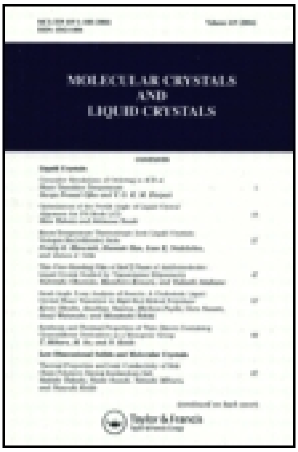

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Aggregation of Cyanobiphenyl Liquid Crystal in Langmuir-Blodgett Multilayers

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Aggregation of Cyanobiphenyl Liquid Crystal in Langmuir-Blodgett Multilayers

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The multilayers containing cyanobiphenyl liquid crystal (4-cyano-4-octybiphenyl) with stearic acid as a matrix have been fabricated by the Langmuir-Blodgett technique. The surface pressure-area isotherms and x-ray diffraction datas reveal that the multilayers have a close packed layer structure. Optical absorption spectra and morphological observations show that the aggregates of cyanobiphenyl liquid crystal are formed in the multilayers, and the aggregate size depend on the film thickness.

Keywords: aggregate, cyanobiphenyl liquid crystal, Langmuir-Blodgett multilayers

1. INTRODUCTION

The molecular organized systems have been attracting attention since it is possible to develop them as functional devices.[1–3] Liquid crystals have been widely used in display devices, optoelectronic devices and physical investigation because of the self-organizing property of liquid crystals. Recently, there is interest in the construction of liquid crystal molecular organizates by the Langmuir-Blodgett (LB) assembly technique.[4–10] In particular, liquid crystal molecules with the conjugated electron systems and electron donating and accepting chemical groups are excepted for incorporation in LB multilayers as piezoelectric, pyroelectric and non-linear optical materials. The stability of monolayers of various amphiphilic cyanobiphenyl liquid crystals at the air-water interfaces was investigated by Deniel et al.[4] Berkovic et al.[7] and Richardson et al.[8] reported the Second Harmonic Generation in the cyanobiphenyl liquid crystal monolayers and multilayers. Sakuhara et al.[9] fabricated *Y* type and *z* type multilayers by mixing the cyanobiphenyl liquid crystal and long chain fatty acids and observed the pyroelectric effect in the *z* type multilayers. However, the aggregation states of cyanobiphenyl liquid crystal in the multilayers have rarely been observed. For many potential applications, it is important to

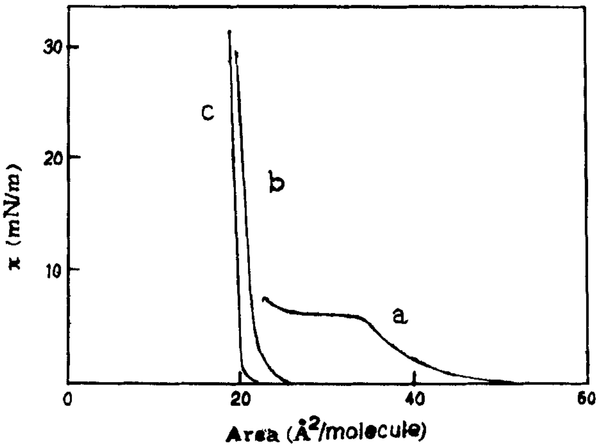

FIGURE 1 Surface pressure-area isotherms, a) pure 8CB; b) 8CB:SA = 1:1; c) pure SA.

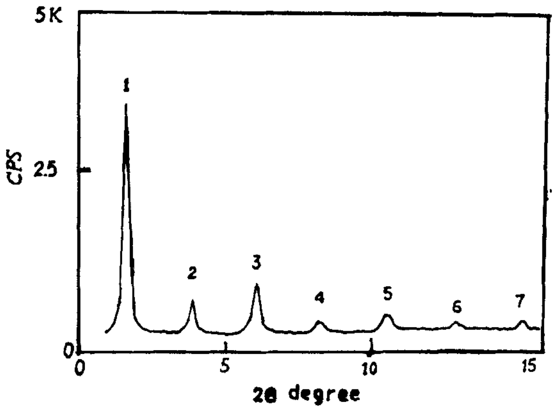

FIGURE 2 X-ray diffraction pattern of the multilayer containing 8CB and SA, (20 layers).

control the aggregation states of molecules in the multilayers. Recent studies[11-13] indicated that two and three dimensional aggregates occurred in monolayers and multilayers containing polar molecules with long chain fatty acids. In this work, we investigated the aggregation states of cyanobiphenyl liquid crystals in LB multilayers by optical absorption spectra and morphological observations.

2. EXPERIMENTAL DETAILS

The cyanobiphenyl liquid crystal used in this work was 4-cyano-4-octybiphenyl (8CB), it was supplied by BDH Chemical Ltd. Stearic acid (SA) was used as a matrix. Mixed solutions of 8CB-SA, total concentration was 1×10^{-3} M in chloroform, were spread on an aqueous subphase including 1×10^{-4} M of $CdCl_2$. The surface pressure-area isotherms of monolayers were measured on a Langmuir trough. Monolayer stability on the subphase was evaluated by changes in the surface area

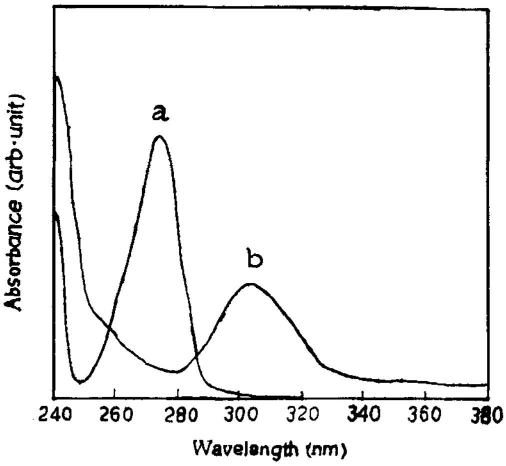

FIGURE 3 Absorption spectra of 8CB, a) in chloroform solution; b) in multilayer.

with time at constant surface pressure. Quartz plates were used as the substrates with hydrophilic surface for depositing multilayers. The surface pressure during monolayer transfer was 27 mN/m. The dipping rate was 5mm/min. The surface morphologies of the multilayers were observed under a Leitz (ORTHOPLAN-POL) microscope with a polarized reflected light illuminator. X-ray diffractions were carried out on a D/max-RA x-ray diffractometer, the x-ray beam was obtained from 40 kv and 50 mA rotating anode CuKα source. Absorption spectra of multilayers were measured with a DU-8B spectrometer.

3. RESULTS AND DISCUSSION

3.1. Monolayers of Cyanobiphenyl Liquid Crystal in Stearic Acid Matrix

For well-defined transfer of monolayers with 8CB, stearic acid, which is known to form a monolayer with a well-defined structure, was used as a matrix. The surface pressure-area isotherms of monolayers of the components and the 1:1 mixture are shown in Figure 1. For pure 8CB, the monolayer collapse is at a comparatively low surface pressure of 4.8 mN/m. The average molecular area is 37 Å^2 molecule. While the isotherm of a 1:1 mixture of 8CB-SA is similar to that of pure SA, the mixed monolayer collapses at 37 mN/m with an average molecular area of 22 Å^2 molecule. The area is almost equal to the cross sectional area of 8CB molecule (20 Å^2 molecule, ref. 4), which indicates that 8CB is closely packed in SA matrix. The mixed monolayer is stable where a detectable decrease in the surface area was not observed, during a period of 1 h.

3.2. Structure of Multilayers of Cyanobiphenyl Liquid Crystal in Stearic Acid Matrix

Figure 2 shows the x-ray diffraction pattern from the multilayer deposited on quartz plates. Many Bragg peaks were observed from the pattern, indicating that the

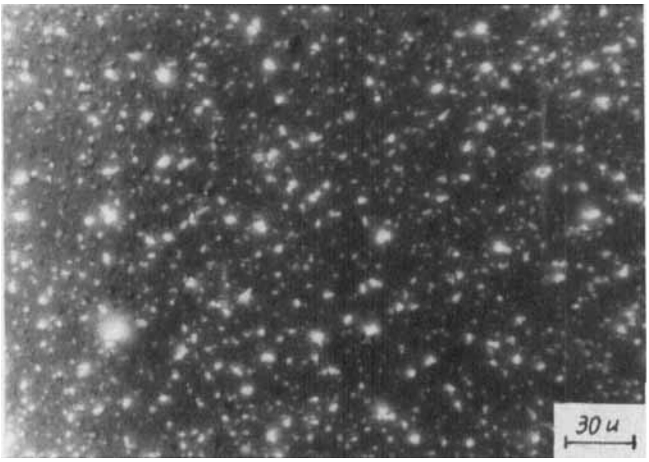

FIGURE 4 Polarizing micrograph of the multilayer containing 8CB and SA, (20 layers, dipping direction: parallel to the polarizer direction).

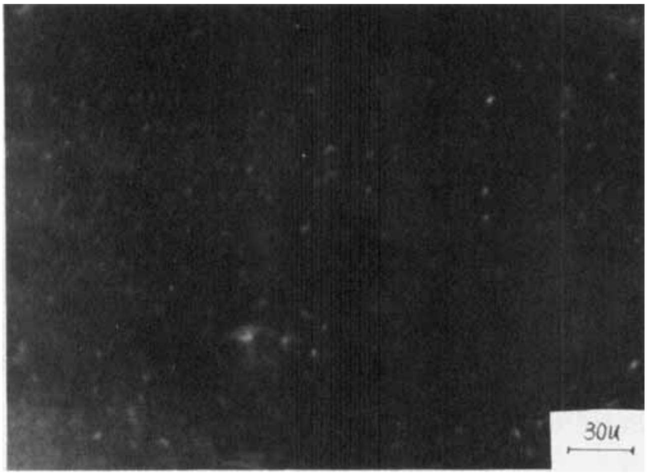

FIGURE 5 Polarizing micrograph of the multilayer containing 8CB and SA, (20 layers, dipping direction: at 45° to the polarizer direction).

multilayer has a well-ordered structure. The angle 2 θ between neighboring peaks is about 1.78°, therefore the spacing d was about 5.01 nm. The value agrees with twice the molecular length of stearic acid. The result suggests that the films deposited are y-type multilayers.

Figure 3 shows the absorption of 8CB in the multilayers in comparison with the spectra in chloroform solution. The absorption around 270 nm of the solution shifts considerably to the longer wavelength in the multilayers. This indicates that the interaction between 8CB molecules is strong, and implies aggregates of 8CB may be formed while still in the monolayers and transfer to the substrates.

3.3 Surface Morphologies of the Multilayers of Cyanobiphenyl Liquid Crystal in Stearic Acid Matrix

Pure SA multilayers are homogeneous, a dark field is observed under a reflection polarizing microscope. For multilayers containing 8CB and SA, many domains are observed. The crystalline domains consisted of anisotropic regions and existed throughout the multilayers. When the multilayers are oriented with the dipping direction parallel to the polarizer direction, the field of view exhibits greater contrast (Figure 4). Whereas the dipping direction is at about 45° to the polarizer direction, the optical extinction occurs in many crystalline domains (Figure 5), indicating that

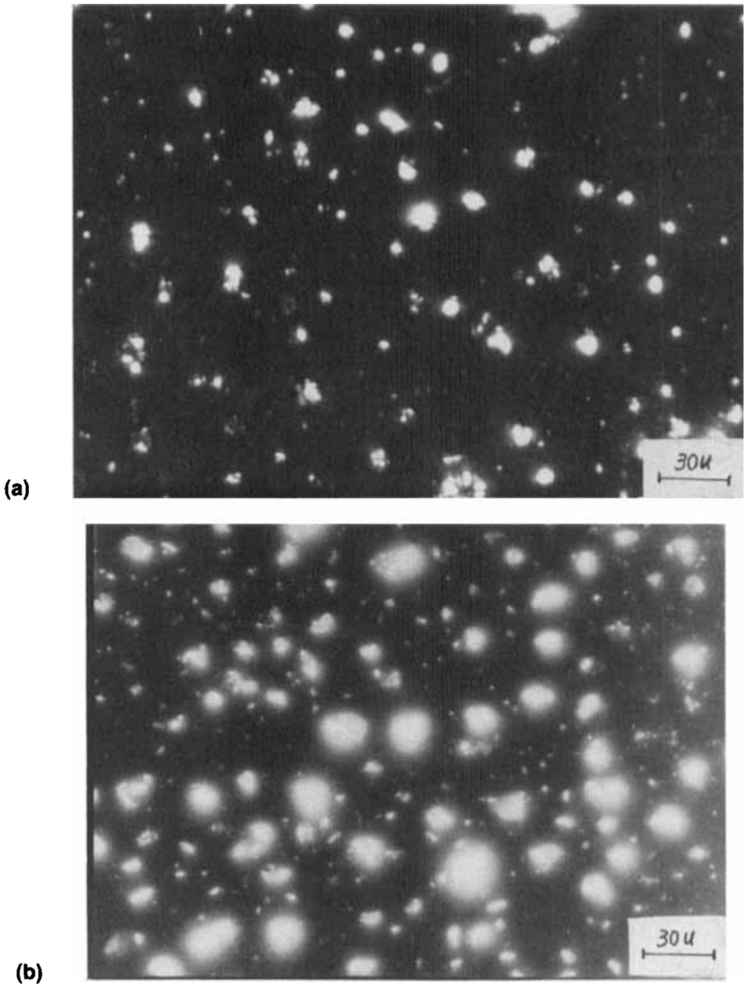

FIGURE 6 Polarizing micrograph of the multilayers containing 8CB and SA. a) 40 layers; b) 60 layers.

these crystalline domains have a uniform extinction angle. The crystalline domains are the segregated 8CB phase. This aggregate size increases with the number of deposition and is approximately 20 μm for 60 layer LB films (Figure 6). In other words, the aggregate states can be controlled by the film thickness.

4. CONCLUSION

The well-oriented multilayers containing cyanobiphenyl liquid crystal 8CB with stearic acid SA as a matrix have been prepared. We have demonstrated that the aggregates of 8CB occur in the multilayers, and the aggregate size depends on the film thickness.

Acknowledgments

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