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Influence of rubbing conditions of polyimide alignment layer on optical anisotropy of immobilized liquid crystal film

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The relationship between the molecular orientation of a rubbed polyimide film (alignment layer) and that of mesogens in a photopolymerized liquid crystal (LC) coated on the film has been investigated using optical measurements. LC monomers were deposited on the alignment layer and were aligned in one direction. The LC monomers were subsequently photocured. Alignment layers under various rubbing conditions were prepared. It was found that the inclination angle of the refractive index ellipsoid and the optical retardation of photopolymerized LC films are strongly related to the optical anisotropy of the rubbed polyimide film. The photopolymerized LC film exhibited high optical anisotropy when alignment layers with an inclination angle of the refractive index ellipsoid smaller than 6° were used.

1. Introduction

Optical retardation films have been used for colour compensation in super-twisted nematic liquid crystal displays (STN-LCDs) since the 1980s. Retardation films for improving the viewing angle have been used in thin film transistor (TFT) LCDs. The retardation film for the twisted-nematic mode has the optical characteristics of an inclined refractive index ellipsoid [1]. Retardation films with various optical properties are needed for the development of thin LCDs.

For coating retardation films, liquid crystalline (LC) monomers are very attractive materials. Retardation films obtained by photopolymerization of LC monomers coated on alignment layers have been reported since 1989 [2–4]. They have also been applied in wide-view LCDs [4]. The fabrication process of a coating retardation film is shown in figure 1. Polyimides are the most widely used materials for the alignment layers. The LC monomers are aligned in one direction by the alignment layer and are subsequently photopolymerized. The optical properties of this film are dominated by the molecular orientation of the mesogens. The relationship between the conditions of the alignment layer and the orientation of mesogens in the photopolymerized LC film has not yet been clarified [5, 6]. This is critical information for the design of optical compensation films. The ordering of mesogens of a photopolymerized LC film originates from the ordering of the LC monomers. In order to align LC monomers in a specific direction, the surface of the polyimide film is rubbed by a velvet cloth. A one-directionally-aligned array of grooves on a submicron scale is formed on the surface and the polyimide molecules at the surface are stretched. The LC molecules flow along the grooves and interact with the stretched polyimide molecules, thereby forming one-dimensionally aligned LC domains. However, details of the alignment of the LC molecules by the rubbed polyimide are still not clear.

A retardation film is optically characterized by the inclination angle of a refractive index ellipsoid β and retardation value Re (figure 2). The retardation value is defined as the difference in the optical path lengths between an ordinary and an extraordinary ray:

$$Re = \mathrm{d}\Delta n \qquad (1)$$

where d is the film thickness and Δn is the optical anisotropy ($\Delta n = na - nb$, figure 2). The optical anisotropy, Δn, arises from the ordering of molecules in a film. Thus, molecular ordering can be evaluated by the retardation value Re of the film. Various measurement techniques have been reported in order to evaluate the molecular orientation of a rubbed polyimide film,

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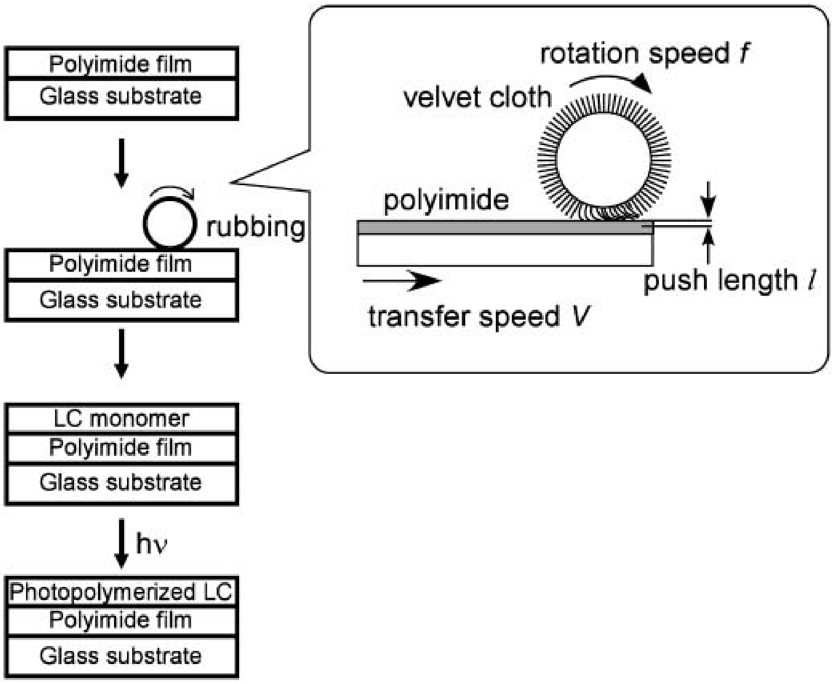


Figure 1. Fabrication of one-dimensionally aligned photopolymerized LC films.

including reflection ellipsometry [7–11], transmission ellipsometry [12] and infrared (IR) absorption spectroscopy [13, 14]. It is known that polarization-modulated transmission spectroellipsometry is suitable for small retardation measurements [15–17].

In this study, we have investigated the relationship between the molecular orientation in an alignment layer (polyimide) and that of mesogens in a photopolymerized LC film. Polarization-modulated transmission spectroellipsometry was applied to characterize the optical properties of the films. 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 the alignment layer and the optical properties of the photopolymerized LC film is discussed.

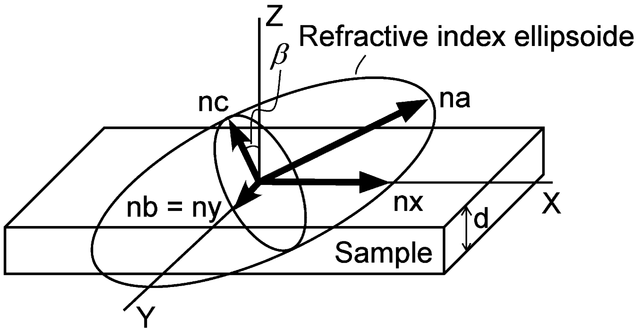


Figure 2. Definition of parameters of a refractive index ellipsoid.

2. Experimental

All samples were prepared on 1737 glass substrates (Corning). The high-pretilt type polyimide PI-1 (figure 3, Nissan Chemical Industries, Japan) was spin-coated on the glass substrates. 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 (figure 1) were as follows: rotation speed f=480 rpm, push length l=0.5 mm, transfer speed V=12 mm s^{-1} 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.

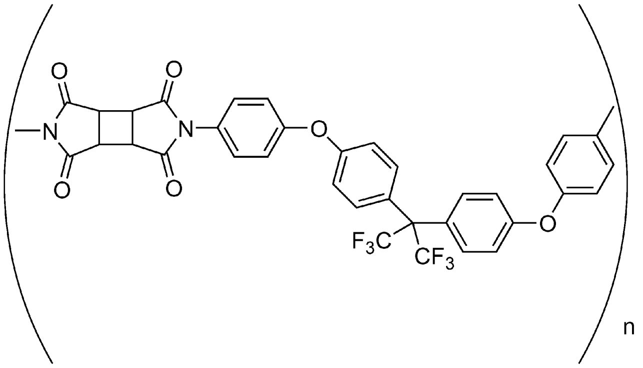
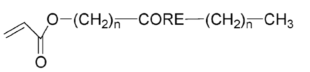
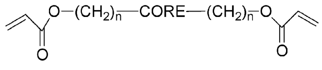


Figure 3. Structure of the polyimide used in this study.

A widely used LC monomer, RMS03-001 (Merck, $T_{\text{N-I}}=70°\text{C}$) was employed in this study. RMS03-001 is a mixture of acrylate-based liquid crystalline monomers with the general structure:





where "CORE" is a rigid, rod-like structure which contains several phenyl rings with several ester groups. 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. In order to align the LC monomers, the LC monomer-coated film was heated at 55°C for 1 min. After the thermal treatment, the samples were kept in a nitrogen atmosphere at room temperature for several minutes and then photopolymerized using an ultra-high pressure mercury lamp with a uniform-radiation optical unit (USHIO, Japan, SPOT-CURE SP-7). The UV-illumination energy used was $20\,\text{mW}\,\text{cm}^{-2}$ and the curing time was 1 min. The conversion of the LC monomer to a polymer was measured by IR spectroscopy (DIGILAB, FTS-65 FT-IR spectrometer). 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 spectroellipsometer (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 (β_{AL}) and that of the photopolymerized LC films (β_{LC}) were measured according to previous studies [18, 19]. Thicknesses of the films were determined using a LEXT OLS3000 confocal scanning microscope (OLYMPUS). The thickness of the polyimide alignment layer was 0.094 µm and that of the photopolymerized LC films was 0.98 µm.

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 surface of the polyimide (PI-1) coated on the glass substrate was rubbed using a velvet cloth (YA-20-A) in a rubbing machine. The push length of the rubbing roller (l), the transfer speed of the rubbing stage (V), the cumulative number of rubs (N) were fixed at $l=0.5\,\text{mm}$, $V=12\,\text{mm}\,\text{s}^{-1}$ and $N=1$, respectively. The rotation speed (f) was 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 (β_{AL}) and the retardation value (Re_{AL}) of the alignment layer increased with increasing rotation speed. The retardation value is related to the ordering of molecules in the film. The 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 increased with rotation speed.

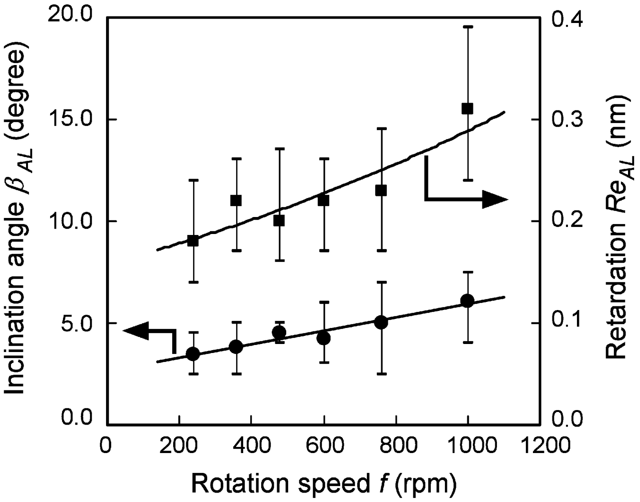


Figure 4. Influence of the rotation speed (f) on the optical properties of the rubbed polyimide films: •, inclination angle (β_{AL}); ■, retardation value (Re_{AL}).

The LC monomer (RMS03-001) was spin-coated on the rubbed polyimide layers and photopolymerized. Photopolymerization of the LC monomer was examined using IR absorption spectra. The IR spectra of the LC film before and after photoirradiation are shown in figure 5. The absorption in the 845–855 cm^{-1} range is attributed to C-H aromatic out-of-plane vibration. The 810–815 cm^{-1} absorption band is attributed to the C=C stretching vibration of the acrylic group [20–22]. The conversion ratio C was calculated from the following equation:

$$C=1-\frac{(P_{810-815}/P_{845-855})}{(M_{810-815}/M_{845-855})} \tag{2}$$

where $P_{wavenumber}$ is the absorbance of polymers and $M_{wavenumber}$ is the absorbance of the monomer. The conversion of LC monomer to polymer was estimated to be 82.2% in the present study.

Retardation values of the LC film (Re_{LC}) before and after photopolymerization were measured to be 170.05 nm and 156.75 nm, respectively. The inclination angles of the refractive index ellipsoid of the LC film (β_{LC}) before and after photoirradiation were 7.6° and 8.0°, respectively. It was thus confirmed that the LC monomer used in this study was photocured while

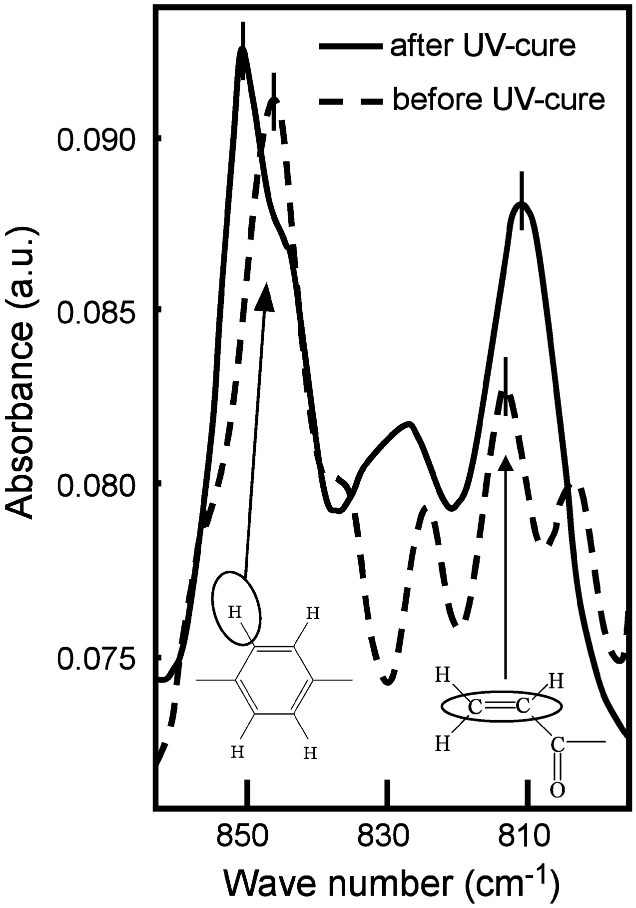


Figure 5. IR spectra of reactive LC material in the wave number range of 865–795 cm^{-1}.

maintaining the molecular alignment of the LC phase produced by the alignment layer. The inclination angle of the refractive index ellipsoid (β_{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 figure 6. With increasing rotation speed, both β_{LC} and Re_{LC} increased. This result is in agreement with the rotation speed dependence of β_{AL} and Re_{AL} shown in figure 4. These results indicate that the ordering of the mesogens of the photopolymerized LC film becomes higher in accordance with the ordering of molecules in the alignment film.

Rubbing conditions, such as push length (l, 0.1–0.7 mm), transferring speed (V, 3–12 mm s^{-1}), rotation speed (f, 240–1000 rpm) and the cumulative number of rubs (N, 1–5), were varied and the values of β 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 figure 7. It was found that the values of β and Re of the photopolymerized LC film are correlated with those of the alignment layer regardless of the rubbing conditions.

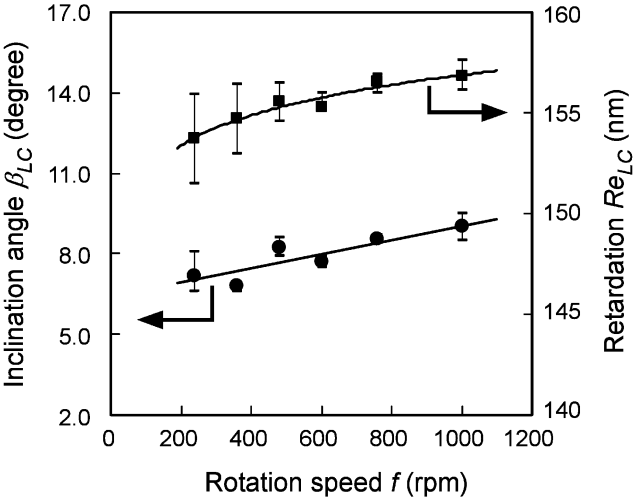


Figure 6. Influence of the rotation speed (f) on the optical properties of the photopolymerized LC films coated on polyimide films: •, inclination angle (β_{LC}); ■, retardation value (Re_{LC}).

3.2. *Influence of properties of the rubbing cloth*

The influence of the properties of the rubbing cloth on the molecular orientations of the alignment layer and 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 cloth properties 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 of l=0.5 mm, V=12 mm s^{-1} and N=1 were used. The rotation speed (f) was varied from 240 to 1000 rpm.

The inclination angles of the refractive index ellipsoid (β_{AL}) and retardation (Re_{AL}) values of the alignment layer subjected to rubbing by the three types of velvet cloth are shown in figure 8. As the rotation speed increased, β_{AL} for YA-19-R and YA-18-R slightly decreased. On the other hand, the values of Re_{AL} for YA-19-R and YA-18-R slightly increased with increasing rotation speed.

Figure 9 shows the inclination angle of the photopolymerized LC film coated on the rubbed polyimide films as a function of the rotation speed. As seen in figure 9, when YA-18-R and YA-19-R were used as the rubbing cloth, the inclination angle of the photopolymerized LC film (β_{LC}) decreased with increasing

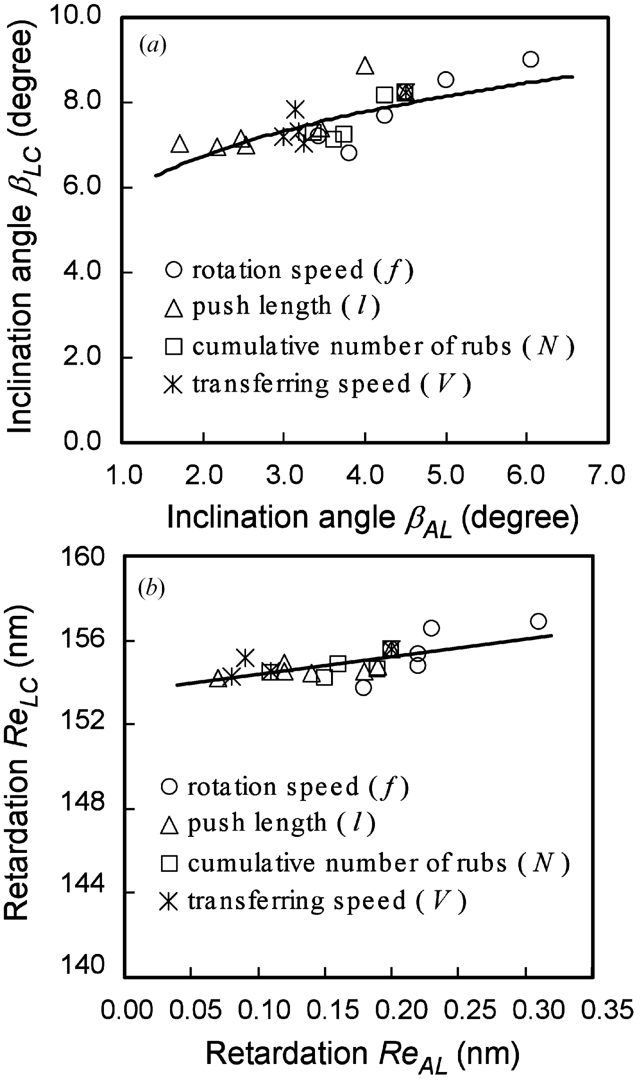


Figure 7. Relationships between the optical properties of the photopolymerized LC film and those of the alignment layer under various rubbing conditions: (a) β_{AL} and β_{LC}, (b) Re_{AL} and Re_{LC}. The standard rubbing conditions used were f=480 rpm, l=0.5 mm, V=12 mm s^{-1} and N=1. ○, f was varied 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 mm s^{-1} to 12 mm s^{-1}.

Table 1. Properties of the different types of rubbing cloths used in this study.

	Thickness (mm)	Mass density of fibres (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 in grams per 9000 m. 1 denier=0.111 mg m^{-1}.

rotation speed. The values of β_{LC} are plotted as a function of β_{AL} in figure 10. The inclination angles of the photopolymerized LC are well correlated with those of the alignment layer regardless of the type of rubbing cloth used.

The influence of the rotation speed on the optical anisotropy of the photopolymerized LC (Δn_{LC}) is shown in figure 11. The optical anisotropy Δn_{LC} increased with rotation speed regardless of the properties of the rubbing cloth. The optical anisotropy originates in the anisotropic ordering of molecules. Thus, the results in figure 11 indicate that the ordering of mesogens is dominated by the rubbing strength of the alignment layer.

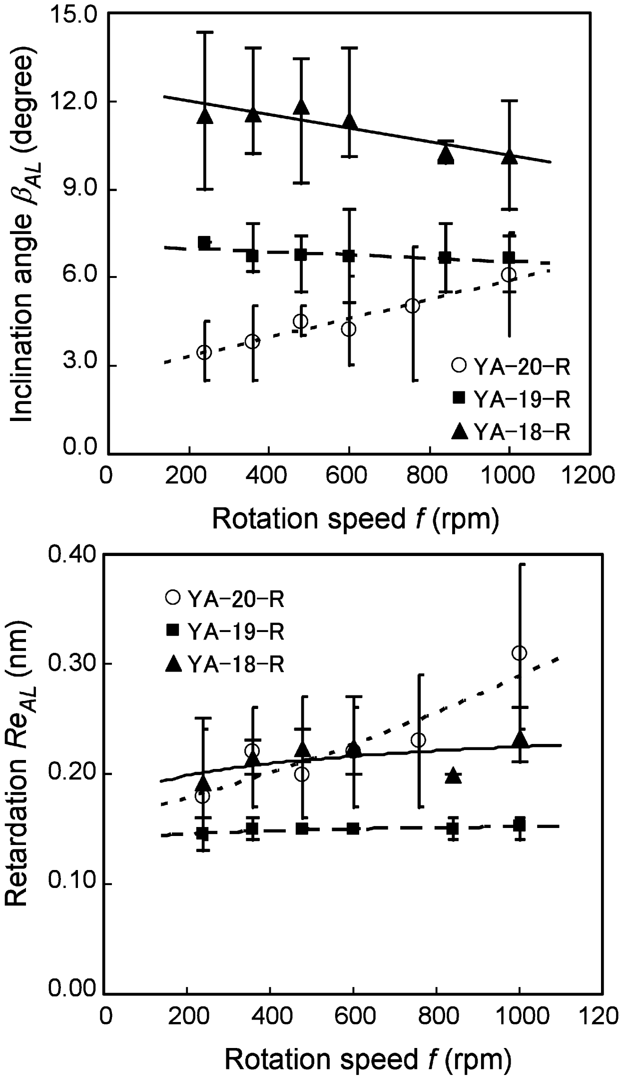


Figure 8. Influence of the rotation speed (*f*) on the optical properties of the rubbed polyimide films using three types of rubbing cloths: (a) inclination angle (β_{AL}), and (b) retardation value (Re_{AL}).

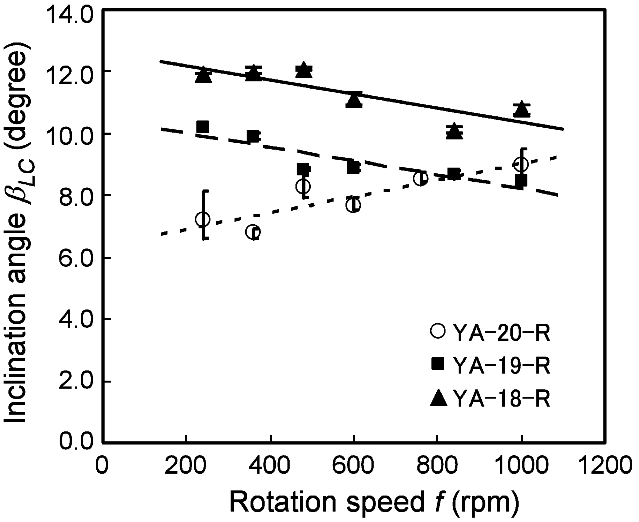


Figure 9. Influence of the rotation speed (*f*) on the inclination angle of the photopolymerized LC film (β_{LC}).

As shown in figures 8a and 9, when YA-18-R and YA-19-R were used, both β_{AL} and β_{LC} values decreased with increasing rotation speed. The value of β is related to the rising angle of the stretched polyimide domains. Thus, the inclination angle of the refractive index ellipsoid (alignment direction) and the optical anisotropy (molecular ordering) of photopolymerized LC film are strongly related to the rubbing conditions of the alignment layer.

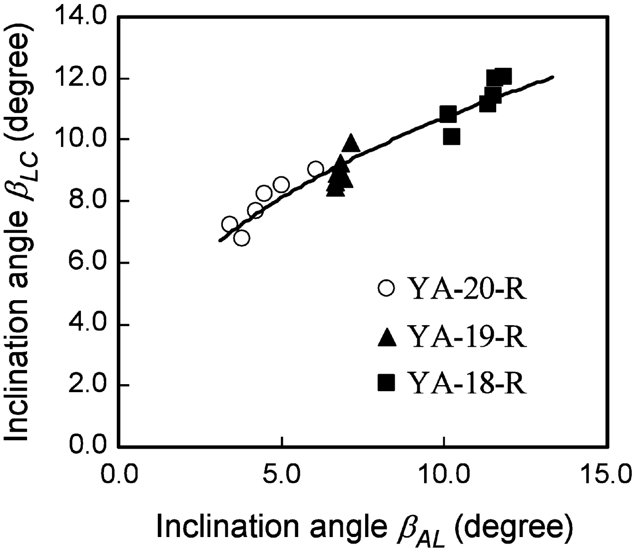


Figure 10. Relationship between the inclination angle of the photopolymerized LC film (β_{LC}) and that of the alignment layers (β_{AL}) rubbed with the three types of rubbing cloths.

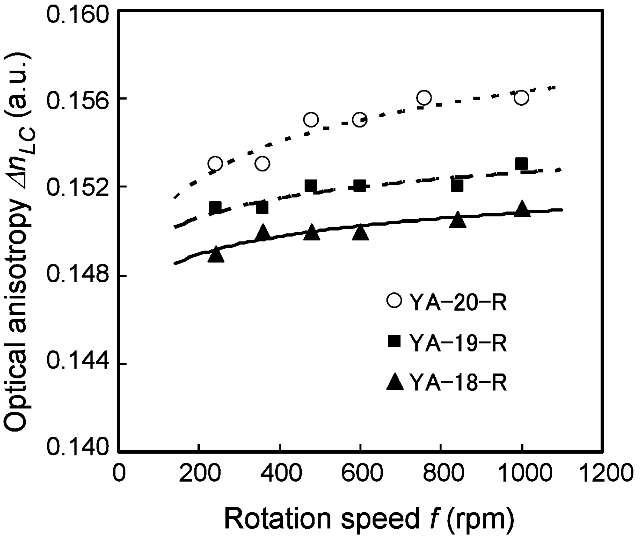


Figure 11. Influence of the rotation speed (*f*) on the optical anisotropy of photopolymerized LC films (Δn_{LC}).

At rotation speeds lower than 500 rpm, both β_{AL} and Re_{AL} of YA-18-R are larger than those of the other two cloth types (figure 8). This indicates that as long as the rotation speed is low, the polyimide molecules are stretched most strongly when YA-18-R is used. However, rubbing with YA-18-R gave the lowest Δn_{LC} value (figure 11). Molecular orientation anisotropy of the alignment layer rubbed by YA-18-A was less reflected in the mesogens in the photopolymerized LC film. The influence of the inclination angle of the alignment layer β_{AL} on the optical anisotropy of the photopolymerized LC film Δn_{LC} is shown in figure 12. Δn_{LC} increased with β_{AL} up to 6°. However, when β_{AL} increased from 6.5° to 7°, Δn_{LC} decreased. Also, the value of Δn_{LC} became small when β_{AL} reached 10–12°. Figure 12 indicates that the influence of the orientation of the rubbed polyimide becomes weak when β_{AL} exceeds 6°.

The dependence of Δn_{LC} on β_{AL} can be interpreted using the model shown in figure 13. The value of β_{AL} indicates the angle between the ordered domains of the polyimide and the surface of the film. A small β_{AL} indicates that the slope of the "hills" formed by rubbing on the surface of the polyimide is small. When the value of β_{AL} is small (figure 13a), the interaction between an LC monomer and the surface of the alignment layer is large. The orientation of mesogens in a photopolymerized LC film becomes high with higher ordering of the molecules in the alignment layer. However, when the value of β_{AL} is large, the angle between the LC molecules and the surface is large. Thus, the interaction becomes small as the value of β_{AL} increases (figure 13b) and this leads to smaller Δn_{LC} values.

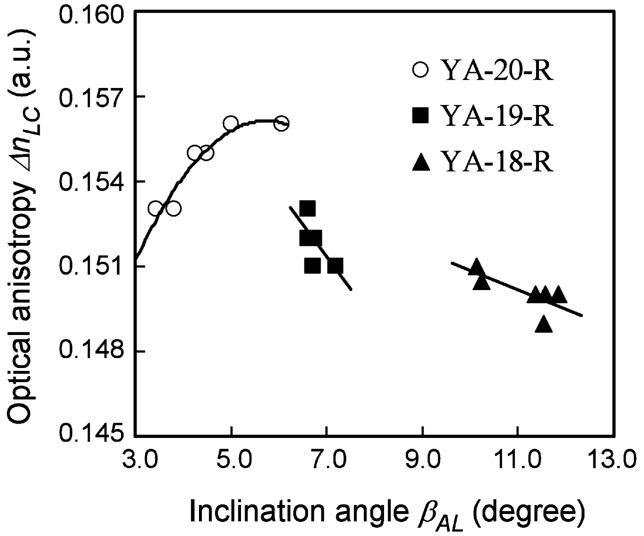


Figure 12. Relationships between optical anisotropy of the photopolymerized LC film (Δn_{LC}) and the inclination angle of alignment layers (β_{AL}) rubbed with the three types of rubbing cloths.

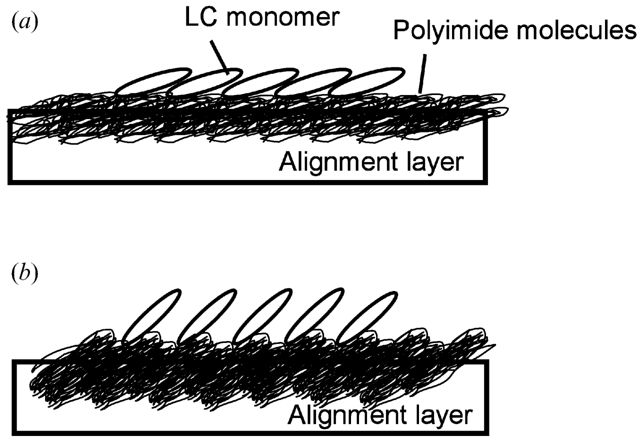


Figure 13. Surface of the rubbed polyimide films and alignment of LC monomers: (a) small inclination angle of the alignment layer (β_{AL}) and (b) large β_{AL}.

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 molecular orientation of the alignment layer was investigated by transmission ellipsometry. The inclination angles of the refractive index ellipsoid of the photopolymerized LC film were correlated with those of the alignment layer regardless of the rubbing conditions. It was found that as long as the values of inclination angle of the alignment layer β_{AL} are smaller than 6°, the mesogens in the polymerized LC films are highly ordered in accordance with the alignment of molecules in the rubbed polyimide films.

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