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Preparation of thin film of TS and PTS by Langmuir–Blodgett techniques

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Thin films of bis-(-*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol monomer (TS) and its polymer, PTS, are successfully prepared by the classic Langmuir–Blodgett techniques. X-ray diffraction reveals highly ordered structures in the films. The three diffracted peaks observed in the range of $2\theta = 5°$ to $25°$ coincide well with those of the (0 1 0) plane in TS single crystal. A trial has been made to prepare a mixed film of TS and arachidic acid, but complete phase separation occurs and TS molecules preferentially tend to form films. Comparison between the *d*-values of TS and PTS film confirms that the polymerization in the TS thin films is also solid-state topochemical polymerization.

1. Introduction

The Langmuir–Blodgett (LB) films have recently become increasingly important in the field of high technology. Monolayers of organic compounds at the gas–liquid interface can be deposited on to a substrate by the Langmuir–Blodgett technique. In this way, high smooth and structural order can be controlled at molecular level. The ultrathin films may exhibit special properties which are of potential importance in the fabrication of integrated optical and submicrometre devices [1].

In order to improve the thermal stability and mechanical strength of the LB films, polymerization is usually employed to obtain polymerized films. Diacetylene compounds are reactive in the solid state and polymer single crystal can be prepared from monomer single crystal. Therefore, it is interesting to investigate the properties of diacetylene films. Polydiacetylene has a conjugated backbone in which dislocated electrons make it exhibit excellent optical, electronic and energy-transfer properties [2, 3].

Bis(*p*-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (TS) is a chemical which is able to form large macroscopic single crystals; therefore, TS monomer and its polymer PTS have been extensively studied [4]. To probe its nonlinear optical property, Thakur and Meyler [5] devised a new technique to prepare TS thin lamina with an optical surface, and McCaffrey *et al.* [6] tried to prepare TS thin film by a modified LB technique. Here we describe the preparation of TS and PTS thin film on a simplified trough using the classical LB technique and the X-ray diffractions from the films.

2. Experimental details

2.1. Synthesis of monomer TS

Monomer TS was synthesized by the method reported by Wegner [7]. TS single crystals were grown from acetone solution at a controlled evaporation rate in the dark [8]. The TS used in the deposition of LB film was in the form of its benzene solution of 2.78×10^{-3} M. Both TS single crystal and TS benzene solution were stored in a refrigerator for future use.

2.2. Spread and deposition of TS at the gas–liquid interface

Spreading was carried out on a simplified trough which was coated with paraffin to make the edge hydrophobic. The trough was filled with doubly-distilled water and the surface was swept by a PTFE bar, then the waxed silks were applied to the surface to divide it into three parts as shown in Fig. 1.

Dilute TS benzene solution was dropped on to Sections II and III until a "lens" was observed which disappeared after a few seconds. Then, castor oil was dropped onto Section I to compact the TS molecules. At this instant, movement of the silks could be observed. It is important that (1) the castor oil is in excess to maintain constant pressure during the whole process, and (2) the temperature be kept at 20° C throughout the experiment.

The substrates used were glass slides which were cleaned using CQ-50 ultrasonic cleaner. The substrate was submerged before spreading, it moved up and down after the operation began. The TS thin films were then obtained in this way.

2.3. X-ray diffraction

X-ray diffraction was obtained using a RIGAKU D/max-γA rotating anionod X-ray diffractometer using copper $K\alpha$ ($\lambda = 0.154\,18$ nm) with DS = 1°, SS = 1/6°, RS = 0.15 mm and $RS_m = 0.3$ mm. The tube current and voltage were 50 mA and 40 kV, respectively.

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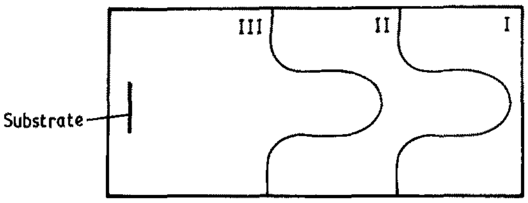
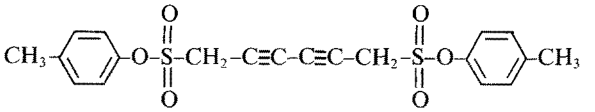


Figure 1 Schematic drawing of the simplified trough.

3. Results and discussion

3.1. Spreading of TS

The monomer TS is a symmetric molecule



$$CH_3\text{-}C_6H_4\text{-}O\text{-}SO_2\text{-}CH_2\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2\text{-}SO_2\text{-}O\text{-}C_6H_4\text{-}CH_3$$

without separated hydrophobic and hydrophilic end groups at both ends, therefore it just floats horizontally on the water surface instead of standing vertically. In spite of this speciality, TS exhibits the same π–A^2 property as in fatty acids [6]. The uniform compression of TS on the water surface begins at 10 dyn cm^{-1}, with a uniform compressibility range of 10 to 18 dyn cm^{-1} in which TS shows properties characteristic of a typical solid film. Meanwhile, the surface pressure of castor oil is 16.5 dyn cm^{-1}, just within the uniform compressibility range of TS. So the use of castor oil as pistol oil is justified to maintain constant pressure.

TS is a highly crystalline compound and its macroscopic single crystal may be prepared by means of solvent evaporation. We previously prepared the TEM sample of TS thin lamina on water surface by toluene evaporation and the TEM results confirmed that the sample so prepared had an excellent ordered structure [8]. This confirms that TS molecules tend to be arranged regularly on the water surface and this tendency is reinforced by applying constant pressure to TS on the water surface. This conclusion is proved and supported by X-ray diffraction.

The TS molecule has two hydrophilic substituents, SO_2, symmetrically distributed in the molecular chain, not at the far ends. These two substituents might have a potential influence on the formation of film on the subphase. In our experiment, we dropped the TS dilute solution on to the water surface until a "lens" was observed and later disappeared. The amount of TS applied to the water surface greatly exceeded the amount theoretically required to form a monolayer. This coincides with the results obtained by McCaffrey *et al.* [6]. We also found that the amount added highly depended on the cleanness of the surface.

TABLE I *d*-values of diffraction peaks of TS and PTS thin film

		010	020	030
TS thin film	*d*-value	1.2779	0.6399	0.4274
	lattice distance (nm)	1.2779	1.2798	1.2816
	length of *b*-axis (nm)	1.453	1.455	1.457
PTS thin film	*d*-value	1.2501	0.6325	
	lattice distance (nm)	1.2501	1.2650	
	length of *b*-axis (nm)	1.417	1.434	

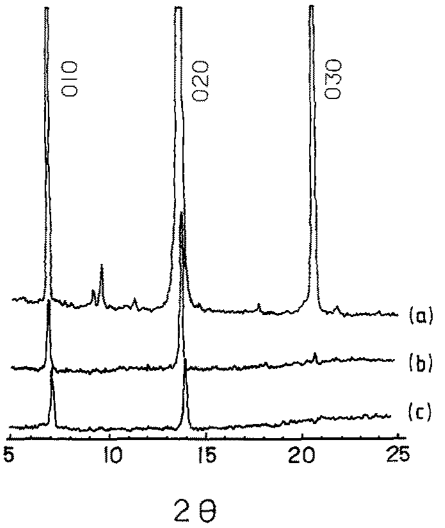


Figure 2 The diffraction profiles for different samples in the range of $2\theta = 5°$ to $25°$. (a) TS single crystal, (b) 11 layers of TS thin film, (c) the corresponding polymer PTS thin film.

3.2. X-ray diffraction of TS thin film

X-ray diffraction method is the most powerful tool in probing the structural order, and is therefore used to characterize the prepared films. The results are encouraging in that three expected diffraction peaks appear in the range $2\theta = 5°$ to $25°$ for thirty-one and eleven layers of TS thin films (in this article, a layer is referred to as the film obtained in one up-journey or down-journey of the substrate, not the true meaning of "layer"). The diffraction profiles for different samples are shown in Fig. 2.

The appearance of the Bragg peak manifests that the TS thin films prepared by the LB technique have a regular periodic structure. To be more certain of this conclusion, we also measured the TS single crystal with an X-ray diffractomer. The uppermost curve in Fig. 2 is the diffraction profile from the (0 1 0) plane in a TS single crystal. By comparison, we can see that the positions of the Braggs peaks from the TS thin film are almost the same as those from the (0 1 0) plane in TS single crystal. This coincidence proves that the TS thin film obtained by the LB technique has the same molecular arrangement as that in the single crystal. By now, we can be certain that TS molecules floating horizontally on the water surface can be transferred to a substrate layer by layer using the LB technique and that the planes in the film which are parallel to the surface of the substrate are (0 1 0). The above results agree well with those of Thakur and Meyler [5] who observed five Bragg peaks from the TS thin lamina

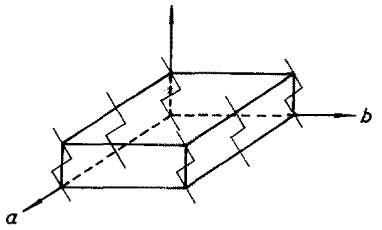


Figure 3 The cell of the monoclinic crystal system of TS single crystal.

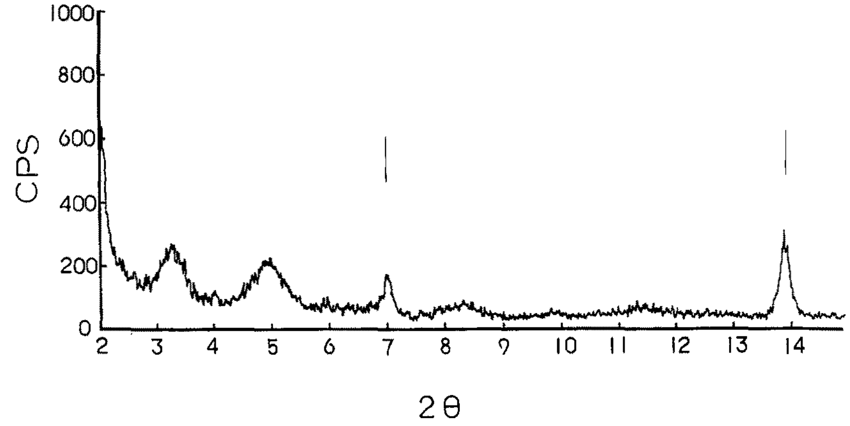


Figure 4 X-ray diffraction from an 11-layer film prepared from TS–arachidic acid mixture solution.

prepared by acetone evaporation under shear stress. This agreement reaffirms that the regular structure in the TS thin film prepared in the laboratory is the same as the crystal structure in the single crystal, crystallized under natural conditions.

3.3. Thermal polymerization of TS thin film

The prepared TS thin film was polymerized at 60° C for 72 h. The X-ray diffraction method was also applied to the PTS thin film thus obtained. Two Bragg peaks were observed which correspond to the first two peaks in TS film, by a slight shift. The third peak was "submerged" due to its low intensity. The results stated above confirm that polymerized PTS thin film possesses the same molecular arrangements as in TS film and also that the polymerization which occurred in TS film is a topochemical one which does not change the arrangement of molecules.

A careful analysis of the X-ray diffraction results reveals that the *d*-values in PTS film are lower than those in TS film (see Table I). The *d*-values reflect the length of the spacings in periodic structures. The decrease in *d*-values indicates a decrease in the spacing after polymerization. This phenomenon agrees with the decrease in cell parameters in TS single crystal when polymerized. The decrease is due to the change of molecular interaction from van der Waals' forces to covalent bonding, resulting in a contraction in the molecular chain direction (*c*-axis). It is known from our previous research [9] that contradictions also occur in the two perpendicular directions (*a*- and *b*-axes) during the process of polymerization. The data in Table I show that the polymerization of TS thin film also obeys the principle stated above. If we postulate that the structure in TS thin film can be illustrated by Fig. 3, the same as in TS single crystal, we can calculate the contradiction rate in the *b*-axis direction to be 2.03%.

3.4. Embedded TS thin film

An attempt was made to prepare TS–arachidic acid embedding film in the hope that TS will somehow form an LB film with the aid of the arachidic acid molecules. A mixture solution with TS molar fraction equal to 0.54 was prepared and subjected to the stated procedures. Fig. 4 shows the X-ray diffraction profile of the mixed film of 11 layers in the range $2\theta = 2°$ to 15°.

From Fig. 4, we can identify two peaks from the TS film ($2\theta \approx 7°$, 14°, respectively) and four peaks from arachidic acid LB film ($2\theta \approx 3.2°$, 5°, 8.3°, 9.8°, respectively) [10]. This excludes the possibility of making TS LB film with other supporting molecules, because complete phase separation occurs in the process of film spreading and deposition. This is because the TS molecules are so highly crystalline that they prefer to form thin crystal films, and at the same time destroy the ability of arachidic acid to form an LB film, resulting in the broadening of the diffraction peaks.

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