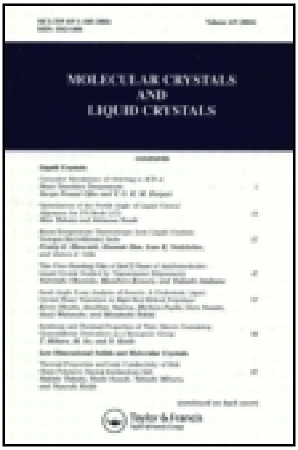

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Relationship between the Optical Properties of Immobilized Liquid-Crystalline Film and Polyimide Alignment Layer

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The relationship between the molecular orientation of a rubbed polyimide film alignment layer and that of mesogens in liquid-crystalline (LC) films coated on the alignment layer before and after photopolymerization has been investigated using optical measurements. LC monomers were coated over the alignment layer and were aligned in one direction. The LC monomers were subsequently photocured. The inclination angle of the refractive index ellipsoid and the optical anisotropy of the immobilized LC film were found to be related to the optical properties of the rubbed polyimide films.

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

1. INTRODUCTION

Optical retardation films are used in almost all liquid-crystalline displays (LCDs) at the present time. In particular, coating-type optical

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retardation films are primarily used for mid- and small-sized LCDs [1]. The coating-type retardation films are fabricated by the polymerization of liquid-crystalline (LC) monomers coated on a substrate. These films have significantly contributed to the thin profiles of current LCDs. Additional coating-type retardation films with various optical properties are needed for further development of thin LCDs and for further reduction in thickness. Control of optical properties of the LC films is essential for many applications, for example, wide-view films designed to increase the field of view of LCDs.

For coating retardation films, LC monomers are very attractive materials. Retardation films obtained by photopolymerization of LC monomers coated on an alignment layer have been reported since 1989 [1–3]. These films have been used in wide-view LCDs [3]. The fabrication process of a coating-type retardation film is shown in Fig. 1. Polyimides are the most widely used materials for the alignment layers. To align LC monomers in a specific direction, the surface of the polyimide film is rubbed with a velvet cloth. One-directionally aligned arrays of submicrometer-scale grooves are formed on the surface, and the polyimide molecules at the surface

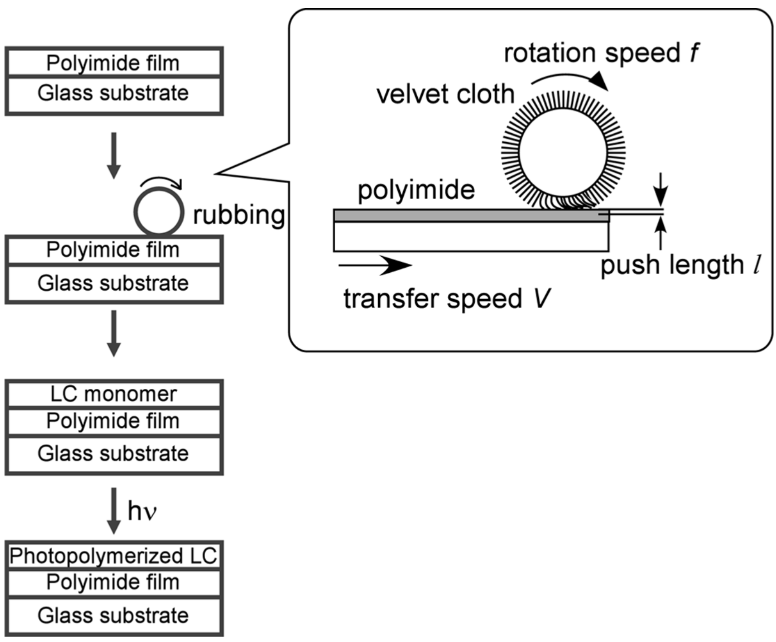


FIGURE 1 Fabrication of one-dimensionally aligned photopolymerized LC films.

are stretched. The LC molecules flow along the grooves and interact with the stretched polyimide molecules, thereby forming one-dimensionally aligned LC domains [4–10]. It is important to understand the relationship between molecular ordering of rubbed polyimide layer and that of the LC monomers, because the optical properties of the film are dominated by the molecular orientation of the LC monomers. However, the relationship has not been studied [11,12]. The retardation value of the LC film changes through photopolymerization [13]. However, details of the effects of photopolymerization on the alignment of the LC monomers have not yet been clarified.

In this study, we investigated the relationship between the molecular orientation in an alignment layer (polyimide) and that of mesogens in an LC film before and after photopolymerization. Polarization-modulated transmission spectro-ellipsometry was applied to characterize the optical properties of the films. The optical properties of the rubbed alignment layer and the LC films were measured, and the factors determining optical anisotropy of the photopolymerized LC films are discussed.

2. EXPERIMENTAL

All samples were prepared on 1737 glass substrates (Corning). High-pretilt and low-pretilt polyimide (Nissan Chemical Industries, Japan: PI-1 and PI-2) were spin-coated on the glass substrates. The structures of these polyimides are shown in Fig. 2. 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 rubbing conditions (Fig. 1) were as follows: rotational speed $f = 240$ to 1000 rpm, push length $l = 0.5$ mm, transfer speed $V = 12$ mm/s, and cumulative number of rubs $N = 1$. YA-20-R velvet cloth (Yoshikawa-Chemical, Japan) was used.

Two widely used LC monomers, Paliocolor LC242 (BASF, $T_{N\text{-}I} = 122$°C) and RMS03-001 (Merck, $T_{N\text{-}I} = 70$°C), were employed in this study. The structure of LC242 is shown in Fig. 3. LC242 is a single compound (Fig. 3a), whereas RMS03-001 is a mixture of acrylate-based LC monomers (Fig. 3b). The LC phase of LC242 and RMS03-001 yields highly transparent films 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

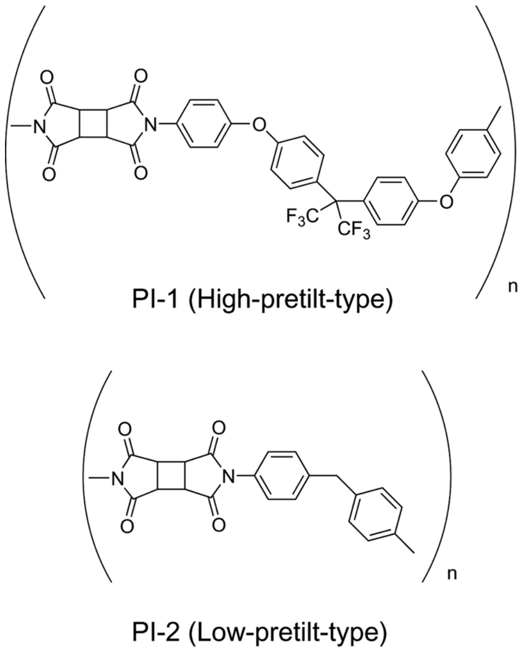


FIGURE 2 Structures of the polyimides used in this study.

with a uniform-radiation optical unit (Ushio, Japan, Spot-cure SP-7). The UV-illumination energy used was 20 mW/cm^2, and the curing time was 1 min. The polar-angle dependence of the retardation values

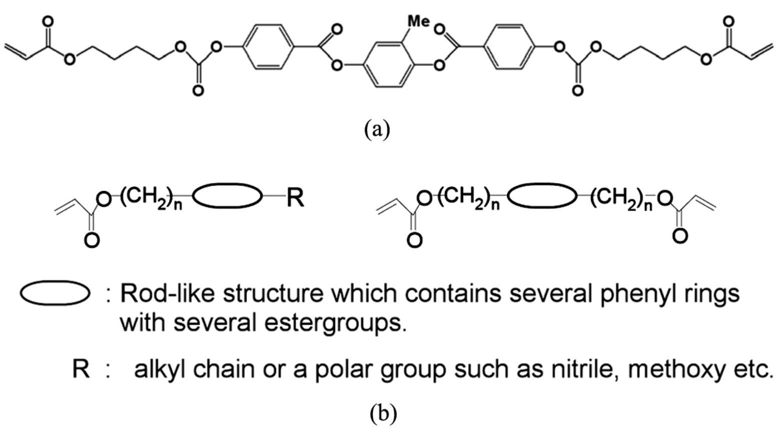


FIGURE 3 Structures of LC monomers LC242 and RMS03-001 used in the study.

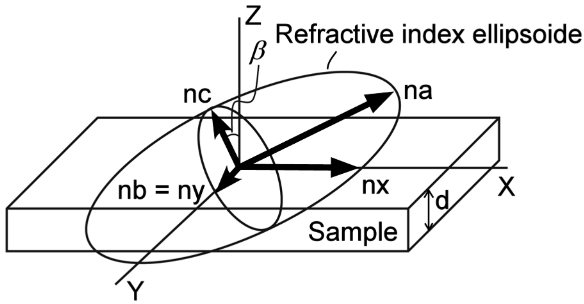


FIGURE 4 Refractive index ellipsoid of the samples.

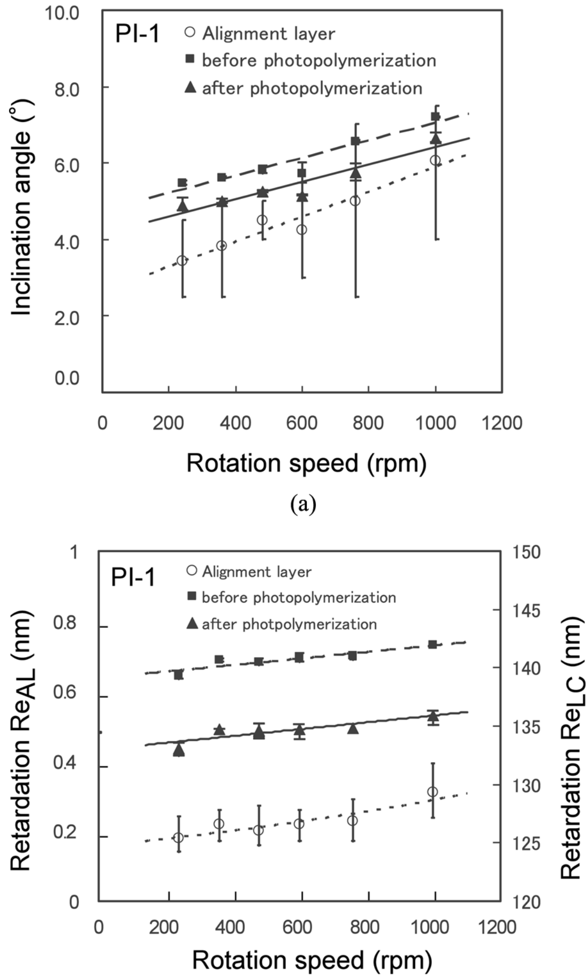
of the rubbed polyimide films and those of the photopolymerized LC films at 590 nm were measured with a M-220 spectro-ellipsometer (Jasco, Japan) and a KOBRA-WR automatic birefringence analyzer (Oji Scientific Instruments, Japan). The inclination angles of the refractive index ellipsoid of the alignment layers (β_{AL}) and the photopolymerized LC films (β_{LC}) were measured as described in previous studies [14,15]. The definition of the inclination angle β is shown in Fig. 4. 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. Single Compound of LC Monomer (LC242)

The influence of the rubbing conditions on the orientation of LC mesogens before and after photopolymerization was investigated. The surfaces of the polyimide (PI-1 and PI-2) coated on the glass substrate were rubbed with a velvet cloth (YA-20-A) by a rubbing machine. Figures 5 and 6 show the influence of the rotation speed of the rubbing roller on the optical properties of the polyimide alignment layers. The inclination angle of the refractive index ellipsoid (β_{AL}) and the retardation value (Re_{AL}) of the alignment films increased with increasing rotation speed. The retardation value is related to the molecular ordering in the film. The results indicate that as the rotation speed increased, the polyimide molecules were stretched strongly because the rubbing force and the number of rubs increased with the rotation speed.

The LC monomer (LC242) was spin-coated on the rubbed polyimide layers and photopolymerized. LC242 is a planar-alignment LC monomer.

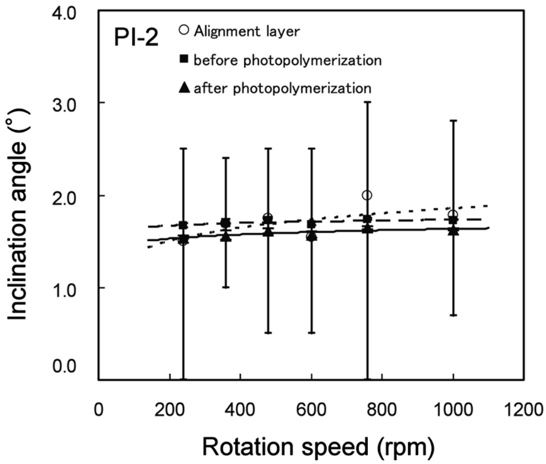


(a)

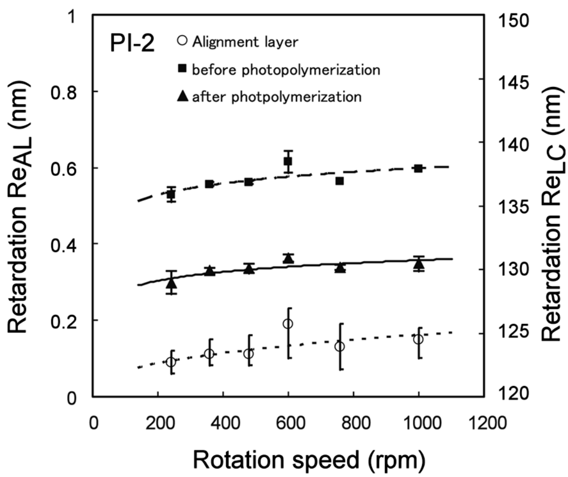
(b)

FIGURE 5 Influence of the rotation speed on the optical properties of the polyimide alignment layer (PI-1) and the LC films (LC242) coated on polyimide films: (a) inclination angle (β_{AL} and β_{LC}) and (b) retardation value (Re_{AL} and Re_{LC}); ○, alignment layer; ■, before photopolymerization; ▲, after photopolymerization.

The conversion of LC monomer to polymer was estimated by IR measurement to be 80.6%. The inclination angle of the refractive index ellipsoid (β_{LC}) and the retardation value (Re_{LC}) of the LC films before and after photopolymerization coated on these polyimide



(a)



(b)

FIGURE 6 Influence of the rotation speed on the optical properties of the polyimide alignment layer (PI-2) and the LC films (LC242) coated on polyimide films: (a) inclination angle (β_{AL} and β_{LC}) and (b) retardation value (Re_{AL} and Re_{LC}); ○, alignment layer; ■, before photopolymerization; ▲, after photopolymerization.

alignment layers are plotted as a function of the rotation speed in Figs. 5 and 6. Both β_{LC} and Re_{LC} before photopolymerization increased with increasing rotation speed in accordance with β_{AL} and Re_{AL}. As shown in Fig. 5a, the dependence of β_{LC} on the rotation speed was smaller than that of β_{AL}. On the other hand, as shown in Fig. 5b, the dependence of Re_{LC} before photopolymerization on the rotation speed is in agreement with that of Re_{AL} on the rotation speed. When the low-pretilt alignment layer (PI-2) was used (Fig. 6), the rotation speed dependence of β_{LC} and Re_{LC} before photopolymerization reflects that of β_{AL} and Re_{AL}. Thus, the inclination angle of the refractive index ellipsoid (alignment direction) and the optical anisotropy (molecular ordering) of the LC monomers (LC242) are strongly related to the ordering of molecules in the polyimide alignment film.

As shown in Figs. 5 and 6, the values of β_{LC} and Re_{LC} are decreased by the photopolymerization. This is because the orientation of mesogens in LC films is changed by the photopolymerization. However, the values of β_{LC} and Re_{LC} after photopolymerization reflect those of β_{LC} and Re_{LC} before photopolymerization. It was thus confirmed that the LC monomer LC242 was photocured while maintaining the molecular alignment of the LC phase produced by the alignment layer.

3.2. Mixture of LC Monomer (RMS03-001)

The LC monomer mixture (RMS03-001) was spin-coated on the rubbed polyimide layers (PI-1 and PI-2) and photopolymerized. RMS03-001 is a planar alignment LC monomer. The conversion of LC monomer to polymer was estimated by IR measurements to be 82.0%. β_{LC} and Re_{LC} before and after photopolymerization are plotted as a function of the rotation speed in Figs. 7 and 8. With increasing rotational speed, both β_{LC} and Re_{LC} before photopolymerization increased in accordance with β_{AL} and Re_{AL}. These results are in agreement with those of the single compound LC242. The values of β_{LC} and Re_{LC} before photopolymerization reflect those of β_{AL} and Re_{AL}. The inclination angle of the reflective index ellipsoid (alignment direction) and the optical anisotropy (molecular ordering) of the LC film before photopolymerization are related to the ordering of molecules in the polyimide alignment film.

As shown in Fig. 7, when PI-1 was used, Re_{LC} decreased by about 8 nm and β_{LC} increased by about 0.7° after photopolymerization. In the case of PI-2 (Fig. 8), Re_{LC} decreased by about 15 nm and β_{LC} increased by about 0.5°. These results show that the ordering of mesogens of the LC film was decreased by the photopolymerization. The decrease in Re_{LC} was larger than that for LC242. In the case of β_{LC}, these trends are opposite those for LC242. These results can be interpreted using the difference in the flexibility of the mesogens of the photopolymerized LC films. In contrast to LC242, RMS03-001

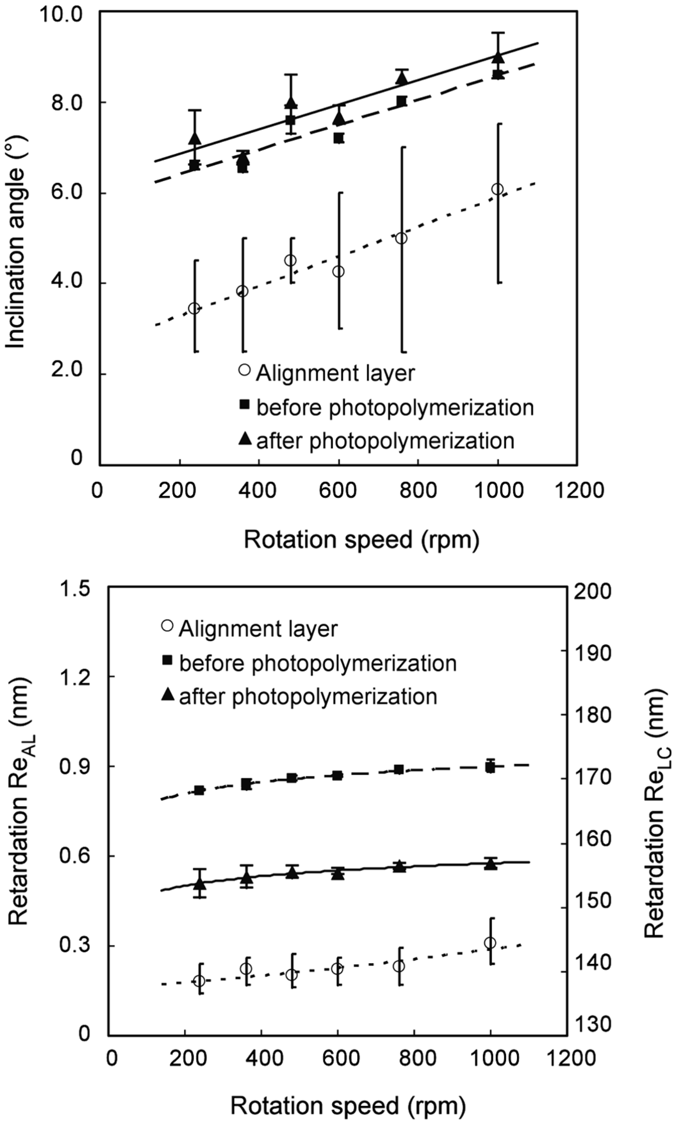


FIGURE 7 Influence of the rotation speed on the optical properties of the polyimide alignment layer (PI-1) and the LC films (RMS03-001) coated on polyimide films: (a) inclination angle (β_{AL} and β_{LC}) and (b) retardation value (Re_{AL} and Re_{LC}); ○, alignment layer; ■, before photopolymerization; ▲, after photopolymerization.

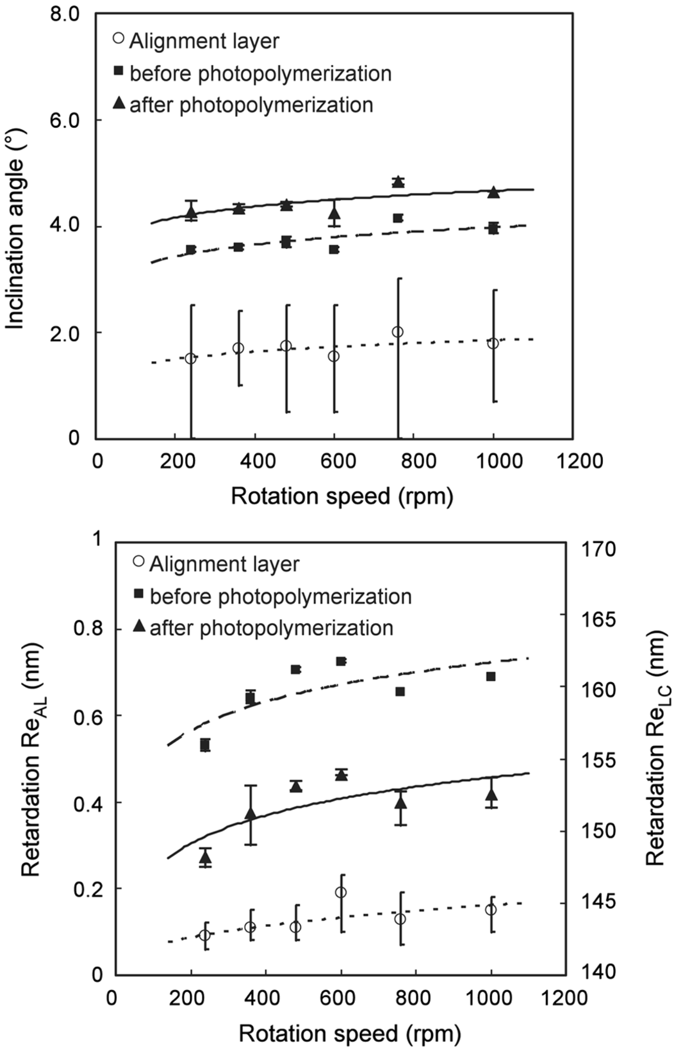


FIGURE 8 Influence of the rotation speed on the optical properties of the polyimide alignment layer (PI-2) and the LC films (RMS03-001) coated on polyimide films: (a) inclination angle (β_{AL} and β_{LC}) and (b) retardation value (Re_{AL} and Re_{LC}); ○, alignment layer; ■, before photopolymerization; ▲, after photopolymerization.

contains monoacrylates and diacrylates. Because of the monoacrylate component, mesogens of the photopolymerized RMS03-001 film are more flexible than those in LC242 (Fig. 9). The change in the structure

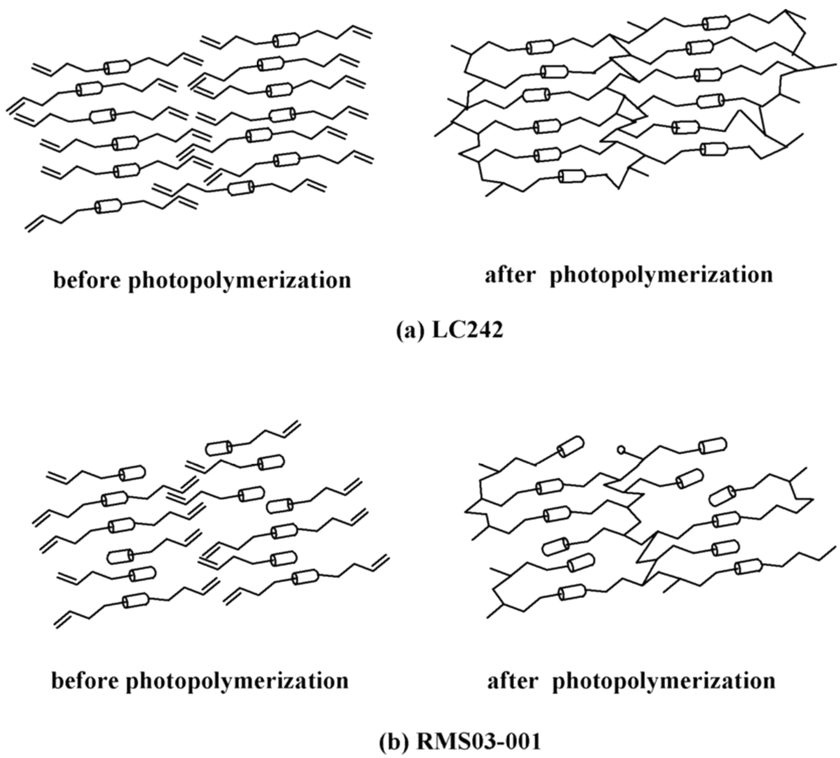


FIGURE 9 Structures of LC films before and after photopolymerization: (a) LC242 and (b) RMS03-001.

of acrylate through polymerization is relaxed because of the flexible structure of the polymer. The alignment of mesogens of RMS03-001 is not disturbed by the polymerization. It was thus confirmed that the LC monomer mixture (RMS03-001) was photocured while maintaining the molecular alignment of the LC phase produced by the molecular alignment condition of the alignment layer.

4. CONCLUSIONS

The relationship between the molecular orientations in an alignment layer (polyimide) and the orientation of mesogens in an LC film before and after photopolymerization was investigated. It was found that the inclination angle of the refractive index ellipsoid (alignment direction) and optical anisotropy (molecular ordering) of the LC film before photopolymerization are related to the ordering of molecules in the polyimide alignment film. The orientation of mesogens of the LC film was changed after photopolymerization regardless of the LC monomer or alignment layer (polyimide) used. The values of β_{LC} and Re_{LC} after photopolymerization were similar to those before photopolymerization. The LC monomer was photocured, maintaining the molecular alignment produced by the alignment layer. It was thus confirmed that the ordering of molecules in the polyimide alignment film is a crucial factor for determining the optical anisotropy of the photopolymerized LC film.

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