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Synthesis and helical twisting property of polymerizable chiral dopant with temperature-dependent solubility in liquid crystal

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Abstract

In this study, right-handed dicinnamate isosorbide was synthesized via the esterification reaction between optically active isosorbide and cinnamate. The chiral dopant was characterized by FT-IR, ^{1}H NMR, elemental analysis, SEM, UV absorption spectrum. After dissolving in a nematic liquid crystal mixture, the chiral dopant exhibited a temperature-dependent solubility in the chiral nematic liquid crystal mixture. Meanwhile, a relatively high value of helical twisting power of the polymerizable chiral dopant was determined. The results show that the chiral dopant has great potential in achieving a polymer stabilized chiral nematic liquid crystal film with a broad-band selective reflection.

Keywords: Chiral dopant; Temperature-dependent solubility; Liquid crystal; Helical twisting power

Chirality in liquid crystals (LC) has been a subject of intense research in science, and is directly responsible for important technological applications [1]. After dissolving a chiral dopant in a nematic LC, a chiral nematic (N*) LC is obtained in which the handedness of the chiral dopant molecules causes the orientation of the local nematic director to vary in space and form a helix. The pitch length, P, of the helix corresponding to a 2π molecular rotation is inversely proportional to the concentration of the chiral dopant [2]. Here, the helical twisting power (HTP) of the chiral dopant can be defined as the slope of $1/P$ versus the concentration of the chiral dopant. Recently, selective reflection property of the N*-LC has attracted considerable attention for its applications in reflective LC displays [3,4], brightness enhancement films of LC displays [5] and other optical elements [6–8]. Temperature has been widely used to adjust the reflection band of the N*-LC, such as temperature-dependent phase transition of N*-LC [9], temperature-dependent refractive index change [10] or temperature-dependent HTP of the chiral dopant [11]. However, not much has been reported on the temperature-dependent solubility of the chiral dopant with polymerizable characteristic.

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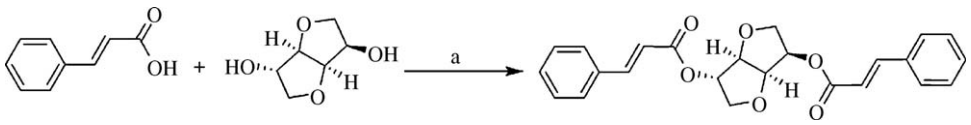

Scheme 1. The synthetic route for the chiral dopant: (a) DCC, DMAP, CH_2Cl_2.

In this communication, we report the synthesis and characterization of a polymerizable chiral dopant with temperature-dependent solubility in LC. We show that temperature-dependent solubility of the polymerizable dicinnamate isosorbide in nematic LC mixture imparts interesting features to obtain a polymer stabilized N*-LC film which are worth being exploited.

1. Experimental

The synthesis of the chiral dopant is outlined in Scheme 1.

Optically active isosorbide (1.46 g, 10 mmol) and dimethylaminopyridine (DMAP) (0.27 g, 2.2 mmol) were dissolved in 50 mL CH_2Cl_2, and then added dropwise to a solution of excessive cinnamate (3.26 g, 22 mmol) and dicyclohexycarbodiimide (DCC) (4.54 g, 22 mmol) in 50 mL CH_2Cl_2. The reaction mixture was continuously stirred at room temperature for 40 h. After the precipitate was filtered off, the resulting solution was washed with dilute hydrochloric acid and water, dried with anhydrous magnesium sulfate. The 2.79 g of white crystals was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) and following recrystallization from ethanol. Yield: 69%. mp: 122.9 °C.

Chemical structure of the chiral dopant was determined by NMR (Bruker DMX-300), FT-IR (PerkinElmer Spectrum One) and elemental analysis (Flash EA 1112). FT-IR (KBr, cm^{-1}): 2904, 2863 (–CH_2–), 1714 (C=O), 1641 (–CH=CH–). ^1H NMR ($CDCl_3$, δ ppm): 7.79–7.70 (dd, 2H), 7.55 (d, 4H), 7.41 (d, 6H), 6.55–6.43 (dd, 2H), 5.39–5.31 (m, 2H), 4.99–4.97 (d, 1H), 4.64–4.63 (d, 1H), 4.15–3.91 (m, 4H). Elemental analysis (%): calcd: C 70.92, H 5.46, O 23.62; found: C 70.90, H 5.57, O 23.53.

The chiral dopant film was prepared by spin-casting a THF solution of the chiral dopant (9.2 wt.%) on ITO glass at 1000 rpm for 10 s. After the THF solvent was removed, the photoreaction of the chiral dopant film was carried out under UV irradiation (0.9 mW cm^{-2}, 365.0 nm). Before viewing under scanning electron microscopy (SEM), the UV cured film was soaked in cyclohexane for extraction of unpolymerized chiral dopant, followed by coating with a thin layer of gold to eliminate any electric charge problem.

A nematic LC mixture of DF-05XX (Chisso Co., Ltd., $T_{N\text{-}I}$ = 115 °C) was used as the LC host of the chiral dopant. The Cano wedge technique [2] was employed to measure the pitch lengths of the N*-LC mixture at different temperatures for

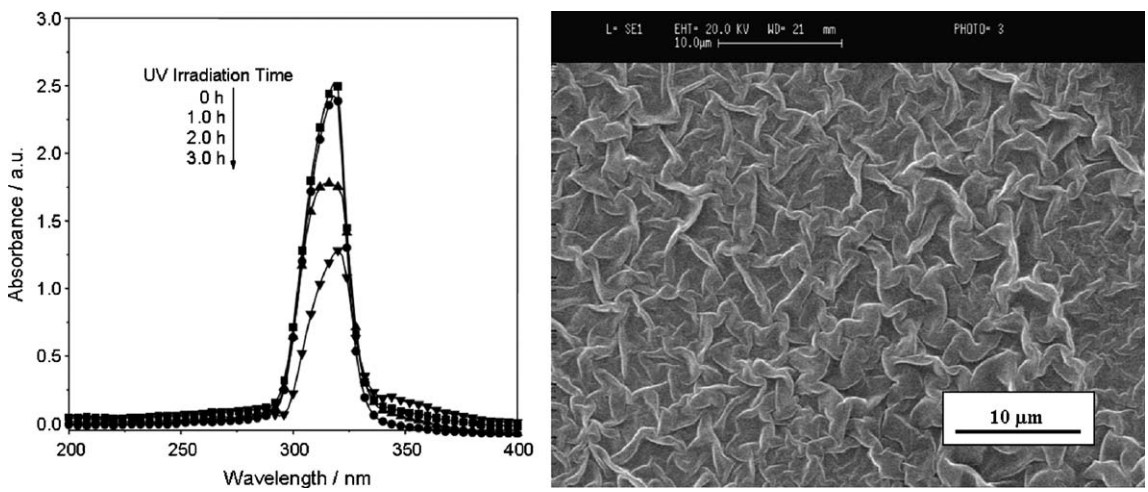

Fig. 1. UV absorption spectrum and SEM photo of the chiral dopant film irradiated by UV light.

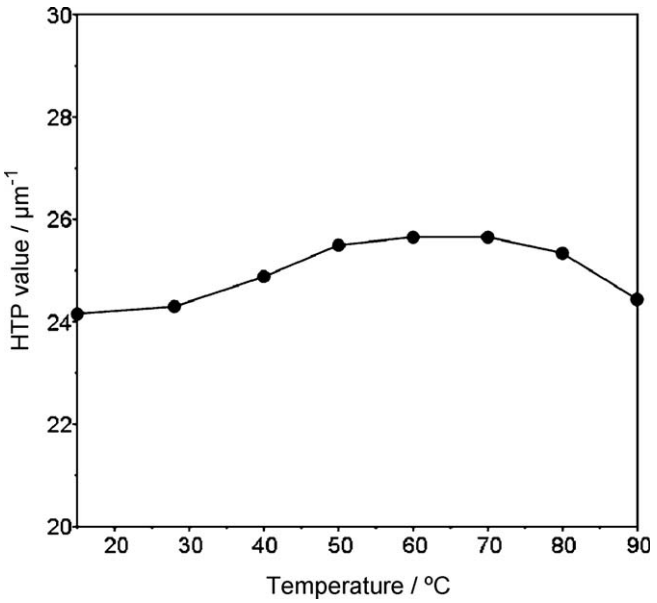

Fig. 2. The HTP values of the chiral dopant as a function of temperature.

determination of HTP values of the chiral dopant. The spectra of selective transmission were obtained by UV/VIS/NIR spectrophotometer (JASCO V-570) while the transmittance of the blank cell was normalized as 100.0%.

2. Results and discussion

Fig. 1 shows the UV absorption spectrum of the chiral dopant film irradiated by UV light. The maximum absorbance (318 nm) attributed to the cinnamoyl groups decreases with the UV irradiation time, as the result of the [2 + 2] photocycloaddition [12] of the C=C bonds of cinnamoyl groups. The SEM photo of the chiral dopant film with the UV irradiation time of 3 h has also shown that the chiral dopant with bifuctionality could be polymerized under UV irradiation.

Fig. 2 shows the HTP values of the chiral dopant as a function of temperature. It is clearly seen that the chiral dopant has a relatively high HTP value of 26 μm^{-1} in the nematic LC of DF-05XX. This means that introduction of a small amount of the chiral dopant in DF-05XX could obtain a short pitch N*-LC, in which small concentration of the chiral dopant has less influence on the properties of LC mixture.

Fig. 3 shows the polarized optical microscopy (POM) photos of the N*-LC mixture with or without UV irradiation and the corresponding transmittance spectra. After introduction into an ITO glass cell of which the inner surfaces had been treated for homogenous orientation of LC molecules, the N*-LC mixture from the chiral dopant adopts a uniformly planar Grandjean texture at high temperature. As for the N*-LC mixture without UV irradiation, the solubility of the chiral dopant decreases with decreasing the temperature. The phase separation and aggregation of the chiral dopant from the N*-LC mixture occur as shown in Fig. 3(a). A noticeable red shift in the transmission spectra has been observed by a UV/VIS/NIR spectrophotometer. This demonstrates that the pitch length of the N*-LC mixture gets longer with temperature decreasing due to the temperature-dependent solubility of the chiral dopant. As for the N*-LC mixture with enough UV irradiation at high temperature, the precipitation of the chiral dopant could be non-apparent after the process of cooling as shown in Fig. 3(b). Red shift after UV irradiation in the transmission spectra could be attributed that the HTP value of the polymerized chiral dopant decreases. The location of selective reflection band did not change even placed the UV cured N*-LC mixture in dark for 23 day. If the differences of pitch lengths of the N*-LC mixture at different temperatures could be anchored by polymer network, a polymer stabilized N*-LC film with a broad-band selective reflection should be obtained. The preliminary research is in progress and will be the scope of a forthcoming report.

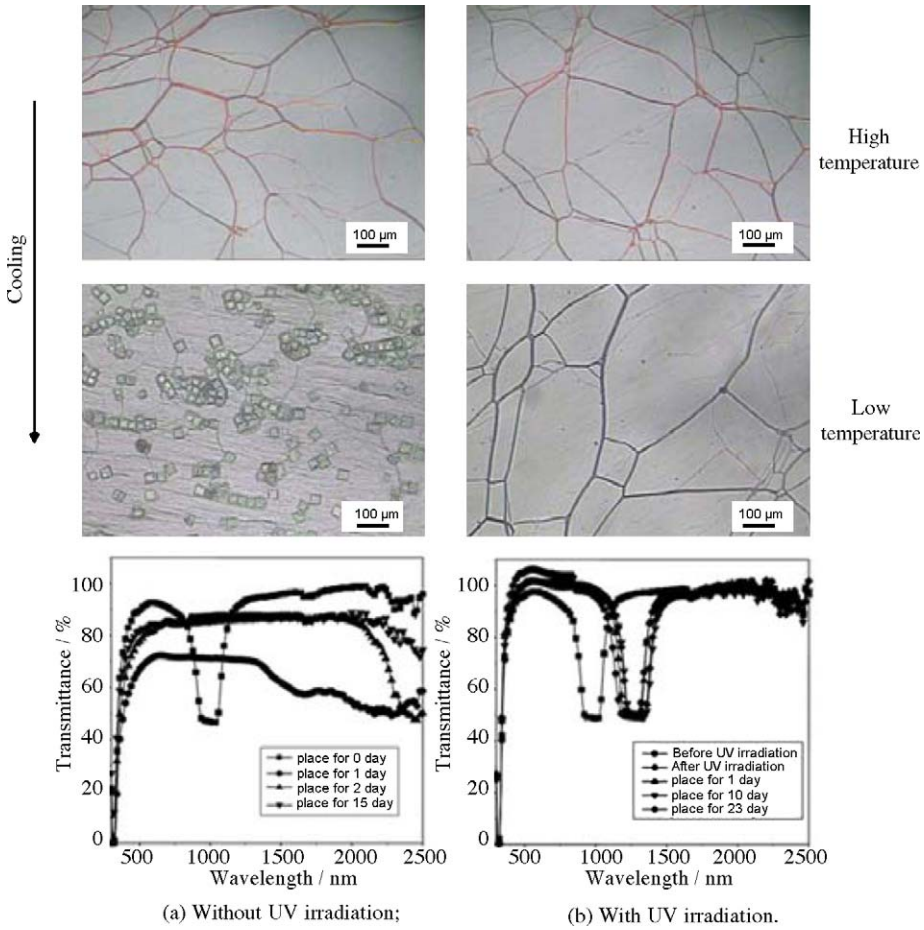

Fig. 3. POM photos of the N*-LC mixture with or without UV irradiation and the corresponding transmittance spectra.

Acknowledgments

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