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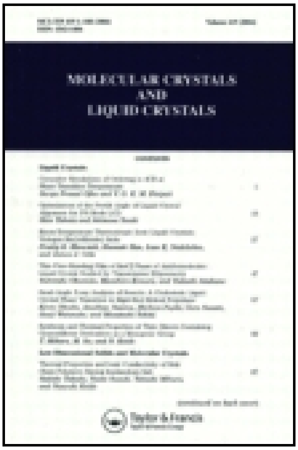

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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# Relationship between Molecular Orientation of Rubbed Polyimide Alignment Layer and That of Liquid-Crystalline Polymer Film Coated on the Alignment Layer

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Version of record first published: 22 Sep 2010

To cite this article: Motohiro Yamahara, Mariko Nakamura, Naoyuki Koide & Takeo Sasaki (2007): Relationship between Molecular Orientation of Rubbed Polyimide Alignment Layer and That of Liquid-Crystalline Polymer Film Coated on the Alignment Layer, Molecular Crystals and Liquid Crystals, 466:1, 39-52

To link to this article: http://dx.doi.org/10.1080/15421400701246275

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*Mol. Cryst. Liq. Cryst.*, Vol. 466, pp. 39–52, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701246275

# Relationship between Molecular Orientation of Rubbed Polyimide Alignment Layer and That of Liquid-Crystalline Polymer Film Coated on the Alignment Layer

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*The molecular orientation of the coating type of retardation film was investigated. The retardation film was created by photopolymerization of a liquid-crystalline (LC) monomer coated on a rubbed polyimide alignment layer. The relationship between the molecular orientation of a rubbed polyimide film and that of mesogens in a photopolymerized liquid crystal coated on the polyimide film has been investigated using optical measurements. It was found that the inclination angle of the refractive index ellipsoide and the optical retardation of photopolymerized LC films are strongly related to the optical properties of the rubbed polyimide film regardless of the rubbing conditions.*

**Keywords:** alignment film; inclination angle; molecular orientation; photopolymerized liquid crystal; retardation; rubbing treatment

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## 1. INTRODUCTION

Optical retardation films are used in almost all the liquid-crystalline displays (LCDs) of the present time. Particularly, coating-type optical retardation films are most used for middle, and small-size LCDs [1]. The coating-type retardation films are fablicated by the polymerization of LC monomers coated on a substrate. The coating-type retardation films have contributed to small size of LCDs. Coating-type retardation films with various optical properties are still needed for the development of even thinner LCDs.

The fabrication process of the coating retardation films is shown in Fig. 1. The LC monomers are aligned in one direction by the alignment layer and are subsequently photopolymerized [2–4]. Polyimides are the most widely used materials for the alignment layers. The optical properties of this film are dominated by the molecular orientation of the mesogens [5,6]. However, the orientation of mesogens in the photopolymerized LC film has not been studied well. The relationship between the conditions of the alignment layer and the orientation of mesogens in the photopolymerized LC film has not yet been clarified [7,8]. This is critical information for the design of optical compensation films.

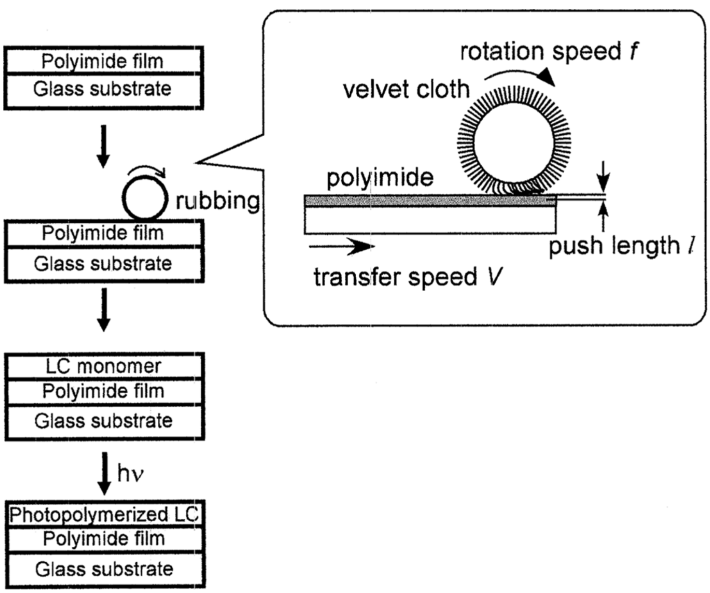


**FIGURE 1** Fabrication of one-dimensionally aligned photopolymerized LC films.

In this study, we investigated the relationship between the molecular orientation in an alignment layer (polyimide) and that of mesogens in a photopolymerized LC film. Polarization-modulated transmission spectro-ellipsometry was applied to characterize the optical properties of the films. Two types of polyimides (high pretilt and low pretilt) were used as the alignment layers. The optical properties of the rubbed alignment layer and those of the photopolymerized LC films were measured, and the relationship between the rubbing conditions of this alignment layer and the optical properties of the photopolymerized LC film is discussed.

## 2. EXPERIMENTAL

All samples were prepared on 1737 glass substrates (Corning). The high-pretilt polimide PI-1 and the low-pretilt polyimide PI-2 (Nissan Chemical Industries, Japan) were spin-coated on the glass substrates. The structures of those polyimides are shown in Fig. 2a. The polyimide-coated glass was heated to 80°C for 5 min and then baked at 200°C for 60 min. The polyimide layer was subsequently rubbed using a velvet cloth in an RM-50 rubbing machine (EHC Co., Japan). The standard rubbing conditions were as follows: rotation speed $f = 480$ rpm, push length $l = 0.5$ mm, transfer speed $V = 12$ mm/s,

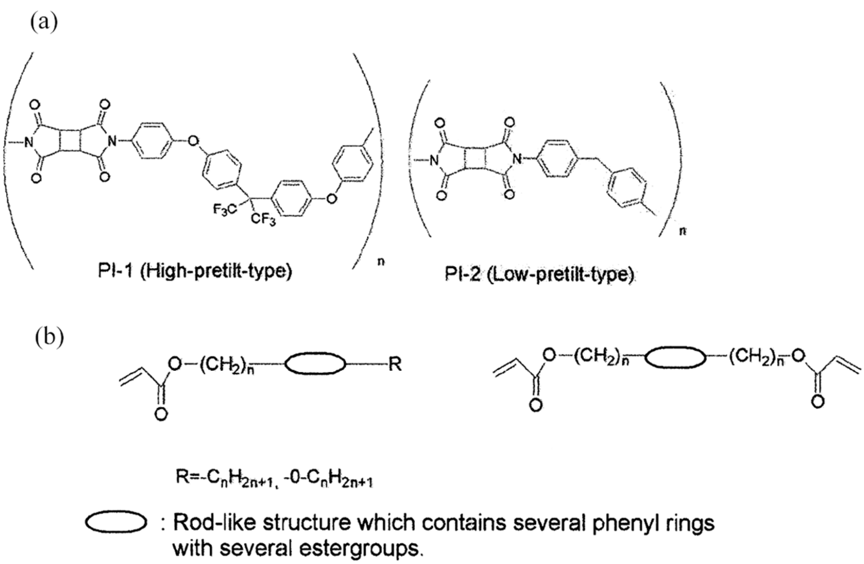


**FIGURE 2** Structures of compounds used in this study.

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and cumulative number of rubs $N = 1$. Three types of velvet cloth (Yoshikawa-Chemical, Japan: YA-20-R, YA-19-R, and YA-18-R) were used.

A widely used LC monomer, RMS03-001 (Merck, $T_{N\text{-}I} = 70°C$) was employed in this study. RMS03-001 is a mixture of acrylate-based LC monomers (Fig. 2b). The LC phase of RMS03-001 yields a highly transparent film even after polymerization. The LC monomer was spin-coated on the rubbed polyimide layers. To align the LC monomers, the LC-monomer-coated film was heated at 55°C for 1 min. After thermal treatment, the samples were kept in a nitrogen atmosphere at room temperature for several minutes and then photopolymerized using an ultrahigh-pressure mercury lamp with a uniform-radiation optical unit (USHIO, Japan, SPOT-CURE SP-7). The UV-illumination energy was $20\,mW/cm^2$, and the curing time was 1 min. The surface of the rubbed polyimide films was examined by an atomic force microscope (Seiko Instruments Inc., Japan, SPI4000, SPA-300HA). The polar angle dependence of the retardation values of the rubbed polyimide films and those of the photopolymerized LC films at 590 nm were measured with a M-220 spectro-ellipsometer (JASCO, Japan) and a KOBRA-WR automatic birefringence analyzer (Oji Scientific Instruments, Japan). The inclination angle of the refractive index ellipsoid of the alignment layers ($\beta_{AL}$) and that of the photopolymerized LC films ($\beta_{LC}$) were measured according to previous studies [9–13]. The definition of the inclination angle $\beta$ is shown in Fig. 3. Thicknesses of the films were measured by a LEXT OLS3000 confocal scanning microscope (Olympus). The thickness of the polyimide alignment layer was 0.096 μm, and that of the photopolymerized LC films was 0.98 μm.

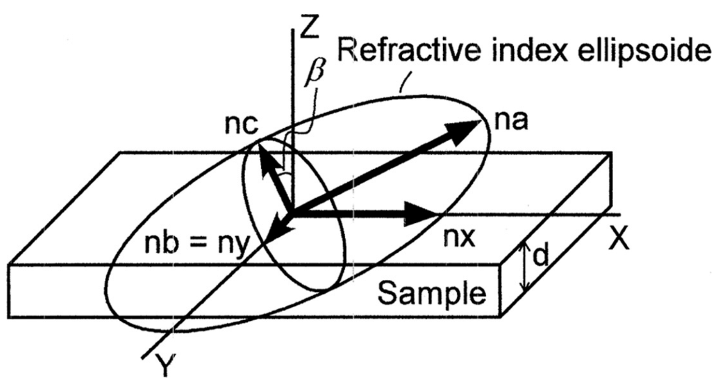


**FIGURE 3** Refractive index ellipsoid of the samples.

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## 3. RESULTS AND DISCUSSION

### 3.1. Influence of Rubbing Conditions on the Ordering of Mesogens of the Photopolymerized LC Film

The influence of the rubbing conditions on the orientation of mesogens of the photopolymerized LC film was investigated. The surfaces of the polyimides (PI-1 and PI-2) coated on the glass substrates were rubbed by a velvet cloth (YA-20-A) using a rubbing machine. The push length of the rubbing roller ($l$), the transfer speed of the rubbing stage ($V$), and the cumulative number of rubs ($N$) were fixed at $l = 0.5\,\text{mm}$, $V = 12\,\text{mm/s}$, and $N = 1$ respectively. The rotation speed ($f$) varied from 240 rpm to 1000 rpm. Figure 4 shows the influence of the rotation speed on the optical properties of the polyimide alignment layer. The inclination angle of the refractive index ellipsoid ($\beta_{AL}$) and the retardation value ($Re_{AL}$) of the alignment layer increased with the rotation speed. These results indicate that as the rotation speed was increased, the molecules of the alignment layer were stretched strongly because the rubbing force and the number of rubs increases with the rotation speed.

The surface of the polyimide films, PI-1 and PI-2, rubbed with standard rubbing conditions were examined using atomic force microscopy (AFM). The AFM images of the rubbed polyimide films (PI-1 and PI-2) are shown in Fig. 5. Many grooves aligned along the rubbing direction were observed on the surface of the polyimide films. The grooves of PI-2 (Fig. 5b) were shallower than those of PI-1 (Fig. 5a). These results indicate that the low-pretilt polyimide film (PI-2) is harder than the high-pretilt polyimide film (PI-1).

The LC monomer was coated on the rubbed surface of the polyimide films and photocured. The conversion of LC monomer to polymer was estimated by IR measurement to be 82%. Retardation values of the LC film ($Re_{LC}$) before and after photopolymerization were measured to be 161.15 nm and 153.10 nm respectively. The inclination angles of the refractive index ellipsoid of the LC film ($\beta_{LC}$) before and after photoirradiation were 3.7° and 4.4° respectively. It was thus confirmed that the LC monomer used in this study was photocured, maintaining the molecular alignment of the LC phase produced by the alignment layer. Although the surface of the coated LC film faced the air, the coated film was very thin, and the alignment layer was a polyimide film for homogenious alignment with large anchoring force. The value of ($\beta_{LC}$) was measured as a average inclination angle over thickness; the effect of the air/LC interface to the measured value of $\beta_{LC}$ is considered to be small. The inclination angle of the refractive index

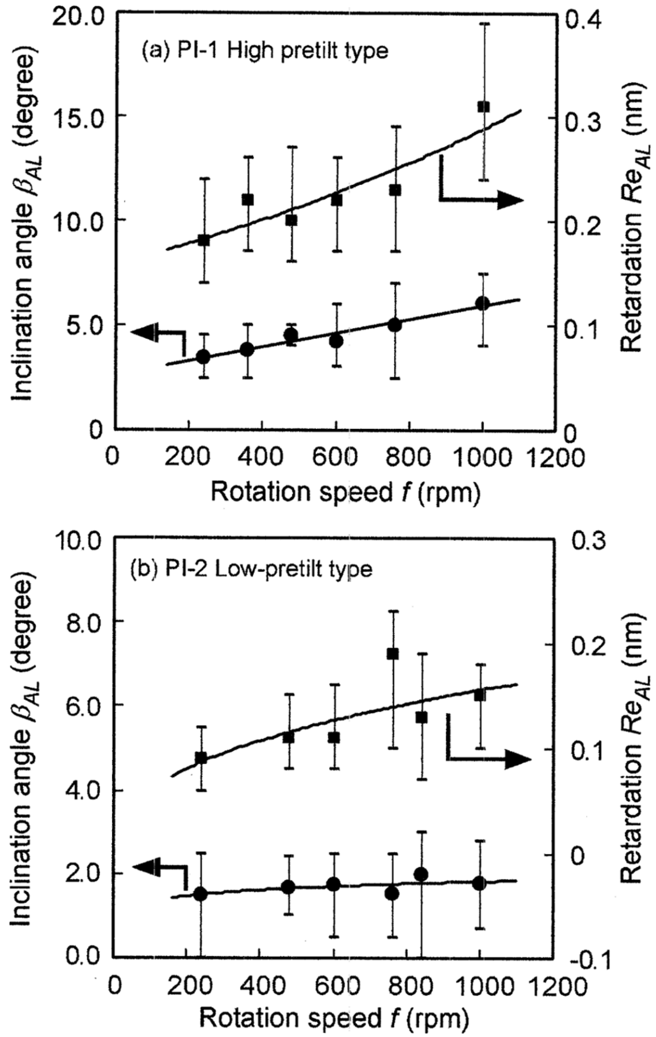


**FIGURE 4** Influence of the rotation speed (*f*) on the optical properties of the rubbed polyimide films; •, inclination angle ($\beta_{AL}$); and ■ retardation value ($Re_{AL}$).

ellipsoid ($\beta_{LC}$) and the retardation value ($Re_{LC}$) of the photopolymerized LC films coated on these polyimide alignment layers are plotted as a function of the rotation speed in Fig. 6. With increasing rotation speed, both $\beta_{LC}$ and $Re_{LC}$ increased. $\beta_{LC}$ and $Re_{LC}$ of PI-2 are smaller than those of PI-1 at the same rubbing condition. These results are in

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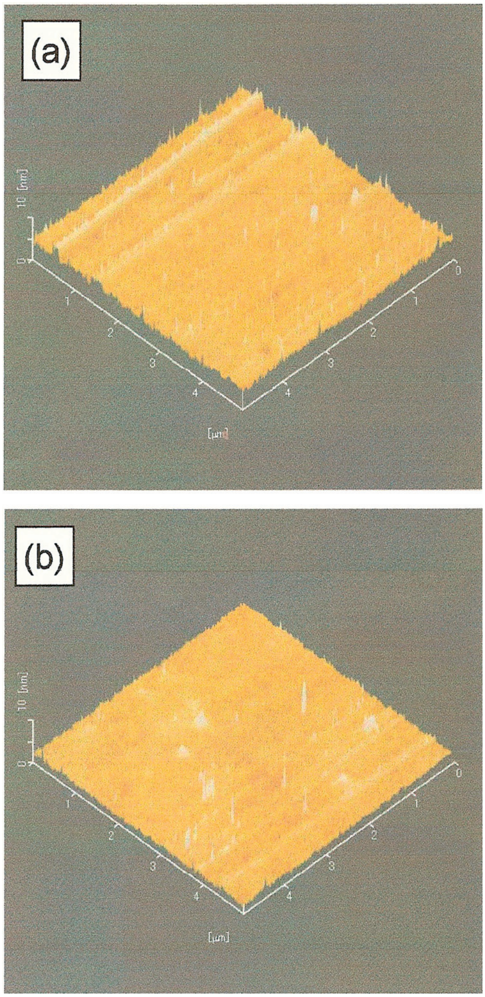


**FIGURE 5** AFM images of the surface of the alignment layers: (a) PI-1 and (b) PI-2.

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agreement with the rotation-speed dependence of $\beta_{AL}$ and $Re_{AL}$ shown in Fig. 4. These results indicate that the ordering of the mesogens of the photopolymerized LC film reflects the molecular ordering of the alignment layer.

Rubbing conditions, such as push length ($l$, 0.1–0.7 mm), transferring speed ($V$, 3–12 mm/s), rotation speed ($f$, 240–1000 rpm), and the cumulative number of rubs ($N$, 1–5), were varied, and the values of

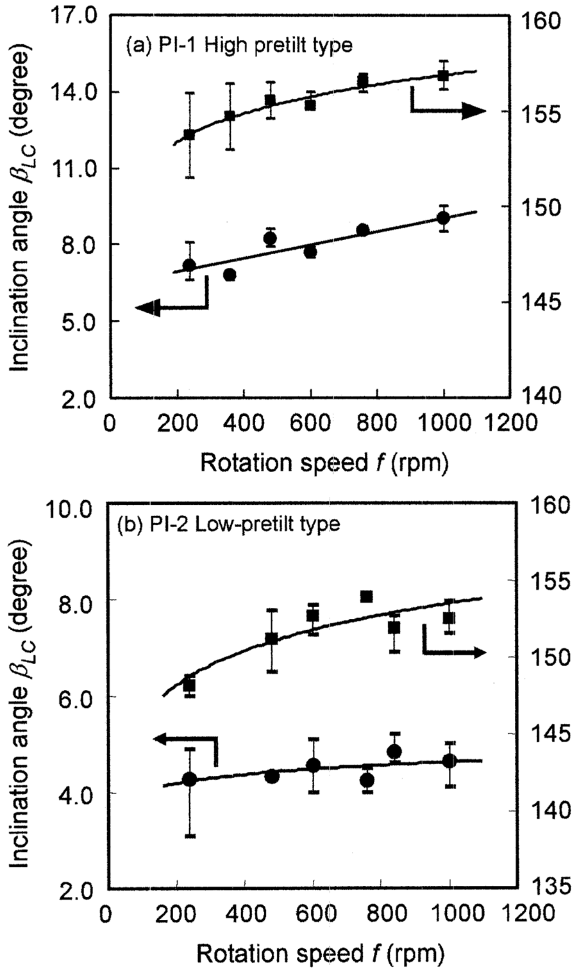


**FIGURE 6** Influence of the rotation speed ($f$) on the optical properties of the photopolymerized LC films coated on polyimide films: ●, inclination angle ($\beta_{LC}$); and ■, retardation value ($Re_{LC}$).

$\beta$ and $Re$ were measured. The molecular ordering (optical anisotropy) and the inclination angle of the index ellipsoid of the alignment layer increased with rubbing strength. The relationship between the optical properties of the alignment layer and those of the photopolymerized LC film under various rubbing conditions are shown in Fig. 7. The values of $\beta$ and $Re$ of the photopolymerized LC film are correlated with those of the alignment layer regardless of the rubbing conditions.

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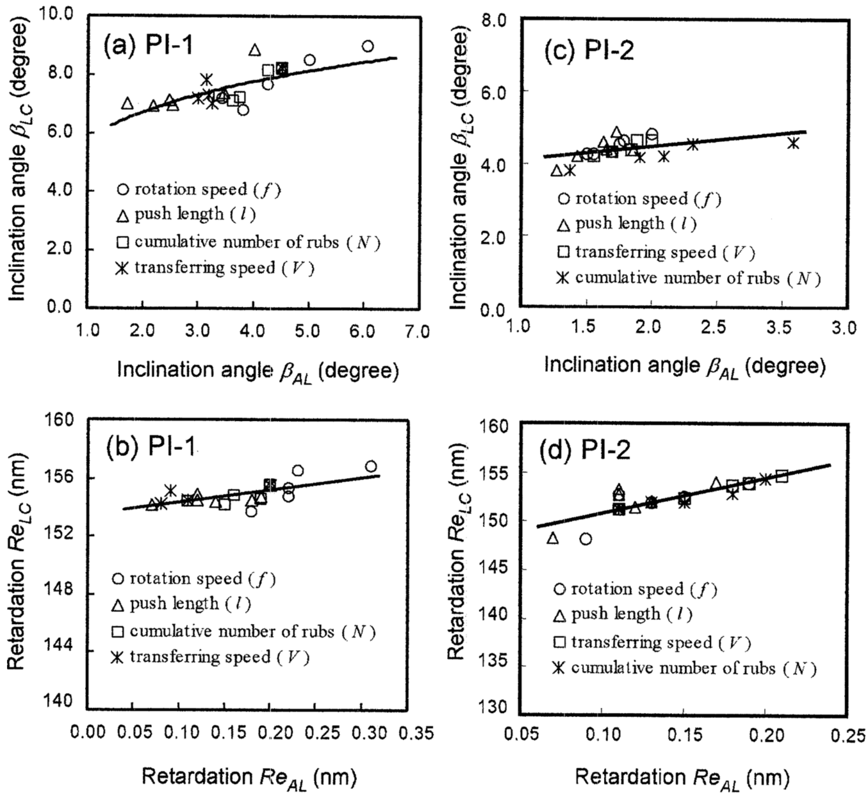


**FIGURE 7** Relationships between the optical properties of the photopolymerized LC film and those of the alignment layer under various rubbing conditions: (a), (c), $\beta_{AL}$ and $\beta_{LC}$; (b), (d), $Re_{AL}$ and $Re_{LC}$. The standard rubbing conditions used were $f = 480$ rpm, $l = 0.5$ mm, $V = 12$ mm/s, and $N = 1$, ○, $f$ was varied from 240 rpm to 1000 rpm; △, $l$ was varied from 0.1 mm to 0.7 mm; □, $N$ was varied from 1 to 5; *, $V$ was varied from 3 m/s to 12 m/s.

## Influence of Properties of the Rubbing Cloth on the Low-Pretilt Type of Polyimide

The influence of the properties of the rubbing cloth on the molecular orientations of the alignment layer and that of the mesogens of the polymerized LC film were investigated. Three types of rubbing cloth, YA-18-R, YA-19-R, and YA-20-R, were used. The properties of these cloths are listed in Table 1. The threads of YA-19-R are more flexible than those of YA-20-R and YA-18-R. Rubbing conditions were $l = 0.5$ mm, $V = 12$ mm/s, and $N = 1$. The rotation speed ($f$) varied from 240 to 1000 rpm.

**TABLE 1** Properties of the Different Types of Rubbing Cloths Used in This Study

| Cloth | Thickness (mm) | Mass density of fibers (denier[a]) | Material |
|---|---|---|---|
| YA-20-R | 1.8 | 3.0 | Rayon |
| YA-19-R | 1.8 | 2.5 | Rayon |
| YA-18-R | 1.6 | 2.5 | Rayon |

[a]Denier is defined as the mass grams per 9000 m. 1 Denier = 0.111 mg/m.

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The inclination angles of the refractive index ellipsoid ($\beta_{AL}$) and retardation ($Re_{AL}$) values of the alignment layer subjected to rubbing by the three types of velvet cloth are shown in Fig. 8. At rotation speed slower than 500 rpm, both $\beta_{AL}$ and $Re_{AL}$ of YA-18-R are larger than those of the other two cloths. This indicates that as long as the rotation speed is low, the polyimide molecules are stretched most strongly when YA-18-R is used. As the rotation speed increased, $\beta_{AL}$ for YA-19-R and YA-18-R slightly decreased. Also, the values of $Re_{AL}$ for YA-19-R and YA-18-R slightly decreased with increasing rotation speed. The values of $Re_{AL}$ for YA-18-R had the lowest point at about 840 rpm. These results show that rubbing force decreases with increasing rotation speed because the threads of YA-18-R and YA-19-R are too soft. However, the threads of YA-18-R are shorter than those of YA-19-R, so the rubbing force in the horizontal direction increases over 840 rpm. Figure 9 shows the inclination angles of the photopolymerized LC film coated on the rubbed polyimide films as a function of the rotation speed. As seen in Fig. 9, when YA-18-R and YA-19-R were used as the rubbing cloth, the inclination angle of the photopolymerized LC film ($\beta_{LC}$) decreased with increasing rotation speed. The values of $Re_{LC}$ for YA-19-R decreased with the rotation speed. $Re_{LC}$ for YA-18-R had the lowest point at about 84 rpm. This result coincides with the rotation-speed dependence of $\beta_{AL}$ and $Re_{AL}$ shown in Fig. 8. Thus, the inclination angle of the refractive index ellipsoide (alignment direction) and the retardation value (molecular ordering) of photopolymerized LC film are strongly related to the rubbing conditions of the alignment layer.

The relationship between the optical properties of the alignment layer and those of the photopolymerized LC film are shown in Fig. 10. The values of $\beta$ and $Re$ of the photopolymerized LC film are well correlated with those of the alignment layer regardless of the rubbing conditions. This shows that the alignment direction and the molecular ordering of photopolymerization LC film are determined by the alignment of molecules in the rubbed polyimide films.

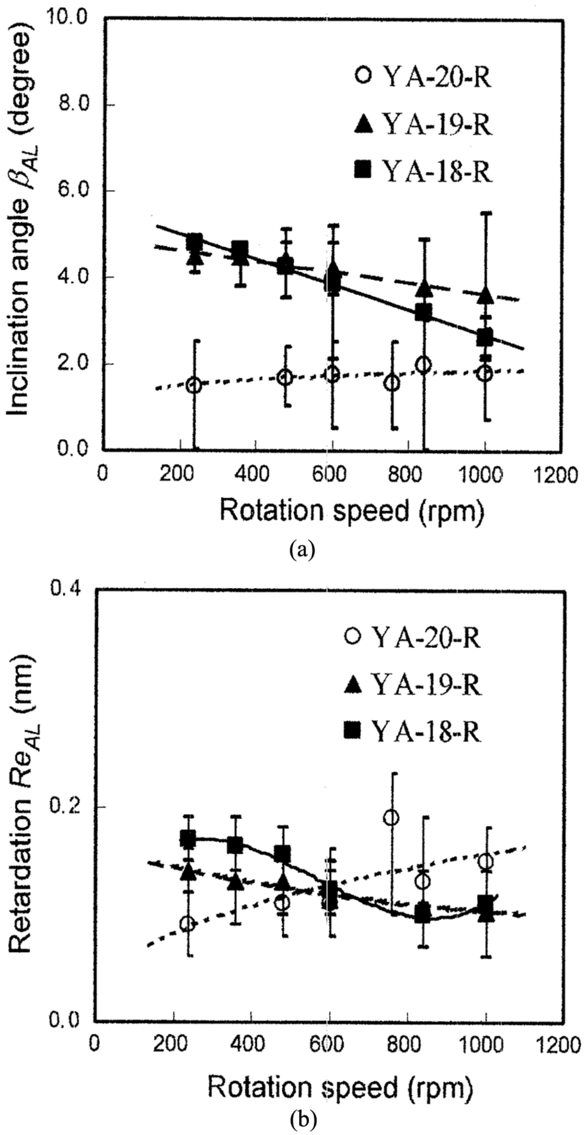


**FIGURE 8** Influence of the rotation speed (*f*) on the optical properties of the rubbed polyimide film using three types of rubbing cloths: (a) inclination angle ($\beta_{AL}$) and (b) retardation value ($Re_{AL}$). PI-2 polyimide was used.

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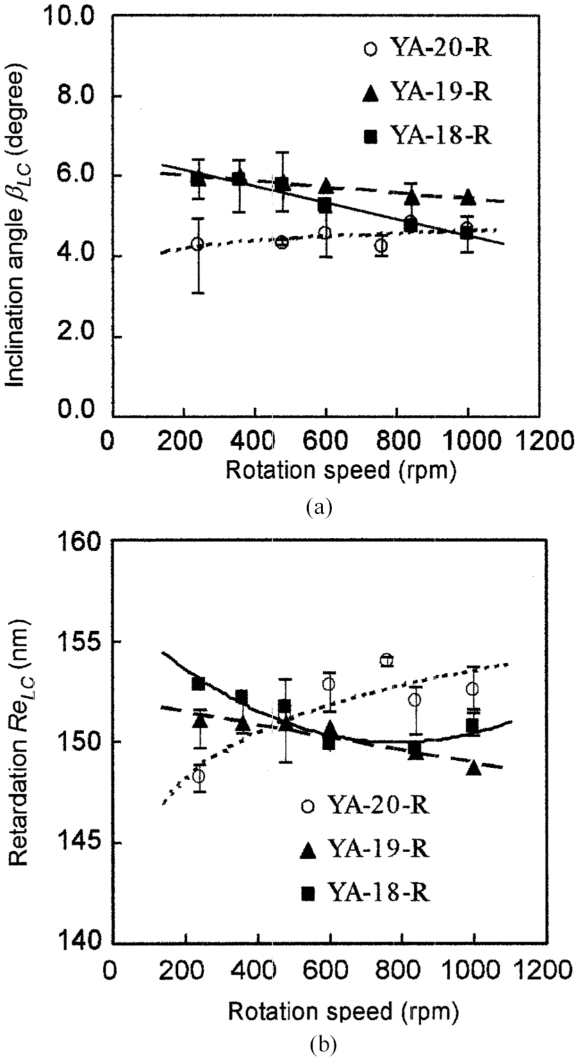


**FIGURE 9** Influence of the rotation speed (*f*) on the optical properties of the photopolymerized LC film using three types of rubbing cloths: (a) inclination angle ($\beta_{LC}$) and (b) retardation value ($Re_{LC}$) PI-2 polyimide was used.

## 4. CONCLUSIONS

The relationship between the molecular orientation of a rubbed polyimide alignment layer and that of a photopolymerized LC film formed on the alignment layer was investigated. The inclination angles of the

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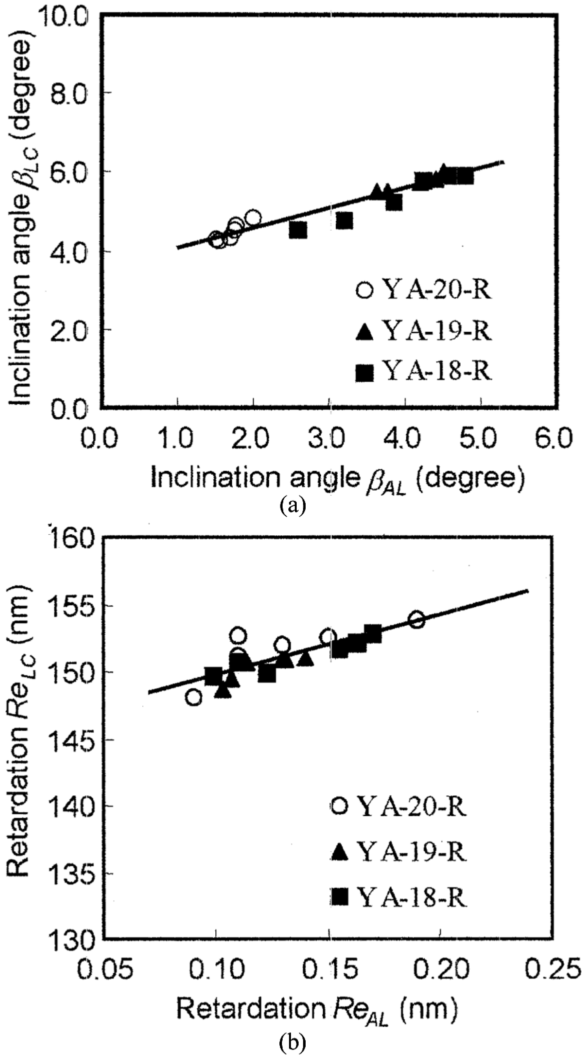


**FIGURE 10** Relationships between the optical properties of the photopolymerized LC film and those of the alignment layer rubbed with the three types of rubbing cloths: (a) $\beta_{AL}$ and $\beta_{LC}$, (b) $Re_{AL}$ and $Re_{LC}$. PI-2 polyimide was used.

refractive index ellipsoid and retardation values of the photopolymerized LC film were correlated with those of the alignment layer regardless of the rubbing conditions. It was found that the mesogens in the polymerized LC films are highly ordered in accordance with the alignment of molecules in the rubbed polyimide films.

## ACKNOWLEDGMENTS

The authors thank Merck Chemicals Ltd., U.K. for supplying the LC monomers and Nissan Chemical Industries, Ltd., for supplying the polyimide.

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