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Effect of chemical structures of polyimides on photosensitivity of liquid crystal alignment using a polarized UV exposure

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Unidirectional liquid crystal (LC) alignment produced by polarized UV exposure was examined using polyimides (PIs) synthesized using different diamines. The dichroic ratio of the resulting LC cells suggests that the UV photosensitivity is primarily controlled by the chemical structures of the PIs used. The UV absorption and fluorescence spectra of the PI films, and molecular conformations of the diamines, indicate that the photosensitivity is controlled by the UV absorption efficiencies and molecular conformations of the PIs.

1. Introduction

Most electro-optic applications of liquid crystals (LCs) require a high level of LC molecular orientation. A good example is the twisted nematic LC display which is fabricated using mechanically rubbed polyimide (PI) alignment films [1]. However, there are several problems with this method such as the creation of contaminating particles and the production of electrostatic charges, which lower the production yield of LC displays. Therefore, alternative non-rubbing techniques to align LCs are required.

Langmuir–Blodgett films [2], stretched polymers [3], micro-grooves [4], stamped polymers [5], and polarized ultraviolet light (PUV) exposure of polymers [6], have been developed to produce unidirectional LC alignment. LC alignment produced using PUV exposure is the most promising non-rubbing technique, overcoming the problems mentioned above and greatly simplifying the production of multi-domain displays [7].

Photo-induced isomerization of azo compounds doped in polymers [6, 8–10], *cis–trans* isomerization [11] or cross-linking [12–16] of poly(vinyl cinnamate) derivatives, and photodecomposition of PIs [17–23], have been shown to produce LC alignment on exposure to PUV. Much effort has been concentrated on the development of photo-reactive PIs, which are more heat resistant than azo compounds and poly(vinyl cinnamate) derivatives. One of the key targets for photo-alignment materials is to increase their photosensitivity as well as the quality of LC alignment. However, the parameters of PI materials which affect their photosensitivity have not yet been clarified. In this paper, we explore the effect of PI chemical structures on their photosensitivity for LC alignment.

2. Experimental

2.1. *Synthesis of PIs*

The PI materials used in this experiment are shown in figure 1. They were prepared by heat curing the precursor polyamic acids, which were synthesized by reaction between equi-molar quantities of cyclobutane tetracarboxylic dianhydride and the appropriate diamines.

2.2. *Preparation of LC cells*

LC cells were prepared for measurement of the dichroic ratios of LCs aligned by PUV-exposed PI films [22]. PI films were deposited by first spin-coating dilute solutions of the respective polyamic acids on ITO glass substrates which were then cured at 250°C for 1 h to complete the imidization [24]. The thickness of the PI film was controlled at 50 nm. The PI films were exposed to PUV incident normal to the surface. We used a

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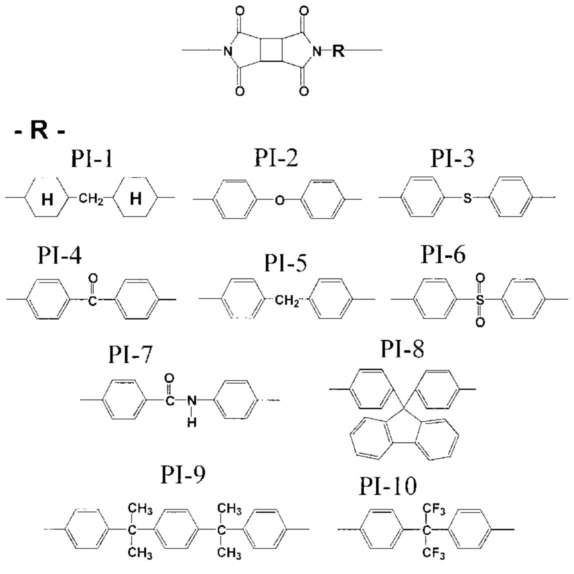

Figure 1. Chemical structures of the PIs used.

450 W-Xe lamp (Oriel, model 6266) as a UV source, and a surface film polarizer (Oriel, model 27320). LC cells for dichroic ratio measurements were fabricated using two PUV-exposed substrates with parallel polarization axes. Dichroic LC, ZLI-2293 (Merck) with 0.5% M-618 (Mitsuitoatsu, $\lambda_{max} = 550$ nm) was filled into the cells in the isotropic state (120°C) and slowly cooled to room temperature to preclude flow alignment.

2.3. *Measurement methods*

The dichroic ratios of the LC cells and UV-visible absorption spectra of the PI films were measured using one polarizer and a Perkin Elmer Lambda 19 UV-visible spectrometer, [22]. The fluorescence spectra of the PI films were measured using a spectra fluorimeter, (Instruments S. A. Fluorolog 270M). The fluorescence spectra were measured in a front-face arrangement and the bandpasses were 1 nm for both the excitation and emission monochromators. The molecular conformations of diamines used in the PIs were calculated by MOPAC Ver. 6 program with AM1 parameters [25].

3. Results and discussion

3.1. *LC alignment on various PI films*

The LC alignment produced by either rubbed or normally exposed with PUV are summarized in the table. In most cases, the LC aligns parallel to the rubbing direction and perpendicular to the UV polarization. This is consistent with results reported previously [17, 18]. However, the LC aligns perpendicular to the rubbing direction and parallel to the exposed UV polarization for PI-8 which contains fluorene diamine.

Table LC alignment on PIs.

	LC alignment direction		
PI	Rubbing	Polarized UV	T_{min}/min
PI-1	Parallel	Perpendicular	92.8
PI-2	Parallel	Perpendicular	2.7
PI-3	Parallel	Perpendicular	2.4
PI-4	Parallel	Perpendicular	2.4
PI-5	Parallel	Perpendicular	7.0
PI-6	Parallel	Perpendicular	92.4
PI-7	Parallel	Perpendicular	64.1
PI-8	Perpendicular	Parallel	23.1
PI-9	Parallel	Perpendicular	22.4
PI-10	Parallel	Perpendicular	57.7

3.2. *Photosensitivity of LC alignment*

Figure 2 shows the dichroic ratios of the LC cells as a function of the PUV exposure time. The dichroic ratios

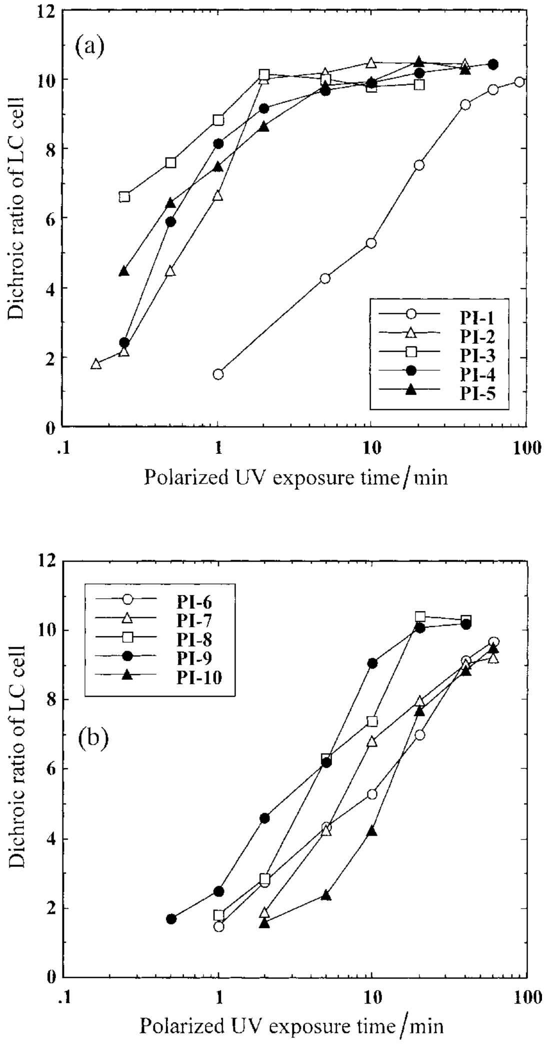

Figure 2. Relationship between UV exposure time and dichroic ratios of LC cells using (*a*) PI-1–5 and (*b*) PI-6–10.

of the LC cells initially increase logarithmically with UV dosage, and then approach a constant value of about 10.5, which is comparable to that of the LC cell with rubbed PI alignment films. Figure 3 shows the typical relationship between PUV exposure time and the dichroic ratios of the LC cells. In this figure, we define the dichroic ratio of the LC cell at lower UV dosage by the following equation:

$$\text{dichroic ratio} = A + B\log(T) \qquad (1)$$

where A is a constant, B the slope of the dichroic ratio of the LC cell, and T the PUV exposure time. Using this equation, we can estimate the photosensitivity of the LC alignment for UV dosage at the minimum PUV exposure time ($T_{\min}$) as 10.5. The photosensitivities of LC alignment ($T_{\min}$) of PI materials are also summarized in the table.

3.3. *Analyses of photosensitivity of LC alignment*

We measured the UV absorption spectra of the PI films prepared on quartz substrates to investigate their photosensitivity. Figure 4 shows the UV absorption spectra of 50 nm PI films.

In previous papers we proposed that selective decomposition of PI by PUV exposure aligns the LC along the optic axis of remaining PI chains [22, 26]. Here we define the absorption efficiency of PI film by the following equation:

$$\text{absorption efficiency} = \int_{200\,\text{nm}}^{400\,\text{nm}} f(x)g(x)h(x)i(x)\,dx \qquad (2)$$

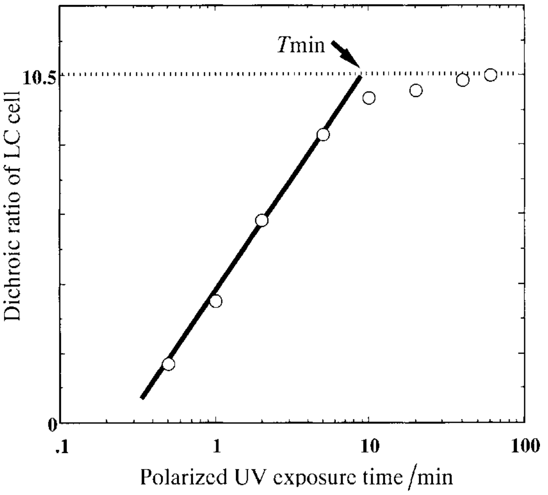

Figure 3. Definition of $T_{\min}$ of photo-alignment.

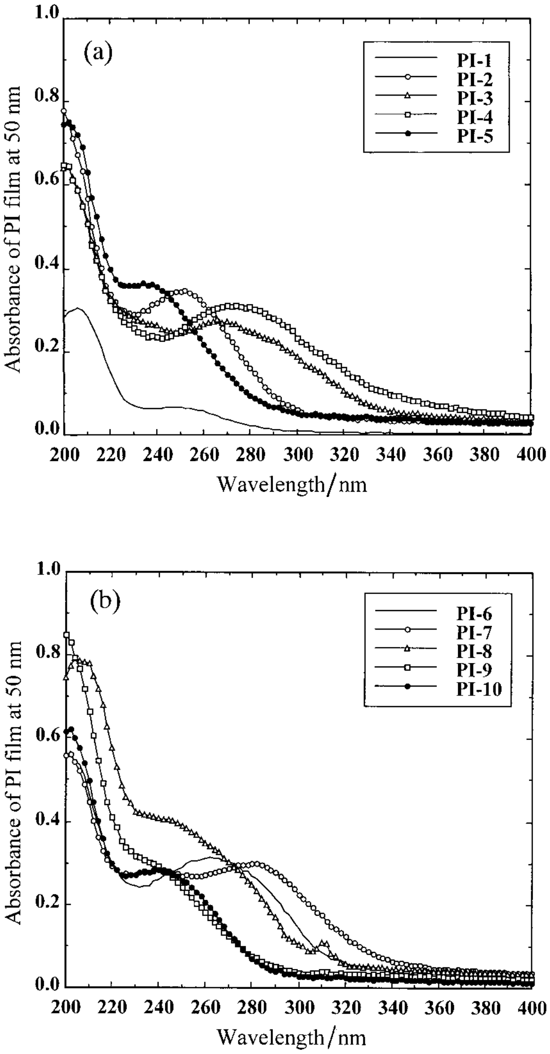

Figure 4. UV absorption spectra of (*a*) PI-1–5 and (*b*) PI-6–10.

where $f(x)$ describes the irradiance of the UV source, $g(x)$ describes the transmittance of film polarizer, $h(x)$ describes the polarization efficiency of film polarizer, and $i(x)$ describes the function of UV absorption of PI film. If the selective decomposition of the PI is related to the UV absorption of the PI film, the absorption efficiency of the PI film is correlated with the sensitivity of the LC alignment to UV dosage. Figures 5, 6, and 7 show the irradiance of the Xe lamp, the transmittance of the film polarizer, and the polarization efficiency of the film polarizer as functions of wavelength. The irradiation of the Xe lamp is taken directly from the manufacturer's catalogue. The transmittance and polarization efficiency of the film polarizer were measured using the UV-visible spectrometer. The polarization efficiency is defined by the following equation:

$$\text{polarization efficiency} = (T_{\text{para}} - T_{\text{per}})/(T_{\text{para}} + T_{\text{per}}) \times 100\,(\%) \qquad (3)$$

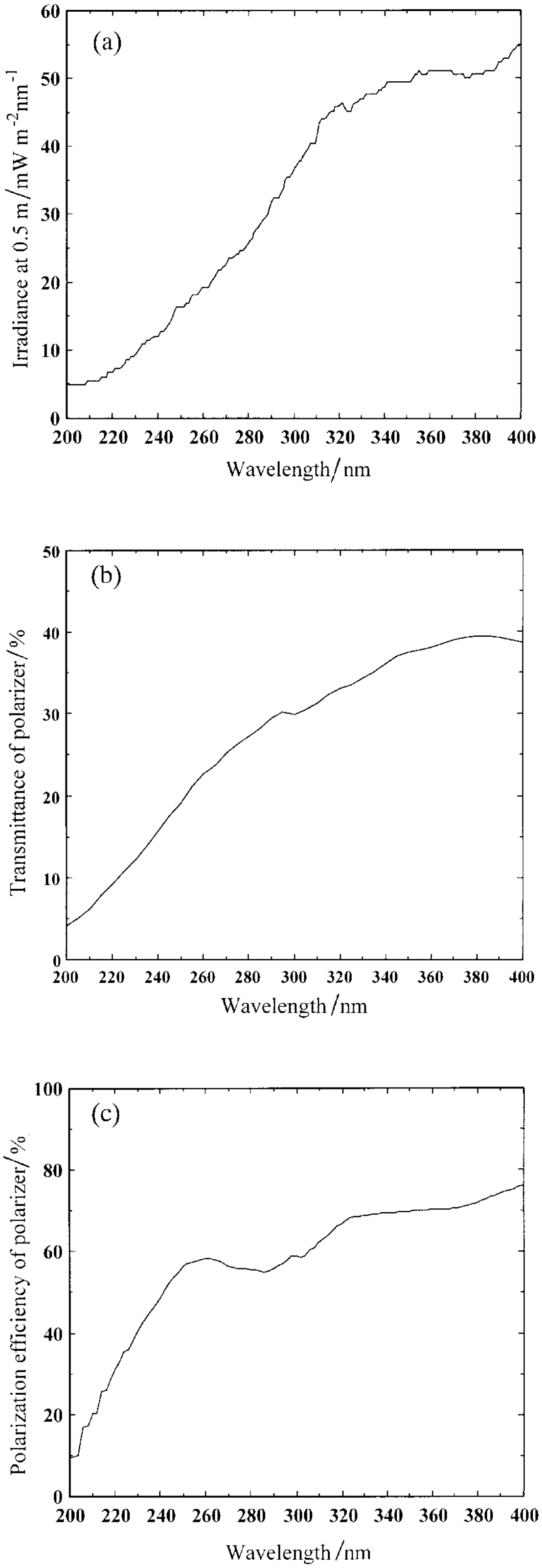

Figure 5. Relationship between wavelength and (*a*) irradiance of Xe lamp, (*b*) transmittance of film polarizer, and (*c*) polarization efficiency of film polarizer.

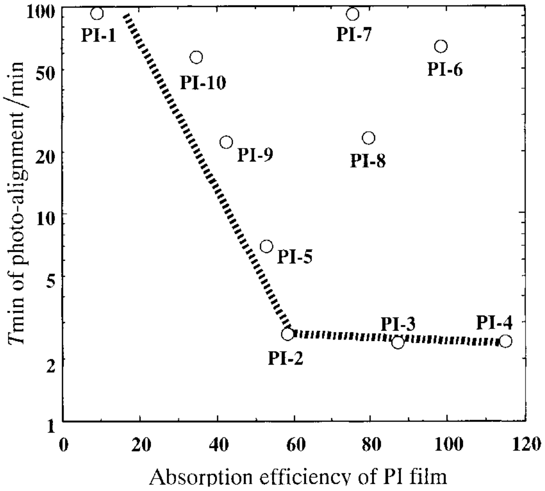

Figure 6. Relationship between absorption efficiencies of PI films and $T_{\rm min}$ of photo-alignment.

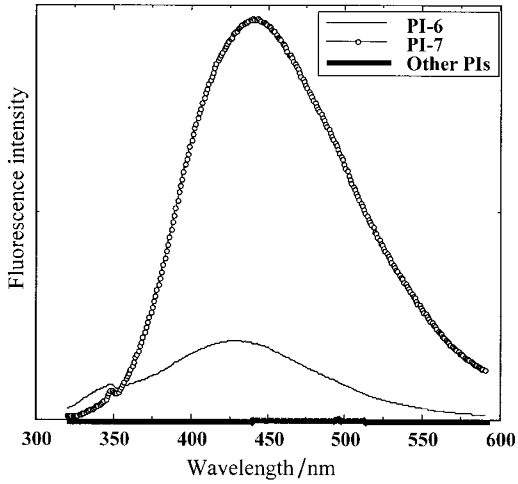

Figure 7. Fluorescence spectra of PI films.

where $T_{\rm para}$ and $T_{\rm per}$ are the maximum and minimum transmittance axes of the film polarizer, respectively.

Figure 6 shows the relationship between $T_{\rm min}$ and the absorption efficiencies of the PI films. The $T_{\rm min}$ tends to decrease with an increase in the absorption efficiency of the PI film, as shown by the dashed line. Previous papers reported that the decomposition of PI containing the cyclobutane moiety was affected by the absorption of the PI material [27, 28]; our results agree. However, PI-6, 7, and 8 deviate from the dashed line shown in figure 8.

To analyse other mechanisms of relaxation from the photo-excited state [29] we measured the fluorescence spectra of 30 μm thick PI films coated on quartz to prevent emission from the substrate. The PI films were excited at their absorption maximum, and the emissions from the PI films were monitored as a function of

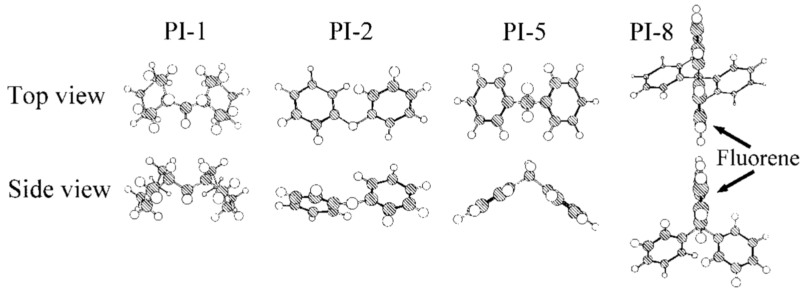

Figure 8. Molecular conformation of diamines in PIs.

wavelength.† Figure 7 gives the fluorescence spectra of the PI films. PI-6 and PI-7 show relatively strong fluorescence compared with the other PI films competing with photoreaction. This could be one reason why PI-6 and PI-7 have relatively lower photosensitivity.

We calculated the molecular conformations of the diamines used in the PIs. Figure 8 shows the typical molecular conformations for diamines used in PI-1, 2, 8, and 9. In most cases, the optic axes in the diamines align along the main chain of the resulting PIs. On the other hand, the diamine in PI-8 has two optic axes produced by the diphenyl methane and fluorene units. This interplay between the two optic axes in PI-8 results in lower photosensitivity for UV dosage. Furthermore, the fluorene unit in PI-8, which has a large birefringence, is aligned perpendicular to the axis of the main chain. The LC aligns in the opposite sense to the other PIs, as shown in the table, because the fluorene units are perpendicular to the main chain.

4. Conclusion

In summary, we have measured the photosensitivity of the LC alignment on various PI films to polarized UV exposure. The photosensitivity of the LC alignment for UV dosage is significantly affected by the chemical structures of PIs. The absorption efficiency of the PI film (defined from the UV absorption of the film, the irradiance of the UV lamp, the transmittance of the film polarizer, and the polarization efficiency of the film polarizer) correlates with the photosensitivity of LC alignment for UV dosage. In addition, the result of the fluorescence spectrum measurements, taken with molecular conformation of the PIs, suggest that charge-transfer in the PI upon UV exposure and the molecular conformation of PI also affect the photosensitivity of the LC alignment.

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† The experimental accuracy of the fluorescence was ±10%.

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