Formation of Langmuir–Blodgett films composed of polydiacetylene and copper tetracynoquinodimethane

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Monolayers containing pentacosa-10,12-diynoic acid and copper tetracynoquinodimethane (CuTCNQ) were formed on a pure water surface. Polymerization of the monolayers rendered polydiacetylene as a matrix in which CuTCNQ molecules were embedded. This result was proved by u.v. absorption spectra and scanning tunnelling microscopy studies of the films.

(**Keywords: Langmuir–Blodgett films; polydiacetylene; copper tetracynoquinodimethane; scanning tunnelling microscopy**)

Introduction

Over the past 10 years, copper and silver tetracynoquinodimethane (MTCNQ, M = Cu or Ag) have received considerable attention due to their optical, electrical and optoelectronic properties[1]. Preparation of high quality thin films of MTCNQ is a key step to obtain the properties desired. Several preparation methods have been reported: reaction of metallic sheet (Cu, Ag) with TCNQ solution; vacuum deposition of M and TCNQ followed by thermal treatment; solid-state diffusion of MTCNQ; and spinning of a MTCNQ solution mixed with polymer[1,2]. In adopting the last method, i.e. embedding MTCNQ in a polymer matrix, a new method was developed in our laboratory by using the Langmuir–Blodgett (LB) technique. Pentacosa-10,12-diynoic acid (DA) mixed with CuTCNQ formed stable monolayers and polymerization of DA under u.v. irradiation occurred when the molecules were arranged with a suitable distance between them[3]. This topochemical reactivity of DA favoured intercalation of CuTCNQ into polymer molecules.

Experimental

The diacetylene derivative used was obtained from Wako Pure Chemical Industries Co. Ltd. CuTCNQ was synthesized according to a known procedure[4] and its purity was determined by elemental analysis. Langmuir films were prepared on a FACE HBM trough under yellow light. U.v.–vis. absorption spectra of LB films were obtained on a Shimadzu UV 2100 instrument. Nanoscope II was used to obtain scanning tunnelling microscopy (STM) images of LB monolayers deposited by a horizontal method onto highly oriented pyrolytic graphite. A solution of CuTCNQ in acetonitrile and of DA in chloroform were mixed at different molar ratios before spreading. Double-distilled water was used as the subphase. The LB films for u.v.–vis. measurement were built up on quartz plates by the vertical dipping method in a Z-type configuration.

Results and discussion

The mixture of CuTCNQ and DA formed stable monolayers on pure water in contrast to DA alone which collapsed easily under the same conditions[5]. CuTCNQ cannot form monolayers either due to the lack of long alkyl chains. The surface pressure–surface area isotherms (at 20°C) of the mixture of CuTCNQ and DA at molar ratios of 0.5:1, 1:1, 2:1 and 4:1 are shown in *Figure 1*. The abscissa is expressed in terms of the area per DA molecule. The effect of the addition of CuTCNQ on the DA isotherm is obvious. The apparent area per DA molecule at a fixed surface pressure increased with increasing proportion of CuTCNQ. This is true even at higher surface pressures. It is worth noting that the magnitude of such an effect is not linearly proportional to the quantity of CuTCNQ added. The apparent limiting area per DA molecule was 37 Å^2 for the 0.5:1 mixture of CuTCNQ and DA (DA on a solution of $CdCl_2$ showed a limiting area per molecule of ~22 Å^2), 50 Å^2 for the 1:1 mixture, and only 52 Å^2 and 54 Å^2 for the 2:1 and 4:1 mixtures, respectively. The plateaux in *Figure 1*, frequently seen in the literature for such isotherms of DA though their origins are not very clear, occurred at relatively high pressure in comparison to the results reported. The slope of the isotherms changed from low to high values after the plateaux. All the mixed monolayers were polymerizable. The deposition of the polymerized monolayer of CuTCNQ–DA at a ratio of 4:1 was not satisfactory due to peeling of the layer during the downstroke.

Figure 2 shows the u.v.–vis. absorption spectra of the mixed LB films. The major maxima at 642 nm with a minor band at 589 nm in spectrum A (for CuTCNQ: PDA = 1:1) is typical for the absorption of PDA in blue form and the small band at 546 nm shows the coexistence of a small quantity of PDA in the red form. The broad band centred at 388 nm represents the absorption of $TCNQ^{\cdot -}$, whilst another absorption band in the visible region is masked by the band of PDA[6]. When the blue form of PDA was transformed to the red form by thermal

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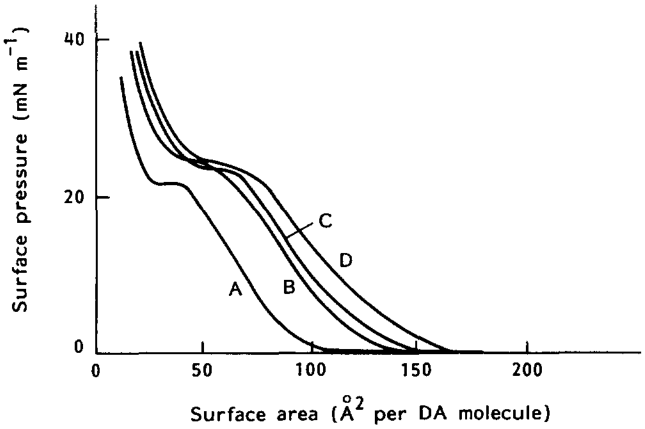

Figure 1 Surface pressure–surface area isotherms of mixtures of CuTCNQ and DA at molar ratios of: (A) 0.5:1; (B) 1:1; (C) 2:1; (D) 4:1

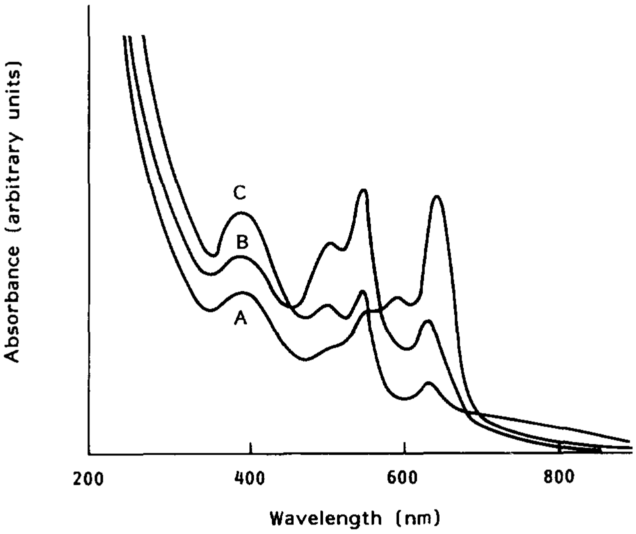

Figure 2 U.v.–vis. absorption spectra of LB films of CuTCNQ–PDA: (A) film (1:1) as-grown; (B) film (1:1) after heating; (C) film (2:1) after heating

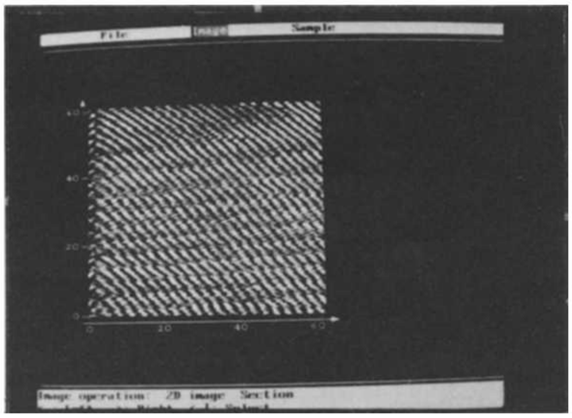

Figure 3 STM image of CuTCNQ–PDA LB film

treatment (80°C for 30 min), the peaks at 546 and 504 nm for the PDA red form increased at the expense of the blue form peaks. The absorption band of $TCNQ^{-}$ at 635 nm appeared (spectrum B). The effect of addition of CuTCNQ should also be observed spectroscopically. On comparison of absorption spectrum C for the LB film of CuTCNQ–PDA at a ratio of 2:1 with the spectrum for the ratio of 1:1, it is seen that the relative intensity of the band at 386 nm over those of PDA increased when the proportion of CuTCNQ was increased.

The hydrophilic surface of the mixed monolayer was studied by STM over the range of 30–180 Å. A representative image of the CuTCNQ–PDA (1:1) monolayer is shown in *Figure 3*. From *Figure 3* (taken at 60 × 60 Å^2), it is clearly seen that the PDA molecules appearing as stripes separated by 2.65 Å were well aligned. No significant distortion or interruption of polymer chains appeared, indicating that the CuTCNQ molecules were miscible with DA rather than in its aggregate form.

On the basis of the above results, the structure of the CuTCNQ-containing PDA LB film can be proposed. The formation of the monolayer composed of CuTCNQ and DA indicates an interaction between them since neither CuTCNQ nor DA can form stable monolayers. The static attraction between the polar head, i.e. the carboxylic acid group of DA and the ionic compound CuTCNQ is expected to be predominant among the various actions. These two species are presumed to be located in the same layer so that the apparent area per DA molecule increased greatly as CuTCNQ was added until the ratio of CuTCNQ to DA reached 1:1. If more CuTCNQ molecules were introduced, excess CuTCNQ was superimposed onto the CuTCNQ which interacted with the carboxylic acid group of DA. This is supported by the very small effect of addition of CuTCNQ on the apparent limiting area per DA molecule for mixtures with ratios of 2:1 and 4:1. After topochemical polymerization of DA, a distance of 4.79 Å between the side chains of PDA[5] may allow the CuTCNQ molecules to intercalate into the polymer matrix. The results suggest that homogeneous films of CuTCNQ–PDA can be prepared by using the LB technique which has the advantage of accurately controlling film thickness. An investigation of optical storage of CuTCNQ–PDA LB films is in progress.

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