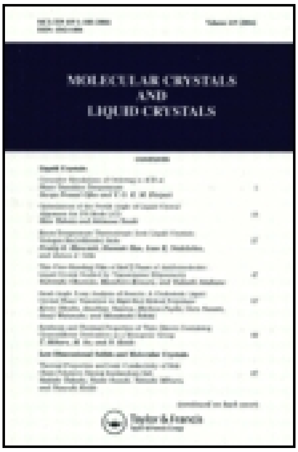

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Effect of Chemical Structures of Polyimides on Photo-Alignment of Liquid Crystals

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Effect of Chemical Structures of Polyimides on Photo-Alignment of Liquid Crystals

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Unidirectional liquid crystal (LC) alignment by a polarized UV exposure was examined using various polyimides (PIs) which consist of different tetracarboxylic dianhydrides and diamines. The dichroic ratios and anchoring energies of the LC cells were measured as a function of polarized UV exposure time. The results suggest that the unidirectional LC alignment for UV dosage is largely affected by the chemical structures of the PIs used. The LC alignment properties are summarized with respect to the UV absorption efficiencies, molecular conformations, and mechanisms of decomposition of the PI films.

Keywords: liquid crystal; polyimide; alignment; polarized UV exposure; anchoring energy

1. INTRODUCTION

Liquid crystal (LC) displays are widely used because of their low-power consumption, thin profile, and full-color capability. To fabricate LC displays, unidirectional LC alignment is typically produced using surface rubbing techniques [1]. However, this method has several problems, such as creation of contaminating particles and production of electrostatic charges, which lower the production yield of LC displays. Therefore, alternative non-rub techniques to align LC are required.

Langmuir-Blodgett films [2], stretched polymers [3], micro-grooves [4], stamped polymers [5], and polarized ultraviolet light (UV) exposure of polymers

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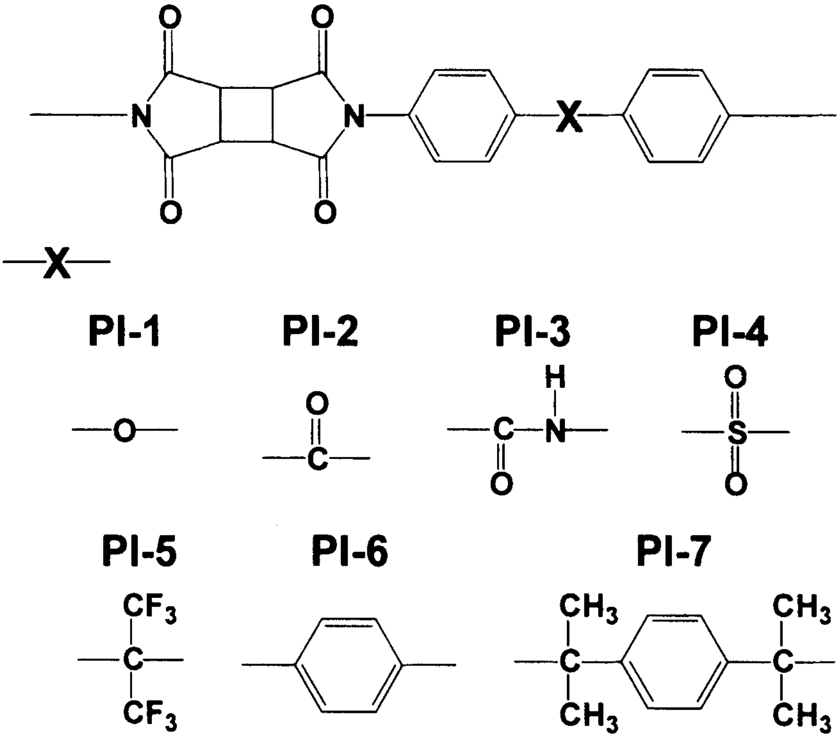

FIGURE 1 Chemical structures of PIs containing various diamines

[6], have been developed to produce unidirectional LC alignment. LC alignment produced using polarized UV exposure is the most promising non-rub technique, overcoming the problems mentioned above and greatly simplifying production of multi-domain LC 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 photo-decomposition of PIs [17–23], have been shown to produce the alignment of LC by a polarized UV exposure. Much effort has been concentrated on the development of photoreactive PIs, which are more heat resistant than azo compounds and poly(vinyl cinnamate) derivatives. One of the key development issues of photo-alignment materials is increasing their photosensitivity and anchoring energies as well as the quality of LC alignment. However, the parameters of PI materials which affect the photosensitivity and anchoring energy have not been clarified yet. In this paper, we explore the effect of the PI chemical structures on the photo-alignment properties of LC.

2. EXPERIMENTS

2.1 Synthesis of PIs

PI materials used in this experiment are summarized in Figures 1 and 2. PI films, except PI-8, were prepared by heat curing of precursor polyamic acids which were synthesized from the equal molar reaction between tetracarboxylic dianhydrides and diamines. PI-8 is an organic-solvent-soluble polyimide synthesized from the reaction reported previously [24].

2.2 Preparation of LC Cells

LC cells were prepared to measure the dichroic ratios and azimuthal anchoring energies of the LCs aligned by polarized-UV-exposed PI films. PI films were deposited by first spin-coating dilute solutions of the respective polyamic acids or polyimide on ITO glass substrates and then cured at 250 °C for 1 hour to accomplish imidization [25]. The thickness of the PI film was controlled at 50 nm.

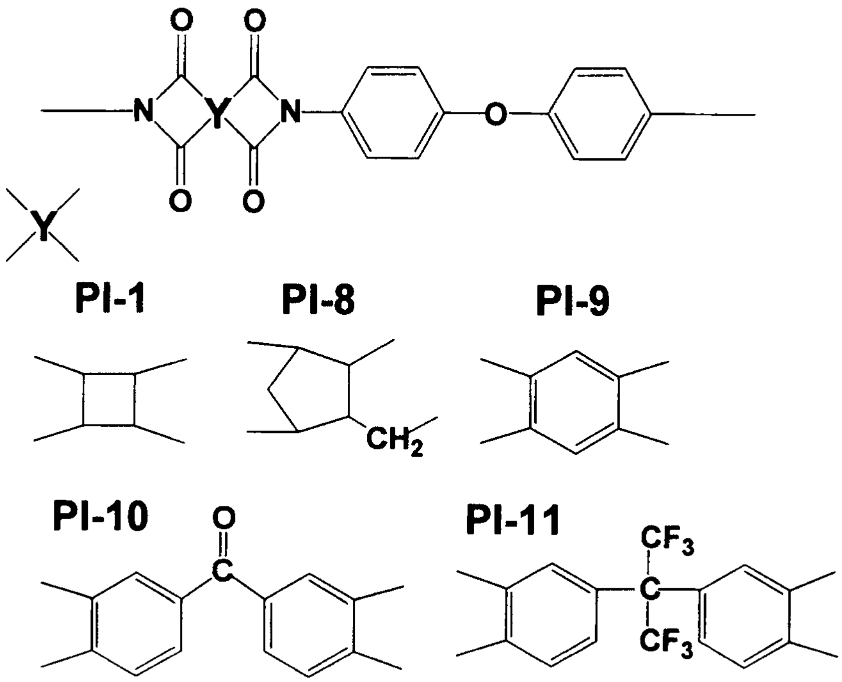

FIGURE 2 Chemical structures of PIs containing various tetracarboxylic dianhydrides

The PI films were exposed with polarized UV incident normal to the surface. We used a 450 W-Xenon lamp (Oriel, model 6266) as a UV source, and a surface film polarizer (Oriel, model 27320) whose effective range is between 230 nm to 770 nm. The intensity of UV after passing through the polarizer was monitored using a photometer, International Light IL1700, and was about 1 mW/cm^2 at 254 nm. LC cells were fabricated using two polarized-UV-exposed substrates with anti-parallel polarization axis. Dichroic LC, 0.5 % M-618 dichroic dye (Mitsuitoatsu, λmax=550 nm) in n-pentylcyanobiphenyl (5CB, EM Industries) solution, and 5CB were filled into the cells in the isotropic state and slowly cooled to room temperature for measurement of the dichroic ratios and azimuthal anchoring energies of the LC cells, respectively.

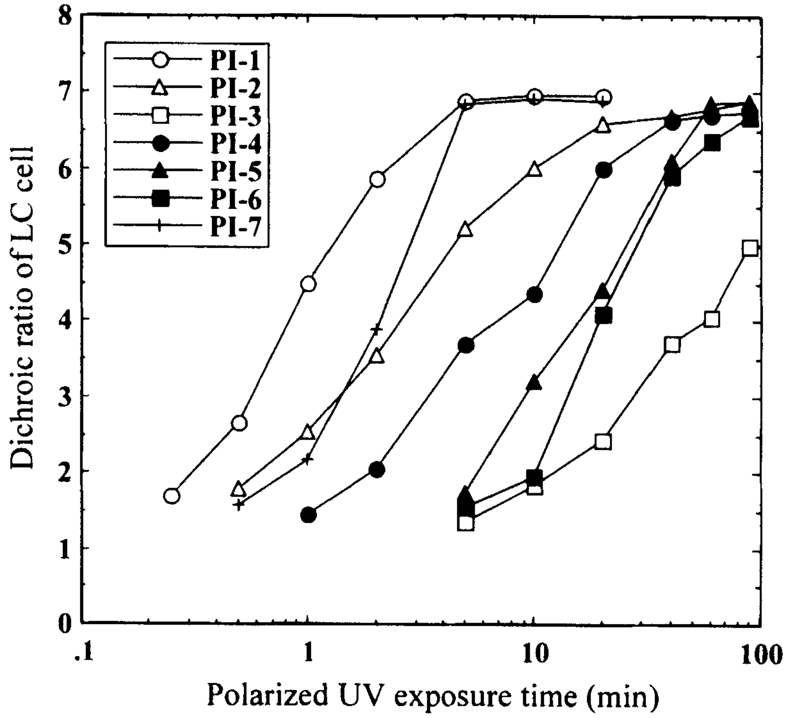

FIGURE 3 Relationship between polarized UV exposure time and dichroic ratios of LC cells with PIs shown in Figure 1

2.3 Measurement Methods

The dichroic ratios of the LC cells were measured using one polarizer and a UV-Vis spectrometer, Perkin Elmer Lambda 19 [22]. The azimuthal anchoring energies of the LC cells were measured utilizing the Neel wall method reported previously [26].

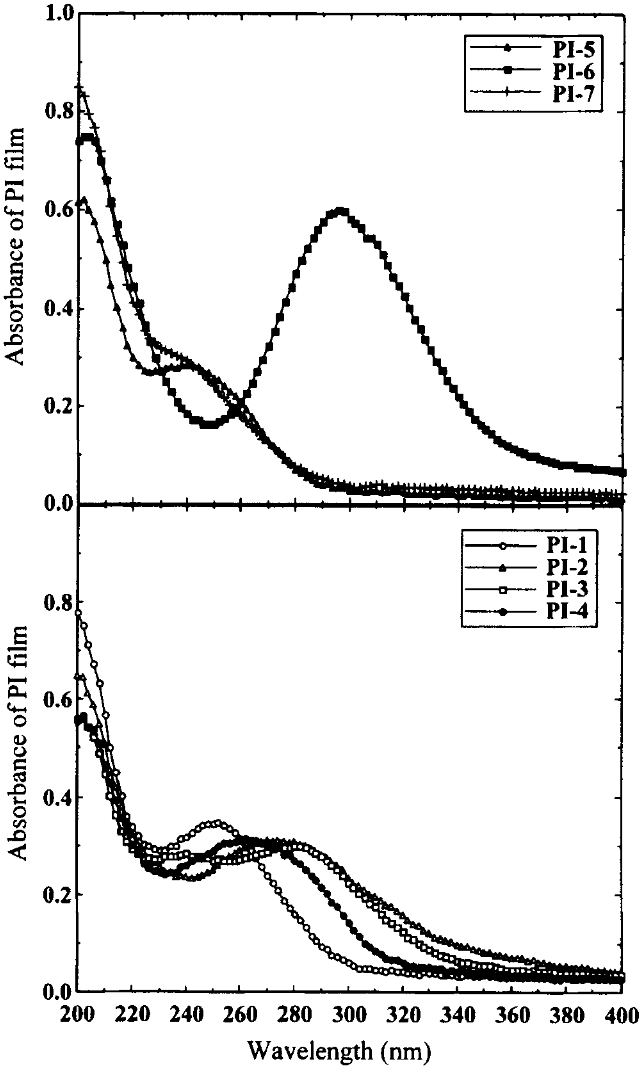

FIGURE 4 UV absorption spectra of PI films shown in Figure 1

The fluorescence spectra of PI films were measured in a front-face arrangement and the bandpasses were 1 nm for both the excitation and emission monochrometers. The PI films were excited at their absorption maximum, and the emission from the PI films were monitored as a function of wavelength. The molecular conformations of the diamines and tetracarboxylic dianhydrides used in PIs were calculated by MOPAC Ver. 6 program with AM1 parameters [27].

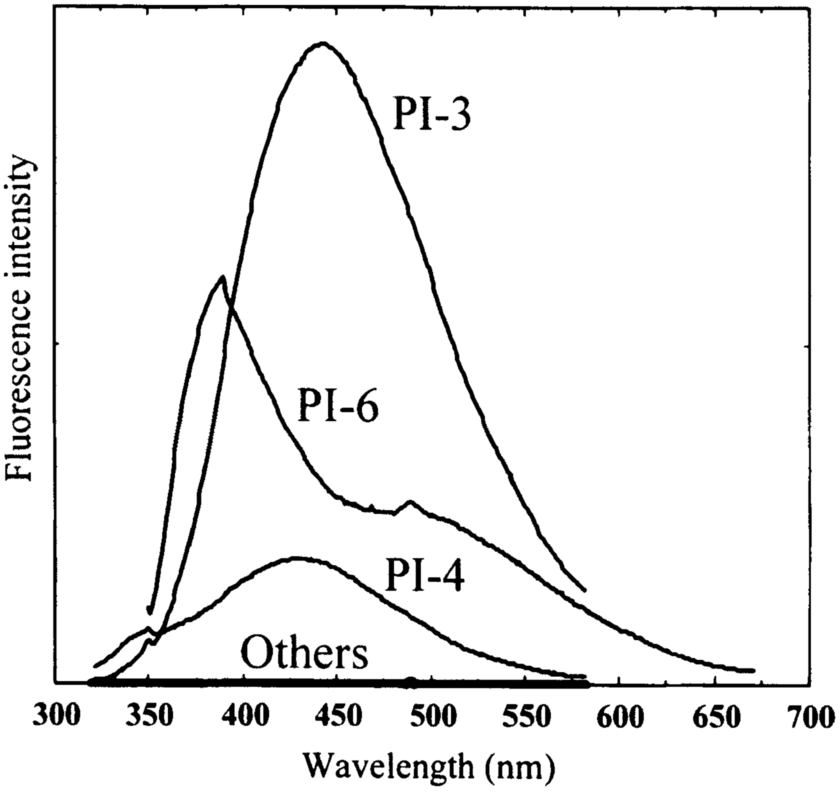

FIGURE 5 Fluorescence spectra of PI films shown in Figure 1

3. RESULTS AND DISCUSSION

3. 1. Effect of Diamines Used in PIs

In this experiment, we used PI materials shown in Figure 1. Figure 3 shows the dichroic ratios of the LC cells as a function of the polarized UV exposure time. The dichroic ratios of the LC cells were defined as A_{per}/A_{para}, where A_{per} and A_{para} are the absorbances of the LC cells at 550 nm perpendicular and parallel to the UV polarization, respectively. The dichroic ratios of the LC cells initially increase logarithmically with UV dosage, and then approach a constant value of about 7.0, which is comparable with that of the LC cell with rubbed PI alignment films. The photosensitivity of LC alignment is largely affected by the diamine structures used in PIs.

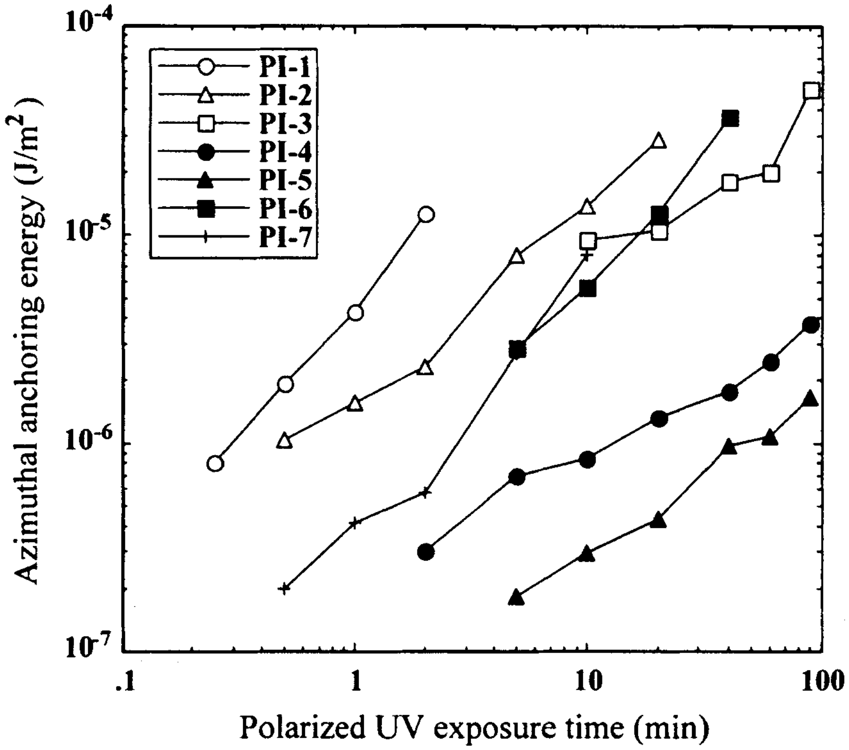

FIGURE 6 Relationship between UV exposure time and azimuthal anchoring energies of LC cells with PIs shown in Figure 1

In our previous paper [28], we reported that the UV absorption efficiency of the PI film defined by the UV absorption and fluorescence of the PI film controls the photosensitivity of the LC alignment for UV dosage: i.e. higher UV absorption or lower fluorescence of PI film results in higher photosensitivity of LC alignment for UV dosage. According to our previous work, we measured the UV absorption and fluorescent spectra of the PI films containing different diamine moieties. Figures 4 and 5 show the UV absorption and fluorescence spectra of the PI films as a function of wavelength, respectively. Measurement of fluorescence spectra suggests that PI-3, PI-4, and PI-6 show relatively strong fluores-

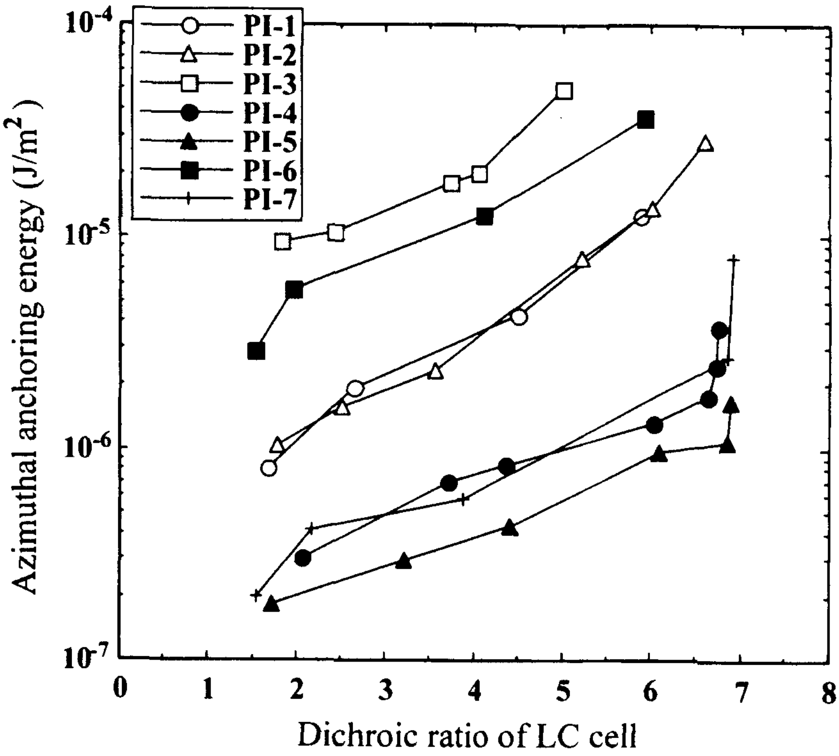

FIGURE 7 Relationship between dichroic ratios and azimuthal anchoring energies of LC cells with PIs shown in Figure 1

cence due to the intra- or intermolecular charge-transfer (CT) [29] compared with the other PI films competing with photodecomposition. This could be one reason why PI-3, PI-4, and PI-6 have relatively lower photosensitivity. On the other hand, the photosensitivity of LC alignment increases with the UV absorbances of the PIs except PI-3, PI-4, and PI-6 as shown in Figure 4.

Figure 6 shows the relationship between polarized UV exposure time and the azimuthal anchoring energies of the LC cells. The azimuthal anchoring energies monotonically increased with UV exposure time. When the azimuthal anchoring energy is above 5×10^{-5}J/m^2, the Neel wall in the LC cell disappears. And when the azimuthal anchoring energy is below 1×10^{-8} J/m^2, we could not detect the Neel wall due to the disordered LC configuration. The azimuthal anchoring energies gradually increase with polarized UV exposure time. Figure 7 shows the relationship between the dichroic ratios and the azimuthal anchoring energies of

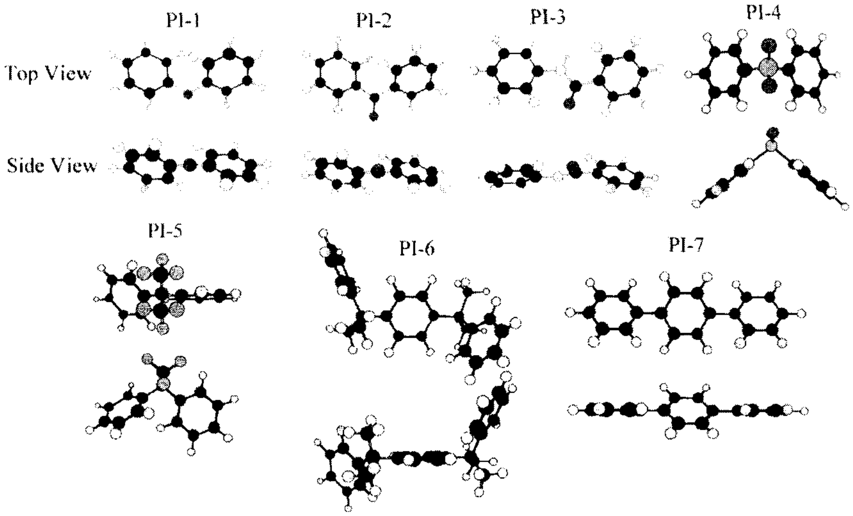

FIGURE 8 Molecular conformations of diamines

the LC cells. The azimuthal anchoring energy and dichroic ratio appear to be logarithmically related. The comparison of the anchoring energies of the LC cells with the same dichroic ratio suggests that the azimuthal anchoring energy is largely affected by the diamine structures in the PIs.

To explain the effect of the diamines used in PIs in more detail, we calculated the molecular conformations of the diamines as shown in Figure 8. The comparison of the molecular conformations suggests that the diamine with bulky molecular conformation tends to show relatively lower azimuthal anchoring energy than those with rigid molecular conformations.

3. 2. Effect of Tetracarboxylic Dianhydrides Used in PIs

In this experiment, we used PI materials shown in Figure 2. Figure 9 shows the dichroic ratios of the LC cells as a function of the polarized UV exposure time. The dichroic ratios of the LC cells initially increase logarithmically with UV. The photosensitivity of LC alignment is also considerably affected by the tetracarboxylic dianhydrides used in PIs.

PI-1 containing cyclobutane tetracarboxylic dianhydride moiety shows higher photosensitivity of LC alignment than those with other PI films. The difference of the photosensitivity can be explained by the main mechanism of the decompo-

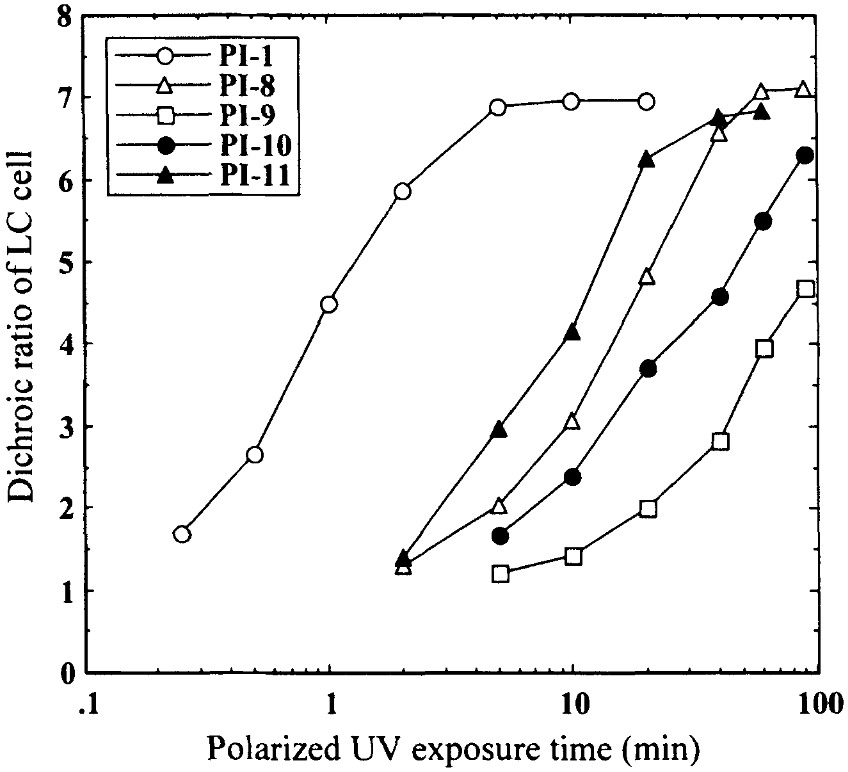

FIGURE 9 Relationship between polarized UV exposure time and dichroic ratios of LC cells with PIs shown in Figure 2

sition of the PIs: cyclobutane ring cleavage [30,31] and imido ring cleavage [32] which requires higher UV dosage, respectively.

We also measured the UV absorption and fluorescence spectra of PI films containing different tetracarboxylic dianhydride moieties. Figure 10 shows the UV absorption spectra of PI films as a function of wavelength. PI-11 shows relatively lower UV absorbance than that of PI-9. Furthermore, the measured fluorescence of these PI films were very small compared to those of other PIs shown in Figure 5. In a series of experiments using PIs composed of cyclobutane tetracarboxylic dianhydride and various diamines [28], we obtained a clear relationship between the absorption efficiency of the PI films and the photosensitivity of the LC alignment for UV dosage. However the data resulting from PI materials containing different tetracarboxylic dianhydrides suggest that this experimental law cannot be applied to the PI materials containing various tetracarboxylic dianhydrides.

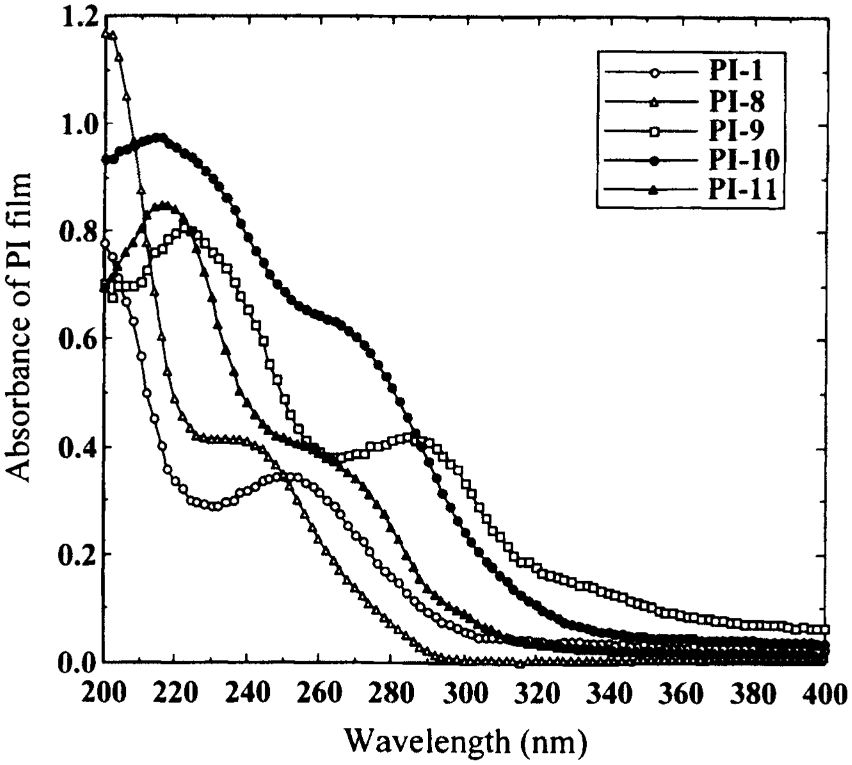

FIGURE 10 UV absorption spectra of PI films shown in Figure 2

Hoyle et al. compared the photodegradation of PIs (PI-9 – 11) upon UV exposure [33], and reported the tendency of PI material to be degradated as the following:

(Sensitive) PI-11 > PI-10 > PI-9 (Less sensitive).

Their results on the photodegradation of PIs coincide with the photosensitivity of LC alignment for UV dosage obtained in this paper. Furthermore, they concluded that the CT characteristics in PIs largely affect the photodecomposition of PI chains [34]. The electron-withdrawing groups, such as ketone in PI-10 and trifluoromethyl in PI-11, affect the CT characteristics in PIs, and result in higher photosensitivity of LC alignment than that of PI-9.

Figure 11 shows the relationship between polarized UV exposure time and the azimuthal anchoring energies of the LC cells. The azimuthal anchoring energies monotonically increased with UV exposure time. Figure 12 shows the relation-

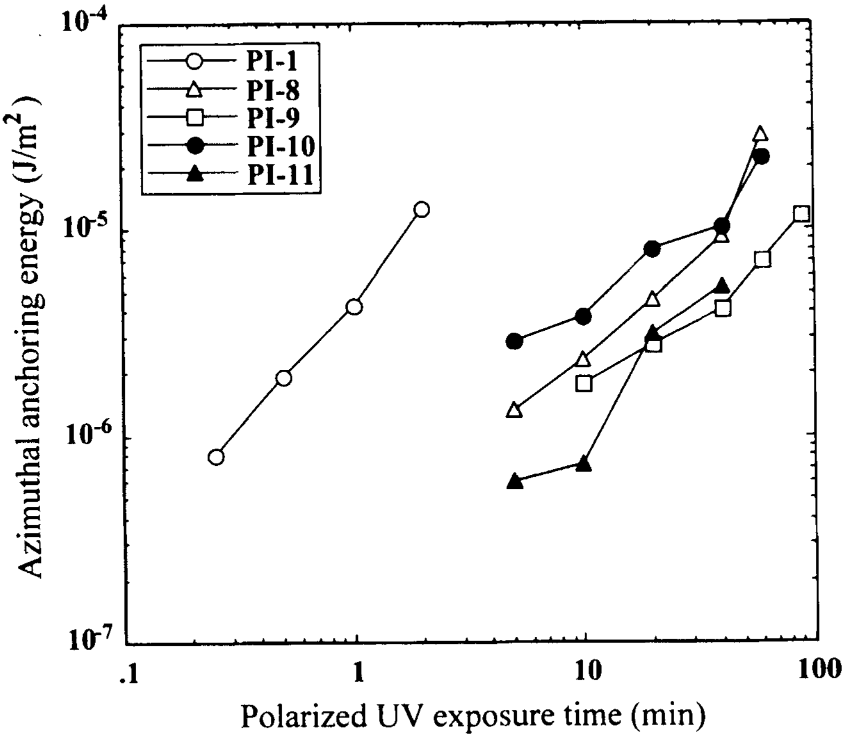

FIGURE 11 Relationship between UV exposure time and azimuthal anchoring energies of LC cells with PIs shown in Figure 2

ship between the dichroic ratios and the azimuthal anchoring energies of the LC cells. The comparison of the anchoring energies of the LC cells with the same dichroic ratio suggests that the azimuthal anchoring energy is also considerably affected by the tetracarboxylic dianhydride structures in PIs.

The molecular conformations of the tetracarboxylic dianhydrides used in PIs were also calculated by the MOPAC Ver.6 program with AM1 parameters. Figure 13 shows the molecular conformations of the tetracarboxylic dianhydrides used in PIs. It seems that the tetracarboxylic dianhydrides with bulky molecular conformations tend to show relatively weak azimuthal anchoring energy. I have reported that the number of benzene in PIs affects the azimuthal anchoring energy due to the anisotropic van der Waals forces [35]. Beside these forces, the steric interaction between PI and LC is also a crucial parameter to control the surface LC alignment.

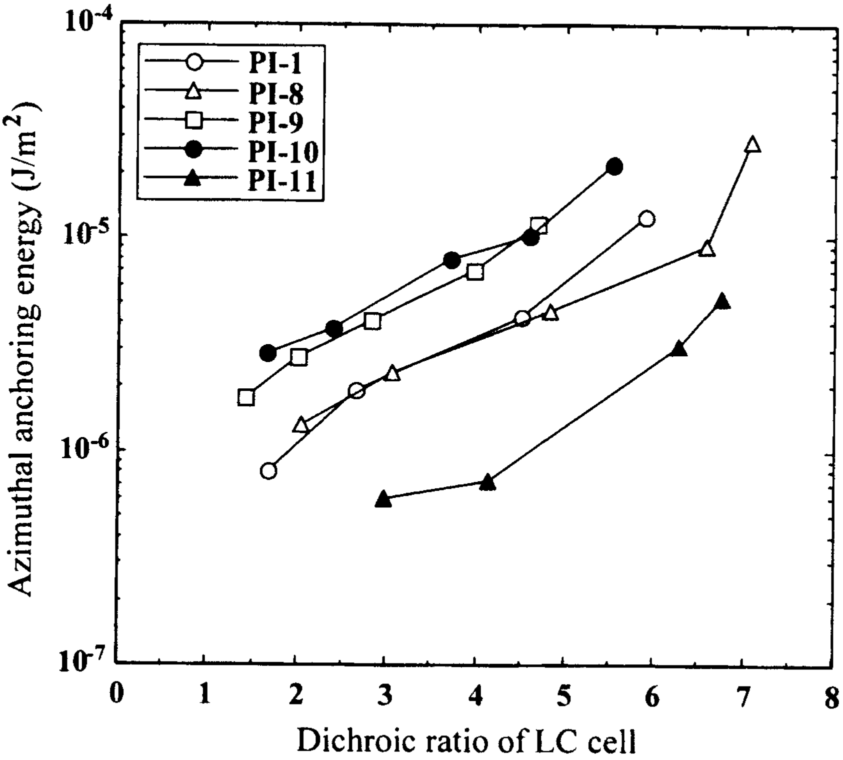

FIGURE 12 Relationship between dichroic ratios and azimuthal anchoring energies of LC cells with PIs shown in Figure 2

4. CONCLUSION

We reported the unidirectional LC alignment properties on PI films with a polarized UV exposure. The photosensitivity of LC alignment and the anchoring energies of the LC cells with various PI materials were measured as a function of polarized UV exposure time. The results suggest that the UV absorption efficiencies, CT characteristics, molecular conformations and mechanisms of decomposition of the PI films considerably affect the photosensitivity and anchoring energy for UV dosage. Further consideration of the azimuthal anchoring energy dependence, such as the relationship with UV dosage and dichroic ratio, is now underway. We will publish it elsewhere.

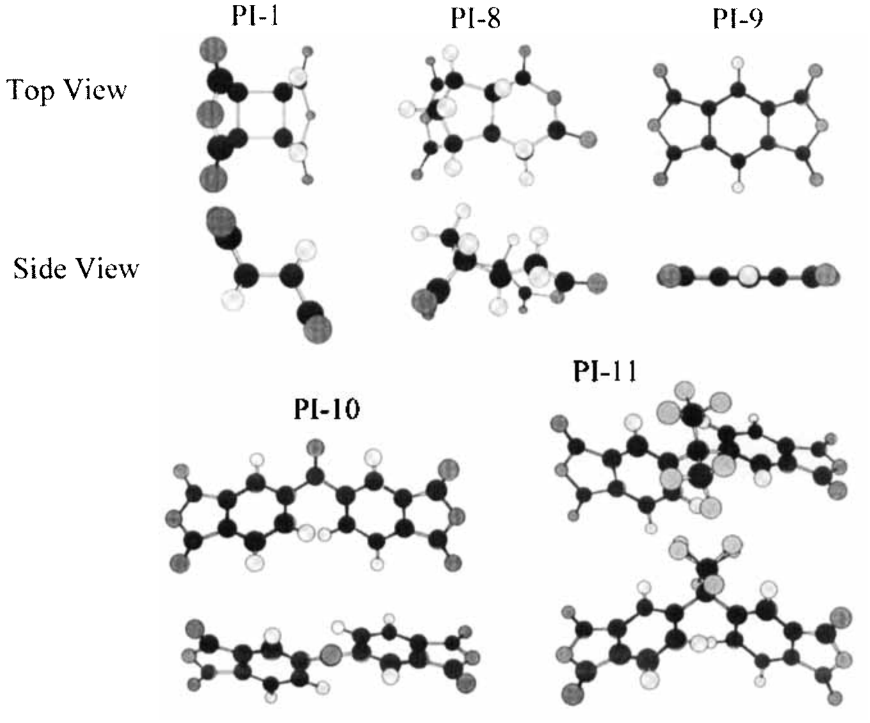

FIGURE 13 Molecular conformations of tetracarboxylic dianhydrides

Acknowledgements

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