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Structural and Thermal Properties of Carboxylic Acid Functionalized Polythiophenes

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Abstract: Polythiophenes functionalized with polar groups at the end of side-chain have emerged as an alternative method to obtain good compatibility between this class of conjugated polymers and electron acceptor compounds. The aim is to prevent phase segregation and to improve the efficiency of the polythiophene technological devices. However, homopolymers synthesized from thiophene rings with high polar groups at the end of the side-chain, such as hydroxyl and carboxylic acid groups, are poorly soluble in common volatile organic solvents. We report on a systematic preparation of copolymers of 3-hexylthiophene (HT) and thiophene-3-acetic acid (TAA), using different feed ratios. The chemical structures of the copolymers were confirmed by FTIR and ^{1}H-NMR. The TAA content in these copolymers were 33, 38 and 54 mol %. HPSEC results did not show any remarkable correlation with TAA contents in the copolymers. In contrast, the thermal analyses showed a decrease in the thermal stability and an increase in rigidity of their backbones, for the copolymers with high amounts of TAA. The solubility and optical property of copolymers were also related to the TAA contents. Thus, the properties of these copolymers can be modulated by a simple control of feed ratio of TAA in the copolymerization.

Keywords: *Conjugated polymer, polythiophene, synthesis, thiophene-3-acetic acid.*

Introduction

Conducting polymers have been extensively studied in the last years because of their unique electronic and optical properties[1]. In this class of polymers, the polythiophenes (PT) are being very exploited because of their good thermal and chemical stability, relative facility of functionalization and chromic properties that have a great potential for applications in technological devices, such as solar cells, electrochromic windows, polymer light-emitting diodes and chemical sensors[2-4]. Unsubstituted polythiophene was extensively considered as model for the study of charge transport in conjugated polymers. However, the strong interchain interaction makes it infusible, insoluble and, consequently, hinders the processability of this material for the fabrication of devices[4].

The problem of the PT solubility was overcome by the introduction of different groups at 3 or 3,4-position of thiophene ring to obtain the polythiophene derivatives. Several polythiophenes derivatives have been synthesized by chemical or electrochemical methods[4-7]. Besides processability, the polythiophene derivatives can also be fully characterized by chemical and physical methods. For example, the poly(3-alkylthiophene)s (PAT) are common polythiophene derivatives that have been the subject of intense research and development over the last years to be used in numerous device applications[8-10].

Current researches have been focused on improving the performance of polythiophene-based devices by the synthesis of new polythiophene derivatives and by the control of their regioregularity[11-15]. In addition, very efficient devices have also been obtained by mixing the polythiophene derivatives and electron acceptor compounds, such as titania, silica and fullerenes[16-21]. An alternative method to achieve the best mix between these materials is the introduction of polar groups in the side-chain of polythiophene derivatives, for example, hydroxyl or carboxylic acid groups[22].

In general, homopolymers with such high polar groups have limited solubility in common volatile organic solvents because of the strong hydrogen bonding[12,23-28]. The key to improve the solubility of these derivatives is the design of amphiphilic copolymers containing both non-polar and polar side-chains. The non-polar side-chain is responsible for the solubility of the copolymer in common volatile organic solvents, while the polar side-chain provides a good mix of the copolymer with electron acceptor compounds.

In this work, we report on the preparation of copolymers of 3-hexylthiophene and thiophene-3-acetic acid using different feed ratios of comonomers. Such approach allowed the comparison among the feed ratios of comonomers, the real compositions of so-obtained materials, their solubility in a common volatile organic solvent and their UV-vis absorption in chloroform solutions. Moreover, it is possible to prepare polythiophenes containing high polar side-chain with good solubility through proper molecular design.

Experimental

Synthesis of copolymers

The monomers 3-hexylthiophene (HT) and thiophene-3-acetic acid (TAA) were purchased from Aldrich and used without purifications. Three

random copolymers were synthesized by oxidative polymerization with ferric chloride as described recently (see Scheme 1)[22]. In such procedure, 3 mmol of monomers were dissolved in 4.6 mL of CH_3NO_2 and solid $FeCl_3$ (12 mmol) was quickly added to the mixture through a powder addition funnel. Then, 30 mL of chloroform was added to the reaction medium that was stirred magnetically for 4 hours. Different feed ratios of comonomers were used in these reactions and their products were identified as P(HT-*co*-TAA) followed by a number that represents the feed ratios of TAA (mol %) for each copolymerization (Table 1). All reactions were conducted under dry nitrogen atmosphere to avoid the deactivation of the oxidizing agent. The products were precipitated into 0.5 L of methanol, filtrated and washed with methanol.

Characterizations

High pressure size exclusion chromatography (HPSEC) analyses were carried out with an Agilent 1100 HPLC equipment using tetrahydrofuran (THF) as solvent (1.0 mL/min) at 35 °C and two PL gel mixed columns calibrated with polystyrene standards. Fourier transform infrared (FTIR) spectra were recorded in transmission mode on a Perkin Elmer Spectrum 2000 using thin films prepared from chloroform solutions of copolymers onto NaCl single crystal windows. Proton nuclear magnetic resonance (¹H-NMR) spectra were obtained on a Varian (300 MHz) using deuterated chloroform

as solvent and tetramethylsilane as external reference. Thermogravimetric analyses (TGA) of powdered copolymers were conducted on a TA Instruments model Q600 equipment. A heating rate of 5 °C/min and nitrogen flow of 100 mL/min was used. Differential Scanning Calorimetry (DSC) measurements were performed on a TA Instruments model Q100 calorimeter using closed aluminum pans filled with about 5 mg of copolymer powders. Thermograms of the heating run were recorded at the rate of 5 °C/min from –80 to 150 °C under nitrogen flow. Uv-vis spectra were recorded on Agilent Technologies/Cary 60 spectrometer from dilute chloroform solutions of the copolymers placed in quartz cuvettes.

Results and Discussion

Solubility and molecular weight distribution

The oxidative copolymerizations of HT and TAA using different feed ratios yielded black powders partially soluble in chloroform. The main features of these products are summarized in Table 1. The overall yield of P(HT-*co*-TAA)25 was consistent with those reported for other copolymers of polythiophene[29]. However, the P(HT-*co*-TAA)50 and P(HT-*co*-TAA)75 have unexpected yields (above 100 wt%), which could be attributed to the high amount of impurities in form of iron residues as determined by the colorimetric 1,10-phenanthroline method. In the polythiophene derivatives the iron residues are known as dopant of the backbones, but they can also act as counter-ions of the carboxylic acid group in the side-chain of the TAA units present in these copolymers[30].

The solubility of these copolymers was verified in chloroform, which is a common organic volatile solvent used to prepare polythiophene-based devices. All copolymers have shown a chloroform-insoluble fraction that depends on the TAA content, as shown in Table 1. All polythiophene derivatives synthesized by oxidative polymerization method have insoluble fractions in all common organic solvent, because of the occurrence of some cross-linking[28,31]. However, the less solubility of P(HT-*co*-TAA)75 in chloroform than other ones can be due to the presence of large amounts of intermolecular hydrogen bonds among TAA side-chains, or the fact that cross-linking reactions are favored as the TAA content is increased in the reaction medium.

The curves of the molecular weight distributions (MWD) of three copolymers, estimated by HPSEC, are shown in Figure 1. The MWD of a homopolymer
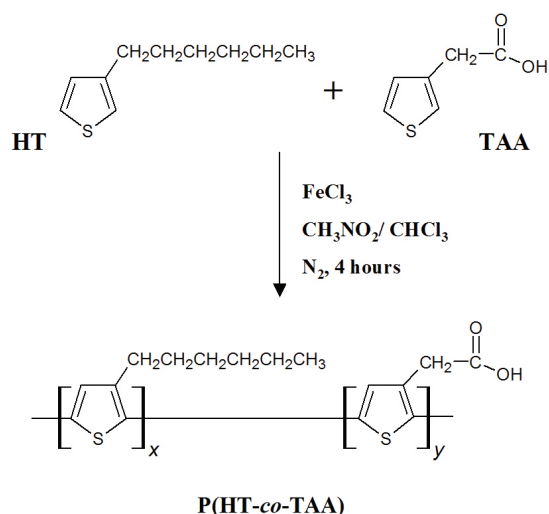
Scheme 1. Procedure to prepare the copolymers, P(HT-*co*-TAA).

Table 1. Main features of the copolymers.

Copolymer	Total Yield[a] (wt %)	CHCl₃ soluble fraction yield (wt %)	TAA Content (mol %)[b]	M_n (g/mol)[c]	PDI[c]	MRUW[d]	DP_n[e]	$T_{5\%}$[f] (°C)	$T_{50\%}$[f] (°C)	Tg[g] (ºC)	λ_{MAX}[h] (nm)
P(*HT*-co-TAA)25	70	65	33	21,100	2.9	157.7	134	310	470	19	420
P(*HT*-co-TAA)50	109	65	38	23,200	2.8	156.4	148	290	477	22	420
P(*HT*-co-TAA)75	110	55	54	22,800	2.6	152.2	150	250	685	28	415

[a]Weight/weight by the starting monomers. [b]Calculated from ¹H NMR. [c]Based on HPSEC measurements. [d]MRUW = mean repetitive unit molecular weight. [e]DP_n=Numerical polymerization degree, calculated as M_n/MRUW. [f]Based on DSC measurements. [g]Based on thermogravimetric analyses. [h]Measured by Uv-vis.

of PHT was included in this figure for comparison. The distribution was slightly narrower for PHT than for the copolymers and the first one shows a shoulder in the MWD about 51,000 g/mol. The number-average molecular weight (M_n) values of copolymers and their corresponding polydispersitivy indexes (PDI) are also shown in Table 1, being lower than that obtained for PHT (M_n = 14,700 g/mol and PDI = 4.6). In addition, the numerical polymerization degrees of copolymers are almost twice than PHT (DPn = 88), but DP_n of the copolymers did not show any remarkable variation with feed ratios of TAA in the copolymerization reactions. These results indicated that the presence of TAA units in the reaction medium influenced positively on the polythiophene chain-growth, possibly because TAA side-chain has less steric hindrance than HT side-chain.

FTIR and ¹H-NMR spectroscopy

Figure 2 illustrates the FTIR spectra of copolymers. The polymerization reactions were confirmed by the decrease of the bands intensity at 730 and 769 cm⁻¹ attributed to the C-Hα out-of-plane deformation vibration of TAA and HT-substituted thiophene rings, respectively. In addition, these spectra show peaks at 839 cm⁻¹
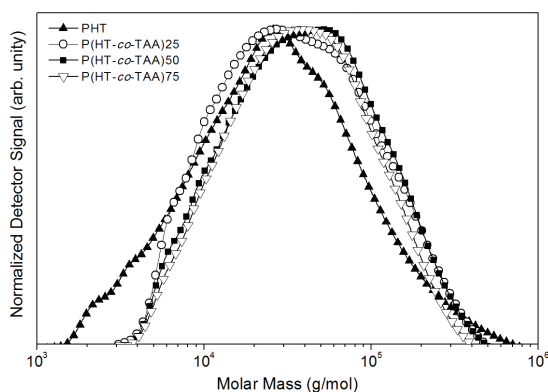
associated with C-Hβ out-of-plane deformation of 2,3,5-trisubstituted thiophene rings, which was attributed to the occurrence of the polymerizations and agreed with the HPSEC results[32].

The bands about 1,462 and 1,375 cm⁻¹ (-CH₃, δ deformation vibration), and 2958 cm⁻¹ (-CH₃, ν_as deformation vibration) evidenced the existence of HT units in these products. Spectral features of TAA units are also clearly seen in the copolymer spectra, in particular the bands at 1,745 and 1,715 cm⁻¹ ascribed to carbonyl (C=O) stretching vibration of free and hydrogen-bonded, respectively[32]. Then, the presence of bands relative of both TAA and HT units in all samples confirm the formation of copolymers.

¹H-NMR was used to characterize the chemical structures of copolymers and to determine the real TAA content in their CHCl₃-soluble fractions. The ¹H-NMR spectra are shown in Figure 3. As it was expected for oxidative polymerization, these spectra indicate that all copolymers have regiorandom linkages due to the presence of two peaks attributed to methylene protons next to the thiophene ring in the HT unit (signal 2)[33]. By comparison with the spectra of two monomers (did not included in this text) the following assignments corresponding to the protons of HT units could be done: 0.93 ppm (Th-CH₂-(CH₂)₄-CH₃), 1.36-1.73 ppm (Th-CH₂-(CH₂)₄-CH₃), and 2.60 and 2.82 ppm (Th-CH₂-(CH₂)₄-CH₃). The peak at 3.74 ppm is assigned to the TAA units (Th-CH₂-COOH) and the peak corresponding

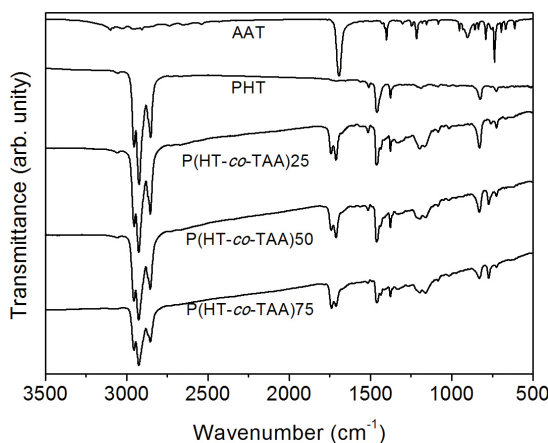**Figure 1.** Molecular weight distributions for the copolymers.

Figure 2. Transmission FTIR spectra of copolymers in form of films onto NaCl windows. The transmission spectra of PHT and AAT monomer were also presented for comparison.
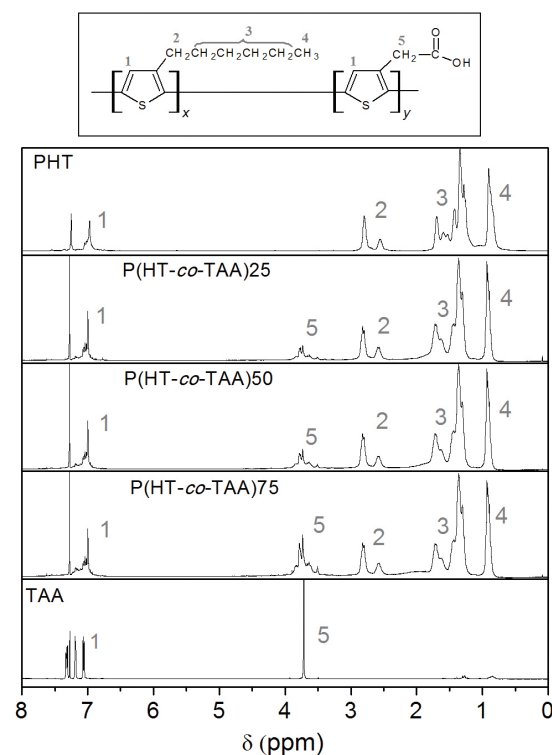

Figure 3. ¹H-NMR (CDCl₃) spectra of copolymers, P(HT-co-TAA). The ¹H-NMR (CDCl₃) of PHT and TAA monomer were also presented for comparison.

to the β'-proton of thiophene ring of both HT and TAA is located at 7.00 ppm.

The compositions of the copolymers can be determined by the area under the peaks attributed to the α-protons of the TAA and HT units. The real contents of TAA in the chloroform-soluble fraction of copolymers are also presented in Table 1. It can be seem from these results that the real molar ratio of TAA units in the P(HT-*co*-TAA)25 was greater than expected. This was assigned to the higher reactivity of the TAA unit in comparison to the HT unit during the oxidative polymerization, because of the highest steric hindrance of the hexyl group in the side-chain of HT unit.

In contrast, the real molar ratios of TAA in the P(HT-*co*-TAA)50 and the P(HT-*co*-TAA)75 are smaller than the feed ratios. This can be associated with the low solubility of chains containing high amounts of TAA, i.e., only chains rich in HT are soluble in chloroform. Despite the highest reactivity of TAA, the soluble fractions of P(HT-*co*-TAA)50 and the P(HT-*co*-TAA)75 have low real molar ratios of TAA.

Thermal analysis (TGA and DSC)

The thermogravimetric curves of all copolymers, shown in Figure 4, exhibit a three-steps weight loss process. The first step (190-330°C) is ascribable to weight loss of the side-chain of the TAA units, as PTAA ($T_{5\%}$ = 180°C) has lower initial temperature of the degradation than PHT ($T_{5\%}$ = 400 °C)[30]. The $T_{5\%}$ of copolymers is slightly lower with the increase of their TAA content, as showed in Table 1.

The second weight loss step, which took place in the temperature range of ca. 360-520 °C, corresponds to the simultaneous degradation of the HT side-chains and the copolymers main-chains. The last weight loss step started around 700 °C and it is assigned to the release of sulfur compounds.

The 5% weight-loss temperatures decrease from 310 to 250 °C as the TAA content increases (Table 1), showing that the copolymers with high TAA contents are more suitable to thermal degradation. In addition, high 50% weight-loss temperatures and residual weight at 980 °C are obtained for P(HT-*co*-TAA)50 and 75, which can be due to the high quantities of iron impurities in these samples.

The DSC curves of the copolymers are shown in Figure 5. Upon heating from –80 to 150 °C, all copolymers exhibited similar profiles with only a simple glass transition. The glass transitions temperatures (Tg) values are presented in Table 1. The P(HT-co-TAA)75 had the highest value of Tg, which can be attributed to the presence of intermolecular hydrogen bond among TAA units[28].

Uv-vis spectroscopy

Optical properties of the copolymers were evaluated by Uv-vis spectroscopy and the results are presented in Figure 6. The spectra of copolymers show the same shape with a broad band derived from the π-π* transitions of conjugated polythiophene main-chain. The wavelengths of maximum absorbance of all copolymers are blue shifted
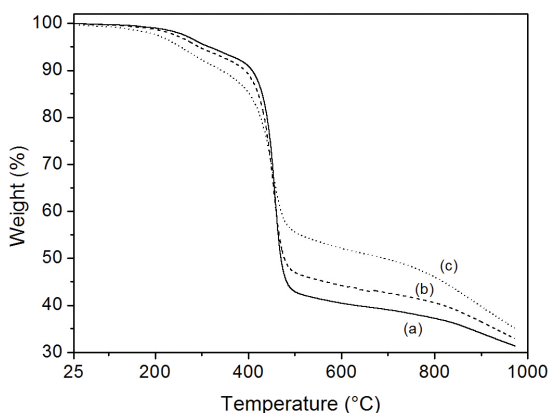

Figure 4. Thermogravimetric (TG) curves of copolymers. (a) P(HT-*co*-TAA)25 (solid curve), (b) P(HT-*co*-TAA)50 (dash curve) and (c) P(HT-*co*-TAA)75 (dot curve).
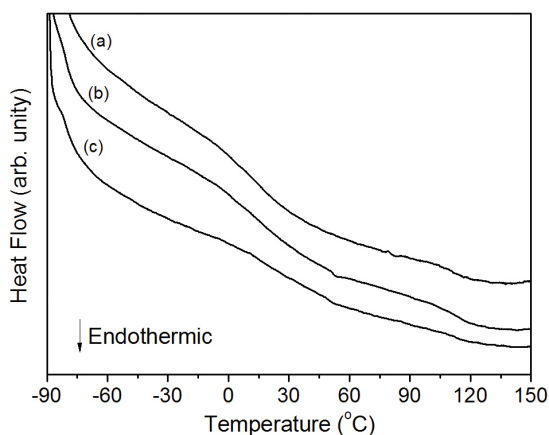

Figure 5. DSC curves of the copolymers. (a) P(HT-*co*-TAA)25, (b) P(HT-*co*-TAA)50 and (c) P(HT-*co*-TAA)75.
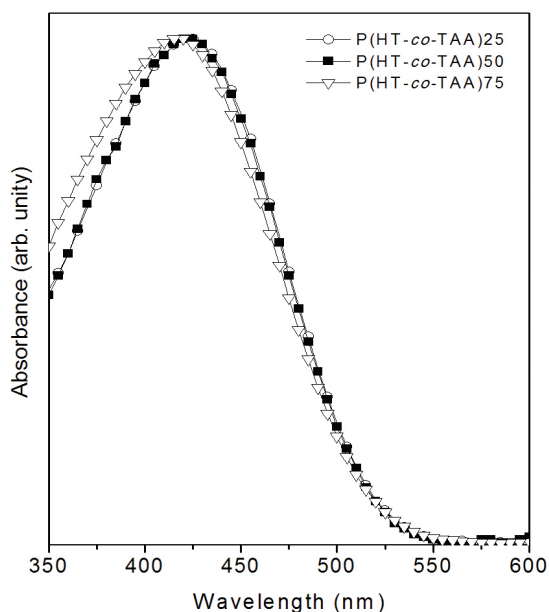

Figure 6. Uv-vis spectra of copolymers in chloroform solutions.

(Table 1) in relation to the value of PHT (495 nm[30]). Furthermore, there is an additional blue shift (5 nm) of the wavelength of maximum absorbance of P(HT-*co*-TAA)75 as compared to other ones. This difference among the band gap of copolymers and PHT probably arises from the presence of hydrogen bond among TAA side-chains that induced the formation of a non-planar conformation, reducing the effective conjugation length[26].

Conclusion

In this work, a series of polythiophene copolymers containing carboxylic acid and alkyl functionalization at the 3-position of the thiophene ring were successfully synthesized. These copolymers combine the good solubility of non-polar polythiophenes derivatives and also present high polar moieties in some side-chains. The amounts of carboxylic acid side-chains in the copolymers could easily be modified up to the maximum of 54 mol% by using 75 mol% of this comonomer in the feed. However, the copolymer with high contents of TAA shows low solubility, low thermal stability, more rigid chains and greater disruption of conjugation length, mainly because of the presence of hydrogen bonding among the TAA side-chains. Thus, these results evidenced that the properties of these copolymers can be tunable by changing the feed ratio of TAA in the copolymerization reaction. Otherwise, by a proper design, it is possible to obtain soluble polythiophenes derivatives bearing high polar groups at the end of side-chain. These copolymers from HT and TAA are being exploited to prepare thin films mixed with electron acceptor compounds, which results will be reported in a future publication.

Acknowledgements

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