

Novel synthesis metal 3-alkylthiophene copolymer

Qi Zhengjian Feng Weidong Sun Yueming Yan Dazhi Xiao Yingbo He Yanfang Yu Jing

(School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096, China)

Abstract: Copolymer, regiorandom and regioregular poly (3-octylthiophene)-co-poly (3-(2-ethyl-1-hexylthiophene))(P3OTIOT) was synthesized by a FeCl_3 -oxidation and GRIM (grignard method) approach. The structure and optical properties were verified by the Fourier transform infrared, ultraviolet visible spectroscopy, NMR (nuclear magnetic resonance), gel permeation chromatography (GPC) and photoluminescence (PL). The results indicate that the band-gap energy of the regioregular HT P3OTEHT was lower than that of the regiorandom copolymer and both of them depict low band-gap energy, high photoluminescence quantum yield, excellent solubility and processability, and might be promising polymer materials for applications in polymer light-emitting diodes, light-emitting electrochemical cells and polymer solar cells, etc.

Key words: 3-alkylthiophene; copolymer; synthesis metal

Conjugated polymers, so-called synthesis metals, have drawn much attention in recent years, due to their promising applications in electrochromics^[1], biosensors^[2], electrochemical supercapacitors^[3], anticorrosion^[4], polymer thin film transistors^[5], polymer light-emitting diodes (PLEDs)^[6], polymer photodetectors and polymer solar cells(PSCs)^[7-11], etc. Soluble polythiophene derivatives(PTs) are the most promising and frequently investigated conjugated systems as a result of their synthetic availability, stability in various redox states, widespread processability, and tunable electronic properties^[12]. However, polythiophene of simplex straight chain alky substituted are unsatisfactory for various applications.

In this paper, our group has synthesized homopolymer poly (3-octylthiophene) (P3OT), poly (3-(2-ethyl-1-hexylthiophene)) (P3IOT) and their regiorandom and regioregular HT copolymer. It is a statistical copolymer of 3-octylthiophene (3OT) and 3-(2-ethyl-1-hexyl thiophene) (3IOT) with a molar ratio of 1 : 1.

All the regiorandom polymers were synthesized by FeCl_3 -oxidation in a chloroform solvent according to a procedure similar to that described in Refs. [12 – 15] (see Fig. 1).

● Poly(3-octylthiophene)(P3OT)

Anhydrous FeCl_3 (4.9 g, 0.03 mol) and chloroform (40 mL) were placed in a 100 mL dry three-neck

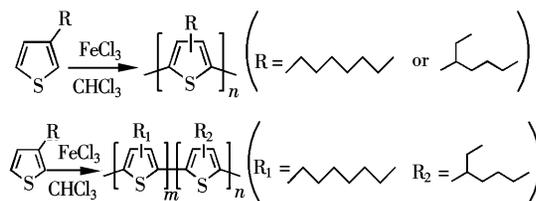


Fig. 1 Synthetic scheme of regiorandom poly(3-alkylthiophene)

round-bottom flask. Under N_2 atmosphere, the mixture was stirred at room temperature till its color turned dark green and 19.6 g 3OT (in 20 mL chloroform) was dripped. After 24 h the product was precipitated in CH_3OH (200 mL) and filtrated. The polymer mixtures were then placed in a 200 mL single-neck round-bottom flask charged with a solution of chloroform (80 mL) and saturated aqueous hydrazine (80 mL), which was stirred and heated up to $65\text{ }^\circ\text{C}$ 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 polymer was collected by filtration and extracted with methanol through a Soxhlet apparatus for 24 h. It was further purified by redissolving in chloroform and precipitating into methanol and the final polymer was dried under vacuum. The yield of the orange solid P3OT was 81%. $^1\text{HNMR}$ δ (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); 7.35, 7.07 (m, 1H). FT-IR (KBr pellet, cm^{-1}): 3057, 2955, 2922, 2852, 1637, 1509, 1457, 1376, 1180, 1077, 828, 721.

● Poly(3-(2-ethyl-1-hexylthiophene)) (P3IOT)

P3EHT was obtained from 3IOT following a procedure similar to that described for P3OT. The yield of the orange solid P3IOT was 78%. $^1\text{HNMR}$ δ (ppm):

Received 2006-10-31.

Foundation item: The Ph. D. Programs Foundation of Ministry of Education of China (No. 20030286012).

Biographies: Qi Zhengjian (1964—), female, doctor; Sun Yueming (corresponding author), male, professor, sun@seu.edu.cn.

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

• Poly[(3-octylthiophene)-co-(3-(2-ethyl-1-hexylthiophene))] (P3OTIOT)

P3OTIOT was obtained from 3OT (0.05 mol) and 3EHT (0.05 mol) following a procedure similar to that described for P3OT. After polymerization, the isolated polymer powders were extracted in a Soxhlet apparatus using hexane to remove short chain oligomers. The yield of the orange red solid P3OTIOT was 72%. $^1\text{H NMR}$ δ (ppm): 0.838, 0.842, 0.868, 0.909; 1.28 to 1.38; 1.66 to 1.69; 2.65, 2.87; 6.72, 6.78; 7.07; 7.23; 7.35; 7.42; 7.47. FT-IR (KBr pellet, cm^{-1}): 3055, 2955, 2925, 2848, 1640, 1500, 1382, 1180, 1077, 828, 800, 700.

• HT poly[(3-octylthiophene)-co-(3-(2-ethyl-1-hexylthiophene))] (TH P3OTIOT)

The regioregular HT copolymer was synthesized by the GRIM approach in a THF solvent according to a procedure similar to that described in Refs. [16–17] (see Fig. 2).

2,5-dibromo-3-octylthiophene (0.05 mol) and 2,5-Dibromo-3-(2-ethyl-1-hexylthiophene) (0.05 mol)

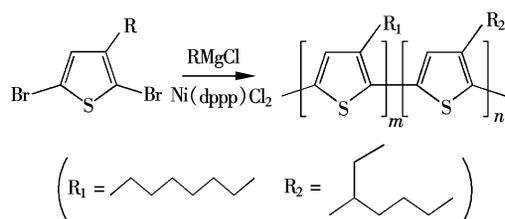


Fig. 2 Synthetic scheme of regioregular HT poly(3-alkylthiophene)

were dissolved in 250 mL of THF. To this solution was added 50 mL of cyclohexylmagnesium chloride (2.0 mol in ether). The mixture was heated to reflux for 1 h at which time Ni(dppp)Cl_2 (100 mg) was added. After 100 min at reflux, the reaction was poured over 300 mL of CH_3OH . The following procedure was similar to that of the regiorandom polymers. The yield of the purple solid HT P3OTIOT was 37%. $^1\text{H NMR}$ δ (ppm): 0.830, 0.858, 0.914; 1.25 to 1.33; 1.56 to 1.69; 2.70, 2.87; 6.95; 7.03; . FT-IR (KBr pellet, cm^{-1}): 3055, 2951, 2928, 2849, 1640, 1500, 1382, 1180, 1077, 828, 800, 700.

The solubility and molecular weights of polymers are shown in Tab. 1. The molecular weight of copolymer P3OTIOT is much lower than that of homopolymer P3OT and P3IOT attributed to the two constituent random polymerization.

Tab. 1 Solubility in organic solvents and average molecular weights, polydispersity indices and polymerization degrees of polythiophene derivatives

Polymer	Solvent				GPC		
	CHCl_3	THF	Toluene	Xylene	Mw	Mn	DP
P3OT	Soluble	Soluble	Soluble	Soluble	116 272	81 156	599
P3IOT	Soluble	Soluble	Insoluble	Insoluble	115 684	76 539	596
P3OTIOT	Soluble	Soluble	Soluble	Soluble	24 361	18 885	125
HT P3OTIOT	Soluble	Soluble	Soluble	Soluble	98 374	39 336	504

In the TGA experiment, all of the polymers exhibited very good thermal stability, losing less than 5% of their weight on heating to approximately 300 $^\circ\text{C}$ under nitrogen atmosphere. The results can be explained by assuming high molecular weights and narrow molecular weight distributions. Obviously, the thermal stability of the polymers was adequate for their applications in TFTs, LEDs and other photoelectronic devices.

In conjugated polymers, the extent of conjugation directly affects the observed energy of the π - π^* transition, which appears as the maximum absorption^[18–19] (see Fig. 3). Their π - π^* transitions are exhibited by the absorption with maximum wavelength λ_{max} at around 415, 395, 410 and 437 nm for P3OT, P3IOT, P3OTIOT and HT P3OTIOT, respectively. Therefore, the absorption of P3OT implied its longest conjugation length of the polymer backbone among regio-

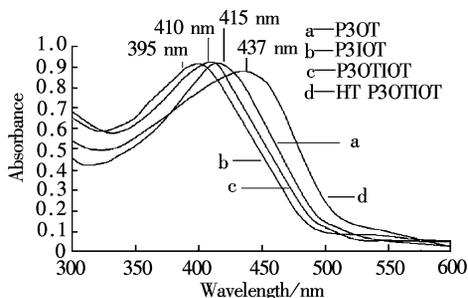


Fig. 3 UV-vis spectra of polythiophene derivatives in CHCl_3

random polymers by the FeCl_3 polymerization approach. The maximum wavelength of P3IOT and P3OTIOT were less than that of P3OT, due to their steric effects being larger than those of P3OT. However, the maximum wavelength of regioregular HT P3OTIOT was shown to be much lower than that of regiorandom polymers. This is attributed to its struc-

tural homogeneity and significantly extended conjugation length. The optical band-gap energy was calculated according to the following formula:

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

where α is the absorbance coefficient, h is the Planck constant, E_g is the optical band-gap energy and n is the transition type, respectively^[20-22]. The value of n is 0.5 in the case of direct band transition, and the absorbance coefficient amount to absorbance for the given sample, so the band-gaps energy were at 2.43, 2.6, 2.45 and 2.11 eV for P3OT, P3IOT, P3OTIOT and HT P3OTIOT, respectively.

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

Photoluminescence emission (PLE) spectra were recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the polymer as shown in Fig. 4. The PLE spectrum of P3OT shows that the emission maximum is 650 nm and emission peaks of P3IOT, P3OTIOT and HT P3OTIOT appeared at around 520, 600 and 620 nm, respectively. The emission of P3IOT, P3OTIOT and HT P3OTIOT are blue-shifted 130, 50 and 30 nm because of sterically induced backbone distortion resulting from branched side chain groups^[23]. The PL intensity of regioregular HT P3OTIOT was similar to that of regiorandom P3OTIOT and about 7 times higher than that of P3OT.

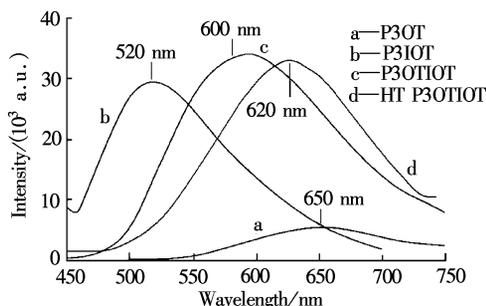


Fig. 4 PLE spectra of polythiophene derivatives

Fig. 5 shows the excitation and emission curves of polymers P3OTIOT and HT P3OTIOT in film states. In the same thickness of films, the excitation curves of all polymers are close to their UV absorption curves^[24], so the film of P3OTIOT and HT P3OTIOT showed π - π^* absorption maxima at about 435 and 452 nm, respectively.

In this paper, two novel constituents of copolythiophene containing branched and straight side chains

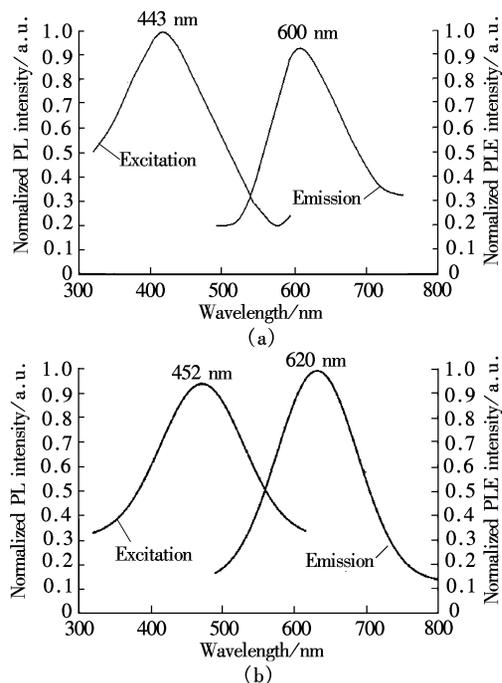


Fig. 5 Normalized excitation and emission curves of P3OTIOT and HT P3OTIOT in spin-coating film states. (a) P3OTIOT; (b) HT P3OTIOT

were synthesized through a FeCl_3 -oxidative and GRIM approach for obtaining the π -conjugated polymers with low band-gap energy, high photoluminescence quantum yield and excellent processability. Compared with the regiorandom copolymer, regioregular HT P3OTIOT depicted structural homogeneity and significantly extended conjugation length. On the basis of these results, the novel conjugated P3OTIOT and HT P3OTIOT might be promising material for applications in polymer light-emitting diodes, and light-emitting electrochemical cells and polymer solar cells, etc.

References

- [1] Sonmez G, Shen C K F, Rubin Y, et al. A red, green, and blue (RGB) polymeric electrochromic device (PECD): the dawning of the PECD era [J]. *Angew Chem Int Ed*, 2004, **43**(12): 1498 - 1502.
- [2] Le Floch F, Ho H A, Harding-Lepage P, et al. Ferrocene-functionalized cationic polythiophene for the label-free electrochemical detection of DNA [J]. *Adv Mater*, 2005, **17**(10): 1251 - 1254.
- [3] Villers D, Jobin D, Soucy C, et al. The influence of the range of electroactivity and capacitance of conducting polymers on the performance of carbon conducting polymer hybrid supercapacitor [J]. *J Electrochem Soc*, 2003, **150**(6): A747 - A752.
- [4] Tuken T, Yazici B, Erbil M. The use of polythiophene for mild steel protection [J]. *Prog Org Coatings*, 2004, **51**(3):

- 205 - 212.
- [5] Ong B S, Wu Y L, Liu P, et al. Structurally ordered polythiophene nanoparticles for high-performance organic thin-film transistors [J]. *Adv Mater*, 2005, **17** (9): 1141 - 1144.
- [6] Ahn S H, Czae M, Kim E R, et al. Synthesis and characterization of soluble polythiophene derivatives containing electron-transporting moiety [J]. *Macromolecules*, 2001, **34**(8): 2522 - 2527.
- [7] Brabec C J. Organic photovoltaics: technology and market [J]. *Solar Energy Materials and Solar Cells*, 2004, **83**(2): 273 - 292.
- [8] Chang J F, Sun B, Breiby D W, et al. Enhanced mobility of poly(3-hexylthiophene) transistors by spin-coating from high-boiling-point solvents [J]. *Chem Mater*, 2004, **16** (23): 4772 - 4776.
- [9] Gadisa A, Svensson M, Andersson M R, et al. Correlation between oxidation potential and open-circuit voltage of composite solar cells based on blends of polythiophenes/fullerene derivative [J]. *Appl Phys Lett*, 2004, **84** (9): 1609 - 1611.
- [10] Ma W L, Yang C Y, Gong X, et al. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology [J]. *Adv Funct Mater*, 2005, **15** (10): 1617 - 1622.
- [11] Li G, Shrotriya V, Yao Y, et al. Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly(3-hexylthiophene) [J]. *J Appl Phys*, 2005, **98** (4): 043704.
- [12] Sanjio S Z, Michael B. Cyclic oligothiophenes: novel organic materials and models for polythiophene. A theoretical study [J]. *J Org Chem*, 2006, **71** (8): 2972 - 2981.
- [13] Cik G, Sersen F L, Bartus L. Anomaly in magnetic properties of poly (3-alkylthiophene)s depending on alkyl chain length [J]. *Synth Met*, 1995, **75** (1): 43 - 48.
- [14] Tamao K, Kodama S, Nakajima I, et al. Nickel-phosphine complex-catalyzed grignard coupling—II: grignard coupling of heterocyclic compounds [J]. *Tetrahedron*, 1982, **38** (22): 3347 - 3354.
- [15] Yoshino K, Nakajima S, Onoda M, et al. Electrical and optical properties of poly(3-alkyl thiophene) [J]. *Synth Met*, 1989, **28** (1): 349 - 357.
- [16] Miroslaw T, Adam P, Malgorzata Z, et al. Effect of molecular weight on spectroscopic and spectroelectrochemical properties of regioregular poly (3-hexylthiophene) [J]. *Macromolecules*, 1998, **31** (15): 5051 - 5058.
- [17] Loewe R S, Ewbank P C, Liu J S, et al. Regioregular, head-to-tail coupled poly(3-alkylthiophene) made easy by the GRIM method: investigation of the reaction and the origin of regioselectivity [J]. *Macromolecules*, 2001, **34** (13): 4324 - 4333.
- [18] Qiao X Y, Wang X H, Mo Z S. The FeCl₃-doped poly (3-alkylthiophenes) in solid state [J]. *Synth Met*, 2001, **122** (2): 449 - 454.
- [19] Fang R C. *Solid state spectroscopy* [M]. Hefei: China University of Science and Technology Press, 2001: 61. (in Chinese)
- [20] Pierrick B, Patrick H. Enhanced infrared properties of regioregular poly (3-alkylthiophenes) [J]. *Macromolecules*, 1997, **30** (9): 2685 - 2692.
- [21] Hao Y Y, Hao H T, Wang H, et al. Preparation and characterization of 2-(8-Hydroxyquinoline)-2 (Phenol) zirconium thin film [J]. *Spectroscopy and Spectral Analysis*, 2004, **24** (12): 1524 - 1527.
- [22] Li J, Zhou H F, Hao Y Y, et al. Spectral analysis and photoluminescence properties of 1,5-naphthalene diamine derivative [J]. *Spectroscopy and Spectral Analysis*, 2006, **26** (2): 235 - 239.
- [23] Chen F, Metha P G, Takiff L, et al. Improved electroluminescence performance of poly(3-alkylthiophenes) having a high head-to-tail (HT) ratio [J]. *J Mater Chem*, 1996, **6** (11): 1763.
- [24] Lu H F, Chan H S O, Ng S C. Synthesis, characterization, and electronic and optical properties of donor-acceptor conjugated polymers based on alternating bis(3-alkylthiophene) and pyridine moieties [J]. *Macromolecules*, 2003, **36** (5): 1543 - 1552.

新型合成金属 3-烷基噻吩共聚物

祁争健 冯卫东 孙岳明 颜大志 肖英勃 何艳芳 虞婧

(东南大学化学化工学院, 南京 210096)

摘要: 用 FeCl₃ 氧化聚合法和 GRIM 置换法合成了无规和规整的 3-辛基噻吩共 3-(2-乙基-1-己基)噻吩共聚物。通过红外、紫外、核磁共振、凝胶色谱和荧光光谱法对其结构和性能进行了分析与表征。结果表明: 头-尾相连的规整 3-辛基噻吩共 3-(2-乙基-1-己基)噻吩共聚物, 带隙能较无规共聚物低, 且 2 种共聚物均表现出能垒低、荧光量子效率高、溶解性好和易于加工处理的特点, 可以是一类应用于发光二极管、电化学电池和太阳能电池等领域具有广泛前景的聚合物。

关键词: 3-烷基噻吩; 共聚物; 合成金属

中图分类号: O658