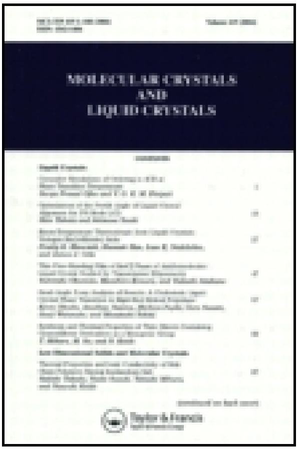

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Dichroism of a Polyimide Chain for Ultraviolet Light

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

[a] Research Institute of Electrical Communication, Tohoku University, Sendai, 980-8577, Japan

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Dichroism of a Polyimide Chain for Ultraviolet Light

KENJI SAKAMOTO, KIYOAKI USAMI, RYUICHI ARAFUNE
and SUKEKATSU USHIODA

*Research Institute of Electrical Communication,
Tohoku University Sendai 980–8577, Japan*

We have determined the absorption coefficient ratio $a_{//}/a_{\perp}$ of a poly [4, 4'-oxydiphenylene-pyromellitimide] (PMDA-ODA) chain in the wavelength range from 240 nm to 380 nm, where $a_{//}$ and $a_{\perp}$ are the absorption coefficients of the polyimide chain for ultraviolet (UV) light polarized parallel and perpendicular to the chain direction, respectively. To accomplish that, we have measured the polarized UV absorption spectra of a rubbed polyimide film whose molecular orientation was previously determined by polarized infrared absorption spectroscopy. The $a_{//}/a_{\perp}$ ratio becomes maximum in the wavelength region from 290 nm to 330 nm : $a_{//}/a_{\perp} \cong 5$. The absorption coefficient peaks at ~290 nm. These results sugest that linearly polarized UV light at 290 nm is most suitable for causing anisotropic decomposition of the polyimide chain. At 266 nm the $a_{//}/a_{\perp}$ ratio was compared with the ratio of the photoinduced decomposition rates of the polyimide chain oriented parallel and perpendicular to the polarization direction of UV light. The anisotropy of the photoinduced decomposition rates of the polyimide chain is much smaller than that of the UV absorption coefficients.

Keywords: photoinduced LC alignment; UV absorption; polyimide; liquid crystal

INTRODUCTION

Liquid crystal (LC) molecules in contact with a polyimide film irradiated with linearly polarized ultraviolet (LPUV) light align perpendicular to the polarization direction [1]. This photoinduced LC alignment does not have the disadvantages, such as creation of dust particles and generation of electrostatic charges, associated with conventional mechanical rubbing. Thus photoinduced LC alignment has recently received much attention as a promising alignment method that can replace the conventional mechanical rubbing method.

It is well known that the exposure of a polyimide film to LPUV light makes the film anisotropic, and that the anisotropy of polyimide film, to be exact, the anisotropy of the polyimide film *surface*, causes LC alignment [1,2]. The film anisotropy arises from anisotropic decomposition of the polyimide chain caused by LPUV light irradiation. The anisotropic decomposition of the polyimide chain originates from its dichroism of ultraviolet (UV) light absorption. Thus the dichroism of the polyimide chain in the UV range provides useful information for the photoinduced LC alignment technique.

In this study we have determined the dichroism of poly [4, 4'-oxydiphenylene-pyromellitimide] (PMDA-ODA) chain in the wavelength range from 240 nm to 380 nm. To accomplish that, we have to measure the polarized UV absorption spectra of a polyimide film with known anisotropic molecular orientation. Here we used a 10 nm-thick rubbed PMDA-ODA film on a CaF_2 substrate as a sample, because the anisotropic molecular orientation of the rubbed film can be determined by polarized infrared (IR) absorption spectroscopy [3].

BACKGROUND INFORMATION

In this section we present the background information for this study. First we describe the orientational distribution function of PMDA-ODA chain in rubbed films. Then we describe the theory that is used to determine the UV absorption coefficient ratio $a_{//}/a_{\perp}$ of the polyimide chain, where $a_{//}$ and $a_{\perp}$ are the absorption coefficients of the polyimide chain for UV light polarized parallel and perpendicular to the chain direction, respectively.

Orientational Distribution Function of the Polyimide Chain

The theory that is used to determine the orientational distribution of PMDA-ODA chain in rubbed films by polarized IR absorption spectroscopy was previously described in detail [3]. Here we only present the form of the orientational distribution function that is used in the theory.

Before we explain the orientational distribution function, we need to define the polyimide chain direction of PMDA-ODA. Figure 1 shows the unit

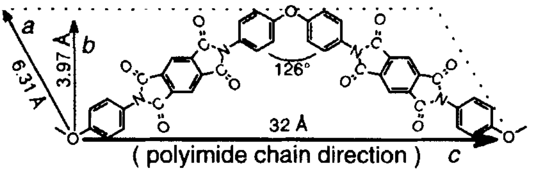

FIGURE 1 Local structure of a PMDA-ODA chain (the unit cell structure of the crystalline PMDA-ODA) [4].

cell structure of the crystalline PMDA-ODA. Although we consider our polyimide film to be amorphous in terms of long range order, the polyimide chain in our film may be assumed to have a similar local structure. The unit cell is orthorhombic with lattice parameters of 6.31, 3.97, and 32 Å along the *a*-, *b*-, and *c*-axes, respectively, and has a second-order helical axis along the *c*-axis. The C-O-C ether linkage angle is 126° [4]. Since the polyimide chain has a zigzag structure along the *c*-axis, we define the polyimide chain direction by the *c*-axis (the average direction of the zigzag polyimide chain).

To specify the orientational distribution function, we define two frames of reference with respect to the sample. One is the laboratory frame labeled by *X*, *Y*, and *Z*-axes, where the *Z*-axis is normal to the surface and the +*X*-direction is the rubbing direction. The other is the frame defined by the principal dielectric axes of the rubbed polyimide film, which are denoted by *x*, *y*, and *z*. Since the rubbed film has a mirror symmetry with respect to the *XZ*-plane, the two principal dielectric axes (*x*- and *z*-axes) lie in the *XZ*-plane. Thus, the *xyz*-coordinates are related to the *XYZ*-coordinates by a single parameter, the inclination angle θ_{incl} of the *x*-axis from the *XY*-plane. The rotation of the +*x*-axis toward the +Z-axis around the *Y*-axis is represented by a positive value of θ_{incl}.

The orientational distribution function $f(\theta,\phi)$ of the polyimide chain is defined with respect to the *principal dielectric axes*, and is assumed to have the following form:

$$f(\theta,\phi) = F\exp\left[-\frac{(\theta-\pi/2)^2}{2\sigma^2}\right]\cdot\left(1+\sum_{n=1}^{\infty}a_n\cos n\phi\right) , \qquad (1)$$

where F is a normalization constant, θ and ϕ are the polar and azimuthal angles that specify the polyimide chain direction, respectively, and σ is the standard deviation for variable θ. Although we express the azimuthal distribution by the Fourier cosine series in Eq.(1), the only term that contributes to the linear dielectric tensor is the cos 2ϕ term. The a_2 coefficient describes the orientational anisotropy of the polyimide chain between the x- and y-axes. A positive value of a_2 means that the polyimide chains are oriented on average along the x-axis. Under the distribution function of Eq.(1) the average inclination angle of the polyimide chain from the surface is represented by θ_{incl}. Thus the orientational distribution of the polyimide chain with respect to the *laboratory frame* is expressed by a_2, σ and θ_{incl}.

UV Dichroic Ratio of a Rubbed Polyimide Film

We consider a case where the variation of the electric field of UV light in a rubbed polyimide film is negligible over the entire film thickness. This is the case for this study. This situation can be realized by designing the sample structure (the polyimide film thickness and substrate material) [5]. At normal incidence the UV dichroic ratio $A_{//}/A_{\perp}$ of the rubbed polyimide film is given by:

$$\frac{A_{//}}{A_{\perp}}=\frac{a_{//}\left\langle\sin^2\Theta\cos^2\Phi\right\rangle+a_{\perp}\left\langle\cos^2\Theta\cos^2\Phi+\sin^2\Phi\right\rangle}{a_{//}\left\langle\sin^2\Theta\sin^2\Phi\right\rangle+a_{\perp}\left\langle\cos^2\Theta\sin^2\Phi+\cos^2\Phi\right\rangle}, \tag{2}$$

where $A_{//}$ and $A_{\perp}$ are the absorbance for UV light polarized parallel and perpendicular to the rubbing direction, respectively; Θ and Φ are the polar and the azimuthal angles that specify the orientation of the polyimide chain with respect to the *laboratory frame*. The angular brackets denote an average over the molecular orientation. When the orientational distribution of the polyimide chain in a rubbed film is known, one can calculate the four angular brackets in Eq.(2). Thus the UV absorption coefficient ratio $a_{//}/a_{\perp}$ of the polyimide chain can be determined by measuring the UV dichroic ratio of the rubbed film whose molecular orientation is already known.

EXPERIMENTAL

The PMDA-ODA film was spin-coated on a CaF_2 substrate (2 mm thick). The film was cured at 300°C for 2 hours in a nitrogen atmosphere. The film thickness deduced from the incident angle dependence of the IR absorption of the phenyl C-C stretching vibration [6] was 10 nm. The rubbing treatment was performed by a homemade rubbing machine. The rubbing condition was identical to that used in our previous study [3,7]. The molecular orientation of the rubbed film was determined by polarized IR absorption spectroscopy. The details of the IR absorption measurements were described elsewhere [7].

The polarized UV absorption spectra were measured by using Shimadzu SPG-100S spectrometer with a photomultiplier (Hamamatsu R928-09) as the light detector and a 150 W Xenon lamp as the light source. The spectral resolution was set at 3 nm. The UV light passed through a colored glass filter (Sigma Koki UTVAF-50S-33U) and a polarizer, and then impinged onto the rubbed film along the surface normal. The UV absorption spectra of the rubbed film were measured for both light polarized parallel and perpendicular to the rubbing direction. The colored glass filter was inserted to minimize the damage (decomposition) of the rubbed polyimide film during the UV absorption measurements. To check the damage, the IR absorption spectra of the rubbed film were measured before and after the UV absorption measurements. We could not detect any damage during the UV absorption measurements.

RESULTS AND DISCUSSION

We have first determined the molecular orientation of the rubbed polyimide film by measuring the IR dichroic ratio at normal incidence and the incident angle dependence of absorption of the phenyl C-C stretching vibration at 1500 cm^{-1}. Due to space limitations we only report the results here. The details of the determination procedure will be found in ref.[3,7]. The orientational distribution of polyimide chains in the rubbed film used in this study is specified by $a_2 = 0.37 \pm 0.02$, $\sigma = 18 \pm 5°$, and $\theta_{incl} = 9.5 \pm 1.5°$.

Figure 2(a) shows the polarized UV absorption spectra of the rubbed polyimide film measured at normal incidence. An absorption band at 287 nm

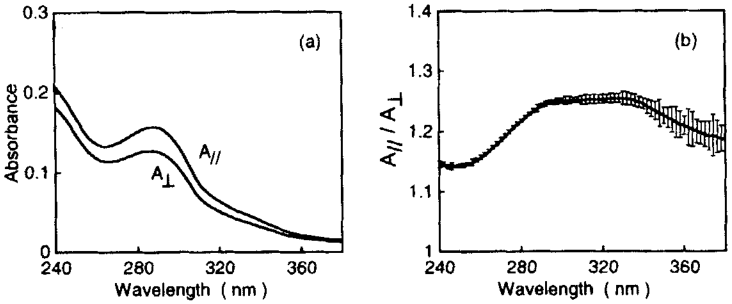

FIGURE 2 Polarized UV absorption spectra (a) and UV dichroic ratio $A_{//}/A_{\perp}$ (b) of the rubbed polyimide film measured at normal incidence. $A_{//}$ and $A_{\perp}$ are the absorbance for UV light polarized parallel and perpendicular to the rubbing direction, respectively. The solid curve in (b) is smoothed over 18 nm.

appears on the tail of strong absroption bands on the shorter wavelength side[8]. In the entire range of our measurement, $A_{//}$ is greater than $A_{\perp}$. Since the polyimide chains in the rubbed film align along the rubbing direction, this result indicates that $a_{//}$ is greater than $a_{\perp}$. Figure 2(b) shows the UV dichroic ratio $A_{//}/A_{\perp}$. The UV dichroic ratio has wavelength dependence, and becomes maximum, $A_{//}/A_{\perp} \cong 1.25$, in the region from 290 nm to 330 nm.

Figure 3 shows the absorption coefficient ratio $a_{//}/a_{\perp}$ of the polyimide chain that was calculated from Eq.(2). As expected from Fig.2(b), the $a_{//}/a_{\perp}$ ratio has a maximum value of ~ 5 in the wavelength region from 290 nm to 330 nm. If the anisotropy of the photoinduced decomposition of the polyimide chain is mainly determined by the $a_{//}/a_{\perp}$ ratio, this result shows that the anisotropy of the photoinduced decomposition depends on the wavelength of LPUV light. LPUV light in the wavelength region from 290 nm to 330 nm is effective in causing the anisotropic decomposition of the polyimide chain. Since the absorption coefficient peaks at ~290 nm, LPUV light at ~290 nm is the most efficient for inducing the anisotropic decomposition of the polyimide chain.

Recently we have investigated the surface anisotropy of a PMDA-ODA film irradiated with LPUV light at 266 nm, and we have determined the ratio

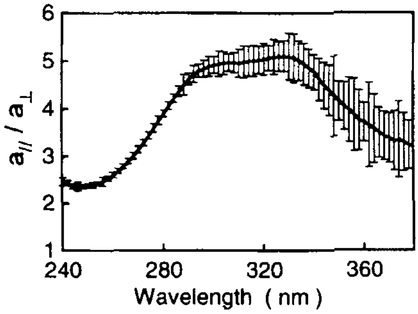

FIGURE 3 Absorption coefficient ratio $a_{//}/a_{\perp}$ of the PMDA-ODA chain. $a_{//}$ and $a_{\perp}$ are the absorption coefficients of the polyimide chain for UV light polarized parallel and perpendicular to the chain direction, respectively. The solid curve is smoothed over 18 nm.

(α/β) of the photoinduced decomposition rates of the polyimide chain: $\alpha/\beta = 1.23 \pm 0.02$ [5]. Here α and β are the decomposition rates of the polyimide chain oriented parallel and perpendicular to the polarization direction of LPUV light, respectively. The α/β ratio is the most important parameter in inducing the surface anisotropy of a polyimide film by irradiation of LPUV light. Thus it is very interesting to compare the $a_{//}/a_{\perp}$ ratio with the α/β ratios. From Fig.3 the $a_{//}/a_{\perp}$ ratio at 266 nm is 2.9 ± 0.1. From the comparison of these ratios, we found that the anisotropy of the photoinduced decomposition of the polyimide chain is significantly smaller than that of the UV absorption coefficients. This means that the surface anisotropy of the polyimide film actually induced by LPUV light irradiation is much smaller than that expected from the $a_{//}/a_{\perp}$ ratio.

When the α/β ratio is close to unity, it is quite difficult to obtain a polyimide film with large surface anisotropy and to control the surface anisotropy by UV light irradiation [5]. If the α/β ratio can be increased by selecting the wavelength of UV light, the controllability of the surface anisotropy by LPUV light irradiation should be improved. Thus we suggest that one should give more attention to the wavelength selection of LPUV light in controlling the surface anisotropy of a polyimide film by photoindiced decomposition.

CONCLUSION

We have determined the absorption coefficient ratio ($a_{//}/a_{\perp}$) of PMDA-ODA chain in the wavelength range from 240 nm to 380 nm. This was achieved by measuring the polarized UV absorption spectra of a rubbed polyimide film whose molecular orientation was previously determined by polarized IR absorption spectroscopy. The absorption coefficient ratio has wavelength dependence, and becomes maximum in the wavelength region from 290 nm to 330 nm. Since the absorption coefficient peaks at ~290 nm, we suggested that LPUV light at ~290 nm is most efficient for inducing anisotropic decomposition of the polyimide chain. The absorption coefficient ratio ($a_{//}/a_{\perp}$) was compared with the ratio (α/β) of the photoinduced decomposition rates of the polyimide chain at 266 nm. From the comparison we found that the surface anisotropy of the polyimide film actually induced by LPUV light irradiation is much smaller than that expected from the $a_{//}/a_{\perp}$ ratio.

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