Layer-by-Layer Assembly of Aqueous Bilayer Membranes on Charged Surfaces

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Multilayer films of cationic bilayer membranes were prepared by means of alternate electrostatic adsorption with sodium poly(styrenesulfonate). Linear film growth was observed for at least 30 layers, as monitored by UV spectroscopy and quartz crystal microbalance (QCM). A regular multilayer film of cationic bilayer membrane with anionic bilayer membrane was similarly prepared.

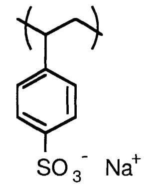
Layer-by-layer assembly of oppositely-charged linear polymers is a rapidly developing technique for the preparation of functional molecular films.[1] This methodology have been applied to a wide range of charged compounds such as proteins,[2] bolaform amphiphiles[3,4] and symmetrically-charged dye molecules.[5,6] Similar multilayer films of ionic amphiphiles have been prepared by combination of layer-by-layer assembly of polyelectrolytes and the LB technique[7] or by build-up of polyelectrolyte-supported monolayers at the air / water interface.[8] Aqueous bilayer membranes are formed by two-dimensional self-assembly of charged amphiphiles.[9] The macroionic nature of charged bilayer membranes appears to be used effectively for the alternate adsorption, though they are bound non-covalently. In order to extend the scope of the layer-by-layer assembly, we examined in this study alternate adsorption of cationic bilayer membranes, **1** and **2**, with either anionic poly(styrenesulfonate) (= PSS) or anionic bilayer membrane **3**. The azobenzene moiety in bilayer components has been used as a spectral probe of the molecular orientation.[10]

Poly(ethylenimine) was adsorbed on a quartz plate or on a silver-coated QCM resonator (9 MHz) as a positively-charged precursor layer using the previously reported method.[2] The charged surface was alternately immersed for 15 min in PSS solution (3.0 mg/ml, MW 88000) and in aqueous dispersion of amphiphile **1** (10 mM). After each adsorption procedure, the surface was rinsed for 1 min with pure water, dried with nitrogen gas. Figure 1a shows absorption spectra of **1**/ PSS film. The absorbance linearly increased during consecutive cycles of the assembly. The absorption peaks at 310 nm and 340 - 360 nm are attributed to the π-π^* transition along the long axis of azobenzene unit with different stacking modes.[10] Therefore, more than one patterns of bilayer assembly exist in the **1**/ PSS film. Figure 1b shows the frequency decrement of the QCM resonator at each adsorption step. The frequency shift of QCM is related to the film formation, as follows.[11,12]

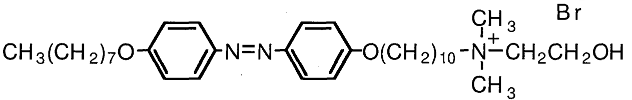
$$\Delta F(\mathrm{Hz}) = -1.832 \times 10^8 M(\mathrm{g}) / A(\mathrm{cm}^2) \quad \text{----} \ (1)$$

$$2d(\text{Å}) = -\Delta F(\mathrm{Hz}) / 1.832\, \rho\ (\mathrm{g/cm}^3) \quad \text{----} \ (2)$$

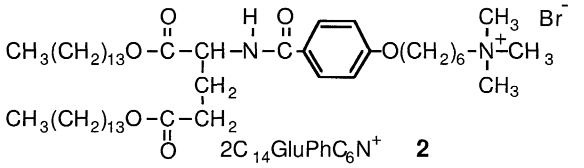
where A, d and ρ represent the surface area of resonator,



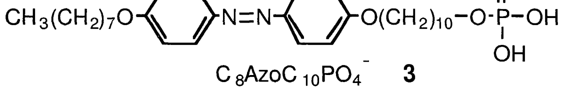
PSS



$C_8AzoC_{10}N^+$ **1**



$2C_{14}GluPhC_6N^+$ **2**



$C_8AzoC_{10}PO_4^-$ **3**

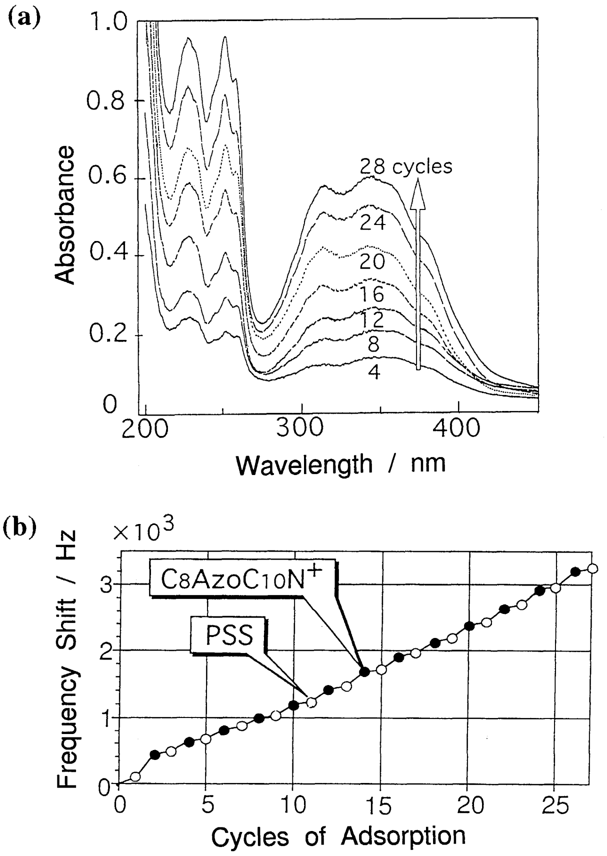


Figure 1. Assembly process of **1**/ PSS film based on UV absorption (a) and QCM frequency shift ($-\Delta F$) (b). (●) bilayer **1**, (○) PSS.

Table 1. Layer-by-layer assembly of bilayer membranes[a]

Components	Frequency Change (and Thickness[b])		Molar Ratio (cationic / anionic)
	1 or **2**	PSS or **3**	
1 / PSS	190±54 Hz (42±12 Å)	41±16 Hz (9± 4 Å)	1.5
2 / PSS	129±15 Hz (30± 6 Å)	28±13 Hz (6± 3 Å)	1.1
1 / **3**	147±21 Hz (32± 4 Å)	137±29 Hz[c] (30± 6 Å)	1.1

[a]Bilayer, 10 mM; PSS, 3.0 mg/ml; 20 ℃. [b]Thicknesses were calculated by the use of eq. (2) and densities.[13] [c]pH 9.2 (Tris buffer).

thickness and density of the adsorbed film, respectively. The frequency change is uniform in each adsorption cycle, with 190 ±54 Hz for component **1** and 41±16 Hz for PSS.[14] These ΔF values correspond to thicknesses of 42 and 9 Å, respectively, from eq. (2).[13] The former thickness is consistent with the long spacing (39 Å) of a multi-bilayer film of **1**[10,13] and indicates the formation of the interdigitated bilayer.

The assembly results are summarized in Table 1. The adsorption was uniform for at least 30 layers. The molar ratio of the two components in each adsorption cycle was estimated from eq. (1) and is included in Table 1. In the case of **1**/ PSS, the molar ratio (i.e., charge ratio of each component) is 3 : 2, indicating that the positive charge of bilayer component **1** cannot be neutralized by PSS alone. The surface charge density of the interdigitated bilayer of **1** may be much higher than the average charge density of PSS. In that case, the surface charge of the bilayer cannot be completely compensated by the linear PSS anion, and the bromide counterion may remain. Double-chain amphiphile **2** produce a smaller charge density at the bilayer surface, because of its greater molecular cross-section, and the molar ratio of the two component becomes unity. The combination of cationic and anionic bilayer membranes with the identical hydrophobic moieties (**1** and **3**) would naturally give an equimolar assembly. This presumption is supported by similar Δ F values for each component.

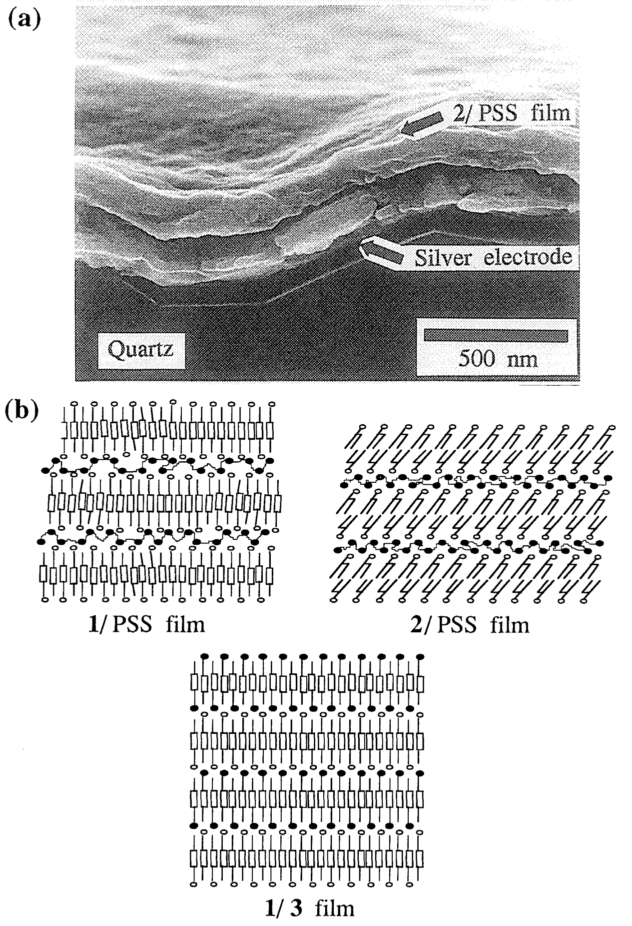


Figure 2. (a) Scanning electron micrograph of **2**/PSS film on the silver-coated resonator (×38000). (b) Schematic illustrations of layer-by-layer architectures of bilayer membranes.[15]

Figure 2a shows scanning electron micrograph of a **2**/ PSS film deposited onto the QCM resonator. The film has a constant thickness of 1200±200 Å on the undulating silver coating. The measured thickness agrees with the thickness estimated from the total frequency shift (5079 Hz) and the film density.[13] Schematic illustrations of these films were shown in Figure 2b.[15]

The present study demonstrates that the layer-by-layer assembly technique is applicable to charged bilayer membranes. Bolaform amphiphiles (i.e., symmetrically charged amphiphiles) are not required for the alternate assembly, since the self assembling nature of synthetic bilayer membranes give rise to new charged surfaces. Thus, the present approach may replace certain aspects of the Langmuir-Blodgett-Kuhn technique if appropriate self assembling amphiphiles are employed. Lvov et al.[7] reported the combination of polycation / polyanion assembly and the LB transfer for construction of superlattice films. The present results show that their two separate processes can be unified in a single approach.

References and Notes

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13 Densities of bilayers **1** and **3** were presumed to be 1.24 g/cm^3 from the crystallographic data of amphiphile **1** : G. Xu, K. Okuyama, and M. Shimomura, *Polym. Prepr. Jpn.*, **38**, 2407 (1989). The bulk density was directly measured for bilayer **2** (1.18±0.1 g/cm^3) and was estimated to be 1.2±0.1 g/cm^3 for PSS.[2]
14 The ΔF change increased for the bilayer **1** after a few days aging.
15 Packing structures of the bilayer component were assumed on the basis of the aggregation structures of its aqueous bilayer membrane.[9,10,13] **1** / PSS and **1** / **3** films were depicted in a parallel stacking mode of azobenzene units.