Layer-by-layer assembly of single-charged ions with a rigid polyampholyte†

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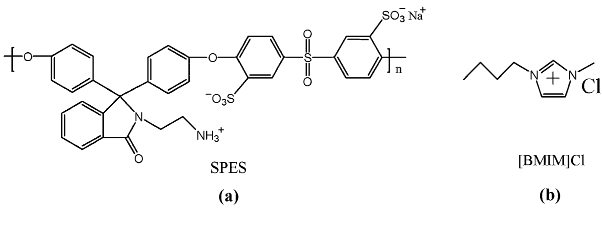
A novel method to produce multilayer films has been developed by layer-by-layer assembly of single-charged ions and a rigid polyampholyte containing unbalanced charges in each of its repeat units.

The layer-by-layer (LbL) assembly technique has attracted a great deal of attention in the last decade largely due to its simplicity and versatility.[1–5] The approach, based on electrostatic interactions between polyelectrolytes, has been extended to incorporation into multilayers of various other species, including biomacromolecules,[6–8] colloids,[9,10] dyes,[11,12] and inorganic nanoparticles,[13,14] to name a few. However, due to their easy extraction from films, incorporation of single-charged species into LbL films remains a challenge, even though there is an increasing need to assemble these species for various functional assemblies.[5,15] Recently, unconventional LbL methods involving more than one step in the assembly process have been developed for this purpose, where a polyelectrolyte was used as a carrier to form a complex with the single-charged molecules first in bulk, which was then assembled with a counter-polyelectrolyte.[15,16] Inspired by this work, we explored a different approach of direct LbL assembly of single-charged species with a polyampholyte. Recently, we reported the synthesis of a rigid charged polymer, sulfonated cardo poly(arylene ether sulfone) (SPES, Scheme 1), used as a membrane material in water treatment, which carries two negative charges and one positive charge in each repeat unit.[17] By taking advantage of the unbalanced charge located in the repeat unit of the polymer, we assembled this polymer directly with a single-charged species, 1-butyl-3-methylimidazolium chloride ($[BMIM]^+Cl^-$, Scheme 1), which is an ionic liquid, to construct a composite multilayer containing single-charged moieties.

Polyampholytes are polyelectrolytes that carry both positive and negative charges in the same chain. One class of polyampholyte is polyzwitterions, with one positive and one negative charge present in each repeat unit of the polymer.[18] These polymers exhibit some unusual properties in solution and at interfaces because of the intra- and intermolecular association of the positive and negative charges of the polymer chains.[19–23] The charge density can also affect the layer-by-layer assembly of polyzwitterions and the stability of the multilayer films.[24] In our case, in each structural unit of SPES, there are two sulfonic groups, which are negatively charged at $pH > 1$, and one ammonium group, which is positively charged at $pH < 10$, based on the pK_a values of these groups. It can be expected that at $pH > 10$ or $pH < 1$, the polymer would behave as a polyanion and a polycation, respectively. When all the ionic groups in SPES are charged, the polymer should exhibit different properties. First we studied the assembly of SPES with a typical polyanion, poly(styrene sulfonate) (PSS), and a typical polycation, poly(diallyldimethylammonium chloride) (PDDA). It has been reported that polyampholytes can adsorb to a surface that carries a charge of the same sign due to the interaction between the surface charges and the local charges of the opposite sign of the polyampholyte.[25,26] However, in the pH range of 1 ~ 12, we observed no multilayer formation between SPES and PSS. On the other hand, multilayers were easily fabricated *via* an LbL assembly process from SPES and PDDA in the same pH range (data in the ESI†). Unlike a normal polyampholyte where the positive and negative charges are located on different monomer units, for SPES, the two negative and one positive charge in the same and every repeat unit of the rigid polymer result in polyanion-like behavior.

We then assembled $[BMIM]^+$, a species carrying a single positive charge, with SPES, and the process was monitored by quartz crystal microgravimetry (QCM). Fig. 1a plots the QCM frequency shift, proportional to the mass of the layer deposited,[27] *vs.* the deposition cycle. As can be seen, the QCM frequency decreases regularly with the successive deposition of



Scheme 1 Molecular structure of SPES (a) and [BMIM]Cl (b).

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† Electronic supplementary information (ESI) available: Experimental details, QCM frequency shifts for alternating adsorptions of SPES and PDDA, UV–vis spectra of SPES–$[BMIM]^+$ multilayers with different numbers of bilayers deposited on quartz, AFM image of SPES–$[BMIM]^+$ multilayers, UV–vis spectra of a quartz substrate (primed with 2 PDDA–PSS bilayers) immersed in PSS and $[BMIM]^+$ solutions alternately for up to 5 cycles. See DOI: 10.1039/b801784k

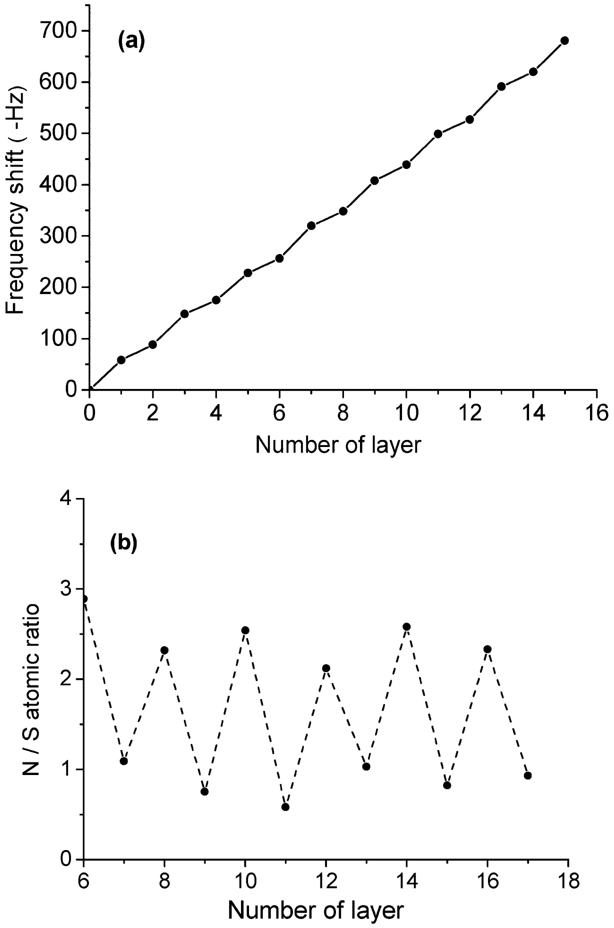


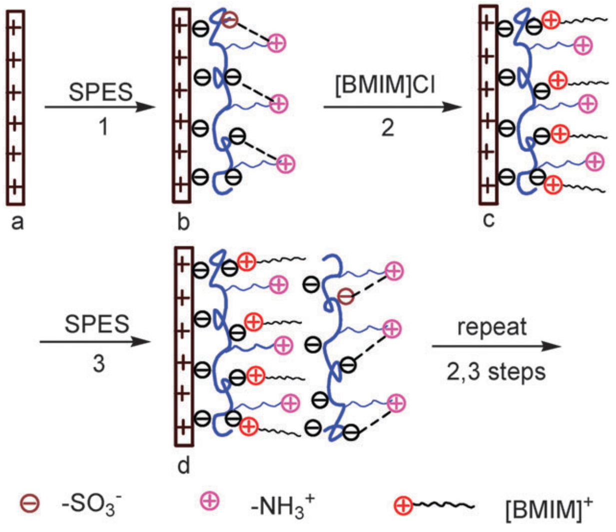
Fig. 1 (a) QCM frequency shifts for the alternating adsorptions of SPES and $[BMIM]^+$, and (b) surface atomic ratios for the multilayers obtained by XPS. The odd layers are SPES.

$[BMIM]^+$ and SPES "layers" on the substrate. The average frequency decrease for the deposition of one SPES layer and one $[BMIM]^+$ layer was 60 ± 7 Hz and 29 ± 2 Hz, respectively, corresponding to a layer thickness of about 2 and 1 nm, respectively, assuming a layer density of 1 g cm^{-3}. These numbers represent significant amounts of the polymer and the $[BMIM]^+$ cation assembled in each cycle. Actually, the QCM average frequency shift for each SPES–$[BMIM]^+$ deposition cycle was almost the same as that for SPES–PDDA. To further prove the alternating deposition of the polymer and the cation, the surface atomic composition of the assembled layers was monitored by X-ray photoelectron spectroscopy (XPS), and the surface nitrogen–sulfur ratio of the multilayer against the assembly step is plotted in Fig. 1b. The zigzag pattern of the N–S ratio clearly shows the surface composition change due to the alternating deposition of the SPES and $[BMIM]^+$ species. The multilayer growth was also verified by UV–Vis (ESI†). In addition, the surface morphology of the multilayers was assessed using atomic force microscopy (AFM), and the rms roughness of the multilayer surface was 6.3 nm (ESI†). These results demonstrate that the assembly between SPES and $[BMIM]^+$ can be repeated indefinitely, and continued growth of this multilayer is possible.

So far the SPES seemed to behave like a normal polyanion. However, there is an ammonium group in each SPES unit besides the sulfonate groups, which can interact with each other to form an inner salt. It was found that SPES is easily soluble in water at higher pH, and when the solution is acidified the polymer precipitates, an evidence of the inner salt formation. To better understand the assembly mechanism between SPES and $[BMIM]^+$, in particular the role of the ammonium group in the process, a control experiment was carried out. LbL assembly between $[BMIM]^+$ and PSS, which carries a sulfonate group in each of its repeat units, the same as the negatively charged groups in SPES, was attempted under various conditions. After the first PSS deposition on the positively charged substrate, no further deposition was detected (details in ESI†).

Based on these observations, we arrived at the assembly mechanism illustrated in Scheme 2. In aqueous solution, the ammonium and sulfonate in each repeat unit of the SPES form an inner salt, and the polymer adsorbs to a positively charged substrate *via* the electrostatic interaction between the substrate charges and the remaining free sulfonate groups in the SPES chains. When this assembled layer is in contact with the $[BMIM]^+$ solution, the $[BMIM]^+$ ion replaces the ammonium in the inner salt, because the concentration of the $[BMIM]^+$ ion is much higher in the solution than that of the ammonium, and also it is a softer base than the ammonium, and the metathesis favors the formation of $[BMIM]^+{\bullet}[R\text{-}SO_3]^-$. The surface of the assembly becomes positively charged due to the liberated ammonium groups, and the next cycle of SPES and $[BMIM]^+$ depositions can be realized. In addition, when the SPES–$[BMIM]^+$ assembly is in contact with the SPES solution again, the surface charges (ammonium groups) and the rigidity of the SPES chains prevent the access of the sulfonate groups in the incoming SPES in the solution to the assembled $[BMIM]^+$ ions, thus the extraction of the $[BMIM]^+$ ions into the solution phase is suppressed, and the assembly process can be sustained.

Furthermore, in a conventional electrostatic LbL process, the surface charge has to be reversed in each step through over-compensation of the original surface charges by the



Scheme 2 Assembly mechanism of the SPES–$[BMIM]^+$ multilayers.

deposited species, so that the next oppositely-charged species can adsorb.[1,5] In our case, the surface charges are generated *via* metathesis of an inner salt in the last assembled layer, *i.e.* the counter ions liberated from the previous layer by the incoming ions of the same sign are still chemically attached to the surface, making them available to charge the surface so that the next species of the opposite charge can adsorb.

In summary, we have demonstrated that using a rigid polyampholyte with unbalanced charges, a single-charged species can be directly incorporated into a multilayer film *via* an LbL electrostatic assembly technique. The extraction of the single-charged species in the assembled layers by polyelectrolyte solution can be effectively suppressed, and continuous growth of the multilayers can be realized. The assembly mechanism, however, is very different from that of conventional LbL assembly. The surface charges are generated *via* metathesis of an inner salt in the last assembled polyampholyte layer by the adsorbed single-charged ion rather than over-compensation of the previous surface charges. This work may provide a new approach to fabrication of functional assembly films.

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