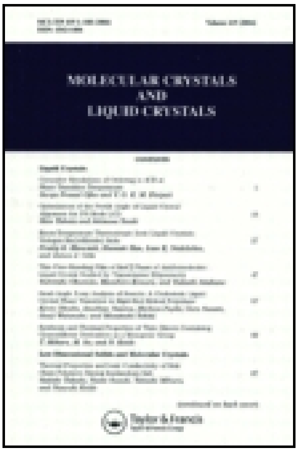

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Preparation and Evaluation of Polyaniline Lb Films

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PREPARATION AND EVALUATION OF POLYANILINE LB FILMS

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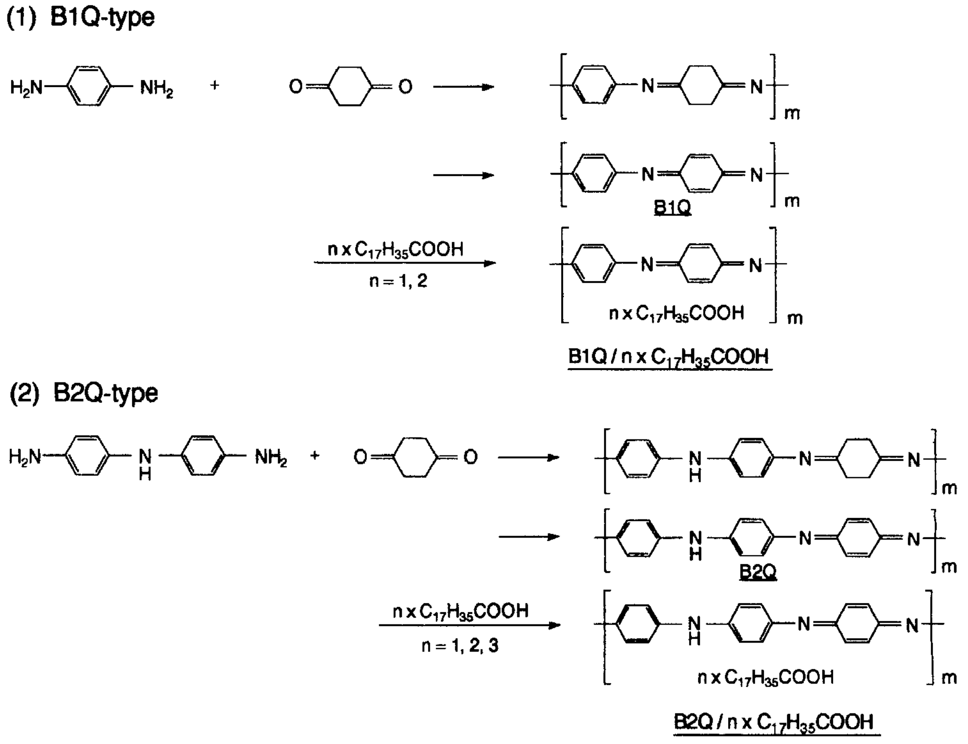
ABSTRACT The mixed Langmuir-Blodgett (LB) films of polyaniline and stearic acid were successfully prepared. They formed stable monolayers at the air-water interface and could be deposited onto solid substrates as Y-type films using a usual LB technique. The stearic acid was removed from the LB films by either immersing the films in organic solvents or heating the films under reduced pressure. The replica method coupled with transmission electron microscopy (TEM) confirmed that these treatments were useful for the preparation of smooth films. The spectroscopic measurements proved perfect removal of the stearic acid after the treatment in solvent. Different electrochemical properties were observed for two kinds of the LB films by cyclic voltammetry. This method made it possible to prepare LB films consisting of polyaniline alone, whose thickness is only 6 A per layer.

INTRODUCTION

Applying the Langmuir-Blodgett (LB) technique to electroactive compounds have great potential to fabricate molecular devices. These compounds can be generally divided into two classes; low molecular charge transfer complex and conjugated unsatured polymers. Up to now, a numerous conductive compounds have been synthesized for each group and a number of researchers have developed them suitable for formation of the LB films. For example, alkyl-substituted TCNQ-TMTTF is one of the most interesting material for the former case.[1] Considering practical use, polymer-based materials are particularly attractive because they exhibit excellent mechanical strength and thermal stability. Actually, conducting polymers such as polypyrrole[2] and poly(p-phenylenevinylene)[3] have been applied to the LB films.

One of the most stable conducting polymers is polyaniline, which has been already applied as a material for batteries. Hitherto poor solubility of polyaniline in organic solvents, however, has made it difficult to prepare the polyaniline LB films. Although some workers introduced substituents such as alkyl chains[4] and sulfonic acid groups[5,6] to improve the solubility, the existence of side chain lead to increase of the thickness between the layers and it would cause lowering of the conductivity of the LB films.

In this paper, we report the preparation of polyaniline LB films containing no substituent. Polyaniline is usually synthesized by the oxidative polymerization of aniline with some oxidizing agents such as ammonium peroxodisulfate.[7] Another way is the polycondensation of p-phenylenediamine or 4,4'-diaminodiphenylamine with 1,4-cyclohexanedione.[8] We found that the polymer remained soluble in dimethyl sulfoxide (DMSO) if proper conditions were selected. Multilayers of mixed LB films of these soluble polyaniline and stearic acid were fabricated, and removal of stearic acid was successfully achieved as shown in Scheme 1.



Scheme 1

EXPERIMENTAL

As shown in the Scheme 1, since the repeating unit of the polymer synthesized from the former condensation reaction consists of one benzene ring and one quinone ring, we call it "B1Q". In a similar manner, the latter polymer is hereinafter called as "B2Q".

Polymer Synthesis

Both B1Q- and B2Q-type polyanilines were synthesized by the polycondensation of p-phenylenediamine and 4,4'-diaminodiphenylamine sulfate respectively,with 1,4-cyclohexanedione. The reaction mixture of the monomers in DMSO at a concentration of 100 mmol/l was heated at 105°C for 12 h under nitrogen.

Preparation of Spreading Solution

The spreading solution for the LB technique of these polymers were prepared as follows: After cooling the reaction mixture to room temperature, the solution was diluted with DMSO to the concentration of 10 mmol/l. Then some definite amount of the stearic acid solution in chloroform (5 mmol/l) was added. Final concentration of the polymer was adjusted to 1 mmol/l, where the solvent was the 1:1 (v/v) mixture of DMSO and chloroform.

Preparation of LB Films

The pressure-area (π-A) isotherms were measured on a San-Esu FSD-20 trough at 20°C with a compression speed of 0.32mm/s. The solution was spread onto distilled and deionized water. The multilayers were built up by the vertical dipping method at 18.5 mN/m for B2Q and 20.0 mN/m for B1Q. A dipping speed of 5 mm/min was used to transfer the films. The first layer was allowed to dry for more than 60 minutes and then they were dried for 10 minutes for subsequent deposition.

Measurements

The IR transmission and reflection absorption spectra of multilayers were measured with a JEOL JIR-MICRO 6000 equipped with a mercury-cadmium-telluride (MCT) detector. In case of reflection absorption spectra (RAS), incidence angle of polarized beam was 10° to the substrate surface. The UV-visible spectroscopy was performed using a Hitachi U-3400 spectrophotometer. Ellipsometric measurements of the thickness of multilayers were done on a NIIC EL-101 ellipsometer. The cyclic voltamograms of LB films deposited on glassy carbon (GC) disc electrode were measured using a Nikko Keisoku NPGFZ22501A potentio-galvanostat equipped with a function generator. A saturated calomel electrode (SCE) and Pt wire were used as the reference and counter electrodes, respectively.

RESULT AND DISCUSSION

Once the polymerization solution was poured into a poor solvent to precipitate the polyaniline, it was difficult to redissolve completely in organic solvents. This is probably because of the change of chemical structure by oxidation with air and the formation of partial crystalline structure during precipitation. So the spreading solutions were prepared directly from the reaction mixture.

The π-A isotherms of the mixture and stearic acid are presented in Figure 1. The ratio of stearic acid to polyaniline repeating unit was changed from 1 to 3 and 1 to 2 for B2Q-type and B1Q-type polyaniline, respectively. The addition of stearic acid not only improved the surface-activity of the monolayer but supported the dispersion of the polymer. Each curve demonstrates that stable condensed monolayers could be formed from a variety of polyaniline/stearic acid mixtures. They were transferred onto a substrate as Y-type films by using a conventional vertical LB technique. When the concentration of stearic acid was low, the transfer ratio of the monolayers during down stroke became worse. This fact might arise from a weaker interaction between the stearic acid on a substrate and that at the air-water interface because the area of the stearic acid occupied in the film is smaller. Thus the stearic acid/polyaniline ratios of the further depositions were adjusted to 3 and 2 for B2Q-type and B1Q-type, respectively.

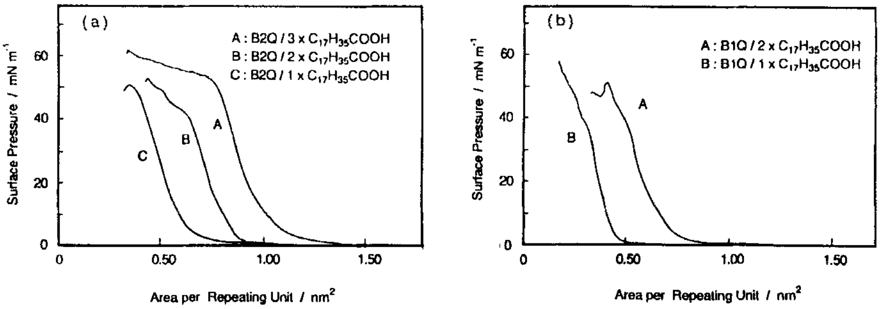


FIGURE 1 π-A curves of B2Q-type(a) and B1Q-type(b) polyaniline with stearic acid.

A comparison of the FT-IR spectra of the B2Q-type LB films in transmission and reflection absorption (RA) modes is shown in Figure 2. Relative intensity of the C-H stretching band is stronger in the transmission mode compared with that in the RA mode. On the other hand, the band progression due to the CH_2 wagging vibration between 1400-1200 cm^{-1} appears more clearly in the RA spectrum. These information indicate that the alkyl chain has some orientation. Furthermore, very broad absorption between 3300-2500 cm^{-1} assigned to O-H stretching vibration was observed in the RA spectrum, which suggests the formation of cyclic dimer of stearic acid between the layers. The transmission and RA spectra of B1Q-type LB films were also measured and the general features of them are similar to those of B2Q-type.

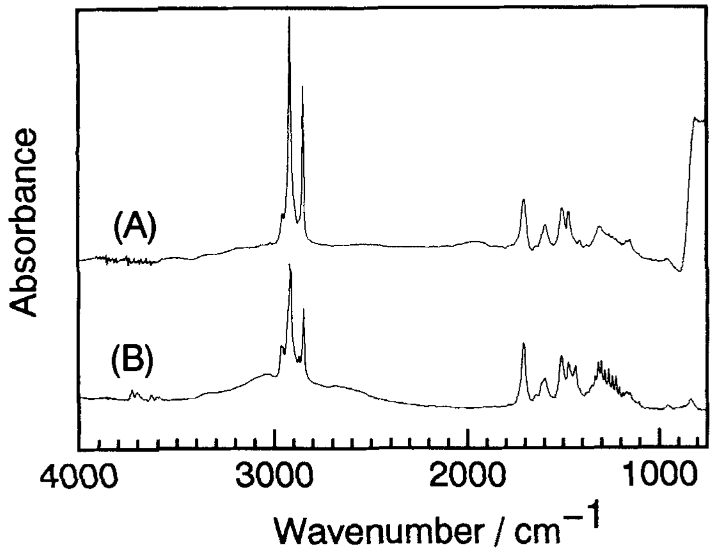


FIGURE 2 Transmission (A) and RA (B) IR spectra of B2Q-type LB film.

The thicknesses of the as-deposited films were measured for the films with various layers by ellipsometry. The average monolayer thicknesses are evaluated to be 16 Å and 18 Å for B2Q-type and B1Q-type, respectively. The thicker nature of B1Q-type originates from the difference of surface pressure during the deposition.

The value of film thickness mainly came from the existence of stearic acid. The removal of the stearic acid from the resulting LB films was attempted by two methods, which consisted of either immersing the mixed LB films in organic solvents or heating the films under reduced pressure. It was possible that rapid dissolution of the stearic acid in organic solvents such as chloroform caused disintegration of the films. Reducing the extraction rate of the stearic acid from the LB films into the solvents, it was achieved by using a mixture of chloroform and n-hexane. Figure 3 represents the RA spectra of B2Q-type LB films before and after the treatment in the solvent of the 1:2 (v/v) mixture of chloroform and n-hexane. The asymmetric and symmetric CH_2 stretching band at 2917 and 2848 cm^{-1}, respectively, disappeared completely. The absorption of C=O stretching at 1704 cm^{-1} and the band progression due to the CH_2 in the RA spectrum also disappeared after the treatment. The absorption bands assigned to stretching of quinone ring, benzene ring, and C-N, which are all associated with polyaniline, appeared clearly at 1594, 1508, and 1315 cm^{-1}, respectively. These changes indicate the stearic acid was extracted from the mixed LB films.

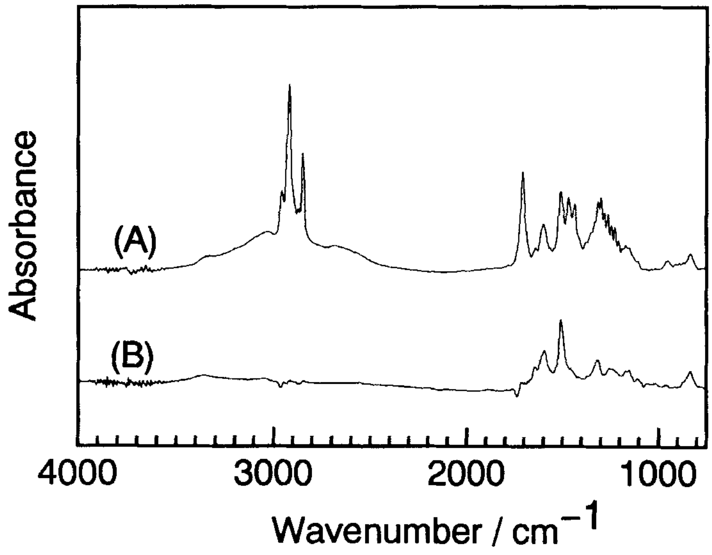


FIGURE 3 RA IR spectra of B2Q-type LB films before (A) and after (B) the solvent treatment.

Figure 4 shows a comparison of the UV-vis spectra of the B2Q-type LB film before and after the treatment described above. These spectra exhibited characteristics of polyaniline and there seems to be no decrease in absorbance at λ_{max} after the treatment. On the basis of the above spectroscopic informations, it is concluded that only stearic acid was completely removed from in the mixed LB films by the solvent treatment.

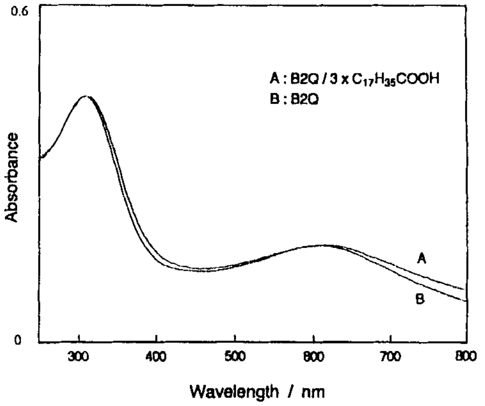


FIGURE 4 UV-visible spectra of B2Q-type LB film before (A) and after (B) the solvent treatment.

The ellipsometric measurements were carried out to evaluate the effect of disappearance of the stearic acid. A remarkable change of the thickness was observed after the solvent treatment. The thickness per monolayer was calculated to be 6.0 Å. Similar treatment in B1Q-type LB films resulted in disappearance of the stearic acid and a small amount of polyaniline as well, which was confirmed by the IR and UV-vis spectra.

Next, the removal of the stearic acid was tried by heat treatment of the LB films. This treatment was performed at some different temperatures under reduced pressure ($< 10^1$ Torr). The change of structure was traced by IR spectroscopy (RAS) as shown in Figure 5 and the relationships of absorbances of the benzene ring and asymmetric methylene stretching vibration (at 1513 and 2915 cm^{-1}, respectively) versus heating temperature were plotted in Figure 6. In all runs the absorbance of the benzene ring remained approximately constant. On the other hand, the absorption of the methylene once became stronger up to 50°C, and then decreased rapidly at about 60°C. The transition dipole moment in the perpendicular direction to the surface of the substrate is strongly absorbed in the RA mode because the S polarized light was used in this measurement. Considering this property, the increase of the absorption meant that the alkyl chain began to lean to the surface with heating and then was removed after that. Nevertheless, judging from the trace of absorption of the methylene, the stearic acid could not be perfectly removed when the LB film was heated at 150°C. Similar results were obtained in case of the B1Q-type LB films, and the thickness per layer of the LB film of polyaniline was estimated to be 6.9 Å from the slope.

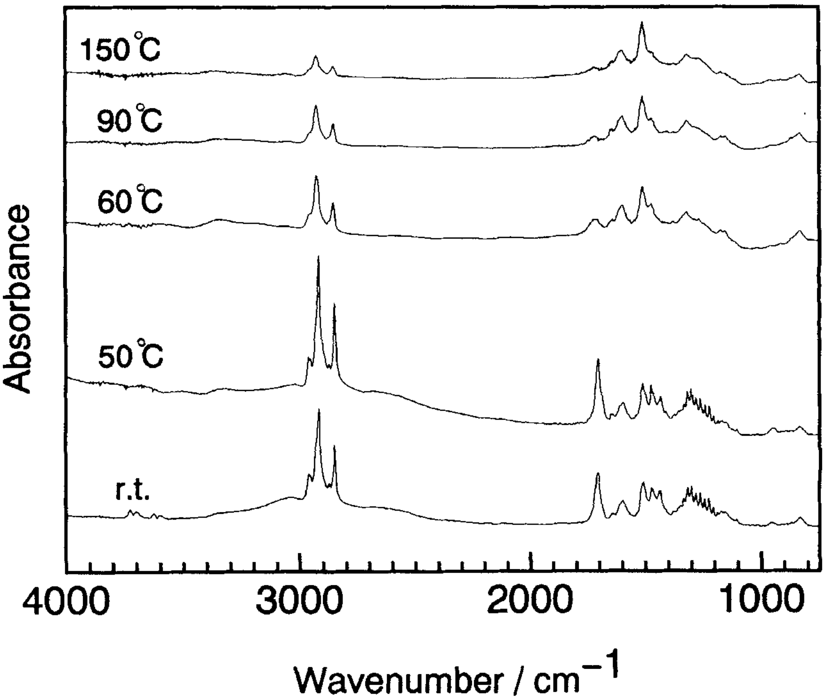


FIGURE 5 Change of IR spectra (RAS) of B2Q-type LB film after the heat treatment.

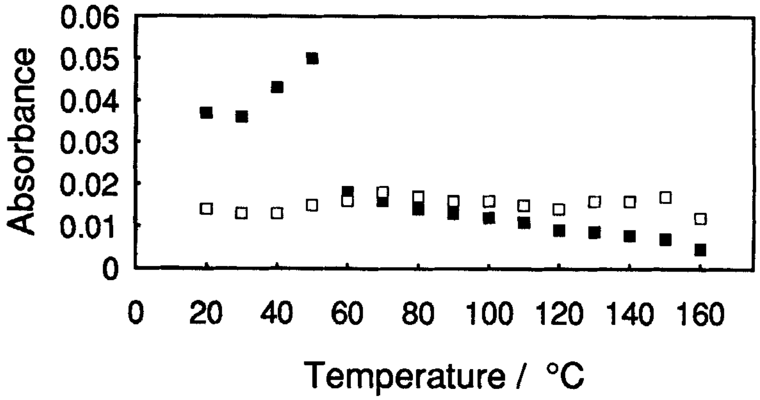
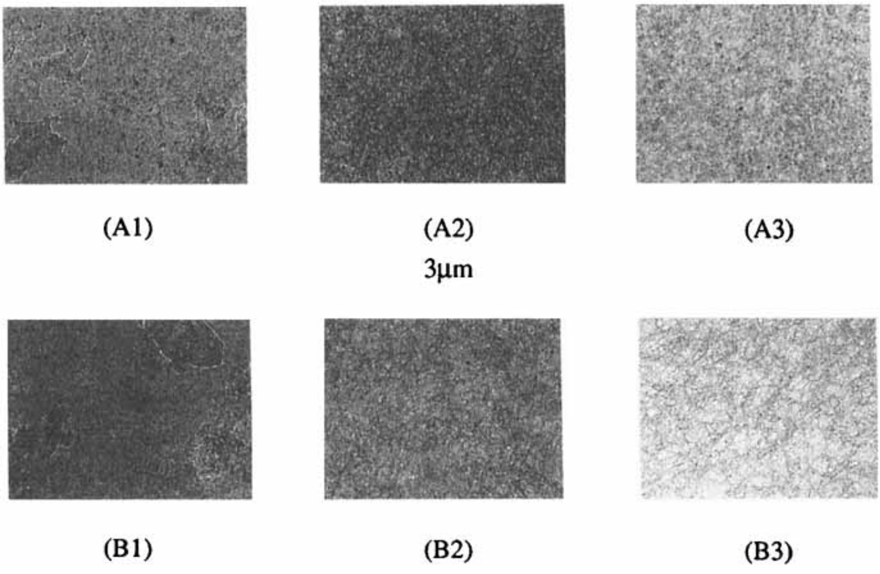


FIGURE 6 Plots of absorbance of B2Q-type LB film after the heat treatment: ■;ν=2917cm^{-1} and □;ν=1506cm^{-1}.

The surfaces of the LB films before and after the above heat treatment were observed by transmission electron microscopy (TEM) using the replica method.[9,10] In the TEM images of **(A1)** and **(B1)** shown in Figure 7, which correspond to the mixed LB films of B2Q- and B1Q-type, respectively, granular structures were observed. From the experimental fact reported by Kato et al. [11], these structures were thought to be crystals. As mentioned above, the oriented stearic acid formed cyclic dimer between the layers. Thus, three dimensional growth of this order would lead to the formation of crystals. On the other hand, no granular structure was found in the films where the stearic acid was removed by either the solvent or heat treatment. So it is concluded that these treatments afforded the smooth and uniform surface.


(A1) (A2) (A3)

3μm

(B1) (B2) (B3)

FIGURE 7 TEM photographs of replica samples. A1, A2, A3; as-deposited, after the solvent treatment, after the heat treatment of B2Q-type films, respectively. B1, B2, B3; as-deposited, after the solvent treatment, after the heat treatment of B1Q-type films, respectively.

In the next stage, the electrochemical properties of the LB films were evaluated by cyclic voltammetry. These measurements were carried out after the removal of the stearic acid by the solvent treatment. As can be seen from Figure 8, two sets of peaks of the redox currents were observed for the B2Q-type film, whereas one set of peak for the B1Q-type. This would be due to the difference of chemical structure of the repeating unit. These electrochemical oxidation-reduction cycles were repeated several times without significant degradation.

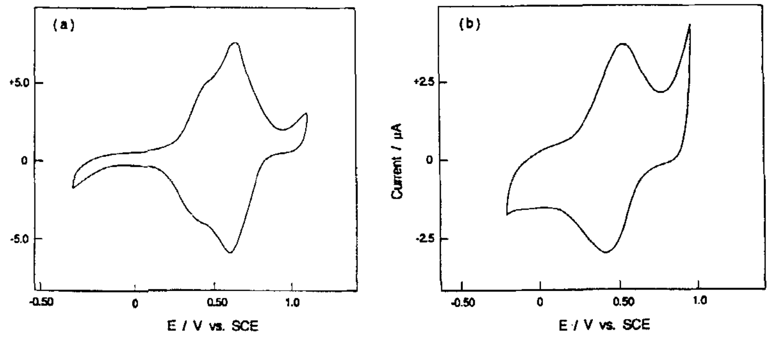


FIGURE 8 Cyclic voltammograms of the LB films (11 layers) after the solvent treatment: (a); B2Q-type in H_2SO_4 and (b); B1Q-type in $HClO_4$.

CONCLUSION

The mixed LB films consisting of polyaniline and stearic acid were successfully prepared as oriented films. The removal of the stearic acid by either immersing the mixed LB films in organic solvent or heating under reduced pressure afforded the polyaniline LB films containing no alkyl chains, whose thickness was only 6.0 Å per layer. The transmission electron microscopic (TEM) observation of replica sample of the LB films confirmed that these treatments resulted in the formation of smooth surface.

The present technique enabled us to prepare ultra thin films consisting of polymers alone even which do not have amphiphilic nature.

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