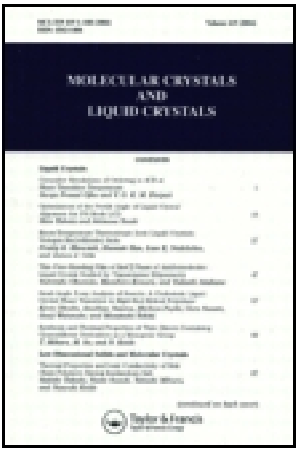


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Properties of Light-Emitting Polythiophene Derivatives Bearing Terphenyl Mesogenic Pendant

Lie Chen [a], Yiwang Chen [a], Weihua Zhou [a], Fan Li [a], Xiaohui He [a] & Ben Zhong Tang [b]

[a] Institute of Polymers/Institute for Advanced Study, Nanchang University, Nanchang, China

[b] Department of Chemistry, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong

Version of record first published: 18 Mar 2010

To cite this article: Lie Chen, Yiwang Chen, Weihua Zhou, Fan Li, Xiaohui He & Ben Zhong Tang (2010): Synthesis and Properties of Light-Emitting Polythiophene Derivatives Bearing Terphenyl Mesogenic Pendant, Molecular Crystals and Liquid Crystals, 518:1, 70-83

To link to this article: http://dx.doi.org/10.1080/15421400903568047

Mol. Cryst. Liq. Cryst., Vol. 518: pp. 70–83, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903568047

Synthesis and Properties of Light-Emitting Polythiophene Derivatives Bearing Terphenyl Mesogenic Pendant

LIE CHEN,[1] YIWANG CHEN,[1] WEIHUA ZHOU,[1]
FAN LI,[1] XIAOHUI HE,[1] AND BEN ZHONG TANG[2]

[1]Institute of Polymers/Institute for Advanced Study, Nanchang University, Nanchang, China
[2]Department of Chemistry, The Hong Kong University of Science & Technology (HKUST), Clear Water Bay, Kowloon, Hong Kong

A series of polythiophenes containing terphenyl mesogenic side chain at the third position through ester bonding was synthesized by dehalogenative polycondensation. The thiophene monomers 2,5-bromo-3-{[(4-(4′-cyano)terphenyloxy)carbonyl]-methyl]}-thiophene [M(CN)] and 2,5-bromo-3-{[(4-(4′-methoxy)terphenyloxy)-carbonyl]methyl}-thiophene [M(OCH_3)] were prepared via Suzuki reation and esterification reactions, in sequence. The structures and properties of the monomers and polymers were characterized and evaluated with nuclear magnetic resonance, infrared spectroscopy, thermogravimetry, differential scanning calorimetry, polarized optical microscopy, ultraviolet spectroscopy, and photoluminescence. All of the polymers were stable, losing little of their weights when heated to ≥300°C. The polymers showed good solubility and could be dissolved in common solvents such as $CHCl_3$, THF, DMF, etc. The monomers exhibited enantiotropic SmA_d phases with a bilayer arrangement in the heating and cooling processes. Due to short spacer methylene ester between the bulk terphenyl mesogenic side chain and rigid polythiophene main chain, the polymers could not exhibit liquid crystallinty at elevated temperature. The existence of the chromophoric terphenyl core endows the polymers with high photoluminescence. When their CH_2Cl_2 solutions were photoexcited, the polymers emitted a strong UV light about 400 nm.

Keywords Liquid crystallinity; photoluminescence; polythiophene; terphenyl

Introduction

Conjugated polymers have been extensively studied for their potential application in light-emitting diodes (LEDs), organic lasers, thin film transistors, and solar cells [1–7]. Among various conjugated polymers, polythiophenes have received considerable attention due to their excellent electrical characteristics [8–10]. The polythiophene family is well known for its environmental stability, melt and solution

---

Address correspondence to Yiwang Chen, Institute of Polymers/Institute for Advanced Study, Nanchang University, Xuefu Rd. 999, Nanchang 330031, China. E-mail: ywchen@ncu.edu.cn processability, and versatile synthesis, which allow us to have a significant control over optical and electronic properties [11].

Conjugated polymers with liquid-crystalline (LC) groups in their side chains are currently drawing interest from the viewpoint of multifunctional electrical and optical materials [12–25]. In side chain type of LC-conjugated polymer, the main chain can be aligned by virtue of spontaneous orientation of the LC side chain. Besides, macroscopic alignment of LC domains is achieved by an external force such as shear stress or electric or magnetic field [26]. Particularly, LC polythiophene derivative is one of the most intriguing polymers, because its electrical and optical properties are expected to be controlled using molecular orientation of the LC side chain. A variety of polythiophenes containing liquid-crystalline mesogens and light-emitting chromophores have been prepared [27–37].

Terphenyls are chemically, electrochemically, and photochemically very stable [38]. Because the strong π-π interaction among phenyl rings favors the self-organization of the calamitic units, they have been widely used to generate liquid crystals with high birefringence [39].

Previously, we have synthesized a series of polythiophene derivatives with the mesogenic units directly attached to the main chain without spacers [40]. In this study, polythiophene derivatives by introducting terphenyl-containing mesogen into the 3-position of the thiophene ring through ester bonding have been synthesized. The influence of the chromophoric terphenyl core on the structures and properties of the monomers and polymers has also been investigated.

Experimental

Materials

Trimethyl borate, *n*-butyllithium, thiophene-3-acetic acid, trimethyl borate, 4-(4-bromophenyl)phenol, 4-bromobenzonitrile, 1,3-dicyclohexylcarbodiimine (DCC), 4-(dimethylamino)pyridine (DMAP), and tetrakis(triphenylphosphine)palladium were purchased from Alfa Aesar and used as received without any further purification. Tetrahydrofuran (THF) and CH_2Cl_2 were dried over sodium. Other chemicals were obtained from Shanghai Reagent Co., Ltd. (Shanghai, China), and used as received.

Techniques

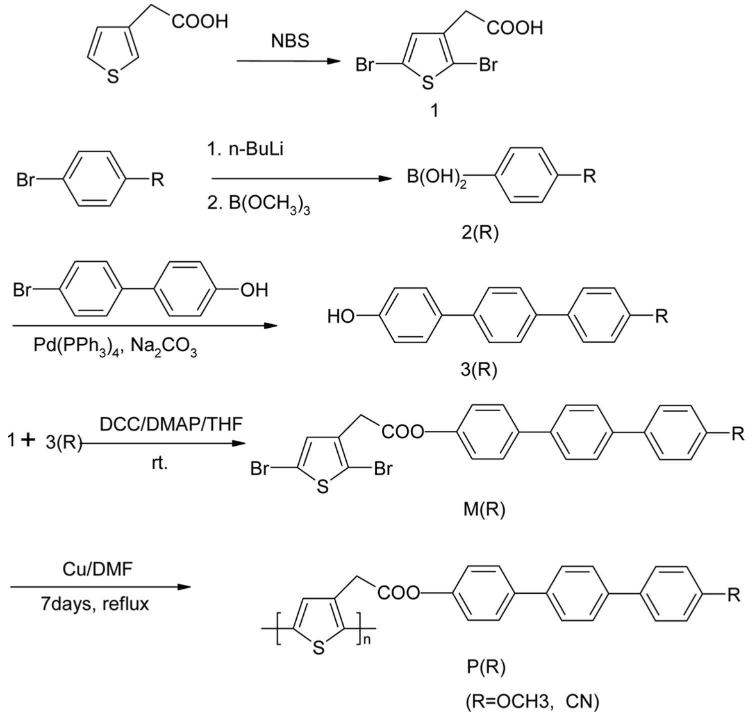
The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR spectrometer (Switzerland) with deuterated chloroform or THF as the solvent and with tetramethylsilane ($\delta = 0$) as the internal standard. The infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 Fourier transform infrared (FTIR) spectrophotometer (Japan) by drop-casting sample solution on KBr substrates. The ultraviolet-visible (UV) spectra of the samples were recorded on a Hitachi UV-2300 spectrophotometer (Japan). Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer (Japan) with a xenon lamp as the light source. The gel permeation chromatography (GPC), so-called size-exclusion chromatography (SEC) analysis, was conducted with a Breeze Waters system (US) equipped with a Rheodyne injector, a 1515 Isocratic pump, and a Waters 2414 differential refractometer using polystyrenes as the standard and THF as the eluent at a flow rate of

1.0 mL/min and 40°C through a Styragel column set, Styragel HT3 and HT4 (19 mm × 300 mm, $10^3 + 10^4$ Å) to separate molecular weight (MW) ranging from 10^2 to 10^6. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 (US) for thermogravimetry at a heating rate of 20°C/min under nitrogen with a sample size of 8–10 mg. Phase-transition temperatures were determined with a Perkin-Elmer DSC 7 differential scanning calorimeter (US) with a constant heating/cooling rate of 10°C/min. Texture observations were made with a Nikon E600POL polarizing optical microscope (Japan) equipped with an Instec HS 400 heating and cooling stage. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer (Switzerland) operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54$ Å) and at a scanning rate of 1°/min.

Synthesis of the Monomers

The synthesis and structures of the monomers are outlined in Scheme 1. All the reactions and manipulations were carried out under a nitrogen atmosphere.

2,5-Dibromothiophene-3-acetic Acid (1). Thiophene-3-acetic acid (10 g, 70.3 mmol) was very slowly added to a solution of N-bromosuccinimide, NBS (30.2 g, 172 mmol), in 50 mL of DMF by a dropping funnel. After the addition, 10 mL of DMF was further added to the reaction mixture and refluxed at 50°C for 20 h under an argon atmosphere. The reaction vessel was wrapped by aluminum foil to shield the reaction from light. When the reaction finished, the reaction mixture was allowed to warm to room temperature. The solution was poured into a large



Scheme 1. Illustration of procedures for synthesis of the monomers and their polymerization.

amount of saturated sodium sulfate cooled by ice water. The yellow precipitate was filtered off and recrystallized from an ethanol: water mixture to yield product as white, needlelike crystals. Yield: 63.0%. IR (cm^{-1}): 3101, 2918, 1707, 1415, 1327, 1232, 1016, 829, 735, 632, 469. ^1H NMR ($CDCl_3$, δ from TMS, ppm): 3.63 (s, 2H, CH_2), 6.95 (s, 1ArH, BrCCHC).

4-Cyanobenzeneboronic Acid [2(CN)]. A solution of *n*-butyllithium (30 mL, 2.87 M in hexane, 0.086 mol) was added dropwise to a stirred, cooled (−110°C) solution of 4-bromobenzonitrile (15 g, 0.082 mol) in dry THF (180 mL) under dry nitrogen. The solution was stirred at below −100°C for 1 h and a solution of trimethyl borate 20.8 mL in dry THF (60 mL) was added at below −100°C. The solution was allowed to warm to room temperature overnight. Ten percent hydrochloric acid was added and the solution was stirred for 1 h at room temperature. The product was extracted into ether and the organic layer was washed with water and dried with $MgSO_4$. The solvent was removed *in vacuo* and the crude product dissolved in THF and precipitated with *n*-hexane to give a yellow solid with yield of 70% [2(OCH_3)], white solid, the synthetic route is the same to [2(CN)].

4-Hydroxy-4′-cyanoterphenyl [3(CN)]. Under a dry nitrogen atmosphere a solution of 2.00 g of 4-cyanobenzeneboronic acid (13.6 mmol) in 10 mL of ethanol was added to a solution of 2.75 g of 4-(4-bromophenyl)phenol (97%, 11.02 mmol) and 0.42 g of tetrakis(triphenylphosphine)palladium(0) (99%, 0.36 mmol) in 20 mL of benzene and 20 mL of aqueous Na_2CO_3 (2 M). The reaction was conducted under reflux overnight. The reaction mixture was then shaken with ethyl acetate and the insoluble parts were filtered off. The organic layer was dried with anhydrous $MgSO_4$, and the solvent was removed by evaporation *in vacuo*. The crude product was recrystallized from acetone to provide a yellow powder, 65% yield.

3(CN), IR (KBr, cm^{-1}): 2215 (C≡N), 3351 (−OH). ^1H NMR (ppm, $CDCl_3$): 7.73–7.65 (four d, aromatic, 8H), 7.53 (d, aromatic, 2H ortho to cyano), 6.93 (d, aromatic, 2H ortho to hydroxyl), 4.91 (s, 1H, −OH).

3(OCH_3), colorless crystal, IR (KBr, cm^{-1}): 3393, 2956, 2835, 1608, 1491, 1251, 1031, 815, 644. ^1H NMR (ppm, $CDCl_3$): 7.60–7.51 (m, aromatic, 8H), 7.00–6.99 (d, aromatic, 2H ortho to hydroxyl), 6.90, 6.93 (d, aromatic, 2H ortho to OCH_3), 5.52 (s, 1H, −OH).

2,5-Bromo-3-{[(4-(4′-cyano)terphenyloxy)carbonyl]methyl}-thiophene [M(CN)]. 2,5-Dibromothiophene-3-acetic acid (3.43 g, 12 mmol) was added to a mixture of 4-hydroxy-4′-cyanoterphenyl (2.71 g, 10 mmol), (dimethylamino)pyridine, DMAP 1.47 g (12 mmol), and dicyclohexylcarbodiimide, DCC (2.46 g, 12 mmol), in 30 mL of absolute THF and further stirred for 24 h at room temperature under an argon atmosphere. Then the solution was filtered to remove the urea crystals, and the solvent was removed by evaporation. The crude product was purified by column chromatography (*n*-hexane/$CHCl_3 = 2/1$) to afford M(CN) as white crystal. Yield = 89%.

M(CN), IR (KBr, cm^{-1}): 2223, 1756, 810, 665, 475. ^1H NMR (ppm, $CDCl_3$): 7.76–7.67 (m, aromatic, 8H), 7.64, 7.62 (d, aromatic, 2H), 7.25, 7.22 (d, aromatic, 2H ortho to −O−), 7.05 (s, aromatic, 1H, BrCCHC), 3.85 (s, 2H, $-CH_2-COO-$).

M(OCH_3), white crystal, IR (KBr, cm^{-1}): 2939, 2861, 1745, 806, 659, 473. ^1H NMR (ppm, $CDCl_3$): 7.63–7.51 (m, aromatic, 8H), 7.19, 7.17 (d, aromatic, 2H ortho to −OOC−), 7.00, 6.98 (d, aromatic, 2H ortho to $-OCH_3$), 7.05 (s, aromatic, 1H, BrCCHC), 3.86 (s, 3H, $-OCH_3$), 3.69 (s, 2H, $-CH_2-COO-$).

Polymerization

All the polymerization reactions and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or in an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymers, which was done in an open atmosphere. A typical experimental procedure for the polymerization of P(CN) is given below.

2,5-Bromo-3-{[(4-(4′-cyano)terphenyloxy)carbonyl]methyl}-thiophene [M(CN)] (0.8 g, 1.3 mmol), 0.346 g (5.4 mmol) of Cu powder, and 5 mL of dry DMF were put into a 100-mL one-necked flask in a dry box. The flask was removed from the dry box and equipped with a magnetic stirring bar and an air-cooled condenser capped with a drying tube. The polymerization was carried out at 145°C for 7 days. The mixture then was cooled, diluted with $CHCl_3$ to about 100 mL, and filtered to remove excess Cu powder. The organic phase was washed with water and dried over $MgSO_4$. The $CHCl_3$ was removed with a rotary evaporator and dried in a vacuum oven to a constant weight.

P(CN), brown powder, IR (KBr, cm^{-1}): 2221, 1749, 802. ^1H NMR (ppm, $CDCl_3$): 7.73–7.62 (m, aromatic, 8H), 7.54–7.52 (m, aromatic, 2H), 7.20–7.18 (m, aromatic, 2H ortho to $-O-$), 6.99–6.92 (m, aromatic, 1H, BrCCHC), 3.49 (m, 2H, $-CH_2-COO-$).

$P(OCH_3)$, brown powder, IR (KBr, cm^{-1}): 2930, 2851, 1745, 803. ^1H NMR (ppm, $CDCl_3$): 7.63–7.52 (m, aromatic, 8H), 7.19–6.77 (m, aromatic, 5H, 2H ortho to –OOC–, 2H ortho to $-OCH_3$, 1H of BrCCHC), 3.86–3.78 (m, 3H, $-OCH_3$), 3.49–3.41 (m, 2H, $-CH_2-COO-$).

Results and Discussion

Synthesis of the Monomers and Polymers

The synthetic routes of the monomers are shown in Scheme 1. The compound of **[3(R)]** was synthesized through Suzuki reaction between the compound of **2(R)** and 4-(4-bromophenyl) phenol using tetrakis(triphenylphosphine)palladium(0) as the catalyst. The monomers were synthesized through an esterification reaction route in the presence of 1,3-dicyclohexylcarbodimine (DCC) and 4-(dimethylamino) pyridine (DMAP). All the intermediate and final products were thoroughly purified and fully characterized, and satisfactory analysis data were obtained (detailed spectroscopic data for the key intermediates and for all the monomers being given in the Experimental Section).

The polymerizations of 2,5-dibrominated thiophenes monomers were carried out via dehalogenative polycondensation, giving poly-(3-position substituted thiophene) derivatives, P(CN), and $P(OCH_3)$. All polymers synthesized were fusible and soluble in common organic solvents including THF, $CHCl_3$, DMF, etc. Number-average (Mn) and weight-average (Mw) molecular weights of the polymers are summarized in Table 1. The chemical structures of the polymers were confirmed by FTIR and ^1H NMR.

Structural Characterization

The monomers and the polymeric products were characterized by spectroscopic methods and all the products gave satisfactory data corresponding to their expected molecular structures (see Experimental Section for details). An example of the IR spectrum of P(CN) is shown in Fig. 1. For comparison, the spectrum of its monomer

Table 1. Molecular weights of the polymers

Polymer	Mn	Mw	MWD[a]	DP[b]
P(CN)	4700	7800	1.66	17
P(OCH_3)	7400	17,600	2.38	27

[a] MWD = molecular weight distribution.

[b] DP = degree of polymerization calculated by Mn/mru (mru: molecular weight of molecular repeat unit).

M(CN) is also given. The monomer absorbs at 2230, 665–475 cm^{-1}, due respectively to the C≡N stretching and C-Br bending vibrations. The C-Br bending vibrations absorption bands (665–475 cm^{-1}) disappeared in the spectrum of its polymer, indicating that the monomer has been transformed to the polymer via dehalogenative polycondensation. The ^{1}H NMR spectra of polymers and monomers are shown in Fig. 2. The resonance peaks in the ^{1}H NMR spectra of polymers are broader than that of monomers and the protons of polymers are upfield-shifted after the monomers. Except for the peaks of solvent and water remained in the spectra, no unexpected signals are observed in the spectra and all the resonance peaks can be assigned to appropriate protons as marked in Fig. 2. This shows that the monomers were polymerized successfully. In ^{1}H NMR of polymers, the integration ratio of thiophen proton and CH_2COO (refer to signals **a** and **b** in spectrum) seems to be relatively low in comparison to other protons due to steric hindrance. However, almost reasonable ratio of integration indicates a correct chemical structure.

Thermal Stability and Liquid Crystallinity

The polythiophenes lose little weight at a temperatures over 300°C (shown in Fig. 3). The thermal stability of the polymers is further substantiated by the differential

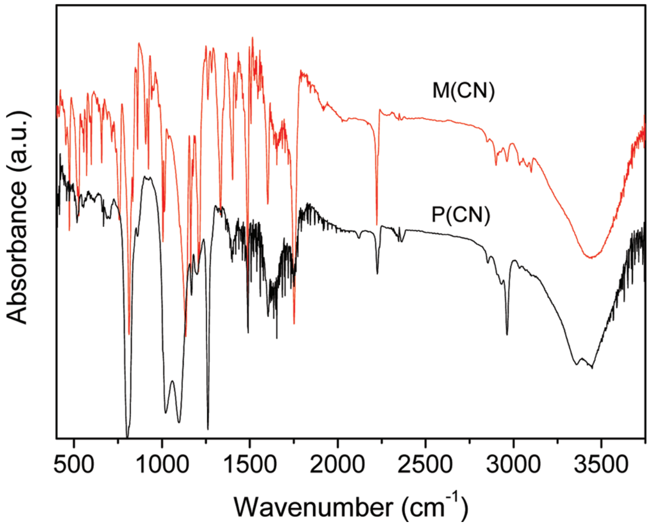


Figure 1. FTIR spectra of the monomer M(CN) and polymer P(CN).

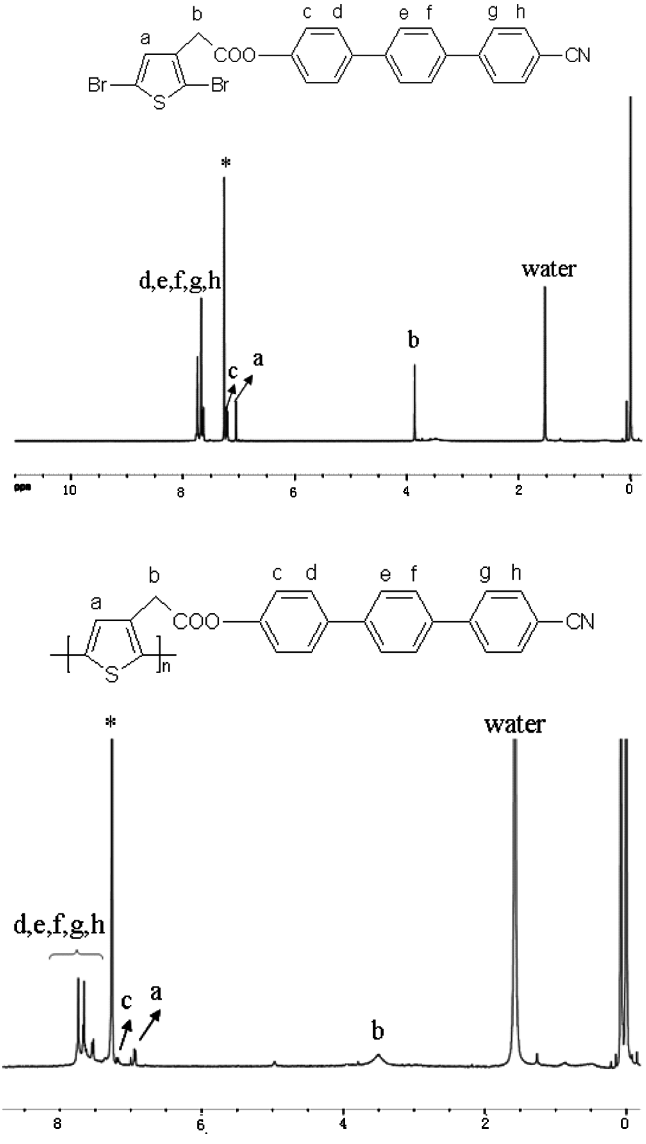


Figure 2. ^{1}H NMR spectra of monomers and polymers (symbol *: $CDCl_3$ as the solvent).

scanning calorimetry (DSC) analysis: no irreversible peaks suspiciously associated with polymer degradation are observed at the high temperatures during the cycles of repeated heating-cooling scans.

All the monomers are white crystals at room temperature and exhibit liquid crystallinity at elevated temperatures. The thermal transition behaviors of the monomers and polymers are examined by DSC and polarized optical microscopy (POM). The POM textures of the monomers are displayed in Fig. 4. When the monomers were cooled from their isotropic state, a large number of anisotropic entities appeared from the dark background of the isotropic liquid, the focal conic fan texture associating to the mesophasic nature of a SmA_d phase. Reheating the monomers regenerates the

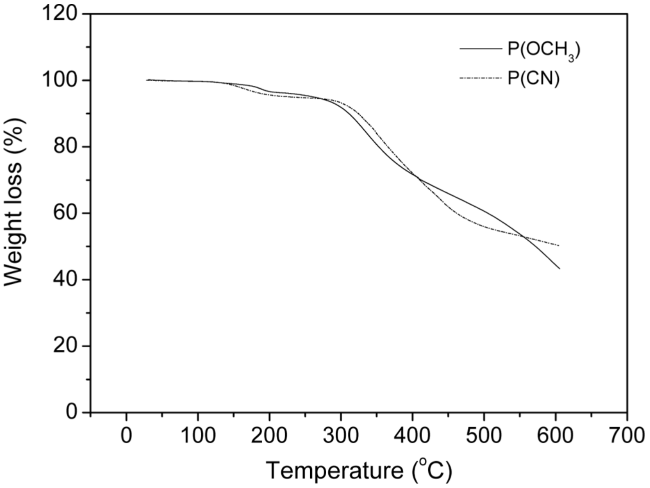
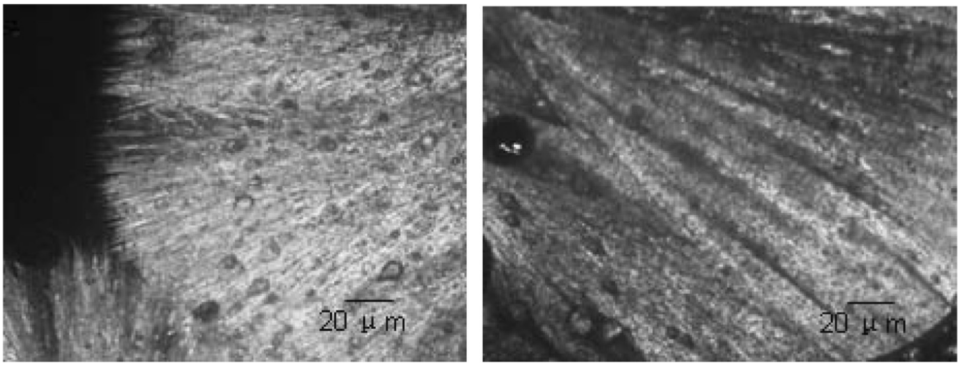
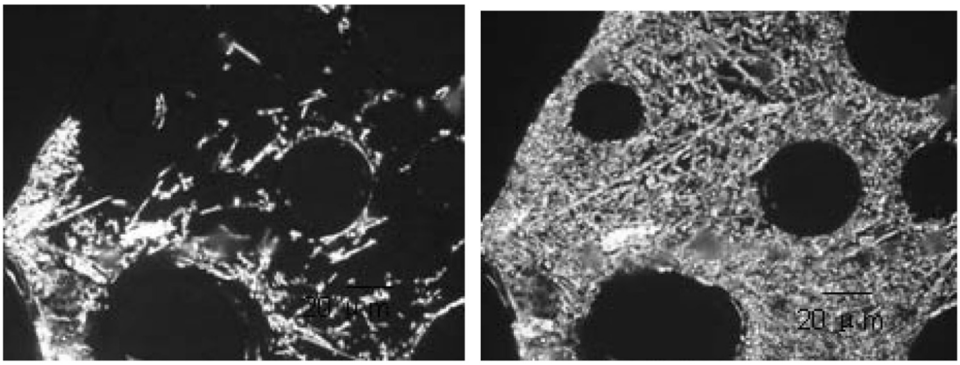


Figure 3. TGA thermograms of polymers under nitrogen at a heating rate of 20°C/min.



M(CN) at 138°C M(CN) at 110°C



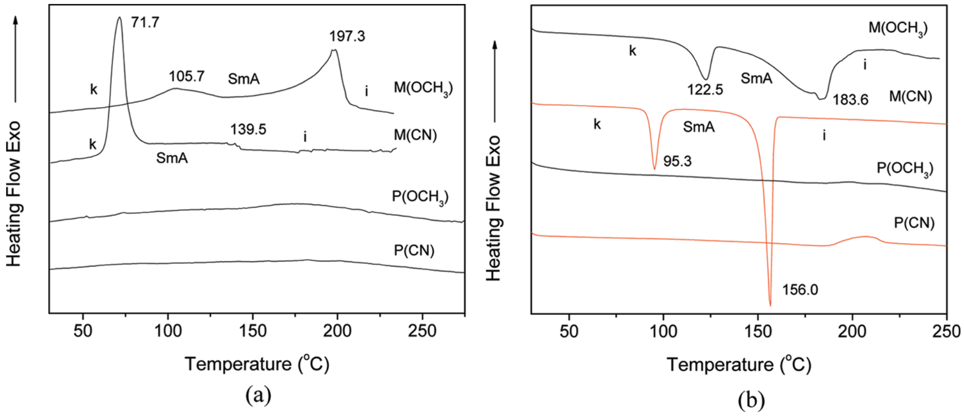
M(OCH$_3$) at 177°C M(OCH$_3$) at 170°C

Figure 4. Mesomorphic textures observed on cooling from the products isotropic states at a cooling rate of 1°C/min.

birefringent texture; that is, the mesomorphism is enantiotropic. However, in sharp contrast to the fact of the monomers, the polymeric products could not exhibit any optical anisotropy when heated or cooled. The results suggest that the thiophene monomers were liquid-crystalline but the polymers were not. It was expected that a liquid-crystalline monomer would result in a polymer with at least one liquid-crystalline phase; however, the expectation was demolished. Because the mesogenic pendant is closely coupled with the rigid backbone, it destroyed the packing arrangements of the mesogens and inhibit the mesogen to move together to pack in a regular fashion.

To learn more about the thermal transitions of the monomers and polymer, we measured their thermograms under nitrogen on a differential scanning calorimeter and the DSC curves are shown in Fig. 5. In the case of monomer M(OCH_3), upon cooling from its isotropic melt, a SmA_d phase with a focal-conic fan texture was observed at 197.3°C. Finally, monomer M(OCH_3) changed into crystal at 105.7°C. The DSC thermogram recorded in the second heating scan also exhibits two peaks at 183.6°C and 122.5°C, a focal-conic fan texture corresponding to a SmA_d phase emerges. M(CN) enters SmA_d mesophase from its isotropic state at 139.5°C. The mesophase is stable in a temperature range over 67.8°C before M(CN) finally solidifies at 71.7°C. The associated k–SmA_d and SmA_d–i transition profiles of M(CN) can be observed at 95.3°C and 156.0°C. The SmA_d phase of the monomers is thus enantiotropic. Different from the monomers, the two resulting polymers show no peaks in the DSC thermograms during the cooling and heating scan, indicating that the polymers are not liquid-crystalline.

With the aid of XRD measurements, the mesomorphic textures of monomers and polymer were identified (Fig. 6). WAXD patterns of all the polymers were obtained at room temperature after the samples had been quenched from liquid-crystalline states with liquid nitrogen. The WAXD pattern of M(OCH_3) shows a sharp reflection at $2\theta = 3.466°$ (d-spacing d = 25.47 Å). The calculated length of one repeat unit of M(OCH_3) is 19.80 Å . Because the d/l ratio is ~1.30, which confirms the SmA_d nature of the mesophase and suggests that the mesogens are interdigitated in an antiparallel fashion with a bilayer structure. The diffractogram of M(CN) showed a sharp reflection at $2\theta = 2.81°$, from which d-spacings of 31.32



(a) (b)

Figure 5. DSC thermograms of the monomers and polymers recorded under nitrogen during the (a) first cooling and (b) second heating scans at a scan rate of 10°C/min.

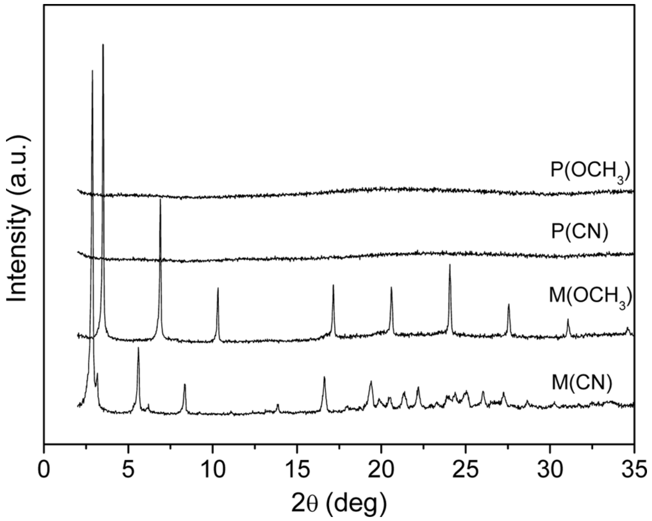


Figure 6. X-ray diffraction patterns of the monomers and polymers quenched from their liquid-crystalline states.

were derived. The d-spacing derived from the low-angle peak was considerably in excess of than the calculated molecule length of M(CN) at its most extended conformation (19.26 Å), thus also providing SmA$_d$ mesophase in a bilayer arrangement, in which the mesogens also arrange in an antiparallel overlapping interdigitated manner. The mesogens of the monomers are packing so well that the high-order secondary reflection at a middle angle at a middle angle at 5–6° were readily detected by the diffractometer, and the d-spacing is about 15.00–16.00 Å, which associated to the distance of the terphenyl mesogen. The diffractograms of the polymers show no peaks, confirming that the polymers are not liquid-crystalline. The short methylene ester spacer between the mesogenic pendant and the polythiophene backbone limited

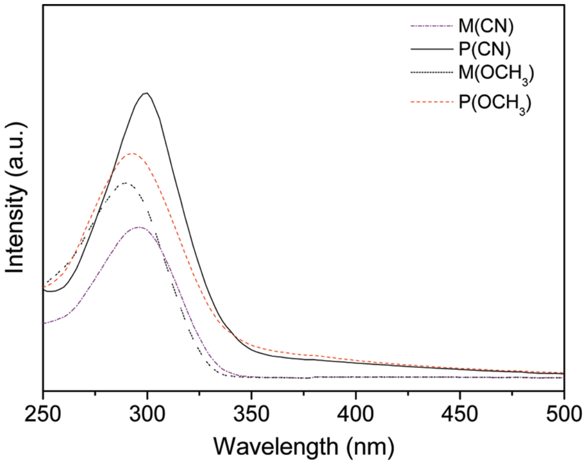


Figure 7. UV spectra of CH_2Cl_2 solution of the monomers and polymers. The concentration was 0.125 Mm.

the mesogens to undergo thermal transitions in a relatively independent fashion. The results are as well as identified with the POM and DSC.

Electronic Absorption and PL

The ultraviolet-visible (UV) and PL spectra of M(OCH_3), M(CN), P(OCH_3), and P(CN) in CH_2Cl_2 are given in Figs. 7 and 8, respectively. The monomers and polymers absorb photons at about 300 nm. The absorptions of the monomers and polymers were assignable to the π–π^* bands of the terphenyl mesogenic pendant because the monomers and polymers had similar absorption wavelengths. Besides, the absorptions of the polymers are stronger than that of its corresponding monomers and the molar absorption coefficient of the polymer P(CN) and P(OCH_3) are 1.83×10^5 and $1.48 \times 10^5\,\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$, respectively. Compared with the high absorption of the the terphenyl mesogenic pendants, the low absorptions of the backbone ($\varepsilon < 1.58 \times 10^4\,\text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$) observed at wavelengths longer than 350 nm may have been due to the reduction of the effective conjugation lengths along the polymer backbone by the bulky pendant groups.

A polymer with both liquid crystal mesogens and light-emitting properties may find unique technological applications [41], we thus investigated the fluorescence properties of the polymers in dilute CH_2Cl_2 solutions. When the polymers were photo-excited at 300 nm, the two strong light-emitting bands at 350 and 415 nm observed for a CH_2Cl_2 solution of P(OCH_3) are assigned to the emitting center of the terphenyl mesogenic core and that of the conjugated polythiophene main chain, respectively. On the other hand, energy transfer from terphenyl mesogenic core to the backbone favors stronger emission in the photoluminescence of polythiophene. The two light-emitting bands of polymer P(CN) was slightly red-shifted to 380 and 425 nm, respectively, due to the favor of cyano auxochrome group linked directly to the terphenyl mesogenic core. The photoluminescence efficiency Φ_F of the polymers was also measured using quinine sulfate as the standard. Thanks to

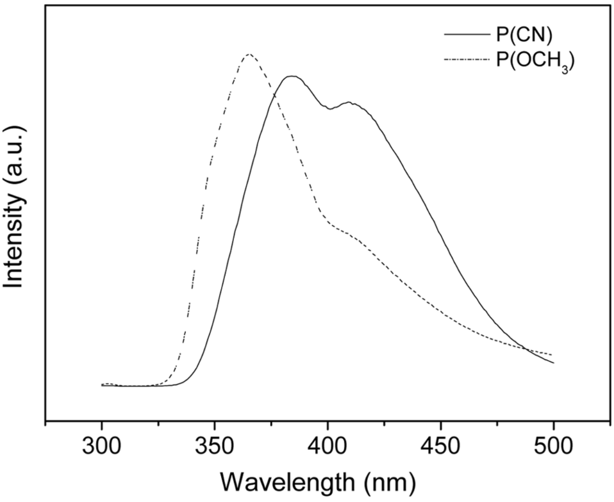


Figure 8. Photoluminescence spectra of CH_2Cl_2 solutions of the polymers. The concentration was 0.125 Mm. Excitation wavelengths: 300 nm.

terphenyl mesogenic favoring the photoluminescence, both of the polymers possessed high quantum efficiency, and Φ_F of polymer P(CN) (82%) was higher than that of P(OCH_3) (74%), which is in agreement with the Tang's observations [42] that the polymers with donor–acceptor pairs luminesce more strongly than those without such push–pull pairs. Most conjugated polymers emit intensely in solution but become weak emitters when fabricated into films [43,44]. This is mainly caused by strong interchain interaction. In the solid state, the polymer strands aggregate together to form less luminescent species such as excimers, leading to red-shifted emissions with low efficiencies [45]. We thus fabricated the polymers into film to check their fluorescence properties. Although we have technical difficulty in measuring the quantum efficiency of the polymers, both of the polymers maintained their strong light-emitting properties and no significant shifts in the peak maximum are observed in comparison to those in the solutions. This is suggestive of little excimer absorption and emission, and the segregation of the backbone effectively by the bulky pendants decreases the strong interchain interaction.

Conclusion

Polythiophenes with terphenyl chromophoric mesogenic side chain were successfully synthesized via dehalogenative polycondensation. The effects of the structural variations on the chemical and physical properties of the monomers and polymers were investigated. The monomers are liquid-crystalline and exhibit enantiotropic smectic A with focal-conic fan textures, but the polymers are not. The short spacers between the mesogenic pendant and the polythiophene backbone limited the mesogens to undergo thermal transitions in a relatively independent fashion, with a consequent loss of liquid crystallinity. On the other hand, the terphenyl chromophoric mesogenic core endows the monomers and polymers with the high absorptivity of UV light and efficient light emission. The polymer P(CN) can emit UV light of 425 nm, which is longer and stronger than that of the polymer P(OCH_3).

Acknowledgment

Financial support for this work was provided by the National Natural Science Foundation of China (50773029), the Natural Science Foundation of Jiangxi Province (2007GZC1727 and 2008GQH0046), Jiangxi Provincial Department of Education, the Program for New Century Excellent Talents in University (NCET-06-0574), the Program for Innovative Research Team of Nanchang University, Program for Innovative Research Team in University of Jiangxi Province, and Program for Changjiang Scholars and Innovative Research Team in University (IRT0730).

References

[1] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., & Holmes, A. B. (1990). *Nature*, *347*, 539.

[2] Gustafsson, G., Gao, Y., Treacy, G. M., Klavetter, F., Colaneri, N., & Hegger, A. J. (1992). *Nature*, *357*, 477.

[3] MacDiarmid, A. G. (2001). *Synth. Met.*, *125*, 11.

[4] Marder, S. R., Kippelen, B., Jen, A. K.-Y., & Peyghambrian, N. (1997). *Nature*, *388*, 845.

[5] Bowman, D., & Mattes, B. R. (2005). *Synth. Met.*, *154*, 29.

[6] Heeger, A. J. (2001). *J. Phys. Chem. B.*, *105*, 8475.

[7] Lee, K., Cho, S., Park, S. H., Heeger, A. J., Lee, C.-W., & Lee, S.-H. (2006). *Nature*, *441*, 65.

[8] Kaneto, K., & Takashima, W. (2001). *Curr. Appl. Phys.*, *1*, 355.

[9] Pandey, S. S., Ram, M. K., Srivastava, V. K., & Malhotra, B. D. (1997). *J. Appl. Polym. Sci.*, *65*, 2745.

[10] Mishra, S. C. K., Ram, M. K., Pandey, S. S., Malhotra, B. D., & Chandra, S. (1992). *Appl. Phys. Lett.*, *61*, 1219.

[11] Ravichandar, R., Thelakkat, M., & Somanathan, N. (2008). *J. Fluoresc.*, *18*, 891.

[12] Shirakawa, H., Kadokura, Y., Goto, H., Oh, S.-Y., & Akagi, K. (1994). *Mol. Cryst. Liq. Cryst.*, *255*, 213.

[13] Lam, J. W. Y., Kong, X., & Tang, B. Z. (1999). *Polym. Mater. Sci. Eng.*, *80*, 159.

[14] Kuroda, H., Goto, H., Akagi, K., & Kawaguchi, A. (2002). *Macromolecules*, *35*, 1307.

[15] Akagi, K., & Shirakawa, H. (1998). In: *Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications*, Wise, D. L., Trantolo, D. J., Altobelli, D. E., Yaszemski, M. J., Gresser, J. D. (Eds.), Marcel Dekker: New York, Vol. 28, 983.

[16] Akagi, K., & Shirakawa, H. (1996). *The Polymeric Materials Encyclopedia. Synthesis, Properties and Applications*, CRC Press: Boca Raton, FL.

[17] Yuan, W. Z., Sun, J. Z., Dong, Y., Haussler, M., Yang, F., Xu, H. P., Qin, A., Lam, J. W. Y., Zheng, Q., & Tang, B. Z. (2006). *Macromolecules*, *39*, 8011.

[18] Xing, C., Lam, J. W. Y., Zhao, K., & Tang, B. Z. (2008). *J. Polym. Sci.: Part A: Polym. Chem.*, *346*, 2960.

[19] Zhou, J.-L., Chen, X.-F., Fan, X.-H., Chai, C.-P., Lu, C.-X., Zhao, X.-D., Pan, Q.-W., Tang, H.-Y., Gao, L.-C., & Zhou, Q.-F. (2006). *J. Polym. Sci.: Part A: Polym. Chem.*, *44*, 4532.

[20] Sanda, F., Aragi, H., & Masuda, T. (2004). *Macromolecules*, *37*, 8510.

[21] Yuan, W. Z., Mao, Y., Zhao, H., Sun, J. Z., Xu, H. P., Jin, J. K., Zheng, Q., & Tang, B. Z. (2008). *Macromolecules*, *41*, 701.

[22] Yuan, W. Z., Qin, A., Lam, J. W. Y., Sun, J. Z., Dong, Y., Haiussler, M., Liu, J., Xu, H. P., Zheng, Q., & Tang, B. Z. (2007). *Macromolecules*, *40*, 3159.

[23] Chen, S. H., Conger, B. M., Mastrangelo, J. C., Kende, A. S., & Kim, D. U. (1998). *Macromolecules*, *31*, 8051.

[24] Percec, V., Asandei, A. D., Hill, D. H., & Crawford, D. (1999). *Macromolecules*, *32*, 2597.

[25] Chen, L., Chen, Y. W., Zha, D. J., & Yang, Y. J. (2006). *Polym. Sci: Part A: Polym. Chem.*, *44*, 2499.

[26] Osaka, I., Goto, H., Itoh, K., & Akagi, K. (2001). *Synth. Met.*, *119*, 541.

[27] Kijima, M., Akagi, K., & Shirakawa, H. (1997). *Synth. Met.*, *84*, 313.

[28] Sohn, H.-S., Yoon, Y.-S., & Lee, J. C. (2008). Seoul, Korea. Abstracts of Papers 236th ACS National Meeting, Philadelphia, August 17–21, 2008, 468.

[29] Dai, X. M., Narihiro, H., Goto, H., Akagi, K., & Yokoyama, H. (2001). *Synth. Met.*, *119*, 397.

[30] Jin, S.-H., Lee, H.-J., Sun, Y.-K., Kim, H.-D., Koh, K.-N., Gal, Y.-S., & Park, D.-K. (1999). *Euro. Polym. J.*, *35*, 89.

[31] Goto, H., Akagi, K., Dai, X., & Narihiro, H. (2007). *Ferroelectrics*, *348*, 149.

[32] Osaka, I., Shibata, S., Toyoshima, R., Akagi, K., & Shirakawa, H. (1999). *Synth. Met.*, *102*, 1437.

[33] Dai, X. M., Goto, H., Akagi, K., & Shirakawa, H. (1999). *Synth. Met.*, *102*, 1291.

[34] Toyoshima, R., Narita, M., Akagi, K., & Shirakawa, H. (1995). *Synth. Met.*, *69*, 289.

[35] Hiroyuki, K., Fumio, S., Takashi, M., & Naoyuki, K. (2003). *Polym. J. (Tokyo, Japan)*, *35*, 945.

[36] Radhakrishnan, S., Somanathan, N., Narashimhaswamy, T., Thelakkat, M., & Schmidt, H. W. (2006). *J. Therm. Anal. Calor.*, *85*, 2433.

[37] Goto, H., Dai, X., Narihiro, H., & Akagi, K. (2004). *Macromolecules*, *37*, 2353.

[38] Goulding, M., Green, S., Parri, O., & Coates, D. (1995). *Mol. Cryst. Liq. Cryst.*, *265*, 27.

[39] Yu, Z. N., Tu, H. L., Wan, X. H., Chen, X. F., & Zhou, Q.-F. (2003). *J. Polym. Sci.: Part A: Polym. Chem.*, *41*, 1454.

[40] Chen, L., Chen, Y.-W., & Zha, D.-J. (2008). *Polym. Mater. Sci. Eng. (China)*, *24*, 52.

[41] ONeill, M., & Kelly, S. M. (2003). *Adv. Mater.*, *15*, 1135.

[42] Lam, J. W. Y., & Tang, B. Z. (2003). *Polym. Sci: Part A: Polym. Chem.*, *41*, 2607.

[43] Li, Y. N., Vamvounis, G., & Holdcroft, S. (2002). *Macromolecules*, *35*, 6900.

[44] Grell, M., Bradley, D. D. C., Ungar, G., Hill, J., & Whitehead, K. S. (1999). *Macromolecules*, *32*(18), 5810.

[45] Lam, J. W. Y., Dong, Y., Kwok, H. S., & Tang, B. Z. (2006). *Macromolecules*, *39*, 6997.