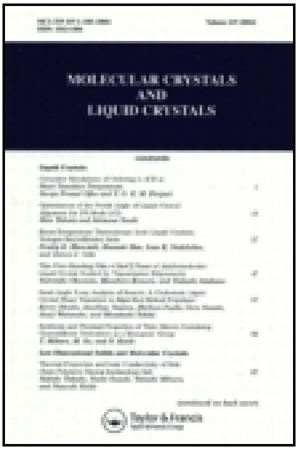

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Orientational Behavior of Ionic Liquid Crystal Polymers and Their Nonionic Family

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Multilayered Langmuir-Blodgett (LB) films were prepared from the monolayers of an ionic liquid crystalline azo-polymer (IP-4) and a nonionic liquid crystalline azo-polymer (NP-4). The multilayer structures in the LB films were completely disturbed by UV light irradiation. However, the periodic layer orderings in the LB films were rebuilt upon a subsequent visible light irradiation. Although NP-4 exhibits a nematic phase in the bulk state at room temperature, the consequent double layered structure with a homeotropic alignment in the LB film of NP-4 was very similar to the smectic layered structures of IP-4.

Keywords: homeotropic alignment; Langmuir-Blodgett film; liquid crystalline polymer; molecular orientation; photoisomerization

1. INTRODUCTION

Liquid crystalline polymers (LCPs) with azobenzene groups have been extensively studied for scientific interests and potential applications in various photonic devices [1–3]. The LCPs having both hydrophilic and hydrophobic parts can suit for fabrication of self-assembled films by Langmuir-Blodgett (LB) method [4,5]. This self-assembly technique has been considered as a powerful tool for construction of ordered ultrathin LCP films. For such LB films, the LCPs exhibiting a smectic phase have usually been used. The periodic ordered structures can be formed through their specific amphiphilic interactions in not only 3-dimensional bulk states but also LB films. However, the photoisomerization of azobenzenes often causes the disordering of the layer structure in LB films [6,7]. From this reason, the preparation of LB films of nematic LCPs is hardly reported.

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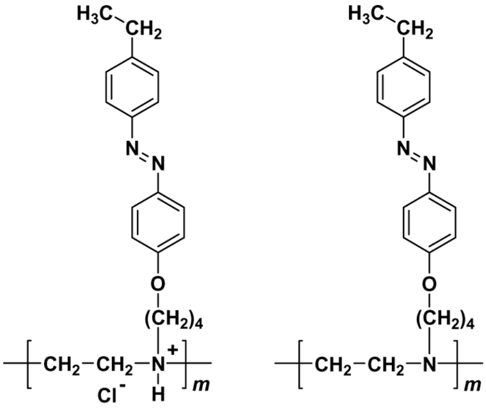

IP-4 NP-4

FIGURE 1 Chemical structures of ionic liquid crystalline azo-polymer (IP-4) and nonionic liquid crystalline azo-polymer (NP-4).

Recently, we reported the formation of the mutilayered LB films of a smectic LCP (IP-4) incorporating the hydrophobic azobenzene pendant groups in the hydrophilic polyethyleneimine (PEI) backbone (Fig. 1) [8]. The periodic ordered structure was rebuilt even after the photoisomerization of azobenzene groups. In this study, multilayered LB films of a nematic LCP (NP-4) were prepared as well as IP-4. The photoisomerizations and the molecular reorientations of the azobenzene groups induced by photoirradiation in the LB films were investigated. Structural parameters of the LB films, including the layer spacings and the alignments of azobenzene groups were estimated by the spectral analysis and X-ray diffraction measurements.

2. EXPERIMENTAL

The structures of a repeat unit of IP-4 and NP-4 are shown in Figure 1. The syntheses and the LC properties of the polymers were reported previously [9].

Surface pressure-area (π-A) isotherms were obtained by using a FSD-300 film balance (USI). The subphase was deionized water, kept at 20°C by means of a water circulating system equipped with a thermostat. The polymers were spread on the water surface from chloroform solutions (0.5 mg/ml), which were kept in a dark place for a day for full conversion of the azobenzene groups to the *trans*-configuration. After the solvent was evaporated, the floating films were compressed at a speed of $36\,cm^2/min$ to record the π-A isotherms. The preparation of LB films was carried out on a FSD-21 (USI). The deposition pressure was 21 mN/m and deposition speed was 5 mm/min. The monolayers were transferred by a vertical dipping method onto hydrophilic quartz plates (19 layers for spectroscopic measurements) or glass slides (39 layers for X-ray diffraction measurements).

The UV-visible absorption spectra were recorded on a U-1800 spectrophotometer (HITACHI). The X-ray diffraction patterns were obtained with a XRD-6100 diffractometer (SHIMADZU). Photoisomerization experiments were carried out at room temperature by using a 300 W high pressure Hg lamp for UV and a 50 W halogen lamp equipped with cut filters (>420 nm) for visible light irradiation.

3. RESULTS AND DISCUSSION

3.1 Film Depositions

The π-A compression isotherms for IP-4 and NP-4 are shown in Figure 2. There are extremely steep regions where the surface pressure increase rapidly with compression. This indicates the formation of condensed Langmuir monolayers. The collapse pressures (π_c) and the limiting areas per repeat unit (A_0) of monolayers were listed in Table 1.

It is a well-known fact that the smallest cross sectional area of azobenzene derivatives is $0.21 \sim 0.25\,nm^2$ [10]. The A_0 of IP-4 was $0.20\,nm^2$. This indicates that the azobenzene groups of IP-4 are tightly packed with the side chains standing upward on water. Althogh the A_0 of NP-4 was slightly larger than the ideal value, NP-4 also formed a monolayer with the azobenzene side chains closely filled.

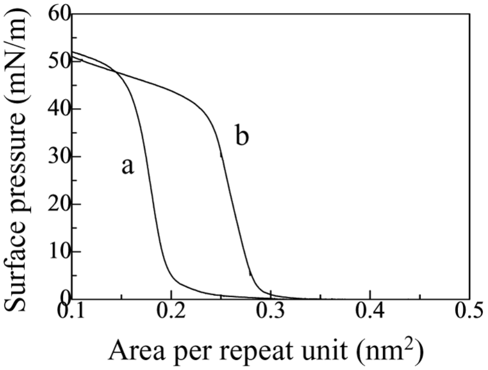

FIGURE 2 π-A isotherms of IP-4 (a) and NP-4 (b) at 20°C.

TABLE 1 Collapse Pressures (π_c) and Limiting Areas (A_0) of Monolayers

Sample	π_c/mNm^{-1}	A_0/nm^2
IP-4	45.0	0.20
NP-4	40.0	0.29

Figure 3 and Figure 4a show the UV-vis absorption spectra of an "as deposited" LB multilayered film of NP-4 on the glas slide and on the quartz plate transferred by the monolayers. The spectrum exhibits two peaks at 316 and 246 nm (Fig. 4a). The peak arising from the π-π^* transition band of azobenzene was observed at 316 nm, which was blue-shifted from that of monomeric state (350 nm). The peak at 246 nm corresponds to the π-π^* transition of the short axis of azobenzene [11]. As shown in Figure 3, the absorbance at 316 nm increased linearly with the number of layers in the deposition procedure. The transfer ratios of both up and down strokes were close to 1.0. The same result was also reported in the LB deposition procedure of the monolayers of IP-4 [8].

The X-ray diffraction patterns of the "as deposited" LB films showed the three small-angle Bragg reflections (Figs. 5a, 6a). These diffraction patterns correspond to the periodic positional orderings perpendicular to the layer planes. The layer spacings d of the "as deposited" LB films of IP-4 and NP-4 were 3.9 nm and 3.8 nm, respectively (Table 2), while the extended lengths (L) of the mosogenic side-groups are 1.9 nm. The relationship between d and L is $d > 2L$. The fact that d-spacings are

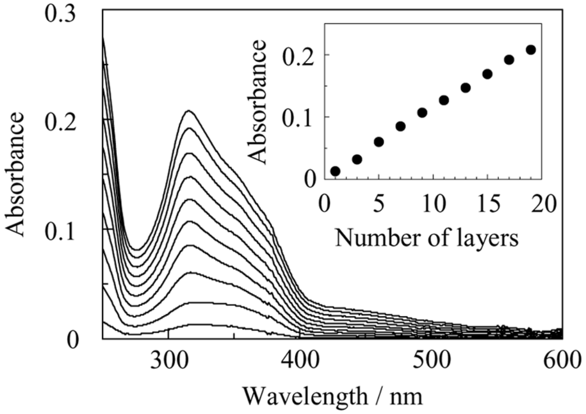

FIGURE 3 UV-vis spectra of the LB film of NP-4 on a quartz substrate for each layer deposition process and plot of absorbance at 316 nm vs the number of layers (inset).

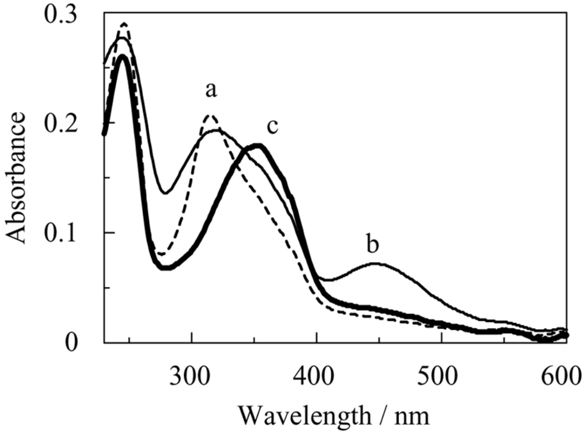

FIGURE 4 UV-vis spectra of the LB film of NP-4: (a) as deposited film; (b) after UV light irradiation; (c) after visible light irradiation.

more than twice the lengths of L indicates a formation of double-layered Y-type LB films (Fig. 7a).

3.2 Orientational Transitions on Irradiations

Upon irradiation with UV light, the layer orderings in the LB films were completely disturbed by the photoisomerizaion of the azobenzene

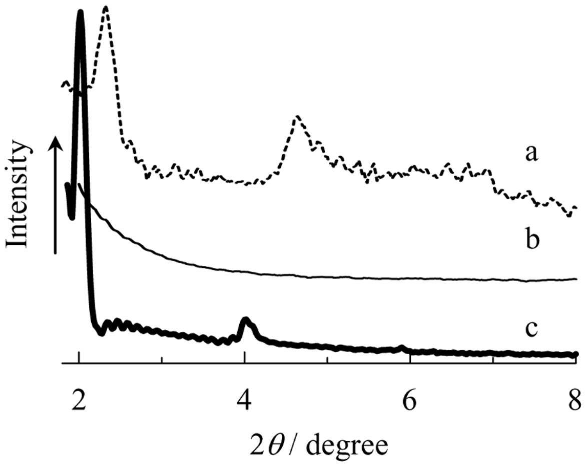

FIGURE 5 X-Ray diffraction patterns of the LB film of IP-4. (a) as deposited film; (b) after UV light irradiation; (c) after visible light irradiation.

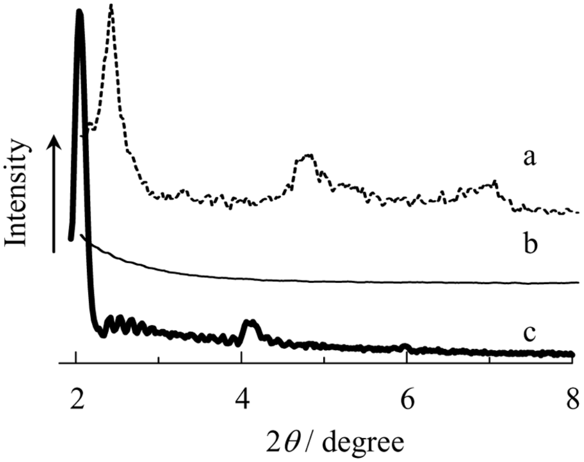

FIGURE 6 X-Ray diffraction patterns of the LB film of NP-4: (a) as deposited film; (b) after UV light irradiation; (c) after visible light irradiation.

groups. Figure 4b shows the UV-vis absorption spectrum of the LB film of NP-4 irradiated for 3.0 seconds. The absorbance increased at 447 nm and decreased at 316 nm. These changes in the UV-vis absorption spectrum indicate the formation of "*cis*-rich" LB film of NP-4.

On the other hand, in the X-ray diffraction patterns of the "*cis*-rich" LB films of IP-4 and NP-4 after UV light irradiation (Figs. 5b, 6b), diffraction peaks at the small-angles corresponding to the periodic layer orderings disappeared. The complete losses of layer orderings are due to great distortions of the layer planes were caused by the changes of geometrical shapes of azobenzene groups (Fig. 7b).

A subsequent visible light irradiation caused the *cis*-to-*trans* photoisomerization of the azobenzene groups in the LB films. Figure 4c shows the UV-vis absorption spectrum of the "reoriented"

TABLE 2 *d*-Spacings and Half Bandwidths of LB Films

Sample	*d*-Spacing[a]/nm	Half width[a]/deg.
IP-4		
As deposited	3.9	0.29
Reoriented	4.3	0.12
NP-4		
As deposited	3.8	0.31
Reoriented	4.3	0.12

[a] Measured by first diffraction.

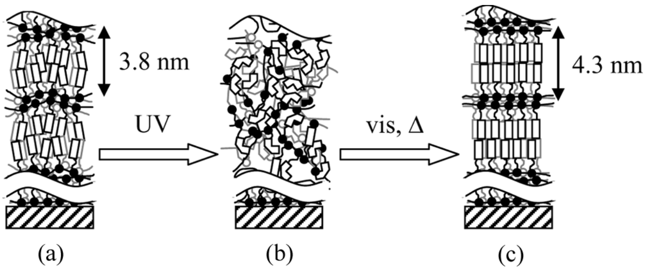

FIGURE 7 Schematic illustration of structural changes for LB film of NP-4. (a) “as deposited” film, (b) “*cis*-rich” film, (c) “reoriented” film.

photostationary state of the LB film of NP-4 after visible light irradiation for 160 minutes. The increase of absorbance at 353 nm and the decrease at 447 nm indicate the formation of *trans* isomer of the azobenzene groups. Since the peak shift to H-aggregated π-π^* band does not occur, the initial “as deposited” LB film is transformed into a new ordered structure.

The periodic layer structures of the LB films were rebuilt upon visible light irradiation. As shown in Figure 5c and 6c, the sharp Bragg reflections reappeared at small-angles in the diffraction patterns of the “reoriented” LB films. These reconstruction of layer orderings are due to the anisotropy formed through the amphiphilic interactions as well as the interactions between the mesogenic *trans* azobenzene groups (Fig. 7c).

The layer spacings and the half bandwidth of the X-ray diffraction in “as deposited” and “reoriented” LB films were listed in Table 2. The layer spacings of LB films were increased upon irradiations. This is due to the reorientation of side chains parallel to the substrate normal. The decrease in the half bandwidth indicates the increase in orderings of side chains within the layer. Note that the directions of side-chains of IP-4 and NP-4 resulted from the reorientation depended on neither the incident angles nor polarizations of visible light. Moreover, the rebuilding and increase of layer orderings occurred not only photochemically but also thermally. From the results, it was found that the reorientation of side-chains and the rebuilding of layer orderings spontaneously took place in the LB films of NP-4 as well as in that of IP-4.

4. CONCLUSION

The scheme proposed in Figure 7 summarizes the results concerning the structural changes within the LB film of NP-4 on irradiation.

The multilayered LB films were successfully prepared from the monolayers of IP-4 and NP-4. The layer structures and the orientations of the azobenzene groups in the LB films were drastically changed upon irradiation with UV and visible light. The periodic ordered structures in the LB films were completely disturbed by UV light irradiation, and it's were rebuilt by visible light irradiation. Although NP-4 exhibits the nematic phase in the bulk state at room temperature, the consequent double layered structure with the homeotropic alignment in the LB film of NP-4 is very similar to that in IP-4.

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