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Mechanism of Orientation of Liquid Crystal Molecules for Polarized UV-exposed Polyimide Alignment Layers

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display (LCD)

(PI) (PUV)

UV, PI 360 nm

PUV가 PI, PI FT-IR

가, 3244 cm⁻¹

가 PUV PI

PUV PI PUV

PI PI

PUV가 PI

PI PUV

ABSTRACT : We studied the mechanism of orientation of polyimide molecules which were irradiated by polarized UV (PUV) using polarized Fourier transform infrared (FT-IR) spectroscopy and ultraviolet (UV) spectroscopy. According to the measured UV spectra, we found PI films mainly absorb UV light less than 360 nm wavelength, therefore, UV light less than 360 nm induces photochemical reaction of PI. PUV irradiation of PI films caused decrease of all peak intensities in the FT-IR spectra, except the newly formed broad peak at 3244 cm⁻¹, due to degradation of the PI molecules. The remaining PI molecules after photo-degradation showed predominantly perpendicular molecular orientation to the irradiated PUV polarization direction, due to the preferential degradation of PI molecules parallel to irradiated PUV polarization direction. However the rubbing of PI films induced reorientation of the PI molecules parallel to the rubbing direction. We also investigated the alignment of the liquid crystal by rubbing or PUV irradiation. Liquid crystals align perpendicular to the PUV polarization direction and parallel to the rubbing direction.

Keywords : polyimide, polarized UV, liquid crystal, FT-IR, orientation.

가

가 3 가

가 (mesomorphic phase)¹

display (cathode ray tube, CRT) display LCD가 LCD CRT display

CRT display LCD

LCD²

가 PI가³

multi-domain LCD⁴

(polarized UV, PUV) PI 가^{5,6} PUV multi domain LCD 가^{7,8}

^{9,10} FT - IR

⁹ FT - IR PUV PI PI¹¹

PI PUV

가

PI PUV

FT - IR PUV

가

PI Nissan 7492 (Nissan Chemical Ind., Ltd.) FTIR CaF₂ poly(amic acid) Nissan 7492 1 500 rpm, 18 2 2500 rpm, 30 CaF₂ 125 PAA가 CaF₂ 70 , 90 230 PI 30 μm FT - IR UV 99.9% CaF₂ PUV UV PI PUV UV/Vis spectrophotometer (UV S-2100; Scinco Co.) PUV PI ZnSe (Graseby Specac Ltd.) FT/IR - 620 (Jasco) 4 cm⁻¹, 200 scan FT - IR FT - IR CaF₂ indium tin oxide (ITO) PI PI texture (Zeiss Jenalab)

PUV UV 1000 W (Nanotek, Inc.) UV model No. 27320 (Nanotek, Inc.) PUV 10 mW/cm² PI PUV UV PUV PI 4 ITO 가 99.9% CaF₂ 70, 90 230, 1 5 PUV UV 1 anti-parallel PUV가 ITO 5 mm 85 E7(K-N = -10, N-I = 60, BDH Chemical Co.) 5 E7 (51% 5CB, 25% 7CB, 16% 8OCB, 8% 5CT) 가 E7 85 30 가 texture FT-IR

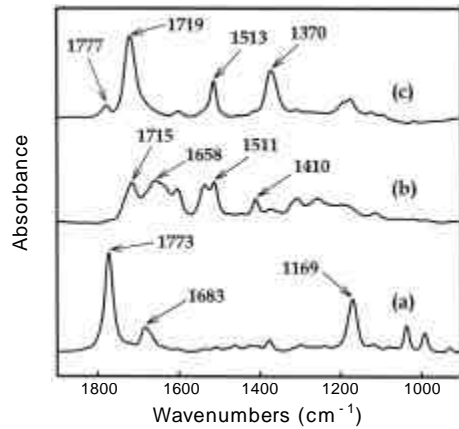


Figure 1. The FT - IR spectra of Nissan 7492. (a) solution, (b) after 90 seconds soft baking at 70 °C, and (c) after 1 hour hard baking at 230 °C.

Table 1. FT-IR Peak Assignment in the 1800 - 1300 cm⁻¹ Region^{9, 12}

material	peak (cm ⁻¹)	polarization	assignment
PAA	1715	-	(C=O), acid
	1658	-	(C=O), amide I
	1536	-	(CNH), amide II
	1511	-	(1,4 - C ₆ H ₄)
	1410	-	(OH), acid
PI	1777	-	(C=O) in - phase (imide I)
	1719	-	(C=O) out - of - phase (imide I)
	1513	-	(1,4 - C ₆ H ₄)
	1370	-	(CNC) (axial - imide II)

* - parallel transition moment tendency ; - perpendicular transition moment tendency.

1900 cm⁻¹ 가
 1900 900 cm⁻¹
 Figure 1 (a) 1773 1169 cm⁻¹
 PAA 가 (b)
 가
 (b) 1715, 1658,
 1511, 1410 cm⁻¹ PAA
 , (c)
 PI 1777, 1719, 1513,
 1370 cm⁻¹ . Table 1

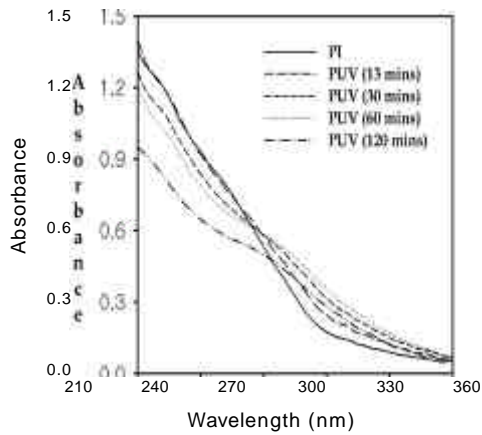


Figure 2. UV spectra change with PUV irradiation time.

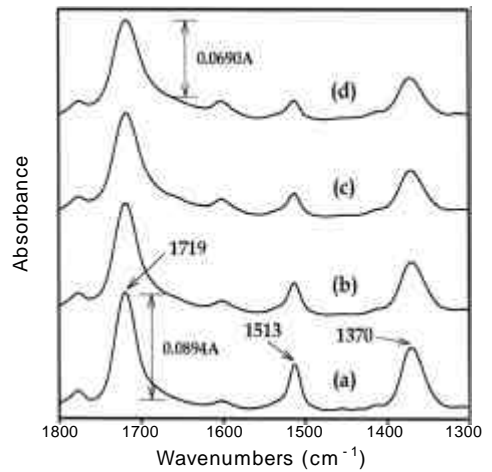


Figure 3. FTIR spectra change with PUV irradiation time (1800-1300 cm^{-1} region). (a) 0 minute, (b) 30 minutes, and (c) 60 minutes, and (d) 90 minutes.

UV PUV
 UV :
 PI :
 PI 가 PUV
 PI UV
 PUV
 PI UV 360 800
 nm 가
 UV 360 nm
 Figure 2 210 360 nm
 Figure 2 360 nm
 PUV PI
 UV 가
 270 nm 230 270 nm
 가 , 270 nm
 가
 PUV PI
 PUV : 230 , 1
 PI PUV FT -
 가 가
 PI 가
 FT - IR

3244 cm^{-1}
 가
 PUV : PUV
 PI FT - IR
 PUV
 Figure 3 PUV 가
 1777, 1719, 1513, 1370 cm^{-1}
 가 1719 cm^{-1} (C=O,
 out - of - phase, imide group) PUV
 PUV PI
 1719 1370
 cm^{-1} 가 PUV 1717, 1372 cm^{-1}
 PUV
 PUV
 (1)
 PUV : 230 , 1
 PI PUV FT -
 가 가
 PI 가
 FT - IR

$$\% \text{ Remaining Peak Area} = \frac{\text{Area}(t)}{\text{Area}(0)} \times 100 \quad (1)$$

$$\text{Area}(t) = \text{PUV} \quad t, \text{Area}(0) = \text{PUV}$$

Figure 4 % remaining peak area 1719, 1513,

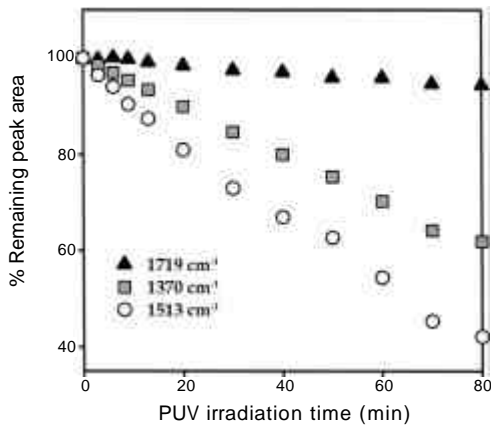


Figure 4. % Remaining peak area changes of several peaks with PUV irradiation time.

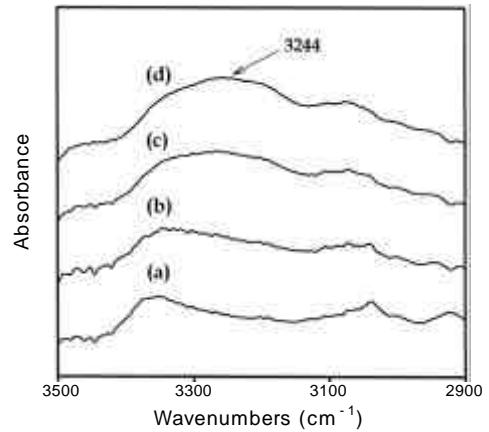


Figure 5. FT - IR spectra change with PUV irradiation time (3500 2900 cm⁻¹ region). (a) 0 minute, (b) 30 minutes, and (c) 60 minutes, and (d) 90 minutes.

1370cm⁻¹
 . PUV aromatic ring imide
 ring -C - N - 1513 1370
 cm⁻¹
 , 1719 cm⁻¹ 30
 가
 . 1719 cm⁻¹
 imide
 C=O COOH 13
 가
 1513 cm⁻¹ 가 1370 cm⁻¹
 -C - N - 1,4 -
 C₆H₄ aromatic ring 가

PUV : Figure 5
 3500 2900 cm⁻¹ PUV가 PI
 FT - IR
 . PUV 가 aromatic C -
 H 가 가 3244 cm⁻¹
 PUV
 가 ,
 3244 cm⁻¹ . 3244
 cm⁻¹ -C - N -
 COOH OH
 OH .¹⁴ PUV
 , PUV

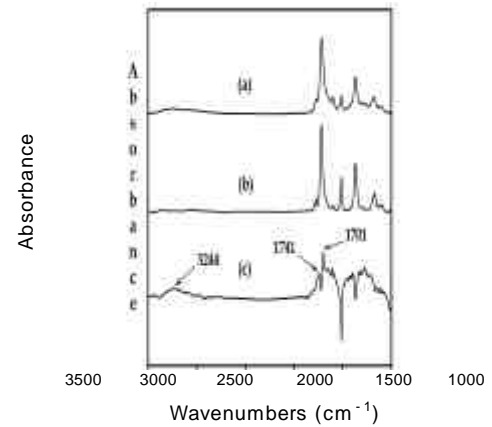


Figure 6. FT - IR spectra of PI. (a) after PUV irradiation, (b) before PUV irradiation, and (c) difference obtained by subtracting (b) from (a). An expanded y - axis scale is used for (c).

FT - IR , PUV
 PUV
 Figure 6(c) . Figure 6(c)
 3244, 1741, 1701 cm⁻¹
 PUV PI
 . 1741
 1701 cm⁻¹ PUV
 -COOH .
 -COOH C=O

1720 - 1680 cm^{-1} ,
 - COOH C=O
 1760 - 1735 cm^{-1} 가
 , 1741 cm^{-1}
 - COOH , 1701
 cm^{-1} - COOH
 - COOH
 . 3244 cm^{-1} - COOH
 - OH - OH
 . PUV , PI - COOH
 가 가
 PUV가 PI : PUV가
 PI , FT -
 IR . Figure 7 90
 PUV가 PI FT - IR
 . Figure 7 (a) PUV
 FT - IR
 , (b) PUV
 FT - IR . Figure 7 (c)
 7(a) 7(b)
 . Figure 7(c) 1719 cm^{-1}
 . Table 1 , 1719

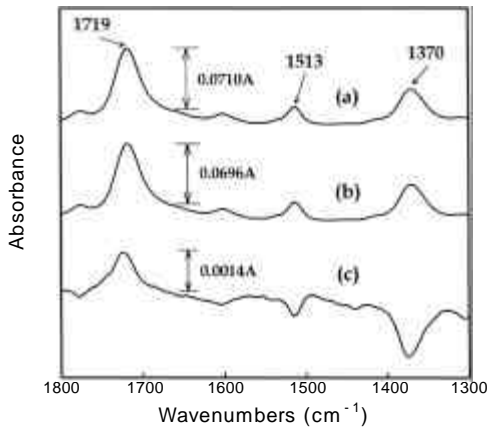


Figure 7. FT - IR spectra of 90 minutes PUV irradiated PI. (a) with polarization parallel to the PUV irradiation direction, (b) with polarization perpendicular to the PUV irradiation direction, and (c) difference obtained by subtracting, (b) from (a).

cm^{-1}
 가 , 1513 1370 cm^{-1}
 가
 , PUV PI PUV
 PI
 PUV
 PUV PI
 . Figure 7(c) PUV 1719
 1513 1370 cm^{-1}
 ,
 (2), (3) (4) dichroic difference (D)
 .¹⁵
 $D(1719) = |A(1719) - A(1719)|$ (2)
 $D(1513) = |A(1513) - A(1513)|$ (3)
 $D(1370) = |A(1370) - A(1370)|$ (4)
 , A PUV
 가 , A PUV
 가
 . 1719 1513 1370 cm^{-1}
 D PUV Figure 8
 . Figure 8 , D PUV
 가 , PUV 40

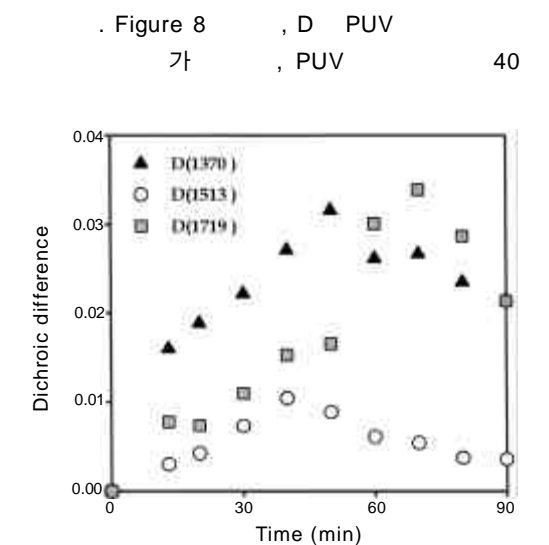


Figure 8. Dichroic difference change with PUV irradiation time.

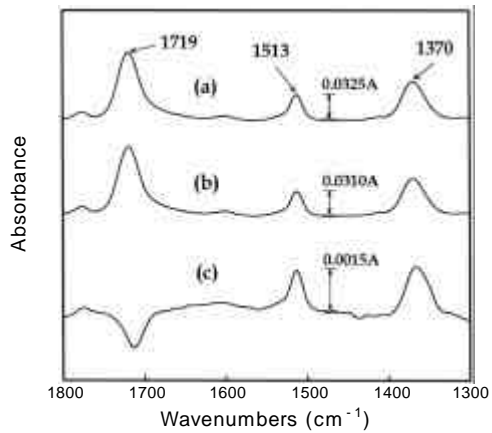
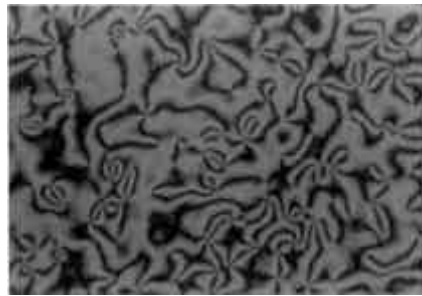
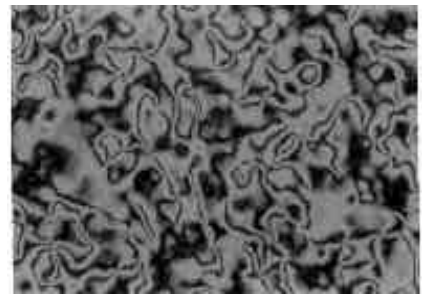


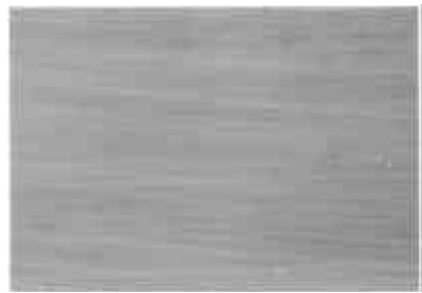
Figure 9. FT - IR spectra of rubbed PI. (a) with polarization parallel to the rubbing direction, (b) with polarization perpendicular to the rubbing direction, and (c) difference obtained by subtracting (b) from (a).



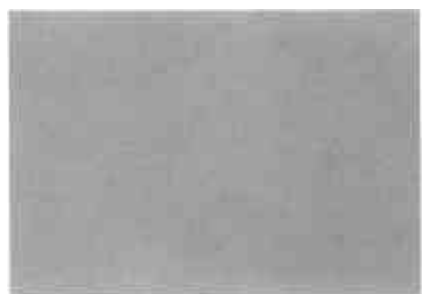
(a)



(b)



(c)



(d)

Figure 10. Photomicrographs of the ITO glass LC cell ($\times 100$). (a) LC cell made of PI without any treatment, (b) LC cell made of 1 hour UV irradiated PI, (c) LC cell made of rubbed PI, and (d) LC cell made of 1 hour PUV irradiated PI.

D(1513) , D(1370)
 PUV 50 , D(1719) PUV
 70 가
 . PUV 가 D가
 가 가 PUV
 D PUV
 PI ,
 PI FT - IR
 . Figure 9 PI FT - IR
 . PUV PI ,
 PI Figure
 9(c) , 1719 cm⁻¹ , 1513
 1370 cm⁻¹ 가 PUV
 PI
 . PI
 .¹⁶
 Texture : PI 가
 PI, UV
 PI, 1 PUV PI, 1 UV
 PI ,
 texture
 . Figure 10

Figure 10 (a) (b) PI UV PI 가 Schli-
 , E7 (c) (d) 17
 uren texture 가 PI PUV PI
 E7 (c)
 (d) (c) scratch
 line (d)
 PUV
 PI PUV PI FT -
 IR FT-IR E7
 가 PUV FT - IR
 Figure 11 PUV
 FT - IR Table
 2 E7 E7
 - C N
 - CH₃ 18

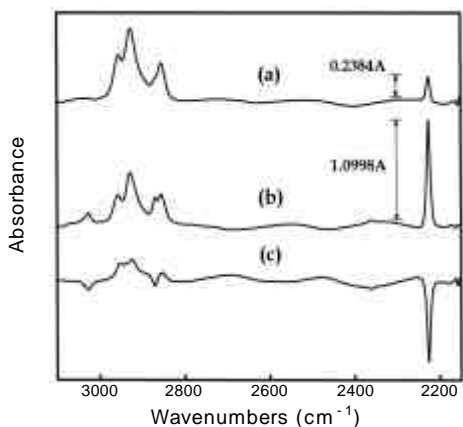


Figure 11. FT - IR spectra of ITO glass LC cell with PUV irradiated PI alignment layer. (a) with polarization parallel to the PUV irradiation direction, (b) with polarization perpendicular to the PUV irradiation direction, and (c) difference obtained by subtracting (b) from (a).

가
 , - CH₂
 19 Figure 11 (a) PUV
 FT - IR
 , - C N
 - CH₂
 Figure 11 (b) PUV
 FT - IR
 , 2927 cm⁻¹ - CH₂
 2227 cm⁻¹ - C N
 E7 PUV
 PI
 Figure 11 (c) (a) (b)

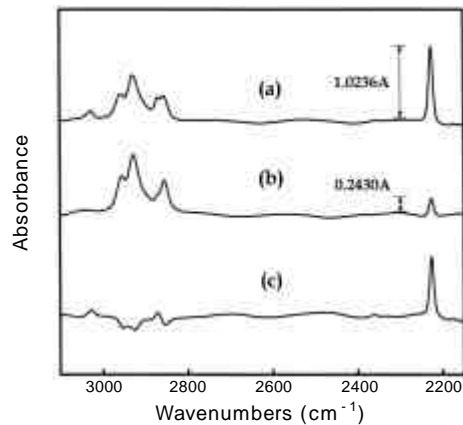
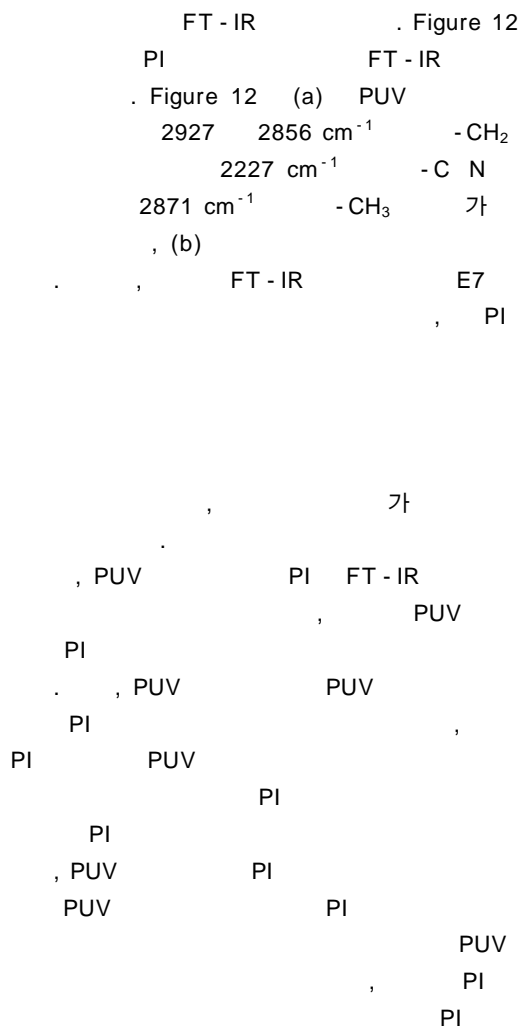


Figure 12. FT - IR spectra of ITO glass LC cell with rubbed PI alignment layer. (a) with polarization parallel to the rubbing direction, (b) with polarization perpendicular to the rubbing direction, and (c) difference obtained by subtracting (b) from (a).

Table 2. Peak Assignment for E7^{19, 20}

peak(cm ⁻¹)	polarization*	assignment
2957	-	asymmetric stretching mode of CH ₃
2927	-	asymmetric stretching mode of CH ₂
2871	-	symmetric stretching mode of CH ₃
2856	-	symmetric stretching mode of CH ₂
2227	-	stretching mode of C N

* - parallel transition moment tendency ; - perpendicular transition moment tendency.



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