Anisotropy of Ionic Conducting Langmuir–Blodgett Films composed of a Poly(oxyethylene)-based Amphiphile

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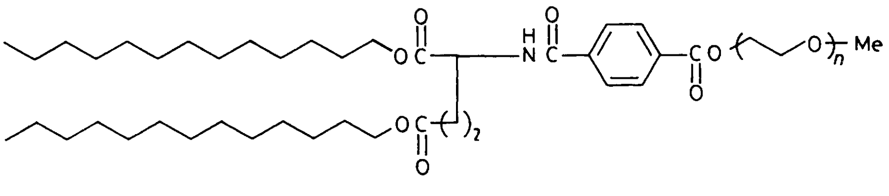
A Langmuir–Blodgett film composed of a poly(oxyethylene)-based double-chain amphiphile–$LiClO_4$ complex showed an extremely high ionic-conduction anisotropy owing to its unusual structural properties.

Since the discovery of fast alkali metal ion conductivity in polymer salt complexes,[1] researchers have been avidly seeking a solid polymeric electrolyte. The Langmuir–Blodgett (LB) technique is a method for the preparation of ultrathin ordered multilayer films of organic molecules,[2] and electrically conducting LB films[2—5] provide an important application in this field. Few reports have appeared, however, on ionic conducting ordered films. Aoki and co-workers[5] reported that cast bilayer films prepared from charged bilayer-forming amphiphiles showed ionic conductivity with a conduction anisotropy, $\sigma_{\parallel}$ (parallel to the film plane)/$\sigma_{\perp}$ (perpendicular) of 10^2. Poly(oxyethylene)–Li^+ systems have been studied most extensively as typical solid polymeric electrolytes. We now report the first preparation of a Li^+ conducting LB film and an ordered cast film composed of poly(oxyethylene)-based solid polymeric electrolyte and the high conduction anisotropy based on the ordered structures.

We employed the hitherto unknown poly(oxyethylene)-



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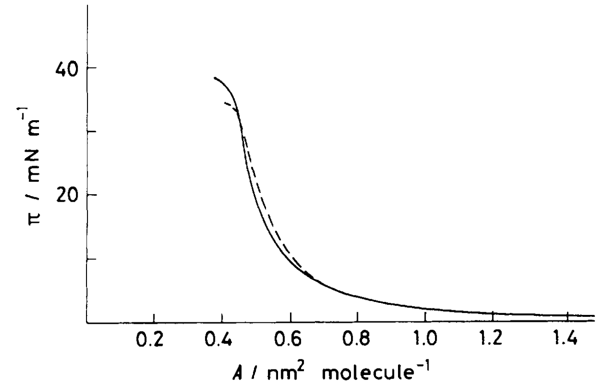

Figure 1. Surface pressure (π)-area (A) isotherms of pure (**1**) (– – –) and (**1**)-Li$^+$ complex (———) on pure water at 20 °C.

Table 1. Ionic conductivities of ordered thin films at 24 °C.[a]

Film	Conductivity/S cm^{-1}		
	$\sigma_{\parallel}$[b]	$\sigma_{\perp}$[c]	$\sigma_{\parallel}/\sigma_{\perp}$
Cast	6.9×10^{-8}	2.2×10^{-11}	3.1×10^{3}
LB (10 layers)	3.4×10^{-6}	1.6×10^{-13}	2.1×10^{7}

[a] O/Li ratio 4 : 1. [b] Ionic conductivity parallel to the film plane. [c] Ionic conductivity perpendicular to the film plane.

based amphiphile (**1**)†–LiClO$_4$ complex as a solid polymeric electrolyte, which is expected to form spontaneously an ordered bilayer structure in cast films owing to the similarity of the molecular structure to that of typical bilayer-forming amphiphiles.[6] Cast films were prepared from tetrahydrofuran (THF)–dioxane–water (2 : 6 : 3 v/v) containing the required amounts of (**1**) and LiClO$_4$. Differential scanning calorimetry (DSC) for the cast film of (**1**) without LiClO$_4$ gave an endothermic peak at 63 °C due to the crystal-to-liquid crystal phase transition of the ordered bilayer structures. The cast film of the (**1**)–LiClO$_4$ complex {[oxyethylene unit]/[LiClO$_4$], O/Li, = 4} also gave a phase transition temperature of 59 °C in DSC, which was slightly lower than that of the pure (**1**) cast film. These imply that the ordered bilayer structure remains in cast films even after complexation with LiClO$_4$.

Spreading experiments of the amphiphiles were performed on a microprocessor-controlled film balance (San-esu Keisoku Co., Ltd., FSD-20). Amphiphiles were spread from ethanol–benzene (1 : 9 v/v), with concentrations of the spreading solutions of ~1.0 mg ml^{-1}. Figure 1 shows the surface pressure (π)–area (A) isotherms of pure (**1**) and (**1**)–Li$^+$ complex (O/Li = 4)‡ on Milli-Q water (Millipore Co.) at 20 °C. Both monolayers of (**1**) and (**1**)–Li$^+$ complex produced condensed films with a collapse pressure of *ca.* 35 mN m^{-1}. Extrapolation of the solidus line of the condensed phase to zero pressure gave molecular areas of 0.53 nm^2 molecule^{-1} for (**1**) and 0.50 nm^2 molecule^{-1} for (**1**)–Li$^+$ complex. These values are

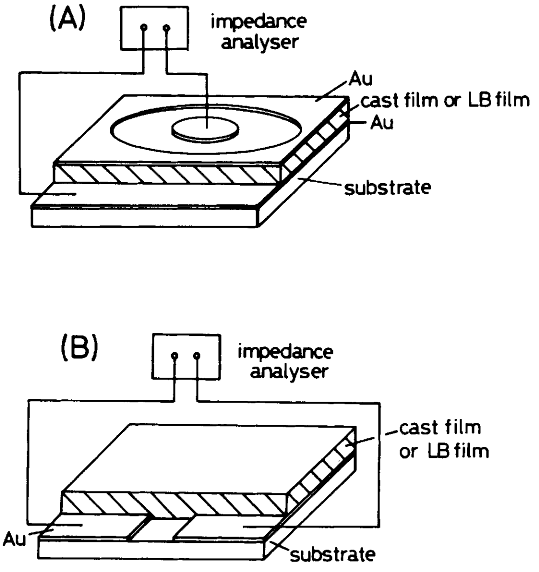

Figure 2. Setup for ionic conductance measurements: (A) perpendicular and (B) parallel to the film plane.

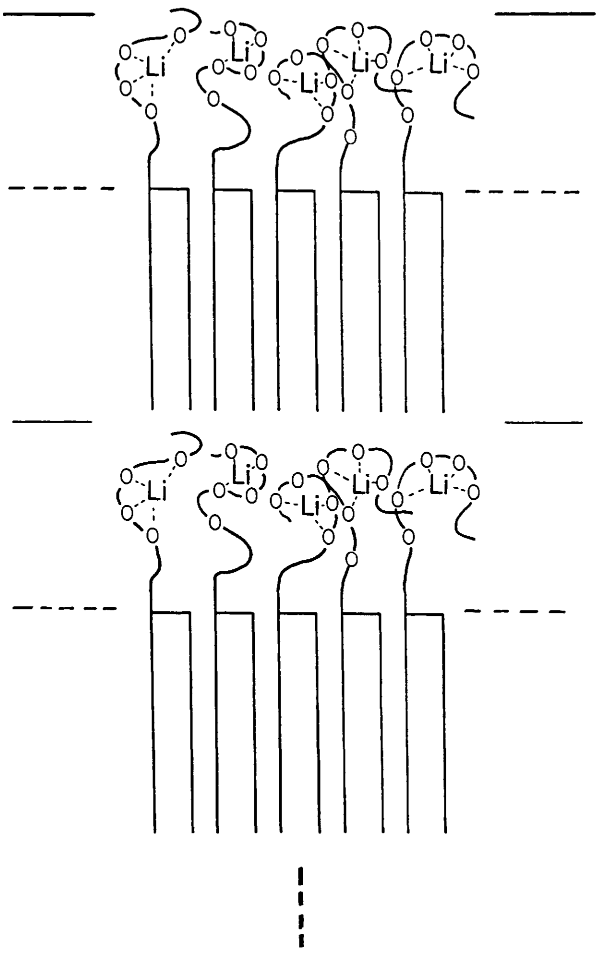

Figure 3. Schematic illustration of the LB film with an ordered alternating structure composed of ionic conductive and insulating layers.

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† Compound (**1**) was prepared as follows. Dioctadecyl L-glutamate[6] was treated with a large excess of terephthaloyl chloride, and then with MeO-terminated poly(oxyethylene) (average degree of polymerization 10; Japan Catalytic Chemical Industry Co., Ltd.) after removal of the unreacted terephthaloyl chloride; yield 30%. The structure of the product was confirmed by NMR spectra and GPC. The details of preparation have been described elsewhere.[7]

‡ The (**1**)–LiClO$_4$ complex was prepared by mixing (**1**) and LiClO$_4$ ([oxyethylene unit]/[LiClO$_4$], 4 : 1 molar ratio) in ethanol.

somewhat larger than the cross section (*ca.* 0.40 nm^2) of the vertically oriented two hydrocarbon chains.

Deposition of (**1**)–Li^+ monolayer onto a quartz plate and an Au electrode§ (prepared by evaporation of gold onto an alumina plate) was examined at a surface pressure of 25 $mN\ m^{-1}$ using the LB technique. In the first down-stroke the monolayer could not be deposited, but in a subsequent stroke the monolayer was transferred in a Z-type deposition. The transfer ratios were found to be 1.00 ± 0.06 and 0.95 ± 0.08 for the quartz plate and the Au electrode, respectively. The UV absorption spectra of the deposited quartz plate supported the formation of a multilayer. The absorbance at 257 nm, which corresponds to the phenyl group of (**1**), was proportional to the number of deposited layers.

Conductivity measurements were made on two types of electrodes as shown in Figure 2, (A): the conductivity perpendicular to the film plane ($\sigma_\perp$); (B): the conductivity parallel to the film plane ($\sigma_\parallel$). Impedance measurements were made from 10 Hz to 10 MHz by using a computer-controlled Hewlett Packard 4192A impedance analyser. Data for the conductivity (σ) at 24 °C for the cast film (film thickness: 20 μm) and the LB film with 10 layers of (**1**)–Li^+ complex monolayer are summarized in Table 1. When conductivities of the cast and LB films without Li^+ were measured, the values of $\sigma_\parallel$ were found to be below 10^{-14} S cm^{-1}. Thus, the conductivities of (**1**)–Li^+ complexed films should be ionic. In the cast film, a conduction anisotropy, $\sigma_\parallel/\sigma_\perp$, of 3.1×10^3 was observed. This is due to the presence of an ionic conductive layer composed of poly(oxyethylene)–Li^+ complex and an insulating layer of alkyl chains based on the oriented film structure. Further amplification of this conduction anisotropy was observed in the LB film; the $\sigma_\parallel$ value increased and the $\sigma_\perp$ value decreased by a factor of *ca.* 10^2 compared with those for the cast film, and the conduction anisotropy surprisingly reached the value of 2.0×10^7.

In conclusion, anisotropy on ionic conduction was observed in the cast film and in the LB film composed of poly(oxyethylene)-based amphiphile–Li^+ complex. In particular, the LB film showed an extremely high conduction anisotropy, reflecting the ordered alternating structure which consists of ionic conductive layers and insulating layers as shown in Figure 3.

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§ The Au electrode was estimated to have a relatively hydrophilic surface, with a surface energy of 50 $mN\ m^{-1}$ by contact angle measurements of water and CH_2I_2 at 20 °C.

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