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The Effects of Different Side Groups on the Properties of Polythiophene

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To investigate the different side groups on the properties of polythiophenes (PTs), three kinds of samples, with alkyl [poly(3-hexylthiophene), P3HT], alkoxy [poly(3-hexyloxythiphene), P3HOT], aryl [poly(3-phenylthiophene), P3PhT], were synthesized with chemically oxidized polymerization in the presence of $FeCl_3$. It was found that the molecular weight (MW) of PTs was influenced by the steric hindrance between side groups. The results of ultraviolet-visible (UV-Vis) and Fourier transform infrared (FT-IR) spectra showed that P3HOT had a longer effective conjugation length than P3HT and P3PhT, due to both the stronger electron-donating property of the alkoxy groups and the coplanar conformation of hexyloxy. Photoluminescence quenching was observed in P3HOT, which was attributed to energy transfer and photochemical reaction. Moreover, the thermal stability of PTs was dependent on the side group, too.

Keywords: conjugated polymer; polythiophenes; P3HT; P3HOT; P3PhT

1 Introduction

Polythiophene (PT) is an important representative class of conjugated polymers that are proclaimed as futuristic new electronic and optical materials (1). PT and its derivatives work very well as solar cell material, electrochromic material, polymer light-emitting diode material etc. (2a–c). It was well known that PTs represented both good solubility and melt processability when the side group (carbon atoms >4) was introduced to a 3-positon thiophene ring. Many workers have reported on the synthesis of thiophene monomers with various side groups. For instance, the desired 3-alkylthiophene could conveniently be prepared by a procedure developed for cross-coupling of Grignard reagents in the presence of nickel (11) catalyzed (3).

3-Alkyoxylthiophene could be prepared by transetherification reaction between 3-methoxythiophene and corresponding primary and secondary alcohols in toluene (4, 5). PTs could be obtained via the electrochemical or chemically oxidized polymerization. The most common route for chemical polymerization was the direct oxidation of 2, 5-position of thiophene ring using $FeCl_3$ as catalysts (1). PTs with alkyl substitution were the most attractive one of their derivatives. The effect of the alkyl length on both molecular chain packing and the value of absorption maximum had been reported (1). Moreover, their optical properties (absorption maximum and visible photoluminescence color) were influenced by regulated by the change of molecular weight (MW) (7).

Although many results had been reported for PTs, the detailed analysis of the effect of different side groups on the properties of PTs had not been summarized. In this paper, poly(3-hexylthiophene) (P3HT) with alkyl, poly(3-hexyloxythiphene) (P3HOT) with alkoxyl and poly(3-phenylthiophene) (P3PhT) with aryl were prepared with chemically oxidized polymerization in the presence of $FeCl_3$. Experimental results of gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectra, ultraviolet-visible (UV-Vis) spectra, photoluminescence (PL) spectra and thermal gravity analysis (TGA) were presented and the effect of a different side group on the properties of PTs were investigated in detail.

2 Experimental

2.1 Preparation of Monomers

3-Bromothiophene was purchased from Zhejiang Shou and Fu Chemical Co. (purity $> 98\%$). 1,3-Bis(diphenylphosphino) propane (DPPP) was purchased from Zhengzhou Ping Yang Chemical Co. (purity $> 98\%$). $Ni(DPPP)Cl_2$ was synthesized by DPPP and $NiCl_2 \cdot 6H_2O$ in the mixture of

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isopropanol and methanol according to the literature (8). All solvents were dried and distilled prior to use. 3-Hexylthiophene monomer was prepared via the Ni(DPPP)Cl_2 catalyzed cross-coupling of 3-bromothiophene and Grignard reagents from 1-bromohexylane, and 3-phenylthiophene from bromobenzene (3). 3-Methoxythiophene was prepared by CuBr-catalyzed methoxylation of 3-bromothiophene (3). 3-Hexyloxythiophene monomer was prepared by transetherification reaction between 3-methoxythiophene and 1-hexanol in toluene in the presence of $NaHSO_4$ (5).

2.2 *Polymerization*

All the polymerizations were performed taking advantage of the direct oxidation of the monomers in chloroform at room temperature. The quantity of catalyst $FeCl_3$ was four times as much as that of the monomers by molar weight (9). The polymers obtained from the precipitation of the reactant in methanol, were washed by Soxhlet extractor with methanol until the solution became colorless, and then dried under vacuum at 40°C to obtain a blue-black powder.

2.3 *Measurements*

MW was evaluated by GPC on an Agilent 1100 column using polystyrene standards as the calibration. The eluent was tetrahydrofuran at a flow rate of 1 ml/min. FT-IR spectra were obtained with a Nicolet 560 Fourier transform infrared spectra, covering the range from 4000 cm^{-1} to 400 cm^{-1}. The samples for measurements were prepared by compression molding with KBr. The thermal stability of samples was investigated with a EXSTAR 6000 TGA in atmosphere at a temperature range from 100°C to 600°C with a scanning rate of 10°C/min. UV-VIS spectra were measured on a UV-1810 PC spectrophotometer with the wavelength from 250 nm to 800 nm at a 1 nm/s scanning rate. PL spectra were obtained on a RF 4500 fluorometer with an excitation wavelength equal to λ_{max}.

3 Results and Discussion

3.1 *Structure and Molecular Weight*

The structures of PTs were characterized by ^{1}H-NMR (400MHz): P3HT ($CDCl_3$, δ_H, ppm): 2.22(t, 2H), 1.31–1.51(m, 8H), 0.9(t, 3H), 6.99(m, 1H). P3HOT ($CDCl_3$, δ_H, ppm): 0.9-2.4(m, 11H), 4.16(m, 2H), 7.1(m, 1H). P3PhT ($CDCl_3$, δ_H, ppm): 6.68(s, 1H), 7.22(s, 2H), 7.34(s, 2H), 7.99(m, 1H). The number average molecular weight (M_n) and the weight average molecular weight (M_w) were shown in Table 1. The MW values of the three PTs, were $M_w = 38{,}196$ and $M_n = 18{,}212$ with a polydispersity index (PDI) 2.10 for P3HT, $M_w = 7.190$ and $M_n = 3{,}164$ with PDI 2.27 for P3HOT, $M_w = 1{,}303$ and $M_n = 580$ with PDI 2.25 for P3PhT, respectively. Though all side groups had six carbons, the MWs were much different and the MW decreased as an order: P3HT > P3HOT > P3PhT.

Table 1. Polymerization Results and MW of PTs

Sample	Yield %[a]	M_n (g/mol)[b]	M_w (g/mol)[b]	PDI[b]	DP[c]
P3HT	60	18,212	38,196	2.10	108.2
P3HOT	30	3,164	7,190	2.27	17.4
P3PhT	68	580	1,303	2.25	3.67

[a] Determined by mass recovered.
[b] Determined by GP.
[c] DP (degree of polymerization) = M_n/mru (mru: mass of repeat unit).

The difference in MW can be explained by steric hindrance obstructing the polymerization. First of all, the phenyl had the largest volume among the three side groups and the coupling reaction between thiophene rings with phenyl was difficult, due to the largest steric hindrance between phenyl and phenyl. Consequently, P3PhT had the lowest MW. And then, the bond angle between side groups and backbone in P3HT (124.4°) was obviously different from that in P3HOT (110.8°). If an oxygen atom rather than an carbon atom was directly attached to the ring, the bond angle between side groups and backbone were changed from 124.4° to 110.8°. While the hexyl was directly attached to the thiophene ring, the bond angle was large and the steric hindrance was small. The introduction of oxygen caused bond angle to become small, which induced a large steric hindrance. So the coupling reaction between thiophene rings with hexyloxy became difficult and MW of P3HOT was lower than that of P3HT. Finally, the order of MW was: P3HT > P3HOT > P3PhT.

3.2 *Infrared Spectra*

The FT-IR spectra of three kinds of PTs were shown in Figure 1. The spectra of PTs reflected their structures

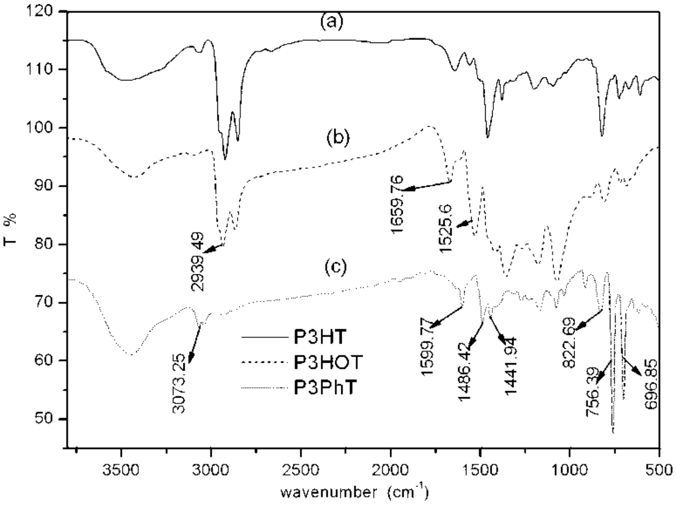

Fig. 1. The FT-IR of (a) P3HT, (b) P3HOT and (c) P3PhT.

clearly. Three PTs showed the similar characteristic IR absorption for the same thiophene ring. The C_β-H stretching in thiophene ring at ca. 3100 cm^{-1}, the C-H out-of-plane bending vibration of thiophene ring at ca. 820 cm^{-1}, and the thiophene ring-stretching vibration at ca. 1513 cm^{-1}, was observed. It was found that the C_β-H band of P3HOT was weaker than that of P3HT, which indicated that some β-defects exist in the polymer. The defects were attributed to the strong electron-donating nature of the alkoxy pendant making the β-position more reactive in 3-alkoxythiophene than in 3-alkylthiophene (12).

As shown in Figure 1(c), P3PhT gave an obvious absorption at 3073 cm^{-1} for the stretching of the C_β-H in benzene. The bands at 1599, 1486, 1441 cm^{-1} were attributed to the stretching vibration of the phenyl ring. Two strong bands at 756 and 696 cm^{-1} were assigned to the monosubstituted benzene ring of the P3PhT (10). In the case of P3HT shown in Figure 1(a) and P3HOT shown in Figure 1(b), great intensity of the bands at 2940 cm^{-1} was observed for C-H stretching vibration of the aliphatic side chain. The bands at ca. 1450 cm^{-1} were ascribable to the bending vibration of -CH_2- in alkyl or alkoxyl. The C-O-C stretching vibration of P3HOT appeared at ca. 1171 and 1066 cm^{-1}.

Furthermore, another great difference in three PTs was the intensity of bands at ca. 1500 and 1650 cm^{-1}. Early work demonstrated that the intensities of bands at ca. 1500 and 1650 cm^{-1} were sensitive to the conjugation length (6). We could infer that the effective conjugation length decrease as order: P3HOT > P3HT > P3PhT, for order of the intensity at ca. 1650 and 1530 cm^{-1} is: P3HOT > P3HT > P3PhT as shown in Figure 1. The effective conjugation length was one of most important factors affecting the optical properties of PTs. The results quite agreed with those of UV-Vis described as follow.

3.3 UV-Vis Absorption and PL Spectra

The UV-Vis and photoluminescence (PL) spectra of PTs were shown in Figure 2. As shown in Figure 2 (A), the maximum absorption (λ_{max}) of P3HT, P3HOT and P3PhT appeared at 436 nm, 472 nm and 418 nm, respectively. At the same time, there was a hump near 300 nm for the π-π^* transition of thiophene unit. Comparison of the spectra, a marked difference in the three kinds of PTs with the various side chains was found. The results of UV-Vis and PL spectra were summarized in Table 2. P3HOT had the largest both λ_{max} and absorption coefficient ($a_m = 2.67 \times 10^4\ L \cdot g^{-1} \cdot cm^{-1}$).

λ_{max} of PTs was attributed to the π-π^* interband transition of unsaturated bond, which was sensitive to effective conjugation length. In our case, all side groups were the electron donor, which was helpful to increase the effective conjugation length. But the order for the electron-donating ability was: hexyloxy > hexyl > phenyl. Therefore, the effective conjugation length of conjugative main chains was: P3HOT > P3HT > P3PhT. The results obtained by FT-IR spectroscopy were further supported by UV-VIS spectroscopy. On the other hand, “zipper effect” in P3HOT which is a side-by-side overlap of the neighboring methylene segments, also influenced the value of λ_{max} (11). The effect would increase the coplanarity of the polymer backbone, which results in longer effective conjugation length. Hence, P3HOT had the

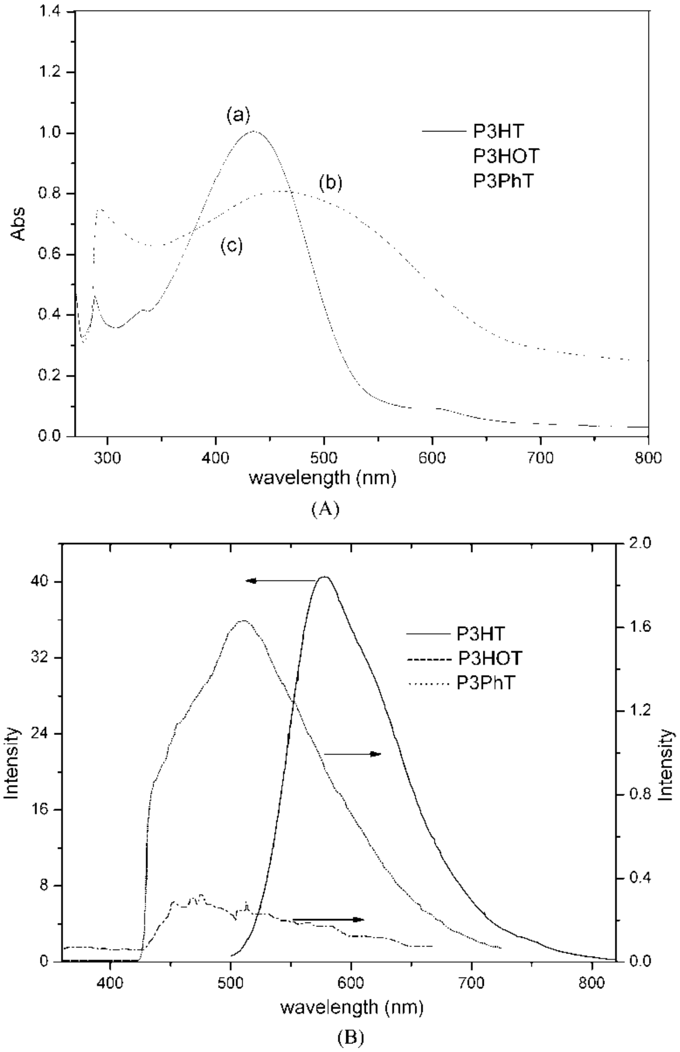

Fig. 2. The UV-VIS absorption (A) and PL spectra (B) of PTs in THT.

Table 2. Optical properties of PTs

Sample	λ_{max}(abs)/ nm[a]	E_g^{op}/eV[b]	a_m/ $L \cdot g^{-1} \cdot cm^{-1}$[c]	λ_{max}(PL)/ nm[d]
P3HT	436	1.90	5.56×10^3	578
P3HOT	472	1.76	2.67×10^4	451,471,510
P3PhT	418	2.27	3.67×10^3	542

[a] c(P3HT) =0.18 g/l, c(P3HOT) = 0.03 g/l, c(P3PhT) = 0.15 g/l.
[b] E_g^{op}= 1240/λ (λ_{max}: absorption maximum).
[c] a_m(absorption coefficient) = A/(c × b) (A: absorbance; c: concentration of solution in mass, b: cell length).
[d] c(P3HT) =0.168 g/l, c(P3HOT) = 0.11 g/l, c(P3PhT) = 0.0334 g/l.

largest both λ_{max} and a_m. Thus, the absorption maximum reflected the ability of electron-donating of the side group and the effective conjugation length of thiophene ring backbone. However, the λ_{max} of PTs was also influenced by the length of side group (6).

In order to study the optical properties of these polymers, the PL measurements of dilute polymer solutions were performed as shown in Figure 2 (B). The emitting peaks of P3HT, P3HOT and P3PhT, appeared at 578 nm, 510/471/451 nm and 542 nm, respectively. First of all, it was apparent from the figure that there was photoluminescence quenching in P3HOT. The photoluminescence quenching may be due to energy transfer by Forster mechanism (the overlap of the polymer photoluminescence with the absorption could end the energy transfer with nonradiative decay) and photobleaching reaction. The photobleaching reaction via a photochemical 1,4-Diels–Alder addition of photosensitized singlet oxygen with thienyl units had accrued in the progress, which induced the formation of products (sulfine or diketone) and a diminished state of conjugation (11). Comparison of P3HT and P3PhT, the strong emitting of P3HT was observed. The different intensity was dependent on the electron-donating ability of side group described above. Therefore, the order of light-emitting ability was: P3HT > P3PhT > P3HOT.

3.4 *Thermal Gravity Analysis*

In order to investigate the thermal stability of PTs, thermal gravity experiments were performed in air. As shown in Figure 3, the onset decomposition temperatures of 3% weight loss were 285.5°C for P3HT, 213.3°C for P3HOT, 304.9°C for P3PhT, while the their ending decomposition temperatures were 550°C, >600°C, 580°C, respectively. It was obvious that the thermal stability of PTs was related to a great extent to the side group. All PTs exhibited two major distinct weight-loss steps. The first step corresponded to the loss of the side chain, and the second step was mainly ascribable to decomposition of thiophene backbone.

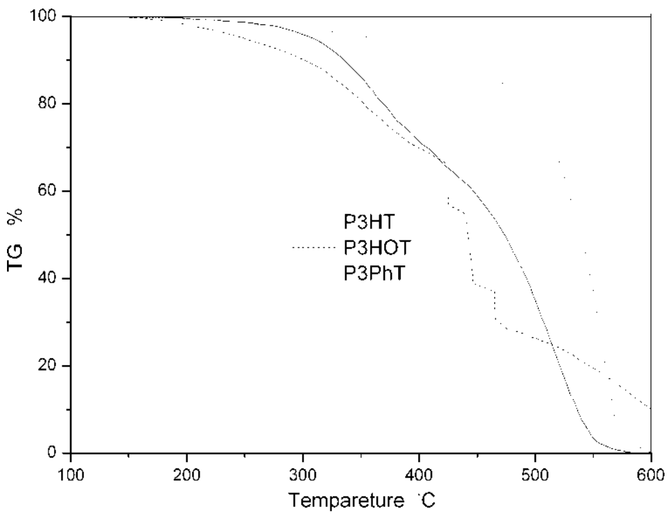

Fig. 3. The thermal gravity analysis of PTs under atmosphere at a heating rate of 20°C/min.

In general, the thermal stability of P3HOT with hexyloxy was weaker than that of P3HT with hexyl; P3PhT was the most stable among three samples. Foremost, the onset temperature of P3HOT was lower than that of P3HT, due to the existence of β-defects in the polymer for the presence of hexyloxy pendant groups. The defects made the system more reactive and easily oxidized (11). The ending temperature of P3HOT was higher than that of P3HT, which was attributed to the occurrence of cross-linking in polymer (11). P3PhT contained a heat-resistant benzene ring, which was more thermal resistant than flexible alkyl or alkoxy. The onset temperature and ending decomposition temperatures were found to decrease with the rigidity of side group. Therefore, the order of thermal stability was as followed: P3PhT > P3HT > P3HOT.

4 Conclusions

Three PTs with different kinds of side groups (P3HT with alkyl, P3HOT with alkoxyl, and P3PhT with aryl) were prepared by chemically oxidized polymerization. MW proved to be related to the steric hindrance between side groups. P3HT had the highest MW for the smallest steric hindrance between hexyl and thiophene backbone. FT-IR spectra showed that the effective conjugation length decreased as order: P3HOT > P3HT > P3PhT. P3HOT had a longer effective conjugation length than P3HT and P3PhT, due to both the stronger electron-donating property of the alkoxy groups and the coplanar conformation of hexyloxy. Photoluminescence quenching was observed while side group was hexyloxy, which was attributed to energy transfer and photochemical reaction. The thermal stability of P3HOT was weaker than that of P3HT, since β-defects in the polymer made the system more reactive and easily oxidized. P3PhT, which contained a heat-resistant benzene ring, was most thermal resistant among three PTs.

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6 References

1. McCullough, R.D. (1998) *Adv. Mater.*, **10**, 93.
2. (a) Huynh, W.U., Dittmer, J.J. and Alivisatos, A.P. (2002) *Science*, **295**, 2425; (b) Perepichka, I.F., Perepichka, D.F., Meng, H. and

Wudl, F. (2005) *Adv. Mater.*, **12**, 2281; (c) Heuer, H.W., Wehrmann, R. and Kirchmeyer, S. (2002) *Adv. Funct. Mater.*, **12**, 89.

3. Pham, C.V., Mark, H.B. and Zimmer, H. (1986) *Synth. Commun.*, **16**, 689.
4. Keegstra, M.A., Peters, T.H.A. and Brandsma, L. (1990) *Synth. Commun.*, **20**, 213.
5. Langeveld-Voss, B.M.W., Jassen, R.A.J., Christiaans, M.P.T., Meskers, S.C.J., Dekkers, H.P.J.M. and Meijer, E.W. (1996) *J. Am. Chem. Soc.*, **118**, 4908.
6. Qiao, X., Wang, X. and Mo, Z. (2001) *Synth. Met.*, **118**, 89.
7. Zhang, Z. and Fujiki, M. (2001) *Poly. J.*, **33**, 597.
8. Hecke, G.R.V. and Horrocks, W.D. (1966) *Inorg. Chem.*, **5**, 9168.
9. Qiao, X., Wang, X. and Mo, Z. (2001) *Synth. Met.*, **122**, 449.
10. Kuila, B.K. and Nandi, A.K. (2004) *Macromolecules*, **37**, 8577.
11. Hu, X. and Xu, L. (2000) *Polymer*, **41**, 9147.
12. Andersson, M.R., Selse, D. and Berggren, M. (1994) *Macromolecules*, **27**, 6503.