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Optically Active Electrochromism of Poly(3,4-ethylenedioxythiophene) Synthesized by Electrochemical Polymerization in Lyotropic Liquid Crystal of Hydroxypropyl Cellulose/Water: Active Control of Optical Activity

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The electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) in a water solution of hydroxypropyl cellulose (HPC) as a polymer lyotropic liquid crystal (LC) gives *poly*EDOT*/HPC hybrid (PEDOT*/HPC) as an optically active polymer. Circular differential interference contrast (C-DIC) microscopy of the polymer reveals a well-resolved ordered structure, and circular dichroism (CD) measurements indicate a Cotton effect for the polymer film. PEDOT prepared using this chiral nematic LC field exhibits good electrochemical stability and switching between a dark blue reduced state and sky blue oxidized state with corresponding changes in Cotton effect. The polymer thus shows "electrochiroptical effect", such as optically active electrochromism, and repeating change in CD through electrochemical redox process. The proposed method represents a new technique for the preparation of chiral conducting polymer films.

Introduction

Chiral polymers have been prepared by a number of research studies through the introduction of an optically active group into an optically inactive polymer main chain.[1−7] In such polymers, the asymmetric carbon locates in the side chain. Recently, the synthesis of main-chain-type chiral conjugated polymers with nonchiral centers has been shown to be possible by polymerization in an asymmetric reaction field. Such a chiral catalytic system was developed, Ti-$(OBu)_4$/ $AlEt_3$/chiral nematic liquid crystal (N*-LC), and has successfully prepared optically active polyacetylene films with high electrical conductivity by iodine doping.[8,9] The insolubility and infusibility of the helical polyacetylene result in a stable chiral structure. This result indicates that stable chiral polymers can be prepared from nonchiral monomers by conformational locking of the repeating units.

Liquid crystal (LC) has significance in biological systems in that life processes require molecular disorder and mobility accompanied by maintenance of the orientation of the functional group. This organization in biological systems is characteristic of the lyotropic LC state. In a few cases, such as in muscles and in the nerve myelin sheath, LC regions with three-dimensional extension are present.[10] Biological reactions occur in asymmetric environments, where ribonucleic acid (RNA), proteins, collagen, and other biopolymers form helical structure. The growth of a nonsubstituted monomer, such as pyrrole, thiophene, or 3,4-ethylenedioxythiophene (EDOT), in an asymmetric environment produced by LC without the introduction of a chiral substituent or use of a chiral catalyst is expected to result in the formation of a conjugated polymer with a chiral structure, and the chirality of the polymer is expected to be preserved due to its insolubility and infusibility. We have previously synthesized *poly*EDOT[11] (PEDOT) and polypyrrole[12] by electrochemical polymerization in low molecular mass N*-LC and the chirality of the products has been confirmed. Also, we reported a new polycondensation method for obtaining chiral polymer from achiral monomer in an inert chiral nematic liquid crystal medium. Although LC exhibits fluid behavior, the crystal-like structural order of N*-LC effectively provides

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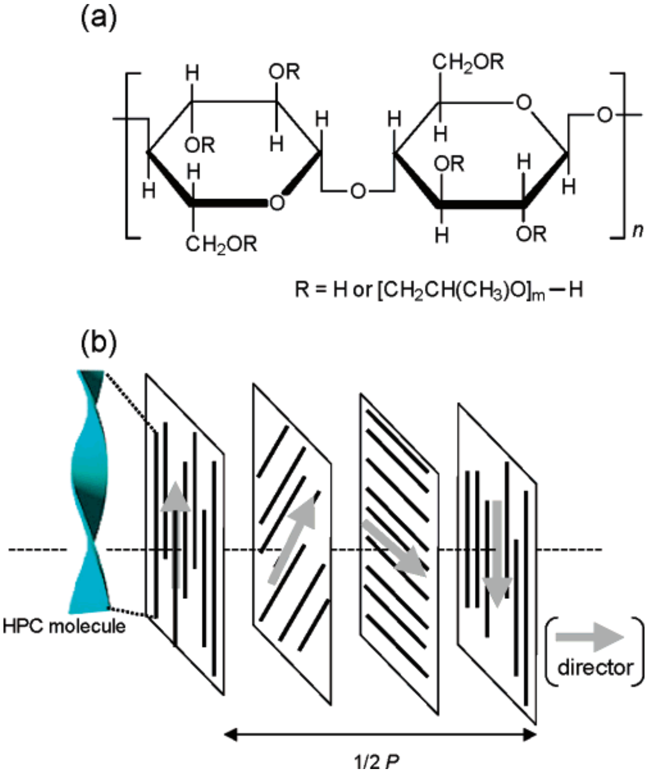


Figure 1. Chemical structure of hydroxypropyl cellulose (HPC) (a) and schematic representation of the N*-LC structure of chiral nematic liquid crystal state of HPC (b). The pitch length (*P*) is typically many hundreds or thousands of times larger than the molecular width.

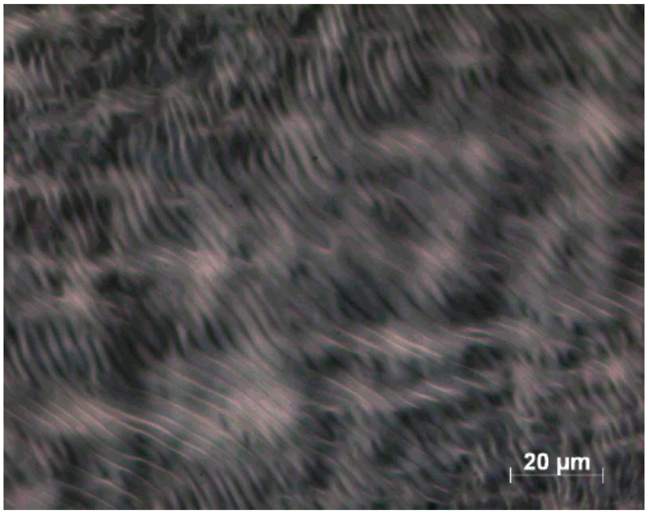
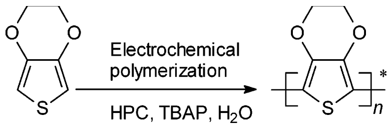


Figure 2. Polarizing optical micrograph of HPC-based electrolyte containing TBAP (supporting salt) and EDOT (monomer).

chiral order for the propagation of the polymerization reaction, in contrast to chiral isotropic liquids.[11,12] Throughout these studies, asymmetric field effect (AFE) in polymerization reaction was confirmed.[13] In the present research, the electrochemical polymerization of EDOT was carried out in a concentrated solution of hydroxypropyl cellulose (HPC) in water to prepare optically active PEDOT. HPC, which is synthesized by reaction between propylene oxide and natural cellulose, forms lyotropic LC in a wide range of solvents.[14−16] PEDOT has been indicated to exhibit the most promising electrochromic properties of the many redox-active conducting polymers (e.g., polythiophene, polypyrrole, and polyaniline).[17−20] HPC in water forms a right-handed helical N*-LC structure.[21] The molecular structure of HPC is shown in Figure 1a. The chirality of HPC expresses itself on the configuration level of macromolecules as well as on the conformation level of helical structures of chain molecules, and both levels will influence the twisting of the self-assembled, supramolecular helicoidal structure formed in the LC state (Figure 1b). We confirmed that polymerization of EDOT in HPC effectively produced optically active polymer. The spectroelectrochemistry in circular dichroism (CD) of the PEDOT*/HPC film prepared in this study is also investigated.

Preparation of Chiral Nematic Electrolyte. A water solution of 65 wt % HPC, 0.1 M EDOT (monomer), and 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting salt was prepared for electrochemical polymerization.



The liquid crystallinity of the HPC solution was confirmed after the addition of TBAP and EDOT through observation of the LC texture by polarizing optical microscopy (POM) using transmitted light. Figure 2 shows the fingerprint or string-like texture of the N*-LC electrolyte under homeotropic anchoring conditions. The helical pitch (*P*) can be determined as twice the distance between the two dark lines. The average pitch of the HPC electrolyte-based N*-LC, calculated from POM observations, was ca. 6−7 μm. These results demonstrate that the HPC solution can be used as an electrolyte for the electrochemical polymerization of EDOT in place of a normal liquid system such as TBAP or lithium perchlorate in acetonitrile.

Polymerization

A three-electrode cell was employed for asymmetric oxidative electrochemical polymerization, with an ITO glass on one side as the working electrode, another ITO glass on the opposite side as the counter electrode, and a silver layer deposited on the glass substrate as a pseudo-reference electrode. As the low dc ionic conductivity of the LC mixture may result in current-resistance (iR) drop, electrochemical polymerization was carried out using a narrow gap (Supporting Information).

The HPC electrolyte and monomer were charged between the electrodes and contained using a 0.19 mm Teflon sheet

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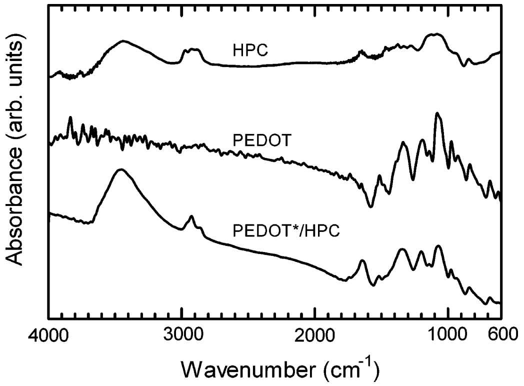

Figure 3. IR absorption spectra of HPC, PEDOT, and PEDOT*/HPC.

spacer. It should be noted that repeated polymerization scanning by cyclic voltammetry destroyed the helical structure in the polymerization of EDOT in *n*-hexylcyanobiphenyl (6CB) with a chiral dopant in our previous work.[11] The optical texture of the present HPC electrolyte, however, was unaffected by repeated scanning, attributable to the higher viscosity of HPC, which exhibits a low orientation response to external electric fields. The silver pseudo-reference electrode was calibrated using a 5 mM solution of Fc/Fc$^+$ in the HPC electrolyte. Potentiodynamic polymerization of EDOT in the HPC electrolyte at a rate of 0.4 mV$\cdot$s^{-1} between -0.8 and $+1.0$ V afforded an insoluble and infusible thin film on the ITO electrode (5 repeat scans). After formation, the polymer was immersed in a large amount of water for 12 h, washed with water, immersed in a large amount of acetone for 12 h, and then washed with water, acetonitrile, methanol, water, and acetone, in order. The sample was then dried under reduced pressure to yield thin film (thickness: 60 nm, reduced state).

Characterization

Infrared Absorption. Figure 3 shows the KBr infrared (IR) absorption spectra of HPC, normal PEDOT (prepared by electrochemical polymerization in acetonitrile solution in the presence of TBAP as a supporting salt), and PEDOT*/HPC, for comparison. The absorption band characteristic to the OH stretching vibration is due to the hydroxy group of HPC. The peaks at 1521, 1348, 1207, and 1074 cm^{-1} in the absorption spectrum of the polymer are characteristic of PEDOT, where the band at 1521 cm^{-1} is ascribed to the stretching of C=C and C$-$C in the thiophene ring. Vibration from the C$-$S bond in the thiophene ring can be seen at 689 cm^{-1}. The peak at 1348 cm^{-1} may be due to the C=C stretching vibration of the thiophene unit in EDOT. On the other hand, the IR spectrum of the polymer does not show the absorption at 1255 and 890 cm^{-1} attributed to the monomer =C$-$H in-plane and out-of-plane deformation vibrations at the 2,2′-position of the EDOT unit, respectively.[22] Therefore, we can determine that the polymerization of EDOT in HPC proceeds through the 2,2′-position of the monomers. The polymer exhibits absorption bands at 3450 (ν_{OH}), 2924 ($\nu_{CH2,\ CH3}$) cm^{-1}. These bands are also observed in the absorption spectrum of HPC. Thus, the results of IR absorption measurements indicate that the polymer film is composed of PEDOT and HPC (hybrid of PEDOT and HPC, denoted PEDOT*/ HPC).

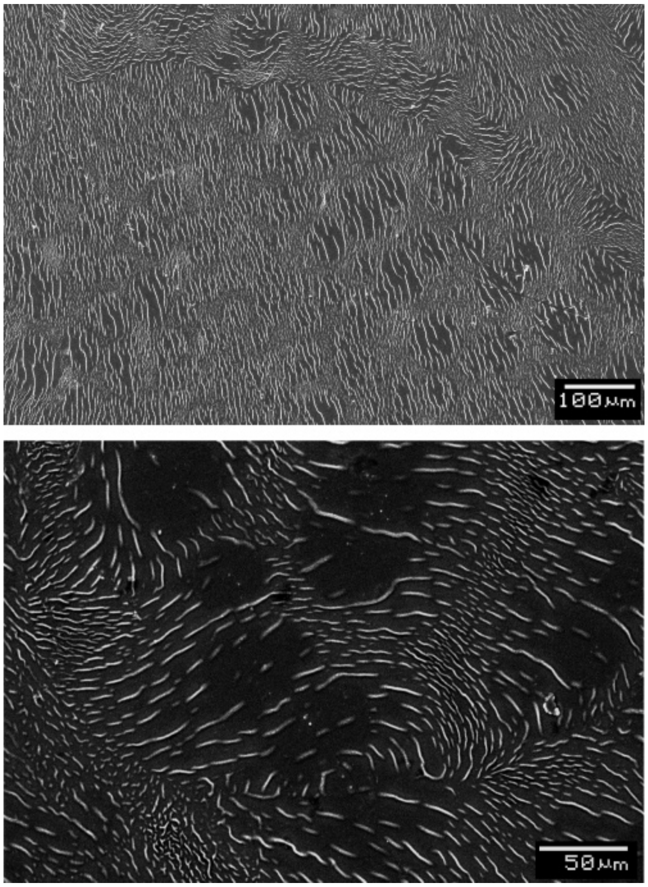

Figure 4. SEM photographs of PEDOT*/HPC (no metal was deposited on the polymer surface to observe surface structure with SEM).

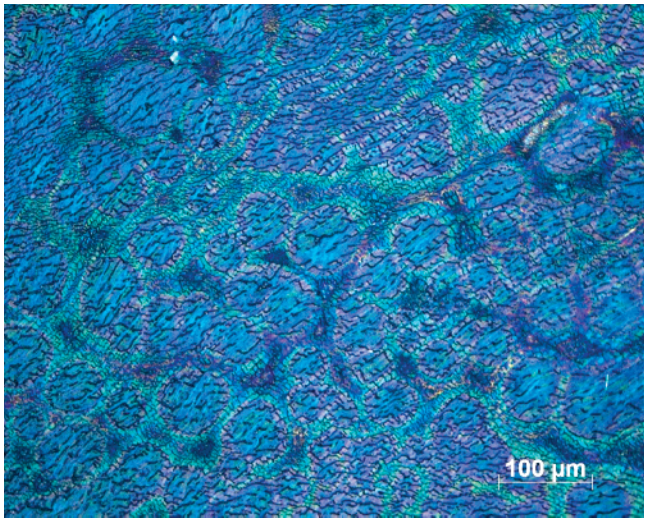

Figure 5. Circular differential interference contrast (C-DIC) optical micrograph of PEDOT*/HPC.

Optical Texture. The scanning electron microscopy (SEM) image (Figure 4) and C-DIC image (Figure 5) of the PEDOT*/HPC reveal a polymer with ordered fibril-like texture. The C-DIC image shows a multicolored surface, a unique pattern that can be attributed to the LC texture of HPC. The circular texture on the surface in particular is

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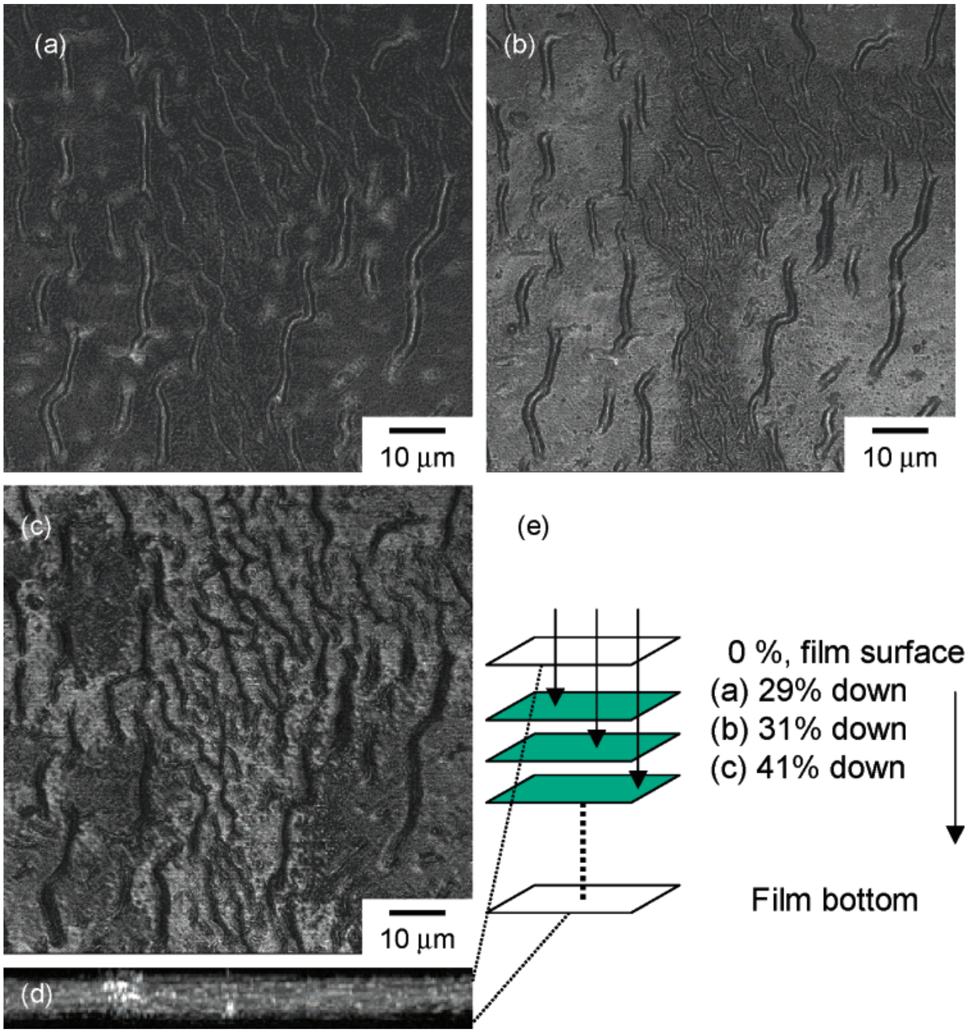

Figure 6. Laser scanning optical photographs of PEDOT*/HPC film. The images (a)−(c) show film surface, (d) displays film cross section, and illustration (e) indicates the structure of the cross section.

considered to be representative of a dissipative structure due to Rayleigh-Bénard convection in the LC during voltage application, which is often observed in LC.[23] Rayleigh-Bénard convection usually induces the formation of hexagonal structures in the LC cell. However, a circular film pattern was produced in this case due to the high viscosity of the polymer LC. This unexpected result imparts a geometric surface structure. As can be seen from the laser scanning optical micrographs, the circular features occur as subsurface structures. The circular features are very indistinct in the topmost layer (Figure 6a, 29% of the film thickness from the top surface), but are quite characteristic at 31% below the surface (Figure 6b). The circular features then begin to shrink further into the film (Figure 6c).

The PEDOT*/HPC film produced in this study exhibited weak birefringence (very dark figure under crossed-polarization conditions) under transmitted-light POM. The PEDOT*/HPC figure under POM suggests a different internal structure compared to the surface structure determined by SEM, C-DIC (reflected light), and optical microscopy (nonpolarized, transmitted light), as shown in Figure 7a. The polymer film possesses LC-like order with weak birefringence under POM (Figure 7b), but exhibits no fibril-like texture under nonpolarized light. The disparity between the surface structure and internal structure may be due to the presence of residual HPC in the film bulk, whereas residual HPC would have been removed from the film surface during the wash procedure.

Cyclic Voltammetry. Figure 8 shows cyclic voltammetry measurements of PEDOT*/HPC films vs Ag/Ag$^+$ at rates of 20, 40, 60, 80, and 100 mV·s^{-1} in 0.1 M TBAP/acetonitrile solution over the potential range −0.8 to +0.8 V. In general, PEDOT displays a broad oxidation peak and two reduction peaks at normal scan rates, but in this case, PEDOT*/HPC exhibits only one broad oxidation and one reduction potential at around −0.1 V. An electrochemical switching model was discussed that includes relaxation of the polymeric structure during redox reactions.[24] The overall process can be understood as a transition of the conducting polymer from two-dimensional to three-dimensional electrode behavior. The electrochemical responses of conducting polymers are affected by both electrochemical laws and the structure and morphology of the film, where conformational changes lead to an increase in the interchain volume, which

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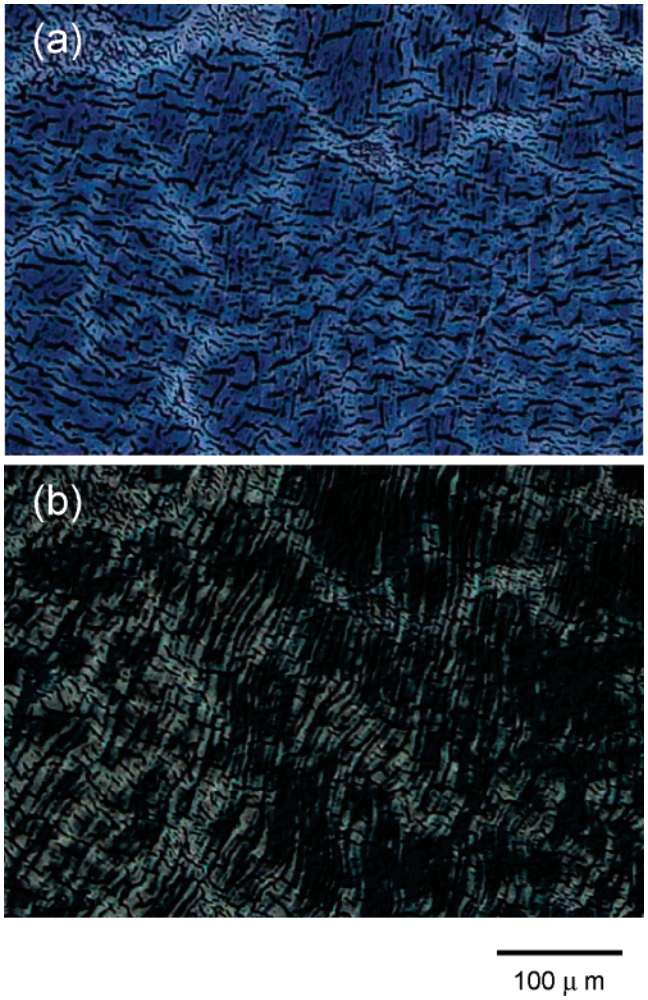

Figure 7. (a) Optical micrograph (no polarizer, transmitted light) and (b) polarizing optical micrograph (transmitted light) of the same part of PEDOT*/HPC.

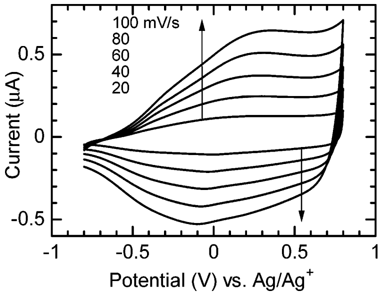

Figure 8. Cyclic voltammetry of PEDOT*/HPC thin film deposited on ITO glass in monomer free 0.1 M TBAP/acetonitrile solution vs Ag/Ag$^+$ at different scan rates.

is occupied by counterions and solvent molecules.[25,26] The PEDOT*/HPC forms a different structure from that of normal PEDOT in terms of both surface morphology and the polymer main chain at the molecular level. This variation results in the deviation of the PEDOT*/HPC redox potential from the standard value for normal PEDOT. Redox switching of the PEDOT*/HPC in monomer-free electrolyte solution gives rise to a well-defined and quasi-reversible redox process. Overall, these results indicate that the polymer is electroactive and well-adhered to the ITO electrode.

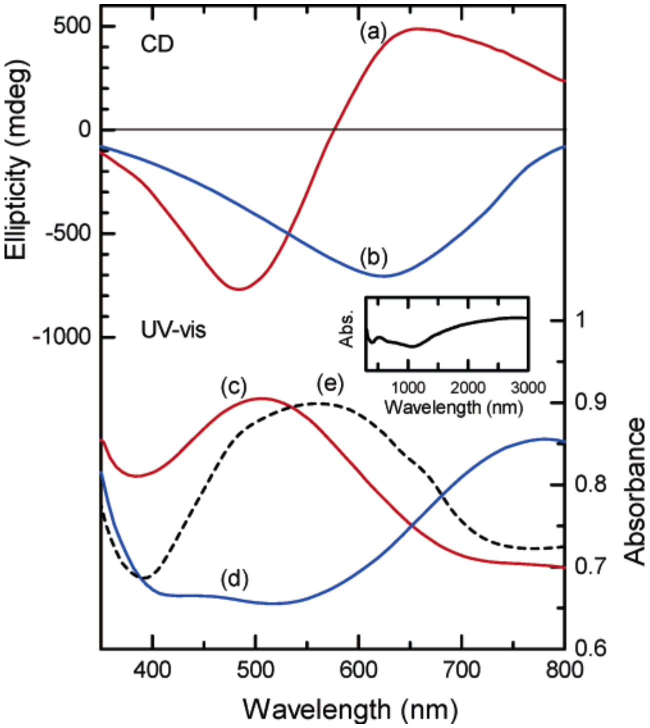

Figure 9. In situ CD spectra (top) and UV−vis (bottom) absorption spectra of PEDOT*/HPC during applications of voltage. (a) and (c) −0.45 V, (b) and (d) +0.64 V vs Ag/Ag$^+$ in monomer free 0.1 M TBAP/acetonitrile. Inset shows absorption spectra (−0.30 V) in longer wavelength region. Dashed line (e) indicates absorption spectrum of the normal PEDOT in reduced state prepared by electrochemical polymerization in TBAP/acetonitrile solution.

Optical Properties. Figure 9 shows the circular dichroism (CD) and ultraviolet−visible (UV−vis) spectra of PEDOT*/HPC during the application of voltage vs Ag/Ag$^+$ in monomer free 0.1 M TBAP/acetonitrile solution. In the reduced state, PEDOT*/HPC shows an absorption maximum at 503 nm (Figure 9, c), while the normal PEDOT film displays an absorption maximum at 560 nm (Figure 9, e). The 57 nm blue shift of PEDOT*/ HPC absorption maximum vs the normal PEDOT may be due to the fact that the dihedral angle between neighboring EDOT units of PEDOT*/HPC in the main chain is larger than that of the normal PEDOT, resulting in a decrease of effective conjugation length. This may be related to the higher order structure of the main chain, such as helical structure. Upon oxidation (application of positive potential), the peak at 503 nm in the absorption spectrum (Figure 9, d), associated with the $\pi-\pi^*$ transition of the polymer main chain weakens, while the peak at 782 nm, corresponding to the generation of radical cations on the polymer main chain, becomes stronger. This is accompanied by the extension of a broad band into the near-IR (NIR) region (Figure 9, inset).

The CD spectra of the polymers are also shown in Figure 9 (top).[27] The PEDOT*/HPC film displayed a bisignate (split type) CD in the reduced state. The positive peak (reduced state) and trough (oxidized state) in the CD of PEDOT*/

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(27) CD measurements were carried out while rotating the sample in order to exclude both artifacts and linear polarization in analysis of chirality.

HPC are located at the inflection point of the corresponding absorption spectra. CD spectra induced by poor solvents or the casting of polythiophene film with an optically active substituent have been interpreted as being due to exciton coupling.[28] Exciton coupling requires the presence of an unconjugated chromophore in the chiral arrangement, which can occur through interchain interaction in the aggregate state.[29−32] The bisignate band in the reduced state of PEDOT*/HPC suggests the presence of an intermolecular process upon aggregate formation.[33] In this case, the aggregate-induced band is a charge transfer-type $\pi-\pi^*$ stacking of the polymer backbone, arising due to electronic communication.[34] Furthermore, the polymer shows a monosignate CD in the oxidized state, which partly released chiral aggregation due to intercalation of perchlorate ion between the main chains by the redox process. This result implies that PEDOT*/HPC in the oxidized state still forms a chiral structure. Therefore, it is possible that the intrusion of the ions does not completely break the chiral aggregation. In the helical aggregation state of the polymer, several hierarchical levels of chiral structure are plausible, including helical main chain structure. We conclude that the optical activity mainly results from the chiral aggregation of PEDOT*/HPC.

The CD observed for PEDOT*/HPC cannot be due to the HPC, which exhibits a CD in the short-wavelength region.[35] The absorption spectra for PEDOT*/HPC is uncharacteristic of selective reflection, but typical of a redox process for normal PEDOT. The reversible inversion of the sign of the CD in the redox process via change of the electronic state of the polymer indicates that the polymer forms a chiral structure, and that the chirality of the polymer can be changed by the application of voltage. The electrochemical potential change to the polymer allows exact doping level, and this process gives changes in electronic state. This phenomenon can be identified as “optically active electrochromism (OAE)”. Thus, it is possible to control chirality of the polymer film by applying an external potential using an electrochemical technique.

Repeating Change in CD. Figure 10 shows in situ optical micrographs (nonpolarized, transmitted light) of the PEDOT*/HPC film in monomer free 0.1 M TBAP under −1.3 and +1.3 V. The polymer changes from dark blue (−1.3 V) to sky blue (+1.3 V) (also see video in Supporting Information).

The large changes in both color and Cotton effect through electrochemical doping−dedoping suggest that PEDOT*/HPC can be used as an electrochromic material. This electrochromic behavior was investigated in more detail by observing the changes in the absorption and CD spectra with applied voltage. Figure 11 shows the changes in absorption for PEDOT*/HPC on ITO glass with repeated scanning between −0.6 and +0.6 V vs Ag/Ag$^+$ as a reference electrode in monomer free 0.1 M TBAP/acetonitrile. The

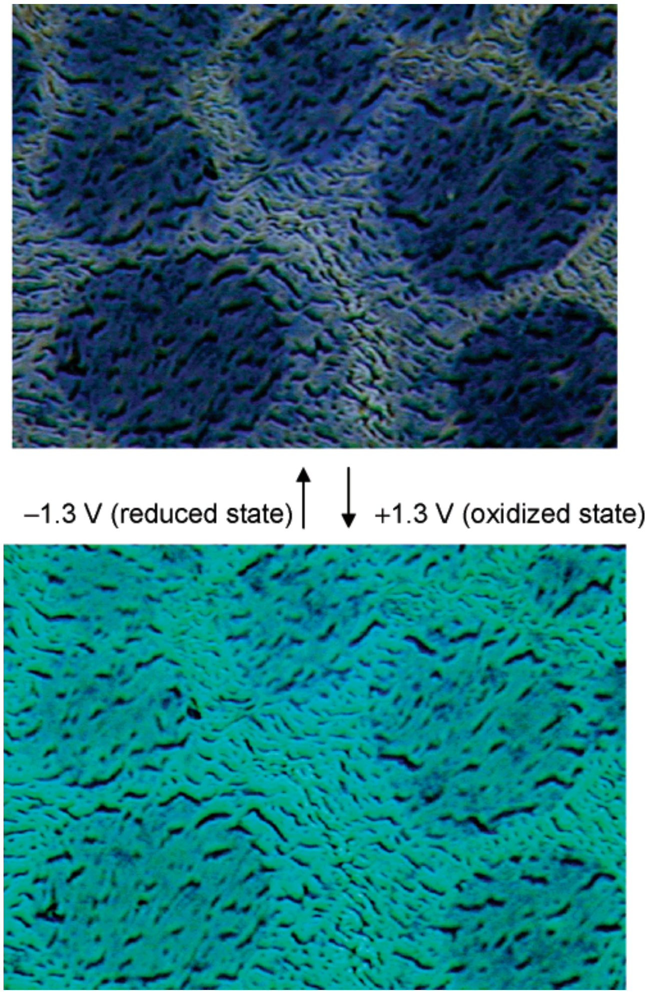

Figure 10. Optical micrographs of PEDOT*/HPC (transmitted light, no polarizer), reduced state (top) and oxidized state in the electrochromic cell (Supporting Information).

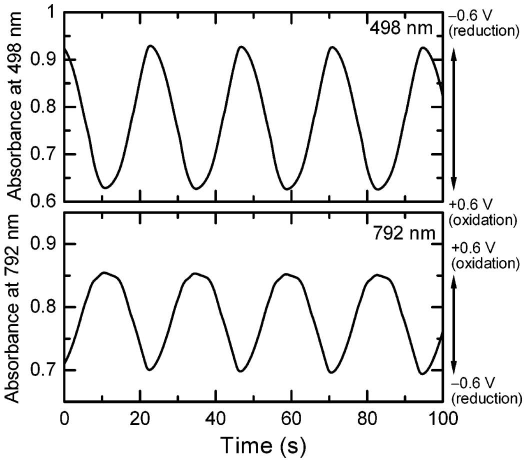

Figure 11. Repeating change of PEDOT*/HPC in absorption spectra at 498 nm and 792 nm during applications of potential with cyclic voltammetry between −0.6 and +0.6 V vs Ag/Ag$^+$ in monomer free 0.1 M TBAP/acetonitrile solution.

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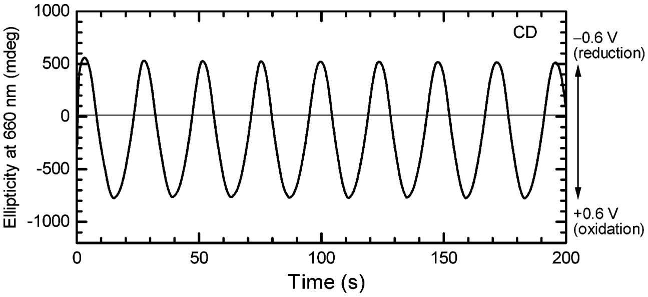

Figure 12. Repeating change of PEDOT*/HPC in CD during applications of potential with cyclic voltammetry between −0.6 and +0.6 V vs Ag/Ag$^+$ in monomer free 0.1 M TBAP/acetonitrile.

absorption intensity was monitored at 498 and 792 nm. In the oxidization process at 0.6 V vs Ag/Ag$^+$, the absorption intensity at 498 nm decreased, while that at 792 nm increased, whereas in the reduction process, the reverse was observed. These changes in absorption intensity were repeatable.

As shown in Figure 12, the CD intensities for PEDOT*/HPC changed reversibly during voltage scanning between −0.6 and +0.6 V in monomer free TBAP/acetonitrile solution. The reduced polymer state produces an opposite sign of the CD with respect to the oxidized state. Thus, altering the redox process allows for a reversible change in the CD intensity.

Optical rotation degree is defined as by

$$\Psi = \omega/2c(n_R - n_L)d$$

where ω, c, n_R, n_L, and d are angular frequency, speed of light in a vacuum, refractive index for right-circularly polarized light, refractive index for left-circularly polarized light , and thickness, respectively (in the case of concentrated sugar solution, $\Psi/d \sim 10°/\text{cm}$). Here, N*-LCs show an extraordinary large "$n_R - n_L$" value because of their helical structure (wave-guiding effect). Accordingly, N*-LCs exhibit intense optical activity compared to chiral compounds in the isotropic state. Although there is the possibility of some involvement of artifacts in the CD measurement of PEDOT*/HPC, these consistent signals of the CD reflect the inherent nature of chirality of the polymer film. The artifacts should be negligible in the CD measurement because PEDOT*/HPC possesses quite strong optical activity compared to the artifacts factor, resulting from its N*-LC like one-handed aggregation structure. The repeatable change in CD through the redox process suggests that the CD results in inherent chirality of PEDOT*/HPC.

The size of the circular structure on the polymer surface remains unchanged during the first several hundred voltage cycles due to the strong adherence of the polymer to the ITO surface. However, after more than 300 cycles with wide range potential changes between −1.3 V and +1.3 V, the adhesion between the polymer and the ITO glass begins to weaken, resulting in a visible and repeatable expansion−contraction phenomenon under voltage cycling. This expansion and contraction causes the size of the circle on the polymer surface to change slightly, as illustrated in Figure 13, driven by the doping and dedoping of TBAP (a supporting salt) during the electrochemical redox process. The mechanical motion causes the slightly concave circular structure to shrink by 2%, with a similar change in size for the entire film. This expansion and contraction change occurs by the same mechanism as for polymer actuators using conducting polymers.

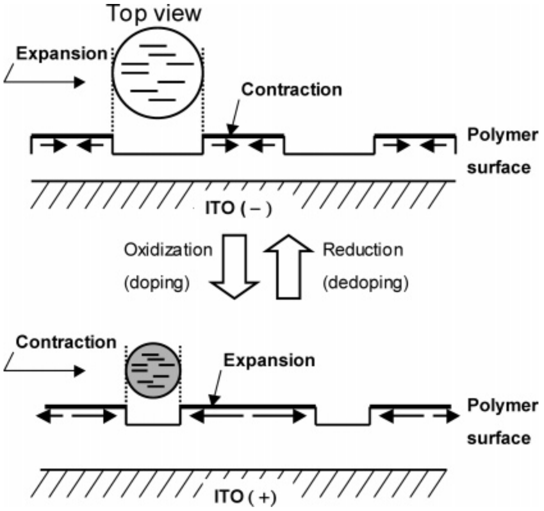

Figure 13. Change in size of circular structure in the redox process.

Optical Rotation. It is well-known that optical rotation occurs as a result of the influence of an external magnetic or electric field by the Faraday, Kerr, Electro-Pockels, and electro-Kerr effects. The effect is utilized in magneto-optical technology, Kerr cells for light shutters, and other applications. Optical rotatory power is also the most interesting physical property of asymmetric chemical materials, allowing the materials to reflect or absorb right- or left-circularly polarized light. The plane of polarization of a chiral medium rotates with the passage of linearly polarized light,[36] and the optical rotatory dispersion (ORD) spectrum provides "a natural optical rotation" of light. Optically active conjugated polymers exhibit interesting properties such as the temperature or solvent polarity control of optical activity[37,38] related to the change in polymer solubility due to variation in the aggregation state. However, for practical application, these methods of controlling optical activity are not convenient due to the difficulty of achieving active and quick control of optical activity through the control of temperature or solvent polarity. Here, we examined the optical rotatory dispersion (ORD) of the polymer during the redox process.

Figure 14 shows the ORD spectra of PEDOT*/HPC in monomer free 0.1 M TBAP/ acetonitrile solution. The optical rotation of the polymer in the reduced state was -1.1×10^5 deg/cm (569 nm, −0.45 V). This value is comparable to the Faraday rotation of magnetic transition-metal materials such as Fe (3.8×10^5 deg/cm at room temperature),[39] $Y_3Fe_5O_{12}$

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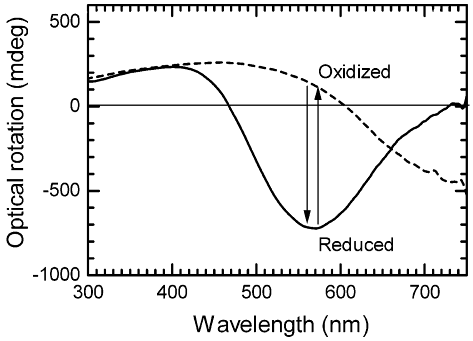

Figure 14. Optical rotation of PEDOT*/HPC at −0.45 V (reduced state) and 0.64 V (oxidized state) vs Ag/Ag$^+$ in monomer free 0.1 M TBAP/acetonitrile.

(250 deg/cm at 100 K),[40] and NdFeO$_3$ (4.7×10^4 deg/cm at room temperature).[40] The optical rotation angle of PEDOT*/HPC is changeable through the redox process. This result demonstrates that active control of optical rotation of the polymer was performed by the electrochemical method. This effect can be regarded as an "electrochemically driven change in optical rotation" of a chiral conducting polymer.

Conclusion

Optically active PEDOT*/HPC was successfully synthesized by oxidative electrochemical polymerization of EDOT in a chiral polymer (HPC) electrolyte without chemical reaction with chiral molecules. The aggregation state of the N*-LC allows epitaxial growth of PEDOT in a three-dimensional chiral field, and the high insolubility and infusibility of PEDOT*/HPC effectively preserves its metastable chiral structure. The PEDOT*/HPC exhibits a strong bisignate CD, electrochemical stability, and reversible color change between a dark blue reduced state and sky blue oxidized state with corresponding changes in the CD measurements. The CD of PEDOT*/HPC derives from N*-LC like aggregation order produced by the matrix N*-LC during the polymerization. The intense optical activity of the polymer allows the electro-chiroptical effects.

Experimental Section

Optical Measurements. Infrared spectroscopic measurements were carried out using a Jasco 550 Fourier transform infrared (FT-IR) spectrometer. Circular dichroism (CD) measurements were performed with a JASCO J-720. ORD spectra for the polymer have been calculated from the CD spectra by the Kramers−Kronig (K−K) transformation. Optical textures were observed by polarizing optical microscopy (POM) using a Nikon ECLIPS E400 POL polarizing microscope equipped with a Linkam TM 600PM heating-and-cooling stage. Circular differential interference contrast (C-DIC) microscopy observations of the polymer were carried out using a Carl Zeiss Axioskop 40 Pol microscope. Scanning electron microscopy (SEM) observations were carried out using a JEOL ED electron microscope, and electrochemical measurements of polymers were obtained using a BAS ALS 660A electrochemical analyzer. Laser scanning optical microscopy observations were performed using a Carl Zeiss LSM510 Laser Scanning System. Film thickness was measured using a ZYGO New View 5032 3-D surface structure analysis interference optical microscope.

Materials. HPC was purchased from Nippon Soda, Japan ($M_w = 3{-}5 \times 10^4$, $\eta = 3.0{-}5.9$ cps, 2 wt % in water at 20 °C). EDOT was obtained from Sigma Aldrich, USA, and was purified by vacuum distillation prior to use. Indium tin oxide (ITO) glasses, having a 0.2−0.3 μm thick ITO layer on glass (9 Ω/cm^2), were used as electrodes.

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Supporting Information Available: (1) The change accompanying the redox process can be confirmed from motion pictures captured during the redox process. (2) The surface structure of the film can be confirmed from laser scanning microscopy and C-DIC images. (3) A video of the change in size of the circular features on the film surface during potential scanning (after 300 scans between −1.3 V and +1.3 V). This material is available free of charge via the Internet at http://pubs.acs.org.

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