# Kinetics of pH Response for Copolymer Films with Dilute Carboxylate Functionality

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We have investigated the effects of film composition and thickness on the rate of pH-induced response of a copolymer film containing predominately polymethylene with randomly distributed carboxylic acid side groups (denoted as PM-CO2H). These responsive films are prepared directly onto a gold electrode surface by surface-catalyzed polymerization and subsequent hydrolysis. We measured electrochemical impedance at fixed frequency (100 Hz) to monitor the barrier properties of the polymer film during a step change in pH. At a 1–3% molar acid content, the copolymer films exhibit a 2 order of magnitude change in impedance at 100 Hz when the contacting solution pH changes from 11 to 4 (or 4 to 11). For all films, the rate of protonation is slower than that of ionization, consistent with a more gradual transfer of protons through an increasingly hydrophobic film at the outermost nanometers during the protonation step. Increased acid content within the film accelerates both the rate of protonation and ionization. Thinner films (50 nm) with the same acid content show faster response rate in both directions, since water and ions have a shorter transfer path. A large and reversible pH response was obtained for all films studied, but selection of appropriate film composition and thickness can greatly influence the rate of response.

## Introduction

Polymer films that respond to pH by altering their barrier properties have potential applications in chemical sensors[1–3] to detect analytes that trigger a change in local pH when reacted and in membrane separations to allow transport through the film only at targeted pH ranges.[4–6] For successful utilization in these applications, the pH-responsive film must exhibit a large, rapid, and reversible response and should be straightforward to process on appropriate substrates. The pH-sensitive films studied to date are most often composed of hydrogels that contain a high fraction of poly(acrylic acid) (PAA).[1,7,8] As a recent example, Cai et al.[7] attached glucose oxidase to the surface of a 1-$\mu$m-thick poly(acrylic acid–isooctylacrylate) hydrogel atop a wireless, mass-sensitive transducer. The sensor tracked glucose concentration from 1 to 15 mM, with a response time of ∼1 h at the highest concentrations. Since the response time of the hydrogel is dependent on diffusion, thinner films are likely to respond more rapidly, as demonstrated by Richter and co-workers[1] who cast ∼400 nm films of a PAA hydrogel onto a quartz crystal microbalance probe and observed a 1 order of magnitude response within 1 s when the pH of the solution changed from 1.8 to 3.2. In cases where ultrathin (70 nm), pH-sensitive inorganic films have been used instead of hydrogels, the response time is rapid but the sensitivity is poor.[9] While these approaches demonstrate the concept of pH-sensitive coatings, current drawbacks include insufficient sensitivity due to the small magnitude of the film response and slow response, most often due to excessive film thickness that enhances the time for water and ion permeation. Films that exhibit large changes in properties upon exposure to a pH stimulus and can be prepared as defect-free thin films have the potential to impact sensor design and performance.

We have recently designed a new class of pH-responsive polymer films on gold surfaces by first developing a controlled, surface-catalyzed polymerization in the presence of diazomethane (DM) and ethyl diazoacetate (EDA) to prepare a random copolymer film consistent with poly(methylene-*co*-ethyl acetate) and subsequently hydrolyzing the ester side chains to varying extents to yield carboxylic acids (denoted as PM-CO2H).[10,11] These films are predominately hydrophobic but contain a controlled, dilute fraction (1–4%) of carboxylic acid groups to exhibit a remarkable change in barrier properties when the pH is increased sufficiently to ionize the acid groups. On the basis of octanol–water partition coefficients, the carboxylate group is ∼$10^4$ times more hydrophilic than the protonated acid.[12] This extreme difference in the affinity of these groups toward water provides the basis for the work described herein. We have shown that at a 1–4% molar acid content, the copolymer film exhibits a 5 order of magnitude change in its resistance to ion transport over 2–3 pH units.[11] The onset pH at which this response initiates can be tailored from pH 5 to 10 by decreasing the acid content in the film from 4% to 1%. We have also shown that this pH-responsive film can be grown atop nanoporous supports to fabricate pH-responsive membranes.[6] To broaden the pH-responsive range and compare the pH-responsive behavior of polyacid and polybases, we can further react the acid groups to obtain amide-linked tertiary amine side chains.[13] We observed and reported that a critical hydrophobicity of the functional side chain is required to produce a large film response.[13]

The ability to precisely control the acid content within the film and tailor the thickness of these surface-catalyzed polymer films from a few to several hundred nm enables a thorough assessment of film composition and thickness on response rate. While film response should be more rapid for thinner films, the film must be sufficiently uniform to function as a defect-free barrier in the uncharged state. Many methods such as the quartz crystal microbalance (QCM),[14] ellipsometry,[8] electrochemical impedance spectroscopy,[15] and optical microscopy[16–18] have been used to study the swelling behavior of polymer films

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and hydrogels. To examine the rate of film response, we measured film impedance at a fixed frequency during a step change in pH, a technique that we[19] and others[20] have previously used to measure the kinetics of self-assembled monolayer formation. This method has also been used to characterize water transport in organic coatings,[21] to evaluate the performance of coatings,[22,23] and to investigate the application of conductive polymer films in pH-sensing.[24] We compared the kinetic rates for the step up in pH with those for the step down to determine if the hydrophobic nature of the uncharged films provides a diffusive barrier for aqueous ions. We expect that protonation of the films will be slower than ionization because, for the former case, water and ions have to penetrate a neutralized region of hydrophobic film formed during the protonation. Through this study, we seek to identify optimal film composition and thicknesses to enhance the magnitude and rate of the response by the film to pH.

## Experimental Section

**Materials.** Potassium hydroxide, diazald (_N_-methyl-_N_-nitroso-_p_-toluenesulfonamide), ethyl diazoacetate (EDA), and poly(ethylene-_co_-ethylacrylate) (PEEA) were used as received from Aldrich (Milwaukee, WI). Benzoic acid, 2-propanol, sodium bicarbonate, potassium hydrogen phthalate, and acetone were used as received from Fisher (Fair Lawn, NJ). Hydrochloric acid and sodium hydroxide were used as received from EM Science (Gibbstown, NJ). Gold shot (99.99%) and chromium-coated tungsten filaments were obtained from J&J Materials (Neptune City, NJ) and R.D. Mathis (Signal Hill, CA), respectively. Silicon (100) wafers (Montco Silicon; Spring City, PA) were rinsed with ethanol and deionized water and dried with nitrogen. Ethanol (absolute) was used as received from AAPER (Shelbyvlle, KY). Nitrogen gas was obtained from J&M Cylinder Gas, Inc. (Decatur, AL). Deionized water (16.7 MΩ· cm) was purified with a Modu-Pure system (Continental Water Systems Corp.; San Antonio, TX) and used for rinsing. Buffer solutions (pH 4 and 11) were prepared according to a literature procedure.[25] In a typical preparation procedure, 0.1 mL of 0.1 M HCl (pH 4) or 22.7 mL of 0.1 M NaOH (pH 11) was added to 50 mL of a solution containing 0.1 M potassium hydrogen phthalate (pH 4) or 0.05 M NaHCO$_3$ (pH 11), and the solution volume was diluted to 100 mL using deionized water.[25] The pH was then measured using a Corning 430 pH meter with 3-in-1 combination electrode and adjusted by addition of HCl, NaOH, or appropriate salts present in each buffer solution.

**Preparation of Gold Substrates.** Gold substrates were prepared by evaporating chromium (100 Å) and gold (1250 Å) in sequence onto silicon (100) wafers at rates of 1–2 Å s$^{-1}$ in a diffusion-pumped chamber with a base pressure of $4 \times 10^{-6}$ Torr. After removal from the evaporation chamber, the wafers were typically cut into 1.2 cm × 4 cm pieces, rinsed with ethanol, and dried in a stream of N$_2$ gas.

**Preparation of Diazomethane.** DM was carefully prepared according to a literature procedure[26] and diluted with ether at 0 °C to prepare solutions of different concentration. _Caution: Diazomethane is toxic and potentially explosive and should be handled carefully![26]_ The concentration of DM was determined by titration with benzoic acid.[27]

**Preparation of Polymer Films.** Polymer films were prepared by exposure of gold-coated silicon substrates to ether solutions containing 0.3 mM DM and 40 mM EDA (to get 50 nm films) or 0.3 mM DM and 80 mM EDA (to get 95 nm films) at 0 °C for 16 h. Film growth was carried out in capped 20 mL vials, and only one substrate was placed in each vial. Upon removal,

the samples were rinsed with ether and ethanol and dried in a stream of nitrogen. The resulting PM-CO2Et film contained 3.6% and 4.2% (molar) of the ethyl ester group for 50 and 95 nm films, respectively.

**Hydrolysis of Polymer Films.** Hydrolysis of the copolymer films was carried out in capped 20 mL vials of 0.2 M KOH in 2-propanol at 75 °C for 40, 80, and 180 min to obtain copolymer films with 1%, 2%, and 3% acid contents for 50 nm films and 1, 2, and 3.5 h to obtain copolymer films with 1%, 2%, and 3% acid contents for 95 nm films. Only one substrate was placed in each vial. The hydrolyzed samples were rinsed with ethanol and DI water and dried in a N$_2$ stream.

**Characterization Methods.** _Reflectance absorption infrared spectroscopy (RAIRS)_ was performed using a Varian 3100 FT-IR spectrometer. The p-polarized light was incident at 80° from the surface normal. The instrument was run in single reflection mode and equipped with a Universal Sampling Accessory. A liquid-nitrogen-cooled, narrow-band MCT detector was used to detect reflected light. Spectral resolution was 2 cm$^{-1}$ after triangular apodization. Each spectrum was accumulated over 1000 scans with a deuterated octadecanethiol-$d_{37}$ self-assembled monolayer on gold as the background.

IR spectra were used to estimate conversion ($\chi$) of the copolymer film by hydrolysis based on the integrated C=O absorbance ($A_{CO,t}$) at 1735 cm$^{-1}$

$$\chi = 1 - \frac{A_{CO,t}}{A_{CO,t=0}} \quad (1)$$

which assumes that any decrease in ester C=O absorbance scales directly with the ester concentration in the film. All the integrated peak areas in this calculation were measured after exposure of the films to pH 11 since the C=O peak due to carboxylate at 1560 cm$^{-1}$ is sufficiently distal in wavenumber from the ester C=O peak at 1735 cm$^{-1}$ and does not affect its integrated intensity.

The molar ester contents of the surface-catalyzed copolymer films were determined from reflectance IR spectra using the integrated area ratios for the carbonyl stretching peak at 1735 cm$^{-1}$ and the combined methylene stretching peaks (symmetric and asymmetric) at 2851 and 2919 cm$^{-1}$, respectively. The basis for the calculation of ester content was the peak area ratio obtained for a cast film of a commercially available random copolymer (poly(ethylene-_co_-ethyl acrylate) (PEEA)). PEEA has a known 18 wt % ethyl acrylate content (2.9% (molar) ethyl ester; 97.1% −CH$_2$−) and exhibited a C=O:CH$_2$ peak area ratio of 0.26. This analysis assumes that the peak area ratio scales linearly with the molar ester content within the film.

_Ellipsometry_ measurements were obtained on a J.A. Woollam Co. M-2000DI variable-angle spectroscopic ellipsometer with WVASE32 software for modeling. Measurements at three spots/ sample were taken with light incident at a 75° angle from the surface normal using wavelengths from 250 to 1000 nm. Optical constants for a bare gold substrate, cut from the same wafer as the samples to be characterized, were measured by ellipsometry and used as the baseline for all polymer film samples. Thickness of the polymer films was determined using a Cauchy layer model. Since the copolymer films are PM rich (ester content <5%), the refractive index for the film was set to 1.5, consistent with the ranges measured for polyethylene.[28]

A Simple Liquid Cell with the M-2000DI system was used to perform ellipsometric measurements on films immersed in a pH buffer solution. Before sample measurement, the liquid cell was calibrated with a 50 mm silicon wafer that contained a

~250 Å thermally grown $SiO_2$ film to ensure that the effects of window birefringence are minimized. After the gold-coated wafer with polymer film sample was mounted and the cell was aligned, a single data scan was acquired to provide a baseline measurement prior to the injection of the solution into the cell. After the pH solution was added to the cell, the alignment was checked again, and a single data set was acquired. A top layer with the optical constants for water was added to the Cauchy layer model to determine the film thickness in the pH solutions.

*Electrochemical impedance spectroscopy (EIS)* was performed with a Gamry Instruments EIS 300 impedance system interfaced to a personal computer. A Flat Cell (EG&G Instruments) was used to expose only 1 cm² of each sample to a pH buffer solution while preventing sample edges from being exposed. The electrochemical cell consisted of a pH buffer solution prepared as described above with an Ag/AgCl/saturated KCl reference electrode, a gold substrate counter electrode, and a gold substrate containing the film to be studied as the working electrode. For the EIS study, all measurements were made at the open circuit potential with a 5 mV ac perturbation that was controlled between 100 mHz and 100 kHz. All data were collected in the range $10^5–10^{-1}$ Hz using 10 points/decade and were fit with an appropriate equivalent circuit model to determine resistance and capacitance values. At each pH value, sufficient time was allowed to make sure that the film reached a stable state as evidenced by the accumulation of repeated spectra that did not change with time.

**Impedance Study at Single Frequency.** Impedance measurements were obtained at 100 Hz. The Flat Cell described above initially contained 6 mL of pH 11/pH 4 buffer solution. After a stable impedance was obtained, the pH solution was removed from the cell and 6 mL of pH 4/pH 11 buffer solution was added immediately. Impedance and phase angle readings were recorded every 3 s. Reported values for $t_{95}$, the time required for the impedance to exhibit 95% of the overall pH-induced response, represent the average and standard deviation of values obtained from at least three measurements on each film with 1, 2, and 3% acid contents.

The magnitude of the impedance, $|Z|$, is related to the real ($Z_R$) and imaginary ($Z_I$) components of the impedance by[29,30]

$$|Z|^2 = (Z_R)^2 + (Z_I)^2 \qquad (2)$$

$$Z_R = R \qquad (3)$$

$$Z_I = 1/\omega C \qquad (4)$$

where $R$ is the resistance, $C$ is the capacitance, and $\omega = 2\pi f$, in which $f$ is the frequency. The phase angle, $\phi$, given by

$$\tan \phi = Z_I/Z_R = 1/\omega RC \qquad (5)$$

expresses the balance between the real and imaginary components in the circuit. For a pure resistance, $\phi = 0°$, for a pure capacitance, $\phi = -90°$, and for a mixture, intermediate phase angles are observed. For the impedance study at fixed frequency, $f$ is a constant (100 Hz in this study). By monitoring the changes of $Z_R$, $Z_I$, and $\phi$ as a function of time when the contacting solution is switched from one pH value to another, we can obtain useful information on the rate of film response.

## Results and Discussion

**Motivation for Single Frequency Measurements.** Figure 1 shows electrochemical impedance spectra in the form of Bode plots for a 95 nm PM-CO2H film with 1% molar acid content
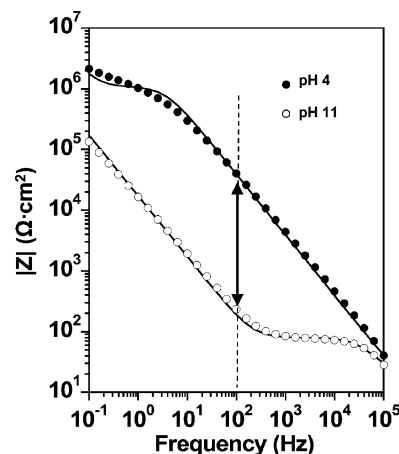


**Figure 1.** Electrochemical impedance spectra in the form of Bode plots for a 95 nm PM-CO2H film with 1% acid content at pH 4 and pH 11 on gold.



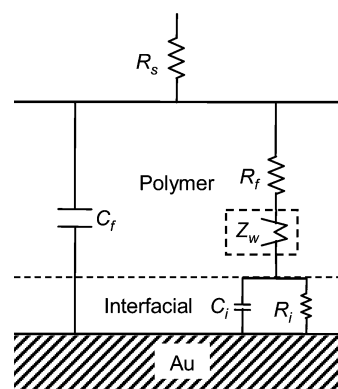**Figure 2.** Equivalent circuit used to model impedance spectra for polymer/metal interfaces.

(99% $-CH_2-$) on gold at pH 4 and pH 11. The spectra can be fitted with a model commonly used for polymer-coated metals[31] as shown in Figure 2. This model contains two time constants, one due to the polymer film and one due to the polymer–metal interface. The following terms are used to denote various film and solution characteristics: solution resistance, $R_s$; interfacial capacitance, $C_i$; interfacial resistance, $R_i$; film capacitance, $C_f$; film resistance, $R_f$; Warburg impedance, $Z_w$. One simplification to the circuit in Figure 2 for this study is that $R_i$ is effectively infinite since no redox probes are present to transfer charge at the electrode; thus, we do not expect to observe a resistance due to the polymer/metal interface in the spectra.

We have reported the effect of pH on the composition of PM-CO2H films using RAIRS.[11] At pH 4, the side chains of PM-CO2H are in the uncharged state ($-CO_2H$) and the film is hydrophobic due to the prevalence of methylene functionality (99%) along the chains. The impedance due to the film dominates the entire frequency region, indicating that the film impedance is much greater than the combined impedance due to the polymer–metal interface. A Warburg component that relates to mass-transfer limited ion diffusion appears at low frequencies. At pH 11, the deprotonation of the carboxylic acid side chains increases the hydrophilicity of the film. The increasing charge of the film with pH results in markedly reduced film resistance such that two time constants appear in the impedance spectrum. The time constant at lower frequencies is from the polymer/metal interface, and the one at higher frequencies is from the polymer film and corresponds to the combined capacitance and resistance of the polymer film. At
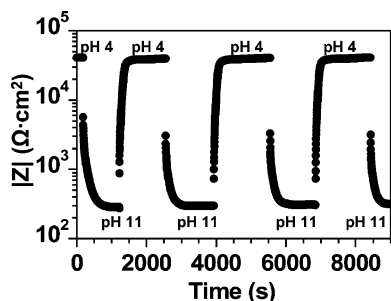
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**Figure 3.** Time-dependence of impedance modulus for a 95 nm PM-CO2H film with 1% acid content on gold when the contacting solution pH cycles between pH 4 and pH 11.

pH 11, the film resistance is still evident from 1 to 40 kHz, representing a small but measurable barrier to ion transfer.

While EIS can be used to evaluate the film performance and extract useful properties such as the film resistance and capacitance, each spectrum requires about 10 min to accumulate, precluding a detailed analysis of kinetics on the time scale of several seconds to a few minutes. To probe the rate of pH-induced response of the copolymer film, a more rapid method to measure film barrier properties is required. One way to achieve a more rapid sampling is to evaluate the pH response at a fixed frequency. Single frequency measurements can probe the impedance change as a function of time by sampling every few seconds, which enables a more effective monitoring of the rate of film response as the film changes from one state to another. As shown in Figure 1, we have drawn a vertical line connecting the two spectra at a frequency of 100 Hz. At 100 Hz, film capacitance dominates the impedance at pH 4 and interfacial capacitance dominates the impedance at pH 11. By the switching of solution pH from 4 to 11, the actual value of impedance modulus is altered by more than 2 orders of magnitude, the largest difference within the studied frequency range. We also expect that the change will be reversible since we have observed repeatable results when we performed EIS over the range from pH 4 to 11 and back.[11]

Figure 3 shows the measured impedance modulus upon exposure of a 95 nm, 1% acid film to pH 4 and 11 buffer solutions in a cyclic manner. The system's impedance at 100 Hz changes by a factor of 150 when the pH of the contacting solution is switched from 4 to 11. For each cycle, the measured impedance values increase upon exposure to the pH 4 buffer and decrease upon exposure to the pH 11 buffer solution. Upon cycling pH, the film returns to the initial impedance value, indicating the reversible nature of the pH response. For all the cycles, the steady-state impedance values at pH 4 are within ∼5% of each other and those at pH 11 are within ∼10% of each other, demonstrating good reversibility. We have previously used EIS to show that the PM-CO2H films exhibit a large response in barrier properties to pH; here, we use fixed frequency impedance measurements to demonstrate that the response is reversible and can be measured in a much more rapid manner to reveal potential information on response rates.

**Response of 1% Acid Films.** Since the impedance changes dramatically with pH, we can monitor changes in the real and imaginary components and phase angles with time to obtain an improved understanding of the response process. Figure 4 shows the time dependence for $|Z|$, $Z_R$, $Z_I$, and $\phi$ at 100 Hz for a 95 nm 1% acid film upon changing pH from 11 to 4 and thereby protonating carboxylates to enhance the hydrophobicity of the film. At pH 11, $Z_R$ and $Z_I$ are each observed, with $Z_I$ being ∼3 times larger. If the polymer/gold interface functions as a pure interfacial capacitor, we would not expect to observe $Z_R$, and
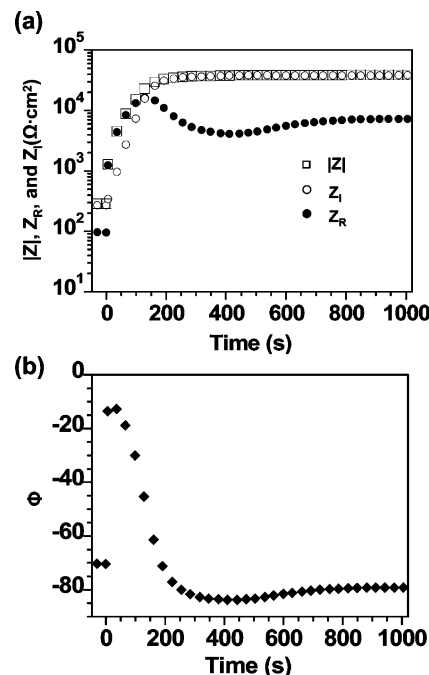


**Figure 4.** Time-dependent changes in (a) $|Z|$, $Z_R$, and $Z_I$ and (b) phase angle ($\phi$) for a 95 nm PM-CO2H film with 1% acid molar content when pH is changed from 11 to 4.

the phase angle should be −90°. However, the fact that $Z_R$ is observed and the phase angle is ∼−70° indicates an easily measurable, albeit minor, contribution due to the resistance of the polymer film against ion transfer with the dominant component being the interfacial capacitance.

When the pH of the contacting solution is changed from 11 to 4, the protonation of the carboxylate side chains within the film increases the film hydrophobicity and leads to an increase of the film impedance. The $|Z|$ changes by 2 orders of magnitude within 160 s after the step change and gradually approaches a steady value after that. The initial change of $|Z|$ is mainly from the large increase of the film resistance ($Z_R$) component as it becomes larger than $Z_I$ in the first 120 s, reflecting a reduction in ion conducting pathways due to the increased hydrophobicity of the protonated film. After this time, $Z_I$ becomes dominant as ion conducting pathways are quenched and the film functions as a dielectric to physically separate the ion-rich solution from the metal electrode.

The change of the phase angle with time also provides very useful information on the response of this system. When the pH is switched from 11 to 4, the phase angle jumps from −70 to −20° within 3 s and reaches a peak value of −11° at 24 s, consistent with the above analysis that the resistance against water and ion diffusion provides the dominant impedance during this intermediate state. After 24 s, although $Z_R$ continues to increase, the phase angle begins to fall gradually, indicating that the relative importance of $Z_I$ is growing and will eventually surpass $Z_R$ as the film behaves more as a dielectric. The phase angle reaches its minimum value (−85°) as $Z_R$ reaches its local minimum at ∼400 s, and the phase angle eventually becomes stable at −80°.

When pH is switched from 4 to 11, the impedance components change more rapidly, returning (within 10%) to their original values at pH 11 before the cycle was initiated. As shown in Figure 5a, $|Z|$ drops from 40 to 2 kΩ·cm² within 10 s. For the entire process, $Z_I$ appears to dominate $Z_R$ as the impedance switches from film-capacitance control to interfacial-capacitance
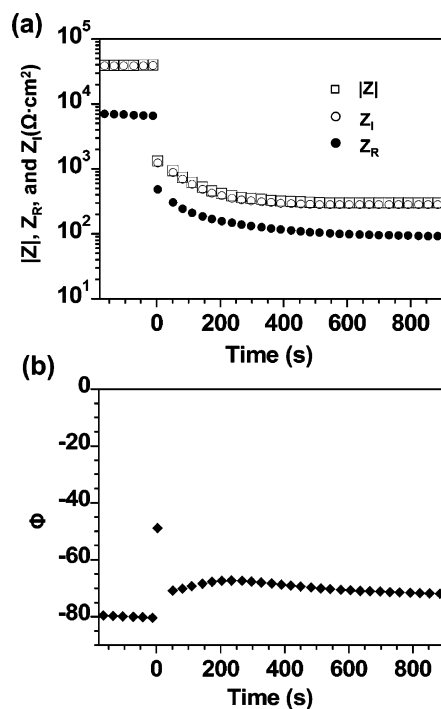
**Figure 5.** Time-dependent changes in (a) $|Z|$, $Z_R$, and $Z_I$ and (b) phase angle ($\phi$) for a 95 nm PM-CO2H film with 1% acid molar content when pH is changed from 4 to 11.



**Figure 6.** Schematic snapshot of a PM-CO2H film at an intermediate time scale after pH has been changed from (a) 11 to 4 and (b) 4 to 11.

control. By observing the time dependence of phase angle, we can also obtain some information about the effect of film resistance during this step change in pH. As shown in Figure 5b, when pH is switched from 4 to 11, the phase angle increases from $-80°$ to a peak value of $-49°$ in 3 s corresponding to an increase in relative contribution by the resistivecomponent as compared to film or interfacial capacitance upon initial deprotonation of the carboxylic acid groups. The brief appearance of this resistive component indicates that the role of film resistance in this process is only significant within the first ∼5 s consistent with very rapid water and ion penetration into this 95 nm film and in contrast to the slower appearance and decay of the resistive component during film protonation (Figure 4b).

To explain the effect of the slower film protonation, we schematically depict a snapshot of the intermediate time scales for water and ions to traverse the film in both protonation (Figure 6a) and ionization (Figure 6b) processes. For protonation, the carboxylate side chains within the film are converted to carboxylic acids. Since the carboxylate group has an octanol−water partition coefficient ($K_{ow}$) of $-5.19$ that is over 4 orders of magnitude lower than that of the carboxylic acid ($K_{ow} = -1.11$),[12] the reacted film becomes dramatically more hydrophobic. At an intermediate time, an outer hydrophobic region of film likely separates the proton-rich aqueous solution from the underlying carboxylate-rich film and impedes the transfer of aqueous protons to further neutralize the carboxylate groups underneath. In addition, once protonation occurs, water and ions trapped in the film may be slow to diffuse out of the film. In contrast, when the pH changes from 4 to 11, the carboxylic acids at the top part of the film will be ionized to carboxylates and the film becomes increasingly hydrophilic to facilitate the transfer of water and ions as a moving front through the film.

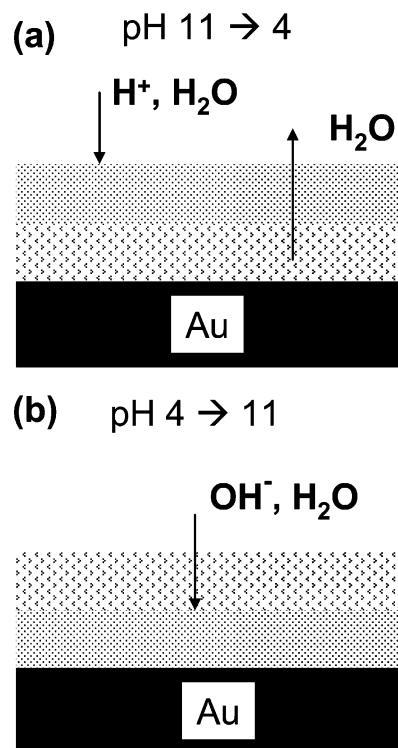The time dependence of $Z_I$ can be used to examine the extent of the protonation/ionization reaction indirectly through the transport of water and ions into or out of the film. Using the Helmholtz model,[30]

$$C = \frac{\epsilon \epsilon_0}{d} \quad (6)$$

where $\epsilon$ is the dielectric constant of the polymer film, $\epsilon_0$ is the permittivity of vacuum, and $d$ is the thickness of the film. With combination of eqs 4 and 6, the imaginary impedance can be written as

$$Z_I = \frac{d}{\omega \epsilon \epsilon_0} \quad (7)$$

Since $\omega$ and $\epsilon_0$ are constants and the film thickness only changes slightly (∼20%)[32] from pH 4 to pH 11 due to swelling, $Z_I$ is mostly a function of the $\epsilon$ of the polymer coated on the gold electrode. Water has a much higher dielectric constant (∼80) than that of the PM-rich film (∼2−3),[33] so an increased water content within the film over time will greatly affect the film capacitance and imaginary impedance. For the ionization, the reaction occurs easily, and the water penetrates into the film very rapidly, observed as a fast drop in $Z_I$. In the protonation, the reaction is hindered by the increasing hydrophobicity of the film which affects the transport of water out of the film; thus, we observe a slower change in $Z_I$ with time.

To assess if the protonation is limited by diffusion or reaction, we performed contact angle measurements on a 1%, 95 nm film after switching the pH of the contacting solution from 11 to 4. The contact angle is only sensitive to the top half nanometer of surface composition.[34] If the process is reaction-limited, we expect the measured contact angle to change with the increasing reaction time as the carboxylic acid content changes within the film and near the surface. We immersed the 1% acid content film that had been placed in pH 11 solution for at least 1 h into a pH 4 solution for 0, 30, 120, and 600 s and measured the contact angles by using a pH 4 solution as the probe liquid.
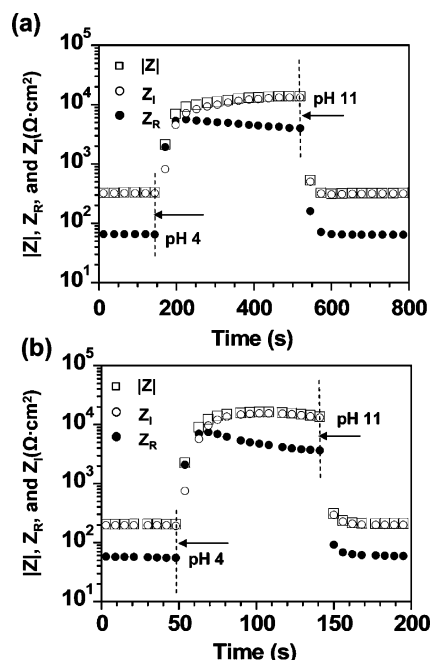
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**Figure 7.** Time-dependent changes in $|Z|$, $Z_R$, and $Z_I$ when the pH changes from 11 to 4 and back to 11 for a 95 nm PM-CO2H film with (a) 2% and (b) 3% acid content. The arrows in the plots indicate when the pH 4 or pH 11 solution was added.

We observed an advancing contact angle of $\sim62°$ for the film prior to immersion into the pH 4 solution and the same advancing contact angle of $\sim78°$ for the samples immersed in pH 4 solutions for 30, 120, and 600 s. Thus, the protonation reaction near the surface occurs on a time scale that is much faster than the $\sim150$ s required for the film to achieve an asymptotic impedance, as shown in Figure 4a. The more rapid conversion of surface carboxylate groups as compared with those throughout the film is consistent with a diffusion-limited process and is qualitatively consistent with Figure 6a.

**Effect of Film Composition on the Rate of Film Response.** To investigate the effect of acid content on the rate of film response, we also measured impedance properties at 100 Hz for 95 nm films with 2 (Figure 7a) and 3% (Figure 7b) molar acid content. These films still yield large responses ($\sim2$ orders of magnitude) when pH is switched between 4 and 11, but the 3% film responds significantly faster, as noted by comparing the time scales on the *x*-axis. Upon comparison of these results with those shown in Figures 4 and 5, an increase in the acid content within the film greatly reduces the response time (vide infra), consistent with the decrease of film hydrophobicity (more carboxylate content) with greater acid content.

To quantify the rate of response, we have determined the time required for a film to reach 95% of the asymptotic impedance modulus ($t_{95}$) as a function of the acid content within the films (Figure 8). This time was chosen because of the widely different transient profiles for the films with different acid contents, which precludes fitting the data with a common model that would enable a simple comparison of rates. As described previously, there are two stages in the film response, an initial, rapid increase/decrease in film impedance and then a gradual increase/decrease until the impedance reaches a stable value. At a film thickness of 95 nm, a 1% acid film requires 420 s to reach 95% of the asymptotic value for the protonation process, while the 2 and 3% films require 210 and 36 s, respectively. By increasing the acid content from 1 to 3%, we can reduce the response time by up to a factor of $\sim12$ but still achieve a large response. The film with 3% acid content is still sufficiently
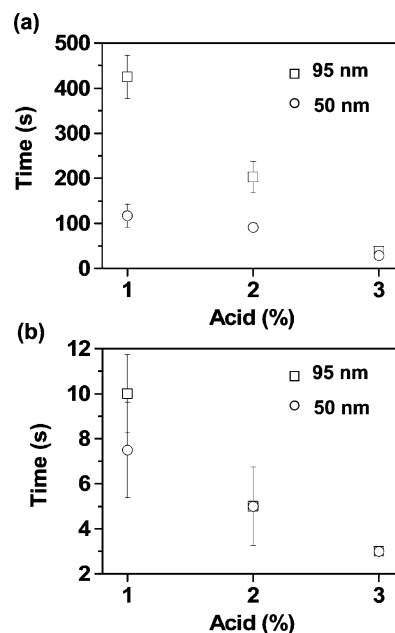


**Figure 8.** Time required for films with 95 and 50 nm thicknesses to reach 95% of the stable impedance as a function of the acid content when the pH changes from (a) 11 to 4 and (b) 4 to 11.

hydrophobic at low pH values (here pH 4) to provide a large film impedance. However, more functional groups are present within the 3% film than in the 1% film to form pathways for water and protons to protonate the unreacted carboxylates so that the response rate is much faster. When pH changes from 4 to 11, the 1, 2, and 3% acid films lose 95% of their impedance in $\sim10$, $\sim5$, and $\sim3$ s, respectively. All films lose more than 1 order of magnitude in $|Z|$ within 3 s.

**Effect of Film Thickness on the Rate of Film Response.** We have also investigated the effect of film thickness on the rate of film response by measuring impedance properties at 100 Hz for 50 nm films with 1, 2, and 3% acid contents and comparing $t_{95}$ values with those of the thick 95 nm films in Figure 8. Upon decrease of the pH from 11 to 4, a 1% acid film at 50 nm requires $\sim115$ s, about a quarter of the time required by the 95 nm film with 1% acid content, to reach 95% of its asymptotic value. For the 1% film, this result is again consistent with a diffusion-limited process during protonation since the time required is proportional to the square of the distance (film thickness). This dependence on thickness was not as prominent for the 2 and 3% acid films. The 2% 50 nm film requires 90 s, which is less than half the time (210 s) required for the 2% 95 nm film, and the 3% 50 nm film requires 27 s, which is only 9 s faster than the 3% 95 nm film. The increased carboxylate content within the film reduces the dependence of the response rate on film thickness by providing additional hydrophilic pathways for water and ion transfer through the intervening hydrophobic barrier at intermediate time scales (Figure 6a). Similar to the 95 nm films, the 50 nm films respond rapidly when pH is changed from 4 to 11. The $t_{95}$ values for 1, 2, and 3% films are $\sim7$, $\sim5$, and $\sim3$ s, respectively.

## Conclusions

We have investigated the rate of pH-induced response for PM-CO2H films with 1, 2, and 3% acid contents and thicknesses of 50 and 95 nm. For all the studied films, the rate of protonation is slower than that of ionization because for the former case, initial protonation produces regions of hydrophobicity that may impede the transfer of water and ions into and/or out of the

film. At the same acid content, the thicker films require a longer time to reach a new stable state since water and ions must diffuse over a longer distance to reach the electrode. With the increase of acid content within the film, these characteristic times can be shortened for both processes because more water and ion pathways exist within the film, and the effect of film thickness on the rate of response becomes muted. By a careful selection of the the acid content and thickness of the polymer film, a fast, large, and reversible pH-response can be achieved within the desired pH range. While these films appear slower in response than some of the more hydrophilic hydrogel films studied with different analytical techniques,[1] the large response (over 2 orders of magnitude) is far greater than that provided by many competing films and could be important in areas where both speed and sensitivity are required.

**Supporting Information Available:** Comparison of atomic force microscopy images for a 95 nm, 3% PM-CO2H film after exposure to pH 4 and pH 11 buffer solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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