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Synthesis of chiral inducers having double stereogenic centers for electrochemical polymerization in cholesteric liquid crystal medium

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ABSTRACT

An enantiomeric pair of chiral inducers with double chiral carbons was synthesized by a simple three-step reaction strategy. The process affords the chiral inducers with good yield, high enantiomeric excess, and good compatibility with nematic liquid crystal. Addition of a small amount of the chiral inducers thus synthesized in this study produced cholesteric architecture. Electrochemical polymerization in the asymmetric liquid crystal environment affords chiroptically active polymers as atropisomers. The electrochemical polymerization under magnetic field of 4 T affords polymer films with linear dichroism. The polymers exhibit a significant color change from dark-green in the oxidized state to light-green in the reduced state. The redox process of the polymer films in an electrolyte provides a reversible absorption, circular dichroism, and linear dichroism spectral changes.

1. Introduction

Conjugated polymers have been extensively studied since the discovery of electrical conductivity in doped polyacetylene [1]. Electrochemically conductive polymers based on polythiophene and polypyrrole led to their use in a wide range of organic electronic devices including ion gates, and electrochemical diodes [2], as well as electrochromic devices [3], electro-luminescent devices [4], electrodes and batteries [5], and sensors [6,7]. Electrochemical polymerization is one of the most useful methods for preparing conjugated polymers because this method provides a polymer film easily and conveniently on an electrode surface [8]. The polymer displays redox properties and electrochromism [9].

The synthesis of optically active polymers has generated great interest in macromolecular science due to a wide variety of potential applications based on the chiral structure. Optically active polymers have been obtained by several methods, including the polymerization of optically active monomers [10], asymmetric selective polymerization [11], and non-covalent interaction between optically inactive polymers and chiral molecules [12]. Macromolecular optical activity originates from the helical structure of the polymer, is an attractive biomimetic technology and holds promise for prospective applications, such as asymmetric separation and recognition properties [13].

In our previous studies, electrochemical polymerization in cholesteric liquid crystal (CLC) phase afforded helically ordered conjugated polymer films [14]. The polymerization proceeds epitaxially on the electrode surface, which enables growth of the polymer film aligned with the liquid crystal (LC) molecular order. The individual molecules of CLC aggregate in a three-dimensional (3-D) one-handed helical structure, resulting in structural chirality. On the other hand, the electrochemical polymerization under magnetic field affords polymer films with linear polarized electrochromism [15]. The polymer transcribes the molecular arrangement of the LC molecules by an applied magnetic field.

The addition of chiral molecules to nematic LC can induce the CLC architecture. Cholesterol esters have been widely used as additives for induction of helical structure in the nematic LC. However, the use of cholesterol derivatives is limited for the construction of a pair of mirror image helical architecture, because of synthetic difficulty for enantiomeric pairs of cholesterol derivatives. Therefore, the synthesis of a pair of mirror image chiral inducers is important, which are easily accessible, chemically more robust, and widely compatible with any type of nematic LC.

In this research, an enantiomeric pair of chiral inducers with two chiral carbons was synthesized using a simple three-step reaction. Mitsunobu reactions were employed to prepare the chiral inducers. This reaction is found to be particularly effective at inverting the configuration of chiral secondary alcohols [16]. Consequently, the chiral inducers were obtained with high enantiomeric excess (ee). Helical twisting power (HTP) of the chiral inducers was estimated by the Cano-wedge cell method [17]. The electrochemical polymerization of 1,4-di(2-thienyl)benzene (TBT) was performed

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in CLC electrolyte under magnetic field. The CLC electrolyte solution was induced using the chiral inducers. Poly(TBT) synthesized under 0 T displayed a fingerprint texture similar to that of the CLC electrolyte solution. Poly(TBT) synthesized under 4 T exhibited a stripe texture.

Addition of a small amount of the chiral inducers thus synthesized in this study produced chiral LC from achiral nematic of LC solvent. Polymerization in the asymmetric LC environment afforded chiroptically active polymers as atropisomers. In other words, induction by the chiral inducers via environmental change resulted in formation of helical structure of the resultant polymer. The polymerization can be referred to as structure-organized polymerization (SOP). The SOP in this study is derived from the inducers with double chiral centers (double chiral inducers). We report synthesis of the double chiral inducers and electrochemical polymerization by using these compounds for asymmetric environment.

2. Experimental

2.1. Instrumentation and materials

The chemical structure of all intermediates and final products were confirmed by the ^{1}H NMR and ^{13}C NMR spectra (ECS 400 spectrometer using $CDCl_3$ as the deuterated solvent, and tetramethylsilane (TMS) as the internal standard), infrared spectroscopy (Jasco FT-IR 500 spectrometer using KBr method) and elementary analysis (Perkin-Elmer 2400 CHN Elemental Analyzer). Enantiomeric excess was determined by HPLC analysis with a chiral column (CHIRALPAK® IC). Optical rotations of compounds were measured with Jasco P-1010 Polarimeter using tetrahydrofuran (THF) as the solvent. Helical twisting power (β) of the CLC was obtained by using the Cano-wedge cell (EHC, KCRK-03, $\tan\theta = 0.0083$). Electrochemical measurements of polymers were performed using an electrochemical analyzer PGSTAT 12 (AUTOLAB, the Netherlands). Optical texture observations were carried out using a Nikon ECLIPS LV 100 high resolution polarizing microscope with a Nikon LU Plan Fluor lens and a Nikon CFIUW lens. Magnetic orientation was carried out with a drum type cryogen-free superconducting magnet (Japan Magnet Technology, JMT). Circular dichroism (CD), linear dichroism (LD) (Jasco, J-720 spectrometer) and ultraviolet visible (UV–vis) spectra (Jasco, U-3500 spectrophotometer) were recorded. The spin densities of the monomer in the radical cationic state was calculated by density functional theory (DFT) method at the B3LYP/631G*.

All reagents were used after further purification by standard methods. Methyl 4-carboxyphenyl carbonate (**1**) [18], TBT [19] and 4-cyano-4′-octyloxybiphenyl (8OCB) [15] were prepared as previously reported. The compounds 2-octanol, diethyl azodicarboxylate, triphenylphosphine, ammonia, cholesteryl oleyl carbonate and tetrabutylammonium perchlorate (TBAP) were purchased from Tokyo Kasei Kogyo Co., Ltd. The 4-cyano-4′-hexylbiphenyl (6CB) was purchased from Merck. Hexane, acetonitrile, chloroform, THF and ethanol (EtOH) were purchased from Nacalai Tesque Co., Ltd. Silica gel 60 N was purchased from Kanto Chemical Co., INC.

3. Synthesis

3.1.1. Syntheses of chiral inducers

3.1.1.1. ***(S)-4*-(1-methyl carbonic acid)-benzoic acid 1-methyl-heptyl ester *(S)-2***

(R)-(−)-2-octanol (1.33 g, 10.2 mmol) and diethyl azodicarboxylate (5.67 g, 28.0 mmol) were slowly added dropwise to a stirred mixture of triphenylphosphine (3.21 g, 12.2 mmol) and methyl 4-carboxyphenyl carbonate (**1**) (2.01 g, 10.2 mmol) in dry THF (20 mL) under argon at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 24 h. After the completion of the reaction was checked by TLC, the resulting solution was extracted with chloroform. After drying over $MgSO_4$ and filtration, chloroform was removed using a rotary evaporator. The crude product was purified by silica gel column with chloroform to give a colorless oil (2.67 g, 8.7 mmol, yield = 87%), which was dried in vacuo. ^{1}H NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 0.80 (t, 3H), 1.25 (m, 11H), 1.59 (m, 2H), 3.85 (s, 3H), 5.07 (sextet, 1H), 7.17 (d, 2H), 8.00 (d, 2H). ^{13}C NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 165.2, 154.3, 153.6, 131.1, 128.7, 120.8, 72.0, 55.6, 36.0, 31.7, 29.1, 25.4, 22.6, 20.1, 14.1. $[\alpha]_{589}^{RT} = -3.21°$ (0.0100 g/mL; THF) for 96% ee.

3.1.1.2. ***(R)-4*-(1-methyl carbonic acid)-benzoic acid 1-methyl-heptyl ester *(R)-2***

This compound was prepared using the same method that was described for **(*S*)-2**. Quantities used: triphenylphosphine (3.19 g, 12.2 mmol), (*S*)-(+)-2-octanol (1.60 g, 12.3 mmol), methyl 4-carboxyphenyl carbonate (**1**) (2.01 g, 10.2 mmol), diethyl azodicarboxylate (5.68 g, 28.1 mmol) and dry THF (20 mL). Quantities yield: colorless oil (2.78 g, 9.0 mmol, yield = 89%). ^{1}H NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 0.89 (t, 3H), 1.38 (m, 11H), 1.68 (m, 2H), 3.94 (s, 3H), 5.16 (sext, 1H), 7.27 (d, 2H), 8.09 (d, 2H). ^{13}C NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 165.3, 154.3, 131.1, 128.7, 120.8, 72.0, 55.6, 36.0, 31.7, 29.1, 25.4, 22.6, 20.1, 14.1. $[\alpha]_{589}^{RT} = +3.00°$ (0.0344 g/mL; THF) for 96% ee.

3.1.1.3. ***(S)-4*-hydroxy-benzoic acid 1-methyl-heptyl ester *(S)-3***

A solution of **(*S*)-2** (2.25 g, 7.3 mmol) in EtOH (10 mL) was added dropwise to 35% ammonia solution (30 mL) at room temperature. TLC analysis showed complete reaction after a period of 1 h. After EtOH was removed using a rotary evaporator, the resulting solution was extracted with dichloromethane, and the organic phase was then dried over $MgSO_4$ and filtered. The crude product was purified by a silica gel column (chloroform/ethyl acetate, 1:3 v/v) to give a colorless liquid (1.65 g, 6.6 mmol, yield = 90%), which was dried *in vacuo*. ^{1}H NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 0.87 (t, 3H), 1.35 (m, 11H), 1.65 (m, 2H), 5.12 (sext, 1H), 6.34 (s, 1H), 6.88 (d, 2H), 7.95 (d, 2H). ^{13}C NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 166.5, 160.1, 131.9, 123.1, 115.2, 71.8, 36.1, 31.8, 29.2, 25.5, 22.6 20.1, 14.1. $[\alpha]_{589}^{RT} = -4.13°$ (0.0166 g/mL; THF) for 95% ee.

3.1.1.4. ***(R)-4*-hydroxy-benzoic acid 1-methyl-heptyl ester *(R)-3***

This compound was prepared using the same method that was described for **(*S*)-3**. Quantities used: **(*R*)-2** (2.41 g, 7.8 mmol), EtOH (10 mL), ammonia (30 mL). Quantities yield: colorless liquid (1.96 g, 7.8 mmol, yield = 99%). ^{1}H NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 0.87 (t, 3H), 1.35 (m, 11H), 1.66 (m, 2H), 5.12 (sext, 1H), 6.35 (s, 1H), 6.88 (d, 2H), 7.95 (d, 2H). ^{13}C NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 166.6, 160.0, 131.9, 123.0, 115.2, 71.8, 36.1, 31.8, 29.2, 25.5, 22.7, 20.2, 14.1. $[\alpha]_{589}^{RT} = +4.16°$ (0.0139 g/mL; THF) for 93% ee.

3.1.1.5. ***(S,S)-4*-(1-methyl-heptyloxy)-benzoic acid 1-methyl-heptyl ester *(S,S)-4***

This compound was prepared using the same method that was described for **(*S*)-2**. Quantities used: triphenylphosphine (1.65 g, 6.3 mmol), (*R*)-(−)-2-octanol (0.68 g, 5.2 mmol), **(*S*)-3** (1.31 g, 5.2 mmol), diethyl azodicarboxylate (2.92 g, 14.4 mmol) and dry THF (20 mL). The crude product was purified by a silica gel column (chloroform/*n*-hexane, 2:3 v/v) to give a colorless oil (1.58 g, 4.3 mmol, yield = 83%), which was dried *in vacuo*. ^{1}H NMR (400 MHz, δ from TMS (ppm), $CDCl_3$): δ 0.81 (m, 6H), 1.29 (m, 22H), 1.51 (m, 2H), 1.66 (m, 2H), 4.37 (sext, 1H), 5.05 (sext, 1H), 6.81 (d, 2H), 7.90