20–30% because of partial loss of hydrogen; pH 5 did not cause much swelling. These results support the hypothesis that the PMAA swelling and deswelling behavior depends on the pH value of the solution and the duration of exposure. The PS capping layer reduced the rate of deswelling so that the film thickness could be accurately measured. These results will be used in future experiments focusing on anionic crosslinking of PMAA and Zn^{2+}. This study was also necessary to prepare for advanced in situ studies (x-ray scattering, etc.) that require the right experimental time scales to collect data. It was shown that the presence of PS allows such time scales to be achieved.

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