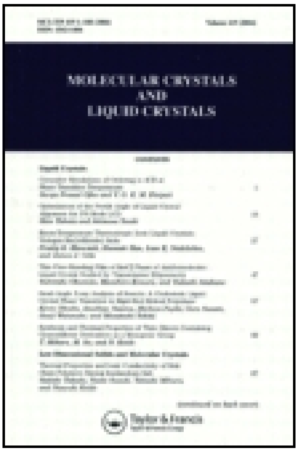

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Fabrication and Characterization of Orientatation-Controlled Alkoxy- and Cyano-Substituted Distyrylbenzene Derivatives in Thin Film

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Distyrylbenzene(DSB) derivatives, trimer of phenylenevinylene, with cyano and alkoxy groups grew epitaxially on the friction-transferred poly(tetrafluoroethylene) (PTFE) layer. DSBs/PTFE double layers indicated the remarkable anisotropic feature in absorption and emission properties.

Keywords distyrylbenzene derivatives;molecular orientation; optical properties

INTRODUCTION

Poly(p-phenylenevinylene) (PPV) is one of the most widely investigated conjugated polymers for use in electroluminescent devices such as light-emitting diodes. However, PPV is obtained as an insoluble material and further processing is difficult. Interest in optical and electronic properties has led to investigation of oligomeric compounds. We have prepared well-ordered thin film of methoxy-substituted distyrylbenzene (DSB) derivatives from vapor phase and discussed the relation between the molecular orientation and the optical properties of the films[1,2].

In this study, three kinds of alkoxy- and cyano-substituted DSB derivatives were vapor-deposited on a friction-transferred poly(tetrafluoroethylene) (PTFE) layer. The molecular orientations and optical properties of DSB derivatives in the film are discussed based on the position of cyano groups at terminal phenyl rings.

EXPERIMENTAL

DSB derivatives used here are 1,4-di(o-cyanostyryl)-2,5-di(2ethylhexyloxy)benzene (DSB-6(2)-o), 1,4-di(m-cyanostyryl)-2,5-di(2-ethylhexyloxy)benzene (DSB-6(2)-m) and 1,4-di(p-cyanostyryl)-2,5-di(2-ethylhexyloxy)benzene (DSB-6(2)-p) shown in Fig.1. These samples were synthesized and characterized in Academia Sinica and were vapor-deposited on a friction-transferred PTFE layer at a pressure of 10^{-3} Pa. The structure and optical properties of the films were investigated by transmission electron microscope (TEM) and UV-VIS absorption and photoluminescence (PL) spectroscopy.

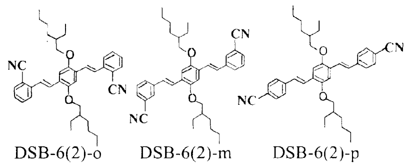

FIGURE 1 Molecular structures of DSB derivatives used here.

RESULTS AND DISCUSSION

Prior to vapor-deposition, the absorption and PL spectra of these samples in $CHCl_3$ solution were investigated. The absorption and emission peaks are found to be at 336 nm and 410 nm and at 479 nm for DSB-6(2)-o, at 327 nm and 399 nm and at 463 nm for DSB-6(2)-m, at 340 nm and 417 nm and at 482 nm for DSB-6(2)-p, respectively, as shown in Fig.2. The wavelength at the lowest energy peak red-shifts as following order: DSB-6(2)-m< DSB-6(2)-o< DSB-6(2)-p. This is good agreement with the results of theoretical calculation using INDO/S-CI method (MOS-F ver.4.1, Fujitsu Labs.). The calculated results indicated that the transition between ground state and first exited state in DSB-6(2)-o and DSB-6(2)-p is delocalised over the whole molecule. In DSB-6(2)-m, on the other hand, the transition is predominantly focused on the central phenyl ring. The electron withdrawing effect of cyano group substituted at meta position of end phenyl ring on the electronic state is not so large.

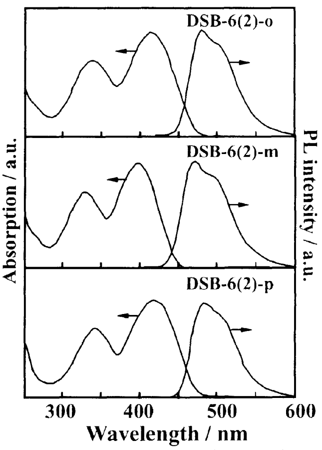

FIGURE 2 Absorption and PL spectra of DSBs in $CHCl_3$ solution.

The friction-transferred PTFE layer has a high potential as a substrate to prepare the uniaxially oriented organic films [3]. Figure 3 shows the electron micrographs and the electron diffraction (ED) patterns of DSBs/PTFE double layer. DSB-6(2)-o deposited on the friction-transferred PTFE layer forms the plate-like crystals aligned along the sliding direction of PTFE. The ED pattern from DSB-6(2)-o/PTFE double layer shows the

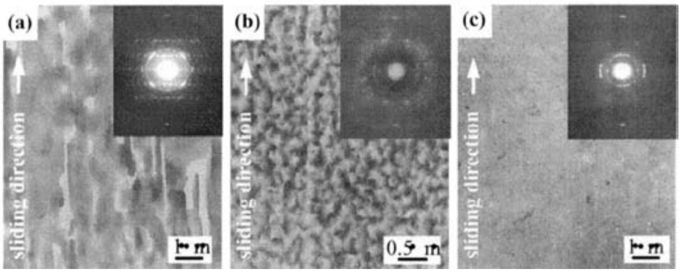

FIGURE 3 TEM and ED pattern of DSB-6(2)-o/PTFE(a), DSB-6(2)-m/PTFE(b) and DSB-6(2)-p/PTFE(c) double layer.

superposition of the reflection spots from the deposited DSB-6(2)-o crystals and those from the PTFE layer. The ED pattern from the DSB-6(2)-o film shows the single net pattern with the diffraction spots corresponding to the lattice spacings of 0.43nm and 2.4nm. These findings indicate that the DSB-6(2)-o grew epitaxially on the PTFE layer. The DSB-6(2)-m film is composed of small rectangular crystallites growing along two directions crossing at 76°. The bisectional direction of crossing angle of these crystallites corresponds to the friction direction of PTFE. Two sets of the single net pattern (0.24nm and 0.8nm) also appear at two directions against to the friction direction of PTFE corresponding such configuration. On the other hand, the DSB-6(2)-p film dose not indicate an obvious crystal habit. However, the DSB-6(2)-p also grows epitaxially on the PTFE layer because the ED pattern of the DSB-6(2)-p/PTFE double layer shows the superposition of single net patterns of the DSB-6(2)-p crystal and the PTFE crystal.

For investigating the effect of molecular orientation on optical properties of DSBs/PTFE double layers, the polarized absorption and PL measurement are carried out. Figure 4 shows the polarized absorption and PL spectra of the DSBs/PTFE double layers together with the experimental setup for polarized PL measurement. The sample is set up where the friction direction of PTFE is parallel to the polarized direction of the incident light.The incident excitation light is inclined to the film plane at an angle of 45°, and emission is detected normal to the film plane.

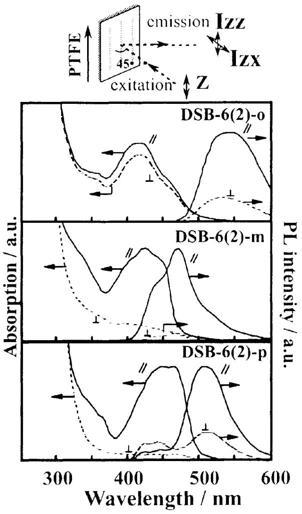

FIGURE 4 Experimental set up for polarized PL mesurement and polarized absorption and PL spectra of DSBs/PTFE double layer.

The absorption spectra of the DSB-6(2)-o, DSB-6(2)-m and DSB-6(2)-p films have broad unstructured peaks around at 413 nm, 430 and 460 nm, respectively. Comparing to the absorption peaks in $CHCl_3$ solution with those in film, the maximum peaks shift to longer wavelength. The absorption intensity of DSB-6(2)-o/PTFE layer is not so dependent on the polarized direction of the incident light. However, the dichroic ratio of PL intensity ($I_{//}$ / $I_{.}$) is about 4. On the other hand, the remarkable anisotropic features of absorption observe in the DSB-6(2)-m/PTFE and DSB-6(2)-p/PTFE layers. The dichroic ratios of absorption intensity are estimated to be 6 and 18, respectively. The DSB-6(2)-m/PTFE layer indicates also anisotropic feature of PL intensity. However, the dichroic ratio of PL intensity of DSB-6(2)-p/PTFE layer is smaller than that of absorption intensity. In DSB molecules, the transition moment of the lowest single exciton associated with • •• * band gap is parallel to the longitudinal direction of the molecules. If the transition moment of DSB molecule is normal to the substrate surface, the absorption peak can not be detected because there is no interaction between the transition moment of molecule and the electric vector of incident light. On the other hand, PL intensity can be detected in this optical set-up even if the transition moment of DSB molecule is normal to the substrate surface because the incident excitation light is inclined to the film plane. Therefore, we concluded that DSB-6(2)-p molecules take two kinds of orientations on the PTFE layer in which the long axes of DSB-6(2)-p are parallel and normal to the substrate surface.

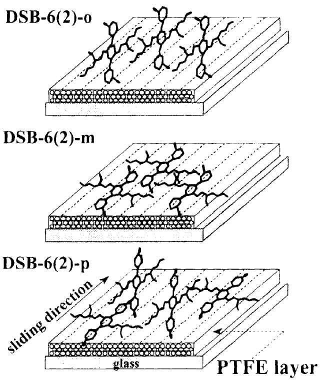

FIGURE 5 Proposed model of molecular orientation of DSBs/PTFE double layer.

The crystal structures of DSB derivatives used here have not been reported yet. However, we can propose their molecular orientations referring the polarized optical properties. Figure 5 shows the proposed molecular orientations of DSB derivatives on the PTFE surface. The long axes of DSB-6(2)-o and DSB-6(2)-m orient inclined and parallel to the substrate, respectively. On the other hand, these orientations coexist in the DSB-6(2)-p film.

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