Thermally Stable Photo-Crosslinking Polymers Bearing Cinnamate Groups for Liquid Crystal Alignment

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Summary: Optically ansiotropic photo-crosslinking polymers were synthesized through reaction between different kinds of epoxy resins and cinnamic acids. Optical anisotropy of the polymer film exposed to linearly polarized UV light (LPUVL) was confirmed from the polarized UV-Visible spectra. The polymer films irradiated by LPUVL showed anisotropic absorbance in the polarized UV-Visible spectra, while the polymer irradiated by unpolarized UV exhibited isotropic absorbance. It was also confirmed that the polymer film exposed to LPUVL could align liquid crystals (LC). LC cell fabricated using the polymer films irradiated by LPUVL showed the anisotropic polar diagram, implying that the polymer films may be applied as the photoalignment layer for LC display.

Keywords: cinnamate group; epoxy; optical anisotropy; photoalignment layer; photoreactive polymer

Introduction

Rubbing polyimide film using velvet fabric is the only technique to align liquid crystals (LC) for mass production of flat-panel LC display (LCD) devices since the rubbing technique is simple and enables LC alignment control.[1,2] However, this process suffers from some shortcomings such as dust generation, electrostatic charge accumulation and difficult control of the rubbing strength.[3,4] Therefore, rubbing-free method has become an important target to overcome the problems arising from the rubbing process.

Photo-induced alignment technique for LCD has received much attention in recent years because of its clean and photo-patternable charateristics.[5] Various kinds of photoreactive polymers have been reported for the alignment of LC. Photo-alignment behaviors of those polymers are mainly based on photo-induced cyclodimerization, photo-induced trans-cis isomerization and photodegradation. For example, nematic liquid crystal can be aligned homogeneously on the photoreactive polymer film such as poly(vinyl cinnamate) (PVCN).[6,7] When linearly polarized UV light (LPUVL) is irradiated to PVCN fim, selective anisotropic [2+2] cycloaddition of cinnamate groups in PVCN takes place, resulting in irreversible low molecular LC alignment.

Different kinds of polymers containing various kinds of cinnamate groups in the side chain were also studied for LC photoalignment layer. Because of poor solubility arising from the rigid-rod nature of cinnamate backbone polymers, most researches have involved only polymers that contain the cinnamate units in the side chain. However, one of the drawbacks of cinnamte polymers was found to be the lack of thermal stability due to low glass transition temperature.

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In this study, we report synthesis of the thermally stable photocrosslinking polymers with optical anisotropy, which can be used for many optical applications, especially as photoalignment layer of LCD. The optical anisotropy, LC alignment behavior and thermal stability of the polymer films were studied by the polarized absorption spectroscopies.

Experimental Part

Three kinds of photocrosslinking polymers (XP2030/CA, XP2030/2-TCA and KWG1-EP/CA) containing cinnamate group were synthesized through a simple reaction between epoxy resin and cinnamic acid, where two kinds of commercial epoxy resins (XP2030 or KWG1-EP) and two kinds of cinnamic acids (trans cinnamic acid or 2-trifluoromethyl cinnamic acid) were used. Figure 1 shows the typical synthesis scheme of the photocrosslinking polymer and the structures of the epoxy resins and cinnamic acids. The reaction was carried out using tetramethyl ammonium chloride (TMAC) as a catalyst in the methylethylketone (MEK) at 75 °C for 120 hours. We confirmed the chemical structures of the photocrosslinking polymers using ^{1}H-NMR and FT-IR spectroscopies.

In order to prepare the polymer films, polymer solutions were prepared by dissolving 0.5 g of the polymers in 10 ml of monochlorobenzene and filtered through 0.2 μm teflon membrane filter. Polymer films were formed on the suitable substrates such as glass or quartz plate using spin-coating method at 1500 rpm for 1 minute. The polymer films were then dried at 70 °C for 60 minutes, leading to an excellent quality of films with a thickness of about 0.7 μm.

The polymer films with optical anisotropy were obtained by exposing the films to the LPUVL. Optical anisotropy of the polymer film was investigated by observing absorbance changes with irradiation time in the directions paralle and perpendicular to LPUVL using polarized UV-Visible spectroscopy. The anisotropy of the films was evaluated by the dichroic ratio defined as the following equation.

$$\text{Dichroic ratio} = [(A_\perp - A_{//})/(A_\perp + A_{//})]$$

where, $A_\perp$ and $A_{//}$ are the absorbances in the direction perpendicular and parallel to LPUVL, respectively. Optical anisotropy was also confirmed by monitoring the absorbance change of the film with the

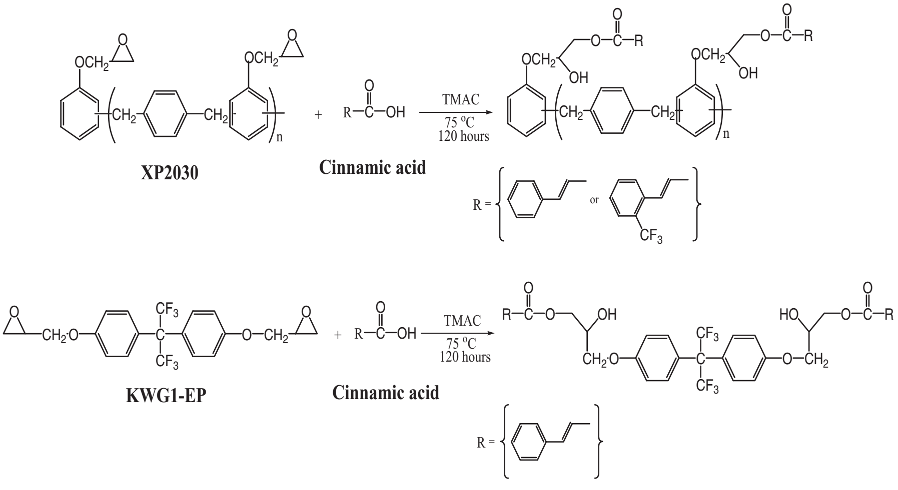

Figure 1.
Synthetic scheme of the photocrosslinking polymers.

rotation angle of the film in polarized UV-Vis spectroscopy.

LC alignment behavior of the polymer films was studied by anisotropic absorption of a dichroic dye in LC cell. Antiparallel LC cell with 25 μm cell gap was assembled with two glass plates coated with LPUVL-exposed polymer film. A nematic LC, E7 (Merck Co.) containing 0.2 wt% Disperse Blue 14 (λ_{max} at 645 nm) as a dichroic dye was injected into the cell. The director of the nematic LC in the cell was determined from the absorption of the dichroic dye in the cell. We also studied thermal stability by observing the change of anisotropy upon thermal treatement at different temperatures for 10 minutes.

Results and Discussion

We confirmed the chemical structures of the photocrosslinking polymers containing cinnamate groups by ^{1}H-NMR and FT-IR spectroscopies. In the ^{1}H-NMR spectra of the Epoxy/CA polymers, the peaks at $2.7 \sim 2.9$ ppm corresponding to the proton of the epoxide ring disappeared and new peaks at 6.5 ppm corresponding to the proton of the cinnamate double bond appeared as shown in Figure 2.

In the FT-IR spectra of Epoxy/CA polymers, new characteristic absorption peaks were observed at $3200 \sim 3600$ cm^{-1} (hydroxyl group), 1720 cm^{-1} (carbonyl group) and 1620 cm^{-1} (cinnamate double bond) as shown in Figure 3. These spectra confirmed the syntheses of the Epoxy/CA with the desired structure.

Figure 4(a) shows the absorbance changes at 278 nm of KWG1-EP/CA film in the directions parallel (solid line) and perpendicular (dot line) to LPUVL with irradiation time, exhibiting clear decrease in the absorbance with UV exposure time. It was also found that the absorbances parallel to the LPUVL decreased much faster than those perpendicular to the LPUVL at all UV exposure time as shown in Figure 4(a). Even though, in general, cinnamate group is known to be a perpendicular director to LPUVL, cinnamte groups in the polymer synthesized in this study was found to be parallel directors. Figure 4(a) indicates that preferred and selective photo-induced cycloaddition of the cinnamate groups parallel to LPUVL took place, confirming that LPUVL produced the optical anisotropy of the film.

Figure 4(b) shows the change of the dichroic ratios of photo-crosslinking polymer films with LPUVL exposure time. The dichroic ratio increased rapidly with increase in exposure time up to 180 seconds and then very slowly increased with further increase in the exposure time. The final dichroic ratios were in the range of 0.03–0.06 depending on the polymer structure. The change in dichroic ratio also confirmed that the cinnamate groups located parallel to the polarization direction of the incident LPUVL were consumed more rapidly than those positioned perpendicular to the polarization direction of

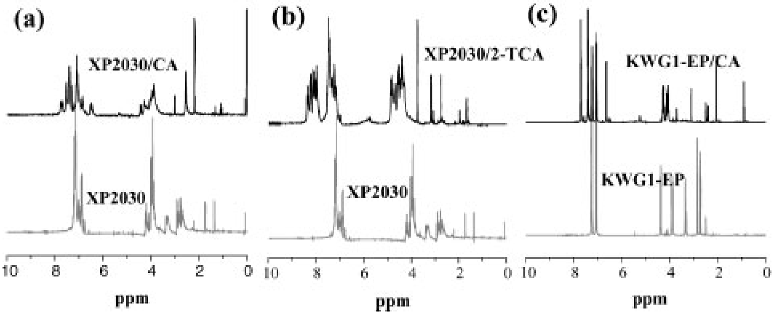

Figure 2.
^{1}H-NMR spectra of (a) XP2030/CA, (b) XP2030/2-TCA and (c) KWG1-EP/CA.

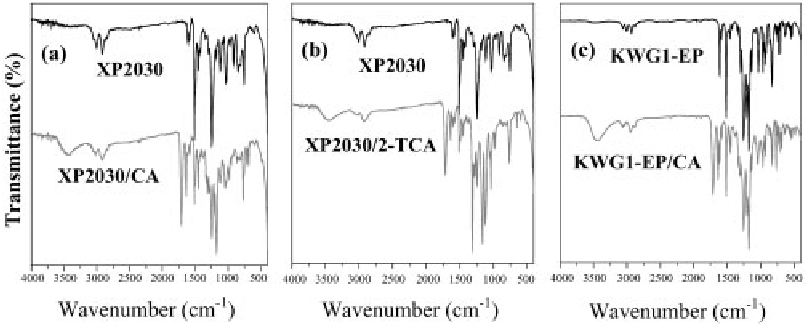

Figure 3.
FT-IR spectra of (a) XP2030/CA, (b) XP2030/2-TCA and (c) KWG1-EP/CA.

the LPUVL. Thus, the directionally selective photoreaction of cinnamate groups in the photocrosslinking polymer films due to LPUVL exposure made cinnamate groups react along the direction parallel to the polarization of the LPUVL. This preferential reaction of cinnamate groups was easily obtained with a LPUVL exposure time of only 180 seconds.

The optical anisotropy of the film due to the selective aligned cycloaddtion of the cinnamate groups in the polymer film was also confirmed by anisotropic absorption of the film in polarized UV-Visible spectroscopy as shown in Figure 5. The polymer film crosslinked by unpolarized UV exhibited isotropic absorption with the rotating angle of the film in polarized spectroscopy as shown in Figure 5(a), while the polymer film crosslinked by LPUVL showed significantly anisotropic absorption with the rotating angle as shown in Figure 5(b). This anisotropic absorption indicates the selective cycloaddition of the cinnamate groups in one direction was formed by the LPUVL. Since only cinnamate groups aligned in a specific direction (parallel or perpendicular) to the polarization direction are usually crosslinked, the absorption pattern of the polymer film crosslinked by LPUVL must be symmetrical. Nevertheless, the polymer film showed a little asymmetrical absorption as shown in Figure 5(b). We consider the cinnamate groups in the film aligned nearly parallel to the polarization direction can also undergo crosslinking, resulting in a little asymmetric absorption pattern.

We confirmed that the polymer film crosslinked by LPUV light could align LC. Figure 6 shows angular dependent absorbances of the dichroic dye in LC cells, which were measured at room temperature and

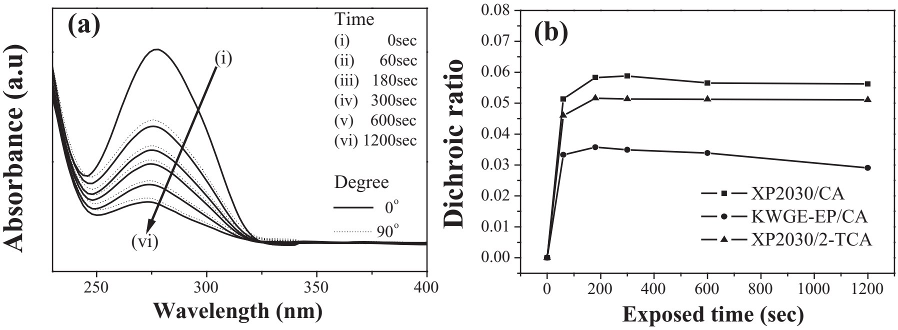

Figure 4.
(a) UV-visible absorption spectra of KWG1-EP/CA (0 and 90° mean the parallel and perpendicular directions to LPUVL) and (b) changes in dichroic ratios with irradiation time.

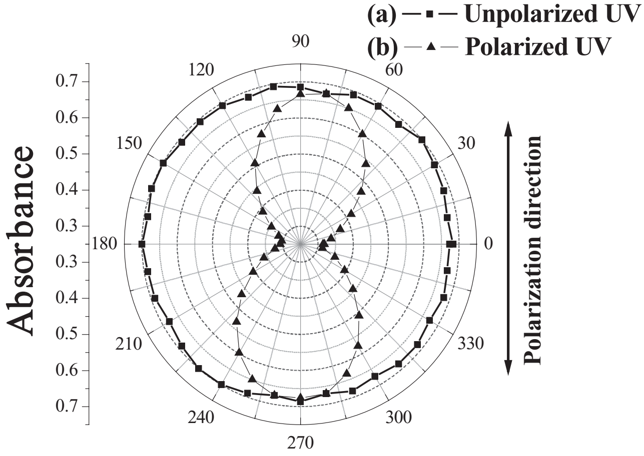

Figure 5.
Polar diagrams of XP2030/CA films exposed to (a) unpolarized and (b) linearly polarized UV.

after isothermal heating at 80, 100 and 120 °C for 10 minutes. At room temperature, LC cells fabricated using the films crosslinked by LPUVL showed significantly anisotropic absorbance of the dye with the rotating angle, confirming that the films could align LC.

However, XP2030/2-TCA and KWG1-EP/CA do not seem to have good thermal stability as shown in Figure 6(b) and (c),

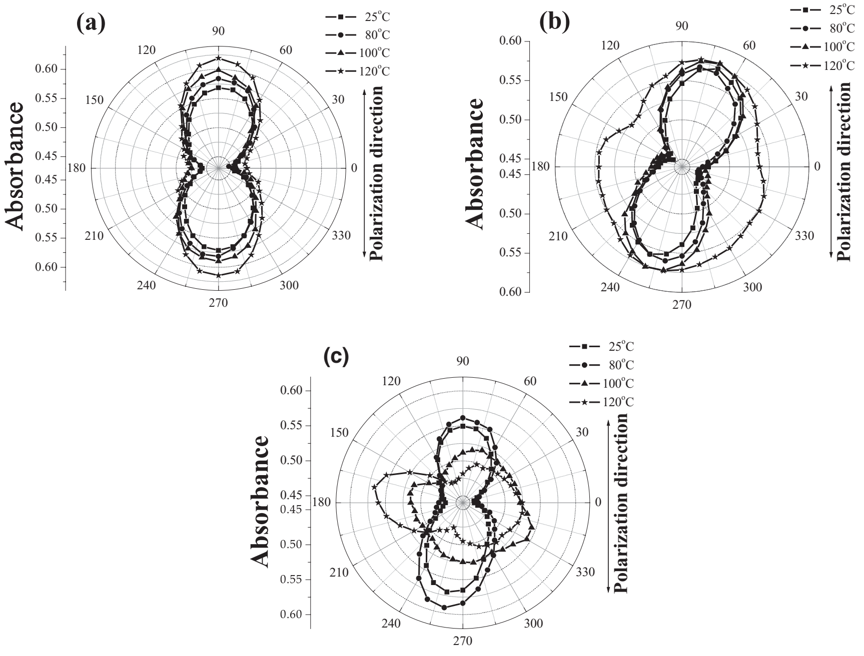

Figure 6.
Circular absorbance diagrams of Disperse Blue 14 ($\lambda_{max} = 648$ nm) in LC cell fabricated with (a) XP2030/CA, (b) XP2030/2-TCA and (c) KWG1-EP/CA.

whereas XP2030/CA possessed excellent thermal stability up to 120 °C, displaying little loss of the anisotropic behavior. The randomization of LC orientation induced by thermal treatment may be resulted from insufficient crosslinking of the polymers.

Conclusions

Photocrosslinking polymers with optical anisotropy were synthesized, which may be applied as the photoalignment layer for LCD. The polymer films irradiated by the polarized UV light showed anisotropic absorbance in the polarized UV-Visible spectra, confirming that LPUVL irradiation induced optical anisotropy of the polymer film by the selective cycloaddition of the cinnamate groups. We also confirmed the photocrosslinking polymer film could align LC. LC cell fabricated using the polymer films irradiated by LPUVL showed anisotropic absorbance of a dichroic dye in the cell. XP2030/CA showed the good thermal stability up to 120 °C. We, therefore, consider the photocrosslinking polymers can be applied to the photoalignment layer for LCD.

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