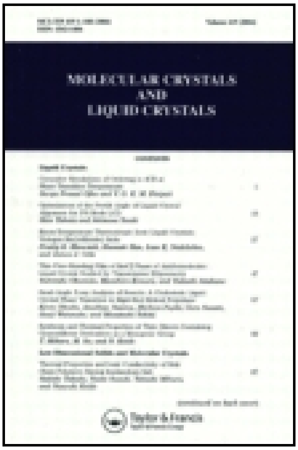

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Photosensitive LB Film of PVA Bearing p-Phenylenediacrylate Ester: Comparative Study on Properties of Monomeric and Polymeric Film

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PHOTOSENSITIVE LB FILM OF PVA BEARING *P*-PHENYLENEDIACRYLATE ESTER: COMPARATIVE STUDY ON PROPERTIES OF MONOMERIC AND POLYMERIC FILM

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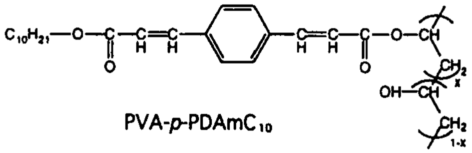
Abstract The manipulation of the LB film was investigated by using poly(vinyl alcohol) bearing *p*-phenylenediacrylate moiety. Its property was characterized with comparison of the monomeric LB film made from corresponding *p*-phenylenediacrylic acid monoester of the side chain. The spectroscopic data showed that the polymer LB film with high photoreactivity was obtained successfully. The result of measurement dynamic contact angle of the polymer LB film revealed its unique surface property, which was shown by a high advancing contact angle (108°) and a low receding contact angle (15°).

Keywords: Langmuir-Blodgett film; PVA; *p*-phenylenediacrylic acid; photoreactivity; contact angle

INTRODUCTION



PVA-*p*-PDAmC$_{10}$

Photoreactive thin films are one of targets to be investigated and developed for applications to electronics and photonics. We have been studying a series of *p*-phenylenediacrylic acid (*p*-PDA) derivatives as the candidate of photofunctional materials[1-4]. By introducing *p*-PDA chromophores into poly(vinyl alcohol) (PVA), we have prepared highly photosensitive polymer (as shown above) and evaluated its property[5]. In this report, the manipulation of Langmuir-Blodgett (LB) film has been investigated with amphiphilic PVA bearing monodecyl ester of *p*-PDA (*p*-PDAmC10), and its characterization has been carried out. The feature of polymeric (PVA-*p*-PDAmC10) LB film was compared with that of monomeric (*p*-PDAmC10) LB film.

EXPERIMENTAL

p-PDAmC10 and PVA-*p*-PDAmC10 were prepared according to previous paper[6]. They were purified by recrystallization or reprecipitation. The degree of esterification of PVA-*p*-PDAmC10 used in this experiment was 28 mol%.

A commercially available film balance (Lauda-MGM) was used as a trough in measurement of surface pressure~area curve and preparation of LB film. Both *p*-PDAmC10 and PVA-*p*-PDAmC10 were dissolved in chloroform at the concentration of 10^{-3} M order. The sample solution was spread on a subphase consisting either of distilled water or 10^{-3} M aqueous solution of $CdCl_2$ / $KHCO_3$. Surface pressure~area curve was measured at 20-21°C. Plates (quartz and glass) treated with an ethanol solution of KOH were used as a substrate. Monolayers were deposited onto a substrate by using the LB method under different surface pressure. The LB films of *p*-PDAmC10 and PVA-*p*-PDAmC10 were irradiated with a 500 W mercury lamp (λ >300 nm). Photoreaction was monitored by measuring their UV spectra with a Shimadzu UV-2500PC UV-VIS Recording Spectrophotometer.

The dynamic contact angle of LB films was measured by the Wilhelmy balance method at 20°C using a Dynamic Contact Angle Analyzer (CAHN). The sample glass plate (32 × 18 × 0.147 mm) on which the monolayers were transferred was vertically immersed into the water and withdrew from the water at a speed of 20 μm / sec. Dynamic contact angle was obtained after calculating and calibrating on the automatically collected date.

RESULTS AND DISCUSSION

Preparation and property of LB films

The surface pressure~area curves of *p*-PDAmC10 and PVA-*p*-PDAmC10 were shown in Figure 1. The surface pressure~area curve of PVA-*p*-PDAmC10 showed the presence of condensed phase with a surface area of 33 Å^2 per polymer unit. PVA-*p*-PDAmC10 monolayer on water subphase is very stable and the monolayer formation is reversible. It can easily be transferred onto a hydrophilic substrate to form a Y-type LB film. There is a linear relationship observed between the absorption intensity and number of layers. The average thickness of a monolayer measured by a Alpha Step 300 Step-Height Profiler with the LB film was 20 Å, which was determined by measuring the thickness of the LB film (25 layers). This suggests that the side chains of *p*-PDAmC10 stand side by side with a tilting angle of about 40° in the LB film. *p*-PDAmC10 monolayer is unstable and irreversible on distilled water, therefore it is difficult to prepare homogeneous LB film. However, as shown in Figure 1, the surface pressure~area curve for *p*-PDAmC10 using $CdCl_2$ aqueous subphase, showed the presence of condensed phase with a surface area of 24 Å^2 per molecule suggesting the formation of a relatively stable monolayer. But this monolayer is not so stable as that of the polymer, its surface pressure is decreasing in the surface pressure~time (π~t) curve even after 16 hours. This indicates that *p*-PDAmC10 has a very strong tendency to aggregate each other on the water surface and surface pressure-area curve may have different shape when the speed of compression is lower than that of aggregation. In the case of *p*-PDAmC10 monolayer on $CdCl_2$ aqueous subphase, it could be transferred onto a substrate to form a Z-type LB film. But *p*-PDAmC10 LB film detached from a substrate when

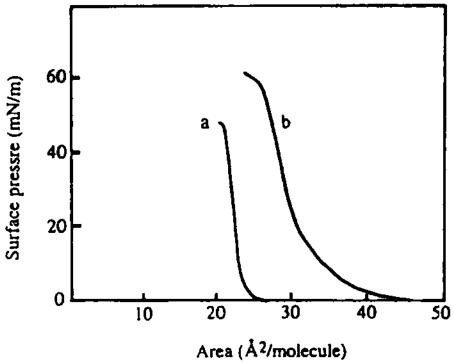


FIGURE 1. Surface pressure–area curves.
a: *p*-PDAmC10 on $CdCl_2$ subphase;
b: PVA-*p*-PDAmC10 on water subphase.

immersed into water slowly, while PVA-*p*-PDAmC10 monolayer could be deposited with a good transfer ratio without peeling from a substrate.

Photoreactivity of LB films

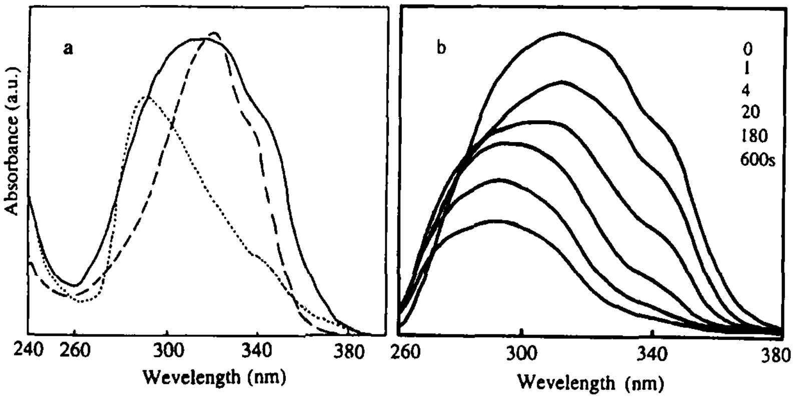


FIGURE 2. UV absorption spectra. a: PVA-*p*-PDAmC10 LB film (——), *p*-PDAmC10 LB film (……) and PVA-*p*-PDAmC10 in THF solvent (------); b: PVA-*p*-PDAmC10 LB film on irradiation with UV light.

The UV spectrum of polymeric LB film is shown in Figure 2. The absorption maximum was observed at 310 nm, which is blue shift compared with that in solution (dotted line). In the case of monomeric LB film, its absorption maximum showed blue shift by 25-nm. When irradiated with a mercury lamp (>300nm), the polymeric LB film showed obvious decrease in absorption intensities and λ_{max} shifted to shorter wavelength (Figure 2). The

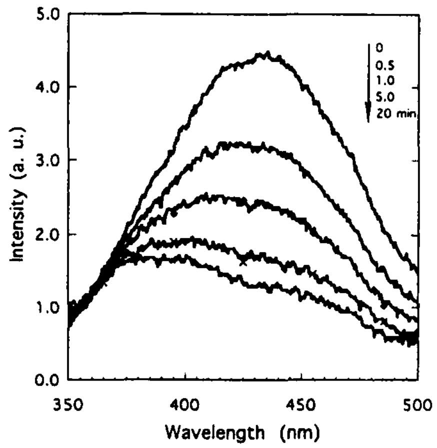


FIGURE 3.Fluorescence spectra of PVA-*p* PDAmC10 LB film on irradiation.

fluorescence spectrum of the polymeric LB film is shown in Figure 3. The broad emission was observed at 420 nm, which is due to the formation of excimers in the LB film. The emission intensity decreased on exposure to exciting light (300 nm). These facts suggest that the double bonds in the polymeric LB film decreased by photoreaction and the conjugation system become shorter. The monomeric LB film was also photoreactive. However, the initial speeds of photoreaction of the polymeric LB film was very fast compared with that of the monomeric LB film. This can be explained as follows: the side chains of *p*-PDAmC10 are easily arranged to the favorable position required for photoreaction, like that in solution.

Contact angles of LB films

Contact angle is a thermodynamic quantity that characterizes the interaction between a solid and a liquid surface at the point of contact. It can provide some information about surface structure and can be used to evaluate the stability of LB film[7,8]. We measured the dynamic contact angles of both monomeric and polymeric LB films by using Wilhelmy balance method[7-9]. Figure 4 shows the hysteresis of dynamic contact angles of the polymeric LB film. The very interesting behavior is that the advancing angle is very high (>100°) and the receding one is very low (<20°). After irradiation, the receding angle increased to 70°~80° and the advancing one decreased

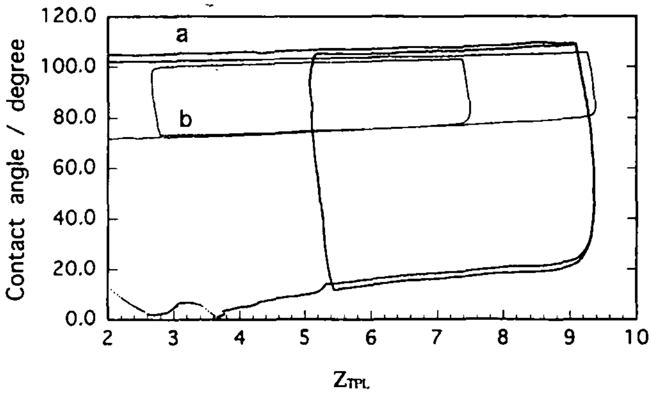


FIGURE 4. Dynamic contact angles of PVA-*p*-PDAmC10 LB film.
a: before irradiation; b: after irradiation.

by 5°. It seems that reorientation of *p*-PDAmC10 side chains takes place through measuring procedure before irradiation. After irradiation, the side chains crosslinked due to photo-cycloaddition[4,6] between the double bonds and this made the LB film less flexible. Therefore the receding contact angle is much higher than that of before irradiated one. For the monomeric film, the advancing angle is 110° and the receding one is 38°. This film is not so stable in water, so detaching of this film was observed during the measurement. On irradiation, the receding contact angle of this LB film did not increase, but film stability does increased.

CONCLUSION

The highly photosensitive LB film was prepared from PVA having *p*-phenylenediacrylate moiety as the side chains. Characterization of the polymer LB film revealed a unique behavior of dynamic contact angles, that is, the advancing angle showed hydrophobic surface, while the receding one showed quite hydrophilic one.

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