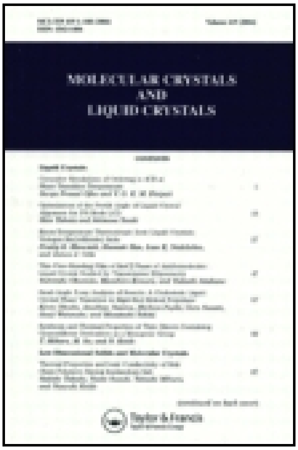

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Inclined Alignment of Polyimide Backbone Structures Induced by Single Exposure of Un-Polarized Light

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We have investigated the alignment of polyimide backbone structures induced by single oblique angle irradiation with un-polarized light (UP-light) of wavelength 340 $\sim$ 500 nm. The polyimide (Azo-PI) used in this study contains azobenzene in the backbone structure. The alignment of the backbone structure occurs through random angular rotation of the azobenzene molecule accompanied by its photo-induced trans-cis-trans isomerization. The photo-alignment treatment was performed on 16 nm thick films of polyamic acid (Azo-PAA) that is the precursor of Azo-PI. Subsequently, the Azo-PAA film was thermally imidized. The UP-light exposure was varied up to 882 J/cm^2. The orientational distribution of the Azo-PI backbone structure was determined, using polarized infrared absorption spectroscopy. We found that the average inclination angle and the in-plane order parameter of the backbone structure increased with UP-light exposure, reaching 51° from the surface plane and 0.1, respectively, at 882 J/cm^2.

Keywords: azobenzene; liquid crystal; photo-induced alignment; photo-isomerization; polarized IR absorption; polyimide

1. INTRODUCTION

Currently a rubbing method is widely used as an alignment technique of liquid crystal (LC) molecules. However, it has serious drawbacks, such as creation of dust particles and generation of electrostatic charge, associated with mechanical rubbing. Since these drawbacks lower the production yield of LC displays, an alternative to the conventional rubbing method is eagerly sought. Photo-induced alignment of LC molecules is a promising alternative, because it is mechanical-contact-free. Up to now various methods of photo-induced alignment have been proposed, and they are actively studied [1–7]. Among them we focus on a method proposed by Park *et al*. in 1998 [8]. This is because the LC alignment obtained by this method is optically and thermally stable. The stability of LC alignment is essential to the practical use of photo-induced alignment.

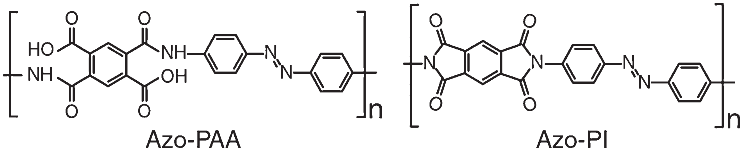
In this method photo-alignment treatment is performed on the film of polyamic acid containing azobenzene in the backbone structure (Azo-PAA). The alignment of the Azo-PAA backbone structure is induced through random angular rotation of azobenzene molecule accompanied by its photo-induced trans-cis-trans isomerization. After the photo-alignment treatment, the Azo-PAA film is converted into the corresponding polyimide (Azo-PI) film by thermal imidization. The molecular orientation of the film becomes stable optically and thermally after imidization. As a result, stable LC alignment is induced by the Azo-PI film.

Previously we reported the alignment of the Azo-PI backbone structure induced by single irradiation with linearly polarized light

(LP-light) [9], and by the double exposure method, where oblique angle irradiation with un-polarized light (UP-light) was performed following LP-light exposure at normal incidence [10–12]. We found that inclined alignment of the Azo-PI backbone structure was realized by the double exposure method. The Azo-PI film with inclined alignment of the backbone structure induced tilted homogeneous alignment of LC molecules. The average tilt angle of LC molecules measured from the surface plane is called the "pretilt angle." The pretilt angle must be controlled to realize high quality LC displays, such as optically compensated bend (OCB) mode LC displays [13]. To accomplish that, one must control the inclination of the polyimide backbone structure [14,15], as well as its in-plane orientation. In principle, inclined alignment of the Azo-PI backbone structure can be induced by single oblique angle irradiation with UP-light. This photo-alignment treatment is the simplest way to generate a finite pretilt angle of LC molecules, and it is suitable for mass production of large-area LC displays, because it requires no polarizing plate. In this study we have investigated the alignment of Azo-PI backbone structure induced by single oblique angle irradiation with UP-light.

2. EXPERIMENT

The molecular structure of Azo-PAA and Azo-PI used in this study is shown in Figure 1. The 16 nm thick Azo-PAA film was formed by spin-coating a solution of Azo-PAA in N-methyl-2-pyrrolidone onto a CaF_2 substrate. Oblique angle irradiation of UP-light was performed on the 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 $340 \sim 500\,nm$ (Asahi Spectra Co., Ltd.). The incidence angle of UP-light was 45°, and the UP-light exposure was varied up to $882\,J/cm^2$. Figure 2 shows the irradiation configuration of UP-light and the definition of the sample coordinate system denoted by XYZ, where the Z axis is the surface normal and the XZ plane is the incidence plane of the UP-light. After the photo-alignment treatment, the Azo-PAA film was thermally imidized



FIGRUE 1 Molecular structure of Azo-PAA and Azo-PI used in this study.

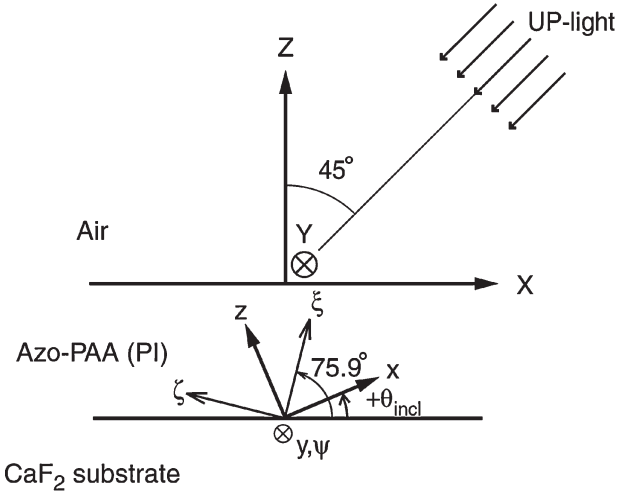


FIGURE 2 Irradiation configuration of UP-light and the definition of three coordinate systems used in this study. The sample coordinate system is denoted by XYZ, where the Z axis is the surface normal and the XZ plane is the incidence plane of the UP-light. The xyz coordinate system is defined by the dielectric principal axes of the Azo-PI film. θ_{incl} is the angle between the x and X axes. The $\xi\psi\zeta$ coordinate system is related to the electric field of UP-light in the Azo-PAA film. The ξ axis is the minimum electric field direction, and the ψ axis is coincident with the Y(y) axis.

at 250°C for two hours in nitrogen atmosphere. The thickness of the Azo-PI film was reduced to $\sim$10 nm.

The orientation of the Azo-PI backbone structure was determined by measuring the polarized infrared (IR) absorption spectra as a function of the angle of incidence [10,16]. Figure 3 shows the experimental geometry for the measurements of the incidence angle dependence of polarized IR absorption. The incidence plane of IR light is the XZ plane, and the sign of the angle of incidence is defined with respect to the propagation direction of UP-light as shown in Figure 3. The incidence angle dependence was measured only for p polarization. At normal incidence the polarized IR absorption spectra were measured for both p(X) and s(Y) polarization.

3. RESULTS

The Azo-PI has a strong IR absorption band at 1365 cm^{-1} [10,12], which is assigned to the C$-$N stretching vibration of the $(OC)_2NC$ bond [17]. Since this band is polarized along the backbone structure,

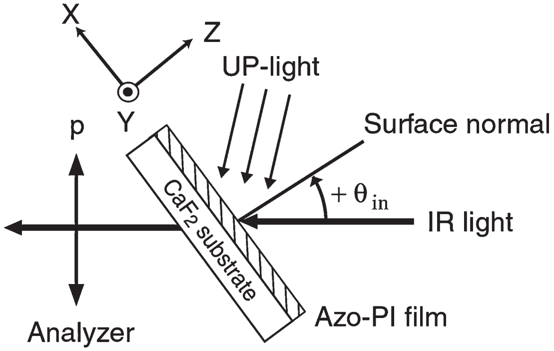


FIGURE 3 Experimental geometry for the measurements of the incidence angle dependence of polarized IR absorption. The sign of the angle of incidence is defined with respect to the propagation direction of UP-light.

we used this band to determine the orientational distribution of the Azo-PI backbone structure. For the Azo-PI films with high inclination of the backbone structure, the spectral shape of the 1365 cm^{-1} band varies with the incidence angle of p-polarized IR light. This is due to the anomalous dielectric dispersion effect of the film [16]. Thus we used the integrated absorbance of the 1365 cm^{-1} band rather than the peak absorbance in the following analysis.

Figure 4 shows the absorbance ratio, $(A_p - A_s)/(A_p + A_s)$, measured at normal incidence as a function of the UP-light exposure, where A_p and A_s are the integrated absorbance of the 1365 cm^{-1} band for p and s polarized IR light, respectively. This absorbance ratio corresponds to the in-plane order parameter Q_Φ of the Azo-PI backbone structure [18,19]. Q_Φ is defined by:

$$Q_\Phi = \frac{\langle \sin^2\Theta \cdot \cos 2\Phi \rangle}{\langle \sin^2\Theta \rangle}, \tag{1}$$

where Θ and Φ are the polar and azimuthal angles, respectively, that specify the orientation of the Azo-PI backbone structure with respect to the XYZ coordinates. Θ and Φ are measured from the Z and X axes, respectively. $Q_\Phi = 0$ means isotropic in-plane molecular orientation; and $Q_\Phi = 1$ and –1 mean that all the Azo-PI backbone structures lie in the XZ and YZ planes, respectively. As shown in Figure 4, Q_Φ gradually increases with the UP-light exposure, reaching 0.1 at 882 J/cm^2. The increase rate of Q_Φ decreases as the UP-light exposure increases. From this result, the average orientation direction of the Azo-PI backbone structure was found to be in the XZ plane, although the in-plane

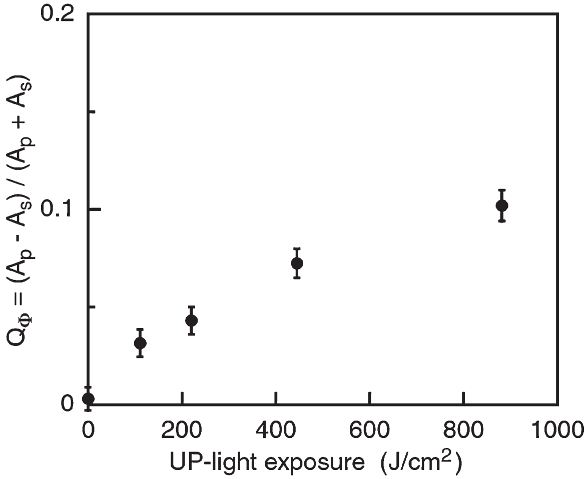


FIGURE 4 UP-light exposure dependence of the absorbance ratio, $(A_p - A_s)/(A_p + A_s)$, measured at normal incidence. A_p and A_s are the integrated absorbance of the 1365 cm^{-1} band for p and s polarized IR light, respectively. This absorbance ratio corresponds to the in-plane order parameter Q_Φ of the Azo-PI backbone structure.

anisotropy was small. (Q_Φ greater than 0.4 can be easily induced by irradiation of LP-light [9,11,12].)

Figure 5 shows the incidence angle dependence of A_p for the untreated film and the film irradiated with UP-light of 220 J/cm^2. The incidence angle dependence for the untreated film is symmetric with respect to normal incidence as expected from its symmetry. On the other hand, asymmetric dependence was observed for the UP-light-exposed film. The integrated absorbance has a maximum at a positive angle of incidence. From this result and the definition of the angle of incidence shown in Figure 3, we see that the Azo-PI backbone structures in the UP-light-exposed film are on average inclined toward the propagation direction of the UP-light. The asymmetry in the incidence angle dependence increased with the UP-light exposure, although the experimental results for the other UP-light exposure are not shown here. We found from the incidence angle dependence that the average inclination angle of the Azo-PI backbone structure increased with the UP-light exposure.

4. DISCUSSION

In this section we will discuss the photo-induced alignment of the Azo-PI backbone structure in detail. The tensor order parameter of the

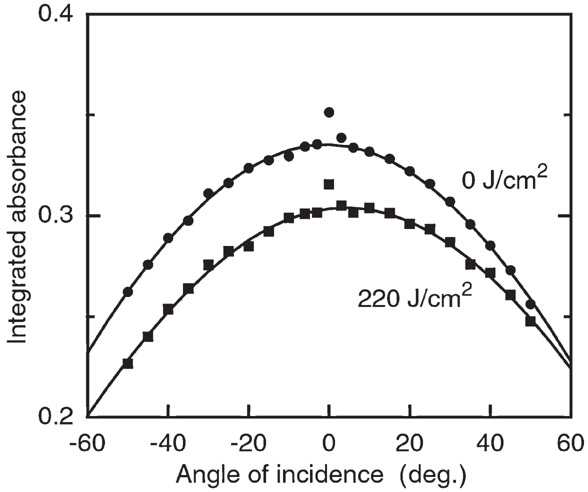


FIGURE 5 Incidence angle dependence of the 1365 cm^{-1} band for p polarization. The filled circles and squares are the data points for the untreated film and the film irradiated with UP-light of 220 J/cm^2, respectively. The solid curves show the best-fit calculated results.

Azo-PI backbone structure can be determined by fitting the experimental data of Figures 4 and 5 with a theoretical calculation [12,20], which was already described elsewhere [10,16]. The element of the tensor order parameter $\overset{\leftrightarrow}{Q}$ with respect to Cartesian coordinates is defined by:

$$Q_{ij} = \left\langle \frac{1}{2}(3\mu_i\mu_j - \delta_{ij}) \right\rangle, \tag{2}$$

where δ_{ij} is the Kronecker delta; μ_i is the i-component of the unit vector $\hat{\mu}$ of the backbone structure direction; and the angular brackets denote an average over its orientation. When $\overset{\leftrightarrow}{Q}$ is defined with respect to the dielectric principal axes (x, y, and z), it is diagonalized into the form [21]:

$$\overset{\leftrightarrow}{Q} = \begin{pmatrix} Q_{xx} & 0 & 0 \\ 0 & Q_{yy} & 0 \\ 0 & 0 & Q_{zz} \end{pmatrix} = \begin{pmatrix} S & 0 & 0 \\ 0 & -(S-P)/2 & 0 \\ 0 & 0 & -(S+P)/2 \end{pmatrix}, \tag{3}$$

where S and P are the two scalar order parameters describing the biaxial ordering, and they are independent. Q_{ii} is the order parameter of the backbone structure around the i axis, which takes a value between 1 and –0.5. $Q_{ii} = 1$ and –0.5 mean that all the Azo-PI backbone structures align parallel and perpendicular to the i axis, respectively. Among Q_{xx}, Q_{yy}, and Q_{zz}, there is a relation of $\sum_{i=x,y,z} Q_{ii} = 0$.

The dielectric principal axis with the largest Q_{ii} corresponds to the average orientation direction of the backbone structure. Here it is denoted by the x axis. The Azo-PI film has mirror symmetry with respect to the XZ plane, and the average orientation direction of the backbone structure is in the XZ plane as stated above. Thus the two dielectric principal axes (x and z axes) lie in the XZ plane as shown in Figure 2. θ_{incl} is defined by the angle between the x and X axes, corresponding to the average inclination angle of the backbone structure measured from the surface plane. Inclination of the +x axis toward the +Z axis is expressed by a positive value of θ_{incl}. The orientational distribution of the backbone structure with respect to the sample coordinate system can be described by a set of S, P, and θ_{incl}, which is the necessary and sufficient parameter set.

Although Q_{xx}, Q_{yy}, and Q_{zz} are redundant, here we use them, instead of S and P, to describe the orientational ordering of the Azo-PI backbone structure. This is because the orientational distribution can be visualized more easily from Q_{xx}, Q_{yy}, and Q_{zz} than S and P. Q_{xx}, Q_{yy}, Q_{zz}, and θ_{incl} determined by the fitting procedure [10,16] are plotted in Figure 6 as a function of the UP-light exposure. The solid curves in Figure 5 are the best-fit calculated results. From Figure 6 we see that the untreated film is isotropic in the film plane, and also that the Azo-PI backbone structures lie flat in the film surface. The average inclination angle of the backbone structure increases almost linearly with the UP-light exposure, reaching 51° at 882 J/cm^2. The order parameter (Q_{xx}) around the average orientation direction is almost constant over the measurement range of the UP-light exposure, while the biaxiality of the orientational distribution varies with the UP-light exposure; i.e., Q_{yy} decreases while Q_{zz} increases. The orientational directionality around the x axis becomes sharper (broader) in the xy (xz) plane as the UP-light exposure increases.

This photo-induced alignment occurs through random angular rotation of the azobenzene molecule accompanied by its trans-cis-trans isomerization reaction. The trans-azobenzene transforms into the cis-isomer by absorbing UV light. The probability of the trans-to-cis isomerization is proportional to $\left|\hat{\mu}_{azo} \cdot \overline{E}\right|^2$, where $\hat{\mu}_{\underline{azo}}$ is the unit vector along the molecular axis of trans-azobenzene; and $\overline{E}$ is the electric field vector of UV light. Then the cis-isomer returns to the trans-isomer form with random orientation thermally or by absorbing visible light.

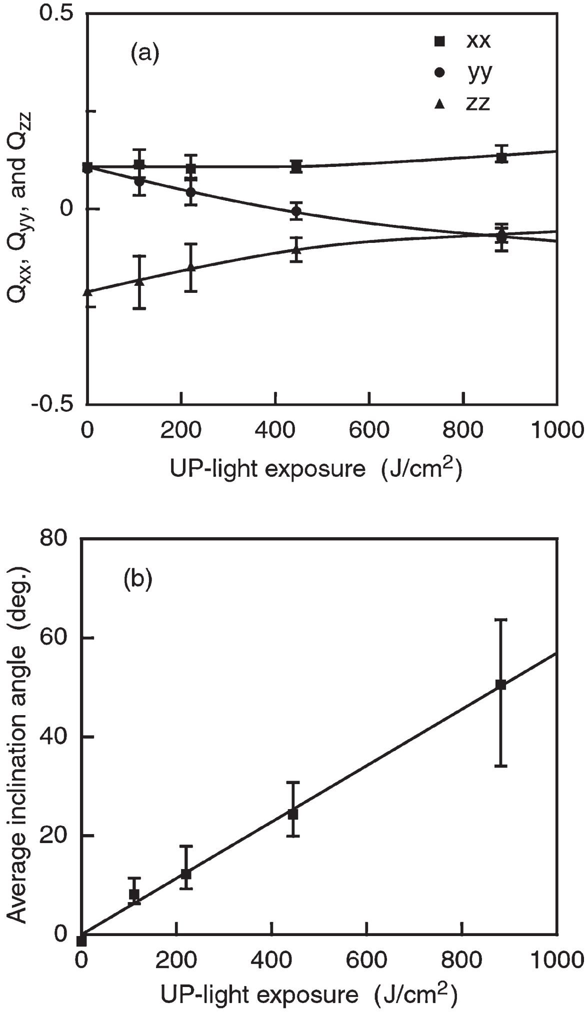


FIGURE 6 (a) Diagonal tensor order parameter (Q_{xx}, Q_{yy}, and Q_{zz}) and (b) average inclination angle θ_{incl} of the Azo-PI backbone structure determined from the IR absorption data shown in Figures 4 and 5. The filled squares, circles, and triangles in (a) are Q_{xx}, Q_{yy}, and Q_{zz}, respectively. The solid curves in (a) and the solid straight line in (b) are guides for the eye.

Since this photo-isomerization cycle is repeated during the UP light irradiation, the number of trans-isomers with their molecular axes oriented to the minimum electric field direction increases with the UP-light exposure. Figure 7 shows the calculated electric field of the

UP-light at the center of the Azo-PAA film. The calculation was performed for wavelength 365 nm, which is a main line of our light source in the UV region. The minimum electric field direction is denoted by the ξ axis, which is in the XZ plane and is directed at 75.9° from the surface plane. Thus the trans-azobenzene gradually rotates toward the ξ axis during the UP-light irradiation. Since the azobenzene is a constituent of the backbone structure, the backbone structure aligns along the same direction.

Since the dielectric principal axes (x, y, and z) rotate around the Y(y) axis as the UP-light exposure increases, Figure 6 is not suitable for understanding the motion of the backbone structure induced by the UP-light irradiation. To confirm the rotation of the backbone structure toward the ξ axis, we calculated the diagonal elements of the tensor order parameter with respect to the $\xi\psi\zeta$ coordinates. Here the ξ axis is the minimum electric field direction of UP-light; and the ψ axis is coincident with the Y axis as shown in Figure 2. Figure 8 shows the UP-light exposure dependence of $Q_{\xi\xi}$, $Q_{\psi\psi}$, and $Q_{\zeta\zeta}$. As expected, $Q_{\xi\xi}$ increases monotonically with the UP-light exposure, while $Q_{\psi\psi}$, and $Q_{\zeta\zeta}$ decreases. This UP-light exposure dependence clearly shows that the backbone structure rotates toward the ξ axis during the UP-light irradiation.

Before closing this section, we mention the LC alignment induced by the Azo-PI films. Uniform LC alignment with the pretilt angle of 2.9° was observed for the UP-light exposure of 882 J/cm^2. This pretilt angle is sufficient for practical application to twisted-nematic LC

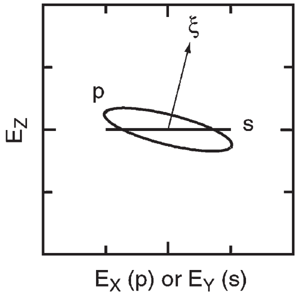


FIGURE 7 Electric field of the UP-light at the center of the Azo-PAA film (16 nm thick), when the UP-light impinges on the film at 45° from the surface normal. The calculation was performed for wavelength 365 nm, which is a main line of our light source in the UV region. The minimum electric field direction is denoted by the ξ axis, which is in the XZ plane and is directed at 75.9° from the surface plane.

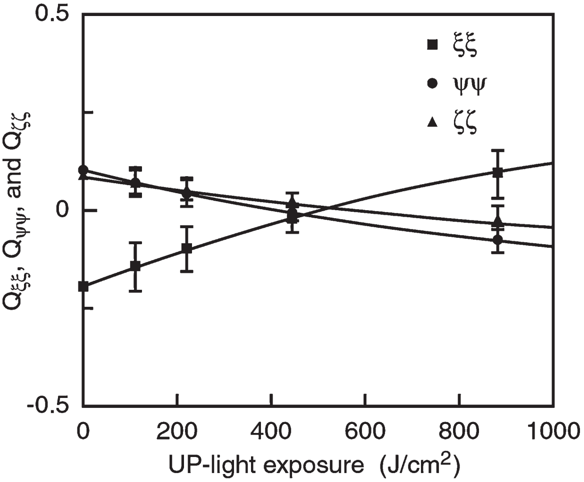


FIGURE 8 Diagonal elements ($Q_{\xi\xi}$, $Q_{\psi\psi}$, and $Q_{\zeta\zeta}$) of the tensor order parameter with respect to the $\xi\psi\zeta$ coordinate system. The ξ axis is the minimum electric field direction of the UP-light, and the ψ axis is coincident with the Y(y) axis (see Fig. 2). The filled squares, circles, and triangles are $Q_{\xi\xi}$, $Q_{\psi\psi}$, and $Q_{\zeta\zeta}$, respectively. The solid curves are guides for the eye.

displays. The UP-light exposure dependence of the pretilt angle will be discussed elsewhere.

5. CONCLUSION

We have investigated the alignment of Azo-PI backbone structures induced by single oblique angle irradiation with UP-light of wavelength 340 $\sim$ 500 nm. We found that the inclined alignment of the backbone structure can be induced by the single oblique angle irradiation. The average inclination angle and the in-plane molecular order parameter increased with the UP-light exposure, reaching 51° from the surface plane and 0.1, respectively, at 882 J/cm^2. This photo-induced alignment can be understood by rotation of the backbone structure toward the minimum electric field direction of the UP-light. The rotation is induced by repeated photo-isomerization cycles of azobenzene in the backbone structure. The in-plane molecular order parameter induced by the single oblique angle irradiation was very small compared to that ($Q_{\Phi} \geq 0.23$) induced by the double exposure method performed in our previous work [11,12]. The double exposure method was found to be effective to induce large in-plane anisotropy of the Azo-PI film with inclined alignment of the backbone structure.

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