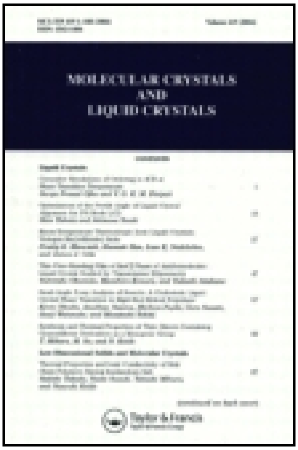

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Effect of Chemical Structures of Polyimides on Unidirectional Liquid Crystal Alignment using a Single Linearly Polarized UV Exposure

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Version of record first published: 24 Sep 2006

To cite this article: M. Nishikawa, B. Taheri & J. L. West (1998): Effect of Chemical Structures of Polyimides on Unidirectional Liquid Crystal Alignment using a Single Linearly Polarized UV Exposure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 325:1, 63-78

To link to this article: http://dx.doi.org/10.1080/10587259808025384

Mol. Cryst. Liq. Cryst., Vol. 325, pp. 63-78
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Effect of Chemical Structures of Polyimides on Unidirectional Liquid Crystal Alignment using a Single Linearly Polarized UV Exposure

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(Received 18 February 1998; In final form 13 April 1998)

Unidirectional liquid crystal (LC) alignment by a linearly polarized UV exposure was examined using various polyimides (PIs) which consist of different tetracarboxylic dianhydrides and diamines. Measurement of dichroic ratios of LC cells suggests that sensitivity of unidirectional LC alignment for UV dosage is largely affected by the chemical structures of PIs used. The results of dichroic ratio measurement of LC cells, UV absorption spectra, birefringences, FT-IR spectra of PI films, and molecular conformations of diamines in PIs calculations using molecular mechanics suggest that the selective photo-decomposition of PI caused the anisotropic van der Waals forces which aligns the LC along its optic axis in residual PI chain.

Keywords: Liquid crystal; polyimide; alignment; polarized UV exposure

1. INTRODUCTION

Almost all liquid crystal displays (LCDs) are fabricated using LC alignment techniques to obtain well-oriented LC molecular conformations. A good example is the twisted nematic LCDs which are fabricated using mechanically rubbed polyimide (PI) films as LC alignment films [1]. However, rubbing may cause static charge, dust, or scratches which lowers the

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production yield of LCDs. Therefore, alternative technique to align LC without rubbing are been developed.

Methods such as Langmuir–Blodgett films [2], stretched polymers [3], micro-grooves [4], stamped polymers [5] and linearly polarized ultraviolet light (UV) exposure of polymers [6], have been used to produce unidirectional LC alignment. LC alignment using a linearly polarized UV exposure is the most promising candidate to overcome the problems with rubbing in addition to greatly simplifying production of multi-domain displays.

Three main types of mateirals for LC alignment using polarized UV exposure have been proposed. First is based on photo-isomerization of azo compounds doped in polymers [6–9]. Second utilizes anisotropic *cis–trans* isomerization [10] or cross-linking [11–15] of poly(vinyl cinnamate) derivatives. Third is based on photo-decomposition of PIs produced by linearly polarized UV exposure [16–20]. Much effort has been concentrated on development of photoreactive PIs which are more heat resistant than azo compounds and poly(vinyl cinnamate) derivatives. However, the mechanism of unidirectional LC alignment using linearly polarized UV exposure has yet to be clarified. In this paper, we explore the mechanism and characteristics of the unidirectional LC alignment using UV exposed PIs with respect to their chemical structures.

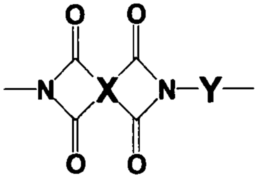
2. EXPERIMENTS

2.1. Synthesis of PIs

PI materials used in this experiments are summarized in Figure 1. PI-1–PI-7 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 [21].

2.2. Preparation of LC Cells

LC cells were prepared to measure dichroic ratios of LCs aligned by linearly polarized UV exposed PI films. PI films were deposited by first spin-coating dilute solutions of the respective polyamic acids and polyimide on ITO glass substrates and then cured at 250°C for 1 hr to accomplish imidization [22]. The thickness of the PI film was controlled at 50 nm. The PI films were



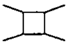
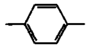
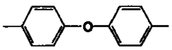
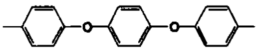
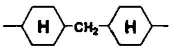
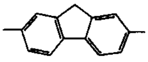
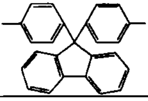
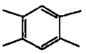
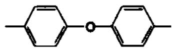
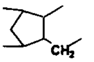
PI No.	**-X-**	**-Y-**
PI-1		
PI-2		
PI-3		
PI-4		
PI-5		
PI-6		
PI-7		
PI-8		

FIGURE 1 Chemical structures of PIs used.

exposed with linearly polarized UV incident normal to the surface. We used a 450 W-Xe 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 in the UV B region after passing through the polarizer was about 6 mW/cm^2. The intensity of Xe lamp monotonically increases with wavelength between 200 to 400 nm; relative intensities of UV light for the light intensity at 250 nm are about 2.2, 2.9 and 3.2 at 300, 350 and 400 nm, respectively [23]. LC cells for dichroic ratio measurement were fabricated using two polarized UV exposed substrates with parallel polarization axis. Dichroic LC, ZLI-2293 (Merck) and 0.5% M-618 (Mitsuitoatsu, azo derivative, $\lambda_{max} = 550$ nm) [24], was filled into the cells in the isotropic state (120°C) and slowly cooled to room temperature to remove flow alignment. LC cells with LC injection in the nematic state showed flow alignment even after LC cells were heated in the isotropic state due to their weak anchoring energies [25].

2.3. Measurement Methods

The dichroic ratios of the LC cells were measured using one polarizer and a UV-Vis spectrometer. PI film birefringences were measured using an instrument described previously [26]. Infrared spectra of PI films were measured using an FT-IR spectrometer, Nicolet 550.

3. RESULTS AND DISCUSSION

3.1. LC Alignment on Various PI Films

The LC alignment produced by various PIs cured at 250°C for 1 hr and either rubbed or normally exposed with linearly polarized UV are summarized in Table I. In most cases, PI shows LC alignment parallel to the rubbing direction and LC alignment perpendicular to the UV polarization. This is consistent with results reported previously [16, 17]. PI-6 containing fluorene diamine, however, aligns LC perpendicular to the rubbing direction and parallel to the exposed UV polarization.

3.2. Effect of Diamine Structures in PIs on LC Alignment

Figure 2 shows the relationship between polarized UV exposure time and the dichroic ratios of LC cells with respect to the number of benzene rings in PIs. The dichroic ratios of LC cells initially increase logarithmically with UV dosage, and approach a constant value at higher dosage. The order of

TABLE I LC alignment on PIs

PI	*LC alignment direction*	
	Rubbing	*Polarized UV*
PI-1	Parallel	Perpendicular
PI-2	Parallel	Perpendicular
PI-3	Parallel	Perpendicular
PI-4	Parallel	Perpendicular
PI-5	Parallel	Perpendicular
PI-6	Perpendicular	Parallel
PI-7	Parallel	Perpendicular
PI-8	Parallel	Perpendicular

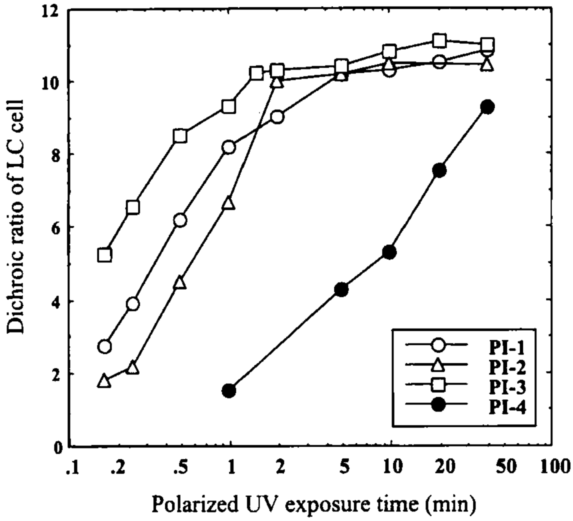


FIGURE 2 Relationship between UV exposure time and dichroic ratios of LC cells on various PI films.

dichroic ratios at lower UV dosage using PI-1 – PI-3 is as below:

PI-3 > PI-1 > PI-2

The order of dichroic ratios of LC cells is not consistent with benzene ring number in PIs. Figure 3 shows the molecular conformations of diamines used in these PIs calculated using molecular mechanics method. Diamine in PI-1 shows the flat molecular conformation with respect to its side view. On the other hand, those of PI-2 and PI-3 are bent because of the ether linkage between benzene rings. The optic axes of benzenes are also shown in Figure 3 as arrows. It is thought that the anisotropic van der Waals forces [27] which would be a main force to align LC increases with the benzene ring number in PI. In the case of PI-2 and PI-3, however, the interplay of optic axes with different vector directions in PIs decreases the magnitude of the anisotropic van der Waals force in UV exposed PI films and results in the decrease of dichroic ratios of LC cells.

Comparison of the dichroic ratios of LC cells using PI with and without aromatic benzene ring suggests that PI without benzene ring (PI-4) shows much lower sensitivity for UV dosage than that with benzene ring (PI-2) as reported previously [28]. UV absorption spectra of these PI films coated on quartz glass are shown in Figure 4. PI-2 shows the absorption around 250 nm, which can be attributed to $\pi-\pi^*$ transitions of benzene ring, and PI-4

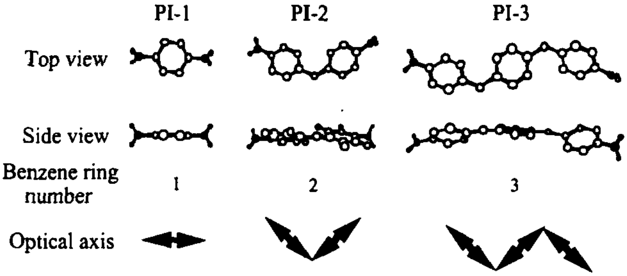


FIGURE 3 Molecular conformations of diamines in PIs calculated using molecular mechanics method.

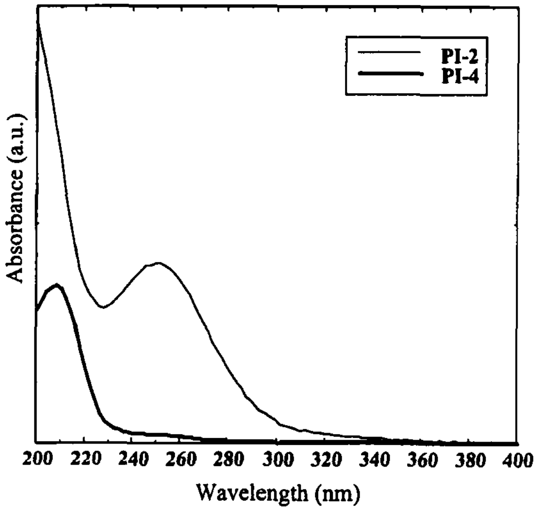


FIGURE 4 UV absorption spectra of PI films.

has very small absorption around 250 nm. Results suggest that PI-4 has the low sensitivity for UV dosage because of no UV absorption in the range over 230 nm where polarizer works effectively.

Figure 5 shows the dependence of the dichroic ratios of LC cells on polarized UV exposure time with respect to PI with fluorene unit located in main chain and side chain. It is found that PI-5 shows higher sensitivity for UV dosage than that of PI-6. In addition, PI-5 shows LC alignment perpendicular to the exposed UV polarization, and that of PI-6 is parallel to the UV polarization. Figure 6 shows the molecular conformations of diamines used in these PIs. Diamine in PI-5 has fluorene unit parallel to its

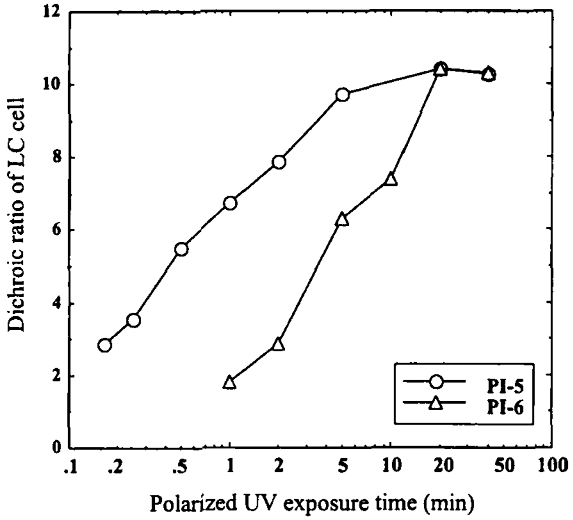


FIGURE 5 Relationship between UV exposure time and dichroic ratios of LC cells on various PI films containing fluorene unit.

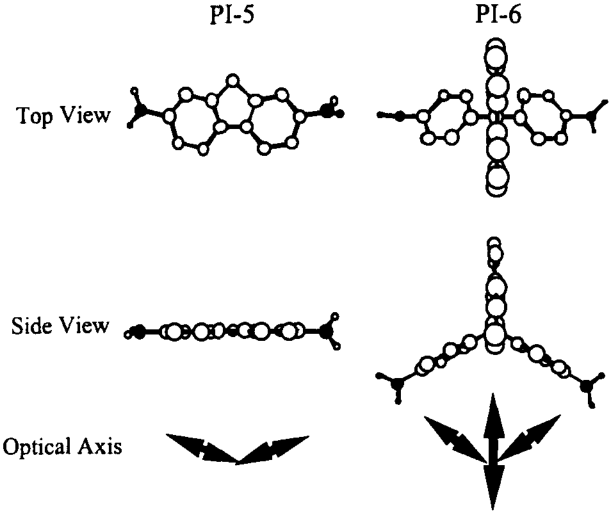


FIGURE 6 Molecular conformations of diamines in PIs containing fluorene unit calculated using molecular mechanics method.

main chain, and that in PI-6 has fluorene unit perpendicular to its main chain. Perpendicular location of fluorene unit in PI-6 to the main chain leads LC molecule to align perpendicular to the rubbing axis as same result observed in poly(styrene) alignment film [29]. Furthermore, the interplay between optic axes of diamine in PI-6, diphenyl methane unit and fluorene unit, results in the lower sensitivity for UV dosage than that of PI-5.

3.3. Effect of Tetracarboxylic Dianhydride Structures in PIs on LC Alignment

Figure 7 shows the relationship between polarized UV exposure time and the dichroic ratios of LC cells. Results show that the chemical structures of tetracarboxylic dianhydrides also considerably affect the sensitivities of LC alignment for UV exposure. In the case of PI-7, the previous paper reported that decomposition of PI chain is restrained due to the charge transfer in PI observed as UV absorption over 300 nm [30]. This charge transfer phenomenon is peculiarly observed in PIs synthesized from aromatic tetracarboxylic dianhydrides and aromatic diamines. However, the difference of sensitivities for UV dosage between PI-2 and PI-8 can not be explained by charge transfer phenomenon, because PI-2 and PI-8 have almost same UV absorption spectra without absorption over 300 nm. To confirm the difference between two samples, dichroic ratios of LC cells were measured using PI films UV exposed in air and nitrogen atmosphere (Fig. 8). In this case of PI-8, the sensitivity for UV exposure largely decreased in

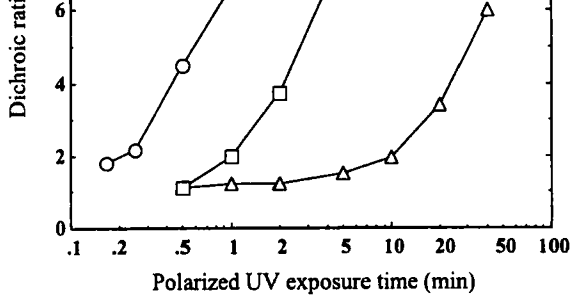


FIGURE 7 Relationship between UV exposure time and dichroic ratios of LC cells on various PI films containing different tetracarboxylic dianhydrides.

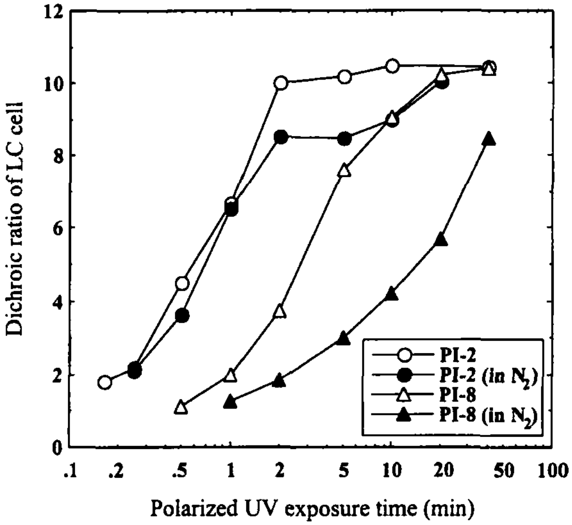


FIGURE 8 Relationship between UV exposure time and dichroic ratios of LC cells on various PI films UV exposed in air and nitrogen atmosphere.

nitrogen atmosphere compared with those in air. In contrast, those of PI-2 showed no difference at lower UV dosage. These results suggest that PI-2 shows two kinds of decomposition, imido ring cleavage [31] which require oxygen and cyclobutane ring cleavage [32] which does not require oxygen. Furthermore, the PI decomposition by cyclobutane ring cleavage is dominant at lower UV dosage. PI-8 shows no cyclopentane ring cleavage in nitrogen atmosphere, so this leads PI-8 into the lower sensitivity for UV exposure compared with that of PI-2.

3.4. Analysis of Mechanism of Unidirectional LC Alignment using Polarized UV Exposure

To elucidate the LC alignment mechanism in more detail, we chose two types of PI which show LC alignment perpendicular (PI-2) and LC alignment parallel (PI-6) to the exposure polarization of UV. We first confirmed the effective axis for LC alignment. Rubbed PI films were normally exposed with polarized UV parallel and perpendicular to the rubbing axis for 0 min to 40 min. Figure 9 shows the relationship between polarized UV irradiation time and dichroic ratios of LC cells. In both PIs, dichroic ratios of LC cells exposed with polarized UV exposure parallel to the rubbing direction gradually decreased with UV irradiation time. On the other hand,

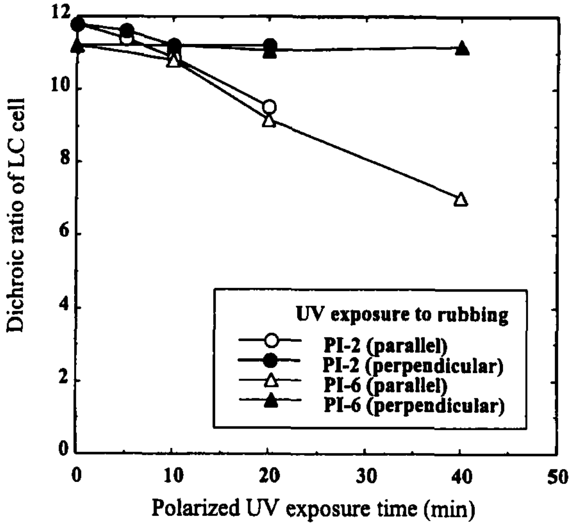


FIGURE 9 Relationship between polarized UV exposure time after rubbing and dichroic ratios of LC cells.

those with polarized UV exposure perpendicular to the rubbing direction showed no change of their dichroic ratios. It is well known that rubbing treatment of PI surface results in the alignment of PI chains parallel to the rubbing direction [21]. These results suggest that polarized UV absorbed parallel to the aligned PI main chains selectively causes the photochemical reaction of PI, and results in the decreases of dichroic ratios of LC cells. Diamine used in PI-6 has two optical axis attributed to fluorene unit and diphenyl methane unit as shown in Figure 6. Electron transfer between fluorene unit and diphenyl methane unit is inihibited because their π-electron orbitals are perpendicular to each other [33]. This means that fluorene unit and diphenyl methane unit in diamine used in PI-6 can individually absorb UV light and diphenyl methane unit directly bonded with cyclobutane tetracarboxylic dianhydride probably causes the decomposition of PI by UV exposure.

UV absorption spectral changes in PI films before and after polarized UV exposure were monitored to measure UV absorption spectra. PI films on quartz substrates were prepared and exposed for 2 hrs with measured normal to the surface. Figure 10 shows UV absorption spectra of PI films before and after polarized UV exposure. After UV exposure, both PI films showed decreases of absorption of 250 nm and increases in the broad absorption above 290 nm. I have not yet determined the photochemical

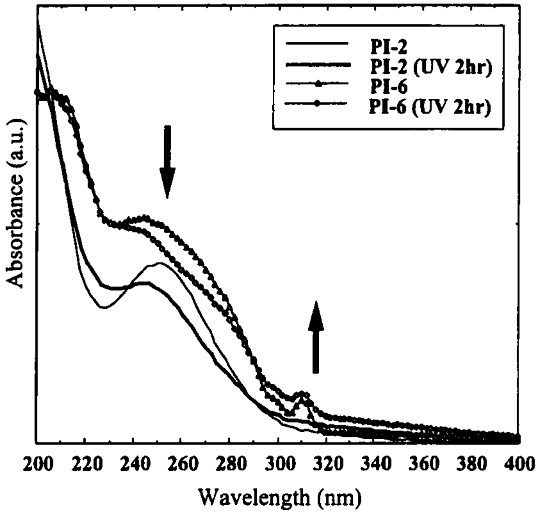


FIGURE 10 UV absorption spectra of PI films before and after UV exposure.

changes in PI films, but it is clear that the broad absorption over 290 nm are generated by the decomposition of PI which corresponds to the absorption of 250 nm. These phenomena are also previously reported on PI material with different chemical structure [16, 17].

Figures 11 and 12 show the dichroic UV absorption spectra of rubbed PI films and polarized UV exposed PI films measured parallel (A_{para}) and perpendicular (A_{per}) to the rubbing direction and the exposed UV polarization, respectively. Dichroic UV absorbance was measured using a surface film polarizer. In the case of rubbing (Fig. 11), PI-2 shows a positive dichroic spectrum, and PI-6 shows a negative dichroic spectrum. The behaviors using polarized UV exposure is opposite to those produced by rubbing (Fig. 12). Furthermore, it should be noted that the subtraction spectra of UV absorption spectra over 290 nm show no dichroism (Fig. 12). Birefringence measurement of PI films after linearly polarized UV exposure also showed that PI-2 had the optical axis perpendicular to the exposed UV polarization, and PI-6 had the parallel optic axis.

Changes in PI films before and after polarized UV exposure were also monitored using FT-IR (Fig. 13). PI films on silicone wafers were normally exposed to polarized UV for 2 hr. Attribution of IR absorption peaks [34] and relative peak intensity [35] of each peak for the peak at 1500 cm^{-1} attributed to ν(1,4-benzene) are summarized in Table II. In both PI films, peak intensities of most of the peaks decrease by UV exposure in air. This

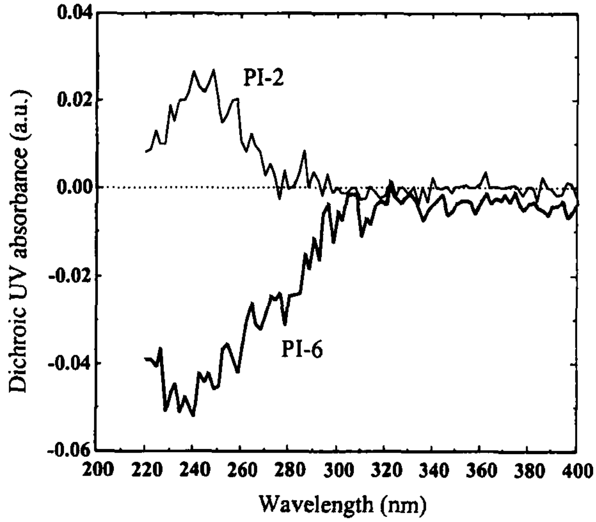


FIGURE 11 Dichroic UV absorption spectra ($A_{para}-A_{per}$) of rubbed PI films measured relative to the rubbing direction.

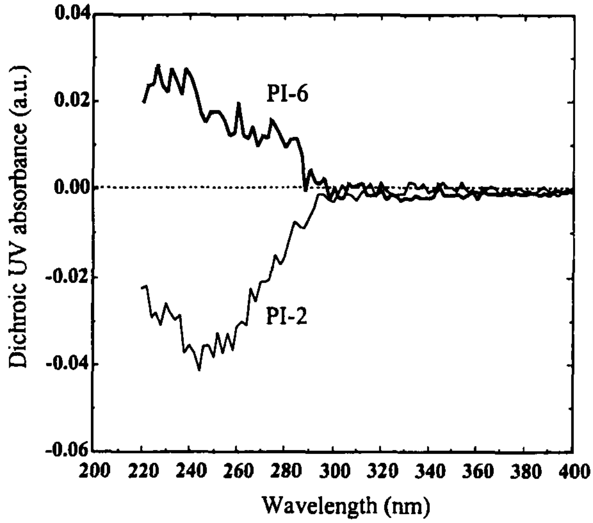


FIGURE 12 Dichroic UV absorption spectra ($A_{para}-A_{per}$) of UV exposed PI films measured relative to the UV polarization.

result shows that surface etching of PI film is caused by UV exposure [36]. Furthermore, relative peak intensities at 1380 cm^{-1} attributed to ν(imide C—N—C) decrease and those at 1720 cm^{-1} attributed to

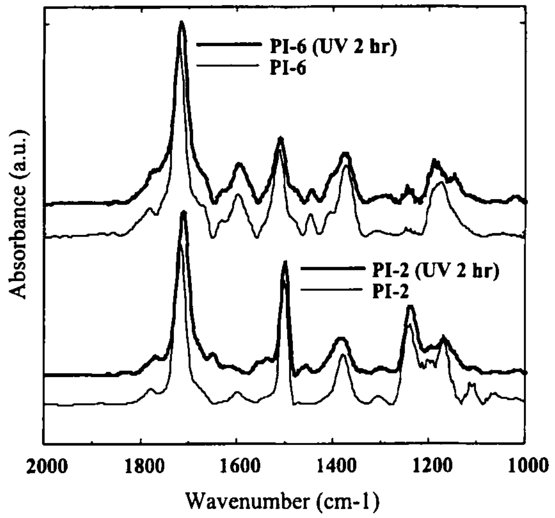


FIGURE 13 FT-IR spectra of PI films before and after UV exposure in air.

TABLE II Attribution of IR absorption peaks and relative intensity

Wavenumber (cm^{-1})	*Attribution*	*Relative peak intensity*					
		PI-2			*PI-6*		
		Before UV	*UV in air*	*UV in N_2*	*Before UV*	*UV in air*	*UV in N_2*
1720	$\nu(C{=}O)$	1.30	1.44	1.24	2.26	2.91	2.13
1500	ν(1,4-benzene)	1.00	1.00	1.00	1.00	1.00	1.00
1380	ν(C —N —C)	0.40	0.30	0.38	0.81	0.74	0.80

$\nu(C = O)$ increase after UV exposure. In the case of UV exposure in air, imide rings in PIs were decomposed by UV exposure, and a new band with IR absorption at around 1720 cm^{-1} was generated by the by-product after the decomposition of PI. In contrast, PI films UV exposed in nitrogen atmosphere show less imide ring cleavage compared with those UV exposed in air. These results also support two kinds of PI decomposition, imide ring cleavage and cyclobutane ring cleavage, by UV exposure.

Taking into account results obtained in this paper we can conclude the mechanism of unidirectional LC alignment by a linearly polarized UV exposure as follows. Figure 14 shows the schematic mechanism of LC alignment by a polarized UV exposure. Before UV exposure, PI chains are randomly aligned. PI chains parallel to the exposed UV polarization are selectively decomposed by UV exposure, and photo-products after UV exposure are randomly relocated in PI films. The residual PI chains

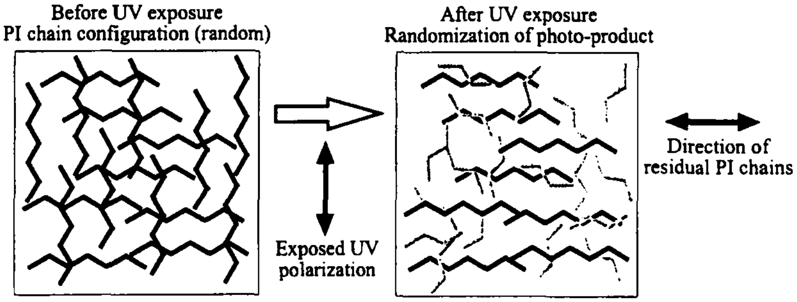


FIGURE 14 Schematic mechanism of LC alignment by a linearly polarized UV exposure; dashed lines shows the by-products of PI after polarized UV exposure.

perpendicular to the exposed UV polarization, which show no photo-decomposition, cause the anisotropic van der Waals force to align LC along its slow axis.

4. CONCLUSION

In this paper, we report unidirectional LC alignment by a linearly polarized UV exposure using various PIs. PI containing fluorene unit in its side chain shows LC alignment parallel to the exposed UV polarization, whose behavior is perpendicular to those of conventional PI materials. Measurement of dichroic ratios of LC cells suggests that sensitivity of unidirectional LC alignment for UV dosage is largely affected by the chemical structures of PIs used. Especially, PI containing diamine with large van der Waals force and PI containing cyclobutane tetracarboxylic dianhydrides show high sensitivity of LC alignment for UV dosage. The results of dichoric ratios of LC cells, UV absorption spectra, birefringences, FT-IR spectra of PI films, and molecular conformations of diamines in PIs calculated using molecular mechanics suggest that the selective photo-decomposition of PI caused the randomization of orientation of photo-products. The residual PI chains perpendicular to the exposed UV polarization, which show no photo-decomposition, cause the anisotropic van der Waals force to align LC along its slow axis.

Acknowledgements

We acknowledge Drs. L. C. Chien, T. Kosa, and X. D. Wang of Kent State University for material synthesis, birefringence measurement, and useful discussion. We also thank Drs. N. Bessho and Y. Matsuki of JSR Co. for their support in this research. Research was supported in part by NSF Science and Technology Center ALCOM, DMR 89-20147.

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