CHEMISTRY LETTERS, pp. 841-844, 1989.

Conductive Langmuir-Blodgett Film Containing Mesogenic Unit.

Phase Transition Accompanied with the Change in Conductivity

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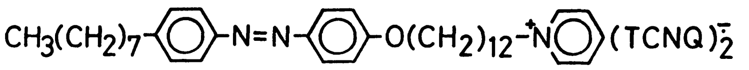
Conductive Langmuir-Blodgett films of charge transfer complex containing azobenzene group in the hydrophobic part exhibited a sharp discontinuity in the temperature dependent conductivity. This discontinuity was accompanied with the change in the aggregation form and the morphology of the films.

Recently mesogen-containing Langmuir-Blodgett (LB) films have attracted much attention.[1-5] But, most of the works are concerned with the orientation of the mesogenic units themselves.[2,3] For example, heat treatment of the LB films of azobenzene derivatives causes a phase transition and a change in the structure of the films.[4] Amphiphilic azobenzene exhibits cis-trans photoisomerization in the LB films of the polyion complex.[5] By introducing a mesogenic unit, conductive LB films would be endowed with various features; change in the structure of the conductive part, generation of long-range order, and occurrence of phase transitions.

In this paper, we will report a first example of the change in the conductivity of the LB films accompanied by the phase transition. This system serves as a useful model for controlling the functions of LB films externally.



azo(8-12)

The amphiphilic charge transfer complex azo(8-12) was synthesized by the method described previously[6,7] with slight modifications. The surface pressure-area isotherm was measured by using a Lauda film balance on pure water at 290 K. A mixture of acetonitrile and benzene (1:1) was used as a spreading solvent. The monolayer was transferred onto quartz plates hydrophobized with 1,1,1,3,3,3-hexamethyldisilazane for conductivity measurement and UV-visible spectroscopy.

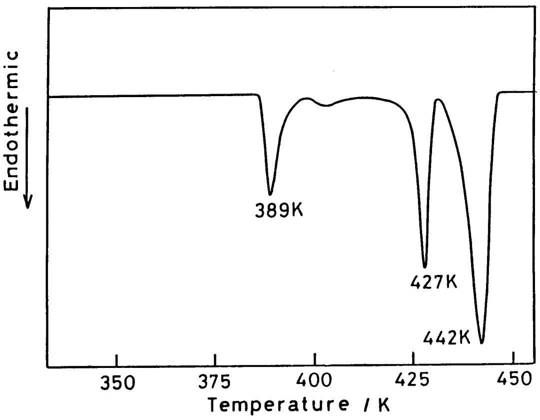


Fig. 1. DSC curve of the powder sample of azo(8-12).

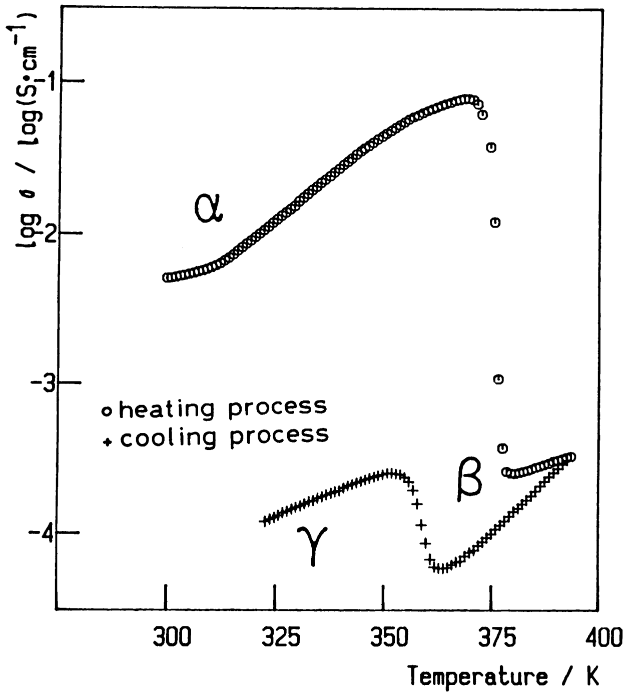


Fig. 2. Temperature dependence of the conductivity of the 100-layered LB film.

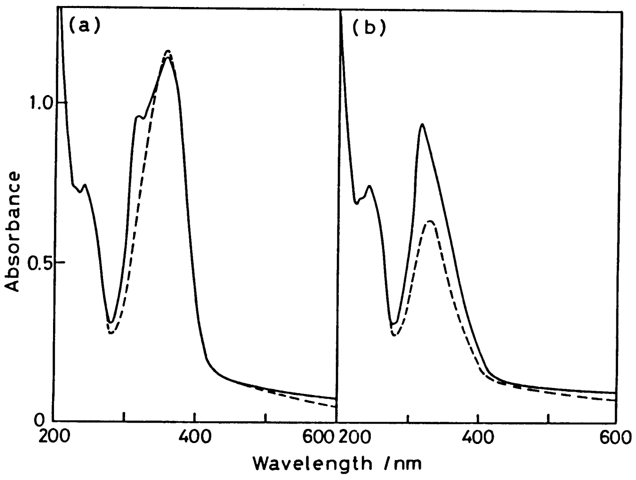


Fig. 3. Polarized absorption spectra of the 60-layered LB films in the α phase (a) and the γ phase (b) at the incident angle of 45° with p-polarized (——) and s-polarized light (---).

The conductivity of LB film on the plate was determined by the DC two-probe method using silver paste as electrodes. Azo(8-12) formed a monolayer with the collapse pressure above 45 mN m^{-1}. The limiting area 0.30 nm^{2}/per complex of azo(8-12) is almost the same as that of N-docosylpyridinium(TCNQ)$_2$, suggesting that the area is governed by the bulky acceptor.6,8) The monolayer was transferred by a horizontal lifting method9) at 25 mN m^{-1}.

Figure 1 shows a DSC curve of the powder sample at the heating process. An endothermic peak at 442 K is identified as the melting point by the polarizing microscope.

The temperature dependence of the conductivity in the lateral direction of the 100-layered LB film is shown in Fig. 2. Two kinds of phase transitions and three distinct phases are recognized; these phases are referred to as α, β, γ as indicated in Fig. 2. The conductivity abruptly decreases around 375 K by a factor of ca. 300 on heating and then increases a little around 360 K on cooling. The sharp decrease in conductivity was irreversible and the α phase could not be recovered even when the LB film was cooled down to room temperature. The γ phase didn't revert to the α phase by the exposure to a high humidity atmosphere.10) The change in conductivity between the β and γ phases was almost reversible. The DSC curve of the powder sample in Fig. 1 exhibited an endothermic peak at 389 K corresponding to the α→β transition.

The polarized UV-visible spectra of the 60-layered LB film in the α and γ phases are shown in Fig. 3 at the incident angle of 45°. The spectra (a) in the α phase show distinct absorptions at 315 nm and 355 nm. The absorption at 315 nm is assigned to the locally excited transition in TCNQ, polarized to the long axis.[11)] Therefore, the TCNQ molecule stands perpendicular to the film surface, because this absorption is seen only when p-polarized light is used. The absorption at 355 nm is assigned to the π-π* transition of azobenzene, polarized to the long axis.[7)] The azobenzene part tilts to the film surface, because the dichroic ratio is around unity. The spectra (b) in the γ phase show strong absorptions at 315 nm and 329 nm when p- and s-polarized light is used, respectively. The spectra in the β phase measured at 393 K were similar to those in Fig. 3(b). The long axis of TCNQ is rather perpendicular to the film surface because the absorption at 315 nm is stronger for the p-polarized light than the s-polarized light. The absorption at 329 nm is assigned to the azobenzene part polarized to the long axis.[7)] The arrangement of the azobenzene part changes considerably as clearly shown in the blue shift and change in absorbance in the absorption spectra. But owing to the overlapping of the absorptions of TCNQ and the azobenzene part, it is difficult to obtain a precise knowledge on the orientation of each part.

Figure 4 shows the IR spectra of the 60-layered LB film in the α and γ phases, which revealed that the sharp discontinuity in conductivity was accompanied with the change in the arrangement of TCNQ molecules. The C≡N stretching band, the C-H bending band and the C-CN stretching band were broad in the α phase, whereas these bands became sharper and shifted to higher energies in the γ phase. The charge transfer band at 2900 cm^{-1} in the α phase shifted to 3500 cm^{-1}, which is consistent with the decrease in conductivity.[12,13)] The IR spectrum in the β phase was almost the same as that in the γ phase. Thus, the sharp change in conductivity in the α→β transition is accompanied with the change in TCNQ column structure as well as the change in the arrangement of the azobenzene part.

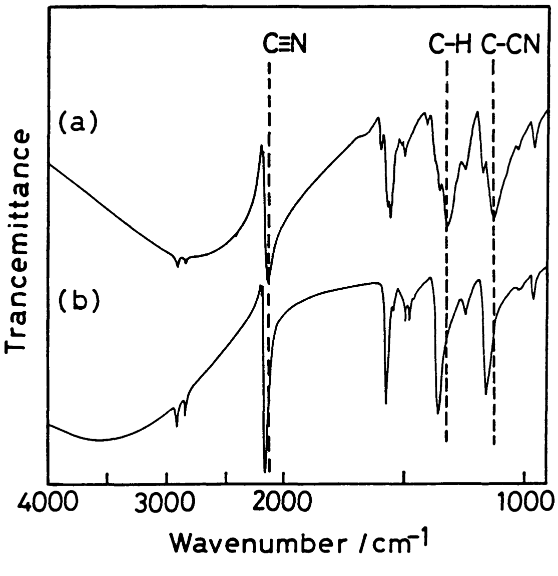


Fig. 4. IR spectra of the 60-layered LB films in the α phase (a) and the γ phase (b).

We investigated the morphology of the 60-layered LB film using the polarizing microscope at various temperatures. No crystallite was seen in the freshly prepared LB film, but on heating the film, small isolated birefringence of crystalline regions began to appear at 373 K and the whole area of the LB film was fully covered with the crystallites at 383 K. The temperature of the change in the morphology agrees with that of the $\alpha \rightarrow \beta$ transition in conductivity. The crystalline structure remained unchanged even when the LB film was cooled down to room temperature and was stable more than six months. Polarizing micrograph of the LB film cooled down to room temperature after heating up to 393 K is shown in Fig. 5. The domain size was approximately 100 μm, i.e., the domains had lateral dimensions about 400 times their thickness.

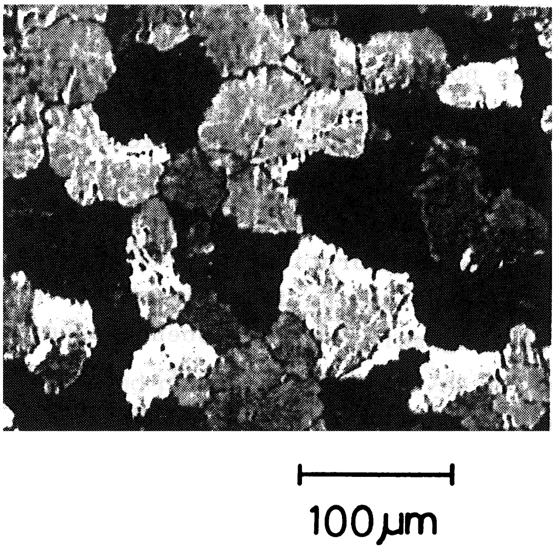


Fig. 5. Polarizing micrograph of the 60-layered LB film cooled down to room temperature after heating up to 393 K (γ phase).

In summary, by introducing the mesogenic unit into conductive LB films, thermal phase transitions appear and are accompanied with the change in the conductivity, the aggregation form, and the morphology of the films. In order to elucidate the mechanisms of the phase transitions and the change in the conductivity, further studies including X-ray diffraction analyses are now in progress.

We are grateful to Dr. M. Sugi for informative comments and helpful discussions.

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(Received February 10, 1989)