X-ray diffraction of pentacosdiyne-8,10 acid-1 Langmuir–Blodgett film

HE PINGSHENG, TIAN QINPING
Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

Pentacosdiyne-8,10 acid-1 (PCDA) was synthesized and deposited by the Langmuir–Blodgett (LB) technique on to glass, quartz and gold-covered glass slides. X-ray diffraction at low angle has been used to investigate the periodic structure of the LB film and the effect of polymerization on the structure. Up to seven Bragg diffraction peaks were observed in the 2θ angle range from 1° to 15°. From these, the spacings of molecules in the LB film and the angle of molecular orientation on the substrate were calculated. A molecular arrangement model was employed to calculate the intensities of diffraction peaks. The calculated result was in qualitative agreement with the experimental phenomenon of the "even–odd intensity oscillation".

1. Introduction

The Langmuir–Blodgett (LB) film technique is becoming an important method in the field of molecular architecture. The monolayers at the air–water interface can be transferred layer by layer onto a substrate to achieve molecular rearrangement by the LB technique. The highly ordered molecular aggregates possess special functions and biological activities. Therefore, the LB films have potential applications in microelectronics, informational optics and molecular biology. [1, 2].

To overcome the low mechanical strength and low thermal stability of the LB film of low molecular weight organic compounds, the inclusion of reactive polymerizable groups in the LB film is the usual practice. Because of their activity 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, the linear diacetylene compounds have been extensively used to prepare polymerized LB films [3, 4]. We began with some basic chemicals and synthesized a long-chain diacetylene acid: pentacosdiyne-8, 10 acid-1 (PCDA). Its LB film on different substrates were deposited, and the periodic structure and the effect of polymerization on the structure was studied by X-ray diffraction. The phenomenon of "even–odd intensity oscillation" of Bragg diffraction peaks was qualitatively explained by calculations based on a molecular arrangement model.

2. Experimental procedure

2.1. Synthesis of pentacosdiyne-8, 10 acid-1

The pentacosdiyne-8, 10 acid-1 was synthesized from the starting chemicals of sebacic acid and 1-hexadecene. The basic routes of synthesis were as follows:

$$\mathrm{HOOC(CH_2)_8COOH \rightarrow HOOC(CH_2)_8COOC_2H_5}$$
$$\mathrm{\rightarrow CH_2{=}CH(CH_2)_6COOC_2H_5}$$
$$\mathrm{\rightarrow CH_2{=}CH(CH_2)_6COOH}$$
$$\mathrm{CH_2Br{-}CHBr(CH_2)COOH \rightarrow HC{\equiv}C(CH_2)_6COOH} \tag{1}$$

$$\mathrm{CH_2{=}CH(CH_2)_{13}CH_3}$$
$$\mathrm{\rightarrow CH_2Br{-}CHBr(CH_2)_{13}CH_3}$$
$$\mathrm{\rightarrow HC{\equiv}C(CH_2)_{13}\,CH_3 \rightarrow IC{\equiv}C(CH_2)_{13}} \tag{2}$$

$$\mathrm{(1) + (2) \rightarrow CH_3(CH_2)_{13}\,C{\equiv}C{-}C{\equiv}C(CH_2)_6COOH} \tag{3}$$

(3) is a light yellow crystal and has been recognized as pentacosdiyne-8, 10 acid-1 by means of infrared (IR) spectroscopy (Fig. 1) and nuclear magnetic resonance (NMR). ^{1}H NMR ($CDCl_3$), $\delta = 0.9$ (3H, t, J = 6Hz, $-CH_3$); 1.3 (30H, S, $(-CH_2-)_{11}$, $(-CH_2-)_4$); 1.4 (2H, M, $-CH_2CH_3$); 2.4 (4H, t, J = 7Hz, $-CH_2C{\equiv}C{-}C{\equiv}C{-}CH_2-$), 2.2 (2H, S, $-CH_2COOH$), 11.5 (1H, BR, $-COOH$).

2.2. Spreading and film preparation of PCDA

PCDA was spread on a simplified trough (Fig. 2) which has an edge coated with paraffin to make it hydrophobic. The water surface was swept several times by a PTFE bar and waxed silks were applied to the surface to divide it into three sections. To stabilize the monolayer on the surface, CdCl salts were added to the water subphase at the concentration of 3×10^{-4} M. The 10^{-3} g/ml PCDA–chloroform solution was dropped on to sections II and III until a "lens" appeared and disappeared in a few seconds. Then,

0022–2461/91 $03.00 + .12 © 1991 Chapman and Hall Ltd.

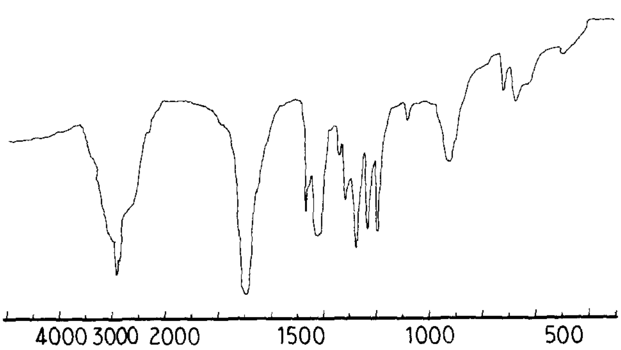


Figure 1 Infrared spectrum of pentacosdiyne-8, 10 acid-1.

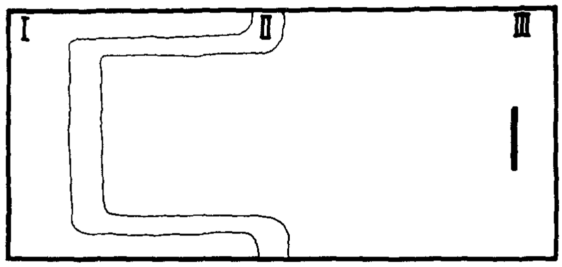


Figure 2 Schematic drawing of the simplified trough. Two waxed silks divided the surface into three sections.

oleic acid as "piston oil" was dropped on to section I in excess and obvious movement of the silks was observed. The excess of the added oleic acid was to maintain constant pressure to the monolayers during the whole process. After an elapse of 30 min, the substrate which was submerged in the water beforehand was pulled out at a speed of 0.4 cm min^{-1} (0.2 cm min^{-1} for the first layer). While the substrate made the up-and-down journey, the PCDA monolayer was gradually transferred on to the substrate to form the Y-type multilayer LB films.

It should be noted that cleanliness was of the utmost importance in our experiment. The trough was cleaned by an NaOH–alcohol solution and rinsed with water and distilled water. Glass slides and quartz slides were immersed in a chromic acid mixture for several hours, then rinsed in water and cleaned in sodium hydroxide–alcohol solution, followed again by rinsing in water and distilled water. The gold-covered glass slide was cleaned by acetone and rinsed in distilled water.

2.3. Low-angle X-ray diffraction of the LB films

The X-ray diffraction was performed on the RIGAKU D/max-γA rotating anionod X-ray diffractometer using a graphite monochrometer and gratings DS = 1°, SS = (1/6)°, RS = 0.15 mm and RS_m = 0.3 mm with tube voltage 40 KV and tube current 60 mA. The Cu K_α line (λ = 0.15418 nm) was used.

3. Results and discussion

3.1. Spreading and LB multilayers of PCDA

The spreading of pentacosdiyne-8, 10 acid-1 on a water surface had not been reported in the literature. Owing to the restriction of experimental conditions we were unable to get its π-A isotherm. Consequently, we had to estimate roughly its range of uniform compressibility. From the π-A isotherms of its homologues with more and fewer numbers of carbons, $C_{12}H_{25}{-}C{\equiv}C{-}C{\equiv}C(CH_2)_8$ COOH and $C_{14}H_{29}{-}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOH$, we knew that they showed uniform compressibility without collapsing in the film pressure range from 10 to 50 mN mm^{-1}. Therefore we proposed that PCDA would form compact monolayer solid films when the film pressure exceeds 20 mN mm^{-1}. This justified our selection of oleic oil acid with a surface pressure of 30 mN mm^{-1} as piston oil. The X-ray diffraction here proved that the preparation of the PCDA LB film in this way was successful.

The depositing speed of the substrate was an important factor in determining the quality of the LB films. The lower moving speed favoured the success of the LB film deposition, especially for the first layer. As a result, we selected 0.2 cm min^{-1} as the pulling speed for the first deposition and 0.4 cm min^{-1} for the following deposition. Our X-ray diffraction results showed that the LB films with more than a hundred layers prepared at these speeds still possess excellent periodic structure.

3.2. X-ray diffraction of PCDA LB films

Good results of X-ray diffraction from the PCDA LB films deposited on a glass slide, quartz slide and gold-covered glass slide were obtained. Fig. 3 showed the diffraction profiles for 70 layers (on a quartz slide) of PCDA LB film. It was evident that the appearance of seven equidistant Bragg peaks proved the presence of a regular periodic structure in the PCDA LB films. Assuming (0 0 1), (0 0 2), . . . , (0 0 l) to the Bragg peaks in Fig. 3 from left to right, the spacing of the LB film could be expressed as follows

$$d = l d_{00l}$$

From this equation, we calculated the average spacings of PCDA LB film on a quartz slide to be

$$d = 5.506 \text{ nm}$$

It should be noticed that the first Bragg peak was in

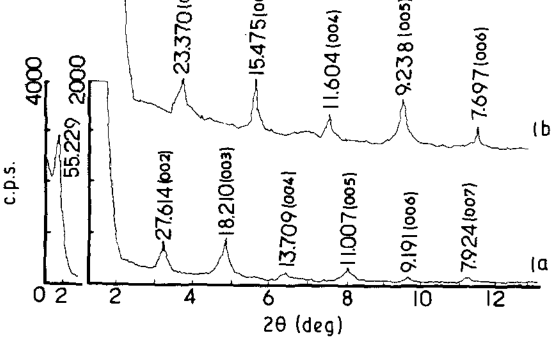


Figure 3 The diffraction profiles of pentacosdiyne-8, 10 acid-1 LB film on a glass slide in the 2θ range of 1° to 15°: (a) monomer (b) polymer.

the very low angle range ($2\theta = 1.6°$), and the detector of the X-ray diffractometer almost received the incidental light with reflecting angle close to the critical angle ($2\theta = 1°$ for the instrument here) of total reflection. In this condition the detector was almost saturated and could not detect the first peak. Even though it appeared, comparable errors would result from the small displacement from the correct sample position. For this reason, the value of the first peak was omitted in our calculation of the average *d*-value.

3.3. Inclination of PCDA molecules on the substrate

The length of the fully extended PCDA molecule could be estimated from the values of bond length. As described above we knew the spacings of PCDA LB film to be 5.506 nm. For Y-type LB film, two molecules made up one period, whereas twice the length of the PCDA molecules was ($2 \times 3.28 + 0.3$) nm. The value of 0.3 nm was the minimum van der Waals' distance between two molecules arranged regularly, and was greater than the value of spacings obtained here. We proposed that the PCDA molecules were not perpendicular to the plane of the substrate, but instead made a angle with the perpendicular direction. Simple calculation gave the value of the angle of molecular inclination to be 36.6°.

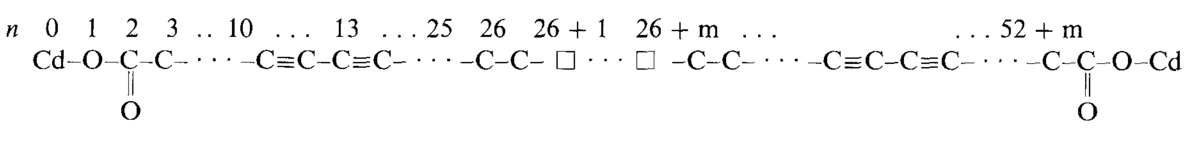
It was rare that the molecules in deposited LB films on the substrate oriented perfectly in the perpendicular direction. For example, the inclination angles were 25° for $C_{21}H_{45}COOH$ [4]; 43° for $CH_3(CH_2)_{17}{-}C{\equiv}C{-}C{\equiv}C{-}COOCu_{1/2}$ [5]; and 31° for $CH_3(CH_2)_9{-}C{\equiv}C{-}C{\equiv}C(CH_2)_8COOCd_{1/2}$ [2]. The inclination angle for diacetylene acid was usually larger. This may be related to the requirement of molecular arrangement for following solid-state polymerization of diacetylene compounds [6].

The spacings for LB films deposited on glass, gold-covered glass and quartz slides were slightly different. The discrepancy showed that the angle of inclination may vary from substrate to substrate.

3.4. Model calculation of X-ray diffraction intensities of LB film

Generally, the intensities of the X-ray diffraction peaks from PCDA LB film were found to decrease as the diffraction angle increased, but the intensities of odd-numbered peaks were higher than the neighbouring even-numbered peaks. We called this phenomenon "even–odd intensity oscillation" and it can be explained qualitatively by a model of molecular arrangement in the LB film [7].

In the Y-type LB films, the molecular arrangement in one period was assumed to be



$$\begin{array}{l} n\quad 0\quad 1\quad 2\quad 3\ ..\ 10\ \ldots\ 13\ \ldots 25\quad 26\quad 26+1\quad 26+\mathrm{m}\ \ldots\qquad \ldots 52+\mathrm{m} \\ \mathrm{Cd{-}O{-}}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}C{-}}\cdots\mathrm{{-}C{\equiv}C{-}C{\equiv}C{-}}\cdots\mathrm{{-}C{-}C{-}}\ \square\ \cdots\ \square\ \mathrm{{-}C{-}C{-}}\cdots\mathrm{{-}C{\equiv}C{-}C{\equiv}C{-}}\cdots\mathrm{{-}C{-}}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}Cd} \end{array}$$

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

$$I \propto |F|^2 \frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta}$$

$$F_{(00l)} = \Sigma f_{\mathrm{cd,o,c}} \exp[2\pi i(lz)]$$

$$f_{\mathrm{cd,o,c}} = A\exp(-aX^2) + B\exp(-bX^2) + C$$

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

where I is the diffraction intensity and θ the diffraction angle; $(00l)$ the diffraction index; z the factor ranging from $1/n$, $2/n$ to n/n; and the constants A, a, B, b, C are the scattering factors which can be found in the literature [8].

Although the Cd layers are the primary scattering layers, the electron density is higher at the end of the chain than it is in the middle part of the chain for long-chain hydrocarbons [9]. In the Y-type LB films, the juxtaposition of two hydrophobic ends of long-chain hydrocarbons will give rise to electron deficient layers in a period. It is the electron deficient layers (which exhibit a difference of electron density along the chain in the period) that will influence the intensity of the diffraction peak. In Fig. 4 the molecular arrangement defined above symbolize the electron deficient layers caused by the adjacent hydrophobic ends of PCDA molecules. The intensities of X-ray diffraction are influenced by the thickness and position of the electron deficiency. We place them in the centre of the period by adjusting the thickness, i.e. by changing the value of m. We can get various relative theoretical diffraction intensities for different m. Comparing the calculated intensities with experimental values, we found that the best agreement could be obtained when $m = 3$. In this way, the "even–odd intensity oscillation" was satisfactorily explained.

In our previous works [10, 11] with long-chain fatty-acids such as stearic acid and arachidic acid, we found that $m = 3$ gave the best agreement between the calculated and the experimental results. Although the pentacosdiyne-8, 10 acid-1 had two short triple bonds, its real situation in LB film could also be explained qualitatively by the model here.

3.5. Effect of polymerization on the periodic structure of PCDA LB film

The polymerization of PCDA LB film was initiated by ultraviolet (UV) light. Monitored by UV spectroscopy, the PCDA film polymerized completely after 150 hours of UV radiation. The X-ray diffraction of the seventy-layer LB film deposited on a quartz slide is shown in the upper part of Fig. 3. The regular diffraction peaks indicate that the PCDA film still maintains

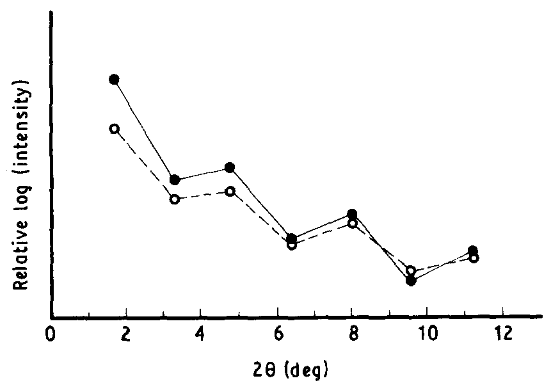


Figure 4 Even–odd intensity oscillation phenomenon of X-ray diffraction in the LB film. (○) experimental; (●) calculated.

its periodic structure after polymerization. The polymerization of diacetylene LB films behaves the same as its solid-state counterpart, i.e. their polymerizations are topochemical and do not destroy the structure of their layer network.

Compared with monomers, the diffraction peaks obviously shift towards large angles after polymerization, indicating the shortening of spacings. It is calculated that the average spacings after polymerization are 4.639 nm, 0.867 nm shorter than the spacings before polymerization. This is due to the distance changes from van der Waals' interactions to chemical bonds after polymerization, causing further inclination of the PCDA molecules on the LB films.

From diacetylene compounds, the activity of topochemical polymerization in the solid state is observed only when the molecules are arranged in an orderly way; they will not polymerize in solution and molten states. Therefore, the success of polymerization of PCDA LB film confirmed unambiguously from an indirect source that the arrangement of molecules on the film is regular and ordered.

Acknowledgement

This project was supported by the National Natural Science Foundation of China and partly by the Structure Research Open Laboratory of the University of Science and Technology of China.

References

1. B. TIEKE, in "Advances in polymer science", Vol. 71 (Springer, Heidelberg, 1985) p. 81.
2. B. TIEKE, G. LIESER and G. WEGNER, *J. Polym. Chem. Ed.* **17** (1979) 1631.
3. G. L. GAINES Jr., "Insoluble monolayers at liquid–gas interfaces" (Interscience Publishers, New York, 1966) p. 58.
4. P-A. CHOLLET, J. MESSIER and C. ROSILLIO, *J. Chem. Phys.* **64** (1976) 1042.
5. F. KAJZAR and J. MESSIER, *Chem. Phys.* **63** (1981) 123.
6. D. BLOOR, in "Developments in crystalline polymers-1", edited by D. C. Bassett (Applied Science, London, 1982) p. 151.
7. M. MATSUDA, M. SUGI, T. FUKUI, S. LIZIMA, M. MAYAHARA and Y. OTSUBO, *J. Appl. Phys.* **48** (1977) 771.
8. J. D. LEE, *Acta Cryst.* **A25** (1969) 712.
9. M. POMERANTZ and A. SEGMULLER, *Thin Solid Film* **68** (1980) 33.
10. H. PINGSHENG, X. BAI, W. YONGZHONG, W. CHANGSUI and Z. GUIEN, *Chinese J. Chem. Phys.* **1** (1988) 64 (in Chinese).
11. H. PINGSHENG, B. JIANMIN, X. BAI, W. YONGZHONG, W. CHANGSUI and Z. GUIEN, *Chem. J. of Chinese Universities* **10**(3), **284** (1989) (in Chinese).

Received 22 June 1989
and accepted 6 June 1990