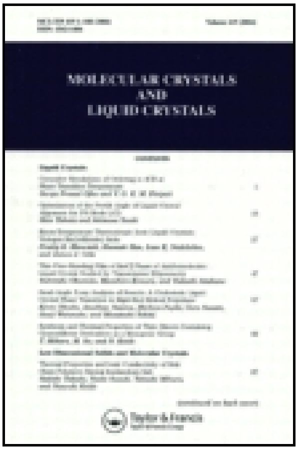

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STRUCTURAL CHANGES OF DIACETYLENE / FATTY ACID HETERO-CYCLIC LANGMUIR-BLODGETT FILMS BY POLYMERIZATION STUDIED BY X-RAY DIFFRACTION

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Abstract Hetero-structured Langmuir-Blodgett (LB) films of stearic acid (C_{18}) and unpolymerized 10-12 pentacosadiynoic acid ($CH_3(CH_2)_{11}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$: PD) were prepared and the structure of unpolymerized and photopolymerized films were investigated by X-ray diffraction. The structural changes by photopolymerization were discussed. The order of deposition was varied systematically. It is found that the interplanar spacings and molecular alignments of the hetero-structured films strongly depend on the order of deposition. For the 3 and 4 layer cycle films, "partially overturned" structure was observed in some unpolymerized films, which means that some molecules turns into Z or X films from Y type. Moreover, polymerized films returned to Y type structure. From the films with rather thick periodicity as long as about 200 Å, satellite reflections were observed suggesting that high order can be achieved over large distances and the macroscopic molecular orientations are highly ordered in spite of the microscopic inhomogeneity.

INTRODUCTION

Recently, fabrication of polar LB[1] films has been investigated with particular emphasis on their physical properties such as piezoelectricity, pyroelectricity[2] and even-order nonlinear optical effect[3]. For such applications, it is of great importance to investigate structure and molecular orientations of the hetero-structured LB multilayers[4]. The relationship between the conditions of fabricating films and the structures of the films, more precisely, the orientation of the molecules in the films is strongly needed.

Of all the classes of materials investigated for polymerization, most attention has been paid to diacetylene derivatives which have the general formula R_1-C≡C-C≡C-R_2 and can be readily polymerized by γ-ray or UV irradiation. Photopolymerized PD, so called polydiacetylene (PDA), can provide large nonlinear optical coefficient. The monomer is suitable for making thin films by the LB technique by which asymmetric crystal structure can be built. The optical behavior of the polymerized films strongly depends on the conformation of the polymer. It is also reported that the third nonlinear optical activity of polymerized diacetylene depends on the density of monomer[5]. Thus the investigation of the structure of unpolymerized diacetylene is of great importance.

However, it is rather difficult to control the orientation of the molecules. Packed molecules of the LB films are not always perpendicular to the substrate. The polydiacetylene LB film is an example, which is a promising candidate of material for organic nonlinear optics. It was also reported that the molecular orientation of the LB films is different between the first layer and the subsequent layers using IR[6] and RHEED[7].

In this paper, we report X-ray analysis of hetero structured LB films of C_{18} and PD in various and systematic deposition order. Further, the structural changes of the alternating films stimulated by the photopolymerization is shown.

EXPERIMENTAL DETAILS

Sample preparation

The trough we used was the KSV-5000 alternate layer system manufactured by KSV corporation (Finland). The surface of the subphase is separated by barriers into three compartments. One is for material A, one for the material B and the other is a pure water surface. The surface pressures are measured with Pt Whilhelmy plates and the subpahse for two film materials was common. A substrate could be moved through any of the compartments in any direction.

Monolayers of PD cadmium salt and cadmium stearate were formed by spreading $CHCl_3$ solutions of PD (Tokyo Kasei Co.,Ltd.) and stearic acid (Tokyo Kasei Co.,Ltd) at a concentration of 1×10^{-3} [mol/l] on an aqueous subphase containing 4×10^{-4} [mol/l] $CdCl_2$ and 5×10^{-5} [mol/l] $KHCO_3$. The reagents were used without further purification. The subphase temperature was maintained at 18.0 °C. The monolayer was then transferred onto a substrate at a constant surface pressure of 25.0 [mN/m] by the vertical dipping method. The transfer rates of the C_{18} and PD were 10 [mm/min] and 5 [mm/min] respectively. The transfer ratios (T_r) of both materials were $0.8<T_r<1.1$. Glass slides were used as substrates. The substrates were cleaned with EXTRAN MA neutral detergent for precise cleaning as a first step of cleaning. Then they were soaked in a saturated solution of KOH dissolved in methanol. The KOH was an analytic grade reagent purchased from Merck Co.,Ltd. The substrates were then washed in water deionized to better than 10 [MΩ/cm]. After drying, they were bathed in hexamethyldisilazane vapor for two days to make the surface completely hydrophobic.

The orders of prepared samples are shown in Table I. C_{18} and PPD are expressed as A and B, respectively. All the samples were Y type with the first layers deposited during the downward stroke. The prepared samples were irradiated by an 8 W UV lamp at a distance of 20 mm for 600 s. The sample preparation was performed in a photo darkroom to prevent photopolymerization of PD before the UV irradiation.

Measurement

The molecular orientations of the prepared samples were measured with a θ-2θ X-ray diffractometer with a rotating Cu target. The wavelength of the monochromized X-ray is 1.5405 Å. The scanning range of 2θ was 1-15 degs. After the measurement, the unpolymerized samples were characterized with a Hitachi 330 UV-visible-IR spectrophotometer and ensured not to be polymerized by the X-ray.

RESULT AND DISCUSSION

Table I: Deposition sequence of prepared samples. 'A' and 'B' represent C_{18} and 10-8 ADA respectively. 'A' and 'B' are half of the interplanar spacings of the Y type homo-films of C_{18} and 10-8 ADA. All the samples are Y type films deposited on the hydrophobic substrates and the first layers were transferred during the downstroke.

period	unit order	repetition	number of layers	expected interplanar spacings
2	[AB] [BA]	20	40	$A+B$
3	[AAB]	14	42	$A+B$, $2A$
	[ABA]			
	[BAA]			
	[BBA]			$A+B$, $2B$
	[BAB]			
	[ABB]			
4	[ABBA]	10	40	$A+B$
	[BAAB]			$A+B$
	[BBAA]			$2A$, $2B$
8	[BBBBAAAA]	4	40	$2A$, $2B$, $4A+4B$

Table II: interplanar spacings of cadmium planes of 2 layer periodic films. [A] and [B] are the half spacing of Y type homo films of stearic acid and PD, respectively.

deposition order	[AB]	[BA]	[A]	[B]
monomer (Å)	53.2	51.2	25.1	28.1
polymer (Å)	53.9	51.8	25.1	28.7

The interplanar spacings of the Cd planes which can appear in the X-ray diffraction pattern is shown in Table I. The half spacings of the Cd planes of C_{18} and PD are indicated as A and B.

2 layer periodic films

The interplanar spacings of Cd planes d of the 2 layer periodic films calculated from the X-ray diffraction patterns are shown in Table II. The calculation is based on the Bragg condition expressed as $d=\frac{n\lambda}{2\sin\theta}$. In the two layer periodic films, the spacings expected to appear in

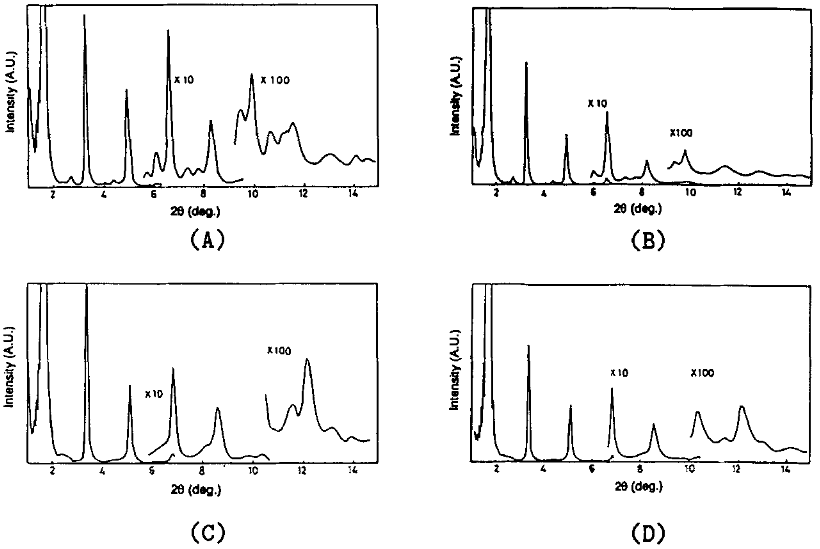
[BAB] and [ABB] types have subsidiary peaks, which suggest some different spacings exist. The peaks other than the major peaks of $A+B$ corresponds the spacing of monolayer of PD plane. In terms of the transfer ratio, the deposition mode of the films were all Y type. Thus it is considered that the unpolymerized alternating films of the combination have "partially overturned structure," which represent the mixture of Y type film and X or Z type film as illustrated in Fig. 2. However, the subsidiary peaks were lowered or extinguished when the films were polymerized and only the superlattce reflections survived. This result means that the overturned PD molecules reoverturn and return to Y type structure.

As a result, some of the PD molecules of the alternating films overturns after the deposition, and the films have the partially overturned structure. When the PD molecules were photopolymerized, the PD molecules that have overturned in the unpolymerized films reoverturn and return to the Y structure. It is widely accepted that molecules in LB films can be overturn in a plane and most of the cases are the transition from X or Z type to Y type. However, it is shown that the transition of the reverse direction can occur in the alternating films.

4 layer periodic films

X-ray diffraction patterns of the 4 layer periodic films are shown in Fig. 3. In the order of these types, the interplanar spacings of the [AABB] and [BBAA] are longer than that of [ABBA] sequence. In this cases, overturning and reoverturning by photopolymerization were also observed. However, the difference of the X-ray diffraction patterns of polymerized and unpolymerized is not so conspicuous as 3 layer periodic films. Other X-ray diffraction patterns are not shown in this paper, but the higher molecular orientations of the films can be obtained with the hydrophobic groups of the same type molecules facing each other and the PD molecules tend to stand upright, which means that the monomer of PD are easier to be polymerized[5].

Molecules in hetero-cyclic LB films of fatty acid and polyisobutyl methacrylate (PIBM) were found to be aggregated and/or crystallized in a layer after the deposition[8]. Lvov *et al.* reported[9] the interlayer



(A) (B)

(C) (D)

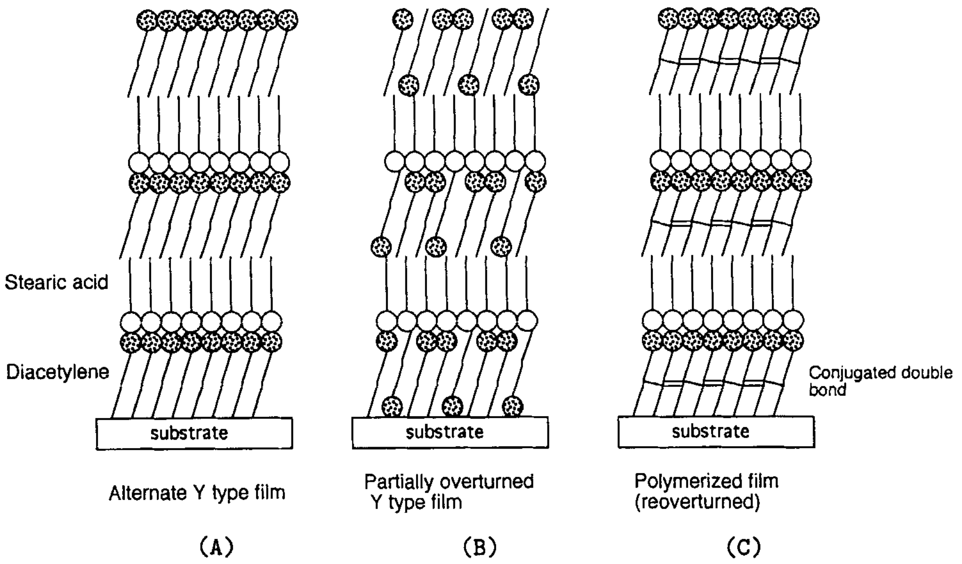
Figure 1: X-ray diffraction patterns of unpolymerized 3 layer periodic films. (A): unpolymerized [ABB], (B): polymerized [ABB], (C):unpolymerized [AAB], (D):polymerized [AAB].

the X-ray diffraction pattern are the length of $A+B$ as shown in Table I. The spacing of the [AB] periodic sample is larger than that of [BA] one in both cases of unpolymerized and polymerized films. The differences between the [AB] type and [BA] one are the first layer and the direction of deposition. In the [AB] type film, C_{18} monolayers are deposited during the downstrokes and [BA] during the upstrokes. Thus the result means that the interplanar spacings depend on the deposition order, *i. e.* the material of the film which is deposited as the first layer. In the 2 layer periodic films, it is considered that the molecular orientation of the first layer affects those of subsequent layers even in the hetero-structured LB films.

3 layer periodic films

X-ray diffraction patterns of the unpolymerized and polymerized 3-layer periodic films are shown in Fig. 1.

In the cases of [AAB] (as shown in Fig. 1), [ABA], and [BAA], almost only the superlattice reflection of averaged spacings of $A+B$ appear in the X-ray diffraction patterns. On the other hand, unpolymerized



Alternate Y type film (A)

Partially overturned Y type film (B)

Polymerized film (reoverturned) (C)

Figure 2: Schematic illustration of partially overturned film drawn as a 2 layer periodic film for simplification. (A): In terms of the transfer ratio, deposition is normal Y type film, (B): Partially overturned monomer film, (C): Return to Y type by photopolymerization.

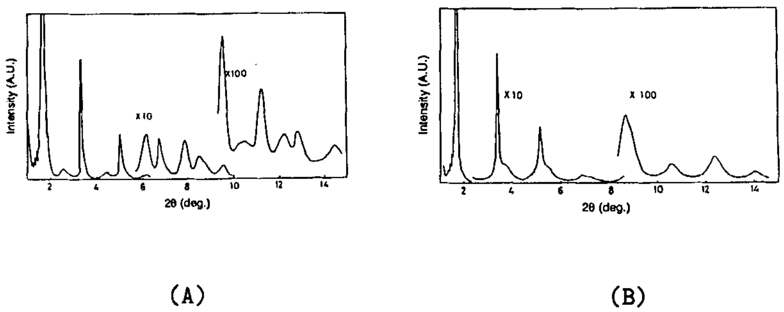


Figure 3: X-ray diffraction patterns of 4 layer periodic [BAAB] films. (A): unpolymerized, (B): polymerized.

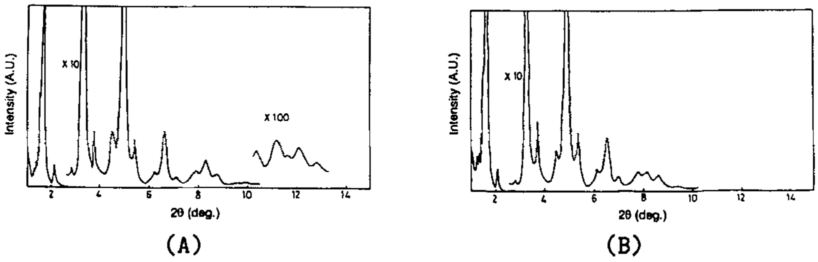


Figure 4: Xray diffraction pattern of unpolymerized (A) and polymerized (B) 8 layer periodic film [BBBBAAAA].

penetration of molecules of hetero-cyclic LB films of some kinds of fatty acid. In the case of C_{18} and PD, it is supposed that a crystallization of the molecules with the hydrophobic groups facing each other should easily occur.

8 layer periodic films

The X-ray diffraction patterns of the 8 layer periodic films is shown in Fig. 4. In these cases, satellite reflections around the main peaks are clearly observed. The satellite reflection is the peaks observed beside the main peaks and is originated from the long cycle periodic structure in multilayered films. In the case of multilayer, the length of averaged interplanar zspacings $(A+B)/2$ and modulation length [BBBBAAAA] corresponds to d_0 and Λ in the eq. (1), respectively. The angles at which main and satellite peaks appear are expressed as

$$\frac{2\sin\theta}{\lambda} = \frac{n}{d_0} + \frac{N}{\Lambda}, \tag{1}$$

where λ, Λ, $n = 1, 2, 3\cdots$, $N = 0, \pm1, \pm2, \pm3\cdots$, d_0 are the wavelength of X-ray, modulation length (long periodic unit length), order of Bragg reflection, order of satellite reflections, and interplanar spacings of crystal, respectively. $N = 0$ represents the main peak and $N = \pm1$ corresponds to the 1st satellite peak. Λ can be calculated directly by the process of elimination of d_0.

$$\Lambda = \frac{(M-N)\lambda}{2(\sin\theta_M - \sin\theta_N)} \tag{2}$$

where θ_M and θ_N are the angles of two peaks appearing in an X-ray diffraction pattern. M and N are the order of satellite peaks.

The period calculated from the satellite peaks is about 200 Å and it agrees well with the designed value of [BBBBAAAA] $(4A+4B)$ length of 210 Å.

On the other hand, the inteplanar spacings observed in the superlattice reflections is only the spacings corresponding to the length of $A+B$, which is the averaged length of $(4A+4B)/4$. Consequently, in the cases of the rather long period unit structure, distinct peaks, which were identified as satellite reflections, were observed. The result is the proof of the highly ordered stacking of hetero-structured films of the C_{18} and PD system and it is shown that the layered structure is kept before and after the photopolymerization.

Microscopic aspects

The results stated above are based on the macroscopic aspects because the information on molecular orientations obtained by X-ray diffraction is averaged over relatively large area. On the other hand, it is reported that the molecular orientations of LB monolayers of PD on SiO_2 substrates were different from place to place microscopically investigated[5] by the atomic force microscopy (AFM). Thus it is considered that averaged macroscopic molecular orientation is very high in all the cases of the sequence of the deposition presented here in spite of the microscopic inhomogeneity.

CONCLUSION

We have investigated the hetero-cyclic LB films of C_{18} and PD system in various and systematic deposition order and characterized by X-ray diffraction. The molecular orientation of the 2 layer cycle films is higher in the case that the first layer is cadmium stearate. For the 3 and 4 layer cycle films, some PD molecules overturns in a plane and form "partially overturned film" and further, the molecules of these films were reoverturned by photopolymerization. From the 8 layer periodic film, the satellite peaks around superlattice reflections and it is determined that rather long periodic well-ordered structure was built in the system fabricated by LB technique. The macroscopic molecular orientations are highly ordered in spite of the microscopic inhomogeneity.

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