JOURNAL OF MATERIALS SCIENCE **34** (1999) 3149–3154

X-ray diffraction analysis of 10,12-pentacosadiynoic acid Langmuir-Blodgett films during polymerization

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10,12-pentacosadiynoic acid (PCDA) LB films were deposited on two different subphases of $CdCl_2$ and $TbCl_3$ respectively and polymerized under UV-irradiation. It is found that the different subphase influenced the molecular packing, and in turn, influenced the polymerization behavior in the LB films. The molecular arrangement structures of unpolymerized and photopolymerized LB films were investigated by low angle X-ray diffraction. The periodic spacing of molecules in the LB films and the inclination angle of molecules on the substrate were calculated from the X-ray diffraction profiles. The unpolymerized PCDA LB film had one set of diffraction peaks, however, two sets of diffraction peaks were clearly observed in partly-polymerized PCDA LB films deposited on $CdCl_2$ subphase and reduced to one set of diffraction peaks corresponding to the polymerized LB films. On the other hand, the PCDA LB films deposited on $TbCl_3$ subphase had only one set of diffraction peaks throughout. This is interpreted to correspond to different mechanisms of chain propagation, i.e., heterogeneous chain propagation for the PCDA LB film deposited on $CdCl_2$ subphase and homogeneous polymerization for the LB film deposited on $TbCl_3$ subphase. A molecular arrangement model in LB film was employed to explain the phenomenon of the "even-odd intensity oscillation" qualitatively.

1. Introduction

Langmuir-Blodgett (LB) films and the monolayer technique have become an important method for investigating a new polymerization mechanism in the two-dimensional state and developing new polymers [1]. Due to the highly ordered molecular arrangement giving smooth structures at the molecular level and ultrathin sample, LB films have a great potential application in microelectronics, informational optics and molecular biology [1]. To overcome the shortcoming of lower mechanical strength and thermal stability of LB films, employment of a polymerizable monomer is the usual practice. The linear diacetylene compounds having the general formula $R'{-}C{\equiv}C{-}C{\equiv}C{-}R$ have been used extensively to prepare polymerized LB films because of their reactivity in the solid state. The absence of protruding "bulges" and their ability to substitute for a length of alkyl chain without interfering with the molecular packing [2]. 10,12-pentacosadiynoic acid (PCDA) monomer is suitable for making thin films by the LB technique. The polymerization reaction process of the PCDA LB films depends on molecular density or arrangement in the film by the energy beam [3]. Besides normal regular X-ray diffraction peaks, the appearance of (an)other diffraction peak(s) in PCDA LB films during photopolymerization has been observed previously [3–5]. Ogawa [3] attributed it to an impurity with a different crystal structure in PCDA crystals. Arisawa *et al.* [4] suggested that the PCDA molecules in LB film that have overturned in the unpolymerized films reoverturn to Y-type structure through polymerizing. Dhanabalan *et al.* [5] gave no explanation at all although he mentioned a weak peak in X-ray diffraction profiles of PCDA LB film. The experimental results presented here indicate a new interpretation of two types of chain propagation in LB films and confirm the topochemical solid-state polymerization nature in long-chain diacetylene acid LB films. It is known that the nature of cations present in the subphase greatly influences the homogeneity and the stability of the resulting fatty acid salt LB films [6]. The different cations in the subphase also should influence the structure of the PCDA films.

In this paper, PCDA LB films were deposited on two different subphases, $CdCl_2$ and $TbCl_3$ respectively, and polymerized under UV-irradiation. The periodic structure of the LB films and the dependence of polymerization on molecular arrangement in the LB films were investigated by low angle X-ray diffraction. The periodic spacing of molecules in the LB films and the inclination angle of molecules on the substrate were

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calculated. The LB films deposited on different subphases have various molecular packing arrangements, which, in turn, influence their polymerization behavior. Two sets of diffraction peaks in PCDA LB film deposited on $CdCl_2$ subphase have been revealed which were based on the different chain propagation. Different behavior between the LB films from $CdCl_2$ and $TbCl_3$ subphase was considered to be closely related to the cation nature in the subphase. The phenomenon of "odd-even intensity oscillation" of Bragg diffraction peaks in PCDA LB films was qualitatively explained by a molecular arrangement model in the LB films.

2. Experimental

2.1. Materials

10,12-pentacosadiynoic acid $CH_3-(CH_2)_{11}-C\equiv C-C\equiv C-(CH_2)_8-COOH$ (PCDA) was obtained from ABCR GmbH (Karlsruhe, Germany) and used without further purification. The PCDA was dissolved in chloroform and filtered in order to remove (very few) polymerized solids. The final concentration of PCDA in chloroform is 0.5 mg/ml. The solution was protected against exposure to light and stored at 4 °C in a refrigerator.

The substrate used was microscopic cover-glass slide. The completely hydrophilic glass slides were firstly immersed in a chromic acid mixture for several hours in an ultrasonic cleaner, then washed in NaOH-alcohol for 10 min with ultrasonic cleaner, and finally rinsed with distilled water several times.

The subphases were 4×10^{-4} mol/dm^3 $CdCl_2$ and $TbCl_3$ (analytical grade) aqueous solution in doubly distilled water prepared by a quartz sub-boiling ultra-purified distiller. All experiments were carried out at room temperature (around 20 °C).

2.2. Spreading and deposition of LB films

A home-built computer-controlled Langmuir system with Whilhelmy Pt-plates was used to perform the pressure-area (π-A) isotherms and deposit LB films within a dust-free glass cabinet covered with an opaque plastic sheet to prevent UV-light entering from the sky. The monolayer was compressed with a barrier rate of 8 mm/min. The multilayer LB films were deposited at a surface pressure of 30 mN/m on the $CdCl_2$ subphase and 22 mN/m on $TbCl_3$ subphase respectively. The substrate was dipped at a constant velocity of 4 mm/min, and lifted at 3 mm/min vertically through the compressed monolayer, except the first layer of 2 mm/min.

2.3. Polymerization of PCDA LB films

The PCDA LB film was polymerized under UV-irradiation. A low voltage mercury lamp with wavelength of 254 nm and a power of 8 W was used. The distance between the sample and the lamp was 11 cm. The polymerization was carried out in air because oxygen had no effect on the polymerization.

2.4. X-ray diffraction analysis of LB film

X-ray diffraction analysis was performed by means of a RIGAKU D/max-γA rotating anode X-ray diffractometer with a graphite monochromater and grating of DS = 1°, SS = 1/6°, RS = 0.15 mm. The tube voltage was 40 kV and the tube current 100 mA. The CuK_α line (λ = 0.15418 nm) was used. The scanning range of diffraction angles (2θ) was in the region of 1.2°–10°.

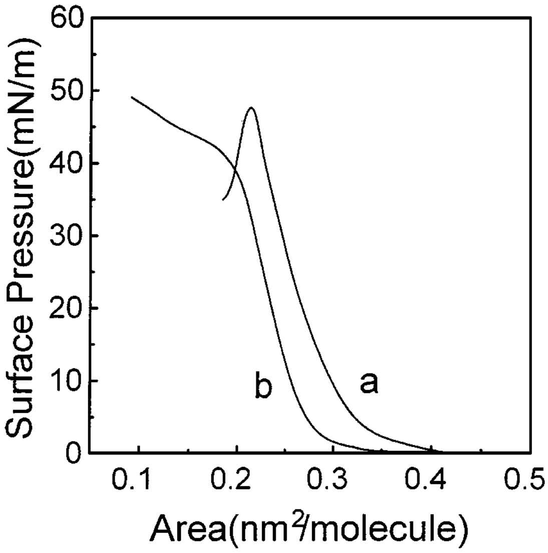

Figure 1 The π-A isotherms of 10,12-pentacosadiynoic acid on subphases of 4×10^{-4} mol/dm^3 $CdCl_2$ (a) and 4×10^{-4} mol/dm^3 $TbCl_3$ (b), 20 °C.

3. Results and discussion

3.1. Surface pressure-area (π-A) isotherms

The surface pressure-area isotherms, π-A curve, of PCDA, on the subphases of 4×10^{-4} mol/dm^3 $CdCl_2$ and 4×10^{-4} mol/dm^3 $TbCl_3$ with the compression rate of 12 cm^2/min were shown in Fig. 1 (curve a and b respectively). Upon compression, the PCDA molecules interact with each other and the surface pressure π increases slowly at the beginning. Then the increase of surface pressure π with compression of the monolayer becomes rapid and the PCDA molecules are arranged more densely. Finally, a closely-packed monolayer is reached in which the individual amphiphilic PCDA molecules are assumed to be perpendicularly (with some angle to normal line of the subphase surface) oriented in the surface. Further compression causes a collapse of the monolayer, i.e., PCDA molecules are pushed out from the air/water interface into the subphase. The cross-sectional area of a PCDA molecule in the close-packed monolayer, as found by the intersection point of the tangent at the π-A curve, just before reaching the collapse point, with the A-axis, could be obtained.

There were considerable differences between the isotherms recorded on the $CdCl_2$ and $TbCl_3$ subphases. The monolayer on $CdCl_2$ exhibited a well-condensed isotherm with a clear collapse pressure of 48 mN/m, and then the surface pressure π started to decrease rapidly. The cross-sectional area of a PCDA molecule in the close-packed monolayer equalled 0.31 nm^2. However, on $TbCl_3$ subphase, the monolayer showed an isotherm with a phase transition around 37 mN/m just prior to the monolayer collapse and without a significant change in collapse pressure. The cross-sectional area of a PCDA molecule was 0.27 nm^2. The observed differences suggest that the type of isotherm is affected by the nature of the subphase. The condensing effect of tri-valent cations Tb^{3+} on molecular packing in the monolayer is stronger than that for the divalent cations Cd^{2+}, indicating that different subphases influence aggregation of film-forming molecules on the subphase surface, and therefore, its polymerization behavior.

3.2. X-ray diffraction analysis of PCDA LB films

The X-ray diffraction profiles of 81-layer 10,12-pentacosadiynoic acid LB films deposited on subphase of $CdCl_2$ on a glass slide before irradiation are shown in Fig. 2 (curve a). Five Bragg diffraction peaks in the range $2\theta = 1.2°–10°$ have been observed, indicating a strong periodicity of the LB films.

The intensity of diffraction peaks of the PCDA LB film decreases with increasing diffraction angle. However, the so-called "even-odd intensity oscillation", i.e., the phenomenon that the intensities of the odd-numbered diffraction peaks are higher than the neighboring even-numbered peaks, has also been observed, which will be explained later.

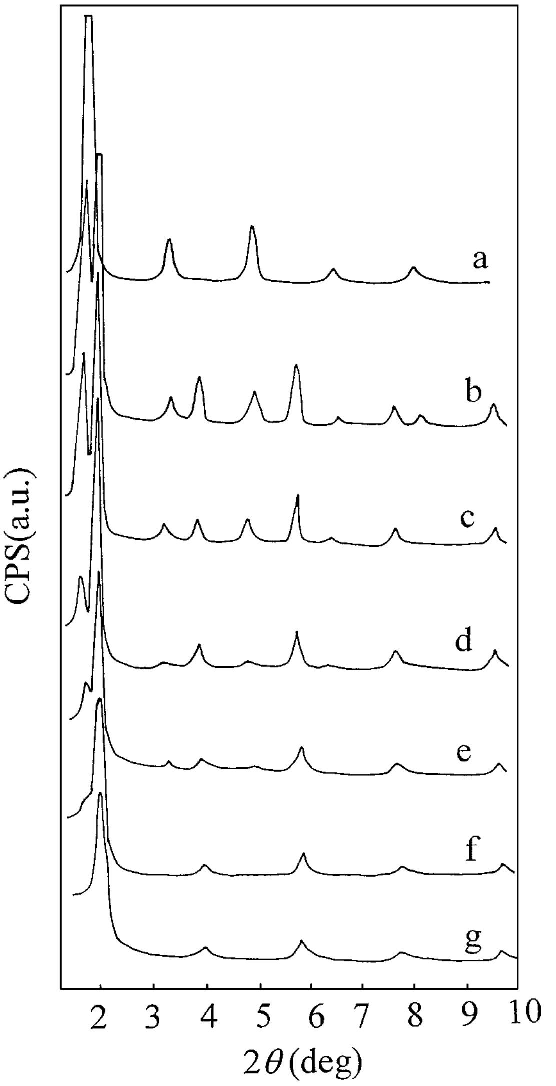

Figure 2 X-ray diffraction profiles of PCDA LB films deposited on $CdCl_2$ subphase under different UV-irradiation time periods. (a) as-deposited (b) 10 min (c) 20 min (d) 40 min (e) 110 min (f) 210 min (g) 400 min.

The periodicity d of the LB films can be calculated from the diffraction peaks as following

$$d = \ell d_{00\ell} \tag{1}$$

where $\ell = 1, 2, 3, \ldots, n$ is the order number corresponding to the number of each diffraction peak. The average spacing of the PCDA LB film deposited on subphase of $CdCl_2$ was found to be $d = 5.45$ nm. It should be pointed out that the first diffraction was in a very low angle range of $2\theta \approx 1.7°$, and considerable errors would result from too strong a reflection because the detector of X-ray diffractometer almost received the incidental light with reflecting angle close to the critical angle of $2\theta = 1°$ of total reflection. For this reason, the value of the first peak was omitted in the calculation of the average spacing.

Fig. 3 (curve a) shows the X-ray diffraction for as-deposited films deposited on the $TbCl_3$ subphase. In the range of 1.2°–10°, five Bragg peaks have also been observed, having "even-odd intensity oscillation" as well. The same calculation gave the average spacing of the PCDA LB film deposited on subphase of $TbCl_3$ $d = 5.40$ nm.

3.3. Inclination angle of the PCDA molecule of the LB films on substrate

Theoretically the amphiphilic film-forming molecules in LB film deposited onto a substate are perfectly

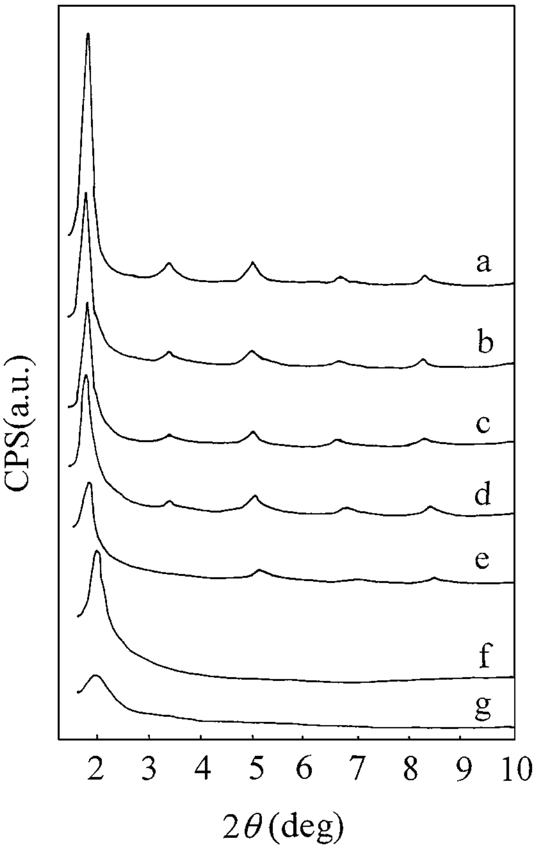

Figure 3 X-ray diffraction profiles of the PCDA LB films deposited on $TbCl_3$ subphase under different UV-irradiation time periods. (a) as-deposited (b) 10 min (c) 30 min (d) 100 min (e) 200 min (f) 350 min (g) 400 min.

oriented in the perpendicular direction, but this is not found. The length of a fully extended PCDA molecule can be theoretically calculated from the bond lengths and bond angles. Compared with the PCDA LB film spacing of 5.45 nm deposited on the subphase of $CdCl_2$, twice the calculated molecular length of 3.28 nm in Y-type PCDA LB film, $2 \times 3.28 + 0.3 = 6.86$ nm (adding 0.3 nm is due to the shortest van der Wall's distance between two PCDA molecules in one period) is greater than the value of the spacing. Therefore the PCDA molecular chains should not lie perpendicular to the plane of the substrate, but have some inclination. The inclination angle of the PCDA molecules on the substrate can be simply estimated and found to be 37.4°.

In the literature, the molecular inclination angles of long-chain diacetylene acid LB films could be also found. Examples are $CH_3-(CH_2)_{17}-C\equiv C-C\equiv C-COOCu_{1/2}$ with the inclination angle of 43° [7]; $CH_3-(CH_2)_9-C\equiv C-C\equiv C-(CH_2)_8-COOCd_{1/2}$ with 31° [8] and $CH_3-(CH_2)_{13}-C\equiv C-C\equiv C-(CH_2)_6-COOCd_{1/2}$ with 36.6° [9]. The larger inclination angle of diacetylene acid LB films may be related to the requirement that the molecular arrangement allows solid-state polymerization of diacetylene compounds in two-dimensional state with closely-packed arrangement [10].

However, the periodic spacing of PCDA LB films deposited on subphase of $TbCl_3$ was 5.40 nm, therefore, the inclination angle of the PCDA molecules was 38.1°. The different subphase, i.e., the different valence cations influenced the inclination angle of PCDA molecules on substrate in LB film.

3.4. Two sets of X-ray diffraction peaks of PCDA LB films deposited on $CdCl_2$ subphase during polymerization

As mentioned above the as-deposited (or unpolymerized) PCDA LB film exhibited one set of regular diffraction peaks. Under UV-irradiation, however, it is interesting to note that two sets of X-ray diffraction peaks could be recognized for partly-polymerized PCDA films deposited on the subphase $CdCl_2$ (Fig. 2, for example, curve b), i.e., the as-deposited PCDA LB film with one set of diffraction peaks initially produced another set of regular diffraction peaks under UV-irradiation. Using the same formula (1), the average spacing of a new set of diffraction peaks in partly-polymerized PCDA LB films can also be estimated to be $d' = 4.649$ nm.

In order to understand the nature of (an)other diffraction peak(s), exposures for different time intervals of UV-irradiation of the PCDA LB film deposited on $CdCl_2$ subphase were carried out and the X-ray diffraction profile changes at each stage were recorded (Fig. 2). With increasing UV-irradiation period of PCDA LB films, the diffraction peaks with the periodic spacing of 5.450 nm were getting weaker until totally disappearing after 210 min UV-irradiation. At the same time the diffraction peaks with the periodic spacing of $d' = 4.649$ nm were getting stronger and becoming an exclusive set of diffraction peaks.

The appearance of two sets of diffraction peaks in partly-polymerized PCDA LB films indicated that there were two different periodic structures in the LB films. The PCDA is a crystal and its pure compound without impurity is easy to obtain with recrystallization, so Ogawa's point of view [3] of the impurity which caused the extra diffraction(s) is not acceptable. In partly-polymerized PCDA LB films deposited on the $CdCl_2$ subphase instead of unpolymerized (or as-deposited) films, the extra set of diffraction peaks with the periodic spacing of $d' = 4.649$ nm would be related to PCDA polymer, i.e., there were two phases (or two crystal structures): PCDA monomer crystal phase and its polymer crystal phase in partly-polymerized PCDA LB films. In as-deposited PCDA LB film only one monomer phase was exhibited; as soon as UV-irradiation was applied, partial PCDA molecules had been polymerized into its polymer and there were two different phases (monomer phase and its polymer phase) in partly-polymerized PCDA LB film due to large mismatch between monomer and polymer lattices. This is the reason why two sets of diffraction peaks appeared, one set belongs to polymerized molecules and another to monomer molecules.

It is well known that the diacetylene compound of PCDA crystal is easy to polymerize in normal conditions [11]. If spreading and deposition are not conducted carefully enough to prevent exposure to UV-light from the sky, the PCDA will be polymerized partly which will result in (an)other diffraction peak(s). Therefore Ogawa [3], Arisawa *et al.* [4] and Dhanabalan *et al.* [5] observation of extra diffraction(s) in their experiments may be because there were no protective measures against UV-light from the sky.

A major question is how to explain why only one set of diffraction peaks is found in PCDA LB films deposited on $TbCl_3$ subphase during the whole polymerization process. As pointed out by Kaiser *et al.* [12], topochemical solid-state polymerization of diacetylene compounds in the bulk would occur in two ways, as showed in Fig. 4, i.e., heterogeneous (Fig. 4a) and homogeneous (Fig. 4b) polymerization. The existence of two sets of X-ray diffraction peaks, therefore two phases, of PCDA LB films deposited on $CdCl_2$

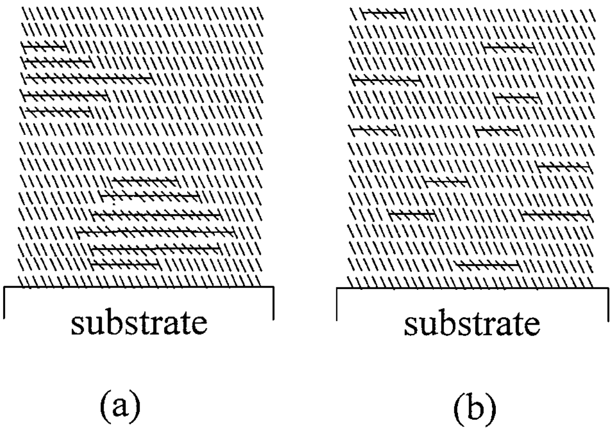

Figure 4 (a) Heterogeneous chain propagation of PCDA LB films deposited on $CdCl_2$ subphase; (b) Homogeneous chain propagation of PCDA LB films deposited on $TbCl_3$ subphase.

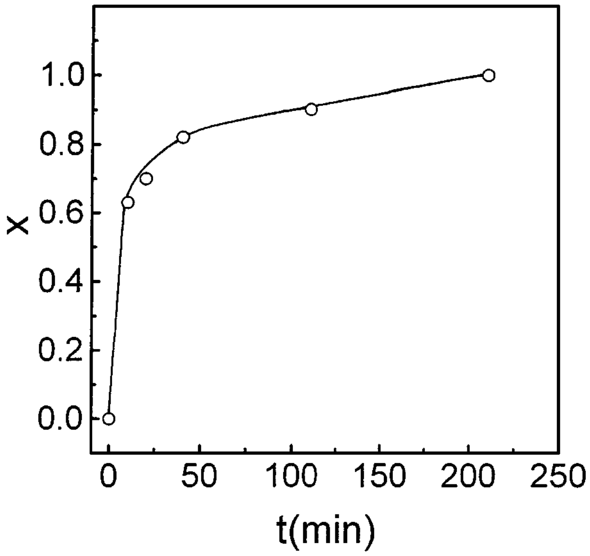

Figure 5 The polymerization conversion rate curve of PCDA LB films deposited on $CdCl_2$ subphase.

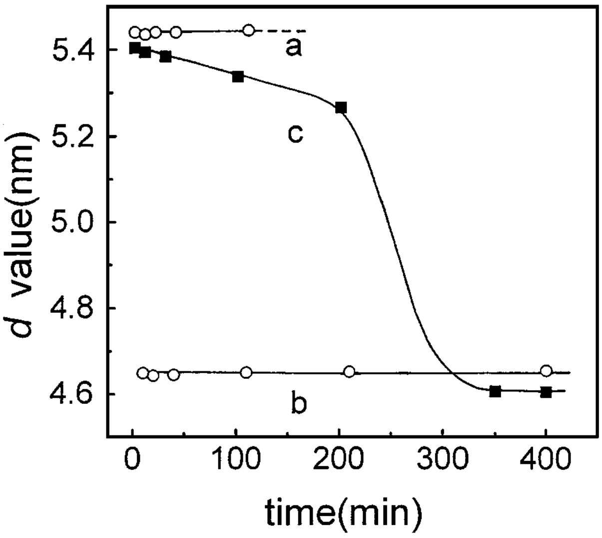

Figure 6 The *d*-values of PCDA LB films deposited on $CdCl_2$ (curve a, b) and on $TbCl_3$ subphase (curve c) as function of UV-irradiation time.

subphase revealed that the chain propagation reaction in the LB films was also heterogeneous, but the presence of only one set of diffraction peaks during the whole polymerization process suggested that the polymerization was a homogeneous chain propagation polymerization in PCDA LB films deposited on $TbCl_3$ subphase as showed in Fig. 4b, in which the polymerized PCDA macromolecules were homogeneously distributed in the PCDA monomers like a solid-solution. The presence of only one set of peaks in Fig. 3 shows that the *d*-value is the average effect of both monomer molecules and polymerized molecules. Most physical phenomena, including diffraction peaks, should be related to the homogeneous solid-solution.

The polymerization conversion curve could be estimated from X-ray diffraction profiles of LB films deposited on $CdCl_2$ subphase (Fig. 5). For simplification, only the third diffraction peaks from the two sets of diffraction peaks were compared. The area percentage of polymerized LB films should represent the polymer content percentage. With increasing UV-irradiation time, the PCDA polymer content increases (Fig. 5). Fully polymerized LB films were obtained after 210 min UV-irradiation.

With increasing UV-irradiation time, the average spacing (*d*-value) of the LB films deposited from $TbCl_3$ subphase became smaller. After UV-irradiation for 350 min, the *d*-value did not reduce. This time gave full-polymerization of the PCDA LB films (Fig. 6 curve c). For the LB films deposited from $CdCl_2$ subphase, two sets of diffraction peaks had separate periodic spacings and almost kept constant (Fig. 6 curve a and b).

3.5. Model calculations of "even-odd intensity oscillation" of the X-ray diffraction profiles

In general, the intensities of the X-ray diffraction peaks of the PCDA LB films decrease from left to right, but the intensities of the odd-numbered peaks are greater than those of the neighboring even-numbered peaks. This phenomenon is known as "even-odd intensity oscillation" and can be explained qualitatively using a model for the molecular arrangement in LB films [13].

In Y-type LB films, the molecular arrangement in one period is assumed to be as shown in Fig. 7. Neglecting the differences between the lengths of chemical bonds and the contribution of hydrogen atoms to the total diffraction intensities, and postulating that the distances of interatomic layers are all equal, we get the following expressions

$$I \propto |F_{(00\ell)}|^2 \frac{(1+\cos 2\theta)}{\sin^2\theta\cos\theta} \quad (2)$$

$$F_{(00\ell)} = \sum_n f_{\mathrm{Cd,O,C}} \exp[2\pi i(\ell z)] \quad (3)$$

$$f_{\mathrm{Cd,O,C}} = A\exp(-aX^2) + B\exp(-bX^2) + C \quad (4)$$

and

$$X = (\sin\theta)/\lambda \quad (5)$$

where I is the intensity of diffraction peaks, $F_{(00\ell)}$ the structure factor of the ℓ-th diffraction peak, θ the Bragg diffraction angle, which could be read from the diffraction profile directly, $f_{\mathrm{Cd,O,C}}$ the scattering factor for the atoms of Cd, O and C. z is a factor whose values range from $1/n$, $2/n$ to n/n, and A, a, B, b, C are the scattering factors, whose values can be read in the literature [14].

In Y-type LB films, the electron density along the long hydrocarbon chains is not homogeneous; the juxtaposition of two hydrophobic ends of the chains produces an electron-deficient layer that will influence the intensities of the diffraction peaks. The small squares in Fig. 7 symbolize the electron-deficient layers. By adjusting the thickness of electron-deficient layers, i.e., by changing the parameter *m*, the intensities of diffraction peaks can be calculated from the formula above. In comparing the calculated intensities with the experimental values (Fig. 8), the best agreement can be obtained when $m = 3$. In this way, the "even-odd intensity

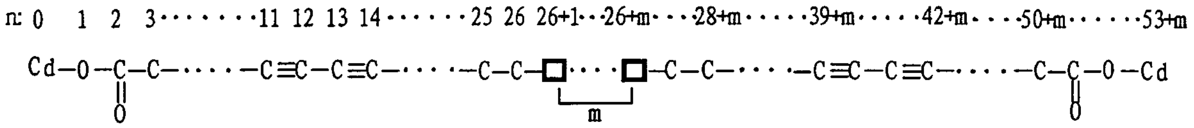

Figure 7 Model arrangement of PCDA LB film in one period.

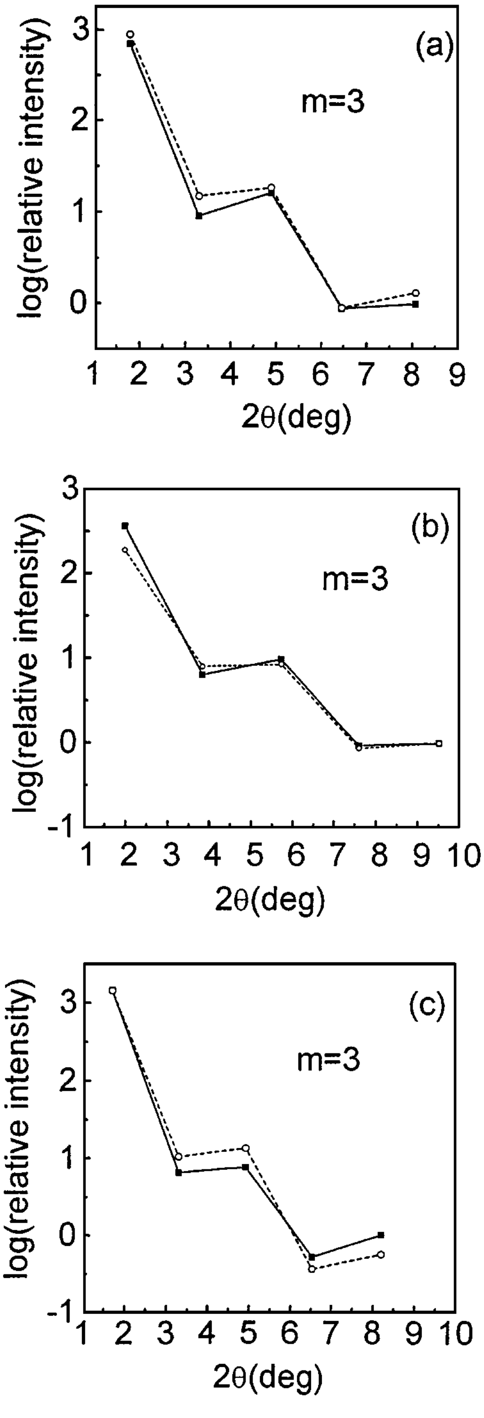

Figure 8 Even-odd oscillation intensities of X-ray diffraction from PCDA LB films (a) PCDA monomer LB films deposited on $CdCl_2$ subphase; (b) its rsulting polymer films; (c) PCDA LB films deposited on $TbCl_3$ subphase. (○: calculated, ■ experimental).

oscillation" of X-ray diffraction from LB films could be accounted for. It is interesting to note that both sets of peaks of PCDA monomer LB films and the corresponding polymer films deposited on $CdCl_2$ subphase and that deposited on $TbCl_3$ subphase fit "even-odd intensity oscillation" when $m = 3$ (Fig. 8a–c). The intermolecular polymerization reacts in a layer, which does not influence the electron-deficient layer along the molecular chain. In Fig. 7, an electron-deficient layer results from the juxtaposition of two hydrophobic ends of the chains, while the cations are connected with the carboxylate group ($-COO^-$) at the hydrophilic end of the chains, thus the different valence cations do not influence the electron-deficient layer, either. That is why m always equals 3 under three different circumstances.

Acknowledgement

Financial support from the National Science Foundation of China (29674027) is greatly acknowledged.

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Received 28 July 1998
and accepted 13 January 1999