Supporting Information

pH-Responsive Membrane Skins by Surface-Catalyzed Polymerization

Dongshun Bai, Steven M. Elliott, and G. Kane Jennings*

Department of Chemical Engineering, Vanderbilt University, Nashville, TN 37235

Preparation of membrane skin

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 chloride, potassium hydrogen phthalate, sodium phosphate monobasic, and acetone were used as received from Fisher (Fair Lawn, NJ). Anodisc™ porous alumina membranes with surface pores of 20 nm diameter were also obtained from Fisher and used as supports for gold deposition and polymer growth. 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 MΩ·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 procedure except that we used NaH$_2$PO$_4$ instead of KH$_2$PO$_4$ and the pH 9 solution was prepared by mixing appropriate volumes 0.1 M Na$_2$CO$_3$ with 0.1 M NaHCO$_3$. In a typical preparation procedure, specified volumes$^1$ 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 NaH$_2$PO$_4$ (pH 6 – 8), or 0.05 M NaHCO$_3$ (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. 0.1 M KCl was added to each pH buffer solution to reduce the solution resistance.

**Preparation of gold coated silicon wafer and membrane:** Gold coated silicon wafers (used for RAIRS and ellipsometry) and alumina membranes were prepared by evaporating chromium (15 Å) and gold (200 Å) in sequence onto silicon (100) wafers and alumina membranes at rates of 1-2 Å s$^{-1}$ in a diffusion-pumped chamber with a base pressure of 4 x 10$^{-6}$ torr.

**Preparation of Diazomethane:** Diazomethane (DM) was carefully prepared according to a literature procedure$^2$ 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!$^2$ The concentration of DM was determined by titration with benzoic acid.$^3$ The DM solution was stored in ether at -17 °C until use.

**Preparation of membrane skin:** Polymer films were formed by exposure of gold-coated membranes to ether solutions containing 2 mM DM and 160 mM EDA at 0 °C for 24 h. Upon
removal, the samples were rinsed sequentially with ether, ethanol, and DI water, dried with N₂, and stored in the laboratory ambient for use.

**Hydrolysis:** Hydrolysis of the copolymer films was carried out in a solution of 0.1 M KOH in 2-propanol at 0 °C for 3 h. The hydrolyzed samples were rinsed with ethanol and DI water, and stored in the laboratory ambient to await characterization.

**Characterization Methods**

**Electrochemical impedance spectroscopy (EIS)** was used to investigate the barrier properties of polymer-modified membranes. EIS was performed with a Gamry Instruments CMS300 impedance system interfaced to a personal computer. The permeation cell used is very similar to that shown by Hou et al⁴ and is schematically depicted in the inset of Figure 2a in the article. The membrane was first mounted between two half U-tubes by using two O-rings to create a water-tight seal. The exposed diameter of the membrane is 20 mm. An Ag/AgCl/saturated KCl reference electrode and a gold substrate counter electrode were placed in one half U-tube and a gold substrate working electrode was placed in the other half U-tube. 50 ml of a pH buffer solution, prepared as described above was poured into each of the half tubes. The measurements were made at the open circuit potential with a 5 mV ac perturbation. All data were collected in the range from 10⁴ to 10⁻¹ Hz using 10 points per decade and were fit with an equivalent circuit model to determine resistance and capacitance values. The equivalent circuit model contained the following elements in series: a solution resistance, a parallel combination of capacitance along with resistance and Warburg impedance to each represent the polymer skin of the
membrane, and an interfacial capacitance at the gold working electrode. The Warburg impedance is related to diffusion-limited ion transport through the membrane.\textsuperscript{5} 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. Reported values and ranges for resistance and capacitance represent the average and standard deviation of values obtained from at least three independent sample preparations.

**Field emission scanning electron microscopy (FESEM)** was used to obtain the surface images of the membrane skins. A Hitachi S4200 high resolution scanning electron microscope equipped with a cold field emission electron gun was performed at an accelerating voltage of 5 kV to observe all the images.

**Reflectance absorption infrared spectroscopy (RAIRS)** was used to determine the composition of films prepared on 2-D Au substrates. RAIRS was performed using a Varian 3100 FTIR 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.
Figure S1 shows reflectance-absorption infrared (RAIR) spectra for the film on a 2D gold surface before hydrolysis and after hydrolysis upon exposure to pH 11 buffer solutions. The 2D gold surface was coated with the same amount of Cr and Au and exposed to the same conditions of 2 mM DM and 160 mM EDA for 24 h in ether solution at 0 ºC, just as the gold-coated alumina membranes were. The ester carbonyl group, represented by a peak at 1735 cm$^{-1}$ in the spectrum for the pre-hydrolysis film, is diminished after hydrolysis in a solution of 0.1 M KOH in 2-propanol at 75 ºC for 3 h. A new peak appears at 1560 cm$^{-1}$ corresponding to the carbonyl stretching vibration in CO$_2$.$^6$ 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 CH$_2$ stretching in the spectra (not shown). The conversion ($\chi$) of the copolymer film on a 2-D substrate by hydrolysis was estimated based on the integrated C=O absorbance ($A_{CO,i}$) at 1735 cm$^{-1}$

$$\chi = 1 - \frac{A_{CO,i}}{A_{CO,j=0}}$$

(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

Figure S1. Reflectance-absorption IR spectra of copolymer films on 2D surface before and after hydrolysis. The 2D flat silicon wafer was coated with the same amount of Cr and Au and exposed to the same polymerization and hydrolysis conditions as the alumina membranes were.
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% \(-\text{CH}_2\)-) 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.

After polymerization, the ester content within the copolymer film is 1.6%, and upon hydrolysis, the conversion (\(\chi\)) of the ester to carboxylic acid is \(~25\%\). Thus, the final acid content within the film is \(~0.4\%\).

**Ellipsometry** was used to determine the polymer film thickness on a 2-D substrate. Ellipsometry measurements were taken 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 and the ester content within the film is < 5%, we set the refractive index to 1.5.\(^7\) For some samples, a refractive index other than 1.5 provided an improved fit, but the refractive index is still in the range of 1.5±0.06.

References