

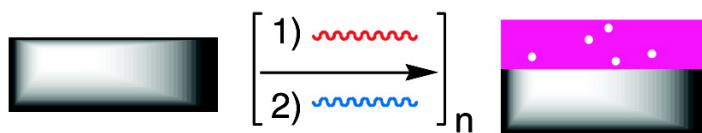
## Defects in a Polyelectrolyte Multilayer: The Inside Story

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### Layer-by-Layer Deposition of Polyelectrolytes



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## Defects in a Polyelectrolyte Multilayer: The Inside Story

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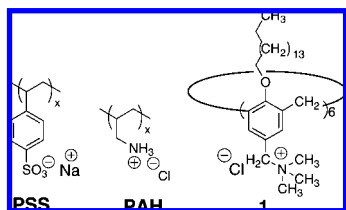
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The deposition of organic and inorganic thin films onto solid surfaces by alternate dipping into aqueous solutions of polycations and polyanions (i.e., the LbL method) has attracted considerable interest in recent years.<sup>1–3</sup> Much of this interest stems from potential applications; e.g., for use in fabricating ultrathin conducting layers, permeation-selective membranes, protective coatings, sensors, and materials for nonlinear optics. Despite extensive studies, relatively little is known about defects (i.e., *gaps*) that exist within these assemblies and the factors that control their formation.

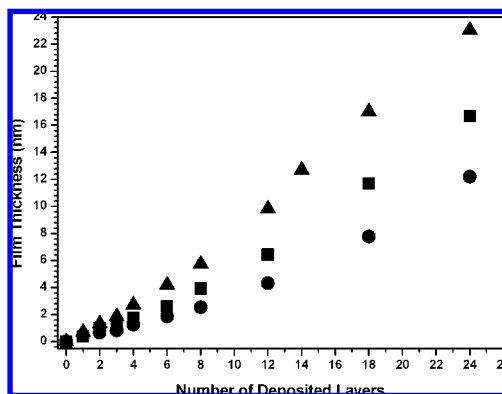
Here, we show how a moderate change in the concentration of poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) can have a dramatic effect on the formation of defects in polyelectrolyte multilayers (PEMs) (Chart 1). Specifically, we show that PEMs made from 14 alternating layers of PSS and PAH under “high” concentration conditions (15.0 mM) exhibit He/N<sub>2</sub> permeation selectivities that exceed 200. In sharp contrast, analogous films of similar thickness that are made from 24 alternating layers of PSS and PAH under “low” concentration conditions (1.0 mM) show no significant He/N<sub>2</sub> permeation selectivity, reflecting the presence of defects. We also provide evidence that *it is the conformation of these polyelectrolytes in solution rather than their concentrations that plays a major role in determining the structure of the resulting PEMs.*

### Chart 1



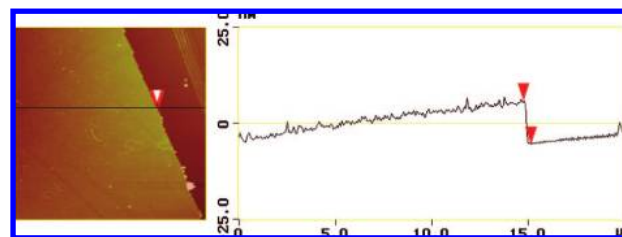
We became keenly interested in the question of defects in PEMs after discovering that the surface viscosity of monolayers of **1** is very sensitive to subphase concentrations of PSS. Specifically, we found that low concentrations of PSS favor high surface viscosities, apparently as the result of increased ionic cross-linking (Chart 1).<sup>4</sup> This observation led us to hypothesize that polyelectrolyte concentrations could also have a significant influence on the formation of defects within PEMs. In essence, we reasoned that a high degree of ionic cross-linking should limit the ability of neighboring polymer segments to associate with one another through hydrophobic forces, which would favor the formation of defects. Conversely, a low degree of ionic cross-linking should allow for “hydrophobic annealing” and the creation of a more coherent film.

To test our hypothesis, we prepared a series of PEMs from PSS and PAH under high (15 mM) and low (1 mM) concentration conditions and measured their barrier properties with respect to He, CO<sub>2</sub>, and N<sub>2</sub>.<sup>5,6</sup> Whereas the permeation of He and N<sub>2</sub> through glassy organic polymers is known to be dominated by their relative size, solubility plays a significant role in the permeation of CO<sub>2</sub>.<sup>7</sup>



**Figure 1.** Plot of film thickness versus number of deposited monolayers using (●) 1.0 mM, (■) 5.0 mM, and (▲) 15 mM concentrations of PSS and PAH. The standard deposition time that was used was 10 min; no differences in film thicknesses were observed when the deposition time was increased to 20 min.

Initially, we examined the thickness dependence of PEMs on the aqueous concentrations of PAH and PSS used. For this purpose, ellipsometry measurements were made using silicon wafers that were silylated in *n*-octadecyltrichlorosilane and coated with one Langmuir–Blodgett (LB) monolayer of (**1**-PSS).<sup>8</sup> As shown in Figure 1, film thicknesses were found to increase with increasing polyelectrolyte concentrations as well as with increasing numbers of layers.<sup>9</sup> Thus, a PEM made under low concentration conditions from 24 alternating monolayers of PSS and PAH had a thickness of  $12 \pm 0.5$  nm. Under high concentration conditions, only 14 alternating layers of PSS and PAH were needed to produce a film of similar thickness (i.e.,  $12.7 \pm 1.4$  nm). Profilometry by atomic force microscopy (after scratching the surface with a razor blade to remove the film and determining step heights) gave a film thickness of  $12.3 \pm 1.0$  nm for the 24-layered film (Figure 2).<sup>10</sup> Similar analysis of the 14-monolayered film gave a thickness of  $13.8 \pm 1.0$  nm (not shown). It should be noted that these AFM values include the (**1**-PSS) layer, which is ca. 2.1 nm in thickness. Thus, the AFM values for these polyelectrolyte multilayers are slightly less than the values determined by ellipsometry.



**Figure 2.** Height image and section profiles (AFM, tapping mode,  $20 \times 20 \mu\text{m}^2$ ) showing the film thickness of 24-layered PEM of PSS/PAH made under low concentration conditions; the *z*-scale is shown to the right.

**Table 1.** Permeances of Gases Across Polymer Membranes<sup>a</sup>

membrane	He	N <sub>2</sub>	CO <sub>2</sub>	He/N <sub>2</sub>	He/CO <sub>2</sub>
S	268	272	1600	0.98	0.16
	268	290	1720	0.92	0.16
S/(1-PSS)	227	252	1380	0.90	0.16
	253	277	1600	0.91	0.16
S/(1-PSS)(PAH-PSS) <sub>4</sub> PAH <sup>b</sup>	30.8	1.36	29.1	22.7	1.10
	37.9	1.81	28.1	20.9	1.35
S/(1-PSS)(PAH-PSS) <sub>7</sub> <sup>b</sup>	29.4	<0.1	13.9	>294	2.12
	23.5	<0.1	18.1	>234	1.30
S/(1-PSS)(PAH-PSS) <sub>12</sub> <sup>c</sup>	157	143	873	1.10	0.18
	163	157	942	1.03	0.17
S/(1-PSS)(PAH-PSS) <sub>7</sub> <sup>d</sup>	30.1	0.40	20.1	75.3	1.50
	66.9	0.86	33.6	77.8	1.99

<sup>a</sup> Permeances at ambient temperature, 10<sup>6</sup> P/l (cm<sup>3</sup>/cm<sup>2</sup>·s·cm Hg), were calculated by dividing the observed flow rate by the area of the membrane (9.36 cm<sup>2</sup>) and the pressure gradient (10 psi) employed, using ca. 30 μm thick PTMSP supports (S). Measurements were made using two different membranes that were prepared, independently, on different days. All measurements were made at ambient temperatures. Values were obtained from 5–10 independent measurements; the error in each case was ±5%. <sup>b</sup> Prepared using 15 mM polyelectrolytes. <sup>c</sup> Prepared using 1 mM polyelectrolytes. <sup>d</sup> Prepared using 1 mM PSS + 30 mM NaCl and 1 mM PAH + 5.5 mM NaCl.

To judge their barrier properties, we deposited a series of PEMs onto supports made from poly[1-(trimethylsilyl)-1-propyne] (PTMSP) that were coated with one LB monolayer of (1-PSS).<sup>8,11,12</sup> Experimental procedures that were used in carrying out alternate dipping with intermediate wash cycles were the same as those used for the silicon substrates. Gas permeation measurements for these PEMs showed a strong dependence on the polyelectrolyte concentration (Table 1). In the absence of PEMs, the bare substrates (PTMSP, S), and also the substrates containing a single LB layer of (1-PSS), showed negligible He/N<sub>2</sub> selectivity but a moderate He/CO<sub>2</sub> reverse-size selectivity. When 14 monolayers of alternating PAH and PSS [i.e., (PAH-PSS)<sub>7</sub>] were deposited under high concentration conditions, the He/N<sub>2</sub> selectivity was greater than 200 and the He/CO<sub>2</sub> selectivity was in excess of 1. Thinner PEMs that were fabricated under high concentration conditions from 9 alternating layers of PAH and PSS [i.e., (PAH-PSS)<sub>4</sub>PAH] had an ellipsometric thickness of 7 nm and He/N<sub>2</sub> and He/CO<sub>2</sub> selectivities that were greater than 20 and 1, respectively. In sharp contrast, 24-monolayered films that were fabricated under low concentration conditions showed a reduced flux for each gas but permeation selectivities that were similar to that found for the bare PTMSP support. From these measurements, it is clear that defect formation is strongly dependent on the concentration of the polyelectrolytes used and that higher concentrations favor a more coherent PEM. The fact that an increase in the number of layers, deposited under high concentration conditions (i.e., on going from S/(1-PSS)(PAH-PSS)<sub>4</sub>PAH to S/(1-PSS)(PAH-PSS)<sub>7</sub>), leads to an increase in permeation selectivity further indicates that defects are present even in these more coherent films.<sup>13</sup>

Since an increase in the concentration of a polyelectrolyte also increases the ionic strength and screening capacity of a solution, it tends to shift the polymer's conformation from a rod-like toward a random coil structure, due to a decrease in charge repulsion between neighboring pendant ions. In an effort to separate conformation from conformational effects, we prepared films from 1 mM solutions

of PSS and PAH having reduced viscosities that matched those of the 15 mM solutions, using appropriate concentrations of NaCl.<sup>14</sup> It is well established that the reduced viscosity of a polymer (i.e., its specific viscosity divided by its concentration) is a function of its degree of polymerization and its conformation. Thus, the conformations of PSS and PAH in these 1 mM solutions with added NaCl, to a first approximation, can be made to match the conformations that exist in the 15 mM solutions without added NaCl. The fact that 14-monolayered films made from these NaCl-containing solutions have the same thickness (13.8 ± 1.0 nm, AFM) and similar barrier properties as the 14-monolayered films made from 15 mM PSS and PAH in the absence of NaCl (Table 1) implies that polyelectrolyte conformation plays a major role in determining the structure of these PEMs.

The combination of gas permeation selectivity and solution viscosity measurements, of the type reported herein, provides a simple yet powerful approach for gaining insight into defects in PEMs and the role that polyelectrolyte conformation plays in their formation. Studies currently in progress are aimed at gaining detailed insight into the nature of these defects and the mechanism by which they are formed. The results of these studies will be reported in due course.

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**Supporting Information Available:** Materials and Methods used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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