



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

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 24 Sep 2006

To cite this article: H. R. Hafiz, J. Zhao, N. Tanigaki & F. Nakanishi (1999): A Study on the Photoreactivity and Structure of LB Films of p-Phenylenediacrylic Acid with an Amide Bond, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 327:1, 111-114

To link to this article: <http://dx.doi.org/10.1080/10587259908026792>

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## A Study on the Photoreactivity and Structure of LB Films of *p*-Phenylenediacrylic Acid with an Amide Bond

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(Received June 30, 1998; In final form July 15, 1998)

Photoreactive LB films of *p*-phenylenediacrylic acid "DCAB" with an amide bond were manipulated under different conditions. As revealed by means of spectroscopy, the type of multilayer structure and photoreactivity are affected by the subphase temperature. The photoreactivity as well as fluorescence of LB films prepared at temperatures in the vicinity of 10 °C are significantly high.

**Keywords:** Amide group; Hydrogen bonding; LB films; Photoreactivity

### INTRODUCTION

Two decades ago until present research is still going for the synthesis and investigation of the photoreactivity of the *p*-phenylenediacrylic acid (PDA) derivatives both in the form of crystals and LB films<sup>[1-5]</sup>. The existence of the bifunctional chromophores in the PDA makes its photochemistry and photophysics indispensable and beneficial in a variety of industrial applicable polymers such as that utilized as thin film photoresists used for microlithography<sup>[6,7]</sup>. In a previous article we have investigated the effect of the temperature on the monolayer formation of PDA bearing an amide bond, that is 4-(4-(2-decyloxycarbonyl)vinyl)cinnammoylamino)benzoic acid "DCAB".



Thermodynamic concept has been utilized to explain the conformational changes of such molecule at the phase transition region between two extremes; bent and erect conformation<sup>[8]</sup>. This result lead us to further investigation on fabrication of the qualified LB films. In this work we investigated the effect of the molecular arrangement on the photoreactivity of LB films manipulated at different temperatures.

### EXPERIMENTAL

The commercial Langmuir balance (Meßgrätewerk Dr. R. Wobser KG, Lauda) was used for manipulation of LB films<sup>[8]</sup>. Distilled water or aqueous  $\text{CdCl}_2$  solution was used as a subphase. Ultra violet and emission spectra were measured using Shimadzu UV-2500PC and JASCO FP-777 spectrophotometers, respectively. Photoreaction was performed using a 500 W super-high pressure mercury lamp (Ushio USH-500 D,  $\lambda=313$  nm). FT-IR measurements were done by a Perkin-Elmer System 2000 FTIR spectrometer, equipped with an MCT detector, at a resolution of  $4\text{ cm}^{-1}$ . X-ray diffractograms were measured using Rigaku Rotaflex computer-controlled Diffractometer with  $\text{CuK}\alpha$  radiation source.

## RESULTS AND DISCUSSION

Judging from the  $\Pi$ -A isotherms at various temperatures, the preparation of the LB film was carried out under a surface pressure of 30 mN/m. It was interesting to find out that the type of LB film depends on the temperature of subphase; at temperatures above  $15^\circ\text{C}$ , X-type film was obtained and below  $15^\circ\text{C}$ , Y-type was obtained (the transfer ratio for all LB films ranged .95 - 1.0). The behavior seems to depend on many factors, such as physical state of both the monolayer and subphase, the chemical structure of the spreading molecules and so on.

At low temperature, under the action of the hydrophobic and cohesion forces between the long alkyl chains and the hydrogen bonding between head carboxyl groups, molecules are arranged in a weakly condensed but rigid monolayer. The situation is converted when we are dealing with the high temperature where a highly condensed but fluid monolayer is obtained. Such two extremes and intermediate molecular conformations were discussed elsewhere<sup>[8]</sup>.

The small angle X-ray diffractograms of Y-type LB films prepared at ca  $9^\circ\text{C}$  did not give a clear diffraction pattern. However, those of the LB film prepared from  $\text{CdCl}_2$  aqueous solution provided some structure order (Figure 1) giving d-spacing value of  $54.15\text{ \AA}$  which confirms the Y-type film. Considering the molecular length of DCAB,  $29.46\text{ \AA}$  (evaluated by bond angle and bond length calculation) and the d-spacing value, DCAB molecules are aligned normal to the substrate with a tilt angle of  $23.2^\circ$ .

The absorption spectra of LB films manipulated at different temperatures (ca.  $9^\circ\text{C}$  and  $20^\circ\text{C}$ ) are illustrated in Figure 2a-b. Depending on the temperature, the shape of spectra was different suggesting different molecular

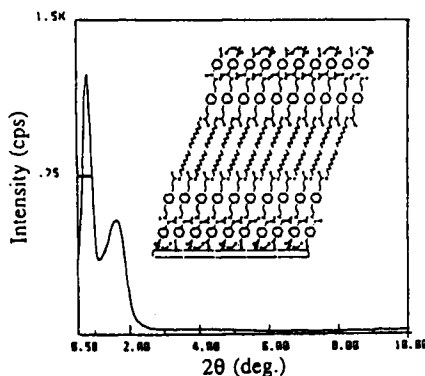


FIGURE 1. X-ray diffractogram of LB film ( $n=98$ ) prepared at the air- $\text{CdCl}_2$  interface. Inset is the proposed bilayer structure.

arrangement in each LB film. When these films were irradiated, the absorption intensity decreased indicating that they are photoreactive.

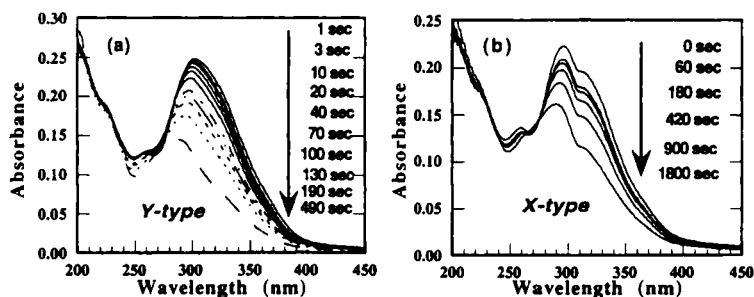


FIGURE 2. Irradiation time effect on the absorption spectrum of LB films ( 14 layers) prepared a) at 9 °C and b) at 20 °C.

The photoreaction of both LB films was also monitored by FTIR spectroscopy as shown in Figure 3a-b. The continuous decrease of the normalized intensity of the bands at  $1628\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{C})_{\text{ester}}$ ) and  $1636\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{C})_{\text{amide}}$ ) indicates that a 2+2 cycloaddition of double bonds occurred upon irradiation. The reaction kinetics can be understood from the relation between the normalized intensity and irradiation time for both bands and at different temperatures shown in Figures 3a-b. It should be noted that the reaction speed of double bonds at ester side is faster than that of amide side and the photoreaction proceeds faster in the LB film prepared at low temperature.

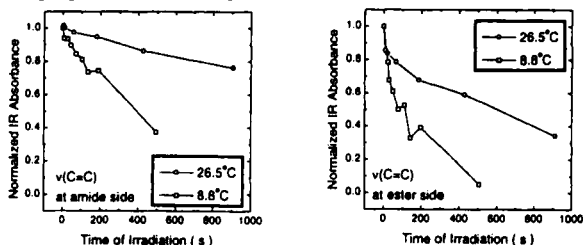


FIGURE 3. Normalized FTIR absorbance of two  $\nu(\text{C}=\text{C})$  modes versus time of irradiation of LB film prepared at different temperatures.

Actually, the latter fact is in agreement with the molecular conformation model described in the previous paper <sup>[8]</sup>, since the LB film prepared at low temperature is assumed to possess a more loose and flexible structure, which causes the photocycloaddition to proceed easily.

Besides, the photoreactivity was confirmed by the room temperature fluorescence spectrum shown in Figure 4a. The broad major peak at ca. 450 nm is a typical characteristics of the excimer emission due to its shape and Stokes shift from the monomer emission <sup>[9]</sup>, which could not be observed by the

presence of an amide group. The fluorescence spectrum for the DCAB in THF solution ( $10^{-5}$  M) is also shown for comparison. The emission spectrum is more structured than that of the LB film. This corresponds to the difference in the vibronic states represented by the excitation spectra in both cases. More details about the fluorescence of DCAB in solution will appear in the coming paper<sup>[10]</sup>. For the LB film, the intensity of the emission peak was shown to decrease upon excitation with the wavelength of 330 nm following the first order kinetics as illustrated in Figure 4b. It is clear that the lower is the temperature the higher is the speed of the fluorescence kinetics.

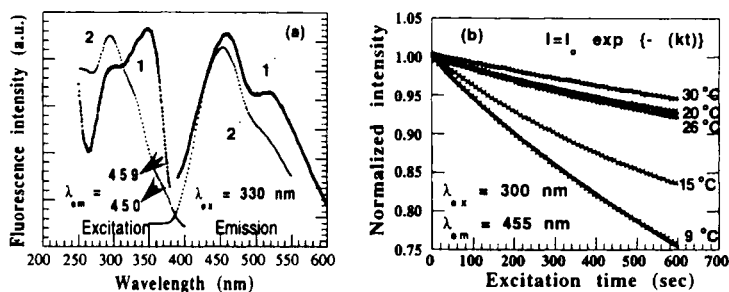


FIGURE 4. a) Fluorescence excitation and emission spectra of LB film (2,2'), and THF solution (1,1'). b) Time decay profiles of maximum emission intensity of LB films prepared at different temperatures.

## CONCLUSION

The type and photoreactivity of LB films depend in a great extent on the manipulation temperature. The more loose LB film architecture obtained at lower temperature, the higher is the photoreactivity. The fluorescence emission is attributable for the excimer formation, and the emission decay follows the first order kinetics upon excitation.

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