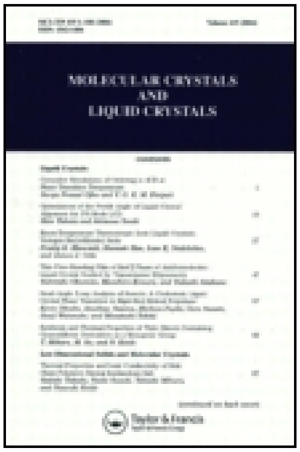

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Infrared Spectroscopic Studies of the Mechanism of Orientation of Polarized UV-exposed Polyimide Films for Liquid Crystal Alignment

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

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Polarized Fourier transform infrared (FTIR) and ultraviolet-visible (UV-VIS) spectroscopy were used to investigate the mechanism of liquid crystal alignment on polarized UV (PUV) irradiated polyimide (PI) films. PI films strongly absorb below 320 nm resulting in photochemical reaction of the PI. PUV irradiation of the PI film caused decrease of all the peak intensities in the IR, except the newly formed 1396 cm^{-1} peak, due to degradation of the PI molecules. The preferential degradation of PI molecules parallel to PUV irradiation direction results in the predominant orientation of the remaining PI molecules perpendicular to the PUV irradiation direction. But the rubbing of the PI films induced reorientation of the PI molecules parallel to the rubbing direction.

Keywords: Polyimide; infrared spectroscopy; dichroic difference; polarized UV

1. INTRODUCTION

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

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*Corresponding author. Phone: (330) 672-2654, (330) 672-2796, e-mail: johnwest@scorpio.kent.edu crystal display (LCD) [1]. Also, production of multi-domain displays to improve the viewing angle characteristics is difficult using standard rubbing techniques.

Polarized UV light irradiation techniques have been developed recently to produce alignment using polyvinylcinnamate films [2–4] and polyimide films [5–8]. Also PUV irradiation can be used to easily manufacture multi-domain LCDs [8, 9]. Much work has been done on the mechanism of the liquid crystal (LC) alignment on the rubbed polymer surfaces [10], but little has been done to understand 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 can be used to evaluate molecular orientation of polymers [11]. Recently, much work has been done to measure the orientation of rubbed PI polymers by polarized IR spectroscopy [13, 14], but only preliminary work has been done to determine the orientation of the PI after PUV irradiation [6]. We studied PUV irradiated PI films using polarized infrared spectroscopy in order to identify the molecular orientation of PI before and after PUV irradiation. PUV irradiation of the PI film caused preferential degradation of the PI molecules parallel to PUV irradiation direction, resulting in the predominant orientation of the remaining PI molecules perpendicular to the PUV irradiation. But the molecular orientation of PI after rubbing became parallel to the rubbing direction.

2. EXPERIMENTAL

A. Materials

Nissan 610 (trade name) was used as the polyimide alignment layer. Nissan 610 is used for high pretilt angle supertwisted nematic (STN) display. To obtain the FTIR spectra, suitable concentrations of the polyamic acid (PAA) form of Nissan 610 solution {usually concentrated Nissan 610 was diluted to 1:3 ratio with 810 solvent (NMP + Butyl Cellosolve mixture)} was spin coated on CaF_2 rectangles. Spin conditions were typically 3000 rpm for 30 seconds. Before spin coating, CaF_2 rectangles were rinsed using isopropyl alcohol, dried thoroughly on a 120°C hot plate. After spin coating, the Nissan 610 coated CaF_2 rectangles were soft baked for 15 minutes at 80°C to remove solvents. After soft baking, they were hard baked in a 250°C convection oven for the desired time, usually 1 hr to accomplish imidization. The resulting film thickness was about 17 nm. After baking, the rectangles were taken from the oven, and put in a vacuum desiccator to cool to room temperature. Usually, polyimide coated rectangles were stored in the vacuum desiccator overnight before taking FTIR spectrum. For the UV–VIS absorption measurements, quartz plates were thoroughly cleaned with absolute methanol and dried on a hot plate. After cooling, they were spin coated, and the imidization reaction was carried out the same way 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 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 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 600 scans were obtained at $4\,cm^{-1}$ resolution.

C. PUV Irradiation

UV irradiation was accomplished using a 450 W Xenon lamp (Oriel) and polarizer (Oriel) for the PUV source. Xenon lamps emit a smooth continuum from the UV through the VIS, with particularly 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 $6\,mW/cm^2$.

3. RESULTS AND DISCUSSION

A. Curing Reaction

1. FTIR Spectral Changes with Curing

To understand the IR spectral features present in the PI film prior to PUV irradiation we begin with discussion of the development of characteristic bands during cure. To check the change of FTIR spectra caused by the imidization reaction, the FTIR spectra of Nissan 610 solution, after soft baking, and after hard baking were obtained. Figure 1 shows the FTIR spectra of, (a) Nissan 610 film, (b) after 15 minutes soft baking at 80°C, (c) after 1 hr hard baking at 250°C. After hard baking, no detectable strong peaks were found between 1900 cm^{-1} to 4000 cm^{-1} region. Therefore, in this paper, we present FTIR spectrum between 1900 cm^{-1} – 1100 cm^{-1} region. By comparing Figures 1(a) and 1(b), we found the strong solvent peaks at 1690 cm^{-1} and 1299 cm^{-1} almost disappeared following soft baking at 80°C for 15 minutes due to the removal of the solvents which do not complex with PAA. After soft baking several peaks, which are characteristic PAA peaks, appeared at 1720, 1666, 1607, 1539, 1502, 1410 cm^{-1}. The peak assignments are shown in Table I [15, 16]. After hard baking at 250°C for 1 hr, the characteristic imide peaks appeared at 1780, 1722, 1377 cm^{-1}. From these results, we monitored the progress of imidization reaction by hard baking. The peaks at 1244, 1207, 1177 cm^{-1} may be tentatively assigned as —C—O—C— asymmetric stretching, absorption by C—F bonds, and tangential ring stretching mode of C_6H_2 [17], respectively. Incorporation of fluorine in the Nissan 610 was also supported by X-ray photoelectron spectroscopy (XPS) results.

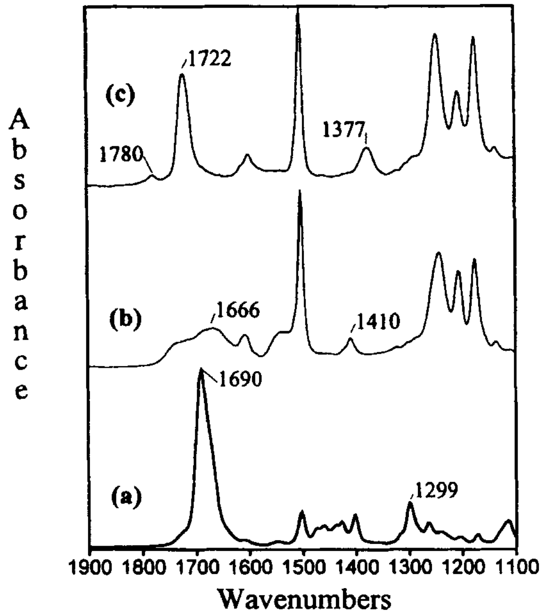

FIGURE 1 The FTIR spectra of Nissan 610: (a) solution; (b) after 15 minutes soft baking at 80°C and (c) after 1 hour hard baking at 250°C.

TABLE I FTIR peak assignment [15, 16] in the 1900–1000 cm^{-1} region

Material	*Peak (cm^{-1})*	*Polarization tendency**	*Assignment*
PAA	1720		$\nu(C=O)$, acid
	1666		$\nu(C=O)$, amide I
	1607		$\nu(1,2,4,5-C_6H_2)$
	1539		δ(CNH), amide II
	1502		$\nu(1,4-C_6H_4)$
	1410		δ(OH), acid
PI	1780	$\parallel$	$\nu(C=O)$ in-phase (imide I)
	1722	$\perp$	$\nu(C=O)$ out-of-phase (imide I)
	1601		$\nu(1,2,4,5,-C_6H_2)$
	1503	$\parallel$	$\nu(1,4-C_6H_4)$
	1377	$\parallel$	ν(CNC) (axial-imide II)

* $\parallel$-parallel transition moment tendency; $\perp$-perpendicular transition moment tendency.

2. Curing Rate at 250°C

We can look at certain bands quantitatively to establish the time to complete imidization and to establish the bands we can observe to follow changes caused by PUV irradiation in the next section. Therefore, to study the curing rate at 250°C, the FTIR spectra were taken after 0, 10, 20, 60, 120, 180 minutes curing at 250°C. The imidization degree can be followed using the 1377 cm^{-1} imide band normalized to the 1503 cm^{-1} band as an internal standard. We used the 1377 cm^{-1} band because it is isolated from other peaks [18]. The curing reaction can be followed using the change of the —COOH group at 1410 cm^{-1} compared to the axial-imide II at 1377 cm^{-1} with both normalized to the 1503 cm^{-1} peak. The results are shown in Figure 2. By increasing the curing time, the peak intensity at 1410 cm^{-1} decreased, and the peak at 1377 cm^{-1} increased. The peak area at 1377 cm^{-1} increased from 0, 0.0342, 0.0349, 0.0371, 0.0372, to 0.0382 with increasing curing time. % Imidization calculated using Eq. (1) [8] were 85.9% (10 minutes curing), 89.3% (20 minutes curing), 94.8% (1 hr curing), 96.4% (2 hrs curing), and 99.0% (3 hrs curing).

$$\%\text{Imidization} = (A_{1377}/A_{1503})/(A_{1377}/A_{1503})_{1\text{hr at }300^{\circ}\text{C}} \times 100 \qquad (1)$$

where A_{1377} and A_{1503} are the peak areas at 1377 cm^{-1} and 1503 cm^{-1}, respectively.

Figure 2 shows the very fast imidization reaction, which is essentially 86% complete within 10 minutes of curing. The fast reaction results from the higher amount of solvent content in the early stage of curing reaction, which

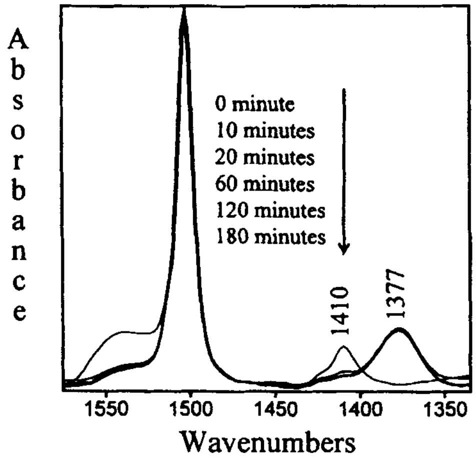

FIGURE 2 FTIR spectra change with curing time at 250°C. (1575–1335 cm^{-1} region).

increases the mobility of the chain. The curing reaction gradually slowed due to the loss of residual solvent and the decrease of molecular mobility by the conversion from the PAA to the more rigid PI [19].

The pretilt angle between LC and PI alignment layer strongly depends on the surface tension of the PI layer [8]. Controlling the % imidization through changing curing time or curing temperature can control the surface tension of the PI layer. Imidization results in a reduction in the concentration of the —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 the resulting change in the pretilt angle.

3. Thickness Measurement

Because of the higher retention of the entrapped solvent by thicker films than that of thinner films, thickness of the film affects the curing rate of the PI. Therefore, we measured the thickness of the film using 1503 cm^{-1} peak as internal standard peak. To measure the film thickness of the PI film after hard baking, interference method by UV–VIS spectra was used to measure two thick film samples (754 and 375 nm). From the interference, the thickness was calculated using Eq. (2). After determining the thickness of the two thick film samples, the remaining sample thicknesses were determined by using the peak area of PI at the 1503 cm^{-1} peak. Typical thickness of the PI film for this study was 17 nm.

$$b(\mathrm{cm}) = N/n \div \{2(\nu_1 - \nu_2)\} \qquad (2)$$

where b = thickness of the film (cm)
N = the number of fringes
$\nu_1 - \nu_2$ = wavenumber difference between the maxima of the sine waves
n = refractive index, for Nissan 610 $n = 1.61$ was used.

B. Effects of PUV Irradiation

1. UV-VIS Spectra Change

Photochemical reactions of PI will depend strongly 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 Nissan 610 after various exposure times with PUV irradiation. All the UV-VIS spectra of PI, 1 hr PUV irradiated PI, 5 hrs PUV irradiated PI showed very little absorption from 350 to 800 nm region; therefore, the PUV at wavelength less than 350 nm will induce most of the photochemical reactions of the PI. We present here only the 200-350 nm region as shown in Figure 3. According to Figure 3, the 250°C 1 hr cured PI absorbs strongly from 320-200 nm region and absorbs little above 320 nm. After 1 hr PUV

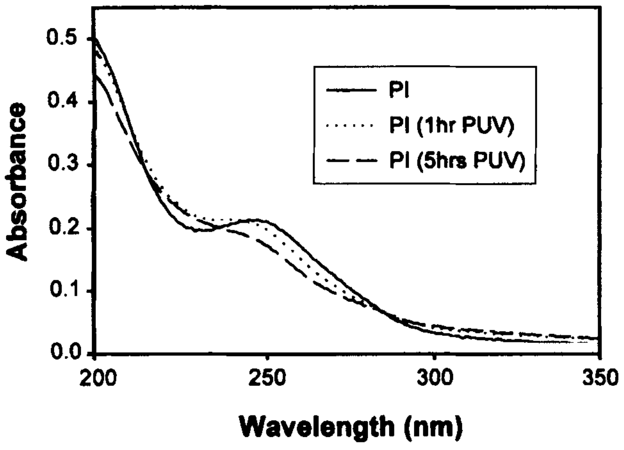

FIGURE 3 UV-VIS spectra change with PUV irradiation.

irradiation on the PI, λ_{max} changed from 246 to 240 nm. Further PUV irradiation resulted in a continued shift of λ_{max} to shorter wavelengths and the decrease in the absorbance intensity. This hypsochromic shift and the hypochromic effect may be caused by the destruction of the conjugation between the imide groups by photoinduced decomposition of the PI [20].

2. *Alignment by PUV Irradiation*

PUV irradiation of the PI cured at 250°C resulted in several changes appearing in the FTIR spectra. First, the absorbance of most PI peaks decreased; Second, a new peak occurred in the 1396 cm^{-1} region; Third, the relative change of polarized IR absorbance peaks occurred showing molecular orientation change. Fourth, the peak at 1722 cm^{-1} before PUV irradiation moved to 1719 cm^{-1} after PUV irradiation.

(a) Changes of the Peak Intensities with PUV Irradiation Time To investigate the effect of PUV irradiation on the PI, the absorbance change of the several characteristic peaks were measured as a function of PUV irradiation time. All the peaks at 1780, 1719, 1503, 1378, 1244, 1207 and 1177 cm^{-1}, except the newly formed peak at 1396 cm^{-1}, gradually decreased with increase of the PUV irradiation time. The peak areas as a function of PUV irradiation time were measured. The % remaining peak area as a function of PUV irradiation time was calculated by the following equation.

$$\%\ \text{Remaining Peak Area} = \text{Area}\,(t)/\text{Area}\,(0) \times 100 \qquad (3)$$

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 at 1780, 1719, 1503, 1377 cm^{-1} are shown in Figure 4. According to Figure 4, the peak areas at 1780 and 1377 cm^{-1} decrease very fast due to cleavage of the —C—N— bond of the imide ring. The peak area at 1719 cm^{-1} initially increased (about 2% after 40 minutes PUV irradiation); after that it decreased. Also the peak position was changed from 1722 to 1719 cm^{-1} by the PUV irradiation. The peak area change at 1719 cm^{-1} may be caused by the contribution of two effects: (1) decrease of the peak area due to degradation of the imide bond, and (2) increase due to formation of $C=O$ containing groups due to photooxidation [21]. It is well known that UV absorption below 250 nm

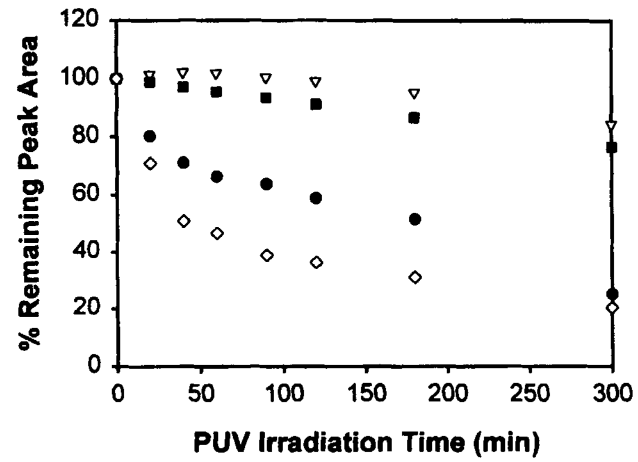

FIGURE 4 % Remaining peak area change of several peaks with the PUV irradiation time: ● -% remaining peak area at 1780 cm^{-1}; ▽-% remaining peak area at 1719 cm^{-1}; ■-% remaining peak area at 1503 cm^{-1} and ◇-% remaining peak area at 1377 cm^{-1}.

($\Delta E = 116$ kcal/mol) can result in the breaking of the carbon — carbon, carbon — halogen, carbon — oxygen, and oxygen — hydrogen bonds in the polymer chain, producing radicals [22]. The photooxidized radicals can be formed by the reaction of the radiation-induced radicals with the oxygen or moisture in the air, which can undergo further photolysis to smaller fragments [23]. This suggests that the PI surface was initially oxidized by the PUV to form C=O containing groups such as C=O and COOH. The major source of the COOH groups may be formed by the cleavage of the comparatively weak —C—N— bond [24]. But after long PUV irradiation, the fragmented material yields very small photooxidation products such as H_2O, CO_2 and CO that will be easily evaporated [20]. Therefore, the decrease of all the peak areas is observed. The peak area at 1503 cm^{-1} showed slower decrease compared to that of —C—N— bond indicating slower degradation and removal of the 1,4 – C_6H_4 group than that of the —C—N— bond.

(b) New Peak Formation with PUV Irradiation After 1 hr hard baking at 250°C, the PI was irradiated with PUV. With increasing PUV irradiation time, the peak intensity at 1377 cm^{-1} decreased gradually and a new peak appeared at 1396 cm^{-1} as shown in Figure 5. Table II shows the curve-fitting results by assuming the peak shape as Gauss–Lorentzian. This data

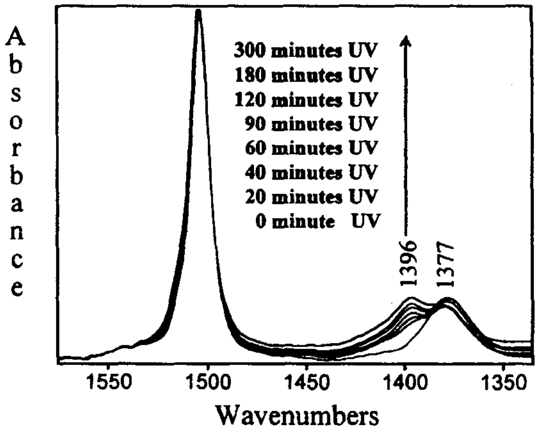

FIGURE 5 FTIR spectrum change with PUV irradiation time (1575 – 1335 cm^{-1} region).

TABLE II Peak area change with PUV irradiation time

PUV irradiation time (min)	*Area at* 1377 *cm*$^{-1}$	*Area at* 1396 *cm*$^{-1}$	% *Area at* 1377 *cm*$^{-1}$ *vs* 1396 *cm*$^{-1}$
0	0.1388	0.0000	100:0
20	0.0761	0.0585	57:43
40	0.0680	0.0648	51:49
60	0.0640	0.0700	48:52
90	0.0560	0.0746	43:57
120	0.0478	0.0770	38:62
180	0.0390	0.0793	33:67
300	0.0237	0.0788	23:77

supports the disappearance of the imide shown at 1377 cm^{-1} and increase of the new functional group shown at 1396 cm^{-1} with PUV irradiation time.

In order to determine what reaction occurs with PUV irradiation, difference spectra were obtained by subtracting the FTIR spectrum of the PI before PUV irradiation from the FTIR spectrum obtained after PUV irradiation. The typical spectrum obtained by subtracting the FTIR spectrum of the PI before PUV irradiation from the FTIR spectrum after 5 hrs PUV irradiation is shown in Figure 6. As shown in Figure 6, all peak intensities in the difference spectrum, except peaks at 1705 and 1396 cm^{-1}, show negative absorbance due to degradation of the PI by PUV irradiation. The 1705 and 1396 cm^{-1} peaks may be caused by the carboxylic acid groups produced by the PUV irradiation. Carboxylic acids which exist as dimers are known to absorb at ~ 1710 cm^{-1} due to C=O stretch and 1440 – 1385 cm^{-1}

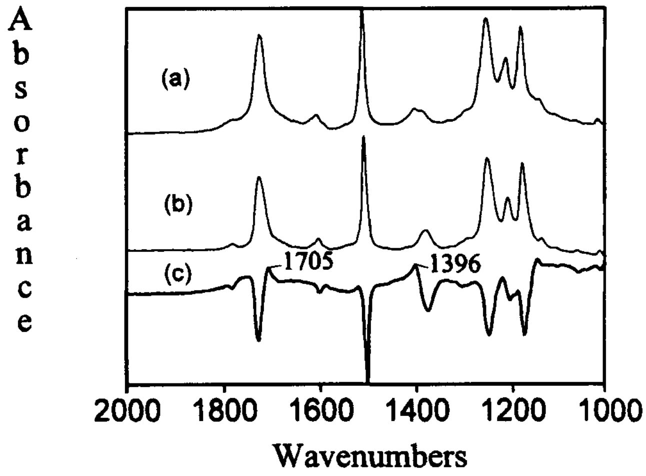

FIGURE 6 FTIR spectra of PI: (a) after 5 hrs PUV irradiation; (b) before PUV irradiation and (c) difference obtained by subtracting (b) from (a).

due to —OH deformation [25]. Therefore, two peaks at 1705 and 1396 cm^{-1} shown in Figure 6 support the production of the —COOH groups by the PUV irradiation.

With PUV irradiation, the production of polar —COOH groups was identified. The increase in surface tension of the PUV irradiated PI film by the formation of the polar —COOH groups may have an effect on the pretilt angle of the LC.

(c) Molecular Orientation of the PUV Irradiated PI To check the molecular orientation change by the PUV irradiation, polarized FTIR spectra were obtained after PUV irradiation. Figure 7 shows the typical polarized FTIR spectra of the PI samples after 90 minutes PUV irradiation. In Figure 7(a), the IR polarization direction is parallel to the PUV polarization and shows a much stronger peak at 1719 cm^{-1} compared to Figure 7(b) where the IR polarization direction is perpendicular to the PUV polarization. According to Table I, the peak at 1722 cm^{-1} has a transition moment perpendicular to the molecular axis. The 1503 cm^{-1} and other remaining peaks have transition moments parallel to the molecular axis. These results support the orientation of the unreacted PI molecules perpendicular to the PUV polarization direction. This PI molecular orientation change after PUV exposure appears to be primarily due to 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. Figure 7(c) shows the difference spectrum obtained by subtracting spectrum (b) from spectrum (a) using subtracting factor 1. This difference spectrum is positive at 1721 cm^{-1}, and negative for the other peaks, clearly supporting perpendicular orientation of the PI chains after PUV irradiation. The area of 1721 cm^{-1} and 1503 cm^{-1} peaks in the difference spectrum can be used to estimate the degree of the orientation of the polymer chains [26]. We used the two strong peaks in the difference spectrum to measure the degree of orientation, one at 1721 cm^{-1} which shows positive and one at 1503 cm^{-1} which shows negative value by the following equations.

$$D(1721) = |A_{\parallel}(1721) - A_{\perp}(1721)| \tag{4}$$

$$D(1503) = |A_{\parallel}(1503) - A_{\perp}(1503)| \tag{5}$$

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

The dichroic difference (D) changes at 1721 and 1503 cm^{-1} with PUV irradiation time are shown in Figure 8. According to Figure 8, D increased

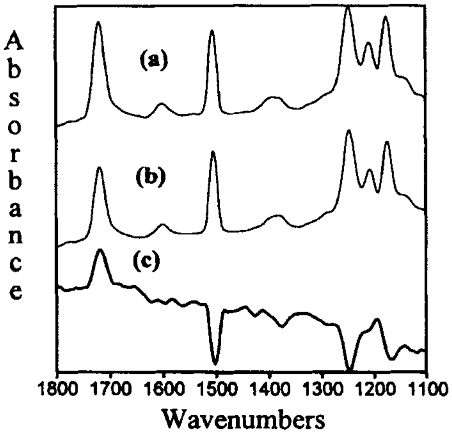

FIGURE 7 FTIR spectra of 90 minutes PUV irradiated PI: (a) with polarization parallel to the PUV irradiation direction; (b) with polarization perpendicular to the PUV irradiation direction and (c) difference obtained by subtracting (b) from (a).

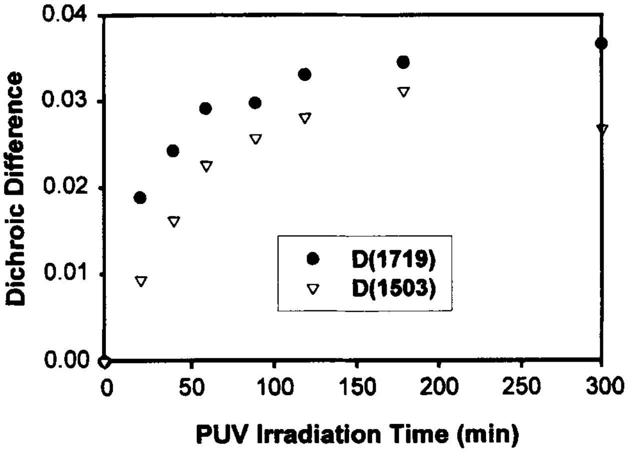

FIGURE 8 Dichroic difference change with PUV irradiation time.

with PUV irradiation time. However, after 5 hrs irradiation, the $D(1503)$ starts to decrease even though the $D(1721)$ still increases. The decrease of the $D(1503)$ at 5 hrs PUV irradiation is caused by the faster decrease of the 1503 cm^{-1} peak intensity compared to 1719 cm^{-1} peak as shown in Figure 4. Therefore, after 3 hrs PUV irradiation, not much unreacted PI parallel to the PUV direction remains and reaction of molecules oriented perpendicular to the PUV direction begins to dominate [27].

To compare the molecular orientation of PI after PUV irradiation with that of PI after rubbing, we measured the polarized FTIR spectra of PI after rubbing with velvet cloth 5 times. The results are shown in Figure 9. Contrary to the PUV irradiated PI, the difference spectrum after rubbing showed the opposite trend, with a positive value at 1503 cm^{-1} and negative value at 1723 cm^{-1}. This result supports that the rubbed PI molecules are aligned along the rubbing direction [28]. We also found the peak at 1722 cm^{-1} before rubbing moved to 1724 cm^{-1} which reflects the change of the polymer-polymer chain interactions between PI chains by rubbing.

4. CONCLUSIONS

The results of these experiments lead to the following conclusions.

1. With increase in the PUV irradiation time, the peak area at 1377 cm^{-1} decreases, and a new peak at 1396 cm^{-1} increases due to disappearance of

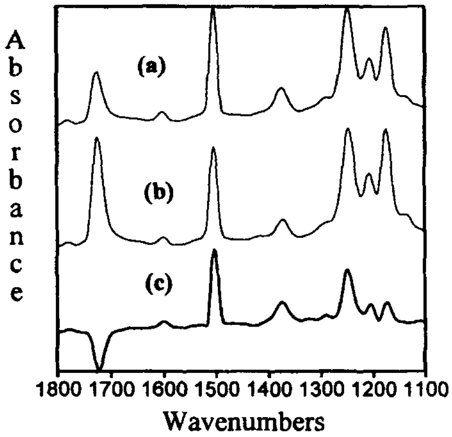

FIGURE 9 FTIR spectra of rubbed PI: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction and (c) difference obtained by subtracting (b) from (a).

imide group and the formation of new functional groups such as —COOH.

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. Rubbing of the PI films physically induces reorientation of the PI chains parallel to the rubbing direction.

Acknowledgements

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