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Synthesis and characterization of side chain cholesteric liquid crystalline polymers containing isosorbide as a chiral centre

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A series of new side chain cholesteric liquid crystalline polysiloxanes was synthesized by grafting copolymerization of a mesogenic monomer (M_1) and a chiral monomer (M_2). The chemical structures of the monomers and polymers obtained were confirmed by FTIR, and ^1H and ^{13}C NMR spectroscopy. The mesomorphic properties were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The influence of the content of the chiral unit on phase behaviour of the polymers is discussed. Monomer M_1 showed nematic and smectic phases on cooling. The polymers P_1 and P_2 showed a nematic phase, P_3 – P_5 showed cholesteric Grandjean texture, and P_6 and P_7 exhibited smectic short-rod texture. The polymers containing more than 7.2 mol% and less than 28.6 mol% of the chiral unit showed an induced cholesteric phase. Experimental results demonstrated that the glass transition, melting and clearing temperatures decreased with increasing content of the chiral unit.

1. Introduction

The interest raised by cholesteric liquid crystalline polymers (LCPs) is essentially connected to the peculiar optical properties of the cholesteric phase, such as the selective reflection of light, thermochromism and circular dichroism, and to their possible applications such as non-linear optical filters, flat panel displays, optical data storage materials, organic pigments, electro-optical materials and fast switching materials stemming from the possibility to couple optical and structural modulations [1–12]. The unique optical properties of cholesteric LC are related to the helical supermolecular structure formed by a rod-like chiral molecule. In general, the chemical structure of the polymer, the concentration of the chiral constituents, the temperature, and the outer field will influence the LC properties and orientation states of side chain chiral LCPs.

Chiral side chain LCPs can be obtained by the combination of a mesogenic unit and a chiral component, or by polymerization of chiral mesogenic units [13–15]. Takashi *et al.* [15] have prepared a new type of induced cholesteric LCPs by copolymerization of the achiral mesogenic monomer with the chiral monomer and have found that the types of LC phase and transition temperature were different depending upon the fraction of the chiral unit.

Any potential application will, of course, be favored by low cost materials. For the synthesis of cholesteric LCPs, isosorbide is an attractive chiral building block because it is accessible from renewable resources in the form of pure enantiomers. Kricheldorf *et al.* have synthesized many photosetting cholesteric main chain copolyesters and copolycarbonates [16–20] which used isosorbide as the chiral group, and have found that although the isosorbide structure was highly unfavourable for the formation of a LC phase because of its non-linear structures, the twisting power was so high that only small amounts (2–10 mol%) were needed to obtain a cholesteric phase.

Some main chain cholesteric LCPs containing isosorbide as the chiral group had been reported previously [18, 19, 21]. In this work, we attempted to use an isosorbide derivative to prepare a series of new side chain cholesteric LCPs. Phase behaviour and mesomorphic properties of the monomers and polymers were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The influence of the concentration of the chiral monomer on phase behaviour of the polymers is discussed.

2. Experimental

2.1. Characterization

Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer. ^1H NMR

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spectra (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were obtained with a Varian Gemini 300 spectrometer. Phase transition temperatures and thermodynamic parameters were determined with a Netzsch DSC 204 equipped with a liquid nitrogen cooling system. The heating and cooling rates were $10^\circ\text{C min}^{-1}$. The phase transition temperatures were collected during the second heating. A Leica DMRX polarizing optical microscope equipped with a Linkam THMSE-600 cool and hot stage was used to observe phase transition temperatures and optical textures of LC monomers and polymers. XRD measurements were performed with a nickel-filtered Cu-K_α ($\lambda=0.1542\text{nm}$) radiation with a DMAX-3A Rigaku powder diffractometer.

2.2. Materials

Polymethylhydrosiloxane (PMHS, $\bar{M}_n=700-800$) was purchased from Jilin Chemical Industry Co. Undecylenic acid was obtained from Beijing Jinlong Chemical Reagent Co., Ltd, and 4-hydroxybenzoic acid from Beijing Fuxing Chemical Industry Co. Isosorbide was purchased from Jiangxi Haohe Chemical Industry Co. and was dried over P_2O_5 before use; 4,4'-dihydroxybiphenyl (from Aldrich) was used as received. Toluene used in the hydrosilylation reaction was first heated under reflux over sodium and then distilled under nitrogen. All other solvents and reagents were purified by standard methods.

2.3. Monomers synthesis

The synthesis of olefinic monomers is shown in schemes 1 and 2. 4-(4-Ethoxybenzoyloxy)benzoic acid was prepared according to similar procedures previously reported [22].

2.3.1. 4-(4-Ethoxybenzoyloxy)-4'-hydroxybiphenyl (1). 4-Ethoxybenzoic acid (8.3 g, 0.05 mol) was reacted at 60°C with 25 ml of thionyl chloride containing a few drops of *N,N*-dimethylformamide (DMF) for 6 h; excess thionyl chloride was then removed under reduced pressure to give the corresponding acid chloride. The acid chloride was dissolved in 10 ml of tetrahydrofuran (THF), and the solution added dropwise to a solution of 55.8 g (0.3 mol) of 4,4'-dihydroxybiphenyl in 200 ml of THF and 20 ml of pyridine with rapid stirring. The reaction mixture was heated under reflux for 15 h. After removing excess solvent, the remaining mixture was poured into water, and neutralized with dilute hydrochloric acid. The crude product was obtained by filtration, and washed successively with 5% sodium hydroxide solution, dilute hydrochloric acid and cold

ethanol. The white solid **1** was obtained by recrystallization from acetone; yield 62%, m.p. 220°C . IR (KBr): 3443 (–OH); 2983, 2850 (– CH_3 , – CH_2 –); 1701 (C=O); 1609, 1497 (Ar–), 1264 cm^{-1} (C–O–C).

2.3.2. 4-10-(Undecylen-1-yloxy)-4'-(4-ethoxybenzoyloxy)biphenyl (M_1). Undecylenyl chloride (12.2 g, 0.06 mol) was added dropwise to a solution of 17.2 g (0.05 mol) of compound **1** in 80 ml of THF and 12 ml of pyridine. The reaction mixture was heated under reflux for 10 h, and the precipitate removed by filtration. The filtrate was then poured into cold water, and neutralized with dilute hydrochloric acid. After standing for 3 h, the crude product obtained was purified by recrystallization from ethanol to give white crystals; yield 68%, m.p. 97°C . IR (KBr): 3075 (=C–H); 2977, 2852 (– CH_3 , – CH_2 –); 1751, 1731 (C=O); 1641 (C=C); 1604, 1492 (Ar–); 1261 cm^{-1} (C–O–C). ^1H NMR (CDCl_3 , TMS), δ (ppm): 1.34–1.79 (m, 13H, – CH_3 and –(CH_2) $_6$ –); 2.03 (m, 2H, = CHCH_2 –); 2.59 (m, 2H, –(CH_2) $_6\text{CH}_2\text{COO}$ –); 4.12 (m, 2H, – OCH_2CH_3); 4.93–5.08 (m, 2H, $\text{CH}_2=\text{CH}$ –); 5.76–5.89 (m, 1H, $\text{CH}_2=\text{CH}$ –); 6.97–8.21 (m, 12H, Ar–H). ^{13}C NMR (CDCl_3 , TMS, δ , ppm): 14.9 (CH_3); 33.2, 29.8, 30.3, 29.5, 25.8, 32.9, 65.6 (methylene–C); 113.6, 121.5, 128.2 (tert. C); 151.6, 134.1, 123.4, 163.7, (quat. C); 114.6 ($\text{CH}_2=$); 139.8 (=CH–); 164.5, 168.7 (C=O).

2.3.3. Isosorbide 10-undecylen-1-ylenate (2). Undecylenyl chloride (10.2 g, 0.05 mol) was added dropwise to a cold solution of 36.5 g (0.25 mol) of isosorbide in 125 ml of THF and 7 ml of triethylamine. The reaction mixture was heated under reflux for 12 h. Excess solvent was removed, and the remaining mixture poured into excess water. The organic layer was washed successively with dilute sodium hydroxide solution, hydrochloric acid and warm water, and then extracted with toluene (dried with anhydrous magnesium sulphate). After removing the toluene by distillation under reduced pressure, the resulting crude product was purified by recrystallization from ethanol/acetone (3/1); yield 73%, m.p. 62°C . IR (KBr): 3401 (–OH); 3079 (=C–H); 2998, 2851 (– CH_3 , – CH_2 –); 1729 (C=O); 1642(C=C); 1247 cm^{-1} (C–O–C).

2.3.4. 4-(4-Ethoxybenzoyloxy)benzoic acid (3). 4-Hydroxybenzoic acid (13.8 g, 0.1 mol) was dissolved in a mixture of 25 ml of carbon tetrachloride and 9.2 g of sodium hydroxide in 55 ml of water. 4-Ethoxybenzoyl chloride (0.1 mol) (laboratory synthesized) was added then dropwise to the cold mixture. After stirring for 6 h at room temperature, the reaction mixture was neutralized with dilute hydrochloric acid, and the resulting precipitate filtered, and washed successively

with warm water, dilute hydrochloric acid and water. The crude product was recrystallized from acetic acid to give white crystals; yield 43%, m.p. 231°C. IR (KBr): 3071 (=C-H); 2995, 2817 (-CH₃, -CH₂-); 2653, 2557 (-COOH); 1746, 1682 (C=O); 1604, 1511 (Ar-); 1259cm⁻¹ (C-O-C).

2.3.5. Isosorbide 2-(10-Undecylen-1-yloxy)-5-(4-ethoxybenzoyloxy)benzoate (M₂). Compound **3** (14.3 g, 0.05 mol) was reacted at 50°C with 35 ml of thionyl chloride containing a few drops of DMF for 6 h, and then excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. Compound **2** (3.12 g, 0.01 mol) and the 4-(4-ethoxybenzoyloxy)benzoyl chloride (3.09 g, 0.01 mol) were dissolved in 40 ml of pyridine. The mixture was stirred at room temperature for 2 h, and then reacted at reflux temperature for 16 h. The mixture was dispersed in H₂O (500 ml) and acidified with 20% HCl, precipitating a crude product which was filtered and recrystallized from ethanol; yield 62%, m.p. 76°C. IR (KBr): 3077(=C-H); 2977–2850 (-CH₃, -CH₂-); 1744, 1728, 1707 (C=O); 1642(C=C); 160, 1490 (Ar-); 1265cm⁻¹ (C-O-C). ¹H NMR(CDCl₃, TMS), δ(ppm): 1.28–1.44(m, 15H, -(CH₂)₆- and -CH₂CH₃); 2.02(m, 2H, =CHCH₂-); 2.31(m, 2H, -CH₂COO-); 3.95–4.03(m, 8H, -OCH₂- and -CH₂O- and -CH₂CH₃); 3.79(m, 2H, -OCH₂-); 4.53(m, 2H, -COOCH₂-); 4.95(m, 2H, CH₂=CH-); 5.24(m, 1H, CH₂=CH-); 6.98–8.13 (m, 8H, Ar-H). ¹³C NMR (CDCl₃, TMS, δ, ppm): 14.1 (CH₃); 33.3, 30.0, 30.2, 29.8, 25.6, 33.7 (methylene-C in (CH₂)₈); 64.5 (methylene-C in isosorbide); 65.3 (methylene-C in CH₃CH₂O); 75.1, 80.2, 82.3, 74.8 (tert. C in isosorbide); 130.1, 121.8, 131.2, 114.5 (tert. C in Ar); 127.3, 157.8, 123.1, 164.3 (quat. C); 114.2 (CH₂=); 140.4 (=CH-); 164.1, 167.7, 171.8 (C=O).

2.4. Polymer synthesis

The polymers **P**₁–**P**₈ were synthesized by equivalent methods. For the synthesis of **P**₄, the monomers **M**₁, **M**₂, and PMHS were dissolved in freshly distilled toluene (feed ratios are given in table 1). The mixture was heated to 65°C under nitrogen and anhydrous conditions, then 2 ml of THF solution of hexachloroplatinat(IV) catalyst (5 mg ml⁻¹) was injected with a syringe. The progress of the hydrosilylation reaction, monitored from the Si-H stretch intensity, went to completion within 48 h as indicated by IR. After the solvent was removed, the crude polymer was purified by precipitation from toluene with excess methanol, and dried under vacuum. IR spectra of

Table 1. Polymerization of polymers **P**₁–**P**₈.

Polymer	Feed/mmol		M ₂ /mol % ^a	Yield/%
	M ₁	M ₂		
P ₁	7.00	0.00	0.0	84
P ₂	6.50	0.50	7.2	83
P ₃	6.00	1.00	14.4	84
P ₄	5.50	1.50	21.4	79
P ₅	5.00	2.00	28.6	76
P ₆	4.00	3.00	35.8	78
P ₇	3.50	3.50	50.0	72
P ₈	0.00	7.00	100.0	72

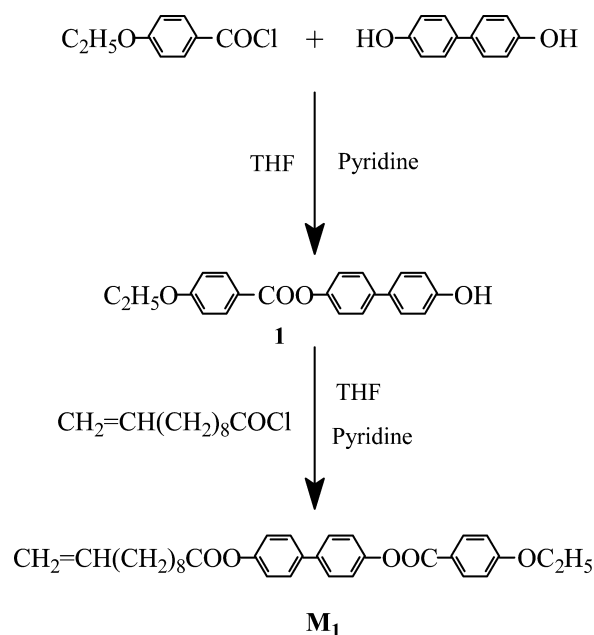
^aMolar fraction of **M**₂ based on (**M**₁+**M**₂).

P₁–**P**₈ were similar, the characteristic peaks for **P**₄ are given as an example. IR (KBr): 2920–2850 (-CH₃, -CH₂-); 1755, 1732 (C=O); 1610, 1490 (Ar-); 1150–1000 cm⁻¹ (Si-O-Si).

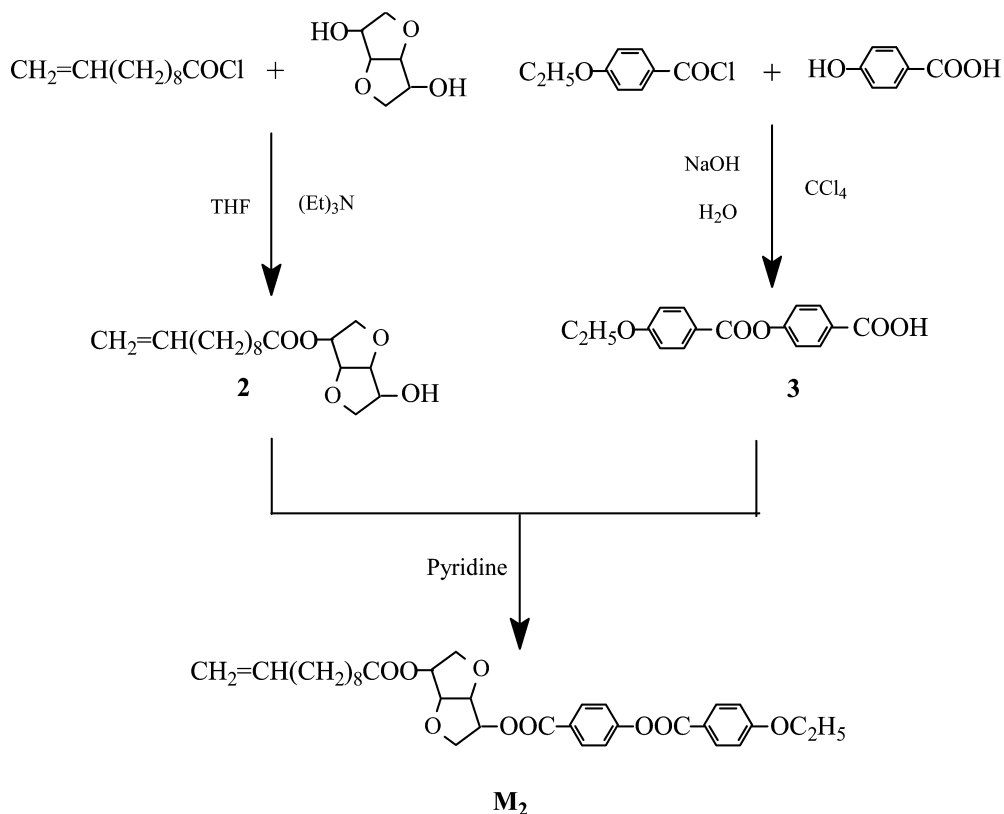
3. Results and discussion

3.1. Syntheses

The synthetic routes to the target monomers are shown in schemes 1 and 2. The structural characterization of the monomers and polymers obtained were in good agreement with the prediction. 4-Ethoxybenzoyl chloride was reacted with 4,4'-dihydroxybiphenyl in THF in the presence of pyridine to give compound **1**; **M**₁ was obtained by the reaction of undecenoyl chloride with **1**, also in THF in the presence of pyridine. Compound **2** was prepared by reacting undecenoyl chloride with



Scheme 1. Synthetic route to the mesogenic monomer.



Scheme 2. Synthetic route to the chiral monomer.

isosorbide in presence of triethylamine in THF; 4-(4-ethoxybenzoyloxy)benzoyl chloride was then reacted with **2** in the presence of pyridine to obtain the chiral monomer **M₂**. The FTIR spectra of the monomers **M₁** and **M₂** showed characteristic bands at 1751–1727 cm⁻¹ due to ester C=O stretching, around 1645–1641 cm⁻¹ due to vinyl C=C stretching, and around 1610–1492 cm⁻¹ corresponding to aromatic C=C stretching. ¹H NMR spectra of **M₁** and **M₂** showed multiplets at 1.28–4.12, 4.95–5.24, and 6.97–8.21 ppm corresponding to methyl and methylene protons, olefinic protons, and aromatic protons, respectively.

The polysiloxanes were prepared by the hydrosilylation reaction between Si–H groups of PMHS and olefinic C=C of **M₁** and **M₂** in toluene, using hexachloroplatinat(IV) as catalyst at 65°C. The IR spectra of the polymers showed complete disappearance of the Si–H stretching band at 2166 cm⁻¹; characteristic Si–O–Si stretching bands appeared at 1200–1000 cm⁻¹. The absorption bands of ester C=O and the aromatic ring still remained. The polymerization and yields of the polymers are summarized in table 1. All the polymers were soluble in hydrocarbons (e.g. toluene, xylene), but were insoluble in hydroxy-containing solvents such as methanol and ethanol.

3.2. Thermal analysis

The thermal properties of the synthesized monomers and polymers **P₁–P₈** were determined by DSC. The corresponding phase transition temperatures, obtained during the second heating cycle, are summarized in tables 2 and 3. Representative DSC curves of the monomers and polymers are presented in figures 1 and 2.

DSC heating curves of **M₁** showed two endothermic peaks, which represented, respectively, melting and nematic–isotropic phase transition. However, on the cooling scan of **M₁**, five exothermic peaks revealed isotropic–nematic, nematic–smectic A (SmA) SmA–smectic C (SmC) SmC–smectic B (SmB) and

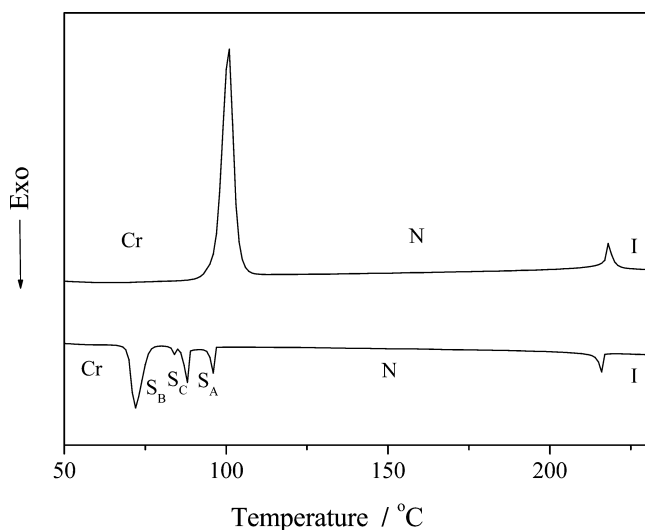
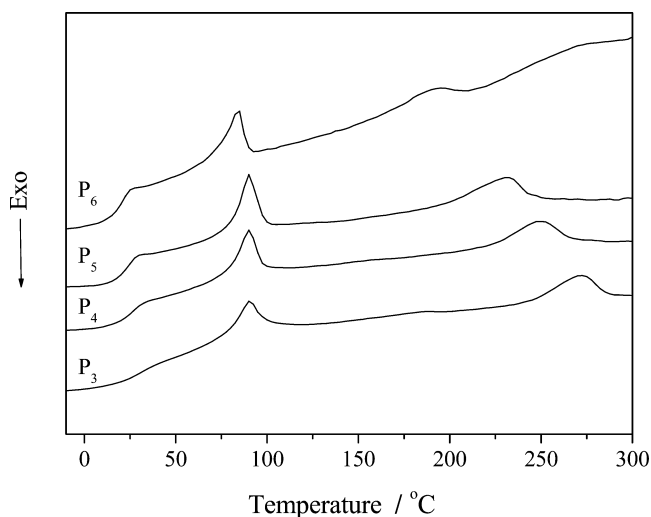
Table 2. Phase transitions of monomers: Cr=solid, N=nematic, S=smectic, I=isotropic. Peak temperatures were taken as phase transition temperatures.

Monomer	Transition temperature/°C (corresponding enthalpy changes/J g ⁻¹)	
	heating	cooling
M₁	Cr97.4(66.0)N218.6(3.5)I	
	I216.0(3.3)N96.0(2.8)S _A 87.9(4.9)S _C 84.2(0.5)S _B 71.6(24.2)Cr	
M₂	Cr76.2(64.50)I	
	I138.6(37.3)Cr	

Table 3. Thermal properties of polymers: N=nematic; Ch=cholesteric; S=smectic.

Polymer	$T_g/^\circ\text{C}$	$\Delta H_m/\text{J g}^{-1}$	$T_m/^\circ\text{C}$	$T_i/^\circ\text{C}$	$\Delta H_i/\text{J g}^{-1}$	ΔT^a	LC phase
P₁	103.4	5.6	127.8	300.2	4.6	172.4	N
P₂	80.2	6.0	115.3	286.5	5.1	171.2	N
P₃	39.4	5.5	90.5	272.5	6.7	182.0	Ch
P₄	29.5	6.8	89.2	250.6	6.7	160.4	Ch
P₅	24.1	5.6	89.8	231.6	3.4	141.8	Ch
P₆	20.0	4.1	84.1	192.6	2.5	108.5	S
P₇	15.3	3.2	76.3	178.4	1.7	102.1	S
P₈	6.6	—	—	—	—	—	—

^aMesophase temperature ranges (T_i-T_m).

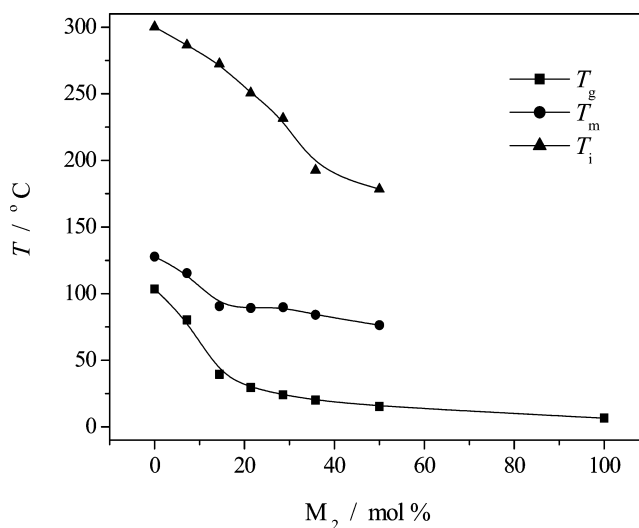
Figure 1. DSC thermograms of monomer **M₁**.Figure 2. DSC thermograms of polymers **P₃–P₆**.

crystallization transitions at 216.0, 96.0, 87.9, 84.2 and 71.6°C, respectively. For **M₂**, the DSC heating thermograms showed only one endothermic phase transition

peak; this represented the melting transition, revealing that **M₂** had no LC properties.

For **P₁–P₇**, a glass transition at low temperature, a melting transition and a mesophase to isotropic transition at high temperature appeared on the DSC curves. This indicates that **P₁–P₇** are semi-crystalline LCPs. The DSC curve of **P₈** showed only a glass transition; no mesophase to isotropic phase transition was seen. Above all, the phase transitions were reversible and did not change after repeated heating and cooling cycles. For **P₁–P₈**, the flexible spacer was the undecenyl group which is so long that the polymers retain a long range orientation order, and have melting transitions.

The glass transition temperature (T_g) is an important parameter in connection with structures and properties. It increases with the decrease in mobility of chain segments in polymers. In polymers **P₁–P₈**, with an increase in the concentration of the chiral unit (similar to the plasticization effect), the chain flexibility increased and T_g decreased. Figure 3 shows the effect

Figure 3. Effect of **M₂** content on phase transition temperatures of the polymers.

of the content of chiral unit on the phase transition temperatures of the polymers. The T_g decreased from 103.4°C for **P**₁ to 6.6°C for **P**₈, as the chiral unit content increased from 0 to 100 mol%.

The chiral monomer content also offered the melting temperature (T_m). The T_m of polymers **P**₁–**P**₇ decreased with increasing concentration of the chiral unit, due mainly to the decrease in content of rigid mesogenic units leading to a decrease in crystalline properties. As shown in table 3, T_m decreased from 127.8°C for **P**₁ to 76.3°C for **P**₇ as the chiral unit content increased from 0 to 50 mol%.

As for the clearing temperature (T_i), the chiral flexible units acted as a diluent and did not favour the formation of mesogenic orientation in the polymers.

Consequently, T_i decreases with increasing concentration of the chiral units. T_i decreased from 300.2°C for **P**₁ to 178.4°C for **P**₈ as the chiral unit content increased from 0 to 50 mol%. For semi-crystalline LCPs, the LC phase appears between the melting point and the clearing temperature. **P**₁–**P**₇ displayed wide mesophase temperature ranges (ΔT), which decreased from 172.4 to 102.1°C with increasing concentration of chiral unit, because T_i fell less than T_g .

3.3. Texture analysis

The optical textures of the monomers and polymers were observed by POM with cool and hot stages. Phase transition temperatures obtained by DSC were

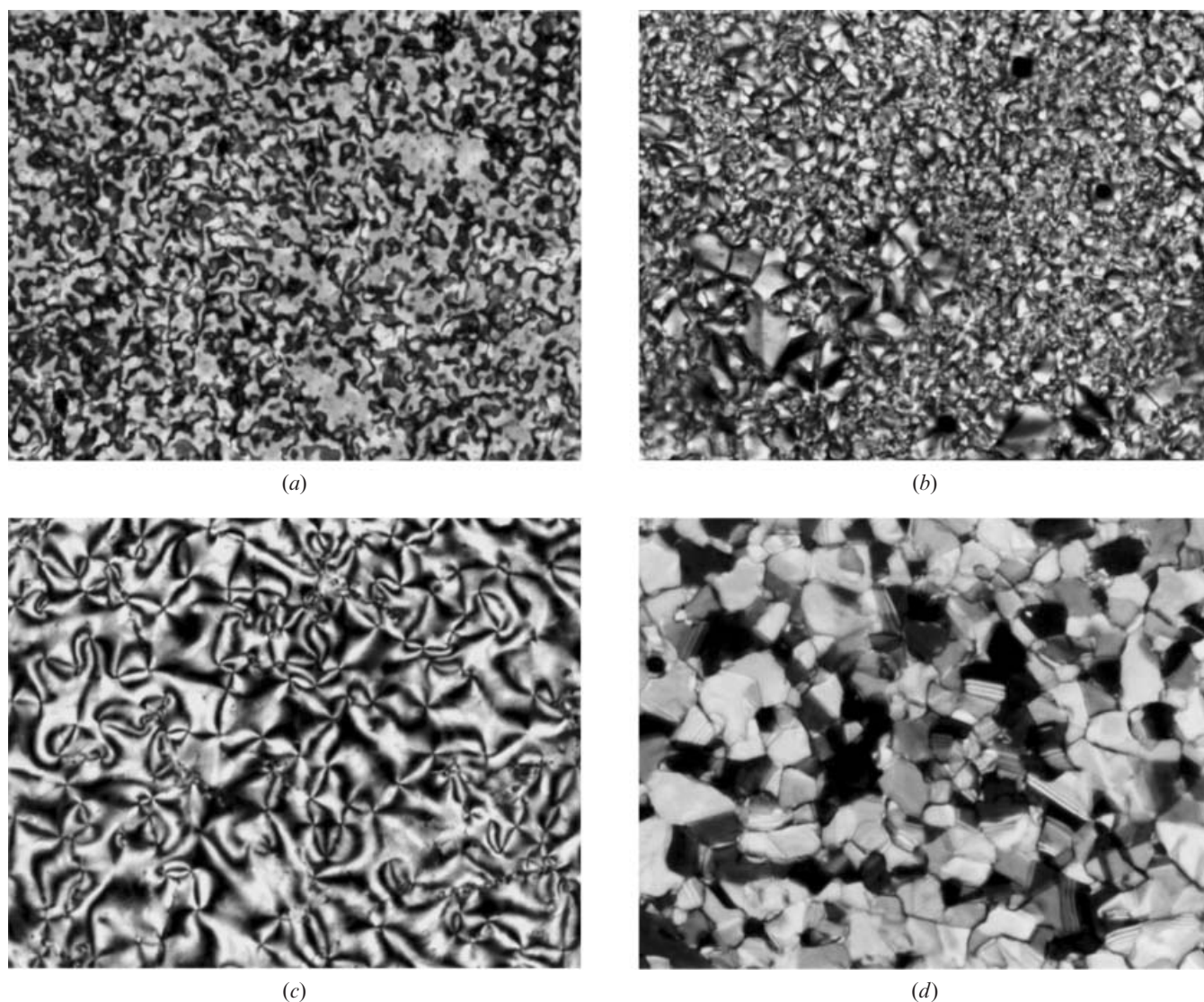
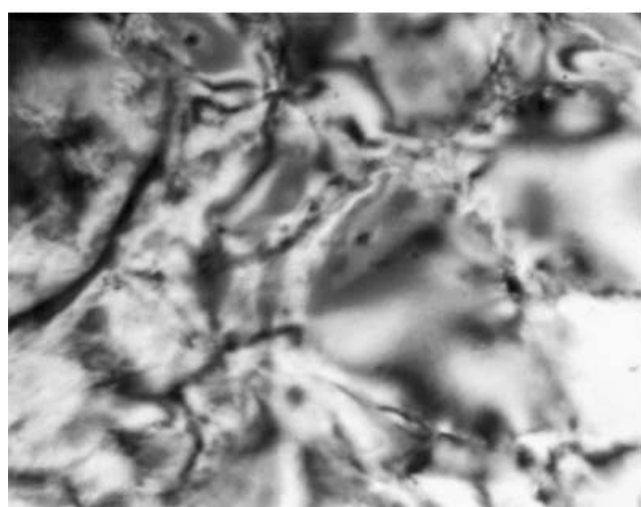


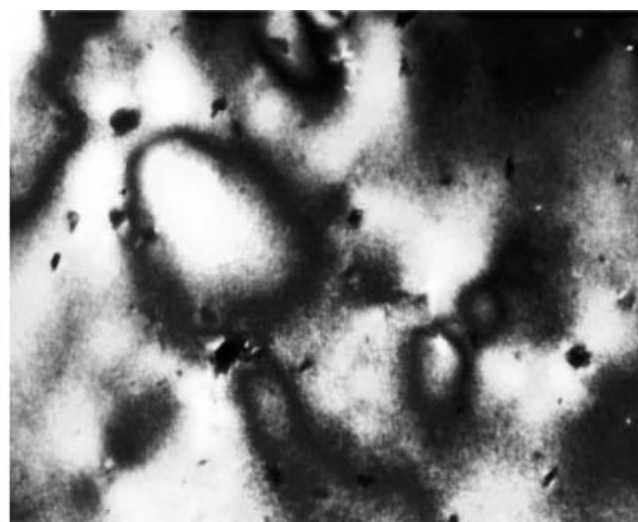
Figure 4. Optical textures of monomer **M**₁ (200 ×): (a) threaded texture on heating to 214.6°C; (b) focal-conic texture on cooling to 93.5°C; (c) schlieren texture on cooling to 85.8°C; (d) mosaic texture on cooling to 83.6°C.

consistent with POM observations. Under POM the monomer M_1 exhibited an enantiotropic nematic phase and a monotropic smectic (SmA, SmC, SmB) phase during its heating and cooling cycles, respectively which agreed with DSC thermograms. When M_1 was heated to about 97.4°C , the typical nematic threaded texture appeared, and the birefringence totally disappeared at 218.6°C . When the isotropic state was cooled to 216.0°C , the threaded texture appeared again. On further cooling to 96.0°C , the threaded texture changed gradually to a SmA focal-conic texture; at 87.9°C , a SmC schlieren texture appeared, and at 84.2°C , a SmB mosaic texture appeared, with crystallization at 71.6°C . Monomer M_2 showed no mesomorphism or texture. Photomicrographs of M_1 are shown in figure 4.

The polymers P_1 and P_2 exhibited nematic schlieren textures, while P_3 – P_5 exhibited induced cholesteric Grandjean textures; P_6 and P_7 showed smectic short-rod texture, and P_8 showed no texture, predictable from its DSC curve. The polymer molecules arranged in helix structures because the chiral group intensity increased to some degree. Thus, the defects, which would produce the various textures, showed not only line-disclinations, but also whorl-dislocations and accompanied by whorl-dispirations. The textures of the cholesteric polymers observed under POM therefore displayed multiple colourful textures. With increasing chiral unit content, the mobility of chain increased, leading to the appearance of the smectic phase. All of this indicated that the copolymer composition affected not only the LCPs



(a)



(b)



(c)

Figure 5. Optical textures of polymers ($200\times$): (a) schlieren texture of P_1 at 213.5°C ; (b) Grandjean texture of P_3 at 266.2°C ; (c) short-rod texture of P_6 at 182.8°C .

phase transition temperatures, but also the mesogenic type and textures. Photomicrographs of the polymers are shown in figure 5.

3.4. XRD analysis

XRD studies are carried out to obtain more detailed information on the mesogenic phase structure. In general, a sharp, strong peak appears at low angles ($1^\circ < 2\theta < 4^\circ$) in small angle X-ray scattering (SAXS) curves only for the smectic structure; a broad peak associated with lateral packing at about $2\theta = 20^\circ$ is observed in wide angle X-ray diffraction (WAXD) curves for nematic, smectic and cholesteric phase structures. Figure 6 shows representative XRD curves of quenched samples of the polymers. For P_6 and P_7 , a sharp peak associated with the smectic layers in the SAXS curves and a broad peak in WAXD curves were observed respectively at $2\theta = 1.30^\circ - 1.50^\circ$ and $21.0^\circ - 22.0^\circ$. According to the Bragg equation, $\lambda_m = 2d \sin \theta$, the corresponding d -spacings were $6.79 - 5.89 \text{ nm}^{-1}$ and $0.423 - 0.404 \text{ nm}$, respectively. For $P_3 - P_5$ no sharp peak at low angles appeared in the SAXS curves; a weak peak and a broad peak were observed, respectively, at $2\theta = 8^\circ - 9^\circ$ and $21.0^\circ - 22.0^\circ$ in WAXD curves. The smectic phase structure of $P_6 - P_7$ and the cholesteric phase structures of $P_3 - P_5$ were therefore confirmed by POM, DSC, and XRD.

4. Conclusions

In this study, a series of new side chain LCPs were synthesized and characterized. Monomer M_1 showed

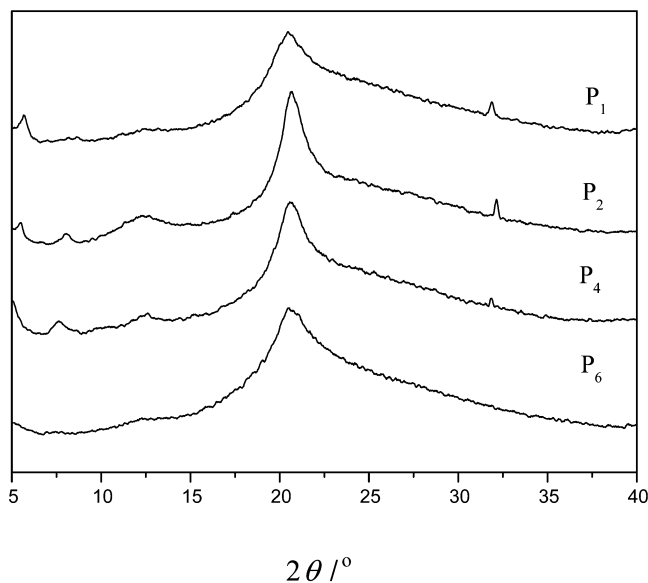


Figure 6. X-ray diffraction patterns of quenched polymer samples.

nematic and smectic (SmA, SmC, SmB) phases on cooling, and M_2 had no liquid crystalline properties. The polymers P_1 and P_2 exhibited nematic phases, while $P_3 - P_5$ showed cholesteric phases, and $P_6 - P_7$ a smectic phase. T_g , T_m and T_i decreased with increasing content of the chiral unit. Polymers containing more than 7.2 mol% and less than 28.6 mol% of the chiral unit showed cholesteric phases.

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