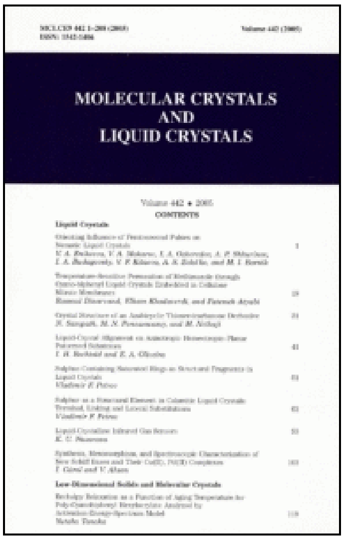

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Polarized Light Emission in a Liquid Crystalline Copolymer Film Comprised of Fluorenevinylene and Photo-Cross-Linkable Mesogenic Side Groups

Jeonghwan Lee[a]; Shigeru Matsuda[a]; Nobuhiro Kawatsuki[a]
[a] Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Shosha, Himeji, Japan

First published on: 12 November 2010

To cite this Article Lee, Jeonghwan , Matsuda, Shigeru and Kawatsuki, Nobuhiro(2010) 'Polarized Light Emission in a Liquid Crystalline Copolymer Film Comprised of Fluorenevinylene and Photo-Cross-Linkable Mesogenic Side Groups', Molecular Crystals and Liquid Crystals, 529: 1, 20 — 24

To link to this Article: DOI: 10.1080/15421406.2010.495653

URL: http://dx.doi.org/10.1080/15421406.2010.495653

Mol. Cryst. Liq. Cryst., Vol. 529: pp. 20–24, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495653

Taylor & Francis
Taylor & Francis Group

Polarized Light Emission in a Liquid Crystalline Copolymer Film Comprised of Fluorenevinylene and Photo-Cross-Linkable Mesogenic Side Groups

JEONGHWAN LEE, SHIGERU MATSUDA, AND NOBUHIRO KAWATSUKI

Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Shosha, Himeji, Japan

*A polymethacrylate copolymer comprised of light-emissive cyano-substituted dihexylfluorenevinylene (CN-DHFV) side groups and photo-cross-linkable 4-(4-methoxycinnamoyloxy)biphenyl (MCB) mesogenic side groups was synthesized and characterized. Irradiating a thin copolymer film with linearly polarized ultraviolet (LPUV) light and subsequent annealing generated a cooperative molecular reorientation of both side groups parallel to the polarization (**E**) of LPUV light. The resulting reoriented film showed a polarized light emission of the CN-DHFV groups with a polarization ratio of 5.6.*

Keywords Photoinduced reorientation; polarized light emission; polymer liquid crystal

Introduction

Polarized light emission has received much attention because it may be applicable to a backlight system in liquid crystal displays (LCDs) and polarized electroluminescent (EL) devices [1]. To obtain polarized light from light-emitting materials, uniaxial in-plane molecular orientation is required. Several reports on light-emitting materials have demonstrated molecular alignment, which was obtained by stretching [2], friction transfer [3], Langmuir-Blodgett deposition [1], and by employing mechanically or optically rubbed alignment layers [4–6]. Another technique to achieve molecular orientation is a photoinduced molecular reorientation of light emitting materials based on an axis-selective photoreaction using polarized light irradiation [7]. We have conducted a systematic study on photo-cross-linkable liquid crystalline polymers (PLCPs) terminated with cinnamate derivatives to generate a large photoinduced molecular reorientation [8], and found that copolymerization with comonomers possessing functional side groups generates cooperative molecular reorientation. This cooperative reorientation is the basis for the molecular

---

Address correspondence to Nobuhiro Kawatsuki, Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji 671-2201, Japan. Tel.: +81-792-67-4886; Fax: +81-792-67-4885; E-mail: kawatuki@eng.u-hyogo.ac.jp

reorientation in these light-emitting materials. A few studies have demonstrated polarized light emission from light-emitting copolymer films [7,9].

Meanwhile, numerous types of polyfluorene derivatives (PFs) have been extensively investigated as emitting materials due to their high photoluminescence quantum yields as well as their chemical and thermal stabilities [10]. Several types of oriented PFs have been obtained using main-chain type polymeric films and a rubbed layer [11]. We previously reported the photoinduced orientation in copolymers with PFs as side groups, but the reorientational order of the PF groups was low [9]. In this paper, to obtain polarized light emission of photo-addressable PF-containing materials, a new polymethacrylate liquid-crystalline copolymer with cyano-substituted dihexylfluorenevinylene (CN-DHFV) side groups and photo-cross-linkable mesogenic side groups are synthesized and characterized. Finally, polarized light emission in the cooperatively reoriented copolymer film is demonstrated.

Experimental

Materials

Figure 1 shows the chemical structure of a copolymer **P1** used in this study. The CN-DHFV side group, which had a CN-substituted fluorenevinylene unit sandwiched between the phenylene units, was designed to achieve blue light emission [9,10a]. Copolymer **P1** was synthesized using methacrylate monomers comprised of a 4-(4-methoxy-cinnamoyloxy)biphenyl (MCB) mesogenic side group [12] and a CN-DHFV side group [9]. Number and weight molecular weight of **P1** were 15,400 and 28,400, respectively.

Photoirradiation

Thin films were prepared by spin-coating a chloroform solution of copolymers (1.4 wt/wt-%) onto a quartz substrate. The film thickness was approximately 0.2 μm. The film was irradiated by light from a 250 W high-pressure Hg-UV lamp that was passed through Glan-Taylor polarizing prisms with a cut-off filter below 290 nm. The light intensity was 10 mW/cm^2 at 365 nm. Degree of the photoreaction (DP) was estimated by monitoring an absorption band at 314 nm (MCB groups) of the UV spectra. For the thermally enhanced molecular reorientation, the irradiated

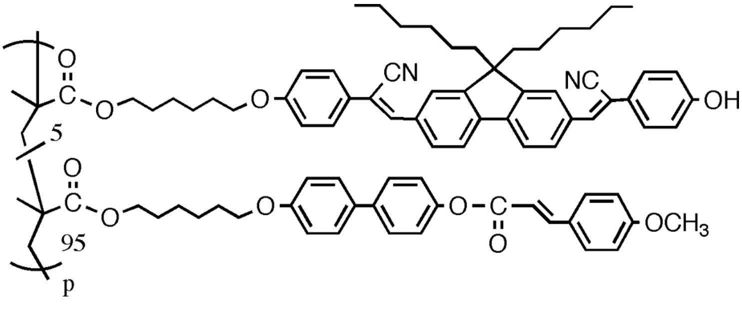

Figure 1. Chemical structure of copolymers used in this study.

film was annealed at elevated temperatures for 10 min. The generated optical anisotropy of the film was measured by polarizing microscopy and polarization UV-vis spectroscopy.

Characterization

Thermal properties were examined using a polarization optical microscope (POM) and a differential scanning calorimetry (DSC) analyzer. Polarization UV-vis spectra were measured using a spectrometer equipped with Glan-Taylor polarizing prisms. The in-plane order parameter, *S*, is expressed in the form of Eq. (1);

$$S = \frac{A_{\|} - A_{\perp}}{A_{\|} + 2A_{\perp}}, \tag{1}$$

where $A_{\|}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to **E**, respectively. *S* was calculated by polarized UV-vis spectroscopy using wavelength of 314 nm (MCB groups). Polarization photoluminescence (PL) spectra were measured using a spectrometer equipped with polarizers.

Results and Discussion

Copolymer **P1** was synthesized by free radical copolymerization, and it revealed a nematic LC phase between 92°C and 261°C. Figure 2 shows the UV-vis absorption and PL spectra of **P1** in a chloroform solution and a thin film. As shown in the figure, the π–π^* transition of the MCB side groups occurred at 292 nm in solution, whereas this transition occurred at 313 nm in the film due to the partial aggregation of the MCB side groups in the solid state. The absorption of CN-DHFV ($\lambda_{max} = 325$ nm in solution) groups was overlapped with the MCB side groups. The PL spectra ($\lambda_{excitation} = 367$ nm) of **P1** in solution and in solid state were similar, and λ_{max} was obtained at 450 nm, indicating aggregation and internal charge transfer of the CN-DHFV side groups did not occur in the solid state.

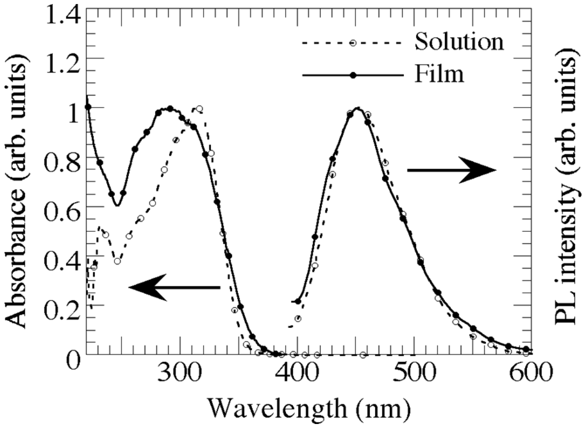

Figure 2. UV-vis absorption and photoluminescence (PL) spectra of **P1** in chloroform solution (dotted lines) and thin film (solid lines).

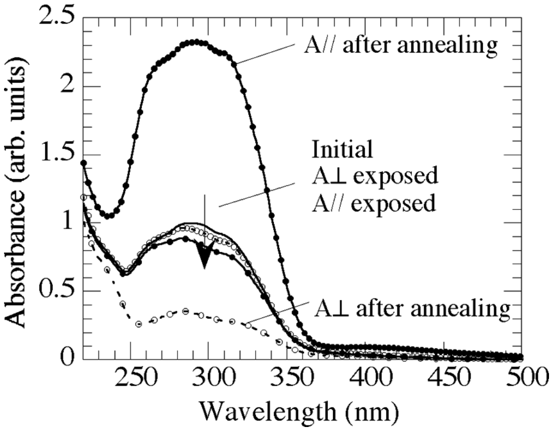

Figure 3. Polarization UV-vis spectra of copolymer **P1** film before and after irradiation for 1.5 J/cm^2, and after subsequent annealing at 150°C for 10 min.

The cooperative molecular reorientation of the CN-DHFV groups was performed based on the axis-selective photoreaction of the MCB side groups and subsequent thermally generated self-organization [12]. Figure 3 shows changes in the polarization UV-vis spectra of a **P1** film before exposure, after irradiating with linearly polarized ultraviolet (LPUV) light with a dose of 1.5 Jcm^{-2}, and subsequent annealing at 150°C for 10 min. In this case, the initial degree of photoreaction of the MCB side groups was approximately 7 mol%. Exposure to LPUV light generated a small negative optical anisotropy ($\Delta A = A_{\parallel} - A_{\perp} < 0$, where $A_{\parallel}$ is the absorption parallel to the polarization, **E**, of LPUV light, while $A_{\perp}$ is the perpendicular to **E**) due to the axis-selective photoreaction of the cinnamate moieties. However, the annealing procedure reversely enhanced ΔA parallel to **E** because the photoreacted MCB groups acted as photo-cross-linked anchors to thermally reorient the remaining side groups parallel to **E** [12]. The thermally enhanced order parameter, *S*, at 314 nm was 0.66, and the mesogenic groups mainly aligned along the in-plane

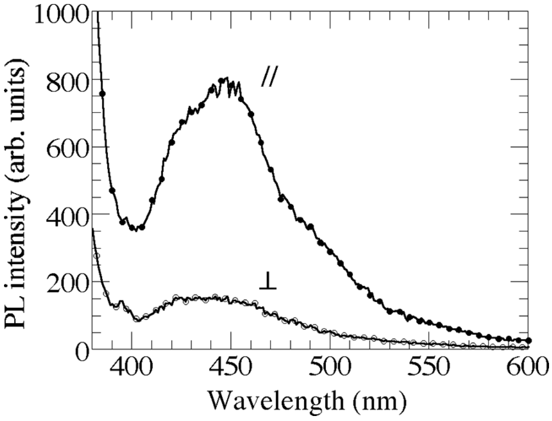

Figure 4. PL spectrum of reoriented **P1** film ($\lambda_{\text{excitation}} = 367$ nm).

direction because the sum of the absorbances ($A_{\parallel} + A_{\perp}$) after reorientation was larger than that before irradiation.

Figure 4 shows the polarized PL spectra of the reoriented **P1** film. It shows that the CN-DHFV moiety emitted in the blue region with a maximum peak at 450 nm, and the emission parallel to **E** of LPUV light was greater than that perpendicular with the polarization ratio of 5.6. This indicates that the CN-DHFV groups cooperatively reorient parallel to **E** of LPUV light, and shows the polarized light emission. Additionally, a primitive EL device, which comprised an oriented **P1** film (thickness = 100 nm) coated on ITO-glass substrate with Al top layer revealed a blue light emission. Further studies on the influence of the copolymer composition on the optical properties, and the fabrication of the EL devices to improve the emission performance are under investigation.

References

[1] Grell, M., & Bradley, D. D. C. (1999). *Adv. Mater.*, *11*, 895.

[2] He, B., Li, J., Bo, Z., & Huang, Y. (2005). *Macromolecules*, *38*, 6762.

[3] (a) Mori, A., Shikuma, J., Kinoshita, M., Ikeda, T., Misaki, M., Ueda, Y., Komura, M., Asaoka, S., & Iyoda, T. (2008). *Chem. Lett.*, *37*, 272; (b) Misaki, M., Ueda, Y., Nagamatsu, S., Yoshida, Y., Tanigaki, N., & Yase, K. (2004). *Macromolecules*, *37*, 6926.

[4] Grell, M., Knoll, W., Lupo, D., Meisel, A., Miteva, T., Neher, D., Nothofer, H.-G., Scherf, U., & Yasuda, A. (1999). *Adv. Mater.*, *11*, 671.

[5] (a) Sainova, D., Zen, A., Nothofer, H.-G., Asawapirom, U., Scherf, U., Hagen, R., Bieringer, T., Kostromine, S., & Neher, D. (2002). *Adv. Funct. Mater.*, *12*, 49; (b) Contoret, A. E. A., Farrar, S. R., Jackson, P. O., Khan, S. M., May, L., O'Neill, M., Nicholls, J. E., Kelly, S. M., & Richards, G. J. (2000). *Adv. Mater.*, *12*, 971.

[6] Sakamoto, K., Miki, K., Misaki, M., Sakaguchi, K., Chikamatsu, M., & Azumi, R. (2007). *Appl. Phys. Lett.*, *91*, 183509.

[7] (a) Rosenhauer, R., Fisher, Th., Stumpe, J., Giménez, R., Serrano, J. L., Vinuales, A., & Boer, D. (2005). *Macromolecules*, *39*, 2213; (b) Rosenhauer, R., Stumpe, J., Gimenez, R., Pinol, M., Serrano, J. L., & Vinnuales, A. (2007). *Macromol. Rapid Commun.*, *28*, 93.

[8] Kawatsuki, N., & Ono, H. (2008). Photo-induced reorientation of photo-cross-linkable polymer liquid crystals and applications to highly functionalized optical devices. In: *Handbook of Organic Electronics and Photonics*, Nalwa, H. S. (Ed.), American Scientific Publishers: CA, Ch. 20, Vol. 2, 301.

[9] Lee, J. H., & Kawatsuki, N. (2009). *Mol. Cryst. Liq. Cryst.*, *498*, 59.

[10] (a) Jin, Y., Ju, J., Kim, J., Lee, S., Kim, J. Y., Park, S. H., Son, S., Jin, S., Lee, K., & Suh, H. (2003). *Macromolecules*, *36*, 6970; (b) Jiang, G., Wu, J., Yao, B., Geng, Y., Cheng, Y., Xie, Z., Wang, L., Jing, X., & Wang, F. (2006). *Macromolecules*, *39*, 7950; (c) Taranekar, P., Abdulbaki, M., Krishnamoorti, R., Phanichphant, S., Waenkaew, P., Patton, D., Fulghum, T., & Advincula, R. (2006). *Macromolecules*, *39*, 3848.

[11] Sirringhaus, H., Wilson, R. J., Friend, R. H., Inbasekaran, M., Wu, W., Woo, E. P., Grell, M., & Bradley, D. D. C. (2000). *Appl. Phys. Lett.*, *77*, 406.

[12] Kawatsuki, N., Goto, K., Kawakami, K., & Yamamoto, T. (2002). *Macromolecules*, *35*, 706.