Ultrathin, Gas-Selective Polyimide Membranes Prepared from Multilayer Polyelectrolyte Films

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Alternating electrostatic deposition of poly(amic acid) salts and poly (allylamine hydrochloride) (PAH) followed by heat-induced imidization yields ultrathin, gas-selective polyimide membranes on porous alumina supports. These membranes are appealing because of the stability and selectivity of polyimides and the fact that alternating polyelectrolyte adsorption allows formation of ultrathin (as low as 35−40 nm), defect-free films that allow high flux. FTIR spectroscopy shows that heating of poly(amic acid)/PAH membranes at 250 °C for 2 h completely converts the poly(amic acid) to the corresponding polyimide, and scanning electron microscopy reveals uniform films with minimal deposition in substrate pores. Permeability coefficients and selectivities (O_2/N_2 up to 6.9 and CO_2/CH_4 up to 68) of three different imidized poly(amic acid)/PAH membranes are comparable to literature values for the corresponding bulk polyimides, provided that the ratio of poly(amic acid) to PAH in the film is high (9:1). Electrostatic deposition of poly(amic acids) thus provides a convenient way to prepare high-flux, gas-selective films on porous supports.

Introduction

Polyimides are attractive membrane materials because of their mechanical and thermal stability,[1,2] and compared with other polymers, certain polyimides exhibit a favorable combination of permeability and gas-transport selectivity.[3−9] Practical application of these materials, however, requires formation of a defect-free polyimide layer on a highly permeable support, and this layer should be as thin as possible to allow high flux through the membrane. Methods for creating ultrathin polyimide skins include phase-inversion processes and formation of composite membranes by deposition of polyimide films on highly permeable substrates. For example, Koros and co-workers prepared cast-sheet[10,11] and hollow-fiber polyimide membranes[12] by a phase-inversion process that yields a dense, selective layer at the surface of a porous material.

Composite membranes offer the advantage that only a thin, selective film of the separation material is used, and thus more expensive, and hopefully more selective, polymers can be employed.[13] In the case of polyimides, composite membranes can be prepared by deposition of a poly(amic acid) followed by imidization to form a selective film. Ding and co-workers coated porous polysulfone hollow fibers with a solution of a poly(amic acid) salt and showed that heating the fibers at 150 °C for 24 h yields fully imidized films that are as thin as 50 nm.[14]

Even with these successes in creating ultrathin membranes, deposition of defect-free polyimide skins that are less than 50 nm thick is still difficult.[15,16] New methods for forming ever-thinner skins will allow creation of membrane systems with higher fluxes, and the recently developed technique of alternating polyelectrolyte deposition (APD) may prove useful in this regard. This method simply involves alternating immersions of a charged substrate into solutions containing oppositely charged polyelectrolytes,[17] and thus film thickness is easily controlled by changing either the number of adsorbed polyelectrolyte layers or deposition variables such as pH, supporting salt concentration, and solvent.[18−20] Because the films self-assemble, surface

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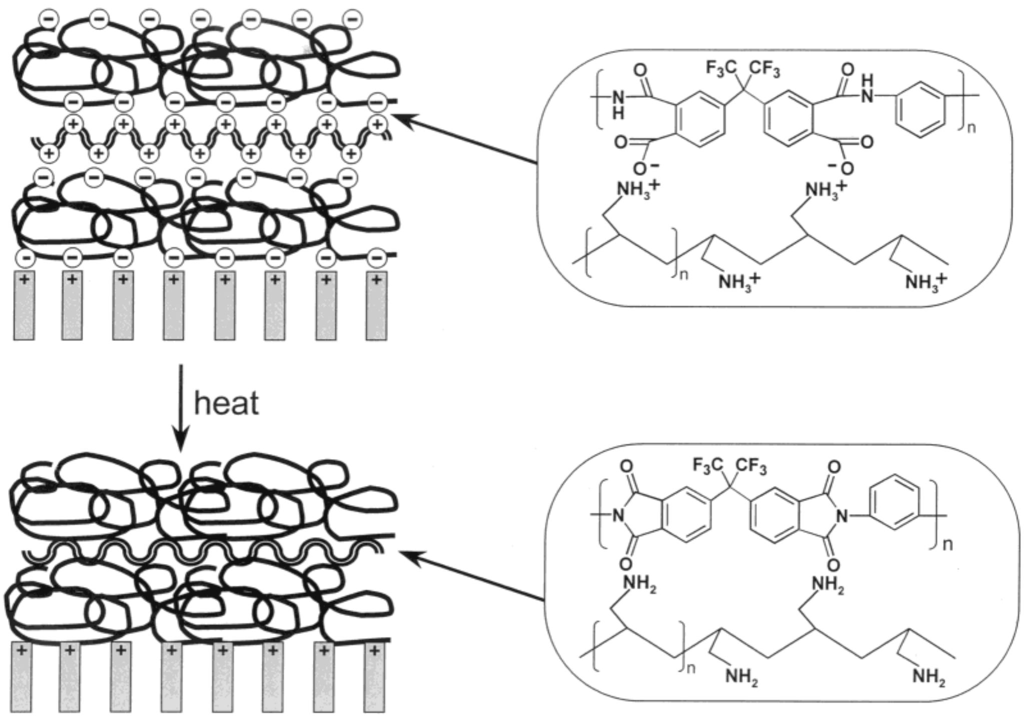

Figure 1. Heat-induced imidization of a poly(amic acid)/PAH film on a porous support. Neutralization of PAH occurs when it contributes a proton for the formation of water. Intertwining of neighboring layers is not shown for figure clarity.

roughness does not greatly affect adhesion, and defect-free films can be obtained on porous supports because each added layer covers defects in the previous layer.[17,21]

A few recent studies demonstrate membrane formation using APD on permeable supports. Successful separation of monovalent and divalent ions with such membranes occurs with various polyelectrolytes and deposition conditions,[22-24] and highly selective separations by pervaporation are also possible.[25-27] In contrast, gas-transport selectivities due to multilayer polyelectrolyte films are relatively modest. Polyelectrolyte films can increase the gas selectivity of nonporous supports,[28-30] but deposition of these films on porous supports yields little increase in selectivity.[30,31] We suspect that the lack of gas-transport selectivity in polyelectrolyte films is inherent in the structure and packing of the polyelectrolytes thus far employed.

In this work, we utilize poly(amic acids) as polyelectrolytes for APD so that these materials can be imidized to produce polyimides that are known to exhibit high gas-transport selectivities and permeabilities. Several previous studies combined APD of poly(amic acids) and a polycation with postdeposition heating to form polyimide films or ion-selective membranes,[22,32-35] but this paper represents the first utilization of this method to form membranes for gas separations. Ionized precursor poly(amic acids) serve as polyanions that form films with poly(allylamine hydrochloride) (PAH) on porous alumina[36] (Figure 1), and subsequent heating yields the polyimide membrane. We chose to study the three polyimides shown in Figure 2 because their gas-transport properties were previously investigated.[7-9] (In this

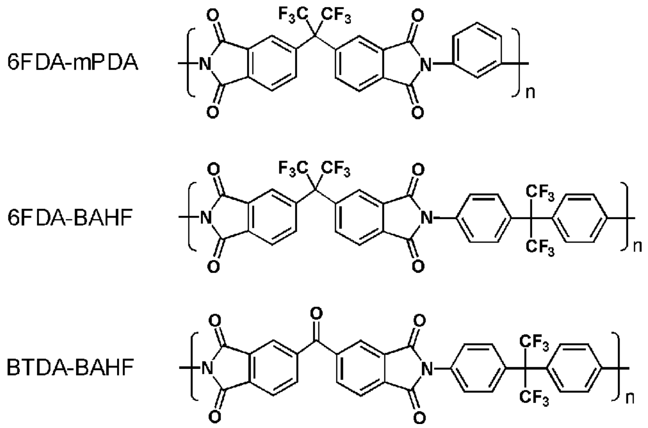

Figure 2. Structures of the polyimides used in this study.

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paper, we use the acronyms in Figure 2 to refer to both the imidized and poly(amic acid) forms of the polymers.) One of the main points that we demonstrate in this study is that the presence of a small amount of PAH in the membrane does not alter the selectivity of the polyimide films. Gas-transport studies clearly demonstrate that 35−50-nm-thick polyimide films prepared using APD have selectivities and permeability coefficients that are the same as those of the corresponding bulk polyimides. Thus APD indeed provides a new tool for development of ultrathin, gas-selective membranes.

Experimental Section

Materials. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-(hexafluoroisopropylidene) dianiline (BAHF), 1,3-phenylenediamine (mPDA), (3-aminopropyl)triethoxysilane, and poly(allylamine hydrochloride) were purchased from Aldrich. DMF (Spectrum) was dried with molecular sieves for at least 24 h, and the 3,3′,4,4′-benzophenonetetracarboxylic dianhydride was purified by vacuum sublimation prior to use. All other chemicals were used as received. Acetone (Vorpak), ethanol (Pharmco, 200 proof), and deionized water (Milli-Q, 18.2 MΩcm) were used for rinsing and preparation of polymer-containing solutions. Porous alumina supports were 25-mm Whatman Anodiscs with 0.02-μm diameter surface pores (Fisher Scientific), and silicon(100) wafers (Silicon Quest) were used as supports for ellipsometry (single-side polished) and Brewster-angle transmission FTIR spectroscopy (double-side polished).

Substrate Preparation. Prior to film deposition, silicon wafers were silanized with (3-aminopropyl)-triethoxysilane to prepare a controlled surface capable of supporting a positive charge. Silanization was accomplished using the method of Petri et al.[37] In the case of porous alumina supports, the polypropylene support ring on the alumina was removed to prevent it from melting into substrate pores during heat-induced imidization. This was accomplished by cutting off as much of the polymer as possible with scissors, and then burning off the remaining ring at 400 °C for 18 h. Subsequently, the alumina supports were rinsed with acetone, dried with N_2, and cleaned for 10 min in a UV/ozone cleaner (Boekel Industries, model 135500). Film formation occurred directly on the alumina.

Polymer Synthesis. The poly(amic acids) were prepared using a typical literature procedure.[38] First, the diamine was dissolved in an appropriate solvent (acetone for 6FDA-BAHF and DMF for both 6FDA-mPDA and BTDA-BAHF). A stoichiometric quantity of the dianhydride was then added to this solution gradually over a period of ~15 min, and the 15 wt % (total dissolved solids) solution was stirred for 24 h. The poly(amic acids) were precipitated twice in either 1:1 hexanes/ethyl acetate (6FDA-BAHF and BTDA-BAHF) or 3:1 chloroform/hexanes (6FDA-mPDA), filtered, and then dried under vacuum for 24 h.

Solution Preparation and Film Deposition. Because of the insolubility of the poly(amic acid) in water, solutions containing 0.005 M 6FDA-BAHF and 0.5 M NaCl were prepared by dissolving 0.039 g of 6FDA-BAHF in 7 mL of ethanol, and then adding 3 mL of 1.67 M aqueous NaCl. The molarities of the polyelectrolytes are given with respect to the repeating unit. The pH was adjusted to 5.0 by adding 0.2 M triethylamine in 7:3 (v:v) ethanol/water. Film deposition began with immersion of the substrate (silanized silicon or porous alumina) into the poly(amic acid) solution for 3 min. The alumina membrane was placed in an O-ring holder so that only the face with 0.02-μm-diameter pores was exposed to solutions. The substrate was removed from solution and rinsed with copious amounts of ethanol and then Milli-Q water. Subsequently, the substrate was immersed in an aqueous 0.02 M PAH solution (0.02 M NaCl, adjusted to pH 5.0 with NaOH) for 3 min and rinsed with Milli-Q water and then ethanol. This process was repeated until the desired number of bilayers was deposited, and all films were terminated with a poly(amic acid) layer. 6FDA-mPDA/PAH films were prepared similarly except that the rinsing solvent was a 1:1 mixture of ethanol and water, and the PAH solution did not contain NaCl. BTDA-BAHF solutions were made by first dissolving BTDA-BAHF in acetone, and then adding water to make 0.005 M BTDA-BAHF in 7:3 (v:v) acetone/water. The pH of this solution was adjusted to 5.0 by adding 0.2 M triethylamine in 7:3 acetone/water. For BTDA-BAHF/PAH films, the poly(amic acid) layers were rinsed with acetone and neither solution contained NaCl.

Film Imidization. Films were heated using a home-built apparatus consisting of a temperature controller, thermocouple, glass chamber, and heating mantle. The heating apparatus was purged with nitrogen for 2 h prior to heating and during heating and cooling. The temperature was ramped at a rate of 5 °C per min and was held at the desired heating temperature for 2 h.

Film Characterization. Ellipsometric thickness measurements on amine-terminated silicon wafers were made using a rotating analyzer ellipsometer (model M-44, J. A. Woollam) and WVASE32 software. Approximate film compositions were determined by measuring the change in thickness upon adsorption of each polymer and assuming that each polyelectrolyte layer had the same density. (For layer-by-layer monitoring of growth, films had to be dried with N_2 after deposition of each layer, but in all other cases films were dried only after deposition of the entire film.) A film refractive index of 1.5 was assumed in all thickness determinations. Transmission FTIR spectra of films on double-side polished Si wafers were measured using a Nicolet Magna-550 FTIR spectrophotometer with a Brewster angle attachment set at 75° (*p*-polarized light). A UV/O_3-cleaned Si substrate was used as a background. Field-emission scanning electron microscopy (FESEM) images were obtained with a Hitachi S-4700 instrument using an acceleration voltage of 15 kV. Samples were fractured in liquid nitrogen and sputter-coated with 5 nm of Au before imaging.

Gas-Transport Studies. Room-temperature (23−24 °C) gas-transport measurements were carried out using a home-built permeation cell consisting of a chamber that sealed onto a membrane via an O-ring. The membrane was supported by a stainless steel frit (Mott), and gas flux was measured using a soap-bubble flow meter (Fisher Scientific, model 420). Using a pressure relief valve, the permeation cell was purged many times with the gas of interest and all measurements with that gas were then taken after a steady-state flux was observed. Fluxes were measured at pressures of 5−45 psig (in 5-psig intervals), and the area of the membrane exposed to the gas was 2.0 cm^2. The fluxes of O_2, N_2, H_2, CH_4, and CO_2 (in that order) were determined for each membrane, and O_2 and N_2 were then tested again to ensure that membrane properties did not change upon exposure to different gases. Permeabilities of the individual gases were calculated for each pressure and then averaged.

Results and Discussion

Film Formation and Composition. The selective layer of gas-separation membranes usually consists of a single, gas-selective polymer,[39] whereas formation of membranes by APD, in contrast, requires two oppositely charged polymers. In the present case, the polyanion is a poly(amic acid) that can be heated to form a gas-selective polyimide, but disruption of the polyimide packing by PAH could significantly reduce selectivity.

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Thus, formation of gas-selective polyimide/PAH membranes will likely require keeping the amount of PAH in the film to a minimum. One of the goals of this study was to obtain multilayer polyelectrolyte films that contain as much as 90% polyimide. We wanted to make the poly(amic acid) layer as thick as possible to both reduce the number of layers that need to be deposited and increase the overall fraction of polyimide in the final film.

Poly(amic acid) layer thickness can be controlled by varying the solvent composition, deposition pH, and supporting salt concentration in deposition solutions. The fluorinated poly(amic acids) employed in this study must first be dissolved in a good solvent (e.g., ethanol or acetone) and then some water can be added to the solution to enhance the deprotonation of −COOH groups. Addition of too much water, however, results in precipitation of the polymer if it is not fully deprotonated. Thus, we deposited films from solutions containing 30% water. Although the addition of salt to polyelectrolyte deposition solutions increased the thickness of some multilayer polyelectrolyte films by as much as an order of magnitude,[19,40] in the poly(amic acid) case, film thickness increased by at most 50% with the addition of up to 0.5 M NaCl. Although small, this difference can increase the overall fraction of poly(amic acid) in the film by 5−10%. Unfortunately, added salt can also change the solubility of the poly(amic acid). This was most apparent for solutions of BTDA-BAHF. When these solutions contained 0.5 M salt, they quickly became cloudy if any of the solvent evaporated. Without the added salt, the solution would stay clear for over 2 h if left uncapped. Thus BTDA-BAHF was deposited in the absence of salt, and 6FDA-BAHF and 6FDA-mPDA were deposited in the presence of 0.5 M NaCl.

For weakly acidic or basic polyelectrolyte systems, adjusting the deposition pH can also have a large effect on layer thickness.[20,41] In the case of poly(amic acids) lower pH values should decrease the fraction of acid groups that are ionized and reduce the number of charged groups per polymer chain. With fewer available charged sites, more polymer strands are required to compensate the charge on the substrate surface, and hence more polymer will be deposited.[20,41] For fluorinated poly(amic acids), pH also affects film thickness by altering polymer solubility. Because deposition solutions are composed of both a good solvent (ethanol or acetone) and water, the polymer is soluble in both the fully protonated and the fully deprotonated forms. However, at intermediate pH values, fluorinated poly(amic acids) are partially protonated and only sparingly soluble. At points near solubility limits, the driving force for film deposition is greatest,[19] and the thickest poly(amic acid) layers form. Thus, we deposited poly(amic acid) films at a pH of 5, because this is the lowest intermediate pH at which polymers reproducibly remain in solution.

The same thought process applies to deposition of PAH, except that we wanted to deposit as little PAH as possible. In this case, the ideal solution might be one that contains the polycation dissolved in a very good solvent, water, at a low pH in the absence of supporting electrolyte.[20,41] However, at some point the amount of PAH deposited is too small to permit deposition of the next poly(amic acid) layer. Thus, for controlled film formation with minimal PAH adsorption, we adjusted the pH of the PAH solution to be the same as that of the poly(amic acid). Also, in the case of films containing 6FDA-BAHF, a small amount of NaCl (0.02 M) was necessary to form layers with consistent thicknesses.

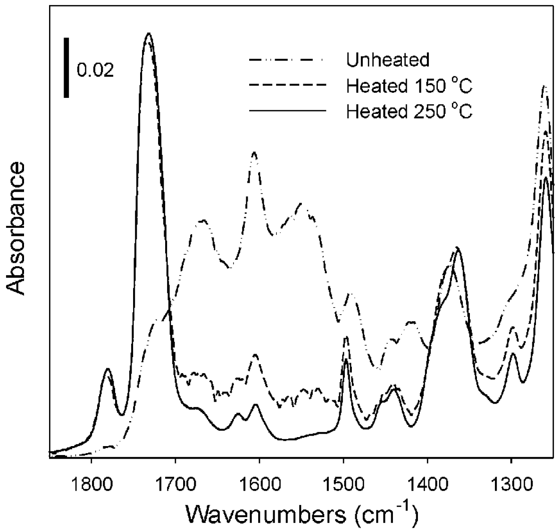

Figure 3. Brewster-angle transmission FTIR spectra of 9.5-bilayer 6FDA-mPDA/PAH films on Si before and after heating at 150 °C or 250 °C for 2 h to induce imidization.

Overall, control over pH and solvent yielded bilayer thicknesses of 34, 38, and 50 Å for 6FDA-BAHF/PAH, BTDA-BAHF/PAH, and 6FDA-mPDA/PAH, respectively. Increases in film thickness after adsorption of PAH were about 11% of those resulting from adsorption of poly(amic acid). Thus, control over deposition conditions allowed formation of films that were ∼90% poly(amic acid).

Film Imidization. To examine the extent of imidization after heating, we measured the Brewster-angle transmission FTIR spectra of poly(amic acid)/PAH films on amine-modified double-side polished Si supports. Figure 3 shows the spectra of films before and after heating at 150 or 250 °C. Unheated films have a broad absorbance band from 1670 to 1520 cm^{-1} primarily due to the overlap of amide and asymmetric $-COO^-$ stretches of the poly(amic acid). 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. In principle, a few amide bonds could form by reaction of the amine groups of PAH and the carboxylate groups of the poly(amic acid), but we see no spectral evidence for this reaction.

Decreases in the carboxylate and amide peak intensities suggest that ∼50% and ∼85% imidization occur for samples heated at 100 °C (not shown) and 150 °C, respectively. Spectra obtained after heating at 250 and 300 °C were essentially identical, implying that full imidization occurs at 250 °C. Thus, complete imidization takes place at temperatures lower than the glass transition temperatures of the polyimides (298 °C for 6FDA-mPDA, 298 °C for 6FDA-BAHF, and 305 °C for

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Table 1. Permeability (Barrers)[a] and Selectivity Coefficients for the Transport of Various Gases through Several Polyimide Membranes Containing ~10% PAH

polymer	P_{O_2}	P_{N_2}	P_{H_2}	P_{CH_4}	P_{CO_2}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}
6FDA-mPDA/PAH[b](9.5 bilayers)	2.8 ± 0.50	0.40 ± 0.08	42 ± 4	0.16 ± 0.06	11 ± 1	6.9	68
bulk 6FDA-mPDA[c,8]	3.0	0.45	40	0.16	9.2	6.7	58
6FDA-BAHF/PAH[b] (14.5 bilayers)	14 ± 0.7	2.6 ± 0.5	110 ± 9	1.4 ± 0.5	53 ± 4	5.2	38
bulk 6FDA-BAHF[c,7]	14	3.1	110	1.3	51	4.6	38
bulk 6FDA-BAHF[c,9]	16	3.5	-	1.6	64	4.7	40
BTDA-BAHF/PAH[b] (10.5 bilayers)	2.2 ± 0.4	0.38 ± 0.09	28 ± 3	0.17 ± 0.06	8.8 ± 1.2	5.8	52
bulk BTDA-BAHF[c,7]	2.5	0.45	31	0.23	10	5.6	45

[a] Barrers = 10^{10}·cm^3 (STP)·cm/(cm^2·s·cm(Hg)). [b] Measured at 24 °C. [c] Measured at 35 °C.

BTDA-BAHF),[7,8] which are typically considered to be the temperatures needed to induce full imidization.[42] Several studies show that complexation of poly(amic acids) with an amine base lowers imidization temperatures and decreases the time needed for full imidization.[43,44] Similarly, we formed poly(amic acid) salts when electrostatically attaching the layers, and thus lower imidization temperatures occurred. Low heating temperatures will prove essential if poly(amic acid) films are to be imidized on temperature-sensitive polymeric supports.

For most gas-transport studies, we employed heating temperatures of 250 °C to achieve full imidization. Temperatures above 250 °C present some risk of decomposition of PAH, which may lead to membrane defects. After heating at 250 °C, film thickness decreases by ~30%, and this change is probably due to both imidization and removal of adsorbed water from the film.

FESEM Studies of Membrane Formation. Figure 4 shows cross-sectional FESEM images of porous alumina substrates before and after deposition of 6FDA-mPDA/PAH films. These images show very little, if any, deposition of polyelectrolytes on the walls of the 0.2-μm pores that make up the majority of the alumina support. There may be some film penetration (10−20 nm) into the 0.02-μm pores at the alumina surface. Cross-sectional images taken at several points along the diameter of the membrane indicate a uniform film thickness, whereas top-view images of the membrane show complete coverage of surface pores. The uncoated backside of the alumina exhibited open pores with no evidence of polyelectrolyte deposition.

Using FESEM images we were able to estimate polyimide film thicknesses to within ~5 nm. The thicknesses of 6FDA-mPDA/PAH (9.5 bilayers), 6FDA-BAHF/PAH (14.5 bilayers), and BTDA-BAHF/PAH (10.5 bilayers) films were all about 50 nm. These thicknesses are about 30% higher than ellipsometric thicknesses of similar films deposited on amine-functionalized silicon wafers. The higher thicknesses on the porous alumina support may be due to a small amount of deposition in the surface pores or differences between charge distributions and roughnesses of the two substrates. The similarity of permeability coefficients determined using these thicknesses and permeability coefficients of bulk polyimides suggests that the thickness values are reasonable (see below).

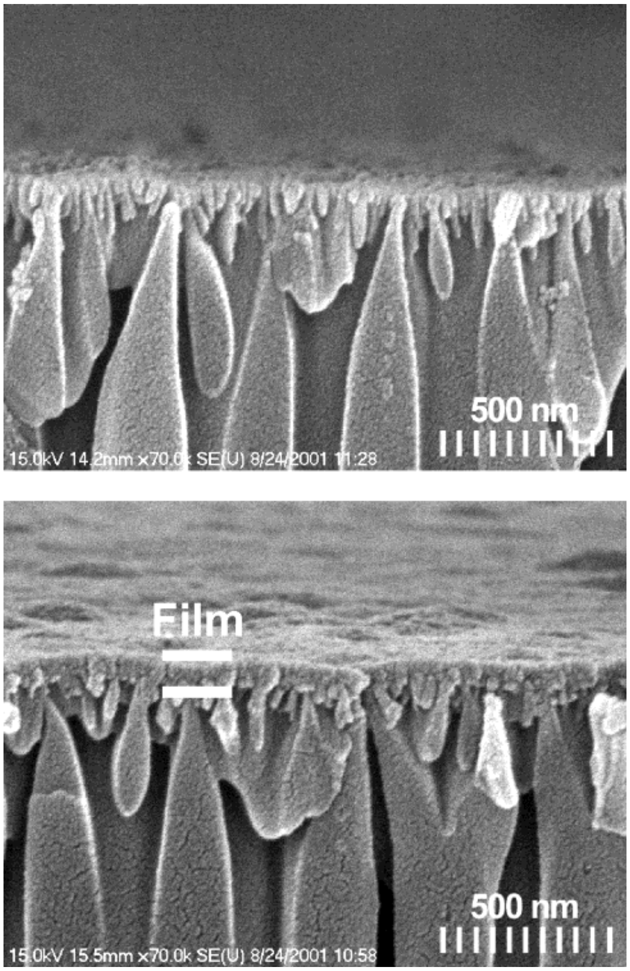

Figure 4. Cross-sectional field-emission scanning electron microscopy images of (a) a bare alumina support and (b) an alumina support coated with an imidized 9.5-bilayer 6FDA-mPDA/PAH film.

Gas-Transport Measurements. Table 1 lists gas permeability coefficients and the ideal O_2/N_2 and CO_2/CH_4 selectivities for polyimide membranes formed by alternating polyelectrolyte deposition and imidization at 250 °C. Permeabilities are presented in barrers (10^{10}·cm^3 (STP)·cm/(cm^2·s·cm(Hg)) and were determined using film thicknesses obtained by FESEM. Selectivities were calculated by dividing the permeabilities of two different gases. All of the membranes were made to be about 50 nm thick, and all data shown represent an average of measurements on 3 replicate membranes.

Within experimental uncertainty, the permeability and selectivity coefficients of the tested membranes are

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Table 2. Gas Permeability[a] and Selectivity Coefficients for 6FDA-mPDA/PAH Membranes Prepared with Different Heating Temperatures and Thicknesses

membrane	P_{O_2}	P_{N_2}	P_{CH_4}	P_{CO_2}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}
9.5 bilayer 6FDA-mPDA/PAH, unheated	0.59	0.68	0.92	0.61	0.86	0.66
9.5 bilayer 6FDA-mPDA/PAH, heated at 150 °C for 2 h	0.57	0.30	0.30	1.4	1.9	4.6
9.5 bilayer 6FDA-mPDA/PAH, heated at 150 °C for 12 h	0.49	<0.2[b]	<0.2[b]	1.8	>2.5	>9
9.5 bilayer 6FDA-mPDA/PAH, heated at 150 °C for 24 h	0.49	<0.2[b]	<0.2[b]	2.1	>2.5	>11
5.5 bilayer 6FDA-mPDA/PAH, heated at 250 °C for 2 h	2.9	1.5	1.5	6.1	1.9	4.1
7.5 bilayer 6FDA-mPDA/PAH, heated at 250 °C for 2 h	2.9	0.43	0.25	13	6.7	51
9.5 bilayer 6FDA-mPDA/PAH, heated at 250 °C for 2 h[c]	2.8	0.40	0.16	11	6.9	68

[a] Data are averages of measurements on two membranes. The difference between the two measurements was <10%. [b] Fluxes were lower than the limit of the flow meter. [c] Data from Table 1.

the same as those of cast, pure polyimide membranes with μm thicknesses. We should note that the transport experiments with the membranes prepared by APD were performed at 24 °C, but the literature data for bulk polyimides were acquired at 35 °C. However, the 10 °C difference in the present case should have little effect on permeability.[45] The high selectivities in these membranes (Table 1) clearly show that the films are free of defects, as even a small fraction of defects would negate selectivity.[46] Annealing that occurs during heat-induced imidization may help to heal defects in these films.

The agreement between the permeability coefficients of membranes prepared by APD and analogous bulk polyimide membranes is somewhat surprising considering that the films prepared by APD contain a mixture of the polyimide and PAH. One would expect lower selectivities and different permeabilities if the two layers were as interpenetrated as is the case for other polyelectrolyte films.[17] Interpenetration may not be as prevalent in these films because each polyelectrolyte is insoluble in the deposition solvent of the other polyelectrolyte. Phase segregation could also occur during heating. Further experiments are required to determine if phase segregation occurs.

Gas Transport as a Function of Film Composition and the Degree of Imidization. To investigate the relationship between extent of imidization and gas transport, we measured gas fluxes through 6FDA-mPDA/PAH membranes before and after heating at 150 °C or 250 °C (Table 2). The unheated membranes exhibited Knudsen diffusion-like selectivities and relatively low permeabilities for O_2 and CO_2 (5- and 18-fold less, respectively, than through membranes heated at 250 °C). Knudsen diffusion occurs in pores with diameters smaller than the mean free path of the gas, and flux in such a system is inversely proportional to the square root of the molecular mass of the gas.[47] Thus, Knudsen diffusion selectivities suggest that transport occurs primarily through a few small defects in unheated films. The relatively low flux through unheated membranes may be due to the ionic cross-links in the film or the presence of residual solvent.

Heating at 150 °C for 2 h increased selectivity relative to unheated films (Table 2), but not to the level found in similar films heated at 250 °C. Fluxes of O_2 and CO_2 were also 5–10-fold lower than for films heated at 250 °C. Increasing heating time (150 °C) to 12 or 24 h did not yield increases in flux, but selectivity appeared to increase. (The fluxes of N_2 and CH_4 through the films heated at 150 °C for 12 or 24 h were too low to be measured with our system, so we could only determine limits for O_2/N_2 and CO_2/CH_4 selectivities.) The differences between membranes heated at 150 and 250 °C could result from a lower (10–15%) degree of imidization, caged solvent that cannot be completely removed at 150 °C, or a change in film structure (polymer segregation) at the higher heating temperature.

To better understand the effect of the polycation on gas transport, we prepared 6FDA-mPDA membranes that contained a higher fraction of PAH (25–30%). This was accomplished by increasing the deposition pH for PAH to 9.0 and adding NaCl (0.5 M) to this solution. In relation to the 6FDA-mPDA/PAH membranes containing only 10% PAH and having the same total thickness, O_2/N_2 selectivity decreased from 6.9 to 2.2 and CO_2/CH_4 selectivity decreased from 68 to 5.8, although the permeabilities of O_2 and CO_2 did not change by an appreciable extent. This change in selectivity could result from greater penetration between the layers due to the higher thickness of PAH. The high pH of the PAH solution should also deprotonate the remaining –COOH groups in the poly(amic acid) layer on the surface, allowing for a greater degree of interpenetration.

Gas Transport as a Function of Film Thickness. Although ion-transport studies suggested that as little as 25 nm of polyelectrolyte film is required to cover the pores of alumina supports,[48] the gas-selectivity of polyimide membranes decreased for films less than 35 nm thick. When polyimide thickness was reduced from 50 nm to 25–30 nm by reducing the number of 6FDA-mPDA/PAH bilayers from 9.5 to 5.5, O_2/N_2 selectivity decreased from 6.9 to 1.9 and CO_2/CH_4 selectivity decreased from 68 to 4.1 (Table 2). Decreases in selectivity result primarily from increases in N_2 and CH_4 flux. The presence of some selectivity suggests that the density of defects is not high enough for transport to occur simply by diffusion through pores, but we think that a few defects result in greatly reduced selectivity by increasing N_2 and CH_4 transport. By making the film two layers thicker (7.5 bilayers), we achieved selectivities similar to those of 9.5-bilayer films, presumably because defects are covered. Thus, we find that a minimum thickness of 35–40 nm is necessary to achieve the highest selectivities. Even thinner selective films might be constructed if nonporous supports or gutter layers are used.

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Conclusion

Alternating electrostatic adsorption of poly(amic acids) and PAH followed by postdeposition heating provides a convenient method for forming ultrathin, gas-selective polyimide films at the surface of porous alumina. By controlling deposition conditions, films can be tailored to contain primarily polyimide, and fully imidized membranes exhibit permeability coefficients and selectivities that are comparable to literature values for the corresponding bulk polyimides. These selectivities can be achieved even with films as thin as 35−40 nm. Future work aims at further reducing the minimum film thickness required for high selectivity and developing gentler imidization conditions that will allow use of polymeric substrates.

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