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Optical Behaviors of Cholesteric Liquid-Crystalline Polyester Composites with Various Chiral Photochromic Dopants

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Supporting Information

ABSTRACT: New developments in the field of chiral nematic liquid crystals, such as color displays, are now being widely proposed. This article describes the tunable incident reflection band based on composite materials of low-molecular-weight chiroptical dopants and polymeric networks. These materials have advantages including easily manageable color according to a change in the helical pitch of the cholesteric liquid crystal upon exposure to light. A series of novel chiral dopants of isosorbide derivatives containing photochromic groups and three new main-chain liquid crystalline polyesters were synthesized and identified using nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and elemental analyses. The phase-transition temperatures and the liquid-crystal phase determination of the synthesized polymers were estimated using DSC, WAXD, and POM analyses. The influence of the dopant concentrations and the solubility in a liquid crystalline polymer blend were also studied. The reflection band of the cholesteric liquid crystalline composites could be adjusted and tuned with a wide range of color variation across the entire visible region. A real image recording of the chiral



photochromic liquid crystalline polymer blend was achieved by exposing it to UV light through a mask.

INTRODUCTION

Systematic studies on main-chain liquid-crystalline polymers (LCPs) did not begin until the mid-1970s.¹ Main-chain LCPs that have repeating rigid mesogenic units in the long main chains, such as benzene rings interlinked at the para position, tend to be infusible crystalline solids.² These types of mainchain polymers usually show quite high melting temperatures above the decomposition temperature and are thus observed to exhibit only lyotropic behavior. The transition temperature of main-chain LCPs can be reduced by structural modifications, such as through the disruption of the perfect regularity and rigidity of the molecular chain by introducing flexible segments or rigid kinks into the straight main chains.³ The most commonly used connecting units joining the rigid core to the disruptors are ester and ether groups. The other strategy is to add a substituent in the aromatic ring, causing a decrease in the crystallinity and lowering the melting point of the polyester.³ In these semiflexible main-chain LCPs, the existence of nematic, cholesteric, and smectic phases has been found.

The synthesis of main-chain LCPs normally follows stepgrowth polymerization techniques, such as polycondensation. Among main-chain LCPs, polyesters are preferred systems because high-molecular-weight polymers can be easily obtained by standard processes. Polyesters are defined as polymers containing at least one ester linkage group per repeating unit. The important properties of polyesters include melt processability, outstanding thermal and chemical resistance, and excellent mechanical properties.

Recently, many photoinduced chiral systems have been studied from experimental and theoretical viewpoints.⁴⁻¹³ The

main goal in preparing photochromic liquid crystals (LCs) is to obtain a material that responds to light such that the chemical and physical properties are affected during photochemical switching of the liquid-crystal phases. There are at least two principal methods to obtain photosensitive LC polymers, including (1) polymers with photosensitive chromophores in side- or main-chain LCPs or (2) polymer mixtures doped with photoresponsive compounds (photochromic dopants). The latter case allows us to control the properties of the guest photochromic dopant by light irradiation without any changes in the polymer matrix itself. The photochromic groups play the role of "switchers" in a liquid crystal, which can induce large changes in their configuration and conformation upon photoisomerization.¹⁴ These changes in the shape of the photochromic groups lead to distortion of the packing of the LC molecules, simultaneously inducing a local phase transition.

It is also well known that adding chiral molecules into an achiral nematic LC host can induce the twisted molecular arrangement to form a self-organized, optically tunable helical structure.^{15–20} Photochemically tunable cholesteric liquid crystals are the most attractive materials. The optical switching of photochromism in cholesteric liquid crystal phases leads to various effects not only on the liquid-crystal phase but also on the helical structure. Adjustment of the cholesteric pitch of the helical structure by light can be utilized in the practical applications of optically addressable displays, recording

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Figure 1. Chemical structures of the chiral dopants D1, D2, and D3 with their transition temperatures and specific rotations. Abbreviations: K = crystalline state, I = isotropic state.



Figure 2. Variations in the UV-vis absorption spectra of the chiroptical dopants (a) D1 and (b) D2 upon 254 nm UV irradiation.

materials, and photonic crystals.²¹ For example, cholesteric color filters that can reveal reflected colors of red, green, and blue via a patterned mask are a good application of the principle.²² Furthermore, the effects of tuning helical twisting power of isosorbide-based chiral dopants on liquid crystals were reported.^{23–25}

The most straightforward approach to develop such a photooptical material would be to synthesize a "hybrid" molecule composed of chiral and photochromic moieties. Here we report the design and synthesis of three new chiral dopants containing photochromic azobenzene or cinnamate with an isosorbide moiety situated at the center of the molecules. As described in Figure 1, the molecular structures of the chiroptical dopants were composed of two different groups: on the two sides, photochromic groups could reversibly respond to lights, and at the center, the presence of an isosorbide group may provide molecular chirality and induce the helix packing. We also investigated the thermal and photochemical behaviors of the photochromic chiral dopants in the synthesized main-chain liquid-crystalline polymer systems. Main-chain liquid-crystalline polymers with and without isosorbide chiral diol were synthesized. The influence of the dopant concentration and the solubility in the main-chain liquid crystalline polymer mixture were also studied.

RESULTS AND DISCUSSION

Synthesis of Chiroptical Dopants (D1, D2, and D3). As illustrated in the Supporting Information Scheme S1, three chiroptical dopants (abbreviated as D1, D2, and D3, Figure 1) containing photochromic azobenzene or cinnamoyl groups and isosorbide as a chiral center were newly designed and synthesized. The detailed synthetic procedures are explained in the Experimental Section of this paper. The chemical structures and the intermediates were confirmed by FT-IR, ¹H NMR (see Figures S1–S3 in the Supporting Information), and elemental analyses.

Photochemistry of Azobenzene- or Cinnamate-Functionalized Chiroptical Dopants (D1, D2, and D3). In this research, the chiral dopants D1 and D2 containing photoisomerizable cinnamoyl groups and D3 containing azobenzene groups were synthesized. To confirm the photoreactivities of the photoisomerizable groups of the synthesized chiral dopants, we investigated the UV absorption spectra of D1, D2, and D3 as a function of the UV exposure time.

The chiral dopant **D1** showed a maximum absorption at ~314 nm in a chloroform solution (5 × 10⁻⁵ M), as seen in Figure 2a. This absorption was attributed to the π - π * transition of the *E*,*E*-form cinnamoyl groups. When the sample solution was exposed to 254 nm light, the π - π * absorbance decreased depending on the increase in the UV irradiation time.



Figure 3. (a) Dependence of the UV-vis absorption spectra of D3 on the irradiation time under 365 nm irradiation and (b) recovery of the UV-vis spectra of D3 in the dark.

The photochemical reaction reached a photostationary state after a 180 s irradiation, holding two isosbestic points at 268 and 342 nm. The presence of the isosbestic points during the photochemical reaction suggested that *E-Z* photoisomerization was the predominant photoreaction in the solution of the chiral dopant **D1**.²⁶ Although most *E-Z* photoisomerizations are reversible, the *Z* to *E* relaxation of **D1** with cinnamate moieties was an irreversible reaction due to the high activation barrier between the two isomers.²⁷ The photoisomerization of the chiroptical dopant **D1** can be seen in the Supporting Information Figure S4.

Figure 2b shows the photoreactivity of the chiral dopant D2 in a CHCl₃ solution (5 \times 10⁻⁵ M). From the UV absorption spectra, the maximum peak intensity was observed at 288 nm, which was the characteristic peak of the cinnamate moiety; the peak decreased as the UV exposure dose increased. The decrease in the peak originated from the E-Z photoisomerization of the attached cinnamoyl groups of D2. From the UV absorption spectra, it was found that the E-Z photoisomerization of the cinnamate moiety of D2 successfully occurred due to the UV exposure. The successive spectral changes in the absorption spectra of D2 were characterized by two isosbestic points at 262 and 318 nm before 20 min of irradiation; however, further exposure led to the disappearance of the isosbestic points, which indicated that not only E-Z isomerization but also another photochromic process occurred. In the case of aryl esters of cinnamic acid, the photodimerization reaction simultaneously occurred with a photo-Fries rearrangement reaction.²⁸ The schematic of the photo-Fries rearrangement of the aryl ester of the cinnamic acid derivative under UV irradiation is shown in Figure S5. Moreover, the absorption bands at approximately 318 to 400 nm slightly increased during the UV irradiation, which was also attributed to the photo-Fries rearrangement of the cinnamate moieties.

The photochemical property of the chiral dopant D3 containing azobenzene groups was studied using UV–vis spectra following by irradiation with 365 nm UV light. Figure 3 shows the steady-state ultraviolet–visible spectroscopy (UV–vis) absorption spectra of D3 in a chloroform solution (5 × 10^{-5} M). The spectral shapes were similar to each other and had characteristics in common with isosorbide complexes that contain azobenzene derivatives as a photochromic group.²⁹ The major absorption band at approximately 292 to 392 nm was assigned to the π – π * transition of the *E*,*E* azobenzene moieties, and a weak absorbance at ~392 to 500 nm was ascribed to the n- π * transition of *Z*,*Z*-form isomers. When the sample solution was exposed to 365 nm light, the π – π * absorbance drastically

decreased depending on the increase in the UV irradiation time, whereas the $n-\pi^*$ band slightly increased in absorbance via *E*-*Z* photoisomerization (Figure 3a). A photostationary state (PSS) was reached after irradiation at 365 nm for ~6 min. The absorption stability of the chiral dopant D3 in the dark is shown in Figure 3b. Theoretically, the *E* form of azobenzene is more stable than the Z form, and the bent Z form may gradually return to the linear E form, even in the dark.³⁰ After 4 days under dark conditions, the absorption band returned to its initial state, which was attributed to the Z to E photoisomerization, revealing that the E-Z photoisomerization of the azobenzene-functionalized chiroptical dopant D3 was a reversible photochemical reaction. The slow Z-E reversion of D3 might be due to the effects of the substituents of azobenzene on the molecular interaction, leading to variations in the speed of the configuration change.

Synthesis of Main-Chain Liquid-Crystalline Polyesters. Various approaches have been successfully carried out for the synthesis of polyesters, which have usually been prepared by solution or interfacial polycondensation and also by the ester exchange reaction at high temperature or reduced pressure. In these usual techniques, monomers should be prepared before polymerization.^{31–33} Direct polycondensation of free carboxylic acids and aromatic diols is a more useful technique because it can be operative under mild conditions. A series of novel polyesters was obtained by direct step growth polymerization (direct polycondensation) involving the use of dicarboxylic acids and an aromatic diol under mild conditions. Three types of diols with different mesogenic groups were employed. Two diol monomers, methyl hydroquinone and 4,4'-bisphenol (abbreviated as MHQ and 2B, respectively, Figure 4), were commercially available. The synthetic routes of the dicarboxylic acid (abbreviated as M1, Figure 4) and chiral-based diol (abbreviated as M2, Figure 4) for the preparation of polyesters are shown in Scheme 1. The detailed synthetic procedures are explained in the Experimental Section. The chemical structures and their intermediates were confirmed using FT-IR, ¹H NMR (see Figures S6 and S7 in the Supporting Information), and elemental analyses.

The polyesters were synthesized by copolymerizing a small amount of the chiral-based diol **M2** because isosorbidecontaining polyesters are known to possess a high helical twisting power (HTP) and are effective for breaking the molecular packing symmetries in a liquid-crystalline matrix.²⁶ In addition, methyl-substituted hydroquinone (**MHQ**) was selected as a diol monomer because the substituted group is useful for lowering the phase-transition temperature.^{34,35}



Figure 4. Chemical structures of the aromatic dicarboxylic acid M1 and the diols M2, MHQ, and 2B for the synthesis of aromatic polyesters by direct step-growth polymerization (direct polycondensation).

The synthesis procedures and possible sequential structures of the oxyethylene-based aliphatic/aromatic polyesters are summarized in Figure 5 and Figures S8 and S9 in the Supporting Information. The properties of the resulting polyesters synthesized from different mixtures of diols are summarized in the Supporting Information. In each synthesis system with a specific diol, dicarboxylic acid (M1)/diol (MHQ, MHQ+M2, or MHQ+M2+2B) feed molar ratios of 1:1 were employed. These polymers had a soft segment, such as an oxyethylene moiety, in the main chain to improve the solubility in organic solvents in comparison with aromatic polyesters.

The actual methyl hydroquinone/M2 molar ratios in the chain structure were calculated from the integration peaks of CH_3 in MHQ at 2.22 ppm and CH in M2 located in the 5.07 ppm region. The high yield, molecular weight, and moderately broad polydispersity index indicated that the use of *p*-TsCl/Py/DMF as a condensing agent for the synthesis of polyesters could successfully induce effective direct polycondensation between dicarboxylic acids and aromatic diols.

Thermal Characterization of the Polyesters. The thermal properties and liquid-crystal phase behaviors of the synthesized polymers were characterized by DSC, TGA, POM, and WAXD. The phase-transition temperatures of the polyesters were characterized by DSC, as shown in Figure S10, and the liquid-crystal phases were determined by hot-stage POM and WAXD. The results are summarized in the Supporting Information Table S2.

The synthesized polyesters with mesogenic units in the main chain consisting of oxyethylene spacers showed liquid-crystal phases. The flexibility of the carbon–oxygen bonds of the oxyethylene spacers in the monomer **M1** and the methyl-substituted mesogenic core decreased the rigidity of these moieties and increased the mobility between polymer chains, resulting in a broadened liquid crystal phase and a low glass-transition temperature $(T_g)^{.36-40}$

Except for P1, which displayed a nematic liquid crystal phase (thread-like texture, Figure 6a), P2 and P3 showed planar and oily streak textures under POM observation, which were the typical textures of the cholesteric liquid-crystal phase, as indicated in Figure 6b–d. This result indicated that the cholesteric liquid-crystal phase could be induced by small amounts of a chiral segment in main-chain polyesters. Moreover, the addition of monomer bisphenol (2B) increased the mesogen length, increased the phase-transition temperature, and broadened the temperature range of the liquid-crystal phase.³⁸ As seen in the Supporting Information Table S2, polymer P3 showed a much broader liquid-crystal phase than polymers P1 and P2.

Figure S11 illustrates the WAXD powder patterns for P3 from 85 to 125 °C that were obtained during heating. At 85 °C, an amorphous scattering halo in the high-angle region at ~20° corresponding to the liquid-like order in the lateral molecular packing was observed. As the temperature increased to 95 °C, a weak peak at 3.29° with a *d* spacing of 26.84 Å was detected in the low-angle region. The WAXD patterns for the polymer P3 at 95 to 115 °C indicated a typical sematic LC phase, and the calculated distance of the layer structure was 26.84 Å.³⁹ In addition, a slight broadening of this scattering halo occurred with increasing temperature. The structural changes of P3 in Figure S11 could be characterized by the *d*-spacing changes, indicating that the phase transition occurred.³⁷ The WAXD results were identical to the DSC and POM results.

The thermal stabilities and thermal degradation patterns of the polymers were investigated using TGA measurements with a heating rate of 20 °C/min under a nitrogen atmosphere. The parameters of the 5% weight loss temperature (T_d^{50}) , and residual weight are summarized in the Supporting Information Table S2. The results showed that the decomposition temperatures at 5% weight loss were >350 °C, and the residues at 600 °C were ~12–15 wt % for all samples, indicating that the synthesized polyesters had high thermal stability. Polymer P3 had a distinct thermal stability up to 388.5 °C (T_d^{5}) , indicating that the incorporation of **2B** monomer into the polymer chain increased

Scheme 1. Synthesis of M1 and M2^a



^{*a*}Reagents and conditions: (i) *p*-toluenesulfonyl chloride, KOH, THF, 30 °C, 24 h; (ii) ethyl 4-hydroxybenzoate, K_2CO_3 , 2-butanone, reflux, 16 h; (iii) KOH, MeOH/H₂O, reflux, 16 h; and (iv) *p*-toluenesulfonic acid monohydrate, xylene, 145 °C, 7 h.



Figure 5. Synthesis route for the main-chain liquid crystalline polyester P1 using p-TsCl/Py/DMF as a condensing agent.



Figure 6. POM textures of (a) P1 at 120 $^{\circ}$ C, (b) P2 at 150 $^{\circ}$ C, and P3 at (c) 115 and (d) 160 $^{\circ}$ C (×400).

the rigidity of the polymer and offered a stabilizing effect against decomposition.

Optical Behavior of Liquid-Crystalline Polyester Composites. In our studies of the optical properties of the systems of chiral photochromic dopant/liquid-crystalline polymer composites, the synthesized compounds D1–D3 were used as photoresponsive chiral (chiroptical) dopants. The photochemical transformations of selective light reflection were studied at elevated temperatures (e.g., in the cholesteric liquid crystal phase) and recorded using an USB-2000 fiber optic spectrometer.

The dynamic optical responses of the nematic polymer P1 doped with different optically active dopants are demonstrated in Figure 7. In the D1/P1 and D2/P1 systems, the cholesteric liquid crystal (CLC) phase was induced at a concentration of 3 wt % addition; however, phase separation was observed in the 3

wt % D3/P1 system, indicating a lack of compatibility between D3 and P1 and resulting in failure to induce the CLC phase. A selective reflection in the visible-light region could be achieved by adding a small amount of chiral dopant, indicating that the isosorbide derivative dopant revealed high helical twisting power (HTP) in the liquid crystalline matrix. The phototuning behaviors of the mixtures D1/P1 and D2/P1 were essentially identical. As seen in Figure 7, exposure to UV light caused a shift in the reflection notch. Tuning bands from 200-250 nm in the visible region were observed. The results provided clear evidence of the alternation of the CLC pitch by the photochemical isomerization of the chiral dopant. UV irradiation of the mixture served to isomerize the cinnamoylcontaining isosorbide molecule, affecting the pitch and resulting in a red shift of the reflection wavelength across the visible region. The phototuning rates of the photoresponsive CLC materials were related to the ability of the generated Z-form isomers to affect the pitch. As the fraction of the chiral dopant was increased to 5 wt %, a clear increase in the tuning rate was observed, as shown in the Supporting Information Figure S12.

The transmission spectra of the CLC mixtures of chiral dopants in cholesteric polymer P2 both before and during phototuning are shown in Figure 8. Here all of the systems (3 wt % of the chiral dopants D1, D2, and D3 in P2) were induced to show the CLC phase. Although a phase separation was brought about by mixing photoisomerizable chiral dopant in the polymer system at a concentration >3 wt %, the high HTP value of the isosorbide derivative dopant brought a high efficiency of reflection light from near-infrared to visible region. In these three systems, only D1/P2 showed a UV-tuning property in the bulk condition. The selective reflections remained in the initial positions for the D2/P2 and D3/P2 samples even after a long photoirradiation. This result could be due to the high viscosity and rigidity of the main-chain



Figure 7. Effect of UV irradiation on the selective reflection bands of the 3 wt % (a) D1/P1 and (b) D2/P1 systems at 120 °C.



Figure 8. Effect of UV irradiation on the selective reflection bands of (a) 3 wt % D1/P2 at 150 °C and (b) 3 wt % D2/P2 in the solution state. (c) Dependence of the transmission spectrum of 3 wt % D3/P2 on UV tuning and thermal recovery at 150 °C. (d) Effects of chiral photochromic dopants on the selective reflection band of P2.

polyester with higher chain entanglement and the distance between the photosensitive and chiral segments. To overcome this problem, the phototuning properties of the D2/P2 and D3/P2 mixtures were studied under solution conditions in chloroform.

Red shifts of the selective light reflection bands were observed with an increase in the UV irradiation time for all doped P2 systems. As shown in Figure 8a, the phototuning of D1/P2 reached a maximum wavelength shift (over 300 nm tuning range), at which point the reflection intensity decreased until the samples were partially isotropic. The D2/P2 mixture in the solution state was observed to have tuning of ~150 nm from exposure to UV light (shown in Figure 8b), which was speculated to be primarily due to the reduction of the polymer viscosity and the extension of the polymer chains in the solvent environment, resulting in the easing tuning of the CLC pitch, which was affected by the conformational change upon generation of the Z-form isomer. There are many photoresponsive chiral materials that have been synthesized and studied that have been observed to reveal a transition from a cholesteric to a photoinduced isotropic state in the photoisomerization of the host molecules upon UV irradiation.⁴¹⁻⁴³ In our system, the main-chain CLC polymers showed lesser influences of the light on the selective light reflection bands compared with the referenced works. The materials showed large-scale tuning as well as the maintenance of the CLC phase upon UV irradiation. This result could be due to the high viscosity of the main-chain polyester with higher chain entanglement, resulting in the local mobility of the chains in the helical structures.

As has been discussed, azobenzene is a photoreversibility photochromic molecule. In the 3 wt % D3/P3 solution system, the initial peak of 3 wt % D3/P3 shifted from 423 to 695 nm after UV irradiation and then showed a blue shift to 591 nm, which was a thermally induced reaction after 3 h treatment at 150 °C (Figure 8c). The slow thermally induced relaxation could be attributed to the effect of the polymer matrix associated with the motion of the polyester polymer backbone. As a result, a slow *Z*-*E* isomerization process of the entire doped polymeric system could be the result of the slow polymer chain rearrangement.⁴⁴

The HTPs of the dopants **D1**, **D2**, and **D3** in **P2** before irradiation (initial) were calculated according to Figure 8d. The highest initial HTP of 126 μ m⁻¹ was obtained for **D3**, which was larger than that for **D1** and **D2** in the same liquid-crystal host (**P2**). The initial HTP of 126 μ m⁻¹ changed to 77 μ m⁻¹ upon 365 nm light irradiation. The changes in the helical pitch and HTP were attributed to the conformational change between *E* and *Z* isomerization of the azobenzene unit in the chiral dopant by photoirradiation.

Figure 9 presents the phototuning properties of doped P3 CLC mixtures. The spectrum of the pure P3 polymer showed a reflection band at 980 nm. The reflection notch of the pure P3 polymer was blue-shifted due to the addition of the chiral dopants. The chiral dopants could exhibit a different ability to twist the LC molecules, showing a different sense of rotation. Compared with the commercially available chiral dopant R811, the synthesized dopants were observed to reveal a marked blue shift of the reflection band under the same concentration. The result indicated that D3 showed a much more efficient ability to induce CLC in the P3 system. It should be noted that the ability to induce the helical arrangement of LC molecules is related not only to the HTP of the chiral dopant itself but also to the solute—solvent interactions between the guest dopant (chiral solution) and the host polymer (LC solvent).^{45,46}

To investigate the practical photochromism of the CLC films, the mixture of the synthesized polymer P3 doped with the chiroptical dopant D1 was coated on a glass substrate. Visible-light reflection could be observed for a mixture of 6 wt % D1 in P3 at the cholesteric mesophase. The initial spectrum

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Figure 9. Effect of chiral dopants on the selective reflection band of P3.

before photoirradiation showed a reflection band at 452 nm (Figure 10a) with a blue color, as shown in Figure 10b. UV



Figure 10. (a) Effect of UV irradiation on the reflection band of the 6 wt % D1/P3 system at 200 °C. (b) Recorded color pattern using the 6 wt % D1/P3 composite at 200 °C with various UV irradiation times.

irradiation of the sample resulted in a shift of the reflection band toward longer wavelengths. The photoinduced switch reached steady state by increasing the UV irradiation time to 20 min. The reflection band shifted to 715 nm, and the reflection color changed to red from green. This system exhibited a wide range of color variation across the entire visible region with exposure to light. This result revealed that the dopant concentration of 6 wt % was sufficient to induce photocontrol of the RGB reflection colors. The efficiency was much more sensitive compared with those of reported chiral photochromic dopants so far.^{47,48}

To correlate the synthesized dopant D3 to other published papers, commercially available E7 and MJ05681 nematic liquid crystals purchased from Merck were used for the evaluation of HTP- of D3-induced cells. Unfortunately, it was found that D3 is insoluble in both E7 and MJ05681 nematic liquid crystals. It is ascribed to molecular structure and intermolecular forces difference. As shown in Figure 1, D3 reveals much higher clearing temperature than that of D1 and D2. The results suggest that molecular interaction between D3 molecules is extremely tough, leading to the decrease in solubility of D3 in both E7 and MJ05681. In the case of D3/P2 system, intermolecular forces between D3 and P2 are compatible,

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leading to the formation of CLC phases.

Instruments. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Jasco VALOR III Fourier transform infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-400 high-resolution NMR spectrometer. Differential scanning calorimetry (DSC) was conducted on a PerkinElmer DSC 7 in a nitrogen atmosphere with the heating and cooling rates of +5 and -5 °C min⁻¹, respectively. A thermogravimetric analyzer (TGA-7) from PerkinElmer was used to record the temperature of thermal decomposition at a heating rate of +40 K min⁻¹ under a nitrogen atmosphere. The cross-sectional morphology of the samples was characterized by transmission electron microscopy (TEM) using a JEOL JEM-1200CX-II microscope with a Cu-grid substrate. The anisotropic properties of the highly ordered, self-assembled samples were investigated using an Olympus BH-2 polarized light microscope (POM) equipped with a Mettler hot stage FP-82, and the temperature scanning rate was determined to be 10 °C min⁻¹. Photoisomerization studies were conducted using UV irradiation with a UVP UVG-54 (254 nm, 6 W) and a UVP UVL-56 (365 nm, 6 W) as the light sources. Samples were irradiated with a distance of 3 cm from UV-lamp. E-Z photochemical isomerizations were investigated using the UV/vis absorption spectra measured using a Jasco V-550 spectrophotometer. The synthesized compounds and polymers were identified using FTIR and '1H NMR.

Synthesis of Isosorbide 2,5-Bis(4-methoxycinnamate) (D1). 4-Methoxycinnamic acid (3.56 g, 20 mmol) and isosorbide (1.46 g, 10 mmol) were dissolved in 60 mL of CH₂Cl₂, and the mixture was stirred at 30 °C. *N*,*N'*-Dicyclohexyl carbodiimide (3.09 g, 15 mmol) and 4-dimethylaminopyridine (0.12 g, 1 mmol) were dissolved in 40 mL of CH₂Cl₂ and dripped into the vigorously stirring solution. The reaction mixture was stirred for 48 h at 30 °C. After filtering out the urea solid that formed, the solvent was removed. The remaining residue was dissolved in CH₂Cl₂ and washed with distilled water. After drying the organic layer over MgSO₄, the product was purified by silica gel column chromatography using ethyl acetate/*n*-hexane (1/5) as the eluent.

Synthesis of 4-(Methoxycarbonyloxy) Cinnamic Acid (1). *Trans*-4-hydroxycinnamic acid (8.21 g, 50 mmol) and NaOH (6.00 g, 150 mmol) were dissolved in 150 mL of H_2O and stirred for 1 h at 0 °C. Methyl chloroformate (8.03 g, 85 mmol) was further added dropwise, and the mixture was stirred for 4 h at room temperature. After completing the reaction, the resulting solution was poured in water and acidified with diluted HCl until weakly acidic. The residue was washed with distilled water twice and recrystallized with ethanol to give the product in 91.7% yield.

Synthesis of Isosorbide 2,5-Bis(4-methoxycarbonyloxy cinnamate) (D2). The mixture of the intermediate 1 (8.00 g, 36 mmol), DMF, and 30 mL of SOCl₂ was heated at reflux for 6 h. After the reaction, SOCl₂ was removed, and the crude product was dissolved in 70 mL of anhydrous THF. The solution was added dropwise to an anhydrous THF solution of isosorbide 2,5-bis (4-hydroxybenzoate) (M2) (6.59 g, 17 mmol) and triethylamine (4.05 g, 40 mmol) under a nitrogen atmosphere at 0 °C. The reaction mixture was stirred for 72 h at 30 °C. After filtering out the precipitate solid that formed, the solvent was removed. The remaining residue was dissolved in CHCl₃ and washed with distilled water. The organic layer was dried over MgSO₄. After removing the solvent, the residue was recrystallized with ethanol to give the product in 13.3% yield.

Synthesis of Isosorbide Bis(4-nitrobenzoat) (2). Isosorbide (3.65 g, 25 mmol) and triethylamine (5.77 g, 57 mmol) were dissolved in 20 mL of CHCl₃, and the mixture was stirred at 0 °C. A solution of 4-nitrobenzoyl chloride (9.28 g, 50 mmol) dissolved in 20 mL of

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CHCl₃ was further added dropwise, and the mixture was stirred for 6 h at 30 °C. After completing the reaction, the resulting solution was poured in water and extracted by CHCl₃. The extracted solution was concentrated using a rotary evaporator under vacuum. The residue was recrystallized with ethanol to give the product in 29.9% yield.

Synthesis of Isosorbide Bis(4-aminobenzoat) (3). The intermediate 2 (4.70 g, 11 mmol) and ammonium chloride (4.50 g, 84 mmol) were dissolved in 50 mL of H_2O and 80 mL of ethanol. A solution of sodium sulfide hydrate (14.40 g, 60 mmol) was further added to the mixture and then heated at reflux for 6 h. After cooling to room temperature, the precipitated solid was collected. The solid was redissolved in an aqueous HCl (10 M) solution (100 mL) and filtered. After ammonium was added to the solution to give pH 8, the precipitated solid was collected and dried. The residue was recrystallized with ethanol to give the product in 48.4% yield.

Synthesis of Isosorbide Bis(4-hydroxy-4'-azobenzoat) (4). The intermediate 3 (0.7 g (1.8 mmol) was dissolved in a mixture of 6 mL of concentrated hydrochloric acid and water. With stirring at 0 °C, 0.4 g (5.8 mmol) of sodium nitrite in water (4 mL) was added to the solution to produce diazonium salt. After the resulting solution was stirred at 0 °C for 1 h, a mixture of phenol (0.55 g, 5.8 mmol) and sodium hydroxide (0.53 g, 13.3 mmol) in 10 mL of water cooled to 0 °C was slowly added. The reaction mixture was stirred at 0 °C for 2 h. After HCl (5%) was added to the reaction mixture to give pH 4, the precipitated solid was collected and dried. The residue was recrystallized with ethanol to give the product in 25% yield.

Synthesis of Isosorbide Bis(4-octoxycarbonyloxy-4'-azobenzoat) (D3). Nonanoyl chloride (0.97 g, 5.5 mmol) was added dropwise to a solution of a mixture of the intermediate 4 (1.5 g, 2.5 mmol) and triethylamine (0.58 g, 5.75 mmol) in anhydrous THF (40 mL). The reaction mixture was stirred at room temperature for 24 h. After completing the reaction, the resulting solution was poured in distilled water and extracted by CHCl₃. The extracted solution was concentrated using a rotary evaporator under vacuum. The residue was recrystallized with THF to give the product in 78% yield.

Synthesis of Tetraethylene Glycol Ditosylate (5). Tetraethylene glycol (11.8 g, 61 mmol) and *p*-toluenesulfonyl chloride (34.5 g, 182 mmol) were dissolved in 90 mL of THF in an ice bath. An aqueous solution of KOH (16 M, 24 mL) was further added dropwise, and the mixture was stirred for 24 h at room temperature. After completing the reaction, the resulting solution was poured in ice water and extracted by CHCl₃. The extracted solution was concentrated using a rotary evaporator under vacuum. The product was purified by silica gel column chromatography using ethyl acetate/*n*-hexane (1/1) as the eluent to give the product in 95.1% yield.

Synthesis of Tetraethylene Glycol Bis(4-carboxyphenyl) Ether (M1). A solution of ethyl 4-hydroxybenzoate (18.3 g, 110 mmol), K_2CO_3 (55.3 g, 400 mmol), and KI (3.0 g, 18 mmol) in 300 mL of 2-butanone was heated at reflux for 2 h under a nitrogen atmosphere. A solution of 5 (27.6 g) in 30 mL of 2-butanone was further added dropwise and heated to reflux for 16 h. The excess K_2CO_3 was filtered off from the hot solution. The solvent was removed under reduced pressure. The product was redissolved in 300 mL of methanol, and a 30 mL aqueous solution of KOH (22.4 g, 400 mmol) was further added to the product. The mixture was heated to reflux for 16 h and then neutralized with conc. HCl to obtain a precipitate. The precipitate was filtered, and the filtrate was washed with hot water and then dried under vacuum. The residue was recrystallized with ethanol to give the product in 82.3% yield.

Synthesis of Isosorbide 2,5-Bis(4-hydroxybenzoate) (M2). A mixture of 4-hydroxybenzoic acid (16.0 g, 116 mmol), isosorbide (8.0 g, 55 mmol), and *p*-toluenesulfonic acid monohydrate (0.44 g, 2.4 mmol) in 100 mL of xylenes was placed in a flask equipped with a Dean–Stark trap, a condenser, and a mechanical stirrer. The reaction mixture was heated to 145 °C for 7 h, at which time an additional charge of *p*-toluenesulfonic acid (0.22 g, 1.2 mmol) was added, and the mixture was heated back to reflux. After 3 h, the reaction was allowed to cool to room temperature. The solvent was removed, and remaining residue was dissolved in 100 mL of ethyl acetate and washed twice with a 1% (w/v) sodium bicarbonate solution. The solvent was

removed under reduced pressure. The product was purified by silica gel column chromatography using ethyl acetate/n-hexane (1/4) as the eluent to give the product in 91.2% yield.

Synthesis of Main-Chain Liquid Crystalline Polyesters. In this study, the liquid-crystalline polyesters containing various proportions of different diols were prepared using the following procedure. For the synthesis of P1, p-toluenesulfonyl chloride (p-TsCl) (1.27 g, 6.7 mmol), N,N-dimethylformamide (DMF) (0.11 g, 1.5 mmol), and 5 mL of anhydrous pyridine (Py) were stirred in a two-necked roundbottomed flask at room temperature for 30 min under a nitrogen atmosphere. The compound M1 (1.00 g, 2.30 mmol) in 5 mL of anhydrous pyridine was added to the mixture. The reaction mixture was stirred at room temperature for 10 min and then stirred at 120 °C for 10 min. Methyl hydroquinone (MHQ) (0.28 g, 2.23 mmol) dissolved in anhydrous pyridine was then added to the mixture and refluxed for 3 h. After the reaction, the mixture was poured in 300 mL of methanol to precipitate the polymer. The polymer was dissolved in chloroform and reprecipitated with methanol twice. The obtained polymer P1 was dried at 70 °C under vacuum for 12 h. The polymers P2 and P3 were synthesized using the same procedure as polymer P1.

CONCLUSIONS

The polymerizable monomer dicarboxylic acid M1, the chiral diol M2, and a series of chiroptical dopants (D1, D2, and D3) were synthesized and identified using NMR, FTIR, and elemental analyses. The synthesized main-chain polyesters were found to exhibit nematic, smectic, or cholesteric liquidcrystal phases. The results from the transmission spectra revealed that the synthesized chiroptical dopants had high HTP values and good compatibilities with the cholesteric liquidcrystalline polymer P3. Stable colorful reflective patterns could be obtained with large-scale tuning through the entire visible region as well as the maintenance of the CLC phase upon UV irradiation. The discovered phenomena suggest the potential use of chiral photochromic dopant/liquid-crystalline polymer composites as UV-light-controllable RGB materials.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.Sb03201.

¹H NMR spectra of D1–D3; photoisomerization of the chiroptical dopant D1; photo-fries rearrangement of the aryl ester of the cinnamic acid derivative; ¹H NMR spectra of M1 and M2; synthesis route for the mainchain liquid-crystalline polyesters P2 and P3 using *p*-TsCl/Py/DMF as a condensing agent; DSC curves of P1, P2, and P3; Synthesis of D1, D2, and D3; results of polymerization; WAXD patterns of P3 at a heating rate of 10 °C/min at various temperatures; comparison of the shift in the reflection notch versus the irradiation time of the D1/P1 and D2/P1 CLC mixtures doped with different ratios of the chiroptical dopants; and phase transition temperature and thermal resistance of polymers. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Gray, G. W. Thermotropic Liquid Crystals; Wiley: New York, 1987.

(2) Preston, J. Rigid chain polymers. Angew. Makromol. Chem. 1982, 109/110, 1–19.

(3) Ciferri, A. Liquid Crystallinity in Polymers: Principles and Fundamental Properties; VCH Publishers: New York, 1991.

(4) Choi, S.-W.; Kawauchi, S.; Ha, N. Y.; Takezoe, H. Photoinduced chirality in azobenzene-containing polymer systems. *Phys. Chem. Chem. Phys.* 2007, 9, 3671–3681.

(5) Tejedor, R. M.; Oriol, L.; Serrano, J. L.; Sierra, T. Chiral photochemical induction in liquid crystals. *J. Mater. Chem.* **2008**, *18*, 2899–2908.

(6) Nikolova, L.; Todorov, T.; Ivanov, M.; Andruzzi, F.; Hvilsted, S.; Ramanujam, P. S. Photoinduced circular anisotropy in side-chain azobenzene polyesters. *Opt. Mater.* **1997**, *8*, 255–258.

(7) Nikolova, L.; Nedelchev, L.; Todorov, T.; Petrova, T.; Tomova, N.; Dragostinova, V.; Ramanujam, P. S.; Hvilsted, S. Self-induced light polarization rotation in azobenzene-containing polymers. *Appl. Phys. Lett.* **2000**, *77*, 657–659.

(8) Iftime, G.; Labarthet, F. L.; Natansohn, A.; Rochon, P. Control of chirality of an azobenzene liquid Crystallin polymer with circularly polarized light. *J. Am. Chem. Soc.* **2000**, *122*, 12646–12650.

(9) Hore, D.; Wu, Y.; Natansohn, A.; Rochon, P. Investigation of circular Bragg reflection in an azo polymer with photoinduced chirality. *J. Appl. Phys.* **2003**, *94*, 2162–2166.

(10) Wu, Y.; Natansohn, A.; Rochon, P. Photoinduced Chirality in Thin Films of Achiral Polymer Liquid Crystals Containing Azobenzene Chromophores. *Macromolecules* **2004**, *37*, 6801–6805.

(11) Tejedor, R. M.; Millaruelo, M.; Oriol, L.; Serrano, J. L.; Alcalá, R.; Rodríguez, F. J.; Villacampa, B. Photoinduced supramolecular chirality in side-chain liquid crystalline azopolymers. *J. Mater. Chem.* **2006**, *16*, 1674–1680.

(12) Choi, S.-W.; Fukuda, T.; Takanishi, Y.; Ishikawa, K.; Takezoe, H. Light-Induced Macroscopic Chirality in Thin Films of Achiral Main-Chain Amorphous Polyazourea System. *Jpn. J. Appl. Phys.* **2006**, *45*, 447–450.

(13) Luo, Q.; Cheng, H.; Tian, H. Recent progress on photochromic diarylethene polymers. *Polym. Chem.* **2011**, *2*, 2435–2443.

(14) Shibaev, V.; Bobrovsky, A.; Boiko, N. Photoactive liquid crystalline polymer systems with light-controllable structure and optical properties. *Prog. Polym. Sci.* **2003**, *28*, 729–836.

(15) Anzai, N.; Machida, S.; Horie, K. Light-induced control of textures and cholesteric pitch in liquid crystals containing chromium complexes, by means of circular and linear polarized light. *Liq. Cryst.* **2003**, *30*, 359–366.

(16) Kihara, H.; Miura, T.; Kishi, R. Polymer Architectures Consisting of Rotating Fibers Prepared by Photopolymerization in a Cholesteric Phase. *Macromol. Rapid Commun.* **2004**, *25*, 445–449.

(17) Goto, H.; Akagi, K. Preparation of Poly(3,4-ethylenedioxythiophene) in a Chiral Nematic Liquid-Crystal Field. *Macromol. Rapid Commun.* **2004**, *25*, 1482–1486.

(18) Li, Y.; Wang, M.; White, T. J.; Bunning, T. J.; Li, Q. Azoarenes with Opposite Chiral Configurations: Light-Driven Reversible Handedness Inversion in Self-Organized Helical Superstructures. *Angew. Chem., Int. Ed.* **2013**, *52*, 8925–8929.

(19) Wang, Y.; Urbas, A.; Li, Q. Reversible visible-light tuning of selforganized helical superstructures enabled by unprecedented lightdriven axially chiral molecular switches. *J. Am. Chem. Soc.* **2012**, *134*, 3342–3345. (20) Li, Q.; Green, L.; Venkataraman, N.; Shiyanovskaya, I.; Khan, A.; Urbas, A.; Doane, J. W. Reversible Photoswitchable Axially Chiral Dopants with High Helical Twisting Power. J. Am. Chem. Soc. 2007, 129, 12908–12909.

(21) Tamaoki, N. Cholesteric Liquid Crystals for Color Information Technology. *Adv. Mater.* 2001, *13*, 1135–1147.

(22) Van de Witte, P.; Brehmer, M.; Lub, J. LCD components obtained by patterning of chiral nematic polymer layers. *J. Mater. Chem.* **1999**, *9*, 2087–2094.

(23) Shin, S.; Park, M.; Cho, J. K.; Char, J.; Gong, M.; Jeong, K.-U. Tuning helical twisting power of isosorbide-based chiral dopants by chemical modifications. *Mol. Cryst. Liq. Cryst.* **2011**, *534*, 19–31.

(24) Xie, K. L.; Su, Y. H.; Zhang, C. X. Synthesis and optical activity of isosorbide chiral derivative containing fluorocarbon group as chiral dopant in liquid crystal materials. *Chin. Chem. Lett.* **2011**, *22*, 1447–1450.

(25) Earl, D. J.; Wilson, M. R. Predictions of molecular chirality and helical twisting powers: A theoretical study. *J. Chem. Phys.* 2003, *119*, 10280–10288.

(26) Bobrovsky, A. Y.; Boiko, N. I.; Shibaev, V. P. New Chiral-Photochromic Dopant with Variable Helical Twisting Power and its use in Photosensitive Cholesteric Materials. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* 2001, 363, 35–50.

(27) Fanghänel, D.; Timpe, G.; Orthman, V. Organic Photochromes; Bureau: New York, 1990.

(28) Kawatsuki, N.; Sakashita, S.; Takatani, K.; Yamamoto, T.; Sangen, O. Synthesis, characterization and photoreaction of side-chain liquid-crystalline polymers comprising cinnamoyl biphenyl mesogen. *Macromol. Chem. Phys.* **1996**, *197*, 1919–1935.

(29) Bobrovsky, A.; Ryabchun, A.; Medvedev, A.; Shibaev, V. Ordering phenomena and photoorientation processes in photochromic thin films of LC chiral azobenzene-containing polymer systems. *J. Photochem. Photobiol., A* **2009**, *206*, 46–52.

(30) Yager, K. G.; Barrett, C. J. Novel photo-switching using azobenzene functional materials. *J. Photochem. Photobiol., A* **2006**, *182*, 250–261.

(31) Sanadhya, S. G.; Oswal, S. L.; Parmar, K. C. Synthesis and characterization of aliphatic-aromatic polyesters using interfacial polycondensation technique. *J. Chem. Pharm. Res.* **2014**, *6*, 705–714. (32) Lin, J.; Sherrington, D. C.; Nield, E.; Richards, R. W. Novel Wholly Aromatic Lyotropic Liquid Crystalline Polyesters. Synthesis, Characterization, and Solution Properties. *Macromolecules* **1992**, *25*, 7107–7118.

(33) Podkościelny, W.; Wdowicka, D. Linear Polyesters Products of Interfacial Polycondensation of Bis(4-Hydroxyphenyl) Ether with Some Aliphatic Acid Dichlorides. J. Appl. Polym. Sci. **1988**, 35, 1779– 1789.

(34) Kricheldorf, H. R.; Probst, N. LC-polyimides 26. Photoreactive, nematic or cholesteric poly(ester-imide)s derived from 4-aminocinnamic acid trimellitimide, isosorbide and various diphenols. *High Perform. Polym.* **1995**, *7*, 471–480.

(35) Schwarz, G.; Kricheldorf, H. R. New polymer synthesis. LXXXIII. Synthesis of chiral and cholesteric polyesters from silylated "sugar diols. J. Polym. Sci., Part A: Polym. Chem. **1996**, 34, 603–611.

(36) Gary, G. W. *Thermotropic Liquid Crystals*; John Wiley & Sons: Chichester, U.K., 1987.

(37) Antoun, S.; Lenz, R. W.; Jin, J.-I. Liquid crystal polymers. IV. Thermotropic polyesters with flexible spacers in the main chain. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1901–1920.

(38) Bagheri, M.; Rad, R. Z. Synthesis and characterization of thermotropic liquid crystalline polyesters with biphenyl unit in the main chain. *React. Funct. Polym.* **2008**, *68*, 613–622.

(39) Jin, S.; Jeong, K.-U.; Tu, Y.; Graham, M. J.; Wang, J.; Harris, F. W.; Cheng, S. Z. D. Structure of Macroscopic Monodomains and Its Soft Confinements of Chiral Smectic Phases on Crystallization in a Main-Chain Nonracemic Liquid Crystalline Polyester. *Macromolecules* **2007**, *40*, 5450–5459.

(40) Jeong, K.-U.; Knapp, B. S.; Ge, J. J.; Jin, S.; Graham, M. J.; Xiong, H.; Harris, F. W.; Cheng, S. Z. D. Structures and Phase Transformations of Asymmetric Bent Main-Chain Liquid Crystalline Polyesters. *Macromolecules* **2005**, *38*, 8333–8344.

(41) Hrozhyk, U. A.; Serak, S. V.; Tabiryan, N. V.; Bunning, T. J. Photoinduced Isotropic State of Cholesteric Liquid Crystals: Novel Dynamic Photonic Materials. *Adv. Mater.* **2007**, *19*, 3244–3247.

(42) White, T. J.; Bricker, R. L.; Natarajan, L. V.; Serak, S. V.; Tabiryan, N. V.; Bunning, T. J. Polymer stabilization of phototunable cholesteric liquid crystals. *Soft Matter* **2009**, *5*, 3623–3628.

(43) Li, Q.; Li, L.; Kim, J.; Park, H.-S.; Williams, J. Reversible Photoresponsive Chiral Liquid Crystals Containing a Cholesteryl Moiety and Azobenzene Linker. *Chem. Mater.* **2005**, *17*, 6018–6021.

(44) Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 3. Effect of Structure of Photochromic Moieties on Alignment Behavior. *Macromolecules* **1998**, *31*, 4457–4463.

(45) Wilson, M. R.; Earl, D. J. Calculating the helical twisting power of chiral dopants. J. Mater. Chem. 2001, 11, 2672–2677.

(46) Ferrarini, A.; Moro, G. J.; Nordio, P. L. Simple molecular model for induced cholesteric phases. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1996**, *53*, 681–688.

(47) White, T. J.; Bricker, R. L.; Natarajan, L. V.; Tondiglia, V. P.; Green, L.; Li, Q.; Bunning, T. J. Electrically switchable, photoaddressable cholesteric liquid crystal reflectors. *Opt. Express* **2010**, *18*, 173–178.

(48) Yoshioka, T.; Ogata, T.; Nonaka, T.; Moritsugu, M.; Kim, S.-N.; Kurihara, S. Reversible-Photon-Mode Full-Color Display by Means of Photochemical Modulation of a Helically Cholesteric Structure. *Adv. Mater.* **2005**, *17*, 1226–1229.