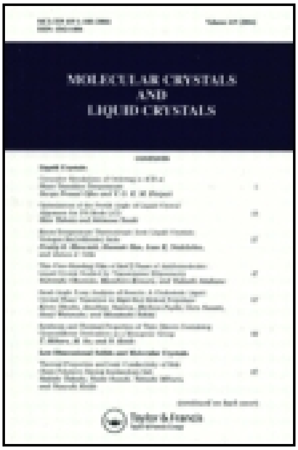

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Two kinds of pyromellitates with different alkyl chains (C 12 and C18) showed characteristic monolayer structures by Brewster angle microscopy, and their Langmuir-Blodgett (LB) films were characterized by FT-IR spectroscopy. The star-like structures on pure water subphase were smoothened on aq. poly(allylamine) subphase. The polyion-complexed monolayer of pyromellitates with poly(allylamine) was transferable on calcium fluoride substrate. The resulting LB films could be networked by heat treatment, and imide structures were produced in the network LB films.

Keywords: pyromellitate; monolayer; network; Brewster angle microscopy

INTRODUCTION

The pyromellitic structure is an important component for polyimides which are employed for various photonic and electronic thin film applications. Specifically, one potential application of interest is a liquid crystal display in which LB multilayers can be used as alignment layers[1-3]. As general technique for polyimides LB films, polyimide precursor LB films have been imidized by thermal or chemical treatments[4].

As for ultrathin polyimide networks, polyion-complexed LB films of oppositely-charged polymers were cross-linked with imides by heat treatment[5]. In the course of studying new polyimide network LB films, we report herein the characteristic structures of pyromellitates monolayers and new LB network films containing pyromellitimide linkage.

EXPERIMENTALS

Materials

Didodecyl and dioctadecyl pyromellitates (2C12PA and 2C18PA) were synthesized by the reaction of pyromellitic dianhydride with dodecanol and octadecanol, respectively. Poly(allylamine) were purchased from Nitto Boseki Co. and the concentration in subphase was adjusted to 10^{-4} M by amino unit.

Measurements

A film balance system (NIMA 611D) and FT-IR spectrometer (Perkin-Elmer) were employed for characterization of monolayer and LB film. A homemade Brewster angle microscope, mounted on the Langmuir film balance, was used to observe the microscopic structures of the monolayers.

RESULTS AND DISCUSSION

Monolayer Properties at the Air-Water Interface

The surface pressure-area (π-A) isotherm of 2C12PA monolayer showed expanded phase, while 2C18PA showed condensed phase (Fig. 1). When poly-(allylamine) (PAA) existed in the subphase, the monolayer showed more expanded phase and enhanced stability against the surface pressure than those of pure water subphase. This PAA effect was clear in 2C12PA monolayer,

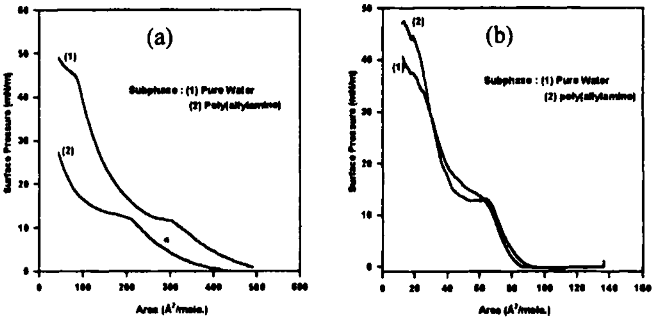

FIGURE 1 π-A isotherms of (a) 2C12PA and (b) 2C18PA.

while not noticeable in case of 2C18PA. It is estimated that the electrostatic interaction of carboxylate and ammonium ions happens actively in 2C12PA monolayer, but much less in 2C18PA one.

During the plateau region of 2C12PA π-A isotherm, a growth of star-like aggregate structure was found on pure water subphase, while the clear-cut structure was smoothened or disappeared on poly(allylamine) subphase (Fig. 2a and 2b). On the other hand, any distinctive images were not found in 2C18PA monolayers both on pure water and on aq. poly(allylamine) subphases (Fig. 2c and 2d).

Fabrication and Characterization of LB Network Films

The polyion-complexed monolayers were deposited on CaF_2 plate as Y type. For the preparation of network LB films, the electrostatic binding between the carboxylates and the ammoniums was forced to imidization by thermal condensation reaction. The FT-IR spectra (not shown here) of the LB films which were taken on the step-by-step treatments showed the incorporation of poly(allylamine) into the LB film and condensation to pyromellitimide structures.

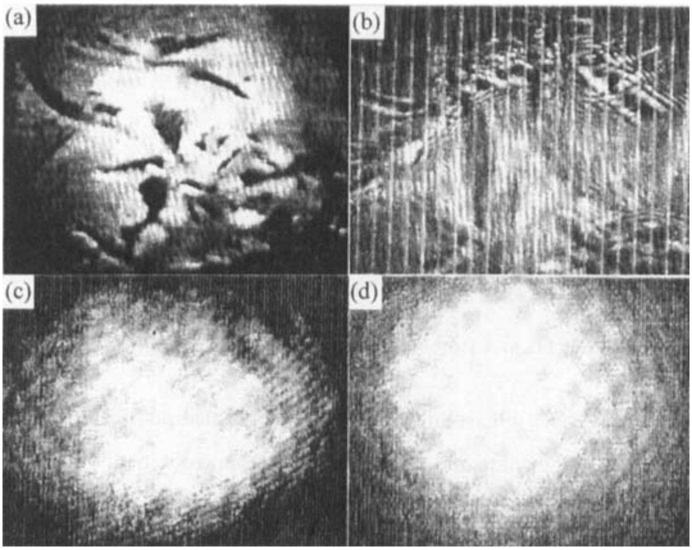

FIGURE 2 BAM images of (a) 2C12PA, (b) 2C12PA/PAA, (c) 2C18PA, and (d) 2C18PA/PAA.

Acknowledgements

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