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Asymmetric polymerisation in liquid crystals and resultant electro-chiroptical effect: Structure organising polymerisation and chiral charge carrier "chiralion"

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Abstract. Electrochemical synthesis in liquid crystal (LC) affords conducting polymers having LC molecular order and electro-activity. The polymerisation method can be referred to as structure organising polymerisation (SOP). The optical textures of the polymers thus prepared appear very similar to that of the LC electrolyte solution used for the polymerisation. Especially, polymers prepared in cholesteric LC (chiral LC) having structural chirality show doping-dedoping (redox) driven change in chiroptical activity (controllable circular dichroism and optical rotation), as "electro-chiroptical effect". The polymer films exhibit interference colour and electrochemically driven refractive index modulations. The chiroptical activity of the polymer prepared in cholesteric LC comes from axial chirality of the helical structure.

1. Introduction
Chiral liquid crystals are fascinating materials due to their liquid-like fluidity, crystal-like order, and hierarchic structure [1]. The helical aggregation of rod-like molecules in cholesteric liquid crystal (cholesteric LC) results in periodicity, and the three-dimensional (3D) molecular arrangement produces structural chirality. Many living organisms possess cholesteric LC structures [2–5]. The exoskeleton of insects with cholesteric order shows selective reflection of light. These are referred to as photonic insects. For example, the exoskeleton of golden beetles has cholesteric order at the microscopic level. A jewel beetle cuticle consists of the alternation of multi-layers having liquid crystal (LC) order [6]. Life forms contain structures related to LCs, e.g., brain, cells, and muscle. Furthermore, DNA shows LC structure at certain concentration in water [7].

The helical arrangement of a cholesteric LC on a macromolecular scale greatly enhances chiroptical properties. The optical rotation of a chiral molecule can be enhanced in the cholesteric LC phase. Therefore, chiral conjugated polymers with cholesteric LC-like macromolecular formations are expected to exhibit optical activity.

LCs can be useful reaction medium, having both liquid-like fluidity and ordered structures that can be imprinted on the forming molecules. A LC can thus function as both a reaction medium and a template. Chemical reactions in cholesteric LCs are particularly effective in producing chiral compounds from achiral materials, since the structural chirality of the cholesteric LC provides a three-dimensional (3D) sequential chiral matrix for the chemical reaction. Polymerisation in cholesteric liquid crystals performs "matrix imprinting" (MAT-I) for the resultant polymer.

The author synthesised mono-substituted polyacetylene derivatives having chiral groups in order to obtain ferroelectric liquid crystalline conjugated polymers based on the original idea of the author in Shirakawa lab (U. Tsukuba). The chiral chemistry and S$_2$2-type Mitsunobu reaction have been introduced in the lab through the idea and experiments in 1994. The polymer thus synthesised showed...
chiroptical activity and beautiful spiral patterns derived from the helical structure with chirality [8,9]. Here, in this lab, synthesis of polyacetylene in nematic LC has been carried out as the previous collaborative study by Araya and Shirakawa et al. [10].

Figure 1. (a) Prototype electrochemical polymerisation in liquid crystal (LC). (b) Sandwich cell LC polymerisation. (c) Detachment of the cell after the polymerisation. ITO = indium tin oxide coated glass. Reproduced by permission of the Royal Society of Chemistry from ref [21] (Figure 1(d,e)).

After several months (November 1994) from the synthesis of the chiral liquid crystal polyacetylene derivative showing spiral structure, synthesis of polyacetylene by using the chiral smectic C (SmC*) for the reaction field was proposed in the lab based on the results obtained by the author. However, at the time, the author mentioned that cholesteric LC (chiral nematic LC, N*-LC) should be employed in place of SmC* LC materials because the synthesis of polyacetylene in the SmC* LC appeared to be difficult. Acetylene gas cannot permeate into the SmC* containing the catalyst due to its high viscosity, resulting in low polymerisation activity at the SmC* reaction field, and synthesis of a large volume of SmC* with multi-step process is required for it. The author suggested the use of an additional chiral dopant (chiral inducer) to nematic liquid crystals for the production of cholesteric LC based on the original idea of the author. At that time, the lab had no concept of the chiral dopants, whereas electro-dopants, such as electron acceptors and donors, for conjugated polymers had been well studied. Therefore, this was the first idea and example of the introduction of the cholesteric LC reaction matrix for production of conjugated polymers (November, 1994). Later, the helical polyacetylene was synthesised with the development of a new chiral inducer [11–14]. In 2000, the synthesis of polypyrrole with a prototype electrochemical polymerisation in LC was carried out in a vial by the author [14,15]. After much effort, the submerged sandwich method was developed. A sandwiched indium tin oxide (ITO) coated glass electrodes were submerged in a LC electrolyte solution containing pyrrole as a monomer, tetrabutylammonium perchlorate (TBAP) as a...
supporting electrolyte, and a chiral dopant (chiral inducer), as shown in Figure 1(a) [14]. The polymerisation was carried out by the applied voltage of 3 V at room temperature. The resultant film displayed fingerprint texture very similar to that of the LC electrolyte solution under scanning electron microscopy (SEM) observations. In 2004, a convenient two-sandwich electrochemical polymerisation method using minimal amounts of LC electrolyte solution with good production efficiency was developed (Figure 1(b,c)) as the original idea of the author, who was assistant professor at the time [15]. This result was published in 2002 as a first report of electrochemical polymerisation in chiral LCs [16]. The film thus prepared shows good electro-activity. Furthermore, chiroptical activity (circular dichroism (CD) and optical rotation) of the film could be tuned by an electrochemical redox process. The redox process is equivalent to electrochemical doping (oxidation) and dedoping (reduction). In other words, the resultant polymer films, as expected for an organic semiconductor, show doping/dedoping-driven electro-chiroptical effect. The electro-controllable optical rotation effect is compared to Faraday rotation and Kerr effect. The chiroptical activity is precisely and rapidly controlled with voltages less than 1 V in these materials. These original findings were obtained by the author on 27 July, 2004. This result and method had not been accepted in the lab, while repeated experiments confirmed the effectiveness of this method and phenomenon. Therefore, the author submitted these findings [17,18].

Electrochemical polymerisation in LC affords electroactive polymers having similar structure to that of the electrolyte solution due to transcription of structural chirality from LC to the resultant polymers. However, the surface structure depends on molecular shape, the affinity to the LC electrolyte solution, and the polymerisation activity of the monomer. Also, crystallinity and film-forming properties are related to the morphology of the resultant polymers. In this paper, the term of “chiral inducer” is employed in place of chiral dopant to avoid confusion with electro-dopants (donors and acceptors). The polymerisation of various monomers in LC and resultant properties are discussed.

2. General method of electrochemical polymerisation in LC
The cholesteric electrolyte solution used as the reaction matrix is prepared by adding a chiral inducer [19] (i.e., cholesteryl pelargonate) to 4-n-pentyl-4'-cyanobiphenyl (5CB) or 4-n-hexyl-4'-cyanobiphenyl (6CB). A nematic LC electrolyte solution is prepared by the same manner but without adding a chiral inducer. Smectic A (SmA) LC having the layer structure of the electrolyte solution is prepared in a mixed LC system (4-n-octyloxy-4'-cyanobiphenyl (8OCB) and 6CB).

Prior to electrochemical polymerisation, the LC electrolyte solution containing monomer (bithiophene, ethylene dioxythiophene, pyrrole, furan, or their derivatives) was heated in a vial to ca. 80 °C under an argon atmosphere in order to completely dissolve the constituents in the LC solvent. The LC mixture was injected between two sandwiched ITO coated glass electrodes with a Teflon sheet (thickness of ca. 0.2 mm) as a spacer by a capillary technique. The reaction cell was initially heated to ca. 40 °C, and then gradually cooled to the LC temperature range. A voltage of 4.0 V was then applied across the cell. After 30 min, an insoluble and infusible polymer thin film was obtained at the sandwiched ITO-coated glass electrode of anode side. Then, the sandwich cell was detached. The polymer film on the ITO was washed with solvents (tetrahydrofuran, hexane, and acetone) and dried.

3. Surface structure
Scanning electron microscopy (SEM) image of poly(2,7-di(2-furyl)fluorene) (PFFLF*, * = chiral) thus prepared in the cholesteric LC shows the labyrinth-like concavo-convex structure (Figure 2(a)), although it should be noted that the molecular structure of the polymer differs from that of the cholesteric LC employed as the electrolyte solution [20,21]. The polymer contains no LC molecules due to phase separation in the polymerisation process.

The laser transmission through the polymer film produces a circular Fourier-transformed interference with distinct separation of red, and green laser light due to a random grating formed by the single-pitch helix-derived stripes of the polymer (Figure 2(b)). Poly(3,4-ethylenedioxythiophene) (PEDOT*) from terEDOT prepared in the cholesteric LC appears to display a vortex pattern [22].
A synthetic scheme for the PEDOT* and a polarising optical microscopy (POM) image of the cholesteric electrolyte solution containing the terEDOT as a monomer are shown in Figure 3(a). The SEM images of the resultant polymer confirm that the polymer imprinted the cholesteric LC structure (vortex structure, Figure 3(b)). The magnification image indicates that the vortex consists of fine lamellas. The optical textures originate from individual molecular ordering of the cholesteric LC matrix. The surface morphologies depend on polymerisation activity of the monomers and the crystallinity of the resultant polymers.

![Poly(2,7-di(2-furyl)fluorene), PFFLF*](image)

**Figure 2.** (a) Scanning electron microscopy (SEM) image of chiral poly(2,7-di(2-furyl)fluorene) (PFFLF*, * = chiral). (b) Diffraction pattern obtained upon irradiation by red and green laser incident light. Reproduced by permission of the Royal Society of Chemistry (RSC) from ref. [20] (Figure 5(d)).

### 4. Electrochemically driven change in chiroptical activity

The polymers thus prepared in cholesteric LC exhibit Cotton effect associated with the $\pi-\pi^*$ transition of the main chain [23]. The circular dichroism (CD) spectra of the reduced (dedoped) polymers reveal a split-type Cotton effect, such as exciton coupling. In the case of the polybithiophene (PBTh*) prepared in cholesteric LC, the CD spectra for the PBTh* film display a positive Cotton effect at 600 nm in the oxidised state. The CD signals cannot be attributed to the cholesteric LC inducer employed in the polymerisation because the weak Cotton effect of the cholesteric LC inducer (cholesteryl pelargonate) is only observed at wavelengths in the range of 240–340 nm. Optical activity of the PBTh* can be changed by adjusting the conditions of the electrochemical redox (electrochemical doping-dedoping) process without changes in optical texture or surface structure. The PBTh* prepared in the cholesteric LC is, therefore, electro-chiroptically active and the CD can be controlled via an
electrochemical process. This phenomenon can be referred to as electrochemically driven chiroptical effect (electro-chiroptical effect). Furthermore, control of optical rotation of the polymer is also possible by the redox process. This electrochemical redox state-induced change in optical rotation can be reasonably explained as being due to electrochemical doping/dedoping of the main chain.

**Figure 3.** (a) Polarising optical microscopy (POM) image of cholesteric liquid crystal (cholesteric LC) electrolyte solution containing monomer and a scheme for preparation of chiral poly(3,4-ethylenedioxythiophene) (PEDOT*). (b) SEM image of the PEDOT* prepared in cholesteric LC electrolyte solution. (c) Magnification image. Reproduced by permission of the Royal Society of Chemistry (RSC) from ref. [21] (Figure 3(a)).

**5. Helical polarons – chirality**

Electron spin resonance (ESR) spectroscopy measurements during the redox process confirm the generation of charge carriers (polarons, radical cations) by electrochemical doping. Increase of applied voltage for the polymer progresses electrochemical doping by perchlorate ion in the electrolyte solution. Figure 4 shows ESR line shapes of the PBTh* prepared in cholesteric LC. The intensity of the ESR signal ($I_{ESR}$) was increased and line width decreased with applied voltage up to 0.4 V because of increase of polarons unit in the main chain. The delocalisation of the polarons along the main chain resulted narrowing of the signals. However, the $I_{ESR}$ was decreased and the signal width was broadened due to generation of bipolarons (dications) by further application of higher voltage.
Figure 4. ESR line shapes of the chiral polybithiophene (PBTh*) prepared in cholesteric LC at -0.1 V, 0.4 V, and 0.8 V vs. Fc/Fc*.

Figure 5 summarises a set of the ESR results. The g-value of the polymer decreased with increase of polarons accompanied by increase of applied voltage. Subsequent application of higher voltage allows increase of the g-value (Figure 5(a)). The $I_{ESR}$ increased with applied voltage up to 0.4 V because of increase of the polarons unit in the main chain. Further applied voltage, as a progress of the electrochemical doping, decreased the $I_{ESR}$ due to the generation of bipolarons (Figure 5(b)). Spin (radical) number ($\rho$) of the polymer once increased, and decreased gradually with the voltage. The maximum of the $\rho$ corresponds to an inflection point of the $I_{ESR}$. The change from polarons to bipolarons is accompanied by change in magnetic properties of the doped polymer from paramagnetism (polarons) to diamagnetism (bipolarons).

Figure 5. ESR results for the PBTh*. (a) g-value vs. $E$. (b) $I_{ESR}$ and $\rho$ vs. $E$. 
Figure 6. (a) ESR results and optical rotation for the PBTh*. Circle: spin (radical) number of the polymer vs. potentials ($E$ vs Fc/Fc$^+$). Square: optical rotation values plotted at 1.7 eV (729 nm) during the electrochemical doping process. (b) ESR line shape at 0.4 V vs. Fc/Fc$^+$. (c) Optical rotation hysteresis effect for the PBTh* as a function of potential vs. Fc/Fc$^+$ reference in 0.1 M tetrabutyl ammonium perchlorate (TBAP)/acetonitrile solution. Reproduced by permission of Elsevier Limited (Figure 6(a,b)), Elsevier, from ref. [24] (Figure 3).

Figure 7. (a) Main chain structure (primary structure) and polarons in the main chain. (b) Intra-main-chain helical twisting and change in the helicity by doping (secondary structure). (c) Chiral aggregation structure (tertiary structure) to show the fingerprint texture observable under POM and SEM.
Figure 6(a) shows change in optical rotation and \( \rho \) of the polymer with applied voltages vs. \( \text{Fc/Fc}^+ \) as a reference. Increase of the optical rotation and \( \rho \) value were observed with increasing of the voltage. The results indicate that polarons on the main chain are in a three-dimensional (3D) chiral environment. The increase of the optical rotation values corresponds to increase of the spins with doping. Optical rotation hysteresis effect was also observed, as shown in Figure 6(c). This demonstrates that the optical rotation is controlled by doping. Polarons distribute on the helically formed main chains at appropriate potentials [24]. Furthermore, introduction of quinonoid structure (polarons unit) of the helical main chain tunes chiroptical activity by the electrochemical doping (Figure 7(b)). Also, intercalation of the dopant between the individual main chains tunes the chiral aggregation. The inter-chains electronic communication is depressed in the doped state due to extension of the inter-chain distance by the intercalation. The intra-chain (generation of polarons in the main chain) and inter-chain (intercalation between main chains) electrochemical doping-redoping (redox process) can control the chiroptical properties. The polarons band of the polymers shows the CD signals, indicating the polarons as charge carrier have chiroptical activity. The polarons with chirality is defined as "chiralion".

Figure 8. [(a) and (b)] Polymer film on ITO under white light at various reflection angles. (c) Natural appearance of polymer film. (d) Diffraction pattern under irradiation with combined red, green, and blue laser light. (e) Green laser diffraction at normal incidence. Black arrow indicates incident direction, white arrows denote reflection directions, and blue arrows denote transmission directions. (f) Schematic of three-dimensional hollow cone drawn by the transmission and reflection of light at normal incidence. (g) Green laser reflection and transmission at \( \theta = 20^\circ \). (h) Transmission colours in CIE colour chromaticity space calculated from transmission spectra for normally incident light at \(-0.6 \text{ V}\) (h) and \(+0.9 \text{ V}\) (i) vs. \( \text{Fc/Fc}^+ \). Detection angles (\( \theta \)): a) 24°, b) 26°, c) 28°, d) 30°, e) 32°, f) 34°, g) 36°, h) 38°, i) 40°, j) 42°, and k) 44°. Reprinted with permission from J. Appl. Phys. 105, 114906 (2009) [25] (Figures 2,3). Copyright [2009], AIP Publishing LLC.
Possible helical aggregation and distribution of polarons along the main chain are displayed in Figure 7. The polymer forms hierarchical chiral structures. The main chain consists of polythiophene with polarons unit in the doped state (primary structure), Figure 7(a). The main chain is twisted. The twist structure is produced by the matrix imprinting (MAT-I) from cholesteric LC during the polymerisation (secondary structure, Figure 7(b)). The main chain aggregates to form helical steps like structure as a chiral aggregation form (tertiary structure, Figure 7(c)).

6. Variable interference colour modulation
The PBTh* reflects rainbow colour upon incident light due to periodic dielectric structure produced by transcription of structural chirality from the cholesteric LC electrolyte solution. The colour of the reflected light varies with the detection angle, indicating that the molecular ordering of the present polymer acts as a reflection grating. Furthermore, the natural colour of the polymer changes from dark red to dark blue according to the oxidation, while the structural colour (interference reflection colour derived from its periodic structure) changes from light blue to orange under obliquely incident white light at a certain angle. The interference colour can be tuned by the electrochemical doping-dedoping. This phenomenon is referred to as "interference electrochromism" [23]. This phenomenon is also observed for the chiral poly(EDOT-benzene-EDOT) (PBEDOT*) [25]. The PBEDOT* shows concavo-convex structure with electro-active properties. The periodic structure based on the helical structure of the polymer produces iridescent reflection of light and diffracts light very well. The polymer film exhibits a rainbow-like appearance upon irradiation of light at certain angles (Figures 8(a)), and appears RGB monochromatic at other incident angles (Figures 8(b)). The natural colour of the polymer is dark brown in the half-doped state (Figure 8(c)). Laser transmission through the polymer film produces a circular Fourier-transformed interference with distinct separation of red, green, and blue laser light (Figure 8(d)) due to the random grating formed by the single-pitch helix-derived stripes of the polymer. The red, green, and blue wavelengths are projected in the outer, middle, and inner parts of the circular diffraction pattern, respectively. The polymer displays $m = 1$ diffraction, as shown in Figures 8(e,g), confirming that the polymer has both transmission and reflection grating functions. Under irradiation normal to the polymer surface, the light trace draws a conic transmission and reflection pattern (Figure 8(f), graphical art). Changes in CIE colour space chromaticity upon electrochemical doping (oxidation) for the PBEDOT* film are shown in Figure 8(h,i). Ellipsometry measurements for the BEDOT* and PBTh* reveal that with increasing positive voltage, the average refractive index of the entire polymer surface decreases at short wavelengths and increases at long wavelengths. This can be regarded as a form of electrochemically driven refraction modulation.

7. Conclusions
The sandwich cell polymerisation method developed by the author allows preparation of electroactive \(\pi\)-conjugated polymers having both electro-activity and liquid crystal-like molecular order. The polymers thus synthesised form periodic patterns displaying periodical dielectric structure (PBTh*), fibril structure (PEDOT*), and labyrinth-like concavo-convex structure (PFFLF*, PBEDOT*). This structure organising polymerisation in LC described here allows production of structural chirality, electro-chiroptical effect, control of refraction, and interference colour tuning. For the first time, the Stille type polycondensations of achiral aromatic monomers in cholesteric LC solution were also carried out based on this idea by the author [26,27]. Furthermore, crystal-LC ordered double layer electroactive polymer has been synthesised with phase transition sequential polymerisation to show metallic electrochromism [28]. The functions derived from the combination of \(\pi\)-conjugated system, liquid crystallinity, chirality, and electro-activity may open a new avenue for further study of optoelectrical functional polymers. Structure-organising polymerisations by using LCs, developed in a set of the studies, can be expected for production of polymers having interesting morphology and optical properties.

Molecular imprinting (MIP) may be occurred in the polymerisation process. The chiral charge carriers in chiral polymers are defined as chirion.
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