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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.

1. Introduction

Asymmetric synthesis of polymers is one of the most interesting research fields in chemistry such as enantioselective syntheses[1] 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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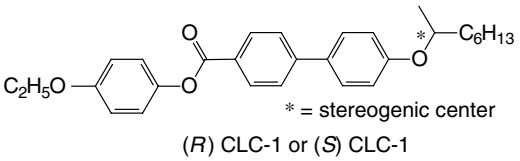


(*R*) CLC-1 or (*S*) CLC-1

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 $Pd(PPh_3)_4$ (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).

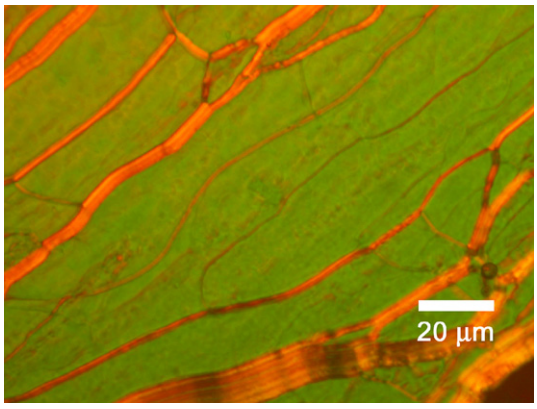
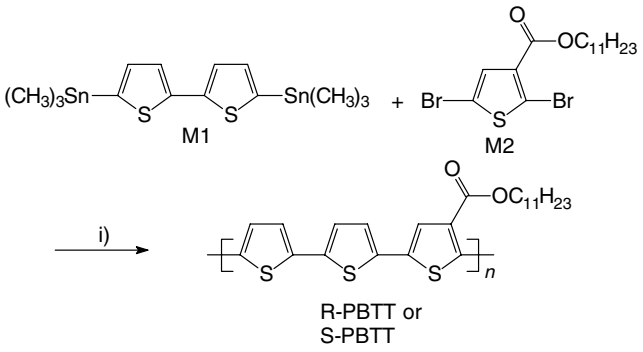


Figure 2. Polarizing optical microscopy image of the reaction mixture in the polymerization process.



Scheme 1. Reagent: (i) $[Pd(PPh_3)_4]$, 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

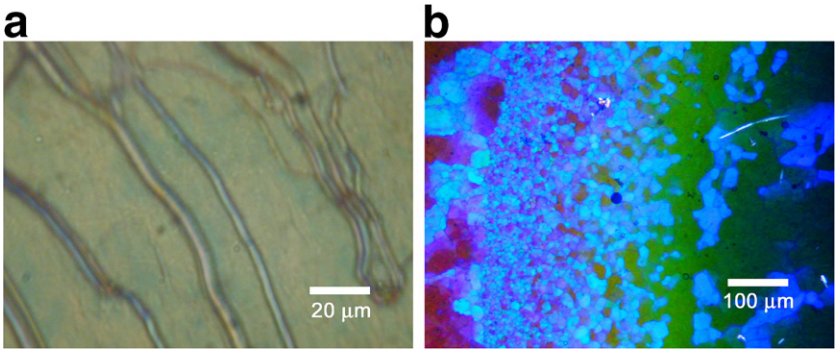


Figure 1. Polarizing optical microscopy images of (*R*) CLC. Oily streak texture of cholesteric phase at 100 °C (a), platelet texture of cubic blue phase at 137 °C (b).