Preparation of Optically Active Pyridine-Based Conducting Polymer Films Using a Liquid Crystal Electrolyte Containing a Cholesterol Derivative

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ABSTRACT: Optically active poly(1,4-di(2-thienyl)phenylene), poly(terthiophene), poly(bithiophene), and poly-(2,5-di(2-thienyl)pyridine) are successfully prepared by asymmetric electrochemical polymerization in a cholesteric electrolyte. The polymers thus synthesized are confirmed by polarizing optical microscopy to assume the double-spiral optical texture of the cholesteric liquid crystal electrolyte. In the reduced state, these polymers exhibit an intense Cotton effect in circular dichroism measurements. This optically active electrochromism is reversible by appropriate adjustment of applied voltage (redox state). Cyclic voltammetry measurements indicate that poly-(2,5-di(2-thienyl)pyridine) has an electrochemical n-dopable property.

Introduction

Conjugated polymers are of significant chemical and physical interest, particularly with respect to application in semiconductor devices.[1] The synthesis of optically active conjugated polymers is also attractive as a specific application of conducting polymer technology. Early research on the synthesis of optically active polyacetylene derivatives[2] has shown that the circular dichroism (CD) spectra of derivatives bearing chiral substituents exhibit optically active bands attributable to the presence of an inherently chiral polyene chromophore in the main chain, implying the formation of a helical conformation.

Several methods have been employed to prepare optically active polymers, including the polymerization of optically active monomers,[3−6] asymmetric selective polymerization,[7,8] and the introduction of a chiral group into an optically inactive polymer via polymer reactions.[9] Polymers thus prepared contain an asymmetric carbon in the side or main chain. More recently, optically active polymers have been prepared from optically inactive monomers using cholesteric liquid crystal (CLC) as a reaction field.[10] Our group has developed a new electrochemical polymerization method in which CLC electrolyte is employed for the preparation of nonsubstituted optically active conjugated polymers with chirality.[11] The polymers thus prepared display intense CD absorption in the reduced state and a much weaker signal in the oxidized state.[12] Control of the electrochemical doping−dedoping (oxidation−reduction) process appears to allow for a reversible change in CD intensity as a form of optically active electrochromism.

In the present study, a set of optically active polymers is prepared from monomers consisting of a three-ring unit (thiophene−arylene−thiophene) with no chiral substituents by electrochemical polymerization in a CLC electrolyte. Phenylene, thiophene, and pyridine are examined as arylene units in the monomer. As polymers containing a pyridine ring in the monomer unit have been reported to have stable n-dopable states,[13] electrochemical n-doping and CD are also investigated for the optically active conducting polymers prepared in this study.

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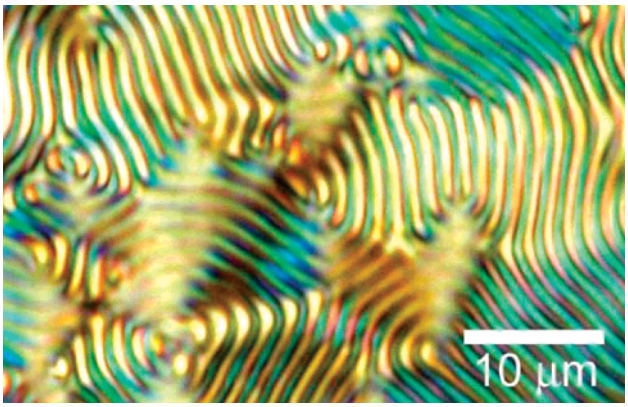

Figure 1. Polarizing optical microscopy (POM) image of CLC electrolyte containing 2,5-TPyT.

Experimental Section

Materials. Terthiophene (3T) and 2-trimethylstannylthiophene were purchased from Sigma Aldrich. Bithiophene (2T) was obtained from Tokyo Kasei (TCI). Cholesteryl oleyl carbonate and tetrabutylammonium perchlorate (TBAP) were purchased from TCI, and 4-cyano-4′-*n*-hexyl biphenyl (6CB) was obtained from Merck. 1,2-Dimethoxyethane and chloroform were purified by distillation prior to use.

General Procedure for Synthesis of Monomers. Thiophene-2-boronic acid (11.7 mmol), dibromoarylene (3.9 mmol), and sodium acid carbonate (11.7 mmol) were mixed into a solution of 1,2-dimethoxyethane/water (48 mL/6 mL) under argon. After refluxing the mixture for 1 h, 0.16 mmol of tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] (0.18 g) was added, and after a further 24 h, the reaction solvent in the mixture was evaporated. The remainder was rinsed with water and extracted using chloroform, and the organic layer was evaporated. Purification by chromatography on silica gel (eluent: chloroform) followed by evaporation afforded the desired material as a solid. Monomer yields: 1,4-di(2-thienyl)phenylene (1,4-TPhT), 92.0%; 2,5-di(2-thienyl)pyridine (2,5-TPyT), 93.8%; 2,6-di(2-thienyl)pyridine (2,6-TPyT), 63.8%; 3,5-di(2-thienyl)pyridine (3,5-TPyT), 92.1%. All compounds were confirmed to be ∼100% pure by thin-layer chromatography.[14]

Preparation of Cholesteric Liquid Crystal Electrolyte. It is generally known that CLC with a helical structure can be formed

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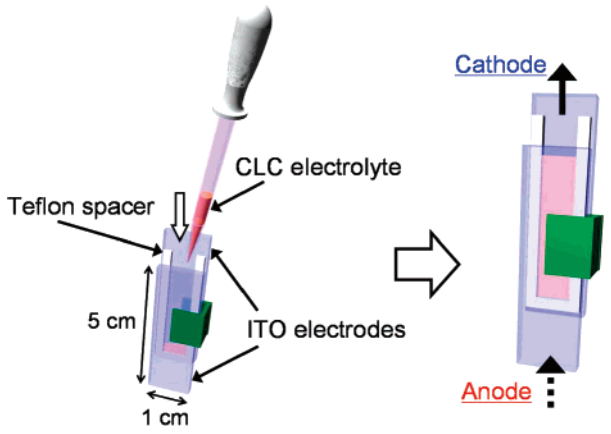

Figure 2. Polymerization cell.

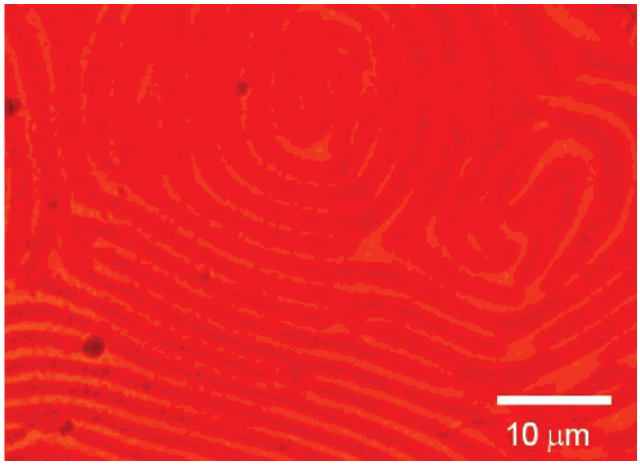

Figure 3. Polarizing optical microscopy (POM) image of poly(2,5-TPyT)*.

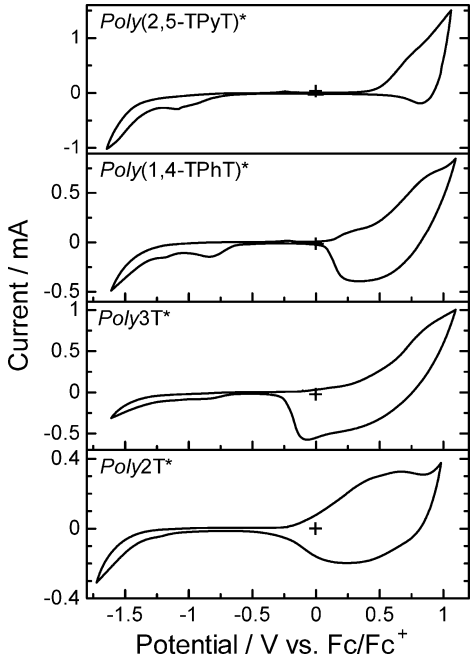

Figure 4. Cyclic voltammetry results (vs Fc/Fc^+) for poly(2,5-TPyT)*, poly(1,4-TPhT)*, poly3T*, and poly2T* on ITO electrodes in monomer-free 0.1 M TBAP/acetonitrile solution (scan rate: 20 mV s^{-1}).

from nematic liquid crystal (NLC) by the addition of a small amount of an optically active molecule as a chiral inducer. Although binol derivatives with axial chirality were used as a chiral inducer in

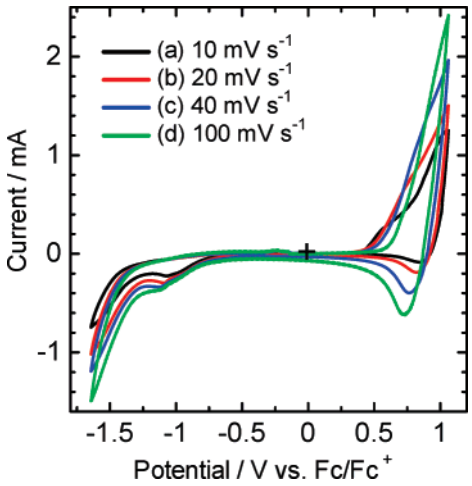

Figure 5. Cyclic voltammetry results for poly(2,5-TPyT)* in 0.1 M TBAP/acetonitrile solution at scan rates of (a) 10, (b) 20, (c) 40, and (d) 100 mV s^{-1}.

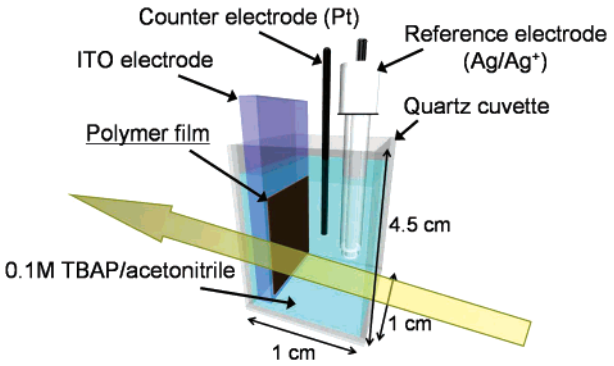

Figure 6. Experimental cell for spectroelectrochemistry.

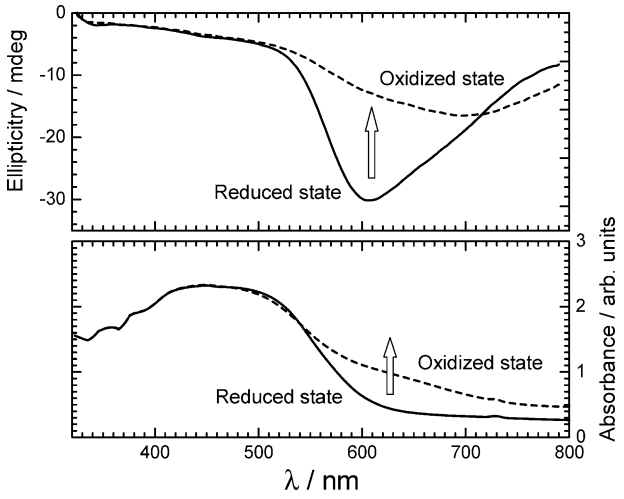

Figure 7. CD spectra (upper) and UV−vis absorption spectra (lower) for poly(2,5-TPyT)* at +1.06 V (oxidized state; dashed line) and −0.14 V (reduced state; solid line) vs Fc/Fc^+ in 0.1 M TBAP/acetonitrile solution.

previous work,[12] a multistep reaction is required for the preparation of the binol derivatives considered here. A cholesterol derivative (cholesteryl oleyl carbonate) was therefore employed in the present study as a convenient chiral inducer offering low cost, strong helical twisting power, and good affinity with 4-cyano-4′-*n*-hexyl biphenyl (6CB), which is used as the NLC solvent.

The CLC electrolyte was prepared from cholesteryl oleyl carbonate as a chiral inducer, tetrabutylammonium perchlorate (TBAP) as a supporting salt, 6CB as an NLC solvent, and a monomer. The molecular structures and composition of the

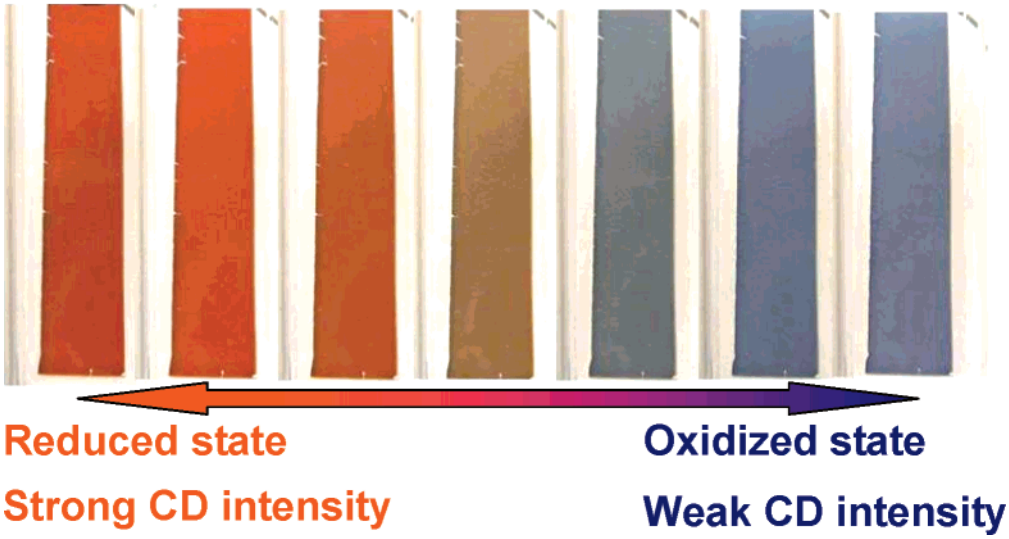

Figure 8. Electrochromism of poly2T* (−0.11 to 1.10 V vs Fc/Fc^{+}) in 0.1 M TBAP/acetonitrile solution.

Table 1. Molecular Structure and Composition of Cholesteric Liquid Crystal (CLC) Electrolytes Containing a Monomer

CLC electrolyte containing monomer			
Monomer	Nematic Liquid crystal NC–C_6H_{13} 6CB[a]	Chiral inducer $CH_3(CH_2)_7$–$(CH_2)_8O$– Cholesteryl oleyl carbonate	Supporting salt $[CH_3(CH_2)_3]_4NClO_4$ TBAP[b]
1,4-TPhT, 2.2 mol%	94.7 mol%	3.0 mol%	0.1 mol%
3T, 2.1 mol%	94.8 mol%	3.0 mol%	0.1 mol%
2T, 3.1 mol%	93.9 mol%	2.9 mol%	0.1 mol%
2,5-TPyT, 4.4 mol%	93.1 mol%	2.1 mol%	0.4 mol%
2,6-TPyT, 4.4 mol%	93.1 mol%	2.1 mol%	0.4 mol%
3,5-TPyT, 4.4 mol%	93.1 mol%	2.1 mol%	0.4 mol%

[a] 4-Cyano-4′-*n*-hexyl biphenyl. [b] Tetrabutylammonium perchlorate.

constituents of the CLC electrolytes are summarized in Table 1. Polarizing optical microscopy (POM) confirmed that the electrolytes exhibited thermotropic LC character and a fingerprint texture typical of CLC. The optical texture of the CLC electrolyte containing the monomer 2,5-TPyT, the helical pitch length of which was ca. 3.9 μm, is shown in Figure 1.

Asymmetric Electrochemical Polymerization. The CLC electrolyte containing a monomer was injected between sandwiched indium tin oxide (ITO)-coated electrodes (surface area: 1 cm × 5 cm) using a Teflon sheet (thickness: 0.19 mm) as a spacer (Figure 2). A constant direct current (dc) voltage of 5 V was then applied to the cell. The application of this polymerization voltage did not affect the optical texture of the CLC electrolyte. However, repeated voltage scanning for cyclic voltammetry was found to destroy the helical structure. During polymerization, the temperature was maintained at 25.5 °C in order to preserve the thermotropic CLC phase. After 1 h of reaction, a thin film had deposited on the anode side of the ITO electrode. The film, which was insoluble in either

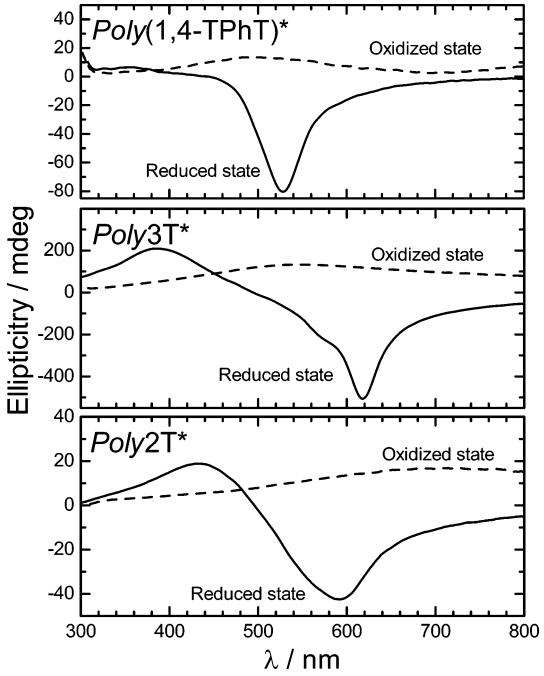

Figure 9. CD spectra for poly(1,4-TPyT)* (upper), poly3T* (middle), and poly2T*(lower) in monomer-free 0.1 M TBAP/acetonitrile solution. Dashed lines denote oxidized state (upper, middle, +1.10 V; lower, +0.98 V vs Fc/Fc^+), and solid lines denote reduced state (upper, middle, −0.11 V; lower, −0.22 V vs Fc/Fc^+).

water or organic solvent, was washed with methanol and acetone and then dried. The CLC electrolyte can be reused repeatedly in this polymerization process.

Poly(1,4-TPhT)*, poly3T*, poly2T*, and poly(2,5-TPyT)* were successfully prepared by this method. However, the polymerization of 2,6-TPyT and 3,5-TPyT did not afford self-standing films, attributable to the low polymerization activity of these monomers, which require the formation of a quinonoid structure of polarons (cation radical) or bipolarons (dication). The poly(2,6-TpyT) film on ITO was very fragile and broke in the washing process, while no poly(3,5-TpyT) film was afforded by in the present polymerization procedure.

Characterization

Optical Texture. Figure 3 shows the double-spiral texture of poly(2,5-TPyT)* under POM (pitch length: 4.0 μm). This pattern resembles the optical texture of the original CLC electrolyte (Figure 1). Poly(1,4-TPhT)*, poly3T*, and poly2T* also display the fingerprint texture characteristic of the CLC. The polymer films exhibit weak birefringence under POM, indicating that the texture is due to the polymer itself, not the LC. The polymers thus appear to replicate the structure of the CLC, demonstrating the effectiveness of CLC as an asymmetric reaction field. The fingerprint texture was observed with transmitted light but not with reflected light, confirming that the optical texture is due to molecular arrangement and not a surface convex−concave structure (i.e., the polymer surface is flat). This suggests that the chiral aggregate was formed upon polymerization.

Cyclic Voltammetry. The electrochemical properties of the poly(2,5-TPyT)*, poly(1,4-TPhT)*, poly3T*, and poly2T* films on ITO were analyzed by cyclic voltammetry in a monomer-free 0.1 M TBAP/acetonitrile solution. Figure 4 shows the cyclic voltammograms for these polymers (vs Fc/Fc^+), and Figure 5 shows cyclic voltammograms for the poly(2,5-TPyT) film at scan rates of 10, 20, 40, and 100 mV s^{-1} in the monomer-free 0.1 M TBAP/acetonitrile solution. The redox switching in the

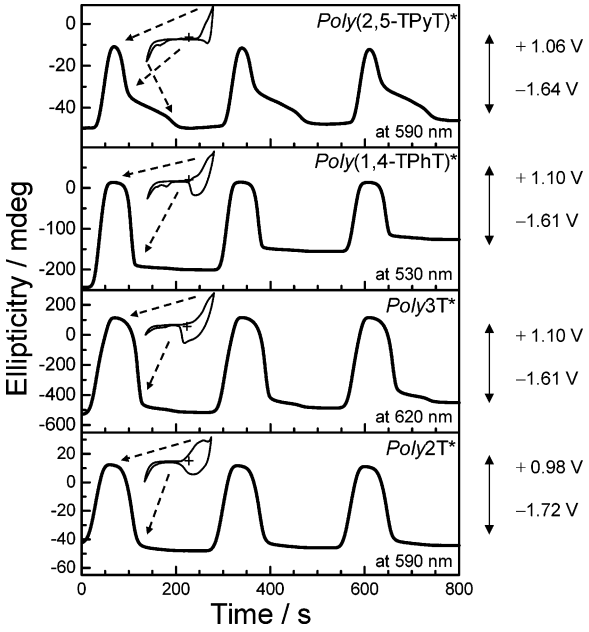

Figure 10. Reversible change in CD intensity for poly(2,5-TPyT)* (−1.64 to +1.06 V vs Fc/Fc^+), poly(1,4-TPhT)* and poly3T* (−1.61 to +1.10 V vs Fc/Fc^+), and poly2T* (−1.72 to +0.98 V vs Fc/Fc^+) (scan rate: 20 mV s^{-1}).

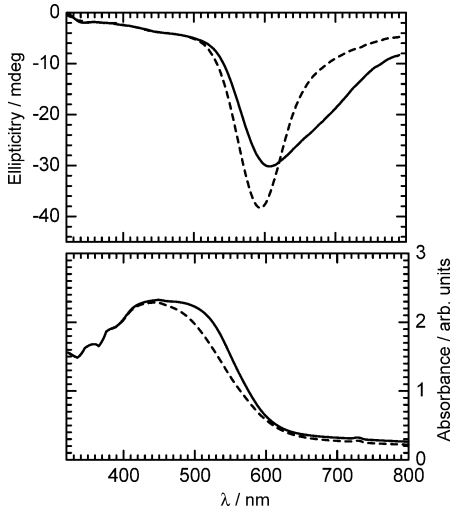

Figure 11. CD spectra (upper) and UV−vis absorption spectra (lower) for poly(2,5-TPyT) at −0.14 V (solid line) and −1.64 V (dashed line) vs Fc/Fc^+ in monomer-free 0.1 M TBAP/acetonitrile solution.

monomer-free electrolyte solution indicates a well-defined and quasi-reversible redox process. These polymers are thus electroactive and were well adhered to the ITO electrode.

Optical Properties. Figure 6 shows the cell employed for in-situ CD and ultraviolet−visible (UV−vis) spectroscopy measurements during the redox process. The polymer on the ITO slide (working electrode), a platinum wire counter electrode, and an Ag/Ag^+ reference electrode were set in a quartz cuvette containing the monomer-free 0.1 M TBAP/acetonitrile solution. CD and UV−vis absorption spectra were then measured while the scanning the voltage applied to the polymer. The spectra for poly(2,5-TPyT)* are shown in Figure 7. The polymer exhibits a strong Cotton effect in the reduced state and reduced CD response in the oxidized state. The color of the polymer also changes from orange to black. In the case of poly2T*, the color was changed from dark red to blue (Figure 8). Poly(1,4-TPhT)*, poly3T*, and poly2T* exhibit similar spectroelectro-

chemistry (Figure 9). The change in CD intensity accompanied by a change in the color of the polymers in the redox process (doping−dedoping) is a form of optically active electrochromism. The synthetic method presented here thus affords polymers with controllable optical activity. The optical texture of the polymer is the same in both the reduced and oxidized states, indicating that the optical texture of the film is independent of the optically active electrochromism.

The n-doping effect of optical activity was examined by observing the change in CD with repeated voltage scanning.[13] The CD intensities were monitored at 590 nm for poly(2,5-TPyT)*, 530 nm for poly(1,4-TPhT)*, 620 nm for poly3T*, and 590 nm for poly2T* (wavelength of maximum CD intensity in reduced state). As shown in Figure 10, only poly(2,5-TPyT)* displays strong shoulders at cathodic potentials, related to n-doping of ammonium ions. An increase in CD intensity was also observed for poly(2,5-TPyT)* at cathodic potentials (−0.14 to −1.64 V; Figure 11). Although the electrochemical n-doping behavior remains to be evaluated in more detail, the electrochemical modulation observed in CD measurements is suggestive of n-doping of the pyridine-based polymer.

Conclusion

Cholesteryl oleyl carbonate, a conveniently available cholesteric derivative, was demonstrated to be an effective chiral inducer for nematic liquid crystal. The CLC electrolyte prepared with the aid of the chiral inducer allows for the synthesis of optically active polymers using cholesteric liquid crystal as a reaction field. The use of cholesterol derivatives as chiral inducers extends the versatility of the asymmetric electrochemical polymerization approach. Polymers thus synthesized are imprinted with the molecular arrangement of the CLC during the growth process and display an optical texture replicating that of the CLC electrolyte. The CD intensity of these polymers can be controlled via an applied voltage to drive the redox process. Sweeping the potential between cathodic and anodic potentials demonstrated a repeatable two-step change in CD for poly(2,5-TPyT)*, which contains a pyridine ring in the monomer unit, implying an n-doping effect. The polymers prepared in this study have potential applications as optical modulators, optical filters, and chiral sensors.

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