This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

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

Synthesis and characterization of side chain cholesteric liquid crystalline elastomers derived from chiral bisolefinic crosslinking units

Xiao-Zhi He[a]; Bao-Yan Zhang[a]; Jian-She Hu[a]; Mei Tian[a]
[a] Center for Molecular Science and Engineering, Northeastern University, Shenyang 110004, PR China

To cite this Article He, Xiao-Zhi , Zhang, Bao-Yan , Hu, Jian-She and Tian, Mei(2005) 'Synthesis and characterization of side chain cholesteric liquid crystalline elastomers derived from chiral bisolefinic crosslinking units', Liquid Crystals, 32: 3, 299 — 306

To link to this Article: DOI: 10.1080/02678290500033844

URL: http://dx.doi.org/10.1080/02678290500033844

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid Crystals, Vol. 32, No. 3, March 2005, 299–305

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of side chain cholesteric liquid crystalline elastomers derived from chiral bisolefinic crosslinking units

XIAO-ZHI HE, BAO-YAN ZHANG*, JIAN-SHE HU and MEI TIAN
Center for Molecular Science and Engineering, Northeastern University, Shenyang 110004, PR China

(*Received 9 May 2004; accepted 18 October 2004*)

In this work we prepared a nematic monomer (4′-allyloxybiphenyl 4′-ethoxybenzoate, $\mathbf{M_1}$), a chiral crosslinking agent (isosorbide 4-allyloxybenzoyl bisate, $\mathbf{M_2}$) and a series of new side chain cholesteric liquid crystalline elastomers derived from $\mathbf{M_1}$ and $\mathbf{M_2}$. The chemical structures of the monomers and polymers were confirmed by FTIR and ^{1}H NMR spectroscopy. The mesomorphic properties were investigated by differential scanning calorimetry, thermogravimetric analysis, polarizing optical microscopy and X-ray diffraction. The effect of the content of the crosslinking unit on phase behaviour of the elastomers is discussed. Polymer $\mathbf{P_1}$ showed a nematic phase, $\mathbf{P_2}$–$\mathbf{P_7}$ showed a cholesteric phase; $\mathbf{P_6}$ formed a blue Grandjean texture over a broad temperature range 145–209.6°C, with no changed on the cooling. Polymers $\mathbf{P_4}$–$\mathbf{P_7}$, with more than 6 mol% of chiral crosslinking agent, gave rise to selective reflection. Elastomers containing less than 15 mol% of the crosslinking units displayed elasticity, reversible phase transition with wide mesophase temperature ranges, and high thermal stability. Experimental results demonstrated that, with increasing content of crosslinking agent, the glass transition temperatures first fell and then increased; the isotropization temperatures and mesophase temperature ranges decreased.

1. Introduction

The development of multifunctional and oriented structures is a continuing aim of materials science. One such supramolecular system comprises liquid crystalline elastomers (LCEs), which combine the properties of the LC phase with rubber-like elasticity [1–6]. Their most outstanding characteristic of mechanical orientability can be applied in many fields, one of which involves chiral LCEs which have unique properties, such as potential ferroelectric properties [7–13]. For chiral, the helical superstructure of a low molar mass LC can be untwisted by the application of a suitable field (typically magnetic or electric). By analogy, this should also occur for polymeric systems. However, in a chiral LCE, there is an additional possible way of untwisting the helical structure. They have the potential to act as a device that transforms a mechanical signal into an optical or electric signal. In order to investigate elastomers with these properties, a range of chiral crosslinkable polymers has been prepared [14–20]. A cholesteric LCE can be achieved by mainly three methods [21]: (a) by directly introducing cholesteric materials and crosslinking agent (liquid crystalline or non-liquid crystalline) into a polymer backbone such as polysiloxane, polyacrylate, polymethacrylate; (b) by photocrosslinking, when suitable reactive groups are present; (c) by introducing chiral materials and nematic LC crosslinking agent with a difunctional moiety into a polymer backbone.

Following previous work in the field of cholesteric LCEs [22–24], we now describe, the synthesis of new side chain cholesteric LCEs derived from 4′-allyloxybiphenyl 4′-ethoxybenzoate ($\mathbf{M_1}$) and, isosorbide 4-allyloxybenzoyl bisate ($\mathbf{M_2}$). Isosorbide was chosen because it possesses a high twisting power and a high molar fraction would generate helixes with a pitch too small (or large) for interaction with visible light [25]. However, to the best of our knowledge, few cholesteric LCE materials bearing a chiral crosslinking agent have so far been described [26–28]. The mesomorphic properties of the monomers and elastomers obtained were characterized by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), polarizing optical microscopy (POM) and X-ray diffraction (XRD). The influence of the content of crosslinking agent on the phase behaviour of the elastomers is discussed.

---

*Corresponding author. Email: baoyanzhang@hotmail.com

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500033844

2. Experimental

2.1. *Characterization*

FTIR spectra were measured on a Nicolet 510 FTIR spectrometer. ^{1}H NMR spectra (300 MHZ) were recorded on a Varian WH-90PFT spectrometer. Specific rotation was performed with a Perkin-Elmer 341 polarimeter. Phase transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 with a liquid nitrogen cooling system. The thermal stability of the polymers was measured with a Netzsch TGA 209C thermogravimetric analyser. 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 optical textures. XRD was performed with nickel-filtered Cu-K radiation with a DMAX-3A Rigaku powder diffractmeter (Rigaku, Japan).

2.2. *Materials*

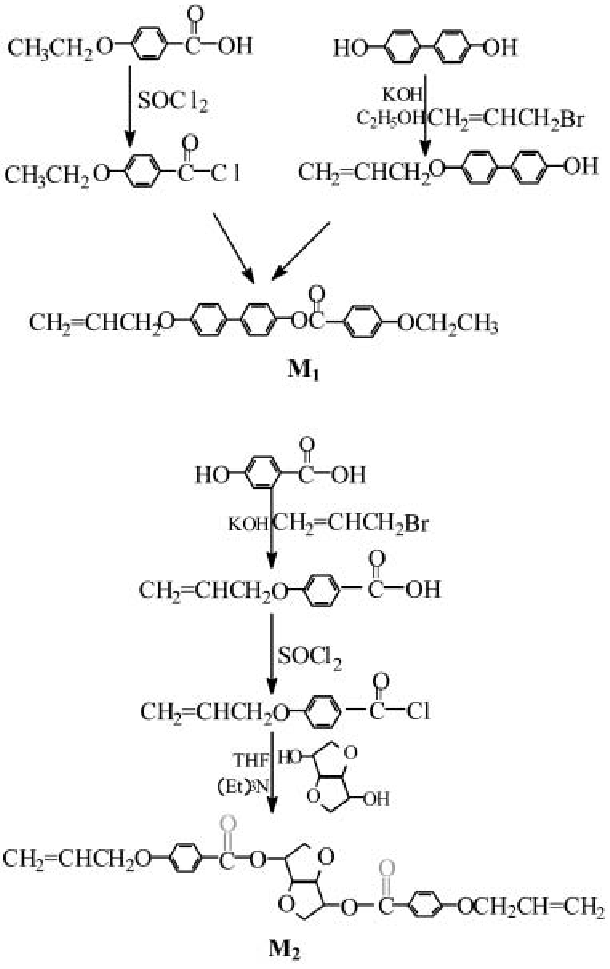
Polymethylhydrosiloxane (PMHS) was purchased from Jilin Chemical Industry Co.(China); 4,4′-Biphenol from Beijing Chemical Industry Co.(China). 3-Bromopropene was purchased from Beijing Fuxing Chemical Industry Co.(China); isosorbide was obtained from Yangzhou Shenzhou New Material Co. Ltd (China). Ethoxybenzoic acid was purchased from Shenyang Xinxi Chemical Reagent Co. (China). Toluene used in the hydrosilication reaction was first heated under reflux over sodium and then distilled under nitrogen. All other solvents and regents were purified by standard methods.

2.3. *Synthesis of the monomer*

The synthesis of the olefinic monomers is shown in Scheme 1. 4-allyloxy-benzoic acid and 4-allyloxy-4′-hydroxy biphenyl were prepared in our laboratory.

2.3.1. 4′-Allyloxybiphenyl 4′-ethoxybenzoate (M_1).

A few drops of *N*,*N*-dimethylfomamide (DMF) was added to a suspension of 4-ethoxybenzoic acid (0.1 mol) in freshly distilled thionyl chloride (40 ml); the reaction mixture was heated under reflux for 5 h, and excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. 4-Allyloxy-4′-hydroxybiphenyl (0.1 mol) was dissolved in a mixture of dry pyridine (10 ml) and dry tetrahydrofuran (THF) (100 ml); the 4-ethoxybenzoic acid chloride was added quickly and the reaction mixture heated under refluxed for 24 h. The cold reaction mixture was stirred into water, and the precipitated product filtered off and recrystallized from ethonol; yield 88%, m.p. 161°C. IR(KBr):3097, 3039(=C–H), 2980–2850(CH_3, CH_2), 1728(C=O), 1648 (C=C), 1605–1450 cm^{-1} (Ar–). ^{1}H NMR($CDCl_3$):δ1.45–1.56(t, 3H, –CH_3), 4.11–4.18(m, 2H, –OCH_2–), 4.59–4.60(d, 2H, –CH_2O–), 5.30–5.48(m, 2H, CH_2=CH–); 6.00–6.20 (m, 1H, CH_2=C*H*–), 6.97–8.19(m, 12H, Ar–*H*).

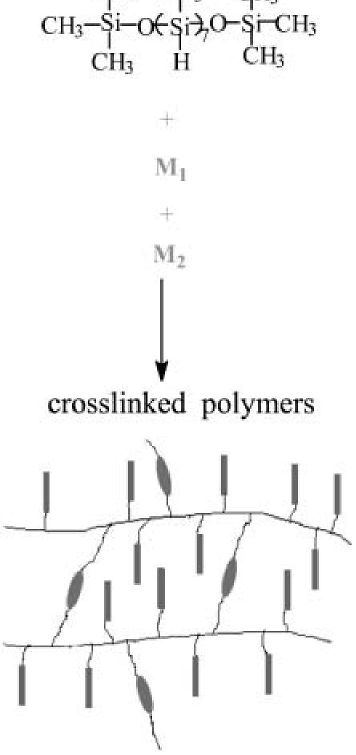


Scheme 1. Synthetic route to the monomers.

2.3.2. Synthesis of Isosorbide 4-allyloxybenzoyl bisate (M_2).

A few drops of DMF was added to a suspension of 4-allyloxybenzoic acid (0.1 mol) in freshly distilled thionyl chloride (40 ml) and the reaction mixture heated under reflux for 10 h; excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride. Isosorbide was dissolved in a mixture of dry triethylamine (10 ml) and dry chloroform(100 ml); the 4-allyloxybenzoyl chloride was then added quickly at ice bath temperature, and the reaction mixture was held for 72 h at room temperature. The cold reaction mixture was mixed with water, and the precipitated product isolated by filtration and recrystallized from ethanol; yield 34%, m.p. 96°C. $[\alpha]_{589}^{17.2} = -75.5°$. IR(KBr): 3038(=C–H), 2980, 2850(–CH_3, –CH_2), 1716(C=O), 1638(C=C), 1605–1450 cm^{-1} (Ar–). ^1H NMR($CDCl_3$):δ4.00–5.04(m, 8H, isosorbide), 4.59–4.68 (d, 2H, CH_2=CHCH_2O), 5.31–5.46(m, 2H, CH_2=CH–), 6.00–6.20 (m, 1H, CH_2=CH–); 6.92–8.06(m, 8H, Ar–H).

2.3.3. Synthesis of the elastomers. The synthetic route to the elastomers is outlined in scheme 2. The mesogenic monomer and chiral crosslinking agent reacted with the Si–H of PMHS to form elastomers in the presence of a Pt catalyst. All the polymers synthesized are listed in table 1. The monomer $\mathbf{M_1}$, $\mathbf{M_2}$ and PMHS were dissolved in dried, freshly distilled toluene. The mixture was heated to 65°C under nitrogen and anhydrous conditions, and then an appropriate amount of THF solution of hexchloroplatinate hydrate catalyst was injected with a syringe. The reaction mixture was held at 60–70°C for three days, and then precipitated with methanol. The products were dried under vacuum at room temperature. IR(KBr): 2980, 2850(–CH_3, –CH_2), 1731(C=O), 1605–1450(Ar–), 1200–1000 cm^{-1} (Si–O–Si).



Scheme 2. Synthesis and schematic representation of elastomers $\mathbf{P_2}$–$\mathbf{P_7}$.

3. Results and discussion

3.1. *Synthesis*

We have synthesized two novel monomers: a nematic monomer ($\mathbf{M_1}$) and a chiral crosslinking agent ($\mathbf{M_2}$). The reaction pathways to $\mathbf{M_1}$ and $\mathbf{M_2}$ are shown in scheme 1. $\mathbf{M_1}$ was prepared by (1) etherification of 4,4′-hydroxybiphenyl with 3-bromopropene to give 4-allyloxy-4′-hydroxybiphenyl; (2) esterification of 4-ethoxybenzoic acid chloride with 4-allyloxy-4′-hydroxybiphenyl to give $\mathbf{M_1}$. $\mathbf{M_2}$ was prepared by (1) etherification of 4-hydroxybenzoic acid with 3-bromopropene to give 4-allyloxybenzoic acid; (2) esterification of 4-allyloxybenzoic acid chloride with isosorbide to give $\mathbf{M_2}$.

The chemical structure of each monomer was characterized by FTIR and ^1H NMR spectroscopy. The FTIR scans of $\mathbf{M_1}$ and $\mathbf{M_2}$ showed characteristic bands at 1728–1716 cm^{-1} originating from ester C=O stretching, 1648–1638 cm^{-1} due to olefinic C=C stretching, and 1605–1450 cm^{-1} corresponding to aromatic C=C stretching. The ^1H NMR spectra of $\mathbf{M_1}$ and $\mathbf{M_2}$ showed multiplets at 6.97–8.19, 5.30–6.11, 4.0–5.6 and 1.56–1.45 ppm, corresponding to aromatic, olefinic protons and methylene, isosorbide, methyl protons.

The new series of elastomers $\mathbf{P_2}$–$\mathbf{P_8}$ were prepared by a one-step hydrosilation reaction between Si–H groups of PMHS and olefinic C=C of the nematic monomer and difunctional chiral crosslinking agent, in toluene using hexachloroplatinate as catalyst at 60°C. The yields and properties of $\mathbf{P_2}$–$\mathbf{P_8}$ are summarized in table 1. $\mathbf{P_2}$–$\mathbf{P_8}$ retained elasticity and were in a rubber-like state at room temperature. The FTIR spectra of $\mathbf{P_1}$–$\mathbf{P_8}$ showed complete disappearance of Si–H stretching band at 2166 cm^{-1}. Characteristic absorption bands appeared at 1740–1728, 1605–1450 and 1200–1000 cm^{-1}, corresponding to the stretching of ester C=O, aromatic and Si–O–Si bonds, respectively. It can

Table 1. Polymerization of polymers $\mathbf{P_1}$–$\mathbf{P_8}$.

Polymer	Feed/mmol $\mathbf{M_1}$	Feed/mmol $\mathbf{M_2}$	$\mathbf{M_2}$/mol%[a]	Yield/%
$\mathbf{P_1}$	3.500	0.000	0	82.5
$\mathbf{P_2}$	3.360	0.070	2	81.0
$\mathbf{P_3}$	3.220	0.140	4	85.2
$\mathbf{P_4}$	3.080	0.210	6	88.0
$\mathbf{P_5}$	2.940	0.280	8	90.3
$\mathbf{P_6}$	2.800	0.350	10	79.2
$\mathbf{P_7}$	2.450	0.525	15	73.5
$\mathbf{P_8}$	2.100	0.700	20	79.1

[a] Molar fraction of $\mathbf{M_2}$ based on $\mathbf{M_1}$+$\mathbf{M_2}$.

be concluded that the chemical structures of the monomers and polymers are consistent with expection.

3.2. *Thermal properties*

Phase transition temperatures and corresponding enthalpy changes are summarized in table 2; DSC curves of elastomers **P$_3$**, **P$_5$**, **P$_8$**, and TGA thermograms of **P$_4$**, **P$_5$**, **P$_6$** are shown in figures 1 (*a*) and 1 (*b*) respectively. A melting transition and a nematic to isotropic phase transition for **M$_1$** appeared in the range 161.0–253.6°C. For the elastomers **P$_2$**–**P$_7$**, a glass transition and a cholesteric to isotropic transition appeared on DSC curves. As can be seen from table 2, a low content of crosslinking agent did not significantly affect the phase behaviour of the elastomers, and reversible phase transitions were observed because of sufficient molecular motion. In contrast, a higher content of crosslinking agent had a strong influence on the phase behaviour; it could cause the LC phase to disappear due to the disturbance of mesogenic order. DSC curves of **P$_8$** showed only a glass transition. Above all, the phase transitions are reversible and do not change on repeated heating and cooling cycles.

Crosslinking imposes additional constraints on the segmental motion of polymer chains, and might be expected to raise the glass transition temperature. However, the effect is small for lightly crosslinked samples, and opposing this effect may be the plasticising influence of the flexible crosslinking units. As a consequence, lightly crosslinked polymers often have reduced glass transition temperatures compared with the parent polymer. Taking the crosslinking and plasticization effects into account, T_g is given by

$$T_g = T_{go} - K_x .\ \rho_x \qquad (1)$$

$$T_g = T_{go} + K_x .\ \rho_x \qquad (2)$$

where T_g and T_{go} are the glass transition temperatures of crosslinked and uncrosslinked polymers, respectively, K_x is a constant, and ρ_x is the content of crosslinking agent. When the content of crosslinking agent is less than certain critical value, the plasticization effect of the flexible crosslinking chain is predominant; equation (1) is then adopted. Conversely, when the crosslinking effect is predominant, equation (2) will take effect. Figure 2 shows the effect of the concentration of crosslinking units on the phase transition temperatures of **P$_1$**–**P$_8$**. It can be seen that the T_g value of **P$_1$** is the highest, which is chiefly due to its rigid structure; the T_g value of **P$_2$**–**P$_4$** reduced quickly from 86.0 to 69.7°C, under the influence of the plasticization of crosslinking. It can be seen that the parent polymer is hard; so at the beginning, introducing the non-LC crosslinking agent brought about significant plasticization. The T_g value of

Table 2. Thermal properties of polymer.

Polymer	T_g/°C	T_i/°C	ΔH/J g^{-1}	ΔT[a]	T_d/°C[c]
P$_1$	88.6	288.6	3.05	200.0	416.8
P$_2$	86.0	278.8	1.99	192.8	416.7
P$_3$	79.4	260.6	1.42	181.2	414.7
P$_4$	69.7	241.3	0.91	171.7	409.3
P$_5$	68.9	225.4	0.66	156.5	403.7
P$_6$	65.4	209.6	0.50	144.2	408.9
P$_7$	67.2	202.1[b]	—	134.9	398.7
P$_8$	76.9	—	—	—	407.1

[a] Mesophase temperature ranges (T_i–T_g).

[b] Temperature at which the birefringence disappeared completely.

[c] Temperature at which 5% weight loss occured.

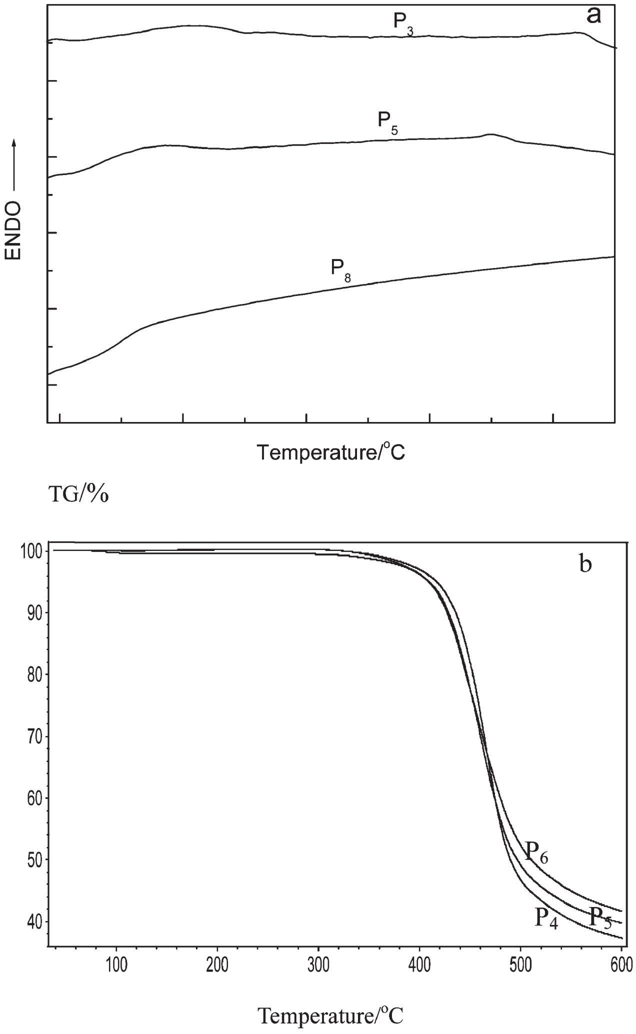


Figure 1. Thermographs of elastomer liquid crystal polymers: (*a*) DSC, (*b*) TGA.

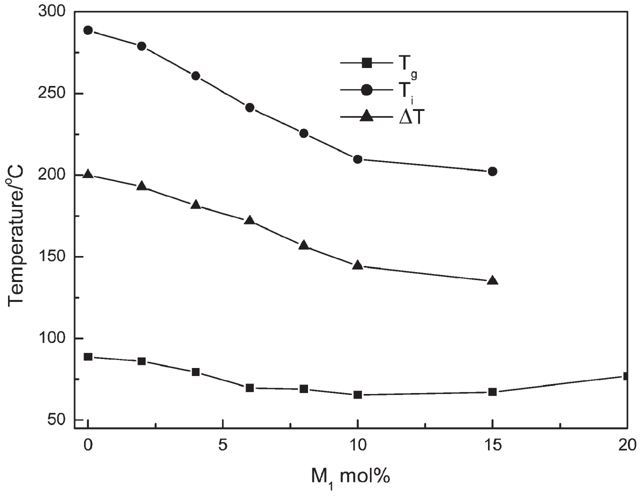


Figure 2. Effect of $\mathbf{M_2}$ content on phase transition temperature of the elastomers.

$\mathbf{P_4}$–$\mathbf{P_6}$ reduced slowly from 69.7 to 65.4°C, showing that the diluted influence of plasticization and the crosslinking effect become equivalent. The T_g value of $\mathbf{P_7}$ rose slowly and $\mathbf{P_8}$ rose quickly compared with $\mathbf{P_6}$; it can thus be concluded that the crosslinking effect gradually becomes predominant as the content of crosslinking agent reaches a certain critical value.

As with the T_g, crosslinking may influence the clearing point (T_i) in two ways. Firstly, crosslinking units may act as a non-mesogenic diluent and lead to a downward shift in the clearing point as increasing proportions are added to a liquid crystalline polymer. For a crosslinked sample, chemical crosslinking may prevent the motion and orientation of mesogenic moieties and thus inhibit the formation of mesogenic orientational order in the elastomers with increasing content of crosslinking agent. Secondly, heating a crosslinked sample to the isotropic state requires additional energy to distort the polymer backbone from the crosslinked anisotropic state, leading to a forward shift in the clearing point with increasing proportions of chiral crosslinking agent. In this study, a non-LC crosslinking agent is introduced into the polymer backbone, so the first factor is predominant. It can be seen that T_i values fell with increasing content of crosslinking agent. From table 2, it can be seen that the T_i value disappeared when the content of crosslinking agent reached a certain critical value; the T_i of $\mathbf{P_1}$–$\mathbf{P_7}$ decreased from 288.6 to 202.1°C when the concentration of crosslinking units increased from zero to 15%. A T_i value for $\mathbf{P_7}$ cannot be seen on the DSC curve, but it was shown to be mesogenic through POM; we therefore used the T_i value of $\mathbf{P_7}$ as measured by POM. Polymers $\mathbf{P_1}$–$\mathbf{P_7}$ displayed wide mesophase temperature ranges (ΔT); the ΔT of the elastomers decreased with increasing content of crosslinking agent. It can be seen that the temperatures at which 5% weight loss occurred (T_d) were greater than 400°C for $\mathbf{P_2}$–$\mathbf{P_8}$, showing that the synthesized elastomers have a high thermal stability.

3.3. *Optical properties*

It is well known that a cholesteric LC phase can be obtained when a nematic phase is doped with chiral molecules; the long axis of the liquid crystal molecules (the director **n**) rotates about a helix. In this phase a band of incident circularly polarized light, having the same sense as the cholesteric helix, is reflected whereas a band with the opposite sense is transmitted. The wavelength of selective reflection of light λ obeys the Bragg condition

$$\lambda = nP$$

The reflected band width($\Delta\lambda$)is given by

$$\Delta\lambda = \lambda_{\max} - \lambda_{\min} = P(n_e - n_o)$$

where n_e and n_o are the extraordinary and the ordinary refractive indices, respectively, of a uniaxially oriented phase.

Although the microscopic origins of pitch are still a subject of study, it is well known that the pitch and reflected colours depend on temperature. Two technologically relevant questions about cholesterics are how to adjust the pitch and how to keep it constant at the correct value. We expected to obtain cholesteric LCEs by introducing a chiral non-LC crosslinking agent and nematic LC monomers. The optical textures of the monomers and polymers were studied by POM with a hot stage, under a nitrogen atmosphere. POM observation results showed that $\mathbf{M_1}$ exhibits an enantiotropic nematic phase. When $\mathbf{M_1}$ was heated to 142°C, the sample began to melt, a typical nematic threaded texture gradually appeared and the texture disappeared at 252°C. When the isotropic state was cooled to 250°C, a small schlieren texture gradually appeared, disappeared quickly, and then a droplet texture appeared and step by step a large schlieren texture appeared at 196°C; a threaded texture appeared again at 176°C. Photomicrographs of $\mathbf{M_1}$ are shown in figure 3.

The uncrosslinked polymer $\mathbf{P_1}$ showed a typical nematic threaded texture, as expected, see figure 4(*a*). Elastomers $\mathbf{P_2}$ and $\mathbf{P_3}$ exhibited cholesteric Grandjean texture when shearing; $\mathbf{P_4}$–$\mathbf{P_7}$ displayed a cholesteric Grandjean orange/green/blue colour with increasing temperature, and also a transmitted colour. $\mathbf{P_8}$ displayed stress-induced birefringence. The LC property

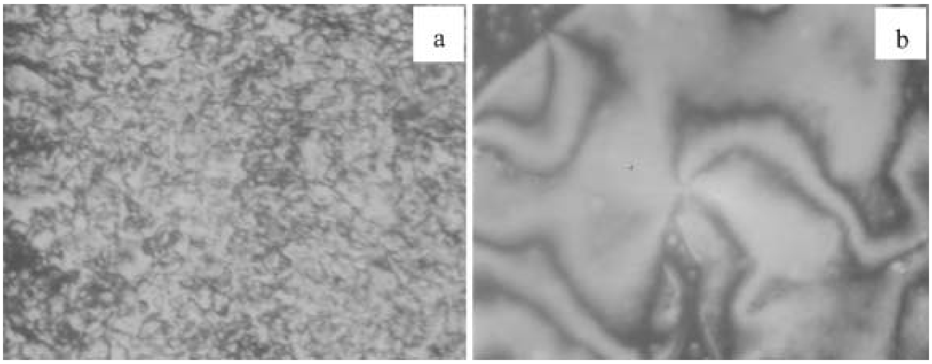


Figure 3. Optical texture of monomer(200X): (*a*) thread-like texture of $\mathbf{M_1}$ on heating to 242°C; (*b*) schlieren texture of $\mathbf{M_1}$ on cooling to 200°C.

of $\mathbf{P_6}$ was extraordinary; heated to 117°C, a bright orange–yellow colour appeared, changing gradually to green, when it reached 145°C, became light green changing a duck blue at 163°C and remained thus until the isotropic state. On cooling, the duck blue color remained and at the same time a colourful transmitted light could be seen. Photomicrographs of $\mathbf{P_6}$ are shown in figure 4 (*b*), 4 (*c*). It can be seen that the pitch of the cholesteric helix became shorter with increasing temperature and that $\mathbf{P_2}$–$\mathbf{P_7}$ are in the cholesteric phase as expected. Thus an appropriate concentration of chiral crosslinking agent with a nematic LC can bring about typical cholesteric LCEs.

3.4. *XRD analysis*

XRD can give information about the orientation of the polymer and can establish the idea of small crystalline domains within the liquid crystalline phase. Samples were quenched from the liquid crystal phase. In general, smectic, nematic and cholesteric structures have a broad peak associated with lateral packing at $2\theta \approx 16$–$20°$ in wide angle XRD (WAXD) curves. A sharp and strong peak at low angle ($1° < 2\theta < 4°$) in small angle X-ray scattering(SAXS) curves can be observed for the smectic structure, but cannot be seen for nematic and cholesteric structures. For $\mathbf{P_1}$–$\mathbf{P_8}$, no sharp low angle peak

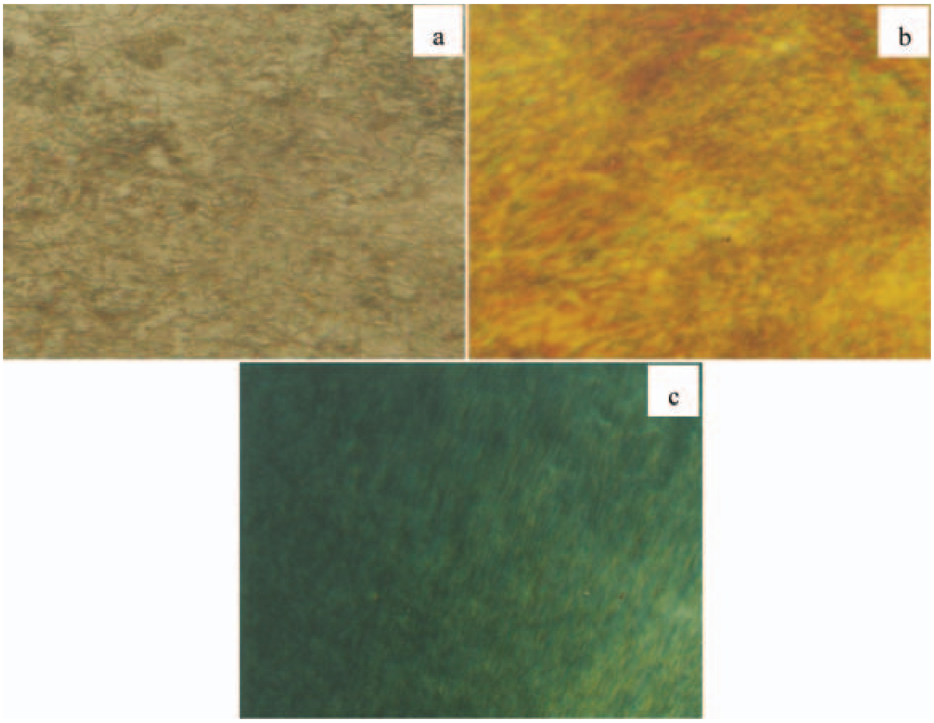


Figure 4. Optical texture of polymers(200x): (*a*) threaded texture of $\mathbf{P_1}$ at 187°C; (*b*) orange/yellow Grandjean texture of $\mathbf{P_6}$ at 117°C; (*c*) blue Grandjean texture of $\mathbf{P_6}$ at 163°C.

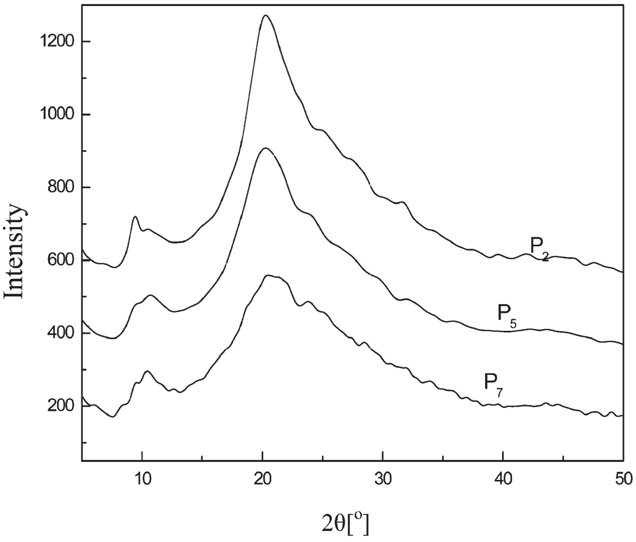


Figure 5. X-ray diffraction patterns of quenched samples.

associated with smectic layers appeared in the SAXS curve; for $\mathbf{P_2}$–$\mathbf{P_8}$ a weak peak and a broad peak were observed, respectively, at $2\theta=9.5$–$11.5°$($d=8.4$–9.7 A°) and 16.0–20.8°($d=4.2$–5.7 A°) in WAXD. As the level of crosslinking agent increased, these broad peaks became weaker; this is simply related to the difference between the intrachain scattering of the mesogenic repeat and the crosslinking unit. A representation of XRD patterns is shown in figure 5. From analysis by XRD, we can exclude the possibility of a smectic phase for the polymers. The nematic phase structure of $\mathbf{P_1}$ and the cholesteric phase structures of $\mathbf{P_2}$–$\mathbf{P_7}$ were confirmed by optical texture and XRD results.

4. Conclusion

In this study, a series of new side chain cholesteric LCEs containing the nematic liquid crystal monomer $\mathbf{M_1}$ (4-allyloxybiphenyl 4′-ethoxybenzoate) and chiral crosslinking agent $\mathbf{M_2}$ (isosorbide 4-allyloxybenzoyl bisate) side groups were synthesized and characterized. All of the polymers obtained showed very wide mesophase temperature ranges and high thermal stability. Light chemical crosslinking did not markedly affect the phase behaviour of the elastomers; but introducing a chiral crosslinking agent changed the polymer phase from nematic to cholesteric. Elastomers containing less than 15% of crosslinking units showed elasticity, reversible phase transition and Grandjean texture during heating and cooling; selective reflection of light can be seen for $\mathbf{P_4}$–$\mathbf{P_7}$. Polymer $\mathbf{P_6}$ showed blue Grandjean texture over a broad temperature range and held this texture on cooling. For $\mathbf{P_1}$–$\mathbf{P_8}$, with increasing content of crosslinking agent, the glass transition temperature first reduced and then increased; the isotropization temperature and mesophase ranges decreased.

Acknowledgement

The authors are grateful to the National Natural Science Fundamental Committee of China, the HI-Tech Research and Development Program (863) of China, the National Basic Research Priorities Program (973) 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] R. Zentel. *Angew.Chem.adv.Mater.*, **101**, 1437 (1989).
[2] R. Loffler, H. Finkelman. *Macromol.Chem.rapid Commun.*, **11**, 321 (1990).
[3] J. Davis. *J. mater.Chem.*, **3**, 551 (1993).
[4] R. Zentel, G. Reckert. *Makromol.Chem.*, **187**, 1915 (1986).
[5] R. Mitchell, J. Davis. *Polymer*, **28**, 639 (1987).
[6] W. Meier, H. Finkelman. *Condens. Matter News*, **1**, 15 (1992).
[7] D.J. Broer, I. Heynderickx. *Macromolecules*, **23**, 2474 (1990).
[8] R. Zentel. *Polymer*, **33**, 4040 (1992).
[9] D.J. Broer, J. Lub, G.N. Mol. *Nature*, **378**, 467 (1995).
[10] G. Maxein, S. Mayer, R. Zentel. *Macromolecules*, **32**, 5747 (1999).
[11] R.A.M. Hikmet, H. Kemperman. *Nature*, **392**, 476 (1998).
[12] P. Thomas, K. Kurschner, P. Strohriegl. *Macromol.Chem.Phys.*, **200**, 2480 (1999).
[13] P.M. Peter. *Nature*, **391**, 745 (1998).
[14] H. Kihara, T. Kato, T. Uryu. *Liq. Cryst.*, **24**, 413 (1998).
[15] H.R. Kricheldorf, T. Krawinkel. *Macromol.Chem.Phys.*, **199**, 783 (1998).
[16] R. Zentel, M. Benalia. *Makromol.Chem.*, **188**, 665 (1987).
[17] H. Dirk, F. Holger, M. Rolf, J.E. Klee. *Adv.Mater*, **11**, 864 (1998).
[18] T. Pfeuffer, K. Kurschner, P. Strohriegl. *Macromol.Chem.Phys.*, **200**, 2480 (1999).
[19] J.E. Stockley, G.D. Sharp, S.A. Serati, K.M. Johnson. *Opti. Lett.*, **20**, 2441 (1995).
[20] J. Lub, D.J. Broer, R.A.M. Hikmet, K.G.J. Nierop. *Liq.Cryst.*, **18**, 319 (1995).
[21] R. Zentel. *Polymer*, **33**, 4040 (1992).
[22] J.S. Hu, B.Y. Zhang, K. Sun, Q.Y. Li. *Liq.Cryst.*, **30**, 1267 (2003).
[23] B.Y. Zhang, J.S. Hu, Y.G. Jia, B.G. Du. *Macromol.Chem.Phys.*, **204**, 2123 (2003).
[24] J.S. Hu, B.Y. Zhang, Y.G. Jia, S. Chen. *Macromolecules*, **36**, 9060 (2003).
[25] B. Sapich, J. Stumpe, T. Krawinkel, H.R. Kricheldorf. *Macromolecules*, **31**, 1016 (1998).
[26] H. Finkelmann. *Adv. Mater.*, **13**, 1069 (2001).
[27] M. Brehmer, R. Zentel. *Mol. Cryst. liq. Cryst.*, **243**, 353 (1994).
[28] S.M. Kelly. *J. mater. Chem.*, **5**, 2047 (1995).