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Improved Stability by Two-Dimensional Crosslinking of Langmuir-Blodgett Films of a Polyamine / Polycarboxylate Salt

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A polyion complex of a maleic acid copolymer with poly(allylamine) was transferred onto solid substrates by the Langmuir-Blodgett technique, and converted by heating at 150 °C in vacuo to a two-dimensionally crosslinked film. The pinhole-free, imide-crosslinked LB film (6 layers) on a Fluoropore membrane did not deteriorate when immersed in water or in benzene.

Polymerization has been effective means to improve stabilities of fragile monolayers and Langmuir-Blodgett films.$^{1-3)}$ The methods include polymerization of monolayers at the air-water interface, polymerization of deposited LB films, and the use of monolayers of pre-formed polymers. The use of polymeric counterions is yet another preparative method of polymeric monolayers and multilayers.$^{4,5)}$ Further stabilization of monolayer films will be achieved by crosslinking reactions. Rosilio and Ruaudel-Teixier used solid state polycondensation of octadecyl urea multilayers,$^{6)}$ and Bauer, Heckmann and others used crosslinking of hydroxy moieties with epichlorohydrin.$^{7,8)}$ We reported formation of salt bridges between a polymerized ammonium monolayer and an anionic polymer at the air-water interface.$^{9)}$

In this paper, we describe well-characterized crosslinking of monolayer films by imide formation, and stability of the resulting multilayers. A closely related monolayers of poly(octadecene-1-co-maleic anhydride) was reported by Tredgold and Winter.$^{10)}$ Nishiyama and Fujihira used poly(allylamine) as counterion of a carboxylate monolayer.$^{11)}$

A copolymer of maleic anhydride (Wako Pure Chem.) and *n*-octadecyl vinyl ether (Tokyo Kasei) was prepared in benzene at 60 °C with 2,2'-azobis(isobutyronitrile) as initiator. It was reprecipitated from benzene and methanol and dried at 35 °C in vacuo. The weight-average molecular weight was 9.0 x 10^4 as determined by gel permeation chromatography (poly(styrene) calibration) and the composition was determined to be 54 % maleic anhydride unit by elemental analysis. The anhydride unit was then converted to the monoester by sodium methoxide (about 3 times excess) in tetrahyrofuran at 50-55 °C, neutralized with hydrochloric acid, and precipitated from water and dried at 50 °C in vacuo. Commercial poly(allylamine) hydrochloride (Nitto Boseki, PAA-HCl-L) was treated with a strongly basic ion exchange resin (amberlite IRA-402) to obtain free polyamine **2**.

Figure 1 shows surface pressure-area isotherms of copolymer **1** on pure water and on aqueous

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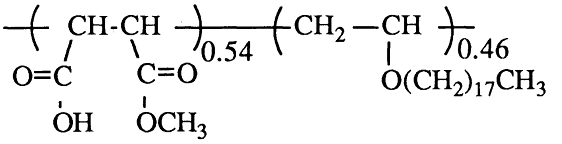
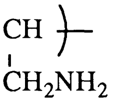


$-\!\left(\mathrm{CH(COOH)\text{-}CH(COOCH_3)}\right)_{0.54}\!\left(\mathrm{CH_2-CH(O(CH_2)_{17}CH_3)}\right)_{0.46}-$

1



$-\!\left(\mathrm{CH_2-CH(CH_2NH_2)}\right)\!-$

2

poly(allylamine), which were obtained by a computer-controlled film balance (San-esu Keisoku, FSD-50) at a compression rate of 0.4 mm/s. These monolayers give expanded phases. The change between the two isotherms is attributed to formation of polyion complex at the interface and the consequent change of the monolayer organization, as already described for other systems.[4,12,13)

The complexed monolayer can be transferred onto various solid substrates at 25 mN/m and 4 mm/min in the Y type deposition (instrument, San-esu Keisoku FSD-51). The transfer ratio tends to decrease with the deposition cycle: 1.5 to 0.9 on a slide glass for 7 layer deposition, and 1.9 to 0.8 on a CaF_2 plate for 12 layer deposition.

The formation of an ion complex was confirmed by means of XPS measurement (Perkin Elmer PHI5300 ESCA system). The N_{1s} peak observed (Fig. 2a) is made of two components (in the 1:1 ratio) which are attributed to NH_3^+ (binding energy, 404.8 eV) and NH_2 (402.7 eV). The content of the N atom in the film is estimated to be 1.8 per maleic acid unit, from the relative area of the N_{1s} and O_{1s} peaks. Therefore, the content of the ammonium nitrogen is 90% of the carboxylate anion, and the remaining nitrogen is in the form of free amine.

The LB films were subsequently treated at 150 °C in vacuo for 6 h. Figure 3 compares FT-IR spectra (instrument, Nicolet 710) of films before and after the treatment. A broad absorption due to the carboxylate salt at 1560 cm^{-1} diminishes by the treatment, and a new peak ascribable to imide carbonyl appeares at 1702 cm^{-1}. These IR data are reinforced by the

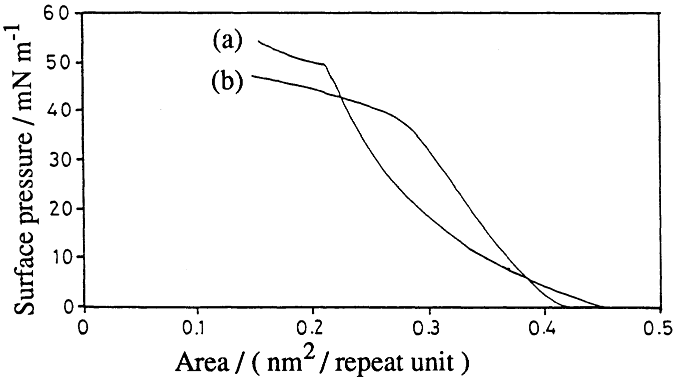


Fig.1. Surface pressure-area isotherms of **1** at 30 °C
(a) on pure water, (b) on aqueous **2** (2×10^{-4} M/-NH_2)
The average molecular weight per repeat unit of **1** is 374.4.

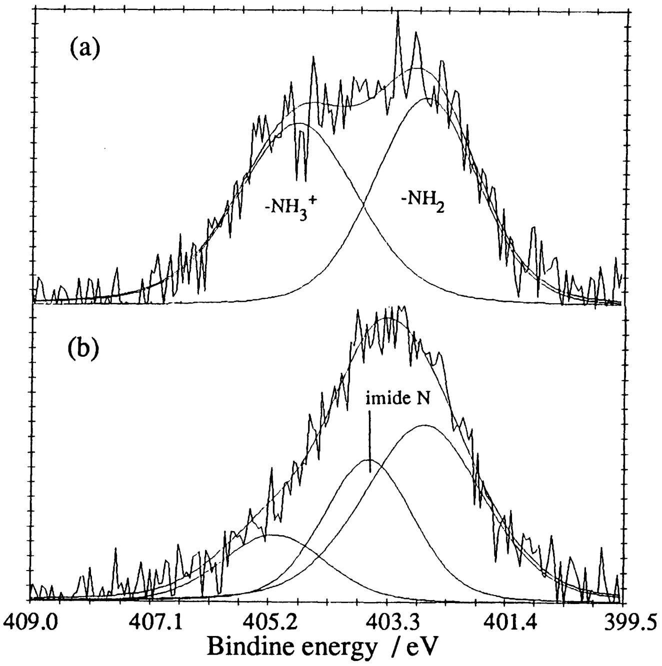
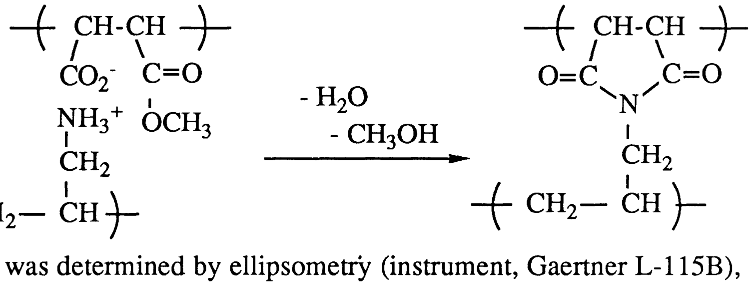


Fig.2. XPS spectra of N_{1s} region of the 10 layer LB films on a fluorocarbon membrane filter (Sumitomo Electric, FP-010), (a) as-deposited film, (b) after the treatment at 150 °C for 6 h in vacuo. The charging shift was not corrected. Take-off angle, 45 °.

XPS data. After the heat treatment, a third peak appeares at 403.6 eV in the N_{1s} region (Fig.2b). The area ratio is approximately 1:2:3 (ammonium / imide / amine). Thus, the content of the free amine (ca. 50% of nitrogen) does not change by the heat treatment, and two thirds of the ion pair are converted to the imide unit. The one third of the ion pair remains intact in spite of the heat treatment.



The layer thickness was determined by ellipsometry (instrument, Gaertner L-115B), as shown in Fig. 4. The film thickness is proportional to the number of deposited layers. The unit thickness of the as-deposited and heat-treated films was estimated from the slopes to be 21.4 Å and 16.6 Å, respectively. Apparently, the formation of covalent bonds between the polymeric ions resulted in more tightly bound LB layers.

Figure 5 shows SEM photographs (instrument, Hitachi S-900) of LB films on porous fluorocarbon membranes (FP-010), observed at an acceleration voltage of 2 kV. We can readily observe that the original pores of the substrate membrane (Fig. 5a) are covered by a thin surface film upon deposition of two LB layers (Fig. 5b). Defects with sizes of 0.1-0.3 µm are seen as dark spots. An enlarged photograph of Fig. 5c shows these defects more clearly. Deposition of 6 LB layers completely removes the defect (Fig. 5d). This appearance does not change upon imide formation. Immersion of this film in water or in benzene for 1 day (before and after imide formation) did not cause any change in its appearance.

In conclusion, we obtained stable, ultrathin films by two dimensional salt bridges and covalent crosslinking. It should become possible to prepare ultrathin polymer films with predetermined molecular pores by the present technique.

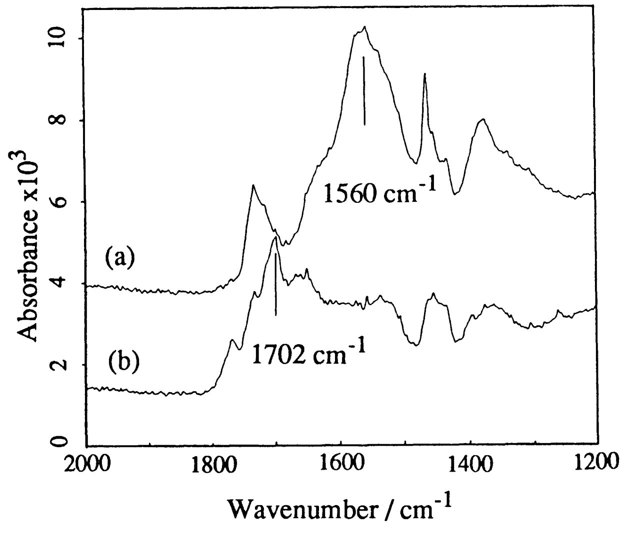


Fig.3. Transmission FT-IR spectra of 12x2 layer LB films on a CaF_2 plate(deposited on both sides) (a) as-deposited sample,(b) treated at 150 °C for 6 h in vacuo.

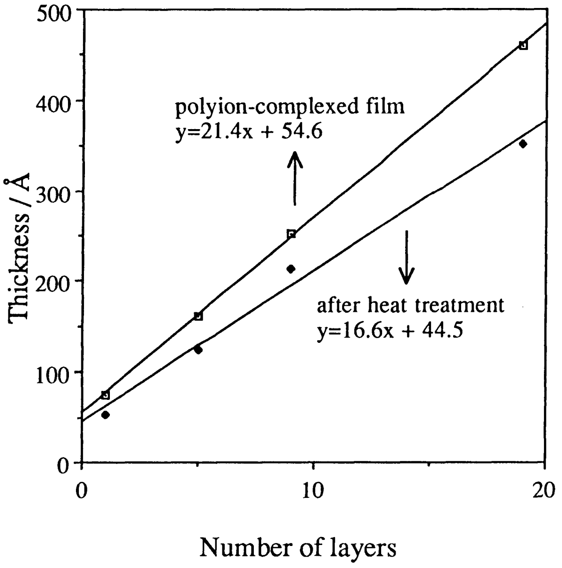


Fig. 4. Thickness of LB films on a Si wafer determined by ellipsometry.

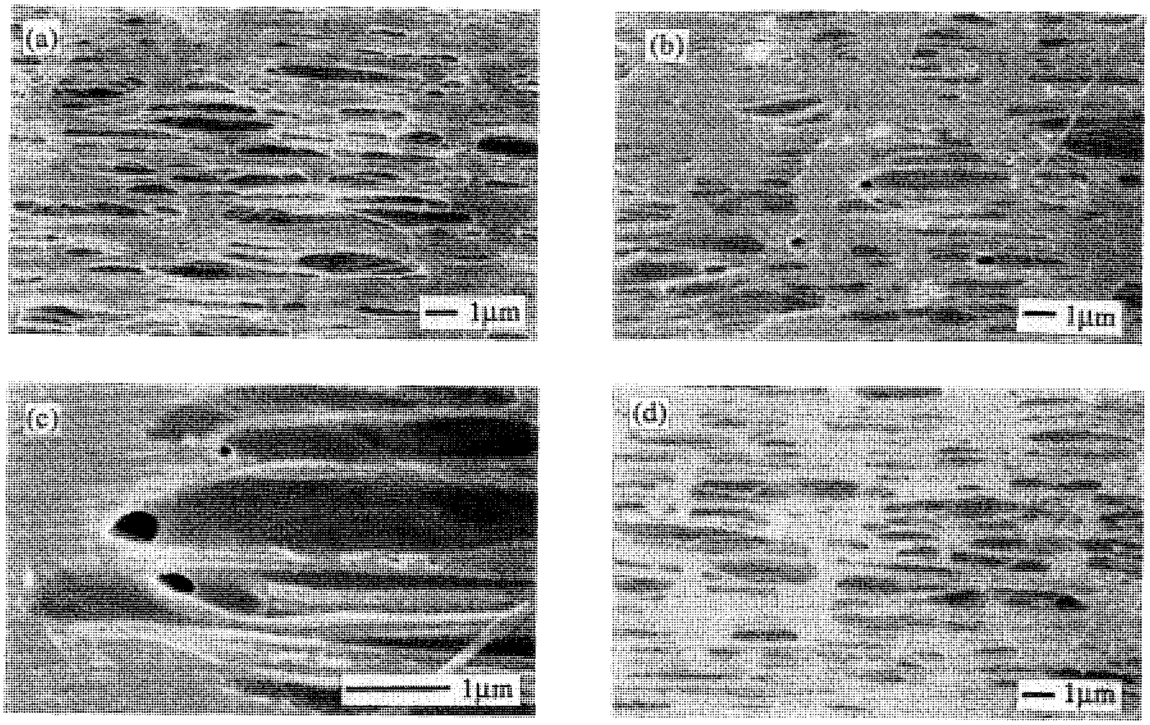


Fig.5. SEM photographs of a fluorocarbon membrane filter (FP-010) and polyion-complexed LB films on FP-010 (before heat treatment). (a) FP-010 only, (b) 2 layer film, (c) enlarged picture of (b), (d) 6 layer film. The samples were sputtered with Pt/Pd and observed at 2 kV.

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