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## Liquid Crystals

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## Cholesteric liquid crystal inductive asymmetric polymerisation of thiophene monomers

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The thermotropic properties of cholesteric liquid crystal as a polymerisation medium for the synthesis of chiral polymers from achiral monomers were clarified. The chiral reaction medium was successfully employed to synthesise chiral polymers from thiophenes as achiral monomer. The polythiophenes thus prepared exhibit intense circular dichroism imparted by the physical chiral continuum of the reaction field. The chiral aggregate of the present polymers displays structural chirality, with optical activity derived not from the chirality of the individual main-chain but from the chiral architecture. The chiral polymers do not exhibit a thermotropic cholesteric liquid crystal phase but nematic liquid crystal character due to the release of the chiral architecture upon heating.

**Keywords:** chiral conjugated polymers; liquid crystal polymers; matrix; molecular imprinting

### 1. Introduction

Experiments examining chemical reactions in cholesteric liquid crystal reaction media were first performed several decades ago for the preparation of chiral compounds from achiral materials (1–3). However, even when asymmetric induction was successful, the optical yields of the resultant materials were very low, with the resultant compounds exhibiting only minor optical rotation (4, 5). Furthermore, the reported asymmetric syntheses of low-molecular-weight compounds in cholesteric liquid crystals were not always reproducible, suggesting that the induction of chirality from the cholesteric environment was inefficient, or that the molecular axis of the guest molecule underwent free rotation during reaction (i.e. racemisation) (4). In such cholesterics, the helical twist angle of directors is relatively small, yet the architecture has distinct one-handed helicity.

The polymerisation of achiral monomers in cholesterics has been investigated by the present authors in an attempt to synthesise chiral conjugated polymers. The properties of the polymerised material are enhanced by the polymer effect. For example, the electrical conductivity of polyacetylene is enhanced by the increase in main-chain length and accompanying shift of the  $\pi-\pi^*$  transition to longer wavelengths (lower energy). It is also possible to enhance the optical activity of the polymer by the polymer effect.

In the present study, following from the successful synthesis of optically active poly(phenylene-*co*-thiophene) from an achiral monomer in a cholesteric

liquid crystal medium (6), the thermotropic behaviour of the liquid-crystalline chiral reaction medium was investigated, and optically active polythiophenes were synthesised by polycondensation in a cholesteric reaction field.

### 2. Experimental

All experiments were performed under an argon atmosphere using Schlenk/vacuum line techniques. Tetrahydrofuran (THF), ethanol, acetone and ether were distilled prior to use. High-purity chloroform (Wako) was used without purification for optical measurements of polymers.  $^1\text{H}$  NMR spectra were measured in  $\text{CDCl}_3$  using a Bruker AV-600 FT-NMR spectrometer or JASCO 270 MHz EX-270 spectrometer. Chemical shifts were recorded in parts per million downfield from tetramethylsilane (TMS) as an internal standard. IR spectra were measured using a JASCO FT-IR 550 spectrometer by the KBr method. Optical absorption spectra were measured at room temperature using a HITACHI U-2000 spectrometer with a quartz cell. Circular dichroism (CD) spectra were obtained using a JASCO J-720 spectrometer. Phase-transition temperatures were determined using a Seiko EXTRA 6000 differential scanning calorimeter at a constant heating/cooling rate of  $10^\circ\text{C min}^{-1}$ . Texture observations were made using a Nikon ECLIPS LV 100 optical microscope equipped with a Linkam TM 600PM heating and cooling stage. Temperature calibration of the heating stage was carried out by differential scanning

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calorimetry (DSC). The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Shodex A-80M column, and Polymer Laboratories PL-gel 5  $\mu$ m MIXED-D column, and a JASCO HPLC 870-UV detector with THF as a solvent. The instrument was calibrated using a polystyrene standard.

Compounds (+)-**3**, (-)-**3**, (+)-**4** and (-)-**4** were synthesised by the previously reported method (6). The synthetic route and molecular structure of the compounds considered for use as cholesteric reaction media in this study are shown in Scheme 1.

#### Synthesis of 2,5-dibromothiophene-3-carboxylic acid undecyl ester (**1**)

A solution of azodicarboxylic acid diisopropyl ester (DIAD, in 40% toluene, 2.8 g, 5.52 mmol) was very slowly added to a solution of 2,5-dibromothiophene-3-carboxylic acid (1.3 g, 4.55 mmol), triphenyl phosphine (1.45 g, 5.52 mmol) and 1-undecanol (0.86 g, 5.05 mmol) in THF (10 ml) under an argon atmosphere using a pressure-equalised dropping funnel. The mix solution was stirred at room temperature for 24 h, after which the THF in the mixture was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane/*n*-hexane=1/1) to afford 1.86 g of the desired material (**1**). Yield=92.8%.  $^1\text{H NMR}$  (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.88

(t, 3 H,  $J=6.6$  Hz,  $-\text{CH}_2\text{CH}_3$ ), 1.27 (m, 16 H,  $-(\text{CH}_2)_8-$ ), 1.77 (quint, 2 H,  $J=7.7$  Hz,  $-\text{COOCH}_2\text{CH}_2-$ ), 4.33 (t, 3H,  $J=6.8$  Hz,  $-\text{COOCH}_2-$ ), 7.43 (d, 2H,  $J=6.3$  Hz, *phH*). Elemental analysis: calculated for  $\text{C}_{16}\text{H}_{24}\text{Br}_2\text{O}_2\text{S}$ , C 43.65, H 5.49; found, C 43.86, H 5.47%.

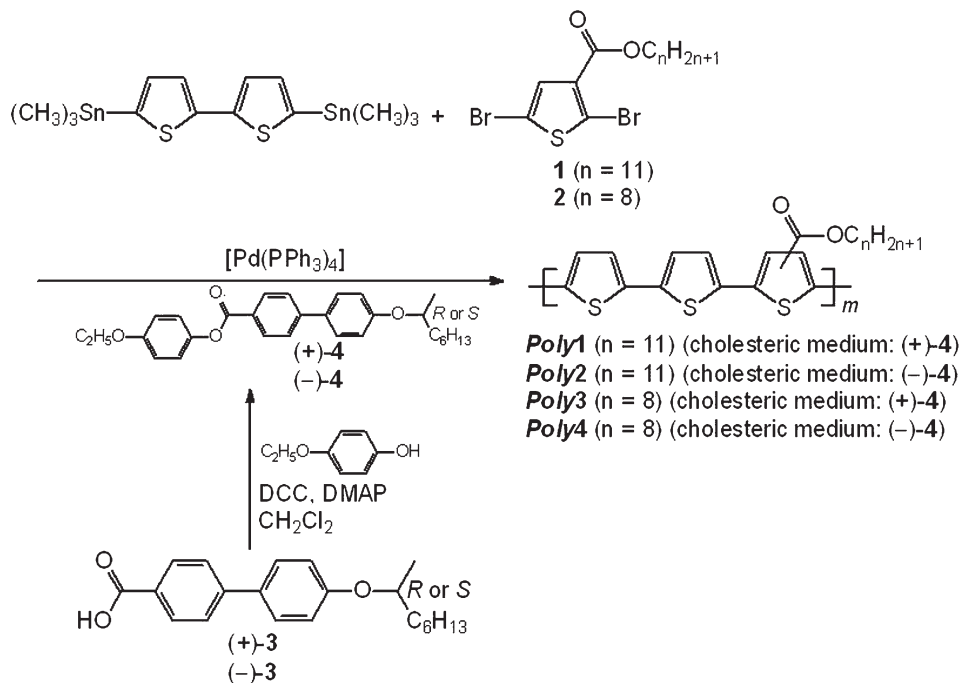
#### Synthesis of 2,5-dibromothiophene-3-carboxylic acid octyl ester (**2**)

This compound was prepared by a similar method to that described for compound **1**. Quantities used were 2,5-dibromothiophene-3-carboxylic acid (1.43 g, 5 mmol), triphenylphosphine (1.31 g, 5 mmol), octanol (0.65 g, 5 mmol) and DIAD (40% in toluene, 2.53 g, 5 mmol). Yield 67% (1.47 g).  $^1\text{H NMR}$  (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.88 (t, 3 H,  $J=4.8$  Hz,  $-\text{CH}_2\text{CH}_3$ ), 1.28 (m, 10 H,  $-(\text{CH}_2)_5-$ ), 1.77 (quint, 2 H,  $J=7.8$  Hz,  $-\text{COOCH}_2\text{CH}_2-$ ), 4.33 (t, 3H,  $J=6.6$  Hz,  $-\text{COOCH}_2-$ ), 7.44 (d, 2H,  $J=6.1$  Hz, *phH*). Elemental analysis: calculated for  $\text{C}_{13}\text{H}_{18}\text{Br}_2\text{O}_2\text{S}$ , C 39.22, H 4.56; found, C 39.21, H 4.36%.

### 3. Results and discussion

#### Liquid crystalline properties of cholesteric medium

The DSC curves for (+)-**3**, a cholesteric LC with a  $-\text{COOH}$  moiety as a precursor of compounds **4**, are shown in Figure 1. The compound exhibits phase



Scheme 1. Synthesis of (+)-**4** and (-)-**4** and polymerisation of thiophene monomers in cholesteric media [DCC=1,3-dicyclohexylcarbodiimide; DMAP=4-(dimethylamino)pyridine].

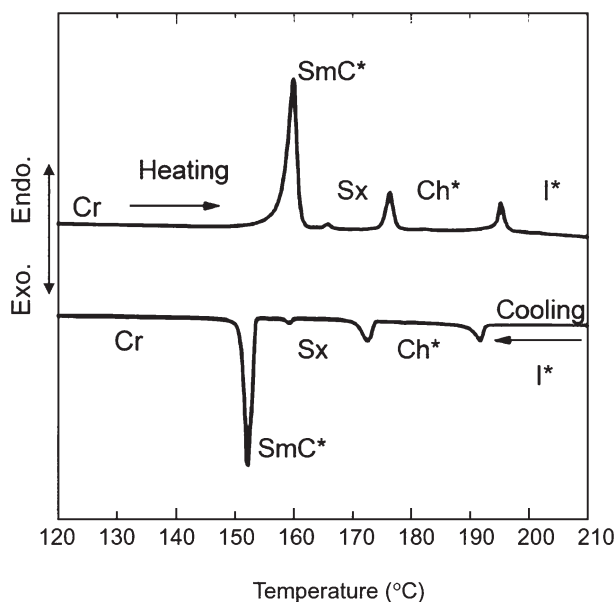


Figure 1. DSC results for (+)-3.

transitions with the phase sequence Cr 160 (152) S<sub>x</sub> 166 (159) SmC\* 176 (173) Ch\* 195 (192) I\*. A sanded texture was observed at 172°C upon heating, and a fan-shaped texture typical of the cholesteric phase was clearly observed at 190°C.

The phase transition behaviour of (+)-4 and (-)-4, the cholesteric medium employed for polymerisation, was similarly determined by DSC and polarising optical microscopy (POM), yielding phases Cr 97 (72) Ch\* 135 (133) BP (134) I\* (6). The DSC curves for (+)-4 are shown in Figure 2. Both compounds exhibit the platelet texture of the blue phase and the fan-shaped texture of the cholesteric phase under POM. No clear transition point was observed for the blue phase (a frustrated mesophase) in DSC measurements.

### Miscibility test

Cholesteryl oleyl carbonate with an anticlockwise helical architecture was employed as a standard cholesteric for determining the helical direction of (+)-4 and (-)-4 through miscibility tests. No boundary was observed between the (+)-4 region and the cholesteryl oleyl carbonate region on a glass cell at 90°C. As shown in Figure 3, however, a distinct contact boundary with the Schlieren texture of the nematic phase was observed by POM between cholesteryl oleyl carbonate and (-)-4. As compounds with opposing helical direction will produce an interface of reduced helicity when in contact (7), these results confirm that (+)-4 has an anticlockwise helical molecular architecture, whereas (-)-4 has a clockwise architecture in the temperature range of the cholesteric LC phase. These results are summarised in Table 1.

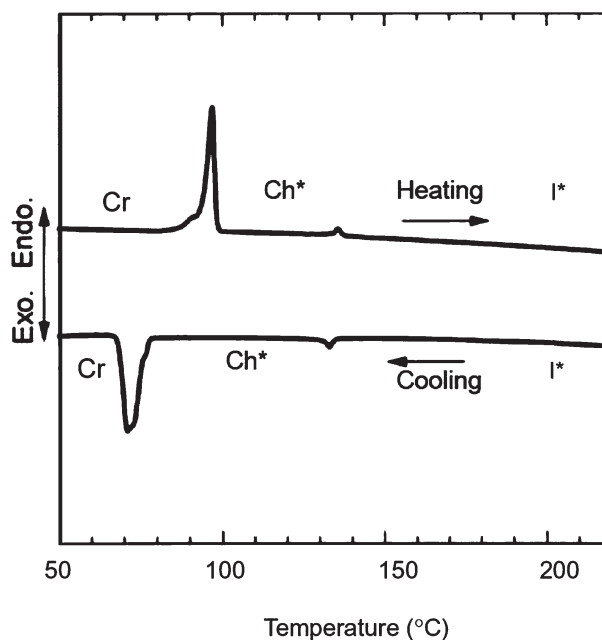


Figure 2. DSC results for (+)-4.

### Polymerisation in cholesteric medium

To maintain the cholesteric LC phase during the polymerisation reaction, the monomers and catalyst must be soluble in the cholesteric medium, the stirring speed should be maintained as low as possible in order to prevent destruction of the helical structure and the reaction temperature must be set appropriately. In the present study, chiral polymers were prepared by the polycondensation of 5-trimethylstannyl-2,2'-bithiophene (8) with 2,5-dibromothiophene-3-carboxylic acid undecyl ester

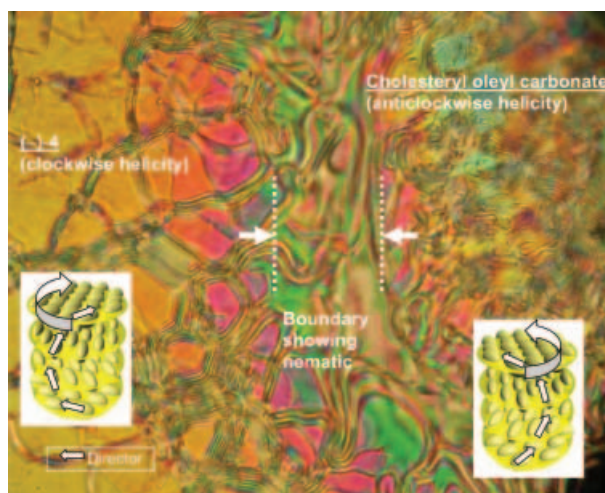
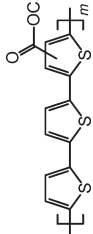
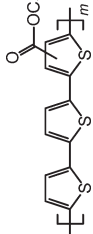
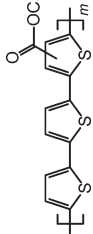
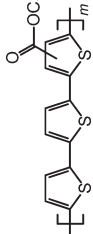


Figure 3. Miscibility test for determination of helical direction of (-)-4 at 90°C. POM images of (-)-4 and cholesteryl oleyl carbonate are also shown along with a schematic illustrating molecular ordering.

Table 1. Polymerisation results.

	Molecular structure	Helicity of cholesteric medium <sup>a</sup>	Transition moment direction of chromophore <sup>b</sup>	$M_n$ (g mol <sup>-1</sup> ) <sup>c</sup>	$M_w$ (g mol <sup>-1</sup> ) <sup>c</sup>	MWD
<i>poly1</i>		Anticlockwise [(+)-4] Clockwise [(-)-4]	Anticlockwise Clockwise	4200 3800	5200 5200	1.23 1.37
<i>poly2</i>		Anticlockwise [(+)-4] Clockwise [(-)-4]	Anticlockwise Clockwise	2650 2200	3600 3700	1.35 1.68
<i>poly3</i>		Anticlockwise [(+)-4] Clockwise [(-)-4]	Anticlockwise Clockwise			
<i>poly4</i>		Anticlockwise [(+)-4] Clockwise [(-)-4]	Anticlockwise Clockwise			

<sup>a</sup>Cholesteric medium used for polymerisation. Helicity was determined with the miscibility test. <sup>b</sup>Determined with CD spectroscopy. <sup>c</sup>Relative to polystyrene standard.

in cholesteric solvents (+)-**4** (to yield *poly1*) and (-)-**4** (*poly2*). The reaction was performed in a small Schlenk flask ( $\phi=1.2$  cm) under argon flow at a temperature of 93°C maintained by placing the flask in a heated and vigorously stirred silicone oil bath. The temperature was chosen such that the cholesteric mixture would be in the liquid crystalline state throughout synthesis. The molar ratio of cholesterics to monomers was set at 5:1 to ensure that the helical structure was not destroyed by the excessive addition of monomer (two monomers: 0.1 mmol each; cholesteric solvent: 0.5 g, 0.11 mmol). The achiral monomers were added to the medium after visual confirmation of the selective reflection of light from the cholesterics. After further confirmation of the selective reflection of this mixture, the Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (1.6 mg) was added under continuous stirring with a 1 cm magnetic stirring bar at 75 min<sup>-1</sup>. The selective reflection of light was visually confirmed after 24 h of reaction, indicating that the mixture maintained the cholesteric phase. The oily streak texture of the cholesteric phase was also confirmed by POM at all stages of the reaction. Similar reactions were performed using 2,5-dibromothiophene-3-carboxylic acid octyl ester to afford *poly3* and *poly4*. DSC curves for the cholesteric LC reaction mixture are shown in Figure 4.

The transition temperature of pure (+)-**4** changes upon addition of the monomer and catalyst. The Cr–Ch\* transition temperature decreased with polymerisation, whereas the Ch\*–I\* transition temperature increased. This can be attributed to the effect of impurities in the cholesteric

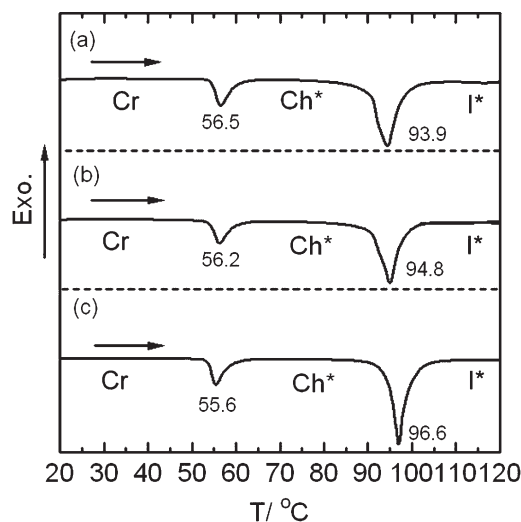


Figure 4. DSC curves of cholesteric solutions on heating. (a) Cholesteric solution before addition of polymerisation catalyst (Pd(PPh<sub>3</sub>)<sub>4</sub>). (b, c) Cholesteric electrolyte after addition of catalyst and reaction for (b) 5 h and (c) 24 h.



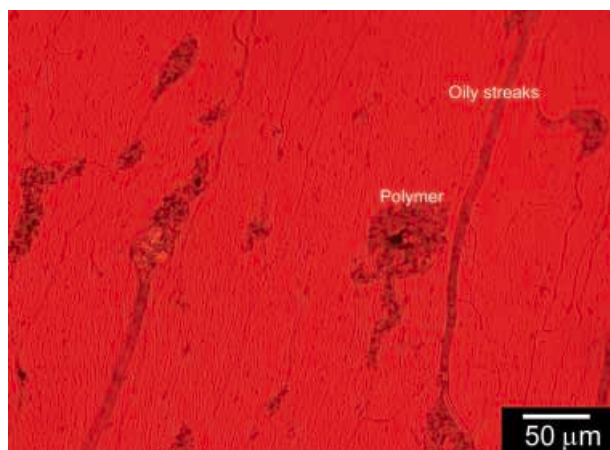


Figure 5. POM image of cholesteric electrolyte during polymerisation at 93°C.

LC, which expand the LC temperature range. Figure 5 shows a POM image of the reaction mixture at 93°C. Polymer fractions can be observed as an insoluble bulk in the cholesteric medium. The bulk was afforded during polymerisation due to the insolubility of the higher-molecular-weight fractions in this reaction system. The polymer bulk is surrounded by the oily streak texture of the cholesteric solvent, and the reaction mixture is red in colour due to the  $\pi-\pi^*$  electronic transition of the main-chain of the oligomer dissolved in the cholesteric mixture.

After cooling naturally to room temperature, a small amount of  $\text{CHCl}_3$  was added to the reaction mixture in preparation for purification. As the cholesteric LC is not soluble in methanol, the polymer was purified in this study using acetone, in which the cholesterics are soluble while the polymer is not. The mixture was poured into a large volume of acetone and washed for ca. 4 h to remove the cholesteric compound and low-molecular-weight fractions of the product. The acetone was then decanted off, and the crude product was washed in a large volume of methanol. The insoluble fraction was collected by decanting off the methanol to afford the desired polymer. The polythiophenes **poly1** (22 mg) and **poly2** (21 mg) were obtained in 50% yield. The polymerisation of thiophenes in the blue phase could not be achieved due to the instability of the blue phase.

The chemical structures of the products synthesised in this study were confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR absorption spectroscopy. The molecular weights were evaluated by GPC with THF eluent relative to a polystyrene standard. The number-average molecular weights ( $M_n$ ) of **poly1** and **poly2** were  $4200 \text{ g mol}^{-1}$  and  $3800 \text{ g mol}^{-1}$ , respectively, and the weight-averaged molecular

weights ( $M_w$ ) were  $5200 \text{ g mol}^{-1}$  in both cases. The polymers in THF solution were separated by filtration through a  $0.1 \mu\text{m}$  membrane filter prior to GPC as the molecular weights of insoluble materials cannot be estimated by GPC. The molecular weights of the polymers determined by GPC thus represent the THF-soluble fraction of the polymer product and are somewhat lower than expected. The insoluble fraction may consist of high-molecular-weight chains or large aggregates.

The long flexible alkyl side-chain has good affinity with the cholesteric medium, and improves solubility in the cholesterics. The solubility is related to the molecular weight of the polymer, as poor solubility results in precipitation of the polymer in the polymerisation solvent during the reaction before sufficient growth of the main-chain. The molecular weights of **poly1** and **poly2** are therefore higher than those for **poly3** and **poly4** (see Table 1).

#### Optical absorption and CD spectra

UV/visible optical absorption spectroscopy measurements of **poly1** and **poly2** in  $\text{CHCl}_3$  solution revealed absorption maxima ( $\lambda_{\text{max}}$ ) at 476 nm (**poly1**) and 473 nm (**poly2**). Cast films of these polymers exhibit an absorption maximum at 518 nm, attributable to in-plane alignment in the cast film (9). Cast films of **poly3** and **poly4** bearing short alkyl chains ( $\text{C}=8$ ) display a  $\lambda_{\text{max}}$  of 522 nm. The longest peak wavelength of the present polymers is greater than that for chiral poly(thiophene-*co*-phenylene) ( $\lambda_{\text{max}}=436 \text{ nm}$ ) prepared in cholesterics, implying that introduction of the phenylene ring in the monomer repeat unit reduces coplanarity.

CD measurements of the polymers reveal complementary mirror-image Cotton effects, as shown in Figure 6. The observation of Cotton effects suggests that the polymers are inherently chiral, despite the absence of asymmetric carbon in the molecular structure.

The cholesteric medium, having a macroscopic chiral architecture, thus produces chirality in the synthesised polymer (chiral aggregation) during the growth process. The chirality of the polymer originates from the helical structure of the synthesis medium, and is maintained in common organic solvents in the absence of cholesteric compounds.

An increase in reaction temperature is likely to extend the helical periodicity of the cholesteric medium, resulting in polymers with weak CD intensity. Deviation from the temperature range of liquid crystallinity in the polymerisation reaction would also prevent successful synthesis of the desired

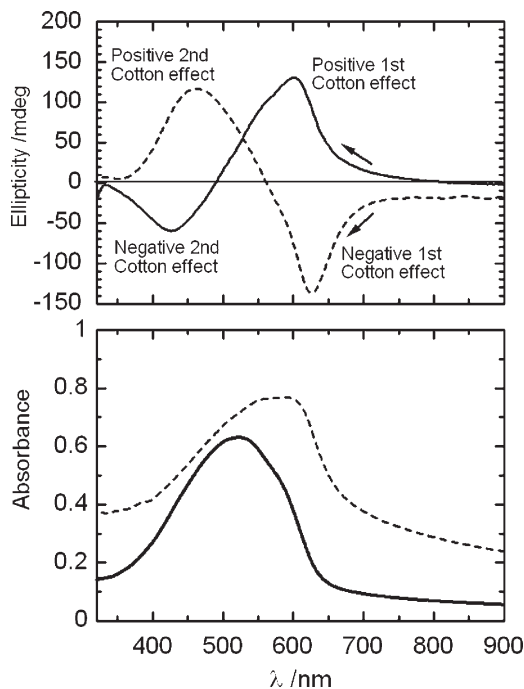


Figure 6. UV/visible absorption spectra and CD spectra for films of *poly3* (dashed line) and *poly4* (solid line) cast on quartz from chloroform solution.

polymers. Polymerisation in the isotropic phase of the cholesteric compound does not produce chiral polymers, while polymerisation in the solid (crystal) state of the cholesteric compound does not allow polymerisation to proceed.

Although the cholesteric medium employed in this study displays liquid crystallinity over a wide temperature range, a reaction temperature of close to 93°C is required to ensure the asymmetric polymerisation. The relationship between the helical pitch of the cholesteric LC and the optical activity of the resultant polymer thus cannot be examined using the present system. It should be noted that the products are quite stable, with no changes in optical absorption or CD intensity over time. This is due to the fact that a  $\pi$ -stacking of the main-chains locks the chiral architecture of the polymer.

Recently, the induction of chirality of achiral polymers in a cholesteric liquid crystal (CLC) was successfully carried out by our group (10). However, the asymmetric polymerisation in the CLC in the present study is a different mechanism from chirality induction by dissolution of the achiral polymers in CLC. In the polymerisation process, the small size achiral monomers with good solubility in the CLC grow to the chiral polymer system with poor solubility in the CLC. The polymer product precipitates in the CLC during the reaction. In other

words, progress of the polymerisation in the CLC gives rise to phase separation between the polymer and the CLC during the reaction. As a result of this reaction, optically active conjugated polymers forming chiral aggregation are produced.

#### Exciton chirality

Defining clockwise chirality of transition moments as positive, the CD signal is split into a positive first (longer wavelength) and negative second (shorter wavelength) Cotton effect, and separation between the two component CD signals of opposite sign is defined as the Davydov split (11, 12). The CD spectra of the present polymers exhibit such a Davydov split pattern (exciton chirality). *Poly3* displays a negative first and positive second Cotton effect (Figure 6), suggesting that the chromophore (main-chain) of *poly3* forms an anticlockwise chiral structure. *Poly4* exhibits the opposite change in Cotton effect sign and thus has clockwise chirality. The CD results suggest that the transition moments of *poly1* and *poly3* prepared in cholesteric medium (+)-4 form an anticlockwise architecture, consistent with the helical direction of the cholesteric medium employed for synthesis. Similarly, the chirality of transition moments of *poly2* and *poly4* corresponds to the helicity of (-)-4. These results, as summarised in Table 1, further support the conclusion that the chirality of the polymers is produced by the transcription of chirality from the cholesteric medium during the polymerisation reaction. The split pattern of the polymer arises from chiral aggregation produced by the chiral continuum of the cholesteric reaction medium in the course of polymerisation. The cholesteric medium is therefore not involved chemically in this asymmetric polymerisation reaction, and the chiral properties of the synthesised polymer can be entirely attributed to the physical structure of the cholesterics. Chiral aggregation of the polymers can be considered to be an “inter-helical structure” between individual main-chains, similar to that of cholesterics. A possible chiral aggregation structure of the polymers, with a stiff and predominantly planar structure of individual main chains, prepared in the cholesteric medium is shown in Figure 7. The helical organisation of the present polymer chains may resemble that of cholesteric liquid crystals.

#### Photoluminescence and circular polarised luminescence

The photoluminescence spectrum of *poly1* in  $\text{CHCl}_3$  solution is shown in Figure 8. An emission



Figure 7. Possible chiral aggregation model of the polymer produced in cholesteric liquid crystal medium.

maximum can be seen at 579 nm, accompanied by a shoulder at 628 nm. The polymer produced an orange emission.

The circularly polarised luminescence (CPL) of the product polymers was analysed with respect to the proportions of left and right components. This technique is widely employed to probe the conformation of an excited state. The radiative transition probabilities for left (L) and right (R) photons in spontaneous emission are unequal in chiral molecules:

$$\Delta I = I_L - I_R. \quad (1)$$

The average luminescence intensity is expressed by

$$I = (I_L + I_R)/2 \quad (2)$$

and the degree of circular polarisation in the emission is defined by

$$g_{em} = 2(I_L - I_R)/(I_L + I_R) = V_{AC}/V_{DC}, \quad (3)$$

where  $g_{em}$ ,  $V_{DC}$  and  $V_{AC}$  are the dissymmetry factor in the emission, the measured fluorescence and CPL, respectively.

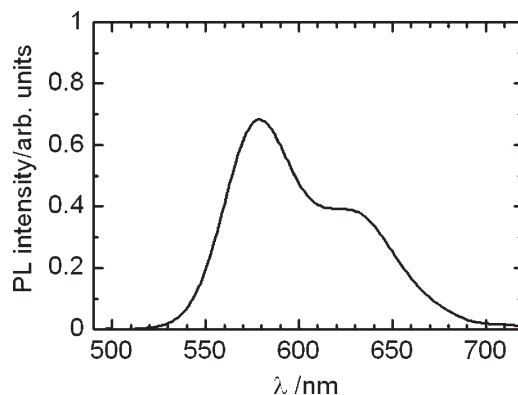


Figure 8. Photoluminescence spectrum for *poly1* in chloroform solution.

Figure 9 shows the CPL for *poly1* and *poly2* in  $\text{CHCl}_3$  solution. This result demonstrates that the polymers produced by the cholesteric medium display circularly polarised emission derived from their chirality.

#### Liquid crystalline properties of polymers

*Poly1* and *poly2* display the Schlieren texture of the nematic phase over a wide temperature range. POM images of *poly1* on first heating (Figures 10 a–10 c) and first cooling (Figures 10 d–10 f) are shown in Figure 10. The polychromic appearance characteristic

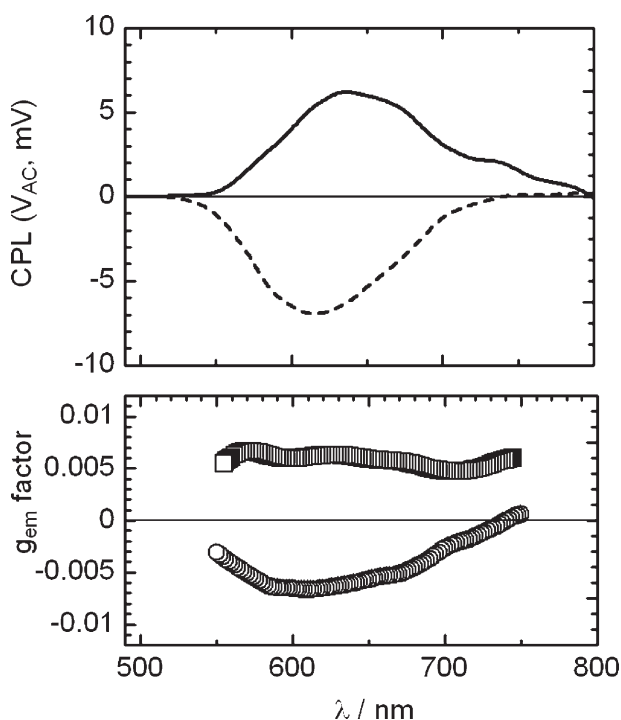


Figure 9. (Top) CPL spectra of *poly1* (solid line) and *poly2* (dashed line). (Bottom)  $g$ -emission factors for *poly1* (squares) and *poly2* (circles).



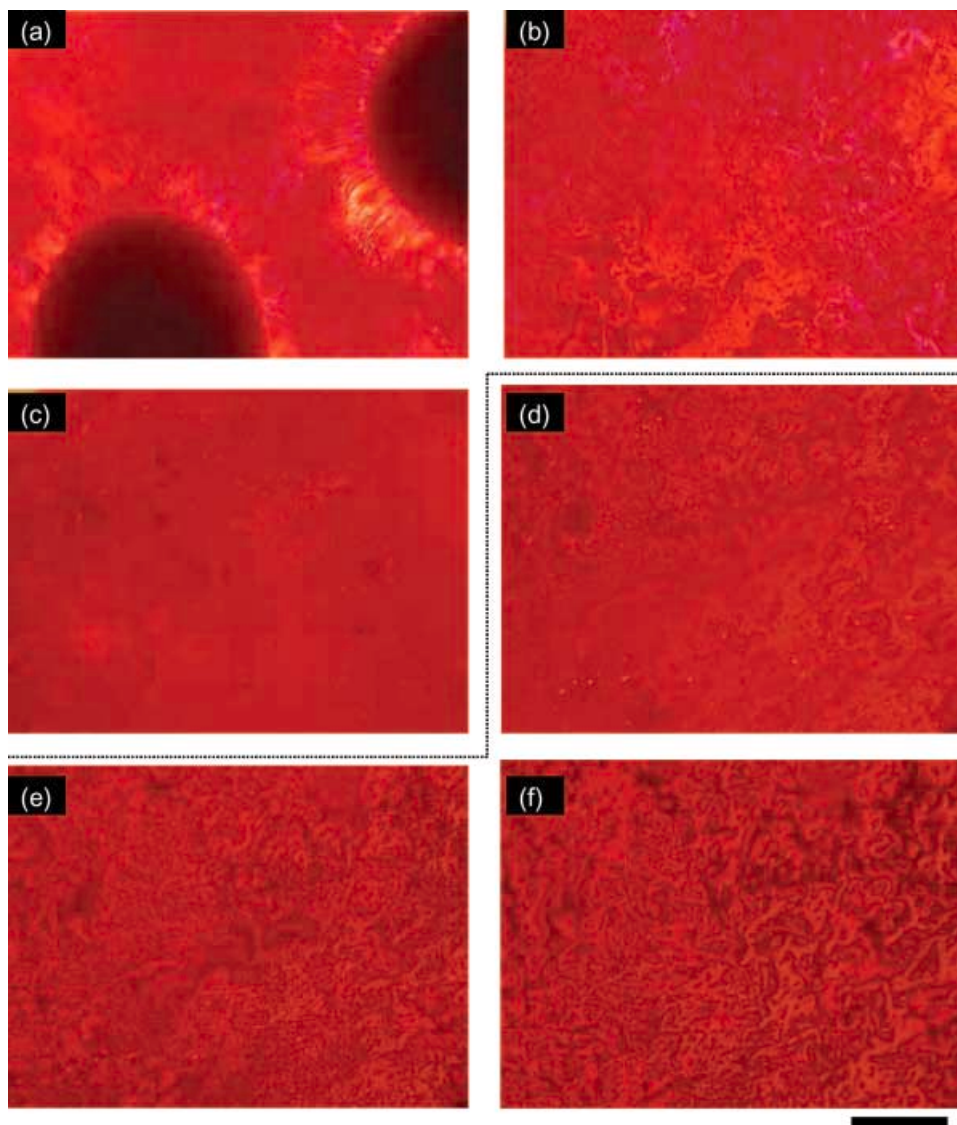


Figure 10. POM images of *poly1* at (a) 102°C, (b) 165°C and (c) 190°C on first heating and at (d) 165°C, (e) 160°C and (f) 150°C on first cooling. Magnification:  $\times 500$ . Scale bar indicates 50  $\mu\text{m}$ .

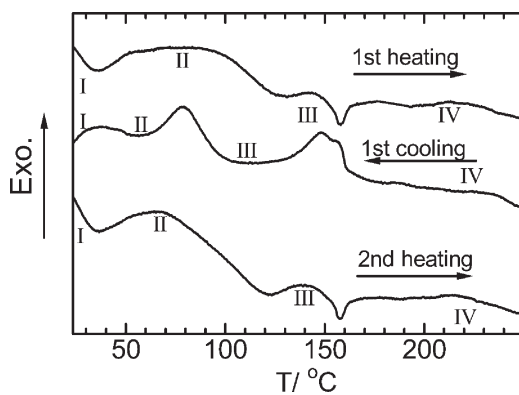


Figure 11. DSC curve for *poly4*.

of LCs was not observed by POM, as the entire region was red due to the  $\pi-\pi^*$  transition of the main-chain. The optical transition of the polymer is thus located at visible wavelengths. The polymer gradually melted (Figure 10 a) and exhibited Schlieren texture (Figure 10 b) in the first heating process. The polymer showed no characteristic texture at the isotropic temperature range (Figure 10 c). Continuously, the first cooling process allowed formation of clear Schlieren texture again (Figure 10 d–10 f).

The DSC curves of *poly4* in first heating, first cooling and second heating cycles are shown in Figure 11. The first heating process of *poly4* shows a clear endothermic signal at 36°C due to the glass transition. Schlieren texture was observed at the

Table 2. Transition temperatures of the polymers.

Polymer		Phase transition <sup>a</sup> /°C			
		I <sup>b</sup>	II <sup>b</sup>	III <sup>b</sup>	IV <sup>b</sup>
		g	M <sub>x</sub>	N	Iso
<i>poly1</i>	1 <sup>st</sup> cooling	·	–	·	·
	2 <sup>nd</sup> heating	·	–	·	·
<i>poly2</i>	1 <sup>st</sup> cooling	·	–	·	·
	2 <sup>nd</sup> heating	·	–	·	·
<i>poly3</i>	1 <sup>st</sup> cooling	·	79	·	·
	2 <sup>nd</sup> heating	·	80	·	·
<i>poly4</i>	1 <sup>st</sup> cooling	·	35	·	·
	2 <sup>nd</sup> heating	·	36	·	·

<sup>a</sup>Scan rate: 10°C min<sup>-1</sup>. g=glassy state, M<sub>x</sub>=unknown phase, N=nematic, Iso=isotropic. <sup>b</sup>Temperature region in the DSC curves (see Figure 11). <sup>c</sup>Transition temperature is unclear.

temperature range of III (region III) in Figure 11. Although the DSC results of *poly4* implied a phase transition between the region II and III (first heating process: 128°C, first cooling process: 79°C, and second heating process: 122°C), no change in the optical texture were observed. These results suggest that the region I in Figure 11 is the glassy state (g), region II is unknown mesophase (M<sub>x</sub>), region III a nematic phase (N) and region IV the isotropic phase. The results are summarised in Table 2.

*Poly1* and *poly2* display no signals related to the unknown phase (M<sub>x</sub>), which was observable for *poly3* and *poly4*. This may be due to the fact that *poly1* and *poly2* bearing flexible long alkyl side-chain (dodecyl group, C=12) have different crystallinity from that of *poly3* and *poly4* (C=8).

Note that *poly3* shows phase transitions at high temperature range compared to *poly1*, *poly2*, and *poly4*. This may be due to the fact that *poly3* has tight aggregation or high molecular weight (13).

These results indicate that although the polymers exhibit chiroptical properties in organic solvent, the polymers do not display thermotropic cholesteric LC character. This is considered to be attributable to the heating process, which releases the chiral aggregation of the polymer (i.e. racemisation), resulting in a nematic state with no structural chirality. Hence, the chiral architecture of the polymers can be released in the first heating process at the temperature range between glassy state (no fluidity) and LC phase having fluidity.

#### 4. Conclusion

The thermotropic characteristics of three-ring cholesteric liquid crystalline compounds as a polymerisation solvent were clarified. The cholesteric solvent was used successfully to synthesise polymers with

chiroptical properties from achiral monomers. Although the monomers and polymer main-chain are achiral, the polymer aggregate produced in the cholesteric LC solvent during the course of polymerisation is optically active. The chiral aggregate of the present polymers exhibits structural chirality. The optical activity of the polymers therefore appears to be derived from cholesteric LC-like three-dimensional chiral architecture.

The present results demonstrate that cholesteric liquid crystal inductive asymmetric reaction is a reliable synthetic route for the polycondensation of thiophenes as a new type of asymmetric polymerisation.

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