Membrane Preparation of Polysulfonic Acid Complexes by Layer-by-Layer Adsorption

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Summary: The water-insoluble, thermostable and homogeneous polymer complex membrane formation of polysulfonic acids was examined by modifying the preparation conditions of the layer-by-layer adsorption method of the acid and base polymers. The complexation of poly(4-styrenesulfonic acid) in the 0.15 unit mM solution with poly(allylamine) gave a polymer complex membrane on a gold substrate in which one polymer layer was formed with a thickness of 1 nm. Properties including the proton conductivity of the membrane suggested possible applications of the polymer complex membrane.

Keywords: layer-by-layer adsorption; poly(4-styrenesulfonic acid); poly(allylamine); polyelectrolytes; polymer complex

Introduction

It is well known that mixing of the aqueous solutions of an acid polymer and a base polymer immediately yields a water-insoluble aggregate or a polymer complex of the acid polymer and the base polymer (respectively a polyanion and a polycation after the complexation).[1–6] However, the polymer complex is a fibrous material, which lacks molding capability and does not give a membrane or a flexible and self-standing film.

A preparative method for ultra-thin membranes of the polymer complexes had been proposed by Iler[7] and extended by Decher et al.[8,9] Alternating the adsorption of an acid polymer and a base polymer leads to the formation of a multi-layered assembly of the polymer complex with a nanometer thickness, based on the electrostatic attraction of oppositely charged polyelectrolytes. A substrate, of which the surface is modified to be cationic, is dipped in an acid polymer solution and rinsed, then dipped in a base polymer solution and rinsed. This technique is called the ''layer-by-layer adsorption'' method for the ultra-thin membrane formation of polymer complexes and is characterized by the following advantages: (i) the preparative procedure is simple; (ii) a large variety of water soluble polymers are applicable for the membrane formation; and (iii) the thickness is tunable by repeating the dipping, the polymer solution conditions, and so on. Many functional polymers have been assembled by this method to form membranes or surface-coatings by polymer complex formation, which were characterized by their bio-activity,[10] electro-conductivity,[11] electrochromic,[12] and light emitting properties.[13]

This paper describes the dense membrane formation of polymer complexes with both a nanometer thickness for each polymer layer and a submicrometer thickness for the total membrane, by carefully tuning the preparative conditions during the layer-by-layer adsorption experiment. In this study, we used polysulfonic acids as the acid polymer, i. e., poly(4-styrenesulfonic acid) (PSS) and poly(vinylsulfonic acid) (PVS). As the water-soluble base polymer, we selected poly(ethylenimine) (PEI) and poly(allylamine) (PAA). A gold plate modified with an amine derivative was utilized as the substrate on which the

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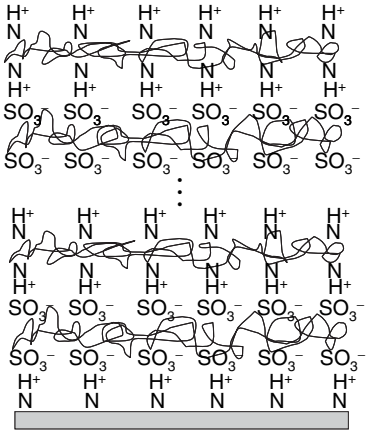

Figure 1.
Illustration of a polysulfonic acid complex membrane on a substrate.

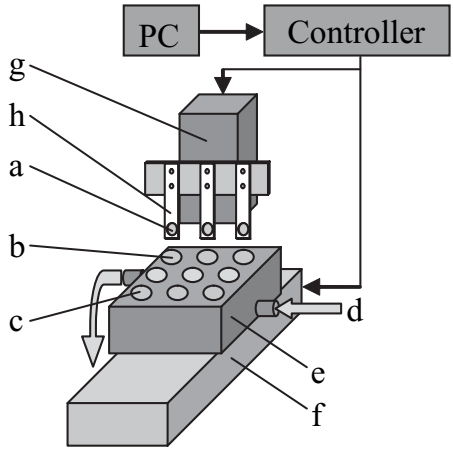

Figure 2.
Apparatus for the layer-by-layer adsorption experiment: a) Au electrodes ($\phi = 15$ mm), b) a vial ($\phi = 40 \times 75$ mm) for the acid polymer solution, c) a vial ($\phi = 40 \times 75$ mm) for the base polymer solution, d) distilled water flow for rinsing, e) a Teflon-coated working stage ($20 \times 20 \times 8.5$ cm), f) an auto X-stage, g) an auto Z-stage, and h) Teflon holders.

polymer complex was assembled by a layer-by-layer structure (Figure 1). The layer-by-layer complexation process was examined using a quartz crystal microbalance (QCM) to yield the polymer complex membrane in which the thickness of each polymer layer was approximately 1 nm. The membranes were characterized by the contact angle of a water droplet, and X-ray photoelectron and infrared reflection-absorption spectroscopies. The thermal property, water insolubility, and proton conductivity of the polymer complex membranes were also demonstrated.

Experimental

PSS (weight-average molecular weight $M_w = 7 \times 10^4$), PVS ($M_w = 7 \times 10^4$), and PEI ($M_w = 2.5 \times 10^4$) were purchased from the Aldrich Co. PAA ($M_w = 6 \times 10^4$) was from the Nitto Boseki Co., Japan. A gold substrate (gold plate, 1.8 cm^2) was cleaned by sonicating in H_2O_2/H_2SO_4 (1/3) and washing with distilled water. The cleaned gold substrate was modified by soaking in an aqueous 2-aminoethanethiol solution, followed by rinsing with distilled water.

The acid and base polymers were dissolved in distilled deionized water. The apparatus for automatically dipping the substrate in the polymer and rinse solution was designed and set up (Figure 2). The layer-by-layer adsorption experiment was carried out by dipping the gold plate in the acid polymer solution at a constant interval using this apparatus, following by rinsing with distilled water, then dipping the gold plate in the base polymer solution, following by rinsing with distilled water.

The QCM measurement was performed using a Seiko EG&G QCA922 microbalance. A quartz plate (7.9×7.9 mm) and the QCM (AT cut, 9 MHz) plate with a gold electrode (0.16 cm^2) were used as the substrates. An alternate adsorption experiment was carried out as described above. X-Ray photoelectron spectra were obtained using a JEOL JPS-9010TR spectrometer with an Al Kα line source. All spectra were calibrated with respect to the position of the carbon 1s peak at 284 eV. The infrared reflection-absorption spectra were recorded using a JEOL JIR-WINSPEC50 spectrometer with an IR-MAU200 microscope. Static contact angles of a droplet of water purified with Millipore Milli-Q on the modified substrate were measured using a

contact-angle meter with a CCD camera. The atomic force microscopic images were taken with a Nanoscope IIIa microscope (Digital Instruments, Inc.). Thermal analyses were performed over the temperature range from 25 to 400 °C for the thermogravimetry using a Rigaku TG8120 thermal analyzer at the heating rate of 10 K min^{-1} under nitrogen. The proton conductivity of the membranes was measured by an Eco Chemie Autolab PGSTAT30 AC impedance analyzer over the frequency range from 1 Hz to 1 MHz.

Results and Discussion

Effects of the polymer species, the polymer solution concentration, and the dipping time on the polymer adsorption on the substrate or the polymer complex formation were studied by measuring the mass change on the gold substrate using a quartz crystal microbalance (QCM) during the layer-by-layer adsorption process. The QCM frequency decrease is proportional to the mass increase on the substrate and provides a nanogram-sensitivity for the mass measurement.[14] In our experiment, the frequency decrease of 1 Hz corresponded to the mass increase of 0.9 ng on the substrate, based on Sauerbrey's equation.[14]

Figure 3 shows the examples of the layer-by-layer adsorption of four alternate acid–base pairs: PSS–PAA, PSS–PEI, PVS–PAA, and PVS–PEI with the aqueous solution concentration of 1.5 unit mM for the acid polymers and 3.0 unit mM for the base polymers. The concentration of the base polymers was twice that of the acid polymers to realize on equivalent and efficient adsorption of the base polymers. The mass changes were plotted vs. the number of adsorption cycles. The mass increase for the 10 bilayers of PSS–PAA was 250 ng mm^{-2}, which was significantly greater than that for the PSS–PEI (106), PVS–PAA (80), and PVS–PEI (20 ng mm^{-2}) adsorptions, respectively. The control experiment using only the PSS solution

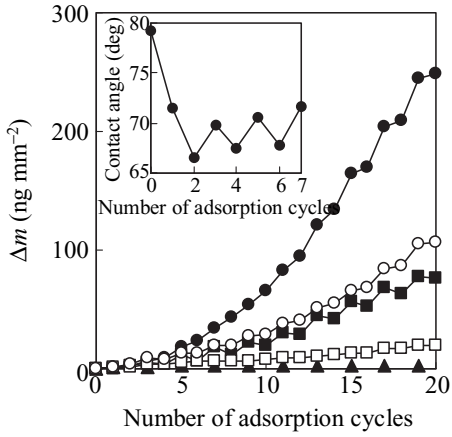

Figure 3.
Mass change (Δm) upon the PSS–PAA (•), PSS–PEI(○), PVS–PAA(■), PVS–PEI(□) alternate adsorption and the PSS (▲) adsorption with the 10-min washing. Odd number step: the PSS or PVS (1.5 unit mM) adsorption, even number step: the PAA or PEI (3.0 unit mM) adsorption. Inset: Contact angle of the PSS–PAA membrane surface vs. number of adsorption cycles.

did not have any mass increase (3 ng mm^{-2}). For the PSS–PAA layer-by-layer adsorption, the mass increase was observed during both the acid and base polymer adsorption steps, indicating an efficient layer-by-layer complexation. In contrast, other acid–base pairs such as PVS–PAA and PSS–PEI showed clear mass increases for the acid polymer adsorptions but not for the base polymer or rather a slight mass decrease for the base polymer adsorptions. For example, the mass decrease in PAA for the 10 bilayers of the PVS–PAA pair was -3.9 ng mm^{-2}. It is presumed that the base polymer extracts the loosely-adsorbed acid polymer from the polymer complex surface that causes the mass decrease.

The water contact angle of the surface on the PSS–PAA bilayered membrane was 67 and 70° for the PSS surface and the PAA surface, respectively (Inset of Figure 3). This result means that the gold substrate was modified by the acid or base polymer adsorbed layer-by-layer.

The average composition or molar and weight [base polymer]/[acid polymer] ratio of the layer-by-layer formed membranes is

Table 1.
Average composition of the 10 bilayered polymer complex membranes[a)]

	PSS–PAA	PSS–PEI	PVS–PAA	PVS–PEI
Molar [base]/[acid] ratio	1.1	0.54	–[b)]	0.80
Weight [base]/[acid] ratio	0.35	0.17	–	0.25

[a)] 20 cycles for the alternate adsorption for 15 min with the intermediate water-rinsing for 10 min.
[b)] Mass change for the PAA adsorption was negative.

summarized in Table 1. The composition was almost unity or almost the same amount of complexation of the acid and base polymer for the PSS–PAA membrane, while the base polymer composition or the adsorption of the base polymer was relatively or significantly low for the other acid–base pair complex membranes. This probably caused the deterioration of the dense membrane formation, which was suggested by the brittleness and turbidity of the membranes composed of other than the PSS–PAA pair. The layer-by-layer PSS–PAA complex formation gave both a nanometer ordered and an acid/base = momolar 1/1 layer structure and a mechanically tough membrane.

The mass change of the substrate during the adsorption process was not influenced by a dipping time longer than 1 min (Figure 4). *In-situ* QCM monitoring of the mass change revealed that the adsorption time course was almost completed within 5 min (Inset of Figure 4). This result was consistent with the previously reported kinetic study of the adsorption process of PSS and PAA.[15] A short dipping time could accelerate the preparation of the multi-layered complex membrane.

The mass increase in the PSS adsorption or one-layer of PSS for the PSS (1.5 unit mM)–PAA (3.0 unit mM) membrane was around 18 ng mm^{-2} (and 7 ng mm^{-2} for one-layer which was more than 10 times greater than the molecular weight of the single-molecular packing of PSS. The mass change increased with the molarity (molar concentration) of the aqueous PSS and PAA solution up to a 1.5 unit mM PSS molarity, and decreased to 24 ng mm^{-2} (1.9 and 0.5 ng mm^{-2} for one-layer of PSS and PAA, respectively) for the 0.15 unit mM PSS solution (Figure 5). This indicates a uniform monolayer formation with around a 1-nm thickness per bilayer for the PSS–PAA complexation.

The 3000 alternate adsorptions of PSS–PAA using the previously selected conditions produced a 3 μm thick membrane. This also supported the formation of the layer-by-layer polymer complex with the nm-thickness of one layer.

AFM images on the PSS–PAA membrane prepared on the substrate by the layer-by-layer method supported a smooth and pinhole-free membrane formation (Figure 6).

X-Ray photoelectron spectroscopy and infrared reflection-absorption spectroscopy

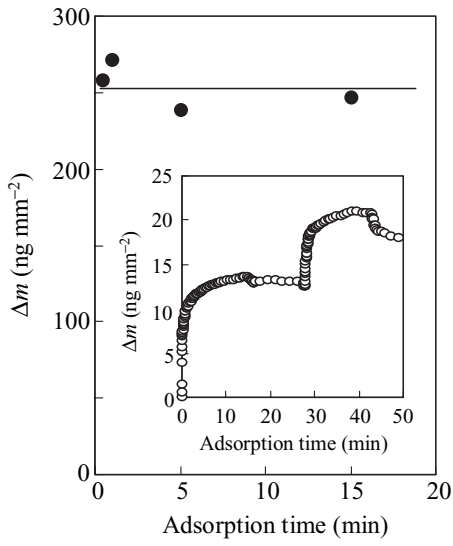

Figure 4.
Mass change (Δm) of the PSS (1.5 unit mM)–PAA (3.0 unit mM) 20 alternate adsorption with the 10-min water rinsing. Inset: *In-situ* QCM monitoring of Δm upon the PSS (1.5 unit mM)–PAA (3.0 unit mM) alternate adsorption with the 10-min water rinsing.

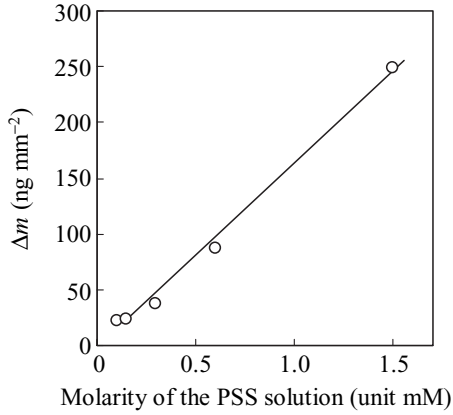

Figure 5.
Mass changes(Δm) upon the PSS–PAA 20 alternate adsorption with the 10-min water rinsing.

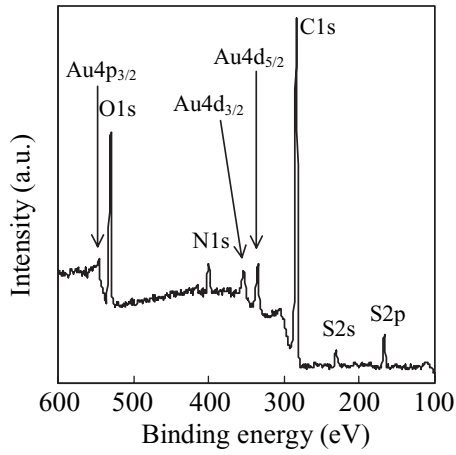

Figure 7.
X-Ray photoelectron spectroscopy spectrum of the PSS–PAA membrane prepared on the gold plate by the layer-by-layer method.

have been reported to be effective to analyze the surface composition of membranes prepared on Au substrates.[16] Figure 7 showed a survey scan of the 100 bilayered PSS–PAA membrane: This identified the presence of the following elements: C (1s, 284 eV), N (1s, 400 eV), O (1s, 530 eV), S (2s, 230 eV; 2p 167 eV), and Au ($4p_{3/2}$ 546 eV; $4d_{5/2}$ 335 eV; $4d_{3/2}$ 353 eV;$4f_{5/2}$ 84 eV; $4f_{3/2}$ 88 eV).[17] The peak of Na (1s, 1070 eV), Cl ($2p_{3/2}$, 200 eV), while other metal ions were not detected. Infrared reflection-absorption spectroscopy on the same PSS–PAA membrane showed the absorption ascribed to the sulfonate (1036 and 1212 cm^{-1}) and amine (1633, 3042, and 3448 cm^{-1}) groups. These analytical results supported a pure acid-base polymer complex formation on the substrate by the layer-by-layer adsorption.

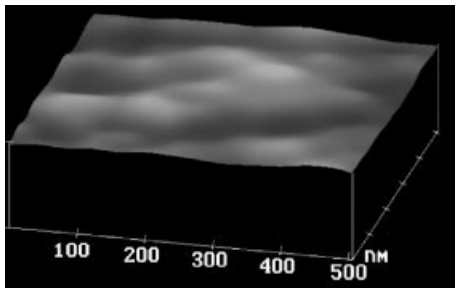

Figure 6.
AFM image on the PSS–PAA membrane prepared on the substrate by the layer-by-layer method.

Thermogravimetry on the PSS–PAA layer-by-layer membrane prepared on the Au substrate is shown in Figure 8. The thermal degradation temperature ($T_{d10\%}$) of the PSS–PAA membrane was 380 °C, and was 115 °C higher than that of PSS itself. The significantly high thermostability of the molecular-leveled and layer-by-layered polymer complex demonstrates an effective network formation through the polymer complex formation.

The PSS–PAA layer-by-layered complex membrane absorbed 35% of water after immersing in water. However, the membrane was completely insoluble in water even after the passage of one week,

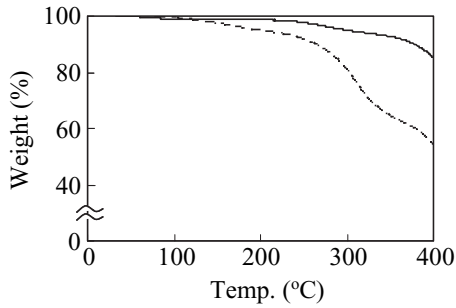

Figure 8.
TG curves of the PSS–PAA (solid line) membrane and PSS (dashed line) recorded under N_2 at a heating rate of 10 K min^{-1}.

while PSS immediately dissolved in the water. The water insolubility of the layer-by-layered polymer complex membrane could be considered to be realized through the molecular- and nm-based complexation between the acid and base polymer.

The PSS–PAA layer-by-layer membrane displayed an anisotropic, but very high proton conductivity of 10^{-3}–10^{-4} S cm^{-1} in the temperature range of 30–180 °C under dry conditions. The proton conductivity will be reported and discussed in our following paper.

Conclusion

The layer-by-layer adsorption method or the polymer complexation process of the acid and the base polymer successfully yielded a polymer complex membrane for the acid and base pair of PSS–PAA in which the thickness of each polymer layer was approximately 1 nm. The thermostability, water insolubility, and proton conductivity of the polymer complex membrane were evaluated in this study. These properties could open up a new function for the layer-by-layered, nm-sized, and molecular-based polymer complex membranes.

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