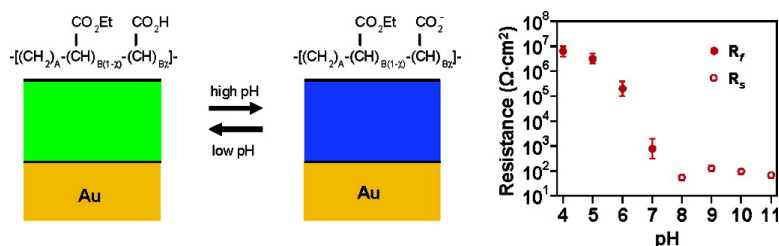


pH-Responsive Copolymer Films by Surface-Catalyzed Growth

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pH-Responsive Copolymer Films by Surface-Catalyzed Growth

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Abstract: We have engineered a new class of pH-responsive polymer films on gold surfaces by first developing a controlled, surface-catalyzed polymerization to prepare a 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). When pH is increased, the acid groups become deprotonated or charged, dramatically increasing their water solubility and greatly altering the film properties. The carboxylic acid content within the copolymer film can be adjusted by changing the monomer concentration ratio used in the polymerization process or the length of time for the hydrolysis. We have designed PM-CO₂H films to consist predominately (>95%) of polymethylene (PM) so that the film is hydrophobic in the uncharged state and, thereby, exhibits an extremely large pH-induced response in barrier properties once ionized. The effect of polymer composition on pH response was investigated by electrochemical impedance spectroscopy (EIS), reflectance-absorption infrared spectroscopy (RAIRS), and contact angle measurements. At a 1%–4% molar acid content, the copolymer film exhibits a 5 orders of magnitude change in its resistance to ion transport over 2–3 pH units. The pH at which this response begins can be tailored from pH 5 to pH 10 by decreasing the acid content in the film from 4% to 1%.

Introduction

Polymer films that respond to pH by altering structure, barrier properties, and/or surface properties have enormous potential to impact chemical sensors,^{1–3} membrane separations,^{4,5} and dynamic surfaces.^{6,7} In many types of chemical sensors and biosensors, pH-sensitive coatings are an integral part of the transduction mechanism to detect the release of H⁺ ions by a chemically specific reaction between an immobilized moiety (e.g., enzyme) and an analyte compound.^{8,9} In separations, pH-responsive polymers can extend/contract to close/open pores in the presence of target molecules and form the basis of smart membranes.⁴ For successful utilization in these applications, the pH-responsive film must exhibit a large, rapid, and reversible response.

Polymer films that respond to pH are most commonly prepared as hydrogels¹⁰ by mixing appropriate polymers^{1,11} or

synthesizing copolymers¹² that can be diluted in solvent and cast onto surfaces. The hydrogels contain carboxylic acid or other ionizable groups, and over a range of pH near the pK_a of the sensitive groups, the film becomes ionized and expands due to additional uptake of water and ions driven by differences in electrochemical potential.¹³ The thicker hydrogel films exhibit rather slow response due to the increased lengths for diffusion, requiring several minutes to hours to completely change chemical states.^{8,9} The concentration of hydrophilic, ionizable groups in these hydrogels is often high,^{11,12} ensuring that water is present in the films at all pH ranges. Therefore, the ultimate response in aqueous-phase barrier properties for these films upon ionization is not expected to be large.

Carboxylic acid groups are commonly used as the pH-sensitive moiety in responsive films as the acid is deprotonated to a carboxylate ion as pH is increased above a certain value. On the basis of octanol–water partition coefficients,¹⁴ the carboxylate group is ~10⁴ times more hydrophilic than the protonated acid. This extreme difference in the affinity of these groups toward water provides the basis for the work described herein. Briefly, polymer films that are predominately hydrophobic but contain a dilute fraction of carboxylic acid groups should exhibit a huge change in barrier properties when the pH is increased sufficiently to ionize the acid groups. At low pH,

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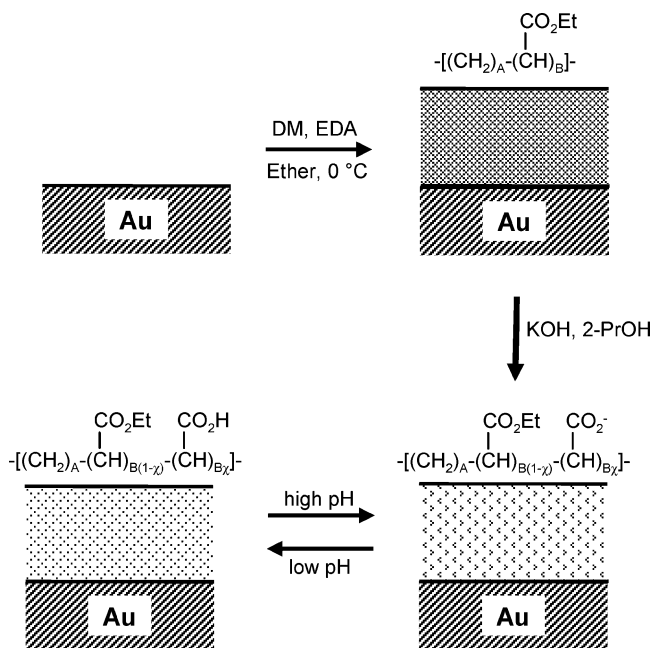


Figure 1. Schematic method for preparing pH-responsive PM-CO₂H films by surface-catalyzed growth and subsequent modification. In these films, $A \gg B$.

the polymers would be mostly dry, but upon ionization, the large difference in hydrophilicity of the carboxylate versus the acid should result in significant water and ion permeation. Such films may provide extremely pH-sensitive materials and could be useful in sensing and separations.

Here, we report a unique approach known as surface-catalyzed polymerization to engineer new classes of pH-responsive copolymer films. The films are prepared by exploiting a selective catalysis at gold surfaces that enables nanometer-level control over film thickness. Briefly, we have recently reported that exposure of gold substrates to a dilute solution containing diazomethane (DM) and ethyl diazoacetate (EDA) (Figure 1) results in a controlled copolymerization of a film containing linear polymethylene (PM) with randomly distributed ethyl ester side groups (denoted as PM-CO₂Et).¹⁵ These films exhibit tunable thicknesses up to several hundred nanometers based on polymerization times and precursor concentrations and controllable film composition based on the solution ratio of the DM and EDA precursors. In the current work, we demonstrate that the hydrolysis of the ester side groups to carboxylic acids with fractional conversion χ provides a film we denote as PM-CO₂H that exhibits unusually large changes in barrier properties when the pH of the contacting solution is altered beyond a film-specific, critical pH range. When the acid groups become deprotonated or charged, the water solubility of the acid functional groups increases markedly to dramatically alter the film properties.¹⁴ We have designed PM-CO₂H films to consist predominately (>95%) of polymethylene (PM) so that the film is hydrophobic in the uncharged state and, thereby, exhibits an extremely large pH-induced response in barrier properties once pH is increased sufficiently to charge the film.

This surface-catalyzed strategy toward pH-responsive films has several advantages over other approaches. (1) Surface-catalyzed polymerizations^{16–18} offer the ability to rapidly grow

films with controlled thicknesses up to the micron level. In fact, film thicknesses for PM-CO₂Et increase linearly with time.¹⁵ (2) The film growth is selective in that polymerization occurs on gold but not on most other materials (silicon, silver, aluminum, plastics, etc.), enabling the patterning of films by directed growth and straightforward integration into bottom-up processing schemes.¹⁸ (3) In contrast to depositing pregrown polymer onto a surface, the chain growth propagates directly from the metal surface and, thereby, enables modification of surfaces of any geometry with a pH-responsive film. (4) Film composition can be tailored to affect the onset and magnitude of the film response without requiring a completely new macromolecular synthesis.

Hydrophobic polymer films that contain carboxylic acid groups have been prepared by surface functionalization of polyethylene.^{7,19} Holmes–Farley et al.¹⁹ exposed bulk polyethylene films to chromic acid/sulfuric acid to produce an acid-rich surface. They used contact angle measurements to determine that the initial ionization of the carboxylic acids occurs at a solution pH of ~ 6 and that the $pK_{a(1/2)}$ is ~ 7.5 and unaffected by salt concentration. The elevation of $pK_{a(1/2)}$ over the pK_a value for acetic acid (4.7), a simple monobasic acid, has been reported by others^{19–22} for acid-containing films and is likely affected by hydrogen bonding between nearby acid groups at a surface^{21,22} or the heterogeneous environment of the acids in a predominately hydrophobic medium.¹⁹ The ability to prepare polymer films with dilute and well-defined fractions of carboxylic acid groups could provide additional insight on the pH-responsive behavior of these films.

In this manuscript, we examine the effect of fractional acid content (1–4%) on the ionization and barrier properties of PM-CO₂H films. An important goal of this work is to engineer the fractional acid content to investigate and perhaps tailor the onset and magnitude of the response in barrier properties. We use reflectance-absorption infrared spectroscopy (RAIRS) to investigate the effect of solution pH on the ionization of the carboxylic acid groups. The fractional ionization greatly affects the barrier properties of the film, which we examine with electrochemical impedance spectroscopy (EIS) to quantify film resistance and capacitance. Since such films have broad applications in amperometric sensors and as membrane skins, the use of EIS enables pertinent insight on how solution pH can affect the resistance of the film against ion diffusion and the capacitive current measured at the electrode surface. Through EIS measurements, we are able to quantify the effect of dilute acid content on the performance and responsiveness of the film.

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, sodium carbonate, potassium hydrogen phthalate, sodium phosphate monobasic, and

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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 (Shelbyville, KY). Nitrogen gas was obtained from J&M Cylinder Gas, Inc (Decatur, AL). Deionized water (16.7 M Ω ·cm) was purified with a Modu-Pure system (Continental Water Systems Corporation; San Antonio, TX) and used for rinsing.

All pH buffer solutions were prepared according to a literature procedure²³ except that we used NaH₂PO₄ instead of KH₂PO₄ and the pH 9 solution was prepared by mixing appropriate volumes of 0.1 M Na₂CO₃ with 0.1 M NaHCO₃. In a typical preparation procedure, specified volumes²³ of 0.1 M HCl (pH 4) or 0.1 M NaOH (pH 5–8, 10–11) were added to 50 mL of a solution containing 0.1 M potassium hydrogen phthalate (pH 4–5), 0.1 M NaH₂PO₄ (pH 6–8), or 0.05 M NaHCO₃ (pH 10–11) and the solution volume was diluted to 100 mL using deionized water. 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 salt.

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 × 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 N₂ gas.

Preparation of Diazomethane. DM was carefully prepared according to a literature procedure²⁴ and diluted with ether at 0 °C to prepare solutions of different concentrations. CAUTION: Diazomethane is toxic and potentially explosive and should be handled carefully!²⁴ The concentration of DM was determined by titration with benzoic acid.²⁵

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 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, ethanol, and DI water, and dried in a stream of nitrogen. The resulting PM-CO₂Et film was 75 nm thick and contained 4.2% (molar) of the ethyl ester group.

Hydrolysis of Polymer Film. 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 1, 2, 3.5, and 24 h to obtain copolymer films with 1%, 2%, 3%, and 4% acid contents, respectively. Only one substrate was placed in each vial. The hydrolyzed samples were rinsed with ethanol and DI water and dried in a N₂ stream.

Effect of pH on Film Composition. PM-CO₂H films with different acid contents were immersed in a pH buffer solution in a 20 mL capped vial for times ranging from 1 h (not in critical pH range) to 12 h (near critical pH range) and then dried with N₂. After IR analysis, the sample was rinsed with DI water and dried with N₂ and then placed into a buffer solution in which pH was one unit higher or lower. Reported peak area ratios for carboxylate (1560 cm⁻¹) to methylene (asymmetric (2919 cm⁻¹) plus symmetric (2851 cm⁻¹)) are based on average peak areas obtained at each pH value upon first decreasing pH from 11 to 4 and then increasing pH from 4 to 11.

Characterization Methods. Reflectance absorption infrared spectroscopy (RAIRS) was performed using a Bio-Rad Excalibur FTS-3000 infrared 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 (χ) of the copolymer film by hydrolysis based on the integrated C=O absorbance ($A_{\text{CO},t}$) at 1735 cm⁻¹

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

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 from 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 reported conversion represents the averages of conversion measured on at least three different samples.

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)). The PEEA has a known 18 wt % ethyl acrylate content (2.9% (molar) ethyl ester; 97.1% -CH₂-) and exhibited a C=O/CH₂ 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 per 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. Film thickness of the polymer layer on samples 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.²⁶

Electrochemical impedance spectroscopy (EIS) was performed with a Gamry Instruments CMS300 impedance system interfaced to a personal computer. A Flat Cell (EG&G Instruments) was used to expose only 1 cm² of each sample to different pH buffer solutions while preventing sample edges from being exposed. The electrochemical cell consisted of a pH buffer solution prepared as described above with a 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. The measurements were made at the open circuit potential with a 5 mV ac perturbation that was controlled between 100 mHz and 10 kHz. All data were collected in the range from 10⁴ to 10⁻¹ Hz using 10 points per 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 spectra that did not change with time. Reported values and ranges for resistance and capacitance represent the average and standard deviation of values obtained from at least three independent sample preparations.

Contact angles were measured on static drops of liquid on the polymer surfaces using a Rame-Hart contact angle goniometer with a syringe graduated in microliter increments. Before the measurement, all the samples were immersed into pH 4 or pH 11 buffer solutions for

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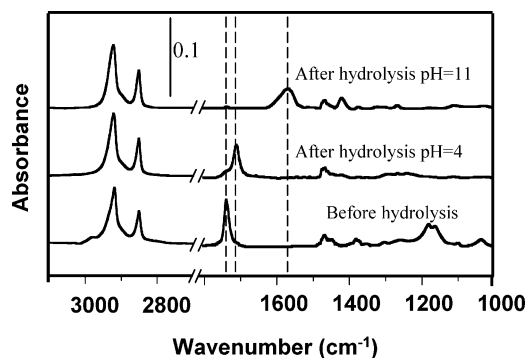


Figure 2. Reflectance-absorption IR spectra of copolymer films (4.2% ester content, 75 nm) before hydrolysis and after hydrolysis (24 h, 0.2 M KOH, 2-propanol, 75 °C) and subsequent exposure to aqueous buffer solutions at pH 4 and 11 for 1 h.

at least 1 h. The probe liquid consisted of pH 4 or pH 11 buffer solutions. The needle tip of the syringe remained inside the liquid drop while measurements were taken on both sides of $\sim 5 \mu\text{L}$ drops. All the contact angles were measured ~ 10 s after application of the drop. Reported values and ranges represent the averages and standard deviations of measurements obtained on at least three films prepared independently.

Results and Discussion

Film Hydrolysis. We exposed 75 nm PM-CO₂Et films (4.2% molar ester content) to a 2-propanol solution of 0.2 M KOH at 75 °C for 24 h and verified that the ester groups can be hydrolyzed to carboxylates (CO₂⁻) with high conversions ($\sim 95\%$). The use of 2-propanol rather than ethanol, used in our previous study,¹⁵ affords higher conversion without adversely affecting film quality. Figure 2 shows reflectance-absorption infrared (RAIR) spectra for the film before hydrolysis and after hydrolysis upon exposure to pH 4 or pH 11 buffer solutions. The ester carbonyl group, represented by a peak at 1735 cm⁻¹ in the spectrum for the prehydrolysis film, is greatly diminished after hydrolysis, and new peaks appear corresponding to the carbonyl stretching vibration in CO₂H (1710 cm⁻¹; pH 4) or CO₂⁻ (1560 and 1420 cm⁻¹; pH 11).²⁷ The hydrolysis and subsequent exposure to buffer solutions does not affect the structure of the film based on the similar peak positions (2919 cm⁻¹) and intensities for CH₂ stretching in the three spectra. The films can be converted between charged (deprotonated) and uncharged (protonated) states repeatedly and reversibly by exposure to the respective buffer solutions.

One approach toward tailoring the acid content of the film is to control the extent of the hydrolysis reaction by controlling the time in which the film is exposed to the KOH solution. To determine the feasibility of such control over acid content, we investigated the kinetics of the hydrolysis reaction. In this study, we used 75 nm copolymer films with an ester content of 4.2% before hydrolysis and exposed them to a solution of 0.2 M KOH in 2-propanol at 75 °C. Figure 3 shows that 70% of the ester groups are converted to acids in the first 3 h, and a nearly linear relationship exists between the conversion and time. For conversion > 70%, hydrolysis occurs more gradually, and a full 24 h is required to achieve 95% conversion. The remaining 5% of the conversion is extremely slow, even for such a thin film.

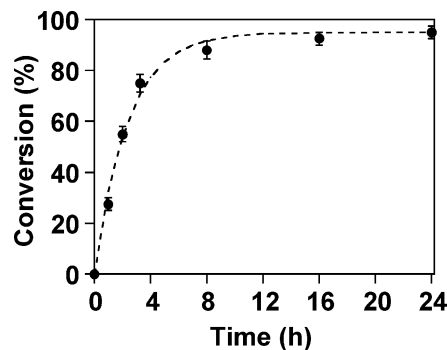


Figure 3. Time dependence of the conversion of ester to acid for a 75 nm PM-CO₂Et (4.2% ester) film upon exposure to 0.2 M KOH in 2-propanol solution at 75 °C. The dashed curve is a fit of the data based on eq 3, where kC is estimated from the fit as $1.17 \times 10^{-4} \text{ s}^{-1}$. The correlation coefficient (R^2) for the fit is 0.99.

Table 1. Advancing Contact Angles on PM-CO₂H Films with Different Acid Contents at pH 4 and pH 11

| acid content | advancing contact angle θ_A | |
|--------------|------------------------------------|---------|
| | pH 4 | pH 11 |
| 0% | 101 ± 3 | 101 ± 2 |
| 1% | 92 ± 3 | 72 ± 2 |
| 2% | 87 ± 3 | 65 ± 2 |
| 3% | 82 ± 3 | 60 ± 1 |
| 4% | 73 ± 2 | 54 ± 2 |

To obtain quantitative kinetics information for hydrolysis of the copolymer film, the conversion data in Figure 3 were fit with a simplest-case, reaction-limited model, which assumes that the rate of hydrolysis is proportional to the concentrations of KOH in solution (C) and accessible ester groups within the film:²⁸

$$\frac{d\chi}{dt} = kC(\chi_f - \chi) \quad (2)$$

or, upon integration,

$$\chi = \chi_f(1 - e^{-kCt}) \quad (3)$$

where t is time, χ is conversion and χ_f is the limiting conversion (0.95 after 24 h). Use of eq 2 provides a good fit to the transient conversion data in Figure 3 (correlation coefficient = $R^2 = 0.99$) and enables an estimate of kC as $1.17 \times 10^{-4} \text{ s}^{-1}$. The long time scale for the hydrolysis of a 75 nm film combined with the good fit of the reaction-limited model to the data suggests that the hydrolysis process is not limited by diffusion.

To provide additional evidence that the hydrolysis process is reaction-limited instead of diffusion-limited, the advancing contact angles for droplets of pH 4 or pH 11 buffer solution on the films with different acid contents are listed in Table 1 (0% represents PM-CO₂Et). All the films show pH-responsive wettability with the carboxylic acid surfaces exhibiting $\sim 20^\circ$ higher contact angles than the carboxylate surfaces. Water contact angles are sensitive to the outer half nanometer of film composition.²⁹ In a diffusion-limited process, the hydrolysis reaction occurs rapidly at the outer surface and the reaction front

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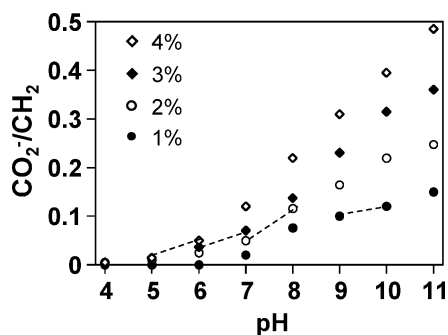


Figure 4. Peak area ratio of the carboxylate stretching band at 1560 cm^{-1} to the sum of the asymmetric (2919 cm^{-1}) and symmetric (2851 cm^{-1}) methylene stretching bands as a function of pH for 75 nm films with acid content ranging from 1% to 4%. The dashed lines in the figure represent the critical pH region (vide infra).

gradually penetrates into the bulk film. If this hydrolysis was a diffusion-limited process, we would expect all the films to exhibit similar contact angles, since their outermost surface would have approximately the same composition. The only difference would be the depth of penetration of the diffusing front. However, the measured contact angles decrease as the acid content of the film increases (Table 1), indicating that surface composition changes with the extent of hydrolysis. Therefore, the good fit of the kinetics data in Figure 3 to a reaction-limited model and the compositionally dependent wettability in Table 1 both are consistent with a reaction-limited hydrolysis process rather than a diffusion-limited one.

In our recent work, we demonstrated that the ester content within the copolymer film could be controlled between $\sim 1\%$ and 5% by varying the monomer concentration ratio. Here, we demonstrate that the ester conversion to acid can be controlled through the hydrolysis time. Combining these two factors, the final acid content within the copolymer film can be controlled over the range of 1% to 5% . All the PM-CO₂H films reported in this manuscript were prepared by controlling the time of hydrolysis for 75 nm PM-CO₂Et films with 4.2% ester content.

pH-Dependence of Film Composition. To obtain an improved understanding of the pH-responsive behaviors of the studied films, we have investigated how the film composition changes after contacting solutions of different pH. We performed RAIRS analysis on 75 nm copolymer films with 1% to 4% acid content at each pH increment between 4 and 11; Figure 4 shows the CO₂⁻ to CH₂ (both asymmetric and symmetric) stretching peak ratio within the films as a function of pH. Since all films have approximately the same CH₂ stretching peak area, the ratios here reflect the relative concentration of carboxylate within the film. For all films at pH 4 and 5, very weak, if any, CO₂⁻ stretching was observed by IR, indicating that the films are predominately in the acid state. At pH 6, carboxylate began to form in films with 2% , 3% , and 4% acid content. From pH 7 to 11, the carboxylate concentration increased almost linearly at each pH step for each film. No large jumps in the carboxylate concentration were observed, indicating that the films are gradually ionized over a broad range of pH.

pH-Responsive Barrier Properties. We have used EIS to measure the effect of pH on the barrier properties of PM-CO₂H films using pH buffer solutions without redox probes. Figure 5 shows the equivalent circuits used to model impedance spectra

for polymer films on gold. 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 ; and Warburg impedance, Z_w . Figure 5a shows a model that is commonly used for polymer-coated metals,³⁰ which contains two time constants, one due to the polymer film and one due to the polymer–metal interface. Figure 5b and 5c show models with a single time constant that represents two simplifications of the overall model in Figure 5a. Figure 5b is used when the impedance due to the polymer film R_f is much smaller than the combined impedance of R_i and C_i in parallel, so only the time constant due to the polymer–metal interface is observed in the impedance spectrum. The equivalent circuit simplifies to R_i and C_i in parallel with one another but in series with R_s . Nonetheless, for the special case of no redox probes (as described here), R_i approaches infinity and thus, the interfacial conductance is purely capacitive in all these circuits. The model in Figure 5c is used when R_f is much greater than the combined impedance of R_i and C_i in parallel, so only the time constant due to the polymer is observed in the impedance spectrum. In Figure 5a and 5c, Z_w represents a Warburg impedance that is occasionally observed and is related to ion transport through the film.³¹

To demonstrate the effect of pH on film barrier properties, Figure 6 shows EIS spectra in the form of Bode plots for a 75 nm PM-CO₂H film on gold with 1% molar acid content. Solid curves in the plot represent best fits of the data with appropriate equivalent circuit models (Figure 5) to provide quantitative information on the effect of pH on film capacitance and resistance (Figure 7a and 7b). For comparison, the spectrum for bare gold exposed to pH 11 buffer solution is also shown and fit with the model in Figure 5b. Since no redox probes are in solution, the spectrum for bare gold is dominated by a double-layer capacitance of $\sim 10^{-5}\text{ F/cm}^2$, similar to the value provided by Loveday and Peterson.³² Changing solution pH had a negligible effect on the spectrum for bare gold. As a second comparison, the spectrum for an unhydrolyzed PM-CO₂Et copolymer film on gold at pH 4 is also shown. Changing solution pH from 4 to 11 had a negligible effect on the spectrum for PM-CO₂Et. The unhydrolyzed polymer film exhibits a straight line of slope -1 with high impedance ($> 10^7\ \Omega\text{ cm}^2$) at low frequency, indicating a strong barrier against ion penetration.^{32–35}

Upon hydrolysis, the impedance spectrum of the PM-CO₂H film changes in a pH-dependent manner. The hydrolyzed film exhibits spectra very similar to that of the unhydrolyzed film from pH 4 to 9, indicating the impedance due to the film dominates the entire frequency region. The slight decrease in the magnitude of the film impedance with increasing pH is consistent with the gradual deprotonation of the carboxylic acid side chains (Figure 4), which increases the hydrophilicity of the film and the effective film capacitance (Figure 7a). Water has a higher dielectric constant (~ 80) than that of the PM-rich

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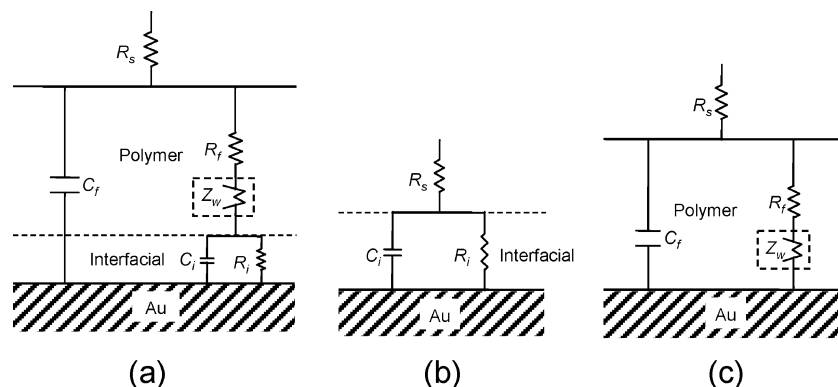


Figure 5. Equivalent circuits used to model impedance spectra for polymer films on gold: (a) model commonly used for polymer/metal interfaces; (b) model used when interfacial components dominate the impedance; (c) model used when the film dominates the impedance spectrum. In the absence of redox probes, R_i approaches infinity and thus, the interfacial conductance is purely capacitive.

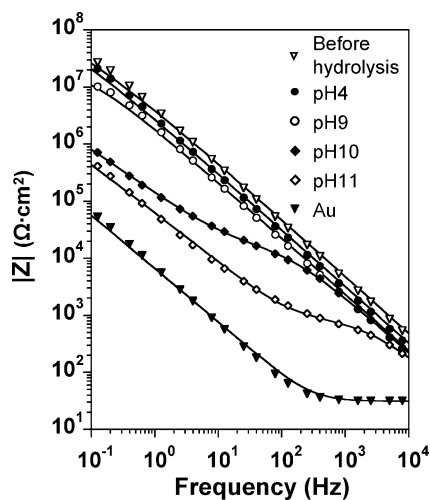


Figure 6. Electrochemical impedance spectra in the form of a Bode plot as a function of pH for a 75 nm copolymer film with 1% acid content on gold. Spectra for uncoated gold and an unhydrolyzed PM-CO₂Et film are shown for comparison. Solid curves represent best fits of the data with appropriate equivalent circuit models.

film (~ 2 to 3),³⁶ so the capacitance of the increasingly wet coating is higher than that of the unhydrolyzed film.

As pH is increased from 9 to 10, the impedance spectrum is greatly affected. The increasing charge of the film with pH results in markedly reduced film resistance such that two time constants appear in the impedance spectrum, and the spectrum is fit by the more complex model shown in Figure 5a. The time constant at lower frequencies is from the interface, and the one at higher frequencies is from the polymer film and corresponds to the combined capacitance and resistance of the polymer film (see Figure 5a).^{33,37,38} This latter time constant provides a measure of the time required for ionic permeation through the film, in this case ~ 0.003 s. As pH is increased from 10 to 11, the film resistance decreases further and the time required for ions to reach the interfacial region becomes even shorter. This spectrum is dominated by the interfacial capacitance. The spectra for pH 10 and 11 are offset at low frequency to represent an interfacial capacitance that increases with pH as the gold/

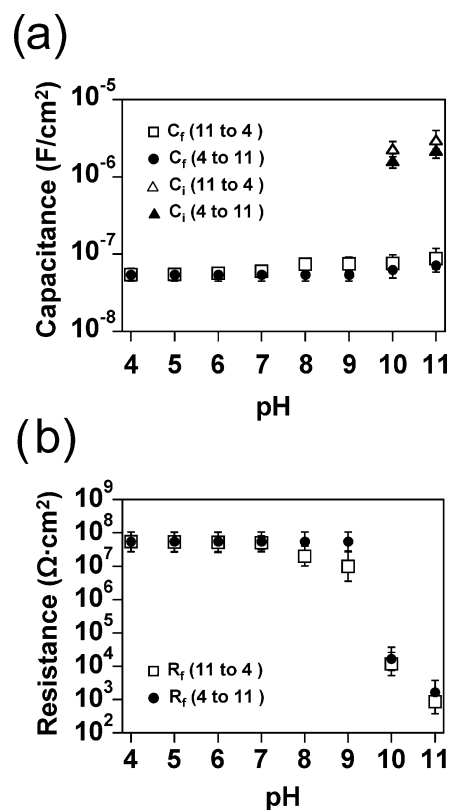


Figure 7. pH-Dependent (a) capacitance and (b) resistance for a 75 nm film with 1% acid content. Open squares represent C_f or R_f , and open triangles represent C_i when pH was incrementally decreased from 11 to 4. Solid circles represent C_f and R_f , and solid triangles represent C_i when pH was incrementally increased from 4 to 11.

polymer interface presumably becomes more concentrated with water and ions.

From pH 9 to pH 11, we did not observe a large increase in the carboxylate composition of the film (refer to Figure 4), but the small amount of carboxylate increase has a profound influence on film resistance, which decreases from $\sim 10^8 \Omega \cdot \text{cm}^2$ at pH 9 to $\sim 10^4 \Omega \cdot \text{cm}^2$ at pH 10 and $\sim 10^3 \Omega \cdot \text{cm}^2$ at pH 11 (Figure 7b). At pH 11, the film resistance is still evident, suggesting a small but measurable barrier to ion transfer. This ~ 5 orders of magnitude drop in resistance over a narrow pH range is much larger than an order of magnitude decrease reported for poly(acrylic acid) thin films³⁹ and could be powerful in applications such as pH-responsive membranes. In contrast,

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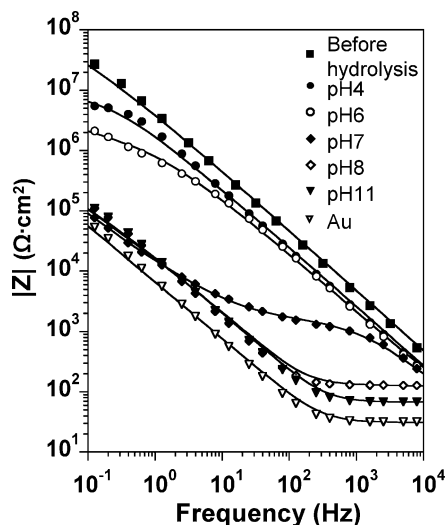


Figure 8. Electrochemical impedance spectra in Bode plot form as a function of pH for a 75 nm copolymer film with 3% acid content on gold. Spectra for uncoated gold and an unhydrolyzed PM-CO₂Et film are shown for comparison. Solid curves represent best fits of the data with appropriate equivalent circuit models.

film capacitance is much less sensitive to pH, remaining $<10^{-7}$ F/cm² for the entire pH range (Figure 7a). This lack of sensitivity in capacitance is due to the predominately hydrophobic nature of the 1% acid film and the high-frequency measurement of film capacitance, which does not allow sufficient time for ions to penetrate the film.

Figure 7a and b show resistance and capacitance values obtained upon first decreasing pH incrementally from 11 to 4 and then upon increasing pH incrementally from 4 back to 11. In general, the closeness of the values, as evidenced by the overlap of error bars at each pH value, combined with the large change in film resistance near the critical pH range suggests a (statistically) reversible pH-induced response of the polymer film. We have also cycled the films ~ 20 times between buffer solutions at pH 4 and pH 11 and measured impedance modulus at a constant frequency (100 Hz) (not shown). For each cycle, the measured impedance values increase upon exposure to pH 4 buffer and decrease upon exposure to pH 11 buffer. For all the cycles, the steady-state impedance values at pH 4 are within $\sim 3\%$ of each other and those at pH 11 are within $\sim 7\%$ of each other, demonstrating good reversibility.

For comparison with the film containing 1% acid, we also show impedance spectra at different pH values for a 75 nm film with 3% acid content in Figure 8 with fitted capacitance and resistance values shown in Figure 9. From pH 4 to 6, only one time constant appears in the spectra, and these can be fitted by the model in Figure 5c. Similar to the more hydrophobic 1% acid film at low pH values, the film impedance dominates the entire frequency range. However, these curves are not straight lines but indicate a film resistance at the lowest frequencies. The 3% acid film is therefore less blocking against ion transfer as compared to the 1% acid film. At pH 7, two time constants appear in the spectrum for the 3% acid film, similar to the 1% acid film at pH 10. Again, the high frequency time constant is attributed to the polymer film, and the low frequency time constant is due to the polymer/metal interface. With the

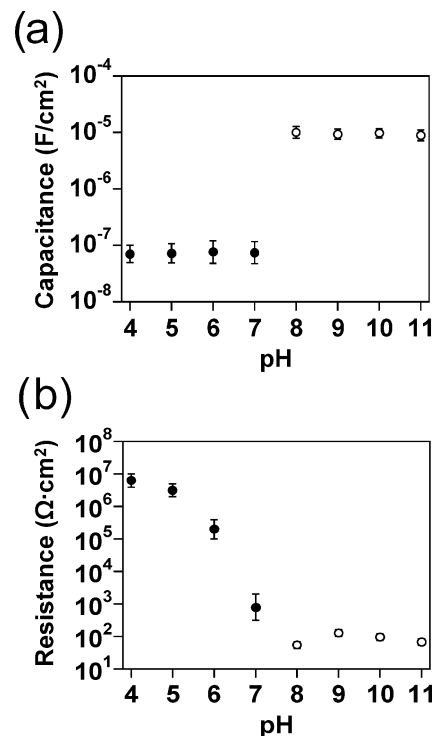


Figure 9. pH-Dependent (a) capacitance and (b) resistance for a 75 nm film with 3% acid content. Solid circles represent C_f or R_f ; empty circles represents the C_i or R_s .

increasing deprotonation of the carboxylic acid groups, aqueous ions can more easily penetrate the film to reach the gold surface, but the film still provides a quantifiable resistance against ion transfer. As shown in Figure 9b, the film resistance drops dramatically from $\sim 10^7$ $\Omega\cdot\text{cm}^2$ at pH 4 to 5 to $\sim 10^5$ $\Omega\cdot\text{cm}^2$ at pH 6 to $\sim 10^3$ $\Omega\cdot\text{cm}^2$ at pH 7 due to the enhanced hydrophilicity of the increasingly charged film. The film capacitance is essentially constant over this same range.

From pH 8 to pH 11, only one time constant due to the polymer/metal interface appears, and the spectra are fit with the model in Figure 5b. At these pH values, the film is not providing any measurable resistance against ion transport, so only R_s values are shown in Figure 9b and C_i values are shown in Figure 9a. Spectra at these pH values approach convergence at low to moderate frequencies due to similar C_i but are distinct at high frequency, where R_s varies due to slight differences in ion concentration and different compositions in the buffer solutions (Figure 9b).³¹

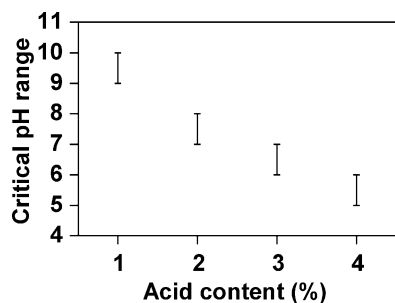
Compared with the film containing 1% acid at the same thickness of 75 nm, the 3% film exhibits lower resistances and higher capacitances at the same pH values from 4 to 7. In addition, comparison of Figures 7b and 9b reveals that the 3% film exhibits a ~ 5 orders of magnitude decrease in resistance over a pH range of 5–8, whereas the transition range for the 1% film is from pH 9–11. These differences imply that the response of the film is extremely sensitive to the acid content or hydrophilicity within the film.

To further explore the effect of acid content within the films, we have also investigated the pH-responsive barrier properties for 75 nm films with 2% and 4% acid contents. The R_f , C_f , and C_i values for the films with 1% through 4% carboxylic acid content are listed in Table 2. All these films have the same composition before hydrolysis, and the only difference among

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Table 2. Effect of Acid Content and pH on the Barrier Properties of PM-CO₂H Copolymer Films When pH Was Incrementally Decreased from 11 to 4

| pH | 1% | | | 2% | | | 3% | | | 4% | | |
|----|---|--------------------------------|--------------------------------|---|--------------------------------|--------------------------------|---|--------------------------------|--------------------------------|---|--------------------------------|--------------------------------|
| | log R_f ($\Omega \cdot \text{cm}^2$) | C_f (nF/cm ²) | C_i (nF/cm ²) | log R_f ($\Omega \cdot \text{cm}^2$) | C_f (nF/cm ²) | C_i (nF/cm ²) | log R_f ($\Omega \cdot \text{cm}^2$) | C_f (nF/cm ²) | C_i (nF/cm ²) | log R_f ($\Omega \cdot \text{cm}^2$) | C_f (nF/cm ²) | C_i (nF/cm ²) |
| 4 | 7.7 ± 0.3 | 55 ± 5 | | 7.4 ± 0.2 | 69 ± 6 | | 6.8 ± 0.2 | 71 ± 10 | | 6.6 ± 0.2 | 130 ± 9 | |
| 5 | 7.7 ± 0.3 | 55 ± 4 | | 7.3 ± 0.4 | 69 ± 6 | | 6.5 ± 0.2 | 72 ± 12 | | 6.4 ± 0.2 | 110 ± 11 | |
| 6 | 7.7 ± 0.3 | 58 ± 4 | | 7.1 ± 0.3 | 71 ± 8 | | 5.3 ± 0.3 | 76 ± 15 | | 4.0 ± 0.3 | 155 ± 19 | |
| 7 | 7.7 ± 0.2 | 60 ± 4 | | 6.8 ± 0.3 | 74 ± 8 | | 2.9 ± 0.5 | 74 ± 15 | | | | |
| 8 | 7.3 ± 0.3 | 74 ± 5 | | 4.5 ± 0.6 | 79 ± 8 | 7200 ± 700 | | | 10200 ± 900 | | | 11000 ± 1000 |
| 9 | 7.0 ± 0.5 | 78 ± 7 | | 3.3 ± 0.5 | 83 ± 10 | 6600 ± 800 | | | 10000 ± 1000 | | | 12000 ± 1100 |
| 10 | 4.1 ± 0.3 | 78 ± 9 | 2300 ± 300 | | | 6500 ± 600 | | | 9800 ± 700 | | | 11000 ± 1300 |
| 11 | 2.8 ± 0.4 | 87 ± 11 | 3000 ± 400 | | | 6200 ± 600 | | | 9300 ± 900 | | | 12000 ± 1000 |
| | | | | | | | | | 8900 ± 800 | | | 13000 ± 1300 |

**Figure 10.** Effect of acid content of PM-CO₂H films on the critical pH, defined as the pH increment over which the largest change in R_f occurs.

them is the hydrolysis time applied. From Table 2, film resistances decrease and film capacitances increase as acid content is increased. In addition, the pH where film properties become immeasurable shifts to lower pH as acid content is increased. From these results, we can extract the critical pH range, the pH increment over which the largest change in R_f occurs. This critical pH region shifts downward as acid content is increased (Figure 10), demonstrating a tunability over the critical pH by careful control over film composition. Interestingly, the pH ranges that result in these dramatic drops in R_f do not yield large increases in carboxylate content, as shown in the compositional results of Figure 4. Upon highlighting these critical pH ranges in Figure 4, we observe that all the dramatic changes in film barrier properties occur between the CO₂⁻/CH₂ peak ratios of 0.03 to 0.12. Films with lower acid content require higher carboxylate contents for their film resistances to break down. This effect is attributed to film hydrophobicity; since the total acid content is reduced (4% down to 1%), a higher fractional deprotonation of the more hydrophobic films is required to produce the same level of ion diffusion pathways and the similar breakdown in film resistance. That the large

change in film resistance occurs over a pH range where carboxylate concentration changes gradually suggests that a critical film hydrophilicity is required to generate these coherent ion pathways.

An important finding of this work is that the critical pH range can be tailored by varying the acid content within the film. This result suggests that PM-CO₂H films can be engineered to open/close at any pH in the range of 5 to 10 to respond in a versatile manner with specific requirements in separations or sensing. The ~5 order of magnitude drop in film resistance should provide high signal-to-noise in sensing and large pH-induced modulation of transport rates in separations.

Conclusions

We have prepared pH-responsive carboxyl-modified polyethylene films by a surface-catalyzed polymerization and subsequent hydrolysis. The films are uncharged and hydrophobic at low pH but become charged at moderate to high pH to facilitate ion transfer. Film resistances decrease by up to ~5 orders of magnitude over the critical pH range, demonstrating the effect of pH and charge on film hydrophobicity. This critical range can be tuned from pH 5 to 10 by varying the acid content within the film. The surface-catalyzed preparation of these films enables selective growth on gold surfaces of any shape, provides a precise control over film thickness, and offers the ability to tune the concentration of the pH-sensitive groups within the film.

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