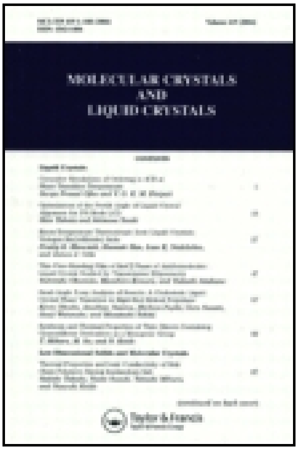

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CHANGE OF IN-PLANE ANISOTROPY OF UV IRRADIATED POLYIMIDE FILMS CAUSED BY WASHING TREATMENT

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CHANGE OF IN-PLANE ANISOTROPY OF UV IRRADIATED POLYIMIDE FILMS CAUSED BY WASHING TREATMENT

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We have investigated the change in the in-plane anisotropy caused by a washing treatment of UV irradiated polyimide (poly[4,4′-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide]) films. The in-plane anisotropy of the films exposed to linearly polarized UV light (LPUVL) was determined by measuring the polarized infrared absorption spectra. We found that part of the polymer fragments produced by photo-induced decomposition are unstable, and that they can be removed by a few minutes of ultrasonic cleaning. In the LPUVL exposure range below $1.5\,J/cm^2$*, the film anisotropy slightly increases after the washing treatment and beyond this exposure it decreases. As a result, the film anisotropy becomes maximum at* $1.5\,J/cm^2$ *for the washed film, while it is maximum at* $\sim 3\ J/cm^2$ *for the unwashed film.*

Keywords: photo-induced liquid crystal alignment; washing treatment; polyimide; photo-induced decomposition reaction; infrared absorption; in-plane anisotropy

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INTRODUCTION

Industrially, rubbing of a polyimide-coated substrate is widely used as a technique to obtain uniform alignment of liquid crystal (LC) molecules. However, this technique has disadvantages such as creation of dust particles and generation of electrostatic charge, which reduce the production yield of LC devices. On the other hand, photo-induced alignment of LC molecules contains no mechanical contact process; i. e. it is dust-free and electrostatic-charge-free. Thus the photo-induced alignment has received much attention as an alternative to the rubbing technique. Among several photo-induced alignment methods reported to date [1–3], alignment methods using photo-induced decomposition reaction are attractive. This is because polyimide films that are widely employed in the practical LC devices can be used as alignment layers.

When a polyimide film is exposed to linearly polarized ultraviolet light (LPUVL), preferential decomposition occurs to the polyimide molecules oriented parallel to the polarization direction of LPUVL. After LPUVL exposure, the average orientation direction of the intact polyimide molecules becomes perpendicular to the polarization direction of LPUVL. Thus the LC molecules align perpendicular to the polarization direction of LPUVL through the anisotropic interaction between the LC molecules and the LPUVL-exposed polyimide film.

Lu *et al*. reported that the top layers of the UV-light-exposed polyimide film could be removed by mechanical rubbing or by a few minutes of ultrasonic agitation [4]. This result indicates that the top layers of the UV-light-exposed film are mechanically unstable. This suggests that there is a possibility that part of the polymer fragments produced by photo-induced decomposition reaction dissolve in LC. Since the dissolution of the polymer fragments increases the concentration of organic contaminants in LC, it might degrade the device performance of active matrix LC displays, such as the voltage holding ratio [5]. In addition, dissolution of the polymer fragments in the top layers causes a modification of the surface properties of the LPUVL-exposed film. Thus the surface alignment properties of LC molecules, such as surface anchoring energy [6] and pretilt angle [7], should be influenced. A change in the surface anchoring energy and the pretilt angle of LC molecules results in degradation of the device performance of LC displays.

To avoid degradation of the device performance, soluble (unstable) polymer fragments must be removed before assembling the LPUVL-exposed alignment film into LC cells. Washing of the LPUVL-exposed film is an effective method for removing the unstable polymer fragments [4]. Thus we have investigated the removal of the unstable polymer fragments and the influence of a washing treatment on the in-plane anisotropy of the LPUVL-exposed polyimide film.

EXPERIMENT

The polyimide used in this study was poly[4,4′-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide] (CBDA-ODA). The molecular structure of the polyimide is shown in Figure 1. The polyimide film was made by spin-coating a solution of the polyamic acid onto a CaF_2 substrate (2 mm thick) and then curing the sample at 300°C for an hour in a nitrogen atmosphere. The film thickness deduced from the incident angle dependence of the infrared (IR) absorption of the phenyl C-C stretching vibration [8] was 12 ± 1 nm. For such a very thin film, the polyimide molecules can be assumed to be decomposed uniformly across the entire film thickness by LPUVL irradiation [9]. Thus we can determine the anisotropic molecular orientation of the LPUVL-exposed film surface by measuring the polarized IR absorption spectra of the film.

The polyimide film was exposed to LPUVL using a 500 W deep UV lamp (Ushio Inc. UXM-501MD). The UV light passed through a bandpass filter of center wavelength 248 nm and band width 10 nm (FWHM) and a Glan-Taylor prism polarizer, and impinged on the polyimide film along the surface normal. The LPUVL-exposed film was washed in isopropyl alcohol with an ultrasonic cleaner, and then rinsed with pure water. The molecular orientation of the LPUVL-exposed film before and after the washing treatment was determined by measuring the polarized IR absorption spectra. The details of the IR measurement were described previously [9].

RESULTS AND DISCUSSION

To monitor the removal of the polymer fragments and the change in the molecular orientation of the polyimide films, we used the 1501 cm^{-1} band assigned to the phenyl C-C stretching vibration of CBDA-ODA [10,11]. This

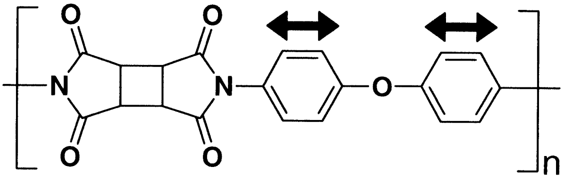

FIGURE 1 Molecular structure of polyimide (CBDA-ODA) used in this study. The arrows show the polarization direction of the 1501 cm^{-1} bands.

is because the 1501 cm^{-1} band is polarized along the polyimide backbone structure and is isolated from the other strong IR absorption bands. In this study the IR dichroic difference was used as a measure of the film anisotropy, because a positive correlation between the dichroic difference and the LC alignment is known [9]. The IR dichroic difference is defined by $A_{\perp} - A_{\|}$, where $A_{\perp}$ and $A_{\|}$ are the absorbance for the IR light polarized perpendicular and parallel to the polarization direction of LPUVL, respectively. They are normalized to the absorbance of the film before LPUVL irradiation, to avoid data scattering due to the difference in the film thickness among the samples used.

First we measured the polarized IR absorption spectra of the polyimide films as a function of the washing time. This measurement was made for a film exposed to LPUVL at 1.0 $\mathrm{J/cm}^2$ and an unexposed film. We repeated the cycle of the washing treatment and the IR measurement for the same sample. Ultrasonic washing in isopropyl alcohol was followed by rinsing with pure water for 5 minutes.

Figure 2(a) shows the washing time dependence of the polarized IR absorbance of the 1501 cm^{-1} band. The horizontal axis is the total ultrasonic washing time. The solid circles and squares are $A_{\|}$ and $A_{\perp}$, respectively, for the LPUVL-exposed film. The crosses are the absorbance for the unexposed film. Both $A_{\perp}$ and $A_{\|}$ for the LPUVL-exposed film decreased after the washing treatment, while the absorbance for the unexposed film did not change. This result shows that part of the polymer fragments

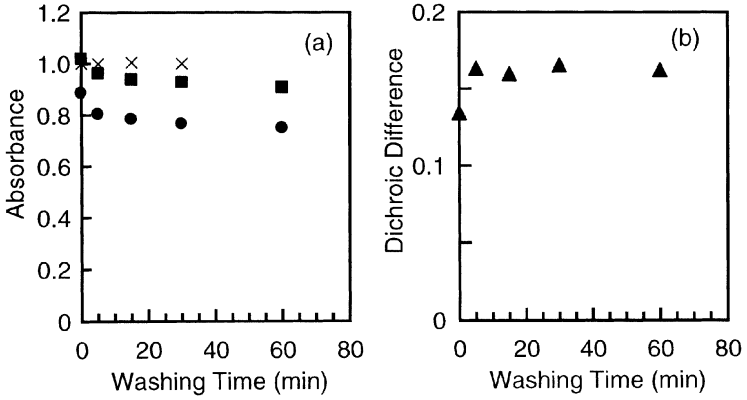

FIGURE 2 Washing time dependence of (a) the polarized IR absorbance and (b) the dichroic difference of the 1501 cm^{-1} band for the LPUVL-exposed film (1.0 J/cm^2). The solid circles, squares, and triangles show {\rm A}_{\l}, $\mathrm{A}_{\perp}$, and $\mathrm{A}_{\perp}$ −{\rm A}_{\l}, respectively. For comparison the absorbance data for the unexposed film are also plotted by the crosses in Figure 2(a).

produced by LPUVL irradiation were removed, indicating that the LPUVL-exposed film contains unstable polymer fragments. In addition, we can see that the decrease of $A_\perp$ and $A_\parallel$ is almost completed in the first 5 minutes. This means that most of the unstable polymer fragments were removed by washing for a few minutes.

Figure 2(b) shows the washing time dependence of the dichroic difference of the 1501 cm^{-1} band for the LPUVL-exposed film. Slight increase in the dichroic difference was observed in the first 5 minutes, and beyond 5 minutes the dichroic difference was constant. This result shows that the anisotropy of the LPUVL-exposed film is stable after removal of the unstable polymer fragments. The increase of the dichroic difference will be discussed later.

Next we examined the change in the in-plane anisotropy caused by the washing treatment for the films exposed to LPUVL at different energy densities. In this measurement 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. Figure 3 shows the LPUVL exposure dependence of the polarized absorbance and dichroic difference of the

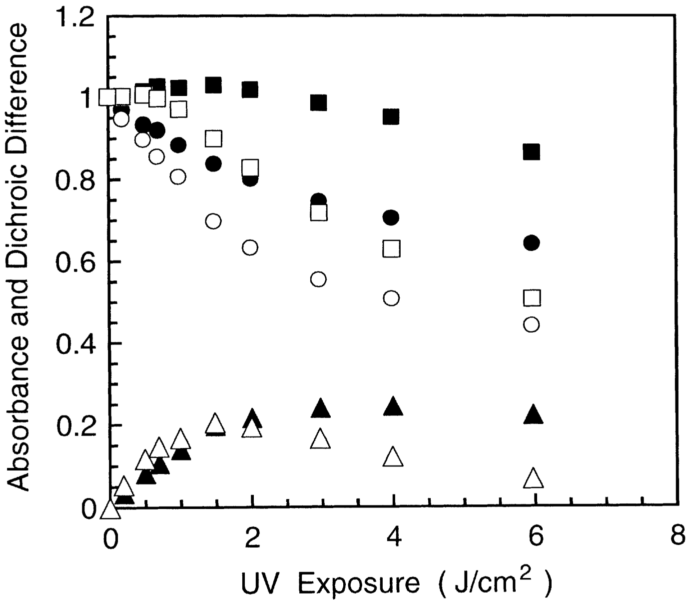

FIGURE 3 LPUVL exposure dependence of the polarized IR absorbance and the dichroic difference of the 1501 cm^{-1} band. The circles, squares, and triangles show $A_\parallel$, $A_\perp$, and $A_\perp - A_\parallel$ respectively. The solid and open symbols are the data points for the unwashed and washed films, respectively.

$1501\,\text{cm}^{-1}$ band for the LPUVL-exposed films before and after the washing treatment. The solid circles, squares, and triangles are the data points of $A_{\|}$, $A_{\perp}$, and $A_{\perp} - A_{\|}$, respectively, for the unwashed films. The open symbols are those for the washed films. For convenience, the polarized absorbance for the unwashed and washed films are denoted by A_i^u and A_i^w, respectively, where $i = \|$ and $\perp$.

For all LPUVL-exposed films examined, both $A_{\|}$ and $A_{\perp}$ decreased after the washing treatment. To see the percentage of the polymer fragments removed, we plotted $\Delta A/A^u$ as a function of the LPUVL exposure in Figure 4, where $A = A_{\|} + A_{\perp}$ and $\Delta A = A^u - A^w$. $\Delta A/A^u$ increases with the LPUVL exposure. This result shows that the unstable polymer fragments in the unwashed film increases with the LPUVL exposure.

Up to $1.5\,\text{J/cm}^2$, $\Delta A_{\|}$ was greater than $\Delta A_{\perp}$. Thus the dichroic difference, i.e. the film anisotropy, increased after the washing treatment. The increase of the dichroic difference can be explained by removal of the unstable polymer fragments. The polyimide molecules oriented parallel to the polarization direction of LPUVL are broken more easily than those oriented perpendicular to it [11,12]. Thus the number of unstable polymer fragments oriented parallel to the polarization direction of LPUVL becomes greater than that oriented perpendicular to it. Hence, the dichroic difference, i.e. the film anisotropy, increases after removal of the unstable polymer fragments.

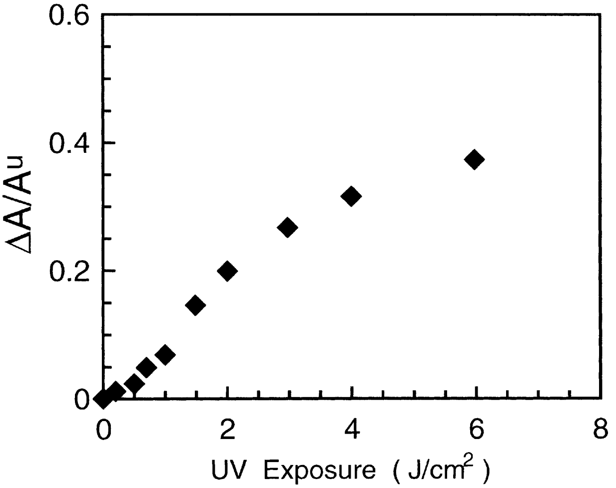

FIGURE 4 Percentage of the polymer fragments removed by the washing treatment. Here, $A = A_{\perp} + A_{\|}$ and $\Delta A = A^u - A^w$.

On the other hand, $\Delta A_{\perp}$ becomes greater than Δ{\rm A}_{\|} beyond $1.5\,\mathrm{J/cm^2}$ as shown in Figure 3. Here we note that the dichroic difference of the washed film rapidly decreases with the increase of LPUVL exposure, while that of the unwashed film is almost constant. This result means that the contribution of unstable polymer fragments to the film anisotropy rapidly increases above $1.5\,\mathrm{J/cm^2}$. Thus the dichroic difference becomes maximum at $1.5\,\mathrm{J/cm^2}$ for the washed film, while the maximum occurs at $\sim 3\,\mathrm{J/cm^2}$ for the unwashed film [11]. Since the LPUVL exposure above $1.5\,\mathrm{J/cm^2}$ reduces the stability of film anisotropy, one should avoid the LPUVL exposure exceeding $1.5\,\mathrm{J/cm^2}$ for the CBDA-ODA film.

CONCLUSION

We have investigated the removal of the unstable polymer fragments produced by photo-induced decomposition and the change in the in-plane anisotropy of the LPUVL-exposed film caused by a washing treatment. We found that the unstable polymer fragments produced by photo-induced decomposition can be removed by a few minutes of ultrasonic agitation in isopropyl alcohol. After removal of the unstable polymer fragments, the film anisotropy was stable under further ultrasonic agitation. For the films exposed to LPUVL below $1.5\,\mathrm{J/cm^2}$, the film anisotropy slightly increased after the washing treatment. The increase of the film anisotropy can be explained by considering the anisotropy in the removal of the unstable polymer fragments. Above $1.5\,\mathrm{J/cm^2}$ the film anisotropy decreased by the washing treatment. The decrement of the film anisotropy rapidly increased with the increase of LPUVL exposure. As a result, the film anisotropy becomes maximum at $1.5\,\mathrm{J/cm^2}$ for the washed film, while the maximum occurs at $\sim 3\,\mathrm{J/cm^2}$ for the unwashed film. We found that the LPUVL exposure exceeding $1.5\,\mathrm{J/cm^2}$ is of no effect for inducing the stable film anisotropy.

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