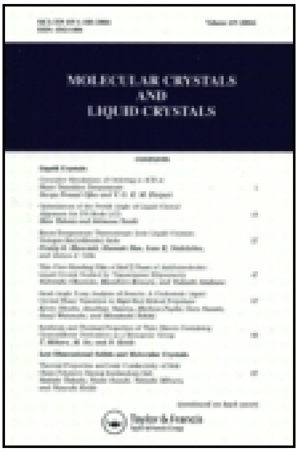

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# Analysis of Rubbed Polyimide Films by Polarized Infrared Spectroscopy

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# ANALYSIS OF RUBBED POLYIMIDE FILMS BY POLARIZED INFRARED SPECTROSCOPY

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Abstract Polarized infrared spectroscopy was applied to the analysis of rubbed polyimide films. $N_2$ purge of a sample chamber and increased substrate thickness enhanced the detection sensitivity. Dichroic differences were measured for the rubbed polyimide films at varied translating speed of the rubbing roller and at varied substrate temperature. The results suggest that the orientation of the polyimide was enhanced by increased polyimide surface temperature brought about by the heat of friction or the external heat. Moreover, a correlation between the LC alignment and the orientation of the polyimide chains was revealed by the analysis of the dichroic difference of the rubbed polyimide films immersed in organic solvents and the LC alignment on the films.

## INTRODUCTION

Liquid crystals (LCs) have recently been studied extensively because of their electro-optic properties and their widespread use in display devices. In order to obtain homogeneous alignment of LC molecules, unidirectional rubbed polymer films or SiO obliquely evaporated films are commonly used. The rubbing method is used in liquid crystal display production because of its high productivity.

Nematic liquid crystals are well known to align on the rubbed polyimide films along the rubbing direction. However, the mechanism of the LC alignments on rubbed polymers is not well understood. There are two classes of hypothesis to explain the interaction between the rubbed surface and LC molecules. Berreman[1] observed micro grooves on the surface of the glass substrate rubbed with diamond paste. He hypothesized that LC alignment was induced by the elastic interaction with the micro grooves. On the other hand, Geary et al.[2] proposed that the rubbing process oriented polymer chains, and LCs grew epitaxially on the oriented polymer. As concerns LC alignment on the rubbed polymer surface, the results of microscopic and spectroscopic analysis suggest that the epitaxial growth mechanism due to the interaction between LC molecules and the oriented polymer is more predominant.[3,4]

To evaluate the orientation of polymers in the rubbed films, birefringence and dichroic measurements have been applied.[4,5] Birefringence is a simple method for evaluation of the overall anisotropies of the sample film, which might include morphological and substrates' anisotropies. Infrared (IR) dichroic measurements can evaluate the orientation of the polymers at molecular level.

In this study, we applied polarized infrared spectroscopy to the analysis of the rubbed polyimide films and evaluated their orientation degree from the measurements of the dichroic difference. Our system for dichroic measurements was improved to enhance detection sensitivity, and the effect of the rubbing conditions and substrate temperature during the rubbing process were examined.

Moreover, we analyzed a correlation between the orientation degree of the rubbed polyimide and the LC alignments to investigate the mechanism of the LC alignment on the rubbed polyimide. To obtain the varied orientation degree of the polyimide chains, we introduced rubbing strength and organic solvent treatments as experimental parameters. Organic solvent immersion of the polyimide films can modify the intermolecular interaction between the polyimide chains in the films, and thus can modify the orientation degree of the polyimide after rubbing.

## EXPERIMENTAL

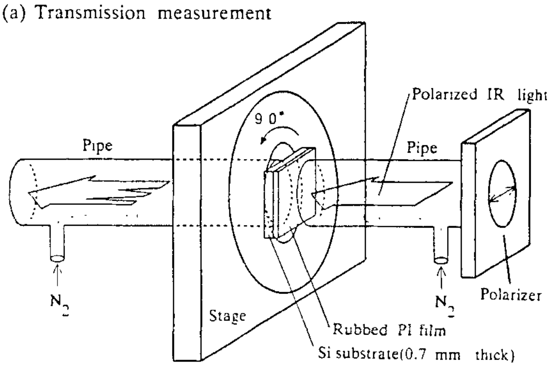
A Bio-Rad FTS-60A FT-IR spectrometer equipped with a polarizer was used in this study. All spectra were measured at 4 $cm^{-1}$ resolution, and interferograms were accumulated 1024 times.

Schematic drawings of the sample chamber for IR dichroic measurements are shown in Figure 1. IR dichroic differences were measured at both transmission and reflection[6] modes.

In our system, some improvements were made to enhance the detection sensitivity and to reduce the measurement error. Sample substrates were rotated to select a polarization (parallel or perpendicular to the rubbing direction) and the polarizer was kept fixed in order to avoid instrumentation errors caused by polarization-dependent properties of optical components in the spectrometer. IR light path was covered with pipes and was purged by dry nitrogen gas to eliminate water vapor. Thick silicon substrates (0.7 mm thick) were used at transmission measurements to reduce interference fringes in the spectra.

Glass substrates coated with indium tin oxide (ITO) on one side were used successfully at reflection measurements. We constructed sample LC cells by using the ITO coated glass

(a) Transmission measurement



(b) Reflection measurement

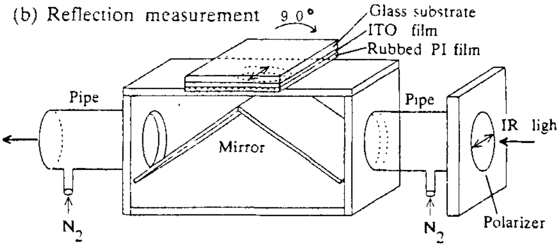


Figure 1 Schematic drawings of sample chamber for IR dichroic measurements.

substrates with the rubbed polyimide films for the reflection measurements, and the LC alignments in these cells were analyzed. The ITO thickness was approximately 150 nm and the reflectance of the ITO film was about 80 % at IR region compared to that of a gold substrate, which was used as a reference of 100 % reflectance.

Polyimide films on the Si substrates and the ITO coated glass substrates were formed as follows. Polyamic acid solution (SE-4140) which is commercially available from Nissan Chemical Ltd., Japan, was spin-coated onto the substrates. The substrates were subsequently heated at 100 ℃ for 3 minutes to evaporate the solvents and were imidized by heat treatment at 260 ℃ for 30 minutes. The thickness of the resulting polyimide films was measured with Tencor Instruments Alpha-Step 200 surface profilometer. The polyimide thickness on the Si substrates was 165 nm, and the polyimide thickness on the ITO coated glass substrates was 210 nm.

The polyimide films were rubbed using the rubbing machine illustrated in Figure 2. Rubbing strength is determined by the number of repeated times of rubbing N, the translating speed of the roller v [mm/s], the depth of the deformed region of the rubbing cloth M [mm], the number of revolutions per minute of the roller n [r.p.m.], and the contact length of the rubbing roller $\ell$ [mm]. The total length of rubbing cloth which contacts a certain point of the substrate L [mm] is defined as[7]

$$L = N \cdot \ell \cdot \left( 1 + \frac{2 \cdot \pi \cdot r \cdot n}{60 \cdot v} \right) \quad (1).$$

We changed such parameters as N, v and M, and measured the dichroic difference.

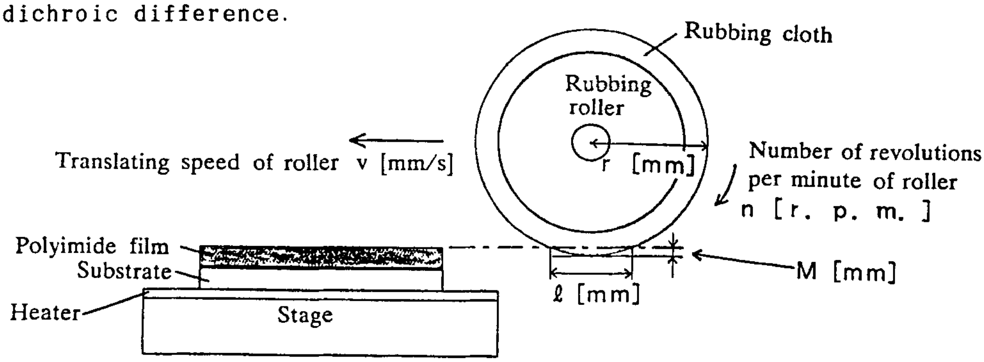


Figure 2 Schematic drawings of rubbing machine.

## RESULTS AND DISCUSSION

### Dichroic spectra and experimental improvements

Figure 3 shows the polarized IR transmission spectra of the rubbed polyimide film. Assignments of IR bands in the spectra were as follows: the C=O stretching vibration of imide ring at 1721 cm$^{-1}$, the phenyl C-C skeleton vibration of the para-substituted benzene rings at 1501 cm$^{-1}$, the C-N stretching vibration of imide unit at 1379 cm$^{-1}$, and the C-O-C stretching vibration at 1243 cm$^{-1}$.

In the dichroic spectrum (c), the absorbance of phenyl C-C, imide C-N, and C-O-C stretching bands increased. The vibrational moments of these bands are parallel to the polyimide chains, so it is concluded that the polyimide chains were preferentially oriented parallel to the rubbing direction by rubbing. The absorbance of C=O stretching band decreased. This result indicates that the vibrational moment of C=O stretching is perpendicular to the polyimide chain.

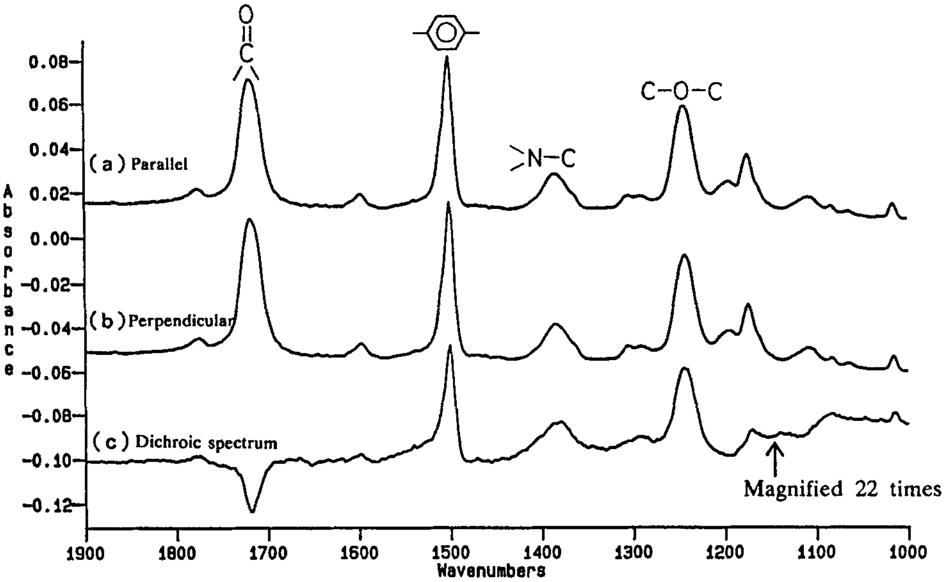
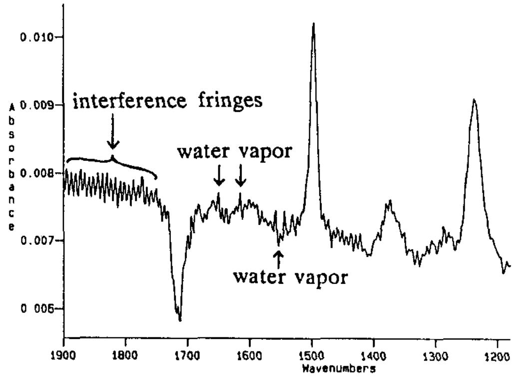


Figure 3 Polarized IR transmission spectra of rubbed polyimide film. (a) absorption spectrum with polarization parallel to rubbing direction; (b) absorption spectrum with perpendicular polarization to it; (c) dichroic spectrum by subtracting (b) spectrum from (a) spectrum. Rubbing conditions were N=3, n=300 r.p.m., r=125 mm, v=12.5 mm/s, and M=0.75 mm.

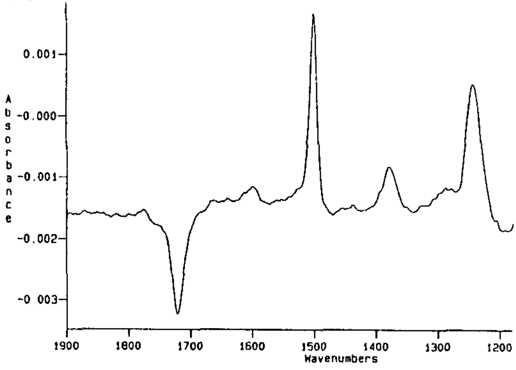
The effect of the experimental improvements on the dichroic spectrum is presented in Figure 4. The spectrum (a) was measured using a 0.4 mm thick Si substrate, and $N_2$ purge of the IR light path was not sufficient. The base-line included interference fringes and the peaks of water vapor, which could reduce the measurement precision. In the spectrum (b), full $N_2$ purge reduced the influence of water vapor, and a 0.7 mm thick Si substrate eliminated the interference fringes. The interference fringes were originating from multiple reflection inside the substrate. By use of the thicker (0.7 mm) substrate, the intensity of the fringes became weaker and the pitch of the fringes became shorter. The fringes could not detected at 4 $cm^{-1}$ resolution because the pitch was too short.

(a)



Substrate thickness: 0.4 mm, not sufficient $N_2$ purged

(b)



Substrate thickness: 0.7 mm, fully $N_2$ purged

Figure 4 Effect of experimental improvements on dichroic spectrum. Rubbing conditions were N=3, n=300 r.p.m., r=125 mm, v=12.5 mm/s, and M=0.9 mm.

The orientation degree of polymer chains can be estimated by the dichroic difference. The dichroic difference is given as $A\parallel - A\perp$, where $A\parallel$ is the absorbance of a characteristic vibration with polarization parallel to the rubbing direction and $A\perp$ is that with polarization perpendicular to it.

The polyimide used in this study has intensive absorption at 1501 $cm^{-1}$(phenyl C-C) and 1721 $cm^{-1}$(C=O). Thus, the dichroic difference of the rubbed polyimide films described in the following section of this paper is defined as $\{A\parallel(1501) - A\perp(1501)\} + \{A\perp(1721) - A\parallel(1721)\}$, where A(1501) is the absorbance at 1501 $cm^{-1}$.

## Effects of rubbing conditions

The polyimide films rubbed under several rubbing conditions were analyzed by polarized IR transmission spectroscopy. Figure 5 shows the relationship between the IR dichroic difference and the number of repeated times of rubbing at slow translating speed of the rubbing roller (v=12.5 mm/s) and at fast speed (v=37.0 mm/s). As the number of repeated times increased, the dichroic difference increased and leveled off.

When the dichroic differences at the saturated region or at the same total length of rubbing L were compared, it was found that the rubbing at the slow translating speed of the roller provided larger dichroic difference than the rubbing at the fast translating speed. This result suggests that the polyimide film surface temperature is increased by rubbing at the slower roller speed. The higher temperature could be brought about by heat of friction during the rubbing process.

In order to test the hypothesis mentioned above, the relationship between the dichroic difference and the substrate temperature during the rubbing was examined (Figure 6). The Si substrates with the polyimide film were heated by a sheet heater put on the stage of the rubbing machine. Thermal conductivity of Si is higher than that of glass, so Si substrates were used.

As shown in Figure 6, IR dichroic difference increased with higher temperature of the substrates. The results presented in Figures 5 and 6 indicate that the orientation of the polyimide chains during the rubbing treatments was enhanced by increased polyimide surface temperature brought about by the heat of friction or the external heat. It is supposed that the polyimide surface softens with the increase in temperature and the polyimide chains become easy to orient by rubbing.

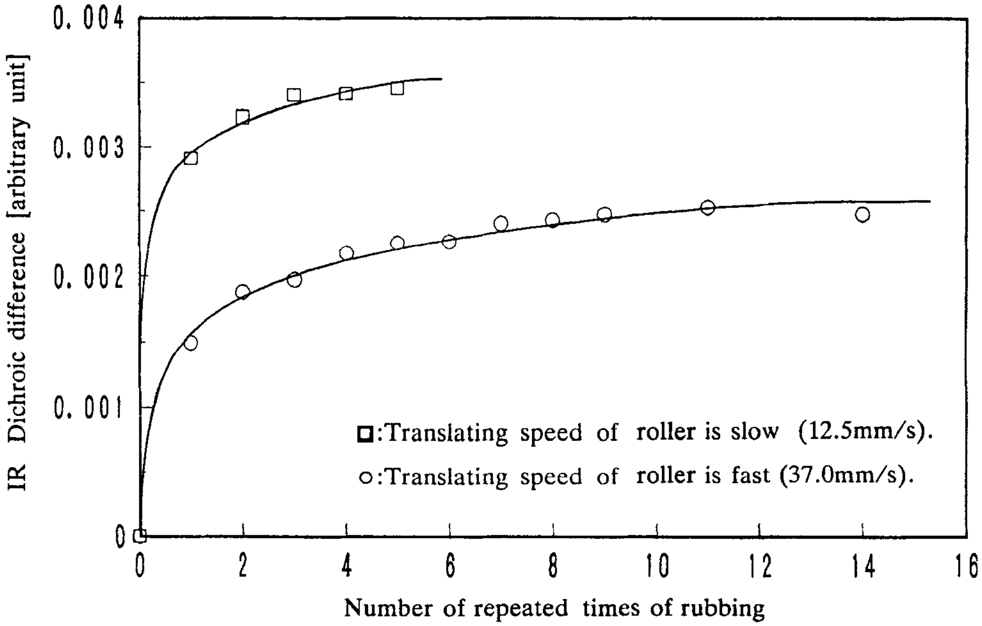


Figure 5 Relationship between IR dichroic difference and number of repeated times of rubbing. Rubbing conditions were n=300 r.p.m., r=125 mm, and M=0.75 mm.

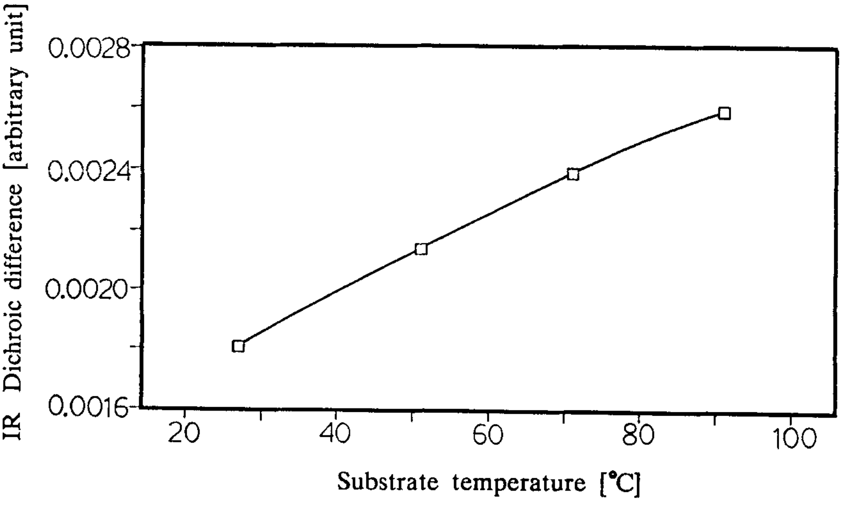


Figure 6 Effect of substrate temperature during rubbing process on orientation of polyimide film. Rubbing conditions were N=1, n=300 r.p.m., r=125 mm, v=12.5 mm/s, and M=0.6 mm.

## Influence of immersion in organic solvents

The influence of immersion in several organic solvents on the rubbed polyimide films was analyzed by IR dichroic measurements. The ITO coated glass substrates were used to observe LC alignment on the same substrates.

As shown in Figure 7, immersion of the rubbed polyimide film in $\gamma$-butyrolactone drastically reduced the dichroic difference of the film. It is suggested that the molecules of $\gamma$-butyrolactone penetrated into the oriented polyimide chains (swelling) and the orientation degree decreased. On the other hand, immersion in xylene did not change the dichroic difference.

The rubbed polyimide films were immersed in a mixture of $\gamma$-butyrolactone and xylene at various mixing ratio. The IR dichroic difference of the films and the LC alignments on the films were analyzed as shown in Figures 7 and 8.

As the concentration of $\gamma$-butyrolactone increased, the IR dichroic difference decreased. The LC alignments on the films immersed in less than 40 wt% $\gamma$-butyrolactone were uniform. The LC alignment was partly degraded for 67 wt% $\gamma$-butyrolactone. The LC alignment was remarkably degraded for 100 wt% $\gamma$-butyrolactone and the LC molecules were preferentially aligned along the injected direction. Thus, with increasing the concentration of $\gamma$-butyrolactone, the IR dichroic difference decreased and the LC alignments were degraded.

The polyimide films rubbed at various rubbing strength were immersed in 67 wt% $\gamma$-butyrolactone diluted with xylene. The rubbing strength was controlled by changing the depth of the deformed region of the rubbing cloth M. The IR dichroic difference of the films and the LC alignments on the films were analyzed as illustrated in Figures 9 and 10.

As the value of M decreased, the IR dichroic difference decreased and the LC alignments were degraded. The LC alignments were uniform for $M \geq 0.8$ mm, partly degraded for $M=0.6-0.7$ mm, and obviously degraded for $M=0.5$ mm.

These results indicate that the IR dichroic difference of the rubbed polyimide films immersed in $\gamma$-butyrolactone correlated with LC alignment capability of the films. We found a correlation between the LC alignment and the orientation degree of the polyimide chains through the immersion of the rubbed polyimide films in organic solvents, which is consistent with the hypothesis[2,3] that LC molecules align by interaction with the oriented polymer.

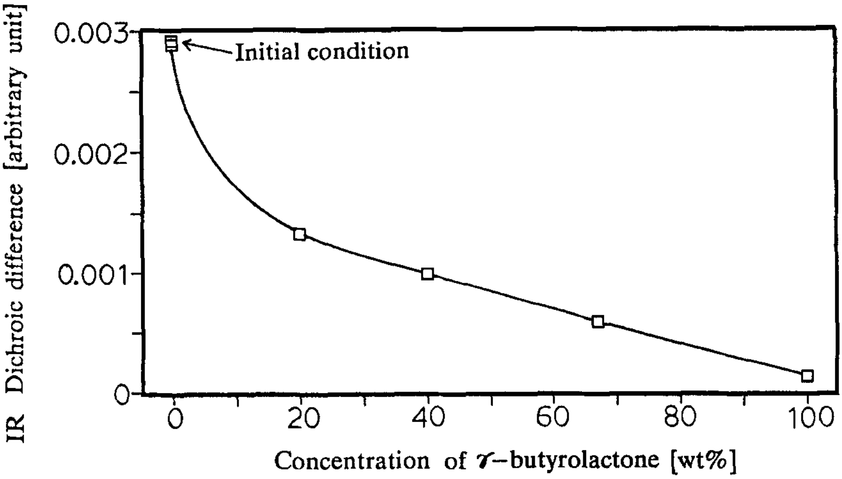


Figure 7 Relationship between concentration of γ-butyrolactone and IR dichroic difference of rubbed polyimide films immersed in mixture of γ-butyrolactone and xylene for 3 minutes. Rubbing conditions were N=3, n=300 r.p.m., r=125 mm, v=12.5 mm/s, and M=0.6 mm.

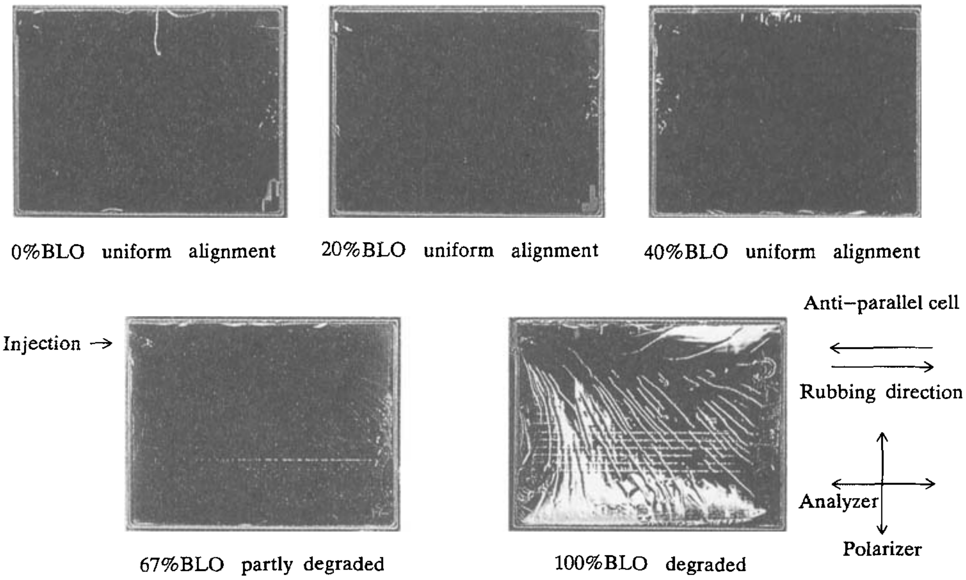
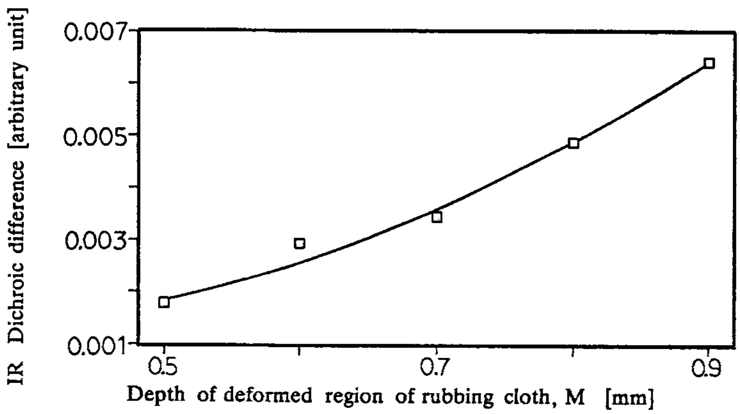


Figure 8 Nematic LC alignments on rubbed polyimide films immersed in mixture of γ-butyrolactone and xylene for 3 minutes, which were observed in anti-parallel cell and crossed nicol.



(b)Immersion in 67% $\gamma$-butyrolactone

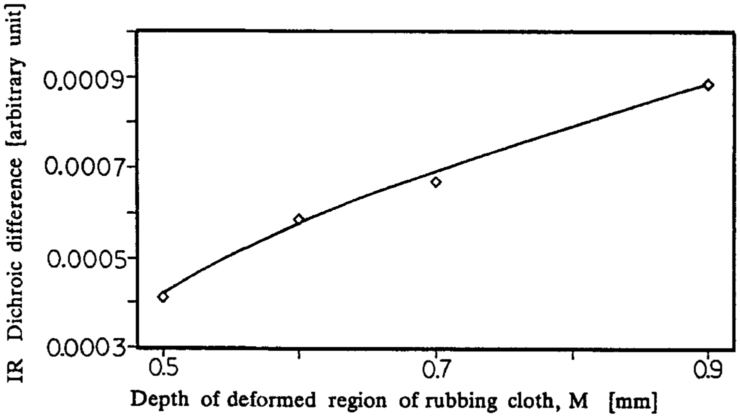
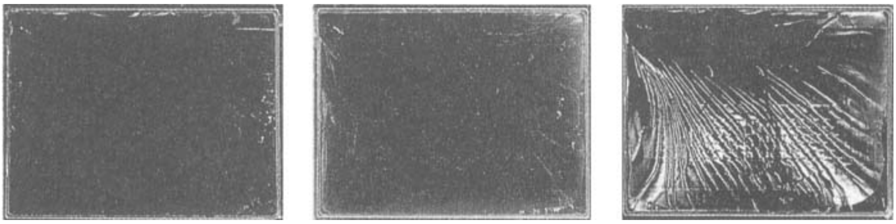


Figure 9 Relationship between rubbing strength and IR dichroic difference of rubbed polyimide films immersed in 67 wt% $\gamma$-butyrolactone diluted with xylene for 3 minutes. Rubbing conditions were N=3, n=300 r.p.m., r=125 mm, and v=12.5 mm/s.



(a) M=0.8 mm
uniform

(b) M=0.7 mm
partly degraded

(c) M=0.5 mm
degraded

Figure 10 Nematic LC alignments on rubbed polyimide films immersed in 67 wt% $\gamma$-butyrolactone diluted with xylene for 3 minutes, which were observed in anti-parallel cell and crossed nicol.

## CONCLUSION

Polarized infrared spectroscopy was applied to the analysis of rubbed polyimide films. The improvements of the sample chamber and the use of thick substrates enabled enhancement of the detection sensitivity as well as reduction of the measurement error.

The rubbing treatments at the slower translating speed of the rubbing roller or at the higher temperature of the substrates increased the dichroic difference. These results suggest that the orientation of the polyimide chains during the rubbing treatments was enhanced by increased polyimide surface temperature brought about by the heat of friction or the external heat.

We found a correlation between the LC alignment and the orientation degree of the polyimide chains by the dichroic measurements of the rubbed polyimide films immersed in organic solvents and the observation of LC alignment on the films.

Polarized infrared spectroscopy (i.e. IR dichroic measurement) can be a useful tool for estimating LC alignment capability of rubbed polyimide films.

## REFERENCES

1. D. W. Berreman, Phys. Rev. Lett., 28, 1683 (1972).
2. J. M. Geary, J. W. Goodby, A. R. Kmetz and J. S. Patel, J. Appl. Phys., 62, 4100 (1987).
3. S. Ishihara, H. Wakemoto, K. Nakazima and Y. Matsuo, Liquid Crystals, 4, 669 (1989).
4. N. A. J. M. van Aerle, M. Barmentlo and R. W. J. Hollering, J. Appl. Phys., 74, 3111 (1993).
5. F. Hide, K. Nito, A. Yasuda, Thin Solid Films, 240, 157 (1994).
6. S. Ishibashi, H. Sasaki, R. Hasagawa, The 19th Symposium on Liquid Crystals, Japan, 3D10, 374(1993).
7. Y. Sato, K. Sato, T. Uchida, Jpn. J. Appl. Phys., 31, L579 (1992).