

Preparation of Iridescent-reflective Poly(furan-*co*-phenylene)s by Electrochemical Polymerization in a Cholesteric Liquid Crystal Medium

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Abstract—Optically active poly(4,4'-di(2-furyl)biphenyl) is successfully prepared by asymmetric electrochemical polymerization in a cholesteric liquid crystal (CLC) electrolyte. The polymer thus obtained forms a fingerprint optical texture similar to that of the CLC electrolyte and a convexo-concave surface structure along the fingerprint pattern. The polymer displays iridescence under irradiation with white light, and circular diffraction upon laser irradiation.

1. Introduction

Optically active polymers are generally synthesized by polymerization of optically active monomers [1-9]. Recently, however, optically active conjugated polymers have been prepared from optically inactive monomers using cholesteric liquid crystal (CLC) as a

reaction solvent [10-14]. In previous work, our group developed a new electrochemical polymerization method based on such a CLC electrolyte for the preparation of optically active conjugated polymers with no substituent [15]. This method is referred to as “asymmetric electrochemical polymerization”. Electrochemical polymerization is a useful and convenient method that produces a polymer film on the electrode surface [16,17]. The polymers prepared by asymmetric electrochemical polymerization display intense circular dichroism (CD) in the reduced state, and weaker CD in the oxidized state [18-21].

Iridescent reflection is seen widely in nature, such as in insect wings, produced by a surface structural effect [22-25]. The industrial synthesis of polymers exhibiting iridescent reflection [26-35] and diffraction [36-44] is of broad interest, with many potential applications of such biomimetic technology. In a previous study, the electrochemical preparation of poly(1,4-bis(2-(3,4-ethylenedioxy)thienyl)benzene (poly-BEDOT-B) showing selective reflection of white light and diffraction property was successfully performed using a CLC electrolyte [45]. In the present study, novel optically active poly(furan-co-phenylene) with no chiral substituent is prepared by asymmetric electrochemical polymerization. The polymer film obtained exhibits iridescence, which is confirmed to be due to the surface structure. The diffraction properties of the polymer are also discussed.

2. Results and discussion

2.1. Electrochemical polymerization in cholesteric liquid crystal

It is generally known that CLC with a helical structure can be formed from nematic liquid crystal (NLC) by the addition of a small amount of an optically active molecule as a chiral inducer. The CLC electrolyte employed in the present study was prepared by the addition of cholesteryl oleyl carbonate as a chiral inducer, along with tetrabutylammonium perchlorate (TBAP) as a supporting salt, to 4-cyano-4'-*n*-hexyl biphenyl (6CB) as the NLC solvent. To

this electrolyte 4,4'-di(2-furyl)biphenyl (4,4'-FBF) was added as a monomer [46]. The molecular structures and composition for the CLC electrolyte are shown in Table 1. The electrolyte was heated to 80 °C and stirred for 30 min to completely dissolve the cholesteryl oleyl carbonate, TBAP, and 4,4'-FBF in the 6CB. The electrolyte exhibited thermotropic LC character, and a fingerprint texture under polarizing optical microscopy (POM) observation at 26 °C, as shown in Fig. 1(a) [47].

The CLC electrolyte containing the monomer was injected between sandwiched indium tin oxide (ITO) coated electrodes (surface area: 1 cm × 5 cm) using a Teflon sheet (0.19 mm thick) as a spacer [21]. A constant direct current (DC) voltage of 4 V was then applied to the cell. The application of this polymerization voltage did not affect the optical texture of the CLC electrolyte. The polymerization reaction was performed at ambient temperature (26 °C) in order to preserve the thermotropic CLC phase. After reaction for 1 h, an insoluble and infusible polymer film, abbreviated as poly(4,4'-FBF)*, (Scheme 1) was obtained on the anode side of the ITO electrode. The film was washed with methanol, then acetone, and then dried.

2.2 Surface structure

Fig. 1(b) shows the fingerprint texture of poly(4,4'-FBF)* under POM (transmitted light). This pattern resembles the optical texture of the original CLC electrolyte (Fig. 1(a)), except that the polymer has no fluidity. The polymer exhibits birefringence, and it was visually confirmed that the polymer had assumed the molecular arrangement of the CLC electrolyte exactly. This result can be attributed to the good affinity of 4,4'-FBF (monomer) toward the CLC electrolyte (solvent) due to rigidity of the solvent molecules.

Fig. 1(c) shows scanning electron microscopy (SEM) images of the surface structure of poly(4,4'-FBF)*. The SEM image matches the POM image well, indicating that the visual

fingerprint texture is due to a convexo-concave surface structure. An atomic force microscopy (AFM) image of the polymer supports this result (Fig. 1(d)). The center part of the fingerprint structure is deeper than that at distant from the center in these images.

For comparison, the electrochemical polymerization of 4,4'-FBF was also conducted in an NLC electrolyte containing no chiral inducer. The polymer film prepared in the NLC, abbreviated as poly(4,4'-FBF), produced exhibits a Schlieren texture very similar to that of the NLC electrolyte. This result implies that poly(4,4'-FBF) can be imprinted with various kinds of liquid-crystal molecular ordering by electrochemical polymerization.

2.3. Optical properties

Fig. 2 shows the CD, optical rotatory dispersion (ORD), and ultraviolet-visible (UV-vis) absorption spectra for poly(4,4'-FBF)*. The polymer exhibits an intense CD and ORD response. In contrast, the poly(4,4'-FBF) film prepared in the NLC electrolyte displayed no CD response, indicating that the polymer prepared in optically inactive liquid crystal is itself optically inactive. Because the signal of the CD spectrum and the absorption spectrum for cholesteryl oleyl carbonate (chiral inducer) is only observed between 200 nm and 300 nm, it can be concluded that the polymer synthesized in the CLC has structural chirality.

2.4. Iridescence and diffraction

The convexo-concave structure of the poly(4,4'-FBF)* film produces two optical effects; the iridescent reflection of light, and the diffraction of light. Iridescent reflection occurs under irradiation with white light, and the reflected color varies with the angle of incidence and the color of the incident light. The inherent color of the polymer (reduced state) is light green. This iridescent reflection originates from the convexo-concave structure of the polymer surface. The iridescence properties can be modified by changing the helical pitch of the CLC

electrolyte during the polymerization reaction.

The diffraction of light can be observed by irradiating the poly(4,4'-FBF)* film on the ITO electrode with a laser set perpendicular to the film surface and observing the transmitted pattern on a screen set at a distance of 100 mm. A circular diffraction pattern is produced, as shown in Fig. 3. Three wavelengths of laser were tested (red, green, blue), and each produced a diffraction circle of characteristic radius (e.g., green, 47 mm; blue, 39 mm). The grating constant of the polymer was calculated to be 1.25 μm based on the radii of these diffraction circles. This grating period corresponds to the distance between adjacent convexo-concave features of the polymer film (Fig. 1(b-d)). It can thus be expected that the diffraction constant can be controlled by changing the helical pitch length of the CLC electrolyte employed for electrochemical polymerization.

3. Conclusion

Polymerization of 4,4'-FBF was carried out in the CLC or NLC electrolytes. The polymers imprinted original texture of the liquid crystal electrolyte during the polymerization process. Poly(4,4'-FBF)* exhibits intense CD and ORD signals, and has the convexo-concave surface structure along the fingerprint texture. The poly(4,4'-FBF)* displayed iridescent reflection upon white light irradiation, and the diffraction property. The polymer prepared by the asymmetric electrochemical polymerization has potential to be applied for optical filters, display devices, and optical diffraction devices.

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References and notes

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- [46] 4,4'-Di(2-furyl)biphenyl (4,4'-FBF): 2-(Tributylstannyl)furan (10 mmol) and 4,4'-dibromobiphenyl (5 mmol) were mixed into toluene (6 mL) under nitrogen. After refluxing the mixture for 30 min, tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] (0.088 mmol) was added. After a reacted 24 h, the toluene in the mixture was evaporated. The purification by chromatography on silica gel (eluent: dichloromethane) and the recrystallization from chloroform followed by evaporation afforded the desired 4,4'-di(2-furyl)biphenyl as white solid. The synthetic yield was 72 %. Elemental analysis calcd (%) for C₂₀H₁₄O₂: C 83.90, H 4.93; found: C 83.34, H 5.06; ¹H NMR (270 MHz, CDCl₃): δ = 6.50 (m, 2H, C(fu4,4')H), 6.70 (d, 2H, C(fu3,3')H, J = 3.3 Hz), 7.50 (dd, 2H, C(fu5,5')H, J = 0.9 Hz), 7.65 (d, 4H, C(ph3,3',5,5')H, J = 7.9 Hz), 7.75 (d, 4H, C(ph2,2',6,6')H, J = 8.3 Hz).
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Figure Captions

Scheme 1.

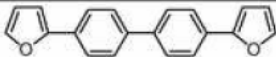
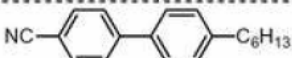
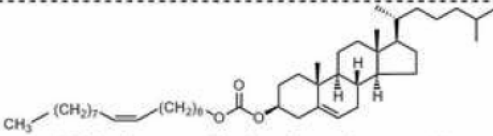
Table 1. Molecular structures and composition of cholesteric liquid crystal (CLC) electrolyte

Fig. 1. (a) Polarizing optical microscopy (POM) image of CLC electrolyte containing the monomer at 26 °C. (b) POM image of poly(4,4'-FBF)*. (c) SEM image of poly(4,4'-FBF)*. (d) AFM image of poly(4,4'-FBF)*.

Fig. 2. In-situ circular dichroism (CD) spectrum (top), optical rotatory dispersion (ORD) spectrum (middle), and UV-vis absorption spectrum (bottom) for poly(4,4'-FBF)* on an ITO electrode.

Fig. 3. Diffraction pattern produced by poly(4,4'-FBF)* under irradiation with (a) blue, (b) green, and (c) combined red, green and blue laser light.

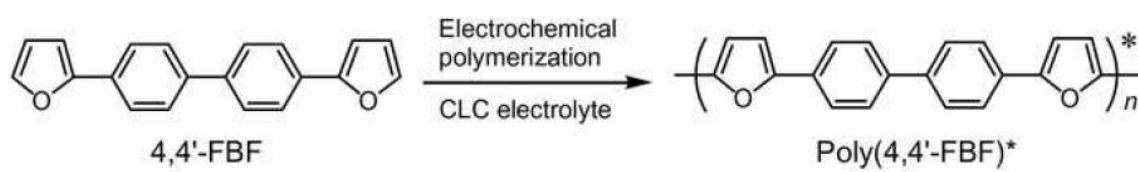
Table 1

	Molecular structure	Mole ratio (mol%)
Monomer	 (4,4'-FBF ^d)	0.8
Supporting salt	$[\text{CH}_3(\text{CH}_2)_3]_4\text{NClO}_4$ (TBAP ^b)	0.3
LC solvent	 (6CB ^c)	95.2
Chiral inducer	 (Cholesteryl oleyl carbonate)	3.7

^a4,4'-Di(2-furyl)biphenyl. ^bTetrabutylammonium perchlorate.

^c4-Cyano-4'-*n*-hexyl biphenyl.

Scheme 1



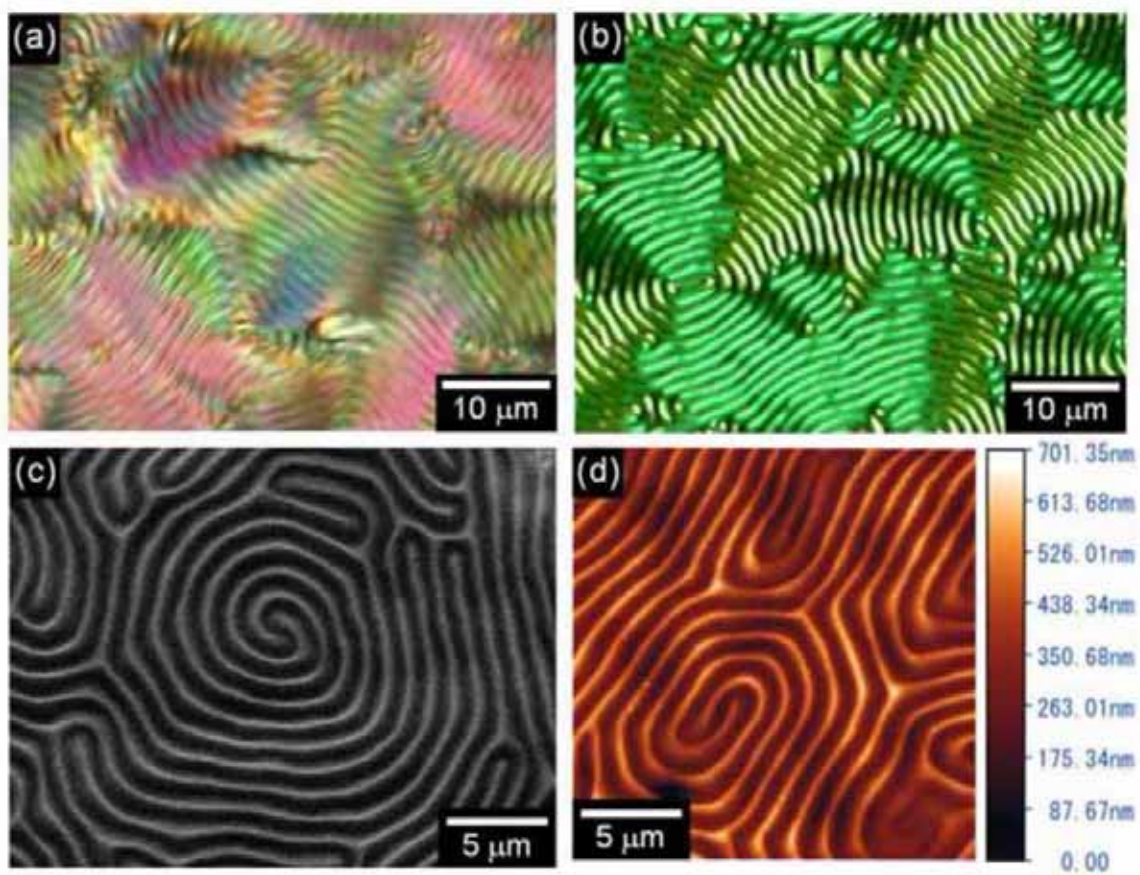


Figure 1

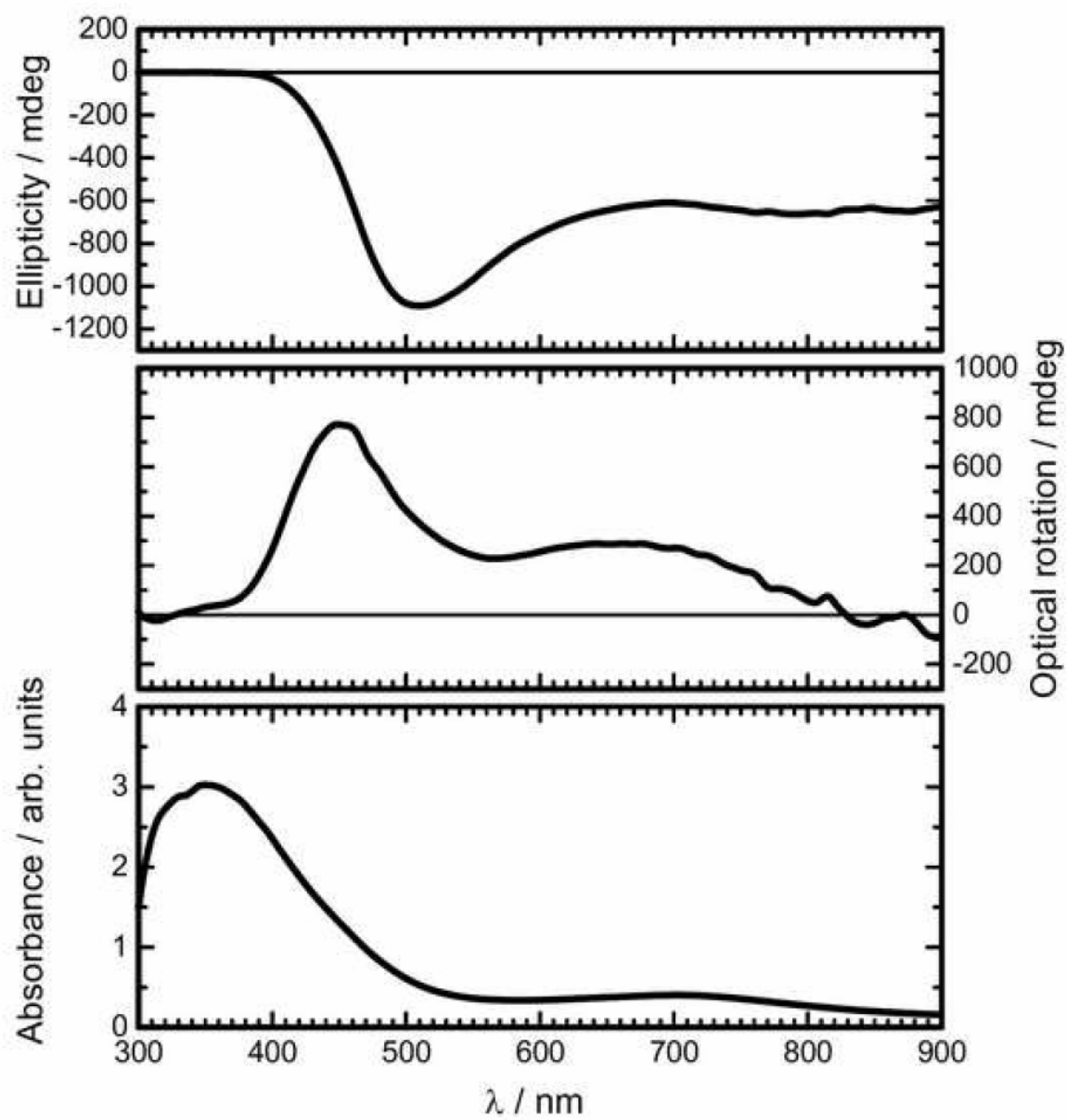


Figure 2

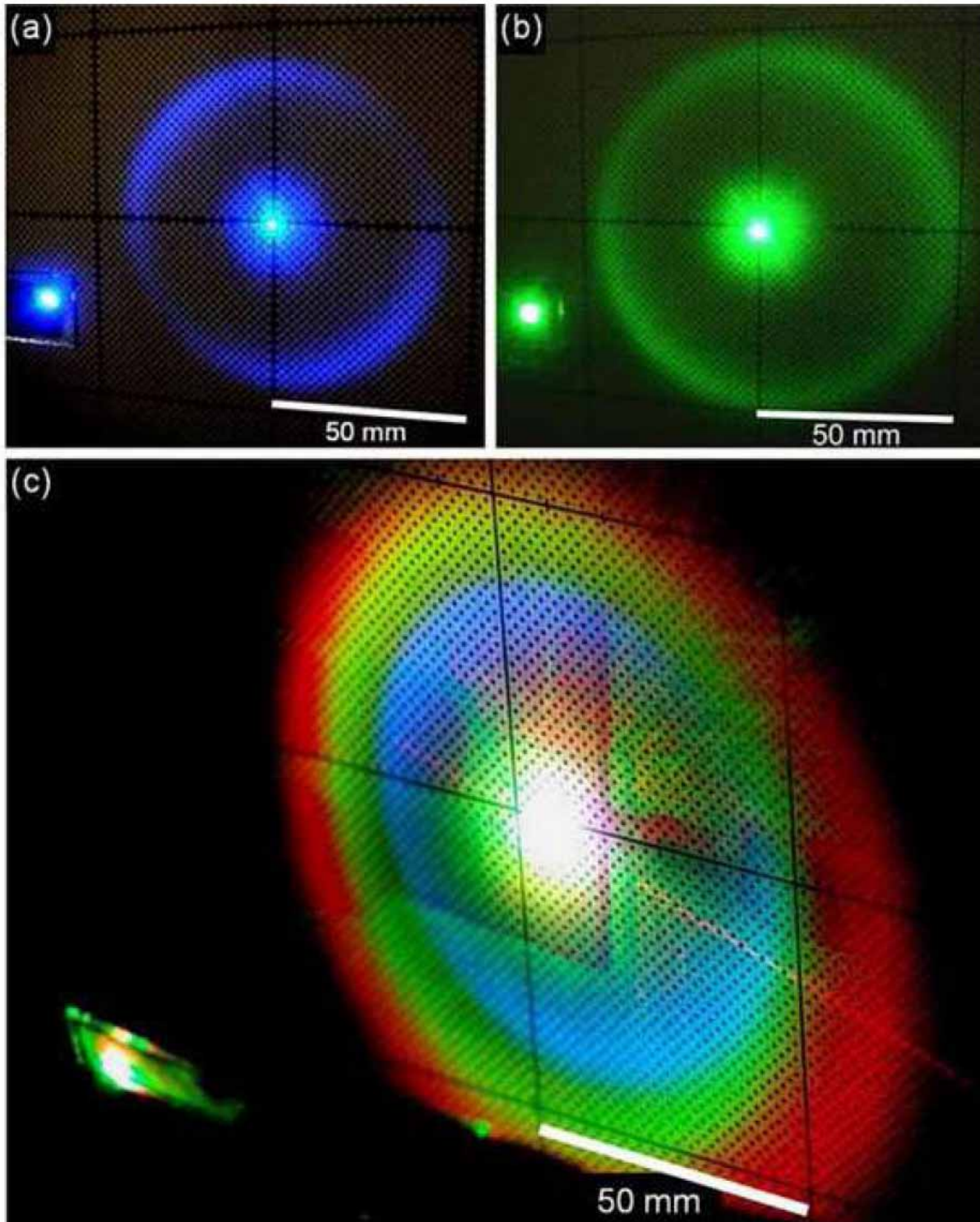


Figure 3