

Cholesteric medium inductive asymmetric polymerization: preparation of optically active polythiophene derivatives from achiral monomers in cholesteric liquid crystals

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Abstract—This Letter reports the synthesis and optical properties of polythiophenes prepared in cholesteric liquid crystal (CLC) medium. The polythiophenes prepared from achiral monomers in the CLC display consistent optical activity. In the first step of this research, we prepared CLCs for a reaction solvent. Next, Stille-type polycondensation reaction in the CLC was carried out. The resultant polymers show intense circular dichroism (CD). The CD results suggest that the polymers form a chiral structure. © 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Asymmetric synthesis of polymers is one of the most interesting research fields in chemistry such as enantioselective syntheses¹ and asymmetric transitions.² Especially, application of conjugated polymers with optical activity is expected for polymer EL showing circular polarized luminescence, and chiral sensors.³ There are various techniques for producing conjugated polymers with optical activity.⁴ In this research, we carried out a new type of asymmetric polymerization to afford optically active polythiophenes by using cholesteric liquid crystal (CLC) as a reaction medium. CLCs have the characteristic structure where the individual CLC molecules in a pseudo-layer orient in the same direction, and each pseudo-layer gradually rotates with a certain angle to form a helical structure. This macroscopically asymmetric architecture of CLCs can function as a chiral guide during polymerization reaction for formation of a chiral structure. We prepared three-ring type CLC materials for the polymerization reaction solvent instead of common organic solvents such as tetrahydrofuran (THF). It can be expected that the optical absorption

maximum due to π - π^* transition of the main chains of the polythiophenes synthesized in this study locates at longer wavelengths compared with the thiophene-phenylene type polymers, previously reported by Goto,^{5a} and the polymers consisting of thiophene monomer repeat units show good film-forming property. Polythiophenes thus synthesized in the CLC display circular dichroism (CD) in the UV-vis region. The CD results suggested that the polymers form a chiral structure.

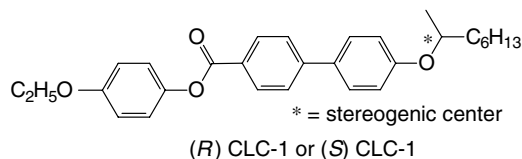
2. Results and discussion

2.1. Synthesis of cholesteric solvent

(*R*) and (*S*) CLC-1, which comprise a three-ring core with an optically active terminal alkyl group were prepared, according to the method previously reported in the Letter.^{5a} Both CLCs display a stable cholesteric liquid crystal phase in a wide temperature range. Differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) confirmed their cholesteric liquid crystallinity at between 78 °C and 137 °C. Therefore, the CLC materials can be employed as a cholesteric reaction solvent. The (*R*) and (*S*) CLCs exhibit a typical oily streak texture of cholesteric liquid crystal, and a cubic blue phase as a frustrated platelet texture under POM observations (Fig. 1a and b).

Keywords: Chirality; Circular dichroism; Conjugated polymer; Liquid crystals.

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2.2. Synthesis of polymers

5-Trimethylstannyl-2,2'-bithiophene (49 mg, 0.1 mmol),⁶ 2,5-dibromothiophene-3-carboxylic acid undecyl ester (49 mg, 0.1 mmol) (M1),⁷ and 0.5 g of (*R*) or (*S*) CLC-1 were placed in a small Schlenk flask under argon flow at 93 °C. The reaction mixture was stirred with a 1-cm Teflon-coated magnetic stirrer. Visible selective reflection of light was confirmed. An addition of a large amount of a monomer into CLC may destroy the helical structure of the system. Therefore, we carried out the reaction under the condition of mole ratio of CLCs/monomers = 10/1. Then a catalytic amount of Pd(PPh₃)₄ (1.6 mg) was added to the mixture to initiate polycondensation. The selective light reflection (rainbow color), derived from the cholesteric phase, was confirmed again. Stirring was conducted exactly at 72 rpm to maintain the cholesteric phase of the reaction mixture. High-speed stirring of the cholesterics destroys its helical structure. On the other hand, the oil in the oil bath was stirred at high speed with a mechanical stirrer for maintaining constant temperature. After 24 h, color of the reaction mixture turned red with selective reflection, which confirmed preservation of the cholesteric phase (Fig. 2). The reaction mixture was allowed to cool to room temperature and dissolved in a small amount of acetone. The solution was poured into a large volume of acetone to remove CLC, monomers, catalyst, and low molecular weight reactant. After filtration, the red powder thus obtained was washed with a large volume of methanol. Filtration, and drying under vacuum afforded the desired polymer. The polythiophenes prepared in (*R*) CLC-1 and (*S*) CLC-1 are abbreviated as *R*-PBTT and *S*-PBTT, respectively (*R*-PBTT: 22 mg, yield = 50%; *S*-PBTT: 21 mg, yield = 50%) (Scheme 1).

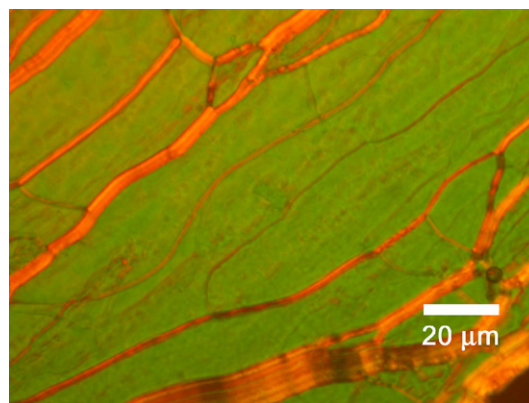
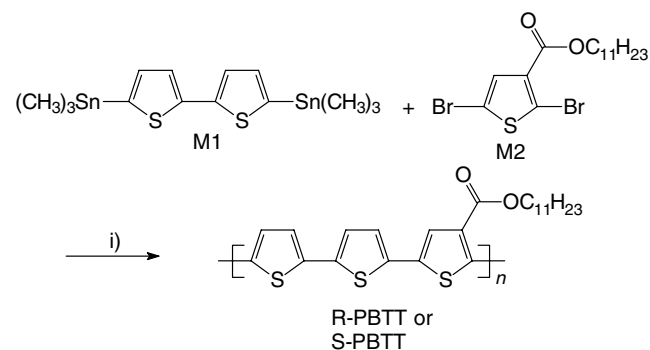


Figure 2. Polarizing optical microscopy image of the reaction mixture in the polymerization process.



Scheme 1. Reagent: (i) [Pd(PPh₃)₄], and (*R*) or (*S*) CLC (as a reaction solvent).

3. Results and discussion

3.1. Molecular weights

Polymerization results are summarized in Table 1. The molecular weights are evaluated with gel permeation chromatography (GPC) relative to polystyrene standard (eluent: THF). The number-average molecular weights (M_n) of *R*-PBTT and *S*-PBTT are 4200 g/mol and 3800 g/mol, respectively. The weight-average molecular

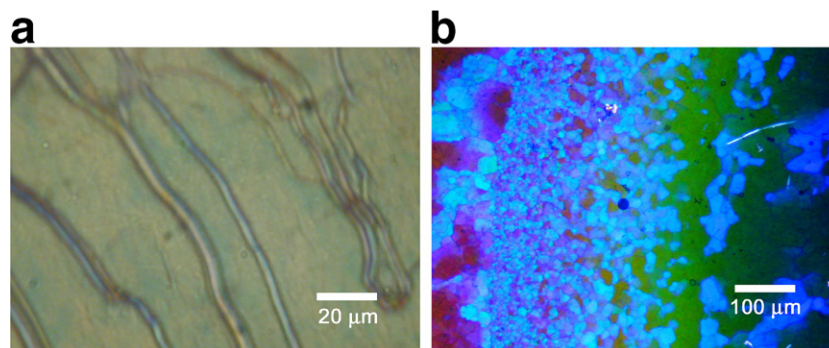


Figure 1. Polarizing optical microscopy images of (*R*) CLC. Oily streak texture of cholesteric phase at 100 °C (a), platelet texture of cubic blue phase at 137 °C (b).

Table 1. Polymerization results^a

Polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n	DP ^b
R-PBTT	4200	5200	1.2	8.9
S-PBTT	3800	5200	1.3	8.0

^a M_n and M_w were evaluated with a gel permeation chromatography (GPC) relative to polystyrene standard.

^b DP (degree of polymerization) was calculated by M_n/mru , mru : molecular weight of monomer repeat unit.

weights (M_w) of both polymers are 5200 g/mol. At this time, filtration of the polymers in THF solution was carried out with a 0.1 μm membrane filter prior to the GPC measurements because GPC cannot estimate molecular weights of insoluble materials. Consequently, the molecular weights of the polymers appeared relatively low value because only the THF soluble part of the polymer was measured with GPC. The insoluble fractions may consist of high molecular weights chains, or form a large size aggregation.

3.2. Optical properties

UV–vis absorption and CD spectroscopy measurements of R-PBTT and S-PBTT in CHCl_3 solution and cast films (Fig. 3) were carried out. Both R-PBTT and S-PBTT in CHCl_3 solution exhibit absorption maximum (λ_{max}) at 474 nm in the UV–vis. The absorption band is assignable to π – π^* transition of the main chain. The absorption band due to the conjugated main chain of the polymers was 60 nm red-shifted to 534 nm in the case of cast films. This may be due to the fact that in-plane alignment occurred in the cast films. The absorption tails off toward the IR region.

In the CD measurements, the polymers display complementary mirror image Davydov split type Cotton effect.⁸ R-PBTT displays a negative first and a positive second Cotton effect, whereas polymer S-PBTT a positive first and a negative second Cotton effect. PBTTs in the solution exhibit signals at 380 nm and 534 nm in the CD,

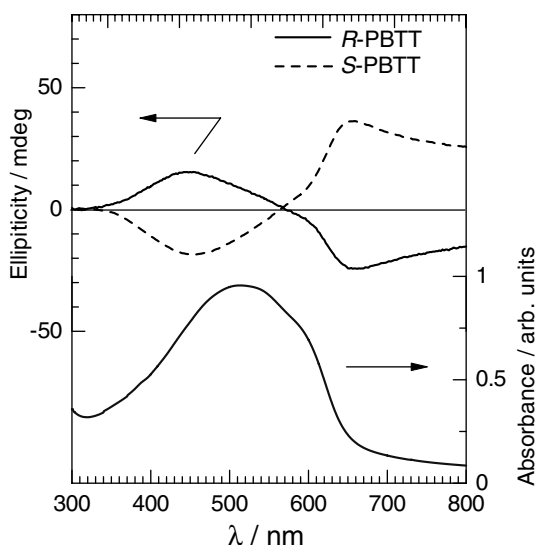


Figure 3. CD (upper) and UV–vis absorption spectra (lower) of PBTT films.

which are assigned to the bisignate exciton coupled band associated with the absorption band at 474 nm. PBTT films show CD bands at 460 nm and 660 nm, which are associated with the absorption band at 518 nm. A set of these results strongly suggests that the polymer is inherently chiral, although the polymers have no asymmetric carbon in the molecular structure. Therefore, we conclude that the CLC medium having a macroscopic chiral architecture produces chirality of the polymer in the growing process. The chirality of the polymer can be originated from helical structures.

It is considered that rise in temperature extends the helical periodicity of the CLC medium. This would result in the production of polymers having a weak CD intensity. Furthermore, a deviation from the liquid crystalline temperature range in the polymerization reaction gives no desired polymers. For instance, polymerization in the isotropic phase of the CLC system gives no chiral polymers, and a polymerization in the solid (crystal) state of the CLC system allows no polymerization reaction.

Although the CLC medium employed in this study displays liquid crystallinity in a wide range, reaction temperature maintenance at around 93 °C is required in this polymerization because the CLC medium containing the reactants and the product exactly displays the liquid crystal phase at 93 °C. Therefore, at this stage, we did not examine the relationship between the helical pitch of the CLC and optical activity of the resultant polymer. The products are quite stable. The optical absorption and CD intensity of the polymers show no change over time. However, heat treatment of the polymer in cumene (high boiling point) solution for 24 h at 150 °C resulted in a significant decrease in CD intensity. This can be due to the fact that release of the chiral structure of the polymers occurred by the heat treatment in the solvent. This intensity change in CD of the polymers accompanied by the heat treatment in cumene is irreversible.

Here, three-type helical structures for the present polymer are considered such as an ‘intra-helical structure’ of the main chains (monomer units gradually twist in one direction along the main chain), ‘winding-helical structure’ of the main chain (like a spring structure such as the secondary structure of DNA), and ‘inter-helical structure’ between the main chains [chiral aggregation (like spiral stairs) consists of individual polymer chains].

4. Conclusion

Asymmetric medium was employed as a reaction solvent for producing chiral polymers from achiral monomers. The polythiophenes show good film-forming property. Polymerizations in the cholesterics produced chiral polymers showing consistent CD. The CD spectra of the polymers thus prepared in this method displayed complementary mirror image Cotton effect. This polymerization method can be referred to as ‘cholesteric medium inductive asymmetric polymerization’ (C-MAP).

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- Experimental procedure for 2,5-dibromothiophene-3-carboxylic acid undecyl ester*: A solution of azodicarboxylic acid diisopropyl ester (DIAD, in 40% toluene, 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) with a pressure equalized dropping funnel under an argon atmosphere. The mix solution was stirred at room temperature. After 24 h, THF in the mixture was evaporated under reduced pressure. The crude product was purified with a column chromatography (silica gel, dichloromethane) to afford 1.86 g (95.9%) of desired material (yield = 92.9%). Anal. Calcd for C₁₈H₂₄S₃Sn₂: C, 43.65; H, 5.49. Found: C, 43.86; H, 5.47. ¹H NMR (270 MHz, δ from TMS, CDCl₃): 0.38 (s, 18H, CH₃), 7.08 (d, 4H, ThH), 7.26 (d, 2H, ThH).
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