Synthesis and Characterization of Copolythiophene

Jie He, Zhongji Su, Binyu Yu, Li Xiang, Bin Yan, Yinghan Wang

State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, People's Republic of China

ABSTRACT: Copolythiophenes (Co-PTs), poly(3-hexyl-thiophene-*co*-3-thiophene carboxylic acid) (P3HT-TCa), poly(3-hexyloxylthiophene-*co*-3-thiophene carboxylic acid) (P3HOT-TCa), and poly(3-phenylthiophene-*co*-3-thiophene carboxylic acid) (P3PhT-TCa), were synthesized by chemical oxidized polymerization to investigate the effect of copolymerization on the properties of polythiophenes (PTs). Gel permeation chromatography showed that the molecular weight (MW) of Co-PT was lower than that of homopolythiophene. Fourier transform infrared (FTIR) spectra indicated that the copolymerization was successful between the monomers. The λ_{max} of Co-PTs gave a ''blue shift'' in ultraviolet-visible (UV-VIS) spectra. Photolumi-nescence (PL) spectra showed that the PL intensity of Co-PT became weaker than that of homopolythiophene and the disappearance of PL had been observed in P3HOT-TCa. The thermal stability of Co-PT was influenced by the carboxyl for its low decomposition temperature. Furthermore, the copolymerization between multi-wall carbon nanotube containing thiophene ring (MWNT-Th) and 3-hexyloxylthiphene could also take place successfully. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3543–3550, 2007

Key words: polythiophene; copolythiophene; MWNT; chemical oxidized polymerization

INTRODUCTION

Poly(3-alkylthiophene) (P3AT) become a soluble and processible conjugated conducting polymer,[1–3] because of the introduction of the alkyl group (≥4) at the 3-position of thiophene ring. P3AT-based devices, such as light emitting diode (LED), solar cell (SC), have been developed for application widely.[4–6] Polythiophenes (PTs) could be prepared by the 2,5-dihalothiophene in the presence of Grignard reagents and nickel(II)/zinc.[7] However, their derivatives containing carboxyl could not be obtained by those reagents for the reactivity of carboxyl. PTs containing carboxyl can always be obtained by polymerization of the derivatives of monomers (usually, methylate of monomers) with nickel(II),[8] or the monomer itself in the presence of FeCl₃.[9–10]

PTs bearing carboxylic groups were self-assembled through self-molecular recognition by forming carboxylic acid dimer pairs between chains.[11] PTs containing carboxylic groups could link to the other particle surface conveniently. Jiu et al. developed a new class of hybrid inorganic/organic materials containing ZnO and different thiophene acid. Different shapes of ZnO particles were controlled by organic thiophene acids containing different number of thiophene units. Furthermore, PTs with carboxyl as side groups usually were water-soluble, which can be used in the water system. They could be used as labels in homogeneous competitive immunoassays for antigens and haptens.[9] The copolythiophenes (Co-PTs) containing carboxyl usually had amphiphilic properties.[12] Narizzano et al. have reported the Co-PT was prepared with 3-hexylthiophene and 3-thiopheneacetic acid. The film of copolymer can be used as polymer matrix for semiconductor CuS nanoparticles.[10]

The special water-solubility and amphiphilic property were the peculiar for those Co-PTs contained carboxyl. However, those kinds of Co-PTs always obtained only by electrochemical methods[13–15] and few researches have been done with chemical oxidized methods. In this article, we reported Co-PTs prepared by chemical oxidized methods. We used chemical copolymerization with FeCl₃ as catalyst and three kinds of Co-PTs with different types of side groups were prepared. The properties of copolymer were investigated particularly. Furthermore, a copolymer containing multi-walled carbon nanotube (MWNT) was prepared successfully, which could be used in photovoltaic device widely.
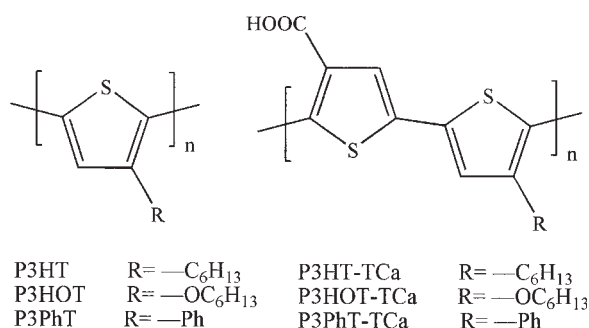
EXPERIMENTAL

Materials

3-Bromothiophene (purity >98%) was purchased from Zhejiang Shou and Fu Chemical. 1,3-Bis(diphenyl-

Scheme 1

P3HT   R= —C₆H₁₃   P3HT-TCa   R= —C₆H₁₃
P3HOT   R= —OC₆H₁₃   P3HOT-TCa   R= —OC₆H₁₃
P3PhT   R= —Ph   P3PhT-TCa   R= —Ph

phosphino) propane (DPPP) (purity >98%) was purchased from Zhengzhou Ping Yang Chemical. 3-Thiophene carboxylic acid (purity >99%) was purchased from Anhui Hua Fu Chemical. MWNT (purity >95%, —OH content: 0.71% wt) was purchased from Chengdu Organic Chemistry, and the MWNT was used without treatment.

3-Hexylthiophene was prepared by cross-coupling of 3-bromothiophene and Grignard reagents from 1-bromoalkanethe in the presence of Ni(DPPP)Cl₂ as catalyst, 3-phenylthiophene from bromobenzene.[16] 3-Methoxythiophene was prepared by CuBr-catalyzed methoxylation of 3-bromothiophene.[17] 3-Hexyloxythiophene monomers were prepared by transetherification reaction between 3-methoxythiophene and 1-hexanol in toluene in the presence of NaHSO₄.[18]

The molecular structures of homopolythiophenes and Co-PTs were shown in Scheme 1. The polymerization was performed taking advantage of the direct

oxidation of 3-thiophene carboxylic acid and other thiophene monomers in equal molar ratio in chloroform at room temperature in the presence of catalyst FeCl₃. The quantity of FeCl₃ was four times as much as that of the total monomers by molar weight.[19] 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 in vacuum at 40°C to obtain a blue–black powder.

3-Thiophene carbonyl chloride was prepared by 3-thiophene carboxylic acid with SOCl₂ at 60°C for 2 h.[20] A dark red liquid was obtained after the solvent was removed by evaporation. Then, 3-thiophene carbonyl chloride with MWNT-OH (MWNT containing —OH) in pyridine was stirred for 10 h at room temperature. The reaction mixture was filtered and the powders which connected with thiophene ring (MWNT-Th) on the surfaces were obtained. MWNT-Th was copolymerized with 3-hexyloxyl thiophene in CHCl₃ in the presence of FeCl₃ for 20 h. Then, the black powder (MWNT-PTh) was obtained after the reaction mixture was poured into methanol. The MWNT-PTh powder was washed by tetrahydrofuran (THF) until the solution became colorless, and then dried in vacuum at 40°C. The detailed route to synthesize the MWNT-PTh was shown in Scheme 2.

Characterization

Molecular weight (MW) was measured by gel permeation chromatography (GPC) on an Agilent1100
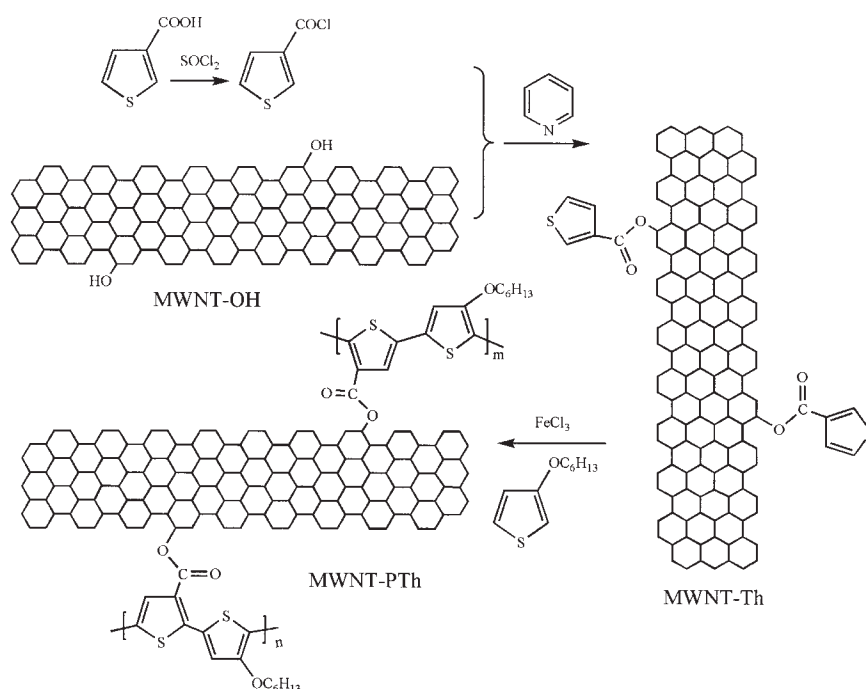
Scheme 2

column using polystyrene standards as the calibration. The eluent was THF at a flow rate of 1 mL/min. Infrared spectra were investigated with Nicolet 560 fourier transform infrared (FTIR) spectrometer from 4000 to 400 cm^{-1}. The samples for measurements were prepared by compression molding with KBr. The thermal stability of samples was obtained in an EXSTAR 6000 thermal gravity analysis (TGA) in atmosphere from 100 to 600°C at a scanning rate of 10°C/min. Ultraviolet-visible (UV-VIS) spectra were evaluated on a UV-1810 PC spectrophotometer with the wavelength from 250 to 800 nm at a 1 nm/s scanning rate. Photoluminescence (PL) spectra were tested on a RF 4500 fluorometer with λ_{max}. as an excitation wavelength. The ^{1}H-NMR was characterized at 400 MHz using a Brucker-400 MHz NMR spectrometer.

RESULTS AND DISCUSSION

Molecular weight and structure

The number average molecular weight ($\overline{M}_n$) and the weight average molecular weight ($\overline{M}_w$) had been measured by GPC. As shown in Table I, The MW values of the PTs, were $\overline{M}_w$ = 38,196 and $\overline{M}_n$ = 18,212 with a polydispersity index (PDI) 2.10 for P3HT, $\overline{M}_w$ = 10,435 and $\overline{M}_n$ = 1752 with PDI 5.96 for P3HT-TCa, $\overline{M}_w$ = 7190 and $\overline{M}_n$ = 3164 with PDI 2.27 for P3HOT, $\overline{M}_w$ = 4848 and $\overline{M}_n$ = 2449 with PDI 1.97 for P3HOT-TCa, $\overline{M}_w$ = 1303 and $\overline{M}_n$ = 580 with PDI 2.25 for P3PhT, $\overline{M}_w$ = 692 and $\overline{M}_n$ = 402 with PDI 1.72 for P3PhT-TCa, respectively.

Above all, MW was influenced by the side groups. The effect of side groups on MW was described elsewhere. Then, it was obvious that the MW decreased after copolymerization. We hypothesize that the results were related to the reactivity of 3-thiophene carboxylic acid. Masuda had reported that poly(3-thiophene carboxylic acid) was prepared by methyl 3-thiophene carboxylate in the presence of nickel(II) bromide, zinc, and triphenylphosphine in

DMF. $\overline{M}_n$ of the poly(3-thiophene carboxylic acid) was below 2000.[8] Therefore, it was inferred that the thiophene monomers with carboxyl in 3-position possess worse reactivity than the other thiophene derivates and was hardly oxidized. In addition, P3HT-TCa had a broader PDI than other copolymers. The probable reason was the great difference of reactivity between two monomers.

The Co-PT not the homopolythiophene was obtained, which can also be proved in the GPC for no signal of two types of homopolythiophene and in UV-Vis spectrum for no signal at $\sim$ 380 nm (the absorption peak for poly(3-thiophene carboxylic acid)). Another important phenomenon was that the Co-PTs could not solve in basic water which indicated that the homopolythiophene of poly(3-thiophene carboxylic acid) did not exist in the Co-PT. The structure of PTs was characterized by ^{1}H-NMR: P3HT-TCa (CDCl$_3$, δ_H, ppm): 2.24(t, 2H), 1.315–1.512(m, 8H), 0.897(t, 3H), 6.98(m, 1H). P3HOT-TCa (CDCl$_3$, δ_H, ppm): 0.901–2.402(m, 11H), 4.159(m, 2H), 7.06(m, 1H). P3PhT-TCa (CDCl$_3$, δ_H, ppm): 6.669(s, 1H), 7.211(s, 2H), 7.31(s, 2H), 7.99(m, 1H). In fact, Co-PTs contained only a small amount of 3-thiophene carboxylic acid. The broad peaking of the proton in carboxyl was covered up as the intensity of proton was so weak.

FTIR spectroscopy

The FTIR spectra of PTs were shown in Figure 1. IR spectrum was a useful method to characterize the structure of polymers. All of PTs showed the similar characteristic IR absorption for thiophene ring. The C—H out-of-plane bending vibration of thiophene ring appeared at ca. 820 cm^{-1}. The absorption bands at $\sim$ 1520 and 1640 cm^{-1} were corresponded to the thiophene ring-stretching vibration. The C$_\beta$-H stretching vibration in thiophene ring was located at ca. 3100 cm^{-1}. The intensity of C$_\beta$-H band of P3HOT and P3HOT-TCa as shown in Figure 1(B) was weak in comparison with that of P3HT and P3HT-TCa as shown in Figure 1(A), which indicated that some β-defects exist in the polymer. The β-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.[21] On the other hand, P3PhT and P3PhT-TCa as shown in Figure 1(C), gave a great absorption at 3025 cm^{-1} for the stretching of the C$_\beta$-H in benzene.

P3HT, P3HT-TCa, P3HOT, and P3HOT-TCa contained long alkyl as side groups. As shown in Figure 1 (A,B), the absorption band at $\sim$ 2923 cm^{-1} was ascribable to —CH$_2$— asymmetry stretching vibration, and the shoulder at $\sim$ 2850 cm^{-1} corresponded with —CH$_2$— symmetry stretching vibration. The bands at $\sim$ 1450, 1420, and 1340 cm^{-1} were

TABLE I
Polymerization Results and Molecular Weight of PTs

Sample	Yield (%)[a]	$\overline{M}_n$ (g/mol)[b]	$\overline{M}_w$ (g/mol)[b]	PDI[b]	DP[c]
P3HT	60	18,212	38,196	2.10	128.9
P3HT-TCa	56.3	1,752	10,435	5.96	–
P3HOT	30	3,164	7,190	2.27	17.4
P3HOT-TCa	20	2,449	4,848	1.97	–
P3PhT	68	580	1,303	2.25	3.67
P3PhT-TCa	82	402	692	1.72	–

[a] Determined by mass recovered.
[b] Determined by GPC.
[c] DP (degree of polymerization) = $\overline{M}_n$/mru (mass of repeat unit).
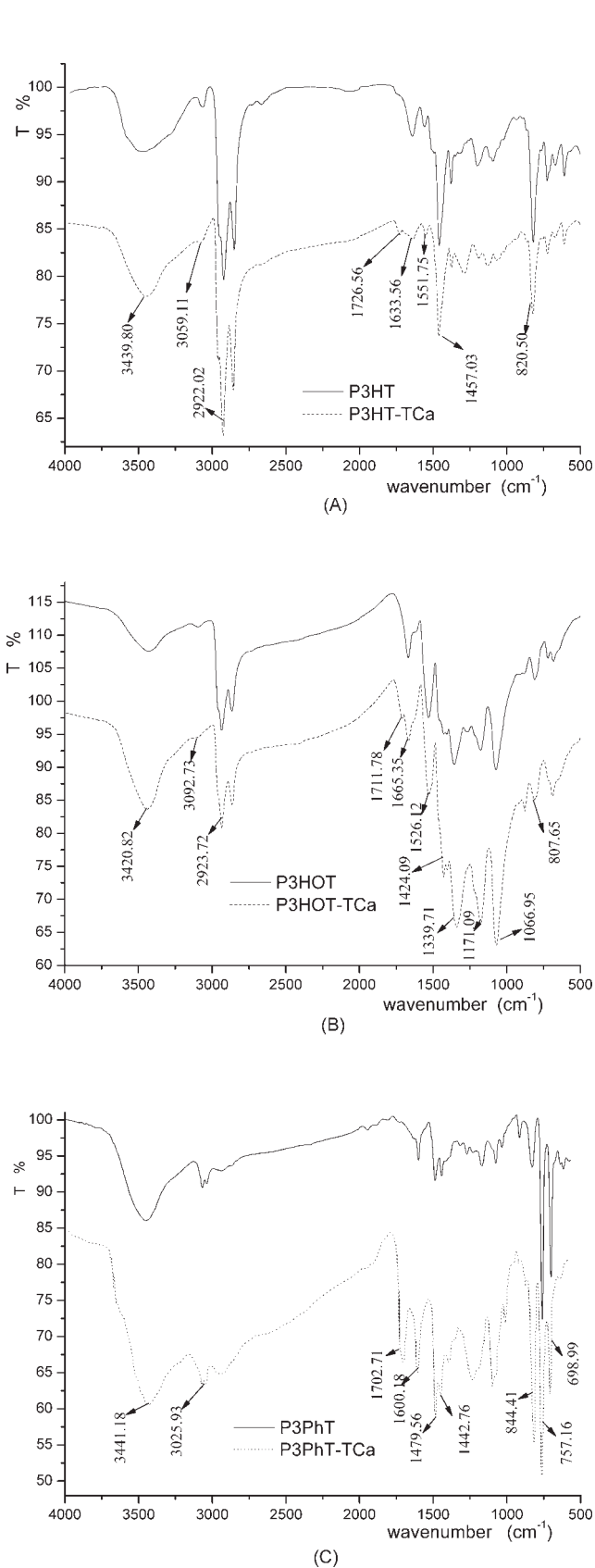
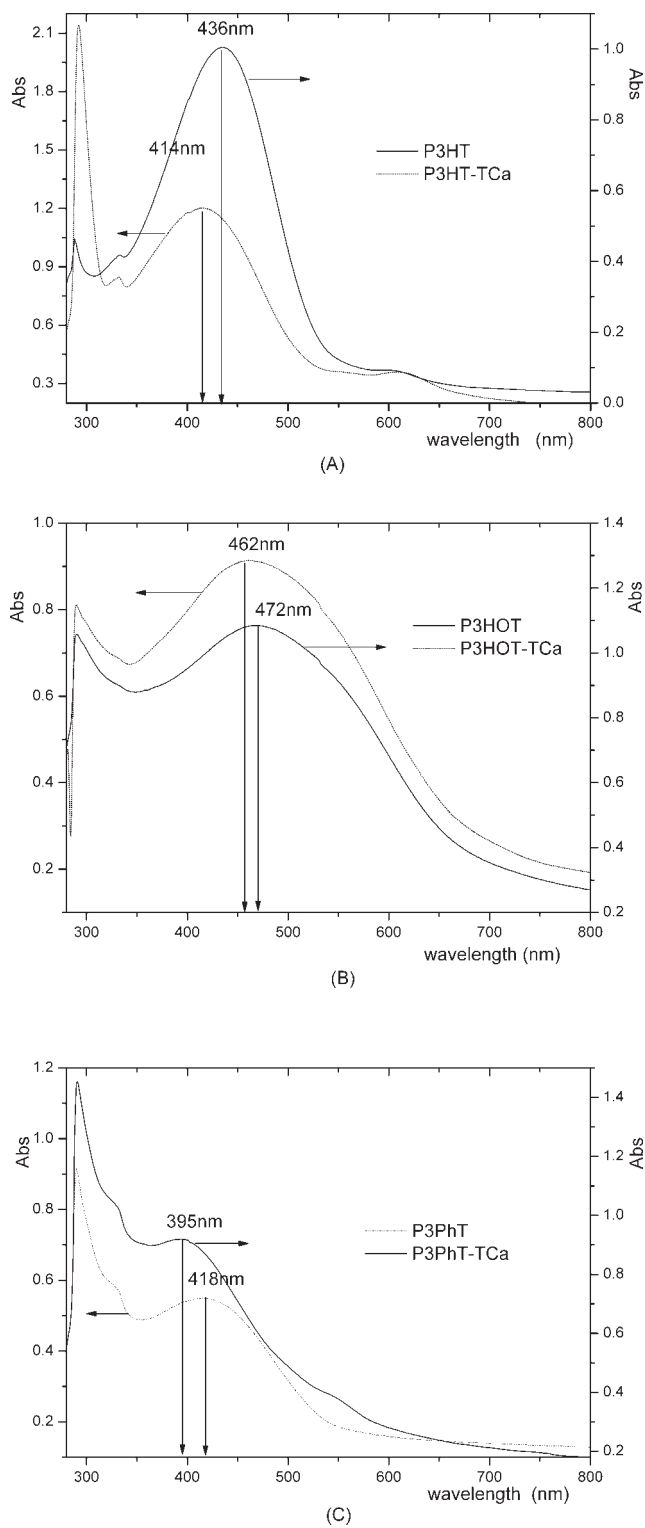**Figure 1** The FTIR spectra of P3HT and P3HT-TCa (A), P3HOT and P3HOT-TCa (B), P3PhT and P3PhT-TCa (C).

Figure 2 The UV-VIS spectra of P3HT and P3HT-TCa (A), P3HOT and P3HOT-TCa (B), P3PhT and P3PhT-TCa (C).

attributed to —CH$_2$— bending vibration. P3HOT and P3HOT-TCa with alkoxyl as side groups showed the catechistic peaks compared with P3HT and P3HT-TCa. The C—O—C stretching vibration ap-

TABLE II
Optical Properties of PTs

Sample	λ_{max} (abs)/nm[a]	E_g^{op}/eV[b]	a_m /L g^{-1}cm^{-1} [c]	λ_{max} (PL)/nm[d]	K/L g^{-1} [e]
P3HT	436	1.90	5.79×10^3	578	244
P3HT-TCa	414	1.77	5.46×10^3	652/572	50
P3HOT	472	1.76	2.67×10^4	510/471/451	3
P3HOT-TCa	462	1.75	1.31×10^4	–	–
P3PhT	418	2.27	3.67×10^3	542	49.4
P3PhT-TCa	395	2.14	3.11×10^3	563	43.34

[a] c(P3HT) = 0.35 g/l, c(P3HT-TCa) = 0.22 g/l, c(P3HOT) = 0.03 g/l, c(P3HOT-TCa) = 0.07 g/l, c(P3PhT) = 0.15 g/l, c(P3PhT-TCa) = 0.23 g/l.
[b] E_g^{op} = 1240/λ (absorption maximum).
[c] a_m(absorption coefficient) = A/(c $\times$ b) (A, absorbance; c, concentration of solution in mass; b, cell length).
[d] c(P3HT) = 0.168 g/l, c(P3HT-TCa) = 0.34 g/l, c(P3HOT) = 0.11 g/l, c(P3HOT-TCa) = 0.09 g/l, c(P3PhT) = 0.0334 g/l, c(P3PhT-TCa) = 0.0923 g/l.
[e] K = F/c, (K, PL coefficient; F, the intensity of PL; c, the concentration of solution in mass).

peared at 1171 and 1066 cm^{-1}.[21] In the case of P3PhT as shown in Figure 1(C), the bands at $\sim$ 1600, 1479, and 1442 cm^{-1} were attributed to the stretching vibration of the phenyl ring. Two strong bands at $\sim$ 757 and 699 cm^{-1} were assigned to the monosubstituted benzene ring of the P3PhT or P3PhT-TCa.

The copolymer containing carboxylic group can be identified by the —OH stretching vibration at ca. 3400 cm^{-1} or C=O stretching vibration at $\sim$ 1700 cm^{-1}. While the samples for IR were prepared by compression molding with KBr crystal, the intensities and values of bands at 3400 cm^{-1} were probably influenced by H$_2$O from KBr crystal. Therefore, we can distinguish the copolymer with homopolymer by the C=O stretching vibration at $\sim$ 1700 cm^{-1}. The C=O bands of P3HT-TCa, P3HOT-TCa, and P3PhT-TCa were 1726, 1711, and 1702 cm^{-1}, respectively. Therefore, it can be inferred that the 3-thiophene carboxylic acid had been introduced to the copolymer successfully.

Furthermore, another great difference between homopolythiophene and Co-PTs was the intensity of bands at $\sim$ 1500 and 1600 cm^{-1}. Early work demonstrated that the intensities of bands at $\sim$ 1500 and 1600 cm^{-1} were sensitive to the conjugation length, which was depended on MW of polymer.[19] Therefore, the intensities of bands at $\sim$ 1500 and 1600 cm^{-1} were weaker in Co-PT than that in homopolythiophene, which indicated the shorter conjugation length in Co-PTs. Because of the difference in conjugation length, the optical properties of homopolythiophene and Co-PT were distinctly different as described later.

UV-VIS spectroscopy

The UV-VIS absorption spectra of PTs were shown in Figure 2. As shown in Figure 2, the absorption peaks of P3HT, P3HT-TCa, P3HOT, P3HOT-TCa, P3PhT, and P3PhT-TCa appeared at 436, 414, 472, 462, 418, and 395 nm, respectively, because of the π-π* interband transition. 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 obvious and a slight variation between homopolythiophene and Co-PTs was observed. As shown in Table II, P3HOT had the largest absorption maximum (λ_{max} = 472 nm) and absorption coefficient (a_m = 2.67 $\times$ 10^4 L g^{-1} cm^{-1}) among the homopolythiophenes, while P3HOT-TCa had the largest absorption maximum (λ_{max} = 462 nm) and absorption coefficient (a_m = 1.31 $\times$ 10^4 L g^{-1} cm^{-1}) among the Co-PTs.

The λ_{max} of PTs was affected by the kinds of sides group, which was discussed in detail elsewhere. UV-VIS absorption spectrum was sensitive to the electronic conjugation length. As aforementioned, the conjugation length of homopolythiophenes was longer than that of Co-PTs, which was observed clearly in FTIR. The copolymerization with 3-thiophene carboxylic acid gave the λ_{max} of PTs a "blue shift" which is a symbol of decrease of conjugation length. The results obtained by IR spectroscopy were further supported by UV-VIS spectroscopy. The main reason may be the decrease of MW. As aforementioned, the MW of copolymer was lower than that of the homopolymer. Another probable reason was the introduction of carboxylic group. The λ_{max} was also influenced by the electron number of conjugation. As the carboxylic group is an electron-drawing group, the electron number of conjugation decreased after the carboxylic group was introduced. Especially, the λ_{max} of poly(3-thiophene carboxylic acid) shifted to 380 nm around.[9] Therefore, the λ_{max} had a "blue shift" after copolymerization.

PL spectroscopy

The PL experiments were performed in THF to investigate the light-emitting properties of PTs. The PL spectra of P3HT, P3HT-TCa, P3HOT, P3PhT, and P3PhT-TCa were exhibited in Figure 3. The emitting peaks of P3HT, P3HT-TCa, P3HOT, P3PhT, and
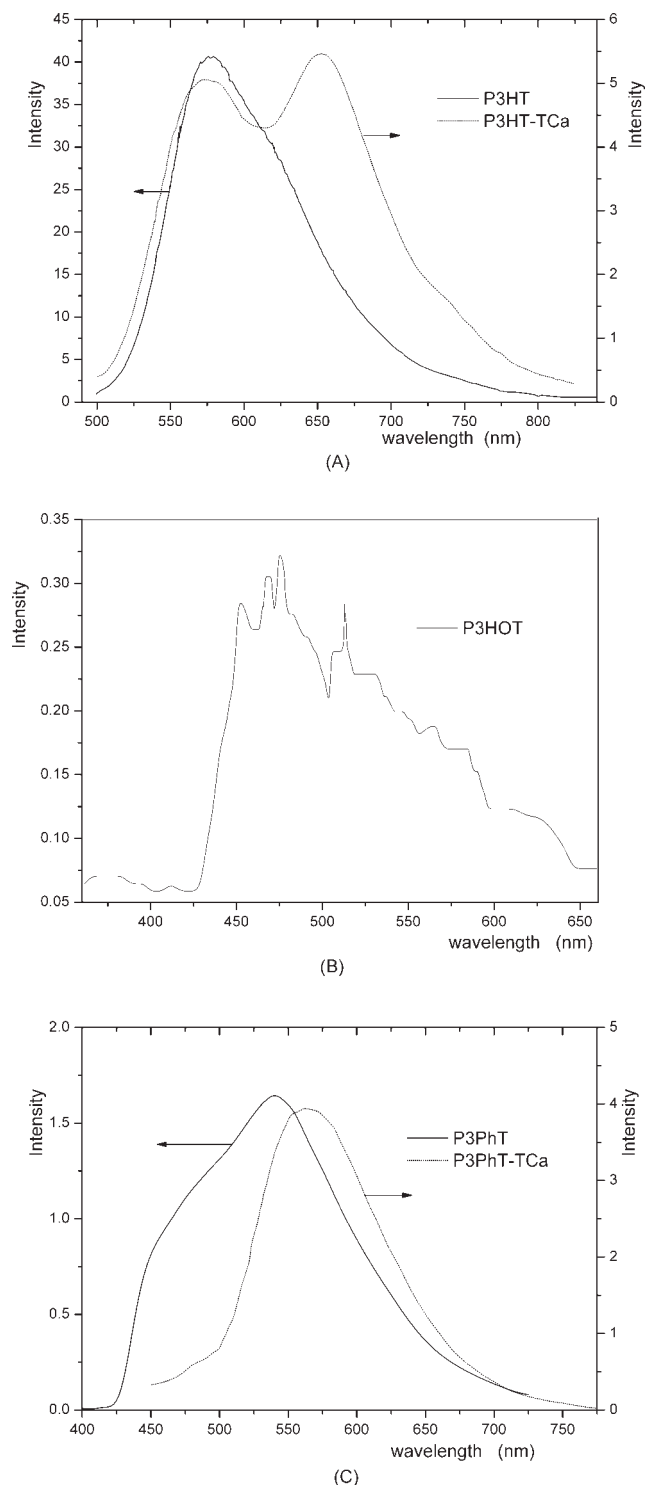

Figure 3 The PL spectra of P3HT and P3HT-TCa (A), P3HOT (B), P3PhT and P3PhT-TCa (C).

P3PhT-TCa were 578, 652/572, 510/471/451, 542, and 563nm, respectively. Particularly, the PL intensity of P3HOT was rather weak, and the PL intensity of P3HOT-TCa could hardly be tested. The possible reason was that the "photo bleaching," via a photochemical 1,4-Diels–Alder addition of photosensitized singlet oxygen with thienyl units, occurred during experiments.[21] The double peak was observed in the PL spectrum of P3HT-TCa. The origin of this phenomenon is unclear and a more systematic investigation is under way.

The intensity of PL decreased after copolymerization. To characterize the light-emitting ability of PTs, the PL coefficient K was defined ($K = F/c$, F defined as the intensity of PL, c defined as the concentration of solution). The significance of K was the intensity of PL of per unit mass concentration. As shown in Table II, the values of K for P3HT, P3HT-TCa, P3HOT, P3PhT, and P3PhT-TCa were 244, 50, 3, 49.4, and 43.34, respectively. The values of K decreased after copolymerization, that is, the ability of light-emitting of PTs decreased after copolymerization, which was attributed to the introduction of carboxylic group. The carboxylic group was electron-drawing, so the intensity of PL decreased after copolymerization.

TGA

To investigate the thermal stability of PTs, thermal gravity experiments were performed in air. As shown in Figure 4, the onset decomposition temperatures of 3% weight loss were 285.5, 283.7, 213.3, 210.9 304.9, and 270.15°C, for P3HT, P3HT-TCa, P3HOT, P3HOT-TCa, P3PhT, and P3PhT-TCa, while the their ending decomposition temperatures were 550, 475.4, >600, 584.0, 580, and 569.1°C, respectively. All PTs showed two weight-loss steps including decomposition of the side chain and thiophene backbone.

P3PhT was the most stable among three samples. P3HOT had a lower onset decomposition temperature but a higher ending decomposition temperature than P3HT. The reason was discussed in detail elsewhere. It was clear that the thermal stability of PTs became weaker after copolymerization. The carboxyl, whose decomposition temperature was at ~ 400°C, was badly heat-resistant. On the other hand, the MW of Co-PT had decreased and the regular arrangement of main chain had been destroyed.

Copolymerization with MWNT

3-Hexyloxythiophene was used to copolymerize with MWNT containing thiophene to disperse MWNT in conductive polymer matrix as shown in Scheme 2. Although lots of studies have focused on dispersion
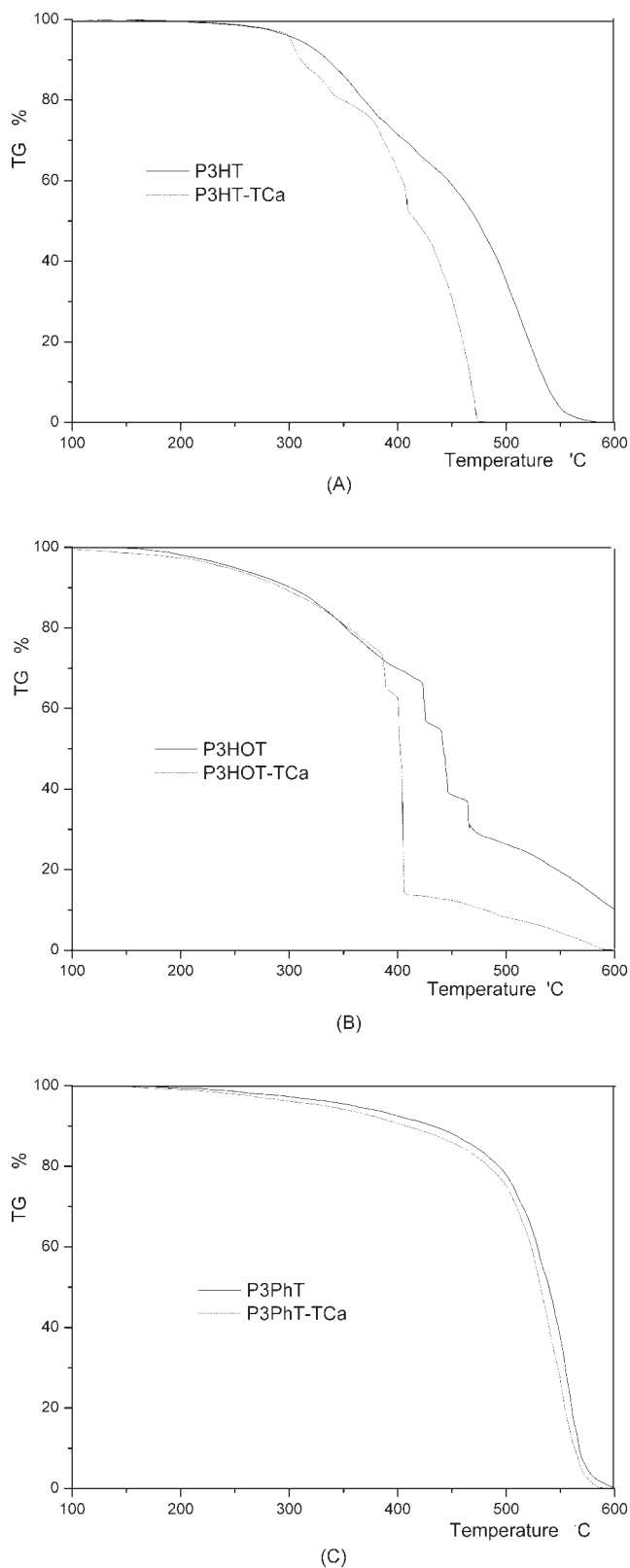
(A)

(B)

(C)

Figure 4 Thermal analysis of P3HT and P3HT-TCa (A), P3HOT and P3HOT-TCa (B), P3PhT and P3PhT-TCa (C).

of carbon nanotube, complete dispersion of carbon nanotube in a polymer matrix can rarely be achieved. The composition containing carbon nano-
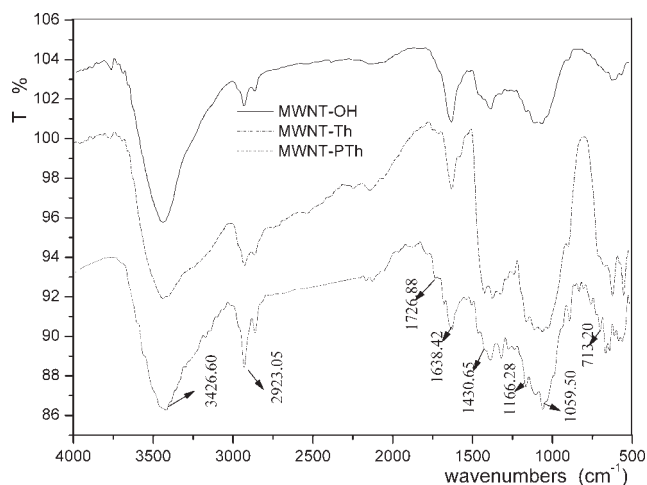

Figure 5 The FTIR spectra of MWNT-OH, MWNT-Th and MWNT-PTh.

tube, which had high carrier mobility and efficient charge transfer, was particularly attractive in photovoltaic device.[22,23] The carbon nanotubes are used as electrodes, or blended/connected with a polymer as bulk-heterojunction devices.[23] Therefore, we aim to synthesize an MWNT functionalized by PTs, which can be used as hole transport or electrode in photovoltaic device. The results could also prove the copolymerization more convincingly.

Figure 5 showed the FTIR of MWNT with hydroxyl (MWNT-OH), thiophene (MWNT-Th) and polythiophene (MWNT-PTh). The stretching vibration of carboxyl appeared at ~ 1700 cm^{-1} after the thiophene rings were introduced. The band at 2923 cm^{-1} was ascribed to the stretching vibration of alkyl group. The intensity of the bands became stronger in MWNT-PTh than that in MWNT-OH. The bands at 713 and 1166 cm^{-1} were corresponded to the in-plane and out-plane rocking vibration of (—CH$_2$—) group. Those bands appeared in MWNT-PTh for the long length alkyl. Therefore, we can conclude that 3-hexyloxythiophene copolymerize with MWNT-Th successfully. TGA showed that the Co-PT was less than 10 wt % in MWNT powders.

CONCLUSIONS

Three kinds of Co-PTs, P3HT-TCa, P3HOT-TCa, and P3PhT-TCa, were prepared and the effects of copolymerization on the properties of PTs were investigated in detail. MW of Co-PT was rather lower than that of homopolythiophene. The mainly reason was ascribed to the low reactivity of 3-thiophene carboxylic acid. P3HT had the highest MW among the homopolythiophene and P3HT-TCa had the highest MW among the Co-PTs. Because of the decreasing of MW and the electron-drawing ability of carboxyl,

the λ_{max} of Co-PTs gave an obvious ''blue shift.'' PL quenching was observed after copolymerization and there was a PL disappearance in P3HOT-TCa. According to TGA, the thermal stability was also affected by copolymerization. Moreover, 3-Hexyloxy-thiophene could copolymerize with MWNT-Th. Though the copolymerization had been achieved in chemical method, the ratio of 3-thiophene carboxylic acid was so low that the Co-PTs could not be dissolved in water. The detailed research results will be reported later.

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