ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 775–784

polymer

www.elsevier.com/locate/polymer

A poly(alkylsulfany)thiophene functionalized with carboxylic groups

R. Cagnoli, A. Mucci *, F. Parenti, L. Schenetti **, M. Borsari, A. Lodi, G. Ponterini

Dipartimento di Chimica, Centro SCS, Università di Modena e Reggio Emilia and INSTM, via G. Campi 183, 41100 Modena, Italy

Received 1 September 2005; received in revised form 6 December 2005; accepted 6 December 2005

Abstract

Different routes, based on the Stille coupling, to the obtainment of a polythiophene bearing a carboxyhexylsulfanyl chain every two thiophene rings (PTCOOH) are here reported and discussed. Two PTCOOHs with different chain lengths were obtained: the shorter by hydrolysis of a polymeric ester precursor and the longer by direct Stille coupling from suitable monomers. They possess similar electrochemical properties but behave differently when aggregation and fluorescence are concerned. The PTCOOH obtained by hydrolysis is found to be fluorescent in a good solvent such as THF, and its fluorescence quantum yield decreases as the extent of aggregation increases. The polymer obtained by direct Stille coupling is less fluorescent, consistently with its proneness to aggregate. The PTCOOH obtained by hydrolysis is therefore more promising in view of the build-up of solid-state devices with exploitable fluorescence properties.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Polythiophene; Alkylsulfanyl groups; Carboxylic acids

1. Introduction

The design, synthesis and characterization of organic semiconducting materials able to detect and transduce physical or chemical information into electrical or optical signals represent by now one of the most interesting fields of research [1]. Substituted polythiophenes (PTs) play a relevant role in the field of organic semiconductors, having good stability and permitting the insertion of functionalities which allow processability in different environments [2]. These materials combine the electroactive properties of PTs with those due to the side chain groups, and PT-based devices, as modified electrodes or sensors, have been developed for applications both in gas phase and in solution in order to identify organic compounds, ions and biomolecules [2,3]. Moreover, in spite of an efficient singlet-to-triplet intersystem crossing, associated with the enhancement of spin–orbit coupling due to the S atoms [4], oligo- and PTs often exhibit rather high fluorescence quantum yields in solution: values between 0.1 and 0.4 are commonplace [4a,5] although much lower values were found for poly-disubstituted thiophenes [5,6]. When such compounds are deposited as cast or spin-coated films a batochromically shifted fluorescence is emitted by aggregated traps. Its intensity is often reduced with respect to that of solutions but it is not completely quenched in many instances [5,7]. This characteristic is exploited in the fabrication of electroluminescent devices [8].

Polymers bearing a carboxylic side chain are very intriguing since they possess sites for molecular interaction, metal-ion detection and self-assembling through hydrogen bond formation. Furthermore, they can be employed as the negatively charged part of polyelectrolyte multilayers [9] and multicomponent devices, such as solar cells [10], organic thin-film transistors [11], chemo- [12] and biosensors [2,13].

The coupling of the carboxylic group with an alkylsulfanyl chain, bonded through its sulfur atom to the β-position of the thiophene ring, was chosen on the basis of our previous studies on oligo- and poly(alkylsulfanyl)thiophenes, which have shown that the sulfur atom positively influences the characteristics of these PTs in comparison to polyalkylthiophenes, especially when filmability and p- and n-doping are concerned [14]. Moreover, we recently reported the synthesis of a cysteine-functionalized polythiophene, obtained from the Stille copolymerization of *N*-(*tert*-butoxycarbonyl)-*S*-(2,5-dibromothien-3-yl)-L-cysteinate and 2,5-bis(trimethylstannyl)thiophene, which showed a high self-assembling behaviour probably associated not only with the presence of the cysteinic side chains but also with the alternation of substituted and unsubstituted thiophene rings [15]. We then turned our

---

* Corresponding authors. Tel.: +39 59 2055077; fax: +39 59 373543.

** Tel.: +39 59 2055076; fax: +39 59 373543.

E-mail addresses: mucci.adele@unimo.it (A. Mucci), schene@unimo.it (L. Schenetti).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.12.016

attention towards PTs carrying alkylsulfanyl chains functionalized with carboxylic moieties (carboxyalkylsulfanyl groups), in order to deeper understand the role of carboxylic and related groups in the physical properties of PTs carrying one substituent in every two thiophene rings.

Here, we report on the synthesis and properties of a carboxyalkylsulfanyl PT (PTCOOH), bearing a side chain every two thiophenes, which has been recently tested in photoactive devices in conjunction with single wall carbon nanotubes, proving to be a material of high current interest [16]. Different synthetic routes were explored, two based on the post-functionalization from polymeric precursors, namely a nitrile and a methyl carboxylate, and one on the direct Stille coupling of suitable monomers. 7-(3-Thienylsulfanyl)heptanenitrile (**1**), 7-(3-thienylsulfanyl) heptanoic acid (**2**) and methyl 7-(3-thienylsulfanyl) heptanoate (**3**) are the base units of the PTs involved in the present work (Scheme 1).

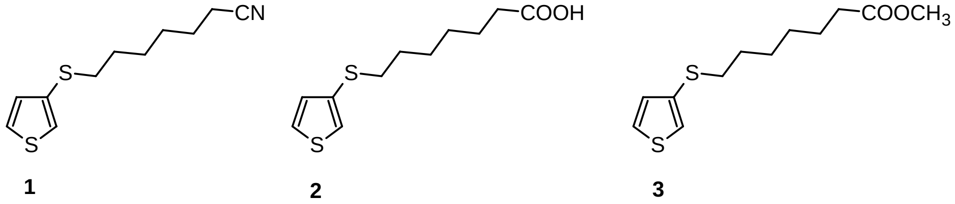
The Stille reaction was utilized at the first stage to copolymerize the 2,5-dibromoderivatives of **1** and **3** with 2,5-bis(trimethylstannyl)thiophene and the resulting polymers, poly[7-(3-thienylsulfanyl)heptanenitrile-*co*-thiophene] (PTCN) and poly{[methyl 7-(3-thienylsulfanyl)heptanoate]-*co*-thiophene} (PTCOOMe), were then hydrolyzed. The hydrolysis of the nitrile polymer presented a number of difficulties, whereas that of the ester proceeded in a much simpler way, generating the desired poly{[7-(3-thienylsulfanyl)heptanoic acid]-*co*-thiophene} (PTCOOH). Eventually, the Stille coupling was directly applied to the 2,5-dibromoderivative of **2**. All the polymers synthesized were characterized through gel permeation chromatography (GPC), NMR and UV–vis spectroscopy. We also give an account on the cyclic voltammetric (CV) properties of cast films of PTCOOH and on the steady-state fluorescence properties of PTCOOH in solution and in solid films.

2. Experimental section

2.1. Materials and methods

All air- or moisture-sensitive reactions were performed under argon with dry glassware. All solvents were dried by standard procedures. All reagents were purchased by Aldrich and Acros and used as received unless otherwise indicated. 2,5-Bis(trimethylstannyl)thiophene **4** was obtained according to Ref. [17].

GPC was carried out on a Hewlett–Packard system equipped with a Hewlett–Packard 5μ mixed PLgel column and a diode-array UV detector, using THF as the eluant, with a flow rate of 1.0 mL min^{-1}, at room temperature. The GPC system was calibrated using a series of monodisperse polystyrene standards. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 operating at 400.13 and 100.61 MHz, respectively. UV–vis spectra were recorded using a Perkin–Elmer Lambda Bio 20 and a Varian Cary 100 Scan UV–visible spectrophotometers. Cyclic voltammetric measurements on a properly coated working electrode were performed in CH$_3$CN solutions of the base electrolyte tetrabuthylammonium tetrafluoborate (TBABF$_4$) 0.1 M under argon atmosphere at 25 °C. All the measurements were carried out with a PAR 273A Model potentiostat/galvanostat. The synthesized polymers were deposited on a glassy carbon working electrode (GCE) by evaporation at 35 °C of a DMSO solution. Before the deposition, the GCE were polished with 0.05 μm alumina powder and then treated in an ultrasonic pool for 10 min before use. As the reference and the counter electrode, a saturated calomel electrode (SCE) and a Pt ring were used, respectively. All the peak potential values are referred to SCE and found reproducible within ±0.01 V. Steady-state fluorescence spectra were measured with a Jobin Yvon-Spex Fluoromax 2 spectrofluorometer. Emission spectra were corrected for the instrumental sensitivity, while excitation spectra were only corrected for the xenon lamp spectral profile. Throughout the paper the term fluorescence quantum yield (Φ_F) is given an operational meaning: $\Phi_F = \Phi_F^{st}\mathrm{Ar}/\mathrm{Ar}^{st}$, where Ar are the integrated areas of the whole corrected emission observed upon exciting at a wavelength at which the sample and the standard (st) had the same absorbances. Due to the complexity of the absorption and emission spectra of some of the samples investigated, we did not attempt to resolve such spectra and obtain the information necessary to calculate quantum yields of single species (as we did, for simpler systems, in Ref. [18]). Fluorescein in 0.1 N aqueous NaOH ($\Phi_F = 0.85$ [19]), acridine orange HCl in ethanol ($\Phi_F = 0.46$ [19]) and diethyloxadicarbocyanine in ethanol ($\Phi_F = 0.49$ [20]) were employed as standards. For these measurements, solution absorbances were below 0.15, while film maximum absorbances did not exceed 0.23. Φ_F values of films were estimated using thin layers (0.1 mm) of solutions of three standards above kept within two quartz plates as the reference systems. The usual refractive index correction (n^2) was applied for all the samples in solution. All fluorescence measurements on solid films or thin solution layers (from 0.1 to 1 mm) were performed at an incidence angle of about 60° or about 30° so as to maximize the fluorescence vs. scattered light ratio. Small fluctuations of the results associated with small differences in excitation geometry



Scheme 1. Derivatives **1–3**.

from one sample to the other were averaged out over several measurements, from two to five.

2.2. Synthesis of 7-(3-thienylsulfanyl)heptanenitrile **1**

To a solution of 3-bromothiophene (4.29 g, 26.3 mmol) in anhydrous Et_2O (24 mL) cooled to −78 °C under argon atmosphere, a solution of *n*-butyllithium (1.6 M in hexane, 17.3 mL) was added dropwise and the mixture was stirred at −78 °C for 30 min. Elemental sulfur (0.88 g, 27.6 mmol) was then added in one portion, and stirring was maintained for an additional 40 min at the same temperature. The reaction mixture was allowed to warm to 20 °C and stirred at this temperature for 5 min. A solution of 7-bromoheptanenitrile (10.0 g, 52.6 mmol) was slowly added to the mixture cooled to 0 °C, which was then left under stirring overnight at room temperature. After addition of HCl 1 N to pH 3, the reaction mixture was extracted with CH_2Cl_2 (2×15 mL), the organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. The excess of 7-bromoheptanenitrile was separated by distillation (0.01 mm Hg, 86 °C). The resulting oil was purified by flash chromatography on silica gel (petroleum ether/Et_2O 95:5 → 80:20) to give pure compound **1** as a brown-orange oil (4.21 g, 71%). ^1H NMR (400.13 MHz, $CDCl_3$, TMS): $\delta = 1.45$ (m, 4H, 2γ-CH_2), 1.63 (m, 4H, 2β-CH_2), 2.34 (t, 2H, $J = 6.8$ Hz, CH_2CN), 2.85 (t, 2H, $J = 6.9$ Hz, CH_2S), 7.02 (dd, 1H, $J = 1.3$, 5.0 Hz, H-4), 7.13 (dd, 1H, $J = 1.3$, 3.0 Hz, H-2), 7.32 (dd, 1H, $J = 3.0$, 5.0 Hz, H-5). ^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): $\delta = 17.1$ (CH_2CN), 25.2 (CH_2CH_2CN), 27.7 ($CH_2CH_2CH_2S$), 28.2 ($CH_2CH_2CH_2CN$), 29.0 (CH_2CH_2S), 35.1 (CH_2S), 119.7 (CN), 123.4 (C-2), 126.2 (C-5), 129.7 (C-4), 131.9 (C-3). Anal. Calcd for $C_{11}H_{15}NS_2$: C, 58.62; H, 6.71; N, 6.21; S, 28.46. Found: C, 58.53; H, 6.78, N, 6.17; S, 28.08.

2.3. Synthesis of 7-[(2,5-dibromothien-3-yl)sulfanyl]heptanenitrile **1a**

N-Bromosuccinimide (NBS) (0.98 g, 5.5 mmol) was added to a solution of **1** (0.50 g, 2.2 mmol) in CH_2Cl_2 (24 mL). The reaction mixture was warmed to reflux and stirred for 18 h. After cooling, the organic solution was washed with water ($2\times$ 15 mL), dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography on silica gel (petroleum ether/Et_2O 95:5 → 80:20) to give pure compound **1a** as a brown oil (0.57 g, 68%). ^1H NMR (400.13 MHz, $CDCl_3$, TMS): $\delta = 1.45$ (m, 4H, 2γ-CH_2), 1.63 (m, 4H, 2β-CH_2), 2.32 (t, 2H, $J = 6.8$ Hz, CH_2CN), 2.81 (t, 2H, $J = 6.9$ Hz, CH_2S), 6.90 (s, 1H, H-4). ^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): $\delta = 17.1$ (CH_2CN), 25.2 (CH_2CH_2CN), 27.6 ($CH_2CH_2CH_2S$), 28.2 ($CH_2CH_2CH_2CN$), 29.1 (CH_2CH_2S), 35.1 (CH_2S), 111.1 (C-5), 113.4 (C-2), 119.6 (CN), 132.4 (C-4), 133.6 (C-3). Anal. Calcd for $C_{11}H_{13}Br_2NS_2$: C, 34.48; H, 3.42; N, 3.66; S, 16.74. Found: C, 34.43; H, 3.40; N, 3.56; S, 16.54.

2.4. Synthesis of 7-[(2,5-dibromothien-3-yl)sulfanyl]heptanoic acid **2a**

To a solution of nitrile **1a** (0.31 g, 0.78 mmol) in EtOH (2 mL), 40% aqueous KOH (1.5 mL) was added, and the reaction mixture was stirred at 78 °C for 18 h. After cooling to room temperature, 10% aqueous H_2SO_4 was added and pH adjusted to 3. The white solid formed was filtered, washed with water and dried to give 0.31 g (99%) of **2a**. ^1H NMR (400.13 MHz, $CDCl_3$, TMS): $\delta = 1.35$ (m, 2H, $CH_2CH_2CH_2COOH$), 1.44 (m, 2H, $CH_2CH_2CH_2S$), 1.59 (m, 2H, CH_2CH_2S), 1.64 (m, 2H, CH_2CH_2COOH), 2.35 (t, 2H, $J = 6.8$ Hz, CH_2COOH), 2.82 (t, 2H, $J = 6.9$ Hz, CH_2S), 6.89 (s, 1H, H-4). ^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): $\delta = 24.5$ (CH_2CH_2COOH), 28.5 ($CH_2CH_2CH_2COOH$), 28.1 ($CH_2CH_2CH_2S$), 29.3 (CH_2CH_2S), 33.8 (CH_2COOH), 35.2 (CH_2S), 111.0 (C-5), 113.2 (C-2), 132.4 (C-4), 133.8 (C-3), 179.3 (COOH). Anal. Calcd for $C_{11}H_{14}Br_2O_2S_2$: C, 32.85; H, 3.51; S, 15.95. Found: C, 32.92; H, 3.46; S, 15.75.

2.5. Synthesis of methyl 7-[(2,5-dibromothien-3-yl)sulfanyl]heptanoate **3a**

To a vigorously stirred solution of acid **2a** (0.273 g, 0.68 mmol) in CH_3OH (2.5 mL) cooled to −10 °C, $SOCl_2$ (88 μL, 1.21 mmol) was added dropwise while keeping the solution at a temperature below 0 °C. The reaction mixture was left to warm to room temperature and stirring continued for another 45 min. The solvent was then partly evaporated to small volume, CH_2Cl_2 (5 mL) added, and the organic solution washed with water (5 mL), dried ($MgSO_4$) and evaporated to afford ester **3a** (0.277 g, 98%) as a yellow oil. ^1H NMR (400.13 MHz, $CDCl_3$, TMS): $\delta = 1.39$ (m, 4H, 2γ-CH_2), 1.61 (m, 4H, 2β-CH_2), 2.31 (t, 2H, $J = 6.8$ Hz, CH_2COOH), 2.82 (t, 2H, $J = 6.9$ Hz, CH_2S), 3.67 (s, 3H, OCH_3), 6.90 (s, 1H, H-4). ^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): $\delta = 24.7$ ($CH_2CH_2COOCH_3$), 28.1 ($CH_2CH_2CH_2S$), 28.6 ($CH_2CH_2CH_2COOCH_3$), 29.2 (CH_2CH_2S), 33.9 (CH_2COOCH_3), 35.2 (CH_2S), 111.0 (C-5), 113.0 (C-2), 132.4 (C-4), 133.9 (C-3), 174.0 (CO). Anal. Calcd for $C_{12}H_{16}Br_2O_2S_2$: C, 34.63; H, 3.87; S, 15.41. Found: C, 34.75; H, 3.66; S, 15.25.

2.6. Synthesis of poly[7-(3-thienylsulfanyl)heptanenitrile-co-thiophene] PTCN

In a screw capped Schlenk tube equipped with a perforable septum, a solution of **1a** (0.77 g, 2.0 mmol) and **4** (0.82 g, 2.0 mmol) in 6 mL of anhydrous THF/DMF 1:1 was added dropwise to 50.0 mg (4.3×10^{-2} mmol) of $Pd(PPh_3)_4$ in 2 mL of anhydrous THF/DMF 1:1 under argon. The mixture was stirred at 90 °C for 60 h and concentrated to small volume, then CH_3OH (5 mL) was added. The red precipitate was filtered and extracted in Soxhlet with CH_3OH (14 h), *n*-pentane (10 h) and $CHCl_3$ (14 h). $CHCl_3$ was removed under vacuum giving 0.35 g (60% yield) of PTCN as a dark reddish film. IR (KBr) ν 3066 (β-CH), 2968, 2930, 2862 (CH_2), 2244 ($C\equiv N$), 1484, 818, 792 (Th) cm^{-1}.

2.7. Synthesis of poly{[methyl 7-(3-thienylsulfanyl)heptanoate]-co-thiophene} PTCOOMe

Dibrominated ester **3a** (0.58 g, 1.39 mmol) was reacted with **4** (0.73 g, 1.78 mmol) as described for **1a** to give, after analogous workup, 0.20 g (43% yield) of PTCOOMe as a dark golden-reddish film. IR (KBr) ν 3065 (β-CH), 2960, 2930, 2856 (CH_2), 1737 (C=O), 1482 (Th), 1260 (CH_2S), 1200, 1172 (C–O–C), 820, 794 (Th) cm^{-1}.

2.8. Hydrolysis of PTCOOMe

To a solution of PTCOOMe (0.20 g) in THF (20 mL), a methanolic solution of NaOH (10%, 20 mL) was added. The mixture was stirred at 70 °C for 3 h, diluted with water (20 mL), the organic solvent were evaporated under reduced pressure, and 10% aqueous H_2SO_4 was added to adjust pH to 3. The red solid formed was filtered, washed with water and dried to afford poly{[7-(3-thienylsulfanyl)heptanoic acid]-*co*-thiophene} (**PTCOOH**) (0.19 g, 99%) as a dark reddish powder. IR (KBr) ν 3067 (β-CH), 2959, 2930, 2856 (CH_2), 1708 (C=O), 1485 (Th), 1261 (CH_2S), 820, 793 (Th) cm^{-1}.

2.9. Direct synthesis of PTCOOH

Dibromated acid **2a** (0.54 g, 1.34 mmol) was reacted with **4** (0.714 g, 1.74 mmol) as described for **1a**. The purple-red precipitate formed was left to settle from the reaction mixture and decanted. Addition of CH_3OH to the surnatant enabled a second portion of precipitate to be recovered after 12 h. The two solid fractions were washed with water and CH_3OH, solubilized in the minimum amount of saturated aqueous NaOH and re-precipitated by adding 10% aqueous H_2SO_4 to pH 3, filtered, and dried to obtain 62 mg (14%) of a dark purple powder and 162 mg (37%) of a golden scaly solid, respectively. IR (KBr) ν 3067 (β-CH), 2930, 2862 (CH_2), 1702 (C=O), 1486 (Th), 1255 (CH_2S), 832, 792 (Th) cm^{-1}.

3. Results and discussion

3.1. Synthesis of starting monomers

The Stille coupling is based on the reaction between a halo- and a stannyl derivative in the presence of a palladium catalyst [21]. The introduction of these complementary functionalities onto two different thiophene rings enables the synthesis of PTs alternating substituted and unsubstituted thiophene rings to be achieved. We generated copolymers of unsubstituted thiophene and derivatives **1–3** by coupling 2,5-bis(trimethylstannyl)thiophene **4** and the 2,5-dibromo derivatives **1a–3a**, whose synthesis is outlined in Scheme 2.

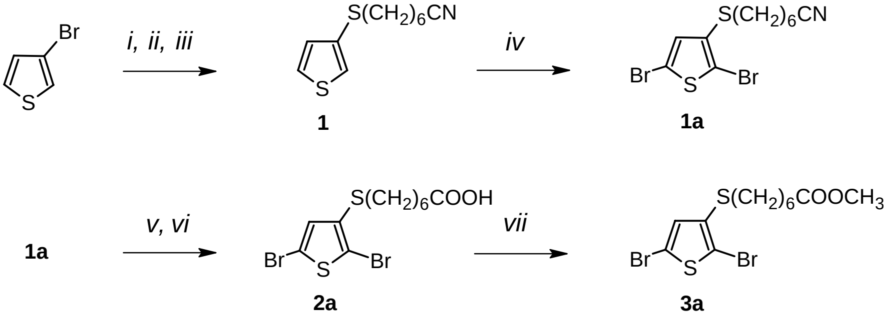
7-(3-Thienylsulfanyl)heptanenitrile **1** was prepared (71% yield) through a one pot reaction from 3-bromothiophene after lithium–bromine exchange with *n*-butyllithium at low temperature, followed by treatment with elemental sulfur which generated the lithium salt of 3-mercaptothiophene, that was then allowed to react at room temperature with 7-bromoheptanenitrile [22]. Bromination with NBS of **1** gave 7-[(2,5-dibromothien-3-yl)sulfanyl]heptanenitrile **1a** in a 68% yield. Hydrolysis of **1a** in basic conditions enabled 7-(3-thienylsulfanyl)-heptanoic acid **2a** to be obtained (99%), from which the methyl ester **3a** was synthesized by treatment with methanol and thionyl chloride (98%).

The reaction pathway here reported is characterized by only one bromination step, and it requires only a chromatographic purification in order to separate the by-products (especially monobrominated derivatives). The successive conversions of the nitrile **1a** into the carboxylic acid **2a** and the methyl ester **3a** afford products pure enough to be utilized without further purification. On the contrary, bromination of **2** and **3** requires a chromatographic purification step for each product and leads to **2a** and **3a** in lower yields (46 and 63%, respectively).

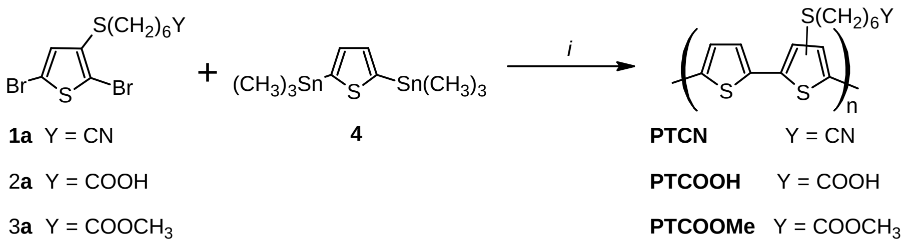
3.2. Polymerization through Stille coupling

The Stille coupling was, at a first stage, applied to **1a** and **3a** (Scheme 3), with the aim of obtaining PTCOOH after hydrolysis of PTCN and PTCOOMe. In fact, we have no knowledge of the application of the Stille coupling to substrates carrying free carboxylic groups, and even recently a paper has reported on the application of this reaction to an ester functionalized thiophene, from which the carboxylic function was thermally restored [10a].

The coupling of **1a** or **3a** and **4** was done in anhydrous THF/DMF at 100 °C for 60 h in the presence of $Pd(PPh_3)_4$ as



Scheme 2. Reagents and conditions: (i) *n*-BuLi, Et_2O, −78 °C, 30 min; (ii) S_8, −78 °C, 40 min; (iii) 7-bromoheptanenitrile, room temperature, overnight; (iv) NBS, CH_2Cl_2, 50 °C, 18 h; (v) EtOH/KOH 40%, 75 °C, overnight; (vi) H_2SO_4 10%; (vii) $SOCl_2$, MeOH, room temperature, 45 min.



Scheme 3. Reagents and conditions: (i) $Pd(PPh_3)_4$, THF/DMF 1:1, 90 °C, 60 h.

catalyst (60 and 43% yield, respectively). The free standing films result soluble in $CHCl_3$, CH_2Cl_2, THF, DMSO, *N*-methylpyrrolidone, and insoluble in CH_3CN, H_2O and CH_3OH.

After a number of attempts in different acidic and basic conditions, the hydrolysis of PTCN was effective in glycerol (KOH 30%, 125 °C, 7 days), but the purification of the product from the solvent presented serious problems due to the formation, during the work-up, of dense jelly phases, corresponding to the retention of glycerol up to about one hundred times the weight of the polymer.

Hydrolysis of PTCOOMe with sodium hydroxide (10% in CH_3OH) in THF afforded much more easily the desired polymer, denoted PTCOOH (99% yield). PTCOOH is soluble in DMSO, DMF and *N*-methylpyrrolidone, partially soluble in THF, and insoluble in $CHCl_3$, CH_2Cl_2, CH_3OH, CH_3CN.

Confiding on the success of the Stille reaction with **1a** and **3a** as substrates, we applied it directly on the acid **2a**. Two fractions were obtained, the former insoluble (14% yield) and the latter soluble (37% yield) in the reaction medium, with an overall yield analogous to that of the same reaction applied to **3a**. The molecular weight analysis show that spontaneous fractionation of PTCOOH occurred in the reaction medium and that only the former fraction, characterized by a lower solubility in THF/DMF with respect to that of the PTCOOH obtained by hydrolysis, is polymeric.

3.3. NMR characterization

The ^1H NMR spectra of PTCN, PTCOOMe and of hydrolyzed PTCOOH are reported in Fig. 1. The thienyl protons are found around 7.1 ppm in $CDCl_3$ and 7.3 ppm in DMSO-d_6, whereas the aliphatic regions show the typical signals due to the protons of the alkylsulfanyl chains terminating with three different functionalities. Signal from the $CH_2(\alpha)$ to the nitrile group of PTCN is found at 2.29 ppm, very close to that of the $CH_2(\alpha)$ to the ester group of PTCOOMe, which is characterized by the CH_3O signal at 3.64 ppm. ^1H NMR spectrum of hydrolyzed PTCOOH (DMSO-d_6 solution) displays the characteristic signal from the carboxylic group at 11.85 ppm and the disappearance of that of CH_3O, confirming the complete hydrolysis of PTCOOMe. Broad components are found both in the aromatic and in the aliphatic regions of ^1H NMR spectra of three polymers, indicating the presence of aggregated phases. It is to be noted that these broad features heavily affect the ^1H NMR spectrum of the PTCOOH obtained from the direct Stille coupling between **2a** and **4**, suggesting a higher aggregation degree for this polymer (Fig. 1(d)).

^1H, ^{13}C inverse-detection NMR spectroscopy, which has been routinely applied by us to the regiochemical characterization of PTs, since 1995, [23], fails in the detection of carbon signals of the thiophene rings of the present polymers, due to the short spin–spin relaxation times induced by the aggregation process, and only the assignment of the aliphatic chain proton and carbon signals is achieved (Table 1).

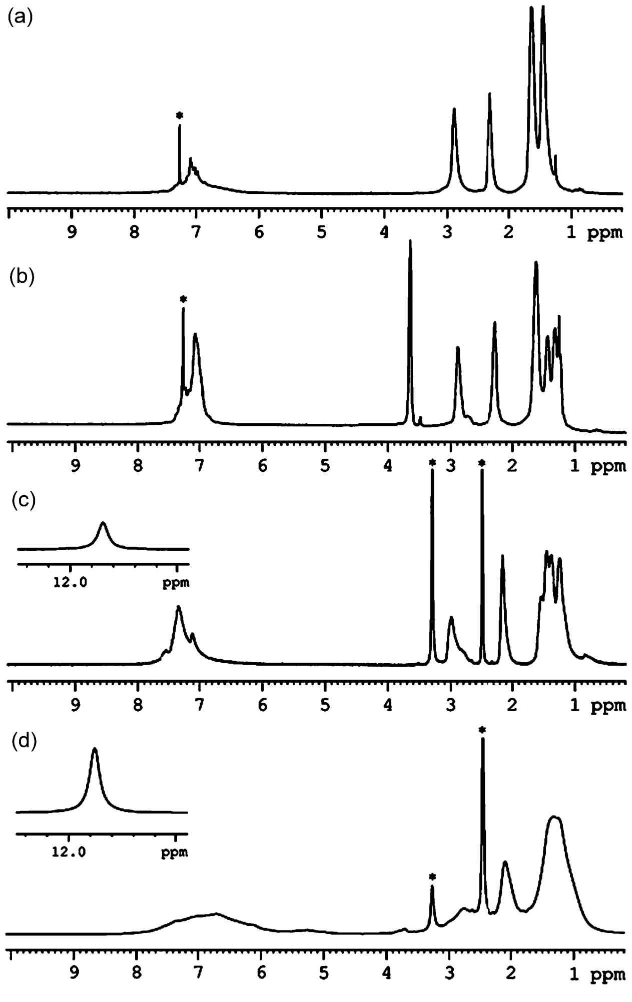


Fig. 1. ^1H NMR spectra of (a) **PTCN** in $CDCl_3$, (b) **PTCOOMe** in $CDCl_3$, (c) hydrolyzed **PTCOOH** in DMSO-d_6 and (d) **PTCOOH** derived from Stille coupling of **2a** and **4** in DMSO-d_6. Asterisks denote solvent and water signals.

Table 1
^1H and ^{13}C chemical shifts (δ in ppm, TMS)

Polymer (solvent)	$\mathrm{S}CH_2$	$\mathrm{SCH_2}CH_2$	$\mathrm{SCH_2CH_2}CH_2$	$CH_2\mathrm{CH_2CH_2Y}$	$CH_2\mathrm{CH_2Y}$	$CH_2\mathrm{Y}$	CN/C=O	Me/H
PTCN ($CDCl_3$)								
^1H	2.89 (HT); 2.86 (HH)	1.64	1.44	1.44	1.64	2.29		
^{13}C	36.1	29.3	27.7	28.3	25.2	16.5	119.5	
PTCOOMe ($CDCl_3$)								
^1H	2.89	1.63	1.44	1.32	1.62	2.28		3.64
^{13}C	36.2; 35.1	29.3	28.2	28.6	24.8	34.0	173.8	51.4
PTCOOH (DMSO-d_6)								
^1H	2.99	1.55	1.38	1.25	1.46	2.16		11.85
^{13}C	34.7	28.4	27.0	27.9	23.8	33.4	173.8	

3.4. Molecular weight characterization

The molecular weights of the synthesized polymers are slightly lower than those reported for alkyl PTs obtained through Stille coupling, probably due to the presence of electron-donor groups on the brominated ring and to the use of THF as polymerization solvent [24]. Number-average molecular weight M_n ranges from 2.2 to 4.1 10^3 Da and weight-average molecular weight M_w from 2.7 to 4.7×10^3 Da, with polydispersity indexes between 1.2 and 2.1. PTCN and PTCOOMe also show a resolved low intensity high mass peak (M_n 17.0 and 22.0 kDa and M_w 18.2 and 28.0, respectively) indicative of the formation of an aggregated phase, whereas PTCOOH displays a M_n similar to that of its parent PT, PTCOOMe, but higher M_w and polydispersity due to the presence of an unresolved aggregated phase peak at higher masses. We recently found [15b] that PTs carrying a β-substituent every two rings can form aggregated phases that coexist with the isolated chains in solution. This behaviour is particularly evident in the case of cysteine side groups [15a] and gives rise to bimodal GPC elugrams.

The two fractions obtained through direct synthesis from **2a** show different molecular weight distributions: that precipitated from the reaction medium is characterized by a molecular mass higher than that of PTCOOH obtained by hydrolysis and very similar to that measured for a cysteine functionalized PT [15a], whereas the more soluble and abundant fraction revealed to be an oligomeric mixture. The results of the GPC analysis are summarized in Table 2.

3.5. UV–vis characterization

UV–vis spectra in good solvents confirm the presence of aggregated phases in low amounts for the PTs here synthesized, except for the PTCOOH fraction precipitated from the reaction medium during direct Stille coupling of **2a** and **4**. PTCN, PTCOOMe ($CHCl_3$ solutions) and PTCOOH obtained by hydrolysis (DMSO solution) show UV–vis spectra characteristic of the prevalence of a random coil form [14,26], with absorption maxima at 489, 491 and 484 nm, respectively, and a shoulder at about 592 nm (Fig. 2).

UV–vis measurements show that the polymeric PTCOOH fraction obtained by direct Stille coupling is strongly aggregated in DMSO: the absorption maximum moves to 538 nm and the shoulder around 590 nm becomes very prominent. The spectral shape becomes that characteristic of an aggregated PT [14,26], and is very similar to that reported for an analogous cysteine-functionalized PT with similar molecular weight [15a]. The UV–vis spectrum in THF indicates a higher amount of a random-coil form with respect to the DMSO solution. A further disruption of aggregates is achieved upon prolonged stirring and refluxing in THF, as inferred by the shift of the absorption maximum from 499 to 497 and then to 482 nm (Fig. 3).

Some remarks on the self-assembling behaviour of the present polymers are necessary. PTs carrying a substituent every two thiophene rings, such as **PTCN** and **PTCOOMe**, display a higher tendency to form aggregates with respect to PTs carrying a substituent on each thiophene ring. This was

Table 2
Summary of molecular weight distribution of the synthesized polythiophenes (measured by GPC relative to monodisperse polystyrene standards)

Polythiophene	$M_n\times10^{-3}$ g/mol	$M_w\times10^{-3}$ g/mol	d[a]
PTCN	2.2	2.7	1.2
PTCOOMe	2.6	3.6	1.4
PTCOOH[b]	2.6	5.4	2.1
PTCOOH[c]	4.1	4.7	1.2

[a] Polydispersity index.

[b] Obtained by hydrolysis of **PTCOOMe**.

[c] Fraction precipitated in the reaction medium during the direct synthesis [25].

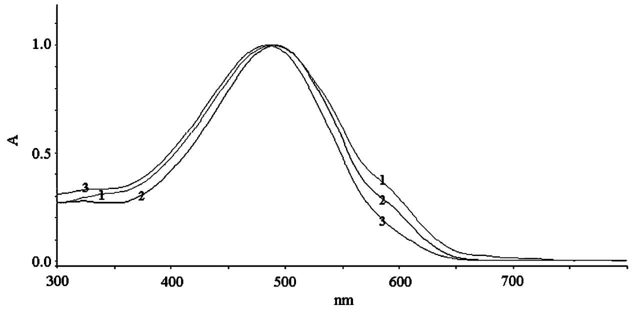


Fig. 2. UV–vis spectra of: (1) **PTCN** and (2) **PTCOOMe** in $CHCl_3$, and (3) **PTCOOH** obtained by hydrolysis in DMSO (2 10^{-5} g mL^{-1}, 1 cm path length).

already found for a tosylated PT [15b], and attributed to a π-stacking favoured by the low substituent density. Also **PTCOOH** obtained by hydrolysis behaves in a rather similar way, whereas **PTCOOH** obtained by direct coupling is more prone to self-assembling like an analogous cysteine-functionalized PT of similar length [15a]. This behaviour of the latter two longer polymers is likely associated with an increase in the strength of both inter-chain dispersive interactions and cooperative hydrogen bonds relative to the shorter ones.

3.6. Cyclic voltammetric measurements on **PTCOOH**

The electrochemical characterization was performed on **PTCOOH** obtained by hydrolysis of **PTCOOMe** and by direct synthesis. CV measurements were obtained from films cast from DMSO solution, by dipping the coated working electrode into a CH_3CN solution containing $TBABF_4$ as base electrolyte. The two polymers display the same oxidation and reduction potentials (within ±0.01 V), and the CV curve of a film of **PTCOOH** obtained by hydrolysis is reported in Fig. 4. One distinct anodic–cathodic peak couple (I) is observed ($E_{pa}(I) = +0.87$ V, $E_{pc}(I) = +0.52$ V) in the anodic region. The anodic signal suggests that the electron transfer process could give a p-doping process with formation of polarons [14,27] and render conductive the polymer coating. In the backwards scan the cathodic counterpart correspond to the neutralization of the doped state.

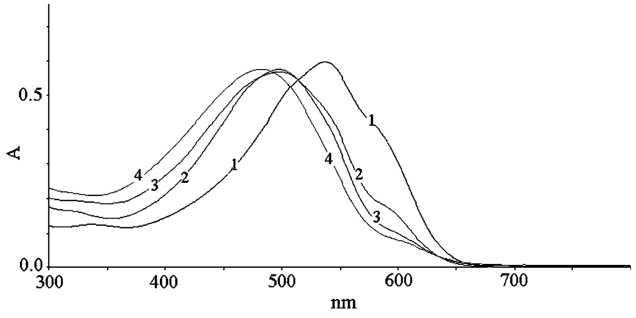


Fig. 3. UV–vis spectra of the high molecular weight fraction of **PTCOOH** obtained by direct Stille coupling of **2a**: (1) DMSO solution, (2) THF solution, (3) THF solution after overnight stirring, and (4) THF solution refluxed overnight.

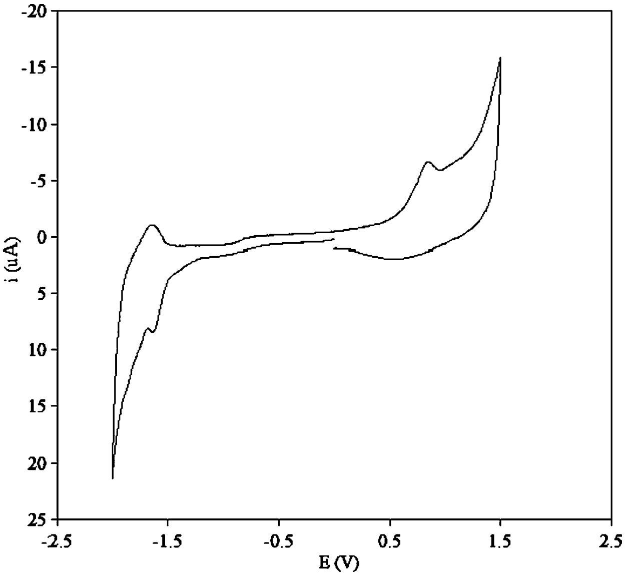


Fig. 4. CV curve performed on a electrode coated with **PTCOOH** obtained by hydrolysis in CH_3CN solution. Base electrolyte $TBABF_4$ 0.1 M, scan rate 0.05 V s^{-1}, $T=25$ °C.

Also in the cathodic region one well-shaped peak couple (II) can be observed ($E_{pa}(II) = -1.64$ V, $E_{pc}(II) = -1.66$ V). An n-doping process can be associated to the cathodic part of (II), while the anodic one corresponds to the neutralization of the adsorbed negatively charged polymer.

The CV curves show notable differences in the anodic region with respect to other alkylsulfanyl PT films [14], in particular the p-doping process seems to occur at more positive potential values while the neutralization of the doped polymer is achieved in the same potential range. The remarkable peak-to-peak separation (about 0.35 V) indicates differences in the electron transfer rates of the oxidation and reduction processes and/or changes in the properties of the film following the p-doping oxidation. In fact, neutralization of the oxidized (and therefore positively charged) film can occur through deprotonation of the carboxylate groups of the polymer chain. In this case, the reduction process (corresponding to the cathodic peak I) should involve the deprotonated form of the starting polymer [28]. Also in the cathodic region the n-doping process of **PTCOOH** takes place at potentials less negative (about 0.2 V) than those reported for polymerized (+)-4,4′-bis[(*S*)-2-methylbuthylsulfanyl]-2,2′-bithiophene but the neutralization of the charged polymer occurs at a very similar potential value [14a]. In this case, however, the peak-to-peak separation is rather small and corresponds to a reversible electron transfer process of a single redox couple. It is worth to note that the difference in E_p values corresponding to p- and n-doping processes ($E_{pa}(I)$ and $E_{pc}(II)$, respectively) of the two polymers are nearly the same (about 2.53 and 2.45 V, respectively) suggesting similar band gap values [29].

3.7. Photoluminescence measurements on **PTCOOH**

The absorption and steady-state emission and excitation spectra in THF of the **PTCOOH** obtained by hydrolysis

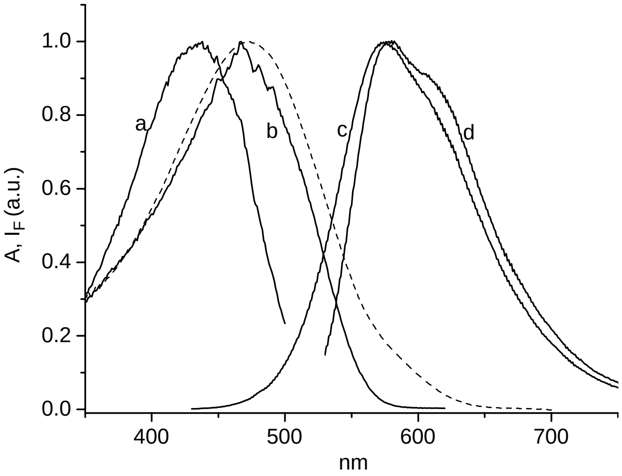


Fig. 5. Normalized absorption (dashed), excitation ((a), $\lambda_{em} = 510$ nm; (b), $\lambda_{em} = 635$ nm) and emission ((c), $\lambda_{exc} = 420$ nm; (d), $\lambda_{exc} = 540$ nm) spectra of **PTCOOH** obtained by hydrolysis in THF.

(maximum absorbance, $A_{max} = 0.14$ at 469 nm) are shown in Fig. 5.

The emission spectrum is dominated by a species with maximum around 566 nm and exhibits a very small dependence on the excitation wavelength. The excitation spectrum (curve b) is essentially independent on the emission wavelength between 565 and 750 nm, i.e. across most of the emission, with the exception of a blue-shifted excitation (curve a) with maximum around 435 nm which corresponds to the emission onset between 450 and 550 nm. We attribute these spectral features to a highly fluorescent species, possibly a fraction with a lower conjugation length. The contribution of this species to the overall absorption and fluorescence excitation and emission spectra of the polymer increases as THF solutions are left both in the dark and at room light for several days. Therefore, this species is likely identifiable as a product of thermal degradation of **PTCOOH** in solution. Excitation at the absorption red tail (580 nm) results in a slightly enhanced emission between 620 and 670 nm (curve d). This emitting species will acquire a much larger relevance in aggregating solvents and in solid films of **PTCOOH**. The species that dominates emission in THF is attributable to the un-aggregated polymer. Its fluorescence quantum yield, determined as 0.20 relative to fluorescein and 0.19 relative to acridine orange HCl, does not change upon moving the excitation wavelength from 470 to 505 nm. This value is well within the range reported for PTs in solution, though rather to the low side, possibly due to some extra spin–orbit coupling favoured by the additional S atom on the ring substituent [4].

In DMSO **PTCOOH** exhibits a stronger tendency to form aggregates. In addition to a solvatochromic shift of the absorption maximum of the un-aggregated polymer (484 nm relative to 469 nm in THF), we observe a dependence of the shape of the absorption spectrum on concentration even for rather diluted solutions. The normalized spectra of three samples having $A_{max} = 0.25$ over a 1 cm path and 1 and 2.1 over a 1 mm path are shown in Fig. 6.

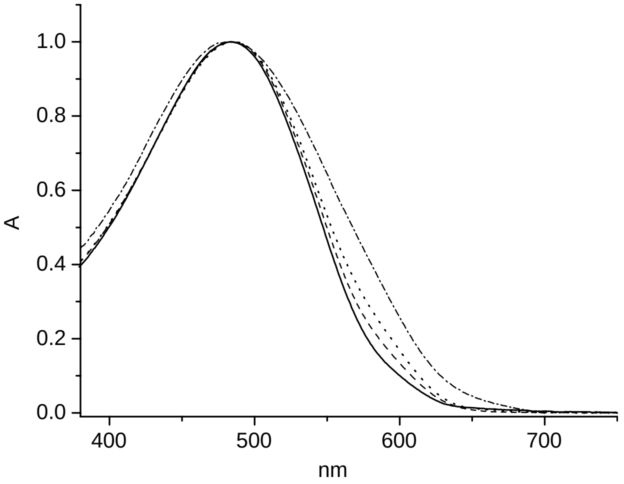


Fig. 6. Normalized absorption spectra of **PTCOOH** obtained by hydrolysis in DMSO at increasing concentrations ($A_{max} = 0.25$ over 1 cm (solid), $A_{max} = 1$ (dashed) and 2.1 (dotted) over 1 mm) and as a spin-coated film ($A_{max} = 0.13$).

The absorption in the 550–650 nm region which grows with concentration is attributable to inter-chain aggregates. These play a major role in steady-state fluorescence observations. For all three samples, but particularly for the most concentrated one, a marked dependence of the emission spectra on the excitation wavelength and of the excitation spectra on the emission wavelength is observed. The effect of sample concentration on the emission and excitation spectra of **PTCOOH** in DMSO is exemplified in Fig. 7.

Here we can see that when the excitation wavelength is set at 530 nm, the emission spectrum is still mainly that of the un-aggregated polymer (maximum at 585 nm) for the least concentrated sample, while it is dominated by a red-shifted emission (maximum at 650 nm) for the most concentrated one. The spectrum of the latter is rather narrow and somewhat structured. Because of this and the fact that this emission has a counterpart in the absorption and excitation spectra between 550 and 640 nm, we rule out the possibility that it may be due to excimers and assign it to inter-chain aggregates. An increase in

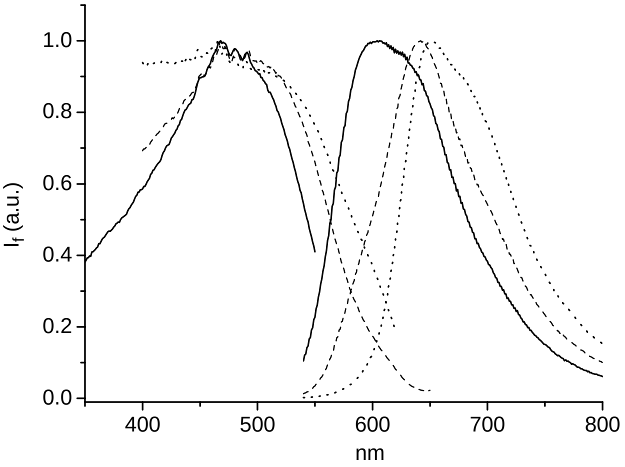


Fig. 7. Normalized excitation ($\lambda_{em} = 650$ nm) and emission ($\lambda_{exc} = 530$ nm) spectra of DMSO solutions of **PTCOOH** obtained by hydrolysis at different concentrations (same as in Fig. 6).

concentration also leads to a reduction of the emission quantum yield. This decreases to about 0.1 in THF when the concentration is increased by a factor of about 20, from a maximum absorbance of 0.2 over 1 cm to 0.4 over 1 mm. At the latter concentration, the quantum yield is lower by a factor of about 0.6 in DMSO relative to THF, a fact that parallels the larger contribution from aggregated species in the emission spectrum in the former solvent. The quantum yield in DMSO also shows some tendency to decrease when moving the excitation wavelength from 480 to 500 and to 550 nm (roughly from 0.06 to 0.04), thus going together with the increase in the absorption and emission contributions of the aggregated polymer form.

Films of **PTCOOH** obtained by casting or spin-coating (A_{max} were adjusted between 0.05 and 0.5 for the former and between 0.12 and 0.23 for the latter) feature a marked broadening of the absorption spectra towards the higher wavelength side relative to solution spectra (Fig. 6), suggesting a much higher contribution from aggregated polymer. Indeed, as shown in Fig. 8, the fluorescence spectra of **PTCOOH** films are dominated by the previously mentioned aggregate emission with maximum around 650 nm (for some samples, this was found at slightly longer wavelengths, 660–670 nm).

This emission is the only one observed in cast films, since the emission spectra are independent of the excitation wavelength across the whole absorption band and, conversely, the excitation spectra are independent of the emission wavelength. However, fluorescence quantum yields are very low for all films: they are typically of the order of 0.005, ranging between roughly 0.0025 and 0.008 for different samples and excitation wavelengths. Such values are very close to the quantum yield attributed to inter-chain aggregates of poly(3-octylthiophene) [30]. Therefore, in these films electronic excitation is mainly lost non-radiatively: only a very weak emission comes from traps corresponding to the inter-chain aggregates already observed in DMSO solution. In spin-coated films, a small contribution to the overall emission in the 500–590 nm region is still observed when exciting on the blue onset of the lowest-energy absorption band, i.e. around 400–420 nm. This is likely attributable to residual un-aggregated polymer that does not transfer excitation to the aggregated traps.

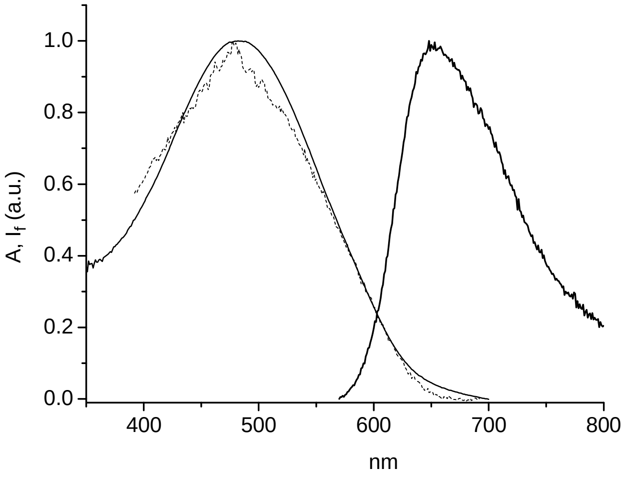


Fig. 8. Normalized absorption (solid), excitation (dashed, $\lambda_{em}=700$ nm) and emission ($\lambda_{exc}=540$ nm) spectra of a spin coated film of **PTCOOH** obtained by hydrolysis ($A_{max}=0.13$).

Concerning the **PTCOOH** obtained by direct Stille coupling, we investigated the steady-state fluorescence properties of THF solutions of the high molecular weight fraction before and after overnight refluxing (the samples characterized by the absorption spectra 2 and 4 in Fig. 3). The emission spectra of these samples, measured by exciting at 505–510 nm (some dependence on the excitation wavelength was observed), show maxima around 580 and 575 nm, respectively. They are therefore red-shifted by 10–15 nm relative to the spectrum of THF samples of the polymer obtained by hydrolysis, a behaviour similar to that exhibited by the absorption spectra (Fig. 3). The emission spectra of both samples feature a strong aggregate shoulder around 645 nm, which is more pronounced for the solution not refluxed overnight. The fluorescence quantum yields obtained by exciting at 510 nm are 0.10 and 0.12, respectively, i.e. about half the quantum yield of the **PTCOOH** obtained by hydrolysis. All these findings agree with the previously drawn conclusion that the high-molecular-weight fraction of the **PTCOOH** obtained by direct Stille coupling contains polymeric units which tend to form aggregates more efficiently than the polymer obtained by hydrolysis of the ester, a prolonged refluxing probably yielding some de-aggregation. Because of the fluorescence quenching effects of inter-chain exciton coupling within polymer aggregates we did not deem it useful to further investigate the fluorescence properties of this polymeric fraction in other solvents and in films.

4. Conclusions

We reported on the synthesis and the characterization of a carboxyhexylsulfanyl PT, **PTCOOH**, which has recently been tested in photoactive devices in conjunction with single wall carbon nanotubes, proving to be a material of high current interest [16]. The most satisfactory yield was obtained through the hydrolysis of **PTCOOMe**, an alkylsulfanyl PT functionalized with methoxycarbonyl groups. The direct Stille coupling of 7-(3-thienylsulfanyl)heptanoic acid **2a** with 2,5-bis(trimethylstannyl)thiophene **4** gave a **PTCOOH** with a higher molecular weight (about 25 thiophenic moieties), but in a lower yield, being this fraction accompanied by an oligomeric one. Our study also points out that a higher tendency to spontaneous self-assembling is observed in PTs carrying a substituent every two rings (hydrolyzed **PTCOOH**, **PTCN**, **PTCOOMe**, and a tosylate PT already reported [15b]) with respect to alkyl- and alkylsulfanyl PTs carrying a substituent on each ring. This inclination to form aggregates is probably to be related to the formations of π-stacks favoured by the low substituent density. On the other hand, longer polymers, such as the **PTCOOH** obtained by direct synthesis and PTs functionalized with cysteine moieties previously reported by some of us [15], exhibit enhanced aggregation, likely because of increased inter-chain dispersive interactions and a more extensive formation of inter-residue hydrogen bonds.

The electrochemical properties of the two **PTCOOH**s here studied appear to be unaffected by their different chain length, whereas the same is not true for their fluorescence. **PTCOOH** obtained by hydrolysis is an efficient fluorophore in THF solution, but its quantum yield decreases from 0.2 to about 0.04 upon inter-chain aggregation in DMSO solutions. Aggregation becomes more extensive in cast and spin-coated films of **PTCOOH** which, correspondingly, exhibit a marked decrease of fluorescence quantum yield, down to about 0.005. In these films, electronic excitation is mainly dissipated non-radiatively. Consistently, the **PTCOOH** obtained by direct Stille coupling, whose stronger tendency to form aggregates in solution is demonstrated by both absorption and fluorescence spectra, featured lower emission quantum yields in THF solution relative to the polymer obtained by hydrolysis of the ester. We must therefore conclude that the build-up of solid-state devices containing PTs able to exhibit good fluorescence properties must rely on the use of a polymer with an appropriate chain length and on procedures that minimize inter-chain exciton formation. In this respect, the **PTCOOH** obtained by hydrolysis is more promising [30], while the observation of some residual emission from un-aggregated polymer in spin-coated films of **PTCOOH** suggests that faster solvent evaporation and/or lower temperatures may, at least to some extent, help to go to the right direction. Also, alternative methods for preparing solid films of PTs (e.g. alternate self-assembly or spin-coating of a sample diluted in a polymer matrix [30]) may prove more efficient to the purpose. A more complete study, also including time-resolved measurements, of the fluorescence properties of this and related polymers in solution and in variously prepared solid films will be given elsewhere.

Acknowledgements

We thank the Centro Interdipartimentale Grandi Strumenti of the University of Modena and Reggio Emilia for the use of the Bruker Avance400 spectrometer. The Fondazione Cassa di Risparmio di Modena is also greatly acknowledged for the financial support given for the acquisition of the Bruker Avance400 spectrometer.

References

[1] (a) Guiseppi-Elie GA, Wallace G, Matsue T. In: Skotheim TA, Elsenbaumer RL, Reynolds JR, editors. Handbook of conducting polymers. New York: Marcel Dekker Inc.; 1998. p. 963–91.
    (b) McQuade DT, Pullen AE, Swager TM. Chem Rev 2000;100:2537.
[2] Kossmehl G, Engelmann G. In: Fichou D, editor. Handbook of oligo- and polythiophenes. Weinheim: Wiley-VCH; 1999. p. 491–524.
[3] Wallace GG. W.O.9002829, AU 88-294; 1990 [Chem Abstr 1990;113:112000h].
[4] (a) Becker PRS, Seixas de Melo J, Maçanita AL, Elisei FJ. Phys Chem 1996;100:18683.
    (b) Rossi R, Ciofalo M, Carpita A, Ponterini G. J Photochem Photobiol A: Chem 1993;70:59.
[5] Theander M, Inganäs O, Mammo W, Olinga T, Svensson M, Andersson MR. J Phys Chem B 1999;103:7771.
[6] Seixas de Melo J, Burrows HD, Svensson M, Andersson MR, Monkman AP. J Chem Phys 2003;118:1550.
[7] (a) Ruseckas A, Namdas EB, Ganguly T, Theander M, Svensson M, Andersson MR, et al. Phys Chem B 2001;105:7624.
    (b) Ruseckas A, Namdas E, Theander M, Svensson M, Yartsev A, Zigmantas D, et al. Synth Met 2001;119:603.
    (c) Ruseckas A, Namdas EB, Theander M, Svensson M, Yartsev A, Zigmantas D, et al. J Photochem Photobiol A: Chem 2001;144:3.
[8] Ackelrud L. Prog Polym Sci 2003;28:875 [references therein].
[9] Viinikanoja A, Lukkari J, Ääritalo T, Laiho T, Kankare J. Langmuir 2003; 19:20768.
[10] (a) Liu J, Kadnikova EN, Liu Y, McGehee MD, Fréchet JMJ. J Am Chem Soc 2004;126:9486.
    (b) Allard D, Allard S, Brehmer M, Conrad L, Zentel R, Stromberg C, et al. Electrochim Acta 2003;48:3137.
[11] Chen XL, Bao Z, Schön JH, Lovinger AJ, Lin Y-Y, Crone B, et al. Appl Phys Lett 2001;78:228.
[12] McCullough RD, Ewbank PC, Loewe RS. J Am Chem Soc 1997;119:633.
[13] (a) Baek M-G, Stevens RC, Charych DH. Bioconjugate Chem 2000;77: 777.
    (b) Nilsson KPR, Rydberg J, Baltzer L, Inganäs O. PNAS 2004;101: 11197.
[14] (a) Iarossi D, Mucci A, Parenti F, Schenetti L, Seeber R, Zanardi C, et al. Chem Eur J 2001;7:676.
    (b) Iarossi D, Mucci A, Schenetti L, Seeber R, Goldoni F, Affronte M, et al. Macromolecules 1999;32:1390.
[15] (a) Mucci A, Parenti F, Schenetti L. Macromol Rapid Commun 2003;24: 547.
    (b) Cagnoli R, Lanzi M, Mucci A, Parenti F, Schenetti L. Polymer 2005; 46:3588.
[16] Rahman GMA, Guldi DM, Cagnoli R, Mucci A, Schenetti L, Vaccari L, et al. J Am Chem Soc 2005;127:10051.
[17] van Pham C, Macomber RS, Mark Jr HB, Zimmer H. J Org Chem 1984; 49:5250.
[18] Caselli M, Latterini L, Ponterini G. Phys Chem Chem Phys 2004;6:3857.
[19] Parker CA. Photoluminescence of solutions. Amsterdam: Elsevier; 1968. p. 266–267.
[20] Dempster DN, Morrow T, Rankin R, Thompson GF. J Chem Soc Faraday Trans 2 1972;68:1479.
[21] Stille JK. Angew Chem, Int Ed Engl 1986;25:508.
[22] Blanchard P, Jousselme B, Frère P, Roncali J. J Org Chem 2002;67:3961.
[23] (a) Mucci A, Schenetti L. Macromol Chem Phys 1995;196:2687.
    (b) Schenetti L, Mucci A. In: Atta-ur-Rahman, editor. New advances in analytical chemistry, vol. 3. New York: Taylor and Francis Inc.; 2002. p. 1–40.
[24] (a) Bouachrine M, Lère-Porte J-P, Moreau JJE, Serein-Spirau F, Torreilles C. J Mater Chem 2000;10:263.
    (b) Iraqi A, Barker GW. J Mater Chem 1998;8:25.
    (c) Zhang QT, Tour JM. J Am Chem Soc 1998;120:5355.
[25] A high mass peak associated with the aggregated phase was not detected by GPC in the case of **PTCOOH** obtained by direct synthesis because its low solubility in THF imposed the filtration of the examined solution prior to the analysis.
[26] (a) Wu X, Chen T-A, Rieke RD. Macromolecules 1996;29:7671.
    (b) Raymond F, Di Césare N, Belletête M, Durocher G, Leclerc M. Adv Mater 1998;10:599.
    (c) Rughooputh SDDV, Hotta S, Heeger AJ, Wudl F. J Polym Sci, Polym Phys Ed 1987;25:1071.
    (d) Roux C, Bergeron JY, Leclerc M. Makromol Chem 1993;194:869.
    (e) Bouman MM, Havinga EE, Janssen RAJ, Meijer EW. Mol Cryst Liq Cryst 1994;256:439.
[27] Heinze J. Synth Met 1991;41–43:2805.
[28] Ikenoue Y, Chiang J, Patil AO, Wudl F, Heeger AJ. J Am Chem Soc 1988; 110:2983.
[29] Ng S-C, Miao P, Chan HSO. Chem Commun 1998;153.
[30] Kanemoto K, Shishido M, Sudo T, Akai I, Hashimoto H, Karasawa T. Chem Phys Lett 2005;402:549.