

# Synthesis and Characterization of Novel Two-Component Conjugated Polythiophenes with 3-Octyl and 3-Isooctylthiophene Side Chains

Weidong Feng, Zhengjian Qi, Yueming Sun

*Applied Chemical Laboratory, College of Chemistry and Chemical Engineering, Southeast University, Nan-Jing, 210096, People's Republic of China*

Received 22 July 2006; accepted 1 November 2006

DOI 10.1002/app.25751

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** With copolymerization functionalization, a novel solution-processable polymer, poly{(3-octylthiophene)-*co*-[3-(2-ethyl-1-hexyl)thiophene]} (P3OTIOT), combining the electrochemical properties of poly(3-octylthiophene) (P3OT) and poly[3-(2-ethyl-1-hexyl)thiophene] (P3IOT) was synthesized by the FeCl<sub>3</sub>-oxidative approach. The characterization of the polymers included Fourier transform infrared, <sup>1</sup>H-NMR, gel permeation chromatography, thermogravimetric analysis (TGA), ultraviolet-visible spectroscopy, and photoluminescence (PL). P3OTIOT had excellent solubility in common organic solvents. Investigations of the optical properties showed that the optical band-gap energy of P3OTIOT was similar to that of P3OT (2.43 eV) at 2.45 eV and 6% lower than that of

P3IOT in CHCl<sub>3</sub> solutions. The bandwidth of the P3OTIOT absorption approached that of P3OT, ranging from 370 to 570 nm, and the emission maximum of P3OTIOT was only 50 nm blueshifted with respect to that of P3OT. However, the PL intensity of P3OTIOT was 7 times higher than that of P3OT. TGA studies showed that P3OTIOT had very good thermal stability, losing 5% of its weight on heating to 300°C. It is suggested that P3OTIOT has low band-gap energy, a high PL quantum yield, and processability. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1169–1175, 2007

**Key words:** conducting polymers; copolymerization; light-emitting diodes (LED); luminescence; UV-vis spectroscopy

## INTRODUCTION

Conjugated polymers have drawn much attention in recent years because of their promising applications in electrochromics,<sup>1</sup> biosensors,<sup>2</sup> electrochemical supercapacitors,<sup>3</sup> anticorrosion,<sup>4</sup> polymer thin-film transistors,<sup>5</sup> polymer light-emitting diodes,<sup>6</sup> polymer photodetectors and polymer solar cells,<sup>7–11</sup> and so forth. Soluble polythiophene derivatives are the most promising and frequently investigated conjugated systems as a result of their synthetic availability, stability in various redox states, widespread processibility, and tunable electronic properties.<sup>12</sup> Moreover, the solubility enables easy characterization and understanding of the physical and chemical structures and properties in great detail. The alkyl side-chain modification makes their color tuning easy.<sup>13</sup>

Among the various properties of polythiophene derivatives, the absorption spectrum, quantum yield, and optical band-gap energy ( $E_g$ ) are of crucial importance for their applications in photoconductors. As photoactive materials in polymer solar cells, first the conjugated polymers need effective absorption of visible light; second, the bandwidth of their absorption must be broad enough.<sup>11</sup> A high luminescence intensity and a low drive voltage are adequate for their applications in displays. However, polythiophenes of simple straight-chain alkyl substitution are unsatisfactory for various applications.

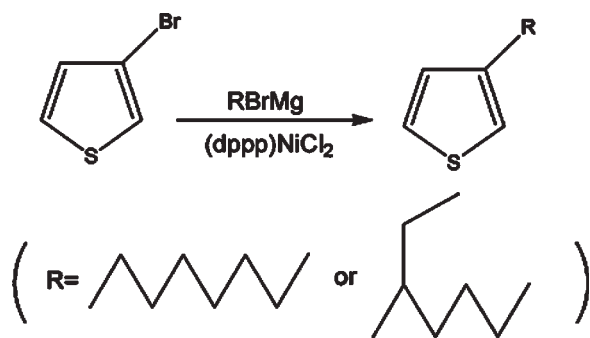
In this work, poly(3-octylthiophene) (P3OT), poly[3-(2-ethyl-1-hexyl)thiophene] (P3IOT), and their two-component (2-C) copolymer, poly{(3-octylthiophene)-*co*-[3-(2-ethyl-1-hexyl)thiophene]} (P3OTIOT), were synthesized by FeCl<sub>3</sub>-oxidative polymerization at room temperature. A critical length of the alkyls is needed for sufficient solubility and processability of the polymer from solution. High-molecular-weight batches of P3OT dissolve quickly in common organic solvent such as chloroform, tetrahydrofuran (THF), and toluene at room temperature. On the other hand, P3IOT is quite soluble in chlorinated solvents such as chloroform but only weakly soluble in nonchlorinated solvents such as toluene or xylene. P3OT has a broad bandwidth of absorption and low band-gap energy in comparison with P3IOT; however, it exhibits lower

Correspondence to: Z. Qi (qizhengjian@sohu.com).

Contract grant sponsor: Doctor Foundation of the Ministry of Education of China; contract grant number: 20030286012.

Contract grant sponsor: Foundation High-Tech Item of Jiang-Su Province of China; contract grant number: BG 2005034.

*Journal of Applied Polymer Science*, Vol. 104, 1169–1175 (2007)  
© 2007 Wiley Periodicals, Inc.



**Scheme 1** Synthetic scheme of 3-alkylthiophene.

intensity of luminescence. An alternative approach to combining the desirable properties of two polymers is copolymerization of the respective monomer units. Here we report the performance of highly soluble P3OTIOT as a photoconductor material. It is a statistical copolymer of 3-octylthiophene (3OT) and 3-(2-ethyl-1-hexyl)thiophene (3IOT) with a molar ratio of 50 : 50. This report shows a path toward a suitable compromise between the sufficient solubility of the polythiophene derivatives and the photoluminescence (PL) quantum yield.

## EXPERIMENTAL

### Materials

3-Bromothiophene (99%), 1-bromooctane (98%), 2-ethylhexylbromide (95%), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) [Ni(dppp)Cl<sub>2</sub>; 98%], and FeCl<sub>3</sub> (97%) were purchased from Aldrich Chemical Co., Inc (NJ).

### Instruments

<sup>1</sup>H-NMR spectra were recorded at 500 MHz on a Bruker DRX-500 (Ettlingen, Germany) in CDCl<sub>3</sub> at room temperature. Fourier transform infrared (FTIR) spectra of the synthesized polymers were recorded on a Nicolet 700 FTIR spectrometer (Waltham, MA). High-resolution mass spectroscopy (HRMS) measurements were taken with a JEOL JMS 700 spectrometer

(Tokyo, Japan). High-performance liquid chromatography (HPLC) was performed with a PerkinElmer Spheri-5 RP-18 column (4.6 × 250 mm i.d., 5-μm coating) (Boston, MA), and the compounds were eluted with methanol and detected by a UV spectrophotodetector at 254 nm. Gel permeation chromatography (GPC) was performed with a PerkinElmer series 200 apparatus (a mixed 10-μ polystyrene column with a length of 750 mm and a refractive-index detector). THF acted as the eluant at a flow rate of 1.0 mL/min at 40°C. The polymer solution was filtered through a 0.45-μm polytetrafluoroethylene filter before being injected into the column. Calibration was conducted with polystyrene standards. Thermogravimetric analysis (TGA) was performed on a DuPont 9900 analyzer with a heating rate of 10°C/min under a nitrogen atmosphere. Ultraviolet-visible (UV-vis) spectra of the polymers with chloroform as a solvent were recorded on a UV-2201 (Kyoto, Japan) in a laboratory atmosphere at room temperature. PL spectra were recorded on a Spex (NJ) FL-2T2.

### 3OT

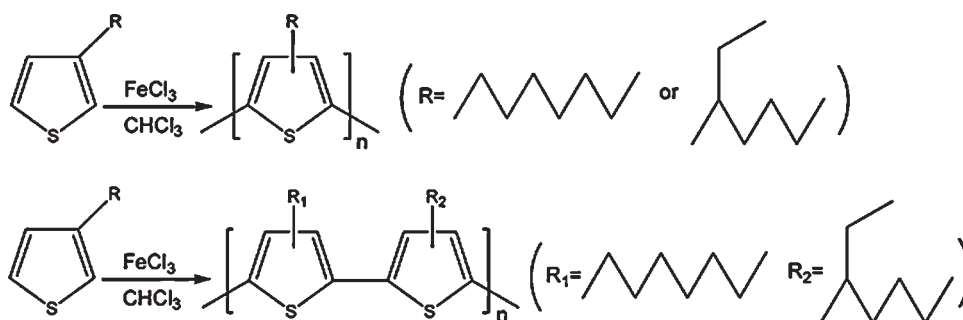
The synthesis of 3OT was performed according to the literature<sup>14</sup> as shown in Scheme 1.

Yield: 76%. White crystalloid (purity: 98.5%, HPLC). <sup>1</sup>H-NMR (δ, ppm): 0.88 (t, *J* = 5.8 Hz, 3H); 1.65 (m, 2H), 1.31 (m, 10H); 2.65 (t, *J* = 7.0 Hz, 2H); 6.96 (m, 2H); 7.25 (s, 1H). HRMS: *m/e* = 195.3570 (calcd 195.3574). ANAL. Calcd: C, 73.41%; H, 10.19%; S, 16.40%. Found: C, 73.38%; H, 10.18%; S, 16.12%.

### 3IOT

3IOT was obtained from 3-bromothiophene and 2-ethyl-1-hexylbromide with a procedure similar to that described for 3OT.

Yield: 72%. White crystalloid (purity: 98.5%, HPLC). <sup>1</sup>H-NMR (δ, ppm): 0.851–0.887 (m, 6H); 1.32 (m, 1H); 1.56–1.67 (m, 8H); 2.67 (d, *J* = 7.0 Hz, 2H); 7.09 (m, 2H); 7.29 (s, 1H). HRMS: *m/e* = 195.3568 (calcd 195.3574). ANAL. Calcd: C, 73.41%; H, 10.19%; S, 16.40%. Found: C, 73.30%; H, 10.00%; S, 16.09%.



**Scheme 2** Synthetic scheme of poly(3-alkylthiophene).

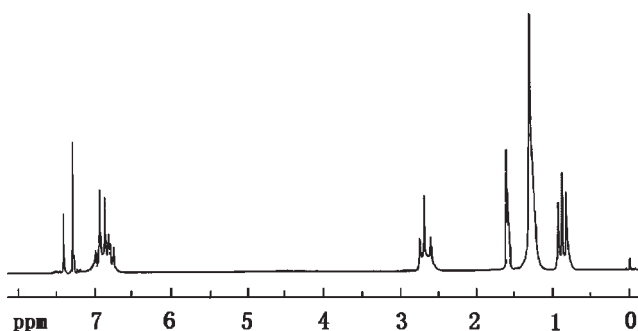


Figure 1  $^1\text{H-NMR}$  spectrum of 3OT.

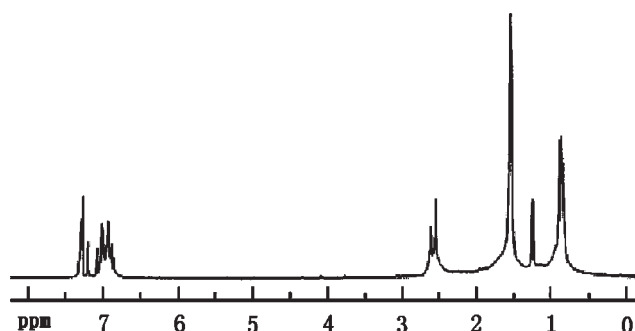


Figure 2  $^1\text{H-NMR}$  spectrum of 3IOT.

### Synthesis of the polymers

All polymers were synthesized by  $\text{FeCl}_3$  oxidation in chloroform as a solvent according to a procedure similar to that described in the literature,<sup>15–18</sup> as shown in Scheme 2.

#### P3OT

Anhydrous  $\text{FeCl}_3$  (4.9 g, 0.03 mol) and chloroform (40 mL) were charged into a dry 100-mL, three-necked, round-bottom flask under an  $\text{N}_2$  atmosphere, and the mixture was stirred at room temperature until it became dark green; then, 19.6 g of 3OT (in 20 mL of chloroform) was dripped. After 24 h, the product was precipitated in  $\text{CH}_3\text{OH}$  (200 mL) and filtered. The polymer mixtures were then placed in a 200-mL, single-necked, round-bottom flask charged with a solution of chloroform (80 mL) and saturated aqueous hydrazine (80 mL) and were stirred and heated to  $65^\circ\text{C}$  for 60 min. The chloroform phase was then concentrated to 10 mL by vacuum distillation and poured into 600 mL of methanol. The orange precipitate of the polymer was collected by filtration and extracted with methanol through a Soxhlet apparatus for 24 h. It was further purified by redissolution in chloroform and precipitation in methanol, and the final polymer was dried *in vacuo*. The yield of the orange solid (P3OT) was 81%.

$^1\text{H-NMR}$  ( $\delta$ , ppm): 0.838 (t,  $J = 7.4$  Hz, 3H); 1.32 (m, 8H); 1.66 (m, 4H); 2.87 (t,  $J = 7.4$  Hz, 2H); 7.07, 7.35 (m, 1H). FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3057, 2955, 2922, 2852, 1637, 1509, 1457, 1376, 1180, 1077, 828, 721.

#### P3IOT

P3IOT was obtained from 3IOT with a procedure similar to that described for P3OT. The yield of the yellow solid (P3IOT) was 78%.

$^1\text{H-NMR}$  ( $\delta$ , ppm): 0.838–0.851 (m, 6H); 1.31–1.33 (m, 1H); 1.56–1.66 (m, 8H); 2.86 (d,  $J = 7.4$  Hz, 2H); 7.07, 7.43 (m, 1H). FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3055, 2950, 2925, 2856, 1630, 1509, 1460, 1400, 864, 819, 705.

#### P3OTIOT

P3OTIOT was obtained from 3OT (0.05 mol) and 3IOT (0.05 mol) with a procedure similar to that described for P3OT. After polymerization, the isolated polymer powders were extracted in a Soxhlet apparatus with hexane to remove short-chain oligomers. The yield of the straw-yellow solid (P3OTIOT) was 72%.

$^1\text{H-NMR}$  ( $\delta$ , ppm): 0.838, 0.842, 0.868, 0.909; 1.28–1.38, 1.66–1.69; 2.65, 2.87; 6.72, 6.78, 7.07; 7.35, 7.42, 7.47. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3055, 2955, 2925, 2856, 1640, 1516, 1464, 1382, 1180, 1077, 828, 800, 721, 617.

## RESULTS AND DISCUSSION

### Structural characterization

The structures were characterized by spectroscopic methods. The spectral assignments clearly corroborated the proposed structure.

Figures 1 and 2 show the  $^1\text{H-NMR}$  spectra of 3OT and 3IOT, respectively. The peak of 3OT that appears at 7.25 ppm can be ascribed to the  $\text{C}_2$  proton of the thiophene ring between the S atom and the side chain, and a group of peaks that appear around 6.96 ppm can be ascribed the two H atoms between the S atom and the side chain; similarly, those of 3IOT appear at 7.29 and 7.09 ppm, respectively. In the aliphatic zone, the triplet at 2.66, 2.65, and 2.64 ppm corresponds to the two H atoms of the  $\text{CH}_2$  group, which is directly connected to the thiophene ring of 3OT; however, that

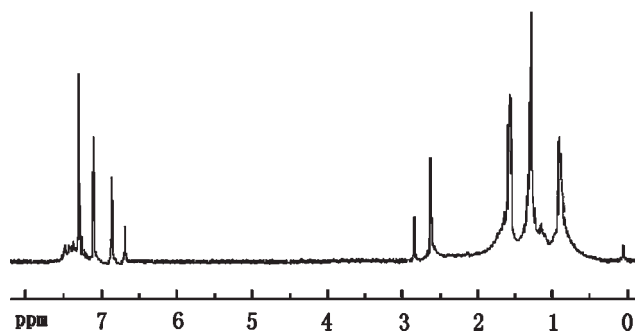


Figure 3  $^1\text{H-NMR}$  spectrum of P3OTIOT.

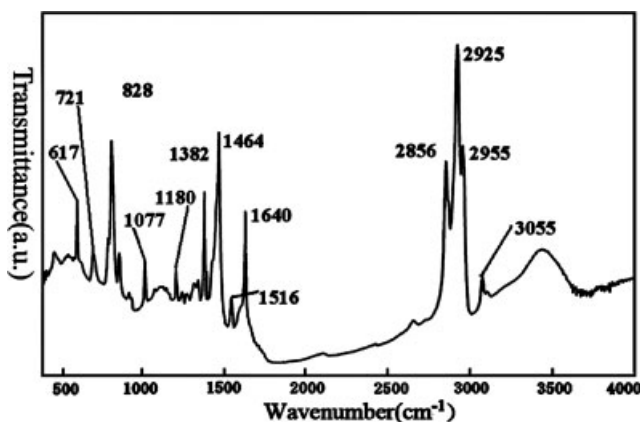


Figure 4 Room-temperature FTIR spectrum of P3OTIOT.

of 3IOT is a doublet that appears at 2.68 and 2.67 ppm. The triplet at 0.89, 0.88, and 0.87 ppm is due to the three H atoms of CH<sub>3</sub> of 3OT, and a group of peaks that appear at 0.851–0.887 ppm is due to the six H atoms of CH<sub>3</sub> of 3IOT. The remaining six CH<sub>2</sub> groups on the octyl chain give absorption bands at 1.65 and 1.31 ppm; likewise, the remaining resonance of 3IOT at 1.32 and 1.56–1.67 ppm can be due to CH and four CH<sub>2</sub> groups, respectively. Figure 3 shows the <sup>1</sup>H-NMR spectrum of the copolymer synthesized by FeCl<sub>3</sub>-oxidative polymerization. The peaks of very low intensity that appear at 7.47, 7.42, and 7.35 ppm can be ascribed to the protons in the terminal thiophene units, whereas the C<sub>β</sub> proton of the thiophene rings appears at 7.07, 6.78, and 6.72 ppm. The remaining resonance at 2.87, 2.65, and 1.69–0.838 ppm can be correlated with the octyl and isooctyl pendant chains on the thienylene units. The differences can be observed in the <sup>1</sup>H-NMR spectra. Both the absorption bands of octyl and those of isooctyl appear in the spectrum of the copolymer. In comparison with the monomers, the proportion of the absorption area around 6.96–7.09 ppm, due to the hydrogen atoms in the aromatic zone, is lessened; moreover, the presence in the spectrum of protons in the terminal thiophene units appears at 7.35–7.47 ppm.

IR spectroscopy is a useful technique for characterizing the structures of polymers. The FTIR spectrum of P3OTIOT is shown in Figure 4. The spectrum of

P3OTIOT reflects obvious alkyl chain substitution. The absorption band at 3055 cm<sup>-1</sup> corresponds to the C<sub>β</sub>–H aromatic stretching mode. The shoulder at 2955 cm<sup>-1</sup> corresponds to the –CH<sub>3</sub> asymmetric stretching vibration. The absorption bands at 2925 and 2856 cm<sup>-1</sup> correspond to the –CH<sub>2</sub>– stretching vibration. The relative intensity of the IR mode at 1640 and 1516 cm<sup>-1</sup> (asymmetric C=C stretching) increases with an increase in the average conjugation length. The thiophene ring stretching mode appears at 1516 and 1464 cm<sup>-1</sup>. The bands centered at 1382 cm<sup>-1</sup> are attributable to the deformation vibration mode of –CH<sub>2</sub>– and –CH<sub>3</sub>. The characteristic in-plane and out-of-plane rocking vibrations of the –(CH<sub>2</sub>)<sub>n</sub>– group (*n* > 3) can be observed at 1180 and 721 cm<sup>-1</sup> in the spectra. The =CH group in-plane and out-of-plane deformation of thiophene is reflected by peaks centered at 1077 and 828 cm<sup>-1</sup>.

### Polymer physical properties

The solubility and molecular weights of the polymers are shown in Table I. P3IOT is insoluble in toluene and xylene, and copolymer P3OTIOT shows good solubility.

The molecular weights and polymerization degrees are presented with a downward trend, which is attributed to the steric exclusion of the substitution in side chains. All the polymers have relatively narrow molecular weight distributions (polydispersity = 1.29–1.51).

In TGA experiments, all the polymers exhibited very good thermal stability, losing less than 5% of their weight on heating to approximately 300°C under a nitrogen atmosphere (Fig. 5). These results can be explained by the assumption of high molecular weights and narrow molecular weight distributions. Obviously, the thermal stability of the polymers is adequate for their applications in thin-film transistor (TFTs), light-emitting diodes, and other photoelectronic devices.

### UV-vis spectroscopy in solution

In conjugated polymers, the extent of conjugation directly affects the observed energy of the π–π\* transi-

TABLE I  
Solubility in Organic Solvents, Average Molecular Weights, Polydispersity Indices (PDIs), and Polymerization Degrees (DPs) of the Polythiophene Derivatives

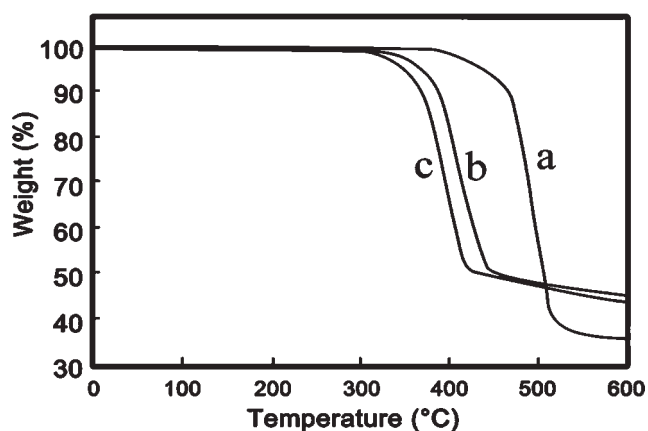
Polymer	Solvent <sup>a</sup>				GPC <sup>b</sup>				
	CHCl <sub>3</sub>	THF	Toluene	Xylene	PMwt	M <sub>w</sub>	M <sub>n</sub>	DP	PDI
P3OT	✓	✓	✓	✓	107,531	116,272	81,156	599	1.43
P3IOT	✓	✓	×	×	99,167	115,684	76,539	596	1.51
P3OTIOT	✓	✓	✓	✓	16,774	24,361	18,885	125	1.29

✓ = soluble; × = insoluble.

<sup>a</sup> PMwt, Peak molecular weight. This means the maximum peak of the PDIs curves in the GPC report.

<sup>b</sup> M<sub>w</sub> = weight-average molecular weight; M<sub>n</sub> = number-average molecular weight.





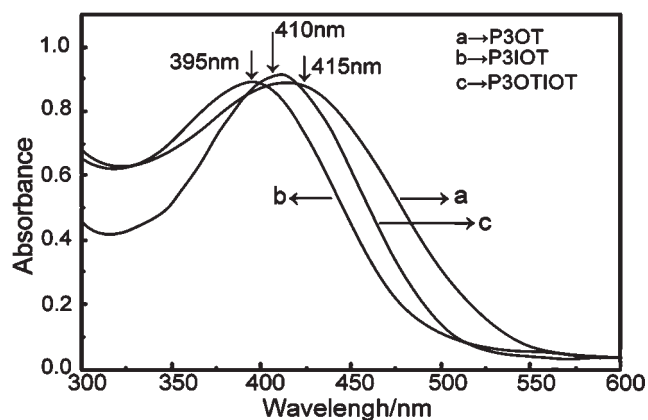
**Figure 5** TGA curves of (a) P3OT, (b) P3IOT, and (c) P3OTIOT.

tion, which appears as the maximum absorption<sup>19,20</sup> (Fig. 6). Their  $\pi$ - $\pi^*$  transitions are exhibited by the absorption with maximum wavelengths around 415, 395, and 410 nm for P3OT, P3IOT and P3OTIOT, respectively. Therefore, the absorption of P3OT implies the longest conjugation length of the polymer backbone. The maximum wavelengths of P3IOT and P3OTIOT are less than that of P3OT because their steric effects are larger than that of P3OT. By the way, it is unnecessary to compare the absorption intensities of the samples. The difference in the absorption intensity is caused only by the concentration of the chloroform solutions.

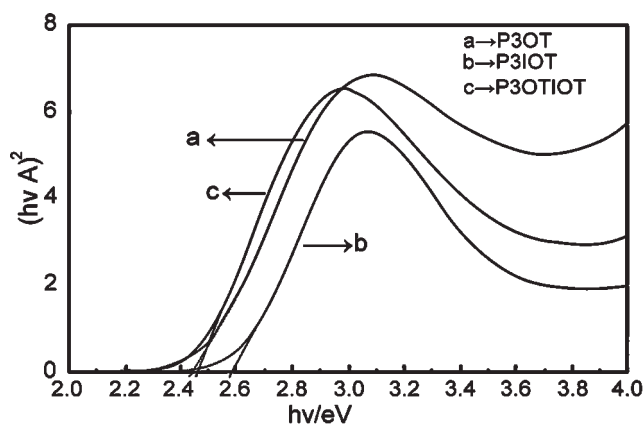
$E_g$  is calculated according to the following formula:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

where  $\alpha$  is the absorbance coefficient,  $h$  is Planck's constant,  $\nu$  is the light frequency,  $B$  is a constant with the given material, and  $n$  is the transition type.<sup>21-23</sup> The value of  $n$  is 0.5 for a direct band transition, and  $\alpha$  amounts to the absorbance for the given sample, so the  $(h\nu A)^2$ - $h\nu$  curves of the polymers can be drawn as



**Figure 6** UV-vis spectra of (a) P3OT, (b) P3IOT, and (c) P3OTIOT in  $\text{CHCl}_3$ .



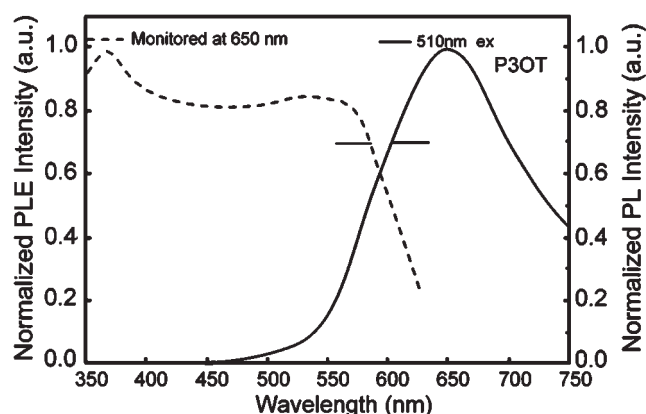
**Figure 7**  $(h\nu A)^2$ - $h\nu$  curves of (a) P3OT, (b) P3IOT, and (c) P3OTIOT.

shown in Figure 7. The linear edge of absorbance is extended and intercrossed with the energy axis, and the  $E_g$  values of P3OT, P3IOT, and P3OTIOT are 2.43, 2.6, and 2.45 eV, respectively. This method shows that  $E_g$  of P3OTIOT is similar to  $E_g$  of P3OT.

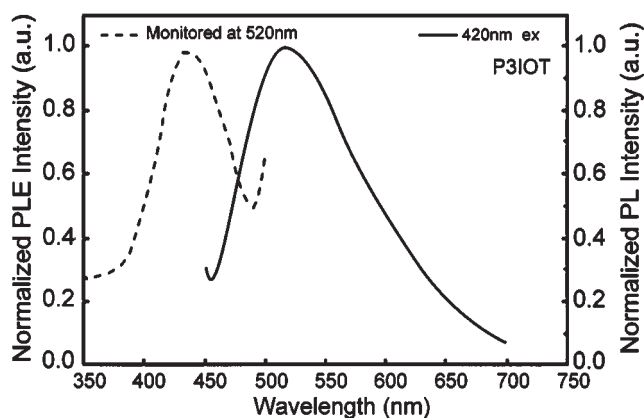
### PL properties

PL spectra can provide a good deal of information on the electronic structures of the conjugated polymers. All the polymers were easily spin-coated onto glass substrates to afford highly transparent, pinhole-free films.

The PL spectra were obtained by excitation at the absorption maxima. Figures 8-10 show the excitation and emission curves of polymers P3OT, P3IOT, and P3OTIOT in the film states, respectively. With the same thickness of the films, the excitation curves of all polymers are closely related to their UV absorption curves,<sup>24</sup> so the films of P3OT, P3IOT, and P3OTIOT show  $\pi$ - $\pi^*$  absorption maxima at about 510, 420, and 435 nm, respectively. It is suggested that the UV-vis absorption maxima of the films are shifted to longer



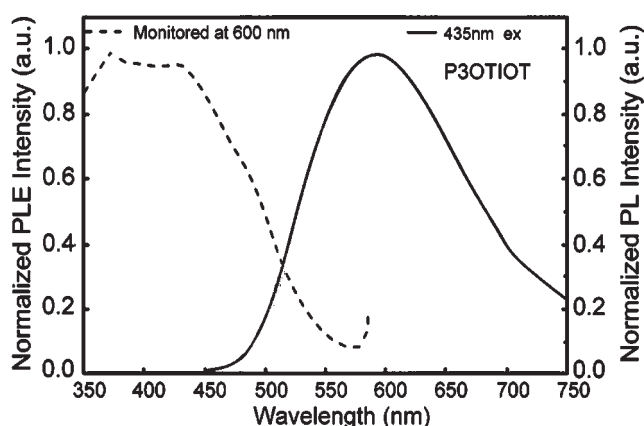
**Figure 8** Normalized excitation and emission curves of P3OT in spin-coating film states. PLE is photoluminescence excitation.



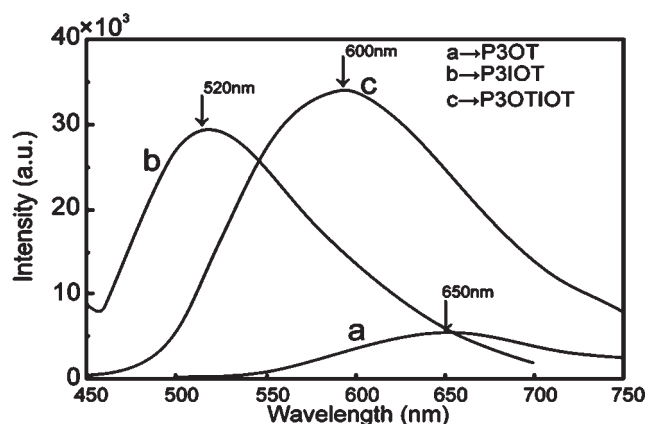
**Figure 9** Normalized excitation and emission curves of P3IOT in spin-coating film states. PLE is photoluminescence excitation.

wavelengths in comparison with those in solution. The results imply that the conformation of poly (alkylthiophene)s in solution can be that of a coil with a small effective conjugation length, and that of the solid state can be a more extended structure with more extensive electronic delocalization.<sup>25</sup> These maximum wavelengths, when correlated with the energy of the  $\pi$ - $\pi^*$  interband transition, indicate a more pronounced planarity of the backbone chains for P3OT and P3OTIOT than that of P3IOT.<sup>26</sup> This is due to the fact that longer side groups restrict the possible rotation of the shared C—C bond of two adjacent thiophene rings.

The PL spectra were recorded with the excitation wavelength corresponding to each absorption maximum wavelength of the polymers, as shown in Figure 11. The PL intensity of P3OTIOT is similar to that of P3IOT and about 7 times higher than that of P3OT because the branched side chain bears higher steric hindrance, the function of the adhesive force between chains has fallen, and the extinction among molecules is reduced. The PL spectrum of P3OT shows that the



**Figure 10** Normalized excitation and emission curves of P3OTIOT in spin-coating film states. PLE is photoluminescence excitation.



**Figure 11** Fluorescence spectra of (a) P3OT, (b) P3IOT, and (c) P3OTIOT.

emission maximum is 650 nm (red), and the emission peaks of P3IOT and P3OTIOT appear around 520 nm (green) and 600 nm (orange), respectively. The emission spectra of P3IOT and P3OTIOT are blueshifted by 130 and 50 nm because of steric-hindrance-induced backbone distortion resulting from branched side-chain groups.<sup>27,28</sup> The bandwidth of P3OTIOT absorption ranges from 370 to 570 nm, which is wide enough for the application of polymer solar cells. Conclusively, we have succeeded in embodying almost full colors from green to red with these polymers by changing the structure of the side chains.

## CONCLUSIONS

In this study, a new copolymer (P3OTIOT) was synthesized successfully through the  $\text{FeCl}_3$ -oxidative approach with low  $E_g$  values, high PL quantum yields, broad bandwidth of absorption, and excellent processability. Our investigations showed that the polymer's electronic and optical properties were consistent with the conjugated backbone structure. On the basis of these results, this novel 2-C conjugated copolymer might be a promising material for applications in polymer light-emitting diodes, polymer light-emitting electrochemical cells, polymer solar cells, and so forth.

## References

- Schwendeman, I.; Hickman, R.; Sonmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chem Mater* 2002, 14, 3118.
- Le Floch, F.; Ho, H. A.; Harding-Lepage, P.; Bedard, M.; Neagu-Plesu, R.; Leclerc, M. *Adv Mater* 2005, 17, 1249.
- Villers, D.; Jobin, D.; Soucy, C.; Cossement, D.; Chahine, R.; Breau, L.; Belanger, D. *J Electrochem Soc A* 2003, 150, 747–752.
- Tuken, T.; Yazici, B.; Erbil, M. *Prog Org Coat* 2004, 51, 205.
- Ong, B. S.; Wu, Y. L.; Liu, P.; Gardner, S. *Adv Mater* 2005, 17, 1141.
- Ahn, S. H.; Czae, M.; Kim, E. R.; Lee, H.; Han, S. H.; Noh, J.; Hara, M. *Macromolecules* 2001, 34, 2522.

7. Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. *Adv Funct Mater* 2003, 13, 85.
8. Kim, Y.; Cook, S.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C. *Chem Mater* 2004, 16, 4812.
9. Gadisa, A.; Svensson, M.; Andersson, M. R.; Inganas, O. *Appl Phys Lett* 2004, 84, 1609.
10. Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. *Adv Funct Mater* 2005, 15, 1617.
11. Li, G.; Shrotriya, V.; Yao, Y.; Yang, Y. J. *Appl Phys* 2005, 98, 043704.
12. Zade, S. S.; Bendikov, M. *J Org Chem* 2006, 71, 2972.
13. Cik, G.; Sersen, F. L.; Bartus, L. *Synth Met* 1995, 75, 43.
14. Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* 1982, 3, 3347.
15. Sugimoto, R.; Takeda, S.; Gu, H.; Yoshino, K. *Chem Express* 1986, 1, 635.
16. Yoshino, K.; Nakajima, S.; Onoda, M.; Sugimoto, R. *Synth Met C* 1989, 28, 349–357.
17. Oesterhoelm, J. E.; Laakso, J.; Nyholm, P.; Isotalo, H.; Stubb, H.; Inganaes, O.; Salaneck, W. R. *Synth Met C* 1989, 28, 435–444.
18. Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol Chem* 1989, 190, 3150.
19. Qiao, X. Y.; Wang, X. H.; Mo, Z. S. *Synth Met* 2001, 122, 449.
20. Pierrick, B.; Patrick, H. *Macromolecules* 1997, 30, 2685.
21. Fang, R. C. *Solid State Spectroscopy*; Press of China University of Science and Technology: Hefei, China, 2001; p 61.
22. Hao, Y. Y.; Hao, H. T.; Wang, H.; Zhou, H. F.; Liu, X. G.; Xu, B. S. *Spectrosc Spectral Anal* 2004, 24, 1524.
23. Li, J.; Zhou, H. F.; Hao, Y. Y.; Wang, H.; Liu, X. G.; Xu, B. S. *Spectrosc Spectral Anal* 2006, 26, 235.
24. Lu, H. F.; Chan, H. S. O.; Ng, S. C. *Macromolecules* 2003, 36, 1543.
25. Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* 1987, 20, 212.
26. Al-Ibrahim, M.; Roth, H. K.; Sensfuss, S. *Org Electron* 2005, 6, 65.
27. Chen, F.; Metha, P. G.; Takiff, L.; McCullough, R. D. *J Mater Chem* 1996, 6, 1763.
28. Ahn, S. H.; Han, S. H.; Noh, J. *Macromolecules* 2001, 34, 2522.