

# Design of a Molecular Bilayer Electrical Device; Dramatic Change of A.C. Impedance Parameters due to Phase Transition of Synthetic Lipid Bilayers on a Patterned Electrode under Air Atmosphere

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A molecular bilayer modified electrode device shows dramatic change of alternating current (a.c.) electrical parameters due to phase transition of the bilayers under an air atmosphere.

Synthetic bilayer membranes<sup>1</sup> possess fundamental physico-chemical properties similar to those of biomembranes and can be immobilized as molecular bilayer films by a simple casting method.<sup>2</sup> Immobilization of bilayer membranes facilitates their use as novel organic thin films with biomembrane-mimic properties. Our current target is to develop novel molecular electrode devices based on organized molecular assemblies. We have recently found unique alternating current (a.c.) impedance characteristics of multi-bilayer coated electrodes in aqueous systems.<sup>3</sup> In the present study, we report the a.c. electrical properties of synthetic lipid bilayer films immobilized on patterned electrodes under an air atmosphere.

A synthetic lipid,  $2C_{18}N^+PSS^-$ , (1),<sup>†</sup> which is water insoluble but retains fundamental bilayer characteristics,<sup>2b,3-5</sup> was prepared from dioctadecyldimethylammonium bromide ( $2C_{18}N^+2C_1Br^-$ ) and sodium poly(styrenesulphonate) (PSS) according to a method described earlier.<sup>2b,5</sup> Transparent thin lipid films were fabricated on patterned Au electrodes of interdigitated form by a simple casting method (Figure 1).<sup>‡</sup> A typical procedure was as follows. A solution of  $2C_{18}N^+PSS^-$  in chloroform (40  $\mu$ l) was spread on the electrodes. The solvent was evaporated at room temperature, and the electrodes were air-dried for one day at ambient temperature (20–30 °C). The amounts of lipid applied were 0.15 mg (electrodes I, II, and III). The modified electrodes (I and II) were then immersed in water (60 °C) for 1 h and air-dried for one day<sup>§</sup> at room temperature, to give electrodes I' and II'.<sup>¶</sup>

Electrical impedance, resistance, and capacitance were measured under an air atmosphere (75% relative humidity)<sup>||</sup> with an LCR meter (YHP, 4284A) assuming a parallel combination of a capacitor and a resistor [a.c. frequency 1 kHz, applied voltage 500 mV]. Figure 2(a) shows the temperature dependence of the electrical resistance of the non-water-annealed  $2C_{18}N^+PSS^-$  modified electrodes I, II, and III. These three electrodes were prepared under the same conditions, but the reproducibility was not good and hysteresis was observed for electrode I.

On the other hand, the resistance for the water-annealed modified electrodes I' and II' exhibited a dramatic temperature dependence [Figure 2(b)]. Below 45 °C, both electrodes

showed very high resistance ( $10^7$ – $10^8 \Omega$ ), but at close to 45 °C this decreased by four orders of magnitude. The two electrodes gave good reproducibility and there was only slight hysteresis (see electrode II'). Note that these data are in sharp contrast with the results for the non-water-annealed electrodes. The present bilayer electrode system is very stable; no change in electrical properties was observed even after 3 months.

Differential scanning calorimetry (DSC) (Seiko Denshi, SSC 560U) was used to examine the thermal transition of  $2C_{18}N^+PSS^-$  cast films under an air atmosphere.  $2C_{18}N^+PSS^-$  films were prepared in the DSC sample vessel by a similar method to that used to fabricate electrodes; *i.e.* casting with a chloroform solution of the lipid and air-drying for one day at room temperature (1.0 mg lipid). Two DSC samples were prepared, neither of which gave any peaks in a 10–70 °C scan. However, after water-annealing treatment as before, they clearly showed endothermic peaks at 42 °C (transition region 33–47 °C, transition enthalpy 7 kcal mol<sup>-1</sup>). The temperature ( $T_c$ ) at the peak maximum was very close to that of the  $2C_{18}N^+PSS^-$  film in an aqueous system ( $T_c$  45 °C) and of the corresponding water-dispersed bilayers of  $2C_{18}N^+2C_1Br^-$  ( $T_c$  45 °C).<sup>6</sup>

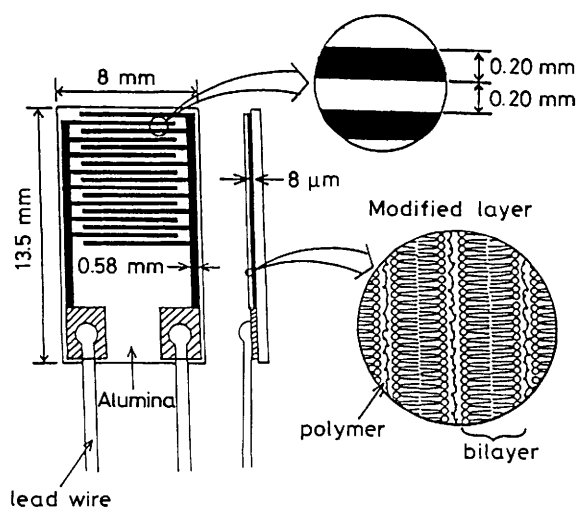
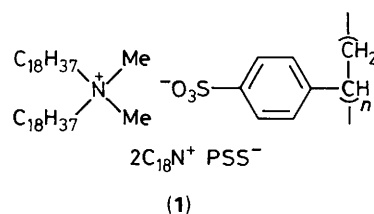


Figure 1. Schematic illustration of a patterned electrode modified with a polyion-complexed lipid bilayer film.

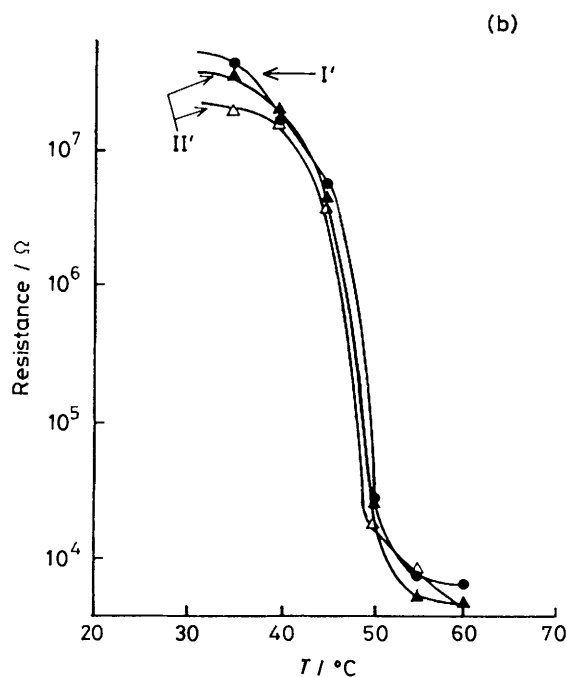
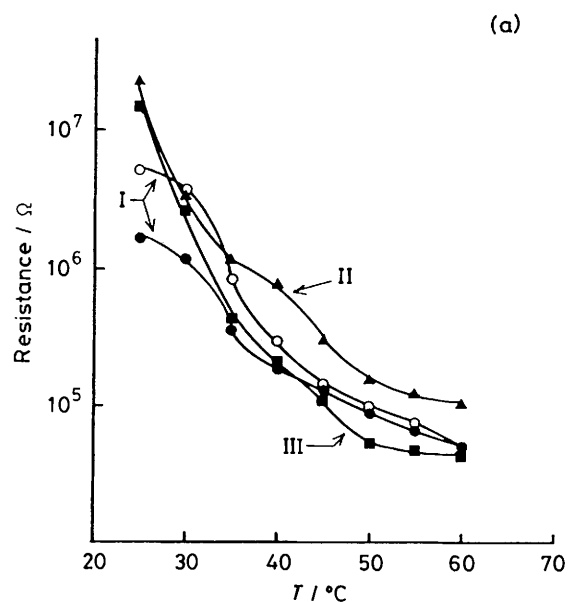
<sup>†</sup> The molar ratio of  $2C_{18}N^+/PSS^-$  evaluated from elemental analysis (C/S) is 1/1.17.

<sup>‡</sup> We propose that the lipid bilayer heads sit on the clean Au surface and the tails adsorb onto the hydrophobic (contaminated) parts of the gold electrode.

<sup>§</sup> We also prepared a sample air-dried for 1 week, which showed almost the same a.c. impedance response as the sample air-dried for 1 day.

<sup>¶</sup> Annealing in water had almost no influence on the elemental analyses.

<sup>||</sup> Saturated  $NaCl_{aq}$  was used to retain constant relative humidity ( $75 \pm 1\%$ ) at 25–60 °C.



**Figure 2.** Temperature dependence of electrical resistance for the non-water-annealed (a) and water-annealed (b)  $2C_{18}N^+PSS^-$  modified electrodes at 1 kHz under an air atmosphere (relative humidity,  $75 \pm 1\%$ ). Cooling cycles  $\circ$  and  $\triangle$ ; heating cycles  $\bullet$ ,  $\blacktriangle$ , and  $\blacksquare$ . Applied voltage, 500 mV.

Thus the water-annealed films retain typical bilayer characteristics (phase transition) even under an air atmosphere and it is apparent that this dramatic temperature dependence of the resistance of the modified electrodes is derived from the phase transition of the bilayer films.

The steep change in resistance near  $T_c$  can be attributed to the increase in ionic conductivity, which is due to the enhancement of mobility of protons and halide ions (the  $2C_{18}N^+PSS^-$  film is contaminated with a small amount of  $Br^-$  ions<sup>11</sup>). The effect of phase transitions on ionic conductivity for solid ammonium amphiphiles has been reported by Aoki *et al.*<sup>7</sup> and Imamura *et al.*<sup>8</sup>

The electrical capacitance for the water-annealed modified electrode also showed dramatic temperature dependence: *i.e.*  $\sim 10^{-5} \mu F$  at temperatures below  $45^\circ C$  and  $10^{-2} \mu F$  at  $50-60^\circ C$ , at 1 kHz. The non-annealed electrode showed no such temperature dependence. Further details, including analyses of the molecular mechanism for impedance and capacitance responses of the lipid films will be published in a following paper.

In conclusion, we have found dramatic  $T_c$  dependence of a.c. parameters for the bilayer-modified electrode device. This is the first example of transduction of the fundamental bilayer characteristics (phase transition) to electrical signals under an air atmosphere using a simple electrode system. These findings should be applicable to the development of functional molecular electrode devices based on self-organized bilayer assemblies.

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