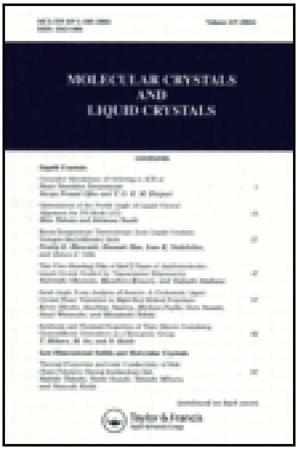

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Anisotropic Molecular Orientation of Liquid Crystal Monolayer in Contact with UV-irradiated Polyimide Film

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ANISOTROPIC MOLECULAR ORIENTATION OF LIQUID CRYSTAL MONOLAYER IN CONTACT WITH UV-IRRADIATED POLYIMIDE FILM

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By polarized infrared (IR) absorption spectroscopy we have determined the in-plane anisotropy in the molecular orientation of a liquid crystal (LC) monolayer in contact with a polyimide film exposed to linearly polarized ultraviolet light (LPUVL). The in-plane anisotropy of the underlying polyimide film surface was also determined. The average orientational directions of the LC molecules and the polyimide molecules were the same, both being perpendicular to the polarization direction of LPUVL. The in-plane molecular order of the LC molecules was smaller than that of the polyimide molecules. This result indicates that the anisotropic orientational distribution of the LC molecules in contact with the LPUVL-exposed polyimide film is induced through a short-range interaction between the LC molecules and the polyimide molecules.

Keywords: infrared absorption; in-plane anisotropy; liquid crystal monolayer; photoinduced decomposition reaction; polyimide; surface alignment

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1. INTRODUCTION

Liquid crystal (LC) molecules in a cell made with two polyimide-coated substrates exposed to linearly polarized ultraviolet light (LPUVL) align parallel to the substrate surface and perpendicular to the polarization direction of LPUVL [1]. This photoinduced LC alignment effect has received much attention as an alternative to the conventional rubbing technique, which is currently used in the fabrication of LC displays. This is because photoinduced alignment methods [1–3] do not have serious problems, such as creation of dust particles and generation of electrostatic charges, associated with mechanical rubbing.

The mechanism of LC alignment induced by the LPUVL-exposed polyimide film is understood in the following way. The preferential photoinduced decomposition occurs to the polyimide molecules oriented parallel to the polarization direction of LPUVL. Thus the orientational distribution of the *remaining* polyimide molecules becomes anisotropic after LPUVL irradiation [4]. This anisotropic orientation induces anisotropic molecular orientation of the first LC monolayer in contact with the LPUVL-exposed polyimide film through a short-range interaction between the polyimide and LC molecules. The anisotropic molecular orientation of the first LC monolayer propagates into the bulk through a long-range (elastic) interaction among LC molecules. As a result LC molecules in the bulk align on average perpendicular to the polarization direction of LPUVL. However, the existence of the short-range intermolecular interaction has not been confirmed yet. The short-range intermolecular interaction is assumed here in analogy with the alignment mechanism of LC molecules for rubbed polyimide films [5]. Since the polyimide molecules are partially decomposed in this photoinduced alignment method, there is no guarantee that the analogy is correct. To clarify the LC alignment mechanism for LPUVL-exposed polyimide films, we have to confirm the existence of the short-range interaction between the LC molecules and the underlying film. To accomplish that, we must find out whether the molecular orientation of the first LC monolayer is anisotropic without the presence of bulk LC [5].

Previously, we investigated the molecular orientation of LC monolayers in contact with polyimide (JSR: AL-1051) films exposed to LPUVL by means of optical second harmonic generation (SHG) [6]. Unfortunately, in that experiment we failed to detect anisotropy in the molecular orientation of the LC monolayer. The main cause for this failure was thought to lie in the extremely small anisotropy of the underlying polyimide film surface. Consequently, the anisotropy of LC monolayer induced by the LPUVL-exposed film was too small to detect with our SHG measurement system. In our later studies [7–9], we found that the photoinduced anisotropy of polyimide films depends strongly on the molecular structure. Poly [4,4′-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide] (CBDA-ODA) films exposed to LPUVL were found to have large anisotropy in the in-plane molecular orientation. The maximum photoinduced anisotropy was about 6 times as large as that of the AL-1051 film used in our previous study [6]. Thus the anisotropy of the LC monolayer in contact with the LPUVL-exposed CBDA-ODA film is expected to be detectable.

In this study, we have determined the in-plane molecular orientation of the LC monolayer in contact with the CBDA-ODA film exposed to LPUVL. As a first step we measured the sample rotation angle dependence of the SHG signal from the LC monolayer. However, the anisotropy in the sample rotation angle dependence could not be detected. It may be hidden by the experimental uncertainty. Thus we decided to use polarized infrared (IR) absorption spectroscopy instead of SHG to determine the molecular orientation of the LC monolayer, as well as that of the underlying polyimide film surface. Indeed, we have succeeded in detecting the anisotropy in the molecular orientation of the LC monolayer. The in-plane anisotropy of the LC monolayer is discussed in relation to that of the underlying polyimide film surface.

2. EXPERIMENT

The molecular structure of CBDA-ODA is shown in Figure 1(a). The CBDA-ODA films were made by spin-coating a solution of the polyamic acid onto CaF_2 substrates (2 mm thick) and then curing the samples at 300°C for an hour in a nitrogen atmosphere. We prepared five identical samples. The film thickness for all samples was 12 nm. This thickness was deduced from the incident angle dependence of the IR absorption of the phenyl C-C stretching vibration at $1501\,\mathrm{cm}^{-1}$ [10]. Then the CBDA-ODA films were exposed to LPUVL in the same manner as in our previous study [7], except that a bandpass filter of center wavelength 248 nm and band width 17 nm (FWHM) was used for wavelength selection in the present study. The LPUVL exposure was $1.8\,\mathrm{J/cm}^2$. To remove the unstable polymer fragments

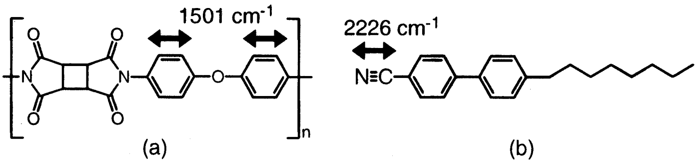

FIGURE 1 Molecular structure of (a) CBDA-ODA and (b) 8CB. The arrows indicate the polarization direction of the IR absorption bands.

created by photo-decomposition of polyimide molecules, the LPUVL-exposed films were washed in isopropyl alcohol with an ultrasonic cleaner for 5 minutes and then rinsed with pure water for 5 minutes [11].

Then approximately a monolayer of LC molecules was deposited onto the LPUVL-exposed films by evaporation in air. The LC molecule used in this study was 4-n-octyl-4′-cyanobiphenyl (8CB), whose molecular structure is shown in Figure 1(b). The deposition quantity was controlled by evaporation time, and it was checked by the IR absorption intensity of the C-N stretching vibration ($2226\,\mathrm{cm}^{-1}$) of 8CB [12]. The IR absorbance corresponding to a single 8CB monolayer was determined from the evaporation time dependence of the SHG signal and the IR absorbance for the same sample. When the SHG signal reached saturation, the IR absorbance of the $2226\,\mathrm{cm}^{-1}$ band was 1.0×10^{-4}. Since the saturation of the SHG signal shows completion of the first monolayer [13], this absorbance corresponds to that of a single 8CB monolayer.

Before deposition of LC molecules, we measured the polarized IR absorption spectra of the LPUVL-exposed CBDA-ODA films at normal incidence. Since the IR absorption intensity of the LPUVL-exposed film is sufficient to determine its in-plane molecular orientation, its absorption spectra were measured for each sample. The details of the IR absorption measurement for the CBDA-ODA films were described previously [4].

In this study we used the 12 nm-thick CBDA-ODA films as described above. For such very thin films, the photoinduced decomposition can be assumed to occur uniformly across the entire film thickness [4]. This means that the LPUVL-exposed film has a uniform molecular orientation across the entire film thickness. Thus the in-plane molecular orientation of the LPUVL-exposed *film* can be regarded as being equal to that in the *surface region* of the film. Therefore, the in-plane molecular orientation in the *surface region* can be determined from the anisotropy in the polarized IR absorption of the *12 nm-thick film*.

In contrast to the LPUVL-exposed CBDA-ODA films, the IR absorption intensity of a single LC monolayer is too weak to determine its anisotropic molecular orientation with sufficient accuracy. To overcome this difficulty, we stacked five identical samples as shown in Figure 2 and then measured the polarized IR absorption spectra of the stack at normal incidence with a $4\,\mathrm{cm}^{-1}$ resolution [14,15]. Furthermore, 7200 spectral scans were averaged to improve the signal-to-noise ratio of the IR absorption spectra.

3. RESULTS AND DISCUSSION

Figure 3 shows the polarized IR absorption spectra of the LPUVL-exposed CBDA-ODA film (sample #1) taken before evaporation of LC molecules. $A_{//}$

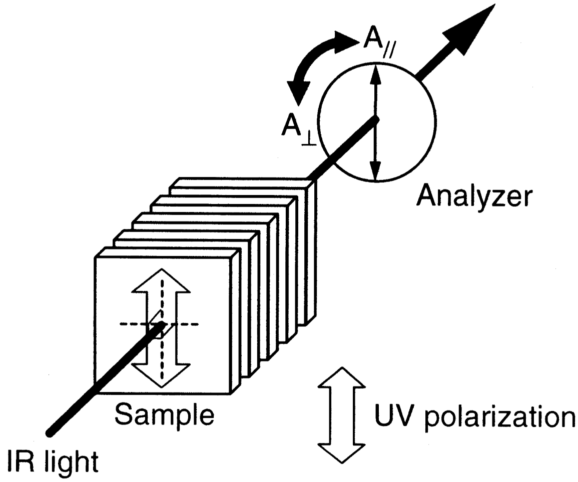

FIGURE 2 Experimental geometry for measuring the polarized IR absorption spectra of the LC monolayer.

and $A_\perp$ are the absorption spectra for the IR light polarized parallel and perpendicular to the polarization direction of LPUVL, respectively. The difference spectrum defined by $A_\perp - A_{//}$ is also shown in Figure 3. To

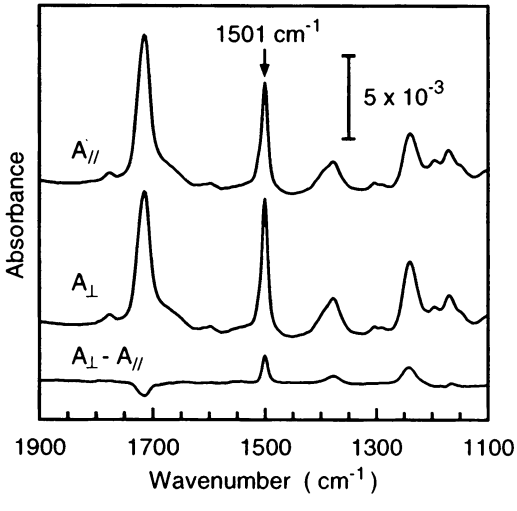

FIGURE 3 Polarized IR absorption spectra ($A_{//}$ and $A_\perp$) and difference spectrum ($A_\perp - A_{//}$) of the LPUVL-exposed CBDA-ODA film (sample #1) without LC molecules.

determine the in-plane orientation of the polyimide backbone structure, we focused on the 1501 cm^{-1} band polarized along the polyimide backbone structure, among several strong IR absorption bands. This is because the 1501 cm^{-1} band is isolated from the other strong IR absorption bands. The 1501 cm^{-1} band is assigned to the phenyl C-C stretching vibration [16]. As seen in Figure 3, $A_\perp$ of the 1501 cm^{-1} band is greater than $A_{/\!/}$. This result shows that the average orientational direction of the remaining polyimide backbone structures is perpendicular to the polarization direction of LPUVL.

In Table 1 we summarized the IR absorption data for the five samples that we prepared for determining the molecular orientation of the LC monolayer. Here A_0 is the IR absorbance of the 1501 cm^{-1} band for the unexposed CBDA-ODA films, and it is proportional to the film thickness. We also listed the normalized dichroic difference defined by $(A_\perp - A_{/\!/})/2A_0$. The meaning of the factor of 1/2 will be mentioned later. From comparison of the normalized dichroic difference of the five samples, one can see that they have almost identical in-plane molecular orientation.

Figure 4(a) shows the polarized IR absorption spectra of the LC monolayer in contact with the LPUVL-exposed CBDA-ODA film. These spectra were obtained by measuring the stack of five identical samples as shown in Figure 2. The intensity scale of Figure 4 is "absorbance per sample." The absorption band assigned to the C-N stretching vibration of 8CB, which is polarized along the molecular axis, was clearly observed at 2226 cm^{-1}. The broad background dip in the absorption spectra arises from the interference of IR light caused by the difference in the substrate thickness of the five samples stacked. The anisotropy in the polarized IR absorption was small for the LC monolayer compared to that of the underlying polyimide film. To clearly see the anisotropy, the difference spectrum $A_\perp - A_{/\!/}$ magnified by a factor of ten is shown in Figure 4(b). From Figure 4(b), one can see that we succeeded in detecting the in-plane anisotropy of the LC monolayer with sufficient accuracy. Since $A_\perp$ of the

TABLE 1 IR Absorption Data for the Five Samples (Without LC Molecules) Prepared for Determining the Molecular Orientation of the LC Monolayer

Sample #	A_0	$A_\perp - A_{/\!/}$	$\frac{A_\perp - A_{/\!/}}{2A_0}$
1	0.0093	0.0016	0.086
2	0.0093	0.0016	0.086
3	0.0093	0.0017	0.091
4	0.0093	0.0016	0.086
5	0.0094	0.0016	0.085
Average			0.087

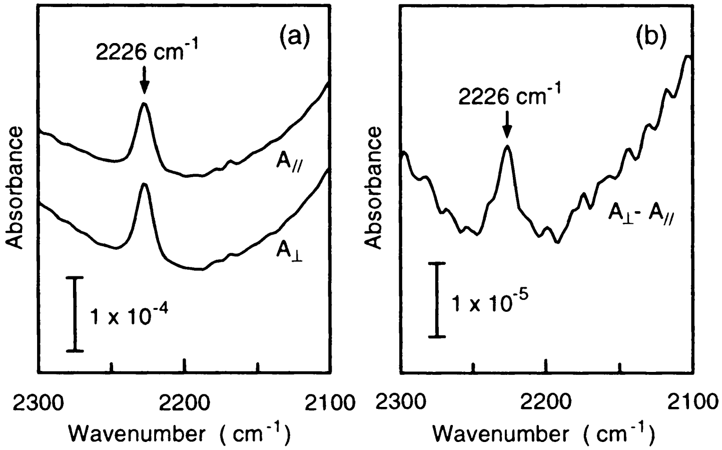

FIGURE 4 (a) Polarized IR absorption spectra and (b) difference spectrum of the LC monolayer in contact with the LPUVL-exposed CBDA-ODA film. The intensity scale is "absorbance per sample."

2226 cm^{-1} band is greater than $A_{//}$, the average orientational direction of LC molecules is perpendicular to the polarization direction of LPUVL. It is the same as the average orientational direction of the underlying polyimide molecules. This result indicates that the LC molecules in contact with the LPUVL-exposed polyimide film align through a short-range interaction between the polyimide and LC molecules.

Finally we quantitatively compare the in-plane anisotropy of the first LC monolayer and that in the *surface region* of the underlying polyimide film. First we quantify the in-plane anisotropy of the LC monolayer by the in-plane molecular order parameter Q_s^{LC} defined by -$\langle\cos 2\phi\rangle$ [17,18]. Here ϕ is the azimuthal angle that specifies the in-plane orientation of the LC molecular axis with respect to the polarization direction of LPUVL, and the angular brackets denote an average over its orientation. Q_s^{LC} can be calculated from the polarized IR absorbance of the 2226 cm^{-1} band: $Q_s^{LC} = (A_\perp - A_{//})/(A_\perp + A_{//})$ [17]. Q_s^{LC} was 0.066 ± 0.010. This value is comparable to the lower limit of Q_s^{LC} that we can determine by using our SHG system, which was previously estimated to be 0.055 [6]. This is the reason why we failed to detect the in-plane anisotropy of the LC monolayer in a preliminary SHG measurement.

Next we have to quantify the in-plane anisotropy of the polyimide film surface. In our previous study [4], we found that the surface density of the *remaining* polyimide backbone structure is an important factor for the LC alignment, in addition to its in-plane molecular order. To reflect the decrease in the surface molecular density caused by photoinduced decomposition, the in-plane molecular order parameter Q_s^{PI} for the LPUVL-exposed polyimide film surface was defined by $(A_\perp - A_{/\!/})/2A_0$. *$(A_\perp - A_{/\!/})/2A_0$ is the product of $(A_\perp - A_{/\!/})/(A_\perp + A_{/\!/})$ and the remaining fraction $((A_\perp + A_{/\!/})/2A_0)$ of the polyimide molecules.* This quantity is half of the dichroic difference normalized to A_0, which was used as a suitable measure of the anisotropy of the LPUVL-exposed polyimide film surface for LC alignment in our previous studies [8,11]. This is the reason why we listed $(A_\perp - A_{/\!/})/2A_0$ in Table 1. Q_s^{PI} was 0.087 ± 0.002. From the comparison of Q_s^{LC} and Q_s^{PI}, we found that the anisotropy in the in-plane molecular orientation of the LC monolayer is smaller than that of the underlying polyimide film *surface*. Before closing this section we wish to note that this relation is opposite to that previously reported for rubbed poly [4,4′-oxydiphenylene-pyromellitimide] (PMDA-ODA) films: i.e. $Q_s^{LC} > Q_s^{PI}$ [14,15,19]. The reason for this difference is not clear at present.

4. CONCLUSION

We have succeeded in detecting the anisotropy in the in-plane molecular orientation of the first LC monolayer in contact with the LPUVL-exposed polyimide film. We found that the average orientational direction of the LC molecules is perpendicular to the polarization direction of LPUVL. It is the same as that of the underlying polyimide molecules. The in-plane molecular order of the LC molecules is smaller than that of the polyimide molecules. This result provides clear evidence showing that a short-range interaction between the LC molecules and the LPUVL-exposed polyimide film is important in orienting the LC molecules.

REFERENCES

[1] Hasegawa, M. & Taira, Y. (1995). Nematic homogeneous photo alignment by polyimide exposure to linearly polarized UV. *J Photopolym. Sci. Technol.*, *8*, 241–248.

[2] Schadt, M., Schmitt, K., Kozinkov, V., & Chigrinov, V. (1992). Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers. *Jpn. J. Appl. Phys.*, *31*, 2155–2164.

[3] Gibbons, W. M., Shannon, P. J., Sun, S. T., & Swetlin, B. J. (1991). Surface-mediated alignment of nematic liquid crystals with polarized laser light. *Nature*, *351*, 49–50.

[4] Sakamoto, K., Usami, K., Watanabe, M., Arafune, R., & Ushioda, S. (1998). Surface anisotropy of polyimide film irradiated with linearly polarized ultraviolet light. *Appl. Phys. Lett.*, *72*, 1832–1834.

[5] Feller, M. B., Chen, W., & Shen, Y. R. (1991). Investigation of surface-induced alignment of liquid-crystal molecules by optical second-harmonic generation. *Phys. Rev. A.*, *43*, 6778–6792.

[6] Kumagai, K., Sakamoto, K., Usami, K., Arafune, R., & Ushioda, S. (1999). Molecular orientation of liquid crystal monolayers on polyimide films exposed to linearly polarized UV light. *Jpn. J. Appl. Phys.*, *38*, 3615–3618.

[7] Sakamoto, K., Usami, K., Araya, T., & Ushioda, S., (1999). Anisotropic molecular orientation of poly[4,4′-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide] films irradiated by linearly polarized UV light. *Jpn. J. Appl. Phys.*, *38*, L1435–L1438.

[8] Usami, K., Sakamoto, K., & Ushioda, S. (2001). Influence of molecular structure on anisotropic photoinduced decomposition of polyimide molecules. *J. Appl. Phys.*, *89*, 5339–5342.

[9] Usami, K., Sakamoto, K., & Ushioda, S. (2001). Cyclobutane ring cleavage of CBDA-ODA polyimide molecules induced by linearly polarized UV light. *Mol. Cryst. Liq. Cryst.*, *368*, 453–460.

[10] Sakamoto, K., Arafune, R., & Ushioda, S. (1997). Incident angle dependence of the infrared absorbance of thin rubbed polyimide films on CaF_2 and Si substrates. *Appl. Spectrosc.*, *51*, 541–544.

[11] Usami, K., Sakamoto, K., & Ushioda, S. (2003). Change of in-plane anisotropy of UV irradiated polyimide films caused by washing treatment. *Mol. Cryst. Liq. Cryst.*, *400*, 71–78.

[12] Hatta, A. (1981). Application of infrared ATR spectroscopy to liquid-crystals. V. Orientation of 5CB molecules in the boundary region of a twisted nematic cell and reorientation by a DC electric field. *Mol. Cryst. Liq. Cryst.*, *74*, 195–207.

[13] Mullin, C. S., Guyot-Sionnest, P., & Shen, Y. R. (1989). Properties of liquid-crystal monolayers on silane surfaces. *Phys. Rev. A.*, *39*, 3745–3747.

[14] Sakamoto, K., Ito, N., Arafune, R., & Ushioda, S. (1999). Determination of the molecular orientation of very thin films on solid substrates: surface liquid crystal layers and rubbed polyimide films. *Vib. Spectrosc.*, *19*, 61–69.

[15] Ito, N., Sakamoto, K., Arafune, R., & Ushioda, S. (2000). Relation between the molecular orientations of a very thin liquid crystal layer and an underlying rubbed polyimide film. *J. Appl. Phys.*, *88*, 3235–3241.

[16] Ishida, H., Wellinghoff, S. T., Baer, E., & Koenig, J. L. (1980). Spectroscopic studies of poly[n,n′-bis(phenoxyphenyl)pyromellitimide]. 1. Structures of the polyimide and three model compounds. *Macromolecules*, *13*, 826–834.

[17] Kaito, A., Nakayama, K., & Kanetsuna, H. (1987). Infrared dichroism and visible-ultraviolet dichroism studies on roller-drawn polypropylene and polyethylene sheets. *J. Macromol Sci. Phys.*, *B26*, 281–306.

[18] Barmentlo, M., van Aerle N. A. J. M, Hollering, R. W. J., & Damen, J. P. M. (1992). Surface induced liquid-crystal alignment studied by optical second-harmonic generation. *J. Appl. Phys.*, *71*. 4799–4804.

[19] Oh-e, M., Hong, S. C., & Shen, Y. R. (2000). Polar ordering at an interface between a liquid crystal monolayer and a rubbed polyimide. *J. Phys. Chem. B.*, *104*, 7455–7461.