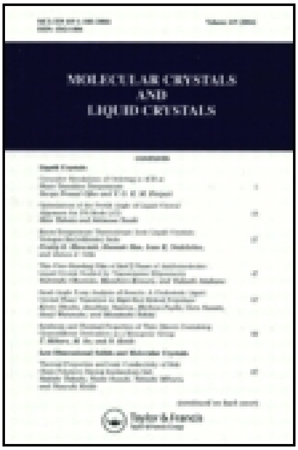

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Photoreactive Polymers Containing Various Kinds of Cinnamate Groups with Optical Anisotropy

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Photoreactive Polymers Containing Various Kinds of Cinnamate Groups with Optical Anisotropy

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Photoreactive polymers with optical anisotropy, which may be applied as the photoalignment layer for liquid crystal display, were synthesized through two-step reaction between several kinds of epoxies and cinnamate groups. The photoreactive polymer film was formed by spin-coating and then exposed to linearly polarized UV light with the wavelength of 254 or 365 nm. The optical anisotropy of the polymer film caused by the selective cycloaddition of the cinnamate groups was confirmed from the polarized UV-vis spectra. The polymer films irradiated by the polarized UV light showed anisotropic absorbance in the polarized UV-vis spectra, while the polymer irradiated by unpolarized UV exhibited isotropic absorbance. We also confirmed the photoreactive polymer film could align liquid crystal. LC cell fabricated using the polymer films irradiated by linearly polarized UV showed anisotropic transmission of the polarized visible light, while the cell fabricated using the polymer films irradiated by unpolarized UV exhibited isotropic transmission.

Keywords: cinnamate group; liquid crystal display; optical anisotropy; photoalignment layer; photoreactive polymer

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INTRODUCTION

Recently, rapid progress of information society has brought about boost in the needs on the flat panel displays, among which Liquid Crystal Display (LCD) is most widely used at present. Especially, alignment layer is one of the most important elements in TFT-LCD. In order to achieve high performance LCD, excellent surface anchoring of LC molecules to the alignment layer is extremely important, which can be hardly obtained by a traditional rubbing method [1–3]. Rubbing method has some disadvantages such as dust generation, electrostatic charge accumulation, poor control of rubbing strength and uniformity [4–6].

In order to overcome these shortcomings, the photoalignment method for LCD has been recently introduced and then gained great attention in both academic and industrial fields [7]. The photoalignment is a touching-free technique [8], which can produce multidomains to overcome the intrinsic viewing angle problems of LCD as well as control liquid crystal alignment at a certain direction. The photoalignment method promises the dust-free process and a possibility of a photopatterning of the LC alignment [9].

In the study, we report the design and synthesis of the photoreactive polymers with optical anisotropy, which can be used for many optical applications, especially as photoalignment layer of LCD. We investigated photocure reaction of the cinnamate double bond of the polymer film using UV-vis spectroscopy. The optical anisotropy of the polymer film and LC alignment behavior were studied by the polarized absorption spectroscopies.

EXPERIMENTAL

We synthesized the photoreactive polymers containing cinnamate groups through two-step reaction. Figure 1 shows the typical synthesis scheme of the photoreactive polymer and the structures of the epoxy resins used in the study. In the first step, Epoxy/Cinnamate polymer (Epoxy/CA) was prepared by reaction between epoxy resin and cinnamic acid. The reaction was carried out using tetramethyl ammonium chloride as a catalyst in the MEK at 80°C for 120 hours. In the second step, cinnamate double bond was incorporated into Epoxy/CA prepolymer by reaction between hydroxyl group of Epoxy/CA and cinnamoyl chloride. The reaction was carried out using triethylamine as a catalyst in THF at room temperature for 12 hours. We confirmed the chemical structure of the photoreactive polymers using ^{1}H-NMR and FT-IR spectroscopies.

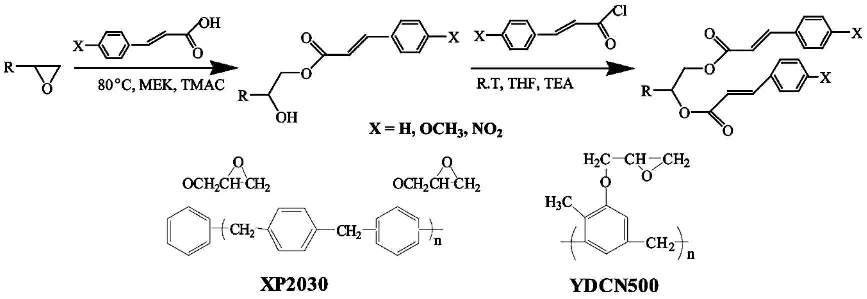

FIGURE 1 Synthetic scheme of the photoreactive polymers.

The photoreactive polymers were completely dissolved in the solvent such as monochlorobenzene, tetrahydrofuran, methyl ethyl ketone or toluene. The solution was filtered through 0.2 μm membrane filter and spin-coated on a quartz substrate. The polymer film was then dried at 70°C for 30 minutes, leading to a excellent quality of film with a thickness of about 1 μm. Photocure of the photoreactive polymer films was carried out by exposing them to 254 or 365 nm UV light with the intensity of 7 mW/cm^2. Photocuring behaviors of the cinnamate, 4-methoxy cinnamate, 4-nitro cinnamate double bonds were studied by monitoring the absorbance change at 275 nm, 310 nm, and 304 nm in UV-vis spectra of corresponding cinnamate groups, respectively.

The photocrosslinked polymer film with optical anisotropy was obtained by exposing the film to the linearly polarized UV light (LPUV). The optical anisotropy of the polymer film was investigated by monitoring the absorbance change of the film during rotating the film in polarized UV-vis spectroscopy. In order to confirm the LC alignment behavior of the polymer film, a parallel LC cell was fabricated using two LPUV photocrosslinked substrates. The cell with 25 μm gap was filled with a nematic liquid crystal (E7:Merck) containing 0.1 wt% of methylene violet (Aldrich) as probing dye at 65°C and then slowly cooled to room temperature. LC alignment in the cell was measured by monitoring the transmittance change of the linearly polarized He-Ne laser beam (632.8 nm) during rotating the LC cell. We studied thermal stability by observing the change in the transmittance of the photocured polymer film upon heating at 250°C for 1 hour.

RESULT AND DISCUSSION

We confirmed the chemical structure of the photoreactive polymers containing various kinds of cinnamate groups by ^{1}H-NMR and

FT-IR spectroscopes. In the ^{1}H-NMR spectra of the Epoxy/CA polymers, the peak at 2.7–2.9 ppm corresponding the epoxide ring proton disappeared and new peaks at 5.5 and 6.7 ppm corresponding to the proton of the cinnamate double bond appeared. In the FT-IR spectra of Epoxy/CA polymers, new characteristic absorption peaks were observed at 3200–3500 cm^{-1} (hydroxyl group), 1720 cm^{-1} (carbonyl group), and 1620 cm^{-1} (cinnamate double bond). These spectra confirmed the syntheses of the Epoxy/CA with the desired structure. Nevertheless, we still observed weak absorption peaks at 3200–3500 cm^{-1} in the spectra of Epoxy/CA/CA, implying all the hydroxyl groups of Epoxy/CA did not react with the cinnamoyl group in the second step reaction.

We found the Epoxy/CA polymers were only partially soluble in the most of the organic solvents, possibly because of hydrophilic nature as well as strong hydrogen bonding of hydroxyl groups of Epoxy/CA polymers. However, the solubility of the Epoxy/CA/CA polymers was dramatically improved, becoming completely soluble in the most of organic solvents. The improved solubility must result from weakening of hydrogen bonding of hydroxyl groups, which reacted with cinnamoyl chloride.

The UV-vis spectral changes can clearly confirm the photo-dimerization of the cinnamate groups as shown in Figure 2(a), where absorbance at 275 nm corresponding to the cinnamate group in Epoxy/CA/CA polymer film decreased with UV exposure time. We also confirmed the effective photocure of the cinnamate double bond in XP2030/CA/CA and YDCN500/CA/CA. Figure 2(b) shows the photocure conversion of the cinnamate double bonds in the polymers with UV irradiation time, exhibiting steep increase of the photocure

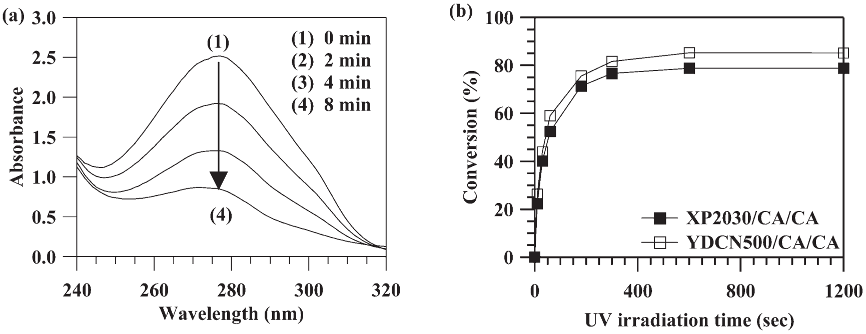

FIGURE 2 (a) UV-visible absorption spectra and (b) photocure conversion of the cinnamate double bond with UV exposure time.

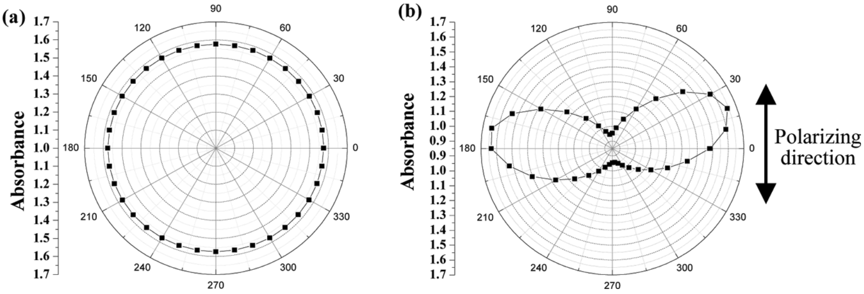

FIGURE 3 Polar diagrams of the polymer films exposed to (a) unpolarized and (b) linearly polarized UV.

conversion during the early UV irradiation period. The conversion reached about 80% after 600 seconds.

The optical anisotropy of the film due to the selective aligned cycloaddtion of the cinnamate groups in the polymer film was confirmed by anisotropic absorption of the film in polarized UV-vis spectroscopy as shown in Figure 3. The polymer film crosslinked by unpolarized UV exhibited isotropic absorption with the rotating angle of the film in polarized spectroscopy as shown in Figure 3(a), while the polymer film crosslinked by LPUV light showed significantly anisotropic absorption with the rotating angle as shown in Figure 3(b). This anisotropic absorption indicates the selective cycloaddition of the cinnamate groups in one direction was formed by the LPUV. Since only cinnamate groups aligned perpendicular to the polarization direction are usually crosslinked, the absorption pattern of the polymer film crosslinked by LPUV light must be symmetrical. Nevertheless, the polymer film showed little asymmetrical absorption as shown in Figure 3(b). We consider the cinnamate groups in the film aligned nearly perpendicular to the polarization direction can also undergo crosslinking, resulting in the little asymmetric absorption pattern.

We also confirmed that the polymer film crosslinked by LPUV could align LC. Figure 4 shows the angular dependent transmittances of the LC cells in the polarized visible spectroscopy. The LC cell fabricated using the films crosslinked by unpolarized UV exhibited isotropic transmittance with the rotating angle of the cell in polarized spectroscopy, while the cell fabricated using the films crosslinked by LPUV light showed significantly anisotropic transmittance with the rotating angle.

Figure 5 displays the transmittance change of the LC cell formed using the pristine polymer films with the LPUV exposure time. Since the LC molecules are isotropically dispersed in the cell before LPUV

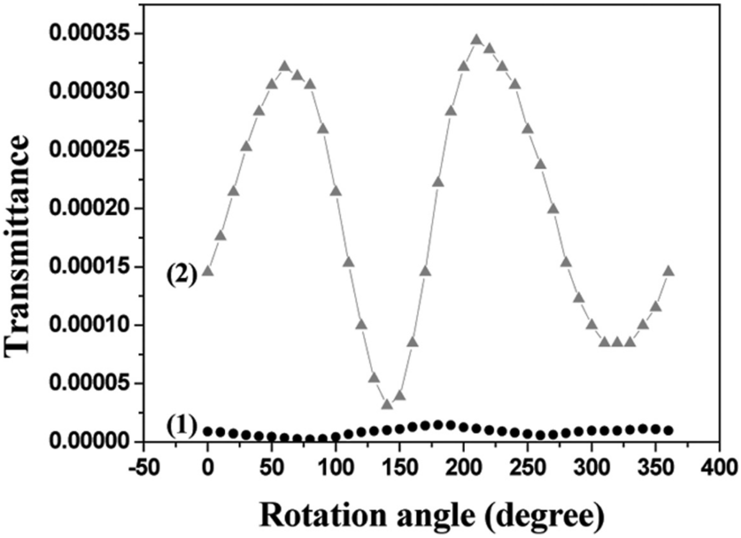

FIGURE 4 Angular dependent transmittance of the polarized visible light through the LC cell fabricated using the films crosslinked by unpolarized UV.

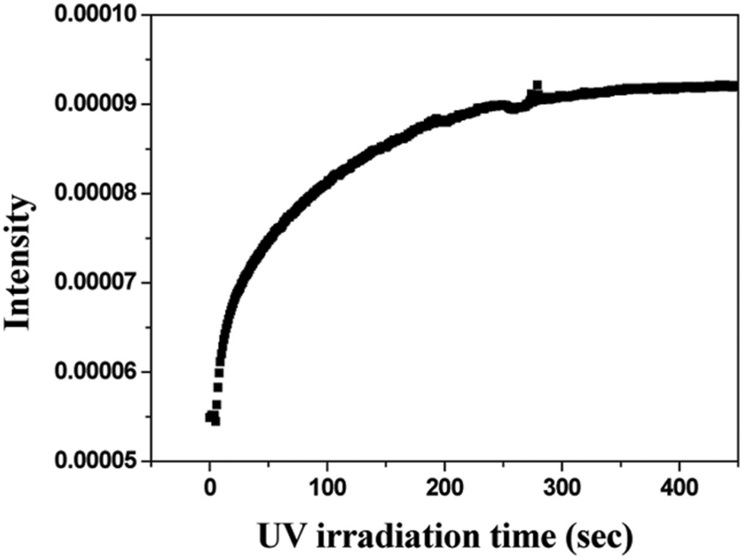

FIGURE 5 Angular dependent transmittance of the polarized visible light through the LC cell fabricated using the films crosslinked by linearly polarized UV.

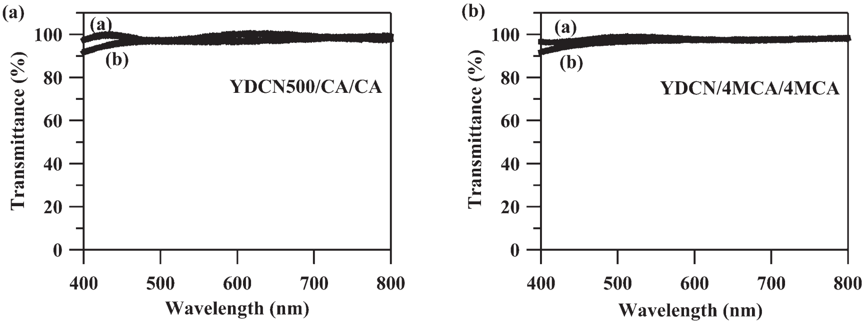

FIGURE 6 Transmittances of the polymer films (a) crosslinked and (b) crosslinked and heated at 250°C for 1 hour.

exposure, the polarized visible light did not transmit through the cell, resulting in low transmittance. However, transmittance of the polarized visible light increased dramatically with the LPUV exposure time because the LPUV produced the selective cycloaddition of cinnamate groups and eventually gave rise to alignment of LC in the cell. As shown in Figure 5, the *in-situ* alignment reached saturation within 400 seconds LPUV exposure, implying very effective photoalignment.

The photocured film showed little change of the transmittance in the visible region even after heating at 250°C for 1 hour compared with the that of the unheated photocured film, implying fairly good thermal stability as shown in Figure 6. We, therefore, consider the photoreactive polymers synthesized in the study can be applied to the photoalignment layer of flat panel display materials.

CONCLUSION

We designed and synthesized photoreactive polymers with optical anisotropy, which may be applied as the photoalignment layer for LCD. The optical anisotropy of the polymer film caused by the selective cycloaddition of the cinnamate groups was confirmed from the polarized UV-vis spectra. The polymer films irradiated by the polarized UV light showed anisotropic absorbance in the polarized UV-vis spectra. We also confirmed the photoreactive polymer film could align liquid crystal. LC cell fabricated using the polymer films irradiated by linearly polarized UV showed anisotropic transmission of the polarized visible light. We, therefore, consider the photoreactive polymers synthesized in the study can be applied to the photoalignment layer of flat panel display materials.

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