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Spectroscopic Studies on the Liquid Crystal Alignment Mechanism for Polarized UV-Exposed Organosoluble 6FDA-TFMB Polyimide Films

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An organosoluble polyimide based on 2,2'-bis(3,4'-dicarboxyphenyl)-hexafluoropropane dianhydride(6FDA) and 2,2'-bis(trifluoromethyl)benzidine(TFMB) was investigated for possible use as a liquid crystal (LC) alignment layer in pre-imidized form. Polarized Fourier transform infrared (FTIR) and ultraviolet-visible (UV-VIS) spectroscopy were used to investigate the effect of polarized UV (PUV) irradiation on the polyimide (PI). PI films strongly absorb UV below 340 nm, resulting in photochemical reaction of the PI. PUV irradiation of the PI film resulted in a decrease of all the peak intensities in the IR, except for newly formed anhydride peaks at 1859 and 1789 cm⁻¹ and the -OH peak at 3266 cm⁻¹ from the -COOH group, due to degradation of the PI molecules. Because the preferential degradation direction of the PI molecules is parallel to the UV polarization direction, the predominant orientation of the remaining PI molecules after PUV irradiation is perpendicular to the polarization direction. Alignment of the liquid crystal on PUV irradiated PI is generally perpendicular to the polarization direction of the PUV. Defects in the LC alignment may result from the liquid crystal dissolving or plasticizing fragments of the PI.

Keywords: Polarized infrared spectroscopy; polyimide; degradation; ultraviolet

I. INTRODUCTION

Most electro-optic applications of liquid crystals require controlled alignment. The most widely used aligning materials are PIs. Two types of PIs can be used for this application. The first group consists of PIs based on polyamic acid precursors, which are baked at 250–350°C to form the PI film. The second type of

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PIs are based on pre-imidized materials, which are dissolved in solvents. These pre-imidized PIs require only a low temperature (180 °C) bake cycle to drive off the solvents [1], since no imidization reaction is required. Therefore, the pre-imidized PIs can be useful for applications involving color filter materials or active matrix elements which could be degraded by the high temperature processing of the imidization reaction.

To give proper alignment of the LC, the PI alignment film can be rubbed mechanically with synthetic velvet cloth [2–4] or irradiated with polarized UV [5–7]. For rubbed PI surfaces, rubbing induces an orientation of the polymer molecules along the rub direction. The LC generally aligns parallel to the rubbing direction [2–4]. With PUV irradiated PI surfaces, however, the molecular orientation of the PI is perpendicular to the PUV polarization direction, due to preferential UV degradation of the PI molecules parallel to the polarization [8]. The LC aligns with the PI molecules, perpendicular to the polarization direction. IR dichroism can be used to evaluate the molecular orientation of polymers [3,9].

6FDA-TFMB PI has been known for its good solubility and high optical transparency [10]. The chemical structure of 6FDA-TFMB is shown in Figure 1.

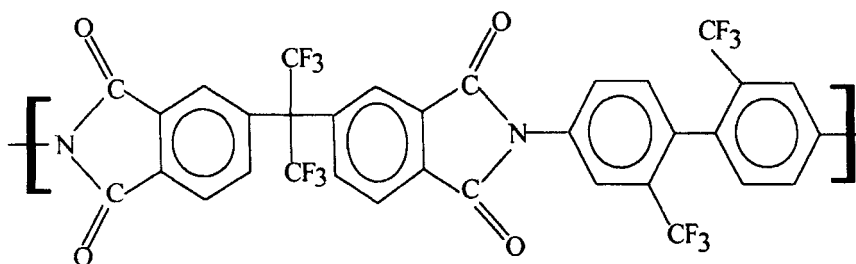


FIGURE 1 Chemical structure of 6FDA-TFMB PI

6FDA-TFMB has been known to have excellent solubility in *N,N*-dimethylacetamide, acetone, tetrahydrofuran (THF), ethyl acetate, etc. Therefore, we investigate the possibility of using 6FDA-TFMB as a LC alignment layer with rubbing and PUV irradiation techniques.

II. EXPERIMENTAL

A. Materials

We used 6FDA-TFMB, which was synthesized at the University of Akron by Dr. Frank Harris' group. A solution of about 2 % 6FDA-TFMB was prepared by dis-

solving 6FDA-TFMB PI powder in THF (inhibitor free). After dissolving, the solution was filtered through a 0.2 μm PTFE filter to remove undissolved particles. To obtain FTIR spectra, the solution was spin coated on CaF_2 rectangles, typically at 3000 rpm for 30 seconds. Before spin coating, CaF_2 rectangles were rinsed with isopropyl alcohol, and dried thoroughly on a 120°C hot plate. After spin coating, the 6FDA-TFMB coated CaF_2 rectangles were heated on the hot plate for 10 minutes at 60°C. Afterward, they were heated in a 120°C convection oven for 1 hr to remove remaining THF. After baking, the rectangles were cooled to room temperature in a desiccator before obtaining FTIR. For the UV-VIS absorption measurement, quartz plates were thoroughly cleaned with methanol and dried on a hot plate. After cooling, they were spin coated using the same method as with CaF_2 .

B. Analytical Instrumentation

To investigate the effect of PUV irradiation on PI films, a Perkin Elmer Lambda 19 was used to take UV-VIS spectra. To study functional group and molecular chain orientation changes by PUV, a Magna 550 FTIR (Nicolet) was used to take transmission FTIR spectra. From the collected FTIR spectrum, the CaF_2 spectrum was subtracted to obtain the sample spectrum. A single diamond IR polarizer (Harrick) was used for this study. To reduce the noise level, over 600 scans were obtained at 4 cm^{-1} resolution. An optical microscope (Leitz) with crossed polarizers was used to investigate the texture of the liquid crystal in contact with PI films.

C. PUV Irradiation

PUV irradiation was accomplished using a 450 W Xenon lamp (Oriental) with a UV linear dichroic polarizer (Oriental). Xenon lamps emit radiation in a smooth continuum from the UV through the VIS, with particularly higher deep UV (DUV, < ~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

Five types of cells were made to investigate the alignment of liquid crystal in contact with the 6FDA-TFMB alignment layers with various surface treatments: untreated PI, rubbed PI, and PUV-irradiated PI with varying irradiation times of 30 minutes, 1 hour, or 2 hours. Rectangular pieces of ITO-coated glass were cleaned with methanol, and 6FDA-TFMB solution was spin coated on the ITO

glass and dried in the same way as with the CaF_2 rectangles. After drying for 1 hr at 120°C, some of the PI-coated substrates were rubbed five times with velvet cloth, while other substrates were irradiated with PUV for 30 minutes, 1 hr, or 2 hrs. A mixture of UV-curable adhesive and 4.0 μm glass fiber spacers was applied to the four corners of the PI-coated ITO glass. Cells were assembled with anti-parallel orientation.

After assembly, the cells were filled with liquid crystal by capillary action in the isotropic phase. With each of the five surface treatment conditions, three different liquid crystals were studied: 5CB (K-N = 24 °C and N-I = 35 °C, BDH Chemical Co.), MBBA (K-N = 21 °C and N-I = 35 °C, synthesized), and E7 (K-N = -10 °C and N-I = 60 °C, BDH Chemical Co.). After filling with LC, the four edges of the cell were completely sealed with 5 Minute Epoxy (Devcon). After the epoxy was cured, the cells were heated about 20°C above the clearing temperature for 30 minutes and slowly cooled to room temperature over 2 hrs to give good homogeneous alignment.

III. RESULTS AND DISCUSSION

A. 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 absorption spectra of the PI after various PUV irradiation times. All of the spectra showed very little absorption from 340 to 800 nm. This indicates that most of the photochemical reactions of the PI are induced by UV radiation with wavelengths below 340 nm. We, therefore present here only the 200 to 340 nm region, as shown in Figure 2.

Before PUV irradiation, absorption peaks were present at 214 and 248 nm, as shown in Figure 2. These two peaks decreased gradually with increasing PUV irradiation time. This is most likely caused by the degradation of the 6FDA-TFMB by UV irradiation.

B. FTIR Spectral Changes

To investigate the effect of PUV irradiation on the PI, we used polarized FTIR spectroscopy. We found several changes appearing in the FTIR spectra with PUV irradiation. First, the absorbance of most PI peaks decreased, except for a broad

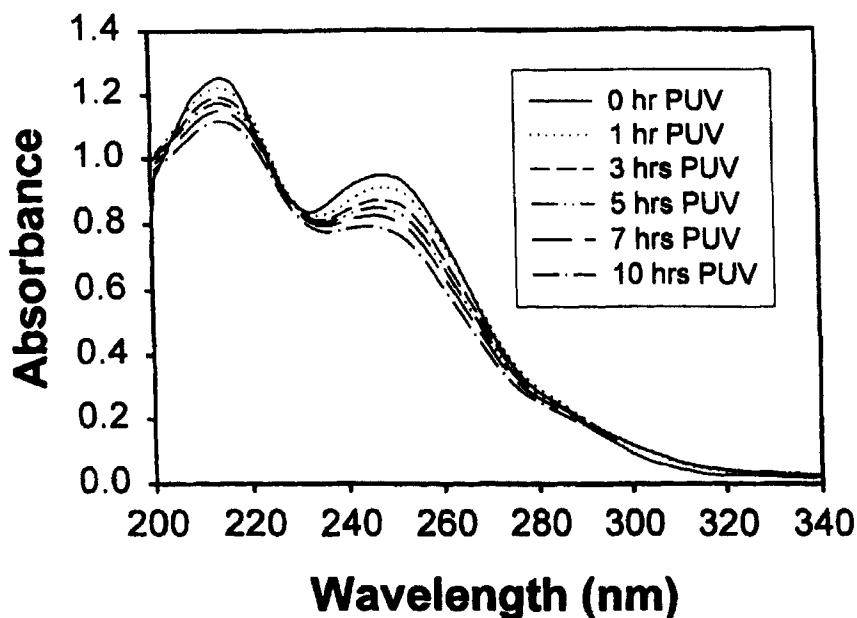


FIGURE 2 UV-VIS spectra change with PUV irradiation time

new peak at 3266 cm^{-1} and two new anhydride peaks at 1858 and 1786 cm^{-1} . Second, the relative heights of the polarized IR absorbance peaks changed, indicating a change in molecular orientation.

1. Changes in peak intensity with PUV irradiation time

To investigate the effect of the PUV irradiation on the PI, FTIR spectra of the PI were taken before and after PUV irradiation. Figure 3 shows changes in the $1900\text{--}1100\text{ cm}^{-1}$ region of the FTIR spectra with increasing PUV irradiation time. As shown in Figure 3, the absorption peak intensities decrease as PUV irradiation time increases, when normalized to the 1731 cm^{-1} peak. In addition, the imide group $\text{C}=\text{O}$ peaks at 1731 and 1787 cm^{-1} became very broad (see Table I for the IR band assignment). After PUV irradiation, a new peak at 1858 cm^{-1} was also found.

In order to determine what reaction occurs with PUV irradiation, difference spectra were obtained by subtracting the FTIR spectrum after PUV irradiation from the FTIR spectrum before PUV irradiation. A typical spectrum obtained by subtracting the FTIR spectrum of the PI after 10 hrs of PUV irradiation from the FTIR spectrum before irradiation is shown in Figure 4.

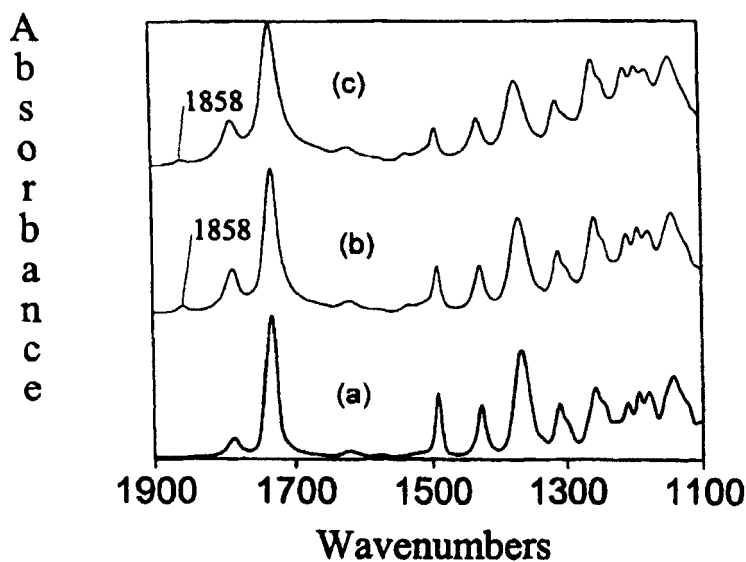


FIGURE 3 FTIR spectra change with PUV irradiation time. (1900–1100 cm^{-1} region): (a) 0 hr PUV; (b) 10 hrs PUV; and (c) 26 hrs PUV

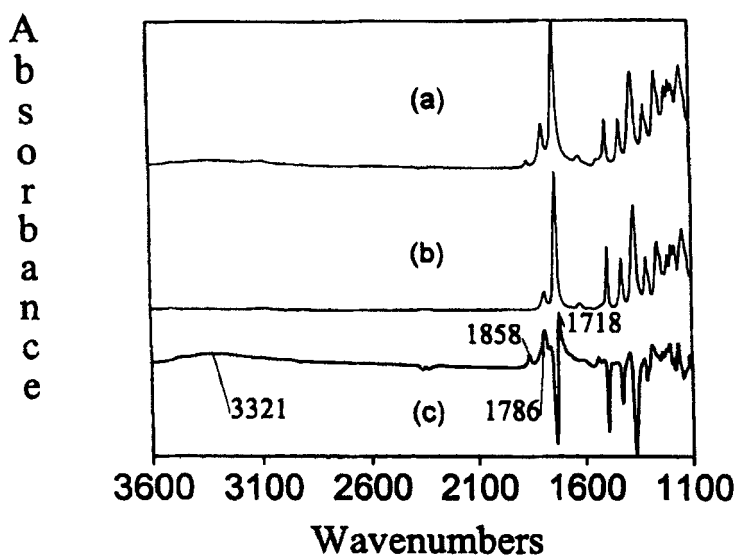


FIGURE 4 FTIR spectra change with PUV irradiation: (a) after 10 hrs PUV irradiation; (b) before PUV irradiation; and (c) difference spectrum obtained by subtracting (b) from (a)

TABLE I FTIR Peak Assignment in the 1900–1100 cm^{-1} Region [11,12]

Material	Peak (cm^{-1})	Polarization Tendency ^a	Assignment
PI	1858		$\nu(\text{C}=\text{O})$ in-phase(anhydride)
	1787		$\nu(\text{C}=\text{O})$ out-of-phase(anhydride) & $\nu(\text{C}=\text{O})$ in-phase(imide I)
	1731	\perp	$\nu(\text{C}=\text{O})$ out-of-phase(imide I)
	1491		$\nu(1,2,4\text{-C}_6\text{H}_3)$
	1426		$\nu(1,2,4\text{-C}_6\text{H}_3)$
	1366		$\nu(\text{CNC})$ (axial-imide II)

|| – parallel transition moment tendency; \perp – perpendicular transition moment tendency

a. ν = Stretching mode.

As shown in Figure 4, all peaks except those at 3321, 1858, 1786, and 1718 cm^{-1} show negative absorbance in the difference spectrum, due to degradation of the PI by PUV irradiation. The 1718 cm^{-1} peak may be caused by the stretching of the $\text{C}=\text{O}$ bond in carbonyl and carboxylic acid groups produced by the PUV irradiation. The peak at 3321 cm^{-1} may be caused by the $-\text{OH}$ stretch of the $-\text{COOH}$ and $-\text{OH}$ groups.

The two peaks at 1858 and 1786 cm^{-1} are characteristic of carbonyl interaction in anhydride groups. The peak at 1858 cm^{-1} (in-phase stretch) is weaker than the peak at 1786 cm^{-1} (out-of-phase), as shown in Figure 4. This means that the anhydride is cyclic [13]. Hoyle et al. [14] also found the appearance of anhydride groups upon irradiation of the 6FDA-TFMB with an unfiltered medium pressure mercury lamp. To investigate the formation rate of the anhydride groups, the peak areas at 1858 and 1786 cm^{-1} were obtained from the difference spectra defined in equation 1:

$$\text{Difference spectrum (t)} = \text{Spectrum (t)} - \text{Spectrum(0)} \quad \dots (1)$$

where:

Spectrum (t) = Spectrum obtained after t hrs PUV irradiation

Spectrum (0) = Spectrum obtained before PUV irradiation

Figure 5 shows a plot of the peak areas as a function of PUV irradiation time. According to Figure 5, anhydride peak areas increase with PUV irradiation until 10 hours of irradiation. After 10 hours of PUV irradiation, the anhydride peaks start to decrease. This means that after 10 hours of PUV irradiation, the degradation rate of the anhydride groups becomes faster than the rate of formation from imide groups, so the degradation of the anhydride predominates.

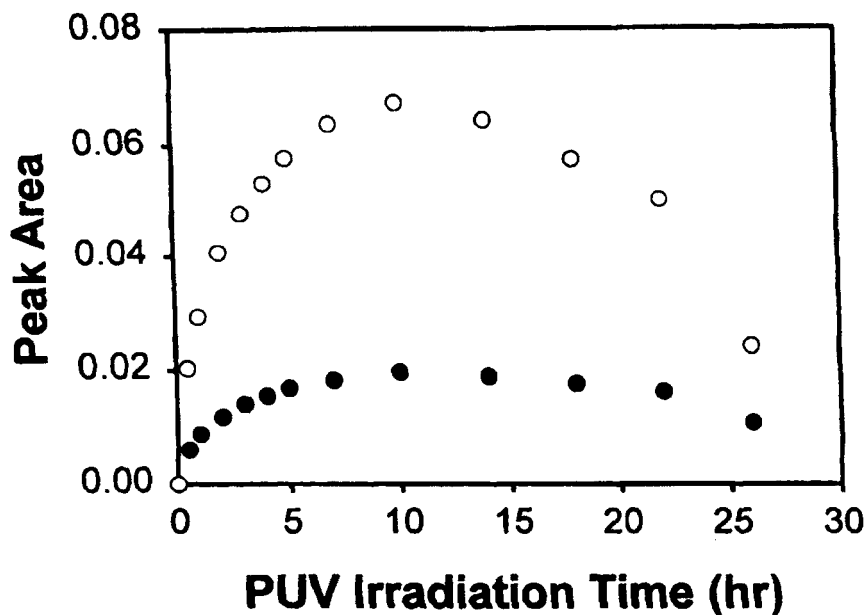


FIGURE 5 Anhydride peak area change with PUV irradiation time: (a) • 1858 cm^{-1} ; and (b) ○ 1786 cm^{-1}

Figure 6 shows the FTIR spectra of the PUV-irradiated PI in the 3600–3000 cm^{-1} region. With increasing PUV irradiation time, we found a decrease in the 3085 cm^{-1} aromatic C-H peak and an increase in the broad peak at 3266 cm^{-1} . With increasing PUV irradiation time, the position of the broad peak also moved from 3344 cm^{-1} (10 hrs PUV) to 3266 cm^{-1} (26 hrs PUV). This new peak at 3266 cm^{-1} may be caused by -OH stretching of the -COOH group, which can be formed from the anhydride groups via decomposition of the arylimide linkage [14], or the peak may result from other -OH groups.

To investigate the absorbance changes of the characteristic peaks with PUV irradiation, the areas of the 1731, 1491, 1366, 1257, and 1210 cm^{-1} peaks were measured as a function of irradiation time. The “% remaining peak area” after a given irradiation time was calculated by the following equation:

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

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

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

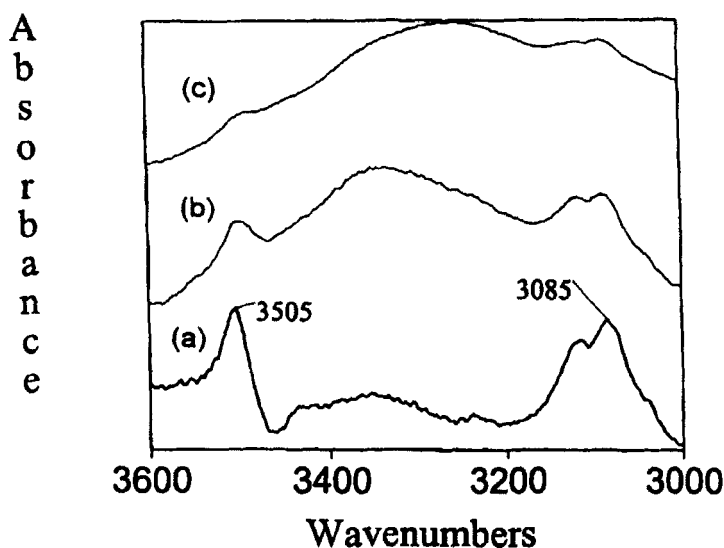


FIGURE 6 FTIR spectrum change with PUV irradiation time: (3600–3000 cm^{-1} region) (a) before PUV irradiation; (b) after 10 hrs PUV irradiation; and (c) after 26 hrs PUV irradiation

Figure 7 shows the % remaining peak areas as a function of PUV irradiation time. The peak areas at 1491 and 1366 cm^{-1} decreased very rapidly, due to the transformation or degradation of the aromatic rings, and the cleavage of the -C-N- of the imide groups, respectively. However, the peak area of the imide group at 1731 cm^{-1} shows a slower degradation rate than that of the 1366 cm^{-1} peak. The slow decrease in peak area at 1731 cm^{-1} with PUV irradiation may be caused by the combination of two opposing effects: 1.) decrease in peak area due to degradation of the imide bond, and 2.) increase in peak area due to formation of -C=O or -COOH groups due to photo-oxidation [15].

Absorption of UV radiation 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 [16]. 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 form smaller fragments [17]. In this case, the PI surface is initially oxidized by the PUV to form groups such as -C=O and COOH. The majority of the -COOH groups may be formed by the hydrolysis of the anhydride groups, which are formed by the cleavage of the comparatively weak -C-N- bonds [18]. 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 [19]. Therefore, a decrease in the areas of all the peaks can be observed.

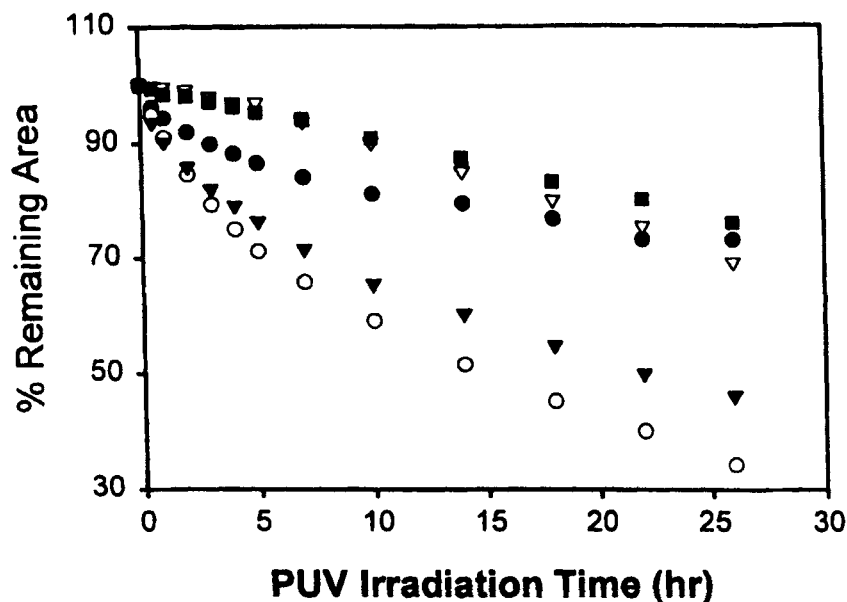


FIGURE 7 % Remaining peak area change of several peaks with the PUV irradiation time: • % Remaining peak area at 1731 cm^{-1} ; ○ % remaining peak area at 1491 cm^{-1} ; ▼ % Remaining peak area at 1366 cm^{-1} ; ▽ % Remaining peak area at 1257 cm^{-1} ; and ■ % Remaining peak area at 1210 cm^{-1}

2. 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 8 shows the typical polarized FTIR spectra of the PI samples after 14 hours of PUV irradiation. Figure 8(c) shows the difference spectrum obtained by subtracting spectrum 8(b) (IR polarization direction \perp PUV polarization direction) from spectrum 8(a) (IR polarization direction \parallel PUV polarization direction). All peaks show negative values in, except for three positive peaks at 1729 , 1311 , and 1257 cm^{-1} . According to Table I, the peak at 1729 cm^{-1} has a transition moment perpendicular to the molecular axis. All peaks showing negative absorbance have transition moments parallel to the molecular axis. This result strongly suggests that the orientation of the PI chains after PUV irradiation is perpendicular to the PUV polarization direction. This PI molecular orientation change after PUV irradiation appears to be primarily due to the preferential degradation of the PI molecules parallel to the polarization direction. Reorientation of the molecular chain due to the imide bond breaking may also play a role.

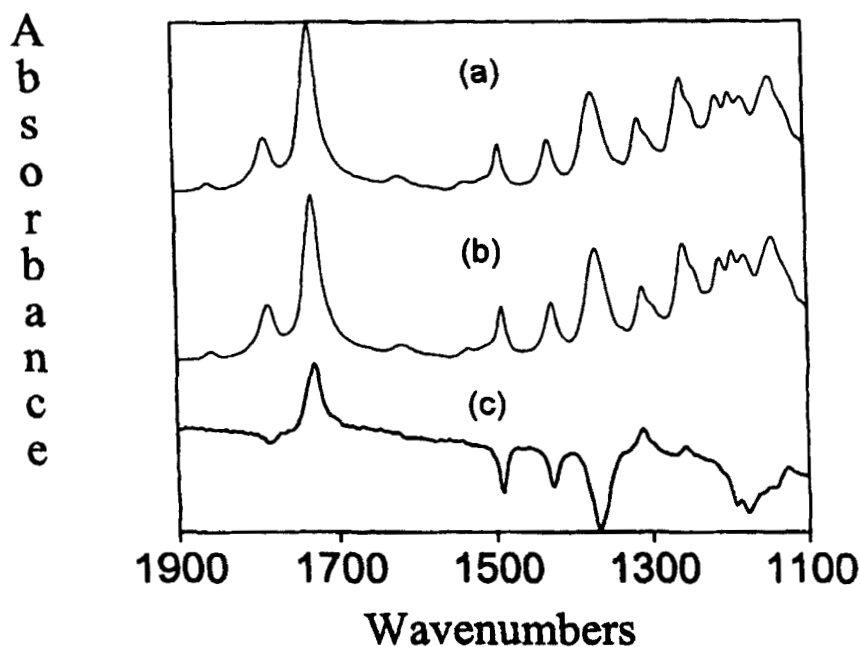


FIGURE 8 FTIR spectra of 14 hrs PUV irradiated PI: (a) with polarization parallel to the PUV irradiation direction; (b) with polarization perpendicular to the PUV irradiation direction; and (c) difference obtained by subtracting (b) from (a)

To estimate degree of orientation of the polymer chains [20], three strong difference peaks (one positive, two negative) were chosen. Dichroic difference values (D) were calculated using the following equations:

$$D(1729) = |A_{\parallel}(1729) - A_{\perp}(1729)| \quad \dots (3)$$

$$D(1491) = |A_{\parallel}(1491) - A_{\perp}(1491)| \quad \dots (4)$$

$$D(1365) = |A_{\parallel}(1365) - A_{\perp}(1365)| \quad \dots (5)$$

where

A_{\parallel} = Absorbance when the FTIR polarization is parallel to the PUV polarization

A_{\perp} = Absorbance when the FTIR polarization is perpendicular to the PUV polarization

The dichroic differences are plotted in Figure 9 as a function of PUV irradiation time. According to Figure 9, the dichroic differences initially increase with

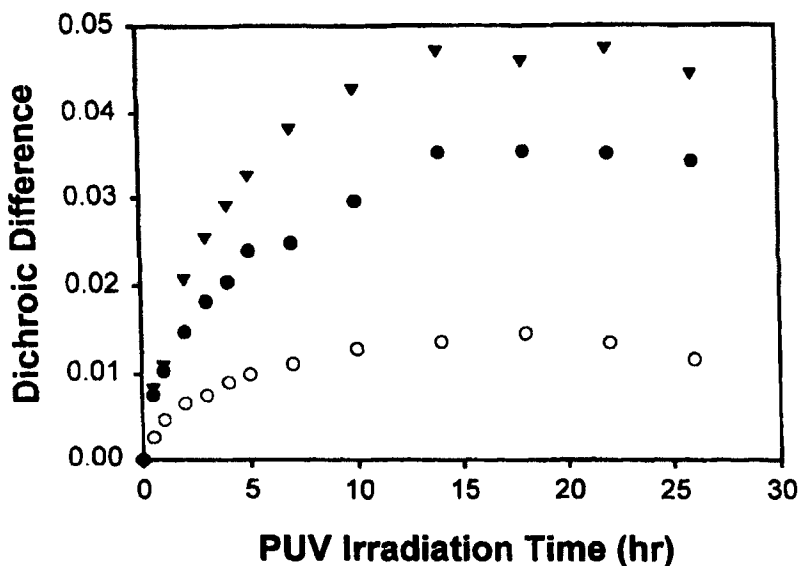


FIGURE 9 Dichroic difference change with PUV irradiation time. • D(1729); ◦ D(1491); and ▼ D(1365)

PUV irradiation time. However, after about 14 to 18 hours of irradiation, the dichroic differences level off, then decrease slightly. This suggests that after 18 hours of PUV irradiation, little unreacted PI parallel to the PUV polarization direction remains, and the reaction of molecules oriented perpendicular to the PUV direction begins to dominate [21].

In order to compare the molecular orientation of PI after PUV irradiation with that of PI after rubbing, we obtained the polarized FTIR spectra of the PI after rubbing 5 times with a velvet cloth. The results are shown in Figure 10. In contrast to the PUV-irradiated PI, the difference spectrum of Figure 10(c) after rubbing showed the opposite trend, with positive values at 1491 and 1363 cm^{-1} , and a negative value at 1734 cm^{-1} . This result clearly shows that the rubbed PI molecules tend to be oriented along the rubbing direction.

C. Alignment Direction of the LC Molecules

1. Texture of the LC

In order to investigate the effects of the treatment of the PI alignment layer on the texture of the LC, we examined five types of liquid crystal cells (see experimen-

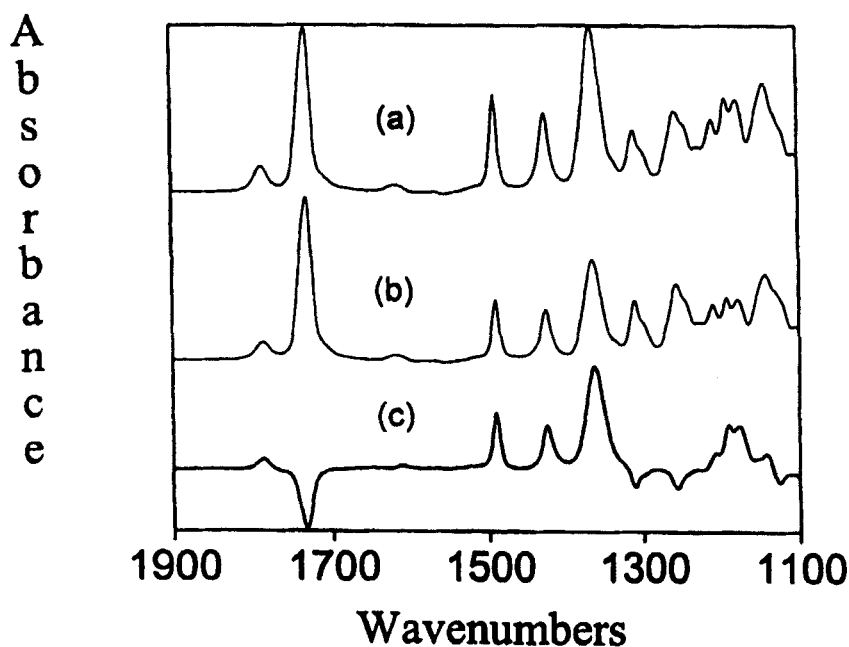


FIGURE 10 FTIR spectra of rubbed PI: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction; and (c) difference obtained by subtracting (b) from (a)

tal section) with optical microscopy under crossed polarizers. Figure 11 shows photomicrographs taken of the five cells filled with 5CB. According to Figure 11(a), Schlieren textures of 5CB, which are due to imperfect homogeneous alignment of the LC [22], appear in the cell with no treatment of the PI. But LC cell made of the rubbed PI show perfect alignment of the 5CB LC as shown in Figure 11(b) with scratches in the direction of rubbing. But LC cells made of the PUV irradiated PI showed some degree of the alignment of LC with defects as shown in Figure 11(c), 11(d) and 11(e). We tried also using MBBA and E7 to find the possibility of getting good alignment of the LC on the PUV irradiated PI. MBBA and E7 LCs showed the same trend as 5CB, some alignment with defects for the PUV irradiated PI.

By the crossed polarizing microscope, we also confirmed the alignment directions of the LC molecules are parallel or perpendicular to the rubbing or PUV irradiation direction. To investigate whether the LC molecules alignment parallel or perpendicular to the rubbing or PUV irradiation direction, we obtained FTIR spectra of two LC cells.

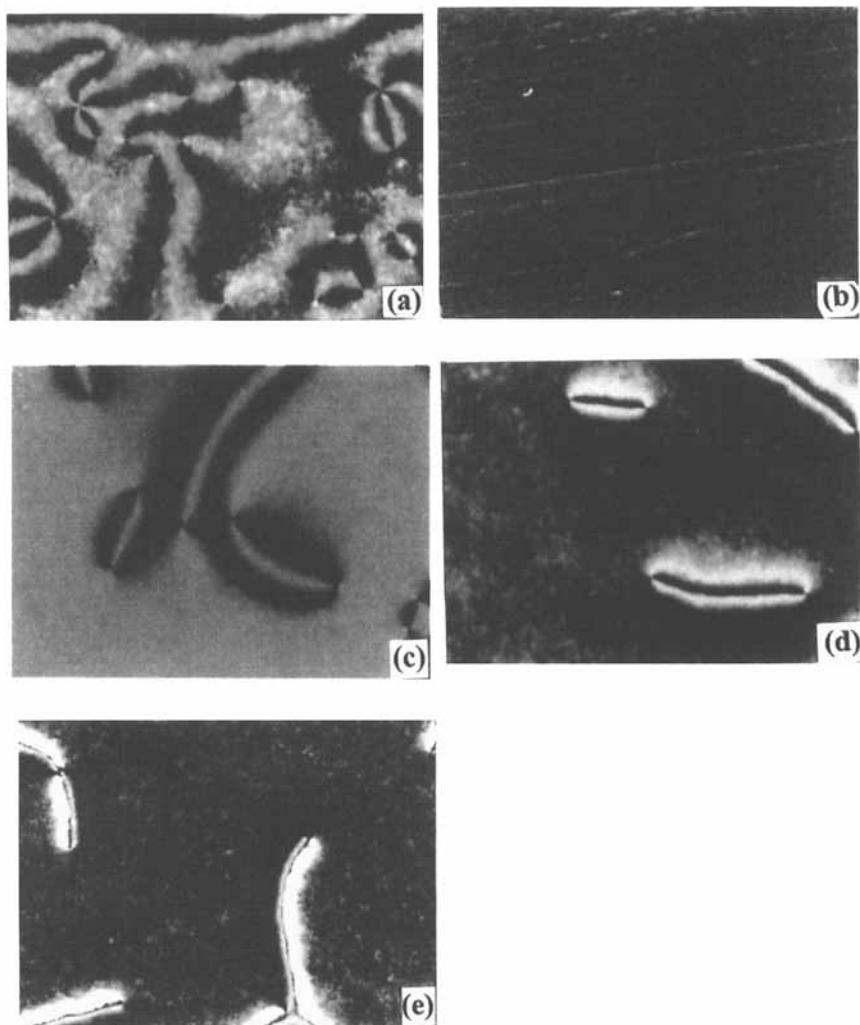


FIGURE 11 Photomicrographs of the ITO glass LC cell (x 110): (a) LC cell made of PI without any treatment; (b) LC cell made of rubbed PI; (c) LC cell made of 0.5 hr PUV irradiated PI; (d) LC cell made of 1 hr PUV irradiated PI; and (e) LC cell made of 2 hrs PUV irradiated PI (See Color Plate V at the back of this issue)

2. FTIR measurement

To investigate the alignment direction of the 5CB, polarized FTIR spectra for the ITO glass cell with PUV irradiated PI alignment layer were obtained and shown in Figure 12. The peak assignments are shown in Table II [23]. The direction of

the transition dipoles of $\text{-C}\equiv\text{N}$ stretching in 5CB is parallel to the long molecular axis of the 5CB molecules [24]. Also the symmetric and asymmetric stretching modes of -CH_3 have components that are parallel and the symmetric and asymmetric stretching modes of -CH_2 are perpendicular to the long molecular axis of the 5CB molecules. Figure 12(a) shows the FTIR spectrum with polarization parallel to the PUV irradiation. In this case $\text{-C}\equiv\text{N}$ stretching mode peak is small compared to those of the CH_2 stretching mode peaks. But Figure 12(b) shows strong symmetric stretching mode peak of -CH_3 at 2871 cm^{-1} and the $\text{-C}\equiv\text{N}$ stretching mode peak at 2227 cm^{-1} compared to the other -CH_2 stretching mode peaks. Therefore, these two results strongly suggest the alignment direction of the 5CB molecules is perpendicular to the PUV irradiation direction, that is, the direction of the PI molecular chain. Figure 12(c) shows the difference spectrum obtained by subtracting spectrum 12(b) from spectrum 12(a) using a subtracting factor 1.

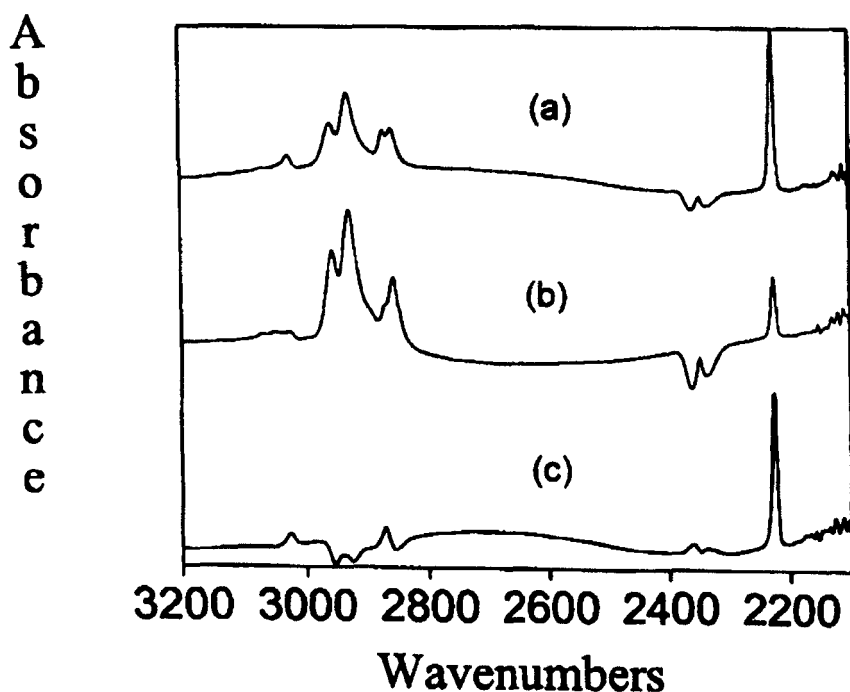


FIGURE 12 FTIR spectra of ITO glass LC cell with PUV irradiated PI alignment layer: (a) with polarization parallel to the PUV irradiation direction; (b) with polarization perpendicular to the PUV irradiation direction; and (c) difference obtained by subtracting (b) from (a)

TABLE II Peak assignment for 4-pentyl-4'-cyanobiphenyl (5CB) [23]

Peak (cm ⁻¹)	Assignment
3071	C-H aromatic stretching
3027	C-H aromatic stretching
2957	asymmetric stretching mode of CH ₃
2929	asymmetric stretching mode of CH ₂
2871	symmetric stretching mode of CH ₃
2857	symmetric stretching mode of CH ₂
2227	stretching mode of C≡N

The dichroic ratios (R) defined as following equation were used to calculate the degree of orientation of the LC.

$$R \text{ (rub)} = A_{\parallel} / A_{\perp} \qquad \dots (6)$$

$$R \text{ (PUV)} = A_{\perp} / A_{\parallel} \qquad \dots (7)$$

R values calculated using -C≡N stretching mode are shown in Table III. According to the results of Table III, 5CB which in contact with rubbed PI gives highest R value compared to PUV irradiated PIs. This data supports the photomicroscopy data of Figure 11. S-T Wu [24] obtained R=3.5 value when 5CB was used to the SiO₂ alignment layer.

TABLE III Effect of the PI treatment method on the R values

PI Treatment Method	R Values
Without any treatment	1.16
30 minutes PUV	2.16
1 hr PUV	3.09
2 hrs PUV	2.86
Rubbed	4.67

Figure 13 show the FTIR spectra of ITO glass LC cell with rubbed alignment layer. In contrary to the spectrum with PUV irradiated alignment layer of Figure 12, Figure 13 spectra support opposite direction trend of the 5CB. Therefore, these spectra support the alignment of the 5CB molecules parallel to the rubbing direction, that is, the PI molecular chain direction.

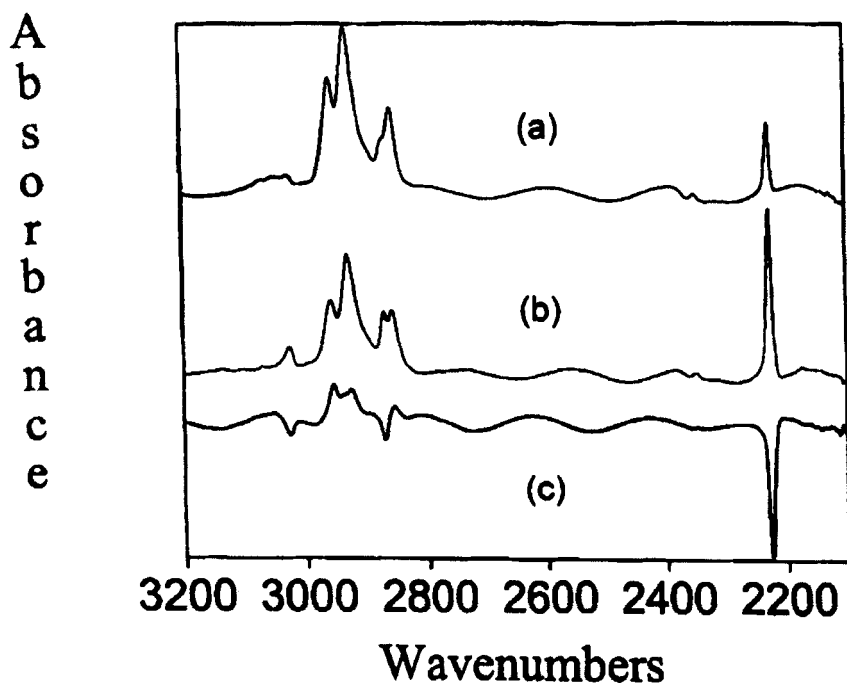


FIGURE 13 FTIR spectra of ITO glass LC cell with rubbed PI alignment layer: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction; and (c) difference obtained by subtracting (b) from (a)

IV. CONCLUSIONS

Through out this experiment, we have arrived at the following conclusions.

1. With the irradiation of the PUV, the 6FDA-TFMB showed formation of cyclic anhydride, indicating degradation via decomposition of the imide linkage.
2. Molecular chain orientation of PUV irradiated PI was perpendicular to the PUV irradiation direction due to the preferential degradation of the PI molecules parallel to the PUV direction.
3. PUV irradiated PI alignment layer showed some alignment of LC with some defects. This may be caused by the increased plasticization or solubility of the 6FDA-TFMB by the decrease of the molecular weight due to photo-degradation. Therefore, using PI with excellent solubility to solvents as an alignment layer, we need careful selection of the LCs which can not plasticize or dissolve PUV irradiated layer of PI.

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References

- [1] J. Varney, *Soild State Technology*, 61–65 (Sept. 1992).
- [2] H. Kikuchi, J. A. Logan, and D. Y. Yoon, *J. Appl. Phys.*, **79**(9), 6811–6817 (1996).
- [3] K. Sawa, K. Sumiyoshi, Y. Hirai, K. Tateishi, and T. Kamejima, *Jpn. J. Appl. Phys.*, **33**(11), Pt. 1, 6273–6276-L1341 (1994).
- [4] J. M. Geary, J. W. Goody, A. R. Kmetz, and J. S. Patel, *J. Appl. Phys.*, **62**(10), 4100–4108 (1987).
- [5] P. J. Shannon, W. M. Gibbons, and S. T. Sun, *Nature*, **368**, 532–533 (1994).
- [6] J. Lu, S. V. Deshpande, E. Gulari, and J. Kanicki, *J. Appl. Phys.*, **80**(9), 5028–5034 (1996).
- [7] J. L. West, X. Wang, Y. Ji, and J. R. Kelly, *SID 95 Digest*, 703–705 (1995).
- [8] K. Ha and J. L. West, *Mol. Cryst. & Liq. Cryst.*, **323**, 129–143 (1998).
- [9] R. Hasegawa, Y. Mori, H. Sasaki, and M. Ishibashi, *Mol. Cryst. Liq. Cryst.*, **262**, 77–88 (1995).
- [10] T. Matsuura, Y. Hasuda, S. Nishi, and N. Yamada, *Macromolecules*, **24**, 5001–5005 (1991).
- [11] H. Isida and M. T. Huang, *Spectrochimica Acta*, **51A**(3), 319–331 (1995).
- [12] S. E. Molis in *Polyimides: Materials, Chemistry and Characterization* edited by C. Feger, M. M. Khojasteh and J. E. McGrath (Elsevier Science Publishers, New York, 1989), p. 659–672.
- [13] N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, (Academic Press, Inc. New York, 1990), 3rd Ed. Chap. 9, p. 311.
- [14] C. E. Hoyle, E. T. Anzures, P. Subramanian, R. Nagarajan, and D. Creed, *Macromolecules*, **25**, 6651–6657 (1992).
- [15] L.-H Chang and N. C. Saha, *Thin Solid Films*, **253**, 430–434 (1994).
- [16] J.F. Rabek, *Photodegradation of Polymers; Physical Characteristics and Applications*. (Springer-Verlag, New York, 1996), p. 2.
- [17] M. A. George, B. L. Ramakrishna, W. S. Glausinger, *J. Phys. Chem.*, **94**, 5159–5164 (1990).
- [18] 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).
- [19] C. E. Hoyle, D. Creed, R. Nagarajan, P. Subramanian, and E. T. Anzures, *Polymer*, **33**(15), 3162–3168 (1992).
- [20] R. Hasegawa, Y. Mori, H. Sasaki, and M. Ishibashi, *Jpn. J. Appl. Phys.*, **35**, 3492–3495 (1996).
- [21] H. G. Galabova, D. W. Allender, and J. Chen, *Phys. Rev. E.*, **55**(2), 1627–1631 (1997).
- [22] D. Demus, L. Richter, *Textures of Liquid Crystals*, (Verlag Chemie, New York, 1978), p. 32.
- [23] C. A. McFarland, J. L. Koenig, and J. L. West, *Appl. Spec.*, **47**(3), 321–329 (1993).
- [24] S-T Wu, *Applied Optics*, **26**(16), 3434–3440 (1987).