

# Studies on the Photodegradation of Polarized UV-Exposed PMDA–ODA Polyimide Films

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**ABSTRACT:** Polarized Fourier transform infrared (FTIR) and ultraviolet-visible (UV-VIS) spectroscopy were used to investigate the photodegradation direction of polarized UV (PUV)-irradiated polyimide (PI) films based on pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). PI films strongly absorb below 350 nm, resulting in a photochemical reaction of the PI. PUV irradiation of the PI film caused a decrease of all existing peaks and formation of new peaks at 3258, 1748, and 1710  $\text{cm}^{-1}$  in the IR, due to degradation of the PI molecules. The preferential degradation of PI mole-

cules parallel to the PUV irradiation direction results in the predominant orientation of the remaining PI molecules perpendicular to the PUV irradiation direction. But rubbing of the PI films induced orientation of the PI molecules parallel to the rubbing direction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3072–3077, 2002

**Key words:** FT-IR; polyimides; irradiation; orientation; degradation

## INTRODUCTION

Polyimides (PIs) based on aromatic dianhydrides and diamines are well known for their thermal stability and chemical resistance. In some cases, PIs are used where prolonged exposure to sunlight is expected. Many articles describing the photochemically induced degradation of PIs irradiated with unfiltered UV light have been published.<sup>1–5</sup> Much work has been done to investigate the effect of a bridging group such as carbonyl, oxygen, or hexafluoroisopropylidene on the photostability of the PIs after unpolarized UV light irradiation. However, only preliminary work has been done to determine the orientation of the PI molecules after polarized UV (PUV) irradiation. IR dichroism measurements have been useful in evaluating the molecular orientation of polymers.<sup>6</sup>

Many kinds of PIs can be used to study the photodegradation direction after PUV irradiation. In this study, we used pyromellitic dianhydride–4,4'-oxydianiline (PMDA–ODA) PI, which is one of the high-temperature-resistant PI films known as Kapton. The chemical structure of PMDA–ODA is shown in Figure 1. In this investigation, we studied PUV-irradiated PMDA–ODA PI films using polarized infrared spectroscopy to identify the molecular orientation of PI before and after PUV irradiation.

## EXPERIMENTAL

### Materials

An amic acid form of a poly(pyromellitic dianhydride-co-4,4'-oxydianiline) solution was obtained from Aldrich (Milwaukee, WI). To obtain the FTIR spectra, suitable concentrations of the poly(amic acid) (PAA) form of PMDA–ODA were spin-coated on  $\text{CaF}_2$  rectangles. A concentrated PAA form of PMDA–ODA was diluted with the *N*-methyl-2-pyrrolidone (NMP) solvent, usually in a ratio of 1 part of the PAA form of PMDA–ODA to 3 parts of the NMP solvent. Spin conditions were typically 3000 rpm for 30 s. Before spin coating,  $\text{CaF}_2$  rectangles were rinsed using isopropyl alcohol and dried thoroughly on a 120°C hot plate. After spin coating, the PAA form of PMDA–ODA-coated  $\text{CaF}_2$  rectangles were soft-baked for 10 min at 85°C to remove the solvents. After soft baking, they were hard-baked in a 260°C convection oven for 1 h to accomplish imidization. After baking, the rectangles were taken from the oven and put in a vacuum desiccator to cool to room temperature. Usually, PI-coated rectangles were stored in the vacuum desiccator overnight before taking the FTIR spectra. 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  $\text{CaF}_2$ .

### Analytical instrumentation

To investigate the effect of PUV irradiation on PI films, a Perkin–Elmer Lambda 19 was used to take the UV-

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VIS spectra. To study the functional group and the molecular chain orientation changes of PMDA-ODA by PUV, a Magna 550 FTIR (Nicolet) was used to take transmission FTIR spectra. From the collected FTIR spectrum, the  $\text{CaF}_2$  spectrum was subtracted to obtain the sample spectrum. A single-diamond IR polarizer from Harrick Co. was used for this study. To reduce the noise level, over 200 scans were obtained at  $4\text{-cm}^{-1}$  resolution.

### PUV irradiation

UV irradiation was accomplished using a 450-W Xenon lamp (Oriol) and polarizer (Oriol) for the PUV source. Xenon lamps emit a smooth continuum from the UV through the VIS, with a higher deep UV (DUV  $\approx 320\text{ nm}$ ) 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  $6\text{ mW/cm}^2$ .

## RESULTS AND DISCUSSION

### Curing reaction

#### FTIR spectral changes with curing

To study changes in the FTIR spectrum caused by the imidization, the FTIR spectra of the PAA form of PMDA-ODA were obtained after soft baking and again after hard baking. Figure 2 shows the FTIR spectra of the PAA form of the PMDA-ODA film (a) after 10-min soft baking at  $85^\circ\text{C}$  and (b) after 1-h hard baking at  $260^\circ\text{C}$ . After hard baking, no detectable strong peaks were found in the  $1900\text{--}4000\text{-cm}^{-1}$  region. Therefore, in this article, we present the FTIR spectrum in the  $1900\text{--}1000\text{-cm}^{-1}$  region. After soft baking, several peaks which are characteristic PAA peaks appeared at  $1725$ ,  $1654$ ,  $1538$ , and  $1409\text{ cm}^{-1}$ . The peak assignments are shown in Table I.<sup>7,8</sup> After hard baking at  $260^\circ\text{C}$  for 1 h, the characteristic imide peaks appeared at  $1777$ ,  $1723$ , and  $1376\text{ cm}^{-1}$ . From these results, we monitored the progress of the imidization reaction during hard baking. The peaks at

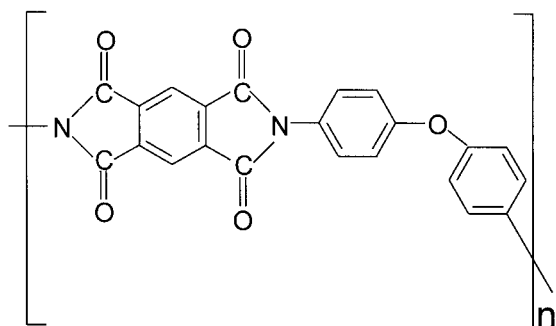


Figure 1 Chemical structure of PMDA-ODA polyimide.

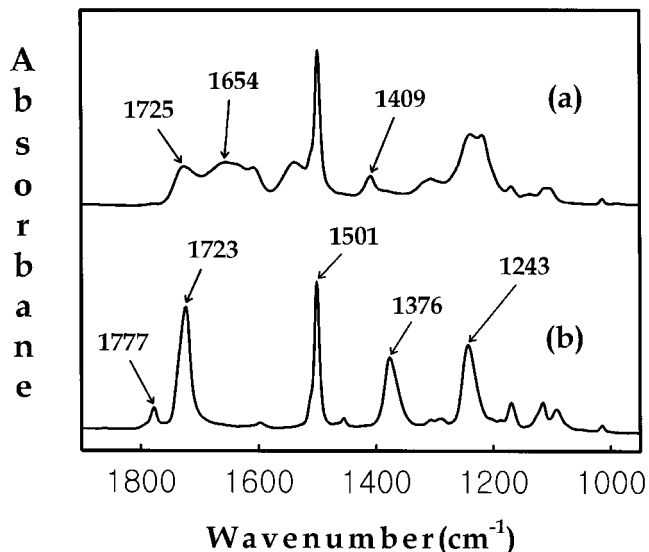


Figure 2 FTIR spectra of PMDA-ODA PAA: (a) after 10-min soft baking at  $85^\circ\text{C}$ ; (b) after 1-h hard baking at  $260^\circ\text{C}$ .

$1243\text{ cm}^{-1}$  may be assigned to  $\text{—C—O—C—}$  asymmetric stretching.

#### Curing rate at $260^\circ\text{C}$

We can look at certain bands quantitatively to establish the time to complete imidization and to establish the bands that we can observe to follow changes caused by PUV irradiation in the next section. Therefore, to study the curing rate at  $260^\circ\text{C}$ , the FTIR spectra were taken after 0, 10, 30, 60, and 180 min curing at  $260^\circ\text{C}$ . The imidization degree can be followed using the  $1376\text{-cm}^{-1}$  imide band normalized to the  $1501\text{-cm}^{-1}$  band as an internal standard. We used the  $1376\text{-cm}^{-1}$  band because it is isolated from the other peaks.<sup>9</sup> The curing reaction can be followed using the change of the  $\text{—OH}$  of the  $\text{—COOH}$  group bending at  $1409\text{ cm}^{-1}$  compared to the axial-imide II at  $1376\text{ cm}^{-1}$ , with both normalized to the  $1501\text{-cm}^{-1}$  peak. The results are shown in Figure 3. By increasing the curing time, the peak intensity at  $1409\text{ cm}^{-1}$  decreased and the peak at  $1376\text{ cm}^{-1}$  increased. The peak area at  $1376\text{ cm}^{-1}$  increased from 0 to 1.009, 1.026, 1.034, and 1.044 with increasing curing time. Relative percents imidization calculated using eq. (1) were 95.3% (10-min curing), 97.4% (30-min curing), 98.5% (1-h curing), and 100.0% (3-h curing):

#### % Imidization

$$= (A_{1376}/A_{1501})/(A_{1376}/A_{1501})_{3\text{h at } 260^\circ\text{C}} \times 100 \quad (1)$$

where  $A_{1376}$  and  $A_{1501}$  are the peak areas at  $1376$  and  $1501\text{ cm}^{-1}$ , respectively.

Figure 3 shows the very fast imidization reaction, which is essentially 95.3% complete within 10 min of

TABLE I  
FTIR Peak Assignment<sup>7,8</sup> in the 1900–1000-cm<sup>-1</sup> Region

Material	Peak (cm <sup>-1</sup> )	Polarization tendency <sup>a</sup>	Assignment
PAA	1725		$\nu(\text{C}=\text{O})$ , acid
	1654		$\nu(\text{C}=\text{O})$ , amide I
	1538		$\delta(\text{CNH})$ , amide II
	1499		$\nu(1,4\text{-C}_6\text{H}_4)$
	1409		$\delta(\text{OH})$ , acid
PI	1777		$\nu(\text{C}=\text{O})$ in-phase (imide I)
	1723	⊥	$\nu(\text{C}=\text{O})$ out-of-phase (imide I)
	1501		$\nu(1,4\text{-C}_6\text{H}_4)$
	1376		$\nu(\text{CNC})$ (axial-imide II)
	1243		$\nu_{\text{as}}(\text{COC})$

<sup>a</sup> ||, parallel transition moment tendency; ⊥, perpendicular transition moment tendency.

curing. The fast reaction results from the higher amount of solvent content in the early stage of the curing reaction, which increases the mobility of the chain. The curing reaction gradually slowed due to the loss of the residual solvent and the decrease of the molecular mobility by the conversion from the PAA to the more rigid PI.<sup>10</sup>

### Effects of PUV irradiation

#### 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 PMDA-ODA PI (1 h cured at 260°C) after various exposure times with PUV irradiation. All the UV-VIS spectra of PI, 6-h PUV-irradiated PI, 12-h PUV-irradiated PI, and 18-h PUV-

irradiated PI showed very little absorption from the 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 200–400-nm region as shown in Figure 4. According to Figure 4, the 1-h cured PI at 260°C absorbs strongly from the 200 to 350 nm region and absorbs little above 350 nm, showing two peaks at 220 and 284 nm. After 1-h PUV irradiation on the PI,  $\lambda_{\text{max}}$  changed from 220 to 224 nm. Further PUV irradiation resulted in an absorbance intensity decrease. This decrease of the absorbance intensity may be caused by photo-induced decomposition of the PI.<sup>4</sup>

#### Alignment by PUV irradiation

PUV irradiation of the PI cured at 260°C resulted in several changes appearing in the FTIR spectra. First, the absorbance of most the PI peaks decreased. Second, new peaks occurred at 3258, 1748, and 1710 cm<sup>-1</sup>.

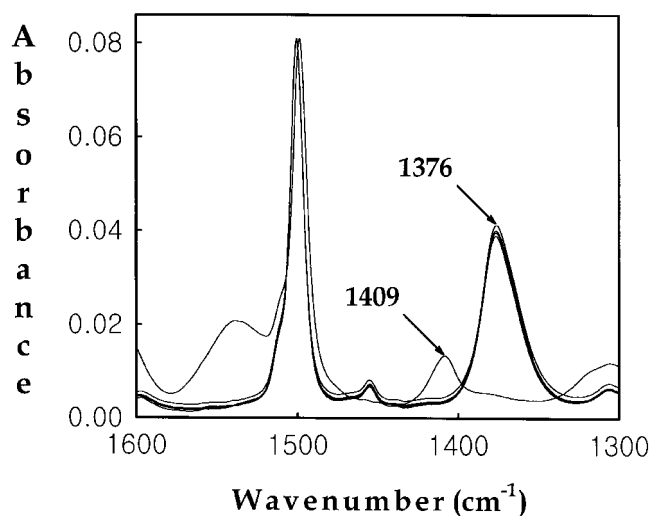


Figure 3 FTIR spectra change with curing time at 260°C (1600–1300 cm<sup>-1</sup> region).

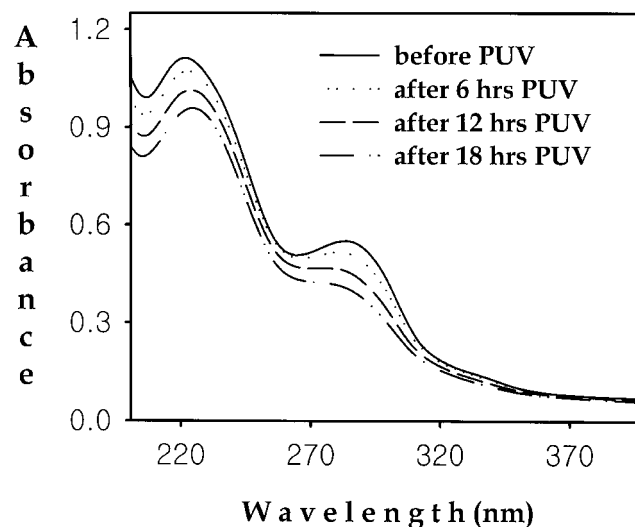
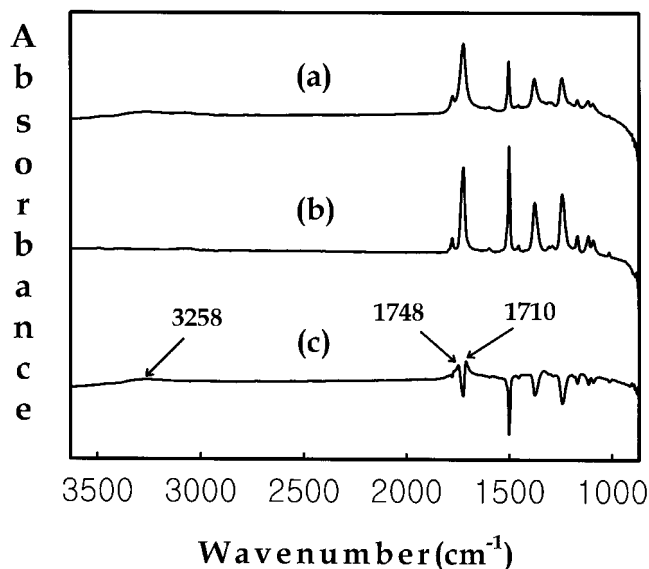


Figure 4 UV-VIS spectra change with PUV irradiation time.

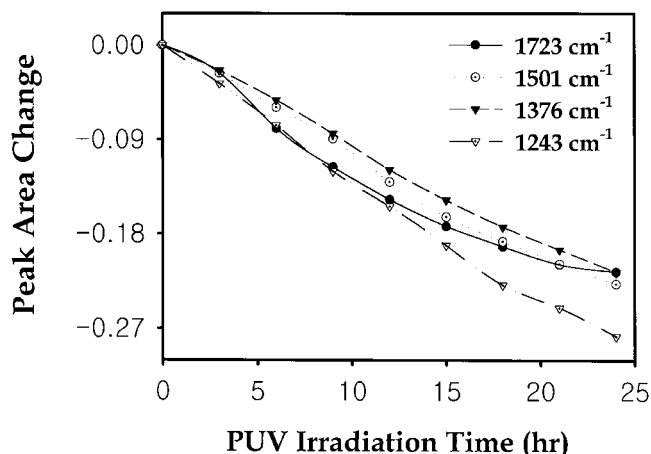
Third, a relative change of polarized IR absorbance peaks occurred, showing a molecular orientation change.

*New peak formation with PUV irradiation.* 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 24 h of PUV irradiation from the FTIR spectrum before irradiation is shown in Figure 5. As shown in Figure 5, all peaks in the difference spectrum, except peaks at 3258, 1748, and 1710  $\text{cm}^{-1}$ , show negative absorbance due to degradation of the PI by PUV irradiation. The 1748- and 1710- $\text{cm}^{-1}$  peaks may be caused by the carboxylic acid groups produced by degradation of the imide bond of PI by PUV irradiation. Carboxylic acids, which exist as dimers, absorb at  $\sim 1710 \text{ cm}^{-1}$ , and free, nonhydrogen-bonded acids, at  $1755 \text{ cm}^{-1}$ . Therefore, the peak at 1748  $\text{cm}^{-1}$  may be caused by the carboxylic acids which form hydrogen-bonded complexes with the adjacent oxygen products.<sup>11</sup> The peak at 3258  $\text{cm}^{-1}$  may be caused by the —OH of the —COOH groups and other —OH groups.

*Changes of the peak intensities with PUV irradiation time.* To investigate the effect of PUV irradiation on the PI, the absorbance change of several characteristic peaks was measured as a function of the PUV irradiation time. The peaks at 1777, 1723, 1501, 1376, and 1243, gradually decreased with increase of the PUV irradiation time. The peak areas as a function of PUV irradiation time were measured. The decrease of major peak areas at 1723, 1501, 1376, and 1243  $\text{cm}^{-1}$  as a



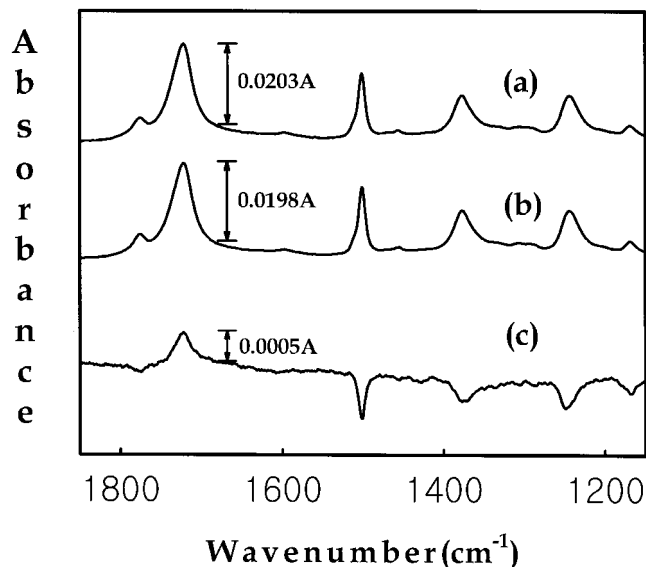
**Figure 5** FTIR spectra of PI (a) after 24 h PUV irradiation, (b) before PUV irradiation, and (c) difference obtained by subtracting (b) from (a). An expanded  $y$ -axis scale was used for (c).



**Figure 6** Decrease of peak area of several major peaks with the PUV irradiation time.

function of the PUV irradiation time are shown in Figure 6. According to Figure 6, the peak areas decrease linearly with the PUV irradiation time for 1501, 1376, and 1243  $\text{cm}^{-1}$  peaks. The area of the peak at 1723  $\text{cm}^{-1}$  decreased nonlinearly. The peak area decrease at 1723  $\text{cm}^{-1}$  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.<sup>5</sup> These combined area changes may be the source of the nonlinear relationship between the PUV irradiation time and the decrease of the peak area. But after long PUV irradiation, the fragmented material yields very small photooxidation products such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and CO that will be easily evaporated.<sup>4</sup> Therefore, the decrease of the all peak areas is observed.

*Molecular orientation of the PUV-irradiated PI.* To check the molecular orientation change by the PUV irradiation, polarized FTIR spectra were obtained after the PUV irradiation. Figure 7 shows the typical polarized FTIR spectra of the PI samples after 1440-min PUV irradiation. In Figure 7(a), the IR polarization direction is parallel to the PUV polarization and shows a much stronger peak at 1723  $\text{cm}^{-1}$  compared to Figure 7(b), where the IR polarization direction is perpendicular to the PUV polarization. According to Table I, the peak at 1723  $\text{cm}^{-1}$  has a transition moment perpendicular to the molecular axis. The 1501- $\text{cm}^{-1}$  and other remaining peaks have transition moments parallel to the molecular axis. 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 1723  $\text{cm}^{-1}$  and negative for the other peaks, clearly supporting perpendicular orientation of the PI chains after PUV irradiation. This PI molecular orientation change after PUV exposure appears to be primarily due to preferential degradation



**Figure 7** FTIR spectra of 1440-min PUV-irradiated PI: (a) with polarization parallel to the PUV irradiation direction; (b) with polarization perpendicular to the PUV irradiation direction; (c) difference obtained by subtracting (b) from (a).

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.

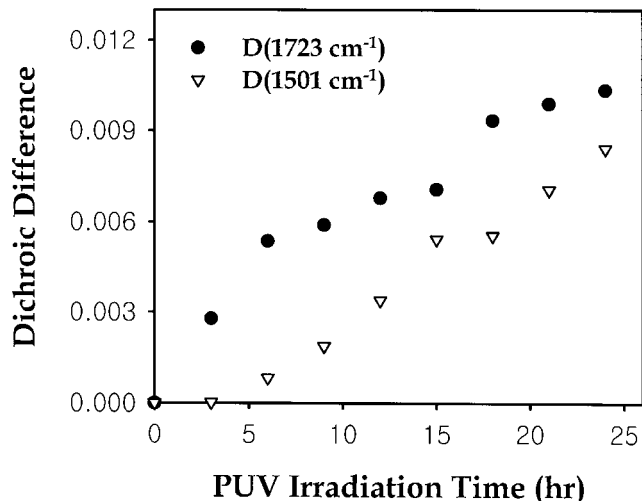
The area of the peaks at 1723 and 1501  $\text{cm}^{-1}$  in the difference spectrum can be used to estimate the degree of the orientation of the polymer chains.<sup>12</sup> We used the two strong peaks in the difference spectrum to measure the degree of orientation, one at 1723  $\text{cm}^{-1}$  which shows a positive value and one at 1501  $\text{cm}^{-1}$  which shows a negative value by the following equations:

$$D(1723) = |A_{\parallel}(1723) - A_{\perp}(1723)| \quad (2)$$

$$D(1501) = |A_{\parallel}(1501) - A_{\perp}(1501)| \quad (3)$$

Here,  $A_{\parallel}$  is the absorbance when the polarization vector is parallel to the PUV irradiation direction or rubbing direction, and  $A_{\perp}$ , the absorbance when the polarization vector is perpendicular to the PUV irradiation direction or rubbing direction. The changes of the dichroic difference ( $D$ ) at 1723 and 1501  $\text{cm}^{-1}$  with the PUV irradiation time are shown in Figure 8. According to Figure 8,  $D$  increased with the PUV irradiation time.

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 a velvet cloth five times. The results are shown in Figure 9. Contrary to the PUV-irradiated PI, the difference spectrum after rubbing showed the opposite trend of a positive value at 1501  $\text{cm}^{-1}$  and a negative value at 1723  $\text{cm}^{-1}$ . This result supports the



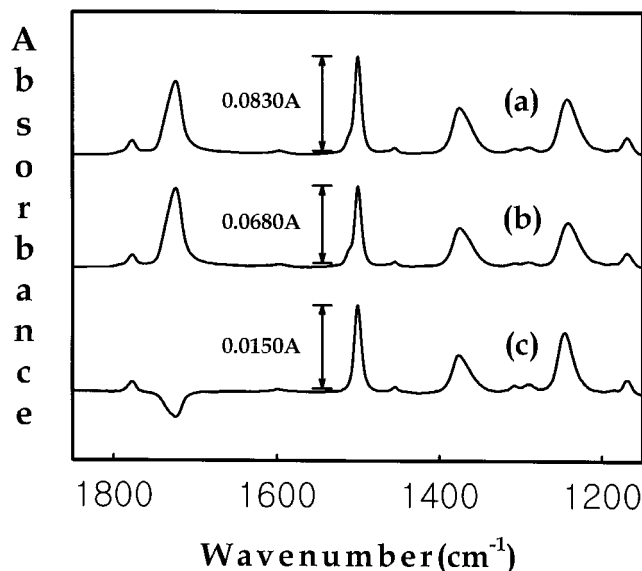
**Figure 8** Dichroic difference change with PUV irradiation time.

conclusion that the rubbed PI molecules are aligned along the rubbing direction.<sup>11</sup>

## CONCLUSIONS

The results of these experiments led to the following conclusions:

1. The imidization reaction is very fast in the early stage of imidization due to a higher amount of solvent content which increases the mobility of the chain.



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

2. Molecular chain orientation of PUV-irradiated PI was perpendicular to the PUV-irradiation direction due to the preferential photodegradation 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.

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## References

1. Hoyle, C. E.; Anzures, E. T. *J Appl Polym Sci* 1991, 43, 1.
2. Hoyle, C. E.; Anzures, E. T. *J Appl Polym Sci* 1991, 43, 11.
3. Hoyle, C. E.; Anzures, E. T. *J Polym Sci Polym Chem Ed* 1992, 39, 1233.
4. Hoyle, C. E.; Creed, D.; Nagarajan, R.; Subramanian, P.; Anzures, E. T. *Polymer* 1992, 33, 3162.
5. Hoyle, C. E.; Anzures, E. T.; Subramanian, P.; Nagarajan, R.; Creed, D. *Macromolecules* 1992, 25, 6651.
6. Sakamoto, K.; Arafune, R.; Ito, N.; Ushioda, S.; Suzuki, Y.; Morokawa, S. *J Appl Phys* 1996, 80, 431–439.
7. Isida, H.; Huang, M. T. *Spectrochim Acta A* 1995, 51, 319–331.
8. Molis, S. E. In *Polyimides: Materials, Chemistry and Characterization*; Feger, C.; Khojasteh, M. M.; McGrath, J. E., Eds.; Elsevier: New York, 1989; pp 659–672.
9. Pryde, C. A. *J Polym Sci Part A Polym Chem* 1989, 27, 711–724.
10. Harris F. W. In *Polyimides*; Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds.; Blackie: Glasgow and London, 1990; p 22.
11. Sawa, K.; Sumiyoshi, K.; Hirai, Y.; Tateishi, K.; Kamejima, T. *Jpn J Appl Phys* 1994, 33, 6273–6276.
12. Hasegawa, R.; Mori, Y.; Sasaki, H.; Ishibashi, M. *Jpn J Appl Phys* 1996, 35, 3492–3495.