Polymer Communication

Magneto-optically active polythiophene derivatives bearing a stable radical group from achiral monomers by polycondensation in cholesteric liquid crystal

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ARTICLE INFO

ABSTRACT

Chiral π-conjugated polymers bearing a stable radical group are successfully prepared by chiral inductive asymmetric polymerization using a cholesteric liquid crystal medium. The polymers thus synthesized form "structural chirality", with the structure of the polymer being analogous to that of the one-handed helical form of the cholesteric liquid crystal. Chirality and magnetic properties of the present polymers were elucidated.

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1. Introduction

The chemistry of polyradicals has attracted considerable interest in many fields of nano-science and industry. Some of the key advancements include the synthesis of polyradicals with strong through-bond interactions among multiple sites in the molecule [1], and the synthesis and magnetic force microscopy (MFM) imaging of purely organic high-spin polyradicals [2]. The magnetic behavior of microcyclic two-strand polyradicals on calix[4]arene rings has also been clarified [3], and a non-conjugated polymer bearing radical groups has been successfully prepared as an electrode for polymer batteries [4]. Plastic electronics, typically involving the synthesis and application of electrical conducting polymers [5], has now extended to the use of magnetically active polymers, for which organic polyradicals are promising magnetically active substituents. Multiple functionalities, such as magnetism and chirality, can be achieved through the introduction of both a radical moiety and an optically active substituent into a π-conjugated polymer. Many helical conjugated polymers have been successfully prepared by inserting an asymmetric carbon in the side-chain [6]. However, the preparation of such conjugated polymers bearing stable radical groups generally involves a multi-step procedure, and the introduction of a chiral group into the polyradical requires further synthetic steps. The relatively large number of steps required limits the total synthetic yield for the desired magnetically active chiral polymer.

As a means of realizing multi-functional polymers in fewer steps, the use of a chiral liquid crystal (LC) medium has been investigated for the synthesis of chiral conjugated polymers from achiral monomers without a chiral initiator [7]. In the present research, an asymmetric polymerization method using a cholesteric LC (CLC) medium is employed for the synthesis of chiral polymers bearing stable radical groups from achiral monomers. Although the polymers synthesized in the CLC do not bear asymmetric carbon atoms, the polymers display consistent chirality due to the formation of chiral aggregates under the influence of the CLC medium. The chirality is maintained by the molecular construction of the chiral aggregate.

The electrochemical polymerization of achiral monomers in cholesteric LC electrolyte to produce conducting polymers with chiroptical properties has been reported previously [8]. The molecular imprinting of chirality during the electrochemical polymerization process in cholesteric LC imparts the properties of consistent circular dichroism (CD) and optical rotation in the resultant electroactive polymers, and the CD character can be altered by appropriate electrochemical doping and dedoping.

In the present study, polythiophene derivatives bearing a stable radical precursor are synthesized using a cholesteric liquid crystal reaction solvent (medium). Chiral π-conjugated radical polymers are then obtained by generating phenoxy radicals.
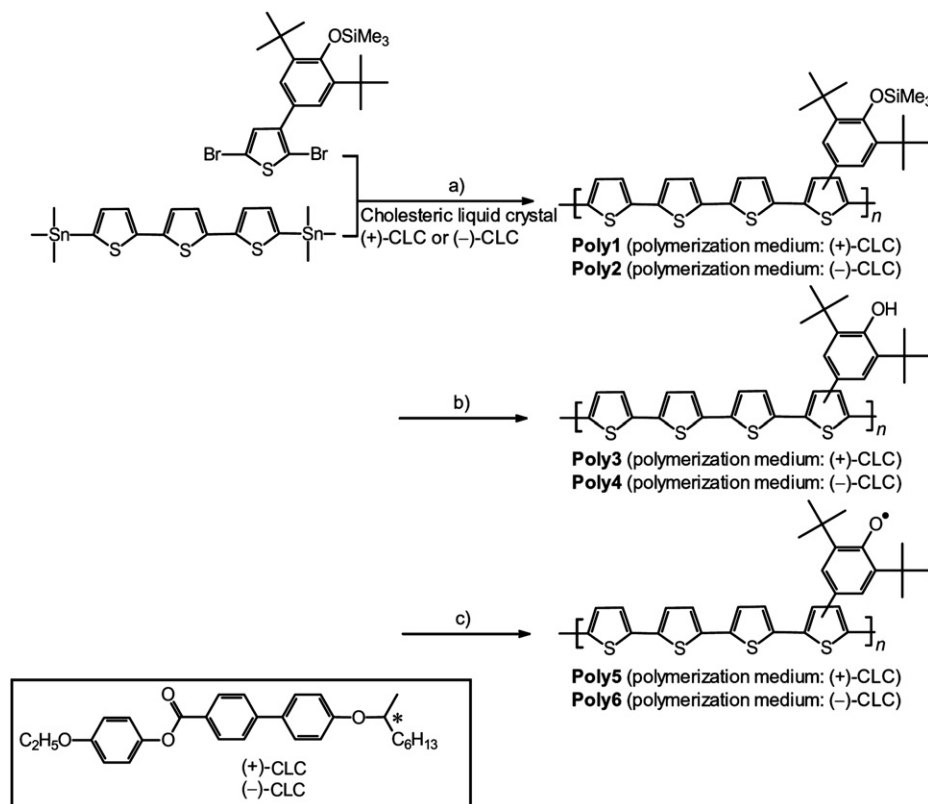
2. Experimental

2.1. Polymerization in cholesteric liquid crystal

Polymerization in a cholesteric medium was carried out by placing 0.5 g of (+)-CLC or (−)-CLC (Scheme 1) in a small test-tube-type

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Scheme 1. Synthetic routes of optically active polyradicals. (a) [Pd(PPh$_3$)$_4$], (+)-CLC or (−)-CLC, SiMe$_3$ = trimethylsilyl. (b) KOH, THF, H$_2$O. (c) PbO$_2$, toluene, * – stereogenic center.

Schlenk flask under an argon atmosphere at 93 °C. The CLC was prepared by the method reported in the literature [7]. Into the medium was dissolved 5,5″-bistrimethylstannanyl[2,2′:5′,2″]-terthiophene (0.05 g, 0.13 mmol) [9], followed by the addition of 2,5-di-*tert*-butyl-4-(2,5-dibromo-thiophen-3-yl)phenoxytrimethyl-silane [10,11] (0.05 g, 0.1 mmol) accompanied by stirring at exactly 80 rpm for 30 min. A catalytic amount of [Pd(PPh$_3$)$_4$] (1.5 mg) was then added to the mixture to initiate polycondensation under constant stirring at exactly 80 rpm to preserve the cholesteric liquid crystallinity. The temperature was maintained at 93 °C throughout the polymerization reaction. The cholesteric liquid crystallinity of the medium was monitored through the reaction by observing the appearance of the medium, which appears rainbow-like when in the desired state. The medium was thus confirmed to retain its cholesteric liquid crystallinity even after 24 h of reaction under the present conditions.

The appearance of the reaction mixture changed from pearl-like before the reaction (Fig. 1(A)) to iridescent dark red after the reaction (B). Polarizing optical microscopic (POM) images of the reaction mixture are shown in Fig. 1(C and D). The polymer fractions are observable as an insoluble dark-red bulk in the cholesteric medium. The bulk, produced during polymerization due to the insolubility of the higher molecular weight fractions in this reaction system, is surrounded by the oily streak texture of the CLC medium. After reacting for 24 h, the mixture was allowed to cool to room temperature, then dissolved in a minimal amount of tetrahydrofuran (THF) and poured into a large amount of acetone to dissolve and remove the CLC medium and the low molecular weight fraction. The product, which was insoluble in acetone, was further washed in a large excess of acetone and then methanol to afford a dark-red solid consisting of **poly1** and **poly2** (Scheme 1) that was soluble in both THF and chloroform.

2.2. Deprotection and oxidation

Trimethylsilyl, added as a protectant for –OH in the side-chain, was removed by suspending the solid (0.1 g each of **poly1** and **poly2**) in a 1:1 water/ethanol solution (5 mL) containing KOH (0.2 mg) for 2 h. The polymer was finally collected by filtration to afford **poly3** (from **poly1**), and **poly4** (from **poly2**) having substituent OH groups (Scheme 1). The products were confirmed to display a sharp infrared absorption band at 3622 cm^{-1} and a broad band at 3420 cm^{-1} assignable to OH vibration, confirming conversion from trimethylsilyl to hydroxyl.

The OH group was subsequently oxidized by suspension of the polymers (5.5 mg each of **poly3** and **poly4**) in toluene (5 mL) containing fresh PbO$_2$ (50 mg) for 10 min under argon flow. The solution was then freeze-dried under reduced pressure to yield **poly5** and **poly6** as chiral polyradicals. The gel permeation chromatography (GPC) results obtained for polymers filtered from THF solution through a 0.2 μm micro-filter are summarized in Table 1. The number-average molecular weights of **poly5** and **poly6** were 8780 and 8120, respectively, with a molecular weight distribution of ca. 1.8.
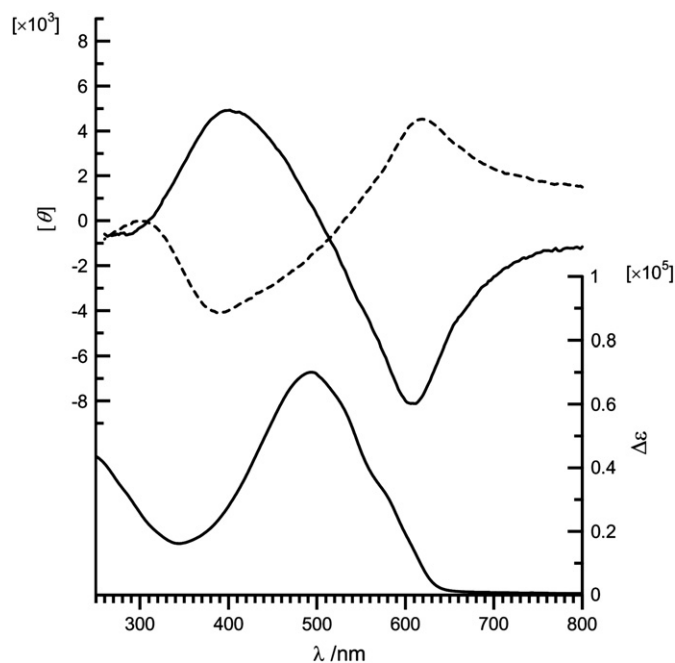
3. Results and discussion

3.1. Ultraviolet–visible absorption spectroscopy

Fig. 2 shows the ultraviolet–visible (UV–vis) absorption spectra of the polymers in chloroform solution. Both **poly5** and **poly6** exhibit a peak wavelength (λ_{max}) of 495 nm. This peak was also partly formed before oxidation of **poly1**. It has been reported that 2,6-di-*tert*-butyl-4-alkyl-phenoxy radicals display a broad absorption band at around 400 nm irrespective of the substituted alkyl group [11], whereas 2,6-di-*tert*-butyl-4-aryl-phenoxy radicals exhibit an
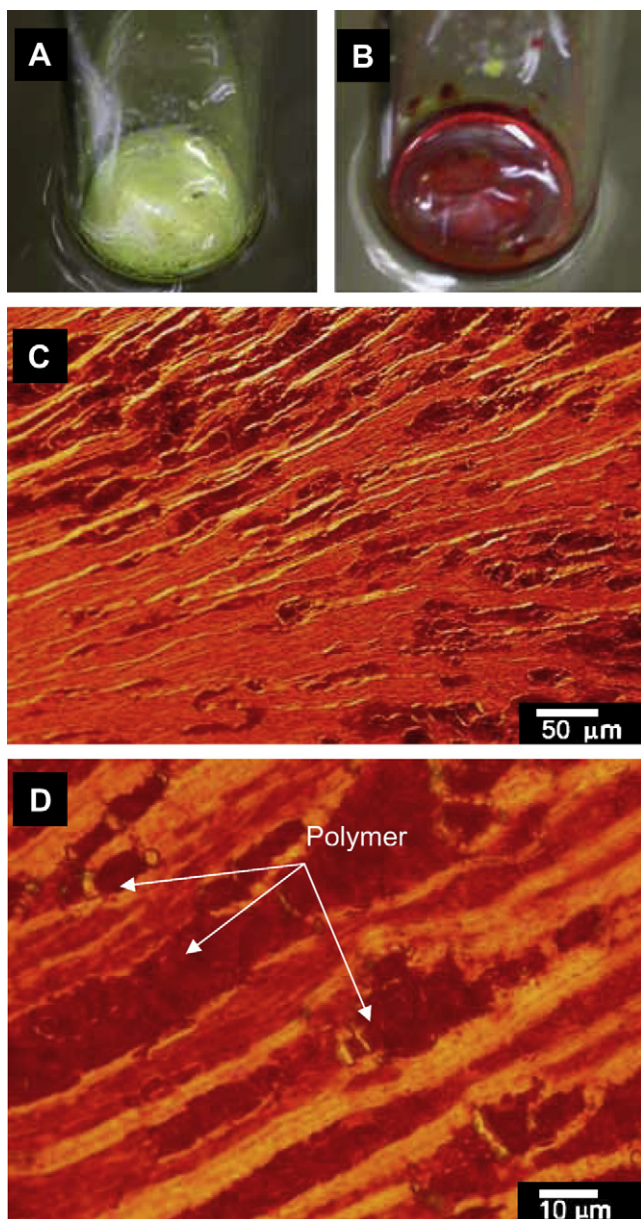
Fig. 1. Photographs of (A) cholesteric solvent containing monomers and (B) reaction mixture 24 h after addition of catalyst, and (C and D) POM images of reaction at magnifications of 100× (C) and 500× (D).

Fig. 2. CD (top) and UV–vis (lower) spectra for **poly5** (solid line) and **poly6** (dashed line) in chloroform solution.

absorption maximum at around 500 nm [12], and polyacetylene-bearing 2,6-di-*tert*-butyl-4-phenoxy radicals have an absorption band at 495 nm [13]. The phenoxy radicals substituted onto the main-chain (polythiophene) of **poly5** and **poly6** thus have a clear electronic effect. It should be noted that the absorption band of the phenoxy radical moiety overlaps that of the double bonds of the

conjugated polymer backbone. Although the radical group is essentially unstable, the two neighboring bulky *tert*-butyl groups protect the phenoxy radical site in this polymer, allowing the radicals to remain relatively stable.

3.2. Circular dichroism spectroscopy

A Cotton effect was observed in CD spectroscopy, indicating that the chirality of the polymers was maintained upon oxidation and that the polymers are inherently chiral, despite the absence of asymmetric carbon in the molecular structure (Fig. 2 (top)). The expected mirror-image relationship between **poly5** and **poly6** is not due to the chiral compound employed as a solvent in this case because the Cotton effect of the CLC is only observed at shorter wavelengths (($+$)-CLC, CD (CHCl$_3$), $\lambda_{max}(\Delta\varepsilon) = 308$ ($+0.51$); ($-$)-CLC, CD (CHCl$_3$), $\lambda_{max}(\Delta\varepsilon) = 308$ (-0.49)) [7]. **Poly5** and **poly6** display mirror-image, exciton-coupled, Davydov-split CD at two exciton levels. This splitting was not detected in absorption spectroscopy, indicating an interchain origin for the optical activity [14,15]. These results suggest that the polymer forms a helical interchain organization. Such chiral aggregation of the polymer main-chains, which bears a resemblance to the form of CLC [16], can be regarded as an "inter-helical structure" among individual main-chains, similar to that of cholesterics. **Poly5** displays a negative first and positive second Cotton effect, while **poly6** exhibits a positive first and negative second Cotton effect, indicating that the transition moments of **poly5** and **poly6** are anticlockwise and clockwise,

Table 1
Molecular weights, ESR results, and helicity

	M_n[a]	M_w[b]	MWD[c]	g value[d]	Spin conc[d] (spin/g)	CLC helicity[e]	Polymer helicity[f]
Poly5	4780	8780	1.83	2.0048	3.4×10^{20}	Anticlockwise	Anticlockwise
Poly6	4610	8120	1.76	2.0047	8.5×10^{19}	Clockwise	Clockwise

[a] Number-average molecular weight.
[b] Weight-average molecular weight.
[c] Molecular weight distribution. All determinations are in reference to polystyrene.
[d] g value and spin concentration were evaluated from ESR measurements.
[e] Helicity of CLC reaction solvent employed for polymerization. Helicity was determined by miscibility test using cholesteryl oleyl carbonate.
[f] The helicity of the chromophore of polymer was determined by CD measurements.

respectively [14]. Miscibility tests using cholesteryl oleyl carbonate as a standard cholesteric with anticlockwise helicity confirmed that the cholesteric medium (+)-CLC has an anticlockwise helical structure, while (−)-CLC has a clockwise structure. The CD results for the present polymers are consistent with the helical direction of the cholesteric medium employed for synthesis. These results are summarized in Table 1.

3.3. Electron spin resonance measurements

The electron spin resonance (ESR) of the polymers was measured in chloroform at room temperature (22 °C). The g value of ca. 2.004 indicates the formation of phenoxy radicals, which produce sharp and unimodal signals ($\Delta H_{pp} = 0.4$ mT) suggestive of a locally high spin concentration within the molecules, as observed for benzenetriyl phenoxy radicals [17].

No intra-chain ferromagnetic spin interaction via the π-conjugated skeleton can be expected for the present polymers, which have no intra-chain spin alignment condition for parallel spin alignment of unpaired electrons [18].

It is possible that PbO_2 as an oxidizer might generate radical cations or dications on the polythiophene main-chain. However, the g value of free electrons in the conduction state of doped polythiophene is lower (2.002–2.003) [19]. Furthermore, the electrical conductivities of the polymers are very low prior to vapor doping of iodine (**poly5**, $\sigma < 10^{-9}$ S/cm; **poly6**, $\sigma < 10^{-9}$ S/cm). These results indicate that the ESR measurements detected phenoxy radicals, and that the radicals on the substituents do not function as carriers. The electrical conductivity of the present polymer after vapor doping of iodine is still relatively low (**poly5**, $\sigma = 1.4 \times 10^{-5}$ S/cm; **poly6**, $\sigma = 1.6 \times 10^{-5}$ S/cm) compared to that for other aromatic-type conducting polymers [20]. This may be due to the disturbance of carrier generation on the main-chain by phenoxy radicals.

Time-dependent ESR spectra for **poly6** in chloroform solution are shown in Fig. 3, and the ESR data are summarized in Fig. 4. The ESR signal intensity for the polymer in chloroform solution under ambient air initially increased, then gradually decreased after 2000 min, possibly due to disaggregation in the solution over time [21]. This result suggests that the structural chirality degraded in the solution, and the radicals were gradually decomposed. In chloroform solution, g and ΔH_{pp} were observed in the present study to remain almost constant.

The formation of a macroscopic helical arrangement of spins along the chiral aggregate can be expected to result in
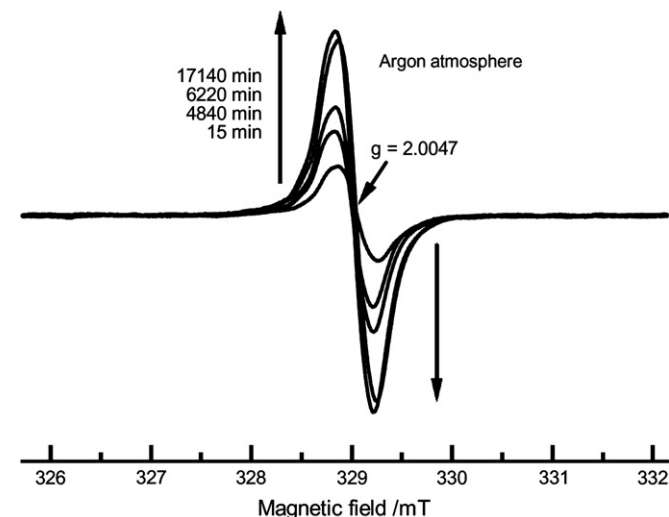

Fig. 4. ESR intensity and g value of **poly6** as a function of time (○, □: ESR data obtained under argon; ●, ■: under ambient air).

diamagnetism [22], which would weaken the ESR signal. However, the release of chiral aggregation (disaggregation) due to dissolution of the polyradicals would enhance the paramagnetic nature and thus strengthen the ESR signal. Under argon, the ESR signal intensity was found to increase with time, then to gradually decrease after 12 days due to decomposition of the radicals. This result appears to indicate that the radicals are stable under argon at room temperature over extended periods, and disaggregation tends to occur in solution. This unexpected phenomenon is thus considered to be satisfactorily explained by helical aggregation and disaggregation in solution.

3.4. Liquid crystalline properties

The precursor polymers (**poly3** and **poly4**) are not soluble in *m*-cresol or *N,N*-dimethylformamide (DMF), a high boiling point solvent, and thus do not display lyotropic liquid crystallinity in these solutions. Although the lyotropic liquid crystallinity of the polymers could not be confirmed, the polymers were confirmed to display thermotropic liquid crystallinity. Fig. 5 shows a POM image of **poly3** at room temperature after gradual cooling from the isotropic state [23]. The polymer exhibits a fine threaded texture reflecting its nematic liquid crystal (NLC) structure. However, the NLC is an achiral LC phase. Thus, although the polymers exhibit
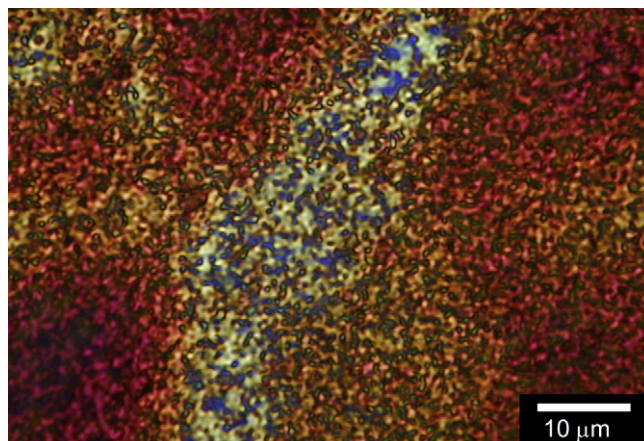

Fig. 3. ESR spectra for **poly6** in chloroform solution under argon.

Fig. 5. POM image of **poly3** at room temperature. Sample was obtained by cooling from mesophase temperatures.

chiroptical properties in organic solvents, the polymer does not display thermotropic cholesteric LC character. This is considered to be due to the heating process, which releases the chiral aggregation of the polymer (i.e., racemization), resulting in a nematic state with no structural chirality.

The film of **poly7** (three thiophene units in the monomer repeat unit; synthesized in (+)-CLC) cast from the chloroform solution displays birefringence, attributable to the enhanced solubility of the polymer by the reduction of thiophene unit number in the monomer repeat unit. The molecular structure of **poly7** and the optical texture of the film cast from chloroform are shown in Figs. 6 and 7. **Poly7** displays lyotropic LC character at high concentrations, achieved by evaporation of chloroform on the glass substrate, and the lyotropic texture is maintained after complete evaporation of chloroform. **Poly7** also displays thermotropic LC character. The optical texture of **poly7** at 120 °C is shown in Fig. 8. The thread-like
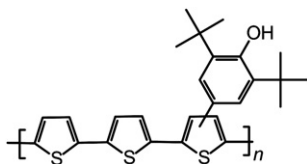

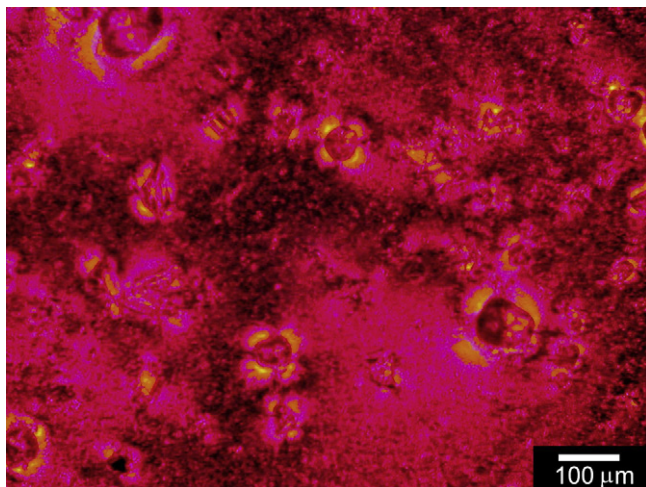**Fig. 6.** Molecular structure of **poly7** prepared in (+)-CLC.

100 μm

Fig. 7. POM image of **poly7** film cast from chloroform.
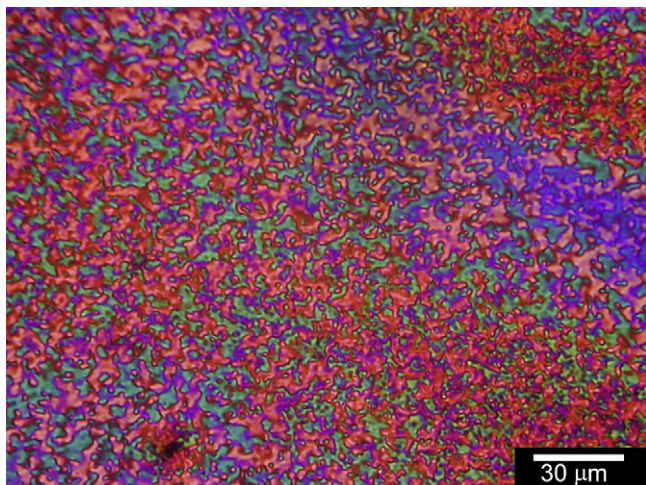

30 μm

Fig. 8. POM image of **poly7** at 120 °C.

texture typical of the nematic phase is clearly apparent. These results suggest that **poly7** has amphotropic LC character [24].

4. Conclusion

Chiral polymers bearing a bulky substituent were successfully prepared by polymerization in a CLC medium. The polymers display complementary mirror-image Cotton effects. The chirality of the polymers is due to chiral aggregation, which occurs during the propagation process in the CLC medium and which is locked by interchain interaction in the π-conjugated system. The chirality is retained even upon oxidation by PbO_2 in toluene to generate spin species. The aggregate form of the polymers is analogous to that of the one-handed helical structure of CLC. The present preparation method may therefore represent a new approach for the synthesis of chiral organic polymers with magnetic properties.

5. Technique and materials

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 the polymer. An EYELA MCS-101 (Tokyo Rika-gaku) low-speed magnetic cell stirrer with digital tachometer was employed for stirring of the cholesteric solution at exactly 80 rpm throughout the polymerization reaction. Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured in chloroform using a Bruker AV-600 or JEOL EX-270 FT-NMR spectrometer. Chemical shifts are represented in parts per million downfield from tetra-methylsilane (TMS) as an internal standard. Infrared spectra were measured using a JASCO FT-IR 550 spectrometer with KBr config-uration. Optical absorption spectra were measured at room tem-perature using a HITACHI U-2000 spectrometer with a quartz cell. CD spectra were obtained using a JASCO J-720 spectrometer. ESR measurements of the samples in chloroform solution were carried out using a JEOL JES TE-200 spectrometer with 100 kHz modula-tion. The sample was charged into a $\phi = 2$ mm quartz tube. Texture observations were performed using a Nikon ECLIPS LV 100 polar-izing microscope equipped with a Linkam TM 600PM heating and cooling stage. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Shodex A-80 M column and a JASCO HPLC 870-UV detector with THF as solvent. The instrument was calibrated using a polystyrene standard. 5,5″-Bistrimethylstannanyl[2,2′:5′,2″]terthiophene, 2,5-di-*tert*-butyl-4-(2,5-dibromo-thiophen-3-yl)phenoxy]trimethylsilane were synthesized by the method reported previously in the literature [9].

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[21] The oxidized solid sample was dissolved in chloroform solution for ESR spectroscopy measurements. This procedure may allow partial disaggregation in chloroform solution.

[22] Although antiferromagnetism for helical magnets is possible, we do not yet confirm it for the polymer prepared in the present study.

[23] During cooling, the polymer LCs transform from mesophase to solid state while maintaining LC texture. The polymer samples show LC optical texture at room temperature after melting and gradual cooling.

[24] Amphotropic LC displays both thermotropic (temperature-dependent) and lyotropic (concentration-dependent) liquid crystallinities.