Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Cholesteric liquid crystalline thermosets: synthesis, structure and properties of ChLCTs/precursor polymers

Jian-She Hu[a]; Bao-Yan Zhang Corresponding author[a]; Dan-Shu Yao[a]; Ai-Juan Zhou[a]
[a] The Center for Molecular Science and Engineering, Northeastern University, Shenyang 110004, PR, China

To cite this Article Hu, Jian-She , Zhang Corresponding author, Bao-Yan , Yao, Dan-Shu and Zhou, Ai-Juan(2004) 'Cholesteric liquid crystalline thermosets: synthesis, structure and properties of ChLCTs/precursor polymers', Liquid Crystals, 31: 3, 393 — 400

To link to this Article: DOI: 10.1080/02678290310001658408

URL: http://dx.doi.org/10.1080/02678290310001658408

LIQUID CRYSTALS, VOL. 31, NO. 3, MARCH 2004, 393–400

Cholesteric liquid crystalline thermosets: synthesis, structure and properties of ChLCTs/precursor polymers

JIAN-SHE HU, BAO-YAN ZHANG*, DAN-SHU YAO and AI-JUAN ZHOU
The Center for Molecular Science and Engineering, Northeastern University,
Shenyang 110004, PR, China

(*Received 9 June 2003; in final form 15 November 2003; accepted 19 November 2003*)

The synthesis of six liquid crystalline monomers M_1–M_6 and three series of side chain cholesteric liquid crystalline polymers P_1–P_3 is described. The chemical structures of the monomers were characterized by FTIR and ^{1}H NMR spectroscopy. The structure–property relationships of M_1–M_6 and P_1–P_3 are discussed. Their phase behaviour and optical properties were investigated by differential scanning calorimetry and polarizing optical microscopy. The monomers M_1–M_3 exhibited cholesteric phases; M_4–M_6 showed nematic or smectic phases. The polymer series P_1–P_3 showed cholesteric phases. Experimental results demonstrated that the selective reflection of the cholesteric monomers and homopolymers shifted to the shorter wavelength region (blue shift) with increasing length of the flexible spacer. The selective reflection of the copolymers shifted to the longer wavelength region (red shift) with increasing content of nematic units.

1. Introduction

In recent years, many studies have centred on liquid crystalline networks (LCNs) with anisotropic properties [1–12]; in particular, LCNs with a cholesteric structure have attracted considerable interest due to their unique optical properties and potential applications in, for example, circular polarizers, non-linear optics and organic pigments [13–17]. The cholesteric phase is formed by rod-like and chiral molecules responsible for macroscopic alignment of cholesteric domains. Depending on chemical structures and external conditions, it may be feasible to achieve a macroscopic alignment of cholesteric domains. Depending on crosslinking density, two new classes of cholesteric LCNs emerge: (i) lightly crosslinked cholesteric liquid crystalline elastomers (ChLCEs); and (ii) highly crosslinked cholesteric liquid crystalline thermosets (ChLCTs). In contrast to ChLCEs, the helical structure of ChLCTs is permanently fixed and optical properties become temperature independent [18–26].

From a technological point of view, two important problems with cholesteric liquid crystals are (1) how to adjust the helical pitch, and (2) how to keep the helical pitch constant once it has been adjusted. The helical pitch of a cholesteric phase can be fixed by three physical or chemical methods: (a) freezing-in by quenching; (b) fixation by photocrosslinking; and (c) fixation by thermal crosslinking. ChLCTs can be obtained by the photocrosslinking of cholesteric main chain [23, 24] or side chain [21] liquid crystalline polymers. They can also be made through the thermally or chemically induced crosslinking of cholesteric mixtures consisting of nematic and chiral monomers [17, 19, 22, 26].

It is well known that acrylate monomers can easily form polymers, whereas allyl monomers polymerize slowly by free radical polymerization. Thus the use of acrylate-allyl monomers, where the acrylate and allyl groups are combined in the same molecule, firstly yields soluble linear precursor polymers, then these precursor polymers form LCTs by special polymerization in the liquid crystalline phase. The aims of our present research are: (i) to study structure and optical property relationships of side chain cholesteric liquid crystalline polymers; (ii) to supply the necessary data to synthesize cholesteric LCNs with specific optical properties; and (iii) to explore their applications in the fields of non-linear optical devices and special coatings. In previous studies, we reported the synthesis and properties of side chain ChLCEs [27–30]. In this study, we have synthesized and characterized three cholesteric monomers, three nematic monomers with acrylate-allyl difunctional groups, and new ChLCT precursor polymers. Their phase behaviour and optical textures were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The influence of the flexible spacer length and

---

*Author for correspondence;
e-mail: baoyanzhang@hotmail.com

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290310001658408

copolymer composition on phase behaviour and optical properties is discussed.

2. Experimental

2.1. *Materials*

Chloroethanol was purchased from Shenyang Xinxi Chemical Reagent Co., 1,6-hexanediol from Beijing Hongyu Chemical Industry Co., and cholesterol from Henan Xiayi Medical Co. All other solvents and reagents were purified by standard methods.

2.2. *Characterization*

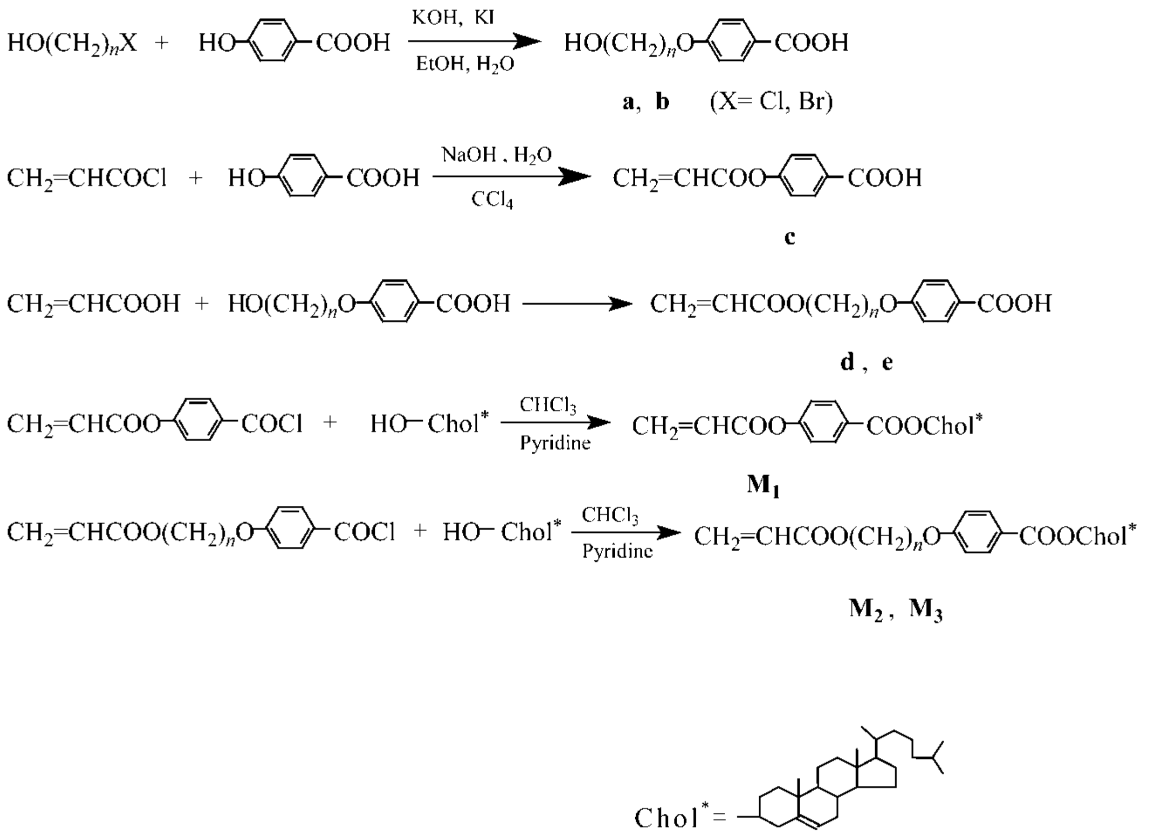
Fourier transform infrared (FTIR) spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Instruments, Madison, WI). ^{1}H NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). The phase transition temperatures and thermodynamic parameters were determined using a Perkin-Elmer DSC-7 (Perkin-Elmer, Foster City, CA) equipped with a liquid nitrogen cooling system. Heating and cooling rates were 20°C min^{-1}. The phase transition temperatures were observed during the second heating and first cooling scans. A Leitz Microphot-FX (Leitz, Wetzlar, Germany) polarizing optical microscope, equipped with a Mettler FP 82 hot stage and FP 80 central processor, was used to observe phase transition temperatures and analyse mesomorphic properties for the liquid crystalline monomers and polymers, through the observation of optical textures.

2.3. *Monomer synthesis*

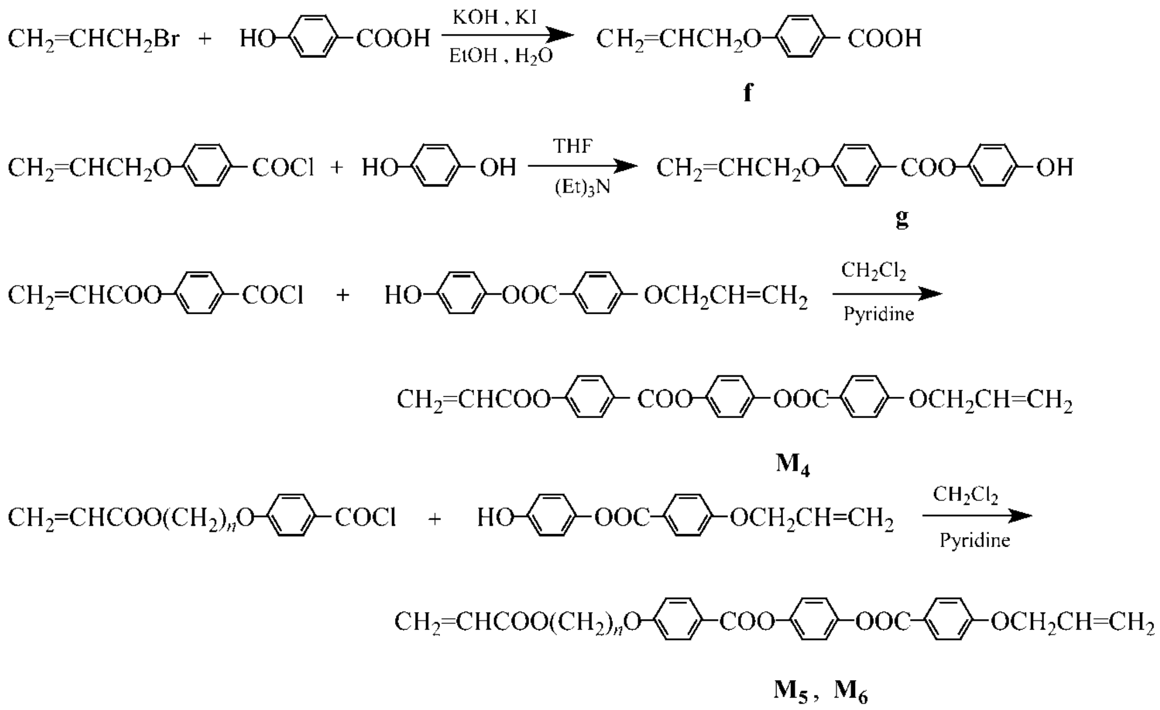
The synthetic routes for cholesteric monomers M_1–M_3 and nematic monomers M_4–M_6 are shown in schemes 1 and 2. The yields and structural characterization of M_1–M_6 are summarized in table 1. 4-(Acryloyloxy-*n*-alkyloxy)benzoic acids **c**, **d**, **e** and 4-hydroxyphenyl-4′-allyloxybenzoate **g** were prepared according to literature procedures reported by Hu *et al.* [31, 32].

2.3.1. *Cholesteryl 4-acryloyloxybenzoate (M_1), cholesteryl 4-(2-acryloyloxyethyloxy)benzoate (M_2), and cholesteryl 4-(6-acryloyloxyhexyloxy)-benzoate (M_3)*

The cholesteric monomers M_1–M_3 were synthesized by equivalent methods. For the synthesis of M_3, 4-(6-acryloyloxyhexyloxy)benzoic acid (29.2 g, 0.1 mol)



Scheme 1. Synthetic routes for cholesteric monomers.



Scheme 2. Synthetic routes for nematic monomers.

Table 1. Yields and characterization of monomers.

Monomer	n	Yield/%	IR (KBr)/cm^{-1}	^{1}H NMR chemical shifts ($CDCl_3$, δ/ppm)
M_1	—	48	3043 (–CH), 2943, 2863 (CH_3, CH_2), 1745, 1714 (COO), 1634 (C–C), 1605, 1510 (Ar)	0.65−2.07 (m, 43H); 5.46 (m, 2H); 5.72 (m, 1H); 6.20 (m, 1H); 7.24−8.21 (m, 4H)
M_2	2	43	3065 (–CH), 2945, 2861 (CH_3, CH_2), 1734, 1713 (COO), 1645 (C–C), 1608, 1511 (Ar)	0.68−2.42 (m, 45H); 3.88 (t, 2H); 4.29 (t, 2H); 4.84 (m, 1H); 5.46 (m, 2H); 6.09 (m, 1H); 6.25 (m, 1H); 6.92−8.11 (m, 4H)
M_3	6	45	3045 (–CH), 2942, 2868 (CH_3, CH_2), 1742, 1712 (COO), 1631 (C–C), 1607, 1512 (Ar)	0.69−2.44 (m, 51H); 3.77 (t, 2H); 4.25 (t, 2H); 4.55 (m, 1H); 5.42 (m, 2H); 6.18 (m, 1H); 6.43 (m, 1H); 6.91−8.02 (m, 4H)
M_4	—	62	3073 (–CH); 2965, 2837 (CH_3, CH_2); 1730 (C–O); 1647 (C–C); 1607, 1509 (Ar)	4.67(t, 2H); 5.33−5.49 (m, 4H,); 6.07 (m, 1H); 6.35 (m, 1H); 7.02−8.27 (m, 12H)
M_5	2	53	3070 (–CH); 2969, 2845 (CH_3, CH_2); 1735 (C–O); 1640 (C–C); 1608, 1512 (Ar)	3.79 (t, 2H); 4.27 (t, 2H); 4.63 (t, 2H); 5.30−5.48 (m, 4H); 6.05 (m, 1H); 6.26 (m, 1H); 6.95−8.18 (m, 12H)
M_6	6	47	3076 (–CH); 2938, 2863 (CH_3, CH_2); 1736 (C–O); 1643 (C–C); 1610, 1513 (Ar)	1.51−1.87 (m, 8H); 3.75 (t, 2H); 4.18 (t, 2H); 4.62 (t, 2H); 5.31−5.48 (m, 4H); 6.01 (m, 1H); 6.20 (m, 1H); 6.96−8.17 (m, 12H)

was reacted at 50°C with thionyl chloride (70 ml) containing a few drops of *N*,*N*-dimethylformamide and a trace of *p*-hydroxyanisole for 4 h. Excess thionyl chloride was removed under reduced pressure to give the acid chloride. The acid chloride was dissolved in 10 ml of chloroform, and the solution added dropwise to a cold solution of cholesterol (38.7 g, 0.1 mol) and 8 ml of pyridine in 150 ml of chloroform. After stirring for 12 h at 50°C, ethanol was added and the precipitate recrystallized from ethanol.

2.3.2. *4-Acryloyloxybenzoyl-4′-allyloxybenzoyl-p-benzenediol bisate (M_4), 4-(2-acryloyloxyethyloxy)-benzoyl-4′-allyloxybenzoyl-p-benzenediol bisate (M_5), 4-(6-acryloyloxyhexyloxy)benzoyl-4′-allyloxybenzoyl-p-benzenediol bisate (M_6)*

The nematic monomers M_4–M_6 were prepared by equivalent methods. For the synthesis of M_6, 4-(6-acryloyloxyhexyloxy)benzoyl chloride (15.5 g, 0.05 mol) was dissolved in 10 ml of dry methylene chloride, and the solution added dropwise to a cold solution of 4-hydroxyphenyl-4′-allyloxybenzoate (13.5 g, 0.05 mol) and 4 ml of pyridine in 100 ml of methylene chloride. After reacting for 8 h and filtering, the crude product was precipitated by adding ethanol to the filtrate; it was then recrystallized from ethanol.

2.4. *Polymer synthesis*

The polymer series P_1–P_3 were obtained by radical polymerization of cholesteric monomer and the corresponding nematic monomer in dry toluene using α,α′-azobisisobutyronitrile (AIBN, 2 mol% to the monomers) as an initiator at 65°C for 24 h under nitrogen. The crude polymers were obtained by precipitation with methanol; they were purified by reprecipitation twice with methanol from toluene and dried in vacuum.

3. Results and discussion

3.1. *Synthesis*

The synthesis of monomers M_1–M_6 was straightforward, and is described above.

It is well known that allyl monomers polymerize only slowly by free radical polymerization because of the dominant effect of chain transfer reactions. However, acrylate monomers can easily form polymers by free radical polymerization, while allyl groups are incorporated in the polymer backbone. Thus the use of acrylate-allyl monomers can lead to soluble polymers. These linear precursors then undergo special polymerization in the liquid crystalline phase, yielding polymer networks.

3.2. *Thermal properties*

The thermal properties of the monomers M_1–M_6 and polymer series P_1–P_3 were investigated by DSC and POM. The phase transition temperatures and corresponding enthalpy changes of monomers M_1–M_6 and polymers of series P_1, P_2 and P_3 are summarized in tables 2, 3, 4 and 5, respectively.

As can be seen from table 2, the length of the flexible spacer strongly affects the phase transition temperatures of M_1–M_6. With increasing length of the flexible spacer, for cholesteric monomers M_1–M_3, the melting temperature (T_m) decreases from 122.7°C (M_1) to 72.9°C (M_3); at the same time, the isotropization temperature (T_i) decreases from 220.8 to 176.4°C, because of reduced intermolecular forces. However, the mesophase temperature ranges (ΔT) increase from 98.1 to 103.5°C because T_i decreases less than T_m. For nematic monomers M_4–M_6, T_m decreases from 141.2°C (M_4) to 76.5°C (M_6), while T_i decreases from 230.0 to 199.0°C, and ΔT widens from 88.8 to 122.5°C.

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

Monomer	n	Transition temperature/°C (Corresponding enthalpy changes/J g^{-1}) Heating Cooling	ΔT_1[a]	ΔT_2[b]
M_1	—	Cr122.7(18.42)Ch220.8(1.14)I I213.8(0.49)Ch98.8(11.72)Cr	98.1	115.0
M_2	2	Cr92.6(15.27)Ch188.2(1.58)I I180.1(0.78)Ch	95.6	—
M_3	6	Cr72.9(18.53)Ch176.4(1.08)I I171.1(0.63)Ch	103.5	—
M_4	—	Cr141.2(29.5)N230.0(0.8)I I221.8(0.5)N117.4(22.7)Cr	88.8	104.4
M_5	2	Cr84.2(13.2)N200.9(1.5)I I194.2(0.9)N51.8(16.8)Cr	116.7	142.4
M_6	6	Cr76.5(22.2)S86.5(3.7)N199.0(2.7)I I194.7(1.5)S77.1(2.2)N36.3(17.2)Cr	122.5	158.4

[a] Mesophase temperature ranges on heating.

[b] Mesophase temperature ranges on cooling.

Table 3. Polymerization and thermal properties of P_1 series.

Polymer[a]	M_4[b]/mol%	Yield/%	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	T_i/°C	ΔT[c]
$P_{1\text{-}1}$	0	94	95.1	156.6	2.6	273	116.4
$P_{1\text{-}2}$	10	89	64.1	146.8	15.8	240	93.2
$P_{1\text{-}3}$	20	93	67.0	143.3	21.1	233	89.7
$P_{1\text{-}4}$	30	92	57.8	141.9	29.7	245	103.1
$P_{1\text{-}5}$	50	93	—	141.3	34.5	252	110.7
$P_{1\text{-}6}$	70	89	—	128.4	33.4	257	128.6

[a] P_1 series were obtained by polymerization of M_1 and M_4.
[b] Molar fraction of M_4 based on (M_1+M_4).
[c] Mesophase temperature ranges.

Table 4. Polymerization and thermal properties of P_2 series.

Polymer[a]	M_5[b]/mol%	Yield/%	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	T_i/°C	ΔT[c]
$P_{2\text{-}1}$	0	96	56.8	—	—	226	169.2
$P_{2\text{-}2}$	10	91	—	71.4	29.6	232	160.6
$P_{2\text{-}3}$	20	94	44.3	70.9	25.5	245	174.1
$P_{2\text{-}4}$	30	93	—	72.4	30.8	240	167.6
$P_{2\text{-}5}$	50	90	—	60.4	25.9	269	208.6
$P_{2\text{-}6}$	70	92	—	59.2	17.6	287	227.8

[a] P_2 series were obtained by polymerization of M_2 and M_5.
[b] Molar fraction of M_5 based on (M_2+M_5).
[c] Mesophase temperature ranges.

Table 5. Polymerization and thermal properties of P_3 series.

Polymer[a]	M_6[b]/mol%	Yield/%	T_g/°C	T_m/°C	ΔH_m/J g^{-1}	T_i/°C	ΔT[c]
$P_{3\text{-}1}$	0	92	48.3	—	—	213.3	165.0
$P_{3\text{-}2}$	10	89	49.4	65.6	9.3	174.0	108.4
$P_{3\text{-}3}$	20	87	47.1	62.4	2.1	174.5	112.1
$P_{3\text{-}4}$	30	90	42.4	61.1	7.5	176.3	115.2
$P_{3\text{-}5}$	50	89	15.8	56.5	12.3	180.1	123.6
$P_{3\text{-}6}$	70	91	17.1	56.4	19.7	185.7	129.3

[a] P_3 series were obtained by polymerization of M_3 and M_6.
[b] Molar fraction of M_6 based on (M_3+M_6).
[c] Mesophase temperature ranges.

The mesomorphic properties and phase transition temperatures of side chain LC polymers depend on the nature of the polymer backbone, the rigidity of the mesogenic units, the length of the flexible spacer, and the copolymer composition. The mesogenic units are usually attached to the polymer backbone by the flexible spacer. The polymer backbone and mesogenic units have opposing tendencies. The polymer backbone is driven towards a random coil-type configuration, whereas the mesogenic units stabilize with long-range orientational order. The flexible spacer, which is generally an aliphatic hydrocarbon chain usually containing more than two methylene units, decouples the mesogenic side groups from the polymer backbone and renders them subject to orientational order.

Similarly to the monomers, the phase behaviour of the homopolymers $P_{1\text{-}1}$, $P_{2\text{-}1}$ and $P_{3\text{-}1}$ is strongly influenced by the flexible spacer length. According to the data of tables 3, 4 and 5, the glass transition temperature (T_g) decreases from 95.1°C ($P_{1\text{-}1}$) to 48.3°C ($P_{3\text{-}1}$), while T_i decreases from 273°C ($P_{1\text{-}1}$) to 213.3°C ($P_{3\text{-}1}$) with increasing length of the flexible spacer.

The copolymer composition also affects the phase transition temperatures of the P_1–P_3 series. When the content of the corresponding nematic monomers increased from 10 to 70 mol%, T_g and T_m of the P_1–P_3 series showed a downtrend. This is because the flexible nematic chains in the copolymers act as a diluent similar to the plasticization effect. However, unlike the changes in T_g and T_m, the T_i of P_1–P_3

increases with increasing content of nematic units. This phenomenon is explained as follows: on the one hand, the flexible nematic chains in the copolymers act as a diluent, and cause a decrease in T_i; on the other hand, the rigid nematic mesogenic core can promote the mesogenic molecular orientational order in the copolymers, and cause an increase in T_i. When the second effect is predominant, T_i increases. In addition, with increasing concentration of nematic units in the copolymers, ΔT of P_1–P_3 increases, because T_i increases and T_g or T_m decreases.

3.3. *Optical properties*

The unique optical properties of cholesteric liquid crystals are related to their helical supermolecular structure. The spatially periodic twisted helical structure of the cholesteric phase selectively reflects visible light, the helical pitch controlling the wavelength of the selectively reflected light. If the helical pitch or reflected wavelength coincides with the wavelength of visible light, the cholesteric phase exhibits a brilliant colour. Due to the angular dependence of the reflection conditions, different colours are seen depending on different observation angles.

The helical pitch is an important parameter in relation to structures and optical properties of the cholesteric phase. Although the microscopic origins of the helical pitch are still a subject of study [33], it is known that the helical pitch and the reflection wavelength of the cholesteric phase depend mainly on the polymer structure such as the polymer backbone, the rigidity of the mesogenic unit, the length of the flexible spacer, the copolymer composition, and external conditions such as temperature, pressure, electric and magnetic field, etc. For M_1–M_3 and series P_1–P_3, on heating a blue shift of the reflection wavelength is observed; thus the helical pitch or reflection wavelength of the cholesteric phase is temperature dependent. However, this temperature dependence of the pitch cannot yet be calculated because the controlling factors are unknown. The selective reflection of the copolymers shifts to the longer wavelength region (red shift) on

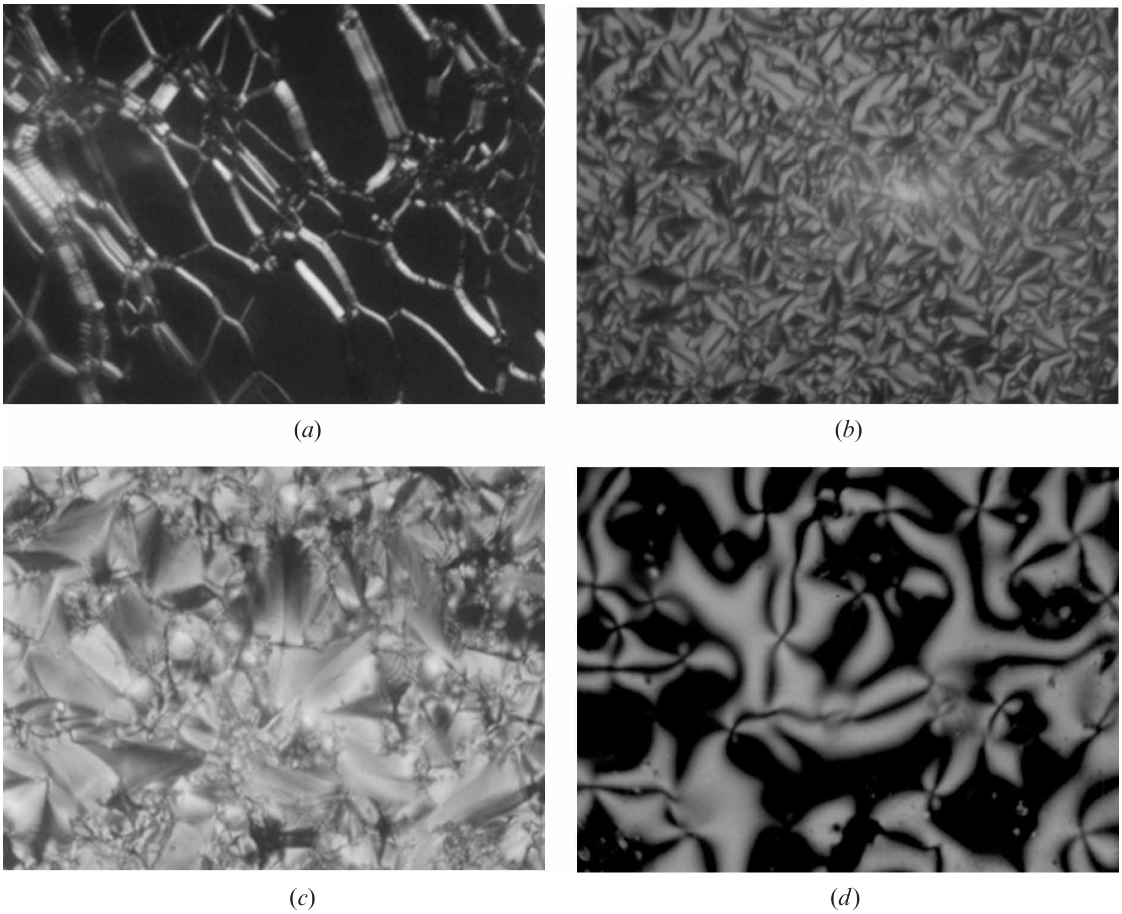
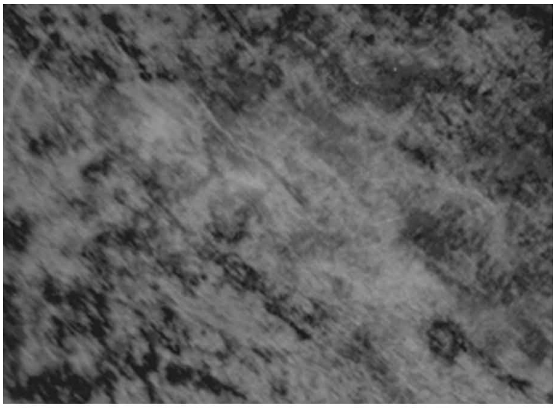

(*a*) (*b*)
(*c*) (*d*)

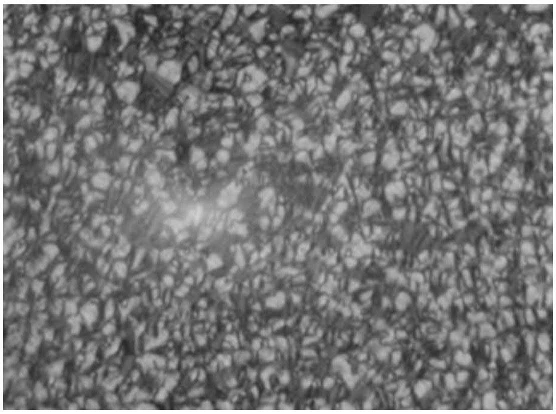
Figure 1. Optical textures of monomers (200 ×): (*a*) oily-streak texture of M_3 at heating to 168°C; (*b*) focal-conic texture of M_3 at cooling to 171°C; (*c*) fan-shaped texture of M_6 at heating to 83°C; (*d*) schlieren texture of M_6 at cooling to 189°C.

increasing the content of nematic units. In addition, the selective reflection displayed a blue shift with increasing length of the flexible spacer.

The helical pitch influences not only the selective reflection wavelength, but also the type of cholesteric texture. In general, a cholesteric phase at zero fields exhibits two optically contrasting stable states: planar texture and focal-conic texture. When the helical pitch lies within the wavelength of visible light, the helical axis is perpendicular to the cell surface and planar oily-streak texture can be observed; when the helical pitch is greater than the wavelength of visible light, focal-conic or finger-print texture is usually observed. In POM the monomers M_1–M_3 exhibited enantiotropic cholesteric textures, while M_4–M_6 exhibited enantiotropic nematic or smectic textures on heating or cooling. On heating monomers M_1–M_3, typical oily-streak textures and a reflection colour in the cholesteric phase were observed, the colour changing from red to blue for M_1, from green to violet for M_2, and from blue to violet for M_3. On cooling samples from the isotropic melt, focal-conic textures were formed, which easily transformed to oily-streak texture on shearing. When monomers M_4–M_6 were heated to T_m, a nematic threaded texture was seen in M_4 and M_5, while a smectic fan-shaped texture appeared in M_6. As heating continued, the threaded or fan-shaped textures changed gradually to nematic schlieren textures. The optical textures of M_3 and M_6 are shown in figures 1 (*a–d*). The polymer series P_1–P_3 exhibited cholesteric Grandjean and focal-conic textures during heating and cooling. Typical photomicrographs of $P_{3\text{-}3}$ are shown in figures 2 (*a*) and 2 (*b*).



(*a*)



(*b*)

Figure 2. POM micrographs of $P_{3\text{-}3}$ (200 ×): (*a*) Grandjean texture on heating to 107°C; (*b*) broken focal-conic texture on cooling to 144°C.

4. Conclusions

Three series of side chain ChLCT precursor polymers containing cholesteric units and nematic units were prepared. The monomers M_1–M_3 and M_4–M_6 showed cholesteric phases, and nematic or smectic phase, respectively. The polymer series P_1–P_3 showed cholesteric phases. All phase transitions were reversible on heating or cooling. The selective reflection of the cholesteric monomers M_1–M_3 and homopolymers $P_{1\text{-}1}$, $P_{2\text{-}1}$ and $P_{3\text{-}1}$ shifted to shorter wavelength with increasing length of the flexible spacer. The selective reflection of the copolymer series P_1–P_3 shifted to longer wavelength with increasing content of nematic units. T_m or T_g and T_i of monomers M_1–M_6 and homopolymers $P_{1\text{-}1}$, $P_{2\text{-}1}$ and $P_{3\text{-}1}$ decreased with increasing length of the flexible spacer. However, T_g and T_m of the copolymer series P_1–P_3 decreased, and T_i increased with increasing content of nematic units.

The authors are grateful to the National Natural Science Fundamental Committee of China, HI-Tech Research and Development Program (863) of China, and the Science and Technology Research Major Project of the Ministry of Education of China for financial support of this work.

References

[1] Finkelmann, H., Meier, W., and Scheuermann, H., 1992, *Liquid Crystals: Applications and Uses*, vol. 3, edited by B. Bahadur (Singapore: World Scientific), p. 353.

[2] Broer, D. J., Boven, J., and Mol, G. N., 1989, *Makromol. Chem.*, **190,** 2255.

[3] Broer, D. J., Lub, J., and Mol, G. N., 1993, *Macromolecules*, **26,** 1244.

[4] Barclay, G. G., and Ober, C. K., 1993, *Prog. polym. Sci.*, **18,** 899.

[5] Douglas, E. P., Langlois, D. A., and Benicewicz, B. C., 1994, *Chem. Mater.*, **6,** 1925.

[6] Warner, M., and Terentjev, E. M., 1996, *Prog. polym. Sci.*, **21,** 853.

[7] Giamberini, M., Amendola, E., and Carfagna, C., 1997, *Macromol. Chem. Phys.*, **198,** 3185.

[8] Kurihara, S., Masumoto, K., and Nonaka, T., 1998, *Appl. Phys. Lett.*, **13,** 160.

[9] LANGLOIS, D. A., BENICEWICZ, B. C., and DOUGLAS, E. P., 1998, *Chem. Mater.*, **10,** 3393.
[10] SYMONS, A. J., DAVIS, F. J., and MITCHELL, G. R., 1999, *Polymer*, **40,** 5365.
[11] HSU, C. S., and CHEN, H. L., 1999, *J. polym. Sci. Part A: polym. Chem.*, **37,** 3929.
[12] CHOI, E. J., AHN, H. K., LEE, J. K., and JIN, J. I., 2000, *Polymer*, **41,** 7617.
[13] BROER, D. J., LUB, J., and MOL, G. N., 1995, *Nature*, **378,** 467.
[14] FREEMANTLE, M., 1996, *Chem. Eng. News*, **74,** 33.
[15] BUNNING, T. J., and KREUZER, F. H., 1995, *Trends polym. Sci.*, **3,** 318.
[16] YANG, D. K., WEST, J. L., CHIEN, L. C., and DOANE, J. W., 1994, *J. appl. Phys.*, **76,** 1331.
[17] PETER, P. M., 1998, *Nature*, **391,** 745.
[18] BROER, D. J., and HEYNDERICKX, I., 1990, *Macromolecules*, **23,** 2474.
[19] LUB, J., BROER, D. J., and HIKMET, R. A. M., 1995, *Liq. Cryst.*, **18,** 319.
[20] DIERKING, I., KOSBAR, L. L., LOWE, A. C., and HELD, G. A., 1998, *Liq. Cryst.*, **24,** 387.
[21] STOHR, A., and STROHRIEGL, P., 1998, *Macromol. Chem. Phys.*, **199,** 751.
[22] HOLTER, D., FREY, H., and KLEE, J. E., 1998, *Adv. Mater.*, **10,** 864.
[23] SAPICH, B., STUMPE, J., KRAWINKEL, T., and KRICHELDORF, H. R., 1998, *Macromolecules*, **31,** 1016.
[24] KRICHELDORF, H. R., and KRAWINKEL, T., 1998, *Macromol. Chem. Phys.*, **199,** 783.
[25] MAXEIN, G., MAYER, S., and ZENTEL, R., 1999, *Macromolecules*, **32,** 5747.
[26] ESPINOSA, M. A., CADIZ, V., and GALIA, M., 2001, *J. Polym. Sci. Part A: polym. Chem.*, **39,** 2847.
[27] ZHANG, B. Y., HU, J. S., WANG, Y., and QIAN, J. H., 2003, *Polym. J.*, **35,** 476.
[28] HU, J. S., ZHANG, B. Y., and SUN, K., 2003, *Liq. Cryst.*, **30,** 1267.
[29] ZHANG, B. Y., HU, J. S., JIA, Y. G., and DU, B. G., 2003, *Macromol. Chem. Phys.*, **204,** 2123.
[30] HU, J. S., ZHANG, B. Y., JIA, Y. G., and CHEN, S., 2003, *Macromolecules*, **36**, 9060.
[31] HU, J. S., ZHANG, B. Y., JIA, Y. G., and WANG, Y., 2003, *Polym. J.*, **35,** 166.
[32] HU, J. S., ZHANG, B. Y., and FENG, Z. L., 2001, *J. appl. polym. Sci.*, **80,** 2335.
[33] HARRIS, A. B., KAMIEN, R. D., and LUBENSKY, T. C., 1997, *Phys, Rev. Lett.*, **78,** 1476.