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A Multi-layered Film of a Two-Dimensionally Crosslinked Acrylate Polymer

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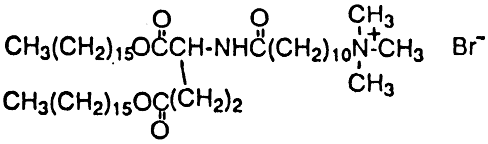
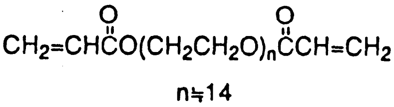
A multilayered film of a two-dimensionally cross-linked polymer of oligoethylene glycol bis-acrylate was prepared by using a cast film of an ammonium bilayer membrane as molecular template.

It has been shown that self-supporting, multilayered films are obtainable by casting of aqueous synthetic bilayer dispersions on solid substrates.[1-6] The highly-regular structure of these cast films is useful for producing macroscopic anisotropy of functional units.[7] We used this structural characteristics to prepare novel two-dimensionally cross-linked polymers.



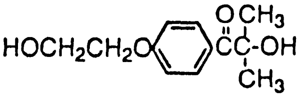
$$\begin{array}{l} CH_3(CH_2)_{15}O\overset{O}{\overset{\|}{C}}CH\text{-}NH\overset{O}{\overset{\|}{C}}(CH_2)_{10}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_3\ \ Br^- \\ CH_3(CH_2)_{15}O\underset{O}{\underset{\|}{C}}(CH_2)_2 \end{array}$$

1



$$CH_2{=}CH\overset{O}{\overset{\|}{C}}O(CH_2CH_2O)_n\overset{O}{\overset{\|}{C}}CH{=}CH_2 \quad n \fallingdotseq 14$$

2



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Bilayer-forming ammonium amphiphile 1 was prepared in these laboratories and identified by IR and NMR spectra and by elemental analyses. It was dispersed in water by sonication (15 mM), and an equimolar amount of monomer 2 (Shin-Nakamura Chemical) and photoinitiator 3 (Merck, 2 mol% of the monomer) were added. The mixture was cast on a fluorocarbon membrane filter for 48 h at 25 °C and 60% relative humidity, and the resulting transparent film was subjected to polymerization by irradiating for 90 s at room temperature with a ultra-high pressure Hg lamp (Ushio, Model UI-501C) at a 46-cm distance. A flexible composite film was thus obtained.

Figure 1 compares X-ray diffraction patterns (Rigaku Denki, Rotaflex, CuKα) of a single-component cast film of 1 and a composite cast film of the equimolar mixture. The cast films were cut into small pieces and X-ray was irradiated toward the edge of the vertically-positioned, stacked pieces. It is clear that highly regular structures are maintained in these films. In particular, the equatorial diffraction patterns in the small angle region indicate the presence of regular multilayers parallel to the film plane, as have been observed in other cast films.[2] The equatorial diffraction patterns were examined more carefully by the reflection method, as shown in Fig. 2. A long spacing of 6.0 nm is found up to the 10th order in Fig. 2a. Since the extended molecular length of amphiphile 1 is 4.3 nm as

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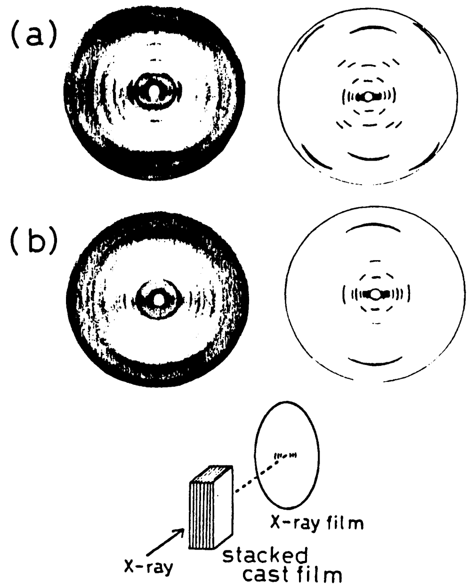

Fig. 1. X-Ray diffraction patterns of cast films. The X-ray beam was directed parallel to the film plane. (a) stacked cast film of **1**; (b) stacked cast film of an equimolar mixture of **1** and **2** (after polymerization)

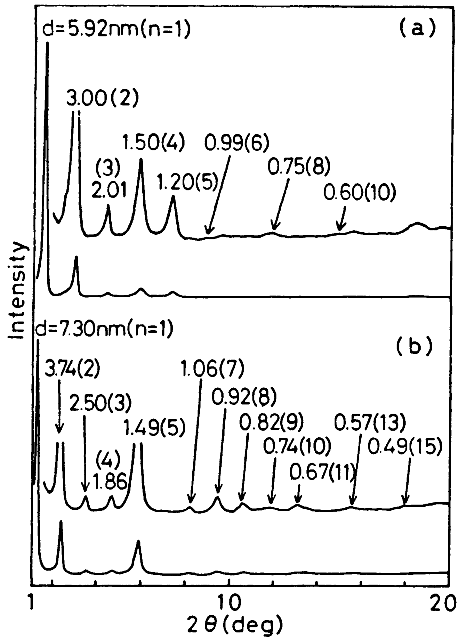

Fig. 2. X-Ray diffraction patterns obtained by the reflection method. (a) cast film of **1**; (b) composite cast film (after polymerization). The observed spacings and their orders of diffraction are given.

estimated from the Corey-Pauling-Koltan model, the observed long spacing suggests that the molecular axis of the bilayer component is considerably tilted against the film plane. When the cast film contains an equimolar amount of the photoirradiated monomer, a long spacing of 7.4 nm is observed up to the 15th order (Fig. 2b). The intensity and sharpness of the diffraction peaks are very close between the two cast films. Therefore, the regular multi-bilayer structure is maintained even after polymerization. Further evidence for this conclusion was obtained by differential scanning calorimetry (DSC ; Seiko Instruments, DSC 100). As shown in Fig. 3, an aqueous bilayer dispersion of **1** gives a DSC peak due to the gel-to-liquid crystal phase transition at 55 °C. This peak shifts to 67 °C with the corresponding cast film. A virtually identical peak is observed upon polymerization of the incorporated monomer in the composite film. All these data establish that monomer incorporation and the subsequent photopolymerization did not disturb the regular chain packing in the original cast film. The polymerization must, therefore, proceed essentially within the two-dimensional interlayer space.

The polymer/multibilayer composite film was subsequently immersed in methanol for 3 h in order to remove the amphiphile component. The remaining clear film is self-supporting (see Fig. 4a) and shows an IR spectrum that is identical with a bulk-polymerized sample of **2** ; the δ_{CH} and γ_{CH} vibrations of the vinyl group are absent. Elemental analysis of the extracted film also indicates complete removal of the amphiphile.[8] Its scanning electron micrograph (Fig. 4b ; Akashi Seisakusho, ISI-DS130) proves the presence of a multi-layered structure with one layer thickness of 50-100 nm. These values are much larger than the thickness of the inter-bilayer space (less than 4 nm) which is estimated from the X-ray diffraction data. It is

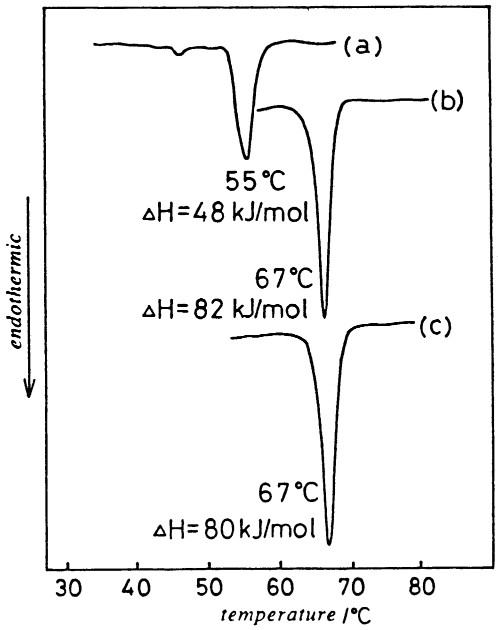

Fig. 3. DSC thermograms of the bilayer of 1. (a) aqueous dispersion(10 mM); (b) cast film of 1; (c) composite cast film (after polymerization).

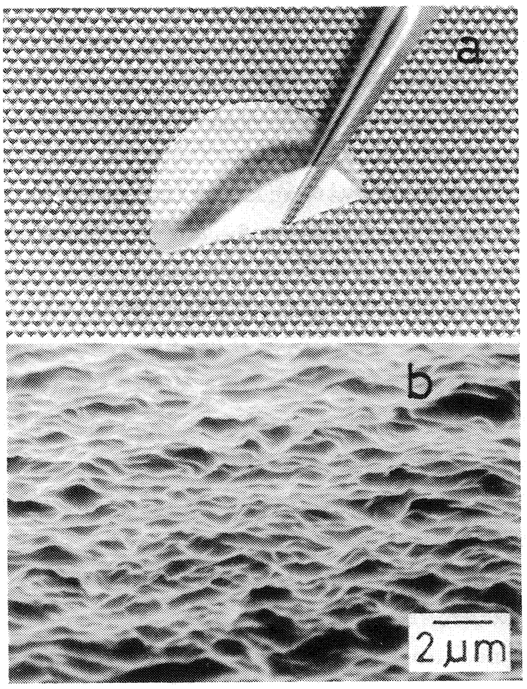

Fig. 4. A multilayerd film of a 2D cross-linked polymer of 2 (a) and its cross-sectional view by SEM (b). The film was cleaved in liquid nitrogen and coated with platinum-palladium.

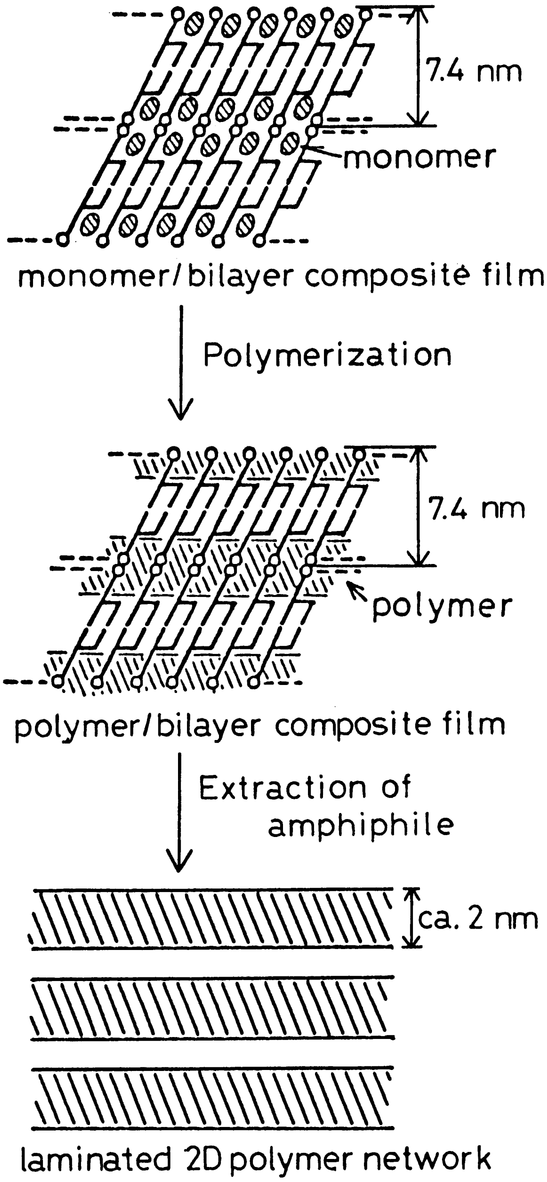

Fig. 5. Schematic illustration of preparation of a laminated 2D polymer network.

not probable that polymerization occurred across the individual bilayer, since the regular multilayer structure of the cast film remained intact after polymerization. The limited resolution of the SEM instrument makes it difficult to observe the individual layer. Since the vinyl group is completely consumed in the polymerization, a two-dimensionally crosslinked polymer is formed. A schematic illustration of the preparative process of a laminated 2D polymer network is given in Fig. 5.

The anisotropic nature of the cross-linking (2D network) is reflected in the ultimate elongation of 48% and tensile strength of 0.60 kg/mm^2 of the film against 11% ultimate elongation and 0.20 kg/mm^2 tensile strength of a bulk polymerized film of **2** (3D network).

Two-dimensionally cross-linked polymers have been obtained by polymerization of aqueous bilayer vesicles,$^{9-12)}$ of adsorbed monolayers at the air-water interface,$^{13-15)}$ and at the oil-water interface,$^{16)}$ and of monomers intercalated into montmorillonite.$^{17-19)}$ In particular, two-dimensional graphite was produced in the latter system. The present approach is unique in demonstrating that a variety of free-standing, multilayered films of the two-dimensional molecular network will be synthesized by appropriate combinations of monomers and synthetic bilayers.

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