Cholesteric Liquid Crystal Inductive Asymmetric Polymerization: Synthesis of Chiral Polythiophene Derivatives from Achiral Monomers in a Cholesteric Liquid Crystal

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ABSTRACT: Inductive asymmetric polymerization from achiral monomers is achieved through the use of cholesteric liquid crystal as an asymmetric reaction solvent. The chirality of the polymers, which have no chiral substituent, is considered to derive from the asymmetry produced by the chiral liquid crystal media during polymerization. No chiral molecules reacted chemically with the monomer during polymerization, and the cholesteric liquid crystal acted solely as a physical reaction environment. Polymers without chiral centers exhibit exciton couple-type circular dichroism and circular polarized luminescence. The chirality of the polymer is due to chiral aggregation, which occurs during the propagation process in the cholesteric liquid crystal medium and which is locked by interchain interaction in the π-conjugated system. Heat treatment of the polymer causes disaggregation and loss of chirality. The present results demonstrate cholesteric liquid crystal inductive asymmetric reaction can be performed by polycondensation in π-conjugated systems.

Introduction

Cholesteric solvents were used more than 30 years ago for the preparation of chiral compounds, including sulfoxide enantiomers,[1] a Claisen rearrangement,[2] and decarboxylation of a non-optically active compound.[3] Following a failed attempt at asymmetric synthesis in cholesteric liquid crystal (LC),[4] the pyrolysis of achiral cyclooctyltrimethylammonium hydroxide in cholesteryl benzoate was achieved by Hofmann elimination.[5] In this case, the extent of asymmetric induction was 7%, and the resultant compounds exhibited little optical rotation. These studies on the chemistry of low-molecular-weight compounds were not always reproducible, and it is considered that the processes were affected by poor effectiveness of chirality induction from the cholesteric environment or by free rotation of the molecular axis of the guest molecule during reaction, resulting in racemization.

Generally, it is assumed that if a chiral polymer with no chiral substituent is obtained, dissolution and washing of the polymer would release the chiral conformational order, erasing any optical activity acquired during growth. Accordingly, some contrivances, such as hydrogen bonding, is required for conformational locking of the chiral order of the polymer upon growth.

To date, there have been little report on the use of cholesteric LC as reaction solvent instead of isotropic solvent, such as tetrahydrofuran (THF), in polycondensation of achiral monomers for preparation of chiral π-conjugated polymers having circular polarized luminescence (CPL) property. To perform chemical polymerization in the cholesteric LC state, the cholesteric liquid crystallinity of the solvent must not be broken by any of the monomers or side products, or the catalyst or resulting polymer, all of which must have good affinity with the cholesteric solvent. The temperature range of the reaction requires careful consideration, as the cholesteric LC state is maintained only within a certain temperature range, similar to the case for thermotropic LC, but the temperature of the reaction must also allow polymerization to proceed. The stirring speed in the reaction also requires careful control in order to maintain the chiral liquid crystallinity throughout the reaction. High shear stress can break the helical structure of cholesteric LC, resulting in a nematic phase with no helical structure. The stirring speed and size of the reaction vessel and stirrer bar should therefore be selected carefully. Finally, after polymerization has been completed, the chirality of the polymer must not be broken by subsequent purification and dissolution in organic solvents.

In the present study, a series of the polymers having monothiophene, bithiophene, and terthiophene in monomer repeat unit were synthesized in the cholesteric LC solvent and confirmed their optical activity with circular dichroism (CD) measurements. Loss of the mesophase upon addition of non-LC compounds has prevented extensive trial of polymerization reactions in cholesteric LC materials. Monomers with good affinity for cholesteric LC were identified for combination with a stable cholesteric compound as a reaction solvent. The cholesteric LC compound prepared in this study is suitable for the polycondensation reaction of aromatic compounds and exhibits a cholesteric phase at around 90 °C. The polymers synthesized from achiral monomers exhibit high optical activity, despite the polymers having no chiral substituent. This method is referred to as cholesteric medium inductive asymmetric polymerization and represents a new type of asymmetric polymerization. The polymerization mechanism and origin of chirality of the polymer obtained in this way are discussed in this report.

Results and Discussion

Synthesis of Cholesteric Solvent. A compound (as solvent) exhibiting cholesteric liquid crystallinity at around 80−100 °C was required. A triple-ring cholesteric LC compound was synthesized as the reaction solvent, as multiple-ring LCs generally exhibit liquid crystallinity at higher temperatures (100−200 °C). The synthetic route for the cholesteric LC having three aromatic rings in the mesogen core is shown in Scheme 1.

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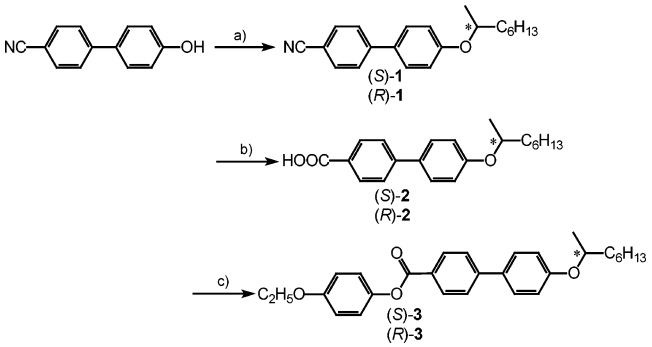
Scheme 1[a]



[a] (a) (*R*)- or (*S*)-octanol, diethylazodicarboxylate (DEAD), triphenylphosphine (TPP), THF; (b) KOH, ethanol, H_2O; (c) 4-ethoxyphenol, 1,3-dicyclohexylcarbodiimide, (DCC) 4-(dimethylamino)pyridine (DMAP), dichloromethane, * = stereogenic center.

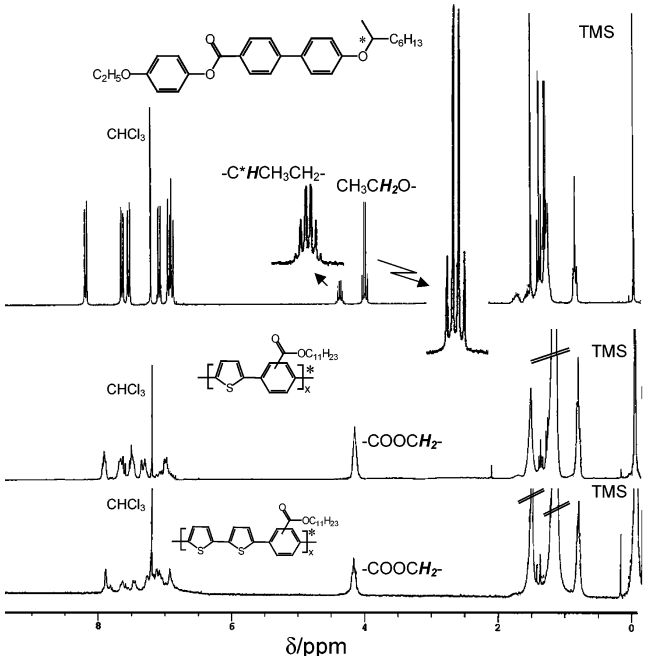


Figure 1. ^{1}H NMR spectra of cholesteric reaction solvent of (*R*)-**3** (top), **poly2** (middle), and **poly3** (lower).

4-Cyano-4′-hydroxybiphenyl and (*R*)- or (*S*)-octanol were coupled according to the Mitsunobu reaction using diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) in THF solution at room temperature. Purification of the crude compound by silica gel column chromatography (eluent: CH_2Cl_2) followed by recrystallized from acetone afforded compound **1** in (*R*) and (*S*) forms. This reaction is characterized by S_N2-type Walden inversion at the stereogenic center but with no racemization, resulting in the formation of an ester with (*S*) or (*R*) configuration.[6]

The cyano group in compound **1** was converted to a carboxyl group by KOH using a mixed solution of KOH/H_2O/ethanol to give compound **2** in (*R*) and (*S*) forms. Compound **2** was subsequently esterified with 4-ethoxyphenol by 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in CH_2Cl_2 to afford (*R*)-**3** and (*S*)-**3**, respectively. Compounds **3** display a sextet absorption at 4.41 ppm from tetramethylsilane (TMS) in nuclear magnetic resonance (NMR) measurements, attributable to a proton attached at the stereogenic center, and six signals in the lower magnetic region due to protons attached to the three benzene rings (Figure 1, top). The circular dichroism (CD) spectra of (*R*)-**3** and (*S*)-**3** in $CHCl_3$ are shown in Figure 2. (*R*)-**3** and (*S*)-**3** display a peak and a trough at around 310 nm, respectively, indicating that both (*R*)-**3** and (*S*)-**3** are optically active.

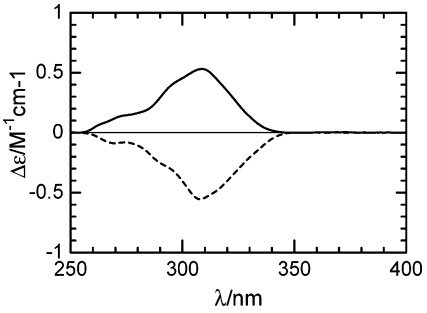


Figure 2. CD spectra of (*R*)-**3** (solid line) and (*S*)-**3** (dashed line) in $CHCl_3$ solution.

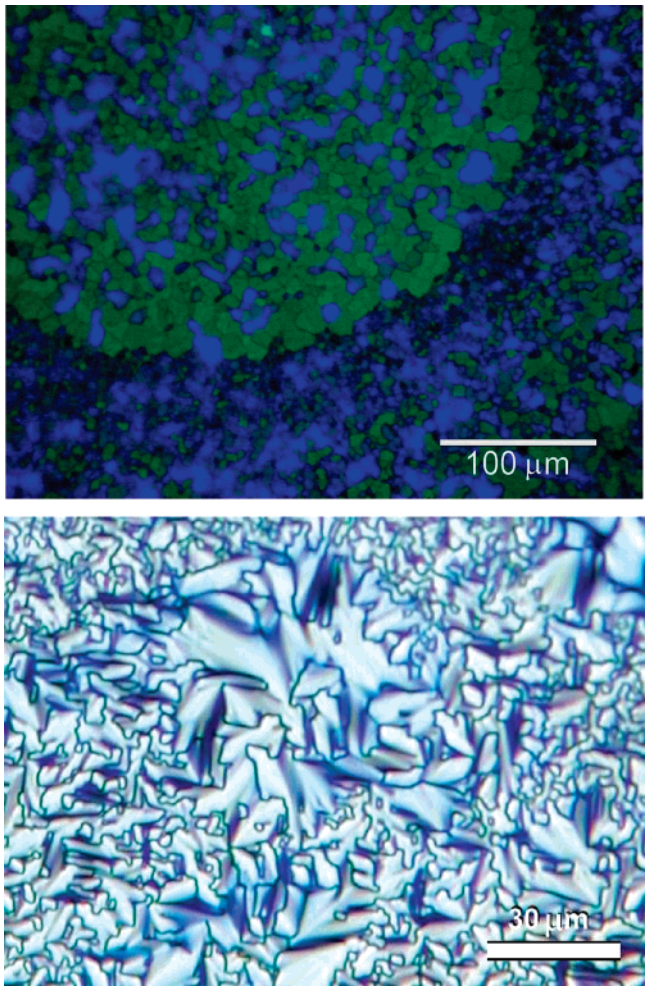


Figure 3. Polarizing optical microscopy (POM) images of (*R*)-**3,** showing platelet texture in Blue Phase (top) and fan-shaped texture (lower) in cholesteric phase.

The phase transition behavior of these compounds was determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) under conditions of K 98 (78) Ch* 138 (136) BP (137) Iso* (K: crystal; Ch*: cholesteric; BP: Blue Phase; Iso*: isotropic; parentheses denote transition temperature in cooling process). Both (*R*)-**3** and (*S*)-**3** exhibit a frustrated platelet texture (blue phase) in the cooling process only and the fan-shaped texture of the cholesteric phase under POM (Figure 3). The Blue Phase is often observed for strongly twisted cholesteric compounds at higher temperatures than for the cholesteric phase. Compounds **3** do not display a fingerprint

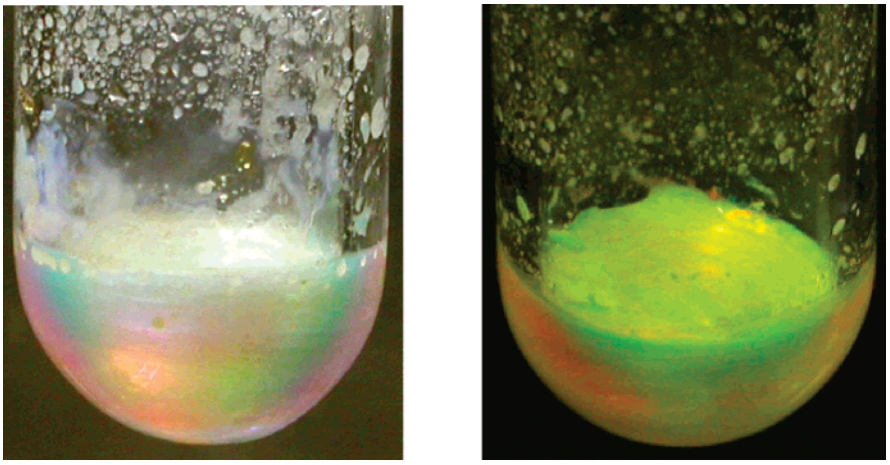
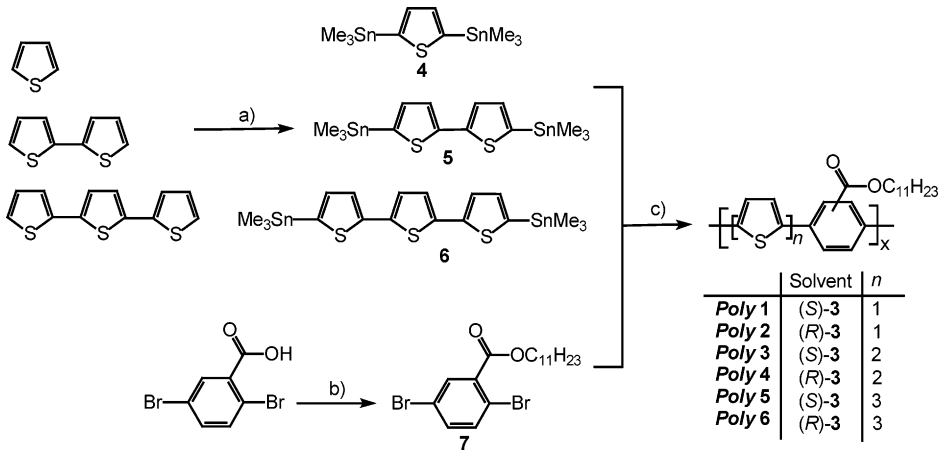


Figure 4. Photographs of reaction flask, showing the cholesteric solvent containing monomers (left), and the reaction mixture after addition of catalyst (24 h later).

Scheme 2[a]



	Solvent	*n*
***Poly* 1**	(*S*)-**3**	1
***Poly* 2**	(*R*)-**3**	1
***Poly* 3**	(*S*)-**3**	2
***Poly* 4**	(*R*)-**3**	2
***Poly* 5**	(*S*)-**3**	3
***Poly* 6**	(*R*)-**3**	3

[a] (a) *n*-Butyllithium, THF, then Me_3SnCl, THF; (b) $C_{11}H_{23}OH$, diethylazodicarboxylate (DEAD), triphenylphosphine (TPP), THF; (c) $[Pd(PPh_3)_4]$, (*R*)-**3** or (*S*)-**3** as a cholesteric solvent.

texture on visual inspection but exhibit an obvious fan-shaped (focal conic) texture with distinct fans.[7]

Synthesis of Monomers. For polycondensation in a cholesteric solvent, rigid and linear monomers are preferable, as the cholesteric solvent consists of linearly arranged molecules. Here, two types of monomers were synthesized such as thiophene-based monomer bis(trimethyltin)monothiophene, bis(trimethyltin)bithiophene, or bis(trimethyltin)terthiophene and that phenylene having an alkyl ester. The thiophene-based monomers were prepared by lithiation of thiophene or bithiophene[8] with *n*-butyllithium (*n*-BuLi) in THF solution. Trimethyltin was then introduced into the α,α′-position of the thiophene unit by an addition of trimethyltin chloride into the mixture. After reaction, the compounds were purified by column chromatography (eluent: *n*-hexane/ethyl acetate = 10) using silica gel treated in advance with triethylamine to avoid elimination of the trimethyltin moiety. The monomers were finally recrystallized from methanol to afford the desired product as green needles.

2,5-Dibromobenzoic acid was coupled with undecanol (not optically active) via the Mitsunobu reaction using DEAD and TPP in THF solution at room temperature followed by silica gel column chromatography (eluent: CH_2Cl_2) and recrystallization from acetone to afford compound **7**.[9]

Polymerization in Cholesteric Liquid Crystal. Polymerization was performed in the cholesteric LC solvent as follows. Stirring at exactly 80 rpm using a Teflon-coated 1 cm magnetic stirrer bar in a $\phi = 1.7$ cm Schlenk tube was confirmed not to break the helical structure of the cholesteric LC. To maintain stirring speed exactly, a low-speed magnetic stirrer with digital speed monitor was employed. The temperature of the reaction was maintained at exactly 93 °C by immersing the reaction vessel in a temperature-controlled silicon oil bath, which was stirred vigorously. The addition of the monomer and the production of the resulting polymer should not affect the liquid crystallinity of the cholesteric LC in this system.

A 1 g sample of (*R*)-**3** or (*S*)-**3** was placed in the Schlenk flask under argon flow at 93 °C, and iridescence due to the selective reflection of light was confirmed (Figure 4, left). Next, 0.1 g of thiophene containing trimethyltin compound (**4**, **5**, or **6**) was added using a custom-made paper funnel (see Supporting Information) and allowed to dissolve completely. 2,5-Dibromobenzoic acid undecyl ester (**7**) with no chirality was then added to the mixture and stirred at exactly 80 rpm for 30 min, after which iridescence was confirmed again. A catalytic amount of $[Pd(PPh_3)_4]$ was then added to the mixture to initiate polycondensation (Scheme 2). The cholesteric liquid crystallinity was confirmed by the selective reflection of the mixture during the reaction. Although the transition temperature of the cholesteric phase may be depressed due to the introduction of impurities such as the monomer, catalyst, or the resulting polymer, this mixture was confirmed to maintain its cholesteric phase at 93 °C. After 24 h, the visible selective reflection of the cholesteric liquid crystal in the reaction flask was confirmed again as evidence of the mixture maintaining its cholesteric

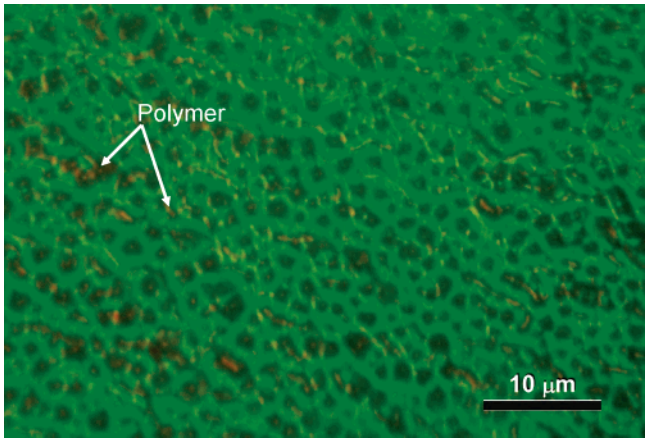


Figure 5. Polarizing optical microscopy (POM) image of reaction mixture (monomer, catalyst [$Pd(PPh_3)_4$], cholesteric solvent [(*R*)-**3**], and polymer, orange fraction) at 93 °C.

phase (Figure 4, right). The cholesteric mixture in the Schlenk flask also fluoresced due to the production of a fluorescent polymer in the cholesteric solvent. Figure 5 shows a POM image of the reaction mixture at 93 °C. Polymer fractions were observed as an insoluble orange bulk in the cholesteric medium. The bulk was afforded during polymerization due to the insolubility of the higher molecular weight fractions in this reaction system. The orange polymer bulks were surrounded by the oily streak texture of the cholesteric solvent. The cholesteric solvent fluoresces yellowish green due to dissolution of the low molecular weight oligomer fraction.

The reaction mixture was allowed to cool to room temperature and then dissolved once in a minimal amount of $CHCl_3$ and poured into a large amount of acetone to completely remove **3** (cholesteric solvent) and the low molecular mass fractions. The product was further washed in acetone and then methanol, leaving a red solid that appeared to be soluble in THF and $CHCl_3$.

The polymers from **4** and **7** prepared in (*S*)-**3** and (*R*)-**3** are abbreviated **poly1** and **poly2**, respectively, and those prepared from **5** and **7** in (*S*)-**3** and (*R*)-**3** are abbreviated **poly3** and **poly4**, respectively. Also, polymers prepared from **6** and **7** in (*S*)-**3** and (*R*)-**3** are abbreviated **poly5** and **poly6**, respectively. Yields of the polymers were in the range 79−86% (Table 1). The number-average molecular weights of **poly1** and **poly2** are 11 000 and 11 500, and those for **poly3** and **poly4** are 7000 and 6100 (eluent: THF). The molecular weight of **poly5** and **poly6** was lower than that of other polymers (M_n = 3400−3600). The degree of polymerization for **poly1** and **poly2** (polymers having monothiophene in the polymer repeat unit) is higher than that for **poly3**, **poly4** (polymers having bithiophene in the polymer repeat unit), **poly5**, and **poly6**, attributable to the higher solubility of **poly1** and **poly2** in cholesteric LC. This lower solubility of **poly3, poly4**, **poly5**, and **poly6** causes precipitates of the polymers in the cholesteric solvent in the relatively early stage of the polymerization. Once the growing polymer becomes a precipitate, the propagation of the polymer no longer advances. Therefore, increase of number of thiophene unit in the polymer repeat unit resulted in low molecular weight. Consequently, **poly5** and **poly6** having three thiophene rings in the monomer repeat unit resulted in low molecular weight. On the other hand, it states later, increase of thiophene rings in the monomer repeat unit of the polymers leads to strong aggregation property.

In this trial, molecular weights of the polymers evaluated by GPC may depend on the size of the individual aggregate of the polymer. The molecular weight of **poly2** was decreased with heat treatment in large amount of THF solution for 30 min at 140 °C (M_n = 2200, M_w = 4000, molecular weight distribution (MWD) = 1.8). Although an occurrence of scission reaction of the polymer by the heat treatment is possible, this result implies that the aggregation consist of chiral organization of low molecular weight oligomers.

Figure 6 shows the DSC results for the cholesteric solvent containing monomers (before polymerization) and the cholesteric solvent containing monomers and the catalyst after polymerization. After polymerization, the phase transition was shifted to lower temperature due to the presence of the product oligomer and polymer. The DSC results indicate that the wide cholesteric temperature range of the reaction mixture allows polymerization to proceed in the cholesteric phase throughout the reaction. These results show that polymerization at 93 °C

Table 1. Polymerization Results

Polymer	Monomer	Cholesteric solvent	Yield (%)	λ_{max}[a] (nm)
***Poly* 1**	**4**, 7	(*S*)-**3**	81	400
***Poly* 2**	**4**, 7	(*R*)- **3**	79	400
***Poly* 3**	**5**, 7	(*S*)-**3**	85	436
***Poly* 4**	**5**, 7	(*R*)-**3**	86	436
***Poly* 5**	**6**, 7	(*S*)-**3**	82	462
***Poly* 6**	**6**, 7	(*R*)-**3**	86	462

[a] Optical absorption maximum in $CHCl_3$ solution.

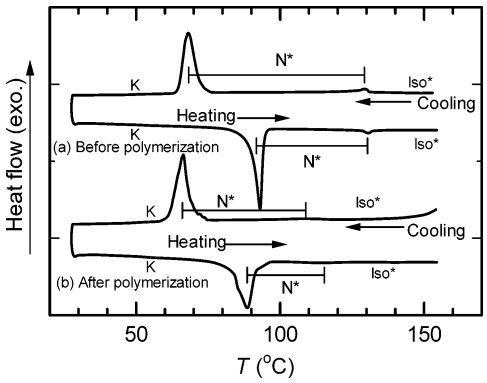


Figure 6. DSC results for chiral nematic solvent (a) containing monomers (before polymerization) and (b) containing monomers and catalyst (after polymerization).

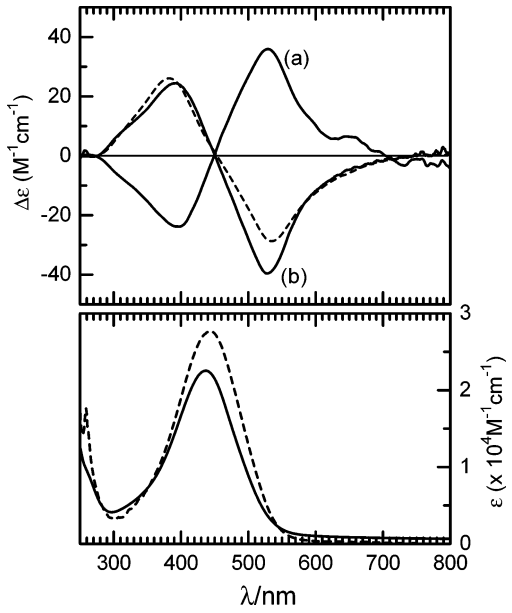


Figure 7. Upper: CD spectra for **poly3** (a, solid line) and **poly4 (**b, solid line) in $CHCl_3$ solution and for **poly4** (dashed line) in THF solution. Lower: UV/vis absorption spectra for **poly4** in $CHCl_3$ solution (solid line) and THF solution (dashed line).

is effective for ensuring that the entire reaction is performed in the cholesteric phase of the solvent.

The sextet signal at around 4.2 ppm from TMS in the polymer is attributable to protons attached at carbon neighboring the ester moiety. **Poly2** and **poly3** display no signals related to (*S*)-**3** (Figure 1). This result indicates that no chiral molecules reacted chemically with the monomer during polymerization and that the cholesteric LC as a reaction solvent functioned only as a physical environment.

Ultraviolet/Visible Absorption and CD Spectra. Poly1 and **poly2** exhibit a peak absorption wavelength (λ_{max}) at 400 nm in the ultraviolet (UV)/visible (vis) absorption spectra in $CHCl_3$ solution, whereas **poly3** and **poly4** display a λ_{max} at 436 nm ascribed to the $\pi-\pi^*$ transition of the main chain (Figure 7 lower, solid line), and **poly5** and **poly6** display λ_{max} at 462 nm in absorption spectra. The addition of one thiophene ring in the monomer repeat unit of the polymer results in ~30 nm red shift in the absorption spectra. The λ_{max} values of the polymer are summarized in Table 1.

In the case of multiple chromophores located in close proximity, the sign of the Cotton effect reflects the energy gap (splitting) between the excited states of chromophores in the chiral molecule. When two energy levels corresponding to dipole−dipole interactions between chromophores are involved, a CD spectrum with two-component Cotton effects of opposite sign is obtained. The distance between the two-component CD curves of opposite sign corresponds to the Davydov splitting, which gives an indication of the interaction among excited states, that is, exciton coupling of the excited states of the chromophores.[10] The strong CD bands at 380 and 530 nm in $CHCl_3$ solution are assigned to the bisignate exciton-coupled band (splitting of the excited state into two exciton levels), centered around the 436 nm absorption band (Figure 7 top, solid lines). This result indicates that the transition moments of **poly3** and **poly4** are oriented clockwise (positive first Cotton effect at longer wavelength and negative second) and counterclockwise (negative first Cotton effect at longer wavelength and positive second), respectively. The expected complementary mirror-image relationship between **poly3** and **poly4** is not due to the chiral compound employed as a solvent in this case because the monosignate CD of **3** is only observed at shorter wavelengths with weak intensity [(*R*)-**3**, CD ($CHCl_3$), λ_{max} ($\Delta\epsilon$) = 308 (+0.53); (*S*)-**3**, CD ($CHCl_3$), λ_{max} ($\Delta\epsilon$) = 308 (−0.55)].

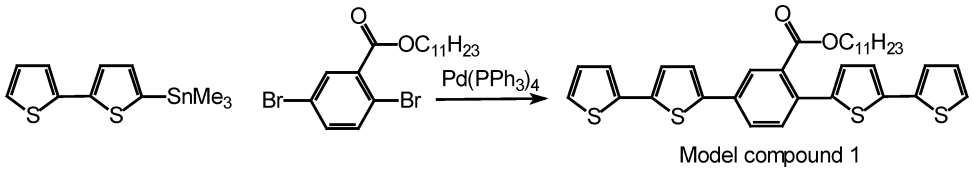
The results above suggest that the polymer forms a helical interchain chiral organization. Such chiral aggregation of the polymer main chains may bear a resemblance to the form of the cholesteric LC. **Poly1** and **poly2**, on the other hand, exhibit no signal in the CD spectra. Although the polymers synthesized in cholesteric LC form chiral aggregates over the course of polymerization, the high solubility of **poly1** and **poly2** resulted in the loss of chiral aggregation upon dissolution in THF or $CHCl_3$ upon conformational equilibration. In contrast, **poly3**, **poly4**, **poly5**, and **poly6** remain optically activity in isotropic solution, despite being polymers with no optically active substituents. The Cotton effect of **poly5** and **poly6** has the same tendency as **poly3** and **poly4**; however, the absorption maximum and CD signals locate at longer wavelength with strong intensity than those of **poly3** and **poly4** [**poly5**: λ_{max} ($\Delta\epsilon$) = 578 nm (183) and 390 nm (−141); **poly6**: λ_{max} ($\Delta\epsilon$) = 578 nm (−87) and 393 nm (76) in $CHCl_3$].

The chiral structure developed during polymerization was thus preserved even after dissolution in solution and washing. This is probably due to the increment of the thiophene ring in the monomer repeat unit, resulting in low solubility, and also to steric hindrance of the ester group attached at the 2-position of the benzene ring, which stabilizes the chiral structure of the polymer.

The monomers involving bithiophene or terthiophene, which often behaves as a mesogenic core, have good affinity for the cholesteric LC solvent compared to the monothiophene unit due to the linearity of the multiring system. Improved interaction between the monomer (**5** or **6)** as a solute and the cholesteric solvent allows effective asymmetric induction from the cholesteric LC to the reactant in the polymer growth process. Furthermore, the cholesteric solvent acts as a poor solvent for the resultant polymer, allowing the polymer to precipitate in the form of chiral aggregates and simultaneously locking the chiral state. The chiral aggregation is thus preserved upon dissolution by strong interchain interaction in the π-conjugated system. The aggregate may act as a single supramolecule.

5-Trimethylstannyl-2,2′-bithiophene[11] and compound **7** were coupled in the same manner as in the preparation of the polymers in cholesteric LC to yield the model compound **1** (Scheme 3). This model compound exhibited no Cotton effect in the CD spectrum which implies that the axial chirality was not produced by the cholesteric LC reaction medium.

Scheme 3



Furthermore, vibrational CD (VCD) of **poly4** was examined. However, no distinct VCD signal at infrared region of the polymers was obtained. This result indicates that the individual chains of polymer prepared in the cholesteric LC may be achiral.

Circular Polarized Luminescence. The CPL of the product polymers was analyzed with respect to the contents 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:

$$\Delta I = I_L - I_R \tag{1}$$

The average luminescence intensity is expressed by

$$I = (I_L + I_R)/2 \tag{2}$$

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

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

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

Poly3 and **poly4** exhibit CPL in chloroform solution at an excitation wavelength of 380 nm (Figure 8). The strong CPL bands in $CHCl_3$ solution are assigned to the bisignate exciton-coupled band; the zero crossing point locates at around the peak top of photoluminescence band. Therefore, it can be defined as both polymers display Davydov-split type CPL. **Poly5** and **poly6** also exhibit CPL in chloroform solution at an excitation wavelength of 380 nm (Figure 9). **Poly5** and **poly6** show the same tendency in CPL as **poly3** and **poly4**, but the CPL signals locate at longer wavelengths. Also, the CPL intensity of **poly5** and **poly6** is stronger than that of **poly3** and **poly4**.

Polymerization under vigorous stirring at 200 rpm produced polymers with no Cotton effect in CD measurements, attributable to the loss of the helical structure of the cholesteric liquid crystal phase due to excessive shear stress and growth of the polymer in the nonhelical medium.

Green et al. showed that chiral solvents such as (*R*)-2-chlorohexane can transfer chirality to the *poly*(*n*-hexyl isocyanate) main chain as an achiral polymer.[12] In the present experiments, the chiral structure of the polymer could not be produced when the reaction solvent was in an isotropic or nonhelical state. This is probably due to the fact that the chirality-inducing property of solvent **3** in the isotropic state has no effect for inducing chiral aggregation of **poly3** because it has no quasi-layer helical structure, while the solvent in cholesteric mesophase with a helical architecture effectively affords a polymer with chiral structure during the polymerization process. This result indicates that the helical structure of the cholesteric LC affords the chiral transformation rather than the effect of individual chiral molecules in direct contact. That is, the cholesteric LC acts as a "chiral organized matrix" consisting of chiral directors of the cholesteric LC, effectively imparting a chiral conformation on the polymer during the polymer growth process. Subsequent interchain interaction in the π-electron system of the polymer locks the chiral aggregation, thereby preserving the chiral formation even after dissolution.

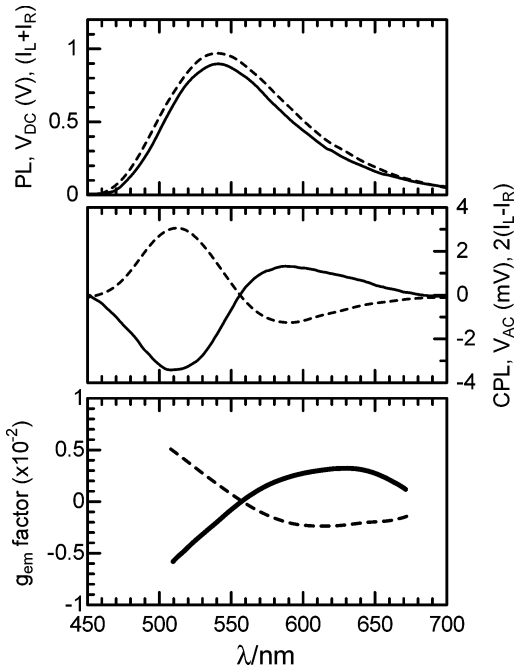


Figure 8. PL spectra (upper), CPL spectra (middle), and dissymmetry factor of emission (g_{em}) (lower) for **poly3** (solid line) and **poly4** (dashed line) in $CHCl_3$ solution.

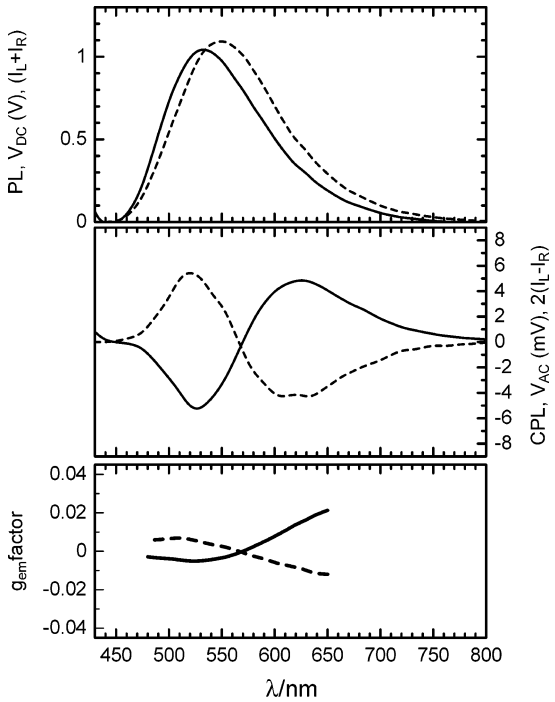


Figure 9. PL spectra (upper), CPL spectra (middle), and dissymmetry factor of emission (g_{em}) (lower) for **poly5** (solid line) and **poly6** (dashed line) in $CHCl_3$ solution.

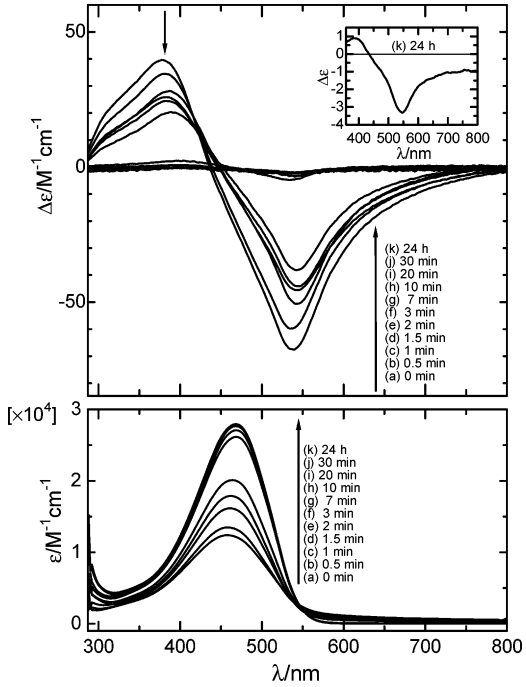


Figure 10. CD spectra (upper) and UV/vis absorption spectra (lower) for **poly4** after heating in cumene for up to 24 h at 120 °C. All spectra were measured at 25 °C in cumene solution.

Disaggregation by Heat Treatment. Heating of the chiral compounds should result in racemization due to random rotation of the polymer main chains and loss of chiral aggregation. To examine this process, **poly4** was heated in cumene (high boiling point). Figure 10 shows the UV/vis and CD spectra of **poly4** in cumene under an argon atmosphere before and after heat treatment. A decrease in the solubility of the polymer in cumene is observed as an increase in the peak intensity in the spectra, since polymer aggregation becomes stronger in cumene at room temperature. The absorption peak of **poly4** is 436 nm in $CHCl_3$ and 458 nm in cumene. The red shift of 22 nm and increase in absorption intensity of the polymer in cumene are caused by solvatochromism.

Heating at 120 °C causes a shift of the absorption peak from 458 to 469 nm and an increase in ϵ (but decrease in $\Delta\epsilon$), along with a shift of the CD extrema to longer wavelengths. The Cotton effect of the heated **poly3** in cumene also weakens, although the UV/vis absorption intensities increase. This result is attributed to disaggregation of the polymer, free rotation of the main chain, and a decrease in the average dihedral angle in the main chain during heating. Random rotation of the monomer repeat unit along the polymer main chain due to heating is considered to improve the average coplanarity of the polymer at 25 °C and increase the effective conjugation length of the $\pi-\pi^*$ system, leading to an increase in the absorption intensity and red shift of the absorption peaks. The change in the CD intensities of the annealed polymer in cumene is irreversible, as reaggregation in the solvent did not occur. Figure 11 shows CD spectra of **poly5** in cumene under an argon atmosphere before and after heat treatment at 150 °C. In the case of **poly5**, heat treatment for 24 h did not break chirality of the polymer. The durability of the chirality of the polymers having triple thiophene rings in the monomer repeat unit comes from strong aggregation property, which produced during the course of the polymerization in cholesteric LC.

Figure 12 shows the PL, CPL, and g_{em} results for **poly4** before and after heating in cumene solution. The PL extrema of the polymer in cumene solution occur at longer wavelengths than

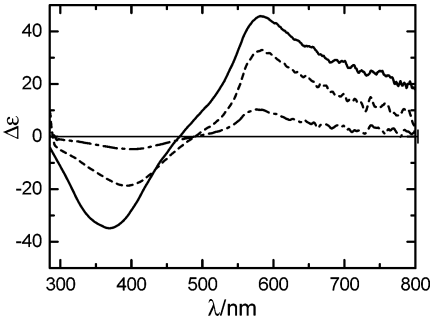


Figure 11. CD spectra of **poly5** after heating in cumene for up to 24 h at 150 °C. All spectra were measured at 25 °C in cumene solution. 0 h, solid line; 6 h, dashed line; 24 h, dot-dashed line.

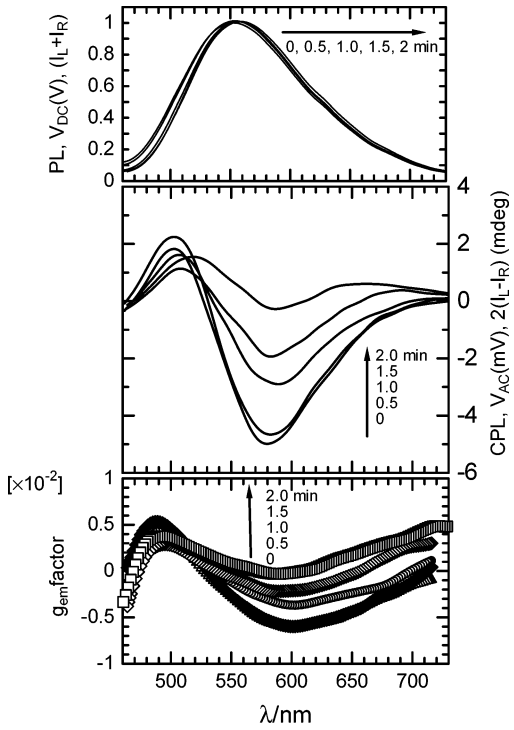


Figure 12. PL spectra (upper), CPL spectra (middle), and dissymmetry factor of emission (g_{em}) (lower) for **poly4** after heating in cumene for up to 2 min.

in $CHCl_3$ solution, and heating reduces the intensity of CPL. The emission peak and extrema in the CPL spectrum are also shifted slightly to longer wavelengths upon heat treatment. The g_{em} factors for **poly4** decrease upon heating. Heat treatment of **poly4** at 150 °C for 3 min resulted in the rapid loss of the CPL signal, although the polymer still exhibited photoluminescence. The change in optical activity by heating is irreversible. This CPL result is suggestive of disaggregation of the polymer and swelling in the solvent upon heating and is consistent with the CD results. The chirality of the polymers, with no chiral substituent, is thus considered to be derived from the asymmetry produced by growth in the cholesteric LC.

The UV/vis absorption and CD spectra for **poly4** in THF (a good solvent) solution are presented in Figure 7 (dashed line). The peak absorption wavelength due to the $\pi-\pi^*$ transition of the **poly4** main chain is red-shifted by 7 nm in THF compared to that in chloroform solution [in $CHCl_3$, λ_{max} (ϵ) = 436 nm (2.3×10^4); in THF, λ_{max} (ϵ) = 443 nm (2.8×10^4)]. This small red shift is due to solvatochromism. The absorption intensity of the polymer is increased in THF, whereas the intensity of the CD spectrum is reduced. This result reflects the increased solubility of **poly4** in THF and consequent partial

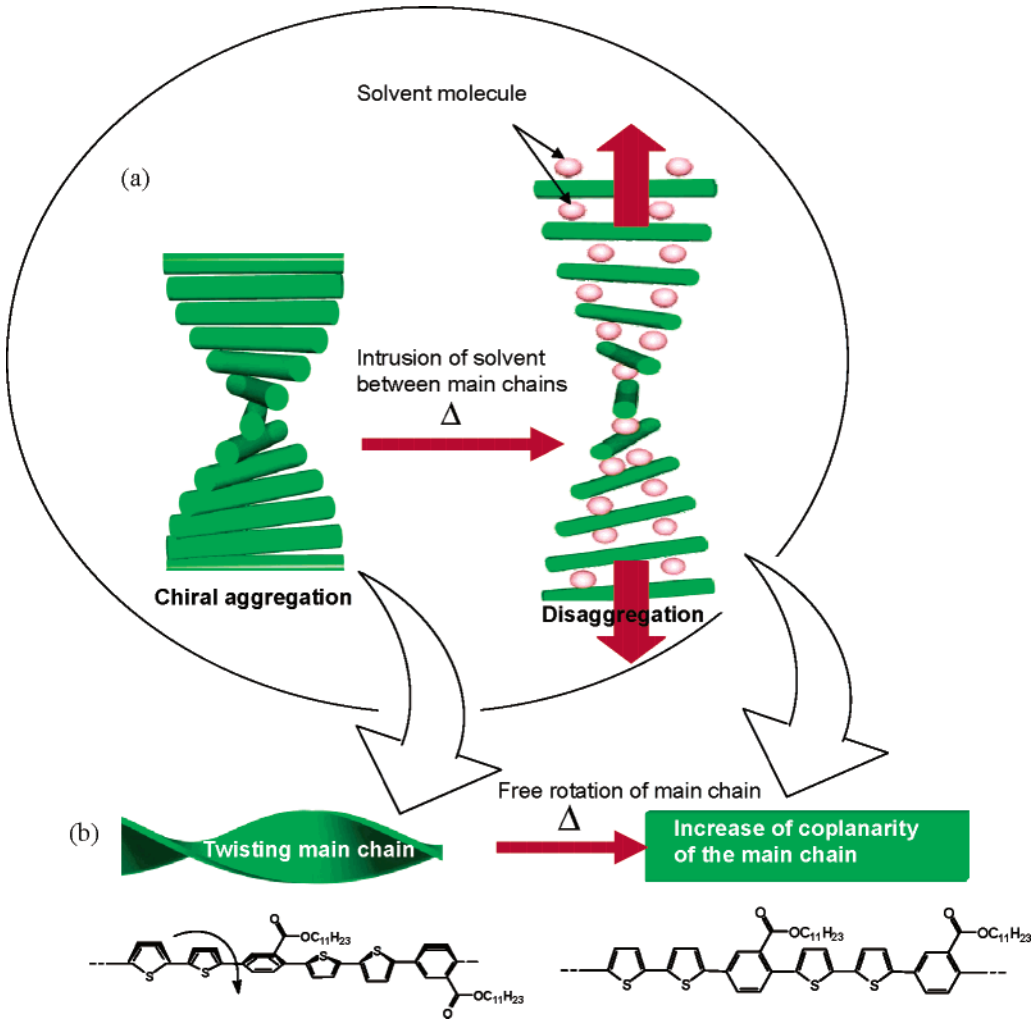


Figure 13. Proposed disaggregation mechanism for chiral aggregates upon heat treatment in cumene. Intrusion of isotropic solvent (cumene) between main chains (a). Increase in coplanarity of main chain through release of aggregation by free rotation of the monomer unit in the isotropic solvent (b).

disaggregation and is consistent with the results of the heat treatment experiment.

Figure 13 shows a disaggregation model for heat treatment in solvent. Intrusion of the isotropic solvent between the main chains leading to disaggregation for loss of chirality of the polymer is plausible.

Conclusion

A cholesteric liquid crystal was shown to provide a molecular matrix with central chirality for polymerization. Growth of a polymer in this three-dimensional chiral environment results in the formation of a chiral aggregate. Although the cholesteric phase has a chiral helical superstructure, on a very long length scale (>400 nm), the twist angle between quasi-layers in the chiral anisotropic reaction field is very small at the molecular level. The solute molecules sandwiched between cholesteric pseudo-layers appear to have little effect, yet the small torsion angle induced between pseudo-layers produces a strong Cotton effect in the CD and CPL spectra of the resultant polymers. The sequential small interchain torsion angle between polymer main chains in the aggregate results in consistent optical activity. The synthesis process, involving formation of chiral aggregates and subsequent conformational locking by the interchain interaction of π-electron conjugated system, affords stable chiral polymers as aggregated polymer units, which in solution behave as single large molecules with optical activity. This type of chiral aggregated polymer can be regarded as "a chiral collective".

It has been thought that it is unlikely to be possible to obtain significant asymmetric induction using a cholesteric solvent.[4] The present results, however, demonstrated that the reproductive cholesteric liquid crystal inductive asymmetric reaction can be realized through synthesis of π-conjugated systems.

Experimental Section

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 for polymer. EYELA MCS-101 (Tokyo Rikagaku) 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 $CDCl_3$ using a Bruker AV-600 or JEOL EX-270 FT-NMR spectrometer. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Infrared spectra were measured with a JASCO FT-IR 550 spectrometer using the KBr method. Vibrational circular dichroism spectra (VCD) were obtained with a Jasco JV-2001. Optical absorption spectra were measured at room temperature using a HITACHI U-2000 spectrometer with quartz cell. CD spectra were obtained with a JASCO J-720 spectrometer. PL and CPL measurements of the polymers were performed with a JASCO CPL 200S spectrometer. Phase transition temperatures were determined using a TA Instruments Q-100 differential scanning calorimeter with a constant heating/cooling rate of 10 °C/min, and texture observations were made using a

Nikon ECLIPS E 400 POL polarizing microscope equipped with a Linkam TM 600PM heating and cooling stage. Temperature calibration of the heating stage was carried out by using DSC. The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Shodex A-80M column and a JASCO HPLC 870-UV detector with THF used as solvent during measurements, with the instrument calibrated by polystyrene standard.

Polymerization in Cholesteric Liquid Crystal. Poly4. (*R*)-**3** (1 g) in a Schlenke flask was stirred slowly (80 rpm) with a magnetic stirrer, which was exactly maintained at 93 °C to exhibit cholesteric liquid crystal phase. Iridescence color of the cholesteric liquid crystal solution due to selective reflection of light was confirmed. Then **5** (0.1 g, 0.2 mmol) was added to the flask very slowly. Subsequently, compound **7** (87 mg, 0.2 mmol) was added to the cholesteric liquid crystal solvent. After 30 min, [$Pd(PPh_3)_4$] (3 mg, 0.0026 mmol) was added to the mixture. The cholesteric liquid crystal solution showed iris color and gradually exhibited fluorescence. The reaction mixture was further stirred very slowly (80 rpm) for 24 h. The reaction mixture was allowed to cool to room temperature and once dissolved in a 1 mL of THF, and this solution was poured into a large amount of acetone to remove the cholesteric liquid crystalline compound and low molecular mass fractions. The product was washed in a large amount of acetone more three times, and finally the polymer was washed in methanol. The red material in the solution was collected by filtration and dried in vacuo to afford red polymer. Yield: 75 mg, 0.17 mmol (86%).

Poly1. This polymer was prepared using the same procedure as described for **poly4**, but collection of the polymer was carried out by the centrifuge technique. Filtration procedure was not valid for the collection of the polymer because it consists of small particles. Quantity used: (*S*)-**3** (1 g), **4** (0.1 g, 0.24 mmol), **7** (0.1 g, 0.24 mmol), [$Pd(PPh_3)_4$] (3 mg, 0.0026 mmol). Yield: 60 mg, 0.17 mmol (71%).

Poly2. This polymer was prepared using the same procedure as described for **poly4**, but collection of the polymer was carried out by the centrifuge technique. Quantity used: (*R*)-**3** (1 g), **4** (0.1 g, 0.24 mmol), **7** (0.1 g, 0.24 mmol), [$Pd(PPh_3)_4$] (3 mg, 0.0026 mmol). Yield: 67 mg, 0.19 mmol (79%).

Poly3. This polymer was prepared using the same procedure as described for **poly4**. Quantity used: (*S*)-**3** (1 g), **5** (0.1 g, 0.2 mmol), **7** (87 mg, 0.2 mmol), [$Pd(PPh_3)_4$] (3 mg, 0.0026 mmol). Yield: 74 mg, 0.17 mmol (85%).

Poly5. This polymer was prepared using the same procedure as described for **poly4**. Quantity used: (*S*)-**3** (0.5 g), **6** (58 mg, 0.1 mmol), **7** (43 mg, 0.1 mmol), [$Pd(PPh_3)_4$] (2.6 mg, 0.0022 mmol). Yield: 43 mg, 0.082 mmol (82%).

Poly6. This polymer was prepared using the same procedure as described for **poly4**. Quantity used: (*R*)-**3** (0.5 g), **6** (58 mg, 0.1 mmol), **7** (43 mg, 0.1 mmol), [$Pd(PPh_3)_4$] (2.6 mg, 0.0022 mmol). Yield: 45 mg, 0.086 mmol (86%).

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Supporting Information Available: A video of the polymerization experiment in cholesteric liquid crystal; synthetic data of low-molecular-weight compounds; figure of custom-made paper funnel for transferring cholesteric liquid crystal compound (powder form in room temperature) to reaction flask. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Pirkle, W. H.; Rinaldi, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3510−3511.
(2) Saeve, F. D.; Sharpe, P. E.; Olin, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 204−205.
(3) Verbit, L.; Halbert, T.; Halbert, R.; Patterson, R. B. *J. Org. Chem.* **1975**, *40*, 1649−1650.
(4) Dondoni, A.; Medici, A. *Mol. Cryst. Liq. Cryst.* **1979**, *55*, 47−51.
(5) Seuron, P.; Solladi, G. S. *J. Org. Chem.* **1980**, *45*, 715−719.
(6) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380−2382.
(7) (a) Strongly twisted cholesteric liquid crystal materials show distinct fan-shaped texture, and slightly smaller twisting materials also show fan-shaped texture but with a somewhat smoother appearance of fans. (b) Dierking, I. In *Textures of Liquid Crystals*; Wiley VCH: Weinheim, 2003.
(8) (a) Goto, H.; Akagi, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 4322−4328. (b) Goto, H.; Akagi, K. *Angew. Chem.* **2005**, *117*, 4396−4402.
(9) Alkyl group was introduced into the phenylene ring due to increase of solubility in the cholesteric solvent.
(10) (a) Freek, J. M.; Jonkheijm, P.; Meijer, E. W. Schenning, A. *Chem. Rev.* **2005**, *105*, 1491−1546. (b) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039−4070. (c) Berova, N.; Borhan, B.; Dong, J. G.; Guo, J.; Huang, X.; Karnaukhova, E.; Kawamura, A.; Lou, J.; Matile, S.; Nakanishi, K.; Rickman, B.; Su, J.; Tan, Q.; Zanze, I. *Pure Appl. Chem.* **1998**, *70*, 377−383. (d) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Christiaans, M. P. T.; Meskers, S. C. J.; Dekkers, H. P. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 4908−4909. (e) Prins, L. J.; Timmerman, P.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2001**, *123*, 10153−63. (f) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227−230. (g) Green, M. M.; Reidy, M. P.; Johnson, R. J.; Darling, G.; O'Leary, D. J.; Willson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6452−6454. (h) Saxena, A.; Guo, G.; Fujiki, M.; Yang, Y.; Ohira, A.; Okoshi, K.; Naito, M. *Macromolecules* **2004**, *37*, 3081−3083. (i) Reinhoudt, N.; Calama, M. C. *Science* **2002**, *295*, 2403−2406. (j) Fiesel, R.; Scherf, U. *Macromol. Rapid Commun.* **1998**, *19*, 427−431. (k) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652−654. (l) Steffen, W.; Köhler, B.; Altmann, M.; Scherf, U.; Stizer, K.; zur Loye, H-C.; Bunz, U. H. F. *Chem.—Eur. J.* **2001**, *7*, 117−126.
(11) (a) Groenendaal, L.; Bruining, M. J.; Hendrickx, E. H. J.; Persoons, A.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Chem. Mater.* **1998**, *10*, 226−234. (b) Henze, O.; Parker, D.; Feast, W. J. *J. Mater. Chem.* **2003**, *13*, 1269−1273.
(12) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860−1866.

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