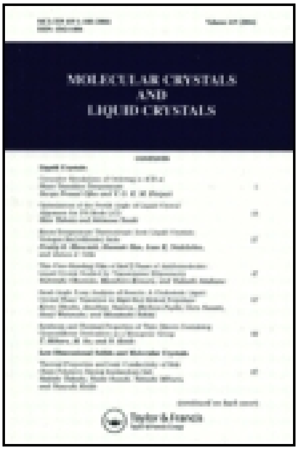

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Polyimide Photo-Alignment Films Applicable to Poly[(9,9-Dioctylfluorenyl-2,7-Diyl)-Co-Bithiophene]

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We have succeeded in forming highly oriented poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-bithiophene] (F8T2) layers by using photo-aligned polyimide films. The polyimide (Azo-PI) contains azobenzene in the backbone structure, which allows us to optically control the alignment of the backbone structure. The photo-aligned Azo-PI films were stable to xylene (a solvent of F8T2) and to annealing at a liquid-crystalline temperature of F8T2. After annealing at 285°C for 15 min followed by quenching to room temperature, the ~20 nm-thick F8T2 layer on the photo-aligned Azo-PI film showed a dichroic ratio of ~14 at 490 nm (the absorption maximum), indicative of a high degree of alignment of F8T2. We conclude that the photo-aligned Azo-PI films are proper alignment films for F8T2.

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Keywords: azobenzene; liquid-crystalline polymers; photo-alignment; photo-isomerization; polyfluorene derivatives; polyimide

1. INTRODUCTION

Poly[9,9-dioctylfluorenyl-2,7-diyl]-co-(bithiophene)] (F8T2) has received much attention as an active layer material of polymer-based field effect transistors (FET's), because of its relatively high charge carrier mobility [1], excellent thermal stability, and ease of thin film formation by wet processes, such as spin-coating and ink-jet printing [2]. The charge carrier mobility can be significantly enhanced by aligning the F8T2 backbone structures [1]. Thus the alignment control is of great importance for improving the switching frequency of polymer-based FET's. Since F8T2 is a liquid-crystalline polymer, its uniaxial alignment can be achieved by depositing F8T2 onto a proper alignment film and then heating the sample to the liquid-crystalline phase [3]. F8T2 has a liquid-crystalline phase above 265°C [1,3–5]. Thus excellent thermal stability is required for the alignment film. Therefore, rubbed polyimide films are often used as alignment films for F8T2 [1–4,6,7], because of the excellent thermal and chemical stability of polyimide [8].

The rubbing technique is widely used to induce anisotropic molecular orientation of polyimide films due to its simplicity and short processing time. However, it has serious drawbacks, such as the creation of dust particles and scratches on the alignment film surface, generation of electrostatic charge, and poor alignment uniformity [9], associated with the mechanical contact between the rubbing cloth and the alignment film surface. Therefore, the development of contact-free alignment techniques is strongly desired.

We are focusing on a photo-alignment method applicable to polyimide films as a contact-free alignment technique. This is because photo-alignment has potential capability for alignment patterning, which is useful in integrating FET's with different source-drain directions in a limited area. In this alignment method, polyamic acid (Azo-PAA) containing azobenzene in the backbone structure, which is the precursor of the corresponding polyimide (Azo-PI), is used as the alignment film material [10,11]. Photo-alignment treatment is performed on the Azo-PAA films. Under irradiation with linearly polarized ultraviolet light (LPUVL), the Azo-PAA backbone structure rotates toward the plane perpendicular to the polarization of the LPUVL. This rotation occurs through random rotation of azobenzene accompanied by its trans-cis-trans photo-isomerization cycle as described previously [11]. After sufficient LPUVL irradiation, the Azo-PAA backbone structure aligns on average perpendicular to the polarization direction of the LPUVL. By imidizing the photo-aligned Azo-PAA film thermally, we can obtain the polyimide photo-alignment film.

Very recently, we have reported that the photo-aligned Azo-PI film is an excellent alignment film for poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) [12,13]. PFO shows the liquid-crystalline phase between ~160 and ~275°C [5,14,15], while the liquid-crystalline phase of F8T2 appears above 265°C. Thus more stringent thermal stability is required for the alignment films for F8T2 than those for PFO. Therefore, in this study we have investigated thermal stability of the photo-aligned Azo-PI film and its alignment ability for F8T2. The tolerance of the photo-aligned Azo-PI film to xylene, which is often used as a solvent of F8T2, has also been examined.

2. EXPERIMENT

Figures 1(a) and (b) show the molecular structure of Azo-PAA and Azo-PI, respectively, used in this study. The polystyrene equivalent weight average molecular weight and the polydispersity of Azo-PAA were $M_w = 24600$ and 2.9, respectively, which were determined by gel permeation chromatography (Shimadzu GPC system). The Azo-PAA film was made on a quartz substrate by spin-coating with a filtered solution of Azo-PAA (1.6 wt.%) in N-methyl-2-pyrrolidone at 3000 rpm for 60 s. Photo-alignment treatment was performed on the

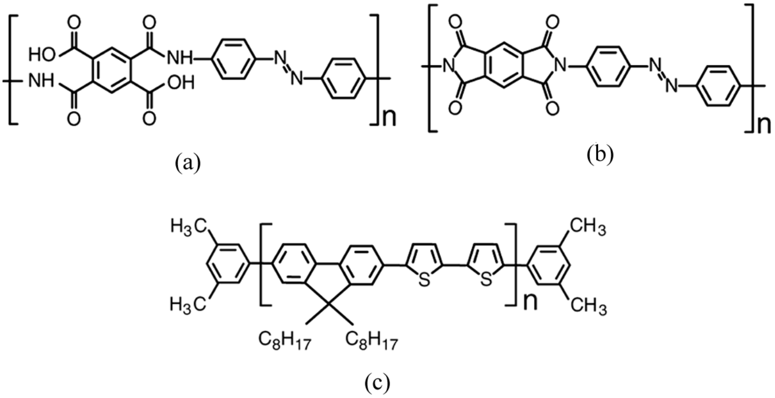

FIGURE 1 Molecular structure of (a) Azo-PAA, (b) Azo-PI, and (c) F8T2 used in this study.

Azo-PAA film using a 500 W deep UV lamp (Ushio Inc. UXM-501MD) as the light source. The wavelength was selected with a band-pass filter of transmission wavelength 340–500 nm (Asahi Spectra Co., Ltd.). To produce linear polarization, a Glan-Taylor prism polarizer was used. The linearly polarized light (LP-L) impinged on the Azo-PAA film at normal incidence. The LP-L exposure was 39 J/cm^2. After the photo-alignment treatment, the Azo-PAA film was thermally imidized at 250°C for 2 h in a nitrogen atmosphere. The thickness of the Azo-PI film was 11 nm. To determine the molecular orientation of the Azo-PI film, the polarized UV-visible absorption spectra were measured at normal incidence in a transmission geometry before deposition of F8T2. Our spectrometer system for the absorption measurements was described previously [13].

F8T2 end-capped with 3,5-dimethylphenyl purchased from American Dye Source, Inc. was used as received. The molecular structure is shown in Figure 1(c). The polystyrene equivalent weight average molecular weight and the polydispersity were $M_w = 44200$ and 4.8, respectively, which were determined with a JASCO GPC system. The 20 nm-thick F8T2 layer was formed on the Azo-PI films by spin-coating with a filtered xylene solution of F8T2 (0.75 wt.%) at 2000 rpm for 60 s. To induce uniaxial alignment of F8T2, the sample was annealed at 285°C for 15 min and then quenched to room temperature. This thermal treatment was performed in a nitrogen atmosphere to prevent thermal oxidation of F8T2 and Azo-PI. The molecular orientation of the F8T2 layer was also determined by measuring the polarized UV-visible absorption spectra at normal incidence.

The thermal stability of Azo-PI was examined using a thermogravimetric analyzer (SII TG/DTA 6200) with a PC station (SII EXSTAR 6000). The thermogravimetric analysis (TGA) was carried out from room temperature to 600°C at a heating rate of 10°C/min under a nitrogen gas stream (300 ml/min). The TGA sample was prepared by pouring the Azo-PAA solution into an aluminum pan and then baking it at 250°C for 2 h in a nitrogen atmosphere. The initial weight of Azo-PI was 8.13 mg.

3. STABILITY OF PHOTO-ALIGNED AZO-PI FILMS

We need to anneal the F8T2/Azo-PI/quartz sample at 285°C to induce uniaxial alignment of F8T2. Thus we first examined the thermal stability of Azo-PI itself. The TGA curve of Azo-PI is shown in Figure 2. No weight loss of Azo-PI occurred below 330°C, and even at 400°C the weight loss was only 1.5%. Beyond this temperature, significant weight loss due to thermal decomposition was observed. From this

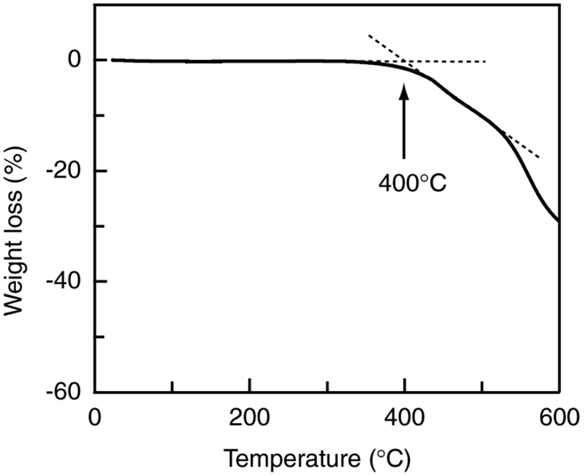

FIGURE 2 TGA curve of Azo-PI measured at a heating rate of 10°C/min under nitrogen gas stream (300 ml/min). The initial weight of Azo-PI was 8.13 mg.

result we see that the thermal stability of Azo-PI is sufficiently high for an alignment film material for F8T2. For reference, we would like to note here that the thermal stability of Azo-PI is inferior to that of a most well-known polyimide, poly [4,4′-oxydiphenylene-pyromellitimide] (PMDA-ODA). The weight loss of PMDA-ODA was reported to be less than 1.5% even at 500°C [8].

Next, we examined the stability of the photo-induced alignment of the Azo-PI backbone structure to xylene, and to annealing at 285°C for 15 min. Figure 3(a) shows the polarized UV-visible absorption spectra of the photo-aligned Azo-PI film. Here, $A_\perp^{PI}$ and $A_\parallel^{PI}$ are the absorption spectra for the light polarized perpendicular and parallel, respectively, to the polarization direction of the LP-L used in the photo-alignment treatment. A strong absorption band was observed at 351 nm, which is assigned to the π–π^* transition of azobenzene in the Azo-PI backbone structure [16]. Since the transition dipole is polarized along the backbone structure, the dichroic ratio $A_\perp^{PI}/A_\parallel^{PI}$ reflects the anisotropy in the in-plane orientation of the Azo-PI backbone structure. From $A_\perp^{PI}/A_\parallel^{PI} = 2.0$, we see that the Azo-PI backbone structures align on average perpendicular to the polarization direction of the LP-L.

To check the tolerance of the alignment of the Azo-PI backbone structure to xylene, the photo-aligned Azo-PI film was washed in

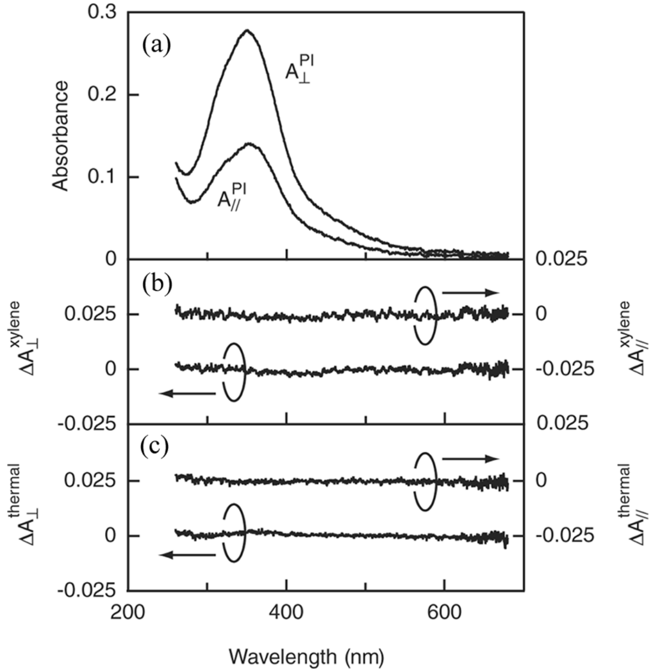

FIGURE 3 (a) Polarized UV-visible absorption spectra of the photo-aligned Azo-PI film. The LP-L exposure in photo-alignment treatment was 39 J/cm^2. $A_{\perp}^{PI}$ and $A_{\parallel}^{PI}$ are the absorption spectra for the light polarized perpendicular and parallel, respectively, to the polarization direction of the LP-L. (b) Difference spectra defined by $\Delta A_i^{xylene} = A_i^{xylene} - A_i^{PI}$, where A_i^{xylene} are the polarized absorption spectra taken after ultrasonic agitation in xylene for 5 min, and $i = \perp$ and $\parallel$. (c) Difference spectra defined by $\Delta A_i^{thermal} = A_i^{thermal} - A_i^{xylene}$, where $A_i^{thermal}$ are the polarized absorption spectra taken after annealing at 285°C for 15 min followed by quenching to room temperature.

xylene with an ultrasonic cleaner for 5 min. Then the polarized absorption spectra A_i^{xylene} were measured, where i is $\perp$ and $\parallel$. The difference spectra, $\Delta A_i^{xylene} = A_i^{xylene} - A_i^{PI}$, of each polarization are shown in Figure 3(b). No change was observed in the absorption spectra of each polarization before and after the xylene treatment. This result indicates that the alignment of the Azo-PI backbone structure is not influenced by the xylene treatment; i. e. the photo-aligned Azo-PI film has high tolerance to xylene. In other words, the alignment of the Azo-PI backbone structure is not influenced by spin-coating with a xylene solution of F8T2.

To confirm the thermal stability of the alignment of the Azo-PI backbone structure, the photo-aligned Azo-PI film was annealed at 285°C for 15 min in a nitrogen atmosphere and subsequently quenched to room temperature. Then the polarized absorption spectra $A_i^{thermal}$ were measured. Figure 3(c) shows the difference spectra defined by $\Delta A_i^{thermal} = A_i^{thermal} - A_i^{xylene}$, indicating that the molecular orientation of the photo-aligned Azo-PI film does not change by the thermal treatment. From the experimental results shown in Figures 2 and 3, we conclude that the photo-aligned Azo-PI films have sufficient thermal and chemical stability as alignment films for F8T2.

4. ALIGNMENT OF F8T2 INDUCED BY PHOTO-ALIGNED AZO-PI FILMS

The polarized absorption spectra, $A_\perp^{F8T2}$ and $A_\parallel^{F8T2}$, of the F8T2 layer formed on the photo-aligned Azo-PI film were measured before and after the thermal treatment (annealing at 285°C for 15 min followed by quenching to room temperature). They are shown in Figures 4(a) and (b), respectively. The absorption spectra were obtained by subtracting those of the Azo-PI film shown in Figure 3(a) from those of the whole sample. The strong absorption in the wavelength region from 300 nm to 600 nm is assigned to the π–π^* transitions of the F8T2 backbone structure, which are polarized along the backbone structure [1].

Before the thermal treatment, no remarkable polarization dependence was observed in absorption, as shown in Figure 3(a). This result indicates that the in-plane orientation of the F8T2 backbone structures is almost random in the as-spin-coated layer. Looking carefully at the absorption spectra in Figure 3(a), it can be seen that small spectral difference exists between $A_\perp^{F8T2}$ and $A_\parallel^{F8T2}$. The spectral difference arises in part from the strong dielectric dispersion of the underlying Azo-PI film due to the strong absorption of azobenzene. It distorts the absorption spectra of the overlying F8T2 layer. Since the photo-aligned Azo-PI film has in-plane anisotropy ($A_\perp^{PI}/A_\parallel^{PI} = 2.0$), the spectral distortion is dependent on the polarization direction. Here, we will not discuss the small spectral difference further, because it does not purely reflect the orientational anisotropy of the F8T2 backbone structure as explained above.

After the thermal treatment, we observed large in-plane anisotropy in absorption, as shown in Figure 3(b). The dichroic ratio defined by $A_\perp^{F8T2}/A_\parallel^{F8T2}$ was $\sim$14 at 490 nm (the absorption maximum). This dichroic ratio corresponds to a uniaxial molecular order parameter of $\sim$0.81 ($= (A_\perp^{F8T2} - A_\parallel^{F8T2})/(A_\perp^{F8T2} + 2A_\parallel^{F8T2})$), indicative of a high

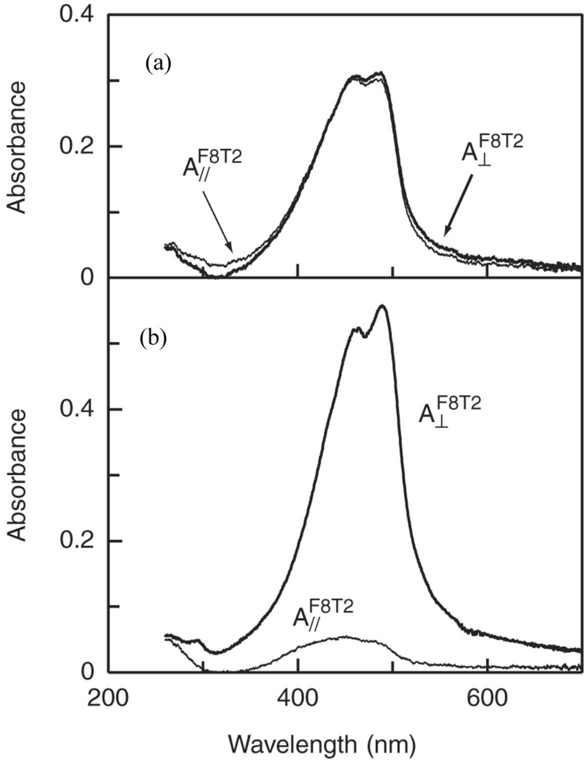

FIGURE 4 Polarized UV-visible absorption spectra, $A_{\perp}^{F8T2}$ (thick curve) and $A_{\parallel}^{F8T2}$ (thin curve), of the F8T2 layer formed on the photo-aligned Azo-PI film. (a) The spectra of the as-spin-coated layer. (b) The spectra taken after annealing at 285°C for 15 min followed by quenching to room temperature. The absorption spectra shown in this figure were obtained by subtracting those of the Azo-PI film shown in Figure 3(a) from those of the whole sample.

degree of alignment. As already discussed in our previous letter [12], the main role of the underlying Azo-PI film is to determine the preferential alignment direction of 'hairy-rod' type liquid-crystalline polymers, such as PFO and F8T2. The preferential alignment direction is the average orientation direction of the Azo-PI backbone structure. The degree of alignment of the liquid crystalline polymers is determined by their self-organization in the liquid crystalline phase. Thus a uniaxial order parameter of 0.81 must reflect the molecular ordering of F8T2 in the liquid crystalline phase. This is the reason why the dichroic ratio (~14) of the F8T2 layer is much higher than that (2.0) of the underlying Azo-PI film. Indeed, $A_{\perp}^{F8T2}/A_{\parallel}^{F8T2}$ is ~14 regardless of $A_{\perp}^{PI}/A_{\parallel}^{PI}$ for $A_{\perp}^{PI}/A_{\parallel}^{PI} \geq 2.0$ as seen from Figure 5, which supports the above discussion. The LP-L exposure dependence of $A_{\perp}^{PI}/A_{\parallel}^{PI}$ and $A_{\perp}^{F8T2}/A_{\parallel}^{F8T2}$ shown in Figure 5 is very similar to that previously reported for the glassy PFO layers on the photo-aligned Azo-PI films, and the detailed discussion was described in ref. [17]. Thus, here we only note that the photo-aligned Azo-PI film with $A_{\perp}^{PI}/A_{\parallel}^{PI} \geq 2.0$ must be used to realize a high degree of alignment of F8T2.

The dichroic ratio of ~14 is higher than that reported previously for the F8T2 layers formed on rubbed polyimide films, which is in the range from 5 to 12 [1,3,4,6,7]. This result might suggest that the photo-aligned Azo-PI films have excellent alignment ability for F8T2 compared to rubbed polyimide films. However, it is pointed out that the degree of alignment of F8T2 is influenced by many factors, such as its molecular weight and polydispersity [4], the layer thickness, and details of the thermal and rubbing treatment [1]. Thus we must evaluate the alignment ability to the exclusion of their influence. To accomplish that, the F8T2 layer was formed on a rubbed PMDA-ODA film in the same procedure, and the polarized UV-visible absorption spectra were measured. The thickness of the PMDA-ODA film was 17 nm, and the rubbing condition was the same as that described in our previous papers [18,19]. The dichroic ratio for the rubbed PMDA-ODA sample was ~15 at 490 nm, which was slightly higher than that (~14) for the photo-aligned Azo-PI sample. We do not think that the slight difference in the dichroic ratio simply reflects the difference in the degree of alignment of F8T2. We believe that the slight

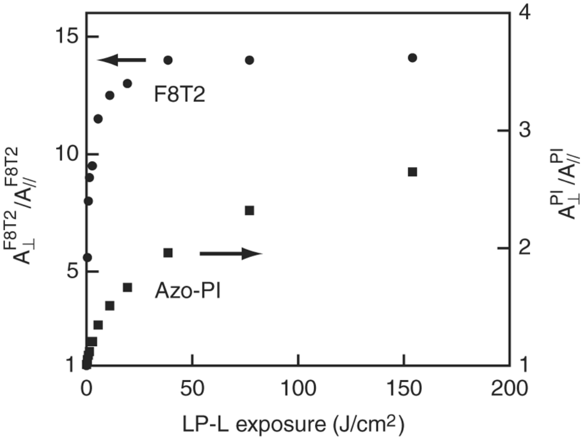

FIGURE 5 LP-L exposure dependence of the dichroic ratios of the photo-aligned Azo-PI film ($A_{\perp}^{PI}/A_{\parallel}^{PI}$) and the F8T2 layer formed on it ($A_{\perp}^{F8T2}/A_{\parallel}^{F8T2}$).

difference is probably caused by the spectral distortion due to the strong dielectric dispersion of the underlying Azo-PI film as discussed above. Therefore, we conclude that the alignment ability of the photo-aligned Azo-PI films for F8T2 is comparable to that of rubbed polyimide films.

5. CONCLUSIONS

We have succeeded in realizing highly oriented F8T2 layers using photo-aligned Azo-PI films. The photo-aligned Azo-PI films were stable to xylene, a solvent of F8T2, and to the thermal treatment performed for aligning F8T2, annealing at 285°C for 15 min followed by quenching. The F8T2 backbone structures aligned on average along the average orientation direction of the Azo-PI backbone structures in the underlying film. The dichroic ratio of the F8T2 layer was ~ 14 at 490 nm (the absorption maximum), corresponding to a uniaxial molecular order parameter of ~ 0.81. Since photo-alignment is contact-free and has potential capability for alignment patterning, the photo-aligned Azo-PI films are proper and attractive alignment films for F8T2.

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