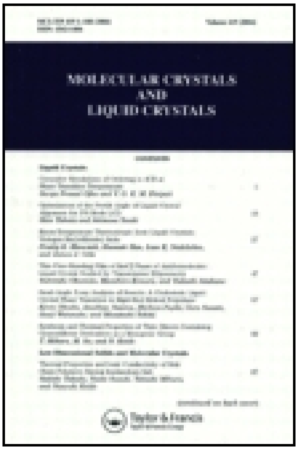

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Stability of a Photoreactive Polymer LB Film

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Stability of a Photoreactive Polymer LB Film

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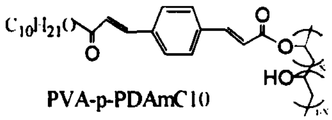
Dynamic contact angles and their hysteresis for LB films of p-phenylenediacrylic acid monodecylester (p-PDAmC10) and poly(vinyl alcohol) bearing p-PDAmC10 as the side chain (PVA-p-PDAmC10) were investigated by the Wilhelmy plate method. The hysteresis loops of the contact angle showed that: (1) PVA-p-PDAmC10 forms a more stable LB film than that of p-PDAmC10 which is casily detached when contacted with water; (2) PVA-p-PDAmC10 LB film transferred at high surface pressure (≥20 mN/m) with more than 3 layers can provide a uniform surface and same wettability; (3) PVA-p-PDAmC10 LB film has a very large contact angle hysteresis (>80°), which means that reorientation of the surface configuration takes place dramatically; and (4) the hysteresis can be greatly reduced (<30°) by UV-irradiation due to the photocycloaddition in the side chains of PVA-p-PDAmC10.

Keywords: p-phenylenediacrylic acid monodecylester; photoreactive polymer; Langmuir-Blodgett (LB) film; contact angle

INTRODUCTION



PVA-p-PDAmC10

p-Phenylenediacrylic acid mono-decylester (p-PDAmC10) is one of the attractive compounds as the candidate of photofunctional materials. The photoreactivity in various organized systems has been studied[1-4]. Recent investigations showed that the poly(vinyl alcohol) bearing p-PDAmC10 (PVA-p-PDAmC10. as shown above) could form highly photoreactive Langmuir-Blodgett (LB) film[5,6]. For developing various applications using such ultra thin films, it is important to clarify their surface properties under the condition of practical use. When these films are used in aqueous environment, stability and wettability are important factors.

There are several reports from this viewpoint. These include desorption of dimethyl dioctadecylammonium bromide molecules on mica surface by contacted with water[7-9], and spontaneous reorganization of stearate and arachidate bilayers during storage in their subphase[10,11]. These phenomena could be easily detected by the change in contact angle of the liquid. Recently we found a unique behavior of dynamic contact angle with polymer LB film of PVA-p-PDAmC10[5]. In this report, to evaluate the wettability and thus stability, further investigation has been carried out with the dynamic contact angle measurement. The monomer LB film of p-PDAmC10 was also prepared and corresponding wettability has been also revealed to provide the information for the preparation of ultra thin films.

EXPERIMENTAL

In the preparation of the LB film, PVA-p-PDAmC10 (esterification degree x=0.28) or p-PDAmC10 chloroform solution was spread on aqueous (in the case of p-PDAmC10, 10^{-4}M $CdCl_2$) subphase, and then a monolayer was transferred onto a microscope cover glass at different surface pressures. The Y-type LB film was obtained for PVA-p-PDAmC10 and Z-type for p-PDAmC10. The dynamic contact angle was measured by the Wilhelmy plate method[7,12-14] using a computer controlled Cahn balance (DCA 322 model).

RESULTS AND DISCUSSION

We have found that the LB film (7 layers) of PVA-p-PDAmC10 shows a unique behavior in measurement of dynamic contact angle (Figure 1). The average advancing angle is about 108° and the receding one around 15° as shown in curve a. The difference (hysteresis) is extremely large. This result can be attributed to the surface configuration of this LB film, in which the whole side chains and hydroxyl groups at the surface can easily change their orientation when the LB film contacted with water due to the loose packing of the side chains (unit area≥33Å^2). In order to find out the effect of preparation condition of LB film on the dynamic contact angle, we have investigated the advancing contact angles of PVA-p-PDAmC10 LB films transferred at different surface pressure as a function of the number of layers (Figure 2). It shows that

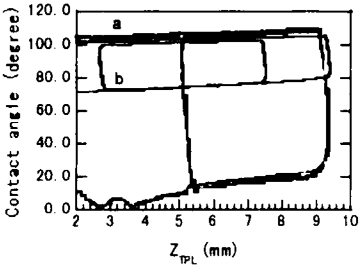


FIGURE 1 Dynamic contact angles of PVA-p-PDAmC10 LB film. a: before irradiation; b: after irradiation

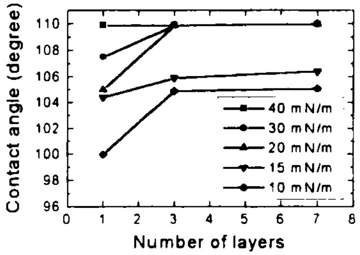


FIGURE 2 The relationship of advancing contact angle with layers of PVA-p-PDAmC10 LB films.

the contact angle increases by increase of the number of layers and reaches the constant value (110°) after the deposition of three layers when surface pressure is higher than 20 mN/m. This suggests that the LB multilayers provide a uniform and reproducible surface under those conditions[15]. When the surface pressure is low (10 or 15 mN/m), the advancing contact angle is low suggesting that the side chains are not closely packed (unit area≥34 and $36A^2$ respectively).

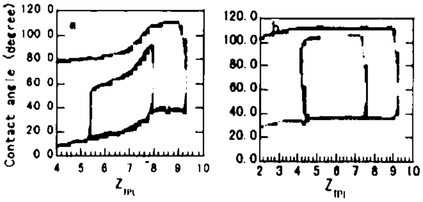


FIGURE 3 Contact angles of p-PDAmC10 LB film. a: before irradiation; b: after irradiation

Figure 3 shows the dynamic contact angle hysteretic loops of p-PDAmC10 LB film (6 layers). The advancing contact angle in the first loop was obviously much larger than that in the second one. This fact indicates that the film detaches or reorganizes when it contacted with water.

After UV-irradiation, the receding contact angle of PVA-p-PDAmC10 LB film increased to about 75° (curve b in Fig.1) suggesting that the film configuration changed greatly due to photocycloaddition of double bonds in the side chains. In the case of the monomer LB film, irradiation improved

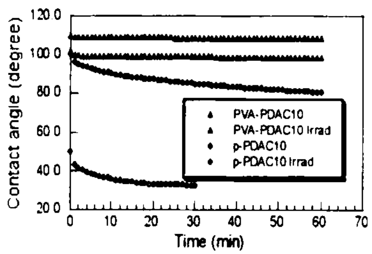


FIGURE 4 The time dependence of the advancing contact angle of LB film

its stability as shown in curve b of Fig. 3. In this case, compared with the polymer LB film, the receding contact angle did not increased so much.

The wettability of the LB film can be illustrated by the advancing contact angle change with time immersed (Figure 4). Both before and after the UV-irradiation, p-PDAmC10 LB films show much larger and faster decrease of the advancing contact angles with time than PVA-p-PDAmC10 LB films. The polymer LB film is more stable than the monomer one.

CONCLUSION

PVA-p-PDAmC10 polymer LB film shows a very high contact angle hysteresis which can be reduced on irradiation. The high contact angle hysteresis is due to the reorientation of surface configuration, which became difficult by photocycloaddition of double bonds in the side chains. The polymer films both before and after UV-irradiation are more stable than the monomer LB films.

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