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Xiaoyu Wang[a]; Daniel J. Sandman[a]; Ferdinando Bruno[a]; Ramaswamy Nagarajan[a]
[a] Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA, USA

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Poly[bis-(p-toluene sulphonate) of 2,4-Hexadiyne-1,6-diol] Langmuir-Blodgett Thin Film Formation and Characterization

XIAOYU WANG, DANIEL J. SANDMAN,
FERDINANDO BRUNO, AND RAMASWAMY NAGARAJAN

Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, MA, USA

Coherent thin films of bis-(p-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (TS) and its polymer, PTS, were prepared by the Langmuir-Blodgett method. Even though TS has no amphiphilic groups at each end, it has an isotherm curve similar to stearic acid and can be transferred to a flat solid substrate under a certain pressure. Polarized UV-Vis spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to characterize this kind of LB thin film's anisotropy, surface morphology, and topography.

Keywords bis-(p-toluene sulphonate) of 2,4-hexadiyne-1,6-diol, polydiacetylene, Langmuir-Blodgett, pressure-area isotherm, surface topography, optical anisotropy

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Introduction

Polydiacetylenes (PDAs) are a class of polymers with quasi-one-dimensional π-electron conjugated backbones. They have attractive optical and electronic properties, such as large third-order nonlinear optical susceptibility and high electron mobility (1–3). All of these properties depend on PDAs' highly ordered supramolecular structures. The precursor monomer diacetylenes (DAs) are relatively easy to deposit as a highly oriented monolayer or multiplayer, on flat substrates (mica, ITO-coated glass substrate, etc.) by using the Langmuir-Blodgett (LB) technique. Topochemical monolayer or multilayer polymerization of suitable monomers can be performed at the air-water interface either directly or after transfer to a flat solid substrate (4, 5). This method can form a highly ordered thin film of conjugated polymer.

Suitable diacetylenes that can form stable and ordered LB thin films normally contain separate hydrophilic and hydrophobic end groups (6). Under compression on the air-water interface, these diacetylene monomers gradually orient themselves with hydrophilic groups remaining in the water and hydrophobic groups protruding from the water to the air.

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Address correspondence to Daniel J. Sandman, Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, One University Ave., Lowell, MA, USA01854-5046. Tel.: 978-934-3835; E-mail: daniel_sandman@uml.edu

In this paper, bis-(p-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (TS) was used to form LB thin film because it shows a similar isotherm curve to stearic acid (7). McCaffrey et al. measured the pressure-area isotherms of PTS LB thin films and used infrared spectroscopy and Raman spectroscopy to characterize such thin films (8). He et al. also studied the PTS LB thin films on a simplified trough. They used X-ray diffraction to analyze TS and PTS LB thin films' molecular structure (7). In this research, we used AFM and SEM to observe and analyze PTS LB thin films' surface topography and image directly, and applied polarized UV-Vis spectroscopy to evaluate the optical anisotropy of such LB thin films.

After polymerization, this kind of LB thin film will be useful for building up thin film crystals and for use as templates to grow films from solution and the melt.

Experimental

Bis-(p-toluene sulphonate) of 2,4-hexadiyne-1,6-diol was synthesized and recrystallized by the method reported by Patel (9). The TS used to deposit LB thin film was in a chloroform solution (1.04×10^{-4} M) and the solution was stored in refrigerator in the dark until used. A TS chloroform solution was spread in different amount on the trough of Langmuir Filmwaage (MGW Lauda) ($1000\,\mathrm{cm}^2$) filled with Milli-Q water. The purified water subphase was kept at a temperature of $20 \pm 0.5^{\circ}$C. All thin films were incubated for $20 \sim 25$ min at 1 atm pressure to ensure that the solvent has evaporated. The compression rate for isotherm and LB thin film preparation was $50\,\mathrm{cm}^2/\mathrm{min}$. The LB thin film was compressed to a surface pressure of $3 \sim 28$ mN/m and equilibrated at the specific pressure for about 30 min. UV light (254 nm) was shined on the compressed films, after $3 \sim 5$ sec following the onset of UV irradiation, the films began to contract and became light blue in $20 \sim 30$ sec. After UV lamps were turned off, the LB thin film stayed on the surface of water for several minutes, and then the water was slowly drained by aspiration. The LB thin film was laid down on the flat surface of substrates, which were submerged horizontally in the subphase prior to thin film spreading. The substrates were removed by forceps and allowed to dry for 24 h at room temperature with a porous cover, and then the LB thin films on these substrates were analyzed.

AFM was accomplished using an Autoprobe CP (Park Scientific Instruments) to obtain topographic images of LB thin films in the contact mode with a silicon nitride cantilever. Scan rate is 1 Hz. Measurements with AFM were under ambient conditions. Scanning Electron Microscope (Amray 1400 SEM with EDXS analysis) was used to image the morphology of LB thin films, polarized UV/Vis/NIR spectrometer (Perkin-Elmer Corporation) was used to characterize the anisotropic optical property of LB thin films. Thin film thickness was measured by Dektak IIA

Results and Discussion

The pressure-area isotherm was used to find the optimum ranges in which to transfer LB thin films to solid substrates. Figure 1 showed isotherm curve for TS (200 μl TS solution in chloroform). We can see that the uniform compression of TS on water surface begins at $12\,\mathrm{dyn\text{-}cm}^{-1}$ with a uniform compressibility range between $12 \sim 25\ \mathrm{dyn\text{-}cm}^{-1}$, which is slightly different from the result McCaffrey mentioned (8). Beyond $25\ \mathrm{dyn\text{-}cm}^{-1}$, a relatively thick collapsed film appeared obviously on the air-water interface. In the

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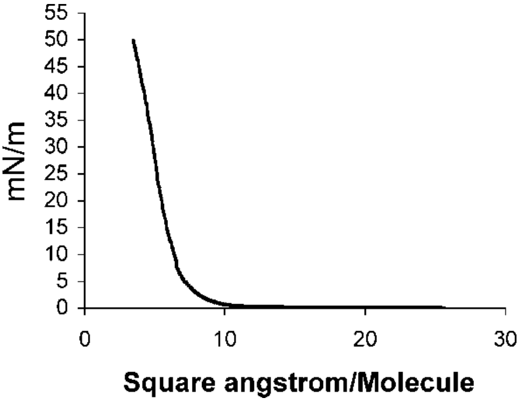

Figure 1. Isotherm curve of TS monomer.

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experiment, 12 dyn-cm^{-1} was set as critical pressure, which was used as a reference. Because TS molecular structure is symmetric without hydrophilic and hydrophobic groups at each end, TS monomers should float horizontally on the air-water interface. Based on the TS unit-cell data obtained by Bloor (10), who estimated the length of the TS monomeric unit should be about 5 Å (c axis) and the unit-cell width about 15 Å (b axis), thus the unit-cell area is approximately 75 Å^2, we can concluded that the formed TS LB thin film were multilayers. Thin film thickness obtained by Dektak IIA was in the range 150 ~ 180 Å, which also confirmed that the film was multilayers.

Figure 2 showed the optical absorption spectra of PTS LB thin film at two different orientations of the polarized incident UV-Vis light, which illustrated the optical anisotropy. In other words, there was orientational effect of TS LB thin film on substrate, which meant this thin film had anisotropic property. In these spectra, exciton absorption range is roughly between 500 nm and 700 nm. The wave number between peaks at 616 nm and 566 nm is about 1435 cm^{-1} and the wave number between peaks 616 nm and 550 nm is about 1949 cm^{-1}, which corresponds carbon-carbon double and triple bond vibronic bands in excitonic state, respectively. In the experiment, it was found that anisotropic effects depended on local area because the absorption ratio varied from one location to another location with the same LB thin film.

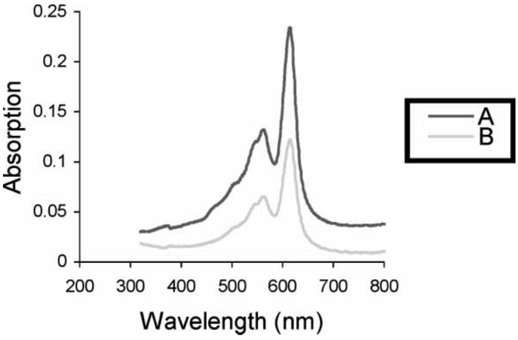

Figure 2. Absorption spectra of PTS LB thin film on Milli-Q water surface ITO-coated glass substrate (A). Polarized light parallel and perpendicular (B) to the polymer main chain.

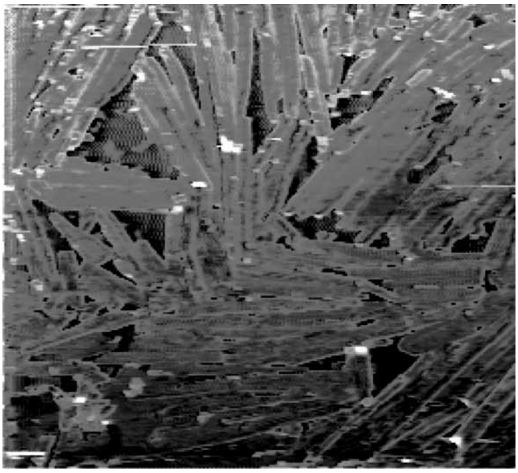

Figure 3. Topographic AFM image of PTS image polymer LB thin film (20 μm × 20 μm).

Figures 3 and 4 showed AFM topography of PTS LB thin film. From Figure 3, it was found that the crystal domain structure sizes were about several square microns, they were discrete thin films on micron scale. Figure 4 showed higher resolution view of PTS LB thin film, which revealed highly regular structure and orientation. The striated patterns observed in Figure 4 should run parallel to the polydiacetylene main chain (11, 12), and their atomic scale image will be explored by AFM equipped with an ultra-thin tip. PTS LB thin films have also been observed by SEM (Figures 5 and 6). These thin films were smooth and their domain sizes were around several square microns.

Conclusions

Multilayers TS LB thin film can be obtained by Langmuir-Blodgett transfer method. Under UV light, TS LB thin film was polymerized to PTS LB thin film in solid state

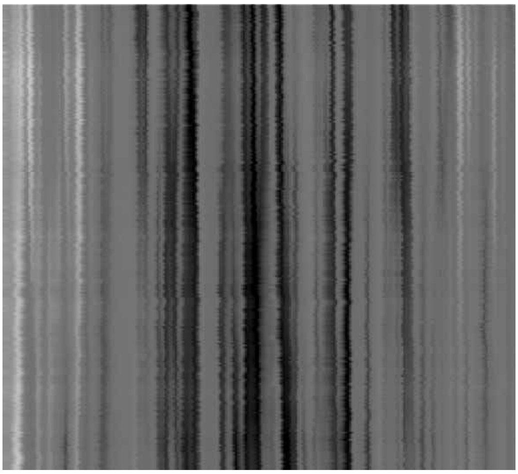

Figure 4. High resolution topographic AFM of PTS polymer LB thin film (1 μm × 1 μm).

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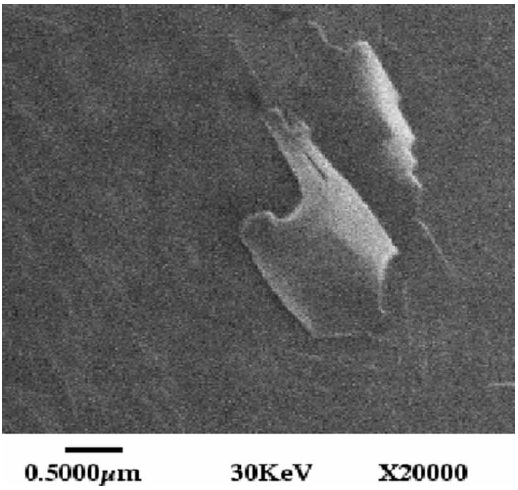

Figure 5. SEM image of PTS polymer LB thin film.

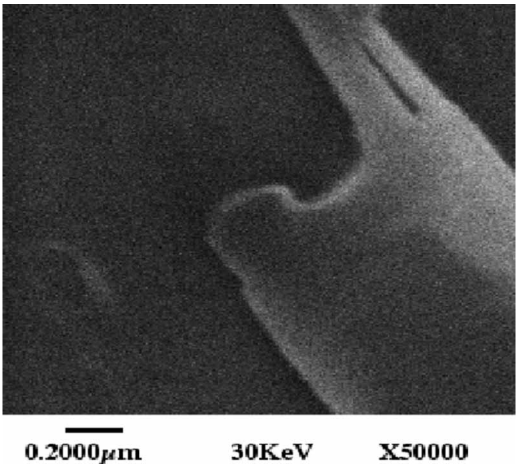

Figure 6. SEM image of PTS polymer LB thin film of higher magnification.

and its color became light blue. This kind of thin film had an anisotropic orientation and their crystal domain sizes were found to be roughly several square microns by AFM and SEM. Further research should be performed to increase the crystal thin film domain size and degree of orientation.

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