Vortex fibril structure and chiroptical electrochromic effect of optically active poly(3,4-ethylenedioxythiophene) (PEDOT*) prepared by chiral transcription electrochemical polymerisation in cholesteric liquid crystal†

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Chiroptical electroactive poly(3,4-ethylenedioxythiophene) (PEDOT) was electrochemically synthesised in a cholesteric liquid crystal (CLC) electrolyte solution from the *ter*EDOT monomer. PEDOT synthesised from *ter*EDOT was found to enable the formation of a fibril structure. In contrast, the EDOT monomer produced PEDOT without fibrils. Electrochemical polymerisation using this method provides a polymer with a distinct fibril structure and vortex texture. This indicates that the individual main chains are arranged by the topological transcription of structural chirality in the epitaxial electrochemical polymerisation in CLC as a one-handed helically twisted matrix. The polymer was confirmed to exhibit chiroptical electrochromism, diffraction, and the generation of a charge carrier in a chiral environment. This suggests formation of helical polarons of PEDOT.

Introduction

Cholesteric liquid crystals (CLC) have phase chirality,[1,2] and thus exhibit strong optical rotary power. The helical arrangement of a CLC on a macromolecular scale greatly enhances the physical manifestation of chiroptical properties to such an extent that the optical rotation of a chiral molecule can be enhanced in the CLC phase. Therefore, chiral conjugated polymers with CLC-like macromolecular formations are expected to exhibit considerable optical activity.

Liquid crystals (LC) are a useful reaction medium, having both liquid-like fluidity and structures that can be imprinted on the forming molecules. A LC can thus function as both a reaction field and a chiral molecular template. Chemical reactions in CLCs may be particularly effective for producing chiral compounds from achiral materials, since the phase chirality of the CLC provides a three-dimensional (3D) sequential chiral field for the chemical reaction.

LC solvents have been employed for many decades for preparing polyacetylenes with high electrical conductivities using the Ziegler–Natta catalytic system.[3–5] The polyacetylene films that are produced display a high degree of fibril orientation. CLCs have been employed to prepare helical polyacetylene.[6] LC materials are widely used in chemistry and physics as molecular templates for synthesising aromatic π-conjugated polymers with supramolecular order.[7–13]

In a previous study, *poly*EDOT prepared in CLCs showed no fibril structure.[14] However, it was successfully polymerised in CLCs; the *poly*EDOT appearing as a partially spiral structure over the entire film surface.[14] This may be because the EDOT monomer has no rigid rod-like molecular shape and was not organized before polymerisation in the CLCs. Herein, polymerisation of *bi*EDOT may improve these drawbacks due to the linearity of *bi*EDOT. Employment of *ter*EDOT for polymerisation in CLCs may further improved these points, and it is expected to produce polymers with high conversion because the number of arylene units in the monomer increases, thus reducing the oxidation potential.

In the present study, electrochemical polymerisation in a CLC electrolyte solution[15] is performed using *ter*EDOT, a triaryl system, to afford a high-performance optically electroactive π-conjugated polymer. A method for producing *ter*EDOT with high-resolution electronic spectra has been previously reported.[16,17] Here, a novel synthetic route for preparing the *ter*EDOT monomer is reported. The rigid rod-like shape of *ter*EDOT provides good affinity for LCs in blends. The *ter*EDOT as a monomer itself can be pre-organized into a chiral sense prior to polymerisation in the CLC medium. The *ter*EDOT is expected to have a high polymerisation activity due to its low oxidation potential.

The fibril-forming result of PEDOT from *ter*EDOT prepared in a CLC electrolyte solution by the transcription electrochemical polymerisation enables the visualization of CLC due to the polymer orientation. The resultant polymer exhibits a coiled fibril structure and the entire surface has a vortex pattern showing chiroptical electrochromism. Furthermore, the diffraction properties and the chiral-spin magnetic structure for the polymer have been evaluated. Polymerisation in a nematic LC (NLC) was also conducted and the birefringence was quantified. This also can provide quantitative information as to how the properties of the polymer reflect those of the liquid crystal host.

The CLC structure occurs in many instances in nature. For example, the cuticle of crusted insects such as *Cetonia* (beetle) exhibits a CLC structure, resulting in the wavelength-selective reflection of circularly polarized light.[18,19] Polymerisation of the organic constituent in the secretion of these insects proceeds in such a manner as to produce CLC order, and the material

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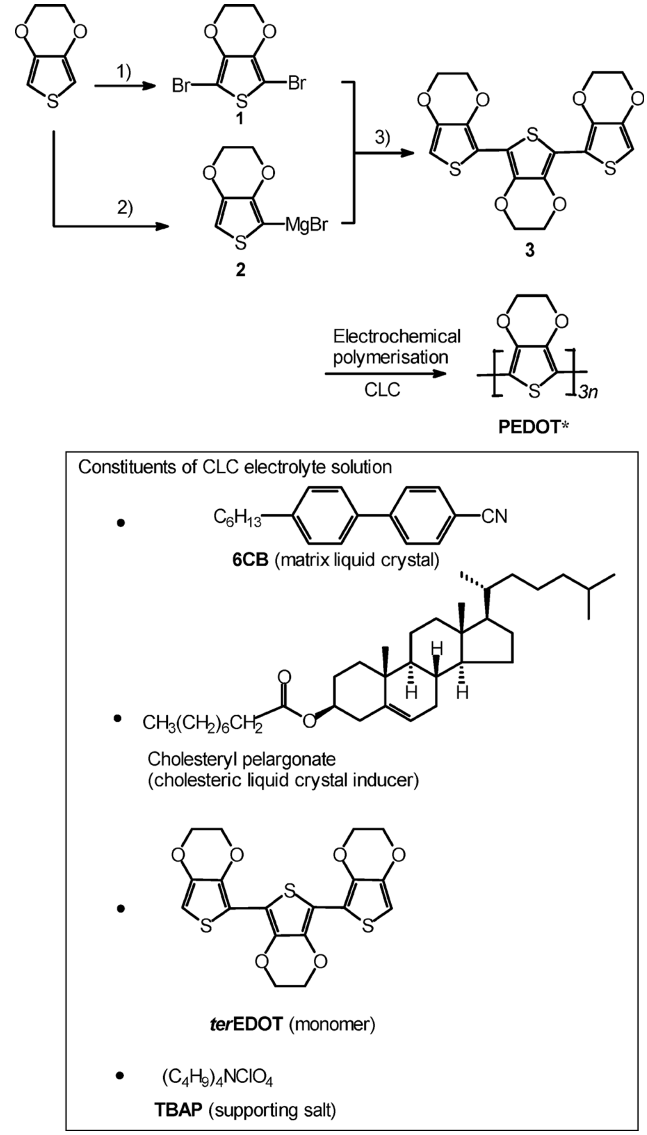
produced is both insoluble and infusible. Similarly, the biomineralization of vaterite in egg yolk proceeds *via* a LC template to produce multilayered shells.[20] Biological LCs thus function both as a reaction field and as a template to guide the formation of the organic structure. The CLC-based polymerisation mechanism considered in the present study attempts to achieve structural chirality by imprinting in a manner comparable to these biological processes as a form of biomimetic technology.

Results and discussion

Polymer synthesis

Scheme 1 shows the synthetic route for monomer 2,3,2′,3′,2″,3″-hexahydro-[5,5′:7′,5″]ter(thieno[3,4-b][1,4]dioxine) (*ter*EDOT). The precursor 5,7-dibromo-2,3-dihydro-thieno[3,4-b][1,4]dioxine (**1**) was first synthesised by bromination using *N*-bromosuccinimide (NBS) in a mixed solvent consisting of chloroform–glacial acetic acid at room temperature according to a method reported in the literature.[21–23] EDOT was then coupled with **1** *via* the Grignard reaction with the aid of a Ni(II) catalyst to yield *ter*EDOT. The cholesteric electrolyte solution used as the reaction field was prepared by adding a CLC inducer (cholesteryl pelargonate) to 4-cyano-4′-hexyl biphenyl (6CB). Tetrabutylammonium perchlorate (TBAP) was then added as a supporting salt. Electrochemical polymerisation of the monomer was carried out in the CLC electrolyte solution between two indium-tin-oxide (ITO) glass electrodes. Molecular structures constituting CLC electrolyte containing EDOT monomer are shown in Scheme 1 (lower). The CLC electrolyte solution displays a typical fingerprint texture under polarizing optical microscopy (POM) observation at 25 °C (Fig. 1). Prior to electrochemical polymerisation, the electrolyte solution was heated in a vial to 40 °C under an argon atmosphere in order to completely dissolve the supporting salt, monomer, and chiral inducer in the 6CB (LC solvent). Electrochemical polymerisation was then performed by injecting the mixture between two sandwiched ITO-coated glass electrodes with a Teflon sheet (thickness, *ca.* 0.2 mm) as a spacer. The reaction cell was initially heated to 40 °C, and then gradually cooled to room temperature (25 °C) to afford the CLCs with a good fingerprint texture. A voltage of 4.0 V was then applied across the cell. The optical texture of the cholesteric mixture remained unchanged upon the application of a voltage. After 30 min, an insoluble and infusible polymer thin film was obtained. It coated the anode side of the ITO electrode. The film on the ITO was then washed with methanol, water, acetonitrile, methanol, water, and acetone in that order, and dried under reduced pressure to afford the chiroptical *ter*EDOT polymer film (PEDOT*).



Scheme 1 Synthetic route for PEDOT* and constituents of the cholesteric liquid crystal (CLC) electrolyte solution. (1) *N*-Bromosuccinimide, chloroform–glacial acetic acid, chloroform. (2) *n*-BuLi, THF, then $MgBr_2$, Et_2O. (3) $Ni(dppp)Cl_2$, THF.

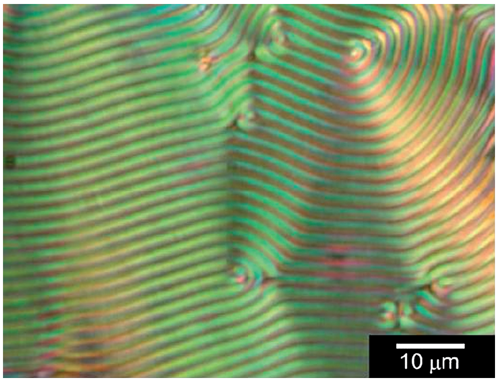


Fig. 1 POM image of cholesteric liquid crystal (CLC) containing the monomer (*ter*EDOT), supporting salt (tetrabutylammonium perchlorate, TBAP), and CLC inducer (cholesteryl pelargonate) at 25 °C.

Polarizing optical microscopic image

POM observations of PEDOT* prepared in the CLC electrolyte solution revealed that the polymer exhibits a fingerprint texture resembling (but not identical to) that of the original CLC system (Fig. 2). In CLCs, the optical texture is closely related to the individual molecular ordering forming the matrix, and the present PEDOT* film exhibits birefringence along with an

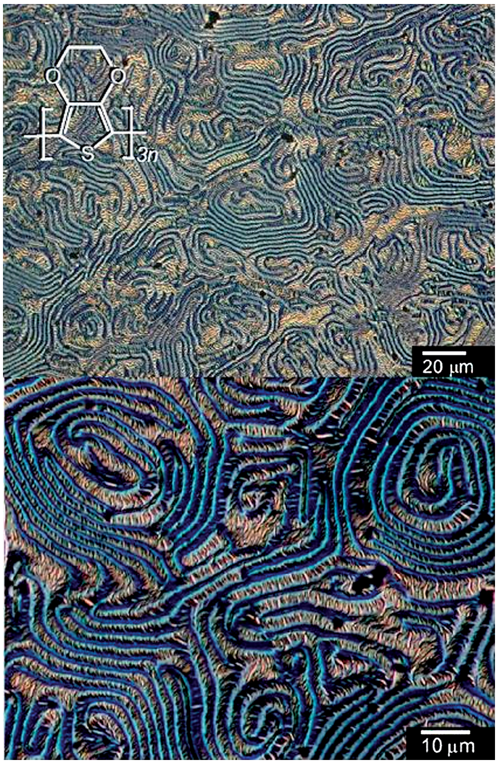


Fig. 2 Polarizing optical microscopic (POM) image of PEDOT* prepared in unoriented cholesteric electrolyte solution at different magnifications.

excellent colour distribution due to optical retardation under POM, similar to that of the CLC. In other words, the molecular arrangement of the individual main chains was oriented in a helical manner, similar to that of the CLC. However, the polymer is not a CLC.

Diffraction

The CLC-like periodic structure of the PEDOT* film produces two optical effects: the diffraction of light and the iridescent reflection of light. Diffraction can be observed by irradiating the PEDOT* film on the ITO electrode with a laser set perpendicular to the film surface and visualizing the transmitted pattern on a screen. A circular diffraction pattern (a Fourier-transformed image) is produced due to the random diffraction function of the present polymer, as shown in Fig. 3(A). Three wavelengths of laser light were tested (red, green, blue), and each produced a diffraction circle of characteristic radius. The circle diameter increases with an increase in the laser wavelength (blue < green < red). The grating period corresponds to the distance between adjacent stripe features of the polymer film. Although the inherent colour of the polymer is dark blue [Fig. 3(B)], a rainbow-coloured iridescent reflection occurs under irradiation with white light, and the reflected wavelengths vary with the angle of incidence and the wavelength composition of the incident light beam [Fig. 3(C)].[13] This iridescent reflection originates from the periodic stripe structure of the polymer surface. Thus, the diffraction by the polymer satisfies Bragg's law, $n\lambda = 2d\sin\theta$, where n is the integral number, λ is the wavelength, d is the lattice constant, and θ is the incident angle (glancing angle). In the case of this system, $P/2$ (distance between the stripes) is the lattice constant.

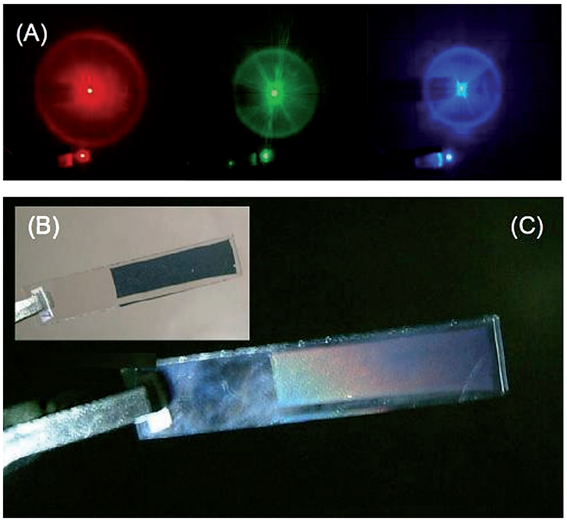


Fig. 3 (A) Laser diffraction patterns of PEDOT*. (B) PEDOT* film under fluorescent light. (C) PEDOT* film showing interference colour with an oblique angle of incidence from a white light emitting diode beam.

Uniaxial PEDOT* prepared in oriented electrolyte solution by shear stress exhibits an oriented optical texture (top) and an oriented laser diffraction pattern (bottom), as shown in Fig. 4.[24]

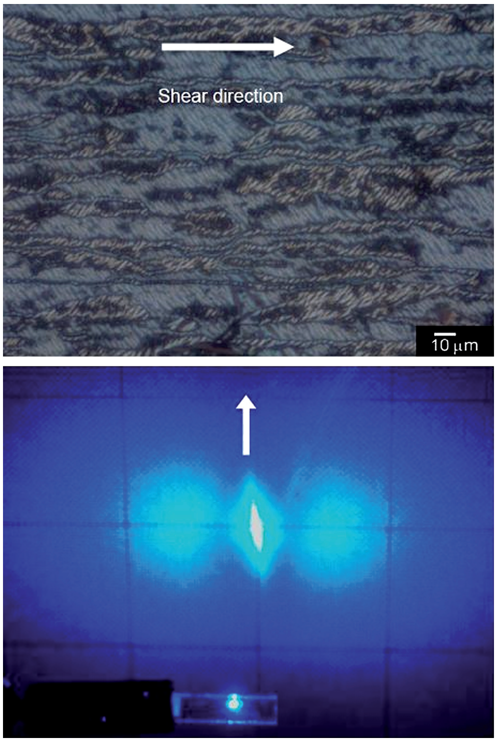


Fig. 4 (Top) POM image of PEDOT* prepared in oriented cholesteric electrolyte solution. (Bottom) Laser diffraction pattern (arrow indicates orientation).

The orientation of PEDOT* is normal to the shear direction of the CLC electrolyte solution (slightly tilted), suggesting that the shear stress aligns the fingerprint pattern of the CLC electrolyte solution, whereas individual CLC molecules are aligned normal to the shear direction. In the polymerisation of *ter*EDOT, the polymer molecules are aligned according to the CLC electrolyte solution, and are thus aligned normal to the shear direction of the CLC electrolyte solution. These results indicate that the laser diffraction effectively expresses the molecular orientation of the polymer.

SEM

Scanning electron microscopy (SEM) images of the present polymer taken at 25° to the surface are shown in Fig. 5 (the four images are from the same sample at different regions). The high conversion and rigidity of the monomer combined with the π-stacking of the polymer, result in a mode of polymer aggregation that produces a fibril structure during electrochemical growth. This structure differs from that of chiral poly*bi*thiophene,[25] chiral polypyrrole,[26] PEDOT synthesised by electrochemical preparation from the EDOT monomer in CLCs,[14] and helical polyacetylenes prepared by acetylene gas–CLC interfacial polymerisation.[27] This difference can be attributed to the difference in molecular shape and crystallinity of PEDOT* prepared by the present route. The SEM observations confirm that the wedge pattern identified by POM corresponds to the assembly of fibrils. Vortices consisting of coil-like fibrils are apparent between the helical bundles. Furthermore, the fibrils between fingerprint features form thin helical bundle structures that are twisted clockwise (Fig. 6(H)).

The characteristic structure may originate from that of individual molecules of the polymer growth along the gradually twisted order of the CLC from the anode (ITO) with the electrochemical epitaxial growth process. The helical formation from the director of the CLC provides a different degree of growth for the polymer on the electrode. It is important to note that the

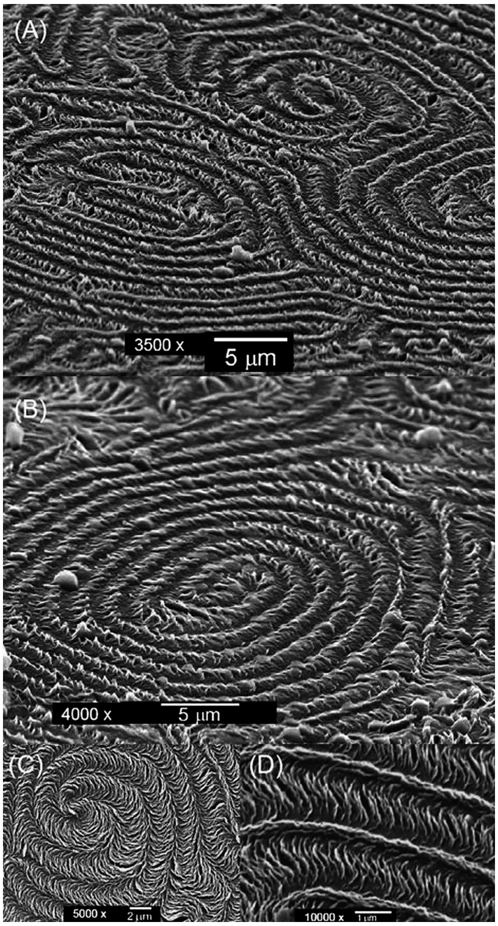


Fig. 5 Scanning electron microscopy (SEM) images of PEDOT* prepared in cholesteric liquid crystal electrolyte solution. SEM images of PEDOT* taken from a direction oriented 25° from the surface [(A) 3500×, (B) 4000×]. (C) SEM image of the polymer surface in the normal direction (5000×). (D) Magnification of surface image (10000×) in the normal direction.

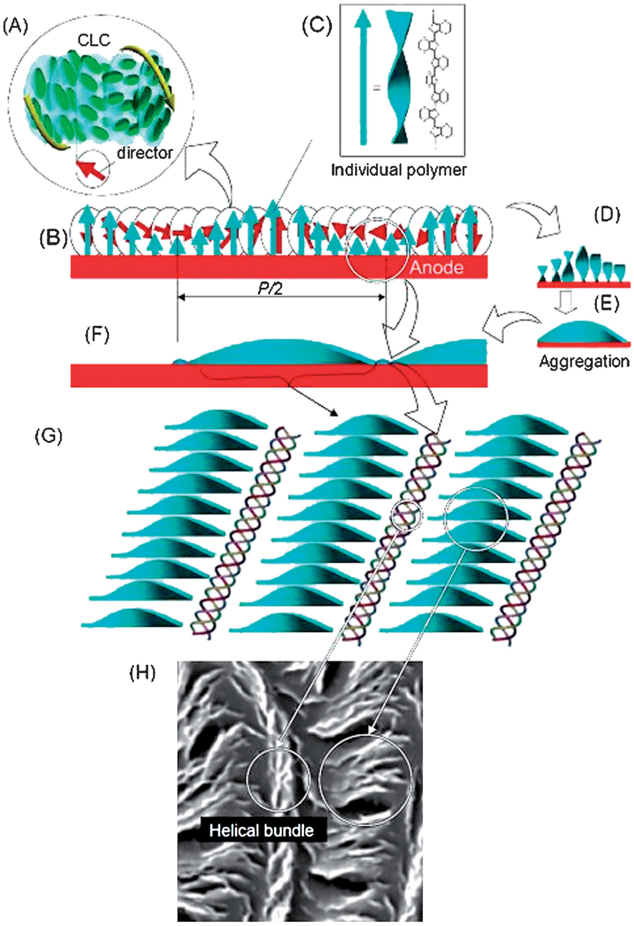


Fig. 6 Plausible polymerisation mechanism of *ter*EDOT in a CLC electrolyte solution. (A) Helical ordering of the CLC. (B) Twisted directors continuum of the CLC (red arrows) and epitaxial growth directions of the polymer from the anode side (sky blue arrows). (C) Helical twist formation of PEDOT*. (D) Formation of individual PEDOT* main chains and (E) aggregation. (F) PEDOT* deposited on ITO. (G) 3D possible structure of the polymer surface. (H) SEM image of PEDOT* showing a helical bundle (polymer grew at the region where directors of the CLC are oriented in parallel to the electrode surface) and lamellar type structure (polymer grew at the region between directors of the CLC oriented in parallel to the electrode surface).

fibrils grow well in the region in which the CLC directors are oriented normal to the electrode surface. The fibrils with helical bundle are observed in the region where the director of the CLC is parallel to the electrode. The fingerprint pattern with the fibril structure observed is similar to the molecular model of the dome-type polygonal texture of CLC materials,[28] and the photo-polymerised polymer obtained in a CLC.[29,30]

The CLC of the biomolecules is solidified during the process of skeletal formation.[31] The characteristic structure is utilized for structural colour in insects such as butterflies. The morphology and polymerisation process of the PEDOT* in the present study may be similar to those for other biological systems. Moreover, the morphology is very similar to the microstructure of the tangential section of tubercles of *Carcinus maenas* (littoral crab)[18] [Fig. 5(C)]. A distinct surface image taken at high magnification is shown in Fig 5(D). In the SEM image, an S-shaped structure is observed between three lines of bundles.

Plausible polymerisation mechanism

A plausible polymerisation mechanism of *ter*EDOT in the CLC electrolyte solution is shown in Fig. 6. The CLC electrolyte solution has one-handed helical ordering [Fig. 6(A)]. Polymerisation is performed in the sequential helical director field [red arrows in Fig. 6(B)] of the CLC electrolyte solution with an electrochemical epitaxial growth mechanism, and the chiral field provides a one-handed twist of the main chain [Fig. 6(C)]. The lamella-like structure can be considered an advanced form of the helical arranged structure. The CLC thus provides a chiral reaction field and functions as a chiral molecular vessel.

Individual twisted PEDOT* main chains [Fig. 6(D)] aggregate to form lamella-like semicircles [Fig. 6(E), 6(F), 6(G)]. The top-view SEM image of the polymer shows a lamellar structure with the "S-shaped" form [Fig. 6(H)]. The right-handed helical bundles of the polymer are located in the region where the directors of CLC are oriented parallel to the electrode surface. This may be due to the fact that the helical torque of the CLC affects the polymer during the growth process in this region. The polymer may thus form a characteristic structure in the CLC electrolyte solution.

Electrochemical polymerisation in a nematic liquid crystal

Electrochemical polymerisation of the monomer was also carried out in the same manner using a nematic LC (NLC) to afford N-PEDOT (PEDOT prepared in a NLC). The electrolyte solution for this polymerisation consisted of 0.29 g 6CB, 0.6 mg TBAP, and 8 mg *ter*EDOT. A POM image of the NLC electrolyte containing the monomer is shown in Fig. 7(A).

The primary feature of molecular organisation in a NLC is the orientational order of the molecular axis, where the average direction of the long axes defines the director (n), which may be treated as a vector. The LC displays a schlieren texture, appearing as a brush-like pattern or thread-like texture, reflecting the disclinations and directors of individual LC molecules in the system.

N-PEDOT film exhibits birefringence and a schlieren texture with two-fold brushes under POM, as shown in Fig. 7(B). The brushes of the schlieren texture on the film visually rotate with the rotation of the POM analyser, as generally observed for NLC, indicating that the present polymer has schlieren-like molecular ordering. These results further suggest that the thread-like pattern of the NLC is imprinted on the polymer during polymerisation, as shown in Fig. 7(C). The fibrils of N-PEDOT are aligned in a thread-like pattern, indicating that the NLC directs the growth of the polymer. The insolubility of the polymer in the NLC electrolyte then facilitates phase separation.[32]

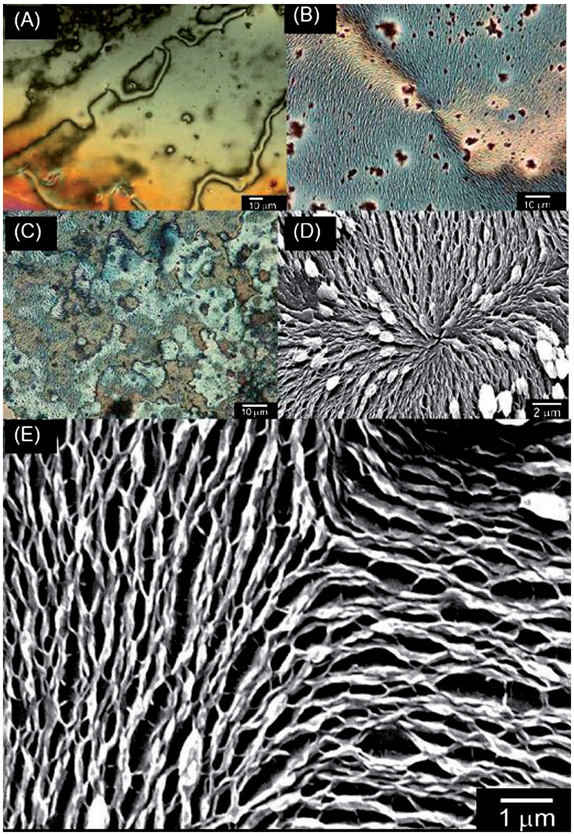


Fig. 7 (A) POM image of nematic electrolyte solution containing *ter*EDOT as a monomer. (B) PEDOT prepared in nematic electrolyte solution (N-PEDOT) in the schlieren texture region. (C) PEDOT prepared in nematic electrolyte solution (N-PEDOT) at a thread-like texture region. (D, E) SEM images of N-PEDOT.

The distribution of the director around the structural defect in NLC has been predicted theoretically,[28a] and the SEM image of N-PEDOT visually confirms the presence of the NLC topology, including the fibril orientation reflecting the vector field around the wedge-type loops near the centre of the defect. The N-PEDOT topology has disclination parameters of $s = -1$ and $s = -1/2$ [Fig. 7(D, E)], where $2\pi s$ is the angle at which the director turns on a closed curve around the centre. The alignment of fibrils in N-PEDOT thus allows the LC directors to be visualized as vectors, and confirms that N-PEDOT growth occurs to form a texture similar to that of NLC in the same manner as observed for the polymerisation in the CLC. That is, transcription of the NLC order occurred at the molecular level in the polymerisation of PEDOT by this method. N-PEDOT is not chiral and exhibits no Cotton effect in circular dichroism (CD) spectroscopy.

Optical activity

In situ optical absorption, CD, and optical rotatory dispersion (ORD) spectra for the polymer films were obtained under various electrochemical conditions in monomer-free 0.1 M TBAP–acetonitrile solution. The measurement cell included a platinum wire as the counter electrode, an Ag/Ag$^+$ reference electrode (calibrated against Fc/Fc$^+$), and the polymer deposited on ITO. The optical absorption spectrum of oxidized (electrochemically doped) PEDOT* exhibits a peak at 538 nm accompanied by a weakening of the π–π* transition of the main-chain and a strengthening of the peaks at 756 nm and 1298 nm due to the generation of radical cations and dications on the main chain (Fig. S1, ESI†). The radical cations and dications on the main chain can be referred to as polarons and bipolarons, respectively.[33–35] The colour of the polymer changed reversibly from dark blue to sky blue upon oxidation, which proceeds by the electrochemical doping of perchlorate ions. This doping–dedoping behaviour is typical for electroactive polymers.[36–38]

As shown in Fig. 8 (top, oxidation process), PEDOT* exhibits a Cotton effect associated with the π–π* transition of the polymer main chain, which is related to the polaron region in electrochemical doping and dedoping. CD spectra of the electrochemical reduction process of the polymer are shown in Fig. S2 (top) (ESI†). These results indicate that the redox process for the CD of the polymer is reversible. The CD signals cannot be due to the CLC inducer, cholesteryl pelargonate, employed in the polymerisation because the weak Cotton effect is only observed at wavelengths in the range 240–340 nm. PEDOT* did not produce any signals related to the CLC inducer in infrared (IR) absorption spectroscopy measurements. The reversible inversion of the sign of the Cotton effect at 450 nm in the doping–dedoping (oxidation–reduction) process *via* a change in the electronic state of the polymer indicates that the polymers have an inherently chiral structure.

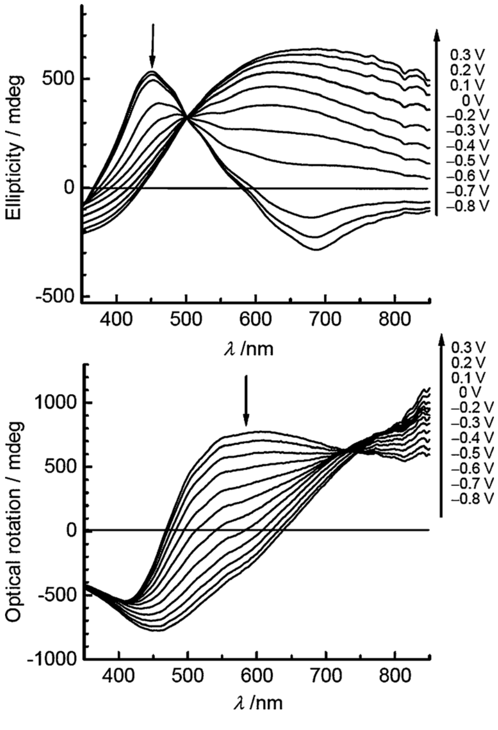


Fig. 8 (Top) CD spectra and (bottom) ORD spectra of monomer-free PEDOT* at various potentials *vs.* Fc/Fc$^+$ during electrochemical oxidation in monomer-free 0.1 M TBAP–acetonitrile solution.

The ORD spectra of PEDOT* at various potentials *vs.* Fc/Fc$^+$ in 0.1 M TBAP–acetonitrile solution is shown are Fig. 8 (bottom) and Fig. S2 (lower) (ESI†). Upon oxidation, an optical rotation trough at 430 nm and a peak at 560 nm appear in the spectrum, with an isosbestic point at 772 nm, which could be attributed to the electrochemical doping–dedoping of perchlorate ions in the redox process. This result confirms that the polymer is electrochiroptically active and that the optical rotation can be controlled *via* the electrochemical process. This property of the polymer can be regarded as an “electrochemically driven chiroptical effect.”

The PEDOT* displayed a bisignate (split type) CD in the reduced state. CD spectra induced by poor solvents or the casting of polythiophene film with an optically active substituent have been ascribed to exciton coupling.[39] Exciton coupling requires the presence of an unconjugated chromophore in the chiral arrangement, which can occur through interchain interactions in the aggregate state. The bisignate band in the reduced state of the PEDOT* suggests the presence of an intermolecular process upon aggregate formation. The aggregate induced band is a charge transfer-type π–π* stacking of the main chain, arising due to electronic communication. Furthermore, oxidation process physically increases the distance between main chains in chiral aggregation due to the intercalation of the perchlorate ion between the main chains. 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 a helical main chain structure produced by transcription from the CLC.

Electrochemical potential change to electroactive π-conjugated polymers reflects the exact doping level, and this process gives changes in the electronic state, resulting in a colour change for polymers. Achiral π-conjugated polymers prepared in isotropic electrolyte solutions show no optical activity, although the polymers display a colour change with the redox process. On the other hand, the PEDOT* thus synthesised in the CLC shows not only a colour change but also tunable chiroptical properties with the redox process.[40,41]

ESR

Fig. 9 (top) shows the electron spin resonance (ESR) spectra of PEDOT* at three potentials. The intensity of the ESR signals changes according to the applied potential, which reflects the state of the electrochemical doping. This result suggests that the spins on the polymer are derived from the induced charge ($S = 1/2$) in the π-electron system. The g value of 2.0027 for the present polymer indicates the formation of charge carriers in the polymer, such as polarons.[35] The ESR result at −0.7 V indicates that electrochemical dedoping is not complete, with ESR signals

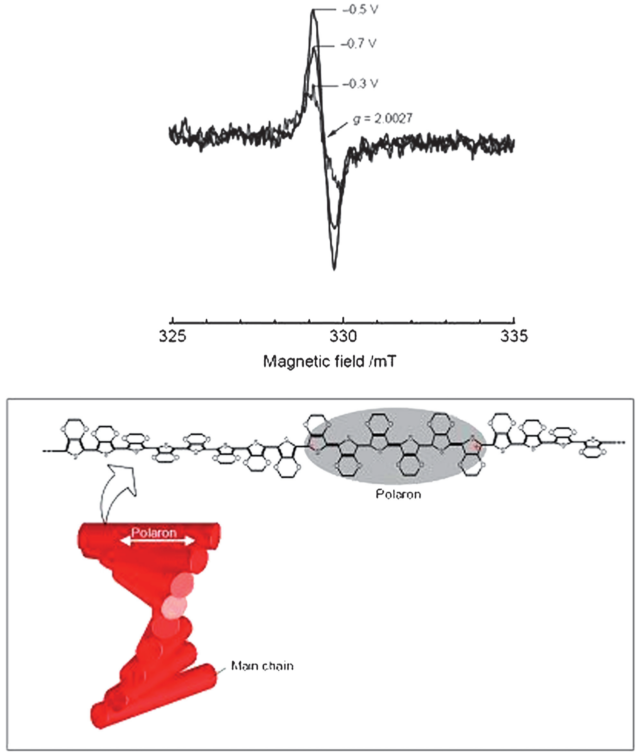


Fig. 9 (Top) ESR spectra of PEDOT* at –0.7 V, –0.5 V, and –0.3 V *vs.* Fc/Fc$^+$. (Bottom) Possible structure of polarons in the main chain and chiral aggregation structure.

indicating the existence of radicals derived from residual polarons. The intensity of the ESR signal at –0.5 V increases with an increase in radical cation concentration, and decreases with the generation of dications (reduction in radical concentration on the main chain). This ESR result is consistent with the absorption spectrum, which reveals the emergence of an absorption band at 756 nm (polaron) with increasing voltage. The CD results for the polymer are also consistent with the ESR spectra. With increasing voltage, the CD signal at 450 nm weakens and the peak at 619 nm strengthens. Furthermore, the CD signals at 850 nm are negative at –0.7 V and positive at –0.5 V. Plausible structures of chiral aggregation forms produced in the CLC electrolyte solution and polaron as a charge carrier in the main chain are shown in Fig. 9 (bottom). Polarons locate individual main chains, and gradually twist in a helical manner to form chiral aggregation polarons. Moreover, the results suggest the formation of inter-chain helical polarons of the conducting polymer.

Conclusions

PEDOT having chiroptical properties was electrochemically synthesised in CLC electrolyte solution from the *ter*EDOT monomer. Electrochemical polymerisation by this method afforded a polymer with a distinct fibril structure and vortex texture imprinted CLC structure indicating that the individual main chains were arranged by the topological transcription of structural chirality in the epitaxial electrochemical polymerisation in CLC as a one-handed helically twisted matrix. The fibril-forming property enables the polymer to direct the LC. The polymer surface may be referred to as a "chiral carpet with vortex" structure. The polymer exhibits chiroptical electrochromism, diffraction properties, and charge carrier generation. The CD and the ESR results suggest the formation of polarons in one-handed helical structures for the polymer. Synthesis of the polymer by the present method is applicable to the fabrication of new optoelectronic devices such as chiral electrochromic displays and optical rotation modulators, and provides valuable insight into the behaviour and structure of liquid crystals.

Experimental

Synthesis of 5,7-dibromo-2,3-dihydro-thieno[3,4-b][1,4]dioxine (dibromo-EDOT) (1)

This synthesis was carried out according to a previously reported method.[423] Quantities used: $CHCl_3$ (50 mL), glacial acetic acid (50 mL), 3,4-ethylenedioxythiophene (EDOT) (3 g, 21.1 mmol), *N*-bromosuccinimide (NBS) (8 g). Yield = 73% (4.63 g, white crystals).

Synthesis of 2,3,2′,3′,2″,3″-hexahydro-[5,5′:7′,5″]ter(thieno[3,4-b]-[1,4]dioxine) (*ter*EDOT) (3)

Into a solution of EDOT (1.9 g, 13.4 mmol) in tetrahydrofuran (THF) a quantity of 5 mL of *n*-butyl lithium–hexane solution was added (2.71 mol L^{-1} in hexane, 13.4 mmol) under argon flow at –79 °C. The reaction mixture was stirred for 60 min. Then, the temperature of the reaction mixture was maintained at 0 °C, and 3.46 g (13.4 mmol) of $MgBr_2$ in Et_2O was added to the mixture and stirred. After 30 min, dibromo-EDOT (**1**) (2 g, 6.7 mmol) was added. Subsequently, $[Ni(dppp)Cl_2]$ (0.14 g, 2.68×10^{-4} mol) was slowly added to the reaction mixture. After 12 h, the solution was evaporated, washed thoroughly with water, and extracted with dichloromethane. After evaporation, the crude product was purified by column chromatography (silica gel, dichloromethane). The silica gel was pretreated by passing through approximately 50 mL triethyl amine to avoid polymerisation of the product during the purification procedure. Yield = 63% (3.6 g, dark yellow powder). The chemical structure of the desired material was confirmed by ^1H NMR in $CDCl_3$ (one drop of triethyl amine was added to the NMR tube to avoid polymerisation). ^1H NMR (δ from TMS, signals of *ter*EDOT): 4.21 (m, 6H), 4.33 (m, 6H), 7.1 (m, 2H).

Preparation of cholesteric liquid crystal electrolyte solution

The cholesteric electrolyte solution used as the reaction field was prepared by adding a CLC inducer (cholesteryl pelargonate, 0.02 g, 0.038 mmol) to 4-cyano-4′-hexyl biphenyl (6CB, 0.459 g), a well-known nematic LC. Tetrabutylammonium perchlorate (TBAP, 1 mg, 0.3×10^{-5} mmol) was then added as a supporting salt. Liquid crystallinity was confirmed to be maintained after addition of the monomer (*ter*EDOT, 20 mg, 0.047 mmol). A scheme of the constituents of the CLC electrolyte solution system employed in this study is provided in Scheme 1. The cholesteric electrolyte solution system exhibits a fingerprint texture typical of the cholesteric phase when observed by polarizing optical microscopy (POM) at room temperature, where the distance between stripes in the optical texture of the cholesteric electrolyte solution corresponds to the helical half-pitch of the CLC. The mixture of LC, monomer, CLC inducer, and supporting salt is employed as an electrolyte solution for electrochemical polymerisation in place of conventional systems containing a supporting salt in isotropic solution.

Techniques

Absorption spectra were obtained using a Hitachi U-2000 spectrophotometer, and circular dichroism and optical rotation measurements were performed using a Jasco J-720 spectrometer with an ORDE-307W ORD unit. Electrochemical measurements of polymers were conducted using an electrochemical analyser (PGSTAT 12, Autolab, Netherlands), and optical textures were observed using a Nikon ECLIPS LV 100 high-resolution polarizing microscope with Nikon LU Plan Fluor and Nikon CFIUW lenses at 1000× and 500× magnifications without immersion oil.

Materials

TBAP and cholesteryl pelargonate were obtained from Tokyo Kasei (TCI) Japan. 6CB was purchased from Merck. EDOT was obtained from Aldrich. The ITO glass (Furuuchi Chemical Corporation) consists of a 0.2–0.3 μm-thick ITO layer on glass (9 $\Omega\ \mathrm{cm}^{-2}$).

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