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pH-Responsive Membrane Skins by Surface-Catalyzed Polymerization

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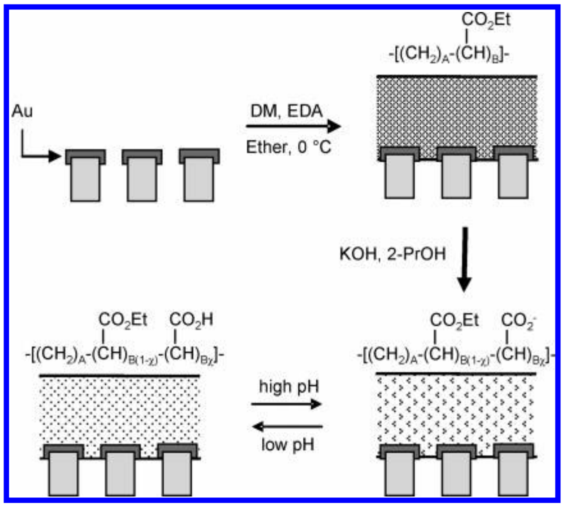
Responsive membranes alter their properties when specific stimuli are present in their environment. These stimuli could include temperature,[1−4] pH,[5−8] ions,[9,10] ultrasound,[11] and electric potential.[12] Responsive membranes have important applications in many areas such as controlled drug delivery,[11,13] ion selection,[5−7] molecular separation,[14−16] and regulation of cell adhesion.[10] Here, we report the modification of alumina membranes with ultrathin polymer skins that exhibit unusually large pH-responsive properties.

To date, many methods have been used in the preparation of dense high-performance skins on mechanically strong membranes, including self-assembled monolayers[5−7,11] and polymer films prepared by surface-initiated,[16,17] photoinitiated[8,18] and plasma routes,[19] by adsorption of polyelectrolyte multilayers,[20,21] as well as by dip coating[22] and solution casting.[23] Recently, we have reported a new surface-catalyzed polymerization process to grow polymethylene (PM)-rich copolymer films with randomly distributed ester side chains (poly(methylene-*co*-ethyl acetate); PM-CO2Et) from two-dimensional (2D) gold surfaces.[24] This process enables growth of copolymer films with controlled film thickness in the range of a few to several hundred nanometers by controlling polymerization time and/or monomer concentrations.[24] The most important aspect of this PM-CO2Et film is that the ester side chains can be hydrolyzed to carboxylic acids (denoted as PM-CO2H) to exhibit pH dependent properties.[25] At a 1−4% molar acid content, the copolymer film exhibits a change in its resistance to ion transport by 5 orders of magnitude over 2−3 pH units. In this paper, we demonstrate that PM-CO2Et films can be grown atop a Au-coated nanoporous alumina support (pore diameter = 20 nm) and hydrolyzed to form a pH sensitive ultrathin membrane skin. Herein, we use these PM-CO2H skins to examine the effect of solution pH on ion transfer.

Scheme 1. Preparation of pH-Responsive Copolymer Films on Gold-Coated Alumina Membranes



Scheme 1 shows the strategy we have developed to prepare pH-responsive membrane skins. First, we deposit a thin layer of chromium (1.5 nm) followed by gold (20 nm) onto the feed side of alumina membranes with 20 nm pore sizes. A top-view scanning electron microscopy (SEM) image (Figure 1b) shows that the pores are still open after the gold deposition, as further verified by electrochemical impedance spectroscopy (EIS). Next, copolymer films are then grown selectively from the gold surface by immersion of the entire membrane in an ether solution at 0 °C containing 2 mM diazomethane (DM) and 160 mM ethyl diazoacetate (EDA) for 24 h to yield a film with ester side chains (Scheme 1). Figure 1c shows the PM-CO2Et coated membrane, and Figure 1d demonstrates a cross-sectional SEM image of a typical membrane construction. The bright clusters on the membrane surface in Figure 1d are gold, which exists at the outer periphery of the pores. From Figure 1d, the average thickness of the polymer skin from 10 different sites on the surface is ∼100 nm. The PM-CO2Et film only grows from the gold surface as evidenced by the open interiors of the pores. We have placed the bare alumina support into the same solution containing both DM and EDA and found that no polymerization occurred. Alumina is not an appropriate

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(1) Fu, Q.; Rao, G. V. R.; Ista, L. K.; Wu, Y.; Andrzejewski, B. P.; Sklar, L. A.; Ward, T. L.; Lopez, G. P. *Adv. Mater.* **2003**, *15*, 1262.
(2) Reber, N.; Kuchel, A.; Spohr, R.; Wolf, A.; Yoshida, M. *J. Membr. Sci.* **2001**, *193*, 49.
(3) Chu, L. Y.; Zhu, J. H.; Chen, W. M.; Niitsuma, T.; Yamaguchi, T.; Nakao, S. *Chin. J. Chem. Eng.* **2003**, *11*, 269.
(4) Lin, S. Y.; Lin, H. L.; Li, M. J. *Adsorption* **2002**, *8*, 197.
(5) Steinle, E. D.; Mitchell, D. T.; Wirtz, M.; Lee, S. B.; Young, V. Y.; Martin, C. R. *Anal. Chem.* **2002**, *74*, 2416.
(6) Lee, S. B.; Martin, C. R. *Anal. Chem.* **2001**, *73*, 768.
(7) Hou, Z. Z.; Abbott, N. L.; Stroeve, P. *Langmuir* **2000**, *16*, 2401.
(8) Geismann, C.; Ulbricht, M. *Macromol. Chem. Phys.* **2005**, *206*, 268.
(9) Ngila, J. C.; Ddamba, W. A. A. *Macromol. Symp.* **2001**, *165*, 73.
(10) Okajima, S.; Yamaguchi, T.; Sakai, Y.; Nakao, S. *Biotechnol. Bioeng.* **2005**, *91*, 237.
(11) Kwok, C. S.; Mourad, P. D.; Crum, L. A.; Ratner, B. D. *J. Biomed. Mater. Res.* **2001**, *57*, 151.
(12) Pile, D. L.; Zhang, Y.; Hillier, A. C. *Langmuir* **2006**, *22*, 5925.
(13) Zhang, K.; Wu, X. Y. *J. Controlled Release* **2002**, *80*, 169.
(14) Masawaki, T.; Taya, M.; Tone, S. *J. Chem. Eng. Jpn.* **1996**, *29*, 180.
(15) Masawaki, T.; Sato, H.; Taya, M.; Tone, S. *Kagaku Kogaku Ronbunshu* **1993**, *19*, 620.
(16) Balachandra, A. M.; Baker, G. L.; Bruening, M. L. *J. Membr. Sci.* **2003**, *227*, 1.
(17) Sun, L.; Baker, G. L.; Bruening, M. L. *Macromolecules* **2005**, *38*, 2307.
(18) Liu, C.; Martin, C. R. *Nature* **1991**, *352*, 50.
(19) Hayakawa, Y.; Terasawa, N.; Hayashi, E.; Abe, T. *J. Appl. Polym. Sci.* **1996**, *62*, 951.
(20) Hammond, P. T. *Adv. Mater.* **2004**, *16*, 1271.
(21) Malaisamy, R.; Bruening, M. L. *Langmuir* **2005**, *21*, 10587.
(22) Yanagishita, H.; Kitamoto, D.; Haraya, K.; Nakane, T.; Okada, T.; Matsuda, H.; Idemoto, Y.; Koura, N. *J. Membr. Sci.* **2001**, *188*, 165.
(23) Hoshi, M.; Kobayashi, M.; Saitoh, T.; Higuchi, A.; Nakagawa, T. *J. Appl. Polym. Sci.* **1998**, *69*, 1483.
(24) Bai, D.; Jennings, G. K. *J. Am. Chem. Soc.* **2005**, *127*, 3048.
(25) Bai, D. S.; Habersberger, B. M.; Jennings, G. K. *J. Am. Chem. Soc.* **2005**, *127*, 16486.

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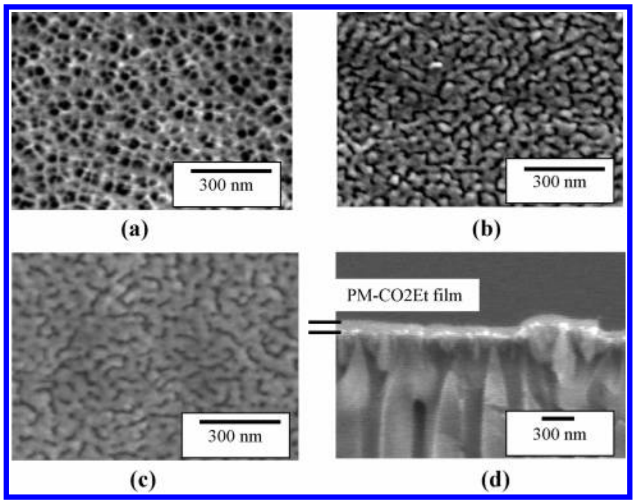

Figure 1. SEM images of the feed side of porous alumina (a) before Au deposition, (b) after deposition of 20 nm Au, and (c) after copolymer growth; (d) shows a cross-sectional image of the membrane from (c).

catalytic surface for promoting the polymerization of diazo molecules whereas gold[26] and atomically modified gold[27] surfaces are very effective catalysts.

In the final step of Scheme 1, the ester side chains within the film are hydrolyzed to carboxylate in a solution of 0.1 M KOH in 2-propanol at 75 °C for 3 h to prepare a pH-responsive membrane skin. To investigate the ester and carboxylate acid content within the copolymer film after hydrolysis, we performed reflectance−absorption infrared spectroscopy (RAIRS) on a 2D flat silicon surface 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 °C. The ester content within the copolymer film is 1.6%, and upon hydrolysis, the conversion (χ) of the ester to carboxylic acid is ∼25%. Thus, the final acid content within the film is ∼0.4%. Higher conversion can be obtained by increasing the KOH concentration and the hydrolysis time, but these conditions may also damage the alumina membrane. More information on the hydrolysis kinetics and IR spectra of the hydrolyzed copolymers on 2D surfaces can be found in our recent articles.[24,25]

To investigate the response of the polymer skins to pH, we obtained electrochemical impedance spectra (Figure 2a) for the PM-CO2H-coated alumina membrane supported between two halves of a U-tube filled with pH buffer solution (see inset of Figure 2a). Solid curves in the plot represent best fits of the data with an appropriate equivalent circuit model to provide quantitative information on the effect of pH on membrane properties. Figure 2b shows that the average membrane resistance decreases as pH is increased. The membrane resistance decreases from ∼10^4 Ω·cm^2 at pH 4 to ∼500 Ω·cm^2 at pH 6 and then gradually decreases to ∼50 Ω·cm^2 at pH 11, suggesting a small but measurable barrier to ion transfer. This resistance at pH 11 corresponds to an impedance that is only 28% higher than that for a gold-coated membrane without the polymer skin. The film response to pH is reversible as evidenced by obtaining similar membrane resistances (within 10%) upon first decreasing pH incrementally from 11 to 4 and then increasing pH incrementally from 4 back to 11.

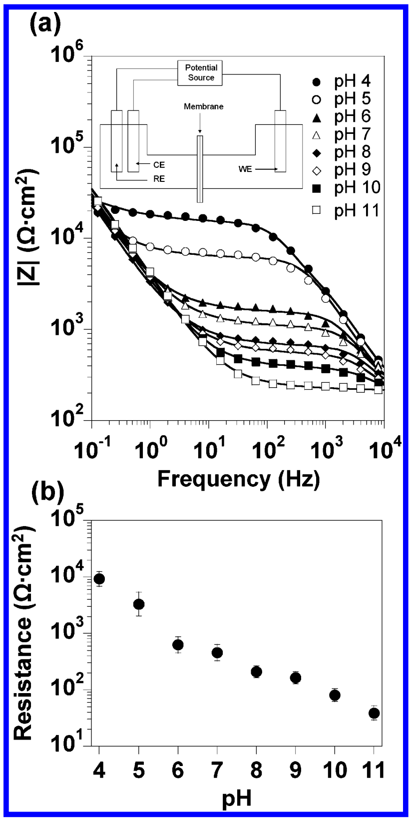

Figure 2. (a) Electrochemical impedance spectra in the form of Bode plots as a function of pH for membrane skins. The inset shows a schematic of the U-tube test cell with counter electrode (CE), reference electrode (RE), and working electrode (WE). (b) Membrane resistance as a function of pH.

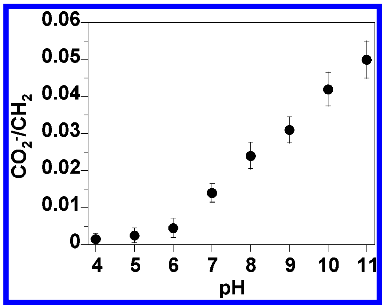

Figure 3. Peak area ratio of the carboxylate stretching band at 1560 cm^{-1} to the sum of the asymmetric (2919 cm^{-1}) and symmetric (2851 cm^{-1}) methylene stretching bands as a function of pH for a film with acid content of 0.4% grown from a 2D gold surface.

The response of the film can be related to its composition, as determined by RAIRS analysis of copolymer films on a 2D surface with 0.4% acid content at each pH increment between 4 and 11; Figure 3 shows the CO_2^- to CH_2 (both asymmetric and symmetric) stretching peak ratio within the films as a function of pH. Since the CH_2 stretching peak area does not change, the ratios here reflect the relative concentration of carboxylate within the film. From pH 4 to 6, a slight increase in CO_2^- content corresponds with a dramatic 20-fold reduction in membrane resistance (Figure 2b). The initial deprotonation of groups in the film has a profound effect on water and ion transport, likely leading to some interconnected pathways for ion conduction. As pH is increased from 6 to 11, the CO_2^- content increases in a nearly

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(26) Seshadri, K.; Atre, S. V.; Tao, Y. T.; Lee, M. T.; Allara, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4698.

(27) Guo, W.; Jennings, G. K. *Langmuir* **2002**, *18*, 3123.

linear manner and membrane resistance drops by another factor of 10, exhibiting a more gradual decay with pH. These results suggest that a percolation threshold[28] is achieved at lower pH and that further increases in pH enhance the density of ion conducting pathways. Over the entire range of pH (4 to 11), the resistance drops by a factor of 200 but is recovered upon decreasing pH back to 4. The pH response of the membrane skins (factor of 200) is less than that for similar films grown from 2D gold surfaces (factor of 10^5)[25] because of the lower resistance (10^4 vs 10^7 Ω cm^2) of the skins at low pH. We attribute this effect to grain boundaries within the skin (see Figure 1c) imparted by surface-initiated growth from the pore-laden surface.

Our approach yields a thin polymer skin covering the pores at one end of the membrane but leaves the pores empty to enable further functionalization. In related work, Steinle et al.[5] have modified the alumina pores with a carboxyl-terminated silane monolayer that yields a decrease of over 4 orders of magnitude in membrane resistance when the membrane is switched from “off” to “on” with increasing pH. Thus, our approach could be used in conjunction with such strategies to prepare membranes with pH-responsive surface and bulk properties.

The surface-catalyzed approach described here enables selective growth on gold surfaces of any shape, provides a precise control over film thickness,[24] and offers the ability to tune the concentration of the pH-sensitive groups within the film.[25] In this particular application, we have prepared pH-responsive PM-CO2H films atop a porous alumina support by a surface-catalyzed polymerization and subsequent hydrolysis. Film resistances decrease by a factor of 200 between pH 4 and pH 11, demonstrating the effect of pH and charge on film hydrophobicity. The surface-catalyzed growth of the pH-responsive copolymer film on a porous membrane support provides a new way to prepare composite membranes.

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Supporting Information Available: Preparation of membrane skins and characterization methods, including EIS, SEM, RAIRS, and ellipsometry (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Mohanty, K. K.; Ottino, J. M.; Davis, H. T. *Chem. Eng. Sci.* **1982**, *37*, 905.