

## Layer-by-layer Deposition of Ionomers with Lipophilic Ion-pairs Dissociated in Less-polar Media

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Two kinds of oppositely charged polystyrene ionomers bearing the bulky and lipophilic phosphazanium cation or diborateimidazolide anion that are soluble and dissociated partially into ions even in nonpolar solvents were prepared. Alternate complexes of them were fabricated in less-polar solvent, acetone, layer-by-layer onto a gold substrate and silica nanoparticles.

Layer-by-layer (LbL) technique is one of the most useful methods for the fabrication of various nanoscale functionalized thin films onto substrates due to controllability and easy accessibility.<sup>1</sup> The wide versatility of this method has permitted us to develop many composite materials from biomolecules,<sup>2</sup> delaminated layered inorganic clays,<sup>3</sup> and colloidal particles,<sup>4</sup> for various applications, such as proton conductive membranes,<sup>5</sup> drug delivery carriers,<sup>6</sup> and microfluidics devices.<sup>7</sup> From their beginning,<sup>8</sup> pairs of polyelectrolytes with opposite charges, such as poly(styrenesulfonate) (PSS) and polyacrylate (PA) for anionic polymers and poly(allylammonium) (PAH) and poly-(diallyl dimethylammonium) (PDA) for cationic polymers, have been predominately used as components for the LbL method due to the reliable Coulombic interaction between them by charge compensation and the release of low-molecular-weight counter ions.<sup>9</sup> They are all soluble in water due to the large number of hydrophilic ionic groups in the polymer chain, and easy dissociation of the ionic groups allows the formation of charged polymers and fabrication of LbL thin films. As the “nonaqueous working” solvents for LbL fabrication, formamide ( $\epsilon = 108$ )<sup>10</sup> and *N,N*-dimethylformamide (DMF,  $\epsilon = 36.7$ )<sup>11</sup> have been used, because these organic solvents have high polarity.

On the other hand, use of LbL technique in lower-dielectric or nonpolar media still remains rare, because the polyelectrolytes are generally less soluble and dissociation of the ionic groups is strongly suppressed due to strong electrostatic interactions. Indeed, only a few reports have documented the formation of LbL multilayers of poly(ethyleneimine) and poly(acrylonitrile-*co*-butadiene-*co*-acrylic acid) in dichloromethane ( $\epsilon = 8.9$ ) by in situ salt formation<sup>12</sup> and some liquid crystalline ionomers in a mixture of THF ( $\epsilon = 7.6$ ) or highly polar solvents.<sup>13</sup> However, in these reports, the dissociation of these polyelectrolytes into macroions remains unclear in these media, and it is unknown whether the LbL multilayers originate from the formation of ion pairs by exchange of their counter ions<sup>9</sup> or aggregation of the ion pairs by dipole–dipole interactions via the same formation mechanism of ionomer–polymer blends.<sup>14</sup> Therefore, we attempted to develop the precise molecular design of LbL multilayers in less-polar media by

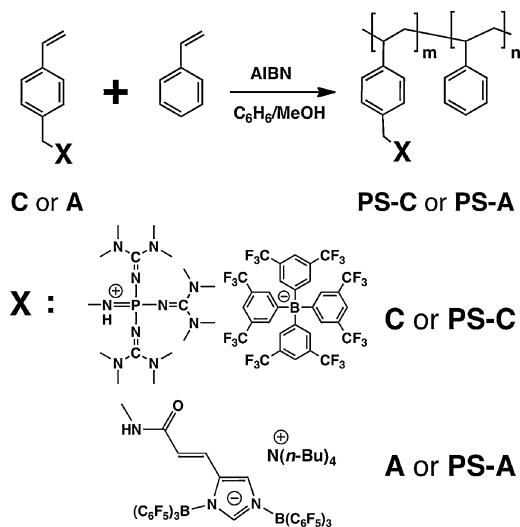
controlling the dissociation of the ion pairs in the ionic polymers in order to expand the applicability of the LbL technique to various hydrophobic ionomers or polyelectrolytes and fabricate LbL multilayers in nonprotic environments.

Our molecular design is based on the utility of bulky and lipophilic ion pairs consisting of the weakly coordinating diborateimidazolide anion or tetraarylborate anion and tetraalkylammonium cation or phosphazanium cation. These ions are known to be large in size and wrapped by hydrophobic groups, and some of their salts are known to be soluble and partially dissociated into ions in less- or nonpolar organic solvents, such as  $\text{CH}_2\text{Cl}_2$  and THF ( $\epsilon < 10$ ).<sup>15</sup> More recently, we reported that crosslinked poly(octadecylacrylate) gels bearing this bulky and lipophilic tetraalkylammonium tetraarylborate ion pair had an extraordinary high swelling ability due to dissociation of the ion pairs followed by extension of the polymer network due to electrostatic repulsion and osmotic pressure.<sup>16</sup> This result prompted us to explore the formation of LbL thin films from ionic polymers with the bulky and lipophilic cationic and anionic ion pairs in less-polar media, in which the Coulombic interaction is expected to be much stronger than those in highly polar media. In this report, we demonstrate the preparation of a pair of new ionic polymers based on polystyrene with bulky and lipophilic ion pairs that are able to dissociate even in less- or nonpolar organic solvents and the formation of LbL thin films by alternating immersions in acetone ( $\epsilon = 20$ ). The bulky phosphazanium cation<sup>17</sup> and weakly coordinating diborateimidazolide anion<sup>18</sup> were selected as ionic groups in the cationic polymer (**PS-C**) and anionic one (**PS-A**), respectively.

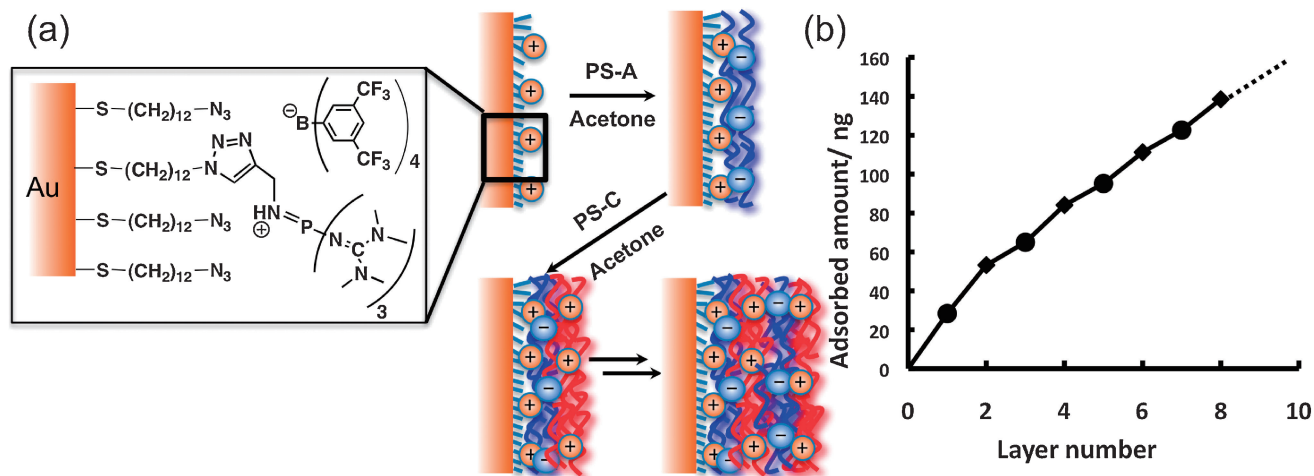
The cationic monomer **C** and anionic monomer **A** were prepared according to Schemes S1 and S2 in the Supporting Information.<sup>25</sup> Both of the monomers had sufficient solubility to measure their conductance in less- or nonpolar organic solvents, such as  $\text{CH}_2\text{Cl}_2$  and acetone, and the conductive measurements revealed that the ionic monomers acted as weak electrolytes in them (Figure S1<sup>25</sup>). We then performed the radical copolymerization of the ionic monomers and styrene initiated by AIBN. The feed ratios between the ionic monomer and styrene were fixed at 7/93, because too many ionic groups might induce the Manning condensation.<sup>19</sup> The resulting polymers were purified by repeated dialysis in acetone, whose structures are shown in Figure 1. The copolymerization ratios were confirmed by the <sup>1</sup>H NMR integration, and the ionic units were found to be 4.1 mol % in **PS-C** and 4.9 mol % in **PS-A** (Figures S2 and S3<sup>25</sup>). In the GPC analysis, the number-average molecular weight ( $M_n$ ) and polydispersity were  $M_n = 1.66 \times 10^4$ ,  $M_w/M_n = 2.12$  for **PS-C** and  $M_n = 1.80 \times 10^4$ ,  $M_w/M_n = 1.78$  for **PS-A**, respectively. AFM observations of the cast film from

an acetone solution indicated their expanded conformations in acetone due to the good compatibility to PS and relatively high dielectric constant for full ion dissociation (Figure S4<sup>25</sup>).

Fabrication of the LbL thin films from **PS-C** and **PS-A** onto the QCM substrate was then attempted (Figure 2a). The phosphazenic cations were first introduced on the QCM substrate by SAM formation of 12-azidododecane-1-thiol followed by a click reaction with **C-2** in the presence of CuBr as a catalyst (Scheme S3<sup>25</sup>). The conversion of the click reaction was monitored by the frequency shift of the QCM and found to be ca. 14% for the number of reactive sites on the QCM substrate. The resulting cationic QCM substrate was alternatively immersed in a 5 mg mL<sup>-1</sup> solution of anionic **PS-A** and cationic **PS-C** in pure acetone for 20 min. After each dip, the substrate was rinsed by repeated immersion into fresh acetone, and then the surface dried with air before measuring the resonance frequency shift. Figure 2b shows the dependence of the frequency shift on the self-assembly steps. This linear



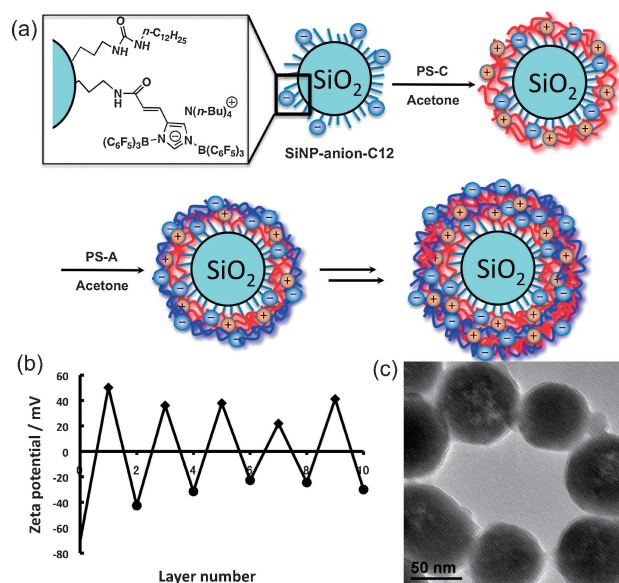
**Figure 1.** Chemical structures of cationic polymer (**PS-C**) and anionic one (**PS-A**).



**Figure 2.** (a) Schematic drawing of the LbL thin film of **PS-A** and **PS-C** onto the QCM substrate. (b) Changes of the adsorbed amount with QCM by the alternative deposition of **PS-A**: ● and **PS-C**: ◆.

decrease in frequency indicated that **PS-A** and **PS-C** were alternately adsorbed without any serious desorption. The amounts of adsorbed **PS-C** and **PS-A** in each step were estimated to be 14.8 and 12.2 ng cm<sup>-2</sup>, respectively. According to the density of the amorphous polystyrene,<sup>20</sup> the thickness of each layer indicated that each layer was close to a monolayer of **PS-C** or **PS-A**. Therefore, the decreased QCM frequency clearly supported the formation of a multilayered thin film on the QCM substrate.

The LbL method of these lipophilic polyelectrolytes was also applied to colloidal silica nanoparticles (Figure 3a). Silica nanoparticles (SiNPs) coated by the weakly coordinated diborateimidazolidine anion, **SiNP-anion-C12**, were prepared from amino-functionalized silica nanoparticles by treatment with



**Figure 3.** (a) Schematic drawing of deposition of **PS-C** and **PS-A** onto the **SiNP-anion-C12** by LbL method. (b) Changes of the  $\zeta$  potential after deposition of **PS-A**: ● and **PS-C**: ◆. (c) A TEM image of silica nanoparticles having ten layers in total.

**Im3** via a condensation reaction, followed by treatment with *n*-dodecyl isocyanate to quench any unreacted amines (Scheme S4<sup>25</sup>). The average diameter of the resulting silica particles was 97 nm from DLS, and the  $\zeta$  potential in ethanol was  $-70.7$  mV, which indicated that **SiNP-anion-C12** was composed of negatively charged particles (Figure S5<sup>25</sup>). Their spherical shapes and diameters were also confirmed by TEM (Figure S6<sup>25</sup>). We then tried the deposition of **PS-C** and **PS-A** on them. A 0.5 mL portion of acetone suspension of **SiNP-anion-C12** ( $2 \text{ mg mL}^{-1}$ ) was alternatively incubated in 0.5 mL of a **PS-C** or **PS-A** acetone solution ( $2 \text{ mg mL}^{-1}$ ) at room temperature for 20 min after gentle vibration. The coated SiNP was washed three times using the following steps; addition of fresh acetone, sonication for redispersion, and centrifugation for isolation. The  $\zeta$  potentials of the resulting SiNP shifted to ca.  $+37.5$  mV after deposition of the **PS-C** and to ca.  $-30.3$  mV after deposition of the **PS-A** as shown in Figure 3b. These alternate changes in the  $\zeta$  potentials were characteristic of the LbL method, which is strong evidence for the stepwise growth of the alternate layers. TEM observations performed for SiNP after the accumulation of ten layers are shown in Figure 3c. The formation of a thin film on the SiNP surface was observed due to an increase in their sizes from the starting **SiNP-anion-C12**. The change in the  $\zeta$  potential clearly indicated the formation of a multilayered thin film. However, we could not determine the thickness of the layers because some parts of the layers had peeled off due to sonication.

We demonstrated the molecular design of ionic polymers using the LbL method in less- or nonpolar organic media with the aid of two kinds of cationic and anionic polymers having lipophilic ion pairs able to dissociate to ions in them. These ionic polymers exhibited high solubility in many less-polar media due to the electrostatic repulsion among the polymer chains. In addition, compared to the conventional LbL method in water,<sup>21</sup> it is noteworthy that the content of the ionic groups in the polymer chain can be reduced to ca. 5 mol %. This could be caused by the stronger Coulombic interaction and longer Bjerrum length. The smaller content (5–10 mol %) of the ionic groups in the polymer chain strongly suggests that the composite films whose chemical and physical properties resemble the analogous nonionic homopolymers can be prepared by using LbL fabrication. With respect to the fabrication of the LbL thin films in less- or nonpolar organic media, our results propose a new tool for the LbL thin films by using an electrostatic interaction among the other interactions such as charge transfer,<sup>22</sup> hydrogen bonding,<sup>23</sup> and host–guest.<sup>24</sup> The utility of bulky and lipophilic ion pairs able to dissociate in them should allow one to fabricate various LbL thin films and other composite materials from various hydrophobic polymers. Moreover, designing ionic groups in the polyelectrolytes should change the solubility and dissociation ability in the media, which increases applications of the LbL thin films. The preparations of various polyelectrolytes or ionomers and applications of the LbL method in various media are currently under investigation.

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