DOI: 10.1002/masy.200650211

Novel Thiophenic Copolymer as a Multi-Purpose Macromolecular Intermediate

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Summary: The preparation of a new thiophenic dimer partially derivatized with a bromohexylic chain is described. Its polymerization under mild oxidative conditions leads to a polythiophene with a degree of functionalization of 50% and highly soluble in organic solvents. The product has been fully characterized by FT-IR, ^{1}H and ^{13}C NMR using one and two-dimensional techniques as well as by SEC and thermal analysis. Solvatochromic effects of the new polymer have been investigated in different mixtures, underlining its self-assembling capability even in solvated states.

Keywords: conjugated polymers; cooperative effects; copolymerization; NMR; polythiophenes; self-organization

Introduction

Polythiophene derivatives have attracted the attention of many research groups due to their peculiar properties such as conductivity in the doped state,[1,2] thermocromism,[2,3] solvatochromism,[3,4] electrochromism,[5,6] photoluminescence[7,8] and electroluminescence.[9,10] For these reasons, several applications have been suggested and attempted in the literature, such as light emitting diodes, electroluminescent devices and polymeric sensory systems.[11] Besides exhibiting a considerable air stability due to the sulphur heteroaromatic ring structure and interesting optical properties that depend on the conformation of the alkyl groups, poly(3-alkylthiophene)s (PATs) are also soluble in some usual organic solvents. In fact, the alkylic side chain disrupts the intermolecular interactions by pushing the chains apart and increases the solvation entropy of the polymer, allowing PATs to become soluble, easily filmable and processable. Moreover, the insertion of functionalized side chains is very intriguing since the properties of the functional group can add to that of the polyconjugated backbone, leading to real multifunctional materials.[12]

The incorporation of a functionalized side chain on the thiophene and the subsequent polymerization via iron trichloride produce configurational defects, which can be avoided by means of alternative complex synthesis using organometallic couplings of thiophenes strategically derivatized in the 2,5 positions of the eteroaromatic ring[13] or by using symmetric (oligo)thiophenes.[14] Low steric repulsion among side chains can also be attained using asymmetric and not wholly substituted bithiophenes, looking for the ideal compromise between solubility and steric hindrance.

To this purpose, in the present work a new thiophenic dimer, namely the 3-(6-bromohexyl)-2,2′-bithiophene (**D**, Scheme 1) has been synthesized and polymerized, to get a better insight on the structure-property relationship of PATs, and to obtain an useful polymeric intermediate easily convertible in other multifunctional

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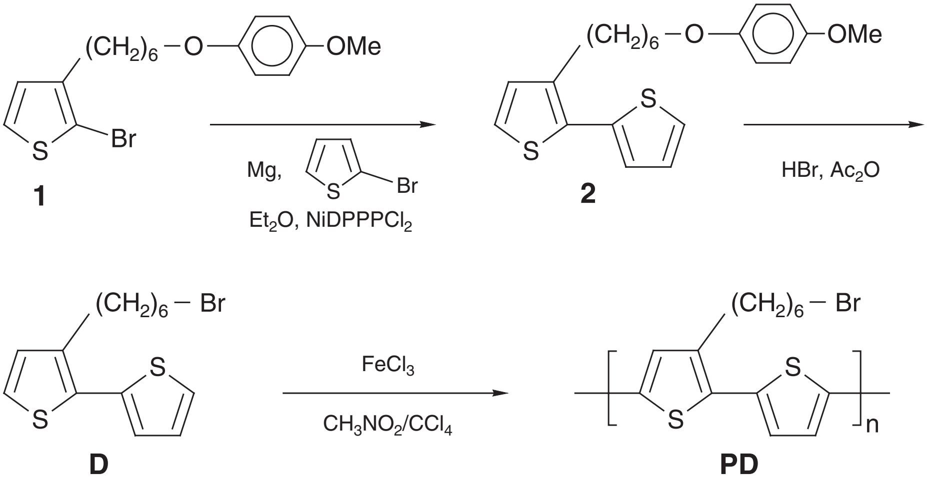

Scheme 1.
Synthesis of dimer **D** and polymer **PD**.

materials by simple reactions of post-polymerization functionalization.

Experimental

Materials and Instruments

All the solvents and reagents used for the synthesis were purchased from Aldrich Chemical Company. IR spectra were carried out using a Perkin Elmer 1750 FT-IR spectrophotometer. The molecular weights were determined by size exclusion chromatography (SEC), relative to polystyrene standards, on a HPLC Lab Flow 2000 apparatus equipped with a Phenogel mixed MXM column and a Linear Instrument (model UVIS-200) UV-Vis detector working at 263 nm, with THF being used as an eluent, at a flow rate of 1.0 mL/min. Thermal analysis was performed on a TA Instruments DSC 2920 and a TGA 2050 and the heating rate was 10 °C/min.

^1H and ^{13}C NMR spectra were obtained on $CDCl_3$ solutions with a Bruker Avance 400 spectrometer operating at 400.13 and 100.61 MHz, respectively. The ^1H and ^{13}C chemical shifts (δ, ppm) are quoted with respect to the $CHCl_3$ signal at 7.26 ppm (for ^1H) and to $CDCl_3$ at 77.0 ppm (for ^{13}C). HMQC[15] parameters were as follows: spectral width (f2) = 7.7 ppm, 2k complex points; spectral width (f1) = 150 ppm, 256 t1 increments with 16 scans per t1 value; relaxation and evolution delays were 0.5 s and 2.78 ms, respectively. HMBC[16] parameters were as follows: spectral width (f2) = 7.7 ppm, 2k complex points; spectral width (f1) = 150 ppm, 256 t1 increments with 32 scans per t1 value; relaxation and evolution delays were 0.5 s and 50 or 100 ms, respectively. TOCSY[17] parameters were as follows: spectral width (f2) = 7.7 ppm, 2k complex points; spectral width (f1) = 7.7 ppm, 256 t1 increments with 16 scans per t1 value; relaxation delay 0.5 s, mixing time 50 ms.

3-[6-(*p*-methoxyphenoxy)hexyl]-2,2′-bithiophene (2)

A solution of 5.65 g (34.65 mmol) of 2-bromothiophene in 57 ml of anhydrous diethyl ether is added dropwise in 1 h under Ar atmosphere to 0.89 g (36.73 mmol) of Mg turnings and then refluxed for 2 h. The mixture is subsequently transferred via cannula to a second apparatus and added dropwise to a mixture of 8.00 g (21.66 mmol) of 2-bromo-3- [6-(p-methoxyphenoxy)hexyl]thiophene (**1**, prepared as in Ref [20]) and 0.1174 g (0.2166 mmol) of [1,3-bis(diphenylphosphino)propane]nikel (II) chloride ($NiDPPPCl_2$) in 57 ml of anhydrous diethyl ether with the temperature being kept at

Table 1.
Polymer yield and characteristic data.

Yield[a)]	M_n	M_w/M_n	Dp_n	HT	I_{sym}/I_{asym}[c)]	λ_{max} film[d)]
%				%		(nm)
74	11000	1.5	66[b)]	50	0.95	512

a) In fractionated polymer.
b) In monothiophenic repeating units.
c) Intensity ratio of the symmetric ring stretching to the antisymmetric one.
d) Film on quartz cast from $CHCl_3$ solution.

−5.5 °C. The reaction mixture is refluxed for 6 h and afterwards quenched with 250 ml of 2% HCl. The aqueous phase is extracted with 4 × 100 ml of diethyl ether, washed to neutrality, dried over $MgSO_4$ and concentrated to give 7.99 g (21.45 mmol, 99% yield) of crude **2**, which is then purified by chromatography (Al_2O_3/n-heptane-diethyl ether 9:1) leading to 7.19 g (19.14 mmol; 88% yield) of the desired product.

^1H NMR ($CDCl_3$, ppm): δ 7.50 (m, 1H); 7.29 (dd, 1H); 7.17 (d, 1H); 7.10 (dd, 1H); 6.92 (d, 1H); 6.82 (s, 4H); 3.83 (t, 2H); 3.68 (s, 3H); 2.68 (t, 2H); 1.82–1.18 (m, 8H).

^{13}C NMR ($CDCl_3$, ppm): δ 154.2, 153.8, 139.9, 130.4, 127.9, 126.5, 125.8, 124.3, 115.9, 115.1, 69.0, 56.2, 31.2, 29.9, 29.8, 29.6, 26.4.

FT-IR (KBr, cm^{-1}): 3 086, 2 988, 2 935, 2 859, 1 510, 1 464, 1 241, 1 181, 1 035, 827, 797, 739, 636, 584.

3-(6-bromohexyl)-2,2′-bithiophene (D)

A mixture of 5.43 ml of 48% HBr and 7.52 ml of acetic anhydride is added under N_2 atmosphere to 3.00 g (8.05 mmol) of **2** and 0.20 g (0.40 mmol) of hexadecyltributylphosphonium bromide. The reaction mixture is heated at 90 °C for 24 h. After dilution with 140 ml of distilled water and ice, the mixture is extracted with 5 × 50 ml of CH_2Cl_2. The organic phase is washed to neutrality with saturated $NaHCO_3$, dried over $MgSO_4$ and concentrated to give 2.53 g (7.81 mmol, 97% yield) of crude **D**, which is then purified by chromatography (SiO_2/n-heptane) leading to 1.72 g (5.23 mmol; 65% yield) of the desired product.

^1H NMR and ^{13}C NMR see Table 3; FT-IR see Table 2.

Poly[3-(6-bromohexyl)-2,2′-bithiophene] (PD)

A solution of 0.46 g (2.81 mmol) of anhydrous $FeCl_3$ in 3.00 ml of CH_3NO_2 is added dropwise over 20 min to a solution of 0.23 g (0.70 mmol) of **D** in 8.50 ml of CCl_4. After stirring for 40 min at 20 °C under a flux of dry Ar, 10 ml of freshly distilled THF and 40 ml of HCl in CH_3OH (5%) are added to the reaction mixture. The liquid phase is removed and the precipitated

Table 2.
Characteristic FT-IR frequencies (cm^{-1}) for **D** and the relative polymer **PD**.

D	PD	Assignment
3104	–	C–H stretching, thiophene α-hydrogen
3068	3062	C–H stretching, thiophene β-hydrogen
2931	2934	C–H stretching methylenes, antisymmetric
2856	2855	C–H stretching methylenes, symmetric
1505	1496	C=C stretching thiophene, antisymmetric
1462	1460	C=C stretching thiophene, symmetric
882, 830, 724	–	C–H 2,3 di-substituted thiophene, bending out of plane
848, 694	–	C–H 2 mono-substituted thiophene, bending out of plane
–	833	C–H 2,3,5 tri-substituted thiophene, bending out of plane
–	791	C–H 2,5 di-substituted thiophene, bending out of plane
Emb.	728	CH_2 rocking
645, 560	645, 562	C–Br stretching

Table 3.
^{1}H and ^{13}C NMR data for **D** (δ, ppm).

Monomer	–	–	H-4	H-5	–	H-3′	H-4′	H-5′
D	C-2	C-3	C-4	C-5	C-2′	C-3′	C-4′	C-5′
^{1}H			6.93	7.18		7.11	7.07	7.31
^{13}C	130.6	139.3	129.8	123.8	136.1	126.1	127.3	125.3
	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	$CH_2(\delta)$	$CH_2(\varepsilon)$	$CH_2(\phi)$		
^{1}H	2.76	1.65	1.48	1.38	1.85	3.39		
^{13}C	28.9	30.4	27.9	28.5	32.7	33.8		

product is dissolved in 150 ml of $CHCl_3$. The organic solution is washed with 2% HCl, with water to neutrality, dried over Na_2SO_4 and its volume reduced to 10 ml. After addition of 150 ml of CH_3OH, the fractionated polymer is filtered over a Teflon septum (0.20 μm pore size) and washed with CH_3OH to give 0.166 g (0.52 mmol, 74% yield) of the desired product.

^{1}H NMR and ^{13}C NMR see Table 4; FT-IR see Table 2.

Results and Discussion

3-[6-(*p*-methoxyphenoxy)hexyl]-2,2′-bithiophene (**2**, Scheme 1) was synthesized in good yield from 2-bromo-3-[6-(*p*-methoxyphenoxy)hexyl]thiophene obtained as reported in Ref. [20], by the cross-coupling Ni(II) catalyzed of **1** with 2-thienylmagnesium bromide. **2** was hence submitted to a cleavage of the etheric functionality leading to 3-(6-bromohexyl)-2,2′-bithiophene (**D**), which has been polymerized using iron trichloride with a procedure involving the addition of the solution of the oxidizing agent in CH_3NO_2 to the dimer in CCl_4. Since the carbonium tetrachloride is a non-solvent for the $FeCl_3$, this method generates the active oxidant *in situ* in a highly dispersed microcrystalline form, avoiding the formation of insoluble polymeric fractions. This polymerization afforded the completely soluble polymer **PD** with a satisfactory yield (74% in purified polymer, see Table 1) and with the expected chemical structure, as testified by spectroscopic analysis.

FT-IR analysis shows that in the ω-brominated polymer the absorption at 3104 cm^{-1} ascribable to the stretching of the thiophenic α-hydrogens is absent, in agreement with the good degree of polymerization and with the absence of α-β or β-β linkages. For clarity sake in Table 2 are reported the frequencies and the assignments of the characteristic bands. Evaluating the intensity ratio I_{sym}/I_{asym} of the IR absorptions of the polymer at 1460 and 1496 cm^{-1}, ascribable to the symmetric and

Table 4.
^{1}H and ^{13}C NMR data for polymer **PD** (δ, ppm).

Polymer	–	–	H-4	H-5	–	H-3′	H-4′	H-5′
PD	C-2	C-3	C-4	C-5	C-2′	C-3′	C-4′	C-5′
^{1}H*			6.99(+)	–	–	7.02–7.04	7.13(+)	–
^{13}C*	129.6	140.0	126.4	134.7	134.7	126.4	124.0	136.5
^{1}H			7.0			7.02–7.04	7.10	
^{13}C	130.5	139.4	126.4	134.8	134.7	126.4	124.0	136.5
	$CH_2(\alpha)$	$CH_2(\beta)$	$CH_2(\gamma)$	$CH_2(\delta)$	$CH_2(\varepsilon)$	$CH_2(\phi)$		
^{1}H*	2.78	1.69	1.47	1.47	1.88	3.42		
	2.80					3.40		
^{13}C	29.4	30.2	27.9	28.6	32.7	34.0		

* More abundant junction.

antisymmetric stretching of the thiophene ring respectively, a lower value for **PD** respect to the ratios of other PATs either reported[21,22] can be found (0.95, see Table 1). This fact can be related to the more extended conjugation length[23,24] of this less sterically crowded polymer, also confirmed by the value of the absorption maximum in film, 512 nm, notably red-shifted respect to other conventional poly(3-alkylthiophene)s reported in literature.[25,26] The polymer has molecular weights lower than those of PATs obtained by the analogous method of oxidative polymerization; this fact essentially depends on the enhanced stability of the radical-cation of the bithiophenic monomer and on the consequent increased probability of the formation of many shorter polymeric chains.[27,28]

The degree of regioregularity of PATs is usually evaluated by ^1H NMR on the basis of the intensity ratio of the two signals relative to methylene protons in α to the thiophene ring[29] but **PD** sample needs a deeper analysis because of the presence, in its backbone, of substituted and unsubstituted aromatic rings linked in a random sequence.

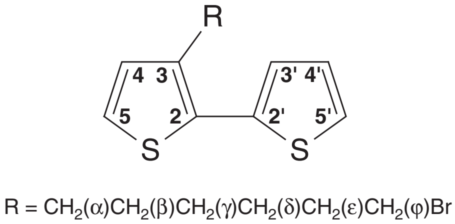

Figure 1.
Structure of **D**.

NMR characterization of D

The structure of the dimer **D** is depicted in Figure 1 and its ^1H and ^{13}C spectra are reported in Figure 2.

The assignment of the aromatic signals to the corresponding protons of the monosubstituted thiophene ring stems directly from the J(H,H) values, whereas that of the protons belonging to the disubstituted thiophene ring has to be based on the $^1J(C,H)$ coupling constants obtained from an inverse-detected heteronuclear multiple-quantum experiment according to Ref. [17]. The doublet at 7.18 ppm displaying a $^1J(C,H)$ of 190 Hz is assigned to H-5, whereas the doublet at 6.93 ppm is attributed to H-4.

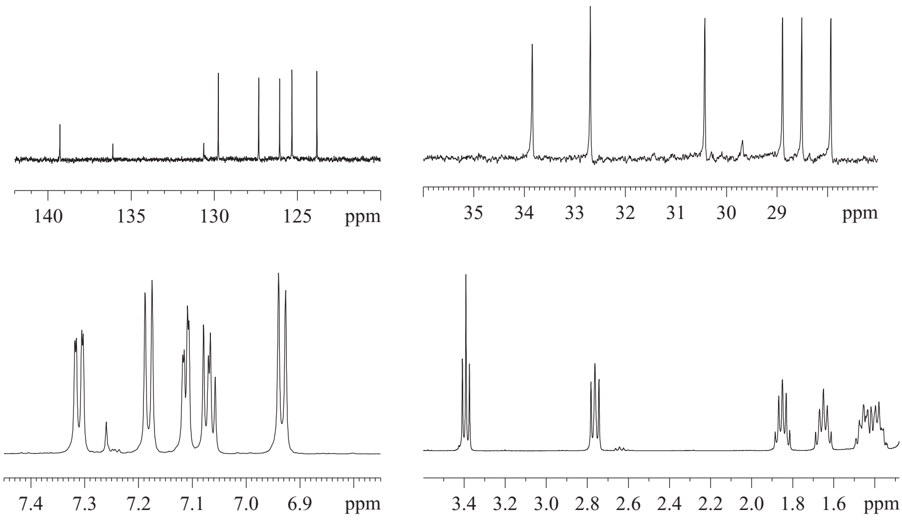

Figure 2.
Bottom trace ^1H NMR and upper trace ^{13}C NMR spectra of **D**.

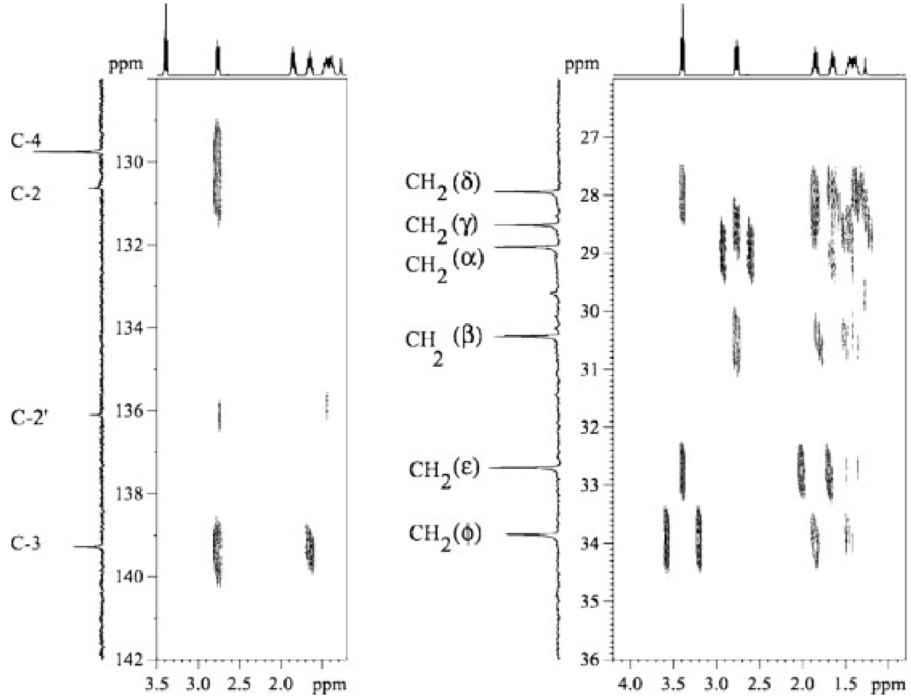

Figure 3.
Partial HBMC experiment; left correlations between aliphatic protons and aromatic carbons; right correlations between aliphatic protons and aliphatic carbons.

The HMBC[18] experiment, reported in Figure 3, permits the complete assignment of the alkyl chain resonances by exploiting the ^{1}H and ^{13}C long-range and residual one-bond correlations. The ^{1}H and ^{13}C NMR data of **D** are reported in Table 3.

NMR assignment of PD

The proton and carbon spectra of the polymer **PD** are reported in Figure 4.

On the basis of polymerized monomer, the spectrum should display singlets due to the H-4 protons of the β-substituted units and two doublets due to the protons of unsubstituted ones. Instead the spectrum shows in the aromatic region between 6.9 and 7.4 ppm overlapped signals, hardly attributable, by a direct inspection, to the corresponding protons. Furthermore, the crowdedness of ^{13}C NMR spectrum does not help in the assignment. Nevertheless, some informations can be achieved through suitable two- dimensional NMR experiments. In order to discriminate between the protons of the un-substituted units with respect those of the β-substituted ones, we performed a TOCSY[19] experiment (Figure 5). This experiment permits to find the pairs of coupled β-protons and the protons belonging to the terminal units.

The signals a 7.13 and 7.10 ppm correlate with the signals centred at 7.01 ppm and are assigned to the β, β' protons. The doublet at 6.93 ppm correlates with the doublet a 7.18 ppm and can be assigned to the terminal β substituted thiophene, whereas proton signals at 7.33 ppm (H-5′), 7.08 ppm (H-4′) and 7.14 ppm (H-3′) are due to non substituted thiophene ring. The singlets at 6.99 and 7.01 ppm are assigned to the H-4s of the β-substituted thiophene.

The HMQC and HMBC experiments permit to find the C-H pairs and the long range correlated carbons. The HMQC experiment (Figure 6) shows that the H-4 protons at 7.02 and 6.99 ppm correlate with carbon at 126.5, and that the protons at 7.13 and 7.10 ppm correlate with carbon at

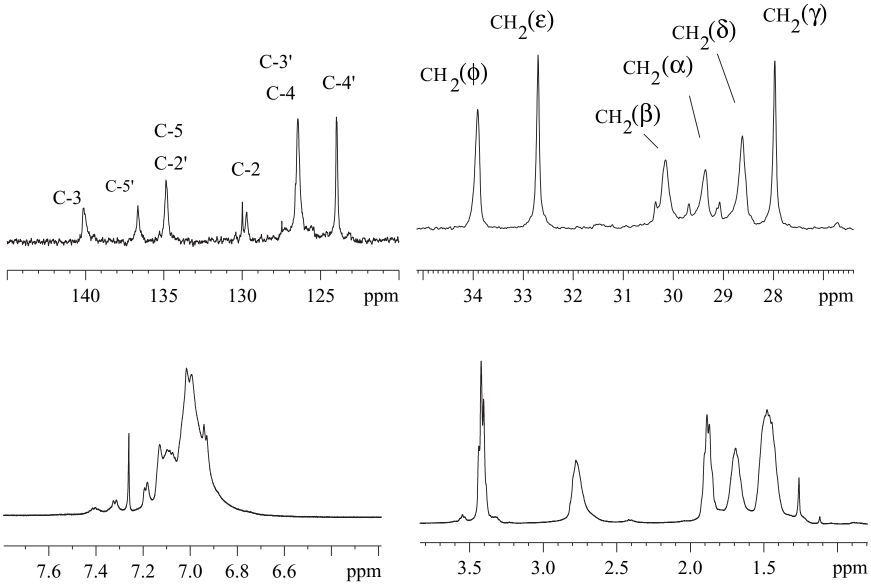

Figure 4.
Bottom trace: ^{1}H NMR and upper trace ^{13}C NMR spectra of **PD**.

124.0 ppm. Furthermore the correlations between the protons of a β-substituted terminal unit (H-4 at 6.93 ppm and H-5 at 7.18 ppm) and the corresponding carbons (129.6 and 124.0 ppm, respectively) are clearly detectable.

The identification of the remaining resonances can be obtained through heteronuclear ^{1}H and ^{13}C long-range correlation experiments. The HMBC performed with an evolution delay of 50 ms (Figure 7a) enables the correlations of H-4 protons

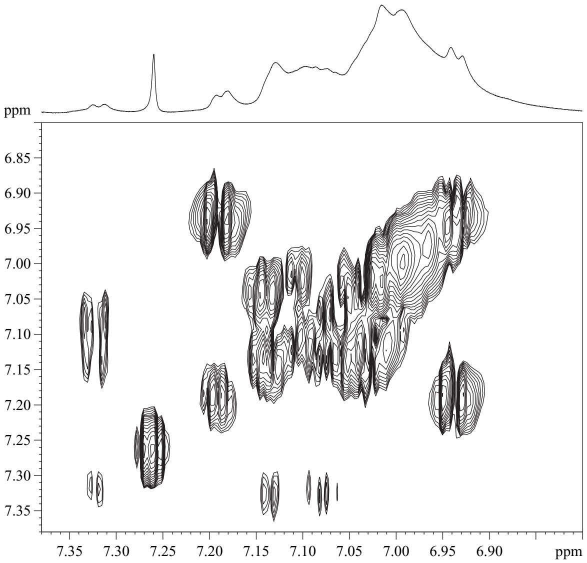

Figure 5.
Aromatic region of TOCSY spectrum of **PD**.

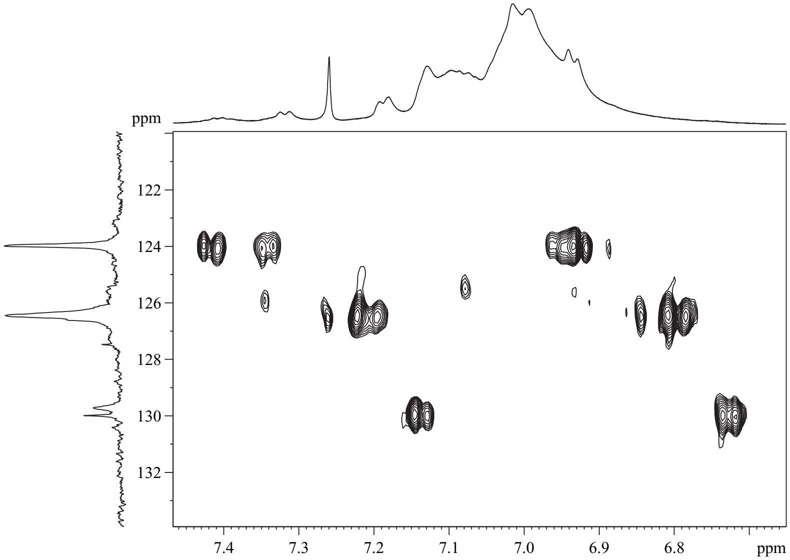

Figure 6.
Aromatic region of ^1H, ^{13}C HMQC spectrum of **PD**.

with C-2 carbons at 129.6 ppm, (this correlation is absent in the HMBC experiment with an evolution delay of 100 ms), with C-5 at 134.8 ppm and C-3 at 140.0 ppm to be found. The C-2 carbons display correlation with H-3′ centered at 7.02 ppm in a HMBC experiment performed with an evolution delay of 100 ms (corresponding to a long-range coupling constant of 5 Hz). Hence the remaining protons are assignable to H-4′. This experiment enables the mono-substituted terminal unit to be identified through the long-range correlations of the carbons at 125.4 (C-5′), 126.0

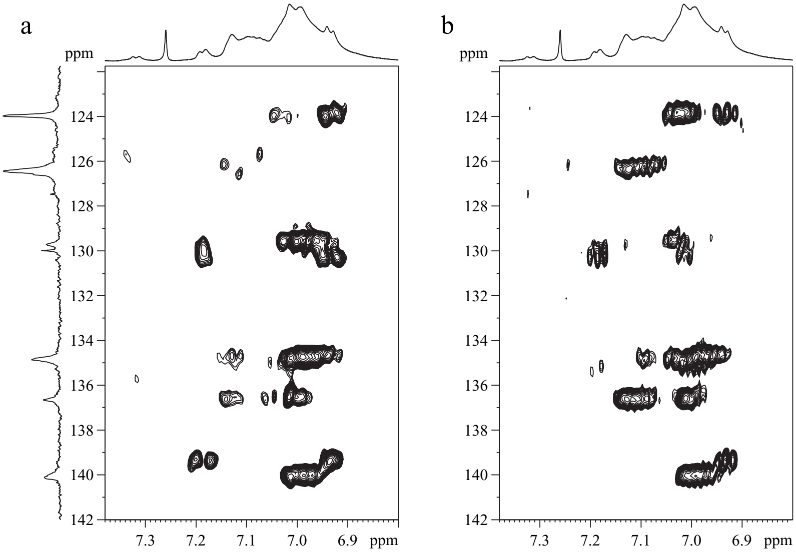

Figure 7.
Partial HMBC experiments performed with: a) 50 ms and b) 100 ms evolution delays.

(C-3′)127.3 (C-4′) with the already attributed protons.

Two types of chains can be detected from HMBC experiment, but the differentiation is only in the proton signals and not in the carbon ones. The more abundant chain is identified through the $CH_2(\alpha)$ at 2.78 ppm which shows correlation besides the proper carbon at 29.4 ppm with C-3 at 140.0, with C-2 at 129.6 and with C-4 at 126.4 ppm. The less abundant chain with $CH_2(\alpha)$ at 2.80 ppm displays correlations with proper C at 29.4 ppm and with C-3 at 139.4, C-2 at 130.5 and with C-4 at 126.4 ppm. The ^1H and ^{13}C NMR data of polymer are summarized in Table 4.

By comparing the carbon chemical shifts of the polymer with those of the monomer we find that the C-5 and C-5′ carbons are deshielded of 12.7 and 11.2 ppm, whereas C-4 and C-4′ are shielded of 3.4 ppm, by the effect of the α,α'-junctions.

As a consequence of the overlapping of the carbon and proton signals, it is difficult to establish a prevalent regiochemistry and the polymer seems to be prevalently regiorandom with a slight prevalence of TT-HH junctions. The average molecular weight evaluated on the basis of the NMR analysis is 9–10 KDa, in good agreement with the value obtained by GPC-SEC (*vide supra*).

Solvatochromism

The chromic behaviour of **PD** has been studied by UV-Vis spectroscopy both in the pure solvents (see Table 5) and in their mixtures with different amounts of MeOH as a non solvent. In absence of methanol, the λ_{max} is anyway influenced by the kind of solvent varying from 452 (orange) to 476 nm (deep red) and showing a good sensitivity of this polymer towards solvents having different polarity. In this framework, low polarity solvents, i.e. with lower Reichardt parameters E_N^T or electrostatic factors EF (the product of the dielectric constant $\varepsilon \times$ the dipole moment μ), seem to be better solvents for **PD** according to the mild polarity of the macromolecules.

Table 5.
UV-Vis absorption maxima of **PD** in different solvents.

Solvent	λ_{max} [a)] (nm)	E_N^T [b)]	EF[c)] (C m $\times 10^{30}$)
CCl_4	452	0.052	0
Dioxane	454	0.164	3.30
THF	462	0.207	44.23
$CHCl_3$	467	0.259	18.45
DMPU	476	0.352	509.65

[a)] Polymer concentration: 7×10^{-5} M.
[b)] Empirical parameter of solvent polarity, see Ref. [30].
[c)] Macroscopical parameter of solvent polarity electrostatic factor.

The addition of methanol to the polymer solution in pure solvents causes a progressive colour change (from orange-red to purple) indicating the attainment of more extensive conjugation lenghts. This solvatochromic transition is more evident in apolar solvents (i.e. CCl_4, $\Delta\lambda_{max} = 50$ nm) than in polar ones (e. g. DMPU, $\Delta\lambda_{max} = 14$ nm), probably because the latter are marginal solvents for **PD**, unable to solvate the polymer to the same extent leaving it in solution in a partly microaggregated form.

From the experimental results reported above we can argue that the probability of more evident solvatochromic effects being generated from pure solvent solutions is higher the higher is the initial solvation degree of the polymer, since the final extended thiophenic chromophore, obtained at high methanol concentrations, is nearly the same.

Moreover, the attainment in solvent/non solvent mixtures of λ_{max} values higher than in solid state (e.g. 535 nm in $CHCl_3$ with a methanol molar fraction of 0.98 vs. 508 nm in film) can be explained considering that, in the condensed state, the polythiophenic backbone of **PD** is more flexible than that of 100% substituted PATs, giving more disordered molecular assemblies not able to afford an average conjugation length typical of the more rigid and ordered conventional thiophene homopolymers. This higher conformational versatility determines a wide range of attainable conjugation lengths and, as a consequence, to a spectrum in solid state completely devoid of structuration (inhomogeneous broadening). On the other hand, the increased rotational mobility of the macromolecules, due to the reduced steric hindrance, operates in favour of longer conjugated chromophores in solvent mixtures. In fact, under partial solvation conditions (in presence of methanol), where the propensity of the side chains to interact with themselves (cooperative phenomena[31]) helps the average conjugation length, this kind of substitution certainly favours the generation of more extended chromophores, evidencing the self-assembling capabilities of **PD** polymer.

Relating to thermal analysis **PD** shows only a second order transition at 31 °C (T_g) according to its essentially amorphous nature, and a decomposition point well above the room temperature (325 °C in air and 350 °C in inert atmosphere).

Conclusions

The new polymer prepared in this study, thanks to the unusual positioning of the flexible side chains possesses very high solubility in common organic solvents, even at low polarity, and a high chromic sensitivity towards the different solvent mixtures, revealing itself potentially useful for chemorecognition purposes. Moreover, the lower average substitution density of **PD**, if compared to the conventional PATs, is able to determine an easy substitution of the halogen group in side chain, a very important feature for post-polymerization processes, thanks to the improved solution and melt tractability. Meanwhile the space close to the backbone can provide more free volume available to accommodate the dopant reducing the thermal instability of the polymer respect to the doped conventional PATs.

Acknowledgements: The financial support by MIUR (funds for selected topics research) is gratefully acknowledged.

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