# Macromolecules

# Control of Chirality and Electrochromism in Copolymer-Type Chiral PEDOT Derivatives by Means of Electrochemical Oxidation and Reduction

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Supporting Information

**ABSTRACT:** Copolymer-type chiral poly(ethylenedioxythiophene) [PEDOT] derivatives were synthesized by two kinds of electrochemical polymerizations of (i) chiral EDOT-based monomers using a cyclic voltammetric method in acetonitrile and (ii) achiral EDOT-based monomers using a potentiostatic method in chiral nematic liquid crystal (N\*-LC) employed as an asymmetric reaction field. The electrochromic and morphological changes of the chiral PEDOT derivatives upon electrochemical doping and dedoping were investigated. Drastic and reversible changes in not only electrochromism but also circular dichroism between neutral and oxidized states of the chiral PEDOT derivatives were observed. This indicates that the helicity of the present polymers can be controlled by the electrochemical doping



and dedoping procedures. It is found that the helically twisted chain and/or helically  $\pi$ -stacked structure formed in the neutral PEDOT derivative are suppressed in the oxidized state, where the main chain becomes planar due to a formation of quinoid structure and the interchain distances are lengthened due to intercalation of dopants into the chains. Spiral morphologies with right-and left-handed screw directions were observed for the polymers synthesized in the N\*-LC and well correlated with spiral textures of the N\*-LCs.

# **1. INTRODUCTION**

Conjugated polymers have many interesting electrical and optical properties and profound applicabilities for inherently transporting materials, light-emitting displays, rechargeable batteries, and electrochemical devices and sensors.<sup>1-6</sup> Electrochemical polymerization for the conjugated polymer is useful because it can be carried out at room temperature and homogeneous polymer films can be formed directly at the electrode surface by which the film thickness is well controlled. One of the most attractive properties of the conjugated polymers is a socalled electrochromism, where the polymer changes in color upon an electrochemical reduction-oxidation (redox).<sup>7,8</sup> Electrochromic polymers give switchable functions and controllable optical properties.<sup>9</sup> Poly(3,4-ethylenedioxythiophene) [PEDOT] is a representative electrochromic polymer with versatile functional properties such as high electrical conductivity, low band gap, redox activity, thermal stability, and excellent transparency in the doped state.<sup>10</sup> It is now desirable to cultivate novel polymerization methods to afford multifunctional and high-performance PEDOT derivatives useful for plastic electronics.

Chiral conjugated polymers are expected to show circularly polarized luminescence when they have chiral centers and/or they form helical structures. There are several methods to induce a chirality on the conjugated polymer. One of them is an introduction of chiral moiety into the side chain of the conjugated polymer.<sup>11–16</sup> The second one is a polymerization of achiral monomer in an asymmetric reaction field consisting of chiral nematic liquid crystal.<sup>17–19</sup> The third one is a usage of both liquid crystalline (LC) conjugated polymer and chiral dopant. That is, when the chiral dopant is added to the nematic LC conjugated polymer, the chiral nematic LC phase is induced in the polymer.<sup>20,21</sup> The chiral conjugated polymers thus prepared are expected to exhibit circular dichroism in absorption and even in fluorescence, yielding circularly polarized absorption and luminescence.

In this work, the chiral PEDOT derivatives were synthesized using two kinds of electrochemical polymerizations, as shown in Table 1. The PEDOT derivatives with chiral side chains were synthesized through the cyclic voltammetric method by electrochemically polymerizing EDOTs derivatives bearing chiral groups at the phenylene moieties. Subsequently, the induced chiral PEDOT derivatives with achiral side chains were synthesized through the potentiostatic method by polymerizing EDOT derivatives bearing achiral groups at phenylene moieties in an asymmetric reaction field consisting of chiral nematic LC (N\*-LC). The copolymer-type chiral PEDOT derivatives thus

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| Polymerization method            | Monomer   | Polymerization components |  | Mole<br>ratio | Polymer  |
|----------------------------------|---|---------------------------|--|---------------|--|
| Cyclic<br>voltammetric<br>method | 0<br>C-0<br>S<br>C-0<br>C-0<br>C-0<br>S<br>C-0<br>S<br>C-0<br>C-0<br>C-0<br>S<br>C-0<br>C-0<br>C-0<br>C-0<br>C-0<br>C-0<br>C-0<br>C-0 | Monomer                   | ( <i>R</i> ), (S)-mono-1   | 0.01          | $\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$ |
|                                  |   | Supporting salt           | ( <i>n-</i> C₄H <sub>9</sub> )₄N <sup>+</sup> ClO₄ <sup>-</sup><br>( <i>n</i> -TBAP) | 0.1           |  |
|                                  | <b>(<i>R</i>), (S)-mono-1</b><br>(chiral)   | Solvent                   | Acetonitrile   | 100           | <b>(<i>R</i>), (S)-poly-1</b><br>(chiral)  |
| Potentiostatic<br>method         | mono-2<br>(achiral)   | Monomer                   | mono-2   | 1.0           | (R), (S)-poly-2 (induced chiral)   |
|                                  |   | Supporting salt           | n-TBAP   | 0.7           |  |
|                                  |   | Chiral<br>inducer         | ( <i>R</i> ), ( <i>S</i> )-PCH506-Binol  | 0.8           |  |
|                                  |   | Solvent                   | 4-cyano-4'-pentyl<br>biphenyl (5CB)  | 100           |  |

| Table 1. Two Kinds of Electrochemical Polymerizat | ons Used for Synthesis of Chiral PEDOT Derivatives |
|---|--|
|---|--|

synthesized were investigated in terms of electrochromic properties, chirality, and morphology upon electrochemical doping and dedoping. We report that the chirality and electrochromism of the copolymer-type chiral PEDOT derivatives are controlled by means of electrochemical oxidation and reduction procedures.

## 2. METHOD

**2.1. Chemicals.** 2,5-Dibromobenzoic acid and tributyltin chloride were purchased from Aldrich and used without further purification. *N*,*N*, N',N'-Tetramethylethylenediamine (TMEDA), azodicarboxylic acid diethyl ester (40% in toluene) (DEAD), and (*R*)- and (*S*)-2-octanol were purchased from Tokyo Chemical Industry without further purification. Tetrahydrofuran (THF), acetonitrile (ACN), and triethylamine were purified by the ordinary method, dried, and distilled immediately before use. 3,4-Ethylenedioxythiophene (EDOT) was vacuum-distilled before use. The chemical compounds (*R*)- and (*S*)-2,2'-dihydroxy-1,1'-binaphthyl (optical purity, 0.99) were purchased from commercially available sources. The mesogenic compound 4- (*trans*-4-*n*-pentylcyclohexyl)phenol [PCH500] was purchased from Kanto Chemical Ltd.

**2.2. Measurements.** NMR spectra of the monomers were recorded on a JEOL-NMR spectrometer (EX-400) using CDCl<sub>3</sub> as a solvent. Electrochemical experiments were carried out using a potentio-stat (Autolab PGSTAT12). UV–vis. absorption spectroscopy (Hitachi U-3500) and circular dichroism (CD) spectroscopy (JASCO J-720) were used to characterize the polymer films. The surface morphologies of the polymer films were investigated using a JEOL JSM-6400 scanning electron microscope. In the electrochemical characterization, a platinum

wire was used as a counter electrode and Ag/Ag<sup>+</sup> was used as a reference electrode. ITO glass (1 cm  $\times$  5 cm, 1 mm in thickness, 10  $\Omega/cm^2$ ) was used as a working electrode. SEM observations were carried out a JEOL 7500F electron microscope. Optical texture observation was performed using a Carl Zeiss polarizing optical microscope equipped with a Linkam THMS 600 heating and cooling stage.

2.3. Electrochemical Polymerization. We used two methods of the electrochemical polymerizations for syntheses of copolymer-type chiral PEDOT derivatives. First, it may be helpful to characterize these methods. The cyclic voltammetric method enables us to control the film thickness by changing the scan number for oxidation and reduction procedures and hence to obtain the polymer thin films with uniform thickness. However, this method is not useful for the electrochemical polymerization using the N\*-LC because the helical twisting structure of the N\*-LC is easily distorted and even destroyed by the repetition of the oxidation and reduction procedures. Thus, this method is only available for the electrochemical polymerization using an isotropic solvent, and in fact it is used for polymerizations of the chiral monomers [(R)- and (S)mono-1] in acetonitrile (see Table 1). On the other hand, the potentiostatic method allowed us to electrochemically polymerize achiral and chiral monomers, although the thickness of the polymer film cannot be so precisely controlled as the cyclic voltammetric method. Nevertheless, one can retrieve the liquid crystals and the chiral dopants for the subsequent polymerizations. Thus, the potentiostatic method is used for the polymerizations of the achiral monomers [(R)- and (S)-mono-2] in the N\*-LC (see Table 1).

Electrochemical polymerizations were performed in a standard threeelectrode cell containing an ITO-coated glass slide as a working electrode, a platinum foil as a counter electrode, and a  $Ag/Ag^+$  as a reference electrode. As shown in Table 1, (*R*)- and (*S*)-**poly-1** were Scheme 1. Synthetic Routes for Monomers [(R)- and (S)-mono-1] and Polymers [(R)- and (S)-poly-1]



synthesized through the electrochemical cyclic voltammetric method from solutions containing 0.01 M of monomers and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) in anhydrous acetonitrile. (R)-and (S)-**poly-2** were synthesized by the potentiostatic method for electrochemical polymerization in the N\*-LC field.

#### 3. RESULTS AND DISCUSSION

**3.1. Synthesis of Monomers.** Chiral compounds of (*R*)- and (S)-1,4-bis(2-(3,4-ethylenedioxy)thienyl)-2-benzoic acid 1-methyl heptyl ester  $\lfloor (R)$ - and (S)-mono-1 were prepared and used as chiral monomers for the electrochemical polymerizations. The synthetic route for mono-1 is described in Scheme 1. The dibromo compounds (R)-1 and (S)-1 were prepared by Mitsunobu esterification reaction by between (R)- and (S)-octanol and 2,5-dibromobenzoic acid with diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) in tetrahydrofuran (THF) solution. The reaction proceeded through an S<sub>N</sub>2-type Walden inversion at the chiral center without racemization, resulting in the formation of the desired compound. 3-Tributylstannyl-3,4ethylenedioxythiophene was prepared by a direct lithiation of an equal molar ratio of 3,4-ethylenedioxythiophene, followed by a reaction with tributyltin chloride. (R)- and (S)-mono-1 were synthesized by Stille coupling using  $Pd(PPh_3)_2Cl_2$  as a catalyst between 3-tributylstannyl-3,4-ethylenedioxythiophene and 2,5-(*R*)- and (*S*)-dibromobenzoic acid 1-methyl heptyl ester.



Figure 1. Electrochemical polymerization using cyclic voltammetric method for synthesis of (S)-poly-1 in acetonitrile including 0.1 M TBAP. Potential scanning of at 20 mV/s was repeated to increase the film thickness according to the cyclic voltammetric method.

**3.2. Polymerization.** The oxidative electrochemical polymerizations for the copolymers [(R)- and (S)-**poly-1**] were synthesized in acetonitrile with 0.1 M tetrabutylammonium perchrolate as electrolyte and 0.01 M monomer on ITO glass electrodes. Figure 1 shows the repeated potential scans for the electrochemical polymerization of the monomer with chiral substituent of (S)-configuration. The results for the electrochemical polymerizations of (R)- and (S)-mono-1 are similar to each other (see Figure S1). During the oxidative scan, two oxidation peaks appeared at -0.12 and +0.58 V for (R)-mono-1 and two



**Figure 2.** Cyclic voltammetry of monomer-free (*S*)-**poly-1** in 0.1 M TBAP/acetonitrile solution: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 mV s<sup>-1</sup>.



**Figure 3.** UV–vis and near-IR absorption spectra of (*S*)-**poly-1** film coated on ITO electrode, measured at different potentials ranging from -0.7 to +0.7 V in acetonitrile with 0.1 M TBAP vs Ag/Ag<sup>+</sup>.

oxidation peaks at -0.11 and +0.58 V for (*S*)-**mono-1** in the first scan. On the return scan, the polymer is dedoped. A growing polymer through the redox process was observed, for instance, by examining changes in absorption intensity at 510 nm of (*S*)-**poly-**1 during the cyclic voltammetric polymerization on ITO-coated glass (see Figure S2). All peaks exhibit an increased current response, indicating the formation of an electroactive polymer film accompanied by an increase of film thickness. After the polymerization, the polymer thin films were washed with an electrolyte solution and acetonitrile.

**3.3. Characterization.** Figure 2 shows the cyclic voltammogram of (*S*)-**poly-1** film at scan rates of 10, 20, 40, 60, 80, and 100 mV s<sup>-1</sup> in 0.1 M TBAP/acetonitrile. The half-wave oxidation potential of the polymer ( $E_{1/2}$ ) was -0.32 V vs Ag/Ag<sup>+</sup> ( $E_{\text{ox/p}} = -0.10$  V and  $E_{\text{red/p}} = -0.54$  V at 100 mV s<sup>-1</sup>), similar to the values for poly[1,4-bis(2-(3',4'-ethylenedioxy)thienyl)-2methoxy-5,2''-ethylhexyloxybenzene] [poly(BEDOT-MEHB)].<sup>22</sup> The polymer exhibited a well-defined and quasi-reversible redox process. It is worthy noting that (*R*)- and (*S*)-**poly-1** display very similar electrochemical behavior, probably because the chirality of the polymers does not affect the redox behavior.

**3.4.** Spectroelectrochemistry of Polymer Films. It is desired at this stage to gain a deeper insight into the relationship between polymer structure and electrochemical properties. The spectroelectrochemistry is expected to give key properties of conjugated polymers such as a band gap  $(E_g)$  and the intergap states that appear upon doping. Therefore, the spectroelectrochemical measurements were performed in the UV—vis and near-infrared (NIR) wavelength range using a quartz cell. The quartz cell includes three electrodes (working, counter, and reference) and the electrolytic solution (0.1 M TBAP). Before the measurement



**Figure 4.** CD spectra of thin films of neutral and oxidized (*R*)- and (*S*)-**poly-1** on ITO glasses.



Figure 5. SEM images of (S)-poly-1 prepared by electrochemical polymerization on ITO glass: (a) neutral state and (b) oxidized state.

of the polymer a spectroscopic blank has been evaluated on an ITO glass without the polymer under the same conditions. The absorbance of the ITO glass is automatically subtracted from the spectroscopic data points by the potentiostat. During the spectroelectrochemical measurement the working electrode potential (ITO) is swept from -0.7 to +0.7 V by the potentiostat.

Figure 3 shows the spectroelectrochemical analysis for the (S)**poly-1** at different voltages varying between -0.7 and +0.7 V. The polymer film in the neutral state (-0.7 V) gives an absorption band at 500 nm. This is assigned to  $\pi - \pi^*$  transition of conjugated main chain and responsible for purple color of the neutral film. In the initial stage of the oxidation (-0.2 V), the band at 500 nm gradually decreases in intensity and new bands at 740 and 1450 nm emerge. This is accompanied by a color change



Figure 6. Electrochemical doping and dedoping processes of chiral PEDOT derivative, (S)-poly-1 in TBAP electrolyte system. Changes in (a) electronic structures between neutral and oxidized states and electrochromic color, (b) interchain helical  $\pi$ -stacking structure, and (c) morphology.

in the polymer from purple to green. As the oxidation proceeds further (from -0.2 to +0.1 V), the two new bands increase in intensity. During the oxidation, the band at 740 nm shows a slight red shift from 740 nm (-0.2 V) to 770 nm (+0.1 V), and the band at 1450 nm shows a large blue shift from 1450 nm (-0.2 V)to 1000 nm (+0.1 V). Finally, these two bands merge into an intense and broad band around 860 nm (+0.5 to +0.7 V); meanwhile, the band at 500 nm disappears. The isosbestic point at 610 nm is observed in the oxidation process, indicating an existence of equilibrium between the neutral and oxidized states. The reverse changes in spectra are observed in the reduction process. At the present time, the assignments of the new bands (740 and 1450 nm) and the intense and broad band around 860 observed in the final stage of the oxidation are not clearly elucidated, remaining them undissolved. However, one may argue that this sort of electrochromism is reversible and can be controllable by the electrochemical doping and dedoping procedures.

**3.5.** CD Spectra of Polymer Films. Figure 4 shows circular dichroism (CD) spectra of (*R*)- and (*S*)-poly-1 films. Cotton effects were observed for absorption region at 450 nm for  $\pi - \pi^*$  transition of the polymer main chain in the neutral state. (*R*)-poly-1 showed a bisignate Cotton effect, i.e., a positive CD band at 452 nm and a negative one at 556 nm. Mirror images in CD

spectra were observed for the neutral (R)- and (S)-poly-1. However, when the polymer was oxidized through a doping, the CD band was markedly weakened in intensity. The application of voltage of -0.7 V for the dedoping restored the CD bands to the original intensities of the neutral state. It is suggested that the changes of CD bands in the neutral and oxidized states might be related to a chirality change in the polymer. In the neutral state, the polymer takes a helically twisted structure because the polymer main chain has a benzonoid structure and a relatively high degree of freedom around the internal rotation of the main chain. Meanwhile, in the oxidized state, the polymer main chain takes a quinoid structure, and the planarity of the main chain is enhanced. The chirality of the polymer weakens as the twisting degree decreases. At the same time, the distance between the polymer main chains is expanded because the dopants  $(ClO_4^{-})$ are intercalated into the main chains (see Figure 6). The increase of interchain distance weakens the helical  $\pi$ -stacking, causing a decrease in CD intensity.

Thus, the CD band observed in the neutral polymer is attributed to the two structural factors: (i) an intrachain twisting (helical conformation) and (ii) an interchain helical  $\pi$ -stacking (chiral stacking). The loss of CD intensity in the oxidized state is due to (iii) an intrachain planarization (planar conformation) of the quinoid structure and (iv) an increase of interchain distance



**Figure 7.** POM images of (*R*)- and (*S*)-N\*-LCs systems containing a monomer, an electrolyte, and a chiral dopant. Images recorded for N\*-LC phase at 23 °C in the cooling process.

(intercalation of dopant into main chains), leading to a vanishing of the helically  $\pi$ -stacked structure. It is not straightforward to discriminate between the two possibilities of intrachain (i and iii) and interchain (ii and iv) structural factors. Nevertheless, by taking account of bisignate shapes of the CD spectra for neutral (*R*)- and (*S*)-**poly-1** shown in Figure 4, the interchain structural factor (ii and iv) is the most likely for the explanation of the CD band.

**3.6.** Morphologies of Polymer Films. Figure 5 shows scanning electron microscope (SEM) images of (S)-poly-1 films prepared by 40 scans on ITO glass. The polymer film in the neutral state has a twisted and shrunk morphology (Figure 5a). Meanwhile, the film in the oxidized state shows a swollen morphology (Figure 5b), since the dopants are contained between the polymer main chains. In fact, the film thickness of the polymer increased by about 20% due to the swelling after the oxidization. The swelling of the oxidized film is attributed to the intercalation of dopants such as  $ClO_4^-$  into the interchains and the porous sites of the film in accompanying with the electrochemical doping. It is of keen interest that the morphological change between the neutral and oxidized states is reversible and hence controllable by the electrochemical doping and dedoping procedures.

3.7. Mechanism of Electrochemical Redox Processes. Upon the electrochemical oxidation, the polymer is oxidized to give a polaron or bipolaron which strongly affects on the electronic band structure.<sup>23</sup> Figure 6 describes electrochemical doping and dedoping processes and the changes in electrochromic color of the chiral PEDOT derivative, (S)-poly-1. In the initial stage of the oxidation, the neutral polymer changes into a cationic polymer with a radical cation corresponding to the polaron. The radical cation is delocalized over the conjugated polymer chain. The color of the polymer film changes from a deep purple to a light purple. In the further oxidation, the doping proceeds and the dication corresponding to the bipolaron is generated. As a result, the color of the film changes from a light purple to an emerald green. The bathochromic shift of the electrochromic color is attributed to an increase of the effective conjugation length, which comes from a formation of a quinoid structure in the oxidized polymer. In Figure 6 is also shown the

schematic representation of the changes in structure and morphology of (S)-**poly-1** upon the electrochemical doping and dedoping procedures. Both the interchain helical  $\pi$ -stacking and the intrachain twisting are weakened by the electrochemical doping. The weakening of the interchain helical  $\pi$ -stacking is accompanied by a considerable expansion between the interchain distances. The expansion of the interchain distances should cause a change in higher-order structure such as morphology. The notable change in morphology between the neutral (shrunk morphology) and oxidized states (swollen morphology), as depicted in Figure 6, could be correlated with the change in the interchain distances.

**3.8.** Preparation of Chiral Nematic Liquid Crystal (N\*-LC). Next, the electrochemical polymerizations in an asymmetric reaction field were performed by using the N\*-LC.<sup>24</sup> Table 1 shows molecular structures of compounds used for the chiral electrochemical polymerization. Synthetic details of the compounds are given in the Supporting Information. 4-Cyano-4'-*n*-pentylbiphenyl (5CB) was used as a parent liquid crystal for the N\*-LC. The liquid crystallinity of 5CB was maintained even after an addition of small amount of the chiral dopant. The N\*-LC system is composed of 0.8 M (*R*)- or (*S*)-binaphthyl-2,2-bis[*p*-(*trans*-4-pentylcyclohexyl)phenoxy-1-1-hexyl] ether [(*R*)- or (*S*)-PCH506-binol] as the chiral dopant, 1.0 M 2,5-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)benzoic acid 1-methylheptyl ester [monomer], and 0.7 M tetrabutylammonium perchlorate [TBAP] in 5CB.

The N\*-LC system was heated up to an isotropic temperature to completely dissolve the monomer, the electrolyte, and the chiral dopant in 5CB. POM images of the N\*-LC systems showed typical fingerprint textures, as seen in Figure 7. (*R*)- or (*S*)-N\*-LC systems showed thermotropic LC behavior. The phase transition temperatures of the (*R*)- and (*S*)-N\*-LC systems are as follows:  $C \rightarrow 6 \rightarrow N^* \rightarrow 28 \rightarrow I$ ,  $C \leftarrow 1 \leftarrow N^* \leftarrow 25 \leftarrow I$  and  $C \rightarrow 5 \rightarrow N^* \rightarrow 27 \rightarrow I$ ,  $C \leftarrow 1 \leftarrow N^* \leftarrow 25 \leftarrow I$  in heating and cooling processes, respectively. Subsequently, the contact tests were carried out to elucidate the screw directions of the N\*-LC systems with fingerprint textures. The cholesteryl oleyl carbonate was used as the standard LC for the contact test. It was found that



Figure 8. UV–vis and near-IR absorption spectra of (S)-poly-2 film coated on ITO electrode prepared at various electrode potentials ranging from -0.7 to +0.7 V in 0.1 M TBAP/acetonitrile vs Ag/Ag<sup>+</sup>.

the (R)- and (S)-N\*-LC systems have left- and right-handed screw directions, respectively.

**3.9. Polymerization in Asymmetric Reaction Field.** The N\*-LC system containing the monomer was injected into a cell composed of sandwiched ITO glasses with a Teflon spacer (140  $\mu$ m). The cell including the N\*-LC system was heated to 50 °C and then slowly cooled to room temperature. The N\*-LC in the cell showed a fingerprint texture at room temperature (Figure S3). DC voltage of 3 V was applied to the cell for 1 h. As the polymerization proceeded, the optical texture of the N\*-LC system became darker owing to the formation of polymer. As a result of the polymerization, a polymer film of dark red color was deposited on the inner glass of the cell. Once the polymerization was complete, the polymer film was washed with methanol, acetonitrile, and toluene, in that order.

3.10. Optical Properties of Polymer Films. The optical textures of the polymers resemble to those of the N\*-LCs. In the spectroelectrochemical measurement, the working electrode potential was controlled by the potentiostat and swept from +0.7to -0.7 V. Figure 8 shows the spectroelectrochemical analysis for the (S)-poly-2 at voltages varying between +0.7 and -0.7 V. When the electrode potential was increased stepwise from -0.7to 0 V, the absorptions in the near-IR region increased in intensity, giving bands at 726 and 1250 nm. From 0 to +0.3 V, a different spectral change was observed; while the bands at 726 and 1250 nm increased, the band at 478 nm decreased. The polymer in the neutral state showed an absorption band at 478 nm, which is due to  $\pi - \pi^*$  transition of the main chain and responsible for the red color. From +0.3 to +0.7 V, the band at 478 nm decreased, while those at 726 and 1250 nm increased. This was accompanied by a change in color of the polymer from red to green.

As shown in Figure 9, (R)- and (S)-**poly-2** exhibit a strong Cotton effect in the neutral state, but no Cotton effect was observed in the oxidized state. (R)- and (S)-**poly-2** gave complementary mirror-image CD spectra. It is suggested that the changes of CD signals in the neutral and oxidized states are related to changes in chirality of the polymers. In the neutral state, the polymer takes a twisted structure because the polymer main chain has a benzonoid structure with a comparatively high degree of freedom in terms of internal rotation of main chains. Therefore, the strong CD intensity originates from the twisted conjugated chain. Meanwhile, in the oxidized state, the polymer takes a quinoid structure and the planarity of the main chain is



Figure 9. CD spectra of (*R*)- and (*S*)-poly-2 in neutral and oxidized states.



Figure 10. POM photographs of (*R*)-poly-2 (upper figure) and (*S*)-poly-2 (lower figure) with left- and right-handed spiral morphologies, respectively.

enhanced (see Figure 6). Thus, the chirality of the polymer is weakened due to a decrease of twisting degree of the main chain. Besides, in the oxidized state the interchain distance is expanded because of existence of intercalating dopant  $(ClO_4^-)$  between the polymer main chains.

Here, it is of interest to discuss the difference in absorption spectrum and band gap between **poly-1** and **poly-2** (see Figures 3 and 8). When the band gap is defined as the onset of the absorption band, the neutral **poly-1** has a band gap of  $\sim$ 1.7 eV, and the wavelength at maximum intensity of absorption band,  $\lambda_{max}$  is 2.44 eV (508 nm). The neutral **poly-2** has a band gap of 1.8 eV, and its  $\lambda_{max}$  is 2.59 eV (478 nm). It is evident that the absorption band of the neutral **poly-1** is located at longer



**Figure 11.** Optical micrographs of (*R*)-**poly-2:** (a) optical micrograph without polarizer; (b) differential interference contrast micrograph.

wavelength by 30 nm than that of the neutral **poly-2**. Namely, the former has a longer effective conjugation length that the latter.

Such a difference can be related to the polymerization method. As mentioned in section 2.3, the cyclic voltammetric (CV) method enables us to control the film thickness by changing the scan number for oxidation and reduction procedures and hence to obtain the polymer thin film with uniform thickness. On the other hand, the potentiostatic method is not capable for controlling the film thickness, although it allows us to perform an electrochemical polymerization even in the N\*-LC. Actually, **poly-1** is synthesized by the CV method, yielding a thin film with uniform thickness. The well-controlled uniform thickness of poly-1 leads to polymer chains with long conjugation length and even small amounts of polymer chains with further longer conjugation length. The latter is responsible for the tailing of the absorption band for poly-1, as found in Figure 3. On the other hand, **poly-2** is synthesized by the potentiostatic method, giving a film with a nonuniform thickness. Hence, poly-2 consists of polymer chains with relatively shorter conjugation length than poly-1, and it gives no tailing in absorption band.

**3.11.** Morphologies and Micrographs of Polymer Films. Figure 10 shows POM photographs of the polymer films in the neutral state; (R)- and (S)-poly-2 have left- and right-handed spiral morphologies, respectively. It appears that the polymer replicates the optical texture of the N\*-LC system. The helical senses of the poly-2 films are quite in agreement with those of the (R)- and (S)-N\*-LC used as asymmetric reaction fields. However, these morphologies showed no change even after the electrochemical doping and dedoping (see Figure 11). The result is in contrast to the case of the poly-1 film. This is because the **poly-2** films are ca. 2 mm in thickness, which being 20 times thicker than those (ca. 0.1 mm) of the **poly-1** films, and they (**poly-2** films) are too thick to be affected in morphology by the electrochemical doping and dedoping. Note that the difference in film thickness between **poly-1** and **poly-2** is attributed to the difference in the electrochemical polymerization techniques between the cyclic voltammetric method and the potentiostatic one. Namely, in the latter (potentiostatic method), it is hard to control the film thickness during the electrochemical polymerization. As a result, the **poly-2** prepared by the potentiostatic method is too thick to enable the dopants to be dispersed homogeneously into the whole of the film, yielding partly doped state.

Figure 11 depicts the optical micrographs of (R)-**poly-2** film. The micrographs are measured without a polarizer (Figure 11a) and using a differential interference contrast technique (Figure 11b). The oxidization was carried out by dipping a half of the film into the electrochemical cell including the electrode. It is clear that the neutral and oxidized areas of the film show reddish and bluish colors, respectively (Figure 11a). Such an electrochromic behavior of **poly-2** is consistent with the results of UV—vis absorption spectra in Figure 8. It is worthy noting that the fingerprint texture of the neutral film of **poly-2** remains unchanged after the oxidation (Figure 11b). In other words, the morphology of the **poly-2** does not change by the electrochromic change on the surface of the film reversibly occurs between the neutral and oxidized states.

#### 4. CONCLUSION

The copolymer-type chiral poly(ethylenedioxythiophene) [PEDOT] derivatives were synthesized by two kinds of electrochemical polymerizations of (i) the chiral EDOT-based monomers using the cyclic voltammetric method in isotropic organic solvent (**poly-1**) and (ii) the achiral EDOT-based monomers using the potentiostatic method in the N\*-LC used as an asymmetric reaction field (**poly-2**).

**Poly-1** exhibited drastic and reversible changes in electrochromism, circular dichroism, and even morphology between the neutral and oxidized states. This implies that the electrochemical doping and doping procedures are useful to control the chiroptical and electrochemical properties of the chiral conjugated polymers.

**Poly-2** showed spiral morphologies with right-and left-handed screw directions which can be correlated to the optical textures of the N\*-LC reaction fields. The chirality and electrochromism of **poly-2** were also controlled by changing the polymer structures between the neutral and oxidized states through the electrochemical doping and doping procedures.

The profiles of Cotton effects in CD spectra imply that the neutral **poly-1** has helically twisted main chain to form helically  $\pi$ -stacked structure, whereas the neutral **poly-2** has helically twisted main chain. These helical structures formed in the PEDOT derivatives are suppressed in the oxidized states because the main chain becomes planar due to a formation of quinoid structure and at the same time the interchain distances are lengthened due to intercalation of dopants into the chains.

The present polymerization methods represent useful approaches for the preparation of chiral conjugated polymers with multifunctional properties such as electrochromism and circular dichroism.

#### ASSOCIATED CONTENT

**Supporting Information.** Synthetic details of compounds, electrochemical polymerization using cyclic voltammetric method

for synthesis of (R)-**poly-1** in acetonitrile including TBAP, changes in absorption intensity at 510 nm of (S)-**poly-1** during the cyclic voltammetric polymerization on ITO-coated glass, electrochemical polymerization cell for synthesis of PEDOT derivative using a potentiostatic method. This material is available free of charge via the Internet at http://pubs.acs.org.

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