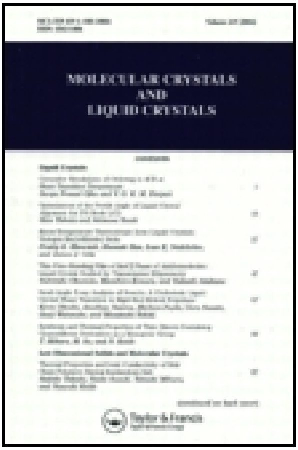

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Infrared Spectroscopic Studies of the Thermal Stability of Alignment Layers of Polarized UV-Exposed Polyimide Films for Liquid Crystal Alignment

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Infrared Spectroscopic Studies of the Thermal Stability of Alignment Layers of Polarized UV-Exposed Polyimide Films for Liquid Crystal Alignment

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Polarized Fourier transform infrared (FTIR) and optical microscopy with crossed polarizer were used to investigate the thermal stability of the alignment layers formed by rubbing and polarized UV (PUV) irradiation on the polyimide (PI) films. The thermal stability of the PUV irradiated PI alignment layer is lower than that of the rubbed PI layer due to the fragmentation reaction of the PI by PUV. We also investigated the alignment of the liquid crystal by rubbing or PUV irradiation. Liquid crystal (LC) molecules align parallel to the predominant orientation of the PI and perpendicular to the PUV irradiation direction.

Keywords: polyimide; infrared spectroscopy; thermal stability; polarized UV

1. INTRODUCTION

Part I of this two-part article has shown the reason of the formation of the alignment layer on the PI by rubbing and PUV irradiation. Here, we compare the thermal stability of the alignment layer formed by PUV irradiation to the alignment layer formed by conventional method of alignment layer formation by rubbing.

The sealing process in the assembling process of liquid crystal display (LCD) cells require heating of the cell between 100–200 °C for curing the sealing adhesive material [1,2]. Therefore, the alignment layer must be stable for half an hour to several hours above 100°C heating.

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The loss of the LC alignment by thermal treatment may be caused by the following three reasons; 1) removal of the alignment layer by oxidative thermal degradation, 2) increased mobility of the molecules in the alignment layer by heating above glass transition temperature (T_g) of the PI or fragmented PI, 3) and LC acting solvent, increasing the mobility or dissolving fragmented PI molecules in the alignment layer in LCD. In this investigation, we studied the factors affecting the thermal stability of the alignment layer.

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 the 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 1hr to accomplish imidization. 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.

B. Analytical Instrumentation

To study peak area and the molecular chain orientation change by thermal treatment, 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. To investigate the texture change of the liquid crystal with heating, optical microscope (Leitz) with crossed polarizer was used.

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, < ~320 nm) output than mercury sources. The PI was irradiated in air for 1 and a half hours. The intensity of the UV in the UVB region after passing through the polarizer was about 6 mW/cm^2.

D. Thermal treatment

To investigate thermal stability of the alignment layer, PUV aligned PIs and the rubbed PIs were heated for 1 hr at the desired temperature.

E. Manufacture of the liquid crystal cell

To investigate the thermal stability of the alignment layer in contact with the liquid crystal, we made two liquid crystal cells using the rubbed PI and the PUV irradiated PI. Four rectangular quartz plates were cleaned with absolute methanol, and Nissan 610 solution was spin coated on the quartz the same method as before. The spin coated quartz substrates were cured at 220°C to avoid homeotropic LC alignment. After curing for 1 hr, two PI coated quartz substrates were weakly rubbed two times with velvet cloth, while the other two PI coated quartz were PUV irradiated for 30 minutes. 3.5 μm glass fiber mixed UV curable adhesive was used as a spacer at four corners of the PI coated quartz. One cell was assembled with parallel rubbing directions and the other cell was assembled with parallel PUV irradiation directions. After assembling cells, 4-pentyl-4′-cyanobiphenyl (5CB, C-N = 24°C and N-I = 35°C) was introduced to the cell by capillary action in the isotropic state. After the 5CB introduction, the four edges of the cell were completely sealed with 5 minute epoxy. After curing of the epoxy, those cells were heated at 90°C for 30 minutes and slowly cooled to room temperature over 2 hrs to give good homogeneous alignment of 5CB.

3. RESULTS AND DISCUSSION

A. The thermal stability of the alignment layers

(1). Peak intensity change with heating temperature

To investigate the thermal loss of the aligning ability of alignment layer, the peak area change with heating were measured. We used two strong peaks in the spectrum to measure the peak area after various thermal treatment temperatures: one at 1719 cm^{-1} {ν(C=O) out-of-phase (imide I)} and the other at 1503 cm^{-1} peak {v(1,4-C_6H_4)}. The peak assignments for the PI are shown in Table I.[3,4] The % remaining peak area after a given thermal treatment temperature was calculated by the following equation:

$$\%\text{Remaining Peak Area} = \text{Area (T)}/\text{Area (0)} \times 100 \qquad ------ (1)$$

Area (T) = The peak area after heating for 1hr at the desired temperature T°C.
Area (0) = The peak area before thermal treatment.

TABLE I FTIR Peak Assignments[3,4] in the 1900–1300 cm^{-1} Region

Material	*Peak (cm^{-1})*	*Polarization Tendency**	*Assignment*
PI	1780	‖	v(C=O) in-phase(imide I)
	1722	⊥	v(C=O) out-of-phase(imide I)
	1601		v(1,2,4,5-C_6H_2)
	1503	‖	v(1,4-C_6H_4)
	1377	‖	v(CNC) (axial-imide II)

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

Fig. 1 shows the % remaining peak area of 1719 cm^{-1} peak and 1503 cm^{-1} peak with the heating for the 1 hour and a half PUV irradiated PI. The % remaining peak area of the two peaks showed a little different trend with heating temperature. For the 1719 cm^{-1} peak case, the % remaining peak area was almost the same or a little increased till 180°C heating, but after that temperature, it showed fast decrease of the remaining peak area. But the % remaining peak area at 1503 cm^{-1} showed decrease of the peak area even beginning from 120°C heating. The % remaining peak area of 1719 cm^{-1} peak may be contributed by 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 thermal oxidation. Therefore, the initial increase of the % remaining peak at 1719 cm^{-1} may be caused by the predominant C=O containing group formation due to thermal oxidation of the PUV irradiated layer. But above 180°C heating, imide bond degradation became predominant than C=O group formation. Therefore, % remaining peak area at 1719 cm^{-1} starts to decrease from above 180°C heating. But peak area at 1503 cm^{-1}, which is due to a skeletal mode of the 1,4 substituted phenyl ring of the PI, showed decrease of the peak area even beginning from 120°C heating due to degradation and removal of the 1,4 substituted phenyl ring of the PI alignment layer.

But for the rubbed alignment layer, the rapid area decrease started to occur from 230°C for 1503 cm^{-1} and from 300°C for 1724 cm^{-1} as shown in Fig. 2. This lower thermal stability of the PUV irradiated layer may be caused by lower

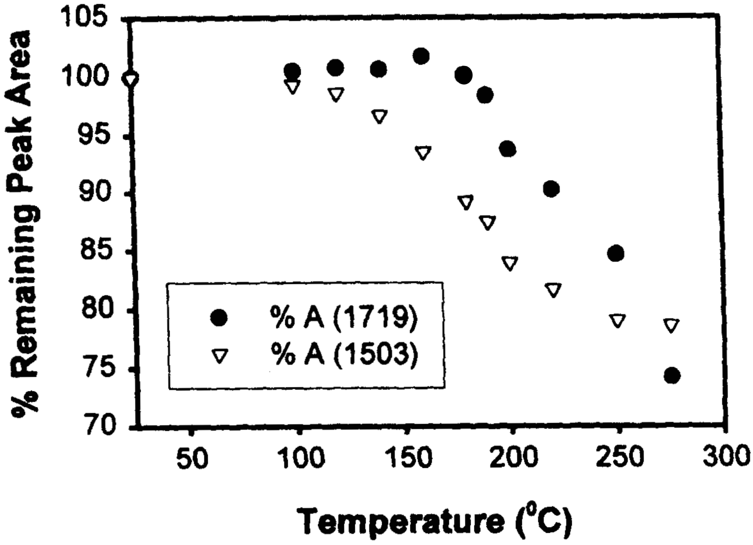

FIGURE 1 % Remaining peak area change with thermal treatment temperature of the PUV irradiated PI

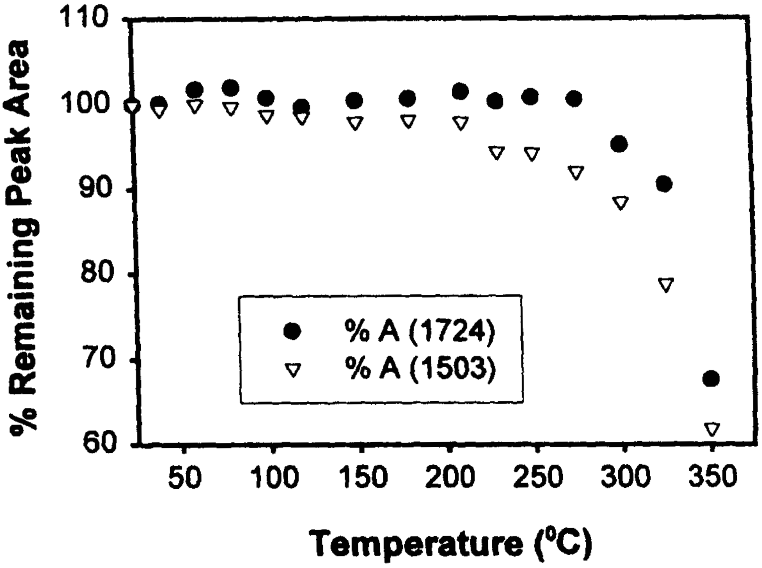

FIGURE 2 % Remaining peak area change with thermal treatment temperature of the rubbed PI molecular weight of the PUV irradiated layer due to main chain scission reactions[5]. After heat treatment, we also found peak area decrease and the returning of the peaks from 1719 and 1724 cm^{-1} to 1722 cm^{-1} which is the peak position before any aligning treatment for both PUV irradiated PI and the rubbed PI. These results support the ablative oxidative thermal degradation of the alignment layer by heating in the air.

(2). Dichroic difference change with heating temperature

To investigate the thermal stability of PI alignment layer formed by PUV irradiation and by rubbing, they were heated for 1 hr in a convection oven. After heating, we took the polarized FTIR spectra. We used two peaks to calculate the dichroic difference (D) using the following eq'ns (2) and (3); One at 1719 cm^{-1}, which has a transition moment perpendicular to the molecular axis, and the other at 1503 cm^{-1}, which has a transition moment parallel to the molecular axis as shown in Table I.

$$D(1719) = |A_{\parallel}(1719) - A_{\perp}(1719)| \qquad ------ (2)$$

$$D(1503) = |A_{\parallel}(1503) - A_{\perp}(1503)| \qquad ------ (3)$$

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 D value change with heating temperature for the PUV irradiated PI is shown in Fig. 3. The D value starts to decrease from 140°C, and after 275°C treatment, D(1719) decreased to 15% of the original value and the D(1503) decreased to 5% of the original value.

The D value change of rubbed PI with temperature is very different from the PUV irradiated PI. The D value change of rubbed PI with temperature is shown in Fig. 4. It shows very slow decrease of the D value with temperature. Even after 275°C heating, D(1724) retains 82% and D(1503) retains 57% of the original value of before heating. It only begins a fast decrease above 300°C heating. After 350°C heating, 19% of the D(1724) value remained compared to the 16% remaining of the D(1503) value. These results support that the rubbed PI alignment layer is thermally more stable than PUV irradiated alignment layer. The decrease of the peak area and loss of dichroism by heating suggest that the degradation of the aligned PI layer at elevated temperatures proceeds through the oxidative thermal degradation which requires oxygen. Therefore, the aligned layer

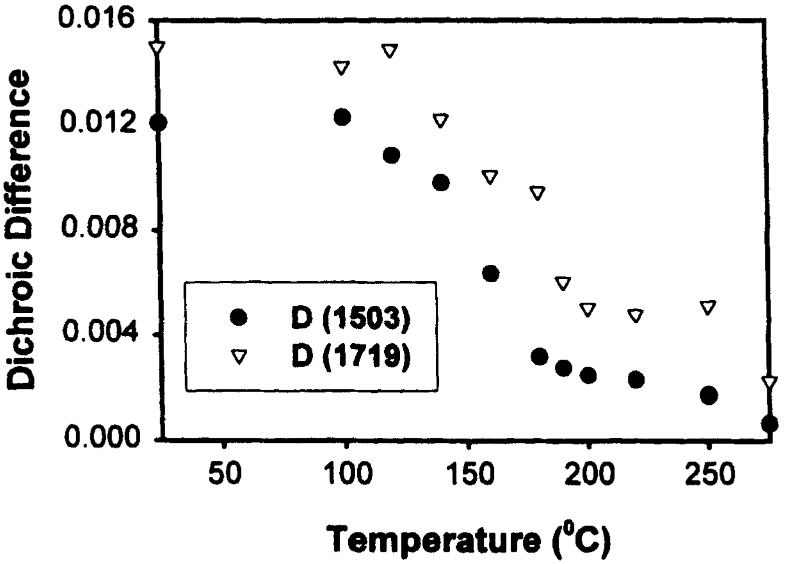

FIGURE 3 FTIR dichroic difference change with thermal treatment temperature of PUV irradiated PI

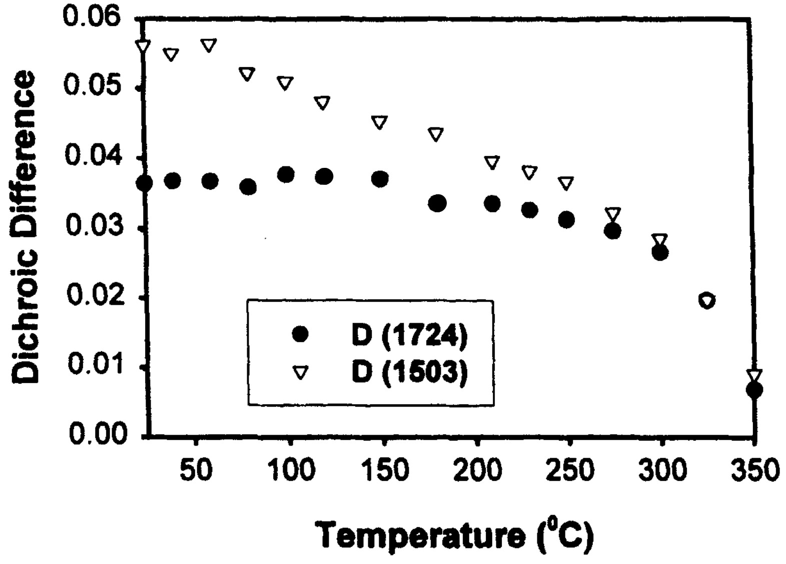

FIGURE 4 FTIR dichroic difference change with thermal treatment temperature of rubbed PI

located on the surface of PI which have much opportunity to contact with oxygen in air will have higher oxidative degradation than in the bulk.

The other interesting facts for the D values from Fig. 3 and Fig. 4 are; 1) D(1503) > D(1724) for rubbed PI, and 2) D(1719) > D(1503) for PUV irradiated PI. For the rubbing alignment by friction, 1,4 substituted phenyl ring part of the PI, which is more flexible than imide group part of the PI, will be better aligned with the rubbing direction. Therefore, D(1503) becomes greater than D(1724) for rubbed PI. But for the PUV irradiated alignment layer, due to preferential photo-degradation of the PI molecules parallel to the PUV direction, remaining PI molecule will align perpendicular to the PUV direction. If carbonyl groups are formed in these remaining aligned PI molecules by chain branching reaction, the dipole moment of this carbonyl becomes perpendicular to the main chain. Therefore, D(1719) can become greater than D(1503) for PUV irradiated PI.

D. Thermal stability of PI alignment layer in contact with 5CB

(1). Alignment direction of 5CB

To investigate the alignment direction of 5CB, polarized FTIR spectra for the quartz cell with PUV irradiated PI alignment layer were obtained and shown in Fig. 5. The peak assignments are shown in Table II.[6] Fig. 5(a) shows the FTIR spectrum with polarization parallel to the PUV irradiation. In this case -C≡N stretching mode peak is small compared to those of the $-CH_2$ stretching mode peaks. But Fig. 5(b) shows strong symmetric stretching mode peak of $-CH_3$ at 2871 cm^{-1} and the -C≡N stretching mode peak at 2227 cm^{-1}compared to the other $-CH_2$ stretching mode peaks. The dipole moments of these two bands in 5CB are parallel to the long molecular axis. Therefore, these two results demonstrate the alignment direction of the 5CB molecules is perpendicular to the PUV irradiation direction, and parallel to the remaining PI molecular chains. Fig. 5 (c) shows the difference spectrum obtained by subtracting spectrum (b) from spectrum (a) using a subtracting factor 1.

Fig. 6 shows the FTIR spectra of a quartz liquid crystal cell with rubbed alignment layer. Opposite to the spectrum with PUV irradiated alignment layer of Fig. 5, these spectra support the alignment of the 5CB molecules parallel to the rubbing direction, and again parallel to the PI molecular chain direction.

(2). Temperature effect on the alignment

To investigate the heating temperature effect on the alignment of the 5CB molecules, the dichroic ratios (R) were calculated using the peak area of 2227 cm^{-1},

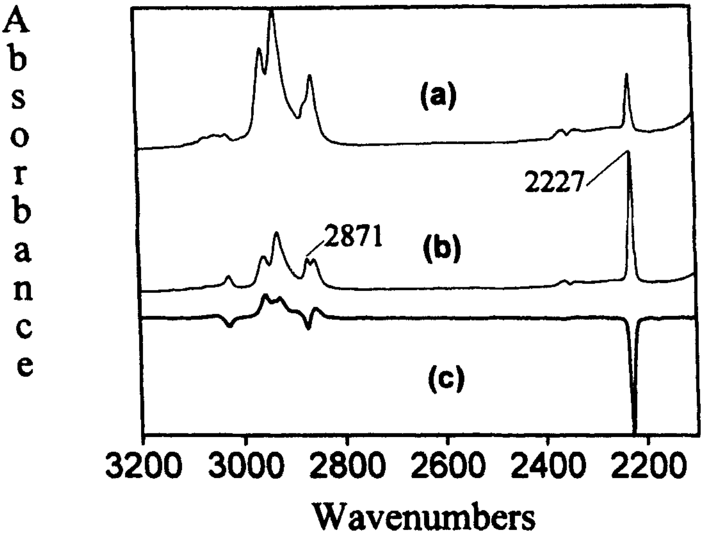

FIGURE 5 FTIR spectra of quartz cell with PUV irradiated PI alignment layer: (a) with polarization parallel to the PUV irradiation direction; (b) with polarization perpendicular to the PUV irradiation direction; and (c) difference obtained by subtracting (b) from (a)

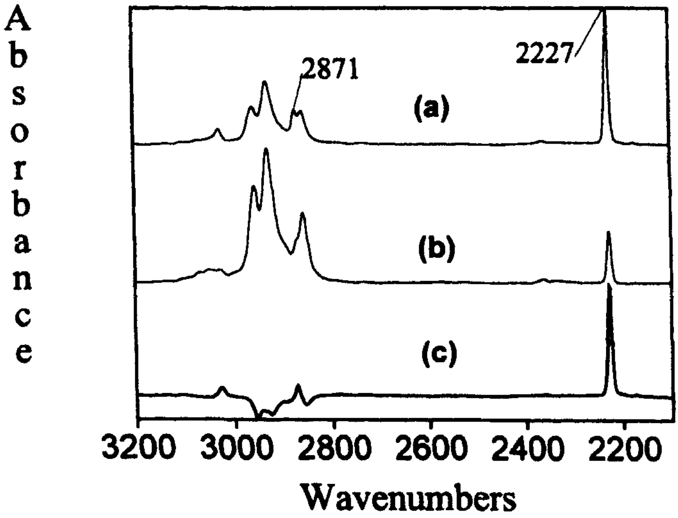

FIGURE 6 FTIR spectra of quartz cell with rubbed PI alignment layer: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction; and (c) difference obtained by subtracting (b) from (a)

which is caused by the -C≡N stretching mode of 5CB. The dipole moment of the -C≡N is known to be parallel to the long molecular axis.

$$R\ (\text{rub}) = A_{\parallel}/A_{\perp} \qquad \text{-----}\ (4)$$

$$R\ (\text{PUV}) = A_{\perp}/A_{\parallel} \qquad \text{-----}\ (5)$$

TABLE II Peak assignments for 4-pentyl-4′-cyanobiphenyl (5CB)[6]

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 results of R change with temperature are shown in Fig. 7. The PUV irradiated PI cell shows faster decrease of the R value after heating to 130°C compared to the almost constant R value of PI rubbed cell. This clearly supports less thermal stability of the PUV irradiated PI cell compared to the rubbed PI cell. It also supports the previous results of thermal treatment of PI alignment layer in air without contact with 5CB. After comparing Fig. 3 to Fig. 7, we found less thermal stability of PUV irradiated layer when it is in contact with 5 CB. The dissolving of the fragmented layer into the 5CB or the increased mobility of the fragmented PI may cause this decrease in thermal stability by the presence of the 5CB.

The R values of 4.19 for rubbed PI layer and the 4.16 for the PUV irradiated PI layer after heating at 90°C are a little bit higher than the commonly reported value of about 3.5[7]. The order parameter calculated by the following equation[8] were 0.64 for the both LC cells before thermal treatment.

$$S = (1.52R - 1)/(1.52R + 2) \qquad \text{-----}\ (6)$$

(3). Texture Change with heating

To investigate the cause of the R decrease for the PUV irradiated PI, a crossed polarizing microscope was used to take microphotographs after each thermal treatment. The results are shown in Fig. 8. According to Fig. 8, at 130°C heating, some Schlieren textures of 5CB, which are caused by imperfect homogeneous alignment of the 5CB start to appear in the PUV irradiated PI cell[9]. After 145°C heating, many Schlieren textures developed. The development of Schlieren tex-

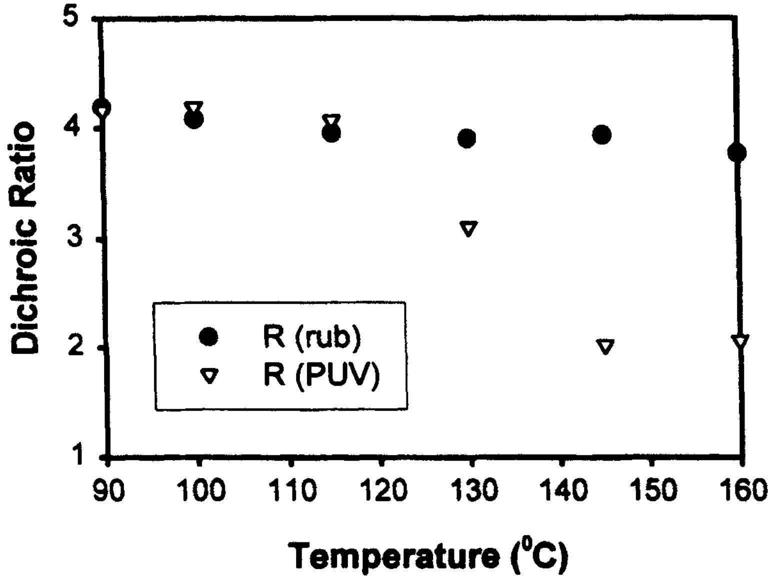

FIGURE 7 Dichroic ratio change with thermal treatment temperature

ture caused by the loss of the aligning ability of the alignment layer was caused by the dissolving of the fragmented parts of the PI layer into the 5CB or by the enhanced mobility of the fragmented alignment layer by the 5CB. This microphotographs clearly support the less thermal stability of the PUV irradiated PI layer compared to the rubbed one.

4. CONCLUSIONS

Through out this experiment, we have arrived at the following three conclusions. First, the UV irradiated alignment layer produced by the PUV irradiation showed less thermal stability than the alignment layer produced by the rubbing. It may be caused by the presence of the small fragments, which are produced by the PUV irradiation. Second, the PUV irradiated PI layer in contact with 5CB showed less thermal stability due to dissolution of the fragmented PI molecules and/or the increase of the mobility of the chain due to plasticization by 5CB. And finally, the sealing materials for the LCD cells with alignment layer formed by PUV irradiation must be curable below 130 °C not impart the aligning ability of the layer.

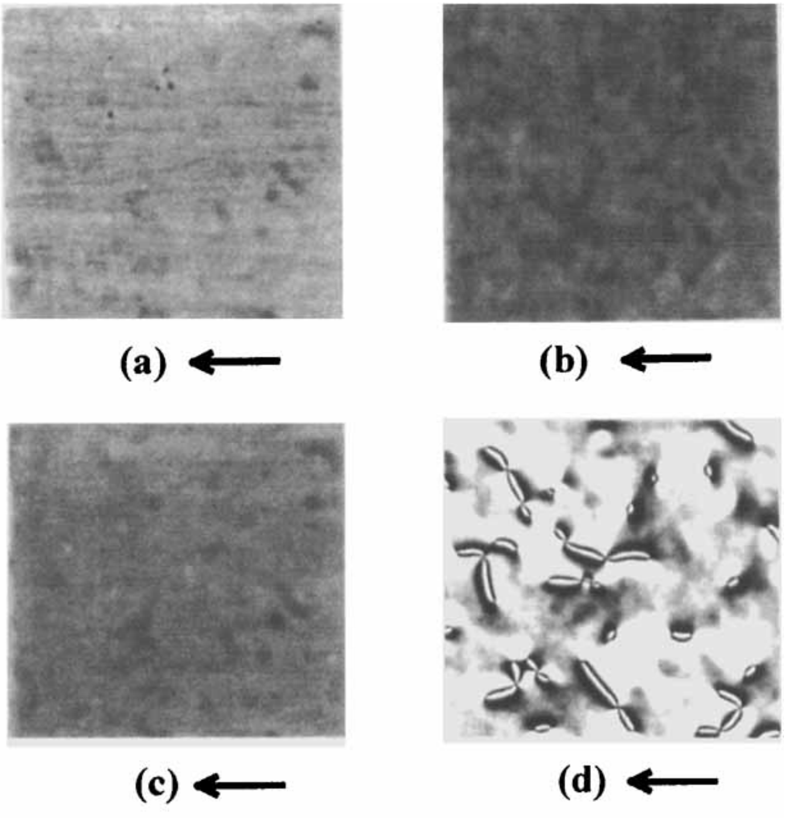

FIGURE 8 Photomicrographs of the quartz LC cell (x 150): (a) LC cell made of rubbed PI after 130°C heating; (b) LC cell made of PUV irradiated PI after 130°C heating; (c) LC cell made of rubbed PI after 145°C heating; and (d) LC cell made of PUV irradiated PI after 145°C heating. Arrow indicates the rubbing or PUV irradiation direction

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References

(1) B. Bahadur, *Mol. Cryst. Liq. Cryst.*, **109(1)**, 1 (1984).
(2) S. Morozumi, *Liquid Crystals: Applications and Uses*, edited by B. Bahadur (World Scientific Publishing Co., 1990), Vol. 1, Chap.7, pp. 171–194.
(3) H. Isida and M. T. Huang, *Spectrochimica Acta*, **51A(3)**, 319–331 (1995).
(4) 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), pp. 659–672.

(5) J. F. Rabek, *Photodegradation of Polymers: Physical Characteristics and Applications* (Springer-Verlag, New York, 1996), p. 62.
(6) C. A. McFarland, J. L. Koenig, and J. L. West, *Appl. Spec.*, **47(3)**, 321 (1993).
(7) J. de Bleijser, L. H. Leyte-Zuiderweg, J. C. Leyte, P. C. M. van Woerkom, and S. J. Picken, *Appl. Spec.*, **50(2)**, 167 (1996).
(8) S. Wu, *Applied Optics*, **26(16)**, 3434 (1987).
(9) D. Demus, L. Richter, *Textures of Liquid Crystals* (Verlag Chemie, New York, 1978), p. 32.