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COMMUNICATION

Splaying Hyperthin Polyelectrolyte Multilayers To Increase Their Gas Permeability

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The concept of splayed, hyperthin polyelectrolyte multilayers (PEMs) is introduced in which a bulky, hydrophilic and charged pendant group is used to increase the gas permeability of a PEM without reducing its permeation selectivity. Proof of principle studies are reported using nm-thick PEMs made from poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) bearing bulky cobaltocenium ions.

The ability to separate gaseous mixtures, efficiently, can have major economic as well as environmental impact. Examples of some mixtures that are of current interest include: H₂/N₂, H₂/CO₂, CO₂/N₂, O₂/N₂, H₂/CH₄, H₂/CO and C₂H₄/C₂H₆.¹⁻³ Although selective adsorption and cryogenic distillation methods can be used to separate such gases, both techniques are expensive in terms of their energy and capital requirements. For this reason, much of the attention has shifted towards membrane-based separations, which can be less costly. Here, the main challenge is to create membrane materials that exhibit a maximum in flux and a maximum in permeation selectivity.^{4,5}

Our own efforts in this area have focused on the fabrication of hyperthin (< 100 nm) polymeric membranes.^{6,7} Our motivation for this work stems from the fact that the flux of a permeant per unit area, J , is inversely proportional to a membrane's thickness, l . Thus, hyperthinness offers the prospect of exceptionally high performance, provided that permeation selectivity is not compromised due to the formation of defects.⁸ In addition to being dependent on a membrane's thickness, the flux of a permeant is also directly proportional to a permeability coefficient, P , which characterizes the membrane/permeant combination, and to the pressure gradient, Δp , which is applied across the membrane (eq. 1).² To date, all of our studies have been based on Langmuir-Blodgett (LB) and Layer-by-Layer (LbL) fabrication methods to produce surfactant bilayers and polyelectrolyte multilayers (PEMs), respectively.^{6,7}

$$J = \frac{P \times \Delta p}{l} \quad \text{eq. 1}$$

In the work reported herein, we demonstrate the feasibility of *increasing the permeability of a hyperthin polyelectrolyte multilayer (PEM) without reducing its permeation selectivity*. The design strategy that we have adopted is reminiscent of one previously used to increase the permeability of *micron*-thick membranes made from cellulose (30-50 μm) and polysulfones (50-75 μm).^{9,10} In both of those cases, bulky adamantyl groups were introduced along the polymer backbone to disrupt the packing of the chains and to increase the free volume within the membrane. Whether a similar strategy could be applied, successfully, to hyperthin PEMs has not, to the best of our knowledge, previously been established (Figure 1).

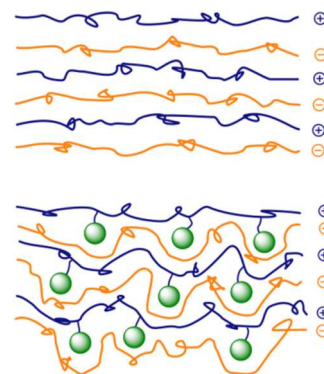


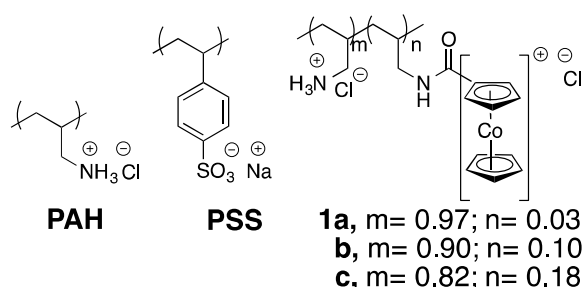
Fig. 1 Stylized illustration of a conventional polyelectrolyte multilayer (top) and a splayed polyelectrolyte multilayer (bottom) made from one conventional polyelectrolyte plus a polymeric counterion bearing bulky pendant groups.

With this aim in mind, we have compared the permeation properties of hyperthin PEMs derived from two commonly used polyelectrolytes, poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) (PSS), with those of analogous PEMs made from PSS plus PAH containing bulky cobaltocenium ions as pendant groups; i.e., **1a**, **1b** and **1c** (Chart 1). The cobaltocenium ion was specifically chosen for this investigation instead of adamantyl groups because of its hydrophilic character, its moderate size, and its net positive charge. Based on bond lengths and van der Waals radii of its atoms, the van der Waals surface of

CoCp₂ can be approximated by a cylinder of 0.65 nm in diameter and 0.69 nm in length.¹¹

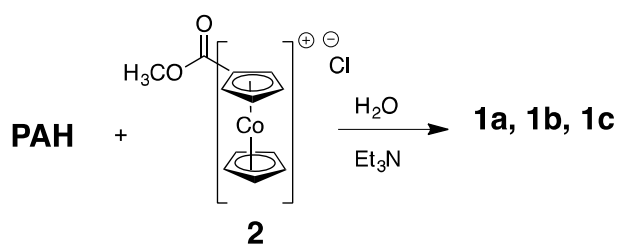
Polymers **1a**, **1b** and **1c** were synthesized by partial acylation of PAH by monomethoxycarbonylbis(cyclopentadienyl)cobalt (III) chloride, **2** (Scheme 1). The latter was prepared by converting monochlorocarbonylcobaltocenium hexafluorophosphate into its methyl ester, followed by ion exchange (not shown).¹² The specific loadings that were obtained were 3, 10 and 18 mol%. These loading have been estimated based on the integrated intensity of two of the aromatic protons (6.3 ppm) of the cobaltocenium ion relative to the integrated intensities of the two protons (3.4 ppm) adjacent to the nitrogen that have been acylated by **2**, and the two protons (3.1 ppm) that have not been acylated.

Chart 1



In Figure 2 are shown the growth curves for polyelectrolyte multilayers formed by LbL deposition of PSS and PAH, **1a**, **1b** or **1c**. In each case, the PEMs were deposited onto silicon wafers that had been silylated with *n*-octadecyltrichlorosilane and surface-modified using branched poly(ethyleneimine) (*b*-PEI).¹³ Unexpectedly, increased loadings of the cobaltocenium ion along the PAH backbone resulted in a reduction in the thickness per deposited bilayer. Thus, the average thicknesses of [PSS/PAH], [PSS/**1a**], [PSS/**1b**] and [PSS/**1c**] were 1.5, 1.3, 1.2 and 1.1 nm, respectively. Although the basis for this decrease in film thickness that accompanies an increase in the cobaltocenium ion content is not presently understood, we suspect that it may be related to conformational differences within these PEMs.

Scheme 1



Polyelectrolyte multilayers that were fabricated from 13.5 bilayers of PSS and PAH (i.e., [PSS/PAH]_{13.5}) showed an ellipsometric film thickness of 21.1 ± 0.4 nm, which includes a contribution of 1.6 ± 0.5 nm from the *b*-PEI anchor layer. When examined by atomic force microscopy after scratching the surface with a razor blade, step height analysis of the same film indicated a thickness of 21.3 ± 1.9 nm. Similar ellipsometry and AFM analysis of a PEM made from 14.5 bilayers of PSS and **1c** (i.e., [PSS/**2c**]_{14.5}) gave film thicknesses of 17.8 ± 0.4 nm and 18.3 ± 1.4 nm, respectively. Thus, these two independent methods of analysis gave excellent agreement.

To assess their permeability properties, hyperthin PEMs made from PSS plus PAH, **1a**, **1b** or **1c** were deposited onto cast films of

poly[1-(trimethylsilyl)-1-propyne] (PTMSP) that were surface-modified *b*-PEI.¹³ In Table 1 are listed the permeances (*P/l*) that were observed with respect to H₂ and N₂.

In the absence of a PEM, the support material showed only a modest preference for the permeation of the smaller H₂ molecule, corresponding to a H₂/N₂ selectivity of 2.3 (Table 1). While the deposition of 7.5 bilayers of PSS/PAH had only a small influence on the membrane's overall permeability and selectivity, the deposition of 10.5 bilayers led to a dramatic decrease in the flux of N₂ and a dramatic increase in H₂/N₂ selectivity. Addition of two more bilayers of PSS/PAH to produce (PSS/PAH)_{12.5} resulted in a slight reduction in permeability and a negligible change in the H₂/N₂ permeation selectivity, which was ca. 300.

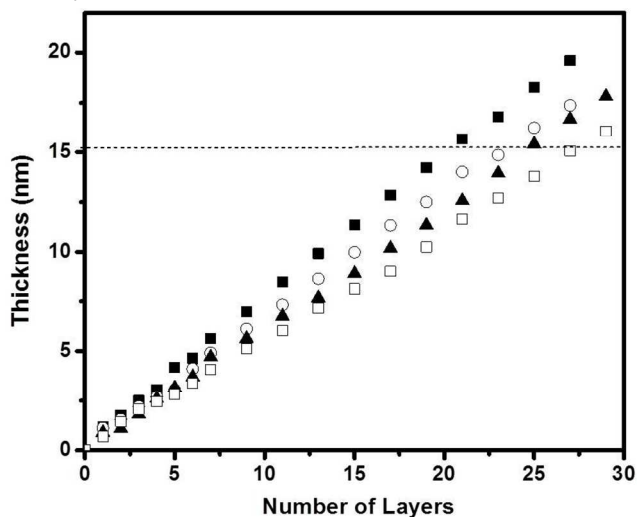


Fig. 2 Plot of ellipsometric film thickness versus number of monolayers deposited onto silylated silicon wafers that were surface-modified with branched poly(ethyleneimine). Here, the odd numbers refer to the deposition of PSS, and the even numbers refer to the deposition of PAH, (**1a**), (**1b**), and (**1c**). In all cases, a repeat unit concentration of 15 mM for each polyelectrolyte was used. The standard deposition time that was used was 10 min.

Deposition of 10.5 bilayers of (PSS/**1c**) afforded a PEM having a similar thickness as that found with 7.5 bilayers of PSS/PAH (ca. 11.5 nm). In this case, however, the permeances were significantly lower and the permeation selectivity significantly higher. Addition of three bilayers of PSS/**1c** to produce (PSS/**1c**)_{13.5} led to a further reduction in permeability and an increase in permeation selectivity. With the addition of two more bilayers of PSS/**1c**, affording (PSS/**1c**)_{15.5}, a slight reduction in permeability could be detected, but the H₂/N₂ permeation selectivity was stable at ca. 300.

To date, only limited studies have been made with PEMs made from PSS/**1b** and PSS/**1a**. However, when compared at a similar membrane thickness of ca. 15 nm, all of the membranes investigated [i.e., (PSS/PAH)_{10.5}, (PSS/**1c**)_{13.5}, (PSS/**1b**)_{12.5} and (PSS/**1a**)_{11.5}] exhibited similar permeation selectivities (ca. 300), and a general increase in permeances as the cobaltocenium content in the membrane increased.

The fact that the H₂/N₂ permeation selectivities for PSS/PAH and PSS/**1c** are stable at ca. 300 at thicknesses of ≥ 15 nm implies that their permeabilities are dominated by their intrinsic membrane properties and that film defects play a negligible role. Thus, the fact the permeances associated with PSS/**1c** are almost twice that found for PSS/PAH membranes (at 15 and 18 nm thicknesses) lends strong support for a splaying action by the bulky pendant cobaltocenium groups.

To place the permeation properties of [PSS/1c]_{15.5} into perspective, we have included this PEM in an upper bound plot for H₂/N₂ (Supplementary Information).^{4,5} Here, the H₂/N₂ selectivity of a large number of polymeric membranes are shown as a function of P_{H_2} . Although our hyperthin membranes lie beneath the present upper bound in this operational comparison, it should be noted that most organic polymeric membranes cannot be fabricated with thicknesses that are less than 100 nm without losing most of their selectivity due to defect formation.

Table 1. Membrane permeances

Membrane ^b	PEM (nm)	H ₂ (GPU) ^a	N ₂ (GPU) ^a	H ₂ /N ₂
[PSS/PAH] ₀ ^c	-----	710	310	2.3
	-----	690	300	2.3
[PSS/PAH] _{7.5}	11.3 ± 0.2	300	72	4.2
		280	68	4.1
[PSS/PAH] _{10.5}	15.6 ± 0.2	67	0.20	340
		53	0.26	200
[PSS/PAH] _{12.5}	18.2 ± 0.3	53	0.17	310
		49	0.17	270
[PSS/1c] _{10.5}	11.7 ± 0.3	120	3.1	39
		100	2.0	50
[PSS/1c] _{13.5}	15.0 ± 0.4	120	0.32	380
		110	0.36	310
[PSS/1c] _{15.5}	17.8 ± 0.4	92	0.32	290
		88	0.31	280
[PSS/1b] _{12.5}	15.4 ± 0.2	98	0.33	300
		87	0.28	310
[PSS/1a] _{11.5}	14.8 ± 0.3	69	0.25	280
		71	0.33	220

^aPermeances are reported as gas permeation units (GPUs), where one GPU = 10⁶ P/l (cm³/cm²-s-cm Hg). These values were calculated by dividing the observed flow rate by the area of the membrane (9.36 cm²) and the pressure gradient (40 psi) employed, using ca. 30 μm thick PTMSP supports. All measurements were made at ambient temperatures. Average values were obtained from 5-10 independent measurements of the same sample; the error in each case was ±5%. Duplicate membranes are reported in all cases. All PEMs were formed using polyelectrolyte solutions that were 15 mM in repeat units and a pH of 8.0 and 4.0 for PAH and PSS, respectively. ^bSubscripts refer to the number of deposited bilayers. ^cPermeances of the support material that was made from PTMSP and one deposited monolayer of b-PEI.

The feasibility of creating splayed hyperthin polyelectrolyte multilayers having enhanced permeability with retention of permeation selectivity, provides considerable incentive for exploring the effects of other perturbing agents on these and related hyperthin PEMs.¹⁴⁻²⁰ This approach toward enhancing the permeability of a PEM raises the possibility of creating new classes of membranes, (including hollow fiber analogs) for gas separations having exceptional performance due to their extreme thinness.²¹ Further studies of splayed polyelectrolyte multilayers are continuing in our laboratory.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Methods used for chemical synthesis, LbL film construction, ¹H NMR spectra and AFM measurements. See DOI: 10.1039/c000000x/

- R. W. Baker and B. T. Low, *Macromolecules*, 2014, **47**, 6999.
- Y. Yampolskii, *Macromolecules*, 2012, **45**, 3298.
- M. Rungta, C. Zhang, W. J. Koros and L. Xu, *AIChE*, 2013, **59**, 3475.
- L. M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390.
- B. D. Freeman, *Macromolecules*, 1999, **32**, 375.
- D. H. III McCullough and S. L. Regan, *Chem. Commun.*, 2004, 2787.
- M. Wang, V. Janout and S. L. Regan, *Acc. Chem. Res.*, 2013, **46**, 2743.
- A. F. Ismail and L. P. Yean, *J. Appl. Polym. Sci.*, 2003, **88**, 442.
- J. Chen, J. Zhang, Y. Feng, J. Wu, J. He and J. Zhang, *J. Membr. Sci.*, 2014, **469**, 507.
- M. R. Pixton and D. R. Paul, *Polymer*, 1995, **36**, 3165.
- L.-J. Li, A. N. Khlobystov, J. G. Wiltshire, G. A. D. Briggs and R. J. Nicholas, *Nat. Mater.*, 2005, **4**, 481.
- L. Ren, C. G. Hardy and C. Tang, *J. Am. Chem. Soc.*, 2010, **132**, 8874.
- C. Lin, Q. Chen, S. Yi, M. Wang and S. L. Regan, *Langmuir*, 2014, **30**, 687.
- R. K. Iler, *J. Colloid Interface Sci.*, 1966, **21**, 569.
- G. Decher and J. -D. Hong, *Macromol. Chem. Macromol. Symp.*, 1991, **46**, 321.
- K. S. Schanze and A. H. Shelton, *Langmuir*, 2009, **25**, 13698.
- J. B. Schlenoff, *Langmuir*, 2009, **25**, 14007.
- J. Park and P. T. Hammond, *Macromolecules*, 2005, **38**, 10542.
- Y. -H. Yang, L. bolling, M. A. Priolo and J. C. Grunlan, *Adv. Mater.*, 2013, **25**, 503.
- W. Chen and T. J. McCarthy, *Macromolecules*, 1997, **30**, 78.
- Ma, C.; Koros, W. J., *J. Membr. Sci.*, 2013, **428**, 251.