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**PREPARATION OF POLYMER LANGMUIR-BLODGETT (LB) FILMS
WITH CYCLOBUTANE RINGS AND THEIR PHOTOCHEMICAL BEHAVIOUR***By Fusae Nakanishi*

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ABSTRACT

Preparation of photoreactive LB films was carried out using polymers/oligomers, which were prepared by "four-center type photopolymerization" and have cyclobutane rings in the main chain. The polymers/oligomers having long-chain alkyl ester residues, formed stable monolayers on the water surface when mixed with arachidic acid. These monolayers could be deposited onto a substrate successfully forming Y-type films. The oligomer LB films were polymerized on irradiation. The polymer LB films showed photo-reversible process between polymers and oligomers, depending on wavelength of irradiating light. This photochemical behaviour was found to be caused by the cleavage and formation of cyclobutane rings.

1. Introduction

The Langmuir-Blodgett (LB) method is an important technique for the preparation of very thin organic films which have a significant role in relation to various electronic and optical phenomena. A number of different kinds of LB films were prepared and their properties were investigated in view of their potential applications. However, in general, the resulting films do not have sufficient mechanical strength for practical use. In order to find a solution to this problem, polymer LB films were prepared¹⁻⁴⁾. This paper focuses on an attempt to prepare photoreactive LB films using polymers/oligomers having cyclobutane rings. The polymer/oligomers, having cyclobutane rings in the main chain, were prepared by the "four-center type photopolymerization"^{5,6)}. We have studied the characteristics of these polymers⁷⁾ and noted several interesting properties of these polymers, which were caused by the presence of cyclobutane rings. Therefore, it is expected that LB films prepared using these polymers will have useful properties which may have applications in the area of recording materials. In this report, the preparation of LB films using such polymers/oligomers and their photochemical behaviour have been described.

2. Experimental**2.1 Materials**

The polymers/oligomers used in this experiment were prepared according to the method described in previous papers^{5,6)}. The polymers prepared from di-*n*-dodecyl ester of *p*-phenylenediacrylic acid (*p*-PDAC₁₂) and di-*n*-hexyl ester of 5,5'-(1,4-phenylene)-bis(2-cyano-2,4-pentadienoic acid) (PCPAC₆) have the reduced viscosities of 1.5 and 1.2, respectively. The oligomers prepared from corresponding monomers, consist of the mixture of trimers and tetramers (oligo(*p*-PDAC₁₂)) and dimers and trimers (oligo(PCPAC₆)).

2.2 Preparation of monolayer or multilayer films

A commercially available film balance (Lauda MGW) was used as a LB equipment. Polymers/oligomers were dissolved in chloroform (Merk, Uvasol) at the concentration of 0.8-1.0 g/L of chloroform. The mixed solution of polymers/oligomers and arachidic acid with unit-molar ratios of 1 : 5 was spread on a subphase consisting of either redistilled water or 10⁻³ M CdCl₂/10⁻⁵ M KHCO₃ aqueous solution. Surface pressure-area isotherms were measured at 20°C. The mixed monolayer was transferred onto either a glass or a quartz plate by the Langmuir-Blodgett method at the surface pressure of 20-30 dyne/cm. The plate used in the experiment, was treated

with sodium alcoholate and washed with redistilled water thoroughly.

2.3 Photoreaction

The polymer/oligomer LB films were irradiated with a spectroirradiator (JASCO CRM-FA) consisting of a 2000 W Xenon lamp and a grating monochrometer. The photoreaction process was monitored by measuring their u.v. spectra using a Shimadzu UV-220 spectrophotometer. An estimate of the molecular weight of the irradiated films was carried out using gel permeation chromatography (Shimadzu LC-5A). For this purpose, the irradiated film was dissolved in tetrahydrofuran and the solution was eluted using tetrahydrofuran.

3. Results and discussion

3.1 Surface pressure-area isotherms of polymers and oligomers

Several polymers for the LB films were prepared from dialkyl esters of *p*-phenylenediacrylic acid (*p*-PDA) and 5,5'-(1,4-phenylene)-bis(2-cyano-2,4-pentadienoic acid) (PCPA). The former compounds have an absorption maximum at 320 nm in solution and they are photo-reactive towards u.v light. The latter compounds showed an absorption maximum at 400 nm in solution and are sensitive to visible light. The polymers/oligomers prepared by irradiating these crystals, have the following structure.

They have benzene rings and cyclobutane rings in the main chain. The polymers prepared by the "four-center type photopolymerization" generally showed high crystallinity and they were difficult to dissolve in ordinary organic solvents. However, in the case of the polymers having long-chain alkyl ester residues, they are soluble in chloroform⁶⁾ and the LB method can be applied to these polymers. Judging from their chemical structure, it appears that these polymers do not readily form stable monolayers. In fact, the surface pressure-area isotherms for the polymer themselves expanded and no condensed

state was observed. However, it was found that the polymers with long-chain alkyl ester residues could form stable monolayers on the water surface when mixed with long-chain fatty acids such as arachidic acid. Poly(*p*-PDAC₁₂) and poly(PCPAC₆) are polymers suitable for LB films and they were chosen for this investigation

Fig. 1 Surface pressure-area isotherms for mixed monolayer.

— poly(*p*-PDAC₁₂)-arachidic acid
 oligo(*p*-PDAC₁₂)-arachidic acid (unit-molar ratio of poly(*p*-PDAC₁₂)/oligo(*p*-PDAC₁₂): arachidic acid=1:5)

Fig. 2 Surface pressure-area isotherms for mixed monolayer.

— poly(PCPAC₆)-arachidic acid
 oligo(PCPAC₆)-arachidic acid (unit-molar ratio of poly(PCPAC₆)/oligo(PCPAC₆): arachidic acid=1:5)

because of ease of synthesis and their film-forming ability. Their oligomer LB films were also investigated for comparison. Figures 1 and 2 show the surface pressure-area isotherms for the mixture of arachidic acid with either a polymer or an oligomer. The condensed states were observed for these mixed monolayers. In the case of poly(*p*-PDAC₁₂) and oligo(*p*-PDAC₁₂), two condensed phases were observed. The average molecular areas in the first condensed state of the mixed monolayers were found to be 27 Å² for poly(*p*-PDAC₁₂), and 25.5 Å² for oligo(*p*-PDAC₁₂). The average molecular areas of the mixed monolayer of poly(PCPAC₆) or oligo(PCPAC₆) were found to be 28 Å² and 27 Å², respectively. Assuming that the molecular area of arachidic acid in the mixed monolayer is the same as in the pure monolayer (19 Å²), the area per unit of the polymers and oligomers was calculated as follows:

poly(*p*-PDAC₁₂) 67 Å², oligo(*p*-PDAC₁₂) 58 Å²,
poly(PCPAC₆) 73 Å², oligo(PCPAC₆) 67 Å²

Though there are differences among these values, they suggest that the unit of polymers or oligomers, which consists of benzene ring and a cyclobutane ring, is located on the water surface and long-chain alkyl ester residues are positioned standing on the water surface as shown below.

3.2 Preparation and properties of polymer or oligomer films

The mixed monolayers of arachidic acid with either polymers or oligomers could be transferred onto a substrate by the Langmuir-Blodgett method. For the successful deposition, the suitable unit-molar ratio of polymer/oligomer-arachidic acid was 1 : 5. Transfer of monolayers was observed on both down and up strokes forming Y-type films. The absorption spectra of the mixed multilayer films thus prepared are shown in Figures 3, 4, 5, and 6. The oligomer films showed an absorption maximum at 280 nm for oligo(*p*-PDAC₁₂) and at 360 nm for oligo(PCPAC₆) (Figures 3 and 4). These absorption maxima are considered to be due to the terminal groups of each oligomers (cinnamic acid ester group for oligo(*p*-PDAC₁₂) and cyano acrylic acid ester group for oligo-

Fig. 3 U. v. spectrum of oligo(*p*-PDAC₁₂) LB film and its change on irradiation of light (280 nm). 1. before irradiation 2. after irradiation for 240 sec.

Fig. 4 U. v. spectrum of oligo(PCPAC₆) LB film and its change on irradiation of light (360 nm). 1. before irradiation 2. after irradiation for 120 sec.

(PCPAC₆)). The linear relationship between the absorbance at 360 nm and the number of layers of oligo(PCPAC₆) LB film, was observed suggesting that each layer was deposited on a substrate successfully.

3.3 Photochemical behaviour of polymer and oligomer LB films

The oligomer LB films were very sensitive to light and their spectra changed on irradiation of light corresponding to their absorption maxima (Figure 3 and 4). The absorption peaks decreased gradually indicating that conjugation through double bonds disappeared by photo-

Fig. 5 U. v. spectrum of poly(*p*-PDA₁₂) LB film and its change on irradiation of light. 1. before irradiation 2. after irradiation with 226 nm for 60 sec. 3. after irradiation with 280 nm for 60 sec.

Fig. 6 U. v. spectrum of poly(PCPAC₆) LB film and its change on irradiation of light. 1. before irradiation 2. after irradiation with 279 nm for 15 sec. 3. after irradiation with 360 nm for 60 sec.

reaction of terminal groups, yielding polymers. The polymer LB films displayed unique behaviour when irradiated with shorter wavelength of light. That is, when poly(*p*-PDAC₁₂) LB film was irradiated with light 226 nm, the u.v. spectrum changed as shown in Figure 5 and was similar to that of oligo (*p*-PDAC₁₂) having the absorption maximum at 280 nm, indicating that terminal groups in the polymer LB film increased on irradiation. By the gel permeation chromatography analysis, the irradiated film was found to be the mixture of dimers and trimers, which has similar molecular weight of the oligomer used for preparation of oligomer LB films. These data indicate that the polymer LB film was depolymerized into the oli-

gomer LB film by the cleavage of cyclobutane rings in the main chain on irradiation of light 226 nm. The resulting oligomer LB film was polymerized again with irradiation of light 280 nm, forming cyclobutane rings as shown below. It is possible to repeat this process (polymer $\rightleftharpoons$ oligomer) several times.

This photochemical behaviour was not observed in the polymer film prepared by casting a poly(*p*-PDAC₁₂) solution and it should be noted that this is characteristic feature of poly(*p*-PDAC₁₂) LB film. The same behaviour was observed for poly(PCPAC₆) LB film. In this case, depolymerization occurred by irradiation of light 279 nm and repolymerization occurred with light 360 nm (Figure 6).

4. CONCLUSION

1. Novel photoreactive LB films were prepared using polymers/oligomers having cyclobutane rings.
2. They formed stable monolayers on the water surface when mixed with arachidic acid and these monolayers could be deposited onto a substrate forming Y-type films.
3. The polymer LB films showed the reversible depolymerization and polymerization process depending on wavelength of irradiating light.

This phenomenon was caused by the cleavage and formation of cyclobutane rings in the main chain.

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シクロブタン環を持つポリマー LB 膜の作製とその光化学的挙動

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光反応性 LB 膜の作製が四点光固相重合によりえられた主鎖にシクロブタン環を持つポリマー/オリゴマーを用いて行なわれた。長鎖アルキルエステル残基を持つポリマー/オリゴマーはアラキジン酸と混合することにより安定な単分子膜を水面上に形成した。これらの単分子膜は基板に Y 型膜として累積することができた。オリ

ゴマー LB 膜は光照射によりポリマー LB 膜と変化した。ポリマー LB 膜は照射する光の波長により、ポリマーからオリゴマーまたオリゴマーからポリマーへの光可逆反応を起した。この挙動は光により主鎖中のシクロブタン環の開裂と形成が起ることに起因することがわかった。