A New Type of Cyclic Alkylacrylamide Polymer Langmuir-Blodgett Film

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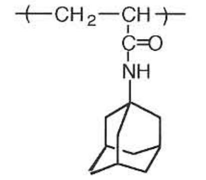
A high quality polymer LB film was newly prepared from adamantylacrylamide polymer without usual long alkyl chain. The measurements with XRD and cyclic voltammetry suggest that the polymer LB film with a thickness of 1.1 nm and well defined molecular orientation is fabricated.

We have succeeded in the preparation of fairly uniform polymer LB films using acrylamide polymers having long alkyl chains (e.g. dodecyl group).[1] In general concept for stable LB film formation, long alkyl chain attached to a hydrophilic moiety is necessary to hold an amphiphilic character.[2] In the present study, a new type of polymer LB film is proposed using cyclic alkylacrylamide polymer with no long alkyl chain, polyadamantylacrylamide (pADA).

Adamantylacrylamide monomer synthesized by the reaction of acryloyl chloride and adamantanamine was polymerized in toluene at 60 °C by free-radical polymerization with AIBN. The molecular weight and polydispersity of the resulting polymer are 1.5 × 10^4 and 1.68, respectively.



polyadamantylacrylamide(pADA)

The pADA was spread from a chloroform solution onto pure water. The surface pressure (π)- area (A) isotherms at 15, 20 and 30 °C are shown in Figure 1. A steep rise in surface pressure was observed and the collapse pressure becomes higher as the temperature decreases. Poor dependence on temperature indicates that molecular packing of pendant substituents often shown in the monolayers having long alkyl chain is not so important. Clearly this polymer forms a stable and condensed monolayer on the water surface in the same manner as others we reported previously.[1,3]

The limiting surface area per monomer unit of the monolayer is determined by extrapolating the linear portion of the steep rise in the π-A isotherms to zero surface pressure. It is approximately 0.28 nm^2/monomer unit in agreement with the value calculated from the CPK model assuming that the polymer main chain is laid on the water surface horizontally and the adamantyl group is oriented perpendicular to the chain. Chart 1 shows the possible molecular orientation on the water surface.

The monolayer on the water surface can be transferred onto a hydrophobic glass plate by a vertical dipping method under a surface pressure of 20 mN m^{-1}. In up- and downward strokes the transfer ratios are almost unity. The layer structure and the film thickness was investigated by X-ray diffraction measurement (XRD). The XRD pattern of the pADA LB film with 40 layers has the Kiessig fringes and two Bragg peaks as shown in Figure 2. Total thickness is determined to be 441 ± 9 Å from the constant spacing of the Kiessig fringes.[5] Monolayer thickness is also determined to be 11 Å from the Bragg peaks. These results exactly agrees with the film thickness estimated from the CPK model based on the structure shown in Chart 1. Furthermore, appearance of well defined Kiessig fringes indicates high flatness of the surface of the LB film.

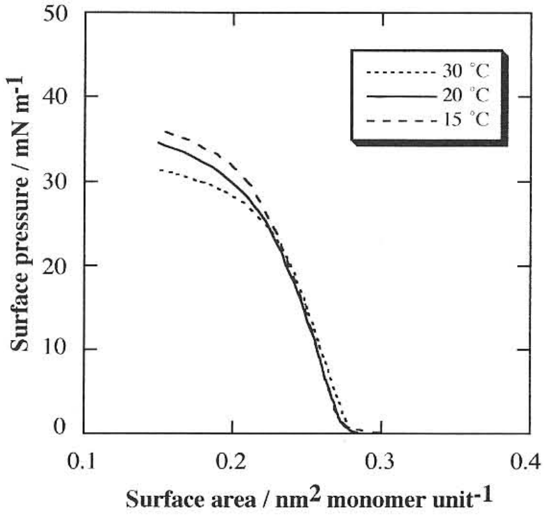


Figure 1. Surface pressure (π)-area (A) isotherms of pADA at various subphase temperature.

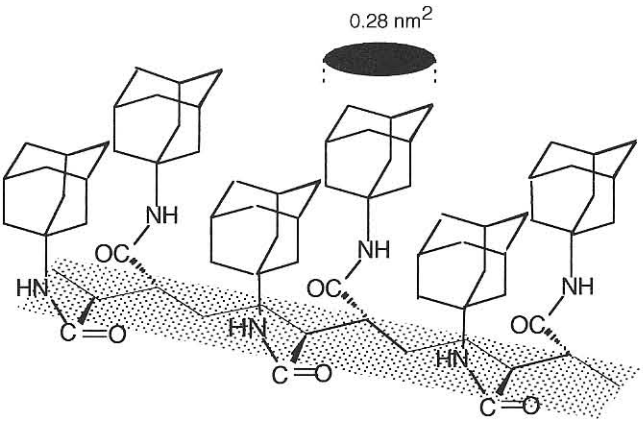


Chart 1. Molecular Conformation of pADA Monolayer on the water surface.

The quality of the polymer LB film was investigated by cyclic voltammetry. Defects formed in the LB film on the electrode surface should be readily evaluated based on the amount of redox peak current, because the redox reaction proceeds only when redox species comes in contact with the electrode surface through the defects.[4] The redox reaction between potassium ferrcyanide

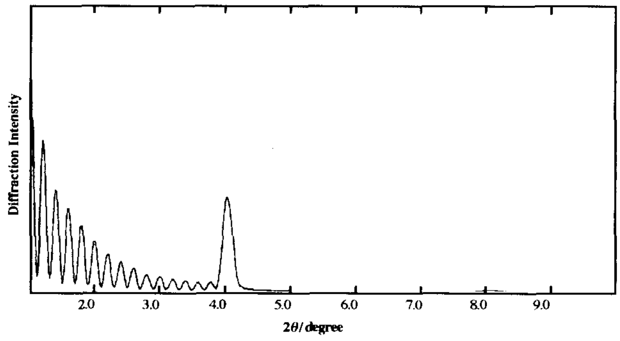


Figure 2. X-ray diffraction patterns of the pADA deposition LB film with 40 layers.

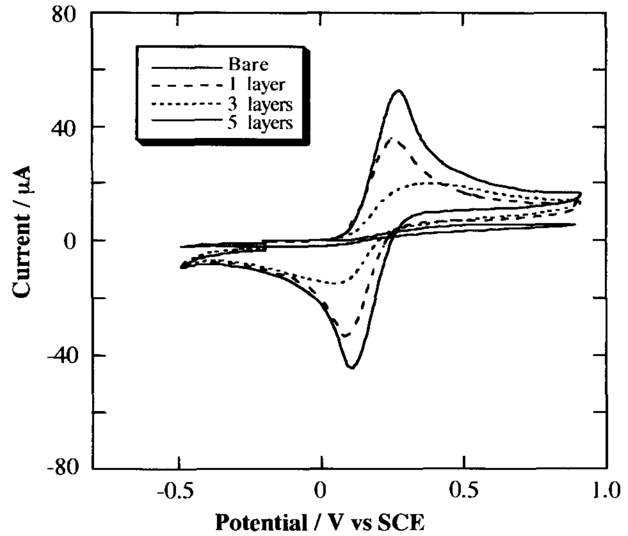


Figure 3. Cyclic voltammograms of 1mM $K_4[Fe(CN)_6]$ aqueous solution: glassy carbon electrode coated with pADA LB film with 0-5 layers. $NaClO_4$ (0.1 mol dm^{-3}) aqueous solutions were used as electrolyte. Scan rate 10 mV sec^{-1}.

$[Fe^{II}(CN)^6]^{4-}$ and ferrocyanide $[Fe^{III}(CN)^6]^{3-}$ was employed for the present work.

The monolayer was transferred onto a glassy carbon disk electrode, and the current induced by the $[Fe^{II}(CN)^6]^{4-}/[Fe^{III}(CN)^6]^{3-}$ redox couple on the electrode was measured under a nitrogen atmosphere at room temperature (Figure 3). The redox peak current apparently decreased with increasing number of layers, indicating that the redox reaction on the electrode is suppressed by deposition of the LB film. With five layers, this LB film can completely restrict the contact of the ferrocyanide ion with the electrode surface.

In conclusion, polyadamantylacrylamide (pADA) forms a stable and condensed monolayer. It can be transferred onto solid supports in both up- and downward strokes, yielding an excellent Y-type polymer LB film. The monolayer thickness of the LB film (11 Å), determined by the XRD measurement, suggests that the adamantyl subsituent is oriented perpendicular to the LB surface. This LB film is of high quality with a small amount defects, and can suppress ion penetration of the redox species with a thickness of 5.5 nm in an aqueous solution. The application is now in studying.

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References and Notes

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