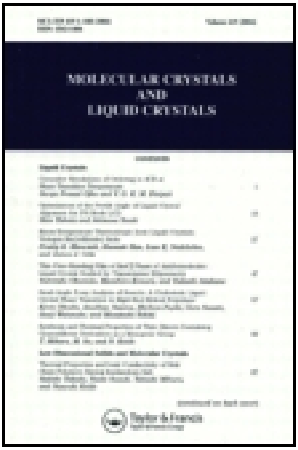


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Preparation of Furan-Based Monomers and Asymmetric Electrochemical Polymerization in Cholesteric Liquid Crystals: Optical Activity and Selective Reflection

Kohsuke Kawabata [a], Hiroyuki Yoneyama [a] & Hiromasa Goto [a]

[a] Graduate School of Pure and Applied Sciences, Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan

Version of record first published: 17 Dec 2009

To cite this article: Kohsuke Kawabata, Hiroyuki Yoneyama & Hiromasa Goto (2009): Preparation of Furan-Based Monomers and Asymmetric Electrochemical Polymerization in Cholesteric Liquid Crystals: Optical Activity and Selective Reflection, Molecular Crystals and Liquid Crystals, 515:1, 3-15

To link to this article: http://dx.doi.org/10.1080/15421400902987636

Mol. Cryst. Liq. Cryst., Vol. 515, pp. 3–15, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902987636

Taylor & Francis
Taylor & Francis Group

Preparation of Furan-Based Monomers and Asymmetric Electrochemical Polymerization in Cholesteric Liquid Crystals: Optical Activity and Selective Reflection

Kohsuke Kawabata, Hiroyuki Yoneyama, and Hiromasa Goto
Graduate School of Pure and Applied Sciences, Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan

1,4-Di(2-furyl)-2,5-substituted phenylenes were synthesized by a Stille cross-coupling reaction. Subsequently, these monomers were electrochemically polymerized in a cholesteric liquid crystal (CLC) electrolyte solution. The polymers thus prepared showed circular dichroism, birefringence, and a fingerprint texture similar to that of the CLC electrolyte. Furthermore, one of the polymers displayed selective reflection under illumination by a white light emitting diode.

Keywords: cholesteric liquid crystals; diffraction; electrochemical polymerization; electrochromism

INTRODUCTION

Conjugated polymers such as polythiophene [1,2], polypyrrole [3,4], polyaniline [5–7], and polyfuran [8] have been studied because of their electrochemical and optical properties, as well as their electrical conductivity. The synthesis of various substituted conjugated polymers or conjugated polymers containing heteroatoms has been studied for various applications such as electrochromic devices [9], photovoltaics [10], organic electro-luminescent devices [11], actuators [12], and biosensors [13]. Although polyethylenedioxythiophene has received significant recent attention, little research has been reported on polymers containing oxygen, with the exception of the electrochemical synthesis of nonchiral polyfurans by Reynolds et al. [14,15].

Address correspondence to H. Goto, Graduate School of Pure and Applied Sciences, Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan. Fax: 81-29-853-4490. E-mail: gotoh@ims.tsukuba.ac.jp

Unfortunately, due to its high oxidation potential, furan monomer requires a relatively high voltage for polymerization compared to other monomers which can form conducting polymers. Polyfurans are expected to exhibit advantageous ionic conductivity due to the high electronegativity of their oxygen atoms [16].

The synthesis of chiral conjugated polymers has been of interest in both chiral chemistry and conjugated polymer research [17,18]; however, few furan-based chiral polymers have been reported. To obtain chiroptical conjugated polymers, a chiral substituent was introduced into the main chain [19]. Recently, a new approach to obtaining chiroptical electroactive conducting polymers, chiral electrochemical polymerization from achiral monomers in a cholesteric liquid crystal (CLC) [20], has been developed. We refer to this method as "cholesteric liquid crystal asymmetric electrochemical polymerization."

We began the present research with the synthesis of 1,4-di(2-furyl)-2,5-substituted phenylene monomers by a Stille cross-coupling reaction with a Pd(0) complex catalyst [21]. From these achiral monomers, optically active conjugated polymers were prepared by electrochemical polymerization in a CLC electrolyte solution. Finally, we examined the spectroelectrochemistry of the polymers prepared by cholesteric liquid crystal asymmetric electrochemical polymerization, and observed their surface using polarizing optical microscopy.

EXPERIMENTAL

Materials

Tetrabutylammonium perchlorate (TBAP), and cholesteryl oleyl carbonate were obtained from Tokyo Kasei Japan. 4-cyano-4′-*n*-hexylbiphenyl (6CB) was purchased from Merck. The indium tin oxide (ITO) glass consists of a 0.2–0.3 µm-thick ITO layer on glass ($9\,\Omega/\text{cm}^2$) was purchased from Furuuchi Chemical Corporation.

Technique

Differential scanning calorimetry (DSC) analysis was carried out with DSC6200 (Seiko Instruments) at scan rate of $5^\circ\text{C}\,\text{min}^{-1}$. Fourier transform infrared (FT-IR) absorption spectroscopy measurement was carried out with FT-IR-300 spectrometer (JASCO). Optical absorption spectra of the polymers were obtained with a HITACHI U-2000. Circular dichroism (CD) measurements were performed with a JASCO J-720. Electrochemical measurements of polymers were performed using an electrochemical analyzer PGSTAT 12 (AUTOLAB, the Netherlands). Optical texture observations were carried out using a Nikon ECLIPS LV 100 high resolution polarizing microscope with a Nikon LU Plan Fluor lens and a Nikon CFIUW lens.

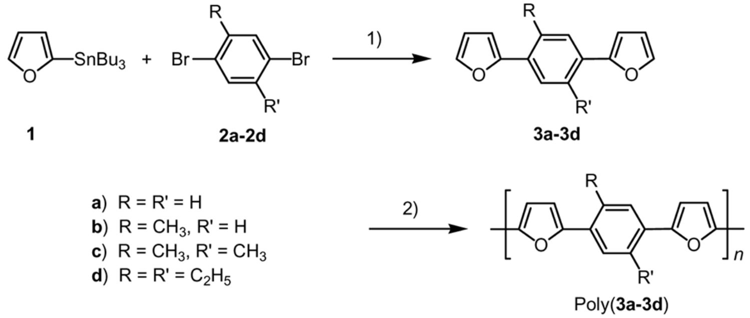
Synthesis of Monomer

Four different 1,4-di(2-furyl)-2,5-substituted phenylenes (**3a–3d**) were synthesized. Mono-substituted furan with tributyltin (**1**) was coupled with dibromophenylenes (**2a–2d**) in the presence of [Pd(PPh_3)$_4$] in toluene solution to afford three-ring type furan based monomers (Scheme 1).

These monomers were electrochemically polymerized in the CLC solvent, which had a 3-D helical structure. It is generally known that the CLC phase has a helical structure and that the addition of a small amount of chiral compound into a nematic liquid crystal (NLC) can induce the formation of a CLC phase [22]. In order to construct a chiral reaction field, we prepared a CLC electrolyte solution, consisting of 6CB as an NLC solvent, cholesteryl oleyl carbonate as a CLC inducer, TBAP as a supporting salt, and the monomers. The molecular formulas and compositions of the constituents of the CLC electrolyte solution are summarized in Table 1.

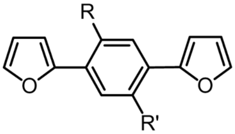
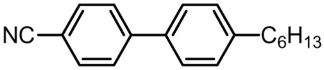
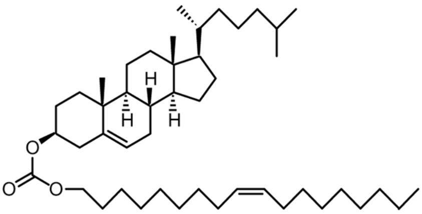
Synthesis of 1,4-Di(2-furyl)phenylene (3a)

1,4-Dibromophenylene **2a** (1.65 g, 7 mmol) and 2-(tributylstannyl)-furan **1** (5.00 g, 14 mmol) were mixed into toluene (13 mL) under nitrogen. After refluxing the mixture for 30 min, tetrakis(triphenylphosphine)palladium(0) [Pd[PPh_3]$_4$] (0.10 g, 0.087 mmol) was added. After a reaction of 24 h at 80°C, the toluene in the mixture was



SCHEME 1 1) [Pd(PPh_3)$_4$], toluene. 2) Cholesteric liquid crystal, electrochemical polymerization.

TABLE 1 Constituents of the Cholesteric Liquid Crystal (CLC) Electrolyte Solution Containing the Monomers

	Molecular structure	Mass ratio	Quantity
Monomer	 1,4-Di(2-furyl)-2,5-substituted phenylene	1.8 wt%	2.5 mg
NLC solvent	 4-Cyano-4'-*n*-hexyl biphenyl	89.8 wt%	0.125 g
CLC inducer	 Cholesteryl oleyl carbonate	8.0 wt%	11.25 mg
Supporting salt	$[CH_3(CH_2)_3]_4NClO_4$ Tetrabutyl ammonium perchlorate	0.4 wt%	0.5 mg

evaporated. The purification by chromatography on silica gel (eluent: dichloromethane) and recrystallization from hexane followed by evaporation afforded **3a** (1.34 g, 6.4 mmol) as a white solid (Yield: 90%). ^{1}H NMR (270 MHz, δ from TMS (ppm), $CDCl_3$): δ 6.48 (m, 2 H), 6,66 (d, 2 H, $J = 3.5$ Hz), 7.47 (m, 2 H), 7.68 (d, 4 H, $J = 0.8$ Hz).

Synthesis of 2,5-Di(2-furyl)toluene (3b)

2,5-dibromotoluene **2b** (0.55 g, 2.2 mmol) and 2-(tributylstannyl)-furan **1** (1.57 g, 4.4 mmol) were mixed into toluene (4 mL) under nitrogen. After refluxing the mixture for 30 min, $[Pd[PPh_3]_4]$ (0.052 g, 0.045 mmol) was added. After a reaction of 24 h at 90°C, the toluene in the mixture was evaporated. The purification by chromatography on silica gel (eluent: chloroform) and recrystallization from hexane followed by evaporation afforded **3b** (0.42 g, 1.9 mmol) as a white solid (Yield: 83%). ^{1}H NMR (270 MHz, δ from TMS (ppm), $CDCl_3$): δ 2.53 (s, 3 H), 6.47 (m, 1 H), 6.50 (m, 1 H), 6.56 (dd, 1 H, $J = 3.5$, 0.7 Hz), 6.66 (dd, 1 H, $J = 3.5$, 0.7 Hz), 7.47 (dd, 1 H, $J = 1.8$, 0.7 Hz), 7.50 (dd, 1 H, $J = 1.8$, 0.7 Hz), 7.54 (m, 2 H), 7.72 (m, 1 H).

Synthesis of 2,5-Di(2-furyl)-p-xylene (3c)

This compound was prepared by the same procedure for synthesis of **3b**. Quantity used: 2,5-dibromo-*p*-xylene **2c** (0.55 g, 2.1 mmol), 2-(tributylstannyl)furan **1** (1.49 g, 4.2 mmol), toluene (4 mL), $[Pd[PPh_3]_4]$ (0.048 g, 0.042 mmol) (0.45 g, 1.9 mmol, light yellow solid, Yield = 89%). ^{1}H NMR (270 MHz, δ from TMS (ppm), $CDCl_3$): δ 2.51 (s, 6 H), 6.50 (m, 2 H), 6.57 (d, 2 H, $J = 3.3$ Hz), 7.51 (m, 2 H), 7.59 (s, 2 H).

Synthesis of 1,4-Diethyl-2,5-di(2-furyl)benzene (3d)

This compound was prepared by the same procedure for synthesis of **3b**. Quantity used: 1,4-dibromo-2,5-diethylbenzene **2d** (0.50 g, 1.7 mmol), 2-(tributylstannyl)furan **1** (1.21 g, 3.4 mmol), toluene (4 mL), $[Pd[PPh_3]_4]$ (0.041 g, 0.036 mmol). (0.37 g, 1.4 mmol, light yellow solid, Yield = 81%). ^{1}H NMR (270 MHz, δ from TMS (ppm), $CDCl_3$): δ 1.26 (t, 6 H, $J = 7.5$ Hz), 2.85 (q, 4 H, $J = 7.4$ Hz), 6.51 (m, 4 H), 7.52 (m, 4 H, C(fu5,5′)H).

Polymerization in a Cholesteric Liquid Crystal

The CLC electrolyte solution was injected between two indium tin oxide (ITO)-coated glass electrodes sandwiching a Teflon sheet (~0.2 mm) spacer. Polymerization was performed with a constant 4.0 V direct-current voltage applied between the electrodes. During polymerization, the temperature was held at 22.0°C in order to maintain the CLC phase. After 20 min, a thin polymer film was deposited on the anodic ITO glass electrode. The residual CLC solution was washed off with hexane to afford a steady green film. GPC measurements for the polymers could not be performed because the polymers are insoluble and infusible.

RESULTS AND DISCUSSION

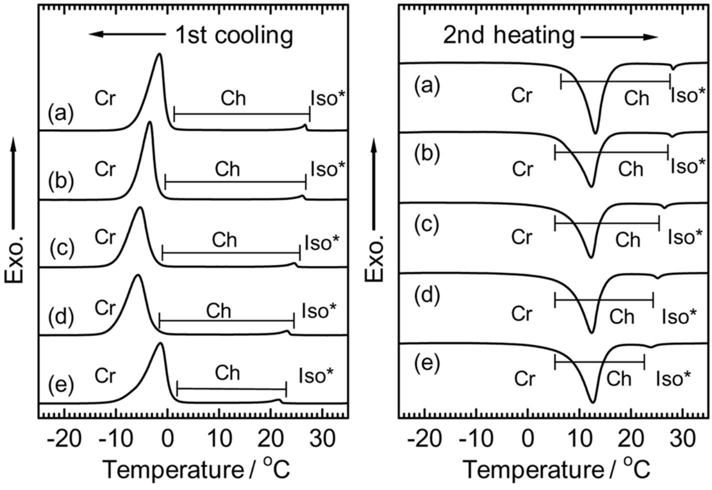
Differential Scanning Calorimetry Analysis

Figure 1 shows DSC curves of 6CB with CLC inducer, and the CLC electrolyte solution containing monomer, supporting salt, and CLC inducer. The CLC electrolyte solutions exhibited stable CLC phase in the temperature range of 7–23°C. In each CLC solution, the

CLC-crystal phase transition temperature in the first cooling was lower than that in the second heating, because of supercooling of the CLC phase. Furthermore, the addition of the monomers and supporting salt into the CLC solutions decrease the phase transition temperatures. However, in the case of the CLC solution containing 1,4-diethyl-2,5-di(2-furyl)benzene, the CLC-crystal phase transition in the first cooling increased. Isotropic-CLC phase transition temperatures decrease with increase of alkyl side chain length of the monomers in the CLC electrolyte solutions.

Infrared Absorption Spectroscopy

FT-IR absorption spectra of 6CB, cholesteryl oleyl carbonate, and poly(1,4-di(2-furyl)phenylene) are shown in Fig. 2. 6CB shows two absorption bands at 2930 and 2845 cm^{-1} assignable to ν_{CH2} of alkyl chain, and an absorption band at 2226 cm^{-1} due to ν_{CN} of CN end group. Cholesteryl oleyl carbonate shows two absorption bands due to ν_{CH2} of alkyl chain similar to that of 6CB, and an absorption band at 1738 cm^{-1} due to $\nu_{\mathrm{C=O}}$ of the ester moiety. Contrary, poly



(a) (b)

FIGURE 1 Differential scanning calorimetry curves of a cholesteric liquid crystal (CLC) solution without supporting salt and monomers (a). CLC electrolyte solutions containing supporting salt and monomers (1,4-di(2-furyl)phenylene (b), 2,5-di(2-furyl)toluene (c), 2,5-di(2-furyl)-*p*-xylene (d), 1,4-diethyl-2,5-di (2-furyl)benzene (e).

(1,4-di(2-furyl)phenylene) prepared in the CLC shows no absorption bands at 2226 cm^{-1} due to 6CB and at 1738 cm^{-1} due to cholesteryl oleyl carbonate. These results suggest that the polymer contains neither 6CB nor cholesteryl oleyl carbonate.

Optical Absorption and CD

Figure 3 shows the CD spectra and optical absorption spectra of the poly(1,4-di(2-furyl)phenylene) at various applied potentials vs. Ag/Ag^{+} reference electrode during oxidation. This polymer at 0 V, in reduced state, exhibited CD signal of −111 mdeg at 472 nm. During the oxidation process, the CD intensity of the polymer decreased to −26 mdeg accompanied by the red shift from 472 nm to 483 nm. At the same time, the absorption band due to $\pi - \pi^{*}$ transition of conjugated main chain increased and shifted to long wavelengths. Furthermore, an absorption band due to polarons at around 700–800 nm appeared. These results indicate that the change in electronic state of the polymer provides change in color and chiroptical property. The electrochemical oxidation process produces polarons and bipolarons on the main chain accompanied by structural change from benzenoid structure to planar quinonoid structure, resulting in increases of coplanarity and rigidity of the main chain. The signal shift in the CD

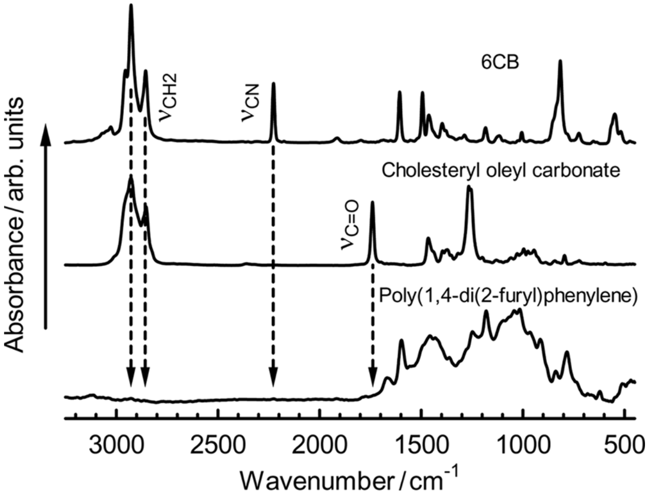


FIGURE 2 Fourier transform infrared (FT-IR) absorption spectra for 6CB, cholesteryl oleyl carbonate, and poly(1,4-di(2-furyl)phenylene).

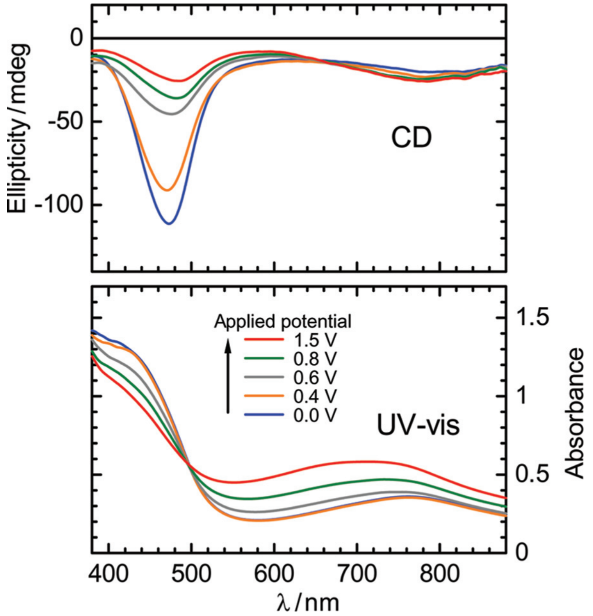


FIGURE 3 CD (top) and optical absorption (bottom) spectra of the poly(1,4-di (2-furyl)phenylene) prepared by cholesteric liquid crystal asymmetric electrochemical polymerization at various applied potentials vs. Ag/Ag$^+$ reference electrode during oxidation process.

of the polymer by the redox process can be explained by the structural change in the main chain.

The poly**3b–3d** in a reduced state also exhibited the negative Cotton effect at 473 nm (poly**3b**), 473 nm (poly**3c**), and 440 nm (poly**3d**) as shown in Fig. 4. The CD signals of the polymers are at nearly identical wavelengths, however, the CD intensities of the polymers are different. An increase of alkyl side chain length of the polymers decreased in the CD intensities. This result suggests that introduction of the alky side chains disturbs the formation of the helical structure, resulting in deformation of helical order structure of the polymers.

Therefore, the present cholesteric liquid crystal asymmetric electrochemical polymerization of furan-based monomer was successfully performed. At the same time, we observed electrochromism in these polymers. The color of the polymers changed from light green to black after the electrochemical oxidation. Furthermore, the intensity of the CD was tuned by application of voltage. This confirmed that the polymer shows optical activity and that this optical activity was changed during the oxidation process by application of voltage to the polymer.

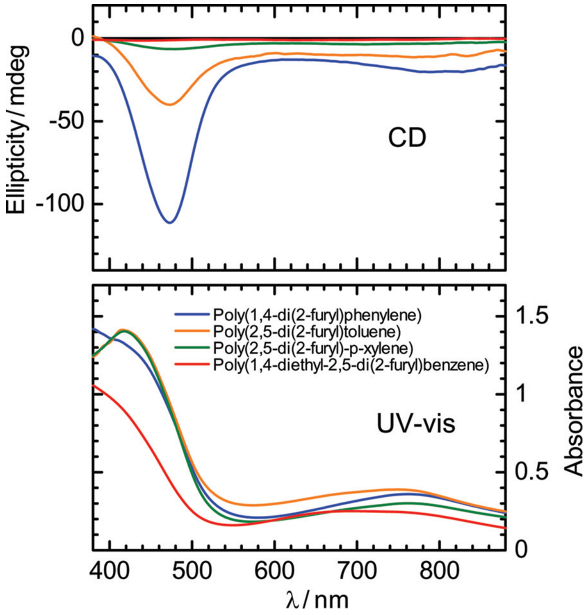


FIGURE 4 CD (top) and optical absorption (bottom) spectra of the polymers at 0 V vs. Ag/Ag$^+$ reference electrode.

Surface Texture

The polarizing optical microscopic (POM) image of the CLC electrolyte solution shown in Fig. 5a. The CLC electrolyte solution displays a fingerprint texture typical of cholesteric phase. Additionally, the polymers synthesized in the CLC show fingerprint texture under cross-Nicol conditions, as shown in Fig. 5b–d, and Fig. 6b. The fingerprint textures of the polymers are similar to that of the CLC electrolyte solution. Although the CLC shows pearl-like multireflection color, the polymers exhibit green. The fingerprint textures of the polymers remained unchanged after annealing at 300°C. These results indicate that the polymers has no CLC property, and that molecular imprinting during the electrochemical polymerization in the CLC resulted in the fingerprint texture. The fingerprint texture of the CLC arises from the helicity of the LC molecules. This suggests that the polymers have a CLC like ordered structure, in which the linear macromolecules are arranged in the 3-D helical structure of the CLC molecules.

Helical pitch of CLC depends on the concentration of CLC inducers. Figure 6 shows a series of POM images of poly**3a** prepared in CLC

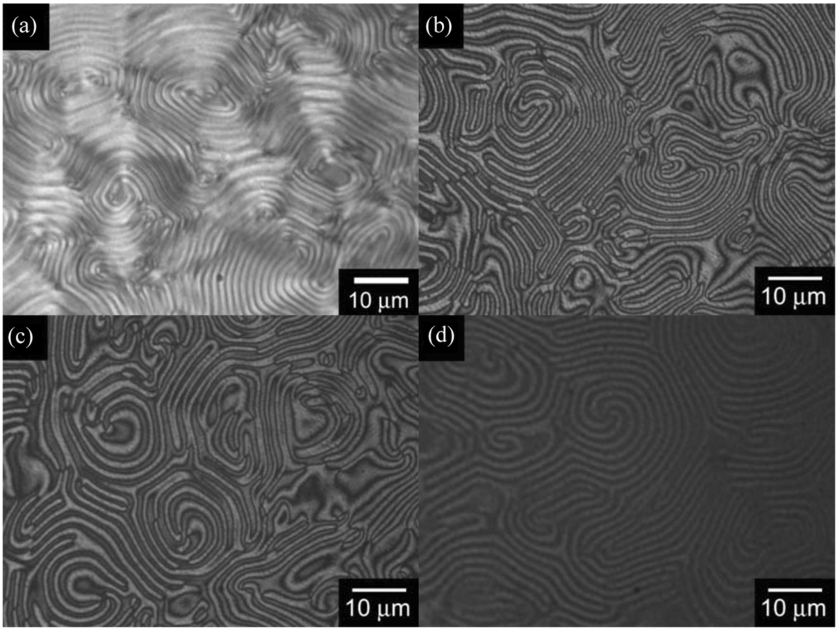


FIGURE 5 Polarizing optical microscopic images of cholesteric liquid crystal (CLC) electrolyte solution containing the monomer (a), poly(2,5-di(2-furyl) toluene) (b), poly(2,5-di(2-furyl)-*p*-xylene) (c), and poly(1,4-diethyl-2,5-di(2-furyl) benzene) (d) under cross-Nicol conditions.

electrolyte solutions at different concentrations of the CLC inducer. Poly**3a** films were prepared in these electrolytes with 4.0 wt%, 8.0 wt%, and 12.0 wt% of the CLC inducer in the electrolyte. The three electrolytes show fingerprint textures with different pitch lengths of ~2.5 μm (Fig. 6a), ~1.6 μm (Fig. 6b), and ~0.8 μm (Fig. 6c), respectively. These results suggest that the fingerprint texture of the polymers thus obtained in the CLC electrolyte solution derives from helical structure of the CLC. Therefore, the pitch length of the fingerprint texture of the polymers is controllable by concentration of the CLC inducer.

Selective Reflection of Light

The surface of poly**3a**, originally green, shows jewel beetle-like iridescent reflection under illumination by white light emitting diode (Fig. 7). This is the structural color derived from the periodic convexo-concave stripes along the fingerprint texture. The polymer

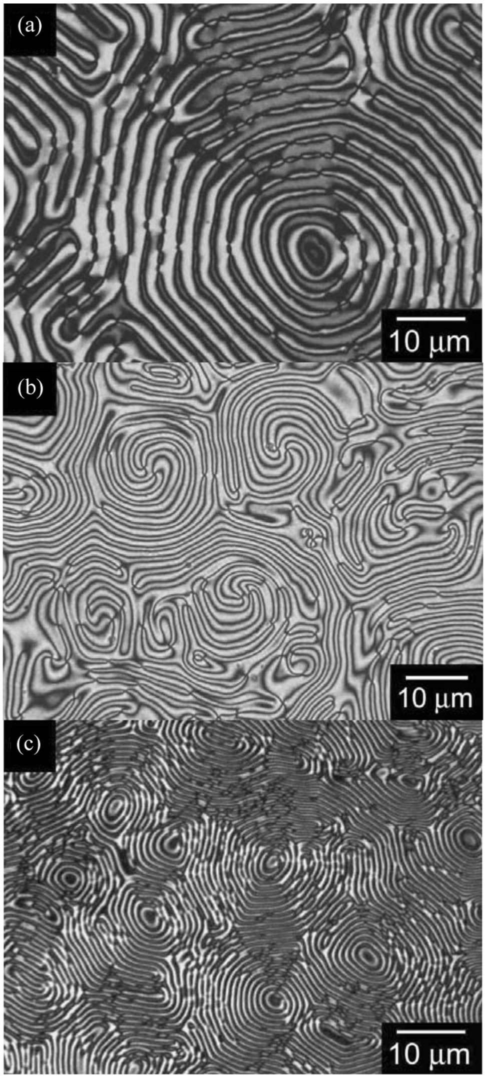


FIGURE 6 Polarizing optical microscopic images of poly(1,4-di(2-furyl) phenylene) prepared in CLC solutions at different concentrations of the CLC inducer. (a; 4.0 wt%, b; 8.0 wt%, c; 12.0 wt%).

synthesized in this study is not CLC, but it can exhibit an interference color reflection phenomenon due to the polymer has a CLC-like periodic structure. In other words, helical periodic structure of the present polymer produced by imprinting from CLC in the course of

FIGURE 7 Iridescent reflection of white light from the poly(1,4-di (2-furyl)phenylene) film prepared by cholesteric liquid crystal asymmetric electrochemical polymerization.

electrochemical polymerization functions CLC type one-dimensional photonic crystals.

CONCLUSION

1,4-Di(2-furyl)-2,5-substituted phenylene monomers were successfully synthesized using a one-pot Stille cross-coupling reaction. Optically active poly(1,4-di(2-furyl)-2,5-substituted phenylene)s were then prepared by cholesteric liquid crystal asymmetric electrochemical polymerization of the achiral monomers in a CLC electrolyte solution. The product polymers showed a fingerprint texture similar to that of the CLC electrolyte solution and exhibited consistent CD. Furthermore, a change in CD intensity of the polymer was observed during oxidation, where the polymers exhibit intense CD signals in the reduced state, and weak signals in the oxidized state. The color of the polymers also drastically changed, from light green to black, during the redox process. The significant color change arises from the furan structure in the main chain, which can provide high-contrast electrochromic properties. These furan-based electro-active polymers can be applied to chiroptical electrochromic displays. Poly(1,4-di(2-furyl)phenylene) shows selective reflection of light, and the periodic convexo-concave surface structure produces the structural color.

ACKNOWLEDGMENTS

The author is grateful to the Chemical Analysis Center of University of Tsukuba, for NMR spectra and elemental analysis data, and the Engineering Workshop of University of Tsukuba, for glasswork.

REFERENCES

[1] Goto, H. *Adv. Func. Mat.*, Accepted.
[2] Zhang, Q. T., & Tour, J. M. (1997). *J. Am. Chem. Soc.*, *119*, 5065.
[3] Zong, K., Abboud, K. A., & Reynolds, J. R. (2004). *Tetrahedron Lett.*, *45*, 4973.
[4] Wu, A., Kolla, H., & Manohar, S. K. (2005). *Macromolecules*, *38*, 7873.
[5] Cheung, J. H., Stockton, W. B., & Rubner, M. F. (1997). *Macromolecules*, *30*, 2712.
[6] Kwon, O., & McKee, M. L. (2000). *J. Phys. Chem. B*, *104*, 1686.
[7] Yan, H., Kajita, M., & Toshima, N. (2002). *Macromol. Mater. Eng.*, *287*, 503.
[8] González-Tejera, M. J., Sánchez de la Blanca, E., & Carrillo, I. (2008). *Synth. Met.*, *158*, 165.
[9] Mudigonda, D. S. K., Boehme, J. L., Brotherston, I. D., Meeker, D. L., & Ferraris, J. P. (2000). *Chem. Mater.*, *12*, 1508.
[10] Bhattacharyya, S., Kymakis, E., & Amaratunga, G. A. J. (2004). *Chem. Mater.*, *16*, 4819.
[11] Boden, B. N., Jardine, K. J., Leung, A. C. W., & MacLachlan, M. J. (2006). *Org. Lett*, *8*, 1855.
[12] Yan, H., Kajita, M., & Toshima, N. (2003). *Macromol. Mater. Eng.*, *288*, 578.
[13] Ramanathann, K., Bangar, M. A., Yun, M., Chen, W., Myung, N. V., & Mulchandani, A. (2005). *J. Am. Chem. Soc.*, *127*, 496.
[14] Reynolds, J. R., Child, A. D., Ruiz, J. P., Hong, S. Y., & Marynick, D. S. (1993). *Macromolecules*, *26*, 2095.
[15] Hong, S. Y., & Marynick, D. S. (1992). *Macromolecules*, *25*, 3591.
[16] Ohsawa, T., Kaneto, K., & Yoshino, K. (1984). *Jpn. J. Appl. Phys.*, *23*, 663.
[17] Tang, K., Green, M. M., Cheon, K. S., Selinger, J. V., & Garetz, B. A. (2003). *J. Am. Chem. Soc.*, *125*, 7313.
[18] Plamas, A. R. A., & Meijer, E. W. (2007). *Angew. Chem., Int. Ed.*, *46*, 8948.
[19] Kajitani, T., Okoshi, K., & Yashima, E. (2008). *Macromolecules*, *41*, 1601.
[20] (a) Yoneyama, H., Kawabata, K., Tsujimoto, A., & Goto, H. (2008). *Electrochem. Commun.*, *10*, 965; (b) Goto, H. (2007). *Phys. Rev. Lett.*, *98*, 253901.
[21] Stille, J. K. (1986). *Angew. Chem., Int. Ed.*, *25*, 508.
[22] Pieraccini, S., Ferrarni, A., & Spada, G. P. (2008). *Chirality*, *20*, 749.