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Synthesis and characterization of chiral polythiophenes: Poly [(*R*)-(−) and (*S*)-(+)-2-(3′-thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate]

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Abstract

(*R*)-(−) (**1**) and (*S*)-(+)-2-(3′-Thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate (**2**) monomers were synthesized, characterized, and polymerized in chloroform using $FeCl_3$ as an oxidizing agent. Molecular weights of 2.6×10^4 and 3.2×10^4 for **poly1** and **poly2**, respectively, were determined by SEC analysis. FTIR spectra of the polymers indicated the coupling of monomers through the α positions. UV–vis spectra showed absorption bands at $\lambda_{max} = 226$ and 423 nm for **poly1** and **poly2**, ascribed to transitions of side groups and polythiophene backbone, respectively. **Poly1** and **poly2** remained stable up to 210 °C. At higher temperatures, a two step weight loss degradation process was observed for both polymers by TGA analysis. ^{1}H NMR, in the presence of **Eu(tfc)$_3$**, and optical rotation measurements indicate the chiral properties of the monomers **1** ($[\alpha]_D^{28} = -76.2$) and **2** ($[\alpha]_D^{28} = +76.0$), and the maintenance of chirality after polymerization (**poly1** $[\alpha]_D^{28} = -29.0$ and **poly2** $[\alpha]_D^{28} = +28.4$, $c = 2.5$ in THF). According to scanning electron microscopic analysis, the polymers are highly porous.

Keywords: Chiral polymer; Polythiophene; Phenylglycine

1. Introduction

The development in the field of conducting polymers, since the first experiments with doped polyacetylene [1–3], is remarkable. Conducting polymer properties have been largely investigated in the last three decades, and a variety of materials have emerged with potential practical applications such as electrochromic devices [4,5], electromagnetic radiation shields [6], light-emitting diodes [7] and gas sensors [8–10]. Research on structural features [11], on electrochemical [12,13] and optical properties [14], on new synthetic methodologies [15–18], as well as on thin film formation [19,20], and other chemical and physical aspects of these materials have been undertaken and reported in the literature.

Polythiophene and its derivatives are among the most extensively studied conducting polymers. Several methodologies have been developed for the synthesis of new thiophene derivatives bearing different functional groups. They have been polymerized by different techniques and methodologies [21–23] giving rise to polythiophenes having properties such as solubility [24,25], self-doping capacity [26], and low band gaps [27,28].

Recently, research on optically active polythiophenes, substituted with stereogenic centers, has become of great interest due to their potential application as materials for enantioselective electrodes and membranes [29,30].

Here, we report the synthesis and characterization of poly[(*R*)-(−)-2-(3′-thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate] (**poly1**) and poly[(*S*)-(+)-2-(3′-thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate] (**poly2**). The monomers (*R*)-(−)-2-(3′-thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate (**1**) and (*S*)-(+)-2-(3′-thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate (**2**) were obtained

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through 3-(2′-iodoethyl)thiophene (**3**) nucleophilic substitution by (*R*)-(−) (**4**) or (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine (**5**) salts (basic medium), which are chiral selectors successfully used in Pirkle's stationary phases [31,32], applied in HPLC enantioselective analysis.

2. Experimental

2.1. Materials and methods

All reagents were purchased from Aldrich and Acros and used as received. The solvents, of analytical grade, were dried by conventional procedures and distilled prior to use [33].

The NMR spectra were recorded in a Varian Unity Plus equipment with frequency of 300 MHz for protons, in $CDCl_3$ solutions. UV–vis spectra were obtained in a Perkin–Elmer lambda 6 spectrophotometer, in THF solutions. FTIR spectra were obtained in a Bruker IFS66 spectrophotometer in KBr pellets. Thermal analyses were performed in a Schimadzu TGA50 thermobalance under air at a heating rate of 10 °C min^{-1}. Optical rotation measurements were carried out in a Perkin–Elmer 241 polarimeter, $c = 2.5$ in THF. Scanning electron microscopy was performed in a JEOL 6360 equipment. Elemental analysis determinations were performed in a Carlo Erba equipment. A Q-TOF mass spectrometer (Micromass, Manchester, UK) was used for fingerprinting and ESI–MS analysis.

Average number and weight molecular weights (M_n, M_w) were measured via size exclusion chromatography (SEC) against polystyrene (PS) standards using two Polymer Laboratories PLGel 5 μm Mixed-C columns, a Shodex RI-71 RI detector and a Shimadzu LC-10 AD pump, in THF, at 1.0 mL/min flow rate.

2.2. Synthesis

(*R*)-(−) (**4**) and (*S*)-(+)-*N*-(3,5-Dinitrobenzoyl)-α-phenylglycine (**5**) [74927-72-3] were synthesized, according to Pirkle's method [34], slightly modified by Navarro et al. [35], with yields of 88% and 91%, respectively.

3-(2′-Bromoethyl)thiophene [570070-76-5] was synthesized as described in the literature [36] with 62% yield (lit. 70%). ^1H NMR ($CDCl_3$): 7.33 (m, 1H, thiophene ring); 7.12–7.03 (m, 2H, thiophene ring); 3.61 (t, $J = 7.5$ Hz, 2H, CH_2) and 3.26 ppm (t, $J = 7.5$ Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 138.82; 127.56; 125.53; 121.61; 33.50 and 33.20 ppm. FTIR (KBr): 3102 ($\nu_{CH\ \alpha}$); 3045 ($\nu_{CH\ \beta}$); 2964 and 2857 (ν_{CH_2}) and 1275 cm^{-1} (ν_{CH_2Br}).

3-(2′-Iodoethyl)thiophene (**3**) [114896-65-0] was prepared using a procedure slightly modified from that described in the literature [37]: 60 mL of a KI (10.1 g, 61.1 mmol) acetone solution was added to the crude 3-(2′-bromoethyl)thiophene (10.6 g, 55.5 mmol) obtained by the procedure described above. The solution was stirred and refluxed overnight. The reaction mixture was filtered and the resulting solution distilled under reduced pressure. Compound **3** (11.2 g, 47 mmol) was obtained in 85% yield (lit. 82%).

^1H NMR ($CDCl_3$): 7.33 (m, 1H, thiophene ring); 7.12–6.99 (m, 2H, thiophene ring); 3.39 (t, $J = 6.9$ Hz, 2H, CH_2) and 3.27 ppm (t, $J = 6.9$ Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): 140.50; 127.55; 125.57; 121.26; 34,40 and 5.12 ppm. FTIR (KBr): 3102 ($\nu_{CH\ \alpha}$); 3045 ($\nu_{CH\ \beta}$); 2961 and 2826 (ν_{CH_2}) and 1169 cm^{-1} (ν_{CH_2I}).

(*R*)-(−) (**1**) or (*S*)-(+)-2-(3′-Thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate (**2**): 3.5 g of **4** or **5** (10.0 mmol) was added to 35 mL of dry CH_3CN solution containing **3** (3.3 g, 13.8 mmol), followed by the addition of 2.1 g (10.0 mmol) of proton-sponge® (1,8-bis(dimethylamino)naphthalene), and stirred at about 50 °C for 3 h. The mixture was separated on a silica gel column (70–230 mesh) eluted with hexane/ethyl acetate (8:2). The separated product was crystallized from $CHCl_3$/ether to give 51% (2.3 g, 5.0 mmol) of (*R*)-(−) monomer **1** (mp. 157–159 °C), *m/z* 456 $[M+H]^+$ or 49% (2.2 g, 4.8 mmol) of (*S*)-(+) monomer **2** (mp. 156–159 °C), *m/z* 456 $[M+H]^+$.

^1H NMR ($CDCl_3$): 9.14 (t, $J = 2.1$ Hz, 1H aromatic); 8.95 (d, $J = 2.1$ Hz, 2H aromatics); 7.71 (d, $J = 6.9$ Hz, 1H, NH); 7.42–7.32 (m, 5H phenyl); 7.18 (t, $J = 3.6$ Hz, 1H thiophene ring); 6.79 (d, $J = 3.6$ Hz, 2H thiophene ring); 5.75 (d, $J = 6.9$ Hz, 1H, CH); 4.44 (m, 2H, CH_2) and 2.96 ppm (m, 2H, CH_2).

^{13}C NMR ($CDCl_3$): 170.48; 161.94; 148.51; 137.12; 136.79; 135.39; 129.17; 128.99; 127.95; 127.43; 127.36; 125.68; 121.77; 121.36; 66.14; 57.36 and 29.20 ppm.

FTIR (KBr): 3292 (ν_{NH} amide); 3110–3050 ($\nu_{CH\ (\alpha\ and\ \beta)}$ thiophene ring and ν_{CH} phenyl); 2946 and 2875 (ν_{CH_2}); 1742 ($\nu_{C=O}$); 1658 ($\nu_{amide\ I}$); 1541 and 1345 (ν_{NO_2}) and 784 cm^{-1} ($\nu_{CH\ (\alpha)}$ thiophene ring).

Anal. Calcd. for **1** $C_{21}H_{17}N_3O_7S$ (455.44): C, 55.38; H, 3.76; N, 9.23; S, 7.04. Found: C, 55.26; H, 3.55; N, 9.03; S, 7.15. For **2**: C, 55.09; H, 3.60; N, 9.04; S, 7.10.

Optical rotation: $[\alpha]_D^{28} = -76.2$ for **1** and $[\alpha]_D^{28} = +76.0$ for **2**, $c = 2.5$ in THF.

2.3. Polymerization of monomers 1 and 2

Poly[(*R*)-(−)-2-(3′-thienyl)ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate] (**poly1**) and poly[(*S*)-(+)-2-(3′-thienyl)-ethyl *N*-(3″,5″-dinitrobenzoyl)-α-phenylglycinate] (**poly2**): **1** or **2** (100 mg; 0.2 mmol) dissolved in dry $CHCl_3$ (10 mL) was added dropwise to an $FeCl_3$ suspension (200 mg; 1.2 mmol) in 20 mL of dry $CHCl_3$ under N_2. The mixture was stirred for 48 h at room temperature. The polymer was then precipitated by the addition of CH_3OH, filtered and purified by Soxhlet extraction with CH_3OH. The purified polymer was dried under vacuum for 12 h. A reddish brown solid was obtained – 60 mg (60%) for **poly1** and 70 mg (70%) for **poly2**.

FTIR (KBr): 3292 (ν_{NH} amide); 3110–3050 ($\nu_{CH\ (\alpha\ and\ \beta)}$ thiophene ring and ν_{CH} phenyl); 2946 and 2875 (ν_{CH_2}); 1742 ($\nu_{C=O}$); 1658 ($\nu_{amide\ I}$); 1541 and 1345 (ν_{NO_2}).

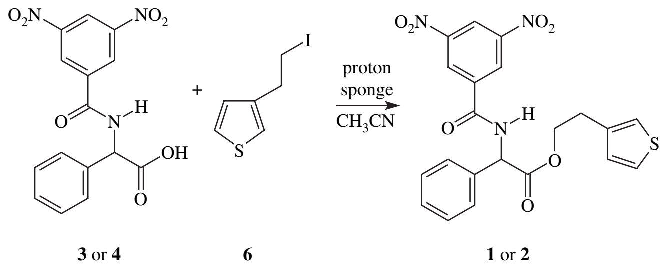
Anal. found for **poly1**: C, 53.32; H, 3.24; N, 8.60; S, 6.87. For **poly2**: C, 53.93; H, 3.25; N, 8.67; S, 6.96.

Optical rotation: $[\alpha]_D^{28} = -29.0$ for **poly1** and $[\alpha]_D^{28} = +28.4$ for **poly2**, $c = 2.5$ in THF.

3. Results and discussion

Monomers **1** and **2**, were synthesized in good yields, 51% and 49% respectively, following procedures described in the literature [34,35] (Scheme 1).

The ^{1}H NMR spectrum of **1** is shown in Fig. 1A. A chiral discrimination study of the enantiomers was done with the aid of the shift reagent [tris-(3-trifluoromethylhydroxymethylene)-(+)-camphorate] europium(III), **Eu(tfc)$_3$** [35]. The spectrum of the (*R*)-(−) enantiomer **1** in the presence of **Eu(tfc)$_3$** (Fig. 1B) showed a visible low field shifting of some specific



Scheme 1.

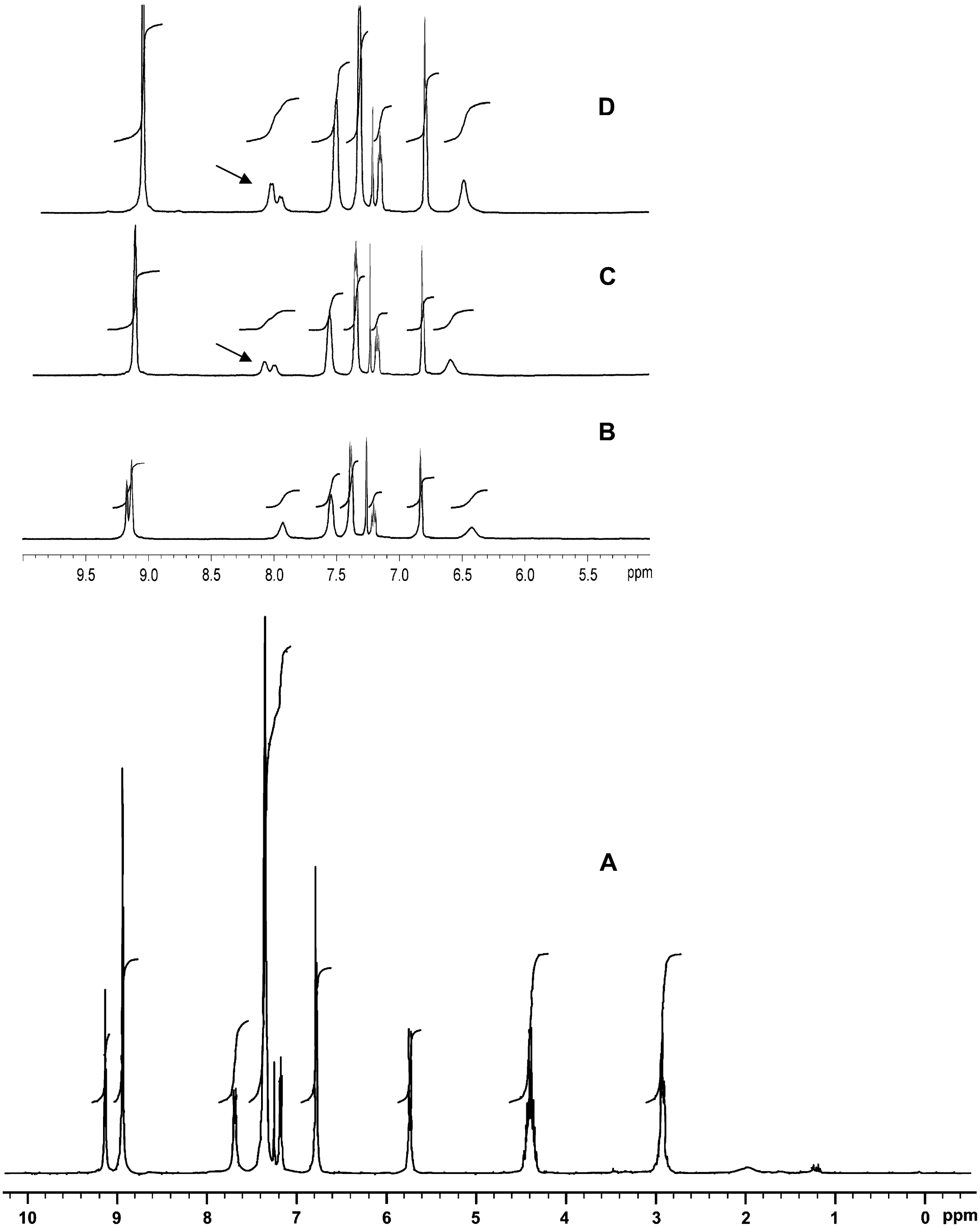


Fig. 1. ^{1}H NMR spectra (CDCl$_3$, 300 MHz) of **1** (A); **1** after addition of **Eu(tfc)$_3$** (B); mixture of **1** + **2** in the presence of **Eu(tfc)$_3$** (C), followed by an increasing amount of **2** (D).

peaks: 8.95 (2H, nitroaromatic), 7.71 (1H, NH), 7.42–7.32 (2H, phenyl) and 5.75 (1H, CH). It was not observed the splitting of any peak. When the same experiment was performed in a mixture of **1** and **2**, it was observed the same behaviour, but with the splitting of the amidic proton (NH) signal (Fig. 1C). Addition of increasing amounts of the (*S*)-(+) enantiomer **2** affects an increase of only one of the signals at 8.12 ppm (Fig. 1D). Therefore, the absence of NH splitting signal for ^{1}H NMR spectra of **1** or **2**, in the presence of **Eu(tfc)$_3$**, indicates a certain optical purity of these compounds.

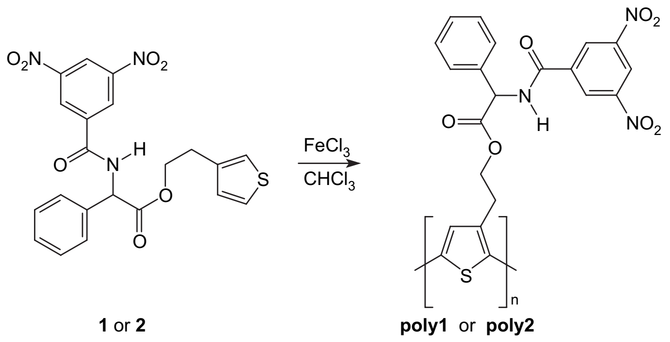
The monomers were polymerized by oxidative coupling with $FeCl_3$ in $CHCl_3$ (Scheme 2). The products **poly1** (60%) and **poly2** (70%) were obtained in good yields.

Polymer molecular weights obtained from SEC analysis were $M_w = 2.6 \times 10^4$, $M_n = 8.4 \times 10^3$, with polydispersity index (M_w/M_n) of 3.1 for **poly1**; and $M_w = 3.2 \times 10^4$, $M_n = 8.6 \times 10^3$, with polydispersity index of 3.8 for **poly2**.

The FTIR spectra of the monomers (Fig. 2B) show characteristic bands at 3292 cm^{-1}, attributed to the N–H stretching of the amide; in the range of 3110–3050 cm^{-1} attributed to the stretching of C–H(α) and C–H(β) of the thiophene ring and C–H of the phenyl group; at 2946 and 2875 cm^{-1} due to the CH_2 asymmetric and symmetric stretching, respectively; at 1742 cm^{-1} due to the carbonyl group and at 1658 cm^{-1} due to the amide groups; at 1541 and 1345 cm^{-1} due to the nitro groups.

As expected, the band at 784 cm^{-1}, attributed to C–H(α) bending deformation of thiophene, is present in the spectra of the monomers but disappears in the polymers spectra (Fig. 2A), indicating polymerization through α–α coupling. The band due to C–H(α) stretching, which is also a diagnostic band for polymer formation through α–α coupling, cannot be used for that purpose here, due various types of C–H aromatic bonds present in the molecule [38,39].

Poly1 and **poly2** exhibited identical UV–vis spectra (Fig. 3), with absorption bands at $\lambda_{max} = 226$ and 423 nm, in THF solution. The broad band with maximum at 423 nm is due to the polymers π–π* absorption indicating a conjugated backbone with low coplanarity of the thiophene rings, as expected for a polythiophene with bulky substituents. The highest energy absorption at $\lambda_{max} = 226$ nm is due to the nitroaromatic substituent groups in the main chain. In the monomers (**1** and **2**), the nitroaromatic group absorption appears at $\lambda_{max} = 248$ nm.



Scheme 2.

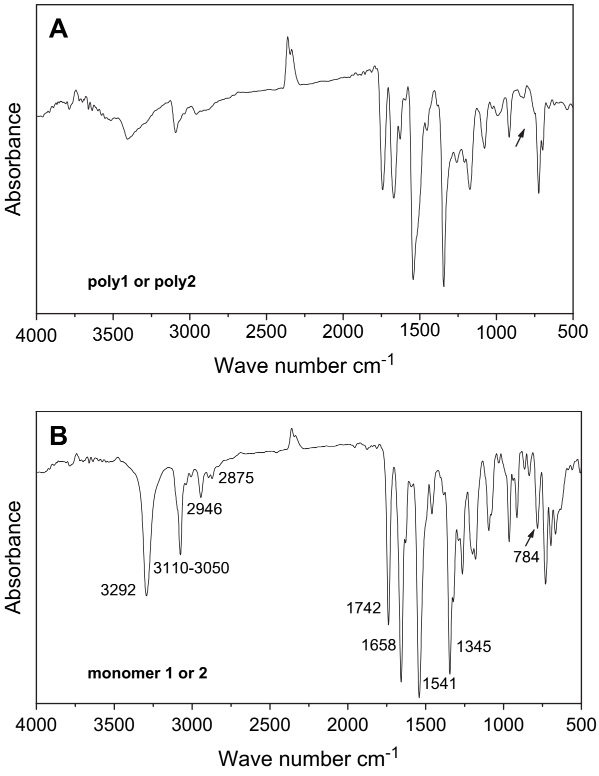


Fig. 2. Infrared spectra of **poly1** or **poly2** (A) and monomers **1** or **2** (B).

The thermogravimetric analysis (TGA) curves (not presented here) are very similar for both polymers. Two decomposition steps are seen after a weight loss step of *ca.* 1% which we attribute to the loss of residual solvent in the samples. The steps representing decomposition of the polymers are detailed in Table 1.

For **poly1**, the first decomposition step begins at 245 °C and goes to 443 °C with maximum weight loss at 326 °C. While for **poly2**, these values are 210, 434 and 325 °C, respectively. For both polymers, this step represents a weight loss of *ca.* 38%, which corresponds roughly to the mass percent of the dinitrobenzoyl moiety. The second decomposition step begins at 443 °C and goes to 946 °C, with maximum weight loss at

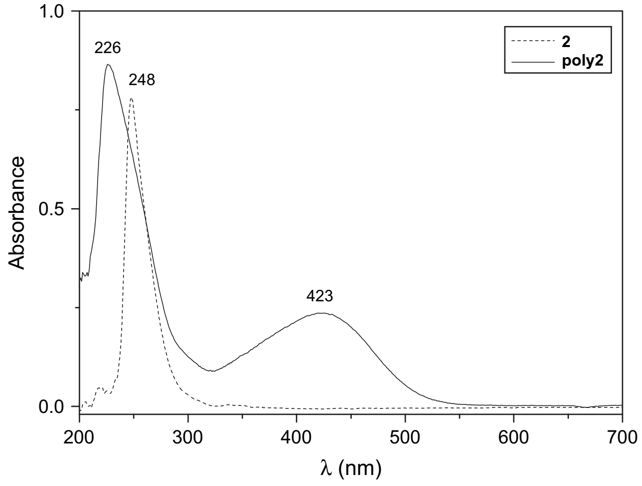


Fig. 3. UV–vis spectra of **2** and **poly2** in THF solution.

Table 1
Results of TGA analysis for **poly1** and **poly2**, under air and heating rate of 10 °C min^{-1}

Polymer	Decomposition temperature (°C)		
	T_i[a]	T_{max}[b]	T_f[c]
Poly1	245	326	443
	443	676	946
Poly2	210	325	434
	435	667	945

[a] Initial temperature.
[b] Maximum temperature.
[c] Final temperature.

676 °C, for **poly1**, and 435, 945, and 667 °C, respectively for **poly2**. This step corresponds to further fragmentation of the polymer including the main chain backbone. A residual mass of 28% remains for **poly1** and 30% for **poly2**, at 950 °C.

Optical activity is maintained after polymerization with similar rotations for **poly1** and **poly2**. The specific optical rotation observed for **poly1** was $[\alpha]_D^{28} = -29.0$, and for **poly2** it was $[\alpha]_D^{28} = +28.4$, both with $c = 2.5$ in THF. The optical rotation was also measured for a copolymer of **1** and **2**, obtained using the same polymerization conditions as those for the synthesis of **poly1** and **poly2**, and a comonomer feeding ratio of 1:1. The value obtained for this copolymer optical rotation was $[\alpha]_D^{28} = -0.3$ ($c = 2.5$ in THF).

Fig. 4 shows the SEM of the polymers. The images of cross-sections revealed high porosity throughout the cross-section with pores ranging in diameter from *ca.* 1 to 10 μm. The surface was nonporous and uniform.

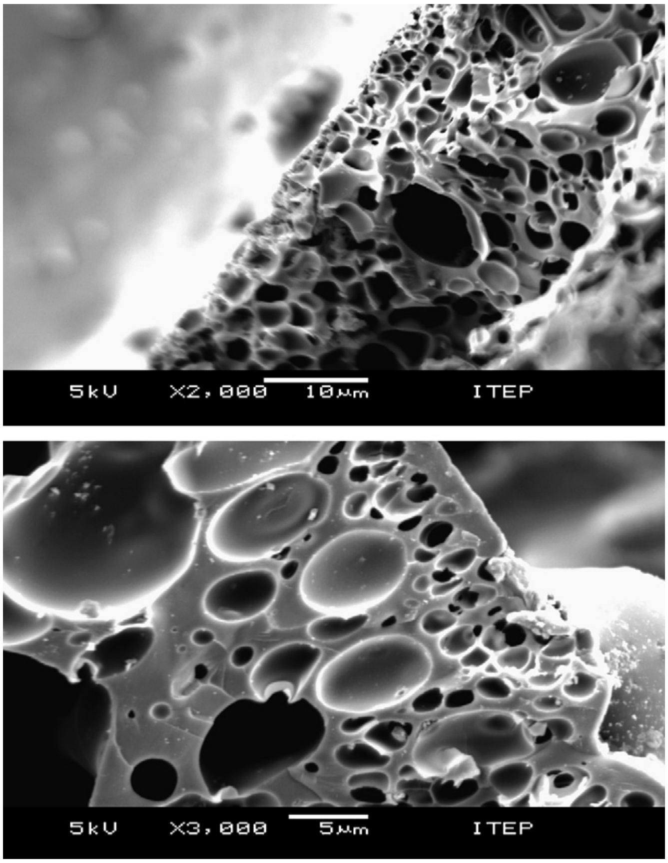


Fig. 4. SEM of the polymers. Top: **poly2**, 2000× magnification (scale bar, 10 μm); bottom: **poly1** 3000× magnification (scale bar 5 μm).

4. Conclusion

Enantiomerically pure thiophenes bearing optically active substituent group (**1** and **2**), as evidenced by ^{1}H NMR (shift reagent) and polarimetric measurements, were polymerized giving rise to optically active polythiophenes (**poly1** and **poly2**). The polymers are highly conjugated and present absorption band (THF) in the UV–vis region typical of β-substituted thiophenes. SEM analysis showed highly porous materials, while TGA indicated good thermal stability, up to 210 °C.

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