

Effect of the Length of the Carbochain on the Phase Behavior of Side-Chain Cholesteric Liquid-Crystalline Elastomers

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ABSTRACT: In this study, we prepared two series of new side-chain cholesteric liquid-crystalline elastomers (**PI** and **PII**) derived from the same chiral bisolefinic crosslinking units and different nematic liquid-crystalline monomers. The chemical structures of the monomers and polymers obtained were confirmed by Fourier transform infrared and $^1\text{H-NMR}$ spectroscopy. The phase behavior properties were investigated by differential scanning calorimetry, thermogravimetric analysis, and polarizing optical microscopy. The effect of the length of the carbochain on the phase behavior of the elastomers was investigated. The polymers of the **PI** and **PII** series showed similar properties. Polymer **P**₁ showed a nematic phase, **P**₂–**P**₇ showed a cholesteric phase, and **P**₄–**P**₇, with more than 6 mol % of the chiral crosslinking agent, exhibited a selective reflection of light. The elastomers

containing less than 15 mol % of the crosslinking units displayed elasticity, a reversible phase transition with wide mesophase temperature ranges, and a high thermal stability. The experimental results demonstrate that the glass-transition temperatures first decreased and then increased; the isotropization temperatures and the mesophase temperature ranges decreased with increasing content of crosslinking agent. However, because of the different lengths of the carbochain, the glass-transition temperatures and phase-transition temperatures of the **PI** series were higher than those of the **PII** series, and the **PI** and **PII** elastomers had their own special optical properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1204–1210, 2005

Key words: chiral; crosslinking; elastomers

INTRODUCTION

As is well known, materials science is directed toward the development of multifunctional and oriented structures. One such supramolecular system is the liquid-crystalline elastomer (LCE), which combine the properties of a liquid-crystal (LC) phase with rubber elasticity.^{1–6} Since the synthesis of LCEs was reported, increasing attention has been paid to novel materials that could be greatly immobilized to give anisotropic solids with unusual properties. The cholesteric LC is probably the most interesting periodic structure because of its history, theory, and practice. The same is true for cholesteric LCEs. Among LCEs, much attention has been paid to cholesteric LCEs, which have

unique properties and potential applications in numerous areas, especially in nonlinear optical materials, electro-optical materials, and fast optical switches. Recently, theoretical and experimental studies have demonstrated that piezoelectric properties can be obtained from cholesteric LCEs. Cholesteric LCEs have the potential to act as devices that transform a mechanical signal into an optical signal.^{7–14} However, to the best of our knowledge, descriptions of cholesteric LCEs bearing chiral crosslinking agents have few so far, so it is necessary and significant to synthesize various kinds of side-chain cholesteric LCEs with chiral crosslinking agents to explore their potential applications.

Our teams have done many studies in the field of cholesteric LCEs.^{15–17} In this study, the synthesis of two new series (**PI** and **PII**) of side-chain cholesteric LCEs derived from two nematic LC monomers, ethoxy-4-allyloxybiphenyl-4'-benzoate (**M**₁) and pentyloxy-4-allyloxybiphenyl-4'-benzoate (**M**₂), and a chiral crosslinking agent, isosorbide 4-allyloxybenzoyl bisate (**M**₃), was performed. The reason we chose isosorbide as the chiral material is that it possesses a high twisting power, and obviously, a high molar fraction of isosorbide generates helices with a pitch that is too small (or large) for an interaction with visible light.¹⁸ The mesomorphic properties of the

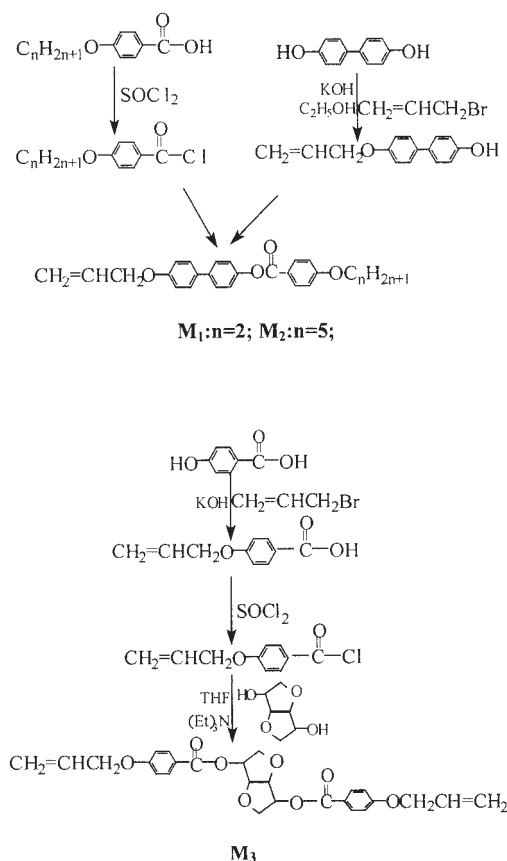
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Scheme 1 Synthetic route of the monomers.

monomers and elastomers obtained were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and thermogravimetric analysis (TGA). The influence of the length of the carbochain on the phase behavior of the elastomers was investigated.

EXPERIMENTAL

Materials

Polymethylhydrosiloxane (PMHS) was purchased from Jilin Chemical Industry Co. (Jilin, China). 4,4'-Biphenol was purchased from Beijing Chemical Industry Co. (Beijing, China). 3-Bromopropene was purchased from Beijing Fuxing Chemical Industry Co. (Beijing, China). Isosorbide was bought from Yangzhou Shenzhou New Material Co., Ltd. (Yangzhou, China). Ethyloxybenzoic acid was purchased from Shenyang Xinxi Chemical Reagent Co. (Shenyang, China). The toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen. All of the other solvents and reagents were purified by standard methods.

Characterization

IR spectra were measured on a PerkinElmer Spectrum One Fourier transform infrared spectrometer (Wellesley, MA). Specific rotation was performed with a PerkinElmer 341 polarimeter (Wellesley, MA). $^1\text{H-NMR}$ spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Palo Alto, CA). Phase-transition temperatures (T_i 's) and thermodynamic parameters were determined with a Netzsch DSC 204 with a liquid nitrogen cooling system (Netzsch, Germany). The heating and cooling rates were $10^\circ\text{C}/\text{min}$. The thermal stability of the polymers was measured with a Netzsch TGA 209C thermogravimetric analyzer (Netzsch, Germany). A Leitz Microphot-FX (Wetzlar, Germany) polarizing optical microscope equipped with a Mettler FP 82 hot stage and an FP 80 central processor was used to observe T_i and to analyze LC properties of the monomers and polymers through the observation of optical textures.

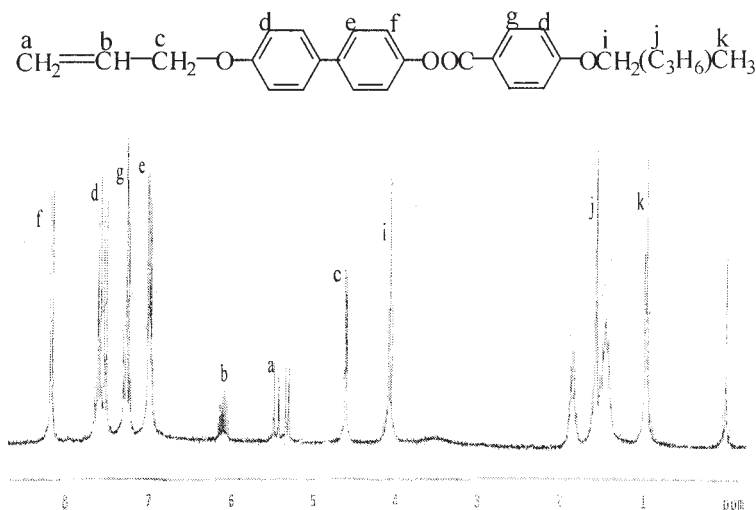
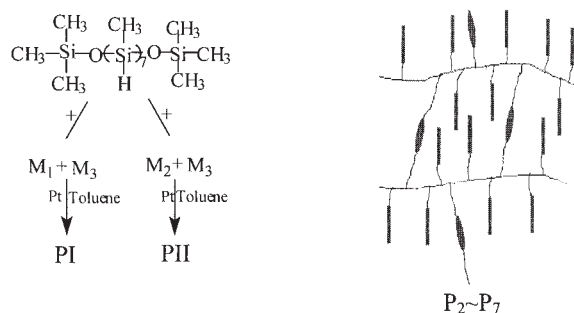


Figure 1 $^1\text{H-NMR}$ spectra of M_2 .



Scheme 2 Synthesis and schematic representation of the elastomers.

Synthesis of the monomers

The synthesis of the olefinic monomers are shown in Scheme 1. 4-Allyloxybenzoic acid and 4-allyloxy-4'-hydroxybiphenyl were prepared in our laboratory.

Synthesis of M_1 and M_2

The synthetic methods of M_1 and M_2 were similar, so we chose monomer M_2 as an example. A few drops of *N,N*-dimethylformamide (DMF) were added to a suspension of 4-pentyloxybenzoic acid (0.1 mol) in freshly distilled thionyl chloride (40 mL), and the reaction mixture was refluxed for 5 h; then, the excessive thionyl chloride was removed under a 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 (100 mL); the 4-pentyloxybenzoic acid chloride was then added at once, and the reaction mixture was refluxed for 24 h. The cold reaction mixture was precipitated into water, and the precipitated product was isolated by filtration and recrystallized from ethanol (yield = 90%, mp = 117.8°C).

IR (KBr, cm^{-1}): 3078, 3038 ($=\text{C}-\text{H}$); 2980–2850 ($-\text{CH}_3, -\text{CH}_2-$); 1727 ($\text{C}=\text{O}$); 1648 ($\text{C}=\text{C}$); 1605–1450 ($\text{Ar}-$); 1258 ($\text{C}-\text{O}-\text{C}$).

$^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 0.93–0.98 (t, 3H, $-\text{CH}_3$), 1.40–1.84 (m, 6H, $-\text{CH}_2-$), 4.04–4.08 (d, 2H, $-\text{OCH}_2-$), 4.59–4.62 (d, 2H, $\text{CH}_2=\text{CHCH}_2\text{O}$), 5.31–5.48 (m, 2H, $\text{CH}_2=$), 6.00–6.20 (m, 1H, $\text{CH}_2=\text{CH}-$), 6.98–8.20 (m, 12H, ArH).

In Figure 1, the $^1\text{H-NMR}$ spectra of M_2 is shown.

Synthesis of M_3

A few drops of DMF were added to a suspension of 4-allyloxybenzoic acid (0.1 mol) in freshly distilled thionyl chloride (40 mL), and the reaction mixture was refluxed for 10 h; then, the excess thionyl chloride was removed under a 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-allyloxybenzoic acid chloride was then added at once in an ice bath, and the reaction mixture was refluxed for 72 h at room temperature. The cold reaction mixture was precipitated into water, and the precipitated product was isolated by filtration and recrystallized from ethanol (yield = 34%, mp = 96°C, $[\alpha]_{589}^{17.2} = -75.5^\circ$). Specific rotation of M_3 solutions of 8 g/ml in the toluene were measured in 2 ml cuvettes of 100 mm length using light of a Na-lamp at $\lambda = 589_{\text{nm}}$ and at 17.8°C.

IR (KBr, cm^{-1}): 3038 ($=\text{C}-\text{H}$); 2980, 2850 ($-\text{CH}_3, -\text{CH}_2-$); 1716 ($\text{C}=\text{O}$); 1638 ($\text{C}=\text{C}$); 1605–1450 ($\text{Ar}-$); 1257 ($\text{C}-\text{O}-\text{C}$).

$^1\text{H-NMR}$ (CHCl_3 , δ , ppm): 4.00–5.04 (m, 10H, isosorbide), 4.59–4.68 (d, 2H, $\text{CH}_2=\text{CHCH}_2\text{O}$), 5.31–5.46 (m, 2H, $\text{CH}_2=\text{CH}$), 6.00–6.20 (m, 1H, $\text{CH}_2=\text{CH}$), 6.92–8.06 (m, 8H, ArH).

Synthesis of the polymers

The synthetic methods for uncrosslinked and crosslinked polymers (elastomers) were similar. The synthetic routes of the elastomers are outlined in Scheme 2. The mesogenic monomers and the different contents of chiral crosslinking agent reacted with Si—H of PMHS to form elastomers in the presence of

TABLE I
Polymerization and Solubility of the PI Polymer Series

Polymer	Feed (mmol)		M_3^a (mol %)	Yield (%)	Solubility ^b		
	M_1	M_3			Toluene	Xylene	DMF
PI-1	3.500	0.000	0	82.5	+	+	+
PI-2	3.360	0.070	2	81.0	–	–	–
PI-3	3.220	0.140	4	86.3	–	–	–
PI-4	3.080	0.210	6	88.0	–	–	–
PI-5	2.940	0.280	8	90.3	–	–	–
PI-6	2.800	0.350	10	79.2	–	–	–
PI-7	2.450	0.525	15	73.5	–	–	–
PI-8	2.100	0.700	20	79.1	–	–	–

^a Molar fraction of M_3 based on $M_1 + M_3$.

^b + = dissolved; – = insolubility or swelling.

TABLE II
Polymerization and Solubility of the PII Polymer Series

Polymer	Feed (mmol)		M_3^a (mol %)	Yield (%)	Solubility ^b		
	M_2	M_3			Toluene	Xylene	DMF
PII-1	3.500	0.000	0	88.5	+	+	+
PII-2	3.360	0.070	2	86.0	—	—	—
PII-3	3.220	0.140	4	85.2	—	—	—
PII-4	3.080	0.210	6	88.0	—	—	—
PII-5	2.940	0.280	8	80.3	—	—	—
PII-6	2.800	0.350	10	75.2	—	—	—
PII-7	2.450	0.525	15	71.5	—	—	—
PII-8	2.100	0.700	20	67.1	—	—	—

^a Molar fraction of M_3 based on $M_2 + M_3$.

^b + = dissolved; — = insolubility or swelling.

Pt catalyst. The monomers (M_1 and M_3) and PMHS were dissolved in dried, freshly distilled toluene. The mixture was heated to 65°C under nitrogen and anhydrous conditions, and then a proper amount of a tetrahydrofuran solution of hexchloroplatinate hydrate catalyst was injected with a syringe. The reaction was carried out at 60–70°C for 3 days, and then, the product was precipitated with methanol. The products of series **PI** were dried *in vacuo* at room temperature. The **PII** series products were synthesized with the same method used for monomers M_2 and M_3 . The obtained elastomers of the **PI** and **PII** series were insoluble in toluene, xylene, DMF, chloroform, and so on but could swell in these solvents. All of the polymers' polymerization solubilities are listed in Tables I and II.

IR (KBr, cm^{-1}): 2980, 2850 ($-\text{CH}_3-\text{CH}_2-$); 1731 ($\text{C}=\text{O}$); 1605–1450 (Ar—); 1200–1000 (Si—O—Si).

RESULTS AND DISCUSSION

Phase behavior

The phase behavior of LC polymers can be readily evaluated by DSC, which provides an effective measurement of the energy required to raise the temperature as a function of temperature. The thermal prop-

erties of polymers P_1 – P_8 of the **PI** and **PII** series are summarized in Tables III and IV. The DSC curves P_2 and P_5 of the **PI** and **PII** series are shown in Figure 2. As shown in the data in Tables III and IV, the general tendencies of the **PI** and **PII** elastomers were concordant. A lower content of crosslinking agent (ρ_x) did not significantly affect the phase behavior of the elastomers, and reversible phase transitions were observed because of enough molecular motion; on the contrary, a higher ρ_x had a strong influence on the phase behavior. It could cause the LC phase to disappear because of the disturbance of mesogenic order. Above all, the phase transitions were reversible and did not change on repeated heating and cooling cycles. In general, the phase behavior of side-chain LCEs mainly depended on the nature of the polymer backbone, the rigidity of the mesogenic monomer, the length of the flexible spacer (L_s), and ρ_x . When the last two factors are taken into account, the glass-transition temperature (T_g) is given by

$$T_g = T_{g0} \pm K_x \rho_x \quad (1)$$

$$T_g = T_{g0} + K_s L_s \quad (2)$$

$$T_g = T_{g0} - K_s L_s \quad (3)$$

TABLE III
Thermal Properties of the PI Polymer Series

Polymer	T_g (°C)	T_i (°C)	ΔT^a	T_d (°C) ^b
PI-1	88.6	288.6	200.0	384.8
PI-2	86.0	278.8	192.8	383.8
PI-3	79.4	260.6	181.2	385.9
PI-4	69.7	241.3	171.7	377.8
PI-5	68.9	225.4	156.5	369.9
PI-6	65.4	209.6	144.2	373.0
PI-7	67.2	202.1 ^c	134.9	355.7
PI-8	76.9	—	—	384.6

^a Mesophase temperature ranges ($T_i - T_g$).

^b Temperature at which the 2% weight loss occurred.

^c Temperature at which the birefringence disappeared completely.

TABLE IV
Thermal Properties of the PII Polymer Series

Polymer	T_g (°C)	T_i (°C)	ΔT^a	T_d (°C) ^b
PII-1	77.2	246.6	169.4	371.5
PII-2	75.1	234.2	159.1	373.5
PII-3	70.6	218.8	148.2	355.5
PII-4	68.7	207.3	143.4	353.2
PII-5	67.1	190.1	125.0	361.4
PII-6	67.3	182.8	115.0	357.8
PII-7	69.3	162.2 ^c	92.9	362.6
PII-8	71.0	—	—	361.9

^a Mesophase temperature ranges ($T_i - T_g$).

^b Temperature at which the 2% weight loss occurred.

^c Temperature at which the birefringence disappeared completely.

where T_g and T_{g0} are the glass-transition temperatures of the crosslinked and uncrosslinked polymers, respectively, and K_x and K_s are constants. When we studied the **PI** and **PII** series separately, the term $K_s L_s$ was omitted, and eq. (1) was used. Crosslinking had the opposite effect on the properties of T_g . On the one hand, the crosslinking effect, which imposed additional constraints on the segment motion of the polymer chains might have been expected to raise T_g ; on the other hand, the flexible crosslinking chain, which may have influenced plasticity, reduced T_g . The two factors interacted, and the result was that T_g first decreased and then increased. When we researched the **PI** and **PII** series and compared their properties, the term $K_x \rho_x$ was ignored, and eqs. (2) and (3) were used. Similarly, the length of the carbochain had two opposite effects on the properties of the LCEs. One was a sterically hindered effect, which may have been to increase T_g ; the other was plasticity, which could have reduced T_g . If the length of the carbochain did not reach a certain critical length, the plasticity was predominant, and eq. (3) was used. Figure 3 shows the effect of the length of the carbochain on the phase temperatures of **P1-P8**. As shown in Figure 3, the T_g values from **PI-1** to **PI-5** were higher than those of the **PII** series, which was due to the influence of the plasticity of the length of the carbochain; the T_g values from **PI-6** to **PI-7** were similar to those of the **PII** series, which showed that the sterically hindered influence and the plasticity of the length of the carbochain were equivalent. The T_g value of **PI-8** was higher than that of the **PII** series again, which caused us to conclude that the plasticity of the length of the carbochain was predominant when it did not reach a certain critical length. Similar to T_g , the length of the carbochain may have influenced the mesophase-transition temperature (T_i) in two ways. First, the long length of the carbochain may have acted as a diluent and led to a downward shift in the T_i value; Second, for a long L_s , heating to the isotropic state required additional energy to distort the polymer backbone from the aniso-

tropic state, which was due to the sterically hindered effect and led to a forward shift in the T_i value. As shown in Tables III and IV, the T_i value of the **PI** series was higher than that of the **PII** series. The reason was that the first factor was predominant. At the same time, **P1-P7** of the **PI** and **PII** series displayed wide mesophase temperature ranges (ΔT 's). The ΔT value of the **PI** and **PII** series decreased with increasing ρ_x . The temperatures at which 2% weight loss occurred (T_d 's) were greater than 350°C for the **PI** and **PII** series, which revealed that the synthesized elastomers had a high thermal stability. Figure 3 shows the effect of M_3 content on phase transition temperature T_i of the **PI** and **PII** elastomers.

Optical properties

The optical textures of the two series of polymers were studied by POM with a hot stage under a nitrogen atmosphere. It is known that the wavelength of reflected light (λ) is related to the pitch (P) of the cholesteric helix and the average refractive index (n) in a Bragg-like manner by

$$\lambda_m = nP \quad (4)$$

The angular dependence of the reflection wavelength (λ_m) is given by

$$\lambda_m(\theta_1, \theta_2) = nP \cos[1/2[\sin^{-1}(\sin \theta_1/n) + \sin^{-1}(\sin \theta_2/n)]] \quad (5)$$

where θ_1 and θ_2 are the angle of incidence and the observation angle, respectively; if λ is in the visible range of the spectrum, the cholesteric phase appears colored. The optical properties of the **PI** and **PII** elas-

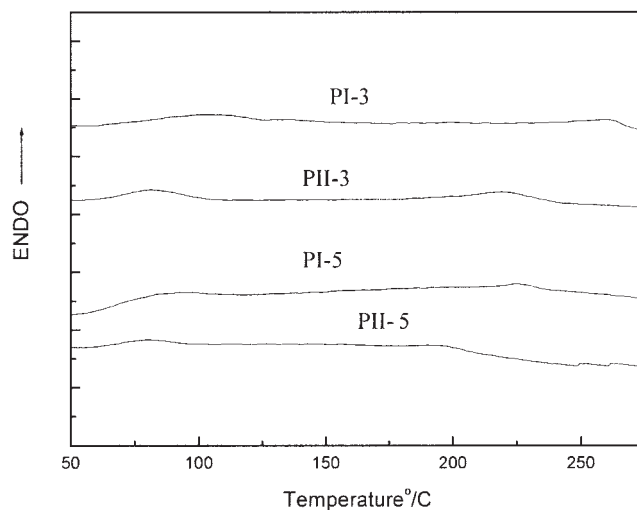


Figure 2 DSC thermograms of the **PI** and **PII** LCEs (second heating).

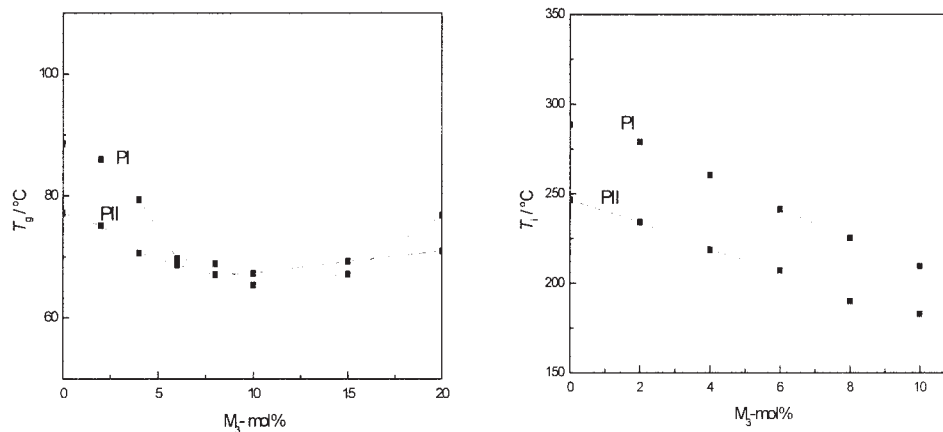


Figure 3 Effect of M_3 contents on the phase transition temperature T_i values of the PI and PII elastomers.

tomers were similar. The uncrosslinked polymer P_1 showed a typical nematic threaded texture as we expected, elastomers P_2 and P_3 exhibited cholesteric Grandjean texture when sheared, and P_4 – P_7 not only showed cholesteric Grandjean orange, green, or blue color with increasing temperature but also the transmitted color could be seen. P_8 displayed stress-in-

duced birefringence. That is, properly chiral concentrations with a nematic LC brought on a typical cholesteric phase just as have expected. When we researched the textures of the two series of polymers, we found that the length of the carbochain of the LC monomer had a great effect on the polymers. The photomicrographs of P_1 and P_6 of the PI and PII series

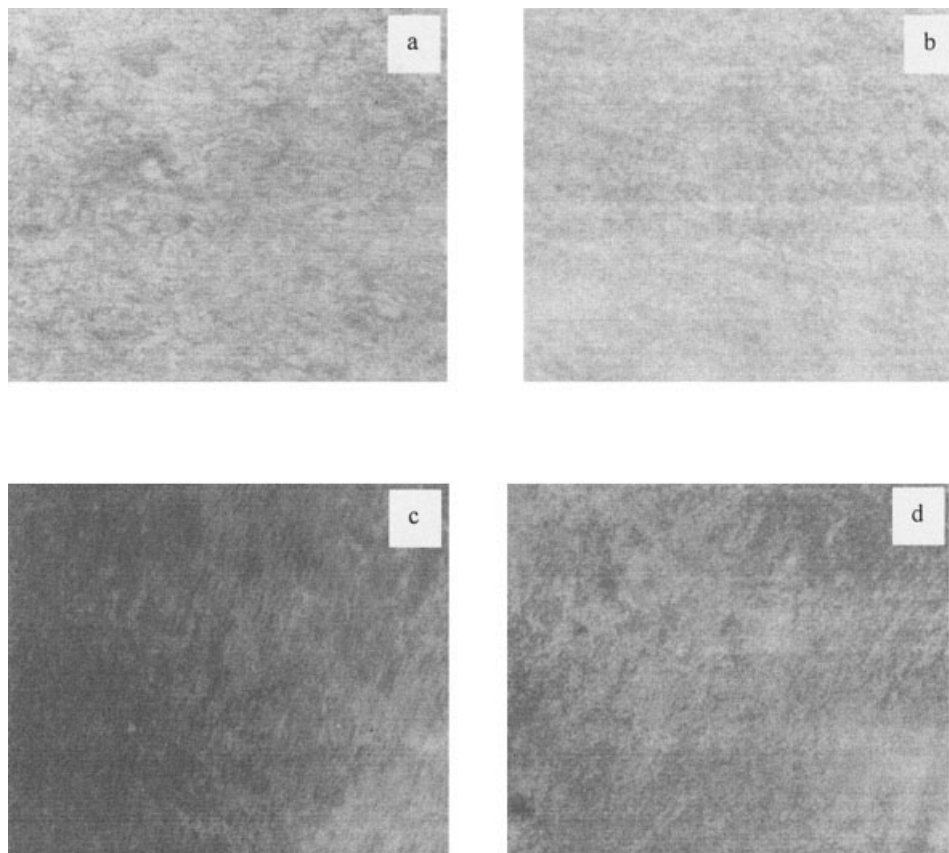


Figure 4 Optical texture of the polymers (200 \times): thread-like textures of (a) PI-1 with heating to 187.0 $^{\circ}$ C and (b) PII-1 with heating to 172 $^{\circ}$ C and (c) Grandjean blue texture of PI-6 with heating to 163.0 $^{\circ}$ C and (d) orange/blue texture of PII-6 with heating to 174.0 $^{\circ}$ C.

are shown on Figure 4. **PI-1** exhibited a pretty and characteristic thread-like texture, whereas the thread-like texture of **PII-1** was not obvious. The reason was that the sterically hindered effect of the long-length carbochain was unfavorable for the formation of a thread-like texture. The Grandjean texture of the **PI** and **PII** elastomers that had the same ρ_x had a bit of difference. We chose **PI-6** and **PII-6** as examples. The optical properties of **PI-6** were extraordinary. The color of the texture changed from Grandjean orange/yellow to duck blue and remained it until it was in an isotropic state. When the sample was cooling, the duck blue color existed so far. **PII-6** exhibited a Grandjean orange/green texture, and the green color gradually increased. The long-length carbochain hindered the formation of a cholesteric helical pitch, which was due to the sterically hindered length of the carbochain, although a short-length carbochain was favorable for the formation of a cholesteric helical pitch. That is, a proper chiral concentration with a nematic LC brought on a typical cholesteric phase just as we expected.

CONCLUSIONS

In this study, two series of new side-chain cholesteric LCEs were synthesized by the reaction of nematic monomers **M**₁ and **M**₂ with the same chiral crosslinking agent, **M**₃, separately. The properties of the two series of new side-chain cholesteric LCEs were characterized by DSC, TGA, and POM. All of the obtained polymers showed very wide ΔT values and high thermal stabilities. Light chemical crosslinking did not markedly affect the phase behavior of the elastomers, but the inclusion of the chiral crosslinking agent

changed the phase of the polymers from nematic to cholesteric. The elastomers containing less than 15% crosslinking units showed elasticity, reversible phase transition, and Grandjean texture during the heating and cooling cycles. The transmission light of **P**₄–**P**₇ was seen. For **P**₁–**P**₈ of the **PI** and **PII** series, the T_g values first decreased and then increased; the isotropization temperatures and ΔT decreased with increasing ρ_x . Through comparison of the two series, we concluded that the T_g and T_i values of the **PI** series were higher than those of the **PII** series and that polymers **PI** and **PII** had their own special optical properties.

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