Splaying Hyperthin Polyelectrolyte Multilayers To Increase Their Gas Permeability

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Supplementary Information

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1. Experimental Procedures

1.1 Materials and Methods

Poly(allylamine hydrochloride) (PAH) (Mw=15 kDa, Sigma-Aldrich Co., St. Louis, MO), poly(4-styrenesulfonic acid), sodium salt (PSS) (Mw=70 kDa, Sigma-Aldrich Co., St. Louis, MO), branched poly(ethyleneimine) (PEI, Mw=70 kDa, Polysciences Inc., Warrington, PA), noctadecyltrichlorosilane (OTS, Sigma-Aldrich Co., St. Louis, MO), poly[1-(trimethylsilyl)-1propyne] (PTMSP, Gelest, Inc., Morrisville, PA) were used as received. House-deionized water was purified using a Millipore Milli-Q filtering system containing one carbon and two ionexchange stages. Other chemicals and solvents used in this study were obtained commercially from various vendors and used without further purification. All ¹H NMR spectra were recorded on a Bruker Avance 500 MHz instrument. Chemical shifts are reported in parts per million relative to residual solvent. Ellipsometry measurements were made using VASE ellipsometer (J.A. Woollam Co., Inc., Lincoln, NE), equipped with variable wavelength (from 250-1700 nm) and angle of incidence $(15^{\circ}-90^{\circ})$ system, a λ of 632.8 nm and an incidence angle of 70° were chosen for measurements. The refractive indices that were used to estimate the thickness of the OTS and polyelectrolyte multilayers were 1.46 and 1.41, respectively. All AFM measurements were made using a tapping mode atomic force microscopy (Solver Next, Multimode SPM, NT-MDT America Inc., Santa Clara, CA), and a minimum of three different locations along the surface were examined. For each sample, 5 x 5 and 10 x 10 μ m²-size images were obtained. Film thicknesses were also determined via AFM by scratching the surface of OTS-modified silicon wafers bearing PEMs with a razor blade to remove the multilayered assemblies, and measure the step heights. The aqueous polymer solutions that were used for layer-by-layer depositions were adjusted to pH 8.0 (polycation solutions) or 4.0 (PSS solution) by addition of a small amount of either 1 M NaOH or 1 M HCl.

1.2 Supports

Experimental methods that were used to prepare PTMSP casting membranes and silicon wafers modified with OTS were the same as reported in our previous paper.^{1,2}

1.3 Layer-by-Layer Depositions

An OTS-modified silicon wafer (or PTMSP support), which was deposited with a PEI (0.1 wt% with 0.1 M NaCl, at pH 10.0) layer on one side and washed with water, was subjected to layer-by-layer depositions. Typically, the substrate was immersed into 200 mL of an aqueous solution of PSS (15 mM repeat unit, at pH 4.0) for 10 min without stirring, and then washed by SI-2

immersing twice in 200 mL of deionized water for 5 min each without stirring, followed by air-drying. In the case of the PTMSP supports, 600 mL of deionized water was used. A similar treatment was then performed using a 15 mM aqueous solution of polycations (1**a**-**c**, at pH 8.0). All the membranes allowed drying in the laboratory ambient for 96 h after the depositions were completed prior to gas permeation measurements.

1.4 Gas Permeation Measurements

Gas permeation measurements were made with a home-built stainless steel permeation apparatus.3 The gases studied were H2 (Ultra High Purity, water <3ppm, Messer Griesheim Industries, Inc., Malvern, PA) and N₂ (prepurified grade, water <3ppm, Praxair, Inc., Danbury, CT). A membrane to be measured was placed in the permeation cell between two Viton rubber O-rings (3.45 cm i.d., Scientific Instrument Services, Inc.) with a support screen (4.70 cm, Millipore Corp.) and held securely with a quick flange clamp (Scientific Instrument Services, Inc., not shown). Membranes were always placed in the cell such that the polyelectrolyte multilayers faced the high pressure side of the pressure gradient. The permeant gas travelled from the gas cylinder to an inline filter (15 m) and elastomer diaphragm regulator (Brooks Instrument, 8601D), which was connected to a Heise gauge port. Another plastic tubing line connected from the Heise gauge outlet to the permeation cell. The pressure gradient that was applied to each membrane was 40 psi. After passing through the membrane, the gaseous permeant was directed into a 40 cm long glass U-tube flowmeter (2 mm i.d.). The volumetric flow rate of the gas was then measured by recording the time $(t_f - t_i)$ that was required for a methyl isobutyl ketone solution containing crystal violet to travel a set distance (d_f - d_i), thereby sweeping out a defined volume. Measurements were taken until steady-state values were achieved (2 h for H₂ and 4 h for N₂). At least five volumetric flow rates were recorded for each membrane, and the mean and standard deviations were determined. The normalized flux was calculated with use of the mean volumetric flow rate, the area that was available for flow (9.36 cm²), and the pressure gradient (2.7 atm) that was employed. This procedure was repeated for the next permeant gas. In general, the permeation properties were first measured for H₂, and then for N₂. To ensure that no damage to the membrane had occurred while these measurements were being made, after the last permeant was investigated, the H₂ and N₂ permeances were measured again and found to be unchanged. To place the permeation properties of [PSS/PAH]_{10.5} and [PSS/1c]_{13.5} into perspective, we then included them in an upper bound plot for H_2/N_2 in Figure SI-1.



Figure SI-1: Upper bound plot for H₂/N₂ selectivity versus H₂ permeability, P_{H2} . The data shown in red are for homopolymers that have been reported to date (Figure adapted by authors from reference 5). Data for (\blacktriangle) [PSS/1c]_{13.5} and (\bullet) [PSS/PAH]_{10.5} have also been included. Here, the permeability coefficient for H₂ has been calculated using the series resistance model, where $1/[P/l]_{\text{composite}} = 1/[P/l]_{\text{PEM}} + 1/[P/l]_{\text{PTMSP}}$.⁶

The typical calculation for the permeability coefficient for H₂ is as below:

According to the data in Table 1, for [PSS/PAH]_{10.5},

1/67(GPU, Composite) = 1/[P/l](GPU, PEM) + 1/710(GPU, PTMSP),

then, $1/[P/l](PEM) = 0.0135 \text{ GPU}^{-1}$, [P/l](PEM) = 74.1 GPU,

since, $l = 15.6 \times 10^{-7}$ cm, $P(PEM) = 74.1 \times 10^{-6}$ cm³/cm²-s-cm Hg x 15.6 x 10⁻⁷ cm = 1.16 Barrers;

for [PSS/1c]_{13.5},

1/120(GPU, Composite) = 1/[P/l](GPU, PEM) + 1/710(GPU, PTMSP),

then, $1/[P/l](PEM) = 6.92 \times 10^{-3} \text{ GPU}^{-1}$, [P/l](PEM) = 144.5 GPU,

since, $l = 15.0 \times 10^{-7}$ cm, $P(PEM) = 144.5 \times 10^{-6} \text{ cm}^3/\text{cm}^2$ -s-cm Hg x 15.0 x 10^{-7} cm = 2.17 Barrers.

1.5 Synthetic Procedures

Scheme SI-1



Synthesis of monocarboxycobaltocenium: Monocarboxycoaltocenium was prepared according to a reported procedure.⁴ ¹H NMR (500 MHz, D_2SO_4 , δ): 7.11 (t, 2H); 6.77 (t, 2H); 6.69 (s, 5H).

Cobaltocenium acyl chloride: Monocarboxycobaltcenium (1.0 g, 2.64 mmol) was dissolved in 15 mL of thionyl chloride. The reaction mixture was refluxed for 2 days. The excess of thionyl chloride was evaporated under reduced pressure to yield a yellow product. The obtained cobaltocenium acyl chloride was subsequently used for the next step without further purification.

Synthesis of methoxycarbonylcobaltocenium (compound **2**): Cobltocenium acyl chloride (1.0 g, 2.52 mmol) was dissolved in a mixture of anhydrous methanol and DMF (v/v, 20 mL/8 mL) and triethylamine (0.54 g, 5.3 mmol) was then injected into the flask. The resulting reaction mixture was stirred overnight at room temperature and then concentrated to ca. 10 mL and cooled in order to precipitate the triethylammonium chloride as a byproduct. After filtration, the solution was added to ca. 50 mL of diethyl ether. The precipitate was collected as a yellow powder which was further purified by recrystallization from water/acetone, and the final product was obtained as red crystals (860 mg, yield: 86.8%). ¹H NMR (500 MHz, D₂O, δ): 6.27 (t, 2H); 5.92 (t, 2H); 5.85 (s, 5H); 3.95 (s, 3H). The hexafluorophosphate salt of methoxycarbonylcobaltocenium was then converted to its chloride salt by stirring with ca. 6 g of Amberlite IRA-402 (Cl) resin in 30 mL of H₂O/acetone (3/1, v/v) for 2 h, followed by filtration and removal of solvent under reduced pressure.

Synthesis of **1c**: Poly(allyamine hydrochloride) (431 mg, 15 kDa, 4.61 mmol NH₃⁺) was dissolved in 1.5 mL of water followed by addition of methoxycarbonylcobaltocenium (1.3 g, 4.61 mmol, Cl⁻ salt). After 1.93 mL of triethylamine (13.8 mmol) was added into the flask, the reaction mixture was heated to 80 °C and stirred for 3 days. The mixture was then evaporated, and the obtained residue was redissolved in 35% ammonia/water (v/v, 5 mL/5 mL). This treatment was repeated twice followed by evaporation under vacuum each time in order to completely remove triethylamine. The resulting residue was dissolved in water at pH 2 (adjusted with 6 M HCl) and purified by dialysis against deionized water for 2 days (changing the dialysate every 12 h, using a Float-A-Lyzer dialysis tube, MWCO 3.5~5 KD). After lyophilization, the final product was obtained as a yellow solid (534 mg, yield: 87.8%, containing 18% Cob⁺ according to NMR). ¹H NMR (500 MHz, D2O, δ): 6.30 (br, 0.36 H, 2H on Cob⁺); 5.95-5.80 (br, 1.28 H, 7H on Cob⁺); 3.70-2.80 (br, 2H); 2.40-1.10 (brm, 3H). The degree of Cob⁺ loading in **1c** is estimated by the integration value of signal at 6.30 ppm. The equivalent integration values of signals at 6.30 ppm and 3.40 ppm confirm that the cobaltocenium unit is covalently attached to the backbone of PAH.

Other cobaltocenium-containing PAH polymers (**1a** and **1b**) were prepared by the similar procedures, but using different equivalents of methoxycarbonylcobaltocenium (0.2 equivalent for 3% Cob⁺ containing PAH and 0.5 equivalent for 10% Cob⁺ containing PAH).

2. NMR Spectra of Compounds

Figure SI-2: ¹H NMR spectrum of monocarboxycobaltocenium



Figure SI-3: ¹H NMR spectrum of compound 2



Figure SI-4: ¹H NMR spectrum of 1a



Figure SI-5: ¹H NMR spectrum of 1b



Figure SI-6: ¹H NMR spectrum of 1c



3. AFM Images of PEMs



Figure SI-7: AFM topographic image (tapping mode, 5 x 5 μ m²) of PEMs formed on OTSmodified silicon wafer: (A) (PSS+PAH)_{13.5}, RMS = 1.94 nm; (B) (PSS+1**a**)_{13.5}, RMS = 1.14 nm; (C) (PSS+1**b**)_{14.5}, RMS = 1.29 nm; (D) (PSS+1**c**)_{14.5}, RMS = 1.36 nm.



Figure SI-8: Height image and section profile (AFM, tapping mode, $10 \times 10 \mu m^2$) showing the film thickness of PEMs formed on OTS-modified silicon wafer: (a) (PSS+PAH)_{13.5}, $\Delta d = 21.3$ nm; (b) (PSS+1c)_{14.5}, $\Delta d = 18.3$ nm. (Note: the thickness of ca. 1.6 nm PEI anchor layer is included in all step height measurements)

4. References

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