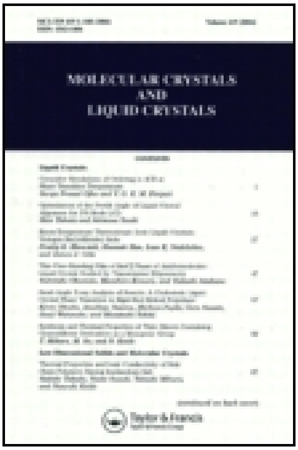

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Cooperative Photoresponse in Azobenzene Polymer/Liquid Crystal Molecular Films

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Cooperative Photoresponse in Azobenzene Polymer/Liquid Crystal Molecular Films

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The orientational properties of hybrid Langmuir-Blodgett (LB) films composed of an amphiphilic azobenzene (Az) side chain polymer and liquid crystal (LC) molecule were investigated to gain insights into the molecular cooperativity in the interface region of the command surface system. Clear in-plane orientational induction directing perpendicular to the LB dipping direction was observed for both the Az side chains and 5CB molecules after an irradiation cycle with non-polarized UV and subsequent visible light in the normal incidence.

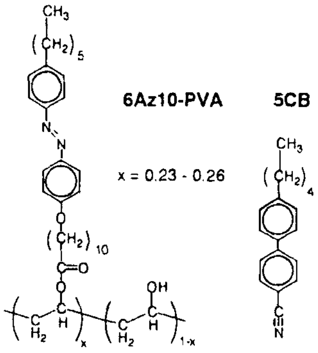
Keywords: azobenzene; liquid crystal; LB film; alignment; cooperativity

INTRODUCTION

Photoresponsive polymers containing Az are currently of interest in view of their use for optical image recording devices. The modification of orientation and its order by means of linearly polarized light has been investigated in films of liquid crystalline polymers[1], amorphous[2], and LB multilayers.[3]

Recently, we have been investigating hybrid LB films composed of an amphiphilic Az side chain polymer (6Az10-PVA) and a LC molecule, 4'-pentyl-4-cyanobiphenyl (5CB) to obtain precise insights of command surfaces,[4,5] which display the surface-assisted alignment regulation of nematic LC. In our previous papers,[6] we reported on the hybrid LB films which can provide a model of the interface region of the command surface system involving the out-of-plane alignment changes.

In this paper, we report on a newly found property in the hybrid multi-layered LB film. An in-plane anisotropic orientation was clearly observed after a cycled photoirradiation.



6Az10-PVA **5CB**

$x = 0.23 - 0.26$

EXPERIMENTAL

The synthesis of 6Az10-PVA was described previously.[7] 5CB was obtained from Merck.

Hybrid LB and spincast films were prepared from an equimolar mixed solution of 6Az10-PVA and 5CB. Multi-layered Y-type 6Az10-PVA/5CB (1/1) LB films were prepared by the successive vertical deposition onto a CaF_2 substrate at 30 mN m^{-1}. The hybrid films were irradiated with 365 nm (UV) or 436 nm (visible) light from a Hg-Xe lamp (SAN-EI Electronics, SUPER-CURE 203S) combined with optical filters for wavelength selection. Their molecular orientational changes were evaluated by polarized UV-visible and FTIR absorption spectra taken on a Hewlett-Packard diode array spectrometer 8452A and a Biorad FTS6000 spectrometer, respectively. They were observed under a polarized optical microscope (OLYMPUS BH-2) equipped with a glass filter (R-63).

RESULTS AND DISCUSSION

Mixing properties

DSC diagrams and π-A isotherms given from mixtures at various molar ratios implied that 6Az10-PVA can accommodate up to two 5CB molecules per Az side chain unit without phase separation.

Induction of in-plane anisotropy

Figure 1 presents polarized UV-visible absorption spectra of a 83-layered 6Az10-PVA/5CB hybrid LB film. As shown in the Figure 1 (a), in the initial state, in-plane anisotropy was hardly noticed. UV light irradiation led to a complete disappearance of the in-plane anisotropy (b).

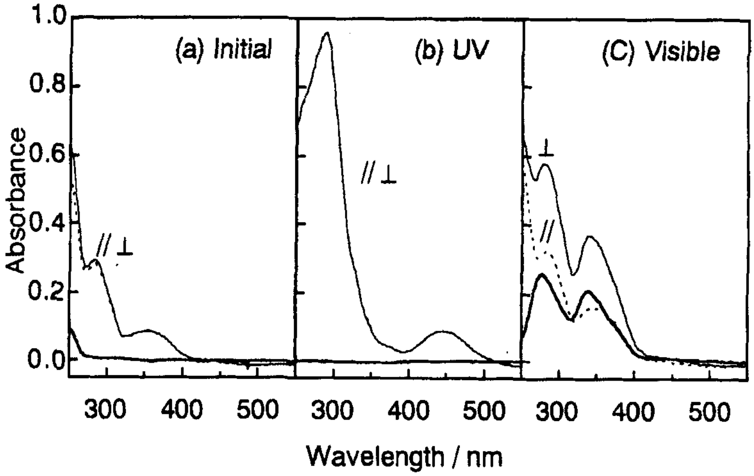


FIGURE 1 Polarized UV-visible absorption spectra of hybrid LB film. (a), (b), and (c) represent the initial state, after UV light irradiation, and subsequent visible light irradiation, respectively. The symbols, // and ⊥, denote the electric vector of probing light in parallel (broken line) and perpendicular (solid line) to the dipping direction, respectively. Bold lines denote difference spectra (⊥ - //).

Upon irradiation with subsequent non-polarized visible light, a clear dichroism was generated in the wavelength region assignable to the π-π* bands of the long axis of Az (ca. 350 nm) and cyanobiphenyl (ca. 280 nm) (c). This demonstrates that the Az and cyanobiphenyl moieties are aligned in the same direction orienting perpendicular to the dipping direction.

Similar experiments were also carried out by polarized FTIR spectroscopy. The initial hybrid LB film scarcely showed a dichroism with the exception of the carbonyl group adjacent to the main chain of 6Az10-PVA which oriented slightly perpendicular to the dipping direction. The UV light irradiation gave rise to perfect disappearance of the dichroism. However, upon exposure to the visible light, the obvious in-plane anisotropy was observed in the hybrid LB film (Figure 2). More intense signals were obtained with the polarization

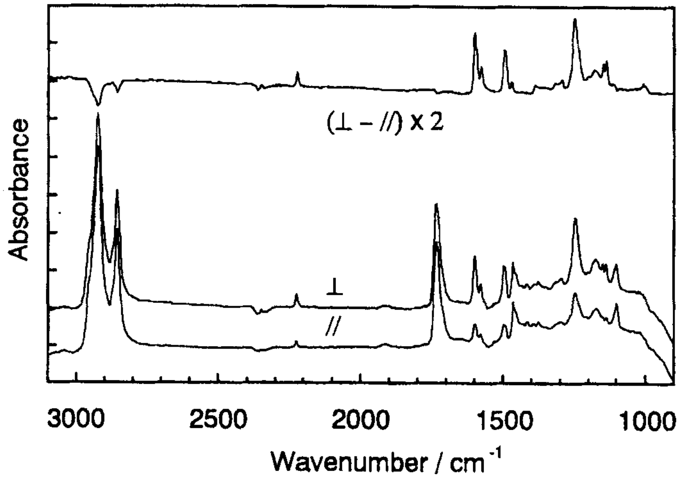


FIGURE 2 Polarized infrared absorption spectra and difference spectrum of hybrid LB film after cycled photoirradiation. The symbols, // and ⊥, denote the electric vectors of probing light in parallel and perpendicular to the dipping direction, respectively.

beam set perpendicular to the dipping direction than with those set parallel for the stretching bands of the cyano (2226 cm^{-1}), benzene ring (1601 cm^{-1}, 1497 cm^{-1}), phenyl ether (1250 cm^{-1}), and C-N (1153 cm^{-1}, 1140 cm^{-1}). On the contrary, the antisymmetric (2926 cm^{-1}) and symmetric (2854 cm^{-1}) stretching bands of CH_2 exhibited the reverse tendency. These results obviously indicate that the Az side chains and 5CB molecules were aligned preferentially perpendicular to the dipping direction in the substrate plane.

In the spincast film of the hybrid material, on the other hand, no in-plane anisotropy was observed at any stages.

The orienting mechanism in hybrid LB films can be assumed as follows. The LB process by the vertical dipping method give rise to a uniaxial orientation of the PVA main chain, perhaps parallel to the dipping direction. However, appearance of the optical in-plane anisotropy in this stage is minor because the molecules are fixed highly perpendicular to the substrate plane. The *E-to-Z* photoisomerization of Az side chain induces the complete orientational randomization of Az side chains and 5CB molecules. Beyond this step and through subsequent *Z-to-E* isomerization, Az side chains and 5CB molecules now can come to preferential orientation in a cooperative fashion following the orientational memory of the main chain.

Optical image storage

As mentioned above, the in-plane anisotropy was not induced by the visible light irradiation only. It showed that the cyclic irradiation process was required for the attainment of the homogeneous alignment. This property enables us to prepare a patterned image by means of a photolithographic technique. As shown in Figure 3, only the area where pre-irradiation with the UV light was performed showed the induced optical anisotropy. The resolution was ca. 10 μm. Thus, in-plane optical patterning was achieved *with non-polarized light.*

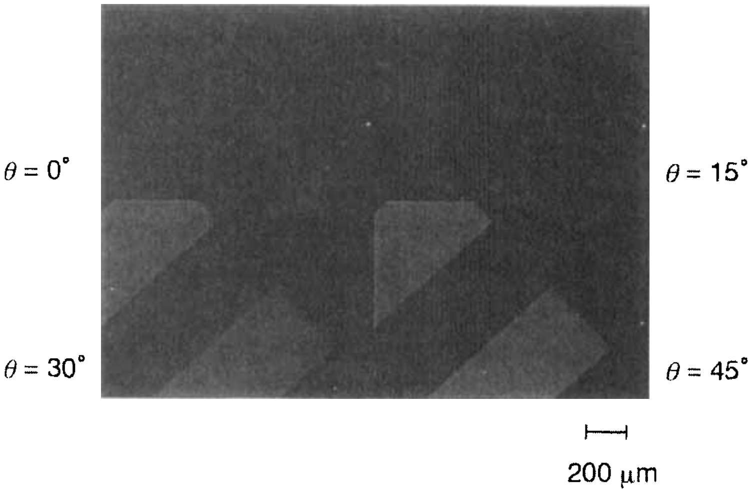


FIGURE 3 Polarized microgaphs of 101-layered hybrid LB film after irradiation with UV light through a photomask and subsequent visible light without a photomask until reaching the photostational state. θ denotes the angle between the crossed polarizer and the dipping directions.

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