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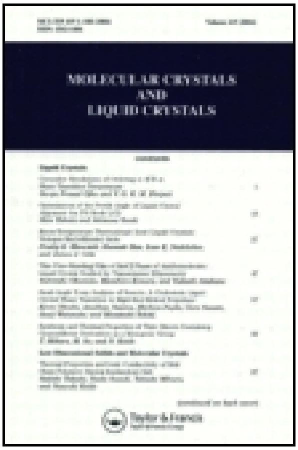

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Cyclobutane Ring Cleavage of CBDA-ODA Polyimide Molecules Induced by Linearly Polarized UV Light

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Cyclobutane Ring Cleavage of CBDA-ODA Polyimide Molecules Induced by Linearly Polarized UV Light

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We have determined the initial cleavage rate of the cyclobutane ring of poly[4,4'-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide] (CBDA-ODA) for linearly polarized ultraviolet light (LPUVL). The initial cleavage rates $\beta_{//}$ and $\beta_{\perp}$ for LPUVL polarized parallel and perpendicular to the polyimide backbone direction, respectively, were determined from the IR absorption data reported previously. $\beta_{//}$ and $\beta_{\perp}$ are 0.70 ± 0.02 and 0.13 ± 0.02 $J^{-1}\cdot cm^{2}$, respectively, for LPUVL of wavelength 248 nm. We found that the anisotropy of the cleavage rate is much larger than that of the phenyl ring decomposition rate for poly[4,4'-oxydiphenylene-pyromellitimide] (PMDA-ODA) that was previously reported. The large anisotropy of the cyclobutane ring cleavage is advantageous to photo-induced alignment of liquid crystals based on the decomposition reaction of polyimide molecules.

Keywords: photo-induced LC alignment; polyimide; CBDA-ODA; liquid crystal; linearly polarized ultraviolet light; IR absorption

INTRODUCTION

Surface alignment of liquid crystal (LC) molecules is an important technology for the fabrication of LC displays. Currently rubbing of polymer coated-substrates is widely used to obtain a homogeneous (uniform and parallel) alignment of LC molecules. However, the

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development of an alternative alignment method is being sought, because the mechanical rubbing has problems, such as creation of dust particles and generation of electrostatic charges. They reduce the production yield of LC displays. Recently, photo-induced alignment of LC molecules has received much attention as a promising method that can replace the conventional rubbing method. This is because the photo-induced alignment contains no mechanical process; i. e. it is dust-free and electrostatic-charge-free. Among the several photo-induced alignment methods that have been reported[1-3], we focus on a photo-alignment technique based on the photo-induced decomposition reaction of polyimide molecules[3]. This technique is attractive, in that the polyimide films that are widely employed in the practical LC displays can be used as alignment layers.

Since the polyimide molecule oriented parallel to the polarization direction of ultraviolet (UV) light is preferentially decomposed, the orientation of the remaining polyimide molecules in the film becomes anisotropic after irradiation with linearly polarized UV light (LPUVL). Through the anisotropic intermolecular interaction between LC and polyimide molecules, the LC molecules align perpendicular to the polarization direction of LPUVL[3]. Thus to achieve a desired LC alignment, we need to control the orientation of the remaining polyimide molecules by LPUVL irradiation. The controllability strongly depends on the anisotropy of the photo-induced decomposition of a polyimide molecule.

Recently Hasegawa reported that poly [4,4'-oxydiphenylene-1,2,3,4-cyclobutanetetracarboximide] (CBDA-ODA) films exposed to LPUVL (wavelength 257 nm) at ~1 J/cm^2 can induce a homogeneous alignment of LC molecules[4]. We investigated the anisotropic molecular orientation of a CBDA-ODA film induced by irradiation with LPUVL of wavelength 248 nm[5]. From the LPUVL exposure dependence of the infrared (IR) absorption spectra, we found that the anisotropic molecular orientation arises from the preferential cleavage of the cyclobutane ring in the polyimide backbone structure oriented along the polarization direction of LPUVL, and subsequent orientational randomization of the cleaved molecules. The anisotropy of the molecular orientation of the LPUVL-exposed film exceeded that of a rubbed CBDA-ODA film around 1 J/cm^2. This result indicates that the anisotropy of the photo-induced cleavage of the cyclobutane ring is very large.

In the present study we have determined two initial (< 1 J/cm^2) cleavage rates of the cyclobutane ring of CBDA-ODA for LPUVL polarized parallel and perpendicular to the backbone direction. This was

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accomplished by analyzing the LPUVL exposure dependence of IR absorption reported in our recent letter[6]. These cleavage rates are useful in systematically determining the LPUVL exposure condition to obtain the desired orientation of uncleaved CBDA-ODA molecules.

THEORY

To describe the anisotropic photo-induced cleavage of the cyclobutane ring of CBDA-ODA, we consider two cleavage rates $\beta_{//}$ and $\beta_{\perp}$[7]. They are the cleavage rates of the cyclobutane ring for the LPUVL polarized parallel and perpendicular to the backbone direction, respectively. Since the thickness of the film used in this study was 10 nm, the variation of the squared electric field of LPUVL across the film thickness is negligible[6]. Thus the cyclobutane ring cleavage can be considered to occur uniformly over the entire film thickness during LPUVL irradiation. Hence we need not consider the variation of the orientational distribution along the film thickness direction. The anisotropic photo-induced cleavage of the cyclobutane rings is described by the following rate equation:

$$\begin{aligned}&\frac{d}{dw}N(\theta,\phi,w)\\&=-[\beta_{//}\cdot(\hat{e}_{UV}\cdot\hat{c})^2+\beta_{\perp}\cdot\{(\hat{e}_{UV}\cdot\hat{a})^2+(\hat{e}_{UV}\cdot\hat{b})^2\}]\cdot N(\theta,\phi,w)\,,\end{aligned}\tag{1}$$

where $N(\theta, \phi, w)$ is the orientational distribution of the backbone directions of *uncleaved* molecules; θ and ϕ are the polar and azimuthal angles that specify the orientation of $\hat{c}$ with respect to the sample coordinates (XYZ) as illustrated in Fig. 1; $\hat{c}$ is the unit vector of the polyimide backbone direction; $\hat{a}$ and $\hat{b}$ are the unit vectors of the directions perpendicular to $\hat{c}$ and orthogonal to each other; $\hat{e}_{UV}$ is the unit vector of the polarization direction of LPUVL; and w is LPUVL exposure. In general, $\beta_{//}$ and $\beta_{\perp}$ are not constant over the whole range of LPUVL exposure. However, since the aim of the present study is to determine the initial values of $\beta_{//}$ and $\beta_{\perp}$, they are treated as constants here. By solving Eq. (1), we obtain:

$$\begin{aligned}&N(\theta,\phi,w)\\&=N(\theta,\phi,0)\exp[-\beta_{//}\cdot w\cdot(\hat{e}_{UV}\cdot\hat{c})^2-\beta_{\perp}\cdot w\cdot\{(\hat{e}_{UV}\cdot\hat{a})^2+(\hat{e}_{UV}\cdot\hat{b})^2\}]\,.\end{aligned}\tag{2}$$

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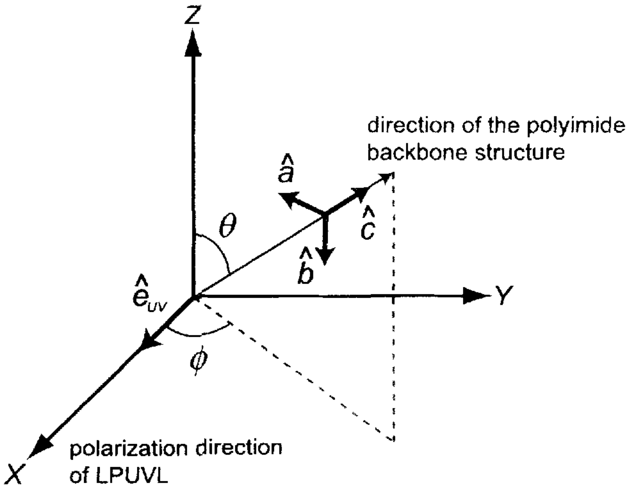

FIGURE 1 Definition of the coordinate system. θ and ϕ are the polar and azimuthal angles that specify the orientation direction of the polyimide backbone structure ($\hat{c}$) with respect to the sample coordinates (*XYZ*). The *Z* axis is the surface normal. The X axis is defined by the polarization direction (e_{UV}) of LPUVL.

RESULTS AND DISCUSSION

Figure 2 shows the LPUVL exposure dependence of the IR absorbance of the 1376 and 1397 cm^{-1} bands measured for a 10-nm-thick CBDA-ODA film on a CaF_2 substrate[5]. The wavelength of LPUVL was 248 nm. Since we will determine the initial cleavage rate of the cyclobutane ring of CBDA-ODA, we present only the IR absorption data up to 2 J/cm^2. The 1376 and 1397 cm^{-1} bands are assigned to the C-N stretching vibration of the $(OC)_2NC$ bond of CBDA-ODA and maleimide, respectively[5, 8]. The maleimide molecule is formed by the cyclobutane ring cleavage induced by LPUVL irradiation[9, 10]. The relevant photochemical reaction is illustrated in Fig. 3. These two bands are polarized along the backbone structure as indicated in Fig. 3.

The open and solid squares in Fig. 2 are the data points of absorbance ($A_\perp$ and $A_{//}$) for the IR light polarized perpendicular and parallel to the polarization direction of LPUVL, respectively. Since the widths of the two bands were constant at 30 cm^{-1} (FWHM) in the measurement range of LPUVL exposure, we plotted the peak absorbance

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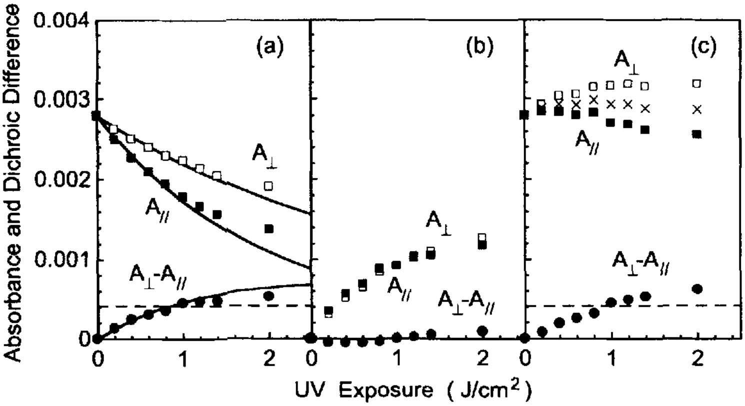

FIGURE 2 LPUVL exposure dependence of the absorption of the two bands: (a) 1376 cm^{-1}, (b) 1397 cm^{-1}, and (c) 1376 cm^{-1} + 1397 cm^{-1}. The open and solid squares are the data points for $A_\perp$ and $A_{//}$, respectively. The solid circles show $A_\perp$ - $A_{//}$. The horizontal dashed lines are the dichroic difference for a rubbed film with the same thickness. The solid curves in (a) are the best fit calculated results ($\beta_{//}$ = 0.70 J^{-1}·cm^2 and $\beta_\perp$ = 0.13 J^{-1}·cm^2).

in Fig. 2. The solid circles show the dichroic difference defined by $A_\perp$ - $A_{//}$. For comparison the dichroic difference for a rubbed CBDA-ODA film[11] with the same film thickness is also shown by horizontal dashed lines in Fig. 2. (The 1397 cm^{-1} band was not observed for the rubbed film.) For both 10-nm-thick LPUVL-exposed and rubbed films, the molecular orientation can be assumed to be uniform across the entire film thickness[6, 12]. Thus we can directly compare the dichroic differences for the LPUVL-exposed and rubbed films.

First let us discuss the cause of the decrease of the 1376 cm^{-1} band shown in Fig. 2(a). There are two processes that cause the decrease of the 1376 cm^{-1} band intensity. One is the direct decomposition of the $(OC)_2NC$ bonds of the CBDA-ODA (uncleaved) molecules. This process decreases the total number of $(OC)_2NC$ bonds (the sum of the numbers of the bonds of uncleaved and cleaved (maleimide) molecules) . The other process is the cleavage of the cyclobutane ring. In this process the decrease of the $(OC)_2NC$ bonds of uncleaved molecules is compensated by the increase of that of cleaved molecules. Thus the total number of the $(OC)_2NC$ bonds does not decrease. To identify the cause for the decrease of the 1376 cm^{-1} band, the sum of the absorbance of the 1376 and 1397

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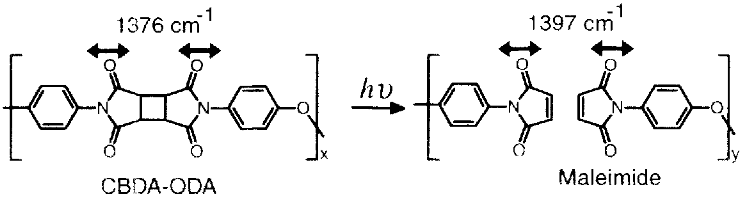

FIGURE 3 Molecular structure and photo-chemical reaction of CBDA-ODA. The polarization directions of the 1376 and 1397 cm^{-1} bands are indicated by the arrows.

cm^{-1} bands is plotted in Fig. 2(c). Since the widths of the two bands are the same, the peak absorbance of the two bands can be added. The sum is proportional to the total number of the $(OC)_2NC$ bonds. The average absorbance $(A_{\perp}+A_{//})/2$, which is shown by the crosses in Fig. 2(c), is almost constant up to ~ 1 J/cm^2. This result indicates that the decrease of the 1376 cm^{-1} band was caused by the cleavage of the cyclobutane ring. Therefore, we can determine the initial cleavage rate of the cyclobutane ring by fitting the LPUVL dependence of the 1376 cm^{-1} band up to 1 J/cm^2.

Before determining the initial cleavage rate of the cyclobutane ring, we describe the anisotropic cleavage of the cyclobutane ring and subsequent orientational randomization of the cleaved molecules. For the 1376 cm^{-1} band, $A_{//}$ decreases about two times faster than $A_{\perp}$. This shows that the cyclobutane ring of the backbone structure oriented parallel to the polarization direction of LPUVL is cleaved much more easily than that oriented perpendicular to it. As expected from this large anisotropy in the cyclobutane ring cleavage, the dichroic difference of the 1376 cm^{-1} band increases, and it exceeds the value for the rubbed film around 1 J/cm^2. On the other hand, both $A_{\perp}$ and $A_{//}$ of the 1397 cm^{-1} band initially increase with the same rate. The dichroic difference is nearly equal to zero. This result shows that the orientation of the maleimide molecule produced by the photo-induced cleavage of the cyclobutane ring is almost random. From the results of the 1376 and 1396 cm^{-1} bands, we found that the orientation of the maleimide molecule is randomized after the cleavage of the cyclobutane ring. The LPUVL exposure dependence of the 1501 cm^{-1} band (not shown here), which is assigned to the phenyl C-C stretching vibration, is similar to that shown in Fig. 2(c). From this result we see that the orientation of the phenyl ring adjacent to the maleimide molecule is also randomized in cleaving the cyclobutane ring. Therefore, for

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CBDA-ODA films the anisotropic orientation of the backbone structure arises from the anisotropic photo-induced cleavage of cyclobutane rings and the orientational randomization of cleaved molecules.

Now we will determine the initial cleavage rates $\beta_{//}$ and $\beta_{\perp}$ of the cyclobutane rings. The IR absorbance A of the 1376 cm^{-1} band is expressed by:

$$A = A_0 \int_0^{2\pi} \int_0^{\pi} (\hat{e}_{IR} \cdot \hat{c})^2 \cdot N(\theta, \phi, w) \sin\theta d\theta d\phi , \qquad (3)$$

where A_0 is a proportionality constant; and $\hat{e}_{IR}$ is the unit polarization vector of the IR light. The initial orientational distribution of the backbone directions of CBDA-ODA molecules was determined by measuring the incident angle dependence of the 1376 and 1501 cm^{-1} bands for the unexposed film[13]: $N(\theta,\phi, 0) = N_0 \cdot \exp[-(\theta-\pi/2)^2/\{2\cdot(\pi/4)^2\}]$, where N_0 is a proportionality constant. The product of A_0 and N_0 is fixed by the IR absorbance of the 1376 cm^{-1} band at $w = 0$. Thus the cleavage rates of the cyclobutane ring, $\beta_{//}$ and $\beta_{\perp}$, can be determined by fitting the LPUVL exposure dependence of the 1376 cm^{-1} band up to 1 J/cm^2.

We obtained good agreement between the calculated results and the experiment for $\beta_{//} = 0.70 \pm 0.02$ J$^{-1}\cdot$cm^2 and $\beta_{\perp} = 0.13 \pm 0.02$ J$^{-1}\cdot$cm^2. The solid curves in Fig. 2(a) are the best fit calculated results with $\beta_{//} = 0.70$ J$^{-1}\cdot$cm^2 and $\beta_{\perp} = 0.13$ J$^{-1}\cdot$cm^2. The ratio $\beta_{//}/\beta_{\perp}$ of the initial cleavage rates is 5.5 ± 0.5. Previously we determined the ratio $\beta_{//}/\beta_{\perp}$ of the decomposition rates of the phenyl ring of poly [4,4'-oxydiphenylene-pyromellitimide] (PMDA-ODA) for LPUVL of wavelength 266 nm: $\beta_{//}/\beta_{\perp} = 1.23 \pm 0.02$[6]. We see that the anisotropy of the cyclobutane ring cleavage is much greater than that of the phenyl ring decomposition of PMDA-ODA. Thus we see that the anisotropy of the photo-induced decomposition of polyimide molecules can be increased by replacing the pyromellitimide in the backbone structure with 1,2,3,4-cyclobutanetetracarboximide. This large anisotropy of the cyclobutane ring cleavage is the reason why the anisotropy of the molecular orientation of the LPUVL-exposed film exceeded that of the rubbed film.

CONCLUSION

We have determined the initial cleavage rates of the cyclobutane ring in the backbone structure of CBDA-ODA. The cleavage rates $\beta_{//}$ and $\beta_{\perp}$ for the LPUVL polarized parallel and perpendicular to the backbone direction are 0.70 ± 0.02 and 0.13 ± 0.02 $J^{-1}\cdot cm^{2}$, respectively. The anisotropy of the cyclobutane ring cleavage is much larger than that of the phenyl ring decomposition of PMDA-ODA. We found that the anisotropy of the photo-induced decomposition of polyimide molecules can be increased by replacing the pyromellitimide in the backbone structure with 1,2,3,4-cyclobutanetetracarboximide. The large anisotropy of the cyclobutane ring cleavage is advantageous to photo-induced LC alignment. By using $\beta_{//}$ and $\beta_{\perp}$ determined in this study, the LPUVL exposure condition for obtaining desired orientation of uncleaved molecules can be systematically deduced.

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