

This article was downloaded by: [Siauliu University Library]

On: 17 February 2013, At: 00:34

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Synthesis of Side-Chain Liquid-Crystalline Cinnamide Polymers Based on Post Polymer Reaction

Mizuho Kondo^a, Yoshiyuki Dozono^a, Kohei Goto^a & Nobuhiro Kawatsuki^a

^a Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha Himeji, Hyogo, 671-2280, Japan

Version of record first published: 02 Aug 2012.

To cite this article: Mizuho Kondo, Yoshiyuki Dozono, Kohei Goto & Nobuhiro Kawatsuki (2012): Synthesis of Side-Chain Liquid-Crystalline Cinnamide Polymers Based on Post Polymer Reaction, *Molecular Crystals and Liquid Crystals*, 563:1, 121-130

To link to this article: <http://dx.doi.org/10.1080/15421406.2012.689142>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis of Side-Chain Liquid-Crystalline Cinnamide Polymers Based on Post Polymer Reaction

MIZUHO KONDO,* YOSHIYUKI DOZONO, KOHEI GOTO,
AND NOBUHIRO KAWATSUKI

Department of Materials Science and Chemistry, Graduate School of
Engineering, University of Hyogo, 2167 Shosha Himeji, Hyogo 671-2280, Japan

We prepared novel photoreactive liquid crystalline (LC) polymer via polymer reaction. The cinnamic acid activated ester easily converted to amide by mixing with amine derivative and solubility of the polymer reduced due to hydrogen bonding. Upon exposure to linearly polarized ultraviolet light and subsequent annealing, the LC cinnamide exhibited axis selective photoreaction and following thermally amplification of molecular alignment. However, photoreactivity, LC stability and thermal amplification behavior of the cinnamide group were lower than that of original cinnamic acid group, suggesting that the lateral hydrogen bonding disturbs molecular reorientation behavior.

Keywords Axis selective photoreaction; polymer reaction; hydrogen bonding; cinnamide

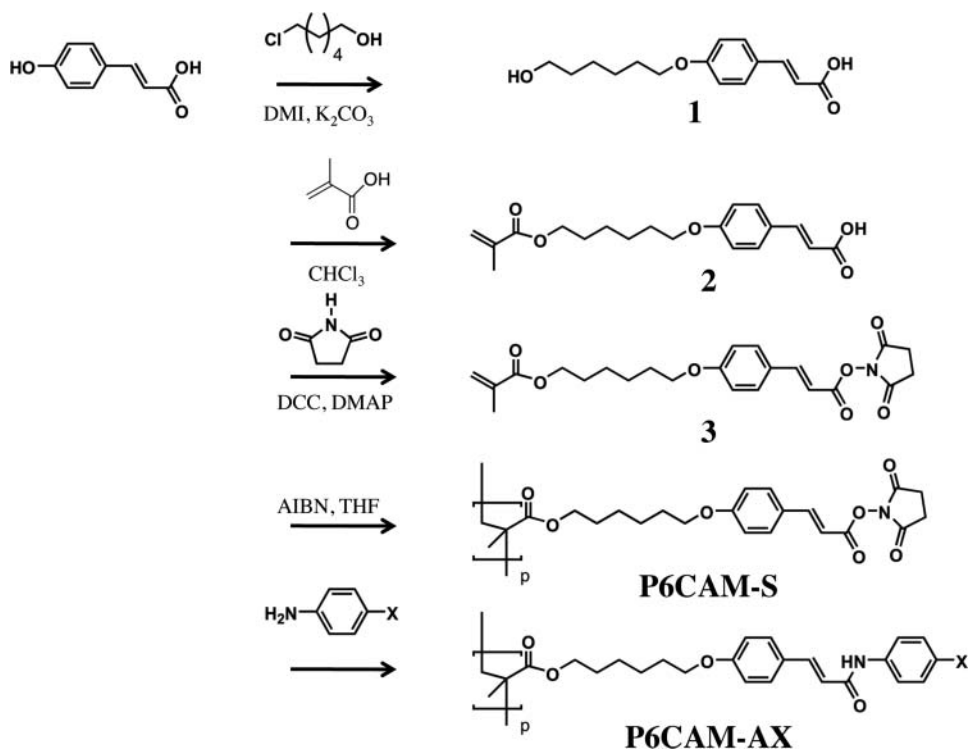
Introduction

Introducing low molecular weight (LMW) functional materials into simple polymer via polymer reaction or noncovalent bonding is a useful method because it can add electrical [1], optical [2,3], and photomechanical [4] functions originated from LMW materials. We have previously studied on enhancement of processibility of π -conjugated LMW combined with photoreactive polymer liquid crystal (PLCP) materials [5,6] and reported that fuluorene derivatives can be aligned along the director of PLCP film by using LC property [5] or hydrogen bonding [6]. PLCPs induce a large photoinduced molecular reorientation when a thin film of them is exposed to linearly polarized UV (LPUV) light and subsequent annealing. PLCPs also change their crosslinking density, acidity and dielectric properties just by tuning the polarization direction and exposing time of the actinic beam. In this work, we focused on activated ester to enhance the reactivity and thermal stability for polymer functionalization. It can be connected to carboxylic molecular terminal and we can functionalize PLCP by LMW compounds containing amine at molecular terminal because it convert to amide bonding by using amine compounds under a mild condition. We synthesized PLCP containing activated ester at molecular terminal and explored their functionalization with primal phenyl amine derivatives and photoresponsive behavior.

*Address correspondence to Assistant Prof. Mizuho Kondo, Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167, Shosha Hi, meji, Hyogo 671-2280, Japan. Tel: (+81)79-267-4014. Fax: (+81)79-267-4014. E-mail: mizuho-k@eng.u-hyogo.ac.jp

Experimental

Figure 1 shows chemical structure of the polymers used in this study. We used phenyl amine to evaluate the effect of liquid crystal property on axis-selective photoreaction of cinnamide group. Synthetic route of the cinnamide polymers are described in Scheme 1. The photoreactive cinnamide was prepared from activated photoreactive polymer ester (**P6CAM-S**) and mixed with various liquid amines to convert to cinnamide derivatives (**P6CAM-A1, A2**). The cinnamic acid polymer (**P6CAM**) was synthesized according to the literature as a reference [7].



Scheme 1. Synthetic route for cinnamide polymers.

4-(6-Hydroxyhexyloxy) cinnamic Acid (**1**)

A mixture of trans-p-coumaric acid (25.0 g, 0.15 mol) and 6-chloro-1-hexanol (52 g, 0.38 mol) was dissolved in 25 g of N,N-dimethylimidazolidinone, potassium carbonate (25 g, 0.18 mol) and a trace amount of potassium iodide were added to the solution. The resulting solution was heated at 130°C for 17 h. After the reaction mixture was cooled to 70°C, 40 ml of water, 30 g (0.53 mol) of potassium hydroxide and 40 ml of methanol was added to the mixture and reflux for 1 h. The resultant solution was cooled to room temperature. After concentrated aqueous hydrochloric acid solution was added to the reaction mixture to give pH 3, the precipitated solid was collected and washed with water. The crude product was recrystallized from a mixture of n-hexane and tetrahydrofane (THF) to give **1** (6.8 g, 22 mmol) in 47 % yield.

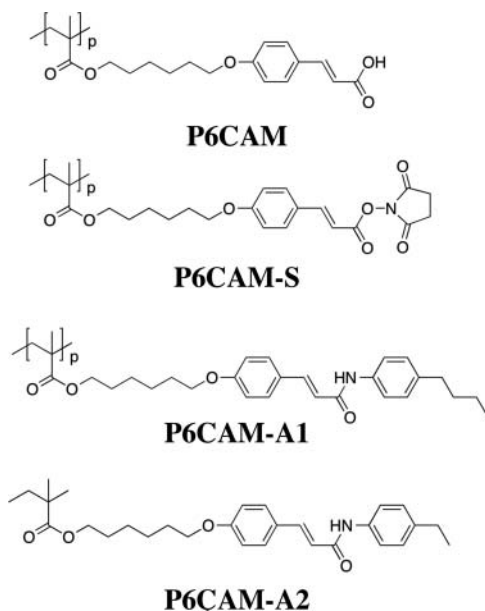


Figure 1. Chemical structure of polymers used in this study.

$^1\text{H-NMR}$ (DMSO): δ (ppm) 1.34–1.36 (d, $J = 6.6$ Hz, 3H), 1.40–1.46 (m, 5H), 1.70–1.73 (t, $J = 7.3$ Hz, 3H), 4.01 (s, 2H), 4.38 (s, 1H), 6.36–6.39 (d, $J = 16$ Hz, 1H), 6.95–6.97 (d, $J = 8.8$ Hz, 2H), 7.53–7.56 (d, $J = 16$ Hz, 1H), 7.62–7.63 (d, $J = 8.8$ Hz, 2H)

4-(6-Methacryloyloxy-1-hexyloxy)-cinnamic Acid (2)

14 g (50 mmol) of **1** and 4.3 g (40 mmol) of p-toluene sulfonic acid was dispersed in a mixture of 5 ml of chloroform and 5.2 g of methacrylic acid (38 mmol). The mixture was reflux at 85°C for 4 h. After the resulting solution was cooled down to room temperature, 40 ml of diethyl ether was added and washed with water for 20 times. After the solvent was removed, a yellow solid obtained was purified by column chromatography on silica gel (chloroform) and recrystallized from ethyl acetate and methanol to give **2** (3.2 g, 6.6 mmol) in 19 %.

$^1\text{H-NMR}$ (DMSO): δ (ppm) 1.40–1.45 (m, 4H), 1.63–1.66 (m, 2H), 1.72–1.74 (m, 2H), 1.89 (s, 3H), 4.01 (s, 2H), 4.10 (s, 2H), 5.66–5.67 (t, $J = 1.6$ Hz, 1H), 6.02 (s, 1H), 6.36–6.39 (d, $J = 16$ Hz, 1H), 6.95–6.97 (d, $J = 8.8$ Hz, 2H), 7.52–7.56 (d, $J = 16$ Hz, 1H), 7.61–7.63 (d, $J = 8.7$ Hz, 2H)

4-(6-Methacryloyloxy-1-hexyloxy)-cinnamic Acid N-Succinimide (3)

2.0 g (6.0 mmol) of **2**, 0.83 g (7.2 mmol) of N-hydroxysuccinimide, trace amount of 4-dimethylaminopyridine (DMAP), and 1.5 g (7.2 mmol) of dicyclohexyl carbodiimide (DCC) was put in 100 ml flask. Then, 40 mL of dried THF was slowly added. The reaction mixture was kept under stirring at room temperature for 19 h. The precipitate formed during the reaction was filtered off and the organic solution was washed with water.

The mixture was dried over sodium sulfate and evaporated under vacuum. The crude product was purified by silica gel column chromatography (ethyl acetate: *n*-hexane = 7:3) and finally recrystallized from *n*-hexane/THF to give **3** (1.3 g, 0.22 mmol) in 50 % yield.

¹H-NMR (CDCl₃): δ(ppm) 1.49–1.56 (m, 4H), 1.63 (s, 2H), 1.73–1.76 (t, *J* = 7.2 Hz 2H), 1.83–1.86 (t, *J* = 7.3 Hz 3H), 1.96 (s, 4H), 2.91 (s, 4H), 4.03 (s, 2H), 4.18 (s, 2H), 5.57(s, 1H), 6.12 (s, 1H), 6.45–6.48 (d, *J* = 16 Hz, 1H), 6.93–6.94 (d, *J* = 8.7 Hz, 2H), 7.53–7.54 (d, *J* = 8.7 Hz, 2H), 7.89–7.91 (d, *J* = 16 Hz, 1H).

Polymerization of **3**

0.8 g (1.9 mol) of **3** and 3.6 mg (0.022 mol) of AIBN were dissolved in chloroform and placed in a polymerization tube. The tube was sealed under nitrogen atmosphere after bubbling with nitrogen for 40 min. Then, the tube was kept at 60°C for 24 h. The resulting solution was cooled to room temperature and poured into diethylether with vigorously stirring to precipitate the polymer. The polymer obtained was purified by repeated reprecipitation from THF into a large excess of diethylether and dried under vacuum to yield 0.52 g of **P6CAM-S** in 65wt% conversion.

GPC (chloroform) : $M_n = 29,000$, $M_w/M_n = 3.7$

Polymer Functionalization

40 mg of **P6CAM-S** and 100mg of phenylamine was mixed at room temperature for 3 h and washed with aqueous hydrochloric acid.

Measurements

¹H-NMR spectra of synthesized compounds were taken on a Bruker DRX500. Thin films of cinnamic acid derivatives were prepared by spin-coating of polymer solutions onto a quartz substrate. The film was irradiated by UV-light from a 250 W high-pressure Hg-UV lamp (Ushio, spotcure UIS 20102) that was passed through Glan-Taylor polarizing prisms with a cut-off filter below 290 nm. The light intensity was about 150 mWcm² at 365 nm. After exposing, the film was annealed at elevated temperatures for 10 min. The optical anisotropy of the film was evaluated with polarizing microscope (POM: OLMPUS, BX-51P) and polarized absorption spectroscopy (Hitachi, U3010). Conversion of succinimide into amide terminal was confirmed with ¹H-NMR, FT-IR spectrometer (Jasco, FT/IR-410) and ATR FT-IR spectrometer (Jasco, FT-IR-480 plus). The thermodynamic properties of the polymers were analyzed using differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C) at heating and cooling rates of 10°C min⁻¹. The molecular weight of the polymer was determined by gel permeation chromatography (GPC; Sugai, U-620 column, Jasco UV-2075, RI-8020, TOSOH Gskgel 4000H, Gskgel α5000; eluent, chloroform) calibrated with standard polystyrenes.

Results and Discussion

Preparation of Cinnamide Group

In the previous work, Zhang *et al.* has been demonstrated a novel method for preparation of crosslinked liquid-crystalline polymers by using N-hydroxysuccinimide carboxylate, activated ester, that can react with primary amines easily under mild reaction conditions

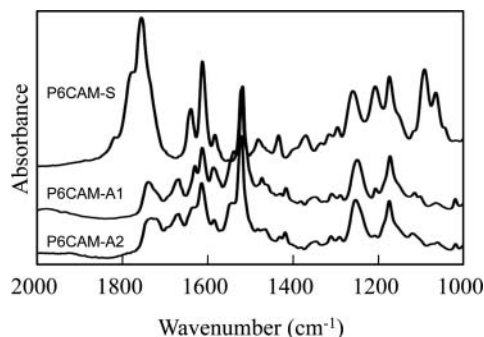


Figure 2. Change in IR spectrum of the activated ester by adding amine derivatives.

[8]. In this work, we applied the activated ester structure for PLCP. Figure 2 shows IR spectra of the **P6CAM-S**, **P6CAM-A1** and **P6CAM-A2** respectively. It is clearly observed that peak around 1739 cm^{-1} for FT-IR spectrometry originating from imide group was reduced and $1700\text{--}1650\text{ cm}^{-1}$ was increased after the reaction. Moreover, the phenyl cinnamide group showed low solubility for chloroform, which can dissolve **P6CAM-S**, indicating that the activated ester converted amide group effectively in a polymer state. Figure 3 shows DSC thermogram of the compounds. **P6CAM** and **P6CAM-A1** showed LC phase while the others showed no mesophase at relevant temperature. In addition, no obvious peak of glass transition was found in **P6CAM-A1** due to strong hydrogen bonding though it became viscous when they were heated above 100°C . Figure 4 displays absorption spectrum of the cinnamic acid derivatives used in this study. The absorbance was normalized in 314 nm , which was a peak of **P6CAM**. It was found that the peak red shifted for the succinimide group while it blue shifted for amide group.

Photoreactivity of the Cinnamide Group

It was known that irradiating a copolymer film with LPUV light induced an axis-selective [2+2] photodimerization reaction of the cinnamic acid groups. Additionally, irradiating a cinnamate-containing polymeric film with LPUV light leads an axis-selective photoreaction, resulting in an induction of small negative optical anisotropy of the film. Change in absorption spectrum of **P6CAM-A1** film and change in absorbance at 320 nm and 280 nm was displayed in Figure 5. A peak around 320 nm reduced upon exposure with UV light, the

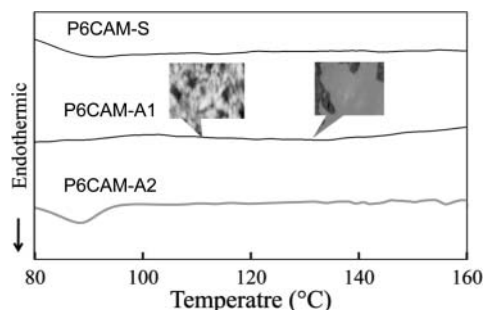


Figure 3. DSC thermogram of the polymers. The inset photograph represents the POM image of the **P6CAM-A1** at 110°C .

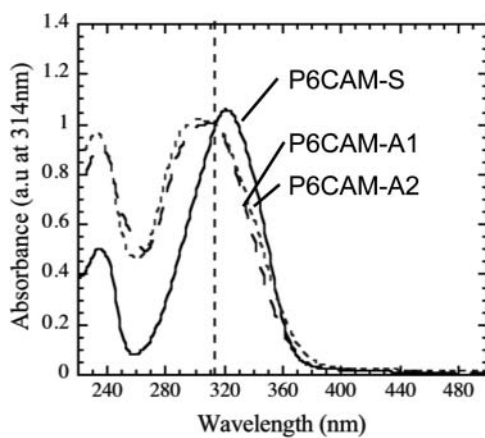


Figure 4. Absorption spectra of the polymer film on quartz substrate.

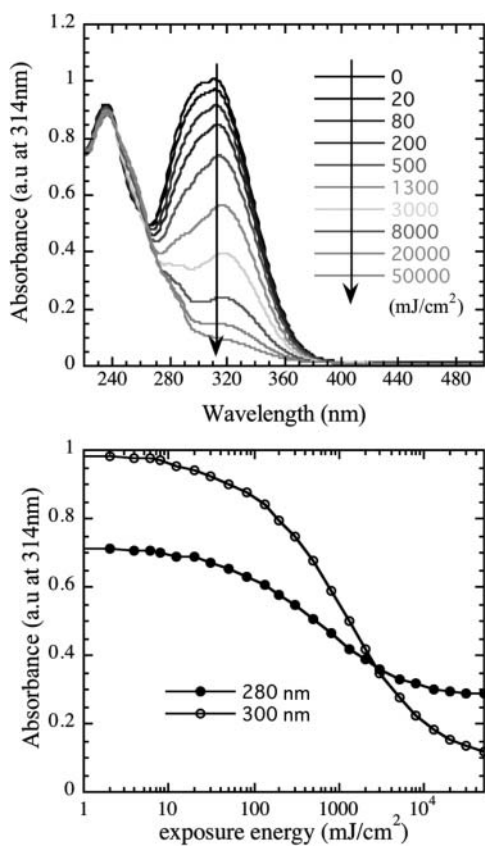


Figure 5. Change in Absorption spectrum of the **P6CAM-A1** film (a) and value of absorbance at 280 nm and 380 nm upon exposure with LPUV light (b).

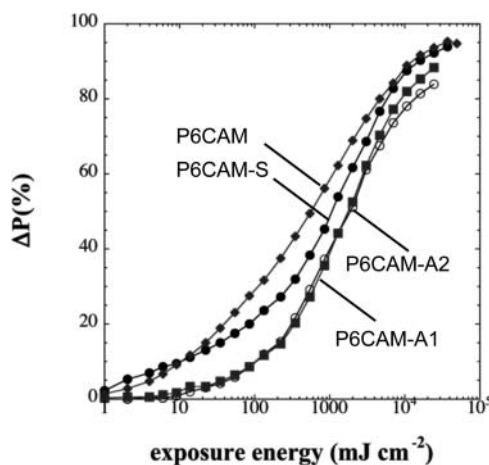


Figure 6. Change in degree of photoreaction of the polymers as a function of dosed energy.

increase in absorbance at longer region (≈ 300 nm) owing to photo-Fries rearrangement was not observed in the polymers [9]. We defined degree of photoreaction as following equation,

$$\Delta P = \frac{(A_{\parallel} + A_{\perp})_{\text{initial}} - (A_{\parallel} + A_{\perp})_{\text{exposure}}}{(A_{\parallel} + A_{\perp})_{\text{initial}}} \times 100 \quad (1)$$

where A_{\parallel} and A_{\perp} are the absorbance at 314 nm parallel and perpendicular to electric vector of linearly polarized light, respectively. Degree of the photoreaction of cinnamic acid films as a function of exposure doses is described in Fig. 6. It was found that the photoreaction of cinnamide groups use larger dose than that of **P6CAM** and **P6CAM-S** indicating that structure of molecular terminal strongly affected photoreactivity of PLCPs.

Figure 7 plots the photoinduced dichroism, $\Delta A = A_{\parallel} - A_{\perp}$, of cinnamic acid and their derivative films as a function of the exposure doses. All the films show a generation of a negative ΔA due to the axis-selective photoreaction though **P6CAM-S** showed small

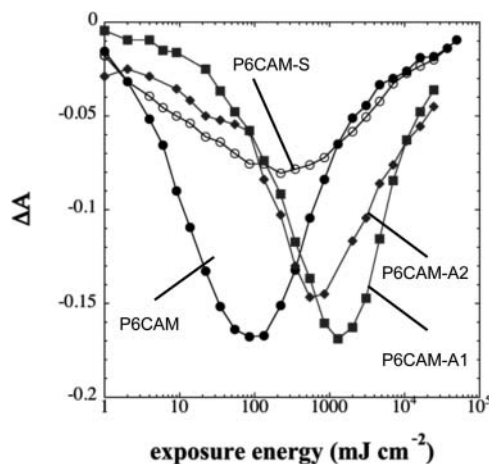


Figure 7. Change in photoinduced optical anisotropy of the polymers.

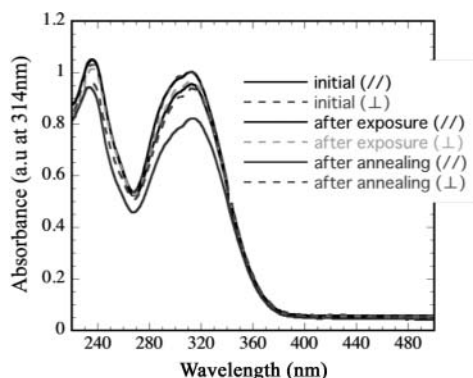


Figure 8. Polarized absorption spectrum of **P6CAM-A1** films before photoirradiation after photoirradiation and subsequent annealing.

dichoroism. It was well known that the annealing process enhanced the photoinduced optical anisotropy of cinnamic LC polymers. Figure 8 shows polarized absorption spectrum of PLCP films before and after photoirradiation and subsequent annealing. In this case, the degree of the photoreaction was fixed to 3% (30 mJcm^{-2}) that induces largest value for **P6CAM** under thermal amplification. It was found that the optical anisotropy between A_{\parallel} and A_{\perp} became larger on annealing. Additionally, the absorption of A_{\parallel} and A_{\perp} after annealing was smaller than that after exposure. These results indicate that the cooperative effect in **P6CAM-A1** is not large enough to reorient the mesogenic side group in the in-plane direction after the annealing procedure even it showed LC phase and containing hydrogen bonding.

The annealing temperature affects the efficiency of the thermal amplification of the molecular alignment of the film. The amplified molecular alignment is evaluated as following equation,

$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{small} + A_{large}} \quad (2)$$

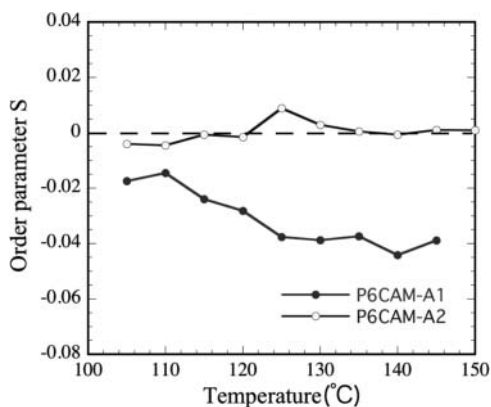


Figure 9. Thermally enhance in-plane order parameter of cinnamide film as a function of annealing temperature. The degree of photoreaction was fixed in 3%.

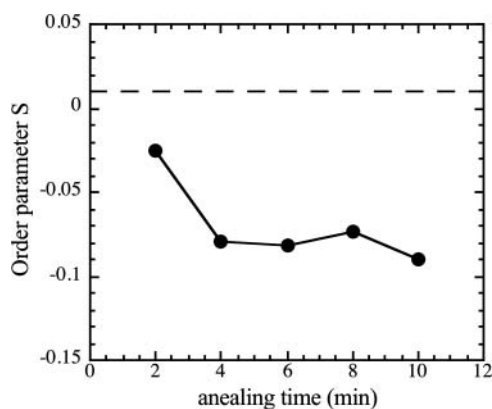


Figure 10. Thermally enhanced S values of **P6CAM-A1** film when the annealing time is varied.

and A_{large} is the larger value of A_{\parallel} and A_{\perp} , and A_{small} is the smaller one. Figure 9 represents the amplified S values of the **P6CAM-A1** and **A2**, when the exposed film is annealed at various temperatures. It is observed that the amplification occurred for **P6CAM-A1** films when the annealing temperature was between 130 and 150°C while **P6CAM-A2** showed no amplification. Although the amplification in **P6CAM-A1** film was induced when the film was heated over 4 minutes, we fixed the annealing time to unify the experimental condition to the previous work (Fig. 10). Additionally, the amplified value was smaller than that of, previous work, **P6CAM**. It can be presumed that the hydrogen bonding perpendicular to the director axis affects the reorientation behavior.

Finally, we dipped **P6CAM-S** film into liquid 4-alkylaniline whether cinnamide group directly convert from succinimide film. **P6CAM-S** showed a strong peak at 1739 cm^{-1} , originating from $\text{C}=\text{O}$ bond at succinic imide. On the other hand, the peak was erased and new broad peaks around 1700–1650 cm^{-1} was detected alternatively when the reaction proceeded similar to reaction in the powder state. These peaks are originating from phenylamide ring indicating that the imide group converted to amide group in a film state (Fig. 11).

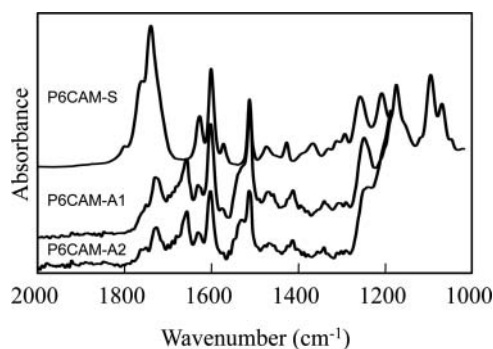


Figure 11. ATR-IR spectra of the **P6CAM-A1**, **A2** and **P6CAM-S** film.

Conclusions

We prepared novel photoreactive LC polymer via polymer reaction. The cinnamic acid activated ester easily converted to amide by mixing with amine derivative and solubility of the polymer reduced due to hydrogen bonding. Upon exposure to UV light and subsequent annealing, the LC cinnamide exhibited axis selective photoreaction and following thermally amplification of molecular alignment. However, photoreactivity, LC stability and thermal amplification behavior of the cinnamide group were lower than that of original cinnamic acid group, suggesting that the lateral hydrogen bonding disturbs molecular reorientation behavior.

Acknowledgment

The authors are grateful to Dr. Yusuke Daiko for important discussions. This work was supported in part by a Grant-in-Aid for scientific research in priority areas “new frontiers in photochromism” from the ministry of education culture sports science and technology and research grant from University of Hyogo.

References

- [1] Rancatore, B. J., Mauldin, C.E., Tung, S.-H., Wang, C., Hxemer, A., Strzalka, J., Fréchet, J. M. J., & Xu, T. (2010). *ACS Nano*, 4, 2721.
- [2] Kondo, M., Miyake, J., Tada, K., & Kawatsuki, N. (2011). *Chem. Lett.*, 40, 264.
- [3] Yaning G., He, Fang, H., Xi, L., Zhiqiang, Z., Wang, Z., & Wang, X. (2007). *Chem. Mater.*, 19, 3877.
- [4] He, J., Zhao, Y., & Zhao, Y. (2009). *Soft. Matter.*, 5, 308.
- [5] Kawatsuki, N., Ando, R., Ishida, R., Kondo, M., & Minami, Y. (2010). *Macromol. Chem. Phys.*, 211, 1741.
- [6] Kawatsuki, N., Hiraiwa, A., Tada, K., Kondo, M., & Ono, H. (2009). *Jpn. J. Appl. Phys.*, 48, 120208.
- [7] Uchida, E., & Kawatsuki, N., (2006). *Macromolecules*, 39, 9357.
- [8] X. Li, X., Wen, R., Zhang, Y., Zhu, L., Zhang, B., & Zhang, H. (2009). *J. Mater. Chem.*, 19, 236.
- [9] Kawatsuki, N., Neko, T., Kurita, M., Nishiyama, A., & Kondo, M. (2011). *Macromolecules*, 44, 5736.