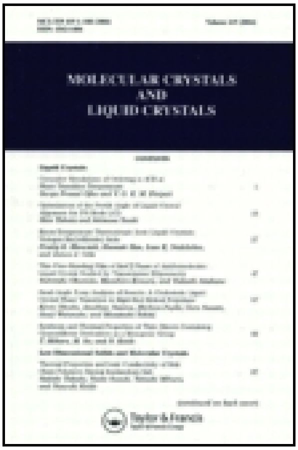

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

IR and AFM Studies on Aging Effects of One-layer Langmuir-Blodgett Films of 2-Alkyl-7,7,8,8-tetracyanoquinodimethane

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IR and AFM Studies on Aging Effects of One-layer Langmuir-Blodgett Films of 2-Alkyl-7,7,8,8-tetracyanoquinodimethane

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Aging Effects of one-layer Langmuir-Blodgett (LB) films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (alkyl-TCNQ) have been investigated by means of infrared (IR) and atomic force microscopy (AFM). Time-dependent infrared (IR) reflection–absorption (RA) spectral changes of a one-layer LB film of pentadecyl-TCNQ on a gold-evaporated glass slide indicate that the alkyl chain becomes more tilted with respect to the surface normal while the TCNQ plane becomes more perpendicular with time. Similar time-dependent changes in the molecular orientation were observed also for a one-layer LB film of pentadecyl-TCNQ on a CaF_2 plate and for one-layer LB films of dodecyl-TCNQ on the gold-evaporated glass slide and CaF_2 plate. However, one-layer LB films of octadecyl-TCNQ did not show a significant change in the molecular orientation. Time-dependent changes in the AFM image of a one-layer LB film of pentadecyl-TCNQ on mica show that the thickness of the LB film varies from 4.6 to 8.2 nm during the time course from 15 to 180 minutes after film deposition.

Keywords: Langmuir-Blodgett films; infrared spectroscopy; atomic force mycroscopy; molecular orientation; tetracyanoquinodimethane

INTRODUCTION

Control of molecular orientation in one-layer Langmuir-Blodgett (LB) films has been a matter of keen interest[1,2]. We have been investigating molecular orientation and structure of one-layer LB films of 2-alkyl-7,7,8,8-tetracyanoquinodimethane (alkyl-TCNQ) by means of infrared (IR) and ultravilolet-visible (UV-vis) spectroscopy[3-6]. The following conclusions have been reached for the molecular orientation and structure in the LB films from our studies[3-6]. (i) The molecular orientation and structure in the one-layer LB films of alkyl-TCNQ change with the length of the hydrocarbon chain substituted. They also show a significant substrate dependency. (ii) The TCNQ planes are tilted considerably with respect to the surface normal in the one-layer LB films due to the intraction between the TCNQ chromophore and the substrate. The hydrocarbon chains are also tilted. (iii) A one-layer LB film of octadecyl-TCNQ consists of a bimolecular layer. In order to obtain the last conclusion atomic force microscope (AFM) was employed[6].

Recently, it was found from the measurements of IR spectra that one-layer LB films of pentadecyl-TCNQ undergo time-dependent orientational change after the film deposition on a CaF_2 plate and gold-evaporated glass slide[7]. The purpose of the present study is to explore further the aging effects for one-layer LB films of the three kinds of alkyl-TCNQ by use of AFM as well as IR spectroscopy. This sort of study should give new insight into the control of molecular orientation in one-layer LB films.

EXPERIMENTS

Experimental procedures for preparing LB films of dodecyl-, pentadecyl-, and octadecyl-TCNQ and measuring their IR spectra were described previously[3-6]. The Langmuir films of alkyl-TCNQ were transferred by the vertical dipping method onto CaF_2 plates, gold-evaporated glass slides, and mica under the surface pressure of 5 mNm^{-1}. AFM images of one-layer LB films of the three kinds of alkyl-TCNQ on the mica were measured with a Shimadzu SPM-9500. We used a silicon nitride tip on a cantilever with a spring constant of 0.16 N/m.

RESULTS AND DISCUSSION

In Figure 1 are shown IR refection-absorption (RA) spectra of a one-layer LB film of pentadecyl-TCNQ on a gold-evaporated glass slide measured at 6, 30,

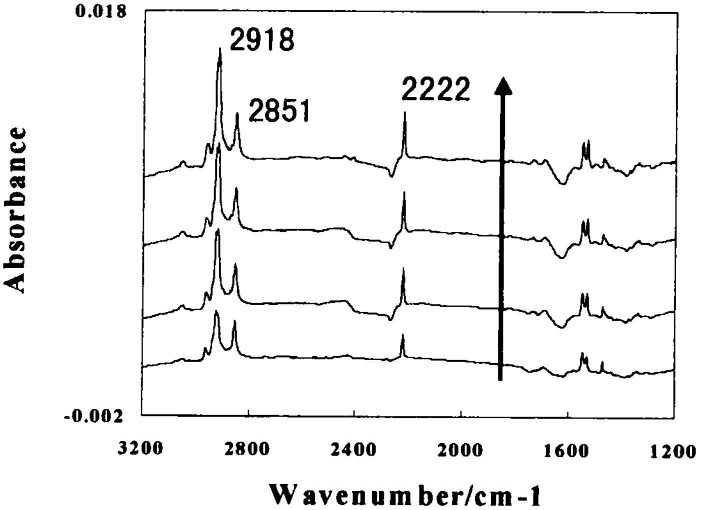

FIGURE 1 Time-dependent IR RA spectra of a one-layer LB film of pentadecyl-TCNQ measured at 6, 30, 45, 131 minutes after the film deposition

58, 131 minutes after the film deposition. It can be clearly seen from Figure 1 that the spectra change with time. The intensities of bands at 2918 and 2851 cm^{-1} due to CH_2 antisymmetric and symmetric stretching modes increase significantly during the time course. According to the surface selection rule in RA spectroscopy[8], this observation suggests that the alkyl chain becomes more tilted with respect to the surface normal with time. A band at 2222 cm^{-1} and a doublet at 1548 and 1531 cm^{-1} are assignable to a CN and C=C stretching modes the TCNQ chromophore respectively. The intensities of these bands also increase with time, indicating that the TCNQ plane becomes more perpendicular with respect to the surface normal. We have also investigated time-dependent changes in an IR transmission spectrum of the one-layer LB film of pentadecyl-TCNQ on a CaF_2 plate. The observed time-dependent changes again indicate that pentadecyl-TCNQ molecules in the LB film on the CaF_2 plate undergo the orientation changes after the film deposition.

One-layer LB films of dodecyl-TCNQ on gold-evaporated glass slide and CaF_2 plate showed similar time-dependent IR spectral changes to those of pentadecyl-TCNQ, but the spectral changes were smaller for the dodecyl-TCNQ LB films than for the pentadecyl-TCNQ LB films. Interestingly enough, one-layer LB films of octadecyl-TCNQ on gold-evaporated glass slide and CaF_2 plate did not show significant time-dependent IR spectral changes. Therefore, the aging effects on the molecular orientation in the one-layer LB films of alkyl-TCNQ depend upon the length of the hydrocarbon chain substituted.

Figure 2 depicts on AFM image of the one-layer LB film of pentadecyl-TCNQ on mica measured at 80 minutes after the film deposition. It can be seen from the image that the film consists of a number of small domains with the size of ~1 μ m. AFM cross sectional profile scanned across a domain reveals that its thickness is 8.2 nm.

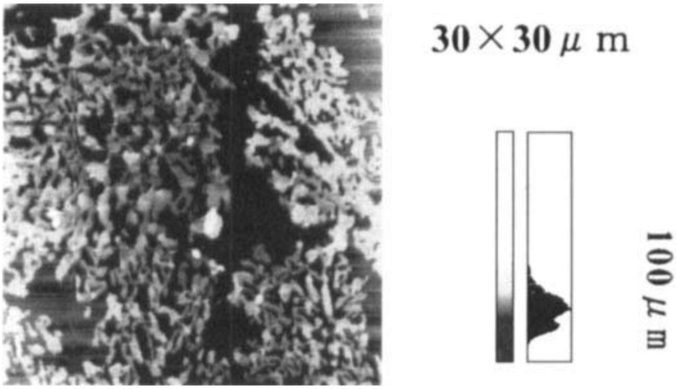

FIGURE 2 An AFM image of a one-layer LB film of pentadecyl-TCNQ on mica measured at 80 minutes after the film deposition (See Color Plate I).

We measured time-dependent AFM changes for the one-layer LB film of pentadecyl-TCNQ and fournd that the thickness changes from 4.6 to 8.2 nm with time. The thickness of 4.6 and 8.2 nm corresponds to a bimolecular layer and its accumulation respectively. The film consists of uniform domain structure just after the deposition, but the domains change into accumulated structures with time. Probably the film is deposited as an unstable bimolucular layer and then changes gradually into more stable accumulated structure.

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