PREPARATION AND PHOTOREACTION OF LANGMUIR-BLODGETT FILM MADE FROM POLY(VINYL ALCOHOL) HAVING p-PHENYLENEDIACRYLIC ACID ESTER

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p-Phenylenediacrylic acid (p-PDA) derivatives is one of the attractive compounds as photoreactive materials. We have studied extensively photopolymerization of p-PDA diesters in the crystalline state[1]. Following this study, we have prepared a series of p-PDA monoesters and studied their photoreaction in various states such as in crystals and Langmuir-Blodgett (LB) films[2,3]. Recently we have synthesized new photosensitive poly(vinyl alcohol)s having p-PDA groups as the side chain[4]. They showed high photosensitivity, which may be due to the polymer effect. In this report, we deal with PVA bearing long-chain alkyl esters of p-PDA, expecting the preparation of photosensitive polymer LB films, which may be useful in various industry fields. p-PDA mono-n-decyl ester (p-PDAmC10) was used for esterification of PVA. PVA with p-PDAm mC10 was prepared from fully saponified PVA of P=1700 and p-PDAmC10 using 1-chloro-2,4,6-trinitrobenzene as the condensing reagents. The degree of esterification estimated by measuring UV spectrum of this polymer (p-PDAmC10-PVA), was 30 mol/%. For the LB film preparation, a commercially available film balance (Lauda-MGW) was used as a trough. p-PDAmC10-PVA is soluble in ordinary organic solvents.
The chloroform solution of p-PDAmC$_{10}$-PVA was spread on a subphase consisting of distilled water and surface pressure-area curve was measured at 20-22 °C. It is shown in Figure 1. The curve showed the presence of the condensed phase. The molecular area for a polymer unit was 33 Å$^2$. This value is larger than that of p-PDAmC$_{10}$ and it seems to be reasonable considering the molecular model of this model. The reproducibility of the curve is good and the monolayer is very stable. The monolayer could be deposited onto a substrate by the LB method under surface pressure of 20-30 dyne/cm and a Y-type film was obtained. The UV spectrum of LB film is shown in Figure 2. The absorption peak was observed at 310 nm, shorter wavelength than that of polymer solution but similar to that of polymer film prepared by spin coating. There is a linear relationship observed between the absorption intensity and number of layers, indicating successful transfer of each monolayer. The thickness of the LB film with 25 layers was measured with an Alpha Step 300. The average thickness of a monolayer was about 20 Å. These facts suggest that the side chains of p-PDAmC$_{10}$ are arranged with some ordering in the layer. On irradiation of p-PDAmC$_{10}$-PVA LB film, the absorption intensity decreased rapidly as shown in Figure 2 by dotted line, indicating photoreaction took place. Thus it was confirmed that p-PDAmC$_{10}$-PVA could provide successfully LB film with high photosensitivity.

References