

Langmuir-Blodgett Film Formation and Photoisomerization of Ionic Liquid Crystalline Polymer with Azobenzene Pendant Groups

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An ionic liquid crystalline polymer (ILCP) with photoactive azobenzene pendant groups was deposited as a multilayered Langmuir-Blodgett (LB) film. The layer structure and the orientation of the azobenzene pendant groups in the LB film were drastically changed upon irradiation with UV and visible lights. The layer order in the LB film was completely disturbed by UV light irradiation, and rebuild by visible light irradiation. Homeotropic molecular alignment with the consequent double layered structure is consistent with that of a smectic A liquid crystalline phase of ILCP.

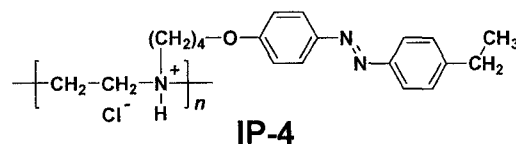
Key words: ionic liquid crystalline polymer, azobenzene, Langmuir-Blodgett film, photoisomerization, reorientation

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]. For these materials, preparation of homogeneous ordered thin films is important. 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. However, the structure of such films is generally different from that of 3-dimensional bulk state [6,7]. Moreover, photoisomerization of azobenzenes often causes the disordering of the layer structure in LB films [8,9].

We have developed various types of amphiphilic LCPs having ionic units and revealed the properties of these ionic LCPs (ILCPs) [10-12]. The ILCPs are attractive and important materials from fundamental viewpoints of the formation of new liquid crystalline phases and the functional new nano-structures. The ionic liquid crystalline systems usually exhibit layered structures due to the segregation of ionic and nonionic groups. These periodic ordered structures can be formed through their specific amphiphilic interactions in not only 3-dimensional bulk states but also LB films. We reported the synthesis and characterization of an ILCP (IP-4) incorporating the hydrophobic azobenzene pendant groups in the hydrophilic polyethyleneimine (PEI) backbone (Fig. 1) [13]. Recently, monolayers prepared from IP-4 at the air-water interface were deposited on solid substrates [14].

In this study, a multilayered LB film of IP-4 that exhibits a smectic A phase in a bulk state, was prepared. We investigated photoisomerization and molecular reorientation of the azobenzene groups induced by photoirradiation in the LB film. Structural parameters of the LB film, including the layer spacing and the alignment of azobenzene groups were estimated by the spectral analysis and X-ray diffraction measurements.



Phase transition temperatures / °C
g 52.5 M 109.5 SmA 210 (Dec)

Fig. 1. Structure and phase transitions of an ionic liquid crystalline azo-polymer **IP-4**. g: glassy, M: mesomorphic, SmA: smectic A, Dec: thermal decomposition.

2. EXPERIMENTAL

The structure and the phase transition temperatures of **IP-4** are shown in Fig. 1. The synthesis of the polymer was described in the reference [13].

A surface pressure-area (π -A) isotherm was 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 polymer was spread on the water surface from chloroform solution (0.5 mg/ml), which was 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 film was compressed at a speed of 36 cm²/min to record the π -A isotherm. 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 monolayer was transferred by a vertical dipping method onto hydrophilic quartz plate (19 layers for spectroscopic measurements) or glass slide (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 LB films 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 Monolayer formation at the air-water interface

IP-4 formed a stable liquid-condensed Langmuir monolayer at the air-water interface. The π - A isotherm for **IP-4** monolayer is shown in Fig. 2. The **IP-4** monolayer exhibit a steep pressure increase at 0.2 nm^2 and a collapse pressure at 45 mN/m with compression on the water surface. We could estimate the occupied area per azobenzene repeat unit of 0.20 nm^2 from the π - A isotherm.

It is a well-known fact that the smallest cross sectional area of azobenzene derivatives is $0.21\text{--}0.25 \text{ nm}^2$ [15]. This indicates that the azobenzene side chain exhibits a closely filled monolayer structure. Therefore, it can be surmised that the azobenzene groups of the **IP-4** are tightly packed with the side chains standing upward on water.

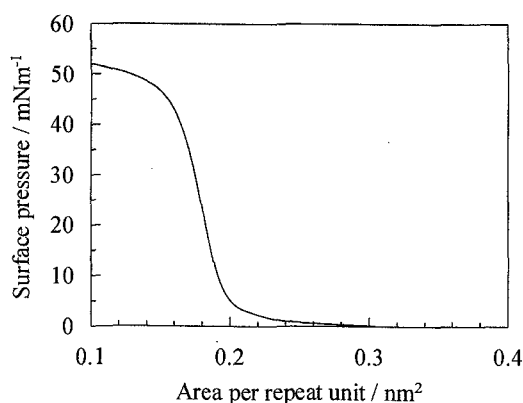


Fig. 2. π - A isotherm of **IP-4** on a pure water subphase at 20°C .

3.2 LB film deposition

Figure 3 shows the UV-vis absorption spectra of "as deposited" LB multilayered films transferred by monolayers. The absorption spectra exhibit two peaks at 318 and 246 nm. The peak arising from π - π^* transition band of azobenzene was observed at 318 nm, which was blue-shifted from that of monomeric state. The peak at 246 nm corresponds to the absorption of the short axis [16]. The intensity of the two bands increased linearly with the number of layers, indicating that the quantities of **IP-4** molecules in each layer were similar, and that the deposition procedure was indeed uniform. As shown in Fig. 4, transfer ratios of both up and down strokes were close to 1.0.

The X-ray diffraction pattern of the "as deposited" LB film was composed of the three small-angle sharp Bragg reflections and a broad reflection in the wide-angle region (Fig. 6a). A set of diffraction pattern observed at the small-angles corresponds to the periodic positional order perpendicular to the layer plane. This diffraction pattern resembles that of a typical liquid crystalline

smectic phase. The layer spacing (d) was 3.9 nm, while the extended length (L) of the mesogenic side-group is 1.9 nm. The relationship between d and L is $d > 2L$. The fact that d is more than twice the length of L indicates a formation of double-layered smectic structure (Fig. 7a).

However, the structure was slightly different from that of the smectic A phase of **IP-4** because the polarized spectroscopy showed a dichroism of azobenzene groups towards the dipping direction. This dichroism is probably due to the influence of gravity upon the deposition process of monolayers.

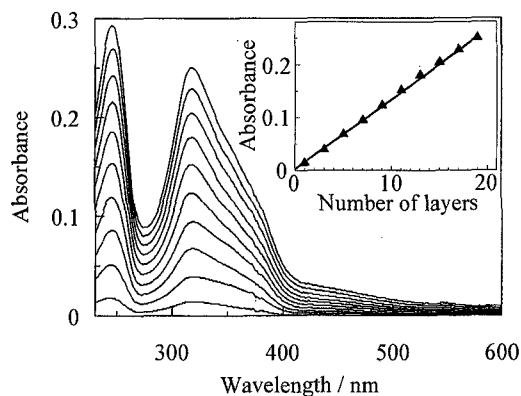


Fig. 3. UV-vis spectra of the LB film deposited on a quartz substrate for each layer deposition process and plot of absorbance at 318 nm vs the number of layers (inset).

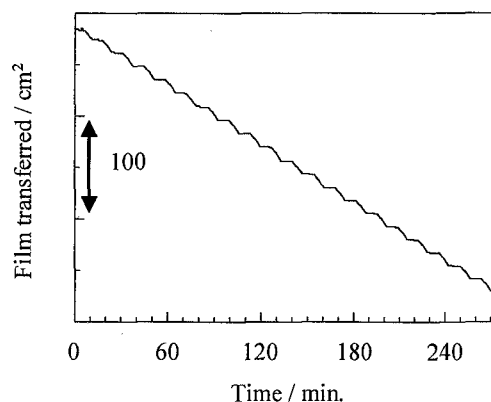


Fig. 4. Deposition trace of 20 deposition cycles for the build up of a 39-layered LB film on a glass slide.

3.3 Structural change on UV light irradiation

Upon irradiation with UV light, the layer order in the LB film was completely disturbed by the *trans*-to-*cis* photoisomerization of azobenzene groups. Figure 5b shows the UV-vis absorption spectrum of the LB film irradiated for 2.5 seconds. In this case, the absorbance increased at 450 nm and decreased at 318 nm. These changes in the UV-vis absorption spectrum indicate an induction of the azobenzene groups with the "cis-rich" photostationary state.

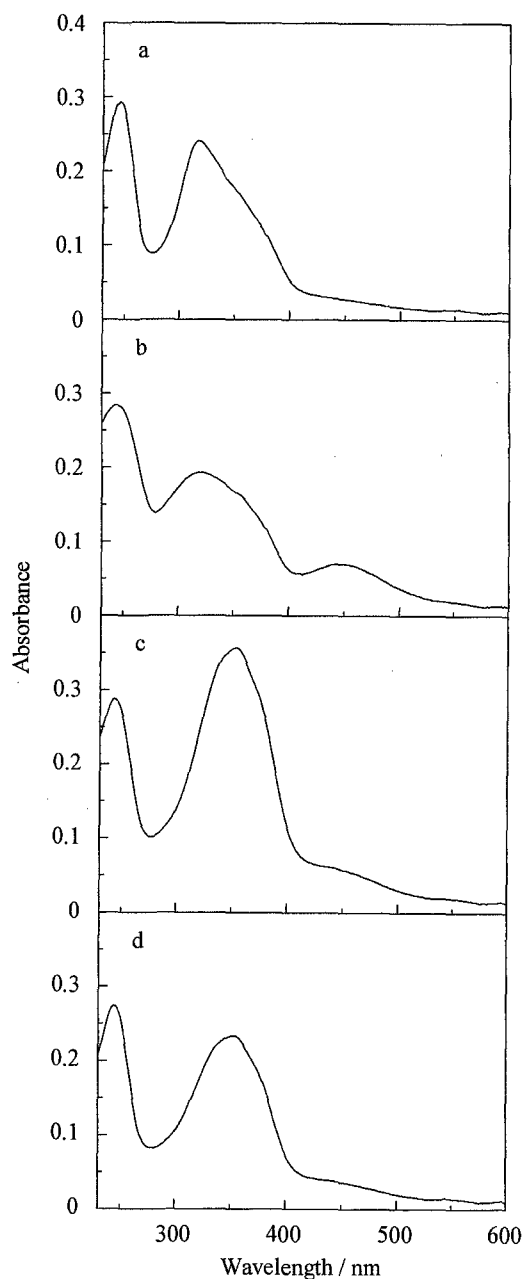


Fig. 5. UV-vis spectra of IP-4 LB film: (a) as deposited film, (b) after UV light irradiation for 2.5 seconds, (c) after visible light irradiation for 45 minutes, (d) after visible light irradiation for 270 minutes.

On the other hand, in the X-ray diffraction pattern of the “*cis*-rich” LB film after UV light irradiation (Fig. 6b), diffraction peaks at the small-angle corresponding to periodic smectic order were disappeared. In contrast, the broad reflection in the wide-angle region was remained. The diffraction pattern is similar to that of a nematic phase which has the short range orientational order but lacks the positional order. The complete loss of smectic order is due to great distortions of the layer planes caused by the change of geometrical shape of azobenzene groups (Fig. 7b).

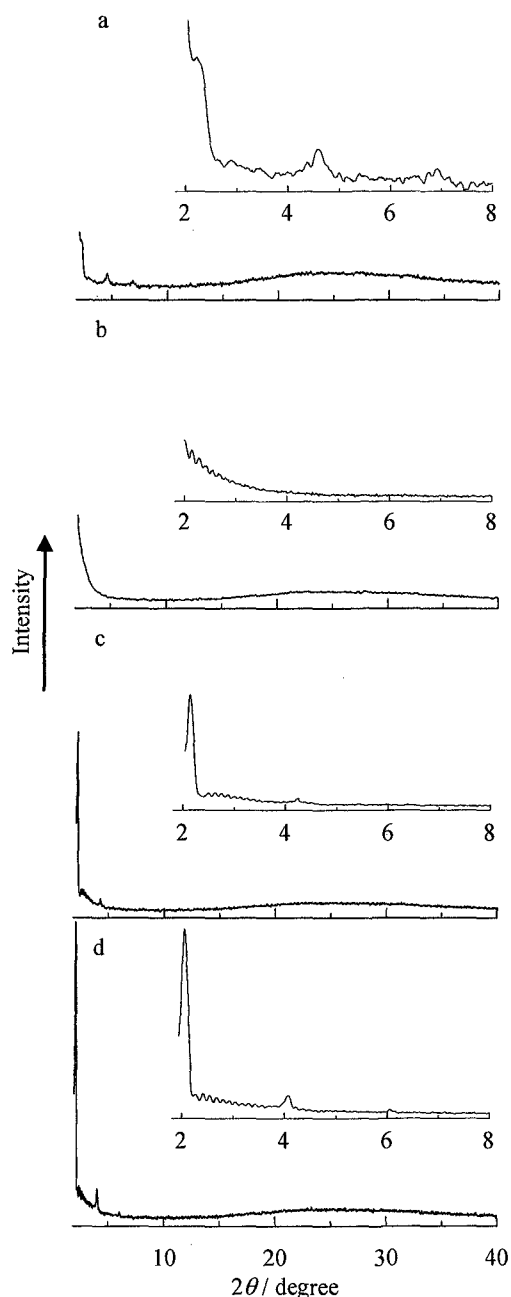


Fig. 6. X-ray diffraction patterns of IP-4 LB film: (a) as deposited film, (b) after UV light irradiation for 2.5 seconds, (c) after visible light irradiation for 45 minutes, (d) after visible light irradiation for 270 minutes. Each inset show enlargement of the small-angles.

3.4 Structural change on visible light irradiation

A subsequent visible light irradiation caused the *cis*-to-*trans* photoisomerization of azobenzene groups and the reorientation of side chains towards the substrate normal. Figure 5c shows the UV-vis absorption spectrum of the “*trans*-rich” photostationary state of the LB film after visible light irradiation for 45 minutes. The increase of absorbance at 354 nm and the decrease at 450 nm indicate the formation of *trans* isomer of

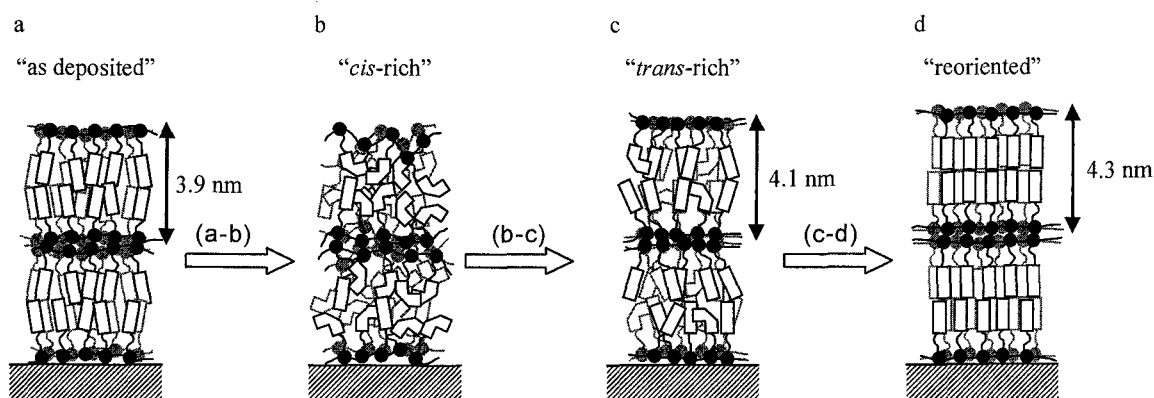


Fig. 7. Schematic illustration of structural change for IP-4 LB film on irradiation: (a - b) UV light irradiation, (b - c) visible light irradiation for 45 minutes, (c - d) visible light irradiation.

azobenzene groups. However, as shown in Fig. 5d, upon further irradiation, the absorbance was decreased over all wavelength range. 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 greater decrease of absorbance at 354 nm compared with 246 nm indicates the formation of the homeotropic molecular alignment (perpendicular orientation) of azobenzene groups.

The periodic layer structure of the LB film was restored on the visible light irradiation. As shown in Fig. 6c, the sharp Bragg reflections reappeared at small-angles in the diffraction pattern of the "trans-rich" LB film. This restoration of layer order is due to the anisotropy formed through the ionic aggregation as well as the interactions between the mesogenic *trans* azobenzene groups (Fig. 7c). Besides, the reorientation of azobenzene groups to the homeotropic alignment was also supported by the X-ray diffraction measurements. The layer spacing of the "reoriented" LB film was 4.3 nm (Fig. 6d), while that of the "trans-rich" LB film was 4.1 nm. This enlargement is due to the reorientation of side chains parallel to the substrate normal (Fig. 7d). The double layered structure with the homeotropic alignment of the "reoriented" LB film is consistent with that of the smectic A liquid crystalline phase of IP-4^[13]. Note that the direction of side-chains resulted from the reorientation depended on neither the incident angle nor polarization of visible light. Moreover, the restoration of layer orderings occurred not only photochemically but also thermally. From the results, it was found that the reorientation of side-chains and the restoration of layer orderings spontaneously took place in the LB film.

4. CONCLUSION

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

The LB film having double-layered smectic structure was successfully prepared from the monolayers of IP-4. The layer structure and the orientation of azobenzene groups in the LB film were drastically changed upon irradiation with UV and visible light. The smectic order in the LB film was completely disturbed by UV light irradiation, and it was restored by visible light

irradiation. The consequent double layered structure with the homeotropic alignment is consistent with that of the smectic A liquid crystalline phase of IP-4.

5. REFERENCES

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