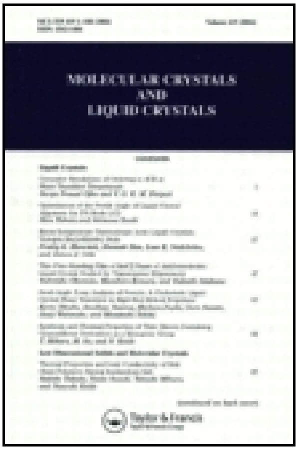

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photochemical Synthesis of a Main-Chain LC Oligomer from an α,ω-Dicinnamoyl-Functionalized LC Monomer: Photoirradiation in the Crystalline State

Hideyuki Kihara [a] & Nobuyuki Tamaoki [a]

[a] Molecular Smart System Group, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki, Japan

Version of record first published: 22 Sep 2010

To cite this article: Hideyuki Kihara & Nobuyuki Tamaoki (2007): Photochemical Synthesis of a Main-Chain LC Oligomer from an α,ω-Dicinnamoyl-Functionalized LC Monomer: Photoirradiation in the Crystalline State, Molecular Crystals and Liquid Crystals, 470:1, 31-37

To link to this article: http://dx.doi.org/10.1080/15421400701492507

Mol. Cryst. Liq. Cryst., Vol. 470, pp. 31–37, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701492507

Taylor & Francis
Taylor & Francis Group

Photochemical Synthesis of a Main-Chain LC Oligomer from an α,ω-Dicinnamoyl-Functionalized LC Monomer: Photoirradiation in the Crystalline State

Hideyuki Kihara
Nobuyuki Tamaoki
Molecular Smart System Group, Nanotechnology Research Institute,
National Institute of Advanced Industrial Science and Technology
(AIST), Ibaraki, Japan

An LC compound 1,4-bis[4-(6-cinnamoyloxyhexyloxy)benzoyloxy]benzene, **1**, *was synthesized, having cinnamoyl groups at the each end of the molecule, and was found to show polymorphism in the crystalline state. A rapid cooling from the isotropic melt of* **1** *to room temperature gave a K1 crystal, while annealing the mesophase of* **1** *at 95°C afforded a K2 crystal. UV irradiation (>300 nm) of both the K1 and K2 crystals at room temperature resulted in the formation of linear LC oligomers with cyclobutane rings in the main chain. ^{1}H NMR spectroscopy revealed that the cyclobutane units of the oligomer obtained from K1 assumed anti and syn head-to-head configurations, whereas those from K2 predominantly formed an anti head-to-tail structure.*

Keywords: cinnamoyl; liquid crystal; liquid-crystalline polymer; photocycloaddition; topochemistry

INTRODUCTION

LC polymer thin films, in which the mesogens are macroscopically aligned, are applied in a variety of materials such as actuators [1], optical compensation films for LCD [2], and so on. Such films usually have a side-chain LC polymer structure and are prepared by in situ polymerization of LC monomers, which show macroscopically-ordered mesophases before polymerization. We recently reported the in situ photopolymerization of an α, ω-dicinnamoyl-functionalized LC monomer **1**, whose structure is depicted in Figure 1, in its LC phase [3].

Address correspondence to Dr. Hideyuki Kihara, Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. E-mail: h-kihara@aist.go.jp

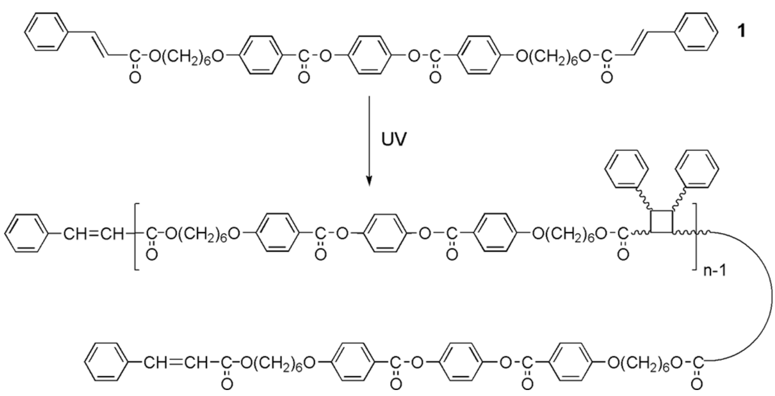

FIGURE 1 The chemical structures of LC compound **1** and the LC oligomer obtained by UV irradiation of **1** in the LC phase.

It was found that the cinnamoyl groups underwent [2 + 2] photocycloaddition intermolecularly, and consequently, the linearly-structured oligomer, which showed a thermally stable LC phase, was obtained. Furthermore, the cyclobutane units in the LC oligomer assumed *anti* and *syn* head-to-head configurations (Fig. 1).

On the other hand, bis(cinnamic acid) derivatives are well known because they have the possibility of being polymerized in the crystalline state via photocycloaddition reactions [4]. Such reactions are based on topochemical principles; therefore, the polymers obtained often have regio- and stereoregularity in the cyclobutane units.

Here, crystalline samples were prepared from **1** and irradiated with UV light in order to elucidate whether or not LC oligomers could be obtained, and if possible, whether or not the reactions are based on topochemistry.

EXPERIMENTAL

Preparation of the Crystalline Samples

The synthesis and properties of **1**, 1,4-bis[4-(6-cinnamoyloxyhexyloxy)-benzoyloxy]benzene, were described in a previous paper [3]. Phase transitions occurred on a cooling scan (I 115 N 83 K (°C)). Thin-layer crystalline samples of **1** were prepared by two different procedures as follows: For both, 2 mg of **1** was placed between glass plates and heated to an isotropic phase at 125°C. In one of the procedures, when the isotropic sample was rapidly cooled to room temperature, a crystal defined as **S1** soon formed (ca. 30 sec). In the other procedure, when the isotropic sample was slowly cooled to and kept at 95°C, a crystal defined as **S2** formed over a longer period of time (ca. 3 h).

Photoirradiation

The crystalline samples were irradiated with UV light (> 300 nm) at room temperature using a 500 W high-pressure mercury lamp. During the irradiation, the sample was turned upside down so that the total irradiation time was equal for both sides of the sample. After irradiation for a prescribed period of time, the sample was immersed in THF, and then a soluble fraction of the THF solution was analyzed with GPC, NMR, and POM.

Measurements

The thermal properties of the samples were evaluated by polarizing optical microscopy (POM) using an Olympus BH2 equipped with a Mettler FP82HT hot stage, and differential scanning calorimetry (DSC) using a Seiko Instruments Inc. DSC 6200. Gel permeation chromatograms (GPC) were recorded on a Shimadzu 10Avp system with Shodex KF800D and KF805L columns using THF as the eluent. ^{1}H NMR spectra were obtained on a Varian Gemini 300 MHz with $CDCl_3$ and TMS as the solvent and internal standard, respectively.

RESULTS AND DISCUSSION

POM images of the thin-layer crystal samples **S1** and **S2** are shown in Figure 2. There is a clear difference in the appearance of the two samples. They also exhibit a remarkable difference in melting behavior. Figure 3 shows DSC thermograms of **1** recorded during heating scans at a rate of 5°C/min. The three thermograms (a), (b) and (c) were

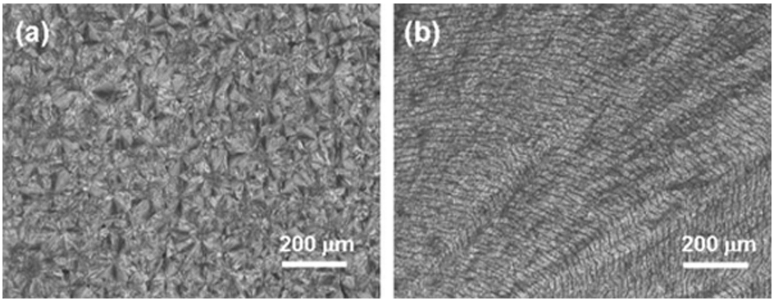

FIGURE 2 POM images of thin-layer crystal samples of **S1** (a) and **S2** (b) taken at room temperature.

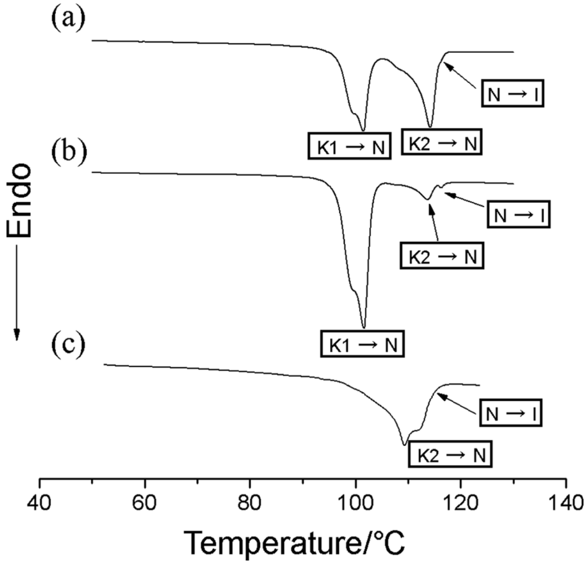

FIGURE 3 DSC thermograms of **1** recorded on heating scans at a rate of 5°C/min: (a) scanned after slow cooling (5°C/min) of **1** from 125°C to room temperature, (b) scanned after rapid cooling (20°C/min) of **1** from 125°C to room temperature and (c) scanned after slow cooling (5°C/min) of **1** from 125 to 95°C and annealing at 95°C for 3 h.

obtained using three different cooling conditions. Thermogram (a) was obtained after cooling of **1** from 125°C to room temperature at a rate of 5°C/min. In thermogram (a), two large endothermic peaks are observed at 101 and 114°C, which correspond to the melting points of two different crystals of **1**. The crystals are defined as K1 and K2, respectively. Thermogram (b) was recorded after rapid cooling (20°C/min) of **1** from 125°C to room temperature. This procedure was the same as that for the preparation of **S1**. In Figure 3(b), the one large endothermic peak corresponds to the melting of K1, and the small peak is associated with the melting of K2 at 102 and 114°C, respectively. Thermogram (c) was obtained after slow cooling (5°C/min) of **1** from 125 to 95°C and annealing at 95°C for 3 h. This process was consistent with that for the preparation of **S2**. In contrast to thermograms (a) and (b), only a large peak corresponding to the melting of K2 was observed at 110°C in thermogram (c). These results indicate that **1** shows polyphormism in the crystal state; that is, it has K1 and K2 crystal forms, and sample **S1** contains a large amount of K1 and a small amount of K2, whereas sample **S2** consists solely of K2.

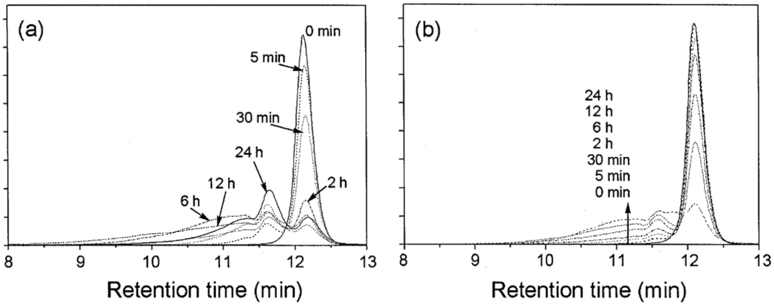

FIGURE 4 GPC charts of polymorphs of 1 (**S1** (a) and **S2** (b)) irradiated with UV light (>300 nm) at room temperature for various lengths of time.

Next, UV irradiation of crystalline samples **S1** and **S2** was carried out at room temperature. GPC charts of the irradiated samples are shown in Figure 4. Although the efficiency of the reaction was very low compared to photopolymerization in the mesophase in the presence of a sensitizer [3], the formation of oligomers in the crystalline phase was quite evident. This result contrasts remarkably with previous studies [5,6], in which LC monomers having two cinnamoyl groups were photopolymerized via cycloaddition in their mesophases, however, no photochemical reaction occurred in the crystalline state. In the photopolymerization of **S2** (Fig. 4(b)), the amount of the oligomer increases linearly as a function of irradiation time, whereas that of **S1** does not show a linear increase (Fig. 4(a)). This is probably because the **S1** preparation method, containing both K1 and K2 crystals, lacks reproducibility.

In order to investigate the stereostructure of the oligomers obtained, ^{1}H NMR spectroscopy was performed. Figure 5 shows the ^{1}H NMR spectra of the irradiated samples of **S1** (b) and **S2** (c) obtained after 24 h of irradiation. The spectrum of the pure compound **1** is also shown (a). Peaks corresponding to cyclobutane units are clearly seen in the spectra of the irradiated samples, which are not observed in that of **1**. According to the literature [5–8], the two peaks at 3.46 and 3.75 ppm in Figure 5(b) could be assigned to a δ-truxinate derivative, that is, an *anti* head-to-head structure, while those at 3.83 and 4.39 ppm can be attributed to a β-truxinate, that is, a *syn* head-to-head structure. This result is similar to that obtained from the photopolymerization of **1** in the LC phase [3]. It is worthwhile noting that the dominant peaks are observed at around 3.75 ppm in Figure 5(c), and that they can be assigned to an α-truxillate derivative, that is, an *anti* head-to-tail structure. It was found that the oligomers prepared from

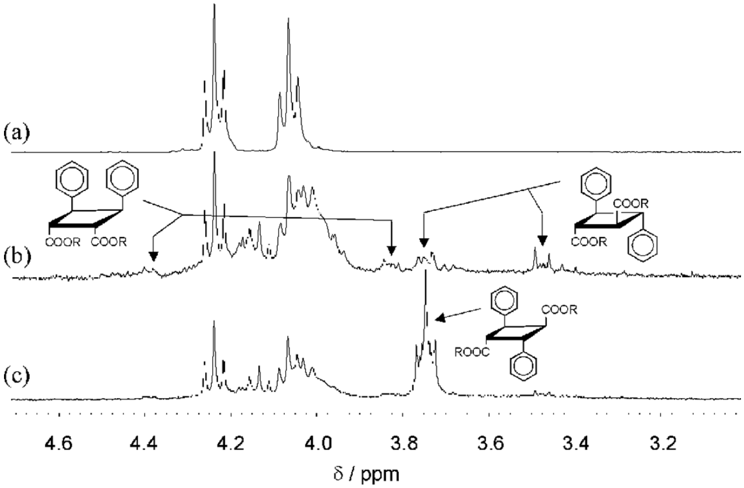

FIGURE 5 Cyclobutane unit signal region of ^{1}H NMR spectra of **1** measured before (a), and after UV irradiation of **S1** (b) and **S2** (c) for 24 hours.

S1 and **S2**, that is, K1 and K2 crystals, have different stereostructures in the cyclobutane units. Consequently, schematic structures of the oligomers can be drawn as shown in Figure 6. The oligomer obtained from K1 has a linear structure in which the mesogens are connected by *δ*- and *β*-type cyclobutane units. In contrast, in the oligomer formed from K2, the mesogens are linked by *α*-type cyclobutane units. The thermal behavior of the oligomers was also studiedby POM measurements, and it was found that the oligomer from K1 showed a nematic phase from 144°C on cooling, while the oligomer from K2 exhibited a nematic phase from 123°C, and upon subsequent cooling, their nematic textures were frozen at room temperature due to a glass transition.

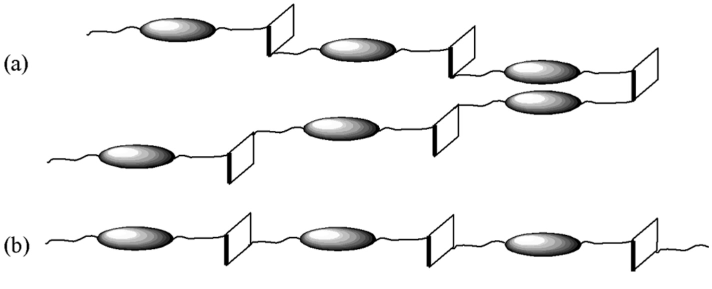

FIGURE 6 Schematic structures of the oligomers obtained from K1 (a) and K2 (b) crystals.

CONCLUSIONS

Main-chain LC oligomers were obtained by UV irradiation of an α,ω-dicinnamoyl-functionalized LC monomer **1** in the crystalline state. **1** shows polymorphism in the crystalline phase, that is, K1 and K2 crystal forms exist. Since the oligomers obtained from K1 and K2 have different stereostructures (in the cyclobutane units), the photopolymerization of **1** in the crystalline state was found to be based on topochemistry.

REFERENCES

[1] Kondo, M., Yu, Y., & Ikeda, T. (2006). *Angew. Chem. Int. Ed.*, *45*, 1378.
[2] Mori, H., Itoh, T., Nishiura, Y., Nakamura, T., & Shinagawa, Y. (1997). *Jpn. J. Appl. Phys.*, *36*, 143.
[3] Kihara, H. & Tamaoki, N. (2006). *Macromol. Rapid Commun.*, *27*, 829.
[4] Dilling, W. L. (1983). *Chem. Rev.*, *83*, 1.
[5] Ikeda, T., Ikeda, T., Sasaki, T., Lee, B., Kurihara, S., & Tazuke, S. (1991). *Liq. Cryst.*, *9*, 457.
[6] Oriol, L., Piñol, M., Serrano, J. L., & Tejedor, R. M. (2003). *J. Photochem. Photobio. A: Chem.*, *155*, 37.
[7] Green, B. S. & Heller, L. (1974). *J. Org. Chem.*, *39*, 196.
[8] Ben-Efraim, D. A. & Green, B. S. (1974). *Tetrahedron*, *30*, 2357.