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**Photo-Induced In-Plane Alignments of Nematic Liquid Crystal Molecules on Azo-Dye Containing Alternate Self-Assembled Films Investigated Using Attenuated Total Reflection Method**

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**1.Introduction**

Evaluation of liquid crystal (LC) molecule orientations is very important for study and development of LC devices. Attenuated total reflection (ATR) measurement [1] is one of the most useful methods for evaluation of LC molecules in LC cells [2,3]. Tilt angles of LC molecules adjacent to the aligning layers and bulk LC molecules in cells can be estimated using the surface plasmon polariton (SPP) [4] and the guided wave excitation modes (GWEM) set-up [5], respectively. However, evaluation of in-plane alignments of LC molecules utilizing the ATR method has been rarely reported until now [6].

Recently, photo-induced alignments of LC molecules using photoisomerization of azo dye have been reported [7] and have been attracting much interest for constructing new optical devices. In this report, photo-induced in-plane alignments of nematic LC molecules have been investigated in LC cells fabricated with alternate Direct Red 80 (DR80: azo-dye) and poly (diallyldimethylammonium chloride) (PDADMAC) self-assembled films [8] on gold electrodes using the ATR method.

He-Ne laser at 632.8nm and also as a function of irradiation time of a linearly polarized light to the cell. High dichroism of the DR80/PDADMAC self-assembled films has been previously observed by polarized UV-vis spectroscopy [9] and is due to the photoisomerization of DR80.

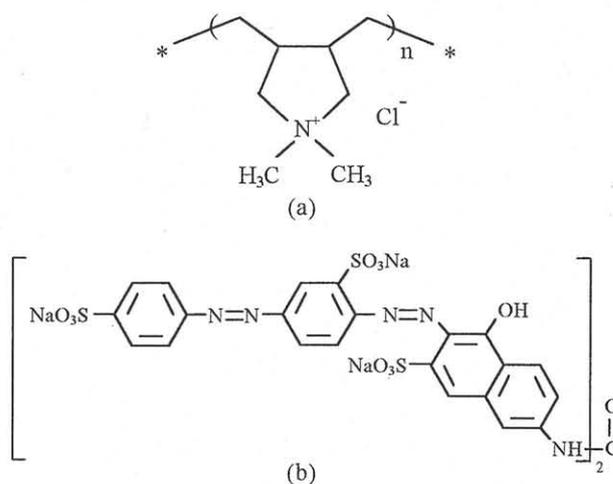


Fig. 1 Chemical structure of PDADMAC (a) and DR80 (b).

**2. Experimental Details**

Chemical structures of PDADMAC and DR80 are shown in Fig.1. DR80 contains azo groups and has been used for photo-induced alignment of LC molecules [8,9]. PDADMAC is used to prepare self-assembled films of well-defined thickness and order.

Figure 2 shows the Kretschmann configuration for the ATR measurement of the LC cell. Half-cylindrical prisms were used for the ATR measurement. Gold films of approximately 50 nm thick were vacuum evaporated onto the flat side of the prism. Initial surface functionalization of the flat surface of the prism with the gold film involved treatment with 3-mercapt-1-propanesulfonic sodium salt, and the layer-by-layer adsorption of the DR80/PDADMAC self-assembled films was carried out. The self-assembled films with 10 pair-layers deposited as aligning layers on the gold-coated prism and the slide glass. The dipping directions of the DR80 and PDADMAC on both the prism and the slide glass were set in the Y direction in the LC cell without any irradiation. The nematic LC molecules were 4-cyano-4'-n-pentylbiphenyl (5CB: Merck Japan Co.).

Reflectivities in the ATR experiments were measured for the LC cell as a function of the incident angle  $\theta$  of a

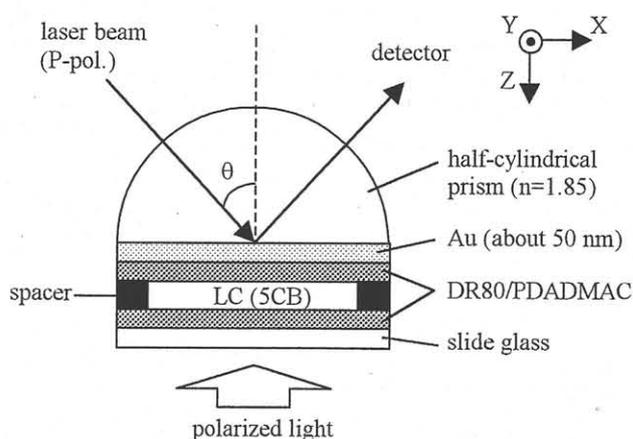


Fig. 2 The Kretschmann configuration for the ATR measurement of the LC cell.

**3.Results and Discussion**

Figure 3 shows the experimental ATR curves in the region of the resonant angles of the SPP for the LC cell. The

experimental procedure was as follows; open circles were measured before irradiation of the linearly polarized visible light. Curves 1 to 4 in the figure were each measured sequentially after one-hour irradiation of the polarized light from a halogen lamp, where the angles  $\theta_D$  between the x-axis of the cell and the direction of the electric field vector of the irradiated polarized light were set to be  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$  and  $90^\circ$  for the curves from 1 to 4, respectively.

Large valleys in reflectivities of the ATR curves were caused by the resonant excitations of the SPP. The results showed that the ATR properties changed with the irradiation of the polarized light, which induced orientation changes of the LC molecules in the cell due to the photoisomerization of DR80. From the theoretical calculations, it was estimated that the LC molecules within the penetration length of the SPP aligned perpendicular to the polarized direction of the irradiation light, and that the tilt angle was almost 0 degree. It was also estimated that the LC molecules aligned along the dipping direction of the self-assembled film before the irradiation.

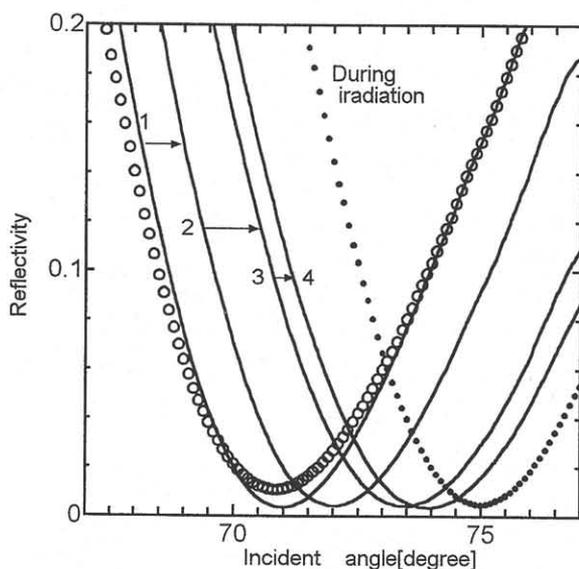


Fig. 3 ATR curves for the LC cell during and after irradiation of the polarized light at the polarized angles  $\theta_D = 0^\circ$ ,  $30^\circ$ ,  $60^\circ$  and  $90^\circ$ .

Figure 4 shows the reflectivity change at  $70.9^\circ$  of the fixed angle in the ATR measurement as a function of the irradiation time of the linearly polarized light. The LC cell was heated locally to about  $40^\circ\text{C}$  during the irradiation making the 5CB layer isotropic. It enabled the irradiated light to pass through the 5CB layer all the way through the self-assembled film on the prism side. The proof of the phase change in 5CB lies on the fact that the reflectivity increased whenever the device was heated and the irradiated light was on, and vice versa. An ATR curve during irradiation is also shown in Fig.3 as dots. The curve shifted to higher angles due to the reflective index of the isotropic 5CB.

The reflectivity changes during the light irradiation in Fig.4 were considered to be due to reorganization on the self-assembled films because the optical properties of

isotropic 5CB did not change with irradiation. It suggests that the photo-induced alignments were caused by the photoisomerization of DR80 in the self-assembled films.

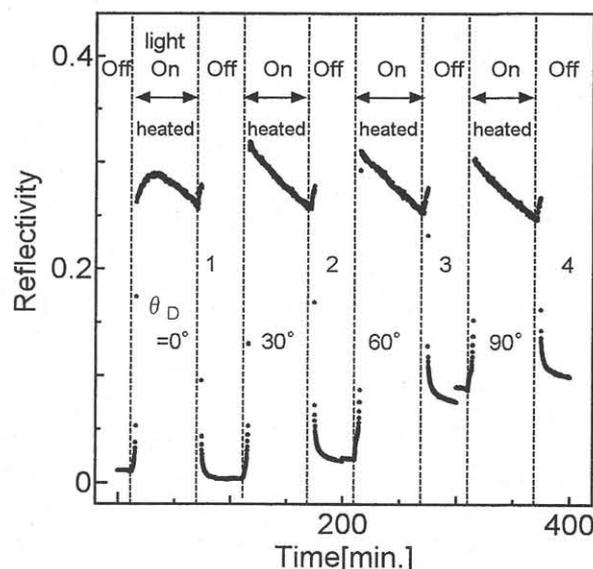


Fig. 4 Reflectivity change caused by irradiation of the polarized light at the fixed angle  $70.9^\circ$  in the ATR measurement.

#### 4. Conclusion

Photo-Induced alignment of nematic liquid crystal 5CB molecules on alternate self-assembled films of azo-dye and polyelectrolyte were investigated using the ATR measurement. It was estimated that the LC molecules aligned along the dipping direction of the self-assembled films when the cell was fabricated. The ATR properties changed with re-orientations of the LC molecules by means of irradiation with linearly polarized light inducing photoisomerization of azo-dye. In-plane alignments of the LC molecules on the self-assembled films could be controlled by the polarized direction of the irradiated light.

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