

Synthesis and Characterization of New 3-Substituted Thiophene Copolymers

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Três polímeros e dois novos copolímeros baseados em derivados de politiofenos 3-substituídos têm sido estudados e todos demonstraram propriedades fotoluminescentes. Todos os polímeros sintetizados, poli(3-metoxitiofeno) (PMOT), poli(3-tiofenoetanol) (PTE), poli(3-tiofenometanol) (PTM), e copolímeros, poli(3-metoxitiofeno-co-3-tiofenoetanol) (PMOT-co-TE) e poli(3-metoxitiofeno-co-3-tiofenometanol) (PMOT-co-TM), foram caracterizados por FT IR, UV-Vis, fotoluminescência (PL), análise térmica (TG e DSC) e difração de raios X. Todos os materiais mostraram emissão de luz na região do laranja do espectro visível. A obtenção dos polímeros e copolímeros foi confirmada por análise espectrométrica na região do infravermelho. A análise térmica mostrou boa estabilidade térmica para os materiais obtidos.

This work reports the synthesis of three polymers and two new copolymers based on 3-substituted polythiophene derivatives, all of them demonstrated photoluminescent properties. All polymers synthesized, *i.e.*, poly(3-methoxythiophene) (PMOT), poly(3-thiopheneethanol) (PTE), poly(3-thiophenemethanol) (PTM), poly(3-methoxythiophene-co-3-thiopheneethanol) (PMOT-co-TE) and poly(3-methoxythiophene-co-3-thiophenemethanol) (PMOT-co-TM), were characterized by FT IR, UV-Vis, photoluminescence (PL), thermal analysis (TG and DSC) and X-ray diffraction (XRD). All materials emitted light in the orange region of the visible spectrum. Spectrometric analysis in the infrared region demonstrated the successful synthesis of polymers and copolymers by the presence of characteristic bands. Thermal analysis showed that the obtained materials had good thermal stability.

Keywords: conjugated polymer, copolymer, 3-substituted thiophene, photoluminescence

Introduction

Intrinsically conductive polymers obtained from thiophenes and their derivatives possess thermal and environmental stability¹ as well as electronic and optical properties that enable applications such as organic transistors,^{1,2} anticorrosives,^{3,4} electrochromic materials⁵ and rechargeable batteries,⁶ leading to intense and increasing interest in these materials by research groups all over the world. The search for new technological materials has significantly contributed to the development of new precursors and synthetic methods that generate materials with desirable properties.⁷⁻¹⁰ These materials can be obtained by different polymerization methods, the most common of which employs ferric chloride as an oxidizing agent under an inert atmosphere,¹¹⁻¹⁷ with other methods including electrochemistry techniques,

such as cyclic voltammetry,¹⁸ chronoamperometry^{19,20} and chronopotentiometry.²¹ The electronic and optical properties of these polymers can be controlled using monomers that have functional groups incorporated into the structure that can contribute to the properties of the polymer chain; for example, poly(3-methoxythiophene) has been extensively studied due to the presence of oxygen in the alkoxy group, which decreases the oxidation potential of the monomer and polymer through its effects as an electron donor substituent.²²⁻²⁴ Other groups such as hydroxyl groups have been described as undesirable ones, because they can behave as nucleophiles, attacking the radical cations presented in the solution and leading to coupled compounds with low electric activity.^{25,26}

The technique of copolymerization has been widely used as a way to obtain materials with properties intermediate between those of the individual homopolymers.^{27,28} Thus, the physical and chemical properties of the final material can be controlled through

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the appropriate choice of monomers that form the polymer chain. We previously studied the influence of alkoxy and hydroxyl groups on the formation and properties of their homopolymers and copolymers, and in this work we report the synthesis of the polymers poly(3-methoxythiophene) (PMOT), poly(3-thiopheneethanol) (PTE), poly(3-thiophenemethanol) (PTM) (obtained previously only through electrochemical polymerization)²⁹ and two new copolymers: poly(3-methoxythiophene-co-3-thiopheneethanol) (PMOT-co-TE) and poly(3-methoxythiophene-co-3-thiophenemethanol) (PMOT-co-TM). Spectrometric measurements in the infrared region exhibited the expected bands, demonstrating the successful synthesis of polymers and copolymers. X-ray diffraction, gel permeation chromatography and thermal analysis were also carried out. Measurements of the absorption and emission of electromagnetic radiation by these materials suggest their potentiality for application in electroluminescent devices.

Experimental

Materials

The 3-methoxythiophene (98%) (MOT), 3-thiophenemethanol (98%) (TM), 3-thiopheneethanol (99%) (TE) and ferric chloride (97%) were obtained from Aldrich. All monomers were used without prior purification. The solvents chloroform (99.8%), dimethylsulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were acquired from Synth.

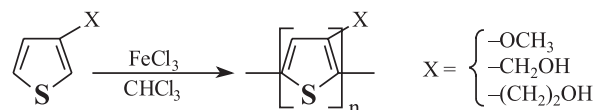
Synthesis

Polymerizations and copolymerizations were carried out at room temperature under an inert atmosphere (nitrogen gas) by adapting the procedures described elsewhere.^{12,17,30}

Polymers

Each monomer (MOT, TE or TM) (0.05 mol L⁻¹) was dissolved in chloroform. A suspension of anhydrous FeCl₃ (0.2 mol L⁻¹), also in chloroform, was added to the flask with magnetic stirring at room temperature under an inert atmosphere (Scheme 1). The monomer solution was slowly dripped into the reaction flask over 30 min. When the addition was complete, the reaction time was monitored by thin layer chromatography (TLC) using chloroform as the solvent and silica gel as the adsorbent. The end of the reaction was determined by the total consumption of monomer. The polymers poly(3-methoxythiophene)

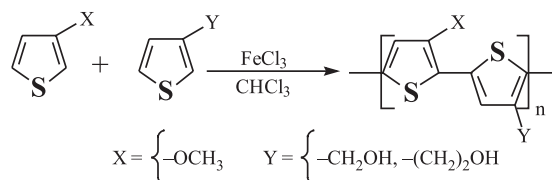
(PMOT) and poly(3-thiophenemethanol) (PTM) were obtained after 2 h reaction. The poly(3-thiopheneethanol) (PTE) was obtained after 3 h.



Scheme 1. Synthetic route of PMOT (X = -O-CH₃), PTE (X = -(CH₂)₂OH) and PTM (X = -CH₂OH).

Copolymers

Copolymers were obtained by the chemical copolymerization of monomers of TE and TM with the monomer MOT at a molar ratio of 2:1. A suspension of FeCl₃ (0.2 mol L⁻¹) in chloroform was added to the flask with magnetic stirring at room temperature under an inert atmosphere. A solution of equal volume containing the two monomers (TE and MOT or TM and MOT) (0.05 mol L⁻¹) was dripped slowly into the reaction flask over 30 min under magnetic stirring (Scheme 2). The reaction was monitored by TLC using chloroform, as the solvent, and silica gel, as the adsorbent. The end of the reaction was determined by the total consumption of monomer. The poly(3-methoxythiophene-co-3-thiophenoethanol) (PMOT-co-TE) and poly(3-methoxythiophene-co-3-thiophenemethanol) (PMOT-co-TM) products were obtained after 4 and 2 h reaction, respectively.



Scheme 2. Synthetic route of the copolymers PMOT-co-TE (X = -OCH₃, Y = -(CH₂)₂OH) and PMOT-co-TM (X = -OCH₃, Y = CH₂OH).

Polymers and copolymers were obtained in the form of dark powders, but the purified PTM appeared redish-brown at the end of the purification process (Figure S1, see Supplementary Information, SI, online). Before spectroscopic analysis, all the samples were submitted to purification to ensure the absence of residues of monomers and other reactants involved in the synthesis process. The PMOT was purified by stirring the polymer with five portions of 40 mL of diethyl ether. The polymers and copolymers PTE, PTM, PMOT-co-TE and PMOT-co-TM were purified by Soxhlet extraction with methanol. Importantly, the homopolymer PMOT is partially soluble in methanol and it disperses quite efficiently in this solvent (blue coloration in the solvent). Because of this,

the purification was performed employing diethyl ether as a solvent. During the purification of polymers PTE and PTM and copolymers PMOT-co-TE and PMOT-co-TM, no solubilization or suspension it was observed using methanol as the solvent. The lack of a blue color in the solvent during the purification of the copolymers suggests either that the homopolymer PMOT it was not formed or those oligomers it was formed from the MOT, indicating that the blends were not formed during the copolymerization.

Analyses

Infrared spectra (FT IR) were recorded for all samples in powder form on a Nicolet 380 spectrometer by attenuated reflectance total (ATR). The thermal behavior of the mass loss (TGA) was investigated in a SDT 2960 simultaneous DTA TGA. Differential scanning calorimetry (DSC) curves for the polymers were obtained with a TA Instruments apparatus, model MTDSC 2920. Approximately 5 mg of each sample was loaded in an aluminum pan, and the analysis was performed according to the following procedure: *i*) ramp heating at 10 °C min⁻¹; up to 110 °C to dry residual volatiles, *ii*) isothermal holding for 1 min, *iii*) quenching (inside the DSC cell) at a rate of *ca.* 10 °C min⁻¹ down to -100 °C, *iv*) isothermal holding for 3 min, and *v*) ramp heating at 5 °C min⁻¹ up to 150 °C. Measurements were carried out using helium as a carrier gas at a flow rate of 50 mL min⁻¹. Analysis of ultraviolet radiation (UV-Vis) was performed in DMF with a HITACHI UVSOLUTION 2010 spectrophotometer. Photoluminescence (PL) spectra of all samples were obtained in DMF at room temperature. The cuvette containing the solutions was mounted on top of an XY driver, which enabled us to move samples with small displacements without losing the optical alignment. A Q-switched Nd:YAG laser emitting at 488 nm was used as the excitation source. The PL emission was collected in a backscattering configuration and focused into an Ocean Optics USB2000 Miniature Fiber Optic Spectrometer. X-ray diffraction (XRD) measurements were obtained from samples in powder form on a Rigaku Geigerflex diffractometer with a cobalt (Co) tube, a voltage of 32.5 KV, a current of 25 mA and 2θ = 5-60°. Gel permeation chromatography (GPC) was performed in a gel chromatography system model Shimadzu LC - 10 AD/CTA - 10 A GPC with a column Shim-Pack 803/804-D Shimadzu (Exclusion limit M_w 7×10⁴ and 4×10⁵) 300×7.8 mm, a 20 μL injection, a flow rate of 1.0 mL min⁻¹, UV-Vis detection at 300 nm, polystyrene standards and DMF as the mobile phase.

Results and Discussion

The polymerization technique employed in this work provided polymers in good yields and it has the advantages of simplicity and a lack of unstable intermediates. PMOT has been obtained by other groups^{17,24} employing the oxidative method with FeCl₃. Some authors²³ have obtained PMOT after 24 h of reaction at room temperature, requiring the addition of methanol as a precipitating agent. Other researchers¹⁷ have shown that keeping the reaction temperature between 0-2 °C yields PMOT after 2 h reaction. The procedure described in this paper yielded PMOT after 2 h reaction at room temperature. This method is interesting because it allowed us to obtain all polymers and copolymers reported in this paper in a short period of time in the form of a powder at the bottom of the reaction system, without the requirement for any precipitating agent. PTE chemical synthesis was reported by Philip *et al.*,³¹ but their study focused on obtaining and characterizing the composite formed between the polymer (matrix) and carbon nanotubes (charge). The polymer yields in our study were 90% (PMOT), 60% (PTE), 77% (PTM), 80% (PMOT-co-TE) and 71% (PMOT-co-TM).

The dissolution of these materials in DMF and in DMSO only was possible after employ magnetic stirring and bath ultrasonically over a period of eight days. In fact, PMOT have total solubilization of 1 mg in 10 mL (0.1 mg mL⁻¹) of DMF or DMSO. For the polymer PTE and copolymers PMOT-co-TE and PMOTco-TM, 1 mg by each of them can be solubilized in 60 mL DMF (0.017 mg mL⁻¹) in Figure S1 (see SI). In DMSO, 0.017 mg mL⁻¹ of the polymer PTE and copolymers PMOT-co-TE and PMOT-co-TM showed a smaller amount of suspended particles, but, we do not know yet how much soluble they are. The PTM is little soluble in both solvents and we observed a small solubilized fraction in both solvents (DMF and DMSO), almost everything stayed in the form of dispersion.

For GPC analyses the samples were dissolved in DMF. Table 1 shows the GPC results for polymers PMOT and PTE and copolymers PMOT-co-TE and PMOT-co-TM. The materials had a high weight average molar mass (\overline{M}_w) between 207,300 and 279,300 g mol⁻¹ and a number weight average molar mass (\overline{M}_n) between 150,000 and 233,000 g mol⁻¹. The polydispersity of these polymers were between 1.19 and 1.38. The result of GPC in DMF for solubilized fraction of PTM showed \overline{M}_w *ca.* 2,000 that is characteristic of oligomers.

Infrared characterization

The spectra of both monomers and homopolymers can be found in Figures S2, S3 and S4 (see SI). Although the

Table 1. Characteristic molecular weight of the polymers and copolymers

Polymers	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
PMOT	233,000	279,300	1.19
PTE	193,300	260,500	1.34
PMOT-co-TE	214,500	263,400	1.22
PMOT-co-TM	150,000	207,300	1.38

PTM presented extremely low solubility in both solvents (DMF/SMSO), it is not possible to obtain GPC results.

bands found in the copolymers can also be found in the corresponding homopolymers, different interactions and vibrational couplings due to the presence of two monomers with different substituents result in the displacement of the copolymer bands when compared to the spectra of their respective homopolymers (Figure 1a). Thus, according to the region of “finger prints” of the spectra of copolymers and homopolymers (Figure 1b), and taking into account that consumption of the two monomers was observed by TLC during the process of copolymerization and that these materials were thoroughly purified, we conclude that the spectral differences between the copolymers and homopolymers are evidence of the formation of copolymers between the MOT and monomers TE and TM. Nevertheless, the following thermal analysis and UV-Vis results show that the copolymers exhibit properties intermediate between those of the homopolymers (expected behavior based on the literature),²⁷ which proves that copolymerization was successful.

The infrared spectra for the polymers and copolymers in Figure 1 shows the expected characteristic bands. PMOT showed absorption bands at 2,930 and 2,873 cm^{-1} corresponding to the C–H stretching of the CH_3 group, demonstrating the presence of methoxy groups. Bands associated with the vibrational modes of the thiophene ring were found at 1,490, 1,469 and 1,434 cm^{-1} . The band at 1,325 cm^{-1} is attributed to the angular deformation of –C–H. The stretching of the $\text{C}_{(\text{ring})}$ –O–C group has been identified as the band at 1,057 cm^{-1} . Bands corresponding to the angular deformation out of the plane of the thiophene ring can be found at 856–701 cm^{-1} .

PTE and PTM present infrared spectra with bands at 3,259 and 3,417 cm^{-1} , respectively, corresponding to the stretching of the hydroxyl group. A shoulder is observed at 3,058 (PTE) and 3,099 cm^{-1} (PTM), corresponding to the =C–H stretching of the thiophene ring. Bands at 2,925 and 2,872 cm^{-1} for PTE and 2,965 and 2,895 cm^{-1} for PTM correspond to the stretching of the – CH_2 – group. Bands associated with the vibrational modes of the thiophene ring were found at 1,511 (PTE) and 1,507 cm^{-1} (PTM). Bands associated with the angular deformation of –C–H are found

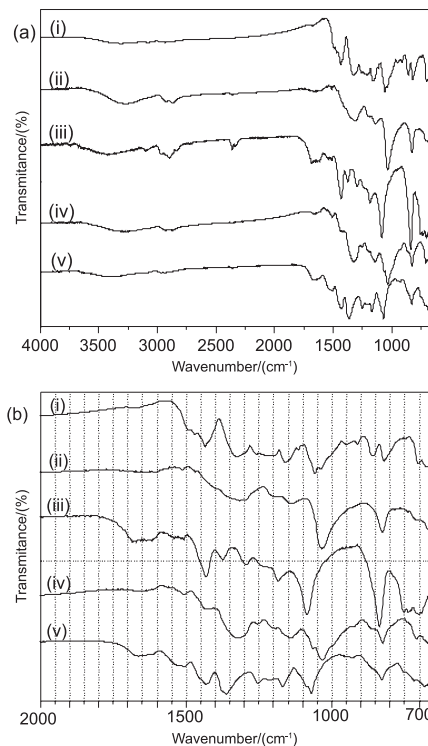


Figure 1. FT-IR spectra of polymers and copolymers: (i) PMOT, (ii) PTE, (iii) PTM, (iv) PMOT-co-TE and (v) PMOT-co-TM.

at 1,315 (PTE) and 1,374 cm^{-1} (PTM). Stretching of the C–O group is associated with the band at 1,032 (PTE) and 1,083 cm^{-1} (PTM). The band corresponding to the angular deformation out of the plane of the thiophene ring can be found at 826 (PTE) and 836–736 cm^{-1} (PTM).

The copolymers PMOT-co-PTE and PMOT-co-TM showed absorption bands at 3,271 and 3,413 cm^{-1} , respectively, corresponding to the stretching of the hydroxyl group. The bands at 3,080 (PMOT-co-TE) and 3,104 cm^{-1} (PMOT-co-TM) are due to the =CH stretching. The bands at 1,324 (PMOT-co-TE) and 1,362 cm^{-1} (PMOT-co-TM) are assigned to the angular deformations of –C–H. The stretching of the C–O group was observed as bands at 1,032, 1,062 (PMOT-co-TE) and 1,069 cm^{-1} (PMOT-co-TM). Bands corresponding to the angular deformation out of the plane of the thiophene ring can be found between 825–707 cm^{-1} (PMOT-co-TE) and 827–715 cm^{-1} (PMOT-co-TM).

The IR spectra obtained for the prepared polymers and copolymers showed enlargement and displacement of the bands and the disappearance of some bands when compared to the IR spectra of the corresponding monomers. The band observed around 1,670 cm^{-1} can be attributed to the couplings associated with the attack by the hydroxyl group of the side chain of monomers TE and TM to the cation radical that occurs during the polymerization process. Pohjakallio *et al.*,³² associate this band to the formation of a carbonyl group with a positive charge concentrated

on oxygen atom 32 (this positive charge is due to the fact that the polymers and copolymers were obtained in their oxidized forms).

In the homopolymers PTE and PTM, beyond the band related to the hydroxyl group, there is a band corresponding to stretching between C–O in 1,032 (PTE) and 1,083 cm^{-1} (PTM). For PMOT²², a stretch $\text{C}_{(\text{ring})}\text{–O–C}$ appears at 1,057 cm^{-1} . For the copolymers, two peaks are observed in the same region due to the presence of groups $\text{C}_{(\text{ring})}\text{–O–C}$, $\text{–CH}_2\text{OH}$ (PMOT-co-TM) and $\text{CH}_2\text{–CH}_2\text{–OH}$ (PMOT-co-TE). In the copolymer PMOT-co-TE, the sharp band at 1,062 cm^{-1} can be attributed to the methoxy group from monomer MOT in the polymer chain, and the other sharp band at 1,032 cm^{-1} is assigned to the group $\text{CH}_2\text{–CH}_2\text{–OH}$ (from monomer TE). For the copolymer PMOT-co-TM, a band is observed at 1,069 cm^{-1} (attributed to the methoxy group) and a shoulder is observed at 1,083 cm^{-1} (corresponding to the monomer TM).

Thermal analysis (TG and DSC)

Figure 2 shows the TG and DTG profiles for the polymers and copolymers. All materials have different behaviors as evidenced by the DTG curves in the temperature range of 33–990 °C. PMOT (Figure 2a) loses mass in four steps: the first one (145–270 °C) may be related to the loss of the alkoxy²¹ group, and the steps afterwards (270–726 °C) to weight loss due to the degradation of the polymeric chain, with a residual mass equal to 32%. PTE (Figure 2b) remained stable up to 200 °C, with weight loss occurring beyond this temperature in steps distinct from those of PMOT. The first step, 200–313 °C, had a maximum rate of mass loss at 304 °C. PTM (Figure 2c) was stable up to 230 °C, with weight loss in one step (230–507 °C), with a maximum rate of mass loss at 402 °C. The difference between the thermal stability observed between PTE and PTM may be related to the large size of the side chains in PTE that could decrease the thermal stability of the polymer, as reported for poly(3-alkylthiophene) and poly(3-alkoxythiophenes).^{22,33} The copolymer PMOT-co-TE (Figure 2d) was thermally stable up to 175 °C and then lost weight in three steps. The first step (175–321 °C) involved a weight loss of 30%, which may be associated with the loss of the side chains –O–CH_3 and $\text{–CH}_2\text{–CH}_2\text{–OH}$. The second mass loss may be related to the degradation of the chain of the copolymer. The copolymer PMOT-co-TM (Figure 2e) was thermally stable up to 200 °C, with mass loss then occurring in two steps. Comparing the two copolymers, their behavior is similar to that of their individual polymers (PTE and PTM), with improved thermal stability over PMOT.

Figure 3 and Table 2 show the DSC results. None of these samples presented DSC signals associated with melting. PTE undergoes a vitreous transition at a T_g of 48 °C, and PTM at 41 °C. According to the literature,²² if only the size of the substituent group influenced the T_g , PTM would display a higher T_g than PTE, but in the case of these samples, the extent of conjugation apparently has a greater influence than the size of the lateral chains, that present sizes differing from of a single CH_2 group. These T_g values also suggest that PTE may have a greater number of hydroxyl groups, resulting in a greater amount of hydrogen bonds compared to PTM and causing the increase in the energy required to weaken these intermolecular interactions. The results obtained from UV-Vis analysis agree with this explanation, as they showed less conjugation for PTM (red shift), which may be related to an increasing amount of coupling caused by attacks from hydroxyl groups in the cation-radical during polymerization.

Copolymers PMOT-co-TE and PMOT-co-TM had T_g values at 56 and 59 °C, respectively. These materials behave as expected,²² with T_g values between those of their individual homopolymers. The values close of the T_g between PMOT-co-TE and PMOT-co-TM and higher than the values observed for PTM and PTE homopolymers demonstrate the contribution of PMOT to T_g . In the synthesis of PMOT-co-TM, the monomer MOT influenced the form in which the TM coupled, disfavoring couplings caused by the attack by hydroxyl groups in cation radicals during the polymerization process. This observation is based on two factors: first, the T_g of this material is greater than that of PMOT-co-TE, and second, the red shift of λ_{max} observed by UV-Vis measurements was greater for PMOT-co-TM than for PTM, indicating that the coupling between the monomers MOT and TM likely have fewer couplings formed by attacks by hydroxyl groups in cation radicals.

X-ray diffraction

Figure 4 shows the X-ray diffratograms obtained. All polymers and copolymers presented a broad and diffuse peak, indicating that the samples are not crystalline materials. This is in accordance with DSC analysis. All samples reach their maximum intensity at $2\theta = 26\text{--}31^\circ$. The presence of an amorphous structure can be attributed to the formation of cross-links (1,3-couplings) between thiophene rings.¹¹

Optical characterization

Table 3 shows a summary of data obtained from absorption (UV-Vis) and photoluminescence (PL)

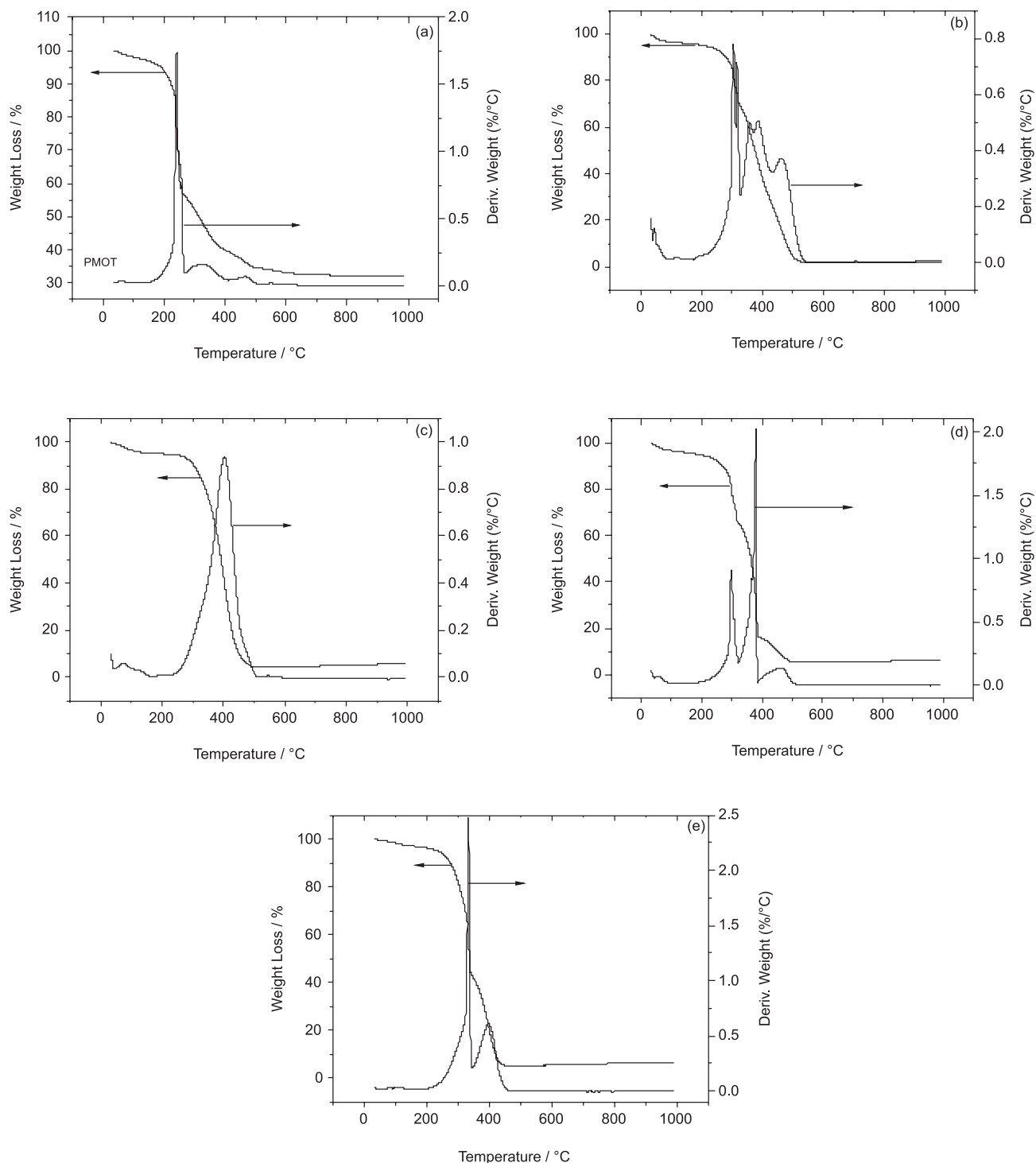


Figure 2. TG-DTG curves of the polymers and copolymers: (a) PMOT; (b) PTE; (c) PTM; (d) PMOT-co-TE; and (e) PMOT-co-TM.

measurements. Figure 5 shows the absorption spectra for the sample solutions. Bands for the homopolymers and copolymers were observed in same range between 400-500 nm. PMOT showed an absorption band at 452 nm (2.75 eV), in agreement with data provided in the literature²² for this material (475-430 nm). PTE and PTM showed absorption bands at 419 nm (2.96 eV) and

405 nm (3.06 eV), respectively. These results show that the effect of the electron donating methoxy group in PMOT increases the wavelength of maximum absorption of PMOT (bathochromic shift or red shift) when compared to PTE and PTM. The difference in the maximum absorption wavelengths between PTE (419 nm) and PTM (405 nm) can be related to two factors: (i) PTE has a more extensive

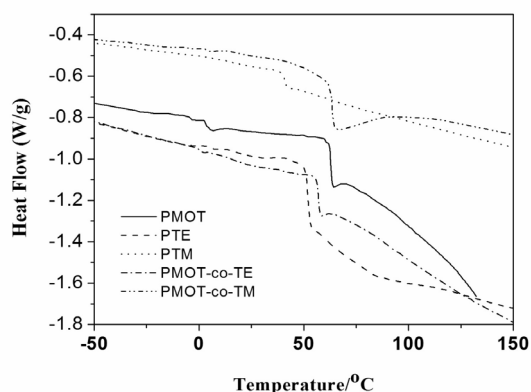


Figure 3. DSC curves of the polymers and copolymers.

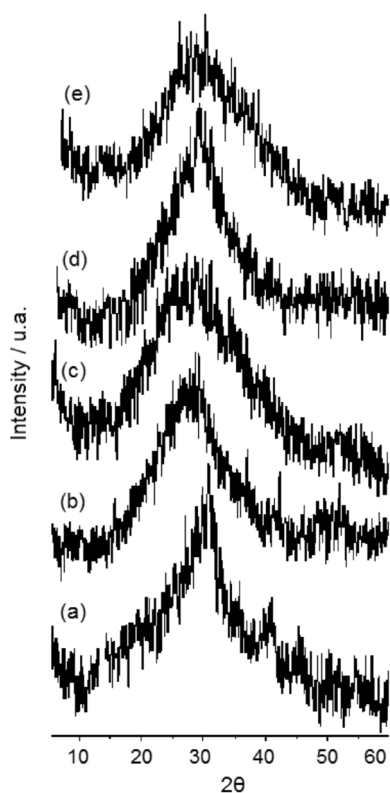


Figure 4. X-ray diffraction patterns of polymers and copolymers: (a) PMOT; (b) PTE; (c) PTM; (d) PMOT-co-TE; and (e) PMOT-co-TM.

Table 2. The TGA results and transition temperatures of the polymers and copolymers (T_d : initial temperature of degradation, T_{td} : temperature of total decomposition, T_g : glass transition temperature)

Polymers	T_d (°C)	Residue (%)	T_{td} (°C)	T_g (°C)
PMOT	145	32.2	726	62
PTE	200	2.4	547	48
PTM	230	5.9	519	41
PMOT-co-TE	175	6.3	536	56
PMOT-co-TM	200	6.6	474	59

π -conjugated system than PTM, which implies a lower energy required for π - π^* transitions, and/or (ii) the ethanol group in PTE favors a more coplanar conformation, resulting in a decrease in the π - π^* transition energy when compared to PTM.³¹ The copolymers obtained had maximum absorption (λ_{max}) values intermediate between those of their homopolymers. PMOT-co-TE showed a λ_{max} at 429 nm (2.89 eV) and PMOT-co-TM showed a λ_{max} at 424 nm (2.93 eV). The observation that PMOT-co-TE has a λ_{max} greater than the PMOT-co-TM one demonstrates that the substituent groups in the monomers TE and TM maintain their effect on the λ_{max} of copolymers.

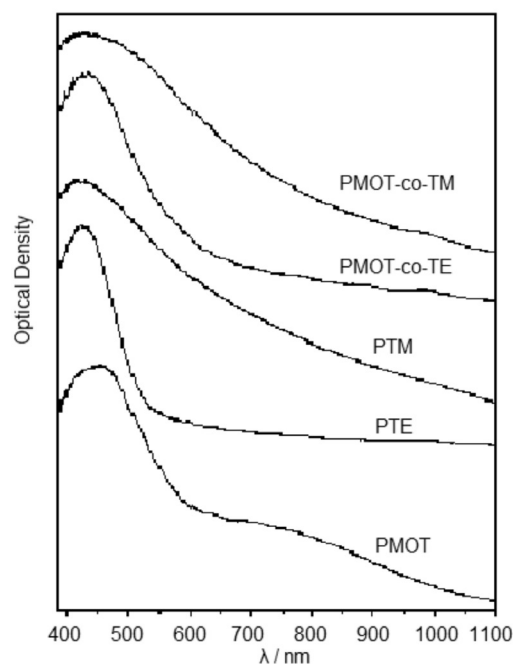


Figure 5. Absorption spectra in DMF as a function of wavelength for PMOT, PTM, PTE and their copolymers.

All polymers and copolymers obtained show an intense orange luminescence above 600 nm that is visible to the naked eye, as shown in Figure 6. The PL spectra of the materials obtained in this work are well resolved for the four transitions (E_{00} , E_{01} , E_{02} and E_{03}) due to their large size and good extension of conjugation, indicating the good structural quality of the materials. The variation of the substituent groups in homopolymers and copolymers did not significantly alter the first vibrational band (E_{01}), λ_{max} ca. 613 nm. All bands showed small changes in the emission intensity of the band with purely electronic transition (E_{00}) and of the second vibrational band (E_{02}). In PMOT, the E_{00} and E_{02} bands presented similar probabilities of transition (similar emission intensities). Compared with PTE, PMOT has a greater probability of transition from the E_{00} band and

Table 3. Absorption and emission data for PMOT, PTE, PTM and their copolymers

Polymers	λ_{\max}	E_{00}	Band		E_{03}
			Absorption	Emission	
PMOT	452 nm	561 nm	613 nm	673 nm	748 nm
	2.7 eV	2.2 eV	2.0 eV	1.8 eV	1.6 eV
PTE	419 nm	562 nm	611 nm	-	-
	2.9 eV	2.2 eV	2.0 eV		
PTM	405 nm	566 nm	614 nm	673 nm	753 nm
	3.0 eV	2.2 eV	2.0 eV	1.8 eV	1.6 eV
PMOT-co-TE	429 nm	562 nm	613 nm	672 nm	745 nm
	2.8 eV	2.2 eV	2.0 eV	1.8 eV	1.6 eV
PMOT-co-TM	424 nm	563 nm	614 nm	675 nm	748 nm
	2.9 eV	2.2 eV	2.0 eV	1.8 eV	1.6 eV

a considerable decrease in emission from the E_{02} band. This behavior indicates that the $-\text{CH}_2-\text{CH}_2-\text{OH}$ group favors the E_{00} band. This was confirmed by the PL spectrum for PMOT-co-TE, where the E_{00} band is more intense than the E_{02} band. The PTM showed behavior similar to its analog PTE: the emission intensity of the E_{00} band is more intense than that of the E_{02} band. In terms of the probability of transitions, PTE favors the E_{00} transition and disfavors the E_{02} transition. Despite the fact that PTM favors the E_{00} transition, the E_{02} transition also has an emission intensity very close to that of E_{00} . Therefore, this observation suggests that the increasing of the size of the hydroxylated side chain can improve the E_{00} transition. This behavior may be linked to the different conformations assumed by the two homopolymers in solution. In the case of the copolymer PMOT-co-TM, the E_{02} band was more intense than the E_{00} band. This observation may be related to the two substituent groups that favor the two transitions almost equally, in which case the E_{02} band is more likely to occur than the E_{00} band.

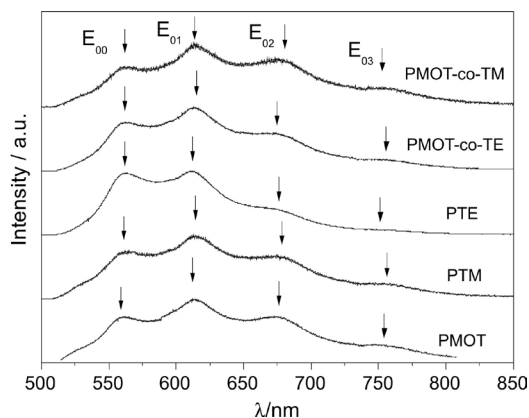


Figure 6. Photoluminescence spectra in DMF for PMOT, PTM, PTE and their copolymers. The labels E_{00} , E_{01} , E_{02} and E_{03} correspond to the pure electronic transition, the first, the second and the third vibronic bands, respectively.

Conclusions

This study compared the influence of different substituent groups on the final properties of thiophene homopolymers and copolymers. The polymerization method which was used it showed itself satisfactory with regard to the obtaining the desired materials at a shorter reaction time and with the material precipitation at the bottom of the own reaction system, with the advantage of not requiring any additional precipitating agent. The effect of alkoxy and hydroxyl substituents on conducting polymers was investigated. Although the TE and TM monomers present hydroxyl groups that could act as nucleophiles in the polymerization process resulting in materials with a low extension of conjugation, in this work, these materials presented interesting thermal and luminescent properties. Thus, all materials obtained showed good thermal stability and photoluminescence properties. The variation of the substituents in both the homopolymers and the copolymers did not significantly alter the λ_{\max} of emission, but they caused interesting variations in the emission intensities of the E_{00} and E_{01} bands, which can be controlled by the appropriate choice of the substituent of the polymer chain. However, more detailed studies of the mechanism of emission of these materials are still needed for a better understanding of the photoluminescent properties, and future tests on the possibility of applications in polymer light emitting diodes (PLEDs) will be carried out.

Supplementary Information

Supplementary data, such as the images of the powders of the polymers studied and their corresponding solutions (Figure S1) and infrared spectra of the monomers and their corresponding polymers (Figures S2, S3 and S4) are available free of charge at <http://jbcs.sbq.org.br>, as PDF file.

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Synthesis and Characterization of New 3-Substituted Thiophene Copolymers

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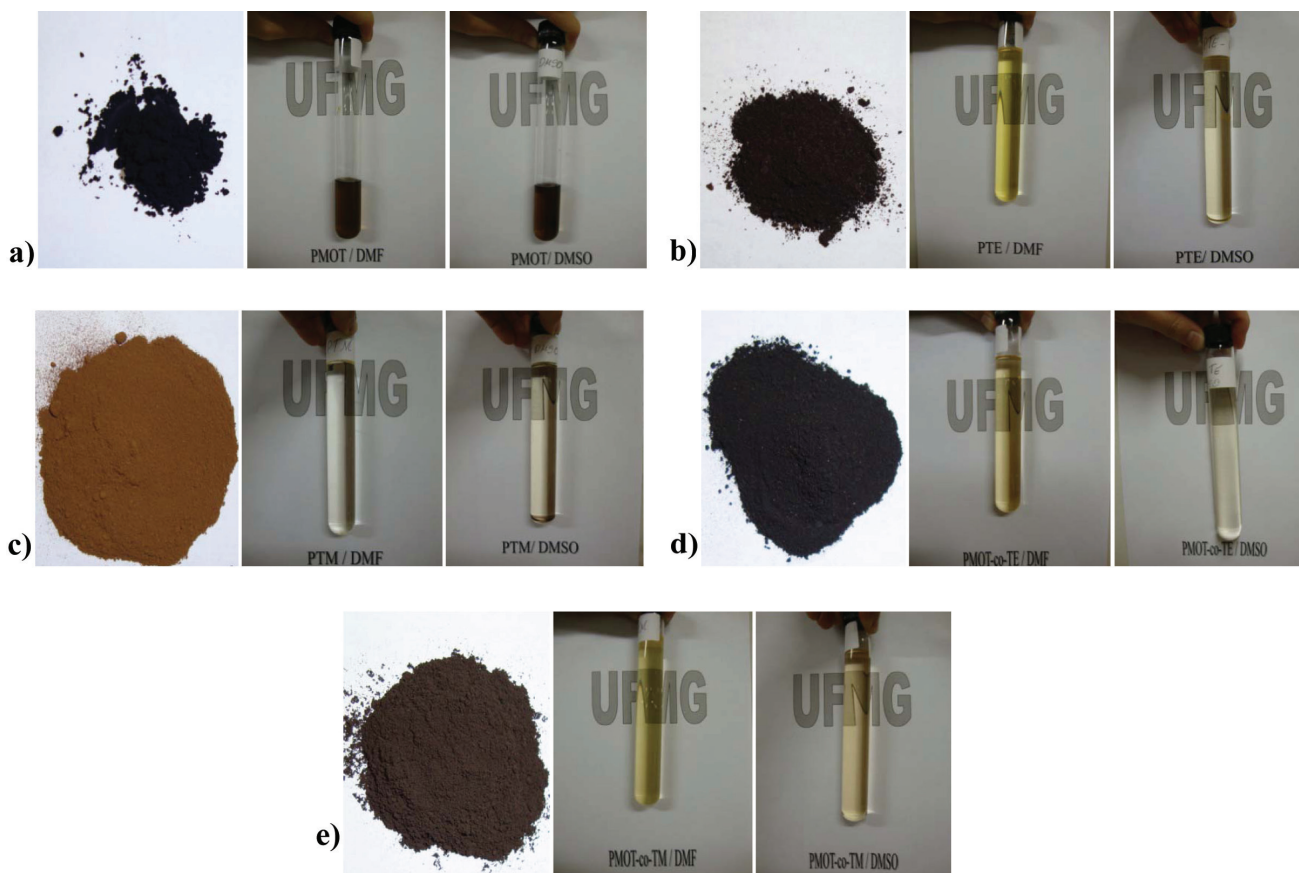


Figure S1. Images of the powders of the polymers and copolymers and their corresponding solutions in DMF and DMSO: a) PMOT/DMF and PMOT/DMSO; b) PTE/DMF and PTE/DMSO; c) PTM/DMF and PTM/DMSO; d) PMOT-co-TE/DMF and PMOT-co-TE/DMSO; e) PMOT-co-TM/DMF and PMOT-co-TM/DMSO. PTM is poor soluble (only a small fraction, maybe with soluble oligomers, it is in solution).

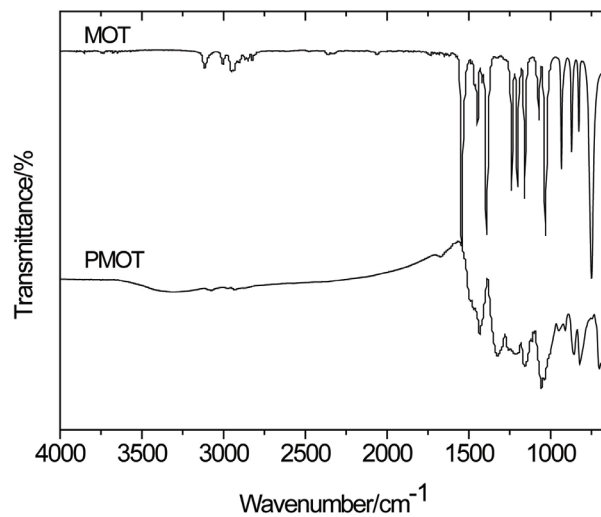


Figure S2. FT IR spectra of the monomer 3-methoxythiophene (MOT) and polymer poly(3-methoxythiophene) (PMOT).

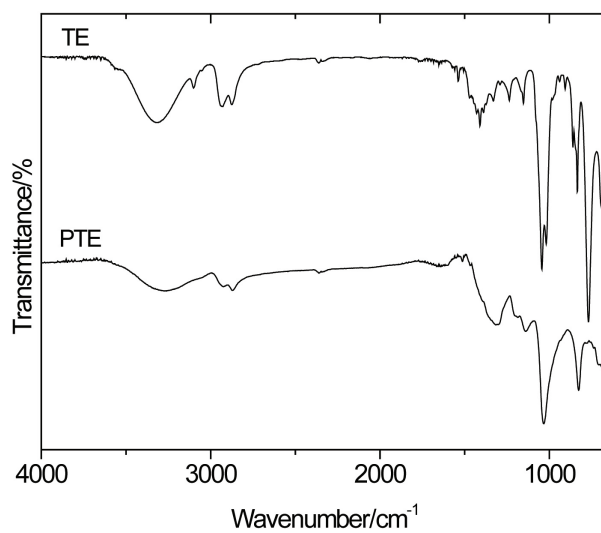


Figure S3. FT IR spectra of the monomer 3-thiopheneethanol (TE) and polymer poly(3-thiopheneethanol) (PTE).

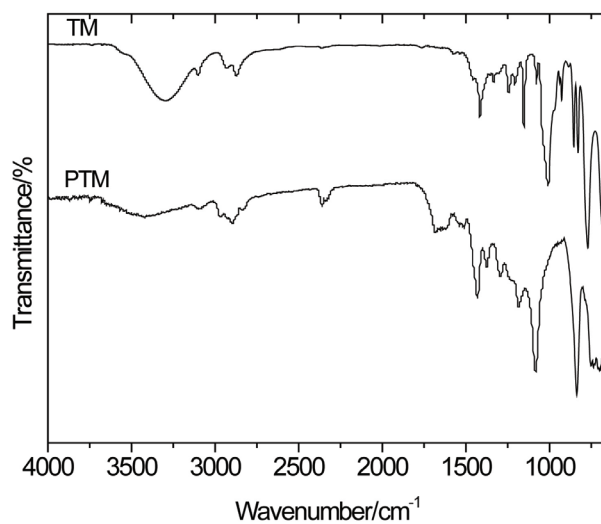


Figure S4. FT IR spectra of the monomer 3-thiophenemethanol (TM) and polymer poly(3-thiophenemethanol) (PTM).