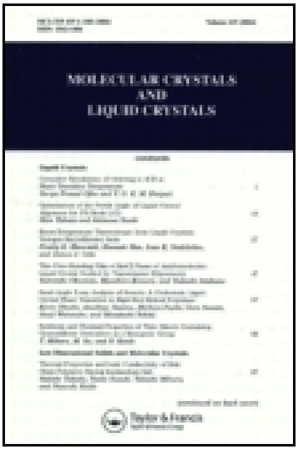

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Anisotropic Decomposition of Polyimide Molecules Induced by Irradiation of Linearly Polarized UV Light

Kiyoaki Usami [a], Kenji Sakamoto [a] & Sukekatsu Ushioda [a]

[a] Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan

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Anisotropic Decomposition of Polyimide Molecules Induced by Irradiation of Linearly Polarized UV Light

KIYOAKI USAMI, KENJI SAKAMOTO and SUKEKATSU USHIODA

Research Institute of Electrical Communication, Tohoku University
2–1–1 Katahira, Aoba-ku, Sendai 980–8577, Japan

We have investigated the anisotropic decomposition of polyimide (poly[bis(4,4′-oxydiphenylene)-dimetylmetyl-pyromellitimide]) molecules induced by exposure to linearly polarized ultraviolet light (LPUVL) of wavelength ~300 nm. The decomposition of the polyimide molecule was monitored by measuring the polarized infrared (IR) absorption spectra as a function of LPUVL exposure. We propose an empirical equation that describes the relation between the orientational distribution of polyimide chains and LPUVL exposure. We consider two decomposition rates $\beta_{//}$ and $\beta_{\perp}$ for the polyimide chains oriented parallel and perpendicular to the polarization direction of LPUVL, respectively. By taking account of the increase of the decomposition rates around 30 J·cm^{-2}, the IR absorption data could be reproduced with $\beta_{//}/\beta_{\perp} = 1.23 \pm 0.02$. The decomposition rate $\beta_{//}$ is $(4.5 \pm 1.0) \times 10^{-3}$J^{-1}·cm^{2} for the LPUVL exposure range up to ~30 J·cm^{-2}, and $(1.6 \pm 0.1) \times 10^{-2}$ J^{-1}·cm^{2} beyond ~30 J·cm^{-2}.

Keywords: liquid crystal; alignment film; polyimide; photo-induced decomposition reaction; infrared absorption; orientational distribution

INTRODUCTION

Recently photo-induced liquid crystal (LC) alignment[1-3] has received much attention as a promising alignment method that can potentially replace the conventional mechanical rubbing method. This is because the photo-induced alignment does not have the disadvantages associated with mechanical rubbing, such as creation of dust particles and generation of electrostatic charge. In the photo-induced alignment method one can control the azimuthal anchoring energy between the alignment film and LC by varying the exposure of light[4,5]. Furthermore this method is suitable for drawing a pattern of LC alignment[1]. The patterning capability is useful in the fabrication of multi-domain LC displays with a wide viewing angle[6-8]. Here we focus on a photo-induced alignment method based on photo-induced decomposition reactions[3]. This method is attractive in that the polyimide widely employed currently can be used as an alignment film material.

LC molecules in contact with a polyimide film exposed to linearly polarized ultraviolet light (LPUVL) align perpendicular to the polarization direction. This photo-induced alignment is explained as follows[3]. The polyimide chain oriented parallel to the polarization direction of LPUVL is broken more easily than that oriented perpendicular to it. Thus the orientational distribution of polyimide chains becomes anisotropic after LPUVL irradiation. Consequently the anisotropy of polyimide chains aligns LC molecules perpendicular to the polarization direction of LPUVL. Thus the control of the orientational distribution of polyimide chains is a key process for the photo-induced alignment method. In this paper we present an empirical equation that describes the relation between the orientational distribution of polyimide chains and LPUVL exposure. The equation is derived from the LPUVL exposure dependence of the infrared (IR) absorption spectra of a polyimide film. We find that the model proposed by Chen et al.[9], which is used for simulation of the orientational distribution of polyimide chains in the LPUVL-exposed film[5,10-12], is not applicable to actual polyimide films.

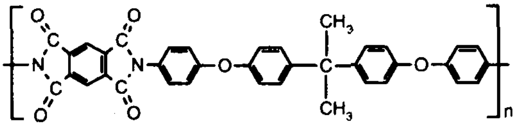

FIGURE 1 Molecular structure of polyimide (A1-PI) used in this study.

EXPERIMENT

The molecular structure of polyimide used in this study is shown in Fig. 1. Following the naming in our previous papers[13,14], this polyimide will be called "A1-PI" in this study. The A1-PI 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 250 °C for an hour in a nitrogen atmosphere. The film thickness was about 13 nm. The thickness and the molecular orientation of the A1-PI film were determined from the incident angle dependence of the polarized IR absorption of the phenyl C-C stretching vibration of the polyimide[15]. For such a very thin film, the variation of the squared electric field of LPUVL across the entire film thickness can be neglected[16]. Thus we can assume the A1-PI film to be decomposed uniformly by irradiation of LPUVL.

The A1-PI film was exposed to LPUVL using a 500 W deep UV lamp (Ushio Inc. UXM-501MD). The UV light passed through an interference filter (Andover Co. 297FS10-50) and a Gran-Taylor prism polarizer (Sigma Koki GYPC-20-17AN), and impinged on the A1-PI film along the surface normal. The interference filter is a bandpass filter with the center wavelength of 296.7 nm and the band width (FWHM) of 10 nm.

The IR absorption spectra were measured at normal incidence by a FT-IR spectrometer with a mercury cadmium telluride detector. For all the absorption measurements 400 spectral scans were averaged with a 4 cm^{-1} resolution. The absorption spectra for the IR light polarized

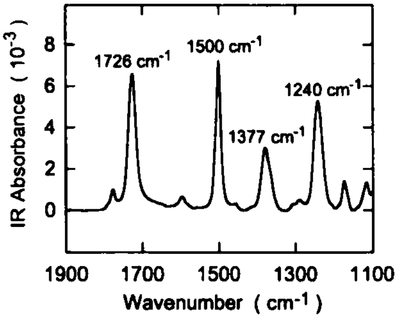

FIGURE 2 IR absorption spectrum of the A1-PI film.

parallel and perpendicular to the polarization of LPUVL were measured as a function of LPUVL exposure.

RESULTS

A1-PI has four strong IR absorption bands as shown in Fig. 2. The bands at 1240 cm^{-1}, 1377 cm^{-1}, and 1500 cm^{-1} are assigned to the C-O-C asymmetric stretching vibration, the C-N stretching vibration of the $(OC)_2NC$ bond, and the phenyl C-C stretching vibration, respectively. They are polarized along the polyimide chain. The polarization direction of the 1726 cm^{-1} band, which is assigned to the C=O asymmetric stretching vibration, is perpendicular to the polyimide chain[17].

The LPUVL exposure dependence of the IR absorption of the four strong bands is shown in Fig. 3. The vertical axis of Fig. 3 is the average absorbance $(A_{//}+A_{\perp})/2$, where $A_{\perp}$ and $A_{//}$ are the absorbance for the IR light polarized perpendicular and parallel to the polarization direction of LPUVL, respectively. All the absorption bands decrease in intensity with the increase of LPUVL exposure, although the reduction rates are different. Since the absorbance is proportional to the number of the corresponding chemical bonds, the observed LPUVL exposure

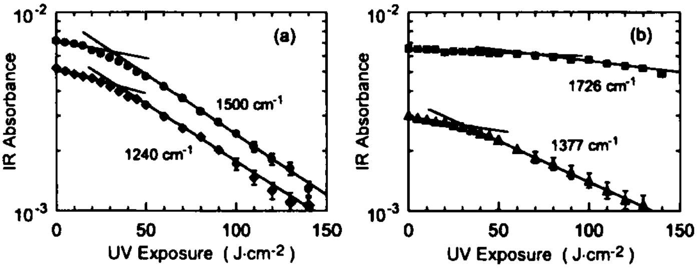

FIGURE 3 LPUVL exposure dependence of the IR absorbance. The solid diamonds and circles in (a) show the average absorbance $(A_{//}+A_{\perp})/2$ of the 1240 cm^{-1} and 1500 cm^{-1} bands, respectively. The solid triangles and squares in (b) are those of the 1377 cm^{-1} and 1726 cm^{-1} bands, respectively. The straight lines are the guide to the eye.

dependence indicates that the bond breaking occurs during the LPUVL irradiation. The relationship among the reduction rates is: 1500 cm^{-1} band ≈ 1240 cm^{-1} band > 1377 cm^{-1} band > 1726 cm^{-1} band. Thus we see that the phenyl C-C bond and the C-O-C ether linkage are broken more easily than the $(OC)_2NC$ and the C=O bonds. In addition, we see that the reduction rates increase by a factor of ~3 around 30 $J{\cdot}cm^{-2}$ for the IR bands polarized along the polyimide chain, and around 70 $J{\cdot}cm^{-2}$ for the 1726 cm^{-1} band. This indicates that the rate of bond breaking is not constant. The variation of the bond breaking rate must be taken into account in formulating an equation that describes the relation between the orientational distribution of the remaining polyimide chains and LPUVL exposure.

To monitor the decomposition of polyimide chains, hereafter we focus on the 1500 cm^{-1} band, which has the fastest reduction rate and is the strongest absorption band polarized along the polyimide chain. Figure 4(a) shows the LPUVL exposure dependence of the polarized IR absorption ($A_{\perp}$ and $A_{//}$) of the 1500 cm^{-1} band. Both $A_{\perp}$ and $A_{//}$ decrease

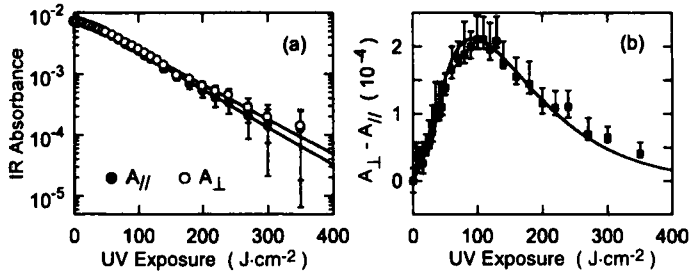

FIGURE 4 LPUVL exposure dependence of (a) the polarized IR absorbance and (b) the dichroic difference of the 1500 cm^{-1} band. The solid curves are the best fit calculated results using Eq. (2) with $\beta_{//}/\beta_{\perp} = 1.22$, $\beta_{//}^{(1)} = 4.5 \times 10^{-3}$ J^{-1}·cm^{2}, and $\beta_{//}^{(2)} = 1.55 \times 10^{-2}$ J^{-1}·cm^{2}.

monotonically with increasing LPUVL-exposure. Although $A_{//}$ decreases slightly faster than $A_{\perp}$, the difference between $A_{//}$ and $A_{\perp}$ is very small. To make the difference clear, the dichroic difference $A_{\perp}$-$A_{//}$ is plotted in Fig. 4(b). To minimize the experimental uncertainty, the dichroic difference was obtained by calculating the difference IR spectra at each LPUVL exposure. The IR dichroic difference increases initially as expected, but it decreases beyond ~100 J·cm^{-2}. The decrease of the dichroic difference is caused by the decrease of the remaining undamaged polyimide chains[16].

RELATION BETWEEN THE ORIENTATIONAL DISTRIBUTION OF POLYIMIDE CHAINS AND LPUVL EXPOSURE

To describe the dependence of the orientational distribution of polyimide chains on LPUVL exposure, two decomposition rates $\beta_{//}$ and $\beta_{\perp}$ are considered. They are the decomposition rates for the polyimide chains oriented parallel and perpendicular to the polarization direction of LPUVL, respectively. Since the thickness of the film used in this study was very thin (~13 nm), the variation of the squared electric field

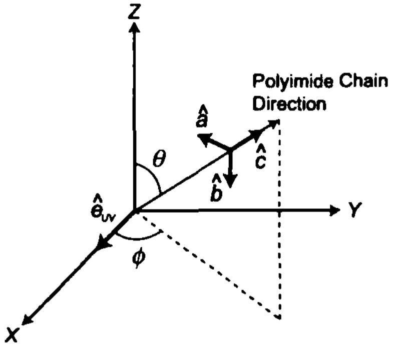

FIGURE 5 Definition of the coordinate system. θ and ϕ are the polar and azimuthal angles that specify the orientation of the polyimide chain direction ($\hat{c}$) with respect to the sample coordinates (*XYZ*). The Z axis is the surface normal. The *X* axis is defined by the polarization direction ($\hat{e}_{UV}$) of LPUVL.

of LPUVL in the film is negligible[16]. Thus the orientational distribution of the polyimide chains can be considered uniform across the entire film thickness even after LPUVL irradiation. Therefore the variation of the orientational distribution along the film thickness direction need not be considered here. The LPUVL exposure dependence of the orientational distribution is expressed by the following rate equation:

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

where $N(\theta, \phi, w)$ is the orientational distribution of the polyimide chain density; 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. 5; $\hat{c}$ is the unit vector of the polyimide chain direction that is defined by the polarization direction of the 1500 cm^{-1} band in this study; $\hat{a}$ 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 the irradiation energy density of LPUVL. By solving Eq. (1), we obtain:

$$\begin{aligned} N(\theta,\phi,w) = N(\theta,\phi,0)\exp[&-(\hat{e}_{UV}\cdot\hat{c})^2\cdot\int_0^w \beta_{//}dw \\ &-\{(\hat{e}_{UV}\cdot\hat{a})^2+(\hat{e}_{UV}\cdot\hat{b})^2\}\cdot\int_0^w \beta_{\perp}dw]. \end{aligned} \tag{2}$$

Here we allow $\beta_{//}$ and $\beta_{\perp}$ to be w-dependent. For A1-PI we have to use this form, because the decomposition rates increase around 30 J·cm^{-2} (see Fig. 3). When the decomposition rates are independent of w, Eq. (2) is simplified:

$$\begin{aligned} N(\theta,\phi,w) = N(\theta,\phi,0)\exp[&-\beta_{//}\cdot w\cdot(\hat{e}_{UV}\cdot\hat{c})^2 \\ &-\beta_{\perp}\cdot w\cdot\{(\hat{e}_{UV}\cdot\hat{a})^2+(\hat{e}_{UV}\cdot\hat{b})^2\}]. \end{aligned} \tag{3}$$

This form was applied for poly [4, 4'-oxydiphenylene-pyromellitimide] (PMDA-ODA)[16].

Next, we demonstrate that Eq. (2) can reproduce the experimental data shown in Fig. 4. The IR absorbance A of the 1500 cm^{-1} band is given by:

$$A = A_0\int_0^{2\pi}\int_0^{\pi}(\hat{e}_{IR}\cdot\hat{c})^2\cdot N(\theta,\phi,w)\sin\theta d\theta d\phi, \tag{4}$$

where A_0 is a proportionality constant; and $\hat{e}_{IR}$ is the unit polarization vector of the IR light. From the incident angle dependence of the 1500 cm^{-1} band for the unexposed A1-PI film, the initial orientational distribution of polyimide chains was found to be isotropic; i.e. $N(\theta, \phi, 0) = N_0/4\pi$, where N_0 is the number density of polyimide chains. Since the product of $A_{//}$ and $N_{//}$ is fixed by the IR absorbance of the 1500 cm^{-1} band at $w = 0$, the only adjustable parameters are the decomposition rates of the polyimide chain, $\beta_{//}$ and $\beta_{\perp}$. The decomposition rates increase by a factor of ~3 around 30 J·cm^{-2} as seen in Figs. 3(a) and 4(a). Thus in our fitting procedure β_i (i = // and ⊥) was set to $\beta_i^{(1)}$ for $w < w'$ and $\beta_i^{(2)}$ for $w \geq w'$. Here w' is the LPUVL exposure where the decomposition rates increase, and it should be around 30 J·cm^{-2}. In addition, the decomposition rate ratio $\beta_{//}/\beta_{\perp}$ was assumed to be constant over the entire measurement range of LPUVL exposure; i.e. $\beta_{//}^{(1)}/\beta_{\perp}^{(1)} = \beta_{//}^{(2)}/\beta_{\perp}^{(2)}$. This assumption is not crucial, because $\beta_{//}^{(1)}/\beta_{\perp}^{(1)}$ is insensitive for the fitting. Therefore, the parameters for the fitting are $\beta_{//}/\beta_{\perp}$, $\beta_{//}^{(1)}$, $\beta_{//}^{(2)}$, and w', which specify the dependence of $\beta_{//}$ and $\beta_{\perp}$ on LPUVL exposure.

The solid curves in Fig. 4 are the best fit calculated results with $\beta_{//}/\beta_{\perp} = 1.22$, $\beta_{//}^{(1)} = 4.5\times10^{-3}$ J^{-1}·cm^{2}, $\beta_{//}^{(2)} = 1.55 \times 10^{-2}$ J^{-1}·cm^{2}, and $w' =$ 30 J·cm^{-2}. The calculated results reproduce the experimental data extremely well. (We can obtain good agreement between the calculated results and the experiment for $\beta_{//}/\beta_{\perp} = 1.23 \pm 0.02$, $\beta_{//}^{(1)} = (4.5 \pm 1.0) \times 10^{-3}$ J^{-1}·cm^{2}, $\beta_{//}^{(2)} = (1.6 \pm 0.1) \times 10^{-2}$ J^{-1}·cm^{2}, and $w' = 30 \pm 5$ J·cm^{-2}.) The good agreement shown in Fig. 4 indicates that for actual polyimide films Eq. (2) is an appropriate expression in describing the relation between the orientational distribution of polyimide chains and LPUVL exposure. Recently, Chen et al. proposed a model for describing this relation[9]. Their model was used to simulate the orientational distribution of polyimide chains in LPUVL-exposed films[11]. They could explain the experimental data on the optical retardation of LPUVL-exposed films as well as the alignment and anchoring energy of the LC molecules in contact with them[5,10,12]. In their model the decomposition rate was assumed to be independent of LPUVL exposure, and $\beta_{\perp}$ was not taken into account. Thus it is obvious that their model cannot reproduce the LPUVL exposure dependence of the IR absorption shown in Fig. 4. We note that Chen's model is too simple to be applied to actual polyimide films. To simulate the orientational distribution for actual polyimide films, first one must determine the two decomposition rates $\beta_{//}$ and $\beta_{\perp}$ experimentally, and then use Eq. (2).

CONCLUSION

The polarized IR absorption spectra of a LPUVL-exposed polyimide film have been measured as a function of LPUVL exposure. We have proposed an empirical equation that describes the relation between the orientational distribution of polyimide chains and LPUVL exposure. The equation was derived by using the two decomposition rates $\beta_{//}$ and $\beta_{\perp}$ for the polyimide chains oriented parallel and perpendicular to the polarization direction of LPUVL, respectively. We have demonstrated that this empirical equation can reproduce the dependence of the IR absorption on LPUVL exposure. This shows that the empirical equation is appropriate in simulating the orientational distribution of polyimide chain in actual LPUVL-exposed films.

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