Articles

Organic- and Water-Soluble Aminoalkylsulfanyl Polythiophenes

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ABSTRACT: Six new aminoalkylsulfanyl polythiophenes (PTs), namely PTNHBoc, PTNMeBoc, $PTNH_2$, PTNHMe, $PTNMe_2$, and PTN^+Me_3, were synthesized. Four of them were obtained through Stille coupling, whereas $PTNH_2$ and PTNHMe were obtained through deprotection via *N*-Boc precursors. The solubility changes going from the protected amines to the quaternary ammonium salt. All the polymers are soluble in DMSO and DMF. PTNHBoc and PTNMeBoc are also soluble in $CHCl_3$, CH_2Cl_2, THF, and DMPU; $PTNH_2$ and PTNHMe are soluble in CH_3OH, whereas $PTNMe_2$ and PTN^+Me_3 are soluble both in CH_3OH and in H_2O. These PTs show a tendency toward microaggregation in solution that does not represent an obstacle to their solubility. NMR, UV−vis, and XRD results prove that they are able to reach very high conjugation lengths and ordered conformations, not only in the solid state but also in solutions of good solvents.

Introduction

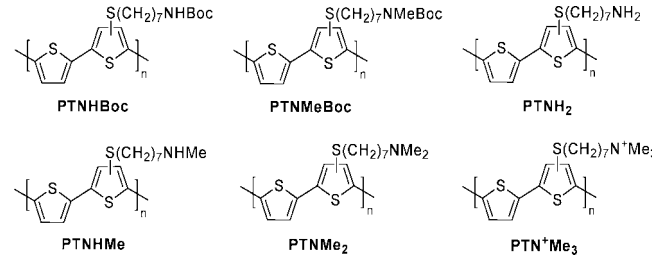
Thanks to their intrinsic structural versatility, polythiophenes (PTs) are important organic semiconducting materials that can be used in many electro-optical applications. In particular, owing to their photophysical properties, lightness, flexibility, processability, and semitransparence, they may represent a less expensive alternative to inorganic semiconductors in photovoltaic[1] and electro-optical[2] devices. Furthermore, organic semiconductors possess an important advantage with respect to the inorganic ones, i.e., the possibility of a chemical modification of the monomeric building blocks that allows both the structural control and the tailoring of the properties of the final materials. The side-chain functionalization offers the attractive possibility of developing PTs which, in addition to their characteristic electronic properties, incorporate the specific qualities of the inserted functional groups. The combination of the conjugate backbone and the modified side chains results in new materials that can be used for sensor applications and in microelectronic or photovoltaic devices. For example, by inserting an amino acid moiety or other ionic groups, it is possible to create a PT that can be used as a biosensor,[3] whereas the presence of ionic groups is fundamental for layer-by-layer deposition,[4] applications in organic photovoltaics, for anchorage to the electrode surface, or for providing amphiphilic behavior in Langmuir−Blodgett films.[5]

With the aim at obtaining materials with a large absorption bandwidth in the visible region, good solubility in organic solvents, and filming properties, we have focused our interest on alkylsulfanyl PTs.[6] We also showed that the presence of an alkylsulfanyl chain is effective in decreasing the oxidation potential with respect to alkyl PTs, stabilizing the oxidized state, and allowing the n-doping of the polymer.[6c,f] The addition of a carboxylic group to the alkylsulfanyl side chain permitted the obtainment of a charged polyelectrolyte belonging to the class of the so-called self-doped conducting polymers.[7] This polymer was indeed tested and proved to be a material of high current interest when used in a photoactive device integrated with single-wall carbon nanotubes (SWNT) functionalized with positively charged (trimethylammoniumacetyl) pyrene groups.[8]

Recently, we turned our attention to PTs bearing alkylsulfanyl chains with amino end groups aiming at producing materials that can be coupled to negatively charged SWNT, or other negatively charged counterparts, used in photovoltaic devices, or as sensitive material in chemical sensors. In this paper, we report on the synthesis and properties of PTs, bearing an aminoalkylsulfanyl moiety every other thiophene unit, where the amino group is present at the end of an heptylsulfanyl chain as *N-tert*-butoxycarbonyl (*N*-Boc) protected (PTNHBoc), *N*-methyl-*N*-Boc-protected (PTNMeBoc), unsubstituted ($PTNH_2$), *N*-methyl- (PTNHMe) and *N,N*-dimethylamines ($PTNMe_2$), and *N,N,N*-trimethylammonium salt (PTN^+Me_3) (Chart 1).

PTNHBoc, PTNMeBoc, $PTNMe_2$, and PTN^+Me_3 were obtained by copolymerization through Stille coupling whereas $PTNH_2$ and PTNHMe were obtained by deprotection from the corresponding carbamates. The solubility of these polymers is strongly dependent on their *N*-substitution: although all of them

Chart 1



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are soluble in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), PTNHBoc and PTNMeBoc are soluble in $CHCl_3$, CH_2Cl_2, tetrahydrofuran (THF), and dimethylpropyleneurea (DMPU), $PTNH_2$ and PTNHMe in CH_3OH, $PTNMe_2$, and PTN^+Me_3 in both CH_3OH and H_2O.

Experimental Section

General Techniques. All air- or moisture-sensitive reactions were performed under argon with dry glassware. All solvents were dried by standard procedures. All reagents were purchased from Aldrich and Acros and used as received unless otherwise indicated. 2,5-Bis(trimethylstannyl)thiophene was obtained according to ref 9.

GPC was carried out on samples dissolved in THF, after filtration on Teflon septum 0.20 μm pore size, with 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. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance400 operating at 400.13 and 100.61 MHz, respectively. UV−vis spectra were recorded using a Perkin-Elmer Lambda Bio 20 and a Lambda 19 UV−vis−NIR spectrophotometers. FT-IR spectra were recorded with a Perkin-Elmer Spectrum One. X-ray diffraction was measured using a Panalytical X'Pert Pro diffractometer. The X-ray beam was nickel-filtered Cu Kα (λ_i = 0.1506 nm) radiation from a sealed tube operated at 40 kV and 40 mA. Data were obtained from 1° to 30° (2θ) at a scan rate of 1° min^{-1} and the incident angle was 0.5°.

Monomers Synthesis. *tert-Butyl N-[7-(2,5-dibromothien-3-yl)-sulfanyl]heptylcarbamate (1).* To a suspension of $LiAlH_4$ (0.40 g, 10.6 mmol) in anhydrous THF (40 mL), a solution of 7-(3-thienylsulfanyl)heptanenitrile[7] (2.2 g, 9.6 mmol) in anhydrous THF (35 mL) was added dropwise under argon atmosphere. The reaction mixture was warmed to reflux and stirred for 8 h. After cooling, 30 mL of H_2O was carefully added and the pH was adjusted to 9. Subsequent extraction with Et_2O (3 × 15 mL), drying ($MgSO_4$), and removal of the volatiles gave pure 7-(3-thienylsulfanyl)heptanamine as a white-yellow solid (2.1 g, 96%). Mp: 71−72 °C. ^1H NMR (400.13 MHz, $CDCl_3$, TMS): δ 1.34 (m, 4H, CH_2CH_2CH$_2$CH$_2$NH$_2$), 1.40 (m, 4H, CH_2CH$_2$CH$_2$S and CH_2-CH$_2$NH$_2$), 1.49 (s, 2H, NH_2),1.63 (m, 2H, CH_2CH$_2$S), 2.70 (t, 2H, J = 6.5 Hz, CH_2NH$_2$), 2.85 (t, 2H, J = 7.3 Hz, CH_2S), 7.02 (dd, 1H, J = 1.3, 5.0 Hz, H-4), 7.12 (dd, 1H, J = 1.3, 3.1 Hz, H-2), 7.32 (dd, 1H, J = 3.1, 5.0 Hz, H-5). ^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): δ 26.6 (*C*H$_2$CH$_2$CH$_2$NH$_2$), 28.7 (*C*H$_2$CH$_2$CH$_2$S), 29.0 (*C*H$_2$CH$_2$CH$_2$CH$_2$NH$_2$), 29.1 (*C*H$_2$CH$_2$S), 33.9 (*C*H$_2$CH$_2$NH$_2$), 35.2 (*C*H$_2$S), 42.1 (*C*H$_2$NH$_2$), 122.9 (C-2), 125.9 (C-5), 129.6 (C-4), 132.1 (C-3).

Et_3N (0.34 g, 3.4 mmol) was added to a stirred solution of 7-(3-thienylsulfanyl)heptanamine (0.79 g, 3.4 mmol) in CH_2Cl_2 (11 mL), followed, after 10 min, by di-*tert*-butyl dicarbonate (0.74 g, 3.4 mmol). The mixture was stirred for 18 h, washed with H_2O, dried, and evaporated under reduced pressure. The crude solid obtained was purified by flash chromatography on silica gel (petroleum ether/Et_2O 90:10 → 50:50) to give pure *tert*-butyl *N*-[7-(3-thienylsulfanyl)heptyl]carbamate as a white solid (0.84 g, 76%). Mp: 50−51 °C. ^1H NMR (400.13 MHz, $CDCl_3$, TMS): δ 1.29 (m, 4H, CH_2CH_2CH$_2$CH$_2$NH), 1.41 (m, 2H, CH_2CH$_2$CH$_2$S), 1.44 (m, 2H, CH_2CH$_2$NH), 1.46 (s, 9H, C(CH_3)$_3$), 1.60 (m, 2H, CH_2CH$_2$S), 2.84 (t, 2H, J = 7.3 Hz, CH_2S), 3.10 (q, 2H, J = 6.6 Hz, CH_2NH), 4.45 (bs, 1H, N*H*), 7.02 (dd, 1H, J = 1.2, 5.0 Hz, H-4), 7.12 (dd, 1H, J = 1.2, 2.9 Hz, H-2), 7.31 (dd, 1H, J = 2.9, 5.0 Hz, H-5). ^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): δ 26.6 (*C*H$_2$CH$_2$CH$_2$NH), 28.4 (C(*C*H$_3$)$_3$), 28.5 (*C*H$_2$CH$_2$CH$_2$S), 28.8 (*C*H$_2$CH$_2$CH$_2$CH$_2$NH), 29.2 (*C*H$_2$CH$_2$S), 30.0 (*C*H$_2$CH$_2$NH), 35.3 (*C*H$_2$S), 40.5 (*C*H$_2$NH), 80.0 (*C*(CH$_3$)$_3$), 123.0 (C-2), 126.0 (C-5), 129.6 (C-4), 132.2 (C-3), 155.9 (C═O).

NBS (0.68 g, 3.8 mmol) was added to a solution of *tert*-butyl *N*-[7-(3-thienylsulfanyl)heptyl]carbamate (0.50 g, 1.5 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was heated at reflux and stirred for 18 h. After cooling, the organic solution was washed with H_2O (2 × 5 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 **1** as a yellow oil (0.53 g, 73%). ^1H NMR (400.13 MHz, $CDCl_3$, TMS): δ 1.30 (m, 4H, CH_2CH_2CH$_2$ CH$_2$NH), 1.43 (s, 9H, C(CH_3)$_3$), 1.47 (m, 2H, CH_2CH$_2$NH), 1.49 (m, 2H, CH_2CH$_2$CH$_2$S), 1.59 (m, 2H, CH_2CH$_2$S), 2.82 (t, 2H, J = 7.3 Hz, CH_2S), 3.10 (q, 2H, J = 6.6 Hz, *CH*$_2$NH), 4.49 (bs, 1H, N*H*), 6.90 (s, 1H, H-4). ^3C NMR (100.61 MHz, $CDCl_3$, TMS): δ 26.6 (*C*H$_2$CH$_2$CH$_2$NH), 28.4 (*C*H$_2$CH$_2$CH$_2$S), 28.5 (C(*C*H$_3$)$_3$), 28.8 (*C*H$_2$CH$_2$CH$_2$CH$_2$NH), 29.4 (*C*H$_2$CH$_2$S), 30.0 (*C*H$_2$CH$_2$NH), 35.3 (*C*H$_2$S), 40.6 (*C*H$_2$NH), 78.8 (*C*(CH$_3$)$_3$), 111.0 (C-5),112.8 (C-2), 132.4 (C-4), 133.6 (C-3), 156.0 (C═O).

tert-Butyl N-{[7-(2,5-dibromothien-3-yl)sulfanyl]heptyl}-N-methylcarbamate (2). A solution of compound **1** (0.30 g, 0.60 mmol) in DMF (3 mL) was added dropwise to a well-stirred suspension of NaH (0.03 g, 1.2 mmol) in DMF (3 mL). After 30 min, CH_3I (0.45 g, 3.0 mmol) was added and the reaction mixture was stirred for 30 h. The reaction mixture was quenched with a saturated NH_4Cl solution (3 mL), and the solution was extracted with CH_2Cl_2 (4 × 5 mL). The combined organic layers were washed with H_2O (2 × 5 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (petroleum ether/Et_2O 100:0 → 70:30) to give pure **2** as a brown-orange oil (0.19 g, 63%). ^1H NMR (400.13 MHz, $CDCl_3$, TMS): δ 1.30 (m, 4H, CH_2CH_2CH$_2$CH$_2$N), 1.41 (m, 2H, CH_2CH$_2$CH$_2$S), 1.44 (s, 9H, C(CH_3)$_3$), 1.47 (m, 2H, CH_2CH$_2$N), 1.57 (m, 2H, CH_2CH$_2$S), 2.81 (t, 2H, J = 7.2 Hz, CH_2S), 2.82 (s, 1H, CH_3), 3.18 (t, 2H, J = 7.3 Hz, CH_2N), 6.89 (s, 1H, H-4).^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): δ 26.6 (*C*H$_2$CH$_2$CH$_2$NH$_2$), 27.6 (*C*H$_2$CH$_2$NH$_2$), 28.5 (*C*H$_2$CH$_2$CH$_2$S), 28.8 (*C*H$_2$CH$_2$CH$_2$CH$_2$NH$_2$), 29.4 (*C*H$_2$CH$_2$S), 34.1 (*C*H$_3$N), 35.2 (*C*H$_2$S), 48.6 (*C*H$_2$N), 79.1 (*C*(CH$_3$)$_3$), 110.9 (C-5), 112.9 (C-2), 132.3 (C-4), 134.0 (C-3), 155.8 (C═O).

N,N-Dimethyl-7-[(2,5-dibromo-3-thienyl)sulfanyl]heptanamine (3). A mixture of **1** (1.5 g, 3.1 mmol) and HBr/CH_3COOH (5.7 M, 1.4 mL, 7.75 mmol) was stirred for 30 min at 26 °C. After addition of 1 N aqueous NaOH until pH = 9, the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to afford 7-(2,5-dibromo-3-thienylsulfanyl)heptylamine (1.1 g, 91%) as a brown oil. A mixture of 7-(2,5-dibromo-3-thienylsulfanyl)heptylamine (0.40 g, 1.0 mmol), formaldehyde (36.5 wt % in H_2O, 0.78 mL, 9.4 mmol), and formic acid (99%, 0.63 mL, 16.5 mmol) were refluxed for 18 h. The solvent was removed under reduced pressure, and the residue was neutralized with 1N aqueous NaOH and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/CH_3OH 100:0 → 5:95) to give **3** (0.23 g, 55%) as a white solid. Mp: 74−75 °C. ^1H NMR (400.13 MHz, $CDCl_3$, TMS): δ 1.26 (m, 2H, CH_2CH$_2$CH$_2$N(CH$_3$)$_2$), 1.27 (m, 2H, CH_2CH$_2$CH$_2$-CH$_2$N(CH$_3$)$_2$), 1.38 (m, 2H, CH_2CH$_2$CH$_2$S), 1.42 (m, 2H, CH_2CH$_2$N(CH$_3$)$_2$), 1.54 (m, 2H, CH_2CH$_2$S), 2.18 (s, 6H, N(CH_3)$_2$), 2.21 (t, 2H, J = 7.3 Hz, CH_2N(CH$_3$)$_2$), 2.78 (t, 2H, J = 7.3 Hz, CH_2S), 6.86 (s, 1H, H-4).^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): δ 27.2 (*C*H$_2$CH$_2$CH$_2$N(CH$_3$)$_2$), 27.5 (*C*H$_2$CH$_2$N(CH$_3$)$_2$), 28.4 (*C*H$_2$CH$_2$CH$_2$S), 29.0 (*C*H$_2$CH$_2$CH$_2$CH$_2$N(CH$_3$)$_2$), 29.4 (*C*H$_2$CH$_2$S), 35.2 (*C*H$_2$S), 45.4 (N(*C*H$_3$)$_2$), 59.7 (*C*H$_2$N(CH$_3$)$_2$), 110.8 (C-5), 112.7 (C-2), 132.2 (C-4), 133.9 (C-3).

[7-(2,5-Dibromothien-3-yl)sulfanyl]heptyltrimethylammonium iodide (4). CH_3I (50 μL, 0.81 mmol) was dropwise added to a solution of **3** (0.11 g, 0.27 mmol) in CH_3CN (3 mL). The reaction mixture was stirred for 4 h. The solution was concentrated to a small volume, and then Et_2O (20 mL) was added. The white precipitate was filtered, washed with Et_2O and dried to obtain **4** (0.11 g, 74%) as a white solid. Mp: 77−79 °C. ^1H NMR (400.13 MHz, $CDCl_3$, TMS): δ 1.29 (m, 2H, CH_2CH$_2$ CH$_2$CH$_2$N$^+$(CH$_3$)$_3$), 1.42 (m, 4H, CH_2CH_2CH$_2$CH$_2$N$^+$(CH$_3$)$_3$), 1.44 (m, 2H, CH_2CH$_2$CH$_2$S), 1.59 (m, 2H, CH_2CH$_2$S), 1.79 (m, 2H, CH_2CH$_2$N$^+$(CH$_3$)$_3$), 2.84 (t, 2H, J = 7.3 Hz, CH_2S), 3.43 (s, 9H, N$^+$(CH_3)$_3$, 3.55 (m, 2H, CH_2N$^+$(CH$_3$)$_3$),

6.91 (s, 1H, H-4).^{13}C NMR (100.61 MHz, $CDCl_3$, TMS): δ 23.2 ($CH_2CH_2N(CH_3)_3$), 26.1 ($CH_2CH_2CH_2N^+(CH_3)_3$), 28.1 ($CH_2CH_2CH_2S$), 28.6 ($CH_2CH_2CH_2CH_2N^+(CH_3)_3$), 29.2 ($CH_2CH_2S$), 35.1 ($CH_2S$), 53.8 ($N^+(CH_3)_3$), 67.3 ($CH_2N^+(CH_3)_3$), 111.9 (C-5), 112.9 (C-2), 132.4 (C-4), 133.8 (C-3).

Poly{tert-butyl N-[7-(3-thienylsulfanyl)heptyl]carbamate-co-thiophene} (PTNHBoc). In a screw-capped Schlenk tube equipped with a perforable septum a solution of **1** (0.25 g, 0.51 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.27 g, 0.67 mmol) in 3 mL of anhydrous THF/DMF 1:1 was added dropwise to a solution of $Pd(PPh_3)_4$ (7.0 mg, 6.0×10^{-3} mmol) in 3 mL of anhydrous THF/DMF 1:1 under argon atmosphere. The mixture was stirred at 90 °C for 56 h and concentrated to a small volume, and then CH_3OH (5 mL) was added. A dark purple precipitate was obtained, which was filtered, washed with CH_3OH, and dried to give 0.18 g (89% yield) of PTNHBoc (golden violet film). IR: 3360, 3080, 2927, 2857, 1667, 1516, 1476, 1397, 1364, 1246, 1164, 860, 780 cm^{-1}.

Poly{tert-butyl N-methyl-N-[7-(3-thienylsulfanyl)heptyl]carbamate-co-thiophene} (PTNMeBoc). As described in the above procedure, from 0.50 g of **2** (1.0 mmol) and 0.53 g of 2,5-bis(trimethylstannyl)thiophene (1.3 mmol), 0.305 g (61% yield) of PTNMeBoc (golden violet film) was obtained. IR: 3079, 2928, 2860, 1666, 1514, 1390, 1365, 1165, 865, 791, 730 cm^{-1}.

Poly[7-(3-thienylsulfanyl)heptanamine-co-thiophene] ($PTNH_2$). To a solution of PTNHBoc (60 mg) in $CHCl_3$ (8 mL), CF_3COOH (3.6 mL, 48.5 mmol) was added dropwise. The mixture was stirred at room temperature for 30 min. A dark purple precipitate was obtained, which was filtered, washed with $CHCl_3$, THF, and Et_2O, and dried to give 45 mg (75% yield) of $PTNH_2$ (dark powder). IR: 3080, 2921, 2880, 1489, 1421, 1121, 920, 840, 790, 728 cm^{-1}.

Poly[N-methyl-7-(3-thienylsulfanyl)heptanamine-co-thiophene] (PTNHMe). As described in the above procedure, from 60 mg of PTNMeBoc, 51 mg (85% yield) of PTNHMe (dark powder) was obtained. IR: 3081, 2930, 2890, 1496, 1435, 1119, 839, 796, 728 cm^{-1}.

Poly[N,N-dimethyl-7-(3-thienylsulfanyl)heptanamine-co-thiophene] ($PTNMe_2$). In a screw-capped Schlenk tube equipped with a perforable septum, a solution of **3** (0.23 g, 0.56 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.25 g, 0.62 mmol) in 5 mL of anhydrous THF/DMF 1:1 was added dropwise to a solution of $Pd(PPh_3)_4$ (7.7 mg, 6.0×10^{-3} mmol) in 3 mL of anhydrous THF/DMF 1:1 under argon. The mixture was stirred at 90 °C for 72 h and concentrated to small volume and then *n*-pentane (15 mL) was added. The dark purple precipitate obtained was filtered, washed with THF, and dried to give 0.125 g (54% yield) of $PTNMe_2$ (golden violet flakes). IR: 3065, 3009, 2958, 2869, 2688, 1490, 1060, 960, 829, 790, 728 cm^{-1}.

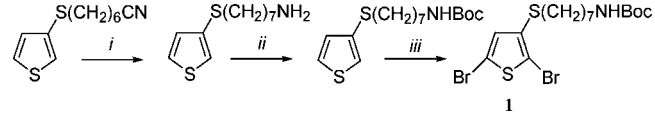
Poly{trimethyl-[7-(3-thienylsulfanyl)heptyl]ammonium iodide-co-thiophene} (PTN^+Me_3). As described in the above procedure, from 90 mg of **4** (0.16 mmol) and 70 mg of 2,5-bis(trimethylstannyl)thiophene (0.18 mmol), 70 mg (80% yield) of PTN^+Me_3 (black powder) was obtained. IR: 3062, 3012, 2963, 2870, 1486, 1387, 1054, 928, 789, 728 cm^{-1}.

Results and Discussion

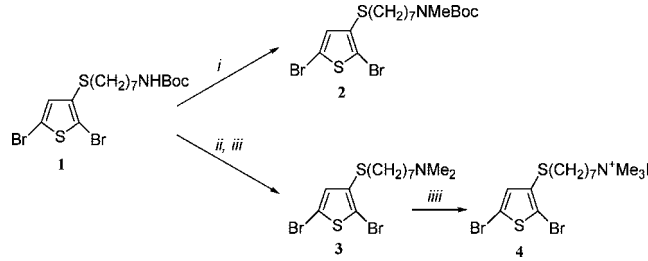
Synthesis. Amino-functionalized PTs are rarely found in the literature and, in particular, there is a very small number of reports dealing with the polymerization of thiophenes bearing a free[10] or a protected amino side chain.[11] In these few examples, the polymerization is achieved by reacting the monomers with $FeCl_3$ or by applying the Stille coupling.

We being currently involved in the study of polymers with alternating substituted−unsubstituted thiophene units,[7,8,12] the Stille coupling seemed to us the best polymerization method, taking into account that the oxidative polymerization with $FeCl_3$, which is the most simple and common method for the synthesis of poly(3-alkylthiophene)s,[13] may not be applied when alkylsulfanyl substituents are present, leading to oligomeric mixtures.[14] The same drawback also occurs with thiophenes functionalized with tertiary amines and is ascribable to the complexation of the oxidant by the lone pair of the nitrogen atom.[15]

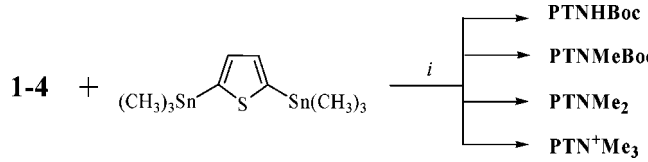
Scheme 1. (i) $LiAlH_4$, THF, 40 °C, 14 h; (ii) Et_3N, $(Boc)_2O$, 25 °C, 18 h; (iii) NBS, CH_2Cl_2, 45 °C, 18 h



Scheme 2. (i) NaH, CH_3I, DMF, room temperature, 30 h; (ii) HBr/CH_3COOH, room temperature, 30 min; (iii) HCHO (36.5 wt %), HCOOH 99%, CH_3OH, 85°C, 18 h; (iiii) CH_3I, CH_3CN, room temperature, 4 h



Scheme 3. (i) $Pd(PPh_3)_4$, THF/DMF 1:1, 90 °C, 56 h



Our first attempts to generate a PT by applying the Stille coupling to thiophenes functionalized with unprotected primary and secondary amino groups produced formylated polymers, because a transamidation reaction between the solvent employed (DMF) and the amino moiety occurred. DMF being the only suitable solvent for this kind of substrates, and in order to avoid the transamidation reaction, we turned our attention to the polymerization of alkylsulfanyl thiophenes bearing *N*-Boc protected and/or *N*-alkylamino-substituted side chains. The 2,5-dibrominated *N*-Boc protected monomer **1** (Scheme 1) was synthesized, starting from 7-(3-thienylsulfanyl)heptanenitrile[7] in four steps. The nitrile group was reduced with $LiAlH_4$ in anhydrous THF[16] giving 7-(3-thienylsulfanyl)heptanamine, which was *N*-Boc protected[17] and then brominated with *N*-bromosuccinimide (NBS).[18]

It is not possible to reverse the order of the synthetic pathway, i.e., bromination and subsequent reduction of nitrile, because the reduction of the 7-[(2,5-dibromothien-3-yl)sulfanyl]heptanenitrile with $LiAlH_4$ leads to the complete debromination at the 2- position of the thiophene ring.

Monomer **1** was employed as intermediate for the synthesis of the *N*-methylated monomers **2**-**4** (Scheme 2). In fact, **2** was obtained from **1** after treatment with NaH and subsequent methylation with CH_3I,[19] **3** was obtained by deprotection of **1** and subsequent methylation (Eschweiler−Clarke reaction with HCHO and HCOOH),[20] and the ammonium salt **4** was generated from **3** by reaction with CH_3I.[11b,21]

The polymerization of monomers **1**−**4** in the Stille conditions (Scheme 3) afforded the related polymers in good yields (PTNHBoc 89%, PTNMeBoc 61%, $PTNMe_2$ 54%, PTN^+Me_3 80%).

After the usual workup, PTNHBoc and PTNMeBoc appeared as golden free-standing films soluble in $CHCl_3$, CH_2Cl_2, THF, DMSO, and DMF.

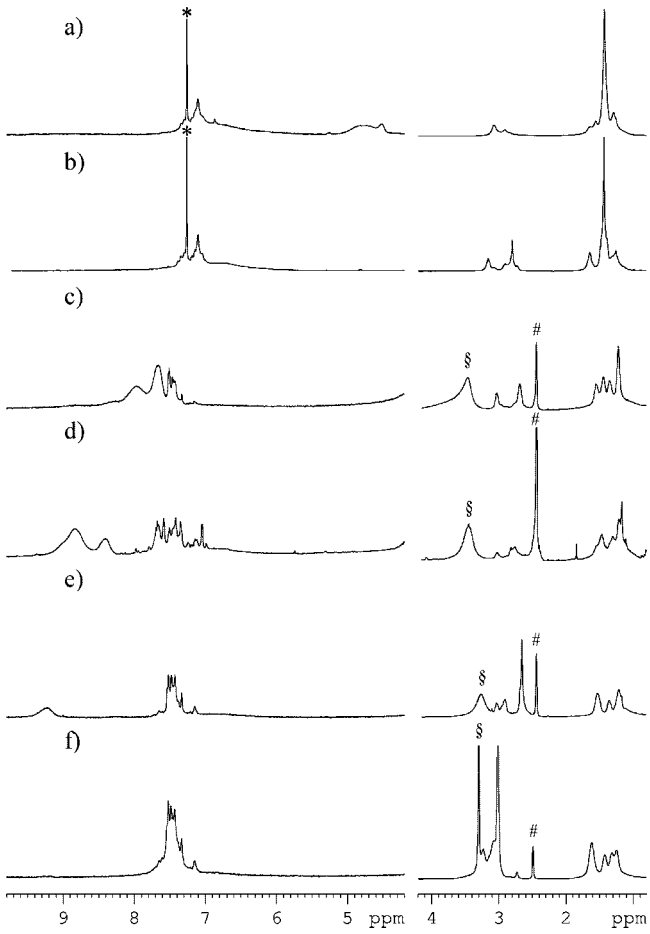


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of (a) PTNHBoc and (b) PTNMeBoc, and in DMSO-d_6 of (c) protonated $PTNH_2$, (d) protonated PTNHMe, (e) $PTNMe_2$, and (f) PTN^+Me_3.* $CHCl_3$ § H_2O, # DMSO residual signals.

Unexpectedly, the addition of CH_3OH to the reaction mixture containing $PTNMe_2$ or PTN^+Me_3 did not cause the precipitation but the dissolution of the polymers, which were recovered from this solvent by addition of *n*-pentane and THF. After removal of the solvent, $PTNMe_2$ and PTN^+Me_3 appeared as dark-golden flakes which showed good solubility in CH_3OH, DMF, and DMSO, and a lower solubility in H_2O. The deprotection of PTNHBoc and PTNMeBoc with trifluoroacetic acid gave the unprotected polymers $PTNH_2$ and PTNHMe in their protonated forms, soluble in CH_3OH, DMF, and DMSO.

GPC Characterization. The molecular weights of PTNHBoc and PTNMeBoc were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. They could not be determined for $PTNMe_2$ and PTN^+Me_3 due to their insolubility in THF. The eluograms show the presence of two peaks, a major one at lower retention times (higher masses) and a minor one at higher retention times (lower masses), which can be attributed to an aggregated and to a free form, respectively, as happens for similar PTs carrying one β-substituent every other thiophene ring.[7,12b] The experimental M_n and M_w, together with the calculated polydispersity index (PD) and the degree of polymerization (DP) of the free forms, are as follows: 4.7 kDa, 6.4 kDa, 1.4, and 23 for PTNHBoc and 3.5 kDa, 4.7 kDa, 1.2, and 16 for PTNMeBoc. M_n and M_w of the aggregated forms are found to be 34 and 41 kDa for PTNHBoc, and 41 and 56 kDa for PTNMeBoc.

^{1}H and ^{13}C NMR Spectroscopic Characterization. The ^{1}H NMR spectra of all polymers in their native forms (Figure 1) display resonances between 6.5 and 7.5 ppm, attributable to the β-protons of the thiophene rings. The aliphatic regions are characterized by two groups of signals, one between 2.7 and 3.2 ppm, due to the methylene protons close to the nitrogen and sulfur atoms, and the other between 1.2 and 1.7 ppm, due to the remaining aliphatic protons. The broad signal between 4.5 and 5.0 ppm in Figure 1, trace a, is attributable to the NH proton of PTNHBoc, whereas broad signals above 7.5 ppm are attributed to the NH proton of the protonated polymer amino groups (see below).

The assignment of the overlapped resonances is obtained through two-dimensional homonuclear ^{1}H,^{1}H (mainly TOCSY and COSY) and heteronuclear ^{1}H,^{13}C inverse-detection experiments.[22] Difficulties are found in the detection of the carbon signals of the thiophene rings, due to the short spin−spin relaxation times induced by the aggregation process, as already reported in similar cases,[7] whereas the same experiments permit to assign the aliphatic chain proton and carbon signals (Table 1).

The ^{1}H NMR spectra of all polymers confirm that they are partially in their aggregated form and that the aggregates are due to π-stacking. In fact, it is possible to note the presence of very broad components, especially in the aromatic region, that are high-field shifted with respect to the main resonances. This feature is more pronounced in the spectra of the two *N*-Boc polymers.

It is worth noting that further information on PTNHBoc can be derived from the NH signal, which splits in two components (Figure 1, trace a), one very broad at about 4.8 ppm and another narrower at 4.53 ppm. A nuclear Overhauser effect (NOESY) experiment evidence that the downfield NHs are heavily involved in a hydrogen bond network and give NOE with *t*-butyl protons, whereas the high-field signal due to free NHs does not give any NOE. This behavior can be explained assuming the formation of inter-residue hydrogen bonds between carbamate groups, as depicted in Chart 2.

The NOESY experiment carried out on protonated polymers, $PTNH_2$ and PTNHMe, shows that the two low-field groups of broad signals ascribable to NH protons behave differently when the exchange with H_2O is monitored. Those at 8.0 and 8.8 ppm are in faster exchange with the (also broad) H_2O signal at 3.5 ppm with respect to NH protons at 7.7 and 8.3 ppm, indicating that they are involved in different hydrogen-bond networks. Similar results are obtained for NH signals (at 9.9 and 9.3 ppm) of protonated $PTNMe_2$ (not reported in Table 1). It should also be noted that the small broad signal at 9.3 ppm (trace e, Figure 1) indicates that $PTNMe_2$ is slightly protonated in its native form in DMSO solution.

In spite of the evidence of the formation of hydrogen bonds only in PTNHBoc, the proneness to aggregation is observed for all the synthesized PTs. We thus conclude that the tendency toward aggregation comes not only from dipolar or ionic interactions among functional groups but also from dispersion forces involved in π-stackings.

UV−Vis Characterization. The chromic properties of the six synthesized polymers were examined in pure solvents, in their mixtures at different molar fractions (mf), and in the solid state, and the absorption maxima wavelengths (λ_{max}) are collected in Table 2. Polymers concentration (8×10^{-5} mol L^{-1}) and temperature (21 °C) were kept constant in all the cases. As already stated, the samples are soluble only in a selected range of polar solvents according to their chemical structure.

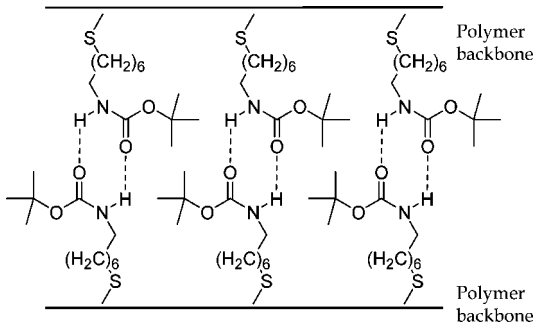
Spectral behaviors among the examined samples are different and strongly dependent on the presence of the amine protecting group (Boc). In detail, PTNHBoc and PTNMeBoc are well soluble in DMPU, an amidic solvent generally able to solvate PTs bearing polar and strongly interacting groups in the side chains, e.g., polyhydroxyalkylthiophenes,[23] but their spectra

Table 1. ^{1}H and ^{13}C Chemical Shifts (δ in ppm, TMS, in $CDCl_3$ or DMSO-d_6) of the Polymers

	S*CH*$_2$	SCH$_2$*CH*$_2$	SCH$_2$CH$_2$*CH*$_2$	*CH*$_2$CH$_2$CH$_2$CH$_2$N	*CH*$_2$CH$_2$CH$_2$N	*CH*$_2$CH$_2$N	*CH*$_2$N	N*H*/N*CH*$_3$	*C*=O	C(*CH*$_3$)$_3$	*C*(CH$_3$)$_3$
PTNHBoc											
^{1}H	2.91	1.65	1.43	1.29	1.29	1.45	3.07	4.53; 4.8[b]		1.43	
^{13}C	36.2	29.5	28.6	28.6	26.7	30.0	40.3		155.9	28.4	78.9
PTNMeBoc											
^{1}H	2.91	1.65	1.43	1.31	1.27	1.48	3.16	2.81		1.43	
^{13}C	35.9	29.3	28.6	28.9	26.6	27.6	48.5	34.0	155.5	28.3	78.8
PTNH$_2$[a]											
^{1}H	3.08	1.59	1.40	1.27	1.28	1.49	2.74	8.0[b]; 7.7[b]			
^{13}C	34.6	28.8	27.9	27.8	25.7	26.9	38.7				
PTNHMe[a]											
^{1}H	3.07	1.59	1.40	1.26	1.26	1.51	2.81	8.80[b];8.35[a]/2.51			
^{13}C	34.7	28.7	27.6	27.6	25.3	24.9	47.8	32.0			
PTNMe$_2$											
^{1}H	3.08	1.60	1.40	1.27	1.25	1.55	2.97	2.71			
^{13}C	34.6	28.5	27.6	27.8	25.4	23.4	56.4	42.1			
PTN$^+$Me$_3$											
^{1}H	3.08	1.60	1.42	1.32	1.24	1.64	3.24	3.01			
^{13}C	34.5	28.4	27.5	27.6	25.2	21.5	64.9	51.8			

[a] As ammonium trifluoroacetate. [b] Broad.

Chart 2



show an unexpected feature. In fact, in this pure solvent, also chosen for its good miscibility with H_2O, PTNHBoc and PTNMeBoc spectral profiles are dramatically red-shifted with respect to those of the hydroxy-functionalized PTs examined in the same pure solvent.[24] Moreover, the two amino polymers show a well evident pure electronic transition (E_{0-0}) at around 590 nm, a value usually observed for highly ordered and planar polyalkylthiophenes in thin films or in solvent/nonsolvent mixtures at very high nonsolvent contents.[25] The UV−vis spectra obtained for PTNHBoc in solution are reported as an example in Figure 2. Progressive additions of CH_3OH or H_2O, acting as nonsolvents for the two polymers, lead to moderate shifts of the λ_{max} of the spectrum: the most evident red shift is obtained using CH_3OH with $\Delta\lambda_{max} = 14$ and 7 nm for PTNHBoc and PTNMeBoc, respectively, and the latter undergoes a bathochromic shift ($\Delta\lambda_{max} = 5$ nm) also in the presence of H_2O (Table 2). The amount of solvatochromic shifts is negligible for the two polymers when they are examined in THF at increasing molar fractions of nonsolvent CH_3OH and the same also occurs when $CHCl_3$ is used as a solvent, maintaining the methanol as nonsolvent.

Differently from the *N*-Boc PTs, $PTNH_2$, PTNHMe, $PTNMe_2$, and PTN^+Me_3 are well soluble in CH_3OH and only swell in DMPU. In this case, spectra are recorded in CH_3OH at increasing molar fractions of DMPU and H_2O and in Figures 3 and 4 are reported the spectral profiles of PTNHMe and PTN^+Me_3 as examples.

$PTNH_2$ and PTNHMe samples appear particularly insensitive to the surrounding solvent system: H_2O additions to CH_3OH solutions did not determine any important effect on the spectral profiles (see Table 2) and also the variation of pH from 1 to 13 does not induce any important change of the spectral features. Only a weak bathochromic shift could be observed at high DMPU content.

In spite of that, the spectral behavior of PTNHMe (Figure 3) is quite noteworthy, showing an evident electronic pure transition at 586 nm almost reaching in intensity the first vibronic quantum at 550 nm, suggesting the ability of this sample to self-assemble in a very ordered planar conformation even in pure CH_3OH.

It is in fact well-known that the presence of ordered chain conformations in polyalkylthiophenes is a necessary condition for the vibronic structure to be observed.[26] The peculiarity of these amino polymers of assuming well-ordered conformations even in good solvents is once again confirmed, a capability which is indeed further enhanced in PTNHMe, giving a spectral profile in solution comparable with those of poly(3-alkylthiophenes) obtained at low temperatures and in the solid state.[27] This is also true for $PTNH_2$ and clearly shows the important role played by the chemical structure of the functional group inserted in the final portion of the side chain in determining the chromic properties of the polythienyl derivatives. The delicate balance among the attractive forces involving the functional amino groups and the repulsive ones ascribable to the sterically demanding side chains is, however, difficult to explain and to predict a priori, but the presence of the unsubstituted thienyl ring in the repeating unit undoubtedly confers unexpected properties to these polymers. Being examined in good solvents in a very dilute regime, polymers chains are able to self-assemble in planar and highly delocalized conformers, mainly through intrachain interactions involving the side-chain amino groups and leading to very soluble, highly conjugated microaggregates which do not precipitate even after months, as testified by the constancy of the absorption values after filtration on Teflon septum 0.20 μm pore size.

In pure CH_3OH, the spectra of $PTNMe_2$ and PTN^+Me_3 are well structured, with a λ_{max} near to those observed for the two Boc-protected polymers.

DMPU additions lead to a marked blue shift of the whole spectral profile (see Table 2). PTN^+Me_3 (Figure 4) is subjected to the most evident chromic effect, with an ipsochromic shift of 38 nm, reduced to 21 nm for $PTNMe_2$ in the same experimental conditions. This behavior is probably ascribable to DMPU ability to solvate strongly polar groups, leading to a partial disruption of the intrachain microaggregates still present in the CH_3OH solution and directly deriving from the solid state. No remarkable chromic transitions were evident going from CH_3OH to H_2O, and also the variation of the pH of the solution did not determine any important change of the spectral features, as occurs for $PTNH_2$ and PTNHMe.

Table 2. UV−Vis Absorption Maxima of the Polymers in Solution and in the Solid State

solvents	PTNHBoc	PTNMeBoc	solvents	$PTNH_2$	PTNHMe	$PTNMe_2$	PTN^+Me_3
DMPU	536	547	CH_3OH	549	549	544	549
DMPU−CH_3OH (0.98 CH_3OH mf)	550	554	CH_3OH−DMPU (0.98 DMPU mf)	556	553	523	511
DMPU−H_2O (0.98 H_2O mf)	536	552	CH_3OH−H_2O (0.98 H_2O mf)	551	551	546	552
film (cast from $CHCl_3$)	550	551	film (cast from CH_3OH)	554	549	544	550

From Table 3 and Figure 5, in which the spectral profiles of the films of all the polymers are reported, it is evident that the λ_{max} and the spectral profiles in film, even if essentially comparable to those obtained in solution, are typical of chromophores with a higher degree of conjugation. Considering now the film, the two Boc-protected samples show the more marked bathochromic shift (up to 14 nm) evidencing, once devoid of the solvent molecules, their ability to self-assemble in a more ordered conformation. For the other samples, even if the bathochromic shift determined going from the solvated to the solid state is not particularly pronounced, the pure electronic transition 0−0, directly proportional to the amount of more conjugated chromophores present in the polyconjugated system, rises its intensity of about 20% (see Table 3). This fact evidences the possibility to further enhance the conformational order of the polymeric chains of all the prepared polymers due to interactions between the macromolecules in conjugated polymeric films obtained by the slow evaporation of the solvent system.

However, the fact that the spectral features of the polymers in film are similar to those obtained in pure solvent solutions strongly validate the hypothesis already stated that the amino polymers are able to reach a very high conformation planarity already in good solvents. This can be a very important feature for obtaining concentrated solutions of preordered planarized PT chains, very useful for the preparation of Langmuir−Blodgett films or for electrospinning processes. Moreover, even if a clear solvatochromic trend among the examined samples is hard to find, it can be concluded that the possibility for all the prepared amino polymers to form highly ordered and still soluble polymeric conformers is an undeniably important feature for the building up of practical devices.

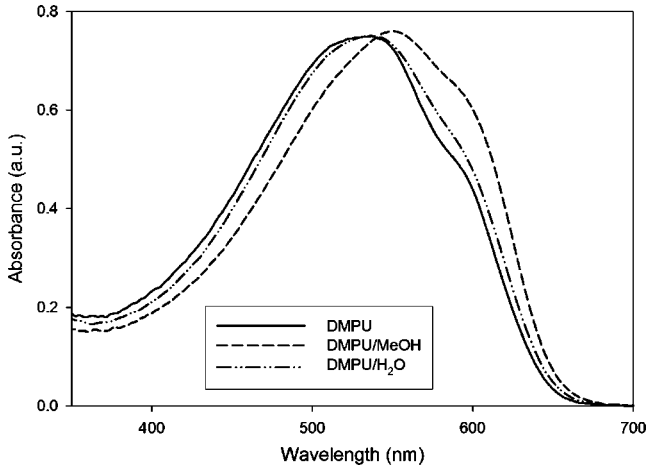


Figure 2. UV−vis spectra of PTNHBoc in different solvent systems.

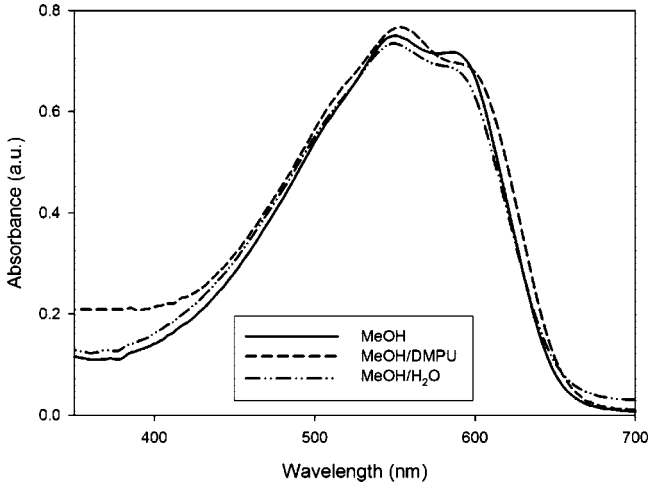


Figure 3. UV−vis spectra of PTNHMe in different solvent mixtures.

X-ray Characterization. X-ray diffraction patterns of all the polymer films cast on alumina from $CHCl_3$ or CH_3OH solutions are reported in Figure 6, and their relevant angles and corresponding d spacings are listed in Table 4. They show two main peaks: one with spacing d_1 in the low-angle region (2θ below 5°) and another spacing d_2 at higher angles. These distinct X-ray diffraction patterns indicate that the polymers assume ordered structures in the solid state.

According to recent literature on alkyl PTs,[28] the first sharp reflection d_1 is assignable to the distance between the polymer backbones separated by their alkyl chains. The observed distance, around 27 Å, is compatible with an end-to-end packing of substituents (Chart 3), rather than with an interdigitated one,[29] and it is quite the same for all our polymers, due to the similar chain lengths. The d_2 spacing is assigned to the stacking face-to-face distance between two successive polymers chains. Another reflection d_3 shown by PTNHBoc ($2\theta = 10.8°$, 8.2 Å)

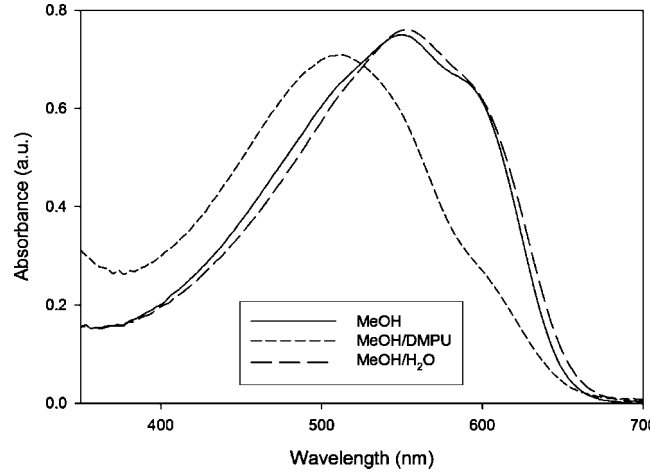


Figure 4. UV−vis spectra of PTN^+Me_3 in different solvent mixtures.

Table 3. Chromic Effects Passing from Solution to Film for the Synthesized Polymers

sample	$\Delta\lambda_{max}$ (nm)[a]	ΔA_{0-0} (%)[b]
PTNHBoc	+14	+35
PTNMeBoc	+7	+30
$PTNH_2$	+5	+22
PTNHMe	0	+18
$PTNMe_2$	0	+18
PTN^+Me_3	+1	+20

[a] λ_{max} film − λ_{max} solution (from which the film was obtained). [b] A_{0-0} film − A_{0-0} solution (from which the film was obtained). The position of the pure electronic transition E_{0-0} was found by the second derivative of the spectral profile.

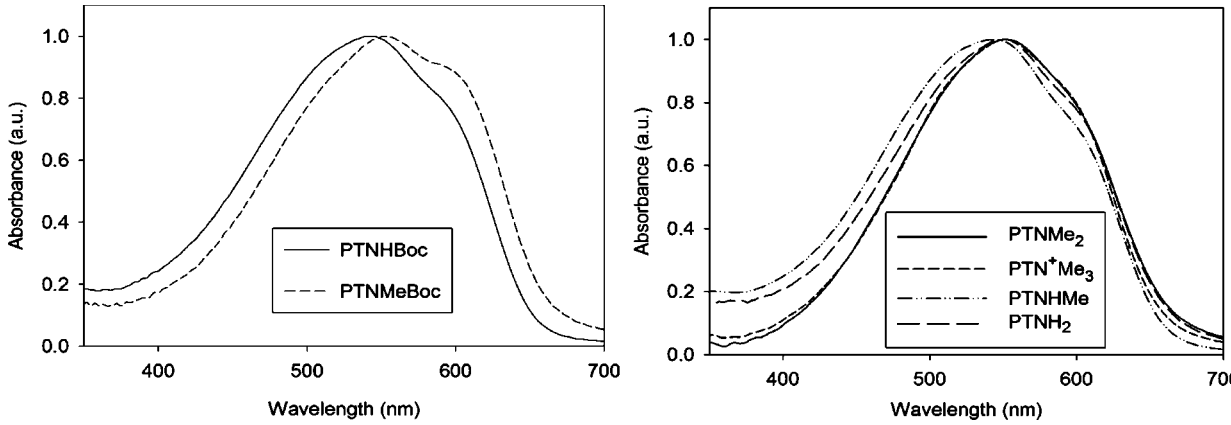


Figure 5. UV−vis spectra of the different polymers in film.

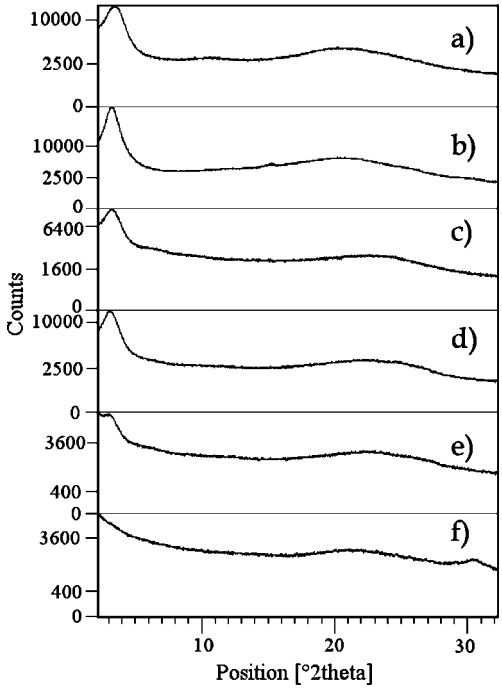


Figure 6. X-ray diffraction patterns of (a) PTNHBoc, (b) PTNMeBoc, (c) $PTNH_2$, (d) PTNHMe, (e) $PTNMe_2$, and (f) PTN^+Me_3.

Table 4. XRD diffraction 2θ angles and calculated *d* spacing

	2θ (deg)/*d* spacing (Å)	
	d_1	d_2
PTNHBoc	3.5/25.0	20.5/4.3
PTNMeBoc	3.3/27.1	20.7/4.3
PTNHMe	3.1/28.9	22.3/4.0
$PTNH_2$	3.2/27.4	22.4/4.0
$PTNMe_2$	3.1/28.9	22.6/4.0
PTN^+Me_3	[a]	21.5/4.1

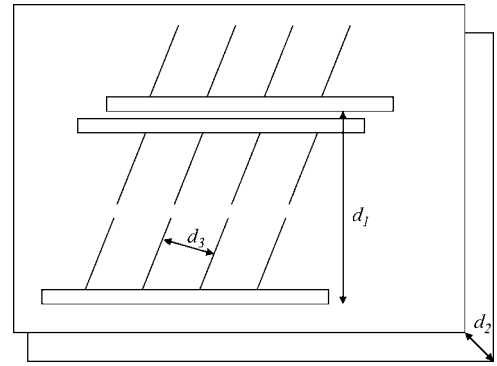
[a] Not resolved.

is not always present in XRD spectra of PTs, and should be related to the lateral separation between the substituent chains on the same polymer backbone. The possibility for the side chains to assume a nematic order, probably promoted by the formation of the hydrogen bonds between the carbamate groups as evidenced by NMR analysis, makes this polymer particularly attractive for its enhanced self-assembling capability.

Conclusions

Starting from novel amino-functionalized thiophenes **1**−**4**, six new aminoalkylsulfanyl PTs, namely PTNHBoc, PTNMeBoc, $PTNH_2$, PTNHMe, $PTNMe_2$, and PTN^+Me_3, were synthesized. PTNHBoc, PTNMeBoc, $PTNMe_2$, and PTN^+Me_3 were obtained through Stille coupling, $PTNH_2$ and PTNHMe from PTNHBoc, and PTNMeBoc through deprotection.

Chart 3. Schematic Representation of Relevant Distances Derived by XRD



The solubility of these polymers is strongly related to the presence and to the type of *N*-substituents and, on going from the protected amines to the quaternary ammonium salt, dramatic changes in solubility are observed. All of them are soluble in DMSO and DMF. PTNHBoc and PTNMeBoc are also soluble in $CHCl_3$, CH_2Cl_2, THF, and DMPU, whereas $PTNH_2$ and PTNHMe in CH_3OH, and $PTNMe_2$ and PTN^+Me_3 in both CH_3OH and H_2O. Being the major part of organic semiconducting polymers soluble in organic solvents, which are complicated and costly to dispose of, the H_2O solubility acquires great importance in view of future industrial applications of these materials. All the synthesized PTs show a proneness to microaggregation in solution, which is not, however, an obstacle for their solubility. We suggest that the tendency toward aggregation mainly comes from dispersion forces involved in π-stacking, from dipolar interactions and, in the case of PTNHBoc, also from hydrogen bonds. NMR, UV−vis, and XRD results show that the prepared polymers are able to reach very high conjugation lengths and ordered conformations, not only in the solid state but also in solutions of good solvents, an undeniably fundamental feature for optical and optoelectronic properties.

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