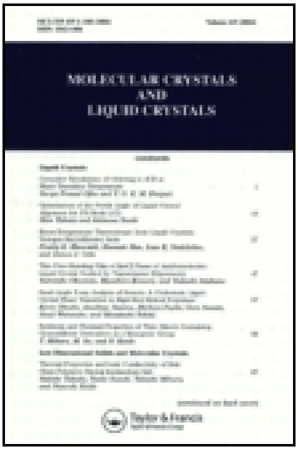

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Novel Photocrosslinking Polymers for Liquid Crystal Alignment

Dong Kyo Seo [a], Oh Hyun Sung [a], Seung Hyun Cho [a], Jun Young Lee [a], Whan Gun Kim [b] & Ki Gook Song [c]

[a] School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, Suwon, Korea

[b] Department of Applied Chemistry, Seokyeong University, Seoul, Korea

[c] Department of Chemical Engineering, Kyunghee University, Yongin, Korea

Version of record first published: 12 Mar 2007

To cite this article: Dong Kyo Seo, Oh Hyun Sung, Seung Hyun Cho, Jun Young Lee, Whan Gun Kim & Ki Gook Song (2007): Novel Photocrosslinking Polymers for Liquid Crystal Alignment, Molecular Crystals and Liquid Crystals, 463:1, 193/[475]-199/[481]

To link to this article: http://dx.doi.org/10.1080/15421400601027924

Mol. Cryst. Liq. Cryst., Vol. 463, pp. 193/[475]–199/[481], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601027924

Novel Photocrosslinking Polymers for Liquid Crystal Alignment

Dong Kyo Seo
Oh Hyun Sung
Seung Hyun Cho
Jun Young Lee
School of Applied Chemistry and Chemical Engineering,
Sungkyunkwan University, Suwon, Korea

Whan Gun Kim
Department of Applied Chemistry, Seokyeong University,
Seoul, Korea

Ki Gook Song
Department of Chemical Engineering, Kyunghee University,
Yongin, Korea

Photocrosslinking polymers with optical anisotropy, which may be applied as the alignment layer for liquid crystal display (LCD), were synthesized through reaction between an epoxy compound and several kinds of cinnamic acids. The photocrosslinking polymer film was formed by spin-coating and then exposed to linearly polarized UV light. 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 unpolarized UV light exhibited isotropic absorbance in the polarized UV-vis spectra, while the polymer films irradiated by the polarized UV light showed anisotropic absorbance. We also confirmed the photocrosslinking polymer film could align liquid crystal (LC). 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; LCD; optical anisotropy; photoreactive polymer; photoalignment layer

This work was supported by the Korea Research Foundation Grant. (KRF-2004-005-D00063)

Address correspondence to Jun Young Lee, School of Applied Chemistry and Chemical Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon 440-746, Kyunggi-do, Korea. E-mail: jylee7@skku.edu

INTRODUCTION

Although the conventional rubbing technique has been widely used for the liquid crystal (LC) alignment, it has several problems such as the dust and static charge accumulation due to the mechanical contact of rubbing cloth. Moreover, the general trend to achieve high performance for LCD applications requires surface anchoring conditions that cannot be provided by a traditional rubbing method. For example, wide viewing angles can be achieved using multiple director orientations within a given pixel [1]. Among non-contact techniques to overcome the problems, photo-alignment method is one of the promising techniques [2]. Poly(vinyl cinnamate) (PVCN) derivatives are the most-well known materials which can align LC in the direction perpendicular to the polarization direction of the light [3–8]. One of the drawbacks of PVCN was found to be the lack of thermal stability due to low glass transition temperature.

In this study, we report the design and synthesis of novel photocrosslinking polymers with optical anisotropy. 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 and their thermal stability of optical anisotropy was also studied.

EXPERIMENTAL

We synthesized the photocrosslinking polymers (YDCN/CA) containing cinnamate derivatives through the simple reaction between a commercial epoxy compound (YDCN) and various kinds of cinnamic acids. Figure 1 shows the typical synthesis scheme of the photocrosslinking polymer and the structures of the epoxy resin and cinnamic acids. The reaction was carried out using tetramethyl ammonium chloride (TMAC) as a catalyst in the methyl ethyl ketone (MEK) at 80°C for 120 hours. We confirmed the chemical structures of the photoreactive polymers using ^{1}H-NMR and FT-IR spectroscopies.

The photoreactive polymers were completely dissolved in the solvent such as monochlorobenzene, tetrahydrofuran, MEK 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 an excellent quality of film with a thickness of about 1 μm. Photocuring of the polymer films was carried out by exposing them to 254 nm UV light with the intensity of 9 mW/cm^2 on the surface of the film. Photocuring behaviors of the YDCN/α-phenyl cinnamic acid (YDCN/α-PCA), YDCN/α-methyl

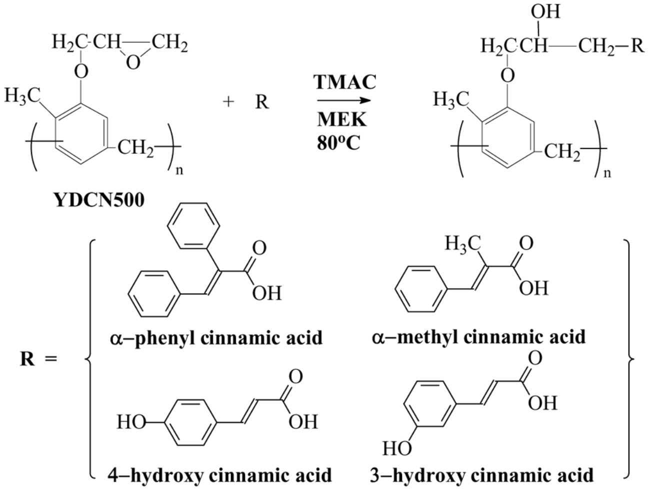

FIGURE 1 Synthetic scheme of the photocrosslinking polymers.

cinnamic acid (YDCN/α-MCA), YDCN/4-hydroxy cinnamic acid (YDCN/4-HCA) and YDCN/3-hydroxy cinnamic acid (YDCN/3-HCA) double bonds were studied by monitoring the absorbance change at 288 nm, 274 nm, 314 nm, and 276 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. The LC cell was constructed with two polymer-coated glass plates after LPUV-exposure. In order to monitor LC alignment, nematic liquid crystal (E7:Merck) was inserted into the LC cell by capillary action with methyl violet as a 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 also studied thermal stability by observing the change of anisotropy after isothermal heating at different temperatures for 10 minutes.

RESULTS AND DISCUSSION

We confirmed the chemical structures of the photocrosslinking polymers containing various kinds of cinnamate groups by ^{1}H-NMR and FT-IR spectroscopies. In the ^{1}H-NMR spectra of the Epoxy/CA polymers, the peak at $2.7 \sim 2.9$ ppm corresponding to the proton of the epoxide ring 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.

The UV-vis spectral changes can clearly confirm the photo-dimerization of the cinnamate groups as shown in Figure 2(a). The absorbances of YDCN/3-HCA cinnamate group at 276 nm in both directions parallel and perpendicular to the polarized direction decreased with LPUV exposure time. However, it was observed that absorbance in the parallel direction decreased much faster than that in the perpendicular direction, indicating preferred and selective photo-dimerization of the cinnamate groups in the polymer by LPUV light. It was also figured out that photocrosslinking could be completed within 1,200 seconds. Figure 2(b) shows the dichroic ratio of photocrosslinking polymers with LPUV irradiation time. Dichroic ratios of the polymer films increased very steeply with the LPUV light exposure time. In the case of YDCN/3-HCA, the dichroic ratio reached the maximum at 180 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, while the polymer film crosslinked by LPUV light showed significantly anisotropic absorption with the rotating angle. This anisotropic absorption indicates the selective cycloaddition of the cinnmate groups in one direction.

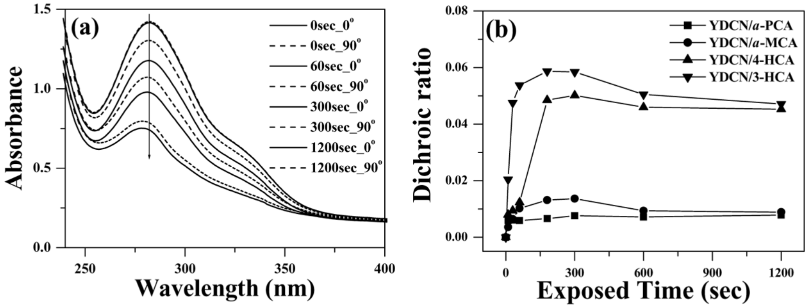

FIGURE 2 (a) UV-visible absorption spectra of YDCN/3- HCA (0 means parallel direction, and 90 means perpendicular direction to polarized direction) and (b) Dichroic ratios of polymer films bearing various kinds of cinnamate groups.

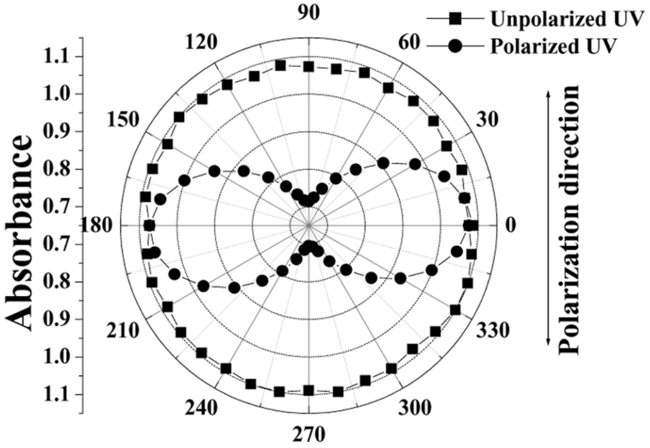

FIGURE 3 Circular diagrams of the polymer films exposed to unpolarized and linearly polarized UV.

We also confirmed that the polymer film crosslinked by LPUV light could align LC. Figure 4 shows the angular dependent transmittances of methyl violet ($\lambda_{\max} = 546\,\mathrm{nm}$) in LC cells observed by the polarized visible spectroscopy. The LC cell fabricated using the films crosslinked by unpolarized UV light exhibited isotropic transmittance with the

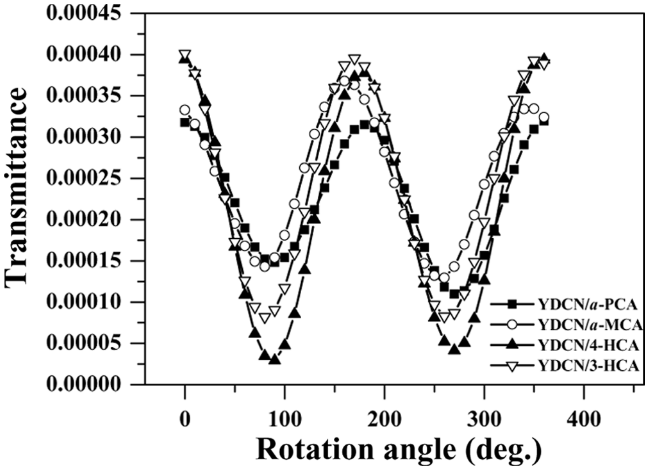

FIGURE 4 Angular dependent transmittance of the polarized visible light through the LC cell fabricated using the films crosslinked by linearly polarized UV.

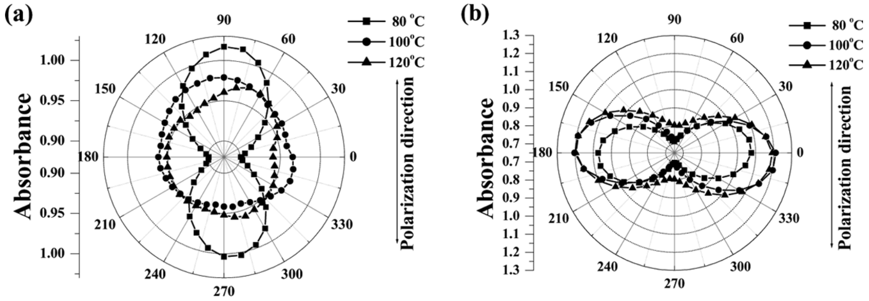

FIGURE 5 Circular diagram of methyl violet absorbance ($\lambda_{\max} = 546\,\text{nm}$) in LC cell fabricated with (a) YDCN/α-PCA and(b) YDCN/3-HCA.

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 shows angular dependent absorbances of the LC cell, which were measured after isothermal heating at 80, 100 and 120°C for 10 minutes. Even though, in general, cinnamate group is known to be a perpendicular director [1,2] as shown in Figure 5(b), the cinnamate groups in YDCN/α-PCA and YDCN/α-MCA worked as parallel director as shown in Figure 5(a). It might be due to the specific structures with the substitutes located at α-position. YDCN/α-PCA and YDCN/α-MCA do not seem to have good thermal stability. The polymers completely lost their anisotropic absorption characteristics upon heating even at 100°C as shown in Figure 5(a). However, YDCN/3-HCA exhibited excellent thermal stability up to 120°C, displaying little loss of the anisotropic behavior.

CONCLUSIONS

We designed and synthesized photocrosslinking 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. It was also confirmed that the polymer films crosslinked by linearly polarized UV light could align LC. LC cell fabricated using the polymer films irradiated by linearly polarized UV light showed anisotropic transmission of the polarized visible light. The polymer films crosslinked by LPUV light maintained the angular dependent absorption behavior even after heating at 120°C, implying good thermal stability. We, therefore, consider the photocrosslinking polymers synthesized in this study can be applied to the photoalignment layer.

REFERENCES

[1] Schadt, M., Seiberle, H., & Schuster, ■. (1996). *Nature*, *381*, 212.
[2] Schadt, M., Shmitt, K., Kozinkov, V., & Chigrinov, V. G. (1992). *Jpn. J. App. Phys.*, *31*, 2155.
[3] Egerton, P. L., Pitts, E., & Reiser, A. (1981). *Macromolecules*, *14*, 95.
[4] Ichimura, K., Akita, Y., Akiyama, H., Hayashi, Y., & Kudo, K. (1996). *Jpn. J. App. Phys.*, *35*, L992.
[5] Ichimura, K. (2000). *Chem. Rev.*, *100*, 1847.
[6] O'Neill, M. & Kelly, S. M. (2000). *J. Phys. D: Appl. Phys.*, *33*, R67.
[7] Kawatsuki, N., Goto, K., Kawakami, T., & Yamamoto, T. (2002). *Macromolecules*, *35*, 706.
[8] Obi, M., Morino, S., & Ichimura, K. (1999). *Chem. Mater.*,*11*, 656.