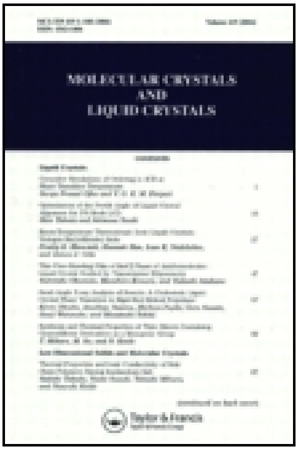

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PHOTOREACTIVE LB FILMS MADE FROM p-PHENYLENEDIACRYLIC ACID DERIVATIVES

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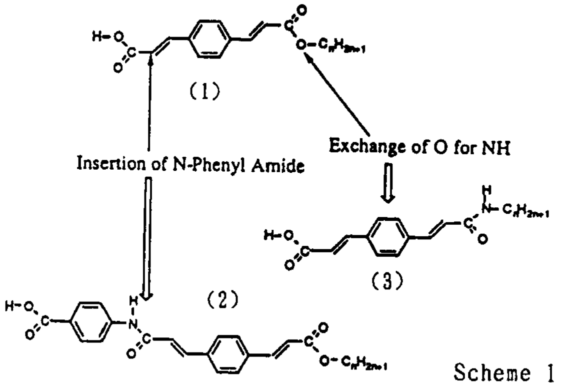
Abstract A new type of photoreactive LB film was prepared from amide derivatives of p-phenylenediacrylic acid. The Y-type of LB films were obtained successfully and they were found to be photoreactive. The photoreaction in the LB film was considered to be oligomerization by cycloaddition of double bonds and decomposition of ester groups.

INTRODUCTION

Photoreaction in the organized systems such as LB films and liquid crystals is of interest and attractive to prepare novel photofunctinal materials. We have investigated the LB films of a series of p-phenylenediacrylic acid (p-PDA) monoesters.(1) with long alkyl chains, which are amphiphilic liquid crystals.[1] In this report the effect of chemical structure on the molecular arrangement and photoreactivity has been studied to design novel photoreactive thin films. For this purpose attention has been paid for introduction of hydrogen bond forming group (amide) into (1). It is expected that hydrogen bonding plays an important role to dictate molecular packings in crystals and LB films resulting in control of photoreactivity. p-PDA amide derivatives (2) and (3) shown in Scheme 1, have been prepared.



Scheme 1

Prepapration and characterization of LB films from these compounds have been carried out and the photoreactivity was elucidated.

EXPERIMENT

The compound (2) with n=10 was prepared by reaction of acid chloride of p-PDA monodecyl ester with p-amino benzoic acid and it was purified by reprecipitaion of its DMSO solution with water. The compound (3) with n=10 was prepared by condensation of N-decyl-p-formylcinnamamide with malonic acid in the presence of piperizine. It was recrystallized from ethanol.[2]
A commercially availablle film balance (Lauda-MGW) was used as a trough. The compounds (2) and (3) were dissolved in ethanol/chloroform solution at the concentration of 10^{-3}M. The sample solutions were spread on a subphase consisting either of redistilled water or $CdCl_2/KHCO_3$ aqueous solution and the surfce pressure-area curves were measured at 20-22°C. The monolayers were transferred onto a quartz plate by the LB technique at a surface pressure of 20-30 dyn/cm.

RESULTS AND DISCUSSION

Preparation and characterization of LB films

The surface pressure-area curves for the compounds (2) and (3) were shown in FIGURE 1. Both compouds could form the stable monolayers on distilled water or aqueous $CdCl_2/KHCO_3$ solution. The monolayer forming behaviour was similar in these compounds. The surface areas of (2) and (3) were 27 Å^2 and 23 Å^2, respectively. The surface area of (2) was larger than that of (3) due to the presence of benzene ring having carboxylic acid group.

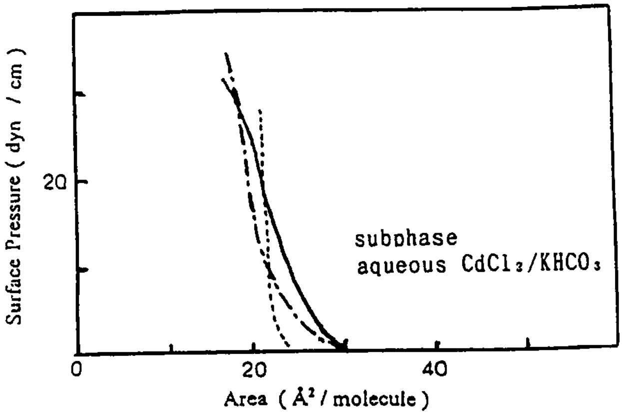


FIGURE 1. The surface pressure-area curves for (1)-(3).
(1) - - - - ·
(2) ———
(3) - — - —

Both monolayers which were formed on $CdCl_2/KHCO_3$ aqueous subphase could be deposited on a quartz plate of which surface was hydrophilic. In both cases LB films with Y-type were obtained. The LB film from (2) gave good linear relationship between the absorbance at its peak and numbers of layers (FIGURE 2), showing the successful transfer of monolayers (2). However, the transfer of monolayers formed on distilled water was not successful with increasing number of monolayer deposited, giving a Z-type film. Therefore, chracterization and photoreactivity were investigated with the LB film of (2) obtained from $CdCl_2/KHCO_3$ subphase intensively. The UV spectrum of the LB films showed the absorption maximum at 284 nm. Compared with that of solution (330 nm) it is blue shifted. This suggests that molecular arrangement in the LB film and in the solution are different each other. The fluorecense spectrum of LB films showed the weak emission at 450 nm. This is different from that of monomers in solution and it was assigned to be an eximer emission as observed in the LB film of p-PDA monodecyl ester. These data indicate that each molecule of (2) in the LB film is arranged side by side as observed in p-PDA monoester LB films, though the distance between component molecules is different in (1) and (2) depending on the presence of hydrogen bond forming group "amide".

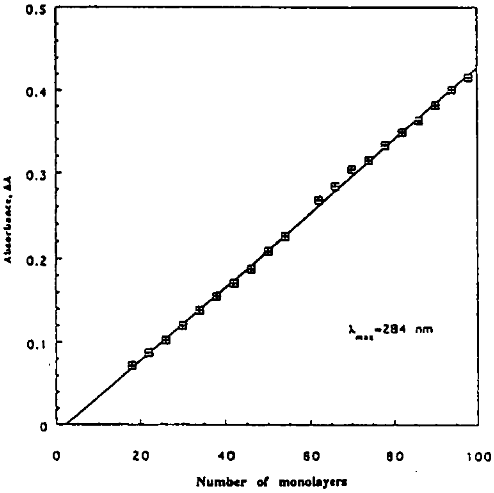


FIGURE 2. The relationship between absorbance and number of layers.

Photoreactivity

When the LB film was irradiated with a 500-W Hg lamp, the absorption intensity of the peak decreased gradually showing the shift of absorption maximum to shorter wavelength (FIGURE 3). The emission was also disappeared gradually. The change of IR spectrum of the LB film on irradiation showed the decrease in intensity of peaks (C=C at 1605 cm^{-1}, alkyl at 2900 cm^{-1}) and broadening of carbonyl group. These data suggest that reaction of double bonds and missing of alkyl chains probably by deesterification took place in the LB film on irradiation. The result of G.P.C. analysis of the irradiated LB film showed that the photoproduct contained two kinds of molecular weight of compounds: one is larger than that of (2) and the other is smaller than (2). Based on above data it is considered that the former is oligomers formed by cycloaddition of double bonds and the latter is decomposed product by deesterification. The latter product was not found in photorection of LB films made from (1). It should be noted that the compounds (2) and (3) are photostable in the crystalline state, however the fabrication of their LB films made them photoreactive.

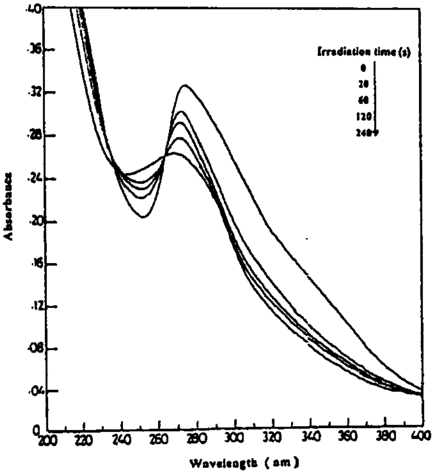


FIGURE 3. The UV spectrum of LB film of (2) and its change on irradiation.

In summary a new type of photoreactive LB film was successfully prepared from amide derivatives of p-PDA and its photoreaction was revealed.

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