Periodic Structure in a Fluorene-based Polymer Prepared by Electrochemical Polymerization

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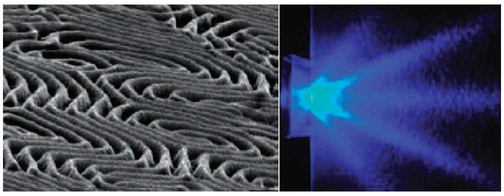
A fluorene-based polymer film prepared by electrochemical polymerization in cholesteric liquid crystal electrolyte solution displays a labyrinthine fingerprint texture, and diffraction grating function.



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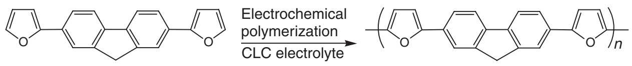
A conjugated copolymer, poly[2,7-di(2-furyl)fluorene], with periodic dielectric microstructure is prepared by electrochemical polymerization using cholesteric liquid crystal as an electrolyte solution. The polymer film thus prepared displays a labyrinthine fingerprint texture formed by a convexo–concave structure, and exhibits a random diffraction grating function. This anisotropic electrochemical polymerization technique is a novel bottom-up approach for preparing one-dimensional photonic crystals.

The manipulation of surface microstructures through micropatterning and other technique[1] is a fundamental process in technologies such as integrated circuits, biosensors, and photonic crystals.[2] Photonic crystals, materials with highly useful optical properties, can be prepared by synthesizing a periodic dielectric surface structure with dimensions comparable to the wavelength of incident light. In recent years, numerous approaches to preparing photonic crystals with periodic nanostructures have been proposed, based on processing methods such as photolithography, etching, and the self-assembly of colloidal crystals.[3] Electrochemical deposition is another technique that can be employed to prepare periodic dielectric structures through the synthesis of various conjugated polymers with optical, electrical, and redox properties.[4] Furthermore, photo-functional materials have been developed.[5,6] Polymerization using cholesteric liquid crystal (CLC) affords a one-dimensional self-assembled photonic structure[7,8] that mimics biological iridescence such as that exhibited by certain Coleoptera beetles.[9] CLC is characterized by a continuous and periodic rotation of the director axis, which results in a helically ordered periodic structure. CLC as a reaction field has thus been applied to the synthesis of photonic crystals for lasing[10] and diffraction gratings. Polymer-stabilized CLC and polymer-dispersed CLC, both polymer/CLC composites, have also been developed as variants of this approach.

Our group has previously reported a method for the preparation of conjugated polymers having cholesteric-like order.[11] The conjugated polymers thus obtained exhibit circular dichroism and a surficial fingerprint texture similar to that of the CLC electrolyte solution. The results of previous studies indicate that the polymers develop a CLC-like helical structure by transcription from the CLC reaction field.

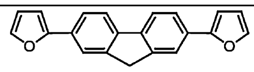
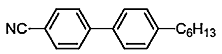
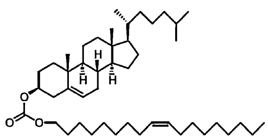
In the present study, a straightforward approach for the preparation of a furan–fluorene conjugated copolymer by electrochemical polymerization using CLC is demonstrated (Scheme 1). The polymer thus synthesized exhibits a distinct labyrinthine convexo–concave surface structure that acts as a periodic dielectric to provide a diffraction grating function.



2,7-Di(2-furyl)fluorene → Poly[2,7-di(2-furyl)fluorene]

Scheme 1.

Table 1. Constituents of CLC electrolyte reaction solution

	Molecular structure	Mass ratio/wt%	Quantity
Monomer	 2,7-Di(2-furyl)fluorene	1.8	2.5 mg
NLC solvent	 4-Cyano-4′-*n*-hexylbiphenyl	89.8	0.125 g
CLC inducer	 Cholesteryl oleyl carbonate	8.0	11.25 mg
Supporting salt	$[CH_3(CH_2)_3]_4NClO_4$ Tetrabutylammonium perchlorate	0.4	0.5 mg

Films of the conjugated copolymer were prepared as follows. The monomer, 2,7-di(2-furyl)fluorene, synthesized via the Stille cross-coupling reaction, was dissolved in a CLC electrolyte solution consisting of 4-cyano-4′-*n*-hexylbiphenyl (6CB) as a nematic liquid crystal (NLC) solvent, cholesteryl oleyl carbonate as a chiral inducer, and tetrabutylammonium perchlorate as a supporting salt (Table 1).

Differential scanning calorimetry measurements confirmed that the CLC electrolyte solution exhibits a stable CLC phase at temperatures in the range of 7–26 °C. A polarizing optical microscopy (POM) image of the CLC electrolyte solution (Figure 1a) shows the characteristic fingerprint texture of the CLC. The polymer was formed on indium tin oxide (ITO) coated glass (used as substrate electrodes) by injecting the CLC electrolyte solution between two ITO glass slides separated by a 190 μm-thick Teflon spacer. A direct-current voltage of 4.0 V was applied between the electrodes for 60 min, resulting in the epitaxial deposition of the polymer film on the anodic ITO glass electrode. The temperature during polymerization was maintained at 20 °C so as to preserve the stable CLC phase. After the reaction, the residual CLC electrolyte solution and low molecular mass fractions were washed off using hexane to afford a stable green film. POM observations under crossed Nicols reveal that the polymer film exhibits birefringence with a fingerprint texture similar to that of the CLC electrolyte solution (Figure 1b).

The observation of birefringence indicates that the individual main chains are assembled so as to produce optical anisotro-

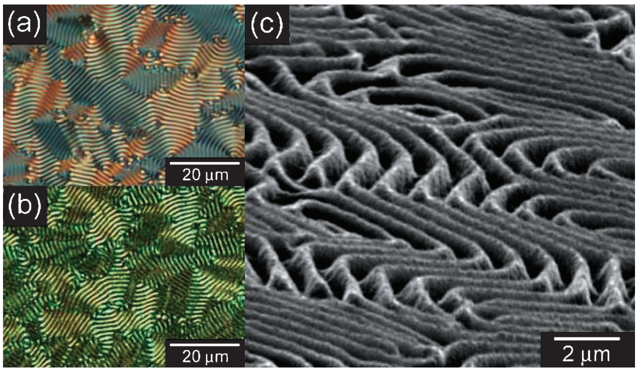


Figure 1. POM image of (a) CLC electrolyte solution and (b) poly[2,7-di(2-furyl)fluorene] film. (c) SEM image of the polymer film.

py, and the fingerprint texture indicates that the main chains of the polymer conform to a CLC-like periodic helical ordering. This helicity-based periodic structure is transcribed from the CLC to afford a periodic dielectric microstructure.

Scanning electron microscopy (SEM) images of the polymer film taken at 45° from the surface normal reveal that the fingerprint texture of the polymer is produced by a labyrinthine convexo–concave surface structure (Figure 1c).

Polymers prepared by electrochemical polymerization using isotropic solutions such as acetonitrile do not exhibit CLC-like structures. Polymerization using CLC therefore makes it possible to prepare anisotropic polymer films with distinct helical structures. This anisotropic epitaxial deposition may occur due to the effect of the continuous change in electric field intensity in the CLC electrolyte solution, or by orientation of the growing polymer according to the LC director. In the former case, the periodic rotation of the director gives rise to a periodic distribution of electrical conductivity within individual CLC molecules, which may affect the rate of polymerization at the molecular level. In the latter case, the rod-like aromatic monomer becomes physically aligned with the helical director in each CLC molecule, causing the individual main chains of the polymer to grow in a helical manner.

The convexo–concave structure of the polymer produces a sequential alternation of dielectric constant between two values (n_1 and n_2), and thus acts as a diffraction grating (Figure 2). Under normally incident blue laser light ($\lambda = 473$ nm), the film diffracts the transmitted beam into five directions (Figure 3).

The regularity of the labyrinthine convexo–concave structure produces second-order diffraction at 54° in addition to first-order diffraction at 24°. From these diffraction angles and

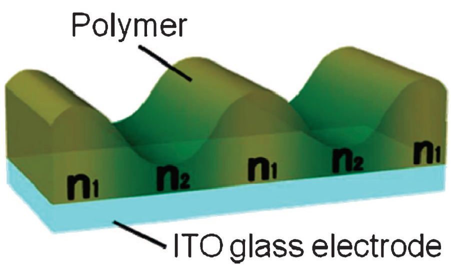


Figure 2. Schematic of periodic dielectric structure forming the polymer fingerprint texture.

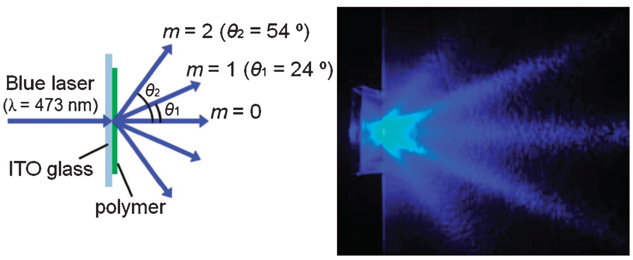


Figure 3. Diffraction of blue laser light by poly[2,7-di(2-furyl)-fluorene] film. (inset) Schematic of optical system.

the laser wavelength, the calculated grating constant is 1.17 µm, which corresponds to the distance between stripes of the fingerprint texture (helical half pitch of the polymer). These results demonstrate that the polymer film prepared in this study has diffraction properties due to the periodic dielectric microstructure. The grating function is random due to the random alignment of stripes comprising the fingerprint texture. The present synthesis thus affords a highly ordered microstructure through transcription from the three-dimensional helical continuum of the CLC reaction field.

In conclusion, electrochemical polymerization using a CLC electrolyte solution was demonstrated to afford anisotropic epitaxially deposited films of a furan–fluorene conjugated copolymer having a periodic microstructure observable by POM and SEM. The polymer films thus obtained exhibit a CLC-like fingerprint texture formed by a labyrinthine convexo–concave structure. This surface structure acts as a diffraction grating, and blue laser light was demonstrated to be diffracted by the film in a manner similar to a one-dimensional photonic crystal. The grating constant of the film was calculated to be 1.17 µm, corresponding to the helical half pitch of the fingerprint texture. The present bottom-up synthesis technique using CLC as an electrolyte solution is expected to be applicable for the preparation of a range of new functional conjugated polymer materials with useful optical properties, and provides an alternate route to top-down processes such as laser-based methods for the preparation of microstructured materials.

References

1 X. Jiang, R. Ferrigno, M. Mrksich, G. M. Whitesides, *J. Am. Chem. Soc.* **2003**, *125*, 2366.
2 J. Yoon, R. T. Mathers, G. W. Coates, E. L. Thomas, *Macromolecules* **2006**, *39*, 1913.
3 R. E. Schaak, R. E. Cable, B. M. Leonard, B. C. Norris, *Langmuir* **2004**, *20*, 7293.
4 H. Goto, *Adv. Funct. Mater.* **2009**, *19*, 1335.
5 A. Urbas, V. Tondiglia, L. Natarajan, R. Sutherland, H. Yu, J.-H. Li, T. Bunning, *J. Am. Chem. Soc.* **2004**, *126*, 13580.
6 J. Z. Vlahakis, M. D. Wand, R. P. Lemieux, *J. Am. Chem. Soc.* **2003**, *125*, 6862.
7 P. V. Shibaev, D. Chiappetta, R. L. Sanford, P. P. Muhoray, M. Moreira, W. Cao, M. M. Green, *Macromolecules* **2006**, *39*, 3986.
8 S. Kurihara, T. Mori, T. Nonaka, *Macromolecules* **1998**, *31*, 5940.
9 P. Vukusic, J. R. Sambles, *Nature* **2003**, *424*, 852.
10 J. Schmidtke, W. Stille, H. Finkelmann, *Phys. Rev. Lett.* **2003**, *90*, 083902.
11 H. Yoneyama, K. Kawabata, A. Tsujimoto, H. Goto, *Electrochem. Commun.* **2008**, *10*, 965.

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