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Synthesis and characterization of side chain liquid crystalline polymers exhibiting cholesteric and blue phases

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A series of cyclosiloxane-based cholesteric liquid crystalline (LC) polymers were synthesized from a cholesteric LC monomer cholest-5-en-3-yl(3 β) 4-(2-propenyloxy)benzoate and a nematic LC monomer butyl 4-[4-(2-propenyloxy)benzoxy]benzoate. All the polymers exhibit thermotropic LC properties and show cholesteric phases. Most of the polymers display four types of phase transition behaviour corresponding to glass transition, melting point, cholesteric phase–blue phase transition and clearing point. The mesophase temperature range of the blue phases are as broad as 20°C. The blue phase was confirmed by the appearance of planar textures and cubic packings. With an increase of non-chiral component in the polymers, the clearing point decreases slightly, while the glass transition and melting temperatures change little. In the reflection spectra of the polymer series the reflected wavelength broadens and shifts to longer wavelength with increase of the non-chiral component in the polymer systems, suggesting that the helical pitch P lengthens.

1. Introduction

Side chain liquid crystalline polymers (LCPs) combine the electro-optical properties of low molecular mass liquid crystals with the mechanical properties and easy processing of polymers [1, 2]. A recent focus of interest in the synthesis of LCP has been the preparation of chiral LCPs. Chirality has become an important and complex topic in liquid crystal research, due mainly to the fact that molecular asymmetry imparts form chirality to the liquid crystalline phases and leads to possible new technical applications for chiral LCPs [3].

Chiral LCPs may exhibit a wide variety of liquid crystalline phases, including the chiral smectic C* (SmC*), cholesteric (N*), and blue phases (BP). Ferroelectricity in liquid crystals is a specific property of some SmC* phases. It was first discovered that a classic liquid crystalline material *p*-decyloxybenzylidene-*p*-amino-2-methylbutyl cinnamate, exhibits a chiral smectic C* phase [4]. Since then considerable experimental and theoretical studies have been carried out in order to understand the various physical properties of this phase [5, 6]. Such polymers can be used as electro-optical materials, for optical storage, and in pyroelectric devices [7–9].

Cholesteric liquid crystals are chiral nematics, where the handedness of the constituent molecules causes the

orientation of the local nematic director to vary in space. In the helical cholesteric structure, the director is perpendicular to the helix axis, and its orientation varies linearly with position along this axis. The spatial period of the structure is the pitch, which is determined by the concentration and helical twisting power of the chiral constituents. As a consequence of the periodicity of the helical cholesteric structure and the birefringence of the liquid crystal, for a range of wavelengths light propagation along the helix axis is forbidden for one of the normal modes. Since propagation is forbidden, incident light with a wavelength in this band and with the same helicity as the cholesteric is strongly reflected. The edges of this reflection band are at wavelengths equal to the refractive indices times the pitch. If the reflected wavelength is in the visible range of the spectrum, the cholesteric phase appears coloured. Cholesteric LCPs with the unique property of selective reflection of circularly polarized light have offered large potential for various optical applications [10–14].

The blue phases (BP), which can be observed between the isotropic and the cholesteric phases, can be considered the three-dimensional counterpart of the cholesteric phase. Two types of BP are known, BP1 and BP2, exhibiting cubic lattices with no positional long range order [15]. They are frustrated phases of chiral molecules, generally occurring over a temperature region of a few tenths of only Kelvins [16]. Compared

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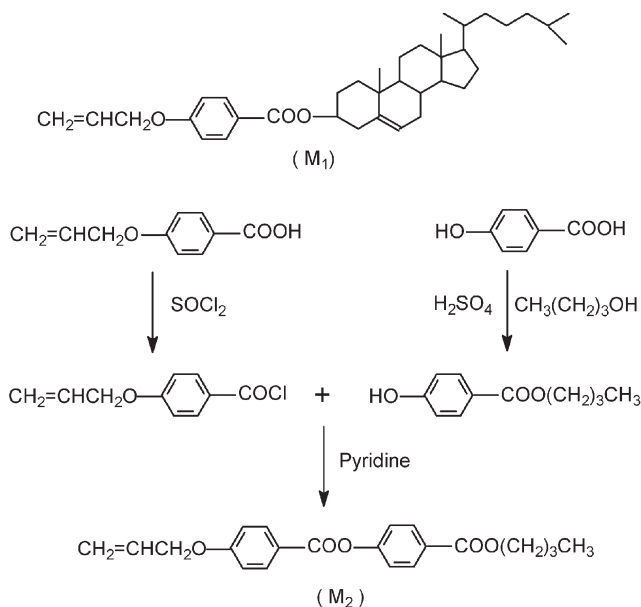
with the SmC* phase and the N* phase, the BP phases have become complex topics in LCP research because of their unique optical properties and potential applications. However, most of described liquid crystals with BP phases are low molar mass liquid crystals, and the BP temperature ranges are extremely narrow. We are interested in cholesteric LCPs with a broad BP using cholesterol as chiral units; and would like to know the fundamental link between chiral component in the polymers and the behaviour of cholesteric mesophases and blue phases. Furthermore, it is of interest to investigate how the chiral components modify liquid crystalline structures of such side chain LCPs. In the present study, a series of cyclosiloxane-based cholesteric LCPs were graft polymerized with a cholesteric LC monomer cholest-5-en-3-yl(3 β) 4-(2-propenyloxy)benzoate and a nematic LC monomer butyl 4-[4-(2-propenyloxy)benzoxy]benzoate.

2. Experimental

2.1. Material and measurements

3-Bromopropene, 4-hydroxy benzoic acid, *n*-butanol, cholesterol and pyridine were purchased from Beijing Chemical Co. Hexachloroplatinic acid hydrate and thionyl chloride were obtained from Shenyang Chemical Co. Cyclo(methylhydrogeno)siloxane (CMHS) ($M_n=200\text{--}300\text{ g mol}^{-1}$) were obtained from Jilin Chemical Industry Company and used without further purification. Pyridine was purified by distillation over potassium hydroxide.

Fourier transform infrared spectroscopy (FTIR) of the synthesized polymers and monomers in the solid state was performed by the KBr method on a Nicolet 510P FTIR Spectrometer. ^1H NMR spectra (300 MHz) were recorded on a Varian WH-90 spectrometer (Varian Associates, Palo Alto, CA). Ultraviolet–visible spectrophotometry was measured with a Perkin Elmer instruments Lambda 900. Reflection spectra of cholesteric mesophases were obtained by reflective light with an incident beam angle of 8°. Thermal transition properties were characterized by a Netzsch Instruments DSC 204 at a heating rate of 10°C min $^{-1}$ under nitrogen. Visual observation of liquid crystalline transitions under crossed polarizers was made with a Leitz Laborlux S polarizing optical microscope (POM) equipped with a THMS-600 heating stage. Small angle X-ray scattering (SAXS) measurements were performed using CuK $_{\alpha}$ ($\lambda=1.542\text{ \AA}$) radiation monochromatized with a Ni filter and a totally reflecting glass block (Huber Small-angle Chamber 701). The intensity curves were measured using a linear position-sensitive detector (Mbraun OED-50M).



Scheme 1. Synthesis route of the monomers.

2.2. Synthesis of liquid crystalline monomers

The synthesis of the LC monomers is shown in scheme 1.

2.2.1. Cholest-5-en-3-yl(3 β) 4-(2-propenyloxy)benzoate (M_1). This was prepared according to a previously reported synthetic method [17]. The yield was 70%, m.p. 107°C. IR (KBr, cm $^{-1}$): 3051 (=C–H), 2971–2854 (–CH $_3$, –CH $_2$ –), 1706 (C=O), 1608, 1511 (Ar–), 1277, 1172(C–O–C). ^1H -NMR (CDCl $_3$, δ , ppm): 7.98–6.92 (m, 4H, Ar-H), 6.02 (m, 2H, CH $_2$ =CH–), 5.36 (m, 1H, =CH–in cholesteryl), 5.18–4.69(m, 1H, CH $_2$ =CH–), 4.47 (t, 2H, –OCH $_2$ –), 2.03–0.67 (m, 43H, cholesteryl–H).

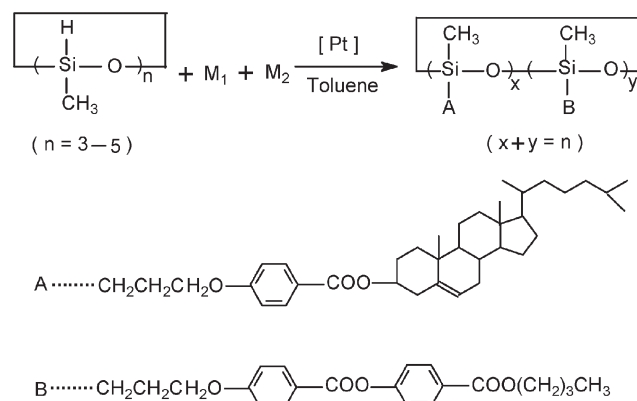
2.2.2. Butyl 4-[4-(2-propenyloxy)benzoxy]benzoate (M_2). Potassium hydroxide (80.0 g, 1.43 mol) and potassium iodide (0.6 g, 0.03 mol) were dissolved in 120 ml water to obtain an aqueous solution, which was then added to a mixture of 4-hydroxybenzoic acid (84.0 g, 0.6 mol) and 300 ml ethanol. 3-Bromopropene (90.0 g, 0.7 mol) was then added dropwise and the mixture was stirred at room temperature for 2 h. It was then heated to 85°C and held for 16 h in a water bath to ensure completion of the reaction, cooled, poured into 500 ml of cold water and acidified with 6N HCl solution. The precipitated crude product was filtered, recrystallized from ethanol and dried overnight at 85°C under vacuum to obtain 4-(2-propenyloxy)benzoic acid as a white powder in 70% yield, m.p. 163°C.

4-(2-Propenyloxy)benzoic acid (20.0 g, 0.1 mol) and thionyl chloride (25.0 g, 0.21 mol) were mixed in a flask

equipped with HCL absorption. The mixture was stirred at room temperature for 2h, then heated to 60°C and held for 3h in a water bath to ensure completion of the reaction. The mixture was then distilled under reduced pressure to obtain 4-(2-propenyloxy)benzoyl chloride at 160–170°C/20 mm Hg in 61% yield.

4-Hydroxy-benzoic acid (69.0 g, 0.5 mol), 200 ml *n*-butanol, 100 ml toluene and 10 ml H₂SO₄ were mixed in a flask equipped with a water separator. The mixture was heated under reflux for 10h and the water separated; it was then neutralized with sodium bicarbonate, and the organic layer distilled under reduced pressure to obtain butyl 4-hydroxybenzoate at 230–250°C/20 mm Hg in 58% yield.

Finally, the butyl 4-hydroxybenzoate (18.2 g, 0.1 mol) was dissolved in 120 ml pyridine; 4-(2-propenyloxy)benzoyl chloride (19.7 g, 0.1 mol) was added and the mixture reacted at 80°C for 6h. It was then cooled, poured into 500 ml of cold water and acidified with 6N HCl. The precipitated crude product was filtered, recrystallized from ethanol and dried overnight at 85°C under vacuum to give butyl 4-[4-(2-propenyloxy)benzoyl]benzoate as a white powder in 70% yield, m.p. 71°C. IR (KBr, cm⁻¹): 3074 (=C–H), 2957, 2932, 2873 (CH₃– and –CH₂–), 1727, 1713 (C=O), 1605, 1509 (Ar–), 1279 (C–C), 1160, 1074 (C–O–C). ¹H NMR (CDCl₃, δ, ppm): 8.15–6.95 (m, 8H, Ar–H), 6.35–6.10 (m, 2H, CH₂=CH–), 5.94–5.5.56 (m, 1H, CH₂=CH–),



Scheme 2. Synthesis route of the polymers.

5.20–5.06 (m, 2H, –CH₂O–), 4.54–4.44 (m, 2H, –COOCH₂–), 2.64–2.51 (m, 2H, –COOCH₂CH₂–), 1.45–1.26 (m, 2H, –CH₂CH₃), 0.85–0.69 (m, 3H, –CH₂CH₃). Elemental analysis: calcd for C₂₀H₂₂O₅, C 70.18, H 6.43; found C 70.11, H 6.51%.

2.3. Synthesis of the liquid crystalline polymers

For synthesis of polymers **P1–P7**, a standard method was adopted, as shown in scheme 2. The polymerization experiments are summarized in table 1; the synthesis of polymer **P4** is given as an example. Cholest-5-en-3-yl(3β) 4-(2-propenyloxy)benzoate (**M1**, 2.06 g, 3.68 mmol) was dissolved in 30 ml of dry, freshly

Table 1. Feed quantities and polymerization of the series of polymers.

Polymer	CMHS /mmol	M ₁ /mmol	M ₂ /mmol	M ₂ / M ₁ +M ₂ %	Yield/%
P1	1.000	4.000	0.000	0.0	93
P2	1.000	3.920	0.080	2.0	95
P3	1.000	3.800	0.200	5.0	94
P4	1.000	3.680	0.320	8.0	95
P5	1.000	3.600	0.400	10.0	93
P6	1.000	3.400	0.600	15.0	95
P7	1.000	3.200	0.800	20.0	94

Table 2. Thermal properties and maximum reflected wavelengths of the polymers.

Sample	T _g /°C	T _m /°C	T _f ^a /°C	T _i /°C	ΔT ^b /°C	λ _{ref} ^c /nm
M2	—	71.6	—	158.3	—	—
P1	52.5	122.5	—	229.2	—	327.74
P2	57.6	121.0	196.1	223.7	27.6	327.79
P3	56.1	122.2	193.7	215.6	21.9	327.86
P4	52.1	119.4	195.0	214.5	19.5	327.94
P5	58.9	119.9	193.0	219.7	26.7	329.15
P6	54.3	122.9	192.0	213.7	21.7	330.29
P7	47.3	118.7	192.7	217.1	24.4	342.98

^aT_f=cholesteric phase–blue phase transition temperature. ^bMesophase temperature ranges of blue phase on heating. ^cMaximum reflected wavelength.

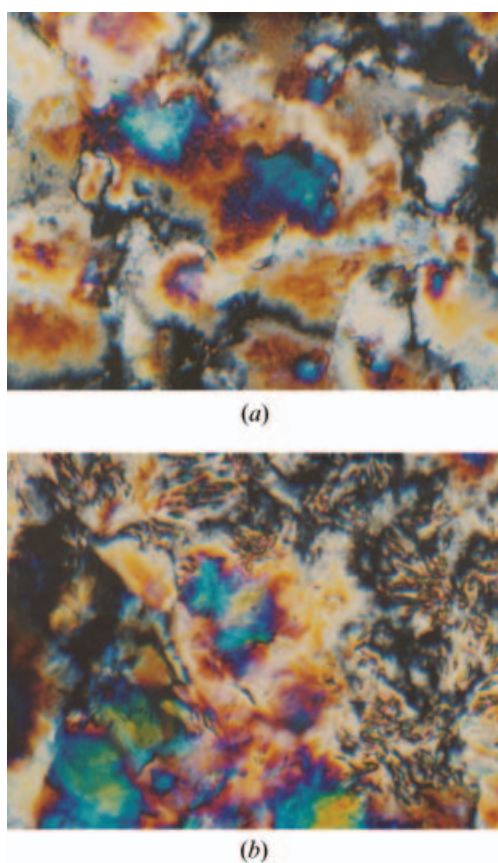


Figure 1. Optical textures of the monomer butyl 4-[4-(2-propenyloxy)benzoxy]benzoate ($200\times$): (a) on heating to 93°C , (b) on cooling to 151°C .

distilled toluene. To the stirred solution were added butyl 4-[4-(2-propenyloxy)benzoxy]benzoate (M_2 , 0.11 g, 0.32 mmol), cyclo(methylhydrogeno)siloxane (CMHS, 0.24 g, 1.0 mmol) and 2 ml of $\text{H}_2\text{PtCl}_6/\text{THF}$

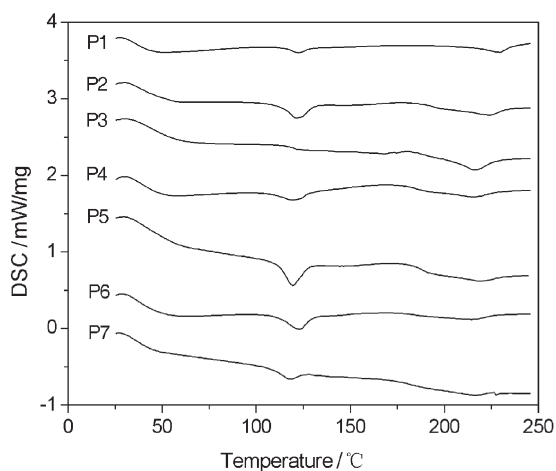


Figure 2. DSC thermograms of the series of polymers on the first heating ($10^\circ\text{C min}^{-1}$).

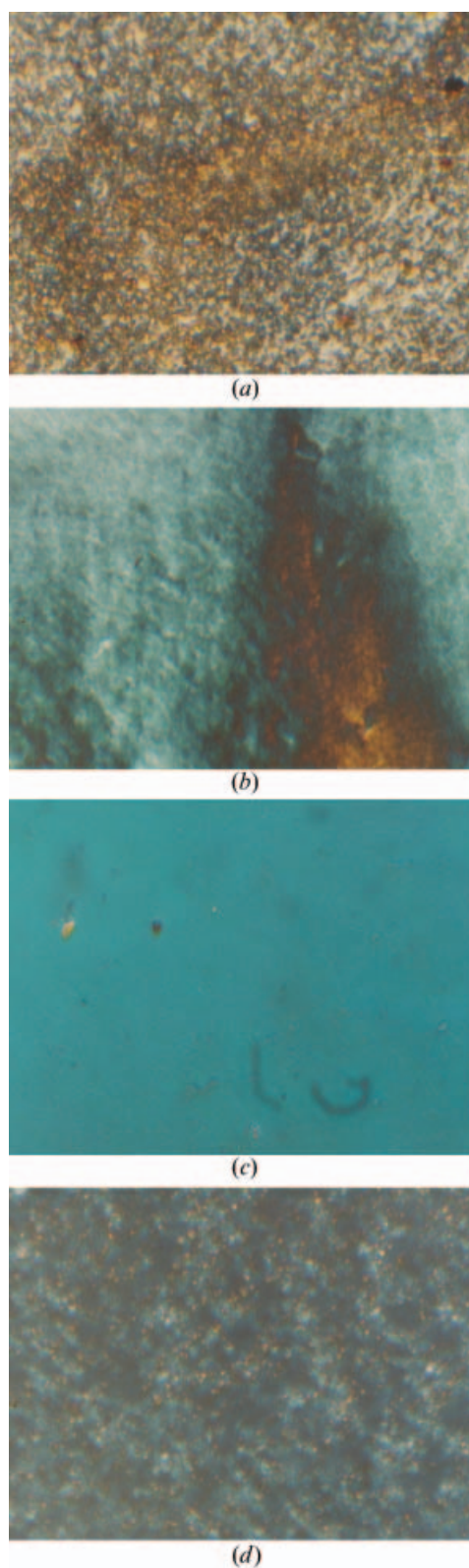


Figure 3. Optical textures of the polymer **P4** ($200\times$): (a) broken focal-conic texture on heating to 121°C , (b) Grandjean texture on heating to 181°C , (c) blue planar texture on heating to 198°C , and (d) broken focal-conic texture on cooling to 191°C .

(0.50 g hexachloroplatinic acid hydrate dissolved in 50 ml THF), and the mixture was heated under nitrogen and anhydrous conditions at 65°C for 72 h. The solution was cooled and poured into 100 ml methanol; after filtration, the product was dried at 80°C for 2 h under vacuum to obtain 2.29 g of polymer in 95% yield. IR(KBr, cm⁻¹): 2946–2887 (CH₃– and –CH₂–), 1713 (C=O), 1606, 1510 (phenyl), 1273 (C–C), 1167(C–O–C), 1103 (Si–C), 1010 (Si–O–Si).

3. Results and discussion

3.1. Liquid crystalline behaviour of the monomers

The LC properties of cholest-5-en-3-yl(3β) 4-(2-propenyloxy)benzoate (**M**₁) were observed as previously reported [18]. The monomer butyl 4-[4-(2-propenyloxy)benzyloxy]benzoate (**M**₂) was studied by DSC, SAXS and POM. The phase transition temperatures obtained during the second heating are summarized in table 2. The DSC heating thermogram of **M**₂ showed two endothermic peaks, representing a melting transition (*T*_m) at 71.6°C and a LC – isotropic phase transitions (*T*_i) at 158.3°C. The corresponding enthalpy changes (ΔH) at *T*_m and *T*_i were 70.66 and 0.42 J g⁻¹, respectively. Under POM **M**₂ exhibited enantiotropic nematic phase on heating or cooling. When **M**₂ was heated to 71°C, the sample began to melt, and the threaded schlieren texture of a nematic phase gradually appeared, as shown in figure 1(a); the texture disappeared at 158°C. When the isotropic state was cooled to 156°C, the threaded schlieren texture appeared again, as shown in figure 1(b). The SAXS profile of **M**₂ showed no strong reflection peak at small scattering angles, suggesting the absence of layered packing of the mesogenic groups. In general, for nematic and cholesteric structures, no peak appears in a SAXS curve. Therefore, the nematic phase structures of **M**₂ can be confirmed according to the X-ray characterization, along with DSC and optical textures.

3.2. Liquid crystalline behaviour of the polymers

The mesogenic properties of the polymers were also studied with DSC, SAXS and POM. The thermal behaviours are included in table 2, and figure 2 displays DSC thermograms of all the polymers synthesized.

In the DSC thermograms, the polymer **P**₁ displays three kinds of phase transition behaviour corresponding to glass transition, melting point and clearing point; the others show four kinds of phase transition behaviour. The special phase transition suggests that there is a LC phase transition between the melting and clearing points. In figure 2, with the increase of non-chiral component in the polymers **P**₁–**P**₇, the temperature of

the clearing point decreases slightly while the glass transition and melting points change only slightly. All the polymers exhibit thermotropic LC properties and a cholesteric phase. Furthermore, for polymers **P**₂–**P**₇, blue phases were observed.

Mesophase identification was accomplished by X-ray measurement and POM. The optical microscopy observations show distinct textures apparently associated with different kinds of structure. All the polymers except **P**₁ showed similar cholesteric and blue phase textures on heating; representative textures are shown in figure 3. When polymer **P**₄ was heated from room temperature, the viewing field became bright and a broken focal-conic texture appeared, see figure 3(a). When it was heated to 185°C, the Grandjean texture gradually appeared, figure 3(b), and the selective reflection colour changed from red to blue with increasing temperature. The Grandjean texture disappeared slowly and a blue planar texture was observed on heating to 198°C, as shown in figure 3(c). The blue planar texture was maintained for almost twenty degrees with increasing temperature, and disappeared at 215°C. When the isotropic state was cooled to 191°C, the broken focal-conic texture appeared, see figure 3(d). The appearance of selective reflection colour indicates the cholesteric mesophase of the sample. On the other hand, the planar texture is characteristic of the blue phase, implying the blue phase structure of the sample [19].

The blue phase was also confirmed by SAXS measurement. The scattering vector lies in the horizontal direction and its length is defined as

$$q = (4\pi/\lambda)\sin\theta \quad (1)$$

where 2θ is the scattering angle and λ is the wavelength of the radiation. The scattering peaks were detected in the SAXS profiles of as-cast films of **P**₃ and **P**₅ which were quenched from the blue phase to room temperature, as illustrated in figure 4. The higher order Bragg reflections of $(4/3)^{1/2}$, $(8/3)^{1/2}$, $(11/3)^{1/2}$, and $(19/3)^{1/2}$ are typical for cubic packings.

The non-chiral component in the polymer systems may influence the liquid crystalline behaviour of the polymers. Because liquid crystalline polymers are most commonly composed of flexible and rigid moieties, self-assembly and nanophase separation into specific microstructures frequently occur due to geometric and chemical dissimilarity of the two moieties. For the polymers **P**₁–**P**₇, the organization of the longer hard segments is easier, resulting in a higher degree of crystallinity of the solid phase. These results demonstrate the melting behaviour of the polymers. For polymer **P**₁, the rigid moieties containing cholesteryl

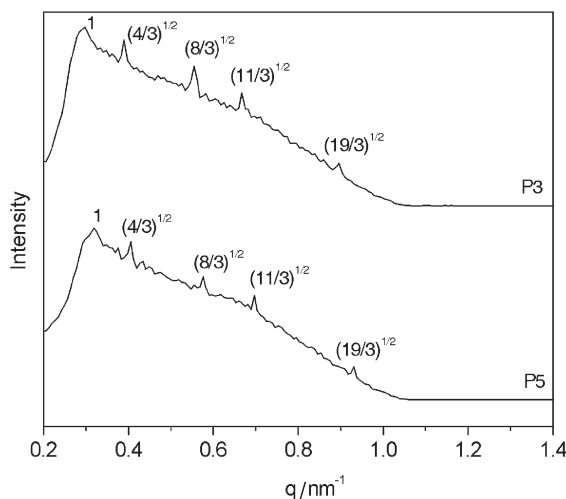


Figure 4. the SAXS profiles of samples **P3** and **P5**.

groups gave the polymers relatively high clearing points due to their steric hindrance. From **P2** to **P7**, with increase of non-cholesteryl groups in the polymer systems, the isotropic transition becomes easier because of lower steric hindrance, leading to a decrease in the clearing point. However, the cholesteric phase–blue phase transition temperatures change only a little for **P2–P7** with increase of non-chiral component. The blue phase temperature range for polymers **P2–P7** is about 20°C, greatly exceeding the temperature range of blue phases reported previously.

3.3. Reflection spectra of the polymers

Cholesteric mesophases exhibit interesting optical properties such as the selective reflection of circularly polarized light and an angular dependence of the reflected wavelength. If the reflected wavelength is in the visible range of the spectrum, the cholesteric phase appears coloured. The wavelength, λ_{\max} , of reflected light from a cholesteric sample is given by

$$\lambda = nP \sin \varphi \quad (2)$$

where n is the average refractive index of the liquid crystalline phase, P is the pitch height of the helicoidal arrangement, and φ is the angle of incidence of the beam. The helical pitch P depends on many factors such as the concentration of the chiral substance, the temperature and any external field of mechanical, electric or magnetic origin [20]. The blue phase (BP) can be considered the three-dimensional counterpart of the cholesteric phase; it is therefore interesting to study its reflection spectra.

Samples were heated in their blue phase (exactly 208.0°C for all the polymers) with no external field; they

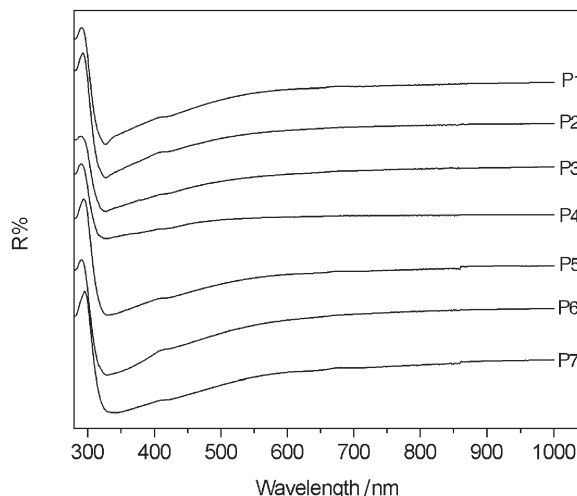


Figure 5. The reflected wavelengths of **P1**, **P4** and **P7** at 128.0°C with no external field.

were quenched in liquid nitrogen and characterized, as listed in table 2. Figure 5 shows the maximum reflected wavelength of all the polymers. It can be seen that the maximum reflection bands broaden from **P1** to **P7** with increase of non-chiral component in the samples. Furthermore, the data show that the reflected wavelength shifts to longer wavelength from **P1** to **P7**, suggesting that the helical pitch P become longer according to equation (2). This is because the helical structure is partially disrupted by the interaction of non-chiral groups.

4. Conclusions

A series of cyclosiloxane-based cholesteric LCPs were synthesized using a cholesteric LC monomer containing cholesteryl groups and a nematic LC monomer containing non-chiral groups. The polymers were prepared in a one-step graft copolymerization with olefinic monomers and cyclohydrogensiloxanes. Their chemical structures and liquid crystalline properties were characterized by FTIR, ^1H NMR, DSC, POM and X-ray measurement.

All the polymers exhibit thermotropic LC properties and show a cholesteric phase. In the DSC thermograms, most of the polymers display four kinds of phase transition behaviour, corresponding to glass transition, melting point, cholesteric phase–blue phase transition and clearing point. The mesophase temperature ranges of the blue phases of the polymers are as wide as 20°C, greatly exceeding the blue phase temperature ranges reported previously. The blue phase was confirmed by planar textures and cubic packing. With the increase of non-chiral component in the polymers, the clearing

point decreases slightly while the glass transition and melting point change only slightly.

Reflection spectra of the series of polymers showed that the reflected wavelength broadens and shifts to longer wavelength with increase of the non-chiral component in the polymer systems, suggesting lengthening of the helical pitch *P*.

Acknowledgements

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