



ChemComm

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Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-06-2018-004550.R1
Article Type:	Communication

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## A Plug and Socket Approach For Tightening Polyelectrolyte Multilayers

Received 00th January 20xx,  
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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**A plug and socket approach for tightening polyelectrolyte multilayers is introduced based on the use pendant  $\beta$ -cyclodextrin groups. Prototypical multilayers derived from poly(sodium 4-styrene sulfonate) and  $\beta$ -cyclodextrin-containing poly(4-vinylbenzyltrimethylammonium chloride) are described. Evidence for tightened multilayers has been obtained from gas permeation, swelling and quartz crystal microbalance with dissipation (QCM-D) measurements.**

The fabrication of polyelectrolyte multilayers (PEMs) *via* the layer-by-layer deposition method continues to attract broad interest from a basic science and an applications standpoint.<sup>1-9</sup> The development of PEMs has been so extensive in recent years that the literature encompassing this area may well be described as vast. Our own interest in PEMs has focused, sharply, on their barrier properties, especially ones that are hyperthin; i.e., less than 100 nm in thickness.<sup>10-13</sup> In principle, such materials could prove useful as protective coatings or as high performance membranes for the separation of gases.<sup>14-18</sup>

In the present work we sought to test the feasibility of increasing the tightness of a PEM and, consequently, its barrier properties by incorporating  $\beta$ -cyclodextrin groups. Specifically, we hypothesized that host-guest interactions between a polycation and a polyanion would lead to enhanced affinity. In a sense, this may be viewed as a "plug and socket" approach for tightening PEMs (Fig.1). Although there have been several reports of cyclodextrin-containing PEMs, to the best of our knowledge, no attempt has yet been made to combine electrostatic affinity with host-guest interactions to increase membrane tightness.<sup>19</sup> Our choice

undergo host/guest complexation with poly(sodium-4-styrene sulfonate) (PSS).<sup>20</sup>

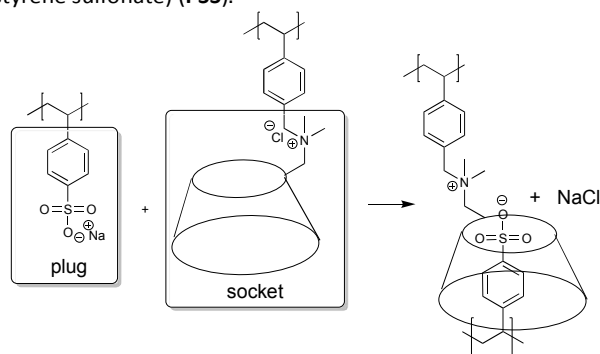


Fig.1 Stylized illustration showing the pairing of a pendant benzene sulfonate group (the "plug") with a pendant  $\beta$ -cyclodextrin cation (the "socket").

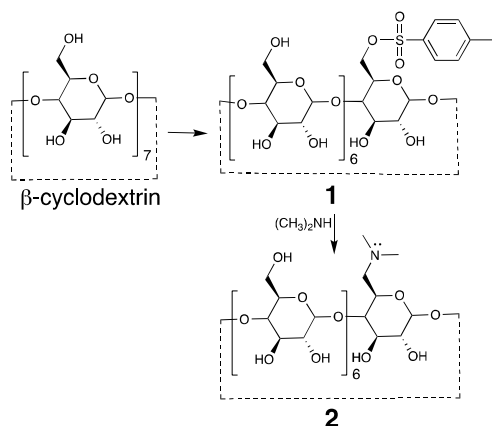
With this goal in mind, we first synthesized 6-O-monotosyl- $\beta$ -cyclodextrin, **1**, using established procedures.<sup>21</sup> Reaction of **1** with excess dimethylamine then afforded the corresponding 6-dimethylamino- $\beta$ -cyclodextrin, **2** (Scheme 1). Subsequent quaternization of poly(*p*-vinylbenzyl chloride) (PVBC, Mw 60 kDa) using limited quantities of **2**, followed by quaternization of the remaining chloromethyl groups with excess trimethylamine yielded a series of polycations containing varying mole percentages of  $\beta$ -cyclodextrin (Scheme 2).

### Scheme 1

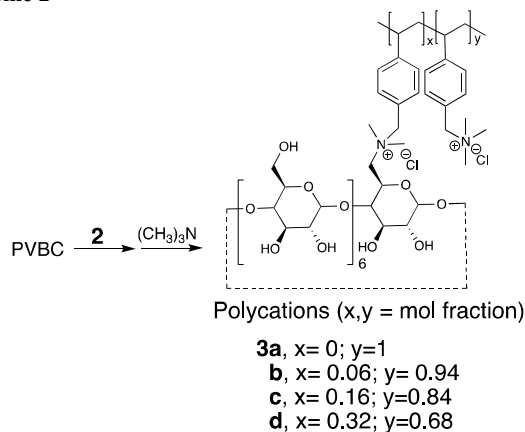
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Electronic Supplementary Information (ESI) available: Experimental procedures used for polymer synthesis, gas permeation, swelling and quartz crystal microbalance with dissipation (QCM-D) measurements. See DOI: 10.1039/x0xx00000x

of  $\beta$ -cyclodextrin for this work was based on its ability to



Scheme 2



Growth profiles that were produced by combining **3a**, **3b**, **3c** and **3d** with poly(sodium-4-styrene sulfonate) (PSS) (Mw 70 kDa) are shown in Fig. 2. In each case, linear growth was observed. In addition, the rate of growth was found to increase as the loading of  $\beta$ -cyclodextrin increased.

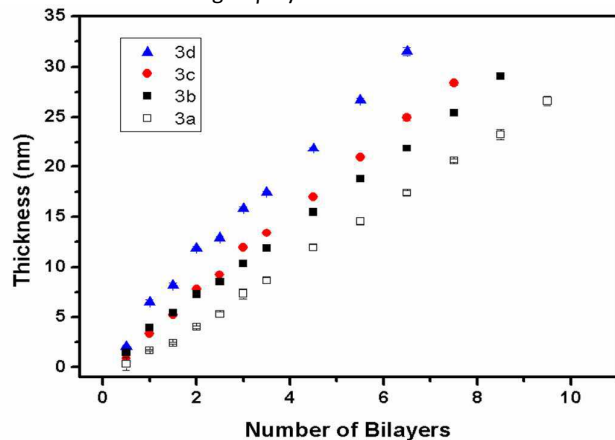


Fig. 2 Growth profiles observed for PEMs made from PSS and **3a**, **3b**, **3c** and **3d** deposited onto silicon wafers that were surface-modified with *n*-octadecyltrichlorosilane plus a layer of branched poly(ethyleneimine). Thicknesses that are shown were determined by ellipsometry. All odd numbers of bilayers refer to PSS being the last deposited monolayer.

To assess the barrier properties of these PEMs we measured their permeabilities with respect to H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>. Thus, each film was deposited onto supports made from poly[1-(trimethylsilyl)-1-propyne] (PTMSP) using procedures similar to those previously described.<sup>12</sup> Specific values of permeances ( $P/l$ ) were determined as a function of the number of deposited monolayers. Here,  $P/l = J/\Delta p$ , where  $P$  is the permeability coefficient for a given permeant,  $l$  is the thickness of the membrane,  $J$  is the flux of the permeant and  $\Delta p$  is the pressure gradient that is applied across the membrane. For purposes of comparison membrane thicknesses of  $21 \pm 1$  nm were used in all cases. Table 1 summarizes our principal findings. For each gas tested, higher barrier properties were found with greater amounts of cyclodextrin in the polycation, reflecting an increase in the tightness of the PEM. It should be noted, in this regard, that if the lumen of these  $\beta$ -cyclodextrins were left unfilled, an increase in permeability would be expected due to a net increase in the void volume within the PEM.

Table 1. Membrane permeances and selectivities<sup>a</sup>

PEM	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
----- <sup>b</sup>	710	1800	310	2.3	5.8
	690	1700	300	2.3	5.7
(PSS/ <b>3a</b> ) <sub>7.5</sub>	124	45	0.44	300	100
	131	49	0.48	250	100
(PSS/ <b>3b</b> ) <sub>6.5</sub>	72	40	0.54	130	74
	78	40	0.55	140	73
(PSS/ <b>3c</b> ) <sub>5.5</sub>	49	17	0.26	190	65
	45	16	0.26	170	62
(PSS/ <b>3d</b> ) <sub>4.5</sub>	42	11	0.25	170	40
	42	12	0.24	170	50

<sup>a</sup>Permeance values,  $10^6 P/l$  (cm<sup>3</sup>/cm<sup>2</sup>-s-cm Hg), were measured at ambient temperature where each value was calculated by dividing the observed flow rate by the area of the membrane (9.36 cm<sup>2</sup>) and the pressure gradient (40 psi) employed, using ca. 30  $\mu$ m thick PTMSP supports. All values are given in GPUs where 1 GPU =  $1 \times 10^{-6}$  (cm<sup>3</sup>/cm<sup>2</sup>-s-cm Hg). All measurements were made using a constant pressure apparatus. Average values were obtained from 5-10 independent measurements of the same sample; the error in each case was  $\pm 5\%$ . Duplicate membranes are reported in all cases. The estimated thickness of these PEMs were ca. 21, 22, 21 and 22 nm for membranes made from **3a**, **3b**, **3c** and **3d**, respectively. <sup>b</sup>PTMSP support with and without the LB anchor layer.

Two other independent measurements also revealed increased tightness due to the incorporation of  $\beta$ -cyclodextrin; i.e., swelling and quartz crystal microbalance with dissipation (QCM-D) measurements. Thus, continuous exposure of PEMs derived from **3a** and PSS to a stream of humidified N<sub>2</sub> resulted in an increase in film thickness due to hydration as revealed by ellipsometry (Fig.3). In sharp contrast, the thickness of an analogous PEM derived from **3d** and PSS was unaffected upon similar exposure to a humidified stream of N<sub>2</sub>.

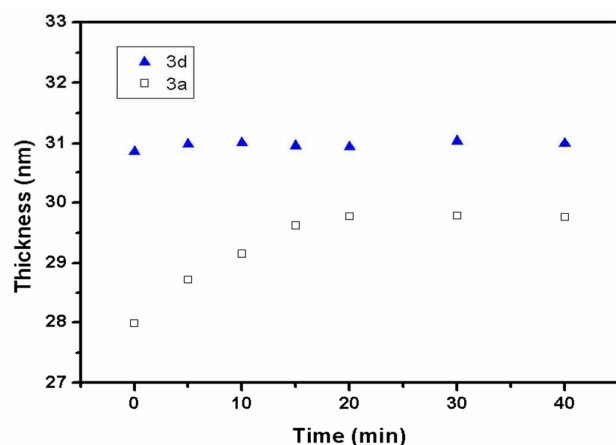


Fig.3 Apparent film thickness of PEMs made from PSS plus 3a or 3d upon exposure to a humidified stream of N<sub>2</sub> as a function of time.

Quartz crystal microbalance with dissipation monitoring (QCM-D) provides a means for measuring mass accumulation on a surface as well as viscoelastic properties of PEMs. Using deposition and washing procedures that were analogous to those used for ellipsometry and gas permeation measurements, QCM-D frequency responses and dissipation signals were measured as a function of time (Fig. 4a, Fig. S-1a). As expected, each injection of polyelectrolyte resulted in a QCM-D frequency that decreased, steadily, over a film growth of 6.5 bilayers. This reflects an accumulation of mass on the sensor surface and the gradual build-up of the PEM.

By modeling these PEMs as viscoelastic film using the Voigt-Voinova mechanical model, we determined film thicknesses, shear elastic moduli and viscosities.<sup>22</sup> Films that were grown to 6.5 bilayers from PSS and 3d showed slightly larger thicknesses ( $40.41 \pm 0.01$  nm) in their hydrated form as compared with ones made from PSS and 3a ( $37.63 \pm 0.01$  nm) (Fig. S-1b). Significantly, these PEMs exhibited markedly different shear elastic moduli and viscosities. In particular, those PEMs derived from PSS and 3d had a greater shear modulus and viscosity ( $441.3 \pm 1.4$  kPa and  $8.473 \pm 0.011$  mPa·s, respectively) as compared with PEMs derived from PSS and 3a ( $258.5 \pm 0.6$  kPa and  $5.189 \pm 0.005$  mPa·s, respectively) (Fig. 4b,c). These findings show that these  $\beta$ -cyclodextrin containing PEMs are stiffer and more viscous than ones that are devoid of the cyclodextrin, reflecting enhanced polycation-polyanion affinity even under hydrated conditions.

Taken together, the present findings show that the covalent attachment of  $\beta$ -cyclodextrin moieties along the backbone of a polycation can significantly enhance the polymer's affinity toward a polyanion in both the dry and hydrated state; the net result being a tighter assembly and increased barrier properties. For those applications of PEMs that rely on their barrier properties (e.g., as coatings for anticorrosion protection, drug protection, drug release, and cytoprotection), this plug and socket strategy represents a

fundamentally new approach that offers significant opportunities for further exploration.<sup>23-27</sup>

This work has been supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences under Award DE-FG02-05ER15720.

### Conflicts of interest

There are no conflicts to declare.

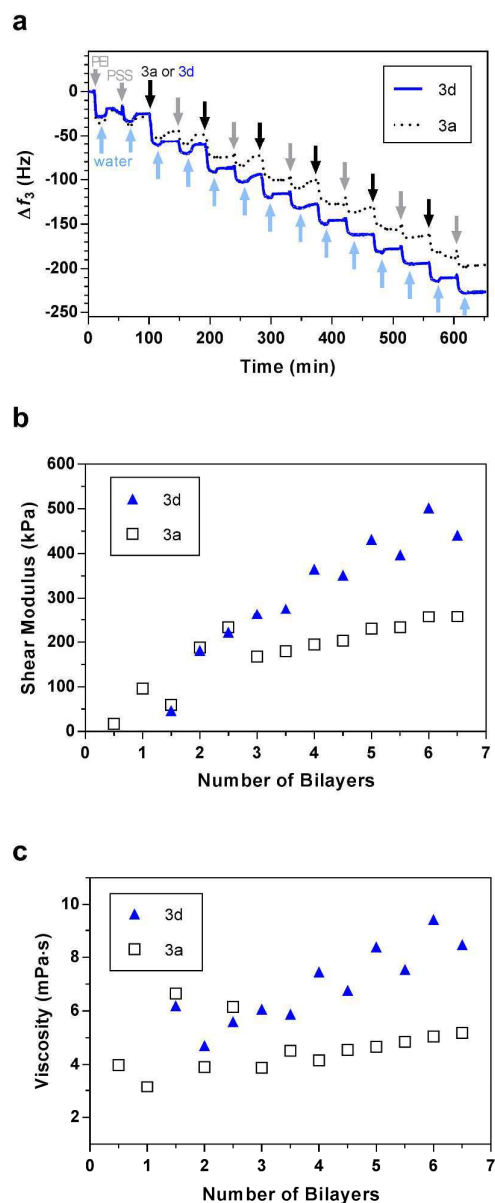


Fig.4 PEM films grown from PSS plus 3a (black dotted line) or 3d (blue solid line) in a QCM-D flowcell: (a) Frequency shifts (3<sup>rd</sup> harmonic) as a function of time where arrows indicate start of injections. After an initial anchor layer was deposited from branched poly(ethyleneimine) (PEI) and PSS, alternating injections

of **3a** or **3d** and **PSS** were made. The black arrows indicate the start of the polycation injections; the gray arrows are the start of the PSS injections. The blue arrows represent the start of the water washing. (**b** and **c**) Modeled shear elastic modulus and viscosity using **3a** or **3d**. Bilayer counting starts after the **PEI** layer has been deposited; i.e., half numbers refer to PSS as the last deposited layer and whole numbers refer to the polycation as the last deposited layer.

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