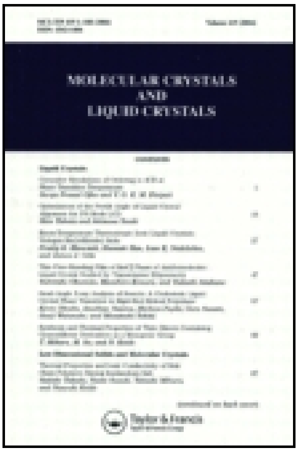

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Clay and a Zwitter Ionic Molecule Hybrid Film: Analysis of the Relationship between the Film Structure and the Conditions for Film Preparation

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We have studied the relationship between the film structure and the conditions for film preparation of a hybrid film of a D-π-A zwitter ionic molecule and a sodium montmorillonite. The films were obtained by means of the modified Langmuir-Blodgett technique. As for the D-π-A zwitter ionic molecule, indoline-TCNQ intramolecular charge-transfer compound (ind-TCNQ) was employed. We have prepared various kinds of hybrid films by changing a parameter during the film preparation. The films thus obtained have been characterized by means of the second-harmonic generation measurements. As a result, a surface pressure at film deposition plays an important role for maintaining the film structure.

Keywords: clay; sodium montmorillonite; zwitter ionic molecule; TCNQ derivative; hybrid Langmuir-Blodgett film; second-harmonic generation

INTRODUCTION

In the last decade, inorganic/organic hybrid films have been providing a stimulus towards the development of advanced materials with desirable optical properties[1,2], electrical properties[2,3], and so forth. The properties of such films are possible to be controlled by changing the layer-by-layer structures of inorganic and/or organic species in an artificial way. Particularly the combination of inorganic and organic components will realize such properties as would not be achieved by the inorganic or organic component alone. Therefore the approach seems to promise the development toward a variety of novel functional materials. In fact, we have recently shown that the hybridization of sodium montmorillonite and D-π-A zwitter ionic molecule or a metal complex with no alkyl chain is achieved by the Langmuir-Blodgett (LB) technique and that the obtained film has a non-centrosymmetric molecular alignment[4-6].

One of the problems of the film is, however, that the structure of such an inorganic/organic hybrid film is quite sensitive to the conditions of the film preparation. Considering the practical importance of a film with uniform thickness and structural order, we have started the systematic investigation on the correlation of the conditions of the film preparation and its structures. We have preliminary revealed that the barrier speed 5mm/min and waiting time for evaporation of the solvent over than 10 min are the most favorable conditions[7]. In the present paper, we have more comprehensively studied the relationship between the surface pressure at deposition and the film structure. The D-π-A zwitter ionic molecule, indoline-TCNQ intramolecular charge-transfer compound (ind-TCNQ; Figure 1) was used as a chromophore. As a result, we have found that the film fabricated at the surface pressure of 20 mN/m maintains its film structure for long time.

EXPERIMENT

Sample preparation was performed by the similar way as reported in the previous papers[4-7]. Waiting time for evaporation of the solvent is 10 min. Optical measurement was made by the same way reported in these papers.

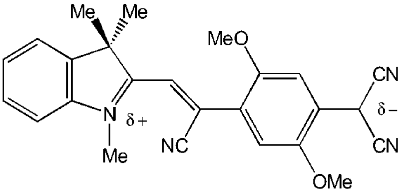

FIGURE 1 Chemical Formula of D-π-A zwitter ionic molecule based on amine and TCNQ derivative.

RESULTS AND DISCUSSION

The measurements of absorption spectra showed that the same spectral shape and peak position were observed both in films and solutions (not shown, reported in reference [6]). This indicated that the charge transfer (CT) degree is the same for the whole samples. The CT degree (δ) estimated by the MOPAC calculation was 0.393. This value is coincident with the fact that the absorption maximum is red-shifted with the increase of the polarity of the solvent.

The π-A isotherm at the barrier speed of 5 mm/min is shown in Figure 2. The surface pressure rises sharply from 0 mN/m to about 15 mN/m, and thereafter undergoes the plateau region from 15 mN/m to 22 mN/m and rises sharply again above 22 mN/m.

As we already have reported[7], these three regions were likely to be assigned as an expanded phase (0 – 15 mN/m), a condensed phase

(15 – 22 mN/m), and a condensed phase (22 ~ mN/m) respectively.

Based on the π-A isotherm, the relationship between the surface pressure and the obtained film structure has been surveyed. We deposited the hybrid films at 15 mN/m, 20 mN/m, 25 mN/m, and 30 mN/m respectively. Figure 3 shows the SHG intensities of the incident angle dependence of the hybrid films. It demonstrates that the conditions of film depositions have been found to give a significant effect on the SHG signal intensity. The film fabricated at the surface pressure of 20 mN/m showed the strongest SHG signal intensity and the film was found to maintain the intensity for 30 hours after the film preparation. The film fabricated at the surface pressure of 25 mN/m showed almost the same SHG signal intensity as that of the one fabricated at 20 mN/m when measured 5 hours after the film preparation. In the former film, however the SHG signal intensity observed 30 hours after the film preparation was found to decrease in intensity. The films fabricated at the surface pressure of 15 mN/m and 30 mN/m showed the SHG signal intensity weaker than those of 20 mN/m and 25 mN/m. However, they stayed with even 30 hours after the film preparation.

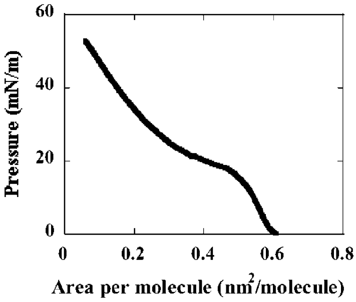

FIGURE 2 Surface pressure versus area per molecule (π-A) isotherm for ind-TCNQ at 20 ℃ on a subphase of 0.01 g/dm^3 sodium montmorillonite. The barrier speed is 5 mm/min. The waiting time for the evaporation of the solvent is 10 min.

These facts suggest the following explanations. The molecular rearrangement took place in the film fabricated at 25 mN/m in a short time. In case of the film fabricated at the surface pressure of 15 mN/m, the molecules in the film should be closely packed, hence the SHG signal intensity is weak. In case of the film fabricated at the surface pressure of 30 mN/m, the molecules in the film should be extremely packed and the film is collapsed, hence the SHG signal intensity is weak.

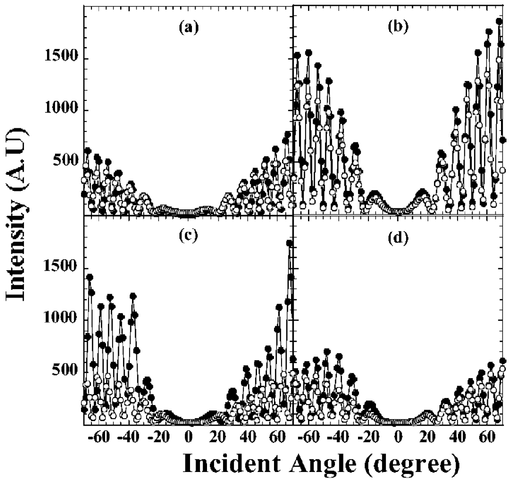

FIGURE 3 Incident angle dependence of the SHG signal intensities from hybrid films fabricated at the surface pressure of (a) 15 mN/m, (b) 20 mN/m, (c) 25 mN/m and (d) 30 mN/m. Waiting time for evaporation of the solvent is 10 min. Barrier speed is 5 mm/min. The solid line serves as a guide. •: 5 hours after the film preparation. ○: 30 hours after the film preparation. The solid line serves as a guide.

As a conclusion, the molecules in the film are orderly arranged at an appropriate density when the film was fabricated at the most favorable surface pressure (or 20 mN/m) for the deposition of the ind-TCNQ and sodium montmorillonite hybrid film.

CONCLUSIONS

The present study has revealed the more optimum conditions for preparing the hybrid LB films of sodium montmorillonite and ind-TCNQ at an air-water interface than the previous study. Namely, the most favorable surface pressure at deposition was 20 mN/m. The present investigation has revealed that the packing and ordering structures of a hybrid film are crucially affected by the conditions of film preparation. These results will help us to make a uniform hybrid LB films on a macroscopic scale.

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