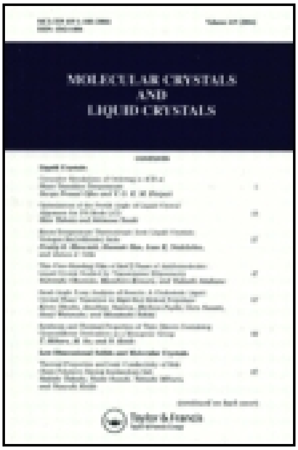

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# Stability of Photo-Induced Alignment of Azobenzene-Containing Polyimides

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# Stability of Photo-Induced Alignment of Azobenzene-Containing Polyimides

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*We have examined the change in the molecular orientation of the photo-aligned film of polyimide containing azobenzene in the backbone structure (Azo-PI) by a washing treatment. The Azo-PI films were washed in 2-propanol with an ultrasonic cleaner for 5 min and then in pure water for 5 min. No noticeable change was observed in the in-plane molecular orientation of the photo-aligned Azo-PI films. On the other hand, the in-plane molecular orientation of a rubbed polyimide (poly[4,4′-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide]) film was relaxed by washing. From these results we conclude that the molecular orientation of the photo-aligned Azo-PI films is more stable than that of the rubbed polyimide film.*

**Keywords:** azobenzene; photo-induced alignment; photo-isomerization; polyimide; stability of molecular orientation

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## INTRODUCTION

At present photo-induced alignment of liquid crystal (LC) molecules is actively studied as a promising alternative to the conventional rubbing technique [1–11]. This is because photo-induced alignment has no disadvantages associated with mechanical rubbing, such as creation of dust particles and generation of electrostatic charge. These disadvantages lead to reduction in the production yield of LC displays. Various methods of photo-induced alignment have been proposed. Among them a method proposed by Park *et al*. [6] is especially attractive, which is based on the photo-isomerization reaction of polyamic acid containing azobenzene in the backbone structure (Azo-PAA). This is because the alignment layer obtained by this method is the corresponding polyimide (Azo-PI) film. Polyimide films are chemically and thermally stable [12], and they have durability required for the fabrication process of today's LC displays. Therefore we focus on this photo-alignment method. Recently we have reported the controllability of the in-plane orientation and the average inclination angle of the Azo-PI backbone structure by optical treatment [13–15]. The LC alignment induced by the Azo-PI film has also been reported [16–18].

The alignment of LC molecules in contact with a polyimide film is mainly induced by the intermolecular interaction between the polyimide and LC molecules [19–22]. Thus the stability of the LC alignment is determined by that of the molecular orientation of the polyimide film; i.e., the alignment stability of the polyimide molecule is essential to LC displays with high reliability. To demonstrate the stability of photo-induced anisotropic orientation of the Azo-PI backbone structure, we have examined the change in molecular orientation of photo-aligned Azo-PI films caused by a washing treatment, ultrasonic agitation in 2-propanol for 5 min and subsequently in pure water for 5 min. This washing treatment is known to relax the orientational distribution of the polyimide backbone structure in rubbed films [23].

## EXPERIMENT

Two Azo-PAA materials were used in this study. One was synthesized from 4,4′-diaminoazobenzene and pyromellitic dianhydride. The other was synthesized from 4,4′-diaminoazobenzene and 4,4′-oxydiphthalic anhydride. In this paper the former and the latter are denoted by Azo-PAA-1 and Azo-PAA-2, respectively. The molecular structure of Azo-PAA's is shown in Figure 1, together with that of the corresponding Azo-PI's.

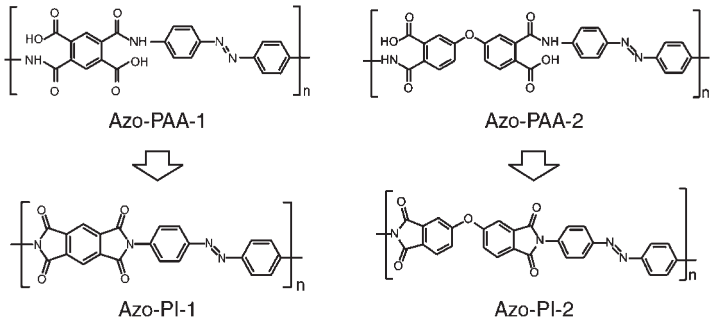


**FIGURE 1** Molecular structure of Azo-PAA's used in this study, and that of the corresponding Azo-PI's.

The Azo-PAA films were formed by spin-coating a solution of Azo-PAA onto $CaF_2$ substrates. Then they were irradiated at normal incidence with linearly polarized light (LP-light), using a 500 W deep UV lamp (Ushio Inc. UXM-501MD) as the light source. The wavelength selection was made with a band-pass filter of transmission wavelength 340–500 nm (Asahi Spectra Co., Ltd.) [15]. A Glan-Taylor prism polarizer was used to produce LP-light. The LP-light exposure was 156 $J/cm^2$ for the Azo-PAA-1 film and 600 $J/cm^2$ for the Azo-PI-2 film. By this LP-light irradiation, anisotropic in-plane orientation of the Azo-PAA backbone structure is induced through random rotation of azobenzene molecule accompanied by its photo-induced trans-cis-trans isomerization. The Azo-PAA backbone structures align on average perpendicular to the polarization direction of the LP-light [13]. After the photo-alignment treatment, the Azo-PAA films were imidized at 250°C in nitrogen atmosphere. The curing duration was two hours for the Azo-PAA-1 film and an hour for the Azo-PAA-2 film. The thicknesses of the Azo-PI-1 and Azo-PI-2 films determined by ellipsometry were 10 nm and 8 nm, respectively.

The Azo-PI films were washed in 2-propanol with an ultrasonic cleaner for 5 min and subsequently in pure water for 5 min. This condition is the same as that in our previous study [23]. Before and after the washing treatment the in-plane molecular orientation of the Azo-PI films was determined by measuring the polarized infrared (IR) absorption spectra at normal incidence. The IR measurements were carried out with a 4 $cm^{-1}$ resolution, using a Fourier transform IR spectrometer with a mercury cadmium telluride detector.

## RESULTS AND DISCUSSION

The spectra (a) and (b) in Figure 2 are the polarized IR absorption spectra ($A^u_{//}$ and $A^u{}_{\perp}$) of the unwashed Azo-PI-1 film. The spectrum (c) is the dichroic difference spectrum defined by $\Delta A^u = A^u_{\perp} - A^u_{//}$. Here, $A^i{}_{//}$ and $A^i_{\perp}$ denote the absorbance for IR light polarized parallel and perpendicular to the polarization direction of the LP-light, respectively. To distinguish between the data for the unwashed (u) and washed (w) films, the superscript i is attached. Three strong absorption bands were observed at 1368 cm$^{-1}$, 1501 cm$^{-1}$, and 1724 cm$^{-1}$, which are assigned to the C–N stretching vibration of the $(OC)_2NC$ bond, the C–C stretching vibration of the para-disubstituted benzene, and the C=O asymmetric stretching vibration, respectively [24]. The 1368 cm$^{-1}$ and 1501 cm$^{-1}$ bands are polarized along the polyimide backbone structure. On the other hand, the polarization direction of the 1724 cm$^{-1}$ band is perpendicular to the polyimide backbone structure.

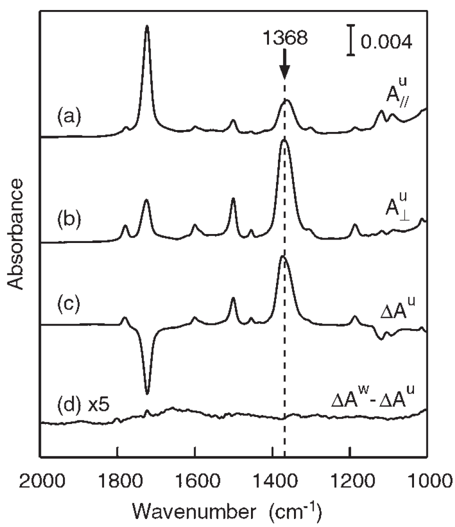


**FIGURE 2** Polarized IR absorption spectra of the photo-aligned Azo-PI-1 film. (a), (b), and (c) are, respectively, the polarized IR absorption spectra ($A^u_{//}$ and $A^u_{\perp}$), and the dichroic difference spectrum ($\Delta A^u = A^u_{\perp} - A^u_{//}$) of the unwashed Azo-PI-1 film, where $A^u_{//}$ and $A^u_{\perp}$ are the absorption spectra for IR light polarized parallel and perpendicular to the polarization direction of LP-light, respectively. (d) is the difference spectrum defined by $\Delta A^w - \Delta A^u$, where $\Delta A^w$ is the dichroic difference spectrum of the washed film.

As seen from the spectra (a) and (b), $A^u_\perp$ is much greater than $A^u_{//}$ for the 1368 and 1501 cm$^{-1}$ bands, while $A^u_\perp$ is much less than $A^u_{//}$ for the 1724 cm$^{-1}$ band. This polarization dependence is clearly seen in the dichroic difference spectrum; i.e., in spectrum (c) the 1368 cm$^{-1}$ and 1501 cm$^{-1}$ bands are positive, and the 1724 cm$^{-1}$ band is negative. From this result one can see that the Azo-PI-1 backbone structures align perpendicular to the polarization direction of the LP-light, and also that large in-plane anisotropy is induced by LP-light irradiation of 156 J/cm$^2$.

The polarized IR absorption spectra of the washed Azo-PI-1 film (not shown here) were the same as those of the unwashed film within the experimental uncertainty. To confirm that there was no change in the anisotropic molecular orientation before and after the washing treatment, we calculated the difference spectrum of the dichroic difference spectra of the unwashed and washed films, which is defined by $\Delta A^w - \Delta A^u$. The calculated result is spectrum (d) in Figure 2, whose vertical scale is magnified by a factor of 5. No noticeable peak was observed. Thus the photo-induced anisotropic orientation of the Azo-PI-1 backbone structure was found to be stable to the washing treatment.

The polarized IR absorption spectra for the Azo-PI-2 film are shown in Figure 3. The three bands assigned to the C−N stretching vibration of the $(OC)_2NC$ bond, the C−C stretching vibration of the para-disubstituted benzene, and the C=O asymmetric stretching vibration were observed at 1362 cm$^{-1}$, 1501 cm$^{-1}$, and 1723 cm$^{-1}$, respectively, although the intensity of the 1501 cm$^{-1}$ band was relatively small. From the same consideration as for the Azo-PI-1 film, one can see that the Azo-PI-2 backbone structures align perpendicular to the polarization direction of LP-light, and that large in-plane anisotropy is induced by LP-light irradiation of 600 J/cm$^2$. We observed no noticeable change in the polarized IR absorption spectra before and after the washing treatment. Indeed, the difference spectrum (d) in Figure 3 has no observable peak. From these results one can see that the in-plane molecular orientation of the photo-aligned Azo-PI-2 film was also stable to the washing treatment.

For comparison we have also carried out the same experiment for a rubbed polyimide film, except for the washing condition. The rubbed film was washed in 2-propanol with an ultrasonic cleaner for 5 min and then rinsed in pure water for 5 min. This washing condition is weaker than that for the photo-aligned Azo-PI films. In this experiment a conventional polyimide film was used instead of the Azo-PI films, because the Azo-PI films are not suitable for mechanical rubbing. For the Azo-PI-1 film, the film thickness was reduced by rubbing;

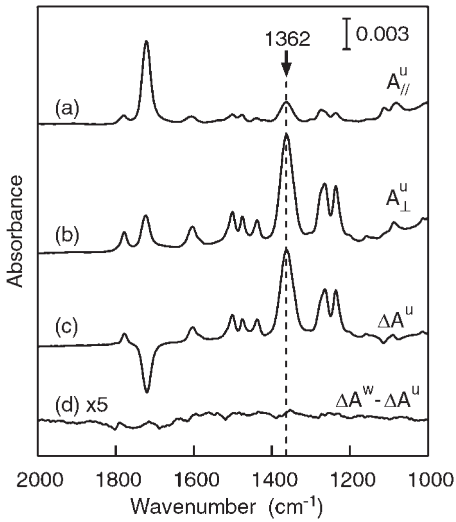


**FIGURE 3** Polarized IR absorption spectra of the photo-aligned Azo-PI-2 film. (a), (b), and (c) are the polarized IR absorption spectra ($A^u_{//}$ and $A^u_{\perp}$), and the dichroic difference spectrum ($\Delta A^u = A^u_{\perp} - A^u_{//}$) of the unwashed Azo-PI-2 film, respectively. (d) is the difference spectrum defined by $\Delta A^w - \Delta A^u$, where $\Delta A^w$ is the dichroic difference spectrum of the washed film.

i.e., the mechanical stability of the Azo-PI-1 film is low. For the Azo-PI-2 film, the in-plane anisotropy induced by rubbing was too small to perform this experiment. Thus poly [4, 4′-oxydiphenylene-1, 2, 3, 4-cyclobutanetetracarboximide] (CBDA-ODA) film (11 nm-thick) was used. The molecular structure of CBDA-ODA is shown in Figure 4. The rubbing treatment was performed in the same manner as in our previous study [23], except that the film was passed five times under the rubbing cylinder. Since the region affected by rubbing is $\sim$12 nm from the surface for the present rubbing condition [25], we can assume that the rubbed film has a uniform molecular orientation across the entire film thickness. This is the reason why we used such a very thin polyimide film in this experiment.

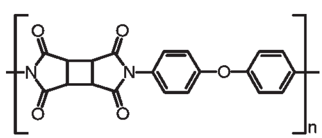

**FIGURE 4** Molecular structure of CBDA-ODA.

The IR absorption spectra for the rubbed CBDA-ODA film are shown in Figure 5. For the rubbed films, $A^i_{//}$ and $A^i_{\perp}$ are the absorbance for IR light polarized parallel and perpendicular to the *rubbing direction*, respectively, and the dichroic difference $\Delta A^i$ is defined by $A^i_{//} - A^i_{\perp}$. The three absorption bands assigned to the C−N stretching vibration of the $(OC)_2NC$ bond, the C−C stretching vibration of the para-disubstituted benzene, and the C=O asymmetric stretching vibration were observed at 1376 $cm^{-1}$, 1501 $cm^{-1}$, and 1717 $cm^{-1}$, respectively. From the spectra (a)–(c), one can see that the CBDA-ODA backbone structures align along the rubbing direction, and that the in-plane anisotropy of the rubbed film is small compared to that of the photo-aligned Azo-PI films.

In contrast to the photo-aligned Azo-PI films, the polarized IR absorption spectra of the rubbed CBDA-ODA film changed by the washing treatment. The in-plane anisotropy was reduced. This reduction can be clearly seen in the difference spectrum (d) in Figure 5; the 1376 $cm^{-1}$ and 1501 $cm^{-1}$ bands are negative, while the 1717 $cm^{-1}$ band is positive. This result shows that the anisotropic

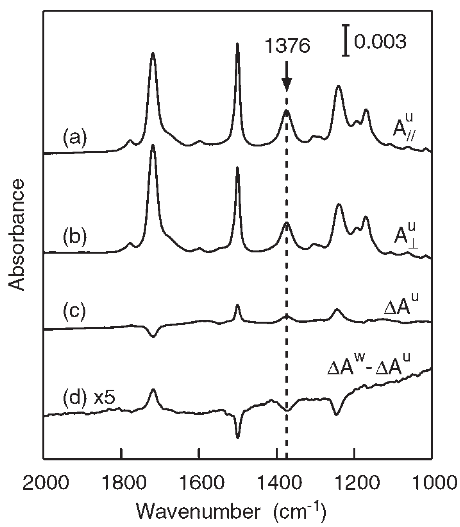


**FIGURE 5** Polarized IR absorption spectra of the rubbed CBDA-ODA film. (a), (b), and (c) are the polarized IR absorption spectra ($A^u_{//}$ and $A^u_{\perp}$), and the dichroic difference spectrum ($\Delta A^u = A^u_{//} - A^u_{\perp}$) of the unwashed CBDA-ODA film, respectively. Here, $A^u_{//}$ and $A^u_{\perp}$ are the absorption spectra for IR light polarized parallel and perpendicular to the rubbing direction, respectively. (d) is the difference spectrum defined by $\Delta A^w - \Delta A^u$, where $\Delta A^w$ is the dichroic difference spectrum of the washed film.

orientation of the CBDA-ODA backbone structure induced by rubbing was relaxed by the washing treatment.

Finally, we quantitatively discuss the change in the in-plane molecular orientation caused by the washing treatment. To accomplish that, we introduce the in-plane molecular order parameter $Q_\Phi$ defined by [26,27]:

$$Q_\Phi = \frac{\langle \sin^2 \Theta \cdot \cos 2\Phi \rangle}{\langle \sin^2 \Theta \rangle},$$

where $\Theta$ and $\Phi$ are the polar and azimuthal angles, respectively, that specify the orientation of the polyimide backbone structure. $\Theta$ and $\Phi$ are defined with respect to the surface normal and the average orientation direction of the polyimide backbone structure, respectively. The angular brackets denote an average over its orientation. For all the samples we calculated $Q_\Phi$ from the polarized IR absorption of the band around $1370\,\mathrm{cm}^{-1}$, which is polarized along the polyimide backbone structure as noted above. $Q_\Phi$ is given by $(A^i_\perp - A^i_{//})/(A^i_\perp + A^i_{//})$ for the photo-aligned Azo-PI films, and by $(A^i_{//} - A^i_\perp)/(A^i_\perp + A^i_{//})$ for the rubbed CBDA-ODA film. To evaluate $Q_\Phi$, we used the integrated absorbance of the $1370\,\mathrm{cm}^{-1}$ band. Here, $Q_\Phi = 0$ means isotropic in-plane molecular orientation. For the photo-aligned films, $Q_\Phi = 1$ and $-1$ mean that all the Azo-PI backbone structures align perpendicular and parallel, respectively, to the polarization direction of the LP-light. For the rubbed film, $Q_\Phi = 1$ and $-1$ mean that all the CBDA-ODA backbone structures align parallel and perpendicular, respectively, to the rubbing direction.

The in-plane molecular order parameters for all the samples are summarized in Table I. From Table I one can see that large in-plane anisotropy was induced by the photo-alignment treatment. The in-plane order parameter $Q_\Phi$ of the Azo-PI backbone structure exceeded

**TABLE I** The In-plane Order Parameter $Q_\Phi$ of the Polyimide Backbone Structures Before and After the Washing Treatment

| | Azo-PI-1[a] | Azo-PI-2[a] | Rubbed CBDA-ODA[b] |
|---|---|---|---|
| Before | 0.50 | 0.68 | 0.10 |
| After | 0.51 | 0.68 | 0.06 |

[a]Washed in 2-propanol with an ultrasonic cleaner for 5 min., and then in pure water for 5 min.

[b]Washed in 2-propanol with an ultrasonic cleaner for 5 min. and then rinsed in pure water for 5 min.

0.50, and it was not changed by the washing treatment. On the other hand, the in-plane anisotropy induced by rubbing was small ($Q_{\Phi} = 0.10$), and it was reduced to 0.06 by the washing treatment. From these results, we conclude that the anisotropic molecular orientation of the photo-aligned Azo-PI films is more stable than that of the conventional rubbed polyimide film.

## CONCLUSION

We have examined the change in the in-plane molecular orientation of the photo-aligned Azo-PI films and the rubbed CBDA-ODA film by the washing treatment. No noticeable change was observed for the photo-aligned Azo-PI films, while the rubbing-induced alignment of the CBDA-ODA backbone structure was relaxed by the washing treatment. From these results we conclude that the photo-induced alignment of the Azo-PI backbone structure is more stable than the rubbing-induced alignment of the polyimide backbone structure.



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