# Optical Properties of Chiral Nematic Side-Chain Copolymers Bearing Cholesteryl and Azobenzene Building Blocks

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**ABSTRACT:** Thermotropic chiral nematic (N\*) side-chain copolymers (CPs) bearing cholesteryl and azobenzene units were synthesized to investigate the structure-property relationships of the acrylates of the chiral, achiral, and photochromic monomers of free radical polymerization-derived polymers. The polar effect of chlorine substitution on the benzene ring of the chiral monomer (M3\*) widened the mesophase transition temperature only at the monomer level, but no remarkable effect on the mesomorphic, optical or thermochromism of the corresponding CPs was observed. An examination of the CPs prepared using differential scanning calorimetry and hot-stage polarizing microscopy showed that all the CPs exhibited a cholesteric nematic phase (N\*), and increasing the content of the

cholesteryl units in the CPs displayed only the N\* phase over a much wider temperature range. On cooling from the isotropic melt of N\* CPs, selective reflections of visible light that changed from short to long wavelengths were observed. The photolysis of CPs revealed that **CP1–CP4** undergo reversible photoisomerization and that **CP5** and **CP6** undergo irreversible photoisomerization. The rate of isomerization depends on the type (-N=N-, -CH=CH-, and both) and content of photochromic units in the CPs. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 770–780, 2011

**KEYWORDS**: chiral; copolymerization; isomer/isomerization; liquid crystalline polymer; photoisomerization; UV-vis spectroscopy

**INTRODUCTION** Thermotropic chiral nematic polymers are represented by a class of macromolecular structures in which chiral moieties contribute to the formation of a cholesteric mesophase.<sup>1,2</sup> From the molecular structure point of view, one would expect that a copolymer (CP) comprised nematogenic- and chiral-monomers that should exhibit cholesteric mesomorphism in view of the common practice in which a chiral nematic material is routinely prepared by mixing a low molar mass nematogen with a chiral dopant.<sup>3,4</sup> The development of materials exhibiting both liquid crystallinity and photochromism is indeed a challenging task. Often, such attempts result in the loss of one or both of these properties. Azo-dye liquid crystals have attracted much attention for their potential use in optical storage applications because of their easy availability and reasonable photo-fatigue resistance as well as the marked transformation of their molecular shape between E and Z photoisomerization.<sup>5-8</sup>

Changes in a material's color can arise from exposure to heat or light.<sup>9–12</sup> These color-change phenomena are known as thermochromism and photochromism, respectively. Thermochromism is a well-known and useful property that is frequently observed with many different materials.<sup>13–15</sup> For example, by quenching the aligned cholesteric phase to a glass state by cooling to room temperature, films exhibiting selective reflection from UV to near-IR have been observed.<sup>16–19</sup> The change in color with temperature is an

aspect that generates much interest in the field of liquid crystals,<sup>16-18</sup> and polymers such as chiral side-chain liquid crystal polymers have rapidly grown in popularity in recent years because of their potential in emerging optical technologies. Many exhibit piezo and pyroelectric effects, some are ferroelectric, and others are capable of the selective reflection of electromagnetic radiation, particularly in the visible region.<sup>20–23</sup> This latter property can be a function of both structure and temperature, and in this work, we used copolymerization as an additional means of fine tuning this behavior. This work deals with the synthesis and characterization of thermotropic side-chain liquid crystalline CPs from a nematogenic monomer with two different photochromic (-N=N- and -CH=CH-) monomers to investigate their structure-property relationships. The effect of the feed ratio of photochromic units/chiral units on mesomorphic optical and thermal properties is discussed in detail.

#### **EXPERIMENTAL**

#### Materials

The 4-hydroxybenzoic acid (99.0%), 6-chloro-1-hexanol (95.0%), acryloyl chloride (98.0%), 4-butoxyphenol (99.0%), (–)-2-methyl-1-butanol (99.0%), (–)-cholesteryl chloroformate (97.0%,  $[\alpha]_D = -28^\circ$ , c = 2 in CHCl<sub>3</sub>), hydroquinone (99.5%), 4,4'-biphenol (97.0%), triethylamine (Et<sub>3</sub>N; 99.0%), *N*,*N*'-dicyclohexyl-carbodiimide (DCC; 99.0%), and 2,2'-

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**TABLE 1** Chemical Structures and Phase Transition Temperature of Monomers

<sup>a</sup> Estimated by DSC thermograms at a scanning rate of 5 K min<sup>-1</sup>.K, crystal; N, nematic; N\*, chrial nematic; SmA, smectic A; I, isotropic phase, heating and cooling cycles.

azobisisobutyronitrile (AIBN; 98.0%) were purchased from Acros Chemical. The 4-dimethylaminopyridine (DMAP; 99.0%) was purchased from Lancaster Chemical. All organic solvents were purchased from Aldrich Chemical. Dichloromethane ( $CH_2Cl_2$ ) was distilled over calcium hydride under argon immediately before use, and other solvents were purified by standard methods. Analytical thin-layer chromatography was performed on Merck aluminum plates with 0.2 mm of silica gel 60F-254. Anhydrous sodium sulfate was used to dry all organic extracts. The AIBN was freshly recrystallized from methanol.

#### Instrumentation

All new compounds were identified by <sup>1</sup>H NMR and Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy and elemental analysis (EA). FTIR spectra were recorded with a KBr disk on a Jasco VALOR III (Tokyo, Japan) FTIR spectrophotometer. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100.6 MHz) spectra were obtained on a Bruker AMX-400 (Darmstadt, Germany) high-resolution NMR spectrometer, and chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Optical rotations were measured at 30 °C in chloroform using a Jasco DIP-370 polarimeter with the Dline of sodium ( $\lambda = 589$  nm) and a precision of  $\pm 0.001^{\circ}$ . The measurements were performed using 1 wt % solutions of the substances in chloroform. The elemental analyses were carried out on a Heraeus CHN-O (Darmstadt, Germany) rapid elemental analyzer. The gel permeation chromatography (GPC) measurements were performed at 40 °C with a Hitachi L-4200 (Osaka, Japan) instrument equipped with TSK gel GMH and G2000H columns. CHCl3 was used as the eluent in these columns, with a rate of elution of 1.0 mL min<sup>-1</sup>. The instrument was calibrated with a polystyrene standard. Differential scanning calorimetry (DSC) was conducted with a PerkinElmer DSC 7 at heating and cooling rates of 10 K min<sup>-1</sup> under a nitrogen atmosphere. The phase transitions were investigated with 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 K min<sup>-1</sup>. Thermal decomposition temperature data were recorded under a nitrogen atmosphere at a heating rate of 20 K min<sup>-1</sup> with a PerkinElmer TGA 7 thermogravimetric analyzer (TGA). UV/Vis absorption spectra were measured with a Jasco V-550 spectrophotometer.

# Synthesis of Monomers

The monomers **M1–M4** in Table 1 were synthesized according to previously reported methods.<sup>24–26</sup> The synthesized monomers and compounds were identified using both <sup>1</sup>H NMR and FTIR. The phase transition temperatures of the above monomers are summarized in Table 1. Synthesis details are as follows: **M1**, yield = 67%; **M2**, yield = 52%,  $[\alpha] = -20.7^{\circ}$ ; **M3**, yield = 52%,  $[\alpha]_D = -18.6^{\circ}$ ; and **M4**, yield = 71%. The remaining monomers, **M5** and **M6**, were prepared as shown in Scheme 1 from 4-(6-acryloyloxyhexyloxy) benzoic acid, respectively, as described below.

# Synthesis of 4-(6-Hydroxyhexyloxy)cinnamic Acid (1)

The above compound was prepared according to an earlier reported procedure.<sup>27</sup> *Trans*-4-hydroxycinnamic acid (7.50 g, 45.7 mmol) was dissolved in EtOH (60 mL). KOH (7.73 g,



SCHEME 1 Synthesis of monomer M4–M6.

137.5 mmol) and trace KI dissolved in  $H_2O$  (20 mL) were added dropwise to the solution. The solution was heated at reflux for 10 min and 6-chloro-1-hexanol (7.47 g, 54.9 mmol) was then added. After the reaction mixture was stirred for 48 h at reflux temperature, the resulting mixture was poured into water and extracted with ethyl ether. The water phase solution was acidified with HCl and diluted with water until weakly acidic. The white precipitate was collected and washed several times with water. The crude product was recrystallized from EtOH in a yield of 46.8%.

The following FTIR bands were measured (cm<sup>-1</sup>): 3254 (OH), 2928, 2850 (CH<sub>2</sub>), 1689 (C=0 in Ar—COO—), 1605, 1520 (C—C in Ar), 1285, 1254 (COC), 2681, 2561 (COOH). The <sup>1</sup>H NMR results were (CDCl<sub>3</sub>,  $\delta$  in ppm): 1.10–1.52 (m, 8H, CH<sub>2</sub>), 3.38–3.42 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>), 4.01–4.03 (t, 2H, CH<sub>2</sub>OPh), 6.26 (dd, 1H, CH=CH), 6.57–7.53 (d, 4H, aromatic), 7.65 (dd, 1H, CH=CH), 12.50 (s, 1H, COOH).

# Synthesis of 4-(6-Acryloyloxyhexyloxy)cinnamic Acid (2)

Compound **1** (4 g, 15 mmol), *N*,*N*-dimethylaniline (2.02 g, 16.7 mmol), and trace 2,6-di-tert-butyl-4-methylphenol were dissolved in distilled 1,4-dioxane (80 mL). The solution was cooled with an ice/salt bath and then acryloyl chloride (2.65 mL, 33.4 mmol) dissolved in distilled 1,4-dioxane (5 mL) was added dropwise with vigorous stirring. After the reaction mixture was stirred for 24 h at room temperature, the solution was poured into cold water and the precipitate was filtered. The crude product was washed several times with water and recrystallized twice from EtOH, resulting in a yield of 66.2%.

The FTIR results were (cm<sup>-1</sup>): 2931, 2856 (CH<sub>2</sub>), 1730 (C=O in Ar–COO–), 1610, 1535 (C–C in Ar), 1290, 1245 (COC), 982 (=C–H), 2675, 2560 (COOH), 1690 (C=C). The <sup>1</sup>H NMR results were (CDCl<sub>3</sub>,  $\delta$  in ppm): 1.25–2.05 (m, 8H, CH<sub>2</sub>), 3.92–4.01 (t, 2H, CH<sub>2</sub>OPh), 4.12–4.19 (m 2H, COOCH<sub>2</sub>), 5.81 (dd, 1H, CH<sub>2</sub>=CH), 6.11 (dd, 1H, CH<sub>2</sub>=CH), 6.37 (dd, 2H, CH=CH), 6.88–6.91 (d, 2H, aromatic), 7.47–7.50 (d, 2H, aromatic), 7.74 (dd, 1H, CH=CH).

# Synthesis of 4-Nitrophenylazophenyl 4-(6-acryloyloxyhexyloxy) Cinnamate (M5)

Compound **2** (2 g, 6.29 mmol), 4-hydroxy-4'-nitro-azobenzene (1.68 g, 6.9 mmol), and DMAP (0.15 g, 1.26 mmol) were dissolved in  $CH_2Cl_2$  (40 mL) at 30 °C. *N*,*N*'-Dicyclohexyl carbodiimide (DCC; 1.56 g, 7.55 mmol) was dissolved in  $CH_2Cl_2$  (30 mL) and then added to the solution. The reaction mixture was stirred for 48 h at 30 °C. The resulting solution was filtered, and the precipitated urea was removed. The filtrate was washed twice with 0.5 N HCl, saturated with aqueous NaHCO<sub>3</sub> solution, and evaporated and dried in a vacuum. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1/5) to give a 68.5% yield.

The following FTIR bands were measured (cm<sup>-1</sup>): 2939, 2857 (CH<sub>2</sub>), 1600 (C=C in Ar), 1517 (NO<sub>2</sub>). The following are the <sup>1</sup>H NMR results (CDCl<sub>3</sub>,  $\delta$  in ppm): 1.27–2.17 (m, 8H, CH<sub>2</sub>), 3.40–4.04 (t, 2H, OCH<sub>2</sub>), 4.16–4.20 (t, 2H, OCH<sub>2</sub>), 5.81–5.84 (dd, 1H, CH<sub>2</sub>=CH), 6.08–6.17 (dd, 1H, CH<sub>2</sub>=CH), 6.38–6.44 (dd, 1H, CH=CH), 6.48–6.53 (dd, 1H, CH=CH), 6.92–6.95 (d, 2H, aromatic), 7.37–7.39 (d, 2H, aromatic), 7.54–7.57 (d, 2H, aromatic), 7.84–7.89 (dd, 1H, CH=CH), 8.02–8.05 (d, 4H, aromatic), 8.38–8.40 (d, 2H, aromatic). Anal. Calcd. for C<sub>30</sub>H<sub>29</sub>N<sub>3</sub>O<sub>7</sub>: C, 66.23; H, 5.39; N, 7.73. Found: C, 66.43; H, 5.25; N, 7.81. The phase transition temperature was: K 127.7 SmA 187.7 N 220.0 I.

# Synthesis of 4-(6-Acryloyloxyhexyloxy) Benzoic Acid (3)

Compound **3** was synthesized in a similar manner to compound **2**, but using 4-hydroxybenzoic acid for a 69.0% yield. FTIR (cm<sup>-1</sup>) bands were measured at: 2933, 2854 (CH<sub>2</sub>), 1733 (C=O in Ar–COO–), 1604, 1528 (C–C in Ar), 1291, 1246 (COC), 2672, 2566 (COOH), 1685 (C=C). <sup>1</sup>H NMR showed the following peaks (DMSO-d<sub>6</sub>,  $\delta$  in ppm): 0.94–1.28 (m, 8H, CH<sub>2</sub>), 4.05 (t, 2H, CH<sub>2</sub>OPh), 4.12 (t, 2H, COOCH<sub>2</sub>), 5.44 (dd, 1H, CH<sub>2</sub>=CH), 5.68 (dd, 1H, CH<sub>2</sub>=CH), 5.86 (dd, 1H, CH<sub>2</sub>=CH), 6.53–7.40 (d, 4H, aromatic), 12.5 (s, 1H, –COOH).

## Synthesis of 4-Nitro-4'-(6-acryloxyhexyloxybenzoyloxy) Stilbene (M6)

Compound **3** (3 g, 10.3 mmol), 4-hydroxy-4'-nitrostilbene (2.73 g, 11.3 mmol), and DMAP (0.26 g, 2.1 mmol) were dissolved in  $CH_2Cl_2$  (60 mL) at 30 °C. *N*,*N'*-Dicyclohexylcarbodiimide (DCC; 2.56 g, 12.4 mmol) was dissolved in  $CH_2Cl_2$  (30 mL) and then added to the solution. The reaction mixture was stirred for 48 h at 30 °C. The resulting solution was filtered, and the precipitated urea was removed. The filtrate was washed twice with 0.5 N HCl, saturated with aqueous NaHCO<sub>3</sub>, and evaporated and dried in a vacuum. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1/5) to give a yield of 72.3%.

FTIR (cm<sup>-1</sup>) bands were: 2943, 2863 (CH<sub>2</sub>), 1596 (C=C in Ar), 1502 (NO<sub>2</sub>). <sup>1</sup>H NMR peaks were (CDCl<sub>3</sub>,  $\delta$  in ppm): 1.48–2.08 (m, 8H, CH<sub>2</sub>), 4.13–4.17 (t, 4H, OCH<sub>2</sub>), 5.84–5.88 (dd, 1H, CH<sub>2</sub>=CH), 6.11–6.18(dd, 1H, CH<sub>2</sub>=CH), 6.32–6.36 (dd, 1H, CH<sub>2</sub>=CH), 7.10–7.12 (d, 2H, aromatic), 7.31–7.33 (d, 2H, aromatic), 7.40–7.44 (dd, 1H, CH=CH), 7.55–7.59 (dd, 1H, CH=CH), 7.76–7.78 (d, 2H, aromatic), 7.87–7.89 (d, 2H, aromatic), 8.11–8.13 (d, 2H, aromatic), 8.34–8.26 (d, 2H, aromatic). The analytical calculations for C<sub>30</sub>H<sub>29</sub>NO<sub>7</sub> were: C, 69.83; H, 5.63; N, 2.72. Found: C, 69.45; H, 5.67; N, 2.61.

# Synthesis of CPs (CP1-CP6)

CPs were obtained through the polymerization of monomers in benzene in the presence of 3 mol % of AIBN at 60  $^\circ$ C for 24 h.28 A feed molar ratio of the comonomers of 83:17 was used to prepare the binary CPs. A typical synthetic procedure is as follows. We started with a solution containing a known amount of monomer in benzene and 3 mol % of AIBN. The monomer solution was poured into a glass polymerization tube equipped with a sealing cap, which was then degassed in a vacuum using the freeze-thaw technique and subsequently sealed. After the completion of polymerization, the polymers were precipitated in a solution containing excess methanol. The crude polymers were then purified via dissolution in benzene, reprecipitated in methanol, and finally dried in a vacuum. The process used to synthesize ternary CPs was very similar to the process described for binary CPs.

#### **Fabrication of Polymer Films for Thermochromism**

The synthesized CPs were dissolved in chloroform and coated on a black treated glass plate. The coated film was dried at 80  $^{\circ}$ C for 3 h. Before testing, the film was heated above its isotropic melting temperature, followed by slow cooling to room temperature. A mask with a "UKN" opening was used to fabricate the patterned films. The polymer was deposited on the black treated glass plate through the mask, similar to a screen-printing process.

#### **RESULTS AND DISCUSSION**

# Synthesis and Mesomorphic Properties of Monomers (M1–M6)

The achiral (**M1**) and chiral (M2\* and M3\*) monomers were synthesized using our previously reported procedures,<sup>24–26</sup> and the photochromic monomers (**M4–M6**) were synthesized



according to Scheme 1. Additionally, the details of the synthetic procedures are described in the experimental section. All the monomers were structurally confirmed by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and EA. The data revealed that the spectroscopy results were in accordance with the structure. Figure 1 shows the <sup>1</sup>H NMR spectrum of monomer **M6**. The results from the spectra agreed with the proposed molecular structure of **M6**.

The <sup>1</sup>H NMR spectrum of **M6** showed peaks at 5.81-6.40 ppm, indicative of the vinyl protons of the terminal acrylate. The multiplet at 1.5-1.9 ppm indicated the presence of alkyl protons that were present in the spacer. The aromatic protons attached to the ether linkages appeared as doublets at 7.25 and 7.40 ppm. The aromatic protons attached to the carbonyl and nitro groups appeared as doublets at 8.34 and 8.25 ppm, respectively. The vinyl protons in the stilbene units were confirmed by the doublets at 7.65 and 7.50 ppm.

The mesomorphic behaviors of all the monomers were studied by DSC and polarized optical microscopy, and the transition temperatures obtained from the DSC analysis are summarized in Table 1. The results revealed that only monomers M1-M4 exhibited liquid crystalline properties. Monomers M2\* and M3\* exhibited chiral nematic liquid crystals (N\*) in which M3 exhibited a much wider temperature range for the liquid crystal phases when compared with M2. The DSC thermogram of monomer M2\* is shown in Figure 2. This may be due to the polar effect of chlorine<sup>29,30</sup> because substitution with chlorine increases spontaneous polarization when compared with nonchlorine compounds, which broadens the mesophase range. In the case of monomers M5 and M6, no significant liquid crystalline behavior was observed by either POM or DSC analysis. This may be explained by the fact that both M5 and M6 contain cinnamic units, which tend to undergo thermal polymerization during heating above their isotropic transition temperatures. On careful consideration of the molecular structure of monomers M4-M6, monomers M4 and M5 contained -N=N- groups, and only M4 exhibited liquid crystalline behavior (SmA) within the range of 127-220 °C. However, M5 and M6 contained the -CH=CH- group but did not exhibited liquid crystalline properties. From this, we concluded that the photochromic -CH=CH- group present in both M5 and M6 affect the liquid crystalline properties. Moreover, not only the geometry



FIGURE 2 DSC thermogram of M2\*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the molecule but also the polarity of the molecule determined the liquid crystalline properties.

Generally, the polarity of a molecule is dependent on the orientation of the ester linking groups.<sup>31</sup> M4, M5, and M6 possess only two ester groups; one is connected with a flexible spacer containing a terminal double bond, and the other acts as a linking group to the mesogen. We introduced one additional ester group in monomers M2 and M3 to connect the chiral group, thus contributing to the polarity of the system. However, because **M1** has two ester groups, the long terminal alkyl chain (butyl group) provided more flexibility to the molecule; thus, it exhibited sharp phase transitions.

For monomer **M3**, an SmA mesophase was expected, but an N\* mesophase was observed, presumably because **M3** has a chloro substituent on the benzene ring, which introduces an additional dipole moment across the long axis of the molecule. This enhances the intermolecular lateral attractions such that the smectic phase should appear for chlorine substituted monomer **M3**. Instead, the observed mesophase was N\*. This may result from the increase in molecular breadth, which forces the molecules further apart, thus reducing the strength of the intermolecular lateral attractions.<sup>32</sup>

The monomer **M4** showed a smectic A (SmA) mesophase between 127 and 187 °C, and thereafter exhibited a nematic mesophase that remained until the isotropic transition temperature was reached at 220 °C. Both applied methods in heating and cooling modes indicated one mesophase with an unchangeable fan-shaped texture that is characteristic of the smectic A mesophase. This type of smectic phase may be expected, as liquid crystals with a nitro group in the *para* position often have a nematic mesophase and perpendicular smectics.<sup>33</sup>

# Synthesis and Characterization of CPs (CP1-CP6)

The copolymerization of a nematogenic- and chiral-monomer was accomplished in benzene in the presence of radical initiator azobis(isobutyronitrile) at 333 K for 48 h under a



Polymer	Composition					
1 01 1 1101	Comonomers	<b>R</b> <sub>1</sub>	R <sub>2</sub>	<b>R</b> <sub>3</sub>		
CP1	M1/M2/M4	Н	-	-N=N-		
CP2	M1/M2/M5	Н	-C=C-	-N=N-		
CP3	M1/M2/M6	Н	-	-C=C-		
CP4	M1/M3/M4	Cl	-	-N=N-		
CP5	M1/M3/M5	Cl	-C=C-	-N=N-		
CP6	M1/M3/M6	Cl	-	-C=C-		

**SCHEME 2** Synthesis of copolymers.

TABLE 2 Results of	Copolymerization
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	Compo	N/ b		
Copolymers	Comonomers	$x/y/z^{c}$	(×10 <sup>4</sup> )	PDI <sup>b</sup>
CP1	M1/M2*/M4	82.5/8.5/9.0	1.55	2.16
CP2	M1/M2*/M5	83.0/5.0/12.0	0.99	1.79
CP3	M1/M2*/M6	85.3/5.1/9.6	1.59	1.44
CP4	M1/M3*/M4	83.0/4.6/12.4	1.11	1.23
CP5	M1/M3*/M5	80.2/3.2/16.6	0.69	1.32
CP6	M1/M3*/M6	83.2/4.1/12.7	1.28	1.32

<sup>a</sup> In benzene at 60 °C for 24 h in the presence of 3 mol % AIBN.

<sup>b</sup>  $M_{\rm w}$  and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl<sub>3</sub>.

<sup>c</sup> Feed molar ratio x/y/z = 83/17/10; final molar ratio was estimated by elemental analysis.

nitrogen atmosphere. The CPs were isolated and repeatedly precipitated from acetone or methanol until the monomers were completely removed. The CPs were then dried in a vacuum oven for several days before analysis. The structures of the CPs synthesized in the present investigation are summarized in Scheme 2. Each CP consisted of a higher amount (about 80%) of **M1** and less chiral monomer (**M2** or **M3**) and photochromic monomer (azo, cinnamic, or both). After polymerization, the corresponding signals of the vinyl group at 5.81–6.45 ppm in the <sup>1</sup>H NMR spectrum of the monomers disappeared, indicating that the polymerization was complete and that no more monomer was present in the polymers. When compared with the monomer <sup>1</sup>H NMR, the peaks of the chemical shifts corresponding to the polymers were broader, which was consistent with the expected polymer structure.

The CP compositions proved difficult to determine with accuracy, so the trends in behavior were expressed in terms of the molar feed composition of the monomer. After polymerization, the monomer contents of each of the repeating units were estimated using EA. The feed molar ratio of the comonomers determined from the EA is given in Table 2. In comparison with the feed molar ratio, the relative polymerization rate of each comonomer was estimated from the results of the composition of the synthesized CPs. From the GPC analysis, it was found that all the CPs synthesized had a moderate molecular weight within the range of  $0.99 \times 10^4$  and  $1.59 \times 10^4$  g mol<sup>-1</sup> and associated polydispersities in the range of 1.23–2.16. All the CPs were found to be soluble in organic solvents such as dichloromethane, chloroform, and Tetrahydrofuran (THF).

#### **Mesomorphic and Thermal Properties of CPs**

The liquid crystalline properties of all the synthesized CPs were studied by hot stage optical microscopy (HOPM) and DSC analysis, and the DSC results are summarized in Table 3. The results obtained from the HOPM analysis were in accordance with the DSC analysis. The DSC traces of CP3 and CP5 are shown in Figure 3. We observed that all the CPs exhibited glass transition temperatures,  $T_{q}$ , ranging from below to above ambient, indicating that the samples were amorphous with no evidence of the crystallinity observed in the monomers. The polymer backbone does enhance the tendency of low molecular mass compounds toward mesomorphism but does so by depressing or even cancelling the ability of low molar mass mesogenic compounds to crystallize after polymerization.<sup>34–37</sup> From the optical microscopy analysis, we found that all the CPs exhibited a chiral nematic (N\*) mesophase. Cowie and Hunter<sup>28</sup> reported that CPs with lower concentrations of the chiral monomer incorporated into the chain do not display a smectic phase. As expected, on cooling from the isotropic melt, all the CPs displayed a pale bluish green color with planar textures and oily streaks, which is characteristic of the cholesteric phase (N\*). The inset picture in Figure 3 shows the N\* mesophase during the heating cycle of CP3 at 124.6 °C. The transition temperatures from both DSC and POM revealed that increasing the ratio of chiral monomer (M2\*/M3\*) widened the liquid crystal mesophase range. On the other hand, decreasing the feed ratio of photochromic monomers (M4-M6, in which M5 and M6 are nonliquid crystal monomers) increased or widened the N\* mesophase range.

From Table 3, it was observed that **CP1** exhibited higher mesophase transition ( $\Delta T = 133.7$ ) than the other CPs,

	Phase Transition Temperature <sup>a</sup> (°C)			TGA		
Copolymers	Heating Cycle	Cooling Cycle	[α] <sub>D</sub> <sup>b</sup>	5% <sup>c</sup>	50% <sup>c</sup>	Char Yield (%) <sup>d</sup>
CP1	G 25.2 N* 158.9 I	l 156.5 N* 27.6 G	-3.37	327	445	5.08
CP2	G 31.9 N* 134.5 I	l 131.3 N* 34.0 G	-6.58	304	420	8.16
CP3	G 26.4 N* 143.5 I	l 140.3 N* 29.1 G	-4.90	283	410	10.01
CP4	G 15.1 N* 124.2 I	l 122.1 N* 18.6 G	-5.63	308	431	6.69
CP5	G 37.4 N* 117.5 I	l 114.3 N* 39.3 G	-6.38	304	425	9.32
CP6	G 20.9 N* 119.9 I	117.3 N* 25.5 G	-3.99	302	415	14.07

**TABLE 3** Thermal Properties and Specific Rotation of Copolymers

 $^{\rm a}$  G, glassy; N\*, chiral nematic; TGA, thermogravimetric analyzer; I, isotropic phase; the phase transition temperature of copolymers was estimated using differential scanning calorimetry, during heating and cooling at a rate of 5 K min^{-1}.

<sup>b</sup> Specific rotation of compounds, 0.1 g in 10 mL CHCl<sub>3</sub>.

<sup>c</sup> Weight loss in %.

<sup>d</sup> Char yield was measured at 600 °C.



FIGURE 3 DSC traces of CP3 and CP5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which is due to the higher degrees of polymerization. It is reported that the increase of mesomorphic phase transition temperatures with increasing degrees of polymerization is because this transition is strongly molecular weight dependant within the range of low molecular weight, whereas it is almost independent for higher molecular weight ranges.<sup>38–40</sup>

The specific rotations  $[\alpha]_D$  of all the CPs were determined in chloroform, and the results are summarized in Table 3. The specific rotations were all negative values and increased with increasing chiral monomers feed ratios. The thermal behavior of the CPs was evaluated by TGA in a nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Because the thermograms of all the CPs were quite similar, only representative TGA traces of CPs **CP1-CP4** are shown in Figure 4, and the data are illustrated in Table 3. The thermal stability of the polymers was evaluated at 5 and 50% weight losses at the corresponding minimum temperatures. The results showed that all the CPs were stable up to 283 °C, and degradation started thereafter in nitrogen. The degradation occurred in a two-step manner; the first step between 300



FIGURE 4 Representative TGA thermograms of CP1-CP4.

and 325 °C corresponded to the cleavage of ester linkage present in the polymer. The second step between 450 and 490 °C may have the outcome of cleavage of the aryl-alkyl-ether linkages present in the polymer chain.<sup>41</sup> The char yields of all the polymers were measured at 600 °C, and the results showed that all the CPs showed a low char yield of 5-10%. The char yield of the CPs was found to increase with the increasing ratio of photochromic monomers or increase with a decrease in the ratio of chiral monomers.

#### **Optical Properties of CPs**

The optical properties of the photochromic monomers (**M4–M6**) and all the CPs were studied in a chloroform  $(10^{-5} \text{ M})$  solution irradiated with 365 nm UV light. The representative spectral changes during the photolysis of **M4** and **CP4** in chloroform are depicted in Figure 5. At room temperature, azobenzene chromophores are expected to be in the more stable *trans* state in the dark. Under these conditions, the absorption spectra of CPs showed a major absorption peak near 350 nm and a weak one at 450 nm, which were assigned to the  $\pi$ - $\pi$ \* electronic transition of the *trans* isomers and the n- $\pi$ \* transition of the *cis* isomers, respectively. On irradiation with UV light, the CP undergoes *trans-cis* photoisomerization. The intensity of the absorption peak at 350 nm progressively decreases with increasing irradiation time



**FIGURE 5** Variation of UV–Vis spectra of **M4** and **CP4**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

until an equilibrium state is reached. At the same time, the weak peak at 450 nm becomes more pronounced. Similar results (UV spectral pattern) were observed for the remaining CPs containing azobenzene groups. A photostationary state was attained as the *cis*-isomer predominated after a suitable irradiation period.<sup>42</sup>

The time required for attaining a photostationary state for the photochromic monomers M4, M5, and M6 in solution was around 30 s, 5 min, and 30 min, respectively. Such variations in the time taken to reach the photostationary states in the monomers was expected because of the varied monomer structures; M4 possessed only the -N=N- group, which isomerizes at a faster rate and reaches the photostationary state in a shorter irradiation time when compared with M6, which possessed only -CH=CH-, and M5, which contained both groups. The --CH=-CH- group usually requires higher energy to invert from a trans to cis configuration. For example, the CP **CP6**, which contained only the -CH=CH- group caused only a 0.03 absorption variation after irradiation for 35 min at 365 nm. All the CPs required more time (>1 h) to attain a photostationary state and exhibited less of a cis-fraction in the stationary state, which was ascribed to the electron withdrawing nature of the nitro group hindering transcis isomerization of the azobenzene unit. This revealed that the nature of the substituent present on the terminal position of the azobenzene unit plays a critical role in the reversible trans-cis isomerization. After attaining a photostationary state, the resultant polymer solution was placed in a dark environment; the absorption band in the range of 350-360 nm increased (up to 90-95% of the initial value) slowly because of the slow thermal cis-trans back isomerization of the azobenzene unit at ambient temperature. In another experiment, after attaining the photostationary state, the resultant polymer solution was irradiated with 560 nm visible light, which caused the *cis-trans* back isomerization to occur rapidly when compared with ambient temperature in the dark. CP3 and CP6, which contain only the --CH=CHgroup, were expected to undergo photocrosslinking during UV irradiation. However, only trans-cis isomerization was observed, but it was irreversible. It was further shown by DSC analysis before and after irradiation that with CP3 and **CP6**, no differences (no shift) in transition temperatures were observed, which was indicative of the photoisomerization process. This may be due to the low -CH=CH- group content (9.6 and 12.7), which may result in the inability to achieve enough conformational freedom to undergo crosslinking.

Figure 6 shows the absorption spectra of **CP2** and **CP5** irradiated with 254 nm UV. As seen in **CP2**, the isobestic point was maintained during the first 5 min of irradiation, and after that, it vanished and there was a significant shift in the UV-Vis spectrum. In addition, the **CP5** isobestic point was not observed, suggesting that 254 nm UV irradiation caused an irreversible configurational isomerization.

The pitch of cholesteric liquid crystals is usually affected by temperature. Figure 7 shows the results of the thermal



FIGURE 6 Variation of UV–Vis spectra of **M4** and **CP4** at 254 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

effects on the reflection bands for **CP1–CP6**. The reflection wavelength and reflection bandwidth can be estimated using the following equations:

$$\lambda_0 = \check{n} \cdot p \tag{1}$$

$$\Delta \lambda = \Delta n \cdot p \tag{2}$$

where  $\lambda_0$  is the central wavelength of the reflected light,  $\check{n}$ is the average refractive index of the liquid crystal, p is the pitch of the cholesteric liquid crystal,  $\Delta \lambda$  is the reflection band width, and  $\Delta n$  is the birefringence difference. The reflection bands of CP1, CP2, and CP3 showed that increasing the temperature caused a blue shift. Higher temperatures usually increase the molecular randomness and decreases ň, resulting in a blue shift. Furthermore, increasing the temperature also decreases  $\Delta \lambda$ , which decreases both the reflection light strength and the reflection bandwidth. As shown in Figure 4 for CP1-CP3, the cholesteric liquid crystals were thermally stable between 30 and 60 °C. CP3 displayed a relatively broad reflection band. All the reflection bands of the CPs were located in visible light. Accordingly, the reflection light must be colorful. CP4 showed a thermally stable reflection between 40 and 60 °C. CP5 and CP6 showed decreased thermal resistances at



FIGURE 7 Dependence of temperature on reflection band of CP1–CP6.

higher temperatures because the reflection bands became narrow and had lower reflection efficiencies.

## **Thermochromism of CPs**

Based on the results from DSC and HOPM analyses, it was concluded that all the CPs exhibited a chiral nematic liquid crystalline phase (N\*). This is a distinct advantage as it is now possible to freeze a particular reflection color into the polymer glass by quenching the CP rapidly from the appropriate temperatures in the N\* phase. For example, **CP4**, on cooling from the isotropic melt, formed a pale bluish green and a homogeneous, planar texture with white, oily streaks, which is a characteristic of the cholesteric phase. The slow cooling of the same sample gave reflected color changes (shown in Fig. 8) in the sequence:

110 °C/blue 
$$\rightarrow$$
 80 °C/green  $\rightarrow$  50 °C/yellow

To investigate the practical thermochromism of the CP films, the synthesized CP **CP4** was coated on a glass substrate. The



FIGURE 8 Real image recorded film of **CP4** at various temperatures and a color scale for relative wavelength.

polymer film was heated to 88 °C and then quenched with an ice water bath. The film was reheated to 110 °C and subsequently quenched in an ice bath. The resulting colors quenched from 110 °C (a), 88 °C (b), and 50 °C (c) are shown in Figure 8 (a–c, respectively). As an additional experiment, the **CP4** material was deposited through a UKN shadow mask onto a black substrate. The plate was heated to 110 °C and then quenched at various temperatures. As shown in Figure 8, we were able to fabricate an UKN printed substrate with various colors, demonstrating that the synthesized CPs and the treating processes have potential for use in the field of colorful, rewritable materials. Figure 8 (d) shows a color scale for the comparison of wavelengths with the reflection color.

#### CONCLUSIONS

It was concluded that the copolymerization of a nematogenic monomer with the two different photochromic monomers (-N=N- and -CH=CH-) made it possible to obtain an N\* CP with different responses to the light irradiation of different wavelengths. According to polarizing optical microscopy, the synthesized CPs were able to produce a chiral nematic phase N\* with an isotropization temperature of 119–158 °C and glass transition temperature of approximately 15-37 °C. The thermal properties of the CPs revealed that all the CPs were thermally stable up to 283 °C, and they then started to decompose in a two stage process. Photolysis studies explained the reversible photoisomerization phenomena. The thermochromism of the CPs displayed different color patterns when quenching at various temperatures. These kinds of multifunctional CPs have potential applications in the field of colorful, rewritable materials.

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