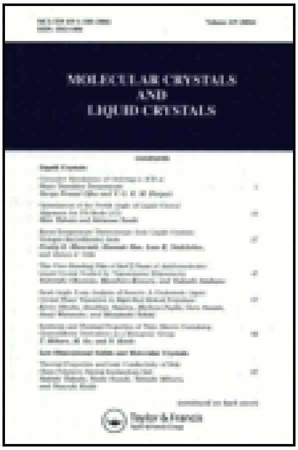

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Temperature Dependent Structure of Conducting Langmuir Blodgett Films Studied by X-ray Scattering

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Temperature Dependent Structure of Conducting Langmuir Blodgett Films Studied by X-ray Scattering

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Electrically conductive Langmuir-Blodgett films were fabricated from mixtures of stearic acid and poly(3-hexylthiophene). The temperature dependent structure of these films as well as that of pure stearic acid LB films was studied using x-ray scattering. We were able to use a crystal analyzer in front of the detector to greatly improve the angular resolution by taking advantage of the high intensity of the x-ray beam from the synchrotron storage ring. A phase separation indicated by a d-spacing change along the stacking direction was observed upon varying the temperature. The in-plane two dimensional structure of these LB films was studied and the temperature dependence indicates a phase transition of the in-plane structure in the temperature range of 90°C to 110°C for the pure stearic acid LB film.

INTRODUCTION

The Langmuir-Blodgett (LB) technique provides a rational approach to fabricate films with well defined composition, structure and thickness as well as a means for engineering electrically and optically active superstructures. However, in order to develop the full potential of this technology, new analytical approaches are necessary which will allow detailed studies of the relationship between the molecular architecture on the one hand and the supermolecular ordering on the other, as well as their effects on the physical properties of the LB films. X-ray scattering has been widely used to study the structure of LB films, especially for the out-of plane structure (along the stacking direction). However, for the in-plane (the planes parallel to the substrate) two dimensional structure study, synchrotron radiation is generally needed as the x-ray source since higher intensities are required. Even for the out-of-plane structure, the high intensity x-rays from a synchrotron provides an opportunity for more detailed studies. In our study, a crystal analyzer was used in front of the detector. The angular resolution therefore was greatly improved. This gave us a chance to study fine structural changes at different temperatures. The phase separation and d-spacing differences between phases along the stacking direction were observed upon changing temperature.

EXPERIMENTAL SECTION

Stearic acid (Fluka Chemical) was purified by recrystallization from acetone. The water used as a subphase was purified with a Milli-Q purification system (Millipore Corp.). Cadmium chloride (Fluka Chemical) was used without further purification. HPLC grade chloroform (Aldrich) was used for the preparation of spreading solutions. Monolayers were spread from chloroform solutions (typical concentration ca. 1 mg of total solute per ml) onto a purified aqueous subphase containing 2×10^{-4} M $CdCl_2$. The surface pressure-area isotherms were measured on a Lauda film balance at 20°C with a compression speed of 5 $Å^2 molecule^{-1} min.^{-1}$. The multi-layers were built up onto a glass slide by the vertical dipping method at 15-28 mN/m and 20°C. A dipping speed of 5 mm/min was used for the first dip and was increased to 10 mm/min for subsequent dips. Drying times of at least 2 hours were used between the first and second dips. This time was reduced to 15 minutes for all subsequent dips. Transfer ratios close to unity were observed for all monolayers. The synthesis of the 3-hexylthiophene monomer and the polymerization were described in earlier publications.[1,2] The molecular weights of the poly(3-hexylthiophene) (P-HT) are $M_n = 18{,}000$ and $M_w = 75{,}700$. It is soluble in organic solvents but is not surface active. The LB films were obtained by spreading a mixture of the P-HT and stearic acid onto the water subphase. Figure 1 shows the components used to form a stable monolayer. The mixtures form very stable monolayers on the water surface. The multi-layers were built up onto a glass slide using the same vertical dipping procedure as described above for stearic acid.

The x-ray diffraction study was carried out on beam lines X-18A and X-7B of the National Synchrotron Light Source using a conventional four-circle Huber diffractometer with a two circle analyzer on the 2θ arm. At x-7b, the incident beam was monochromated by a Si(220) double-crystal monochromator with the wavelength set at 0.94 Å. The layer structure along the stacking direction was studied using θ-2θ radial scans. The scattering geometry is sketched in Figure 2. A Ge crystal analyzer with the (220) Bragg reflection was used in front of a NaI scintillation detector to improve the angular resolution. The in-plane two-dimensional structure was studied by grazing angle diffraction with a fixed incidence angle at or near the critical angle. The in-plane diffracted beams were recorded by scanning the detector in the horizontal plane. A 0.1° Söller slit was used to improve the

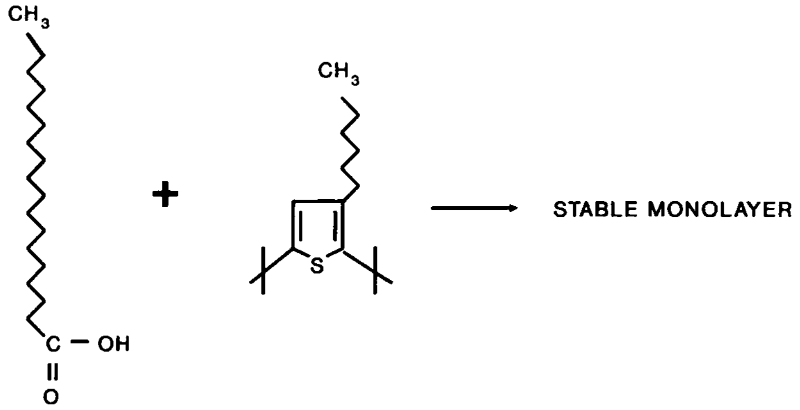

FIGURE 1 Formation of mixed poly(3-hexylthiophene)/stearic acid Langmuir-Blodgett films.

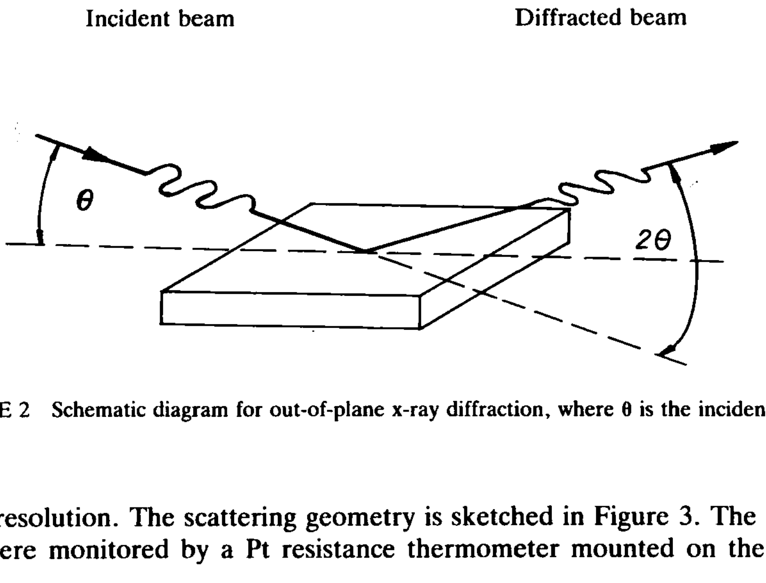

FIGURE 2 Schematic diagram for out-of-plane x-ray diffraction, where θ is the incident angle.

angular resolution. The scattering geometry is sketched in Figure 3. The temperatures were monitored by a Pt resistance thermometer mounted on the sample holder.

RESULTS AND DISCUSSION

The out-of-plane x-ray diffraction patterns for 34 layers of cadmium stearate LB film at different temperatures are shown in Figure 4. The intensity is plotted in arbitrary units vs. $2\sin\theta/\lambda$ with units of 1/Å. We define $Q_z = 2\sin\theta/\lambda$. The peaks shown in Figure 4 are the 2nd, 3rd, 4th, 5th, 6th and 7th order (001) type Bragg reflections. The first order reflection was not collected since it is too close to the direct beam. The intensity of the peaks shows an alternating pattern with weaker peaks at even order reflections. This is a typical feature of a bilayer structure with

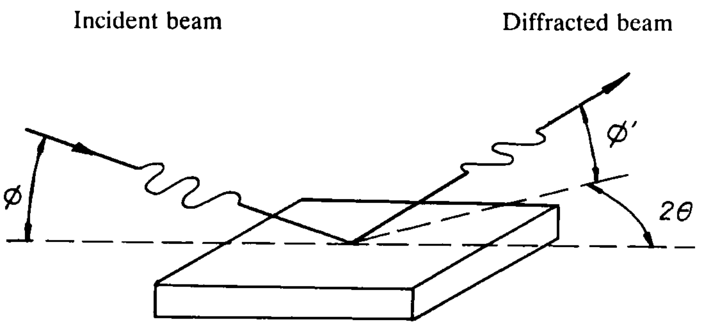

FIGURE 3 Schematic diagram for in-plane x-ray diffraction, where ϕ is the incident angle which was set to be close to the critical angle.

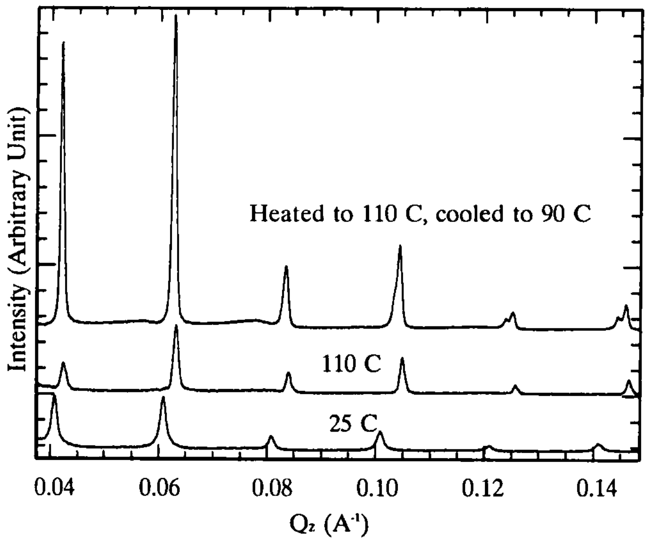

FIGURE 4 Out-of-plane x-ray diffraction pattern for 34 layers of cadmium stearate LB film deposited on a glass slide, where $Q_z = 2\sin\theta/\lambda$.

low electron density at the center of the bilayer.[2] At 25°C, the d-spacing of the bilayer calculated from the diffraction pattern is 49 Å. According to M. Sugi,[3] the d-spacing for the fatty acid salt LB films is linearly related to the number of carbon units (n) as: d(n) = 5.3 + 2.50n (Å). The d-spacing of the cadmium stearate with 18 carbon units should be 50.3 Å. The 49 Å d-spacing calculated from the diffraction pattern is very close to the ideal value. This indicates that the hydrocarbon chains are oriented almost normal to the substrate. This is in good agreement with the result of our NEXAFS study.[4] When the sample was heated to 110°C, the d-spacing reduced to 48.4 Å indicating a tilting of the hydrocarbon tails. This tilting and disordering effect at elevated temperature has been studied by C. Naselli *et al.*[5] on similar systems of LB multi-layers using FTIR spectroscopy. More interestingly, when the sample was cooled to 90°C after being heated to 110°C, a second set of peaks with d-spacing of 47.9 Å appeared in the diffraction pattern. This second set of peaks did not grow at the expense of the first set which corresponds to a d-spacing of 48.6 Å at 90°C. This second set could not be resolved from the first for the lower orders, so, their intensities added to those of the first set making the lower order peaks much stronger compared with those at 25°C and 110°C. This indicates that the total scattering power of the sample has increased, probably due to an annealing of the sample. Similar temperature dependent behavior of x-ray diffraction of fatty acid LB films was observed by M. R. Buhaenko *et al.*[6] In that study, the diffraction pattern of a 40 layer LB film of docosanoic acid with a 2.5×10^{-4} M $CdCl_2$ subphase, dipped at pH 3.0 was a set of peaks with d-spacing of 53 Å at 25°C. This changed into two sets of peaks with a d-spacings of 48 Å and 53 Å on heating to 55°C, probably due to annealing. The study showed that the intensity of the second set increased with time as the sample was being heated to 55°C. For the sample dipped at the same dipping condition except the pH is 6 instead of 3, the diffraction pattern was quite different. The room temperature phase had a d-spacing of 60 Å and the second sets of peaks with a d-spacing of 58 Å started developing with time at 90°C. Although the authors offered no explanation for this pH dependent behavior, we believe this is an effect due to the concentration of the Cd ions in the LB film. As pointed out by M. Bloch *et al.*,[7] the higher the pH, the higher the concentration of the Cd ions in the LB film. It would be reasonable to assume that the phase separation at elevated temperature is due to the redistribution of the Cd ions in the LB film. Since this is a diffusion controlled process, the dynamic effects must be considered. Therefore, the difference between the diffraction pattern at 110°C and 90°C in Figure 4 could be due to a time effect rather than a temperature effect. This dynamic character of the phase separation of Cd containing LB films makes it more difficult to study and is the reason why this phase separation has not been widely investigated. Another factor which limited the study of this phase separation is the angular resolution of the diffractometer. If no analyzer had been used, we would not have been able to resolve the second set of peaks. More extensive x-ray diffraction experiments are planned to study the Cd concentration effects on the structure of LB films. For example, by varying the pH of the subphase during the sample preparation and varying the temperature and heating times during the diffraction experiment.

Because of the layered structure of the LB film, the Cd ion motion would be primarily restricted to the plane of the layer in which they were located. Therefore, if the phase separation we saw in the out-of-plane diffraction is due to the redistribution of the Cd ions, we would expect some change in the in-plane diffraction pattern in the same temperature range as well. Figure 5 shows the in-plane x-ray diffraction pattern for the same sample as in Figure 4. At 25°C, only one peak is observed corresponding to an in-plane d-spacing of 4.13 Å indexed as (110) for a hexagonal structure. At 110°C, this peak splits into two peaks corresponding to d-spacing of 4.26 Å and 3.83 Å. These d-spacing values are very close to those observed by M. Bloch *et al.*[8] for the orthorhombic structure with $d_{110} = 4.15$ Å and $d_{020} = 3.71$ Å. However, in their study, the hexagonal structure was only observed in the monolayer film and the orthorhombic structure was the stable

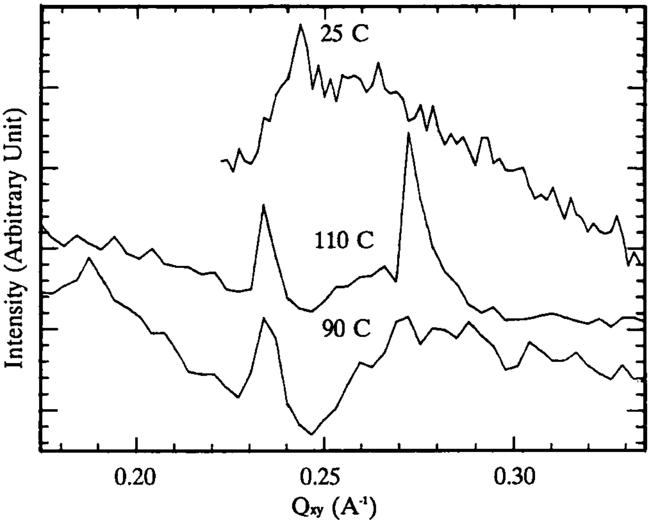

FIGURE 5 In-plane x-ray diffraction pattern for 34 layers of cadmium stearate LB film deposited on a glass slide, where $Q_{xy} = 2\sin\theta/\lambda$ is the in-plane diffraction vector.

phase in the multi-layer film at room temperature. In order to fully understand the two dimensional structure change with temperature, we are planning further experiments with well controlled Cd concentration of the LB film and more carefully monitored heat treatment history.

As mentioned in the experimental section of this paper, the P-HT/stearic acid mixture was used to fabricate the conducting polymer LB films. Whether the P-HT and cadmium stearate are mixed at the molecular level or form separate domains is a very important question in characterizing these films.

Figure 6 shows the out-of-plane x-ray diffraction pattern for 34 layers of the mixture of cadmium stearate/P-HT with a 2:1 ratio. At 25°C, the diffraction pattern is the same as that for pure cadmium stearate with a d-spacing of 49 Å (d(25°C) = 49 Å). At 50°C, the diffraction peaks moved slightly towards higher angle indicating a small d-spacing decrease (d(50°C) = 48.95 Å). At 75°C, a completely new set of peaks with d-spacing of 40 Å (d'(75°C = 40 Å) appeared while the d-spacing of the original set decreased a little (d(75°C) = 48.8 Å). When cooling the sample to 25°C, the d-spacing of the new set decreased (d'(25°C) = 39.9 Å) in contrast to the increasing d-spacing of the original set (d(25°C, cooling) = 48.95 Å).

Figure 7 shows the diffraction pattern of the same film at higher temperature. At 90°C, the d-spacing of the new set decreased even more (d'(90°C) = 37 Å) while the d-spacing of the original set only decreased a little (d(90°C) = 48.3 Å). At 110°C, the peaks of the new set disappeared. All of the diffraction peaks disappeared at 130°C. Since the original set of diffraction peaks has the same d-spacing and thermal behavior as the pure cadmium stearate, we would assume that the diffraction is from cadmium planes located within highly ordered molecular stacks of cadmium stearate molecules. On the other hand, the new set of peaks is

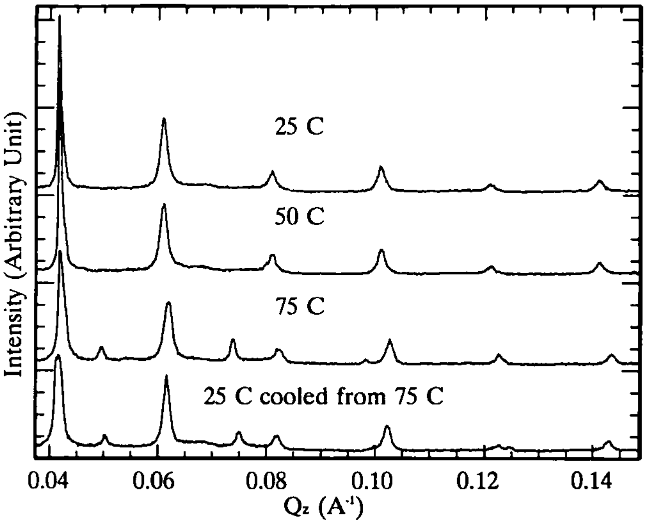

FIGURE 6 Out-of-plane x-ray diffraction pattern for 34 layers of mixture of cadmium stearate and P-HT with 2:1 ratio LB film on a glass slide.

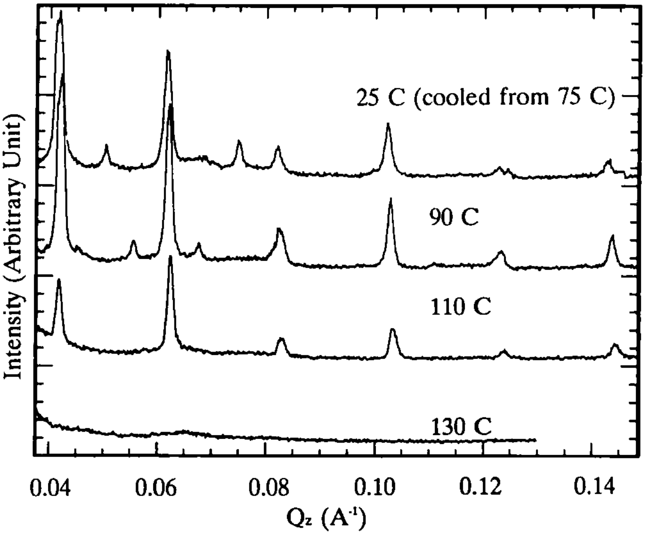

FIGURE 7 Out-of-plane x-ray diffraction pattern for a 34 layer LB film consisting of a mixture of cadmium stearate and P-HT in a 2:1 ratio deposited on a glass slide (heated up to melting temperature).

a unique feature of the mixture since there has been no report of diffraction peaks with a d-spacing of 40 Å at 75°C for cadmium stearate LB films. In addition, the d-spacing of this new set has a completely different thermal behavior from the one corresponding to the pure cadmium stearate, it decreases much faster during heating and keeps decreasing instead of increasing during cooling. It disappears at a temperature below the melting temperature of the film. Although it is clear that the new set of peaks is uniquely related to the mixture properties of the film, it is not clear from what structure the new diffraction arises.

According to our NEXAFS study[4] and FTIR study,[1] the LB films of the P-HT/cadmium stearate mixture is made of a two phase microstructure consisting of well ordered domains of cadmium stearate molecules and relatively disordered polythiophene molecules. The interesting temperature dependent x-ray diffraction pattern we observed in this study is further evidence of this model. Since the Cd ions are much stronger scatterers than any other atoms in the film, and they are well ordered in the cadmium stearate domain, it would be reasonable to believe that both sets of peaks arise from the Cd ion planes. We believe that the different d-spacings is caused by the different thermal behavior between columns made of pure cadmium stearate domains (let us call them the pure column) and columns made of alternative cadmium stearate and P-HT domains (let us call them the sandwich columns). At 25°C, the d-spacing of the pure columns and the sandwich columns is almost the same except that diffraction from the sandwich columns is weaker since the cadmium concentration is about on-half of the pure column. At elevated temperatures, the hydrocarbon chains of the cadmium stearate undergoes a tilting and twisting process through a conformational change causing the d-spacing of the Cd planes to decrease. This process occurs in both types of columns. However, in the sandwich columns, at sufficiently high temperatures, another process could occur, the hydrocarbon chains of the P-HT could move along the stacking direction and penetrate into the neighboring cadmium stearate domains through a conformational change. This is probably what happens at 75°C. This penetration will significantly reduce the distance between the Cd ion planes in the sandwich columns and generate the second set of diffraction peaks. When the sample was cooled to 25°C, the partially reversible conformational change of the hydrocarbon chains of the cadmium stearate makes the d-spacing of the Cd planes in the pure columns increase a little. In the sandwich columns, the hydrocarbon chains of the cadmium stearate had been penetrated by the hydrocarbon chains of the P-HT, making them more difficult to rearrange and increase the d-spacing. On the other hand, the thermal contraction of the P-HT domains between the cadmium stearate domains reduced the d-spacing of the new set further during cooling. At higher temperatures, the hydrocarbon chains of the P-HT penetrate more into the cadmium stearate domains, so the contraction of the new set is greater than the old one. At about 110°C, the d-spacing of the Cd ion planes in the sandwich columns is reduced to one half of the d-spacing of the cadmium stearate bilayer. In other words, the P-HT layer totally penetrates into the adjacent cadmium stearate layers. Therefore, the new set of peaks disappears at this temperature, below the melting temperature of the film.

CONCLUSION

Using synchrotron radiation as an x-ray source, the temperature dependent structural change of LB films of pure cadmium stearate and a mixture of cadmium stearate/P-HT was studied using x-ray diffraction. For the pure cadmium stearate film, there is a phase transition in the temperature range of 90–110°C. This transition produces a second set of d-spacing of the Cd ion planes along the stacking direction and probably a hexagonal to orthorhombic change for the in-plane structure. For the LB films with 2:1 mixture ratio of cadmium stearate to P-HT, a new set of diffraction peaks with a d-spacing of 40 Å appears to 75°C. The appearance of this new set and its thermal behavior supports our model of the two phase microstructure for the LB films of this mixture. It seems that the microstructure of the LB films is far more complicated than was thought before, it depends on the Cd ion concentration and the pH of the subphase as well as the thermal history of the film. The distribution of the Cd ions in the LB films plays a very important role for both the in-plane and out-of-plane structure. Further systematic study would provide more information about the structure of this interesting system and may lead to some new methods to fabricate and control the structure of the LB films.

Acknowledgments

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