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# Transfer of the in-plane molecular orientation of polyimide film surface to liquid crystal monolayer

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We have determined the relationship between the in-plane molecular orientations of a polyimide film and the liquid crystal (LC) monolayer in contact with it. A photoaligned film of polyimide, containing azobenzene in the backbone structure, was used, because its in-plane molecular order can be varied over a wide range without change in the morphology and the chemical nature of the film surface. The in-plane order parameter of the LC molecule was found to be almost equal to that of the polyimide backbone structure. This result shows that the molecular alignment of the LC monolayer is mainly induced by a short-range interaction between the LC and polyimide molecules. © 2005 American Institute of Physics. [DOI: 10.1063/1.1937988]

Polyimide films with anisotropic molecular orientations, e.g., rubbed polyimide films, can induce uniform alignment of liquid crystal (LC) molecules. An understanding of the LC alignment mechanism is not only interesting from the scientific point of view but also of great importance from the industrial point of view. This is because rubbed polyimide films are widely used as alignment layers for LC molecules in present LC displays, and also because determination of the alignment mechanism is very helpful in developing an alignment method that does not have the drawbacks associated with mechanical rubbing. As a result of extensive efforts to understand the mechanism,<sup>1-9</sup> at present it is understood in the following two steps: (i) molecular alignment of the first LC monolayer is induced through a short-range interaction between the LC molecules and the underlying polyimide film. The LC molecules in the first monolayer are strongly anchored to the polyimide film surface; (ii) the molecular alignment of the first LC monolayer propagates into the bulk via a long-range (elastic) interaction among LC molecules. However, the understanding of the first step is still poor, because of the lack of the quantitative information on the relationship between the molecular orientations of the LC monolayer and the underlying polyimide film surface.

In this study, we have obtained the relationship *over a wide range of the in-plane molecular orientation*, and have *excluded the influence of the morphology and the chemical nature of the polyimide film surface on the LC alignment*. This was attained by using photoaligned films of polyimide containing azobenzene in the backbone structure

(Azo-PI).<sup>10-12</sup> This is because the in-plane molecular orientation of the Azo-PI film can be optically controlled over a wide range.<sup>11</sup> Since the photoalignment is a noncontact process, changes in the surface morphology during the alignment treatment can be prevented; i.e., the influence of the surface morphology upon the alignment of LC molecules can be removed. The photoalignment of the Azo-PI backbone structure occurs through random rotation of the azobenzene unit accompanied by its repeated photoisomerization. Thus the chemical nature of the Azo-PI film surface does not change by the photoalignment treatment. On the other hand, for conventional rubbing, the surface morphology significantly changes during the alignment treatment.<sup>2</sup> For the photoalignment method using the photodecomposition reaction of polyimide, the chemical nature of the polyimide film surface is changed by the alignment treatment, and also the controllable range of the in-plane molecular orientation is narrow because of the small anisotropy in the photodecomposition of the polyimide backbone structure.<sup>9</sup> Therefore, if rubbed or photodecomposed polyimide films are used, we cannot obtain the true relationship between the in-plane molecular orientations of the LC monolayer and the underlying polyimide film surface.

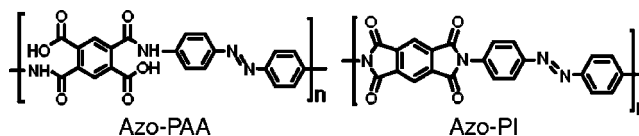


FIG. 1. Molecular structure of Azo-PI and Azo-PAA used in this study.

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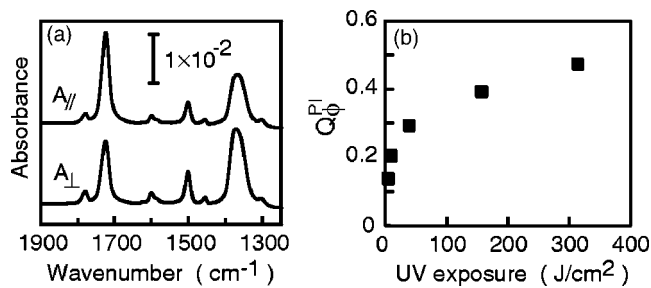


FIG. 2. (a) Polarized IR absorption spectra ( $A_{||}$  and  $A_{\perp}$ ) of the Azo-PI film exposed to LPUVL at  $11 \text{ J/cm}^2$ .  $A_{||}$  and  $A_{\perp}$  are the absorbance for the IR light polarized parallel and perpendicular to the polarization direction of LPUVL, respectively; (b) LPUVL-exposure dependence of the in-plane molecular order parameter ( $Q_{\phi}^{\text{PI}}$ ) of the Azo-PI film.

The molecular structure of Azo-PI used in this study is shown in Fig. 1 together with that of the polyamic acid (Azo-PAA), which is the precursor of Azo-PI. The 22-nm-thick Azo-PAA films were spin coated onto  $\text{CaF}_2$  substrates. The Azo-PAA films were exposed to linearly polarized ultraviolet light (LPUVL) of wavelength 365–400 nm.<sup>11</sup> To prepare the Azo-PI films with different in-plane molecular orientation, the LPUVL-exposure was varied up to  $315 \text{ J/cm}^2$ : 5, 11, 39, 158, and  $315 \text{ J/cm}^2$ . After the photoalignment treatment the Azo-PAA films were baked at  $250 \text{ }^\circ\text{C}$  for 1 h in a nitrogen atmosphere for thermal imidization. The film thickness of the obtained Azo-PI film was  $15 \pm 1 \text{ nm}$ .

Approximately a monolayer of LC molecules, 4-*n*-octyl-4'-cyanobiphenyl (8CB), was deposited onto the Azo-PI film by evaporation in air. The 8CB molecules were heated around  $120 \text{ }^\circ\text{C}$ . The deposition quantity was controlled by the evaporation time. The details of the way to control the deposition quantity were already described.<sup>9</sup>

The in-plane molecular orientation of the Azo-PI film and the first LC monolayer was determined by measuring the polarization angle dependence of the infrared (IR) absorption spectra at normal incidence. The IR absorption spectra were measured by a Fourier transform IR (FTIR) spectrometer with a mercury cadmium telluride (MCT) detector. The spectral resolution was set at  $4 \text{ cm}^{-1}$ . The absorption spectra of the Azo-PI films were measured before deposition of LC molecules, and they were obtained by averaging 400 spectral scans. Since the IR absorption of the LC monolayer is very weak, the IR absorption spectra were obtained by averaging 7200 spectral scans.<sup>9</sup>

Figure 2(a) shows the polarized IR absorption spectra ( $A_{||}$  and  $A_{\perp}$ ) of the Azo-PI film for the LPUVL-exposure of  $11 \text{ J/cm}^2$ . Here  $A_{||}$  and  $A_{\perp}$  are the absorbance for the IR light polarized parallel and perpendicular to the polarization direction of the LPUVL, respectively. To determine the in-plane orientation of the Azo-PI backbone structure, we used the band observed at  $1501 \text{ cm}^{-1}$ . This band is assigned to the phenyl C–C stretching vibration and polarized along the Azo-PI backbone structure.<sup>13</sup> From its polarization dependence ( $A_{\perp} > A_{||}$ ), we see that the Azo-PI backbone structure aligns on average perpendicular to the polarization direction of LPUVL.

To quantitatively express the in-plane molecular orientation, we introduce the in-plane molecular order parameter  $Q_{\phi}$  defined by:<sup>4,14</sup>

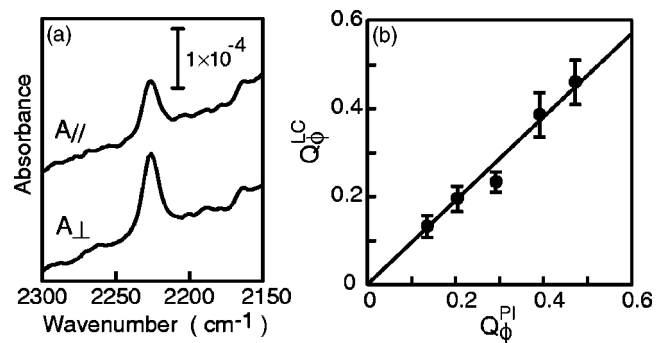


FIG. 3. (a) Polarized IR absorption spectra ( $A_{||}$  and  $A_{\perp}$ ) of the LC monolayer in contact with the Azo-PI film exposed to LPUVL at  $11 \text{ J/cm}^2$ . The definitions of  $A_{||}$  and  $A_{\perp}$  are the same as those in Fig. 2(a); (b) relationship between the in-plane molecular order parameter of the Azo-PI film ( $Q_{\phi}^{\text{PI}}$ ) and that of the first LC monolayer ( $Q_{\phi}^{\text{LC}}$ ). The straight line is  $Q_{\phi}^{\text{LC}} = 0.95 Q_{\phi}^{\text{PI}}$ .

$$Q_{\phi} = - \frac{\langle \sin^2 \theta \cos 2\phi \rangle}{\langle \sin^2 \theta \rangle} = \frac{A_{\perp} - A_{||}}{A_{\perp} + A_{||}}, \quad (1)$$

where  $\theta$  and  $\phi$  are the polar and azimuthal angles, respectively, that specify the orientation of the molecular axis, which is the backbone structure for Azo-PI and the long molecular axis for 8CB.  $\theta$  and  $\phi$  are defined with respect to the surface normal and the polarization direction of LPUVL, respectively. The angular brackets denote an average over its orientation.  $Q_{\phi} = 0$  means isotropic (random) in-plane molecular orientation; and  $Q_{\phi} = 1$  and  $-1$  mean that the molecular axes of all molecules lie in the plane perpendicular and parallel, respectively, to the polarization direction of LPUVL.

The in-plane molecular order parameter ( $Q_{\phi}^{\text{PI}}$ ) of the Azo-PI film is simply obtained from  $A_{\perp}$  and  $A_{||}$  of the  $1501 \text{ cm}^{-1}$  band by using Eq. (1). From the absorption spectra shown in Fig. 2(a),  $Q_{\phi}^{\text{PI}}$  was found to be  $0.20 \pm 0.01$  for the LPUVL exposure of  $11 \text{ J/cm}^2$ .  $Q_{\phi}^{\text{PI}}$  of the five samples prepared in this study is plotted in Fig. 2(b) as a function of the LPUVL exposure. One can see that the in-plane molecular orientation can be optically controlled up to  $Q_{\phi}^{\text{PI}} \sim 0.5$ . (For reference,  $Q_{\phi}$  induced by rubbing and by anisotropic photodecomposition is at most 0.38 (Ref. 6) and 0.16,<sup>15</sup> respectively.)

Figure 3(a) shows the polarized IR absorption spectra of the LC monolayer in contact with the Azo-PI film exposed to LPUVL at  $11 \text{ J/cm}^2$ . The band at  $2226 \text{ cm}^{-1}$  is assigned to the C–N stretching vibration of 8CB, which is polarized along the long molecular axis.<sup>16</sup> From the polarization dependence ( $A_{\perp} > A_{||}$ ), we see that the LC molecules align on average perpendicular to the polarization direction of LPUVL; i.e., the average orientation direction of the LC molecules is the same as that of the Azo-PI backbone structure.

The signal to noise ( $s/n$ ) ratio of the spectra shown in Fig. 3(a) is so high as to allow us to determine the in-plane molecular orientation with sufficient accuracy, even though the IR absorbance of the LC monolayer is much smaller than that of the Azo-PI film [see the intensity scales in Figs. 2(a) and 3(a)]. The high  $s/n$  ratio was achieved by averaging 7200 spectral scans, as mentioned above. The in-plane order parameter ( $Q_{\phi}^{\text{LC}}$ ) of the first LC monolayer was determined from the polarization dependence of the  $2226 \text{ cm}^{-1}$  band.

Figure 3(b) shows the relationship between  $Q_{\phi}^{\text{PI}}$  and  $Q_{\phi}^{\text{LC}}$ . One can see that  $Q_{\phi}^{\text{LC}}$  is almost equal to  $Q_{\phi}^{\text{PI}}$ . The relationship obtained by the least squares method is:  $Q_{\phi}^{\text{LC}} = 0.95 Q_{\phi}^{\text{PI}}$  [the straight line in Fig. 3(b)].

Before reaching a final conclusion we must discuss the relationship between the in-plane molecular orientations of the Azo-PI *film* and its *surface*, because  $Q_{\phi}^{\text{PI}}$  determined here is the in-plane molecular order parameter not of the film *surface* but of the *film*. For the 22-nm-thick Azo-PAA film, the squared electric field of LPUVL is constant within 10% across the entire film thickness.<sup>11</sup> The constant electric field is expected to induce photoalignment of the Azo-PAA backbone structure uniformly. Thus the LPUVL-exposed Azo-PAA film as well as the Azo-PI film can be assumed to have uniform in-plane molecular orientation across the entire film thickness.<sup>17</sup> This assumption is supported by the fact that the in-plane molecular order parameters of the 3-nm-thick and 15-nm-thick Azo-PI films treated by the same LPUVL irradiation are equal within the experimental uncertainty. From this consideration, we believe that the in-plane molecular orientation of the Azo-PI film *surface* is the same as that of the *film*. Therefore, the agreement between  $Q_{\phi}^{\text{LC}}$  and  $Q_{\phi}^{\text{PI}}$  strongly suggests that the in-plane molecular orientation of the Azo-PI film surface is transferred to the first LC monolayer through a short-range interaction between the LC molecule and Azo-PI backbone structure. Recently, Shioda *et al.*<sup>18</sup> pointed out that the interaction among LC molecules plays an important role in the LC alignment even for the first LC monolayer. However, the relationship  $Q_{\phi}^{\text{LC}} \sim Q_{\phi}^{\text{PI}}$  over a wide range indicates that the interaction among LC molecules is negligibly small at least for the present (Azo-PI and 8CB) system.

To conclude, we have determined the relationship between the in-plane molecular orientation of a polyimide film and that of the LC monolayer in contact with it, by using *photoaligned Azo-PI films*. We found that the in-plane order parameter of the LC molecule is almost equal to that of the polyimide backbone structure. This result shows that the in-

plane orientation of the Azo-PI backbone structure is transferred to the first LC monolayer.

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