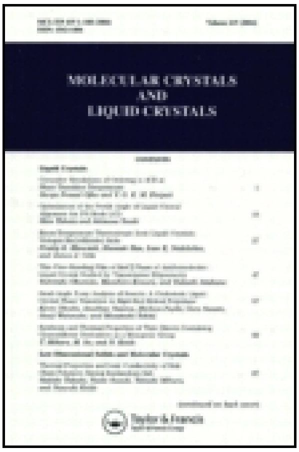

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Photoregulation of Nematic Liquid Crystal Alignment by LB Films of Azobenzene/Polyethylenimine Derivatives

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PHOTOREGULATION OF NEMATIC LIQUID CRYSTAL ALIGNMENT BY LB FILMS OF AZOBENZENE / POLYETHYLENIMINE DERIVATIVES

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Abstract The alignment behavior of a nematic liquid crystal on polyethylenimine-based azobenzene LB monolayers is investigated. Difference in the linkage manner of the azobenzene side chain, covalent bond or ionic bond led to unmatched results in the liquid crystal alignment.

INTRODUCTION

Photochromic molecular films, typically azobenzene (Az) monolayers, on a solid substrate, can induce reversible homeotropic/planar alignment changes of nematic liquid crystals (LCs) by the *cis/trans* photoisomerization reaction (command surfaces[1], Figure 1). Our previous works have been undertaken with poly(vinyl alcohol) (PVA) derivatives containing Az side chains.[2] In this work, we have chosen polyethylenimine (PEI) as the next candidate for the polymer main chain. With this polymer, introduction of the Az side chain

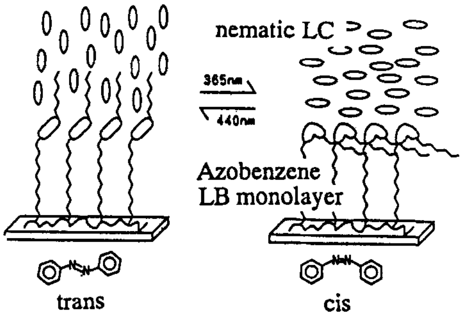
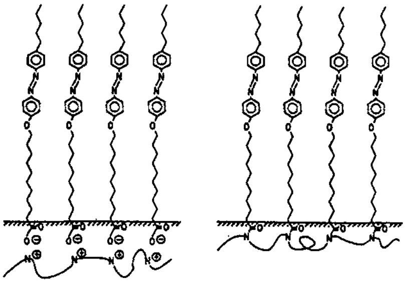


FIGURE 1 Schematic illustration of the command surface comprized of an Az LB monolayer.

is attained by two means, i.e., the covalent linkage and the ionic complexation (see Figure 2). We have already shown that the covalently bonded Az unit the side chain undergoes efficient photoisomerization in the LB films.[3] Similarly Fujihira and coworkers[4] have reported a facile Az LB film preparation method based on polyion complexation at the air-water interface that provides readily photoisomerizable Az unit in the LB film. It seems, therefore, of interest to compare the two methods in terms of the LC alignment photocontrol.



Polyion complex (PIC) Covalent bond (CB)

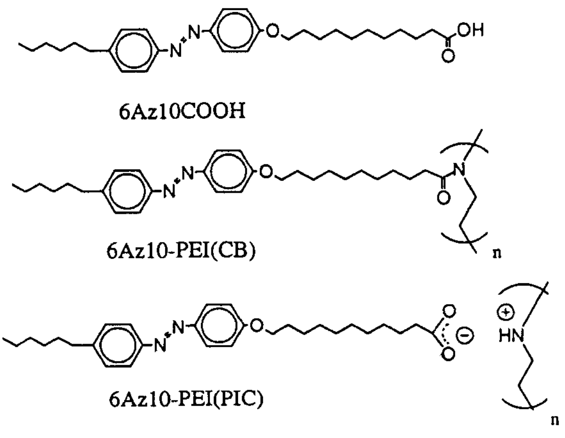
FIGURE 2 6Az10-PEI monolayers spread in different manners.

This paper represents the spreading behavior of these monolayers on the water subphase, UV-visible spectroscopic properties of the LB films, and photochemical commanding behaviors of LC alignment using the above two types of Az monolayers.

EXPERIMENTAL

Materials

Polyethylenimine (PEI, Mw = 7 x 10^4, 30 wt % aqueous solution) was purchased from Wako Pure Chemical Co. The nematic LC used in this study (DON-103) was the product of RODIC. Synthesis of the Az carboxylic acid derivative (6Az10COOH) was reported earlier.[2] 6Az10-PEI(CB) was obtained by coupling between 6Az10COOH and PEI using a water-soluble carbodiimid in N,N-dimethylacetamide. The details of this polymr reaction will be described elsewhere.



6Az10COOH

6Az10-PEI(CB)

6Az10-PEI(PIC)

Materials in this work

Methods

LB experiments and fabrication of LC cells were carried out according the procedure described in the previous paper.[2] Evaluation of the nematic LC alignment was performed using a dichroic dye dissolved in the LC phase.[2]

UV (365 nm) and visible (436 nm) light irradiation was achieved with a 500 W high pressure mercury passed through appropriate glass filters. Polarized UV-visible absorption spectra of Az monolayers were taken on a JASCO HSSP-3. FT-IR measurements were made on a Biorad FTS-60A.

RESULTS AND DISCUSSION

The Spreading behavior at the air-water interface

Figure 3 displays the surface pressure-area curves of 6Az10COOH (a), 6Az10-PEI(PIC) (b), and 6Az10-PEI(CB) (c) on pure water observed at 20 °C. The Az derivatives were spread in the *trans* form (solid line), after pre-irradiation with visible light (*ca*. 90 % *trans* form, dashed line), and UV light (ca. 90 % *cis* form, dotted line). Polyion complexation of PEI and 6Az10COOH at the air/water interface was achieved as follows. PEI was first dissolved in the water subphase (1 x 10^{-4} mol dm^{-3}) and the chloroform solution of 6Az10COOH was spread afterwards. The occupying area of Az unit in the *trans* form and the collapse pressure in the *cis* form of 6Az10-PEI(PIC) resemble those for 6Az10-PEI(CB) rather than for 6Az10COOH, indicating formation of polyion complex at the air/water interface. The polymeric monolay-

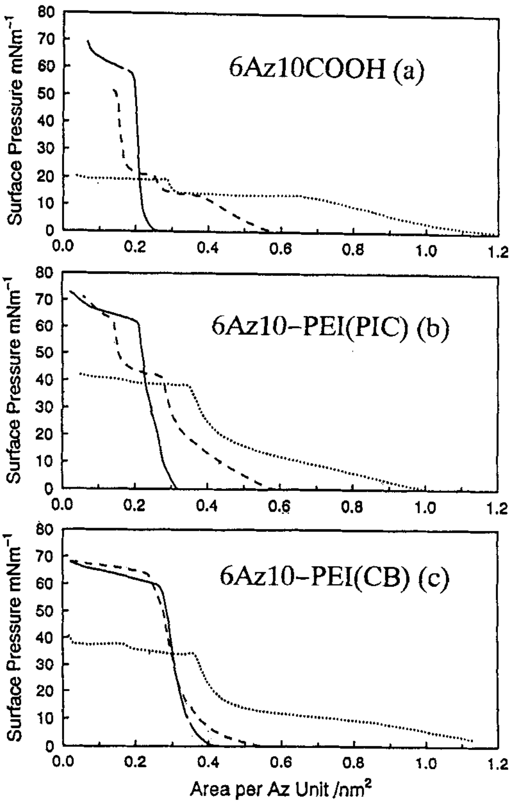


FIGURE 3 Surface pressure area-curves at 20°C. For details, see the text.

ers in the *trans* form (b and c) were somewhat expanded due to lateral steric requirement. These spreading behaviors agree well with that for the analogous poly(vinyl alcohol) derivative.[3]

The polyion complexation between PEI and 6Az10COOH was further confirmed by the FT-IR analysis (Figure 4). In the LB film of 6Az10-PEI(PIC) (twenty five layers on CaF_2), the C=O stretching band around 1700 cm^{-1} observed for the 6Az10COOH powder was replaced by those around 1550 cm^{-1} and 1400 cm^{-1}, indicating conversion from COOH to COO^- due to the ion complexation.

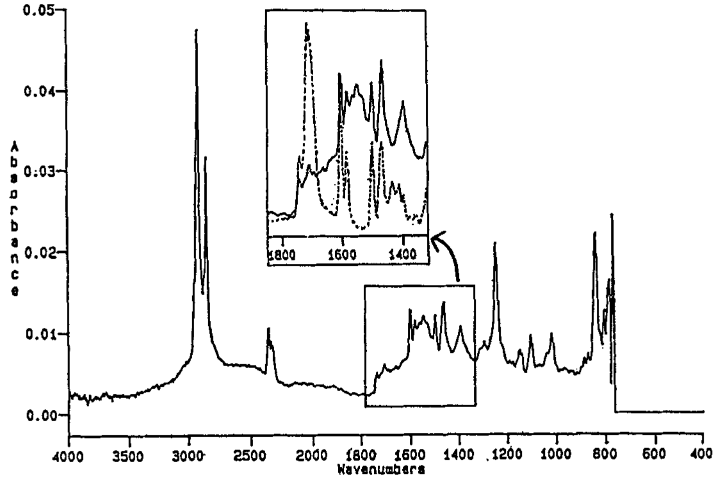


FIGURE 4 IR spectra of 25-layered 6Az10-PEI(PIC) (—) and 6Az10COOH powder in KBr pellet (·····).

Polarized UV-visible absorption spectra of LB monolayers

Monolayers of 6Az10-PEI(PIC) and 6Az10-PEI(CB) were transferred onto a clean quartz plate on both sides and their polarized absorption spectra in the *trans* form were measured (Figure 5). Monolayer deposition was achieved at three different areas. For both series, further compression of the monolayer induced hypsochromic shift of the π-π* long axis band and increased ratio of absorption intensity at the short axis band (243 nm) relative to the long axis band (longer than 300 nm). These changes should be due to stronger interaction among the Az chromophores and induction of normal orientation of the side chain with respect to the substrate plane for the more densely packed monolayer. Although not outstanding, the absorbances in the dipping direction was generally larger than those observed in the perpendicular direction. This dichroic ratio became distinct for the most compressed LB layers. The Az unit in the LB films underwent efficient reversible *trans* to *cis* photoisomerization except for the most densely packed 6Az10–PEI(PIC) in which the aggregation of the Az unit proceeded to the largest extent.

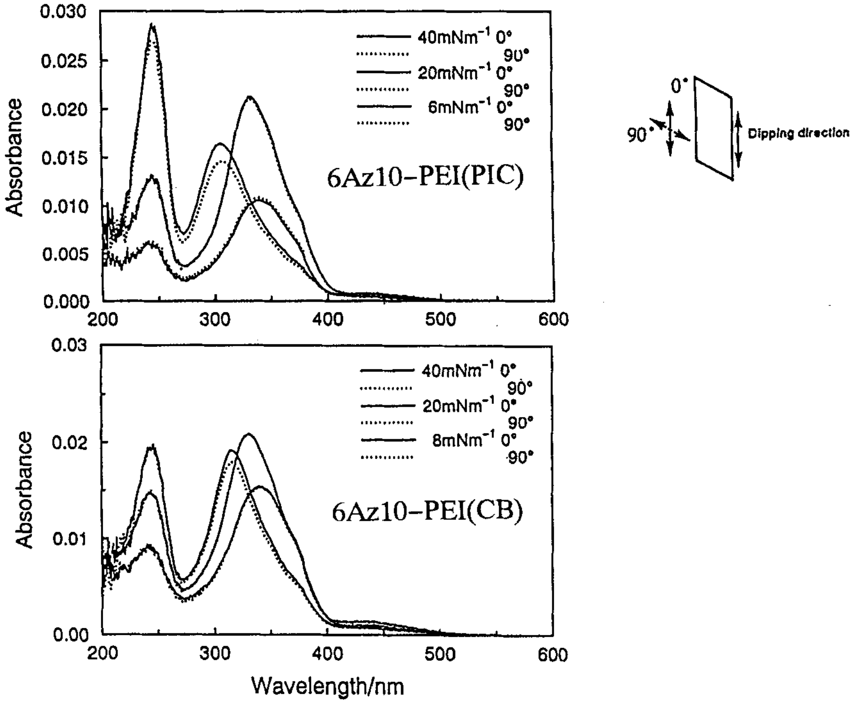


FIGURE 5 Polarized UV–visible absorption spectra of 6Az10–PEI LB monolayers (both sides) on a quartz substrate.

Commanding behaviors of LC alignment on 6Az10–PEI LB monolayers

Table 1 summarizes the alignment behavior of nematic LC on 6Az10–PEI LB monolayers. The most notable result is that, whilst the homeotropic/planar photoregulation is attained on covalent–bond type Az LB films, the polyion complex type LB films induced no alignment changes, giving the persistent planar alignment. The photoreactivity of Az unit in the LB films were almost identical except for the most compressed 6Az10–PEI(PIC). We interpret at moment that this difference arises from mobility freedom of the side chain. For LC alignment photoregulation, fixed anchoring of the side chain onto the substrate seems to important.

The in–plane orientation of all LB films agreed with the dipping direction, and this behavior was insensitive to the Az packing density. This is to be noted when compared to the orientation on 6Az10–PVA LB monolayers. We have recently demonstrated that the LC alignment on 6Az10–PVA LB monolayers are strongly area dependent; for instance, the most densely packed LB films gives orthogonal orientation with respect to the dipping direction.[5] The difference observed between PEI–based and PVA–based Az polymers appears to be an interesting problem to be pursued. This should be involved in the future work.

TABLE I Alignment behaviors of nematic LC on 6Az10–PEI monolayers.

type of monolayer	Az form on spreading (π / mN m^{-1})	alignment of nematic LC		
		Initial	UV irrad.	Vis Irrad
6Az10–PEI	*trans*[a] (40)	//	//	//
(PIC)	*cis*[b] (20)	//	//	//
	cis[b] (6)	//	//	//
6Az10–PEI	*trans*[a] (40)	⊥	//	⊥
(CB)	*cis*[b] (20)	⊥	//	⊥
	cis[b] (8)	⊥	//	⊥

Key: [a] pre–irradiated at 436 nm, [b] pre–irradiated at 365 nm,
⊥; homeotropic alignment, //; planar alignment (along the dipping direction).

In conclusion, an important role of the covalent linkage of the Az side chain to the polymer backbone is proposed to attain the photoregulation of a nematic LC alignment in the homeotropic/planar mode.

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