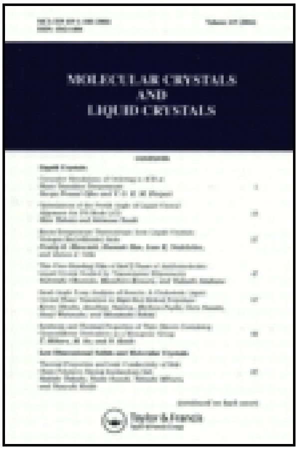

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Polarized Infrared Spectroscopic Studies of Polarized UV-exposed Polyimide Films for Liquid Crystal Alignment

Ki Ryong Ha [a] [b] , John L. West [b] & Gregory R. Magyar [b]

[a] Department of Chemical Engineering, Keimyung University, Taegu, 704-701, Korea

[b] Liquid Crystal Institute, Kent State University, Kent, OH, 44242-0001

To cite this article: Ki Ryong Ha, John L. West & Gregory R. Magyar (1998): Polarized Infrared Spectroscopic Studies of Polarized UV-exposed Polyimide Films for Liquid Crystal Alignment, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 325:1, 13-32

To link to this article: http://dx.doi.org/10.1080/10587259808025380

Mol. Cryst. Liq. Cryst., Vol. 325, pp. 13-32
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

Polarized Infrared Spectroscopic Studies of Polarized UV-exposed Polyimide Films for Liquid Crystal Alignment

KI RYONG HA[a, b], JOHN L. WEST[b,*] and GREGORY R. MAGYAR[b]

[a] *Department of Chemical Engineering, Keimyung University, Taegu, 704-701, Korea;*
[b] *Liquid Crystal Institute, Kent State University, Kent, OH 44242-0001*

(Received 6 August 1997; In final form 3 April 1998)

Polarized Fourier transform infrared (FTIR) and ultraviolet-visible (UV-VIS) spectroscopy were used to investigate the cause of liquid crystal alignment on polarized UV (PUV) irradiated polyimide (PI) films. PI films strongly absorb below 350 nm. PUV irradiation of the PI film caused a decrease in the intensity of the original IR absorbance peaks of the PI, due to degradation of the PI molecules, along with the appearance of a new peak at 3261 cm^{-1}. Because the PI molecules oriented parallel to the direction of UV polarization preferentially degrade, the predominant orientation of the remaining PI molecules after PUV irradiation is perpendicular to the PUV polarization direction. Liquid crystal (LC) molecules align parallel to the predominant orientation of the PI and perpendicular to the PUV polarization direction.

Keywords: PI-2555; polarized UV; liquid crystal; infrared spectroscopy; degradation

1. INTRODUCTION

Most electro-optic applications of liquid crystals require controlled alignment. Control of liquid crystal alignment in LC devices is traditionally produced using mechanically rubbed polymer films. A synthetic velvet cloth is widely used to rub PI films. However, rubbed PI films have several drawbacks, such as particle defects and static charging problems that can destroy a liquid crystal display (LCD) [1].

---

*Corresponding author. Tel.: (330) 672-2654, FAX: (330) 672-2796, e-mail: johnwest@scorpio.kent.edu

PUV irraditation techniques have been developed recently to produce alignment of LC on polyvinylcinnamate films [2–4] and polyimide films. [5–8] PUV irradiation of PI films as an alignment technique for LCDs has the advantage of using the existing PI technology, while eliminating the drawbacks of rubbing. PUV irradiation can also be used to easily manufacture multi-domain LCDs [8, 9]. Although much work has been done to investigate the mechanism of LC alignment on rubbed polymer surfaces [10], little has been done to examine the mechanism of LC alignment on PUV irradiated PI surfaces.

For rubbed polymer surfaces, it is clear that the molecular interactions between LC molecules and the oriented polymer molecules is more important than microgrooves in creating alignment [11, 12]. IR dichroism measurements have been useful in evaluating the molecular orientation of polymers [11]. Recently, much work has been done to measure the orientation of rubbed PI by polarized IR spectroscopy [13, 14], but only preliminary work has been done to determine the orientation of the PI after PUV irradiation [6].

Many kinds of PI can be used as LC alignment layers. In this study, we used DuPont PI-2555 as the LC alignment layer. This material is widely used as an alignment layer in both twisted nematic (TN) and supertwisted nematic (STN) LCDs. PI-2555 is an amorphous polyimide based on BTDA (3,3′, 4,4′-benzophenonetetracarboxylic dianhydride) and a mixture of ODA (4,4′-oxydianiline) and MPD (*m*-phenylene diamine) [15]. The chemical structure of PI-2555 is shown in Figure 1.

In this investigation, we studied PUV irradiated PI-2555 films using polarized infrared spectroscopy to determine the molecular orientation of PI before and after PUV irradiation.

2. EXPERIMENTAL

A. Materials

DuPont PI-2555 was used as the polyimide alignment layer. To obtain the FTIR spectra, suitable concentrations of the polyamic acid (PAA) form of

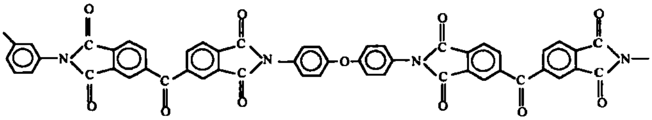

FIGURE 1 Chemical structure of PI-2555.

PI-2555 solution were spin coated on CaF_2 rectangles. Concentrated PI-2555 was diluted with the DuPont T-9039 solvent, a mixture of NMP (N-Methyl-2-Pyrrolidone) and 1-Methoxy-2-Propanol, usually in a ratio of 1 part PI-2555 to 4 parts solvent. Solutions were typically spin coated at 3000 rpm for 30 seconds. Before spin coating, CaF_2 rectangles were rinsed with isopropyl alcohol, and dried throughly on a 125°C hot plate. After spin coating, the PI-2555 coated CaF_2 rectangles were soft baked for 10 minutes at 125°C to remove solvents. After soft baking, they were hard baked in a 275°C convection oven for the desired time, usually 1 hr to accomplish imidization. The thickness of the PI is usually 60 – 70 nm at these conditions. After hard baking, the rectangles were cooled to room temperature in a desiccator. After complete cooling, FTIR spectra were taken.

For the UV-VIS absorption measurements, quartz plates were throughly cleaned with methanol and dried on a hot plate. After cooling, they were spin coated with PI-2555 solution, and the imidization reaction was carried out the same way as with CaF_2 substrates.

B. Analytical Instrumentation

To investigate the effect of UV irradiation on PI films, a Perkin Elmer Lambda 19 was used to take UV-VIS spectra. To study functional group and the molecular chain orientation change by PUV, a Magna 550 FTIR (Nicolet) was used to take transmission FTIR spectra. From the collected FTIR spectrum, the CaF_2 spectrum or twice the ITO glass spectrum was subtracted to obtain the sample spectrum. A single diamond IR polarizer from Harrick company was used for this study. To reduce the noise level, over 300 scans were obtained at $4\,cm^{-1}$ resolution. To investigate the texture of the liquid crystal in contact with PI films with different treatment methods, an optical microscope (Leitz) with crossed polarizer was used.

C. PUV Irradiation

UV irradiation was accomplished using a 450 W Xenon lamp (Oriel) with a UV linear dichroic polarizer (Oriel). Xenon lamps emit radiation in a smooth continuum from the UV through the VIS, with higher deep UV (DUV, $< \sim 320\,nm$) output than mercury sources. The PI was irradiated in air. The intensity of the UV in the UVB region after passing through the polarizer was about $6\,mW/cm^2$.

D. Preparation of Liquid Crystal Cells

Four cells were made to investigate the alignment of liquid crystal in contact with the PI-2555 alignment layers with various surface treatments: rubbed PI, unpolarized UV-irradiated PI, polarized UV-irradiated PI, and untreated PI. Eight rectangular pieces of ITO-coated glass were cleaned with methanol, and PI-2555 solution was spin coated on the ITO glass using the same method as CaF_2 rectangles. The PI-coated ITO glass substrates were cured the same as before. After curing for 1 hr, two PI coated ITO substrates were hand rubbed four times each with velvet cloth, two substrates were irradiated for 1 hr with unpolarized UV, and two substrates were irradiated for 1 hr with polarized UV. A mixture of a UV-curable adhesive and 4.0 μm glass fiber spacers was applied to four corners of the PI-coated substrates. Rubbed and PUV cells were assembled with anti-parallel orientation. After assembly, cells were filled with nematic liquid crystal E7 ($K-N=-10°C$ and $N-I=60°C$, BDH Chemical Co.) by capillary action in the isotropic state at 85°C. E7 is a eutectic liquid crystal mixture of 51% 5CB, 25% 7CB, 16% 8OCB, and 8% 5CT [16]. After filling with E7, the four edges of the cell were completely sealed with 5 Minute Epoxy (Devcon). After the epoxy was cured, the cells were heated to 85°C for 30 minutes and slowly cooled to room temperature over 2 hrs to give good homogeneous alignment of E7.

3. RESULTS AND DISCUSSION

A. Curing Reaction

1. *FTIR Spectral Changes with Curing*

To study changes in the FTIR spectrum caused by the imidization reaction, the FTIR spectra of PI-2555 were obtained after soft baking and again after hard baking. Figure 2 shows FTIR spectra of PI-2555: a) after soft baking for 10 minutes at 125°C, and b) after hard baking for 1 hr at 275°C. After hard baking, no detectable strong peaks were found between $1900\,cm^{-1}$ to $4000\,cm^{-1}$ region except a weak peak at $3068\,cm^{-1}$ caused by the aromatic C—H of the PI. Therefore, in this paper, we present FTIR spectra between $1900\,cm^{-1}-1000\,cm^{-1}$. As shown in Figure 2(a), after soft-baking, several characteristic PAA peaks appeared at 1725, 1665, 1606, 1539, 1499, 1408, $1302\,cm^{-1}$. Two small peaks at 1780 and $1856\,cm^{-1}$ are cyclic anhydride peaks caused by the BTDA, which is present in a slight stoichiometric excess

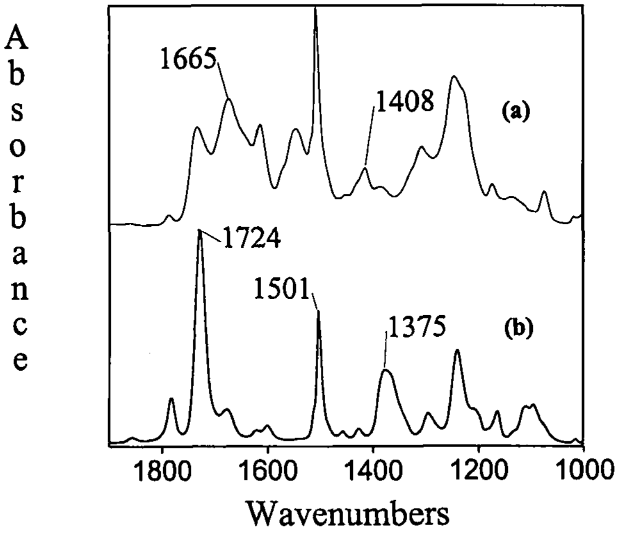

FIGURE 2 The FTIR spectra of PI-2555: (a) after 10 minutes soft baking at 125°C and; (b) after 1 hour hard baking at 275°C.

TABLE I FTIR Peak assignment [18, 19] in the 1900-1000cm^{1} region

Material	*Peak* (cm^{-1})	*Polarization Tendency**	*Assignment*
PAA	1725		$\nu(C=O)$, acid
	1665		$\nu(C=O)$, amide I
	1606		$\nu(1,2,4\text{-}C_6H_3)$
	1539		$\delta(CNH)$, amide II
	1499		$\nu(1,4-C_6H_4)$
	1408		$\delta(OH)$, acid
	1302		$\nu(C{-}OH)$
	1238		ν_{as} (COC)
PI	1780	∥	$\nu(C=O)$ in-phase(imide I) and out-of-phase(anhydride)
	1724	⊥	$\nu(C=O)$ out-of-phase(imide I)
	1676		$\nu(C=O)$-phenyl
	1501	∥	$\nu(1,4-C_6H_4)$
	1375	∥	$\nu(CNC)$ (axial-imide II)

* ∥ – parallel transition moment tendency; ⊥ – perpendicular transition moment tendency.

to enhance the molecular weight [17]. The peak assignments are shown in Table I [18, 19].

As shown in Figure 2(b), after hard baking at 275°C for 1 hr, the characteristic imide peaks appeared at 1780, 1724 and 1375 cm^{-1}. The peak at 1780 cm^{-1} may be assigned to the two different functional groups. One is from the excess cyclic anhydride of unreacted BTDA, and the other is from the $\nu(C=O)$ in-phase(imide I) stretch of the imide group which is formed by the imidization reaction. From these results, we monitored the progress of the imidization reaction during hard baking. The peak at 1238 cm^{-1} may be tentatively assigned as —C—O—C— asymmetric stretching [18].

2. Curing Rate at 275°C

To study the curing rate of PI-2555 at 275°C, FTIR spectra were taken after various times of curing at 275°C. The degree of imidization was followed at the 1375 cm^{-1} imide band, normalized to the 1501 cm^{-1} band as internal standard. We used the 1375 cm^{-1} band because it is isolated from other peaks [20]. The curing reaction can also be followed using the change of the —COOH group at 1408 cm^{-1}.

Figure 3 shows the FTIR spectra before curing and after various cure times at 275°C. As the curing time increased, the peak intensity at 1408 cm^{-1} decreased, while the peak at 1375 cm^{-1} increased. Most of the spectral changes occur during the first 10 minutes of curing. The peak area at

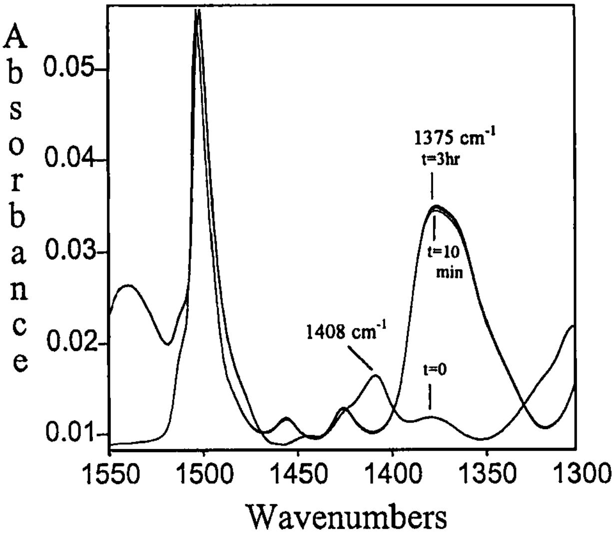

FIGURE 3 FTIR spectra before and after curing at 275°C. The spectrum before curing ($t = 0$) shows a peak at 1408 cm^{-1}. After curing, several curves are shown for cure times ranging from 10 minutes to three hours. These may be most readily distinguished near the 1375 cm^{-1} peak.

1375 cm^{-1} increased from 0 to 0.932, 0.948, 0.958, 0.958, and 0.959 with increasing curing time from 0 to 10, 30, 60, 120 and 180 minutes, respectively. If we assume the degree of imidization of PI-2555 cured for 3 hrs at 275°C to be 100%, we can calculate the degree of imidization with curing time using Eq. (1):

$$\%\ \text{Imidization} = (A_{1375}/A_{1501})/(A_{1375}/A_{1501})_{3\text{hrs at }275^\circ\text{C}} \times 100 \qquad (1)$$

where A_{1375} and A_{1501} are the peak areas at 1375 cm^{-1} and 1501 cm^{-1}, respectively. Percent imidizations calculated using Eq. (1) were 97.9% (after curing 10 minutes), 98.8% (after 30 minutes), 99.4% (after 1 hour), 99.7% (after 2 hours), and 100.0% (after curing 3 hours).

According to Figure 3, imidization reaction is 97.9% complete within the first 10 minutes of curing. The fast reaction in the early stage of the curing results from the higher amount of solvent (NMP + 1-Methoxy-2-Propanol mixture) content in the early stage of curing reaction, which increases the mobility of the chain. The curing reaction gradually slows, due to the decrease in molecular mobility resulting from the loss of residual solvent and from the conversion of the PAA to the more rigid PI [21].

The pretilt angle between LC and PI alignment layer strongly depends on the surface tension of the PI layer [8]. Controlling the % imidization, by changing either the curing time or the curing temperature, can control the surface tension of the PI layer. Imidization results in a reduction in the concentration of the polar — COOH and — CONH — groups, which are converted to — $(C=O)_2N$ — groups. Therefore, this imidization reaction is responsible for the change in surface tension of the PI alignment layer and, thus, for the resulting change in the pretilt angle.

B. Effects of the UV or PUV Irradiation

1. UV-VIS Spectral Changes

Photochemical reactions will depend on the overlap of the emission spectrum of the UV source and the absorption spectrum of the PI. Strong absorption means efficient transfer of energy from the incident light into the PI molecules. Therefore, we obtained UV-VIS spectra of the PI-2555 after various exposure times with unpolarized UV irradiation. All of the UV-VIS spectra of PI before and after UV irradiation showed very little absorption from 350 to 800 nm; therefore, we present here only the 200–350 nm region, as shown in Figure 4. Therefore, the UV light at wavelengths less than 350 nm will induce most of the photochemical reactions of the PI in our experiment.

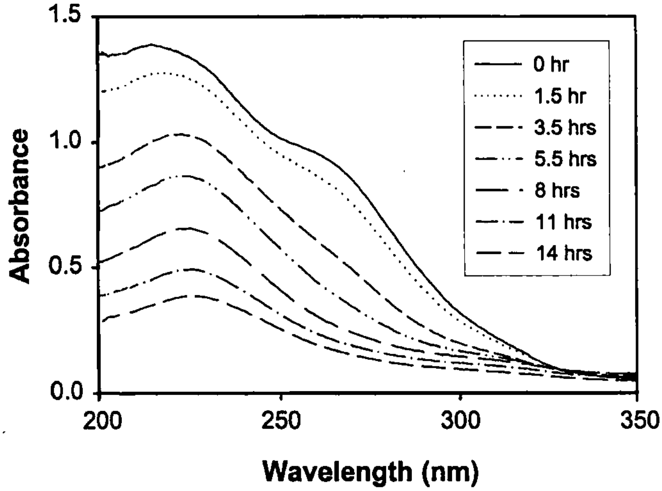

FIGURE 4 UV-VIS spectra after various times of PUV irradiation.

By increasing UV irradiation time, two absorption peaks at 210 and 270 nm, which were present before UV irradiation, decreased, as shown in Figure 4. Particularly, after 3.5 hrs UV irradiation, the shoulder peak at 270 nm almost disappeared as shown in Figure 4. In addition, the color of the PI-2555 changed from a yellowish tint before radiation to transparent after UV exposure.

2. Alignment by PUV Irradiation

PUV irradiation of the PI cured at 275°C resulted in several changes appearing in the FTIR spectra. First, the absorbance of most PI peaks decreased with PUV irradiation, with some of the peaks showing a shift to lower wave number. Second, a broad new peak appeared at 3261 cm^{-1}. Third, polarized IR absorbance spectra showed changes in the relative peak heights, indicating changes in molecular orientation.

a) Changes of the Peak Intensities with PUV Irradiation Time To investigate the effect of the PUV irradiation on the PI, FTIR spectra of the PI before and after PUV irradiation were taken. Figure 5 shows changes in the 1900–1000 cm^{-1} region of the FTIR spectra with increasing PUV irradiation time. Three observations can be made from Figure 5. First, all absorption peak

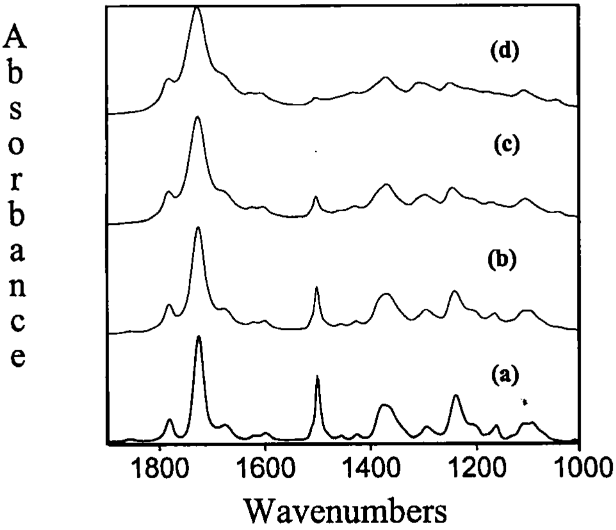

FIGURE 5 FTIR spectra in the 1900–1000 cm^{-1} region after PUV irradiation times of: (a) 0 hr; (b) 10 hrs; (c) 19 hrs; and (d) 35 hrs.

intensities decrease as PUV irradiation time increases. Second, the peak at 1721 cm^{-1} (due to $C=O$ of imide group) became very broad. These features are very similar to spectral changes resulting from the degradation of PI films due to irradiation with ion beams, such as B^+ ions [22]. Third, the peaks initially at 1724 and 1375 cm^{-1} shifted to 1721 and 1367 cm^{-1} after PUV irradiation. This shift may reflect changes in the local environment of the groups.

To investigate the absorbance changes of the characteristic peaks as a function of PUV irradiation time, the areas of the 1855, 1780, 1724, 1501, 1375, and 1238 cm^{-1} peaks were measured after various PUV irradiation times. The % remaining peak area after a given PUV irradiation time was calculated by the following equation:

$$\% \text{ Remaining Peak Area} = \text{Area}(t)/\text{Area}(0) \times 100 \qquad (2)$$

Area (t) = The peak area after t minute of PUV irradiation time.

Area (0) = The peak area before PUV irradiation.

The % remaining peak area changes for each of the peaks are shown in Figure 6. According to Figure 6, those peak areas at 1855 and 1501 cm^{-1} decreased very rapidly due to cleavage of the C(O) —O —(CO) of the cyclic anhydride, and the transforming of the aromatic rings, respectively.

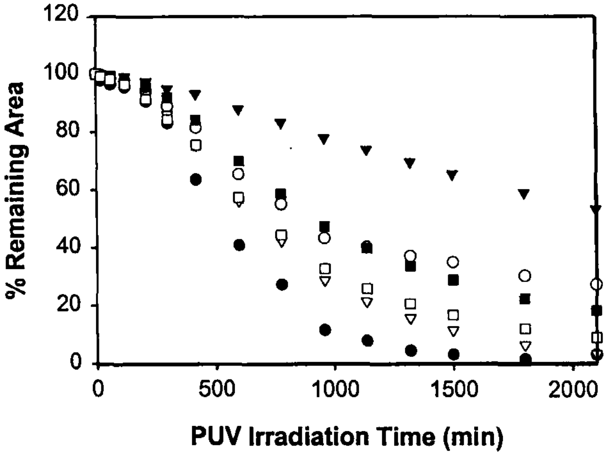

FIGURE 6 % remaining peak area changes of several peaks with PUV irradiation time: ●$1855\,cm^{-1}$; ○ $1780\,cm^{-1}$; ▲$1724\,cm^{-1}$; ▽$1501\,cm^{-1}$; ■$1375\,cm^{-1}$; and □$1238\,cm^{-1}$.

The % remaining peak area changes of the imide group, which shows peaks at 1780, 1724, and $1375\,cm^{-1}$, show different degradation rates among the three peaks. The slow decrease of the $1724\,cm^{-1}$ peak (which moved to $1721\,cm^{-1}$ after PUV irradiation) may be caused by the combination of two effects: 1) decrease of the peak area due to degradation of the imide bond, and 2) increase in peak area due to formation of C = O or COOH groups by photo-oxidation.

It is well known that UV absorption below 250 nm ($\Delta E = 116$ kcal/mol) can result in the breaking of the carbon—carbon, carbon—halogen, carbon—oxygen, and oxygen—hydrogen bonds in the polymer chain to produce radicals [23]. Photo-oxidized radicals can be formed by the reaction of the radiation-induced radicals with oxygen or moisture in the air. These radicals can undergo further photolysis to smaller fragments [24]. This means that the PI surface was initially oxidized by the PUV to form C = O containing groups such as C = O and COOH. The majority of the COOH groups may be formed by the cleavage of the comparatively weak — C —N — bond [25]. After long PUV irradiation, however, the fragmented material yields very small photooxidation products, such as H_2O, CO_2 and CO, that will be easily evolved away [26]. Therefore, a decrease in the areas of all the peaks can be observed. The peak area at $1501\,cm^{-1}$ showed a faster decrease than that of the — C —N — bond at $1375\,cm^{-1}$. It indicates faster transformation and removal of the 1,4-C_6H_4 group than that of the — C —N — bond.

b) New Product Formation with PUV Irradiation Figure 7 shows the FTIR spectra of the PUV irradiated PI in the 3600–2700 cm^{-1} region. By increasing the PUV irradiation time, we found a decrease of the 3067 cm^{-1} peak due to aromatic C—H, along with the appearance of a new broad peak near 3261 cm^{-1}. With increasing PUV irradiation time, the intensity of this peak increased, and its position moved from 3286 cm^{-1} (10 hrs PUV) → 3273 cm^{-1} (19 hrs PUV) → 3261 cm^{-1} (35 hrs PUV), as shown in Figure 7. This new peak at 3261 cm^{-1} may be due to OH stretching of the —COOH group, which can be formed by breaking the —C—N— bond, or the peak may result from other —OH groups [27].

In order to determine what reaction occurs with PUV irradiation, difference spectra were obtained by subtracting the FTIR spectrum of the PI after PUV irradiation from the FTIR spectrum obtained before PUV irradiation. The typical spectrum obtained by subtracting the FTIR spectrum of the PI after 10 hrs of PUV irradiation from the FTIR spectrum before irradiation is shows in Figure 8. As shown in Figure 8, all peaks in the difference spectrum, except peaks at 3274, 1749, and 1708 cm^{-1}, show negative absorbance due to degradation of the PI by PUV irradiation. The 1749 and 1708 cm^{-1} peaks may be caused by the carboxylic acid groups produced by the PUV irradiation. Carboxylic acids which exist as dimers

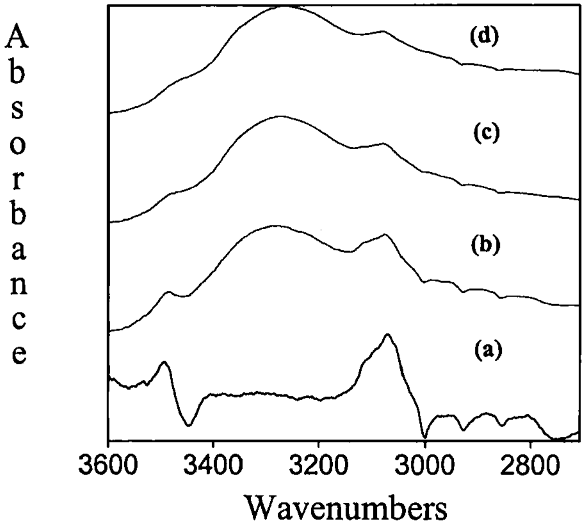

FIGURE 7 FTIR spectra in the 3600–2700 cm^{-1} region after PUV irradiation times of: (a) 0 hr; (b) 10 hrs; (c) 19 hrs; and (d) 35 hrs.

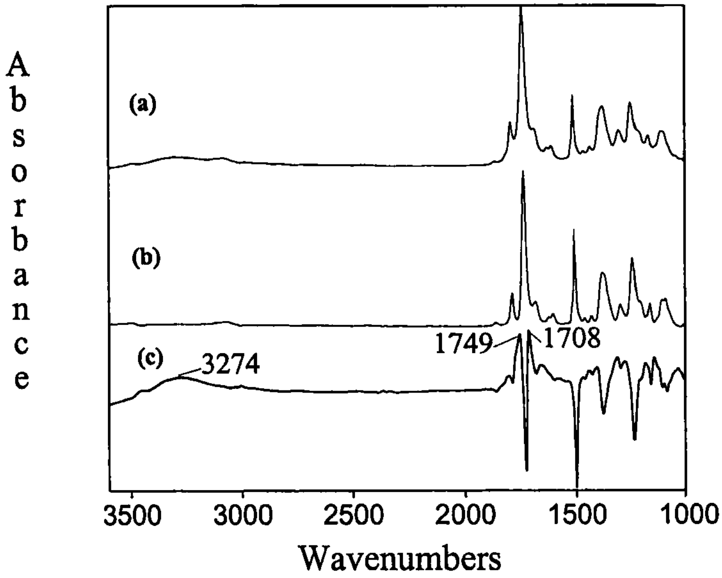

FIGURE 8 FTIR spectra of PI: (a) after 10 hrs PUV irradiation; (b) before PUV irradiation; and (c) difference obtained by subtracting (b) from (a). An expanded y-axis scale is used for (c).

absorb at $\sim 1710\,\text{cm}^{-1}$, and free, non-hydrogen-bonded acids at $1755\,\text{cm}^{-1}$. Therefore, the peak at $1749\,\text{cm}^{-1}$ may be caused by the carboxylic acids which form hydrogen bonded complexes with adjacent oxygen products [28]. The peak at $3274\,\text{cm}^{-1}$ may be caused by the — OH of the — COOH groups and other — OH groups.

With PUV irradiation, the concentration of the more polar — COOH groups increased relative to the less polar groups, such as the benzene rings (see Figs. 5 and 7). This increase in polarity of the PI surface by PUV irradiation may have an effect on the pretilt angle of the LC.

c) Molecular Orientation of the PUV Irradiated PI To determine changes in the molecular orientation of the PI induced by PUV irradiation, polarized FTIR spectra were obtained after PUV irradiation. Figure 9 shows the difference in the polarized FTIR spectra of PI after 10 hrs of PUV irradiation. The difference spectrum is obtained by subtracting the FTIR spectrum with perpendicular polarization from the spectrum with parallel polarization. For a given wave number, the absorbance difference (A_d) in

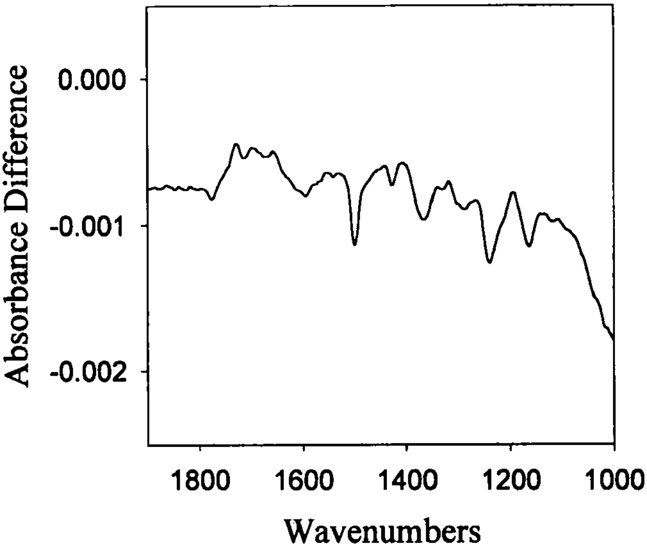

FIGURE 9 Difference in the polarized FTIR spectra of PI after 10 hrs of PUV irradiation. The difference spectrum (A_d) is obtained by : $A_d = A_{\parallel} - A_{\perp}$ where $A_{\parallel}$ is obtained with IR polarization parallel to the PUV polarization direction, and $A_{\perp}$ is obtained with IR polarization perpendicular to the PUV polarization direction.

Figure 9 is given by:

$$A_d = A_{\parallel} - A_{\perp} \tag{3}$$

where $A_{\parallel}$ is the FTIR absorbance obtained with IR polarization parallel to the PUV polarization direction, and $A_{\perp}$ is the absorbance with IR polarization perpendicular to the PUV polarization direction.

All peaks in Figure 9 show negative values, except for a positive peak at 1729 cm^{-1}. According to Table I, the peak at 1729 cm^{-1} has a transition moment perpendicular to the molecular axis. All other remaining peaks have transition moments parallel to the molecular axis. This PI molecular orientation change after PUV exposure appears to be primarily due to the preferential degradation of the PI molecules parallel to the PUV direction. Reorientation of the molecular chain due to the imide bond breaking may also play a role.

In Figure 9, the area of the 1729 cm^{-1} peak is smaller than the other peak areas. The C = O group corresponding to the 1729 cm^{-1} peak may be poorly aligned due to its proximity to the kink in the MDA region of the PI-2555 chain (see Fig. 1). Therefore, measuring the peak area change at 1729 cm^{-1} with PUV irradiation time can result in error. Instead, we used two strong negative peaks in the difference spectrum to estimate the degree of orientation of the polymer chains [29]: one at 1501 cm^{-1} and the other at 1367 cm^{-1}. The dichroic difference (D) at these peaks were determined from the polarized FTIR spectra at various times after PUV irradiation according to Eqs. (4) and (5):

$$D(1501) = |A_{\parallel}(1501) - A_{\perp}(1501)| \tag{4}$$

$$D(1367) = |A_{\parallel}(1367) - A_{\perp}(1367)| \tag{5}$$

where $A_{\parallel}$ = Absorbance when the polarization vector is parallel to the PUV irradiation direction; $A_{\perp}$ = Absorbance when the polarization vector is perpendicular to the PUV irradiation direction.

The dichroic differences (D) at 1501 cm^{-1} and 1367 cm^{-1} are plotted in Figure 10 as a function of PUV irradiation time. According to Figure 10, both D(1501) and D(1367) initially increase with PUV irradiation time. However, after 13 hrs irradiation, both D(1501) and D(1367) start to decrease. This suggests that after 13 hrs PUV irradiation, very little unreacted PI parallel to the PUV polarization direction remains, and the reaction of molecules oriented perpendicular to the PUV direction begins to dominate [30].

In order to compare the molecular orientation of PI after PUV irradiation with that of PI after rubbing, we took the polarized FTIR spectra of PI-2555

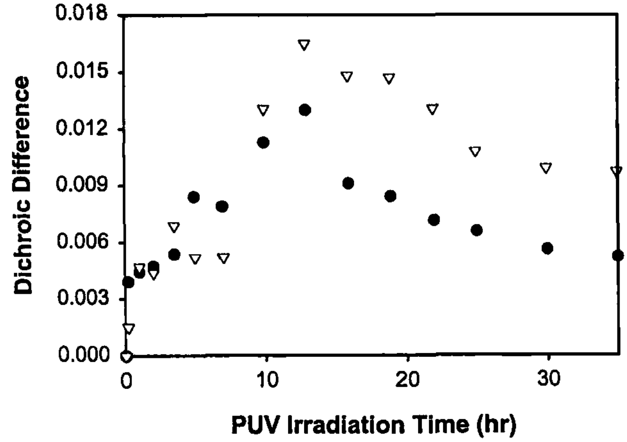

FIGURE 10 Dichroic difference change with PUV irradiation time: ● D(1501 cm^{-1}); ▽ D(1367 cm^{-1}).

after rubbing with a velvet cloth 5 times. The results are shown in Figure 11. In contrast to the PUV irradiated PI, the difference spectrum in Figure 11(c) after rubbing showed the opposite trend, with a positive value at 1501 cm^{-1} and a negative value at 1726 cm^{-1}. This result is consistent with previous work showing that the rubbed PI molecules are aligned along the rubbing direction [31]. As with PUV irradiated PI, the peak at 1726 cm^{-1} is smaller than other major peaks.

3. Alignment Direction of the LC Molecules

a) Texture of the LC In order to investigate the effects of the PI alignment layer treatment on the texture of the LC, four LC cells with different treatment methods were prepared: (a) untreated PI; (b) rubbed PI; (c) PI irradiated with unpolarized UV for 1 hr; (d) PI irradiated with PUV for 1 hr. After filling with liquid crystal, the cells were observed under the microscope using crossed polarizers. The photomicrographs taken under the crossed polarizing microscope are shown in Figure 12. According to Figures 12(a) and (c), Schlieren textures, which are due to imperfect homogeneous

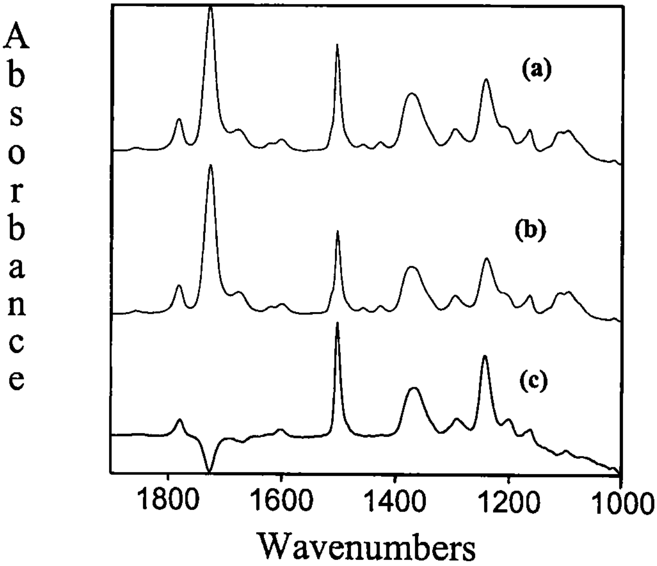

FIGURE 11 FTIR spectra of rubbed PI: (a) with IR polarization parallel to the rubbing direction; (b) with IR polarization perpendicular to the rubbing direction and (c) difference obtained by subtracting (b) from (a). An expanded y-axis scale is used for (c).

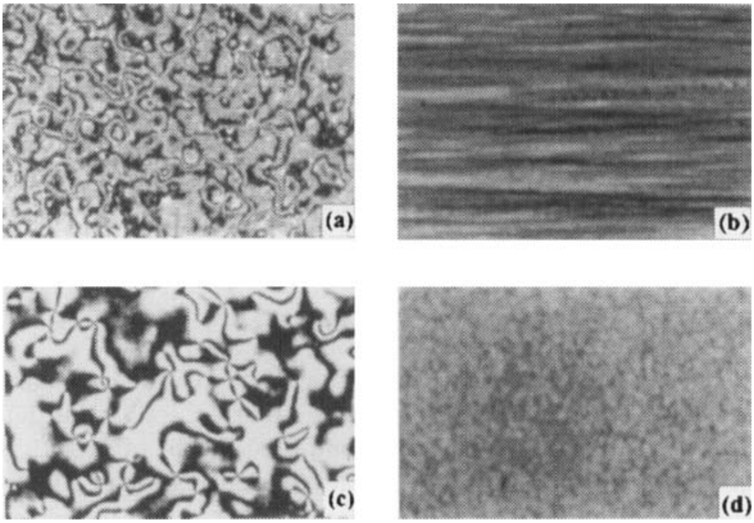

FIGURE 12 Photomicrographs of the ITO glass LC cell (× 110): (a) LC cell made of PI without any treatment; (b) LC cell made of rubbed PI; (c) LC cell made of 1 hr UV irradiated PI and (d) LC cell made of 1 hr PUV irradiated PI. (See Color Plate I).

alignment of the E7 [32], appear in the LC cells which were prepared using the PI without any treatment and the unpolarized UV irradiated PI. In contrast, LC cells with rubbed PI and PUV irradiated PI, show uniform homogeneous alignment of the E7 as shown in Figures (b) and (d). The difference between these two cells is the presence of the scratch lines for the rubbed PI layer, which are not present in the PUV irradiated PI. With the crossed polarizing microscope, we also confirmed that the alignment directions of the LC molecules were either parallel or perpendicular to the rubbing direction or PUV polarization direction. To investigate whether the LC molecules align parallel or perpendicular to the rubbing or PUV polarization directions; we obtained FTIR spectra of two LC cells.

b) FTIR Measurement In order to investigate the alignment direction of the E7, polarized FTIR spectra were obtained for the ITO glass cell with PUV irradiated PI alignment layer. These are shown in Figure 13. The peak assignments are shown in Table II. The direction of the transition dipoles of $—C\equiv N$ stretching in E7 is parallel to the long molecular axis of the LC molecules [33]. Also the symmetric and asymmetric stretching modes of $—CH_3$ have components that are parallel, while the symmetric and

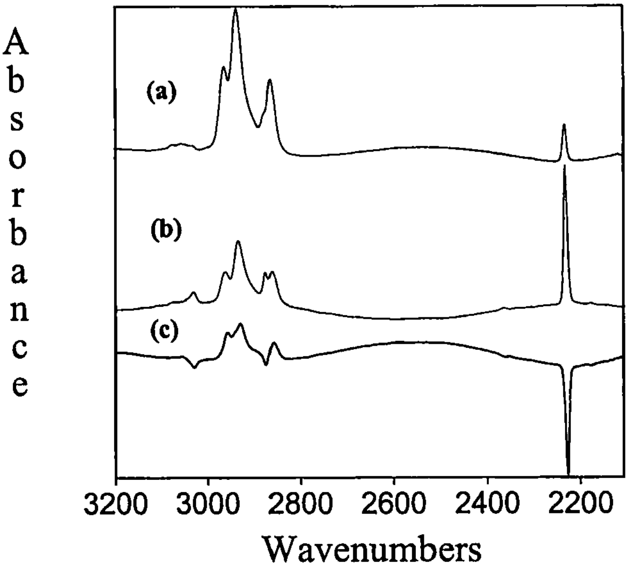

FIGURE 13 FTIR spectra of ITO glass LC cell with PUV irradiated PI alignment layer: (a) with polarization parallel to the PUV irradiation direction; (b) with polarization perpendicular to the PUV irradiation direction; and (c) difference obtained by subtracting (b) from (a).

TABLE II Peak assignment for E7 [16]

Peak (cm^{-1})	*Assignment*
3072	C —H aromatic stretching
3053	C —H aromatic stretching
3041	C —H aromatic stretching
3029	C —H aromatic stretching
2956	asymmetric stretching mode of CH_3
2929	asymmetric stretching mode of CH_2
2871	symmetric stretching mode of CH_3
2858	symmetric stretching mode of CH_2
2227	stretching mode of $C \equiv N$

asymmetric stretching modes of $—CH_2$ are perpendicular to the long molecular axis of the LC molecules. Figure 13(a) shows the FTIR spectrum with polarization parallel to the PUV polarization. In this case the $—C \equiv N$ stretching mode peak is small compared to the CH_2 stretching mode. In contrast, Figure 13(b) shows a strong symmetric stretching mode peak of $—CH_3$ at 2871 cm^{-1}, as well as strong $—C \equiv N$ stretching mode peak at 2227 cm^{-1}, compared to the other $—CH_2$ stretching mode peaks. These two results strongly suggest that the alignment direction of the E7 molecules is perpendicular to the PUV irradiation direction, or parallel to the direction of the PI molecular chain. Figure 13(c) shows the difference spectrum obtained by subtracting spectrum (b) from spectrum (a).

Figure 14 shows the FTIR spectra of the LC cell with rubbed PI alignment layer. In contrast to the spectra with PUV irradiated alignment layer in Figure 13, the spectra in Figure 14 show the opposite trend for E7. Thus, these spectra support the conclusion that the alignment of the E7 molecules is parallel to the rubbing direction, or parallel to the PI molecular chain direction.

4. CONCLUSIONS

In this experiment, we have arrived at the following conclusions:

1. With increasing PUV irradiation time, all peak areas decreased except for a new peak at 3261 cm^{-1}, which may be caused by the production of — COOH and — OH groups. This indicates an overall degradation in the polyimide chain. Figure 6 demonstrates that photodegradation occurs at a faster rate in some functional groups than in others.

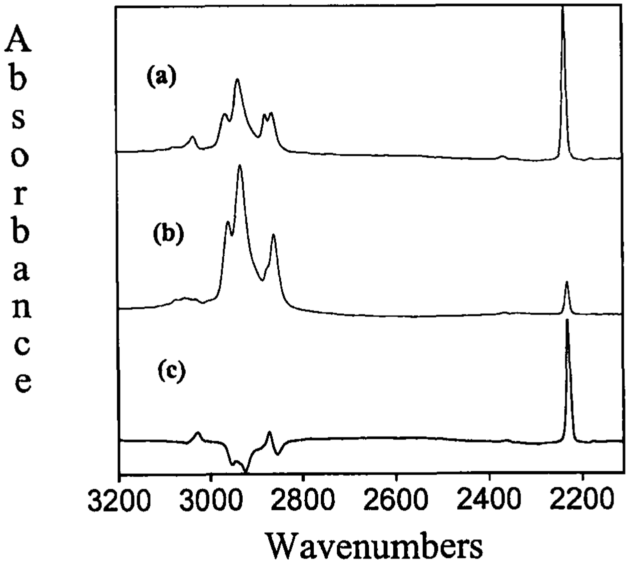

FIGURE 14 FTIR spectra of ITO glass LC cell with rubbed PI alignment layer: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction; and (c) difference obtained by subtracting (b) from (a).

2. The unreacted molecular chains of the PUV-irradiated PI were perpendicular to the PUV polarization direction, due to the preferential degradation of the PI molecules parallel to the PUV polarization direction.
3. The main reason for LC alignment by PUV irradiation is the photochemically induced anisotropy resulting from preferential photodegradation of the PI molecules parallel to the PUV direction. LC aligns with the preferential orientation of the polymer chain, or perpendicular to the polarization of the UV.

Acknowledgments

We would like to thank the Korea Research Foundation and the National Science Foundation (ALCOM DMR-8920147-08) for their financial support for this project.

References

[1] J. Varney, Solid State Technology, pp. 61-65 (Sept. 1992).
[2] H. Schadt, K. Schmitt, V. Kozinkov and V. Chigrinov, *Jpn. J. Appl. Phys.*, **31**, 2155-2164 (1992).
[3] T. Y. Marushi and Y. A. Reznikov, *Mol. Mat.*, **3**, 161-168 (1993).
[4] G. P. Byran-Brown and I. C. Sage, *Liquid Crystals*, **20**(6), 825-829 (1996).
[5] P. J. Shannon, W. M. Gibbons and S. T. Sun, *Nature*, **368**, 532-533 (1994).
[6] J. L. West, X. Wang, Y. Ji and J. R. Kelly, SID 95 Digest, pp. 703-705 (1995).
[7] J. Lu, S. Deshpande, J. Kanicki, A. Lien, R. A. John and W. L. Warren, AMLCD' 95 Digest, pp. 97-100 (1995).
[8] J. Lu, S. V. Deshpande, E. Gulari and J. Kanicki, *J. Appl. Phys.*, **80**(9), 5028-5034 (1996).
[9] A. Lien, R. A. John, M. Angelopoulos, K. W. Lee, H. Takano, K. Tajima and A. Takenaka, *Appl. Phys. Lett.*, **67**(21), 3108-3110 (1995).
[10] J. M. Geary, J. W. Gooby, A. R. Kmetz and J. S. Patel, *J. Appl. Phys.*, **62**(10), 4100-4108 (1987).
[11] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki and S. Morokawa, *J. Appl. Phys.*, **80**(1), 431-439 (1996).
[12] N. A. J. M. van Aerle, M. Barmentlo and R. W. Hollering, *J. Appl. Phys.*, **74**(5), 3111-3120 (1993).
[13] K. Sakamoto, R. Arafune, N. Ito, S. Ushioda, Y. Suzuki and S. Morokawa, *Jpn. J. Appl. Phys.*, Part 2, **33**(9B), L1323-L1326 (1994).
[14] R. Hasegawa, Y. Mori, H. Sasaki and M. Ishibashi, *Mol. Cryst. Liq. Cryst.*, **262**, 77-88 (1995).
[15] C. Feger and H. Franke, In: "Polyimides: Fundamentals and applications" Edited by M. K. Ghosh and K. L. Mittal, Marcel Dekker, Inc., Chap. 24, p. 793, New York (1996).
[16] C. A. McFarland, J. L. Koenig and J. L. West, *Applied Spectroscopy*, **47**(3), 321-329 (1993).
[17] F. W. Harris, In: "Polyimides" Edited by D. Wilson, H. D. Stenzenberger and P. M. Hergenrother (Blackie, Glasgow and London), Chap. 1, p. 7 (1990).
[18] H. Isida and M. T. Huang, *Spectrochimica Acta*, **51A**(3), 319-331 (1995).

[19] S. E. Molis, In: "Polyimides: Materials, Chemistry and Characterization" Edited by C. Feger, M. M. Khojasteh and J. E. McGrath, pp. 659-672, Elsevier Science Publishers (1989).

[20] C. A. Pryde, *J. Polym. Sci: Part A: Polym. Chem.*, **27**, 711-724 (1989).

[21] F. W. Harris, In: "Polyimides" Edited by D. Wilson, H. D. Stenzenberger and P. M. Hergenrother (Blackie, Glasgow and London) Chap. 1, p. 22 (1990).

[22] D. Xu, X. L. Xu, G. D. Du, R. Wang and S. C. Zou, *Nuclear Instruments and Methods in Physics Research*, **B80/81**, 1063-1066 (1993).

[23] J. F. Rabek, *Photodegradation of Polymers: Physical Characteristics and Applications*, p. 2, Springer-Verlag (1996).

[24] M. A. George, B. L. Ramakrishna and W. S. Glausinger, *J. Phys. Chem.*, **94**, 5159-5164 (1990).

[25] D. J. T. Hill, F. A. Rasoul, J. S. Forsythe, J. H.O'Donnell, P. J. Pomery, G. A. George, P. R. Young and J. W. Connell, *J. Appl. Polym. Sci.*, **58**, 1847-1856 (1995).

[26] C. E. Hoyle, D. Creed, R. Nagarajan, P. Subramanian and E. T. Anzures, *Polymer*, **33**(15), 3162-3168 (1992).

[27] A. A. Lin, V. R. Sastri, G. Tesoro, R. Eachus and A. Reiser, *Macromolecules*, **21**, 1165-1169 (1988).

[28] D. J. Carlsson, R. Brousseau, C. Zhang and D. M. Wiles, In: "Chemical Reactions on Polymers" Edited by J. L. Benham and J. F. Kinstle (ASC Symposium Series 364, American Chemical Society, Washington, DC), Chap 27. p. 382 (1988).

[29] R. Hasegawa, Y. Mori, H. Sasaki and M. Ishibashi, *Jpn. J. Appl. Phys.*, **35**, 3492-3495 (1996).

[30] H. G. Galabova, D. W. Allender and J. Chen, *Phys. Rev. E*, **55**(2), 1627-1631 (1997).

[31] K. Sawa, K. Sumiyoshi, Y. Hirai, K. Tateishi and T. Kamejima, *Jpn. J. Appl. Phys.*, **33**, 6273-6276 (1994).

[32] D. Demus, L. Richter, Textures of Liquid Crystals, p. 32, Verlag Chemie, New York (1978).

[33] S. Wu, *Applied Optics*, **26**(16), 3434-3440 (1987).