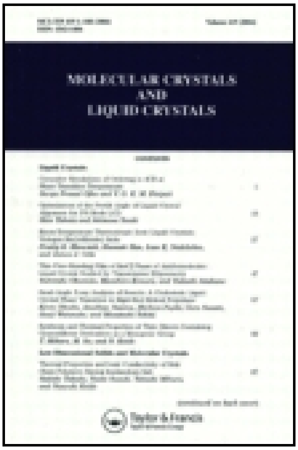

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In-plane Molecular Order of a Photo-oriented Polyamic Acid Film: Enhancement upon Thermal Imidization

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IN-PLANE MOLECULAR ORDER OF A PHOTO-ORIENTED POLYAMIC ACID FILM: ENHANCEMENT UPON THERMAL IMIDIZATION

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We have determined the in-plane molecular order of a polyamic acid (PAA) film irradiated with linearly polarized ultraviolet light (LPUVL), as well as that of the polyimide film obtained by thermally imidizing it. The PAA examined in this study contains azobenzene units in the backbone structure. The in-plane molecular order of the PAA and polyimide films was determined from the anisotropy in the polarized IR absorption of the phenyl C-C stretching vibration polarized along the backbone structure. We found that the photo-induced anisotropy in the in-plane molecular orientation was small, but it increased significantly after thermal imidization; i.e. the in-plane molecular order of the polyimide film was much greater than that of the PAA film. The enhancement of the in-plane molecular order was tentatively attributed to the crystallization of the film caused by thermal imidization

Keywords: azobenzene; in-plane molecular orientation; liquid crystal; photoinduced alignment; polarized IR absorption; polyimide

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1. INTRODUCTION

Recently, photoinduced alignment methods of liquid crystal (LC) molecules have received much attention as an alternative to the conventional rubbing technique, which is currently used in the fabrication of LC displays. This is because photoinduced alignment methods do not have drawbacks, such as creation of dust particles and generation of electrostatic charges, associated with mechanical rubbing. Until now several photoinduced alignment methods have been reported. They are based on photoinduced dimerization [1], isomerization [2,3], and decomposition [4,5] reactions. Among them, photoinduced alignment methods using polyimide as an alignment layer material are particularly attractive, because polyimides are already widely used in today's LC displays. Use of polyimide alignment layers is expected to bring about a smooth transition from the conventional rubbing technique to a photoinduced alignment technique in the manufacturing process.

We are interested in the alignment method that uses photo-isomerization reaction of polyamic acid (PAA) with azobenzene units in the backbone structure. In this method that was recently reported by Park *et al.* [6], a PAA film is irradiated with ultraviolet (UV) light to induce anisotropic molecular orientation. Permanent angular reorientation of the PAA chain occurs through multiple cycles of the trans-cis and cis-trans isomerization of the azobenzene unit. Then the UV-irradiated PAA film is converted into a polyimide film by a thermal imidization process. The LC alignment induced by the polyimide film was reported to be thermally and optically stable. In addition inclined uniform alignment of LC molecules was achieved by oblique angle irradiation of un-polarized UV light. Although the pretilt angle (the average tilt angle of the LC molecules measured from the film surface) was too small (0.17°) [6], this alignment method is quite promising as an alternative to the conventional rubbing technique.

Park *et al.* [6] investigated the orientational change of the PAA chains with azobenzene units in the backbone structure induced by irradiation of linearly polarized UV light (LPUVL). The PAA film exposed to LPUVL was reported to have only small anisotropy in the in-plane molecular orientation. However, the molecular orientation of the film after thermal imidization was not reported. In this study we have determined the in-plane molecular order of a PAA film irradiated with LPUVL and a polyimide film obtained by thermally imidizing it. We found that the photoinduced anisotropy in the in-plane molecular orientation was significantly enhanced by thermal imidization. Although the photoinduced in-plane anisotropy of the PAA film was small, we obtained the polyimide film with in-plane anisotropy much greater than that induced by rubbing.

2. EXPERIMENT

Figure 1 shows the molecular structure of PAA used in this study and that of polyimide obtained after thermal imidization. This PAA has a different molecular structure from that used by Park *et al.* [6]. The PAA film was spin-coated on a CaF_2 substrate (2 mm thick), and then it was exposed to LPUVL of wavelength 365 to 400 nm at normal incidence. The LPUVL exposure was $79\,J/cm^2$. The film thickness determined by ellipsometry was 22 nm. Then the PAA film was cured at 250°C for an hour in a nitrogen atmosphere to convert it into a polyimide film. The film thickness was reduced to 15 nm. The molecular orientation of the PAA and polyimide films was determined by measuring their polarized infrared (IR) absorption spectra at normal incidence with a $4\,cm^{-1}$ resolution.

By polarized microscope and polarized IR absorption measurements performed for an LC cell filled with 4-n-pentyl-4′-cyanobiphenyl (5CB), we confirmed that the polyimide film induced uniform alignment of LC molecules. The average molecular orientation of the LC molecules was parallel to the film surface and perpendicular to the polarization direction of LPUVL.

3. RESULTS AND DISCUSSION

The polarized IR absorption spectra of the PAA film exposed to LPUVL at $79\,J/cm^2$ are shown in Figure 2. Figure 3 shows the IR absorption spectra of the polyimide film that was obtained by thermally imidizing the PAA film. $A_{\parallel}$ and $A_{\perp}$ are the absorption spectra for the IR light polarized parallel and perpendicular, respectively, to the polarization direction of LPUVL. To determine the molecular orientation, we focused on the $1595\,cm^{-1}$ band for the PAA film and the $1501\,cm^{-1}$ band for the polyimide film. These bands are assigned to different modes of the phenyl C-C stretching vibration, but both bands are polarized along the corresponding backbone structures [7,8]. For the PAA film ($1595\,cm^{-1}$ band), $A_{\perp}$ is greater than $A_{\parallel}$, but the difference between them is very small: $A_{\perp} = 0.0045$ and $A_{\parallel} = 0.0039$.

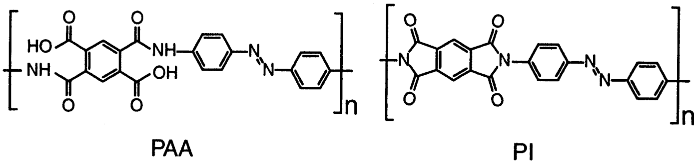

FIGURE 1 Molecular structures of PAA used in this study and polyimide (PI) obtained by thermal imidization of PAA.

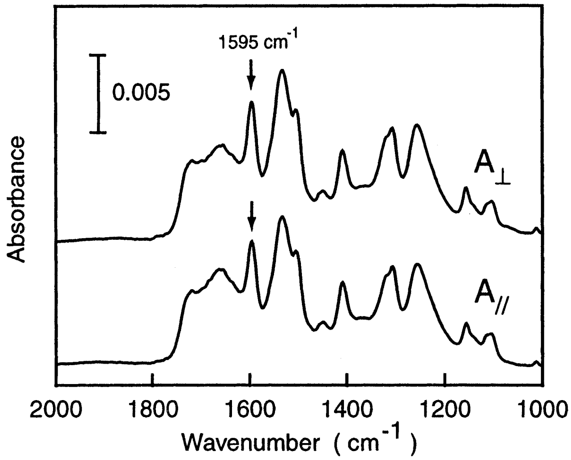

FIGURE 2 Polarized IR absorption spectra of the PAA film exposed to LPUVL at 79 J/cm^2. $A_\perp$ and $A_{||}$ are the absorption spectra for the IR light polarized perpendicular and parallel to the polarization direction of LPUVL, respectively.

The small anisotropy in the polarized IR absorption is consistent with the result of polarized UV absorption reported by Park *et al.* [6]. This result shows that the photoinduced angular reorientation of the PAA chain occurs with a low efficiency.

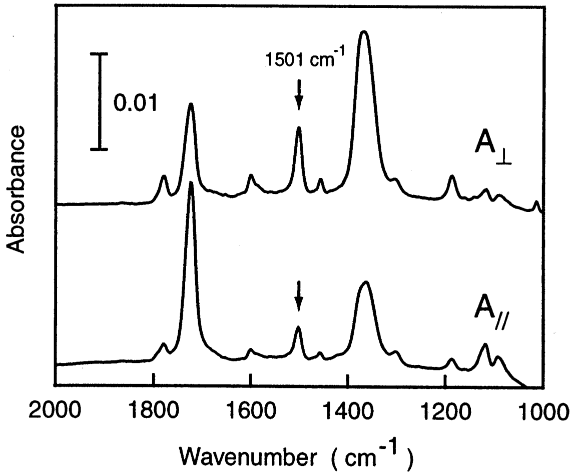

FIGURE 3 Polarized IR absorption spectra of the polyimide film obtained by thermally imidizing the PAA film exposed to LPUVL at 79 J/cm^2. The meanings of $A_\perp$ and $A_{||}$ are the same as in Figure 2.

In contrast to the PAA film, $A_{\perp}$ is much greater than $A_{\parallel}$ for the polyimide film ($1501\,\mathrm{cm}^{-1}$ band): $A_{\perp} = 0.0068$ and $A_{\parallel} = 0.0033$. It is evident from Figures 2 and 3 that the in-plane anisotropy in the molecular orientation was enhanced by thermal imidization. To consider the in-plane order of the PAA and polyimide chains quantitatively, we introduce the in-plane molecular order parameter Q_{ϕ} defined by $(A_{\perp} - A_{\parallel})/(A_{\perp} + A_{\parallel})$ [9,10]. Here, $Q_{\phi} = 0$ means isotropic in-plane molecular orientation, and $Q_{\phi} = 1$ and -1 mean that all polymer chains align perpendicular and parallel, respectively, to the polarization direction of LPUVL. Q_{ϕ} determined from the anisotropy in the polarized IR absorption was 0.07 for the PAA film and 0.35 for the polyimide film. We see that Q_{ϕ} increased by a factor of 5 by thermal imidization. The increase of Q_{ϕ} shows that the backbone structures are self-aligned during the thermal imidization process, becoming parallel to each other. Previously Kikuchi *et al.* reported that a well-oriented crystalline structure of polyimide, poly(p-phenylene biphenyltetracarboximide) (BPDA-PDA), was produced by thermal imidization of an amorphous PAA film that was slightly stretched [11]. This means that the slightly anisotropic orientation of the PAA chains in the film is markedly enhanced by thermal imidization. Since the same effect should occur to our film, we attribute the enhancement of molecular orientation by thermal imidization to the crystallization of the PAA film that initially has slightly anisotropic molecular orientation.

Finally, we compare the in-plane anisotropy of the polyimide film induced by LPUVL irradiation and that induced by mechanical rubbing. To determine Q_{ϕ} of a rubbed polyimide film of the same molecular composition, we measured the polarized IR absorption spectra of a rubbed polyimide film (6 nm thick) on a CaF_2 substrate. The rubbing condition was identical to that reported in our previous work [12,13]. Since the region affected by rubbing is $\sim 12\,\mathrm{nm}$ from the surface for the present rubbing condition [13,14], we can assume that the rubbed film has a uniform molecular orientation across the entire film thickness. Thus Q_{ϕ} of the rubbed film determined from the polarized IR absorbance can be directly compared with that of the LPUVL-exposed film. Figure 4 shows the polarized IR absorption spectra of the rubbed film. Q_{ϕ} of the rubbed film was 0.19. For reference, we note that Q_{ϕ} of rubbed films of polyimides with different molecular structures was reported to be between 0.08 and 0.14 [15]. Thus we see that the photo-alignment process used in this study can induce the in-plane molecular order of the polyimide film greater than that induced by rubbing. We found that the enhancement of the in-plane molecular order caused by thermal imidization plays an important role in the realization of polyimide films with large in-plane anisotropy.

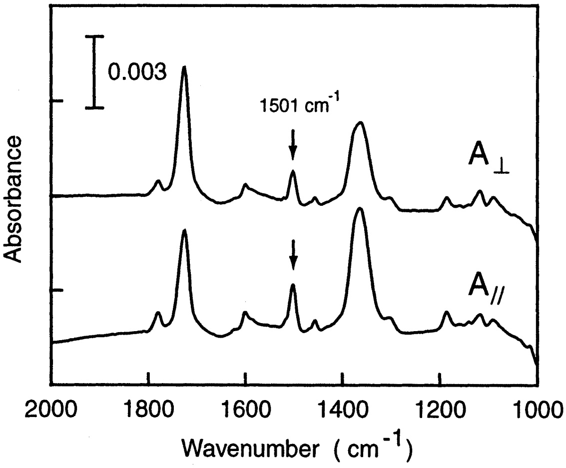

FIGURE 4 Polarized IR absorption spectra of the rubbed polyimide film (6 nm thick). $A_{\perp}$ and $A_{||}$ are the absorption spectra for the IR light polarized perpendicular and parallel to the rubbing direction, respectively.

4. CONCLUSION

We have determined the in-plane molecular order of the PAA film, with azobenzene units in the backbone structure, induced by LPUVL irradiation of $79\,\mathrm{J/cm^2}$ as well as that of the film obtained by thermally imidizing the PAA film. We found that the photoinduced in-plane molecular order of the PAA film was small, but it increased significantly by subsequent thermal imidization. The in-plane molecular order after thermal imidization exceeded that induced by rubbing. The enhancement of the in-plane molecular order was tentatively attributed to the crystallization of the film caused by thermal imidization. The realization of polyimide films with large in-plane anisotropy suggests that the alignment method used in this study is potentially promising as an alternative to the conventional rubbing technique.

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