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Photoregulation of Tilt Angle of Nematic Liquid Crystals by Azobenzene Layers[#,1)]

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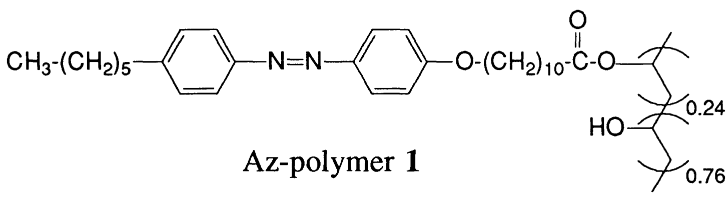
Hybrid-type liquid crystal cells were prepared with glass plates modified with octadecyltrichlorosilane and Langmuir-Blodgett film of azobenzene polymer. The tilt angle of director of the nematic liquid crystals is continuously varied by regulating the fraction of *trans*-azobenzene units by irradiating light wavelength.

It is widely recognized that alignment of liquid crystals (LC) is determined by nature of a surface contacted with the LC. In LC cells composed of glass plates modified with azobenzene (Az) units, the alignment of nematic LC is controlled by the structure of Az units.[2)] On irradiation with 365-nm light, *trans*-Az units isomerize to the cis form to induce a parallel (planar) alignment of the LC. On the contrary, *cis*-Az units isomerize to the trans form on irradiation with 440-nm light inducing a homeotropic alignment.[2)] In this communication we wish to describe regulation of the tilt angle of nematic LC director by irradiating light wavelength.

On UV and visible light irradiation, the Az units of Langmuir-Blodgett (LB) film composed of Az-polymer **1**[3)] on a glass plate isomerize between the cis and trans forms. Figure 1 shows the absorption spectra of LB film of **1** in the photostationary state upon 365- and 440-nm irradiation. This figure suggests that the isomer ratio of Az units is dependent on irradiating light wavelength and regulates alignment of LC contacted to the Az layers. The photostationary state isomer ratio of Az units on the glass plate was determined in the following way. An LB film of **1** on a quartz plate was irradiated with monochromatic light (300–420 nm) and the absorption spectra of the LB film were measured. From the absorbance at 358 nm the fraction of *trans*-Az units was calculated by assuming that **1** is 100% in the trans form in the dark, and that the molar absorptivity of *cis*-Az units at 358 nm is one tenth of that of *trans*-Az units (Fig. 2).[4)]



Az-polymer **1**

Dedicated to Professor Emeritus Osamu Simamura, The University of Tokyo, for the occasion of his 80th birthday.

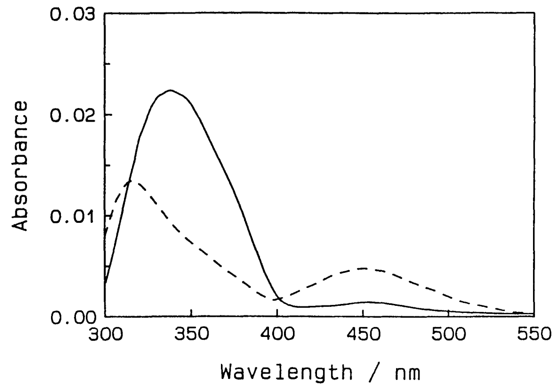


Fig. 1. Absorption spectra of LB film of Az-polymer **1** on a quartz plate in the photostationary state upon 365-nm (------) and 440-nm irradiation (——).

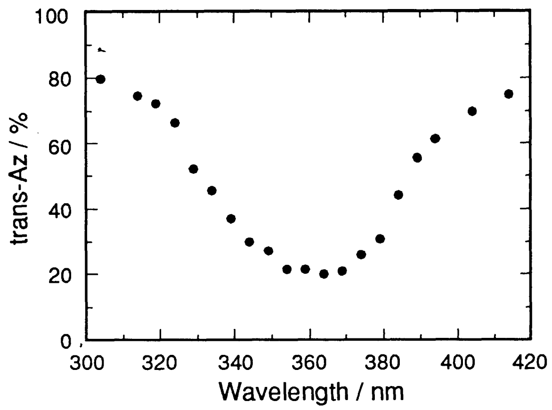
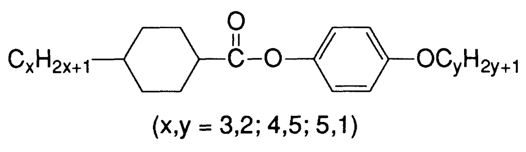


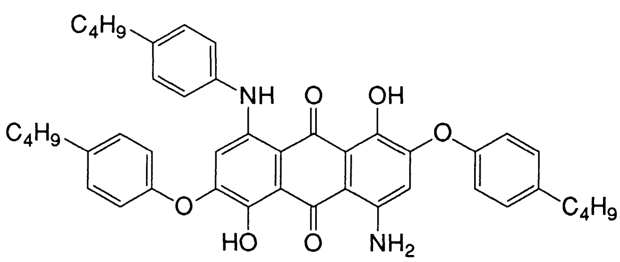
Fig. 2. Fraction of *trans*-Az units in **1** in the photostationary state.

Hybrid-type nematic LC cells were prepared according to the procedures described previously.[5)] One of the glass plates was modified with a commanding LB film of Az-polymer **1**, and the other was treated with octadecyltrichlorosilane (OTS), a homeotropically aligning reagent. Nematic LC **2** (DON-103, Rodic Co.) containing a dichroic dye **3** (1 wt%) was suspended with spherical glass spacers of 8-μm diameter and put between the plates. Monochromatic light (300–420 nm) obtained from a 500-W xenon-lamp and a monochromator was illuminated onto the LB layered side of the LC cell. The tilt angle of LC was determined from the absorbance of dichroic dye contained in the LC.

The LC cell, in which dichroic dye **3** molecules were aligned parallel to LC molecules, was irradiated with monochromatic light. The absorbance of **3** in the cell was measured with a linearly polarized He-Ne laser beam. On irradiation at 334–379 nm, the transmittance was changed depending on the angle (ϕ) between the plane of polarization of the He-Ne beam and dipping direction of the LB film preparation. When ϕ was 0 or π, the transmittance was minimum. These findings suggest that the cell has a homogeneous orientation aligned parallel to the dipping direction of LB preparation. This alignment was not altered by irradiation wavelength in the range of 334–379 nm. At the position of $\phi = 0$ the change in transmittance was measured during irradiation with monochromatic light. Figure 3 shows the transmittance of **3** in the LC cell in the photostationary state (closed circles). The transmittance is changed continuously with the irradiating light wavelength. It may be possible to regulate the transmittance of LC cell by the irradiating light wavelength. It is interesting that there are two wavelength ranges which give the same transmittance. It is also interesting that the patterns of Figs. 2 and 3 (closed circles) resemble each other; the dependence of *trans*-Az fraction on irradiating light wavelength is similar to that of transmittance of the LC cell.



Nematic LC **2**



Dichroic dye **3**

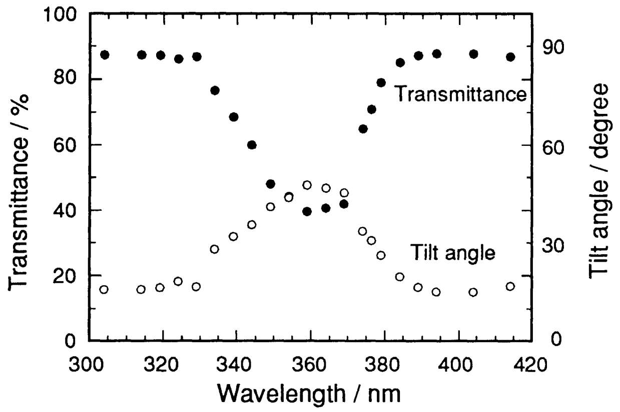


Fig. 3. Plots of transmittance (●) and tilt angle (○) of LC cell in the presence of dichroic dye in the photostationary state as a function of irradiating light wavelength.

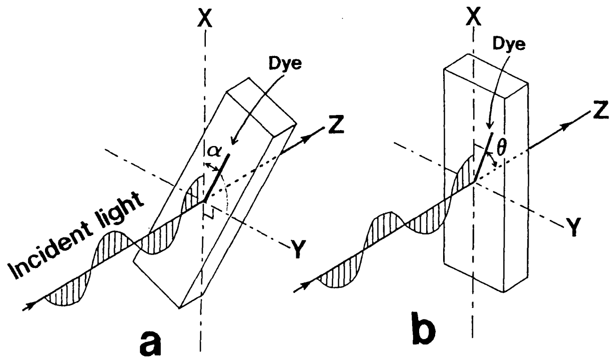


Fig. 4. Measurements of transmittance of dichroic dye **3** with linearly polarized light.

The alignment of LC molecules in plane is not altered, and the transmittance change seems to reflect the tilt angle of nematic LC director. The transmittance of dichroic dye **3** at each tilt angle is estimated as follows. On irradiation with linearly polarized light the absorbed energy (S) is proportional to the square of cosine of the angle (α) between the electric field of light and the transition moment of a molecule. The relation between the transmittance, T, and α is given by Eq. 2.

$$I_0 - I = NS = \beta N I_0 \cos^2\alpha \qquad (1)$$

$$T = I/I_0 = 1 - \beta N \cos^2\alpha \qquad (2)$$

where I_0 and I are the intensities of incident and transmitted light. N is the number of dye molecules and β is a constant.

LC **2** containing **3** (1 wt%) was interposed between two glass plates modified with LB film of Az-polymer **1**. On irradiation with 365 nm-light homogeneous orientation was aligned parallel to the dipping direction of LB preparation. Transmittance of linearly polarized light in the LC cell was measured by rotating the LC cell as depicted in Fig. 4a (Fig. 5). This can be applied to measurements of the tilt angle. Thus, transmittance of linearly polarized light in the LC cell having tilted LC molecules was measured with keeping the molecular plane of **3** on the xz plane (Fig. 4b). The relation in Fig. 5 indicates the correlation between T and α, where α is expressed as $\alpha = \frac{\pi}{2} - \theta$, by using the tilt angle θ, as shown in Fig. 4b (Fig. 5, upper abscissa).

$$T = I/I_0 = 1 - \beta N \cos^2(\tfrac{\pi}{2} - \theta) \qquad (3)$$

In the hybrid-type LC cell the LC molecules near the OTS plate always tend to lie perpendicular to the plate; θ is close to zero. When the Az units are in the cis form, the LC molecules close to the *cis*-Az layer align parallel to the layer; θ is close to 90 degree. The tilt angle may change depending on the distance from *cis*-Az layer. The tilt angle of the hybrid cell is not exactly determined, but the tilt angle exhibiting the same transmittance as that experimentally observed can be estimated from Eq. 3 and the estimated tilt angles are plotted against irradiation light wavelength (Fig. 3, open circles).

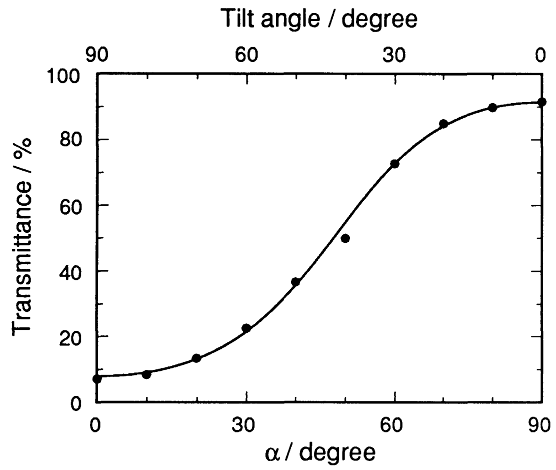


Fig. 5. Plot of transmittance vs. α and tilt angle.

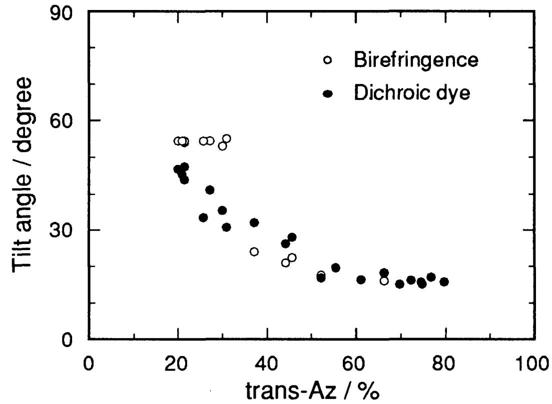


Fig. 6. Dependence of the tilt angle of nematic LC director on the fraction of *trans*-Az.

The tilt angles calculated from the absorbance of dye are plotted against the fraction of *trans*-Az in the photostationary state (Fig. 6; closed circles). The tilt angles on irradiation of shorter and longer wavelength than 360 nm light are in the same region. This means that the tilt angles are governed by the fraction of *trans*-Az units.

Alignment of the LC cell in the absence of dye was also measured by transmittance change due to birefringence. The cell was put in front of a cross polarizer,[6] and the transmittance of linearly polarized light was measured in the photostationary state on irradiation of 300–420 nm light (Fig. 6; open circles). The open and closed circles are aligned in the same region. This means that the tilt angles determined by dichroic dye agree with those by birefringence. The above results suggest that the tilt angle of LC director depends on the ratio of *cis*-Az/*trans*-Az or the absolute *trans*-Az density on the surface layer, which is easily controlled by light wavelength. This is the first example of continuous regulation of the tilt angle of LC director by light wavelength.

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