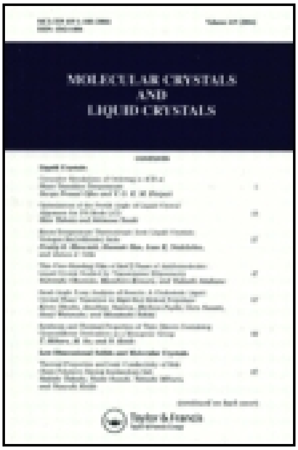

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of Poly(1,4-bis(3′,4′-ethylenedioxythiophene)-phenylene) (PBEDOT-P) in Cholesterics

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Version of record first published: 31 Aug 2012.

To cite this article: Akitsu Tsujimoto & Hiromasa Goto (2008): Synthesis of Poly(1,4-bis(3′,4′-ethylenedioxythiophene)-phenylene) (PBEDOT-P) in Cholesterics, Molecular Crystals and Liquid Crystals, 493:1, 82-92

To link to this article: http://dx.doi.org/10.1080/15421400802406745

Mol. Cryst. Liq. Cryst., Vol. 493, pp. 82–92, 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802406745

Synthesis of Poly(1,4-bis(3′,4′-ethylenedioxythiophene)-phenylene) (PBEDOT-P) in Cholesterics

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Electrochemical polymerization of 1,4-bis(3′,4′-ethylenedioxythiophene)-phenylene (BEDOT-P) was performed in a cholesteric liquid crystal (CLC) as an anisotropic electrolyte solution. The surface morphology and optical properties of the polymer (poly(BEDOT-P)/CLC) thus prepared in the cholesteric electrolyte were examined.

Keywords: cholesteric liquid crystals; conducting polymers; electrochemical polymerization

INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most successful polymers for practical applications, such as capacitors, sensors, light-emitting diodes (LEDs), transistors, and photovoltaics [1–4]. Especially, PEDOT and its derivatives have been studied in regard to electrochromics, which exhibit reversible and highly stable changes in optical properties upon the application of a voltage. The definition of electrochromism was extended from that of a color change in the visible spectrum to a multispectral energy modulation that might cover ultraviolet (UV), near infrared (NIR), mid infrared (mid-IR), and microwave regions, with "color" corresponding to the response of detectors at these wavelengths.

It is remarkable that a monomer such as 1,4-bis(3′,4′-ethylenedioxythiophene)-phenylene (BEDOT-P) having a rigid rod-like shape can have a good affinity for liquid crystals in blends. And poly(BEDOT-P) is expected to be one of the polymers having good electrochromic

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properties. The preparation method and electrochromism of BEDOT-P have been reported previously [5].

This article reports a new synthetic route for preparing the BEDOT-P monomer, polymerization of BEDOT-P in a cholesteric liquid crystal (CLC) electrolyte solution [6–10], observation of the surface structure by scanning electron microscopy (SEM) and polarizing optical microscopy (POM), and the spectroelectrochemical properties of the polymers.

EXPERIMENTAL

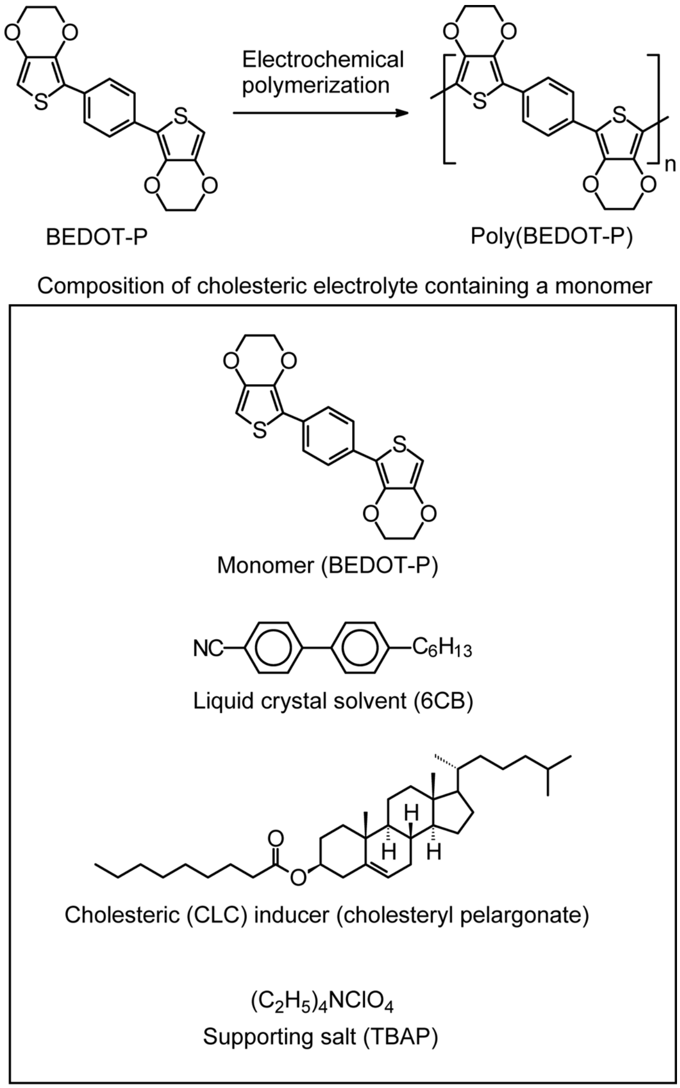
Synthesis

2-Tributylstannyl-3,4-ethylenedioxythiophene (TBS-EDOT)

In a three-necked round bottle flask, *N,N,N′,N′*-tetramethylethylenediamine, TMEDA, (11.96 g, 58 mmol) was slowly added to a solution of 3,4-ethylenedioxythiophene (8.27 g, 58 mmol) in 50 mL of tetrahydrofuran (THF) under dry ice-cooling in an argon atmosphere, and the mixture was stirred for 10 min. Then, a solution of *n*-butyl lithium (22.7 mL, 58 mmol) in *n*-hexane was slowly added to the mixture by a pressure-equalized dropping funnel, and the mixture was stirred for several minutes at room temperature. The mixture was refluxed at 55°C for 30 min. Next, tributylstannyl chloride (11.56 g, 58 mmol) was gradually added to it, and the mixture was stirred for another 3 h. The color of the mixture turned pale brown. The solvent in the mixture was evaporated and washed with water thoroughly. Then the organic layer was extracted with dichloromethane using a separate funnel and was evaporated under reduced pressure to afford a crude product. Purification by column chromatography (silica gel, dichloromethane) followed by evaporation under reduced pressure afforded 12.27 g of the desired material (a transparent yellow liquid) (y = 49.1%). In the purification process, the silica gel in the column was pretreated with triethylamine for protecting the tributhyl tin on the EDOT [11]. ^{1}H NMR ($CDCl_3$, ppm): 0.97 (t, 9H); 1.00–1.22 (m, 6H); 1.34 (sext, 6H); 1.57 (quint, 6H); 4.14 (d, 2H); 4.18 (d, 2H); 6.32 (s, 1H).

1,4-Bis(3′,4′-ethylenedioxythiophene)-phenylene

1,4-bis(3′,4′-ethylenedioxythiophene)-phenylene (BEDOT-P) was prepared via a $Pd(PPh_3)_4$-catalyzed Stille coupling reaction as illustrated in Scheme 1. In a small Schlenk tube, TBS-EDOT (1.21 g, 2.8 mmol) was added to a solution of 1,4-dibromobenzene (0.33 g, 1.4 mmol) in 3.5 mL THF with stirring under an N_2 gas flow. Then, $[Pd(PPh_3)_4]$



SCHEME 1 Constituents of cholesteric liquid crystal electrolyte solution containing monomer.

(0.04 g, 2.8×10^{-2} mmol) was added to the solution quickly, 3.5 mL of THF was added to the reaction mixture, and refluxed for 24 h with stirring. The solvent in the mixture was evaporated, washed with water thoroughly, the organic layer was extracted with chloroform using a separate funnel, and the organic layer was evaporated under reduced pressure to afford a crude product. Purification by column chromatography (silica gel, dichloromethane) followed by evaporation under reduced pressure afforded 0.89 g of the desired material (y ~ 100%). ^{1}H NMR ($CDCl_3$, ppm): 4.15 (d, 2H); 4.24 (d, 2H); 6.29 (s, 2H); 7.7 (d, 2H).

Electropolymerization

Poly(BEDOT-P)/CLC

n-Hexylcyanobiphenyl (6CB) was employed as the solvent for the electrolyte solution for the electropolymerization. The molecular structures of the materials used for the electrochemical polymerization are given in Scheme 1. We prepared the cholesteric liquid crystal (CLC) electrolyte solution with composition of 7.5 wt% of cholesteryl pelargonate (CLC inducer), 9.2 wt% of BEDOT-P (monomer), and 4.2×10^{-2} wt% of tetrabutyl ammonium perchlorate (TBAP). The CLC mixture was sandwiched between indium tin oxide (ITO-coated electrodes using a Teflon Sheet (thickness 0.19 mm) as a spacer. The CLC mixture was charged into the reaction cell using a pipette. The reaction cell was gradually cooled to 14°C to obtain a good fingerprint texture. A constant voltage of $16\ \mathrm{V \cdot mm^{-1}}$ was then applied to the cell, which did not affect the optical texture of the CLC mixture. The polymerization temperature was maintained at 14°C using a Peltier device as a temperature control stage in order to preserve the CLC phase in the course of the polymerization. The surface temperature of the reaction cell was monitored using a radiation thermometer.

After 20 min, a film of insoluble and infusible polymer was deposited on the anode side of the ITO electrode. The film was frequently washed by acetone, water, and CH_2Cl_2, and dried at room temperature to afford the polymer film, abbreviated as poly(BEDOT-P)/CLC.

Infrared Absorption Spectroscopy

Figure 1 shows infrared (IR) absorption spectra of 6CB, cholesteryl pelargonate (CLC inducer), and the PEDOT-P. The PEDOT-P showed an absorption band at $2934\ \mathrm{cm^{-1}}$ assignable to ν_{CH2} of oxyethylene ring. An absorption band at $1590\ \mathrm{cm^{-1}}$ is due to $\nu_{C=C}$ of benzene ring. Absorption band at $1395\ \mathrm{cm^{-1}}$ comes from ν_{CH2} bending of oxyethylene ring. Oxyethylene absorption bands are observable at $1181\ \mathrm{cm^{-1}}$ ($\nu_{C\text{-}C}$ streching) and $1080\ \mathrm{cm^{-1}}$ ($\nu_{C\text{-}O}$ streching). On the other hand, the PEDOT-P displays no absorption bands related to the characteristic absorption bands of 6CB ($2227\ \mathrm{cm^{-1}}$, ν_{CN}, terminal CN group) and

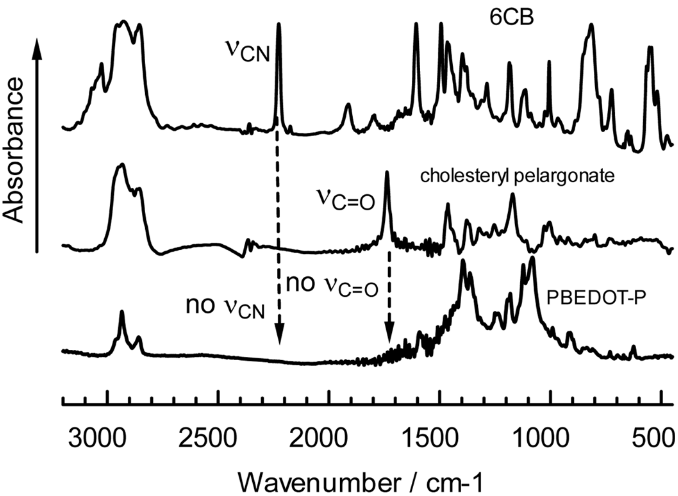


FIGURE 1 IR spectra of 6CB, CLC inducer, and PEDOT-P (polymer).

cholesteryl pelargonate (1737 cm^{-1}, $\nu_{C=O}$, ester moiety). The IR measurements suggest that the polymer contains no cholesteryl pelargonate or 6CB.

RESULTS AND DISCUSSION

Surface Structure

A polarizing optical microscopy image of the CLC electrolyte solution containing monomer is shown in Fig. 2. The liquid crystal electrolyte thus prepared displays a fingerprint texture typical of cholesteric liquid crystals. Figure 3 shows an optical microscopy image of the polymer synthesized in the CLC electrolyte, and Fig. 4 displays a surface image of the polymer obtained with a scanning electron microscope (SEM). The polymer film displays a fingerprint texture quite similar to that of cholesterics. This result indicated that the polymer was an exactly replicated macroscopic arrangement of the CLC as an electrolyte solution during the polymerization.

As can be seen in Figs. 3 and 4, a half-pitch of the polymer was approximately 1 μm (distance between stripes). It can be considered that the CLC field provides a sequential helical pattern as a molecule molds during this polymerization. The CLC field thus provides a “key hole” to the monomer (BEDOT-P) during the polymerization process.

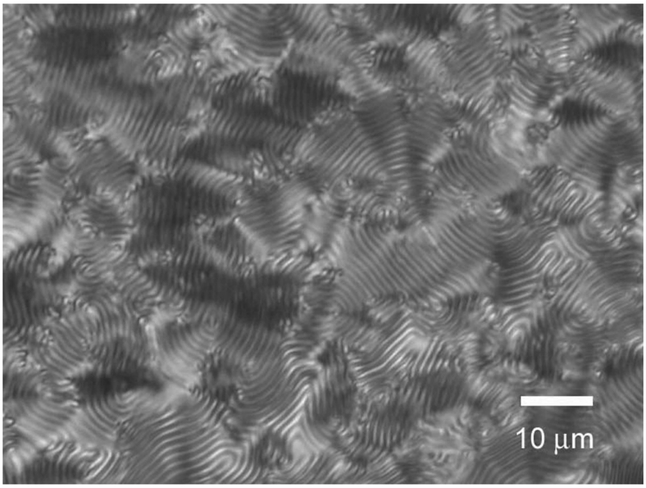


FIGURE 2 Polarizing optical microscopy image of CLC mixture containing monomer at 14°C.

Cylic Voltammetry

Cyclic voltammetry (CV) measurement of the polymer in a monomer-free 0.1 M TBAP/acetonitrile solution was carried out. In the CV, an oxidation peak (E_{pa}) at 0.74 V and a reduction trough (E_{pc}) at 0.33 V

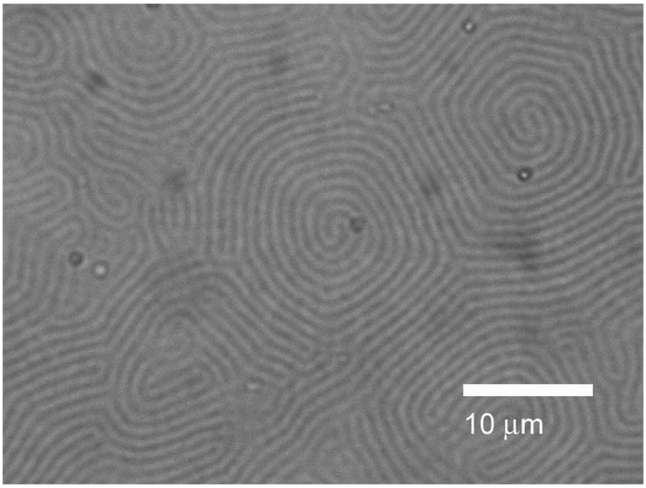


FIGURE 3 Optical microscopy image of poly(BEDOT-P)/CLC.

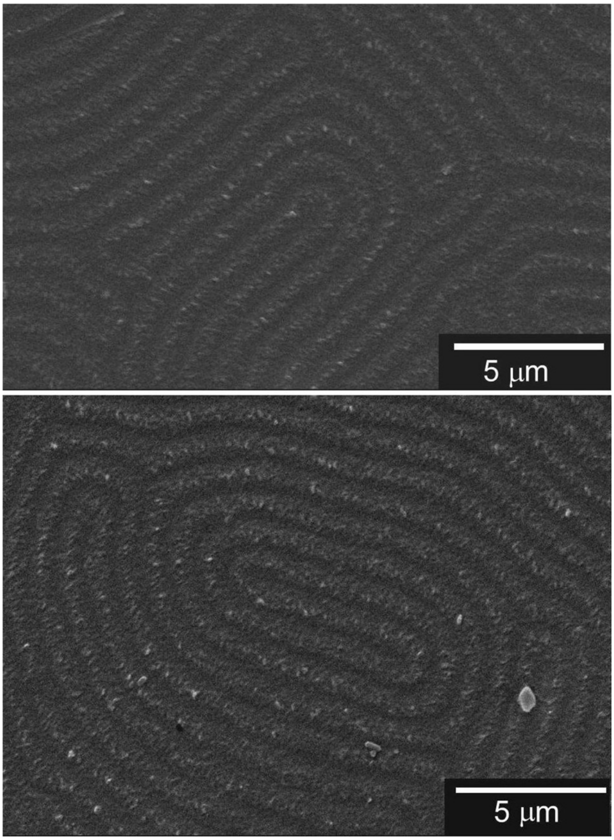


FIGURE 4 Scanning electron microscopy (SEM) image of poly(BEDOT-P)/CLC.

were observed. The signal at 0.74 V is attributable to the generation of a radical cation (polaron) on the poly(BEDOT-P)/CLC. The polymer film is blue-purple in the oxidized state (electrochemically doped), and orange in the reduced state (dedoped). These color changes indicate a change in the electronic structure of the polymer via the electrochemical process.

Colorimetry

In consideration of an electrochromic material for use in display applications, it is essential to precisely define its color [12]. Therefore, we implemented colorimetry techniques to elucidate the optical

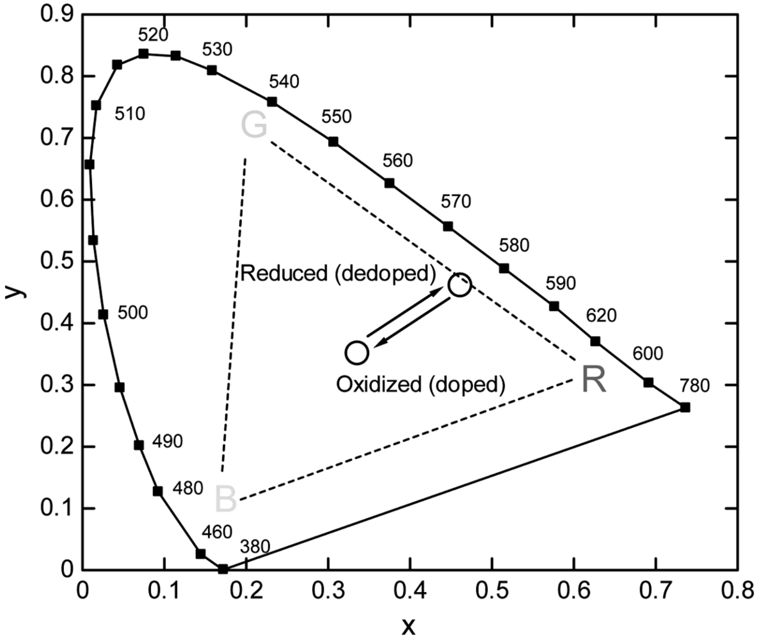


FIGURE 5 CIE $x-y$ diagram recorded while the polymer was held at potentials ranging from 0 V via 1 V to 0 V versus Ag/Ag$^+$.

properties of poly(BEDOT-P)/CLC. Figure 5 represents the Commission Internationale de I'Eclairage (CIE) $x-y$ diagram for poly(-BEDOT-P)/CLC, which displays the polymer switch from the orange reduced state at 0 V to the blue-purple oxidized state at 1 V. The x and y values in the oxidized state are 0.335745 and 0.351146, respectively. The x and y values in the reduced state are 0.461599 and 0.461158, respectively.

Diffraction

The preparation and properties of the gratings and photonic crystals fabricated with CLCs have been reported [13–15]. The polymer synthesized in this study is not CLC, but it can exhibit a diffraction phenomenon because the polymer has a CLC-like periodic structure. The fingerprint structure of poly(BEDOT-P)/CLC produced by molecular imprinting from the CLC electrolyte can lead to two optical effects, the iridescent reflection of light, and the diffraction of light [16].

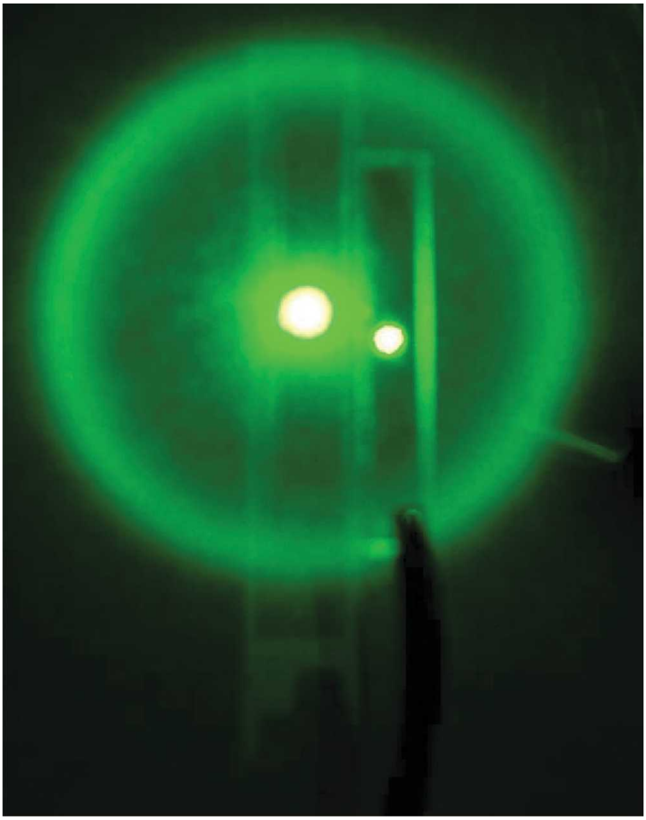


FIGURE 6 Circular diffraction patterns upon irradiation of green laser to the polymer.

Rainbow-colored reflection occurs under irradiation with white light, and the reflected color varies with the angle. This iridescent reflection originates from the periodic fingerprint structure of the polymer surface.

The diffraction of light is observed by irradiating the poly(BEDOT-P)/CLC film on the ITO electrode with a laser set perpendicular to the film surface and observing the transmitted pattern. A circular diffraction pattern is produced, as shown in Fig. 6. The polymer plays the role of random grating, resulting in a circular diffraction pattern. It is expected that the diffraction constant can be controlled by changing the helical pitch length of the CLC electrolyte solution employed for electrochemical polymerization.

CONCLUSION

The CLC electrolyte solution shows a fingerprint texture typical of cholesteric liquid crystals. Poly(BEDOT-P)/CLC, electrochemically polymerized in the CLC electrolyte, displays a fingerprint texture quite similar to that of cholesterics. The helical half-pitch of the polymer was ~1 μm, corresponding to that of the cholesteric electrolyte solution. This result strongly suggests that the electrochemically prepared polymer thus prepared in the CLC replicates the macroscopic helical architecture of CLC. The present polymer displays iridescent reflection upon white light irradiation, and the diffraction of light.

ACKNOWLEDGMENTS

We would like to thank the Chemical Analysis Center of the University of Tsukuba for the NMR spectra and elemental analysis data, and the Engineering Workshop of the University of Tsukuba for the glasswork.

EXPERIMENTAL INFORMATION OF THE OPTICAL MICROSCOPE

Optical texture observations were performed using a Nikon ECLIPS LV 100 high resolution polarizing microscope with a Nikon LU Plan Fluor lens and a Nikon CFIUW lens. The observation of the texture was carried out at ×1000 and ×500 without an immersion oil.

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