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## Liquid Crystals

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### Liquid crystalline and thermo-optical properties of cyclic siloxane tetramers containing cholesteryl-4-allyloxy-benzoate and biphenyl-4-yl 4-allyloxybenzoate

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## Liquid crystalline and thermo-optical properties of cyclic siloxane tetramers containing cholesteryl-4-allyloxy-benzoate and biphenyl-4-yl 4-allyloxybenzoate

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A series of cyclic siloxane tetramers covering the whole composition range were synthesised using cyclotetrasiloxane, cholesteryl-4-allyloxy-benzoate and biphenyl-4-yl 4-allyloxybenzoate, and the effects of the cholesteryl-based mesogenic units on liquid crystalline and thermo-optical properties were studied. The presence of a cholesteric mesogen was observed to widen the mesogenic temperature range and tended to induce smectic A phases in the tetramers containing a higher mole fraction of cholesteryl-4-allyloxy-benzoate ( $X_{\text{chol}}$ ). The selective reflection of cholesteric tetramers shifted to shorter wavelengths with increasing  $X_{\text{chol}}$  and temperature. Blue phases can be easily observed for those tetramers containing more than 50.0 mol% cholesteric mesogen. The shorter pitch sample showed the wider blue phases range. The blue phases range width increased from 2.8°C to 18.5°C as  $X_{\text{chol}}$  increased from 0.5 to 1.0.

**Keywords:** cyclic siloxane tetramer; blue phase; selective reflection

### 1. Introduction

Cyclic liquid crystalline side chain siloxanes (CLCS) have attracted considerable interest because they combine the ordered microstructure of low molecular weight liquid crystals with the processing characteristics of polymers. Due to their well-defined molecular weights and low viscosity compared with other polymers, CLCS exhibit fast electro-optical switching properties [1, 2].

Compared with conventional low molecular weight mesogens, the higher molecular weights of these CLCS allow the mesophase properties to be frozen into a glassy phase. As a result, thin films and fibres possessing the anisotropic mechanical and optical properties of the low molecular weight mesogens can be formed. Due to the helical arrangement of molecules, the cholesteric CLCS exhibits some unique optical properties, which include selective reflection of light, thermochromism and circular dichroism. The most striking one is selective reflection, where circularly polarised light of a specific handedness and wavelength is reflected. When the reflected wavelength is in the range of the visible spectrum, an iridescent colour can be observed. The wavelength,  $\lambda_m$ , of selectively reflected light is given by  $\lambda_m = nP$ , where  $n$  is the average refractive index of the liquid crystalline phase and  $P$  is the cholesteric pitch. Therefore, derivatives of the system containing cholesteryl-4-allyloxy-benzoate

and biphenyl-4-yl 4-allyloxybenzoate (shown in Scheme 1) have been utilised in optical data storage materials [3, 4], optical band gap materials [5] and wide-band reflective polarisers [6–9].

Blue phases (BPs) are of particular interest because they have a fluid lattice, the structure of which is stabilised by lattice defects. There are three blue phases, i.e. blue phase I (BP I), blue phase II (BP II), and blue phase III (BP III). Among these, BP I and BP II have cubic symmetry [10, 11], whereas BP III has the same symmetry as the isotropic phase [12]. They are often observed in a very narrow temperature range ( $\sim 1^\circ\text{C}$ ) between the isotropic phase and cholesteric or smectic phases of highly chiral mesogens, where the low-temperature cholesteric phase is characterised by a pitch well below 1  $\mu\text{m}$  with the wavelength of selective reflection in the visible range of the spectrum [13]. BPs have potential applications as fast light modulators or tunable photonic crystals, but the main obstacle to the application is their narrow stable temperature range. Therefore, extending their range has attracted much attention. In order to solve this problem, there are several effective methods as follows: blue phases in the low molecular weight molecules with specific structures [14–17], oligomers [18–24] and the mixtures between them [25–28], and polymer stabilised blue phases [29–30].

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Although some work has been done on liquid crystalline cyclic siloxane tetramers containing cholesteryl-4-allyloxybenzoate and biphenyl-4-yl 4-allyloxybenzoate (shown in Scheme 1), the component proportion was limited [31, 32] and the thermo-optical properties of only a few were examined. Furthermore, the BPs, which are among the most interesting self-organised structures in the field of liquid crystals, were overlooked for the higher  $X_{\text{chol}}$  samples. Here, a series of liquid crystalline cyclic siloxane tetramers of this system covering the whole composition range ( $0 \leq X_{\text{chol}} \leq 1.0$ ) were synthesised using standard hydrosilylation chemistry, and their liquid crystalline and thermo-optical properties were studied in detail.

## 2. Experimental

### 2.1 Materials

4-Hydroxybenzoic acid, bromopropene, cholesterol, 4-phenylphenol and hexachloroplatinic acid hydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) were purchased from Beijing Chemical Co. (Beijing City, China) and used without any further purification. Cyclotetrasiloxane  $\text{D}_4^{\text{H}}$  (purity  $\geq 98\%$ ) was obtained from Ningbo Runhe Chemical Industry Co., Ltd. (Ningbo City, Zhejiang Province, China). The nematic LC host SLC1717 ( $T_{\text{N-I}} = 91.8^\circ\text{C}$ ) was purchased from Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd. (Shijiazhuang City, Hebei Province, China). All other solvents and reagents were obtained from Beijing Chemical Co. and purified by standard methods.

### 2.2 Characterisation

The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrophotometer.  $^1\text{H}$  NMR experiments were performed on a Bruker DMX-400 high-resolution NMR spectrometer with  $\text{SiMe}_4$  as internal standard in  $\text{CDCl}_3$ . Thermal transition properties were characterised using a Perkin-Elmer pyris-6 differential scanning calorimeter at a heating rate of  $10^\circ\text{C min}^{-1}$  under dry nitrogen atmosphere; phase transition temperatures were collected during the second heating scans. Visual observation of liquid crystalline transitions and optical textures under cross-polarised light were made using an Olympus BX-51 polarised light microscope (POM) equipped with a Linkam Scientific LTS 350 hot stage calibrated to an accuracy of  $\pm 0.1^\circ\text{C}$ . The transmission spectra were measured using a JASCO V-570 UV/Vis/NIR spectrophotometer equipped with a Linkam Scientific LTS 350 hot stage. The pitch of the chiral nematic mixture consisting of SLC1717 and each chiral additive was measured by the Cano wedge method [33].

## 2.3 Synthesis

### 2.3.1 Synthesis of monomers

The structures of cholesteric monomer cholesteryl-4-allyloxybenzoate (M1) and nematic monomer biphenyl-4-yl 4-allyloxybenzoate (M2) are shown in Scheme 1. M1 was made by the literature method [34] in 70% yield. The melting temperature ( $T_{\text{m}}$ ) and clearing temperature ( $T_{\text{c}}$ ) are  $116.5^\circ\text{C}$  and  $245.4^\circ\text{C}$ , respectively.

FT-IR (KBr) ( $\text{cm}^{-1}$ ): 3074 (=C-H), 2944, 2867 (- $\text{CH}_3$ , - $\text{CH}_2$ -), 1707 (C = O), 1651 (C = C), 1607, 1510 (Ar), 1279, 1254 (C-O-C).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.99 (2H, d, Ar-**H**), 6.92 (2H, d, Ar-**H**), 6.05 (1H, m,  $\text{CH}_2 = \text{CH-CH}_2$ -), 5.44 (1H, d, one of  $\text{CH}_2 = \text{CH-CH}_2$ -), 5.40 (1H, t, -C = **CH**- in cholesteryl moiety), 5.31 (1H, d, one of  $\text{CH}_2 = \text{CH-CH}_2$ -), 4.83 (1H, m, -O-**CH**- in cholesteryl moiety), 4.59 (2H, d,  $\text{CH}_2 = \text{CH-CH}_2$ -), 2.45 (2H, d, -O-**CH-CH}\_2**- in cholesteryl moiety), 0.86-2.01 (38H, m, **H** in cholesteryl moiety), 0.69 (3H, s, -**CH}\_3** in cholesteryl moiety).

M2 was synthesised according to the literature [35] in 75% yield.  $T_{\text{m}}$  and  $T_{\text{c}}$  are  $142.0^\circ\text{C}$  and  $143.4^\circ\text{C}$ , respectively.

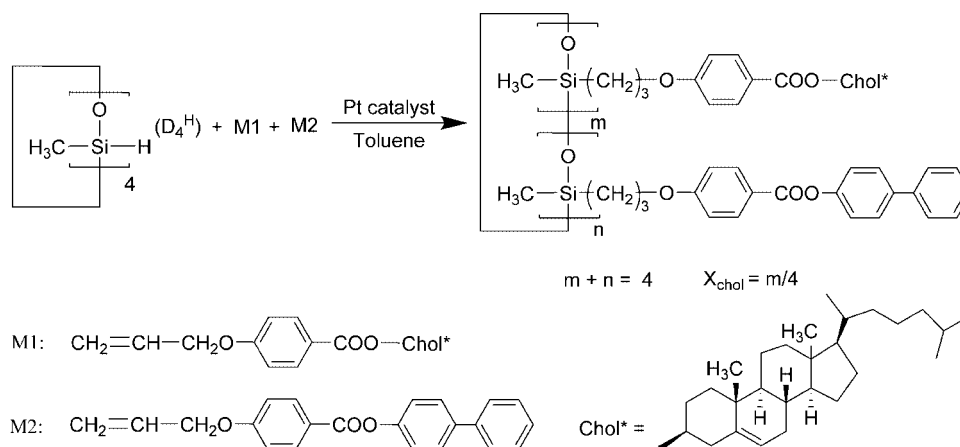
FT-IR (KBr) ( $\text{cm}^{-1}$ ): 3072 (=C-H), 1731 (C = O), 1647 (C = C), 1608, 1511 (Ar), 1261, 1215 (C-O-C).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.18 (2H, d, Ar-**H**), 7.64 (2H, d, Ar-**H**), 7.60 (2H, d, Ar-**H**), 7.45 (2H, t, Ar-**H**), 7.36 (1H, t, Ar-**H**), 7.28 (2H, d, Ar-**H**), 7.01 (2H, d, Ar-**H**), 6.09 (1H, m,  $\text{CH}_2 = \text{CH-CH}_2$ -), 5.46 (1H, d, one of  $\text{CH}_2 = \text{CH-CH}_2$ -), 5.35 (1H, d, one of  $\text{CH}_2 = \text{CH-CH}_2$ -), 4.65 (2H, d,  $\text{CH}_2 = \text{CH-CH}_2$ -).

### 2.3.2 Synthesis of tetramers

The synthesis of the tetramers was performed according to Scheme 1 and Table 1. The same method [36] was adopted for the synthesis of tetramers T1–T9. The synthesis of tetramer T5 is given as an example.

A stirred mixture of  $\text{D}_4^{\text{H}}$  (0.481 g, 2.0 mmol, 8.0 mmol (Si-H)), vinyl monomers M1 (2.406 g, 4.4 mmol) and M2 (1.454 g, 4.4 mmol), i.e. a 10% excess of monomer over a mole ratio of 1:1 based upon siloxane hydrogen, 5.0 wt% hexachloroplatinic acid hydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) in isopropyl alcohol (two drops) and fresh toluene (20 mL) was heated under  $\text{N}_2$  and anhydrous conditions at  $110^\circ\text{C}$ . The progress of the hydrosilylation reaction, monitored from the Si-H ( $2160 \text{ cm}^{-1}$ ) stretch intensity, went to completion within 24 h as indicated by FT-IR. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The crude tetramer was purified by several reprecipitations from



Scheme 1. Synthetic route of the tetramers.

Table 1. Phase behaviours and selective reflection wavelengths of the tetramers.

Tetramer	$X_{\text{chol}}^{[a]}$	Phase transitions <sup>[b]</sup> /°C (Enthalpy changes/J g <sup>-1</sup> )	$\Delta T^{[c]}$ /°C	$\lambda_m^{[d]}$ /nm
T1	0.00	Cr <sub>1</sub> 45.6 Cr <sub>2</sub> 156.9 N 194.4 (1.5) I	37.5	–
T2	0.125	G 55.5 Ch 189.2 (2.0) I	133.7	1190
T3	0.25	G 51.5 Ch 192.7 (1.8) I	141.2	732
T4	0.375	G 53.7 Ch 208.3 (1.8) I	154.6	554
T5	0.50	G 43.4 Ch 205.2 <sup>[e]</sup> BPs 208.0 (1.2) I	164.6	494
T6	0.625	G 55.2 Ch 230.5 <sup>[e]</sup> BPs 234.5 (1.4) I	179.3	476
T7	0.75	G 57.3 SmA 197.7 (0.2) Ch 237.5 <sup>[e]</sup> BPs 242.5 (1.5) I	185.2	438
T8	0.875	G 56.4 SmA 220.2 (0.3) Ch 245.4 <sup>[e]</sup> BPs 251.0 (1.6) I	194.6	415
T9	1.00	G 65.5 SmA 233.1 (1.0) Ch 248.0 <sup>[e]</sup> BPs 266.5 (1.1) I	201.0	408

Notes: <sup>[a]</sup> Mole fraction of M1 based on M1 + M2; <sup>[b]</sup> Cr = crystal, G = glassy, SmA = smectic A, N = nematic, Ch = cholesteric, BPs = blue phases, I = isotropic; <sup>[c]</sup> mesogenic temperature range width; <sup>[d]</sup> selective reflection wavelength measured near ( $\sim 1^\circ\text{C}$ ) the Ch-I (or Ch-BPs) transition; <sup>[e]</sup> determined by POM but too weak to be seen in the DSC scans.

the  $\text{CH}_2\text{Cl}_2$  solution into cold methanol. The procedure was repeated until the product was shown by TLC to be free from monomer. Finally, the product was dried under vacuum and T5 was obtained. FT-IR (KBr) ( $\text{cm}^{-1}$ ): 2944, 2868 ( $-\text{CH}_3$ ,  $-\text{CH}_2-$ ), 1736, 1711 ( $\text{C}=\text{O}$  in different ester linkages), 1606, 1510 (Ar), 1252, 1208 ( $\text{C}-\text{O}-\text{C}$ ), 1100–1000 ( $\text{Si}-\text{O}$ ).

### 3. Results and discussion

#### 3.1 Liquid crystalline properties

The mesophase properties of M1, M2 and tetramers T1–T9 were determined by differential scanning calorimetry (DSC) and POM. Thermal behaviours determined by DSC were consistent with POM observations. The DSC curves of T1–T9 are presented in Figure 1.

The phase behaviours and selective reflection wavelengths of the tetramers synthesised are summarised in Table 1. All the tetramers exhibited thermotropic LC properties and the composition dependence of transition temperature for the cyclic system is shown in Figure 2.

The liquid crystalline behaviours of the mesomorphic tetramers occurred over a restricted temperature range between  $T_c$  and  $T_m$  or the glass transition temperature ( $T_g$ ); the mesogenic temperature range width ( $\Delta T$ ) was determined as  $T_c - T_m$  or  $T_c - T_g$ . Figure 3 shows the effect of  $X_{\text{chol}}$  on  $\Delta T$  for tetramers. As shown in Table 1, in comparison with the  $T_m$  and  $T_c$  of T1, the  $T_g$  and  $T_c$  of T2 decreased by  $101.4^\circ\text{C}$  and  $5.2^\circ\text{C}$ , respectively, when  $X_{\text{chol}}$  increased from 0 to 0.125;  $\Delta T$  of T2 widened by  $96.2^\circ\text{C}$ . When  $X_{\text{chol}}$  increased from 0.125 to 1.0,  $T_c$  obviously increased and  $T_g$  changed a little;  $\Delta T$  widened linearly with a rate about  $0.8^\circ\text{C} (\text{mol}\%)^{-1}$  from T2 to T9. The increase in  $\Delta T$  indicated the reinforced effect of M1 on the mesophase range of this cyclic system.

Homobiphenyl siloxane T1 exhibited a lower temperature crystalline phase above which a nematic mesophase was present. DSC measurements indicated two melting peaks upon heating separated by a recrystallisation endotherm as listed in Table 1. Only one recrystallisation was observed on cooling at  $123.1^\circ\text{C}$ . Within the mesophase, POM revealed only a nematic phase (consistent with a cholesteric with an infinite



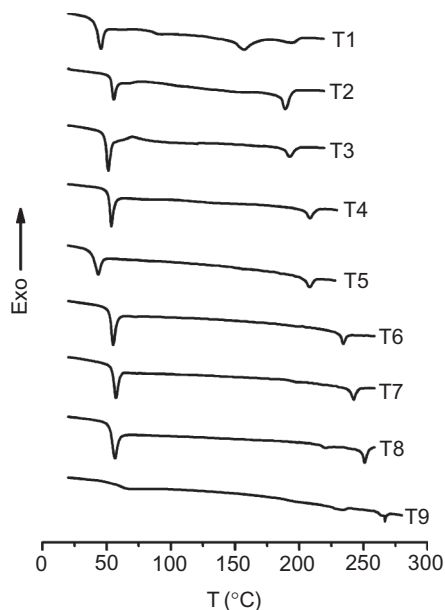


Figure 1. DSC thermograms of T1–T9 on the second heating scans at  $10^{\circ}\text{C min}^{-1}$ .

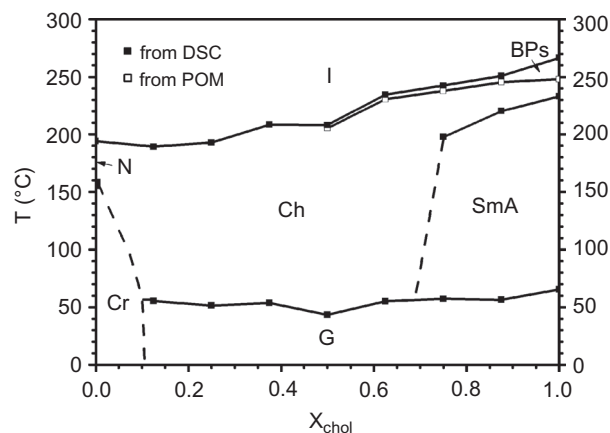


Figure 2. Composition dependence of transition temperature for tetramers shown in Scheme 1.

pitch) (Figure 4(a)) and no signs of other texture appearing upon cooling to room temperature.

A large cholesteric mesophase region above a glassy solid phase was observed on the left side of Figure 2. With increasing  $X_{\text{chol}}$  from 0.125 to 0.625, the cholesteric phase range width increased from  $133.7^{\circ}\text{C}$  to  $175.3^{\circ}\text{C}$ . When T4 was heated from room temperature, the viewing field became bright and a Grandjean texture appeared (Figure 4(b)). On further heating to  $120.0^{\circ}\text{C}$ , the oily streaks texture gradually appeared (Figure 4(c)), and the selective reflection colour changed from red to green with increasing temperature. The oily streaks texture disappeared quickly

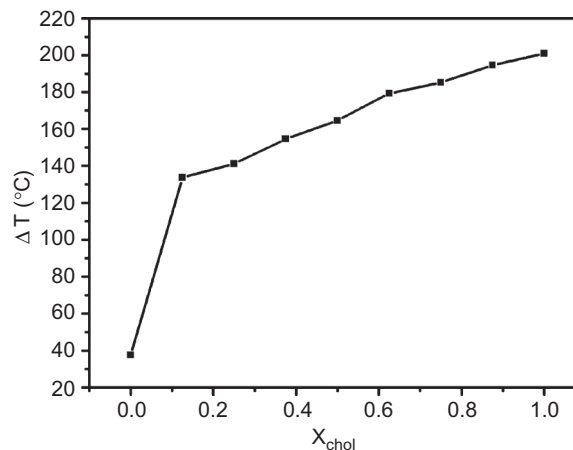


Figure 3. Mesogenic temperature range width  $\Delta T$  versus  $X_{\text{chol}}$  for T1–T9.

on heating to  $208.3^{\circ}\text{C}$  and resulted in a whole dark view of the isotropic liquid phase.

Tetramers containing more than 75.0 mol% cholesteric mesogen formed a lower temperature smectic A (SmA) phase in addition to a narrow upper temperature cholesteric (Ch) phase. When  $X_{\text{chol}}$  increased from 0.75 to 1.0, the enthalpy of SmA to Ch increased from  $0.2 \text{ J g}^{-1}$  to  $1.0 \text{ J g}^{-1}$ , and the SmA phase range width increased from  $140.4^{\circ}\text{C}$  to  $167.6^{\circ}\text{C}$ ; meanwhile the cholesteric phase range width fell from  $40.1^{\circ}\text{C}$  to  $14.9^{\circ}\text{C}$ . Large dark areas of view in slides treated for homeotropic orientation (characteristics of the SmA phases) were observed with POM (Figure 4(d)). All the data and phenomena suggested that the cholesteric mesogen tended to induce a layer packing in this system.

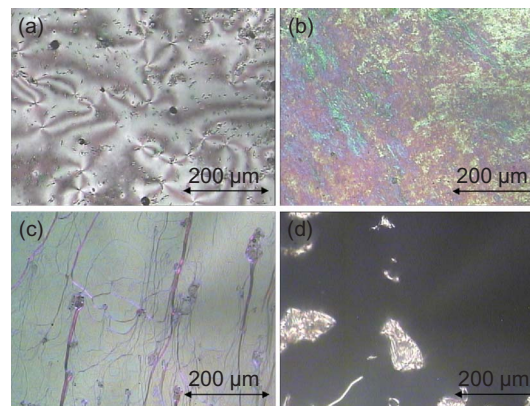


Figure 4. POM photos of T1, T4 and T7: (a) schlieren texture of T1 at  $158.0^{\circ}\text{C}$  on cooling; (b) Grandjean texture of T4 at  $110.0^{\circ}\text{C}$  on heating; (c) oily streaks texture of T4 at  $207.0^{\circ}\text{C}$  on heating; and (d) pseudo-isotropic SmA texture of T7 at  $147.0^{\circ}\text{C}$  on cooling (colour version online).

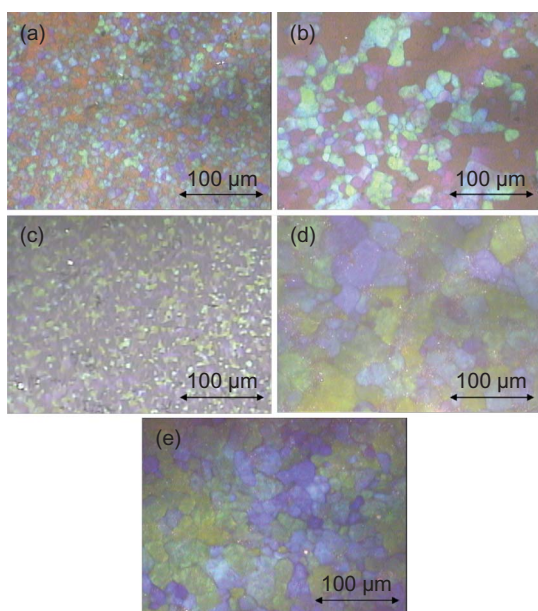


Figure 5. Platelet textures of T5–T9 (on cooling at  $0.2^\circ\text{C min}^{-1}$ ): (a) T5 at  $205.0^\circ\text{C}$ ; (b) T6 at  $230.7^\circ\text{C}$ ; (c) T7 at  $234.0^\circ\text{C}$ ; (d) T8 at  $236.2^\circ\text{C}$ ; and (e) T9 at  $240.2^\circ\text{C}$ .

For tetramers containing more than 50.0 mol% of M1, enantiotropic BPs were found and ascertained by observation of the characteristic textural pattern. When T5 was heated slowly at a rate  $0.2^\circ\text{C min}^{-1}$ , a platelet texture of BP I appeared at  $205.2^\circ\text{C}$ . On further heating, BP I changed to BP III at  $207.3^\circ\text{C}$ , and finally resulted in a whole dark view of isotropic liquid at  $208.0^\circ\text{C}$ . When T5 was cooled from the isotropic phase slowly ( $0.2^\circ\text{C min}^{-1}$ ), cubic BPs with a platelet texture were observed beside the fog phase (BP III) (Figure 5(a)). Similar observations could be made for T6–T9 (Figure 5(b)–5(e)). It can be seen from Table 1 that  $\lambda_m$  decreased as  $X_{\text{chol}}$  increased from 0.5 to 1.0, and that the BPs range width increased from  $2.8^\circ\text{C}$  to  $18.5^\circ\text{C}$ . This indicated that the larger helical twisting power (HTP) could induce the wider BPs range for the higher  $X_{\text{chol}}$  in this system.

In order to better understand the effect of  $X_{\text{chol}}$  on the BPs of chiral tetramers, we investigated the helical twisting power of the chiral monomer M1 and chiral tetramers T2–T9 in nematic LC host SLC1717. The helical pitch for a chiral nematic mixture of SLC1717 and 5 wt% of each chiral compound was measured from  $25.0^\circ\text{C}$  to  $95.0^\circ\text{C}$ . The clearing points of all the chiral nematic mixtures were between  $95.0^\circ\text{C}$  and  $97.0^\circ\text{C}$ . According to the equation  $HTP = (Pc)^{-1}$ , the HTP values of each compound at different temperatures were obtained and summarised in Figure 6.

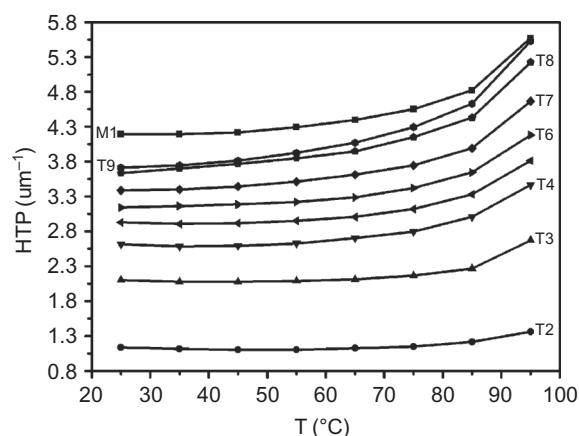


Figure 6. Temperature dependence of the helical twisting power for M1 and T2–T9 in SLC1717.

It can be seen that the HTP value of monomer M1 is the largest among the compounds at the whole temperature range due to the higher content of cholesteryl moiety. However, tetramers T5–T9 showed blue phases whereas monomer M1 showed only a cholesteric phase. Therefore, not only the helical twisting power of the chiral compound but also the molecular structure affects the stability of the BPs. As shown in Figure 6, when the temperatures increased, the HTP values of T2–T5 initially fell slightly and then increased, whereas the HTP values of M1 and T6–T9 increased all the time; compared with the chiral tetramers, the  $dHTP/dT$  value of M1 was relatively medium. Hence, it can be concluded that the siloxane backbone plays a critical role in the blue phases and helical twisting powers for the chiral cyclic siloxane tetramers.

### 3.2 Thermo-optical properties

Figure 7 shows a typical profile of the transmission spectra under normal incidence for tetramer T7 at different temperatures (a minimum of light transmission corresponds to the maximum of selective light reflection of circularly polarised light). When T7 was heated from room temperature in a cell with a planar boundary condition, it remained colourless until the temperature reached the SmA–Ch transition. When the sample was further heated from the SmA–Ch transition to  $237.0^\circ\text{C}$ , the selective reflection colour changed from gradually red to purple.

Figure 8, where the dash lines represent the SmA–Ch transition temperatures, shows the temperature dependences of the selective reflection wavelengths for tetramers T2–T9 in the cholesteric phases. It can be seen that for T2–T6,  $d\lambda_m/dT > 0$ , i.e. with increasing

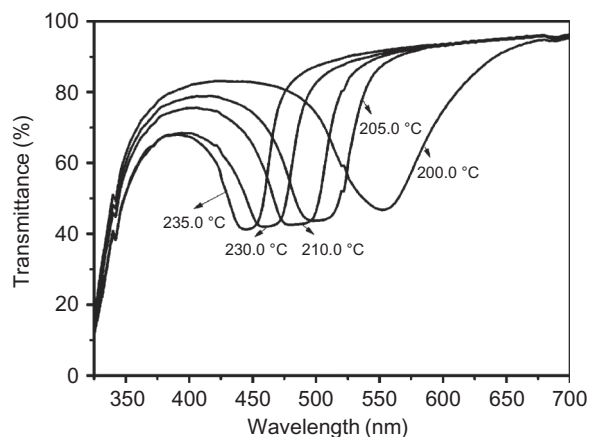


Figure 7. Transmission spectra for T7 from 200.0°C to 235.0°C.

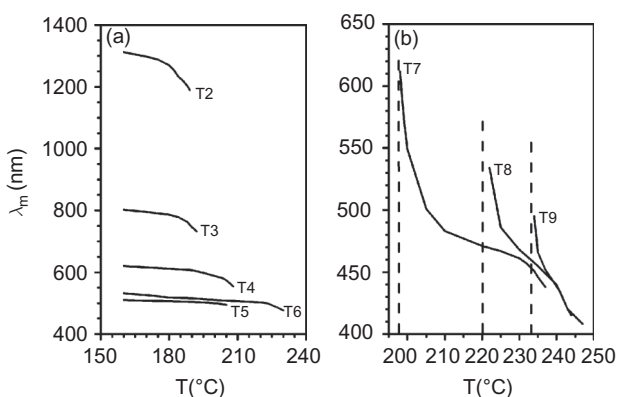


Figure 8. Temperature dependence of the selective reflected wavelength  $\lambda_m$  for T2–T9.

temperature, tightening of the helix is observed; the values of  $\lambda_m$  decreased slightly until the temperatures were close to the Ch–I (or Ch–BPs) transitions. When T7–T9 were heated from the SmA–Ch transitions, pronounced pre-transitional decreases in helix pitch were observed; when heated to the temperatures near the Ch–BPs transition, their pitches decreased abruptly. These results indicated that the helical twist powers of tetramers T2–T9 increased slightly in the lower temperatures and increased markedly in the higher temperatures.

#### 4. Conclusions

Nine cyclic siloxane tetramers, containing cholesteryl-4-allyloxy-benzoate and biphenyl-4-yl 4-allyloxybenzoate, and covering the whole composition range were synthesised and their liquid crystalline and thermo-optical properties were examined in detail.

All the tetramers exhibited thermotropic LC properties. In certain temperature regions, the tetramers

showed cholesteric phases except for the homobiphenyl one which showed only a nematic phase. For the chiral tetramers, the selective reflection wavelengths decreased as temperatures increased, and the helical twist powers increased with increasing  $X_{\text{chol}}$ .

The cholesteryl-based mesogen can broaden the liquid crystal temperature range and introduce SmA phases into tetramers containing  $X_{\text{chol}} \geq 0.75$  between the glassy and the cholesteric phases. Tetramers containing more than 50.0 mol% cholesteric mesogen can exhibit blue phases and the blue phases range width increased from 2.8°C to 18.5°C as  $X_{\text{chol}}$  increased from 0.5 to 1.0.

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