J. Am. Chem. Soc. **2001,** *123,* 11805−11806 11805

Ultrathin, Ion-Selective Polyimide Membranes Prepared from Layered Polyelectrolytes

Daniel M. Sullivan and Merlin L. Bruening*

Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

Received July 2, 2001

We report the formation of selective, ultrathin (4−9 nm) polyimide skins on porous alumina by alternating polyelectrolyte deposition (APD) and subsequent imidization (Figure 1). This method is extremely convenient and affords control over the thickness and selectivity of the polyimide film.[1] These membranes show remarkably selective transport of singly over doubly charged ions (Cl^-/SO_4^{2-} selectivities reach values as high as 1000), and their minimal thickness permits high flux of the monovalent species.

Aromatic polyimides are attractive membrane materials because of their mechanical strength, thermal stability, selectivity, and wide tunability.[2−4] With common processing techniques, however, formation of ultrathin selective membranes with thicknesses less than 40 nm is difficult. APD, in contrast, offers an easy way to deposit ultrathin multilayered films. A few previous studies combined APD of poly(amic acids) and a polycation with postdeposition heating to form polyimide films.[5−7] Here we utilize this approach to form highly selective, ultrathin polyimide membranes on porous supports coated with multilayered polyelectrolyte gutter layers. Because the polyimide portion of such systems is ultrathin, these membranes simultaneously allow high flux and high selectivity. Although several groups studied layered polyelectrolyte membranes for various applications,[8−14] the polyimide films described here show unique ion-transport selectivities with deposition of only a few layers.

The first challenge in forming ultrathin polyelectrolyte membranes is to show that they completely cover a porous substrate without filling underlying pores. To avoid any question as to whether polyimide membranes would cover a porous substrate, we deposited poly(pyromellitic dianhydride-phenylenediamine)[15,16] (PMDA-PDA)/poly(allylamine hydrochloride) (PAH) bilayers on top of a gutter layer consisting of 5-bilayers of poly(styrenesulfonate) (PSS)/PAH (Figure 1a).[17] Previous scanning electron microscopy studies of 5-bilayer PSS/PAH coatings on porous alumina showed complete pore coverage, with little penetration of polymer into the underlying cavities.[8,18] Such PSS/PAH membranes show modest transport selectivity between monovalent and divalent anions ($Cl^-/SO_4^{2-} \cong 5$) and only slight ($\sim$25%) decreases in the flux of monovalent species relative to fluxes through bare alumina. Thus, when using PSS/PAH as a gutter layer, the polyimide portion of the membrane will still be the dominant factor in controlling transport. We recently used a similar approach to form a discriminating skin layer of poly(acrylic acid)/PAH on PSS/PAH.[9]

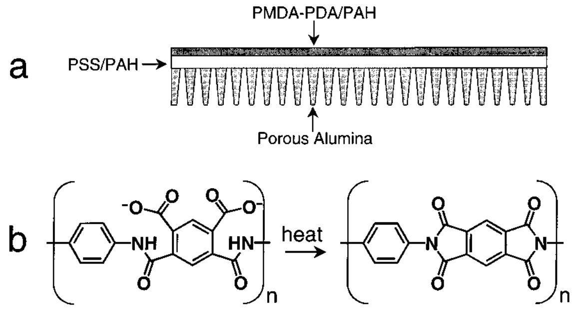

Figure 1. (a) Membrane consisting of a porous alumina support, a PSS/PAH base layer, and a PMDA-PDA/PAH selective capping layer (b) PMDA-PDA structure and heat-induced imidization.

Heating PMDA-PDA under N_2 yields a polyimide membrane (Figure 1b), and the extent of imidization can be controlled to alter ion-transport selectivity. To examine the extent of imidization, we prepared PAH/PSS (4.5 bilayers) + PMDA-PDA/PAH films on gold supports and measured their reflectance FTIR spectra.[19] Figure 2 shows spectra of films containing a 2.5-bilayer top-coat of PMDA-PDA/PAH before and after heating for 2 h under a N_2 atmosphere. Unheated films have a broad absorbance band from 1680 to 1520 cm^{-1} primarily due to the overlap of the amide and asymmetric $-COO^-$ stretches of the poly(amic acid). The symmetric $-COO^-$ stretch appears at 1407 cm^{-1}. Heating of these films results in the appearance of asymmetric and symmetric imide carbonyl peaks (1775 and 1730 cm^{-1}) and the reduction of amide and carboxylate peaks. Higher heating temperatures result in larger imide peaks, showing that one can control the extent of imidization. Ellipsometric studies of films on gold-coated Si wafers indicate a linear growth in thickness due to adsorption of PMDA-PDA/PAH, with a $\sim$26 Å thickness increase per bilayer.

To study ion transport through PMDA-PDA/PAH films, we utilized a diffusion dialysis apparatus where the membrane separates a source phase solution (0.1 F salt, unbuffered, pH 5.3−6.2) from a receiving phase that initially contains deionzed water.[8] Both phases were stirred, and flux was measured by monitoring increases in the conductivity of the receiving phase for 45 min. Selectivity coefficients were determined by dividing the flux values of different salts. The flux of KCl increased slowly during initial transport experiments, so membrane conditioning was

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* To whom correspondence should be addressed. E-mail: bruening@cem.msu.edu.

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[16] PMDA-PDA was prepared using a literature procedure (ref 15) and was precipitated into ethanol twice from HPLC grade *N*,*N*-dimethylacetamide, dried in vacuum, and stored in a desiccator until needed.

[17] To deposit PMDA-PDA, PSS/PAH coated alumina (Anopore 0.02 μm filter) was treated with a solution containing 0.005 M PMDA-PDA (with respect to the repeat unit), 0.015 M triethylamine, and 0.5 M NaCl (pH adjusted to 4.5 with HCl) for 3 min and rinsed with Milli-Q water. PAH (0.02 M, 0.5 M NaCl, pH adjusted to 4.5) was then deposited in a similar manner. This procedure was repeated until 1.5, 2.5, 3, or 3.5 PMDA-PDA/PAH bilayers were deposited. The samples were dried with N_2 only after all of the layers were added. The PSS/PAH deposition procedure was described in ref 8.

[18] The positive surface charge of porous alumina allows direct adsorption of a polyanion. 5-bilayer PSS/PAH films are about 20 nm thick.

[19] Gold-coated Si substrates were modified with a monolayer of mercaptopropionic acid to provide a negatively charged surface. In this case, PAH/PSS deposition begins with PAH.

10.1021/ja016536h CCC: $20.00

Table 1. Selectivity Coefficients for Porous Alumina Coated with a 5-Bilayer PSS/PAH Base and Capped with 1.5−3.5 bilayers of PMDA-PDA/PAH[20]

	KCl flux 10^{-8} mol·cm^{-2}·s^{-1}			α, Cl^-/SO_4^{2-}				α, K^+/Mg^{2+}			
heating temp	1.5 bilayers	2.5 bilayers	3.5 bilayers	1.5 bilayers	2.5 bilayers	3 bilayers	3.5 bilayers	1.5 bilayers	2.5 bilayers	3 bilayers	3.5 bilayers
unheated	3.5 ± 0.2	3.7 ± 0.3	3.5 ± 0.5	4.2 ± 0.2	4.7 ± 1	3.2 ± 0.2	6 ± 0.5	120 ± 12	120 ± 31	210 ± 3.7	110 ± 25
130 °C	4.3 ± 0.8	3.8 ± 0.9	3.4 ± 0.1	16 ± 1.4	24 ± 5.3	−	100 ± 46	91 ± 19	100 ± 4.5	−	130 ± 21
150 °C	4.1 ± 0.5	2.8 ± 0.3	2.2 ± 0.9	51 ± 8	680 ± 153	390 ± 23	790 ± 120	94 ± 24	110 ± 22	130 ± 5	310 ± 73
165 °C	2.8 ± 0.2	2.9 ± 0.6	1.5 ± 0.1	680 ± 33	820 ± 220	−	1000 ± 580	110 ± 20	170 ± 30	−	190 ± 55
180 °C	3.0 ± 0.7	1.6 ± 0.2	0.5 ± 0.03	590 ± 85	1100 ± 150	−	310 ± 140	41 ± 13	93 ± 12	−	60 ± 11

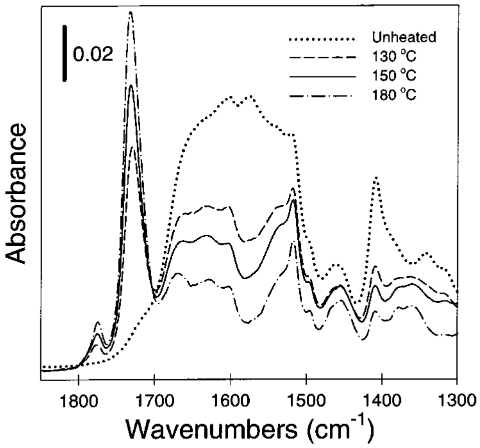

Figure 2. External reflection FTIR spectra of films containing a PAH/PSS base of 4.5 bilayers and a PMDA-PDA/PAH topcoat of 2.5 bilayers. Films were deposited on gold-coated substrates and heated for 2 h under N_2 at the indicated temperature.

required to obtain steady flux values. We repeated measurements of KCl, K_2SO_4, $K_3Fe(CN)_6$, $BaCl_2$, $CaCl_2$, and $MgCl_2$ fluxes twice in this order, with one final KCl measurement. The last two KCl flux measurements differed by less than 10%, and thus we utilized the second set of flux values to calculate selectivitiy.

Table 1 shows the Cl^-/SO_4^{2-} and K^+/Mg^{2+} selectivity coefficients, α, for membranes coated with 1.5, 2.5, 3, and 3.5 PMDA-PDA/PAH bilayers that were heated at various temperatures. Unheated membranes show a Cl^-/SO_4^{2-} selectivity of 3−6. Heating membranes, however, increases Cl^-/SO_4^{2-} selectivities to values as high as 1000. For comparison, Neosepta membranes coated with a single layer of polyanion showed a maximum Cl^-/SO_4^{2-} selectivity of 20.[21] In contrast, the K^+/Mg^{2+} selectivity is relatively high (120) for unheated films, but heating does not increase this selectivity to the same degree as seen for anions.

Donnan exclusion due to surface charge, which is a major factor in the selectivity of some polyelectrolyte membranes,[8,9,14] is not the main reason for the large selectivity values in the present case. This can be seen by changing the sign of the outer-layer charge through termination with PAH rather than PMDA-PDA (Table 1, 3-bilayers). This change in sign has only a small effect on selectivity with either cations or anions.

The selectivity among ions most likely reflects differences in hydration energies and ion sizes. Both hydration energy and hydrated ion radius decrease in the order $Mg^{2+} > Ca^{2+} > Ba^{2+} > SO_4^{2-} > Cl^- > K^+$.[22] Either loss of waters of hydration upon partitioning into the membrane or slower diffusion of large hydrated ions would result in K^+/Mg^{2+} and Cl^-/SO_4^{2-} selectivity. The K^+/Mg^{2+} selectivity should also be greater than that for Cl^-/SO_4^{2-}, as is seen for unheated films. Selective transport of K^+ over Ba^{2+} or Ca^{2+} also occurs through these membranes, but these selectivity values are only about 30% of those for K^+/Mg^{2+}, as would be expected from trends in hydrated radii and hydration energies.

After heating and imidization, the membrane should become denser and more hydrophobic. This would explain the increase in Cl^-/SO_4^{2-} selectivity upon heating. However, we would expect the K^+/Mg^{2+} selectivity to increase with heating to an even greater extent. We speculate that Mg^{2+} may be diffusing through the membrane with only a few waters of hydration, and thus increases in film density may not slow its diffusion as much as that of SO_4^{2-}, which has a larger unhydrated radius.

Membrane selectivity also varies with the number of PMDA-PDA/PAH bilayers. Adding more bilayers appears to decrease the heating temperature at which the onset of high Cl^-/SO_4^{2-} selectivity occurs. Due to interpenetration of polymers, the 1.5-bilayer PMDA-PDA/PAH top-coat likely contains some PSS and may be less selective than thicker top-coats. Remarkably, even a 2.5-bilayer PMDA-PDA/PAH top-coating that is only 70 Å thick can give Cl^-/SO_4^{2-} selectivities of over 1000 after heating at 180 °C.[23] Selectivities as high as 680 for Cl^-/SO_4^{2-} can be achieved with Cl^- flux that is still 50% of that through bare alumina.[9]

In summary, ultrathin polyimide membranes can be formed on porous alumina supports coated with a polyelectrolyte gutter layer, and these membranes exhibit extremely large separation coefficients between monovalent and divalent ions. Future studies should help clarify the mechanism of selectivity in these systems.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9816108) and the Department of Energy Office of Basic Energy Sciences.

JA016536H

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[20] Selectivities and fluxes are the averages of values from at least three membranes.

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[23] Thicknesses of PMDA-PDA films were estimated from the change in ellipsometric thickness upon deposition of PMDA-PDA/PAH on a PAH/PSS-coated Au substrate. Previous SEM studies showed that thicknesses of films on alumina and Au were similar (refs 8 and 9).