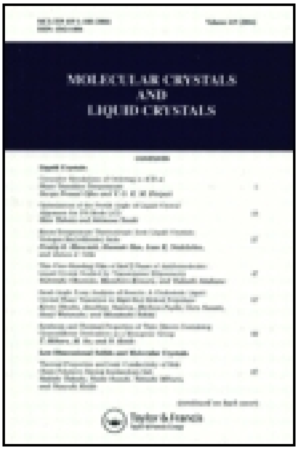

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Jeong Hwan Lee [a] & Nobuhiro Kawatsuki [a]
[a] Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, Shosha Himeji, Japan

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Synthesis and Properties of Photo-Cross-Linkable Polymer Liquid Crystal Containing Fluorene Unit

Jeong Hwan Lee and Nobuhiro Kawatsuki
Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, Shosha Himeji, Japan

Poly(methacrylate) copolymer containing 95 mol% of photoreactive H-bonded mesogenic unit 4-(6-hydroxyhexyloxy)cinnamic acid (6CA) and 5 mol% of luminescent unit 2,7-bis[2-(4-hydroxyphenyl)-2-cyanovinyl]-9,9-dihexyl-9H-fluorene (CN-DHFP) was synthesized and characterized. The irradiation with LPUV light resulted in the induction of a small negative optical anisotropy (ΔA) in the films due to the axis selective photoreaction of the cinnamic acid group. After annealing, the negative optical anisotropies both 6CA and CN-DHFP groups were significantly enhanced. The enhanced reorientation direction of both groups was perpendicular to **E** *of LPUV light. Polarized blue emission was obtained with polarization ratio of about 2.0.*

Keywords: electroluminescence; photoorientation; polarized emission; polymer liquid crystal

INTRODUCTION

Since the first report on polarized electroluminescent (EL) material, polarized light source is of interest for use as a backlight in a liquid crystal (LC) display because of the removal of the backlight and polarizer combination [1]. Irradiation with linearly polarized ultraviolet (LPUV) light in thin polymer films containing photoreactive moieties induces optical anisotropy and has attracted intensive interest from an practical viewpoint due to the alignment of LCs. A large number of photoreactive polymers have been extensively investigated including azobenzene containing polymers and photo-cross-linkable polymers such as coumarin and cinnamate for the application to LC

Address correspondence to Jeong Hwan Lee, Department of Materials Science and Chemistry, Himeji Institute of Technology, University of Hyogo, 2167 Shosha, Himeji 671-2201, Japan. E-mail: kawatuki@eng.u-hyogo.ac.jp

alignment materials [2–6]. Additionally, various types of copolymer have been also synthesized to obtain higher molecular orientation by the cooperative effect [7–9].

In this work we synthesized polymer liquid crystal containing photoreactive H-bonded mesogenic unit of 4-(6-hydroxyhexyloxy) cinnamic acid (6CA), and luminescent unit of 2,7-bis[2-(4-hydroxyphenyl)-2-cyanovinyl]-9,9-dihexyl-9H-fluorene (CN-DHFP) groups, which yields the cooperative molecular reorientation and exhibits polarized emission due to the alignment of CN-DHFP group.

EXPERIMENTAL

Materials

The chemical structure of copolymer is shown in Figure 1. Methacrylate monomers comprising of 6CA and CN-DHFP groups were synthesized according to the literature [10–12]. The radical polymerization was carried out using AIBN as an inhibitor in THF solution at 55°C for one day. The reaction mixture was poured into diethyl ether and the solid was filtered out, washed and dried. The yield was 56 wt%.

Characterization

Thin films of the copolymer were prepared by spin-coating from a solution of the copolymer in THF onto quartz substrate. The films were stored at room temperature for one day. The irradiation was carried out using LPUV light with an intensity of 10 mW/cm^2 at 365 nm. After irradiation, films were annealed at elevated temperature for 10 min. The optical anisotropy of the film was measured by polarization UV-vis spectroscopy. The in-plane order parameter

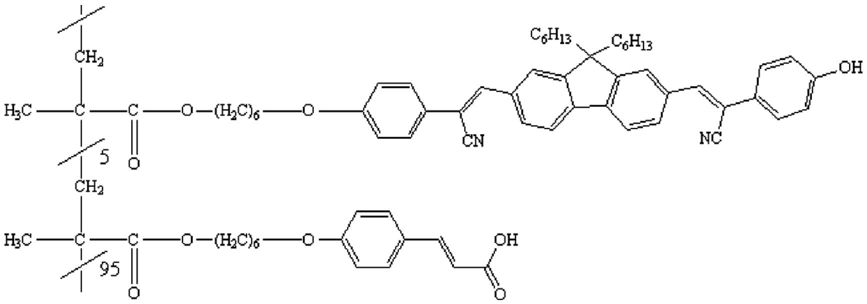


FIGURE 1 The chemical structure of copolymer.

S was calculated from the measured absorbance parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the electric field vector (**E**) of the LPUV light (Eq. (1)). A_{large} is the larger value of $A_{\parallel}$ and $A_{\perp}$, and A_{small} is the smaller one.

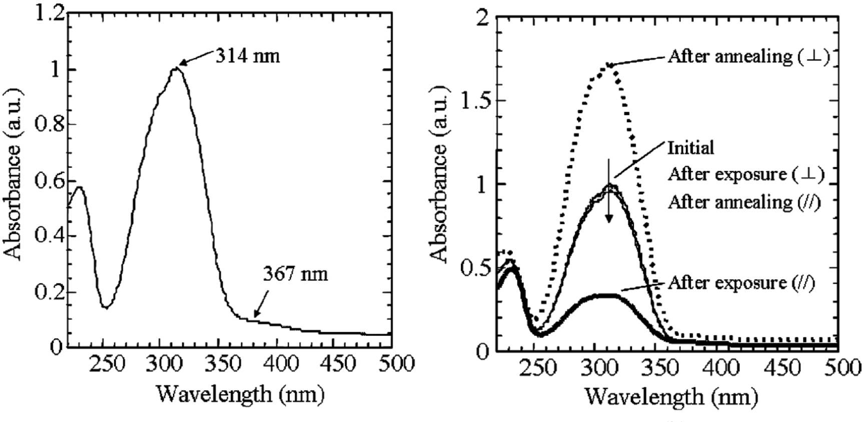
$$S = \frac{A_{\parallel} - A_{\perp}}{A_{large} + 2A_{small}} \tag{1}$$

The polarization ratio R was calculated by fluorescence intensity parallel ($I_{\parallel}$) over intensity perpendicular ($I_{\perp}$) to molecular alignment (Eq. (2)).

$$R = \frac{I_{\perp}}{I_{\parallel}} \tag{2}$$

RESULTS AND DISCUSSION

The synthesized copolymer exhibits LC phase when the comonomer comprising of CN-DHFP is 20 mol% and below because it dose not show LC nature. Therefore, the copolymer containing 95 mol% of comonomer comprising of 6CA group exhibits a nematic LC phase between 130 and 175°. The absorption spectrum of the copolymer film, which was prepared by spin-coating onto quartz plate from the copolymer solution in THF, is shown Figure 2a.



(a) (b)

FIGURE 2 (a) UV-vis absorption spectrum and (b) polarized UV-vis absorption spectra of copolymer film before irradiation, after irradiation (thin lines) with 10 mJ/cm^2 doses of LPUV light, and after subsequent annealing (thick lines) at 150°C for 10 min.

The copolymer exhibit absorption spectrum with a maximum peak at 314 nm attributed to $\pi-\pi^*$ transition of the cinnamic acid and a band at 367 nm due to the $\pi-\pi^*$ transition of fluorene unit. Irradiation of a polymer containing cinnamic acid with LPUV light leads to negative optical anisotropy ($\Delta A = A_{||} - A_{\perp} < 0$), as a result of axis-selective [2 + 2] photodimerization. Figure 2b shows the changes in the polarization UV-vis spectra of a copolymer film irradiated with 7 mJ/cm^2 doses of LPUV light and after subsequently annealed at the 150°C for 10 min. The degree of the photoreaction is approximately 3 mol%. Exposure to LPUV light generates a small negative ΔA due to the axis-selective photoreaction. An enhancement of the negative ΔA is induced by the annealing process and the generated in-plane order parameter S at 314 nm is amplified from -0.001 to -0.57. It is reported the mechanism of the thermally enhanced molecular reorientation of the photoinduced ΔA of 6CA group [9]. Similar to the homopolymer, cooperative molecular reorientation of the CN-DHFP groups occurs. Figure 3 shows the thermally enhanced S as a function of exposure energy. The thermally enhanced reorientation direction of mesogenic group is perpendicular to **E** of LPUV light.

Figure 4 shows polarized PL emission spectra of an aligned copolymer film. The emission of perpendicular direction is obviously higher than that of parallel direction by the alignment of mesogenic groups. This result indicates that the cooperative reorientation of both H-bond mesogenic groups and CN-DHFP side groups. The maximum emission

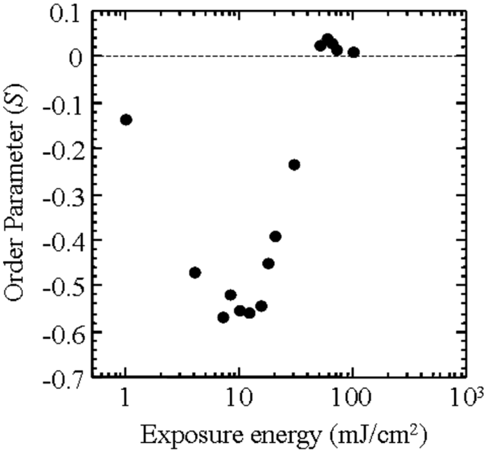


FIGURE 3 Change in in-plane order parameter S of copolymer film.

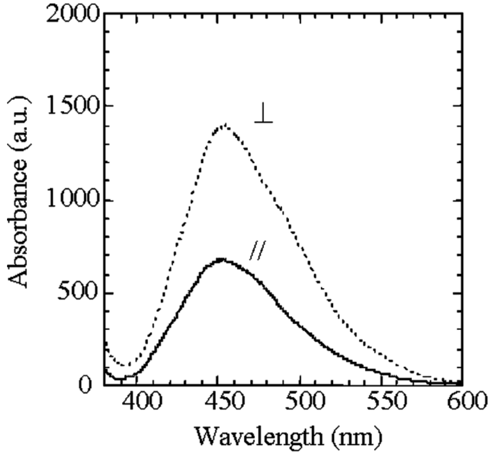


FIGURE 4 Polarized PL spectra ($\lambda_{ex} = 367\,nm$) of copolymer film.

peak is at 451 nm, which corresponds to blue light. The polarization ratio R shows 2.0 at 451 nm.

CONCLUSIONS

Methacrylate copolymer containing photoreactive H-bonded mesogenic 4-(6-hydroxyhexyloxy)cinnamic acid (6CA) and luminescent 2,7-bis[2-(4-hydroxyphenyl)-2-cyanovinyl]-9,9-dihexyl-9H-fluorene (CN-DHFP) side groups was synthesized and characterized. The irradiation with LPUV light causes a small negative ΔA in the copolymer film, which could be amplified by annealing process. The thermally enhanced reorientation direction of mesogenic group is perpendicular to **E** of LPUV light.

The polarized PL emission spectra were obtained by the alignment of 6CA unit. The CN-DHFP emits a blue light with polarization ratio of 2.0. This result indicates the cooperative reorientation of both 6CA and CN-DHFP side groups.

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