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Polymer 41 (2000) 3147–3157

polymer

Synthesis and characterization of neutral newly substituted polyalkylthiophenes

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Received 17 May 1999; received in revised form 22 July 1999; accepted 28 July 1999

Abstract

In this work, two newly substituted polyalkylthiophenes, poly(3,4-dihexyl-2,2′-bithiophene) and its didodecyl analogue have been prepared in order to compare their properties with those of the regioisomeric poly(3-alkylthiophene)s containing the same amount of head-to-tail configuration (conventional PATs). Remarkable differences between the material characteristics of these two kinds of polyalkylthiophene have been observed, thus enabling us to elucidate the side chains effects exclusively attributable to the difference between the side chains distribution along the polythiophene backbone. In the neutral bulk state, compared to that of the conventional PATs, the polymers prepared for this study have been found more thermostable materials exhibiting higher flexibility and less ordered (in the crystallographic sense) molecular assemblies, still able to afford an average conjugation length as long as that of the conventional PATs, but varying between wider limits. This seems to be closely connected with a lower degree of side chains interactions and/or the high proportion (50%) of unsubstituted thiophene rings. Based on these effects of molecular structure on the material properties at room temperature, we have anticipated in the novel polymers, at higher temperatures, the possibility of weaker thermochromism and better conductivity stability than in their regioisomeric conventional PATs. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(3,4-dialkyl-2,2′-bithiophene)s; Poly(3-alkylthiophene)s; Comparative study

1. Introduction

Flexible side chain substituted π-conjugated polymers are easily processible materials which still may have the extended π-electron delocalization typical of the corresponding unsubstituted parent polymer. This extensive π-conjugation gives rise to remarkable optical and nonlinear optical properties in the neutral state, as well as, upon doping, to high electrical conductivity. Owing to these unique physical properties, polyconjugated soluble polymers are currently receiving considerable attention in view of both a still more clear elucidation of the structure–property relationships and the wide variety of their potential technological applications [1–10].

Among the many conjugated polymers, polythiophene derivatives are at present extensively studied [2,4–6,9,10] due to the high environmental stability of both their neutral and doped states as well as to desirable characteristics such as lack of toxicity and low costs. Because of the easy way with which 3-*n*-alkylthiophene monomers can be prepared, a large proportion of papers have been devoted to poly(3-*n*-alkylthiophene)s (PATs). Oxidative coupling of the asymmetric 3-*n*-alkylthiophenes by either electrochemical [2] or chemical [11] polymerization methods always results in a ring chain containing about 70–80% of head-to-tail (HT) configurational dyads, with the remainder of the dyads being head-to-head (HH) or tail-to-tail (TT) coupled monomeric units, as determined by nuclear magnetic resonance (n.m.r.) analysis [12–16]. In the following, these 70–80/30–20 HT/HH or TT PATs possessing alkyl side chains with four or more carbon atoms will be referred to as conventional PATs.

There is now experimental evidence that many properties of PATs are attenuated by larger percentages of HH linkages, that impose limitations on the coplanarity of the ring chain, also decreasing the efficiency of interchain packing in the solid state. For instance, rather poor properties, compared to those of the conventional PATs, have been reported for 100% HH poly(3,4-dialkylthiophene)s [17], for PATs stoichiometrically identical with the conventional PATs, but containing regularly spaced HH (50%) and TT (50%) dyads,

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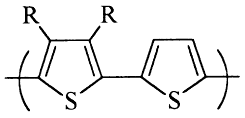
PII: S0032-3861(99)00528-5



R= n-hexyl : DHBT / PDHBT

R= n-dodecyl : DDBT / PDDBT

Fig. 1. Monomer/polymer molecular structures.

prepared from 3,3′-[18] or 4,4′-dialkyl-2,2′-bithiophene [19–21] monomers, and for totally regiorandom (50:50 HT/HH) PATs, prepared by the $Pd(PPh_3)_4$-catalyzed coupling polymerization reaction of 2-bromo-5-halozincio-3-alkylthiophenes [22–24]. On the contrary, regioregular PATs possessing almost exclusively HT couplings, prepared by elegant, but rather complex, synthetic routes, exhibited dramatically improved electrooptical properties [22–29]. Besides the configurational stereochemistry, also the length of the alkyl side chain in the conventional PATs has been extensively studied in view of its influence on both the electronically conjugated system of the main chain and the structural organization of the neutral and doped phases [12,26,28,30–40]. As a result, much weaker control of the electrooptical properties was found for the length of the alkyl side chain, compared to the ratio of HT to HH and TT coupling. However, in contrast to the conventional PATs, for other *n*-alkyl substituted polythiophenes there is considerably less information available on the relationships between the physical properties and the relative amount and distribution of the alkyl side chains [41–46]. In this context, in our previous research [47] we investigated the synthesis of poly(3,3″-and 3′,4′-dialkyl-2,2′:5′,2″-terthiophene)s having the same average side chain density, that is the same ratio of alkyl substituents to thiophene rings, but different regular side chain distributions. Interestingly, these polymers showed electrical and electrochemical behaviors strongly dependent on the specific positioning of the alkyl substituents [48,49].

In this paper, our synthetic attention has been directed to prepare the novel monomers 3,4-dihexyl-and 3,4-didodecyl-2,2′-bithiophene (DHBT and DDBT, respectively) and polymerize them according to the method of Sugimoto et al. [11], in order to obtain the newly substituted polyalkylthiophenes PDHBT and PDDBT which, as shown in Fig. 1, are isomers of PATs and can be viewed as α-linked alternating copolymers of 3,4-dihexyl- or 3,4-didodecylthiophene with unsubstituted thiophene (assuming perfect HT coupling).

For PDHBT and PDDBT we expect, indeed, a proportion of HT configuration very similar to that of the conventional PATs, due to the polymerization method adopted and to the geometric, steric and chemical similarities between the alkyl side chains in the corresponding starting monomers.

Moreover, owing to the specific molecular structure of the monomers DHBT and DDBT, the corresponding polymers are bound to have the same side chains density of the conventional PATs (namely a chain per thiophene ring, on an average) but a quite different and unusual side chain distribution along the polymer backbone, mostly consisting of two chains attached on every second thiophene ring (for all of the HT couplings). These observations indicate that in PDHBT and PDDBT the side chains steric requirements associated to the proportion of non-HT connectivity and to the length and average density of the side chains are comparable to those in the conventional PATs, thus resulting in comparable effects on the side chain induced properties. Consequently, by comparing PDHBT and PDDBT to the conventional PATs, it should be possible to estimate the effects of the steric requirements exclusively attributable to the novel side chains distribution.

2. Experimental

2.1. General and measurements

Since at room temperature the monomers are highly viscous liquids, whose thermal analyses by differential scanning calorimetry (d.s.c.) revealed unexpectedly large and variable undercoolings, the melting points (m.p.) of the monomers have been measured as well by detecting the temperature invariance in a phase transition (heating runs). A few drops of liquid samples at room temperature were poured into a thin walled test tube of 2 mm internal diameter and the cold junction of an iron/constantane thermocouple, calibrated with respect to an exactly measured room temperature of 16.5 ± 0.1°C was immersed in the liquid and connected to a recorder having its full scale settled at 20 mV. By cooling down to about −21°C, the liquid samples rapidly solidified wrapping the cold junction inside and the recorder shifted nearly to its full scale value. The test tubes were then lifted out of their cooling baths and the recorder was started vs time. The inflection point of each recorded heating curve corresponded exactly to the phase transition observed by direct visual inspection, with the m.p. of each monomer being in good agreement with the corresponding d.s.c. result (endothermic peak). Microanalytical results were supplied by Redox Laboratories (Cologno, M., Milan, Italy). The ^{1}H n.m.r. spectra were recorded in $CDCl_3$ on a Varian Gemini (200 MHz) Fourier Transform spectrometer and are reported in ppm as δ relative to internal tetramethylsilane at 0 ppm. The infra-red (i.r.) spectra were recorded on a Perkin–Elmer 1750 Fourier Transform infrared spectrophotometer and the frequencies are reported in cm^{-1} with the spectra being obtained on KBr discs using either neat samples for oily products or film samples for polymers. Mass spectrometry (m.s.) was carried out on a

VG 7070E spectrometer at 70 eV. All compounds first prepared in the course of this study gave elemental analyses (C, H, S, Br) within 0.4% of theory as well as ^{1}H n.m.r., i.r. and m.s. results which agreed with the assigned structures. The optical absorption measurements were performed at room temperature using a Perkin–Elmer Lambda 19 u.v./vis/near i.r. spectrophotometer. Sample preparation in form of thin films of PDHBT and PDDBT was made by casting from chloroform solutions on glass substrates. Thermogravimetric analysis (t.g.a.) was performed under nitrogen and air at a heating rate of 20°C/min; using a Perkin–Elmer TGA 7 analyzer. D.s.c. measurements on the polymers were performed between room temperature and +190°C on a Perkin Elmer DSC 7 apparatus using heating and cooling rates of 10°C/min. Polarizing microscope observations were carried out using a Leitz Orthoplan Pol apparatus equipped with a Leitz 350 hot stage in air at a heating rate ranging from 2 to 5°C/min. X-ray diffraction (x.r.d.) data were collected at room temperature using a conventional source, CuK radiation ($\lambda_1 = 1.5406$ Å, $\lambda_2 = 1.5443$ Å), and a Bragg–Brentano powder diffractometer (Philips PW1050/81-PW1710) equipped with a graphite monochromator in the diffracted beam. A 2Θ range between 2.0 and 90.0° was scanned by 881 steps of 0.1° with a counting time of 15 s for each step. Slits of 0.5°, 0.1 mm, 1° were used to collimate the radiation. The x.r.d. investigation was carried out using films of the polymers, which were cast from toluene solution. Molecular weights were measured by gel permeation chromatography (g.p.c.) on a Waters Model 590 instrument equipped with a TSK Gel G4000HXL column and a u.v.–vis. Perkin–Elmer LC-95 spectrophotometric detector. The molecular weights were obtained in the usual manner from the retention time calibration curve using a series of polystyrene standards.

2.2. Synthesis and characterization of DHBT and DDBT

The monomers DHBT and DDBT were prepared by the general procedure of Tamao et al. [50] using 2-thienylmagnesium bromide (1.25 equiv.), dichloro [1,3-bis(diphenylphosphino)propane]Ni(II) (5 mmol) and the appropriate 2-bromo-3, 4-dialkylthiophene (1 equiv.). The synthetic and purification details previously reported for the corresponding 3′4′-dialkyl-2,2′:5′,2″-terthiophenes [47] gave DHBT [m.p.: 5.4°C. Yield: 85%. Elemental anal. for $C_{20}H_{30}S_2$: calcd.: C: 71.80, H: 9.04, S: 19.17; found: C: 72.05, H: 9.00, S: 19.24. M.s. (m/z): 334 (M^+). ^{1}H n.m.r.: 7.28, dd, ^{1}H (5′), $J_{5'-4'} = 4.98$ Hz, $J_{5'-3'} = 1.42$ Hz; 7.09, dd, ^{1}H (3′), $J_{3'-4'} = 3.59$ Hz, $J_{3'-5'} = 1.42$ Hz; 7.04, dd, ^{1}H (4′), $J_{4'-5'} = 4.98$ Hz, $J_{4'-3'} = 3.59$ Hz; 6.86, s, ^{1}H (5); 2.66, t, 2H (αCH$_2$); 2.53, t, 2H (αCH$_2$); 1.7–1.1, m, 16 H (CH$_2$); 0.89, m, 6H (CH$_3$). I.r.: 3105, 3072, 2955, 2927, 2857, 1512, 1466, 1420, 1378, 1194, 1081, 880, 847, 826, 733, 692] and DDBT [m.p.: 22.4°C. Yield: 68%. Elemental anal. for $C_{32}H_{54}S_2$: calcd.: C: 76.43, H: 10.82, S: 12.75; found: C: 76.6, H: 10.78, S: 12.8. M.s. (m/z): 503 ($M^+ + 1$). ^{1}H n.m.r.: 7.28, dd, ^{1}H (5′), $J_{5'-4'} = 5.07$ Hz, $J_{5'-3'} = 1.31$ Hz; 7.09, dd, ^{1}H (3′), $J_{3'-4'} = 3.59$ Hz, $J_{3'-5'} = 1.31$ Hz; 7.04, dd, ^{1}H (4′), $J_{4'-5'} = 5.07$ Hz, $J_{4'-3'} = 3.59$ Hz; 6.86, s, ^{1}H (5); 2.66, t, 2H (αCH$_2$); 2.53, t, 2H (αCH$_2$); 1.7–1.1, m, 40H (CH$_2$); 0.89, m, 6H (CH$_3$). I.r.: 3106, 3072, 2926, 2853, 1514, 1466, 1420, 1378, 1196, 1080, 877, 825, 735, 723, 691]. The two desired 2-bromo-3,4-dialkylthiophenes were prepared from the corresponding 3,4-dialkylthiophenes by the bromination procedure of Mitchell et al. [51]. Usual work-up and chromatography over silica gel with *n*-hexane as eluent gave virtually pure 2-bromo-3,4-dihyexylthiophene [yield: 75%. Elemental anal. for $C_{16}H_{27}BrS$: calcd.: C: 58.00, H: 8.21, Br: 24.11, S: 9.68; found: C: 58.17, H: 8.17, Br: 24.20, S: 9.72. M.s. (m/z): 330 (M^+). ^{1}H n.m.r.: 6.85, s, ^{1}H (5); 2.5, m, 4H (αCH$_2$); 1.7–1.2, m, 16H (CH$_2$); 0.9, t, 6H (CH$_3$). I.r.: 3106, 2956, 2927, 2857, 1465, 1379, 1093, 974, 869, 727] and 2-bromo-3, 4-didodecylthiophene [yield: 70%. Elemental anal. for $C_{28}H_{51}BrS$: calcd.: C: 67.30, H: 10.29, Br: 15.99, S: 6.42; found: C: 67.50, H: 10.25, Br: 16.00, S: 6.44. M.s. (m/z): 499 ($M^+ + 1$). ^{1}H n.m.r.: 6.85, s, ^{1}H (5); 2.5, m, 4H (αCH$_2$); 1.7–1.2, m, 40H (CH$_2$); 0.9, t, 6H (CH$_3$). I.r.: 3106, 2955, 2925, 2853, 1466, 1378, 1098, 973, 867, 724]. Finally, 3,4-dihexyl- and 3,4-didodecylthiophene were prepared and purified by literature procedures [12,47] and the physical and spectroscopic data were found in agreement with the results previously reported. As far as m.s. is concerned, two features should be noted: (i) for he compounds containing bromine the isotopic abundance ratios were found as expected, and the reported molecular weights are given for the isotope ^{79}Br and (ii) for the dodecyl derivatives the ion corresponding to the expected molecular weight M was almost absent, but the ($M + 1$) peak intensity was well above the isotopic contribution. According to literature reports concerning 2-alkyl and 2,5-dialkylthiophenes [52], this may be due to a rearrangement ion whose intensity increases as the *n*-alkyl chain lengthens.

2.3. Synthesis and isolation of neutral polymers

The monomers DHBT and DDBT were oxidatively polymerized by anhydrous $FeCl_3$ in CCl_4. The oxidant to monomer molar ratio was 4:1 and the weighed amount of oxidant was added all at once, as a solid, to the monomer (1–2 g) solution (0.07 M) in CCl_4 under a gently bubbling N_2 stream. The deep blue-black mixture was stirred at room temperature for 16 h and then poured into about 500 ml of methanol. The resulting brown-red precipitate was recovered by filtration and exhaustively extracted in a Soxhlet apparatus, first with methanol, then with acetone, in order to remove the residual oxidant and oligomers. The unextracted polymer was dissolved using $CHCl_3$ for PDHBT and *n*-hexane for PDDBT and the solution filtered in order to remove traces of insoluble materials. After solvent evaporation, the residue was lifted by methanol in form of a continuous and homogeneous red film of high

Table 1
I.r. data of PDHBT and PDDBT

Polymer	Aromatic C_β–H str.	Aliphatic C–H str.			Ring str.			CH_3 def.	Aromatic C–H out-of-plane def.	CH_2 rocking
					Asym.	Sym.				
PDHBT	3064	2955	2928	2857	1495	1466	1437[a]	1378	793	724
PDDBT	3063	2954	2924	2852	1495	1467	1440[a]	1378	792	721

[a] Clear upward swelling which is assignable not only to ring vibrations, but to CH_2 bending modes of the conformationally slightly distorted aliphatic side chains, as well (see Ref. [57]).

flexibility and toughness. PDHBT (yield: 65%. Elemental anal. for $C_{20}H_{28}S_2$: calcd.: C: 72.23, H: 8.49, S: 19.28; found: C: 72.00, H: 8.45, S: 19.20, Fe $<$ 0.3, Cl $<$ 0.3). PDDBT (yield: 85%. Elemental anal. for $C_{32}H_{52}S_2$: calcd.: C: 76.73, H: 10.46, S: 12.80; found: C: 76.50, H: 10.42, S: 12.75, Fe $<$ 0.3, Cl $<$ 0.3).

3. Results and discussion

3.1. Polymerization and molecular weight analysis

The experimental conditions used for polymerization reactions of DHBT and DDBT are based on the general method of Sugimoto et al. [11]. However, the reaction solvent and the other synthetic details reported in Section 2 were chosen according to recently reported [47] results, in order to achieve not only good yields of neutral soluble polymers, but high molecular weights with the narrowest distribution, as well. Indeed, quite good yields of the soluble fraction of PDHBT and PDDBT have been obtained, with small amounts of the oligomeric fractions and even negligible amounts of insoluble materials being produced. Interestingly, unreacted DHBT and DDBT were absent in the respective oligomeric fractions, as determined by thin layer chromatography (SiO_2, hexane). The g.p.c. studies on the soluble fraction of PDHBT and PDDBT revealed that the weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) are 2.3×10^5 and 8.1×10^4 for PDHBT and 2.1×10^5 and 8.3×10^4 for PDDBT, with the polydispersity index ($\bar{M}_w/\bar{M}_n$) being 2.8 and 2.5, respectively. Although g.p.c. results can be strongly influenced by specific synthetic details and maybe also by the dedoping and fractionation procedures, we noticed that the measured molecular weights were in agreement with those reported for similarly prepared conventional PATs [12,16,18]. However, a lower polydispersity index was obtained for PDHBT and PDDBT, consistent with a less large molecular weight distribution resulting from the improved method of polymerization.

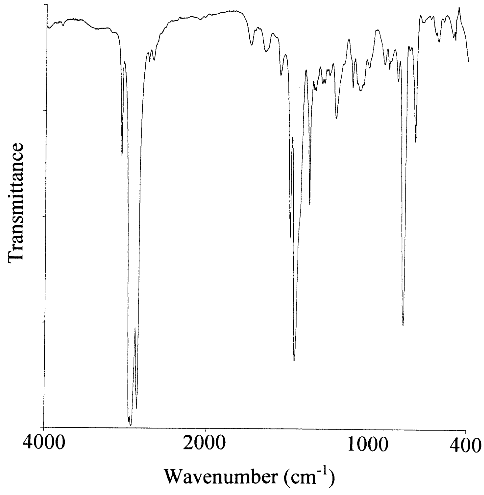


Fig. 2. I.r. spectrum of PDHBT.

3.2. Infrared spectroscopy

I.r. vibrational spectroscopy of neural polythiophene and 3-substituted polythiophenes is well documented [53–57]. The principal i.r. absorption bands of PDHBT and PDDBT and their assignments are summarized in Table 1. Since the peaks were observed in the spectra of both polymers at essentially the same energies, but with the expected differences in intensity, we focus our attention only on the spectrum of PDHBT (Fig. 2).

The C_α–H stretching mode, observed in the spectrum of the monomer DHBT at 3105 cm^{-1}, is absent in the spectrum of PDHBT, clearly indicating a large extent of α,α-couplings in the polymer backbone. Moreover, the out-of-plane C–H deformation modes, observed for DHBT at 826, 733 and 692 cm^{-1}, completely disappeared, with a new sharp and intense band appearing at 793 cm^{-1}, assignable to the C–H out-of-plane vibration of the 2,5-disubstituted thiophene ring [53,54]. This provides further evidence that PDHBT has a dominant poly(2,5-thienylenic) linear structure with an absence of mislinkages through the β-positions. The above observations also suggest a rather high molecular weight for PDHBT, as inferred from g.p.c. analysis. Based on a discussion identical to that described for PDHBT, the same conclusions can be drawn for PDDBT.

It should be noted, however, that the aromatic C–H of the unsubstituted thiophene rings in PDHBT and PDDBT have an out-of-plane deformation mode lying at wavenumbers 3–7 cm^{-1} higher than those observed in vibrational spectra of unsubstituted polythiophenes [53–55]. This is probably due to the fact that in PDHBT and PDDBT the backbone

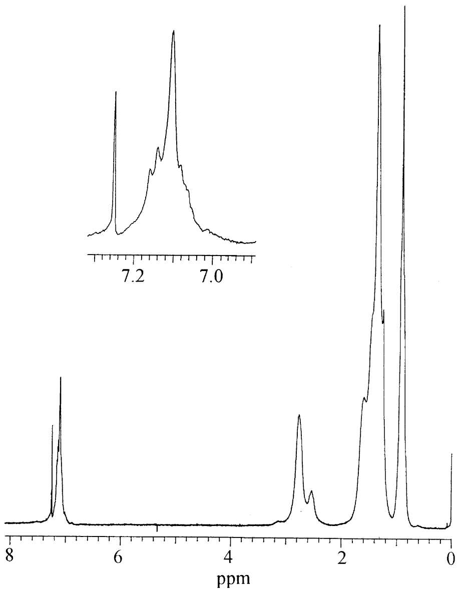


Fig. 3. ^{1}H n.m.r. spectrum of PDHBT in CDCl$_3$. The inset shows an expanded ^{1}H n.m.r. spectrum in the range of aromatic resonances.

conformations are a little more twisted than those in unsubstituted polythiophenes. Indeed, the aromatic C–H out-of-plane vibration of poly(3-alkylthiophene)s was previously reported [24] to shift from 820–822 cm^{-1} towards 827–829 cm^{-1} in going from the slightly twisted backbone conformations of the regioregular PATs to the more twisted conformations of the conventional PATs. In this context, one can also note that even larger shifts (from 817 up to 835 cm^{-1}) were reported [57] as a result of increasing temperature.

Another interesting feature of the vibrational spectra of PDHBT and PDDBT is the intensity ratio of the peak at 1466–1467 cm^{-1}, assigned to the symmetric ring stretching, to the peak at 1495 cm^{-1}, assigned to the asymmetric ring stretching ($I_{\mathrm{sym}}/I_{\mathrm{asym}}$). Based on the analysis of the vibrational spectra of unsubstituted polythiophenes and α-oligothiophenes, the above ratio has been shown [53,54] to be useful for an approximate measure of the effective length of the backbone conjugation, with more extended conjugation resulting in smaller values of the ratio. $I_{\mathrm{sym}}/I_{\mathrm{asym}}$ of PDHBT and PDDBT have almost the same value, which is considerably smaller in comparison with the ratios of the conventional PATs either reported [24] or roughly derived from their published spectra [21,58–62].

However, this does not necessarily involve more extended conjugation in PDHBT and PDDBT and shorter conjugation in the conventional PATs since, in our opinion, $I_{\mathrm{sym}}/I_{\mathrm{asym}}$ is indeed indicative of the relative degree of conjugation, but for polymer samples of a given molecular structure. Thus, the differences between the ratios should be plausibly bound up with the peculiarities of the side chain positioning along the polymer backbones, rather than with significant differences between the conjugation lengths, as also indicated by the optical absorption results.

Finally, in the vibrational spectra of both PDHBT and PDDBT no prominent broad absorption was observed in the range 1390–1030 cm^{-1}, characteristic of doping induced modes and due to charged bipolarons on the polythiophene backbone [21,63–66]. This means that, after the

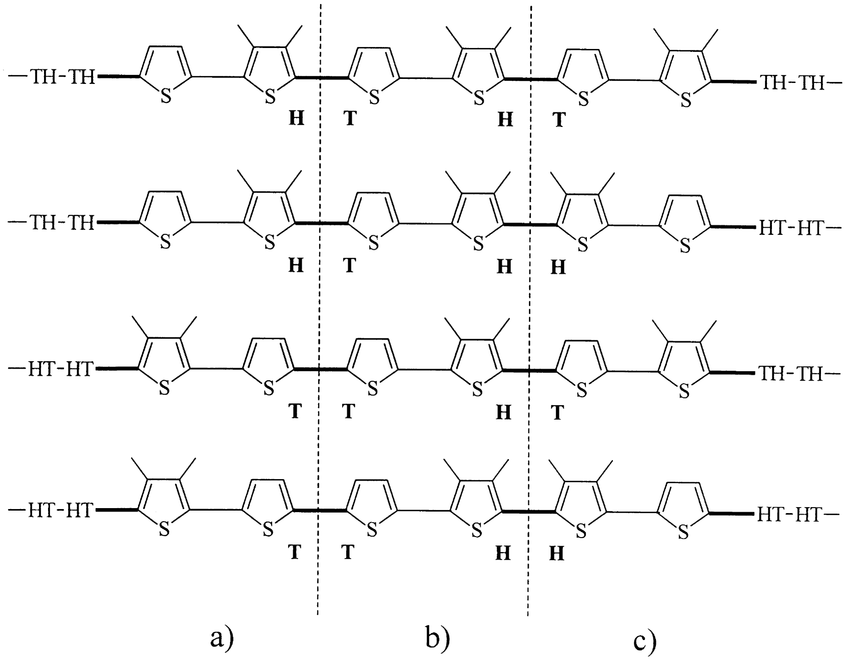


Fig. 4. The four possible configurational triads in poly(3,4-dialkyl-2,2′-bithiophene)s: (a) coupling between regioregular oligomers and the monomer; (b) coupling of the new oligomers with additional monomer; and (c) coupling of a third molecule of monomer followed by regiospecific polymerization.

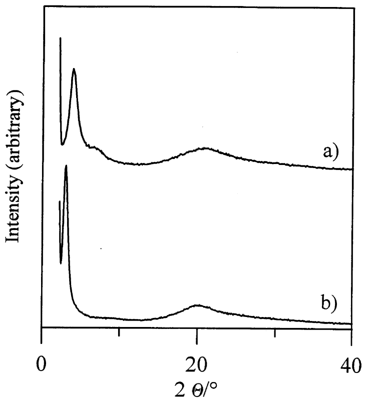


Fig. 5. X.r.d. profiles of solution-cast films of PDHBT (a) and PDDBT (b).

purification steps adopted, only very small amounts of iron chloride residues remained in the polymers, in good agreement with the microanalytical results.

3.3. ^{1}H n.m.r. spectroscopy

The resonance peaks found in the spectra of PDHBT and PDDBT have the same chemical shifts, but relative peak intensities corresponding to hydrogen atoms of the expected side alkyl group.

Therefore, only the spectrum of PDHBT, with an expanded aromatic region, has been reported in Fig. 3 for further discussion of both spectra.

The spectrum in Fig. 3 shows a narrow triplet peak at $\delta = 0.9$ assigned to the methyl protons of the alkyl groups in the monomeric units, a peak with two shoulders between $\delta = 1.1$–1.8 assigned to the subsequent methylene protons, and two peaks at $\delta = 2.54$ and 2.76 assigned to the α(1)-methylene protons relative to the thiophene ring [61]. These two chemical shifts for the α(1)-methylene protons are characteristic of the conventional PATs and were explained by configurational and hence regiochemical defects arising along the polymer backbone from HH and HT coupling of asymmetric 3-alkylthiophene monomers [13,14,61,67]. Taking into consideration the asymmetric nature of the DHBT and DDBT monomers, and on the basis of both their ^{1}H n.m.r. spectra (data reported in Section 2) and the ^{1}H n.m.r. data reported for model polymers [12,13,18], the peaks at $\delta = 2.54$ and $\delta = 2.76$ are assigned to HH and HT configurations, respectively. The relative ratio of the integrated areas of the two peaks suggests that PDHBT and PDDBT contain about 78 mol% HT configuration, a degree of regioregularity which is consistent with previous reports and is typical for the conventional PATs [12–16] and other poly(3-substituted-thiophene)s [68] prepared by the same oxidative method.

In the region of chemical shifts due to the aromatic β-hydrogen atoms, the inset of Fig. 3 shows a major peak at $\delta = 7.1$ and four minor peaks at $\delta = 7.05$, 7.07, 7.13, and 7.15, which account for about 20% of the total signal intensity. The assignment to the β-hydrogen atoms is based on the ^{1}H n.m.r. data of the monomers (see Section 2). Interestingly, peaks due to the terminal α-hydrogen atoms, which should have been observed at $\delta = 6.86$ and 7.28, disappear into background noise. This would imply a large degree of polymerization, which is consistent with the results of the g.p.c. studies described above.

It is known that the analysis of the spectral region corresponding to β-protons in the conventional PATs reveals further regiochemical information, due to the fact that each proton peak arises from a different configuration [14,67,69]. The four configurational triads which can occur during the polymerization of 3,4-dialkyl-2,2′-bithiophene monomers are shown in Fig. 4.

Fig. 4 clearly indicates that only the HT-HT configurational triad could afford a polymer backbone with 100% HT configuration, i.e. regioregular polymers, whereas the remaining three triads give rise to polymers with regioregular segments α-linked to tetrasubstituted or unsubstituted 2,2′-bithiophene spacers. Evidence indicates that only the regioregular segments and the unsubstituted 2,2′-bithiophene spacers can be related to the five aromatic resonances. Since the main configuration of PDHBT and PDDBT is the HT one, as stated above, the most intense peak at $\delta = 7.1$ could be attributed to the regioregular segments of the polymers. As a consequence, the less intense peaks at $\delta = 7.05$, 7.07, 7.13 and 7.15 would be the unsubstituted 2,2′-bithiophene spacer of the TT-HT and the TT-HH configurations. This assignment is supported by ^{1}H n.m.r. data reported for poly(3′,4′-dihexyl- and 3′,4′-didodecyl-2,2′:5′,2″-terthiophene) [47], whose spectra show four aromatic resonances exactly superimposable with the four less intense peaks of PDHBT and PDDBT. This is due to the fact that the two homopolymeric terthiophenes can be viewed as α-linked alternating copolymers of 2,2′-bithiophene with the proper 3,4-dialkylthiophene, and therefore, as shown in Fig. 4, they are the most suitable models of the TT-HT and TT-HH configurational triads in regioirregular PDHBT and PDDBT.

3.4. X-ray diffraction analysis

The room temperature x.r.d. patterns of PDHBT and PDDBT are shown in Fig. 5. The most remarkable features are the intense low-angle reflections at 22.6 Å ($2\Theta = 3.89°$) and 29.9 Å ($2\Theta = 2.94°$) and the broad high-angle halos centered at 4.28 Å ($2\Theta = 20.7°$) and at 4.42 Å ($2\Theta = 20.1°$), for PDHBT and PDDBT, respectively.

As previously reported for the conventional PATs possessing alkyl side chains with six or more carbon atoms [32,34,45,59,70–73], the sharp low-angle crystalline peak corresponds to the first order reflection attributable to the distance between almost parallel polythiophene chains belonging to the same plane. Although, by analogy with PATs, this distance was found to increase with the increase in the length of the alkyl side chain, the value shown by PDHBT is larger compared to the corresponding one reported for poly(3-hexylthiophene) ($d = 16.4$–17 Å), and the same also appears for the distance found for PDDBT, compared to poly(3-dodecylthiophene) ($d = 25$–28Å). This may indicate that, in spite of the same size and average density of the alkyl substituents along the backbones of the compared polymers, the newly substituted main chain of PDHBT and PDDBT can possess certain conformational degree of freedom requiring somewhat higher free volume. As a result, probably from a cooperation of disordering of the side chains and twisting of the main chain, a more difficult lateral packing of the coplanar subchains arises for PDHBT and PDDBT. However, it should be noted that the crystalline peak found in PDDBT (Fig. 5(b)) is significantly sharper and more intense than in PDHBT (Fig. 5(a)), suggesting that for the polymer with the longer alkyl side chain the ordered domains are mainly bigger. In the above-mentioned PATs one can always observe also second- and third-order reflections relative to the polythiophene interchains distance. Their absence in our samples indicates a lower degree of regularity in the lateral packing distance, as noted above.

By examining the x.r.d. patterns at wider angles, we remark that the weak diffraction peak associated with the chain-to-chain stacking distance of about 3.8 Å ($2\Theta = 23.4°$), typical of all PATs previously considered, is not evident in our samples, whereas only the broad amorphous halo near $2\Theta = 20°$, attributed [45,72] to both amorphously packed polythiophene main chains and scattering from disordered alkyl side chains, can be observed.

At this point it is worth noting that PDHBT and PDDBT show an x.r.d. pattern at room temperature quite similar to that found at higher temperatures for the conventional PATs [32,59,73,74] and even for a more regioregular poly-(3-octylthiophene) sample heated up to 160°C [75]. In these cases, as well as in the case of a similar halo observed for different amorphous polyalkylthiophenes [45], both the broad maximum near $2\Theta = 20°$ and the absence of the 3.8 Å spacing have been related to a nematic liquid crystal-like order. Furthermore, the existence of this kind of order in the melt of PATs has been put forward also as a result of calorimetric studies [39,75–77]. All the above observations enable us to reasonably suppose that the polymer chains of PDHBT and PDDBT at room temperature are packed in a nematic fashion, that is in a state in which, though the side chains are highly disordered, the main chains are relatively straight and co-oriented in the plane, but in absence of any significant regular order between chains of different planes. The structural information obtained from the poor x.r.d. patterns observed is in agreement with the d.s.c. and optical absorption results, as will be clarified below.

3.5. Thermal analysis and polarizing microscope observations

The t.g.a. analysis in nitrogen atmosphere showed no weight loss up to 400°C for PDHBT and up to 412°C for PDDBT. In air, the polymers start to decompose near 350 and 367°C, respectively, and both of them lose 99% of their weight at 830°C, thus confirming the insignificance of any residual amount of insoluble materials.

By comparison, poly(3-hexylthiophene) [78], poly-(3-octylthiophene) [79] and poly(3′,4′-dibutyl-2,2′:5′,2″-terthiophene) [80], itself being even more stable than PATs, exhibit lower thermal stability. The improved stability of the dibutylterthiophene polymer as compared to PATs, has been attributed to the fewer average number of alkyl groups per thiophene ring [80]. However, we note that the average density of alkyl groups in PDHBT and PDDBT is the same as that in PATs. Therefore, the excellent thermal stability of PDHBT and PDDBT may be correlated with the specific positioning of the substituents rather than with the average density of substitution.

The d.s.c. thermogram of the first heating scan of PDHBT shows a broad, weak, endothermic peak in the range 80–160°C, whereas an exothermic sharper peak centered at 119°C is observed upon cooling. Both peaks correspond to a same, very small enthalpic change. Exactly the same features also appear for the d.s.c. thermograms of PDDBT, with the exception that the cooling peak is centered at 130°C and a slightly higher enthalpic change is shown.

The thermal transitions of our samples are broader and remarkably weaker compared to those presented for the conventional PATs [15,34,40,73,76] and whereas the latter polymers show marked effects of previous thermal history [32,34,73,76], the structural changes occurring both in PDHBT and PDDBT during the thermal cycles adopted are repeatable. This suggests that a room temperature stable structure is completely recovered in the course of the quenching of samples from the melt. Moreover, the double melting behavior characteristic of conventional poly-(3-dodecylthiophene) [15,32,34,73], generally believed to arise from the separate melting of ordered alkyl side chains (lower temperature peak) and ordered main chains (higher temperature peak), is not observed for PDDBT. All these observations are in agreement with the amorphous structures of PDHBT and PDDBT revealed by the x.r.d. measurements. Nevertheless, due to the lack of any endothermic peak clearly associated with crystallinity of the main chain, we were not able to determine the isotropization temperature. Since this temperature was early identified as a crucial parameter to understand, on a molecular level, the solid state thermochromism of conventional [32,34,40,73] and more regioregular PATs [30,40,75,81], we followed the thermal behavior of PDHBT and PDDBT (thin films on glass) on a hot stage of a polarizing microscope. On heating, the bulk of both samples show a continuous, weak change of colour, from red-brown to yellow-orange, with the high temperature colour remaining almost unchanged well above the isotropic melting. In agreement with the d.s.c. results, this weak and gradual change of colour occurs in a broad, undefined range of temperatures and is clearly insufficient to precisely detect the temperature of the transition to the isotropic melting. In order to overcome this drawback, we took into account the optical behavior of a number of stressed points of the film surface such as tears, artificially cut borders and also surroundings of impurity traces. Indeed, around these points, a bright-yellow birefringence and sharp conoscopic brushes (isogyres) rotating in opposition with respect to the stage are shown. This local birefringence may be attributed to small anisotropic domains of slightly ordered chains, either resulting from local stretching processes or due to local stress within the bulk of amorphous regions. We examined carefully the optical behavior of these birefringent points exploiting them as spies of chains dynamics during the transition to the isotropic melting. On heating, in a small range of temperatures (about 5°C) a progressive darkening of this birefringence is observed, together with a rapidly smearing of the sharp and thin conoscopic brushes. Above this range, every local birefringence disappears and a completely uniform yellow-orange colour is shown by both polymers: clearly the softening process mostly rerandomizes the majority of local anisotropic domains and relaxes nearly all the stressed points, thus extinguishing every birefringence effect. Based on these observations, we were able to consider the isotropization temperatures of PDHBT and PDDBT precisely centered at 121 and 132°C, respectively, in quite good agreement with the d.s.c. results.

3.6. Optical absorption spectroscopy

It is well known that thin films of electrochemically prepared poly(3-methylthiophene) and much thicker films of nearly 100% HT regioregular PATs bearing longer *n*-alkyl substituents can easily adopt coplanar backbone conformations with extensive electronic delocalization and quite high wavelength for the maximum intensity of the $\pi-\pi^*$ absorption band ($\lambda_{\max}$) [26]. This is due to the negligible steric repulsion caused by the methyl group and even by the longer, but fully HT sequenced, alkyl groups. On the other hand, a shorter $\lambda_{\max}$ is found for film samples of the conventional PATs, since these polymers can adopt less coplanar backbone conformations owing to some steric repulsions caused by the remarkable content of non-HT connectivity. In this regard, however, it is worth noting that PDHBT and PDDBT should not show the same $\lambda_{\max}$ data of the conventional PATs, even if the same amount of non-HT connectivity characterizes both kinds of polymers. Indeed, some difference between the steric requirements of the alkyl side chains might well arise from the different side chains positioning along the polythiophene backbones.

The room temperature spectra of PDHBT in $CHCl_3$ solution and in the solid state show broad $\pi-\pi^*$ absorption bands with $\lambda_{\max}$ at 435 and 478 nm, respectively; the corresponding absorption bands of PDDBT appeared slightly red shifted at 437 and 485 nm, indicating a little better electronic delocalization for the polymer possessing the longer alkyl side chains. This may be a consequence of a slightly higher HT content in PDDBT, which nevertheless was impossible to determine due to the limited sensitivity of the ^{1}H n.m.r. measurements. However, at least for the film sample, also some occurrence of the so-called zipper effect [37] should be considered.

An objective comparison of the $\lambda_{\max}$ values of PDHBT and PDDBT with those of the conventional PATs from the literature is almost impossible, because of the large number of available publications and the great dispersion of the data caused by specific and quite different experimental conditions used in the various laboratories, even for the same polymerization method. In this context, it was remarked that polymer reprecipitation can lead to fractions with improved regioregularity [26]. Moreover, also the film thickness [26,82] and the method of film preparation [82,83] can have significant influence on the preferred conformations of the solid state molecular assemblies and hence on the optical properties of the films.

However, by inspection of the literature one can list three main observations: (i) the $\lambda_{\max}$ data in solution found for PDHBT and PDDBT are identical to the corresponding data reported so far for all the conventional PATs [12,19,26,55,79,84–86], even including the reprecipitated ones [16,18,62,67,69,87]; (ii) the solid state $\lambda_{\max}$ data of PDHBT and PDDBT are virtually identical to those of the electrochemically prepared PATs [12,55,84,85] and to those of many PATs prepared by the oxidative coupling using $FeCl_3$ [6,19,26,85]; (iii) the remainder of the latter PATs [12,40,88,89] and, of course, the reprecipitated ones [16,18,67,87,90] show slightly red shifted maxima.

The absence of any significant difference between the spectra of PDHBT and PDDBT in $CHCl_3$ solution and those of the conventional PATs either in $CHCl_3$ or tetrahydrofuran solution indicates that, in such good solvents and at room temperature, the alkyl side chains may exhibit large and similar conformational changes and therefore they can drive the twisting of the main chain up to a comparable degree and independently of their specific positioning on the thiophene rings. Also the red shifts involved in the solution-to-solid state transition of both PDHBT and PDDBT are as large as those displayed by the conventional PATs. This indicates that, in going from the solution to the bulk solution-cast films, comparable disorder–order transitions of the side chains can occur, favouring the nonplanar-to-planar conformational changes of the backbones up to a comparable average degree.

Thus, the results obtained by comparing PDHBT and PDDBT to the conventional PATs are rather surprising, since they indicate that the remarkably different side chains distribution along the polymer backbones are not accompanied by any different steric requirement of the alkyl side chains and hence by any discernible different effect on the electronic conjugation. On the contrary, these results are simply accounted for by the almost identical content of

HT configuration in the two kinds of alkyl substituted polythiophenes. This strongly suggests that, as previously observed for PATs, the regiochemistry of substitution is of first importance in determining the room temperature absorption maxima also for PDHBT and PDDBT, both in $CHCl_3$ solution and in the condensed state.

However, it is worth also noting that, contrary to the conventional PATs, the $\pi-\pi^*$ absorption band observed for the bulk solution-cast films of both PDHBT and PDDBT does not show any resolvable vibronic fine structure, which is known to be characteristic of the spectra of all PATs and to be indicative of the extent of backbone coplanarity and π-stacking in bulk material (films or stable colloidal particles) [26,91,92]. This difference indicates that, in the condensed state, the polythiophene backbone of PDHBT and PDDBT is more flexible than that of the conventional PATs. Hence it appears that the specific steric requirements of the newly sequenced side chains result in some more flexible and disordered molecular assemblies, which nevertheless are still able to afford an average length of conjugation typical of the more rigid and ordered conventional PATs. A plausible explanation for this subtle difference in conformational structure between the compared polymers may be found in the hypothesis that, in spite of a similar average torsional angle between adjacent thiophene rings, in PDHBT and PDDBT a broader distribution of the inter-ring twist angles is caused by the specific positioning of the substituents, probably as a result of both a lower degree of side chains interactions and the remarkable amount (50%) of unsubstituted thiophene rings in the backbone. This broader conformational variability may, of course, give rise to a broader range of conjugation lengths and, correspondingly, to structureless absorption (inhomogeneous broadening), as observed.

The results of the optical absorption measurements performed in the solid state at room temperature corroborate well with the x.r.d. and d.s.c. results, which have shown that PDHBT and PDDBT are more amorphous materials, compared to the semicrystalline conventional PATs. On the other hand, this lower degree of crystallinity is not in contrast with the comparable λ_{max} found for the two regioisomeric versions of alkyl substituted polythiophenes, as previously shown also for other amorphous octyl substituted polythiophenes compared to the conventional poly(3-octylthiophene) [45].

4. Conclusions

It should be emphasized at the end of this comparative study that, besides the morphological, thermal and optical properties that we have studied, other relevant side-chains-affected properties characteristic of the almost coplanar bulk state of all conjugated polymers bearing flexible side chains (namely solvato- and thermochromism in the neutral state and conductivity and thermal undoping in the doped state) should change remarkably in going from the conventional PATs to the corresponding poly(3,4-dialkyl-2,2′-bithiophene)s. Thermal undoping of doped conductive conventional PATs, mainly consisting in the thermally driven reversal of the doping process occurring with the ejection of the dopant anions, is a serious problem for many applications of these materials. This intrinsic thermodynamic instability of the doped state, as well as the pronounced thermochromic blue shift of the neutral state, are now considered to be due to thermally increasing steric interactions of the long and flexible alkyl side chains directly attached on every thiophene ring, and therefore easily driving the conjugated main chain towards highly twisted conformations.

As concerns the polymers prepared for this study, the ways in which the unusual positioning of the flexible side chains can drive this planar to non-planar transition at elevated temperatures are hardly predictable, at least from the theoretical point of view, since too many factors affecting the thermal and morphological properties of the bulk state should be considered [89,93]. However, from the results of all our characterizations performed at room temperature on PDHBT and PDDBT in comparison with the conventional PATs, we cannot exclude, even at higher temperatures, the possibility of either lower side chains interactions or a polythiophene backbone intrinsically less prone to highly twisted conformational changes.

As a result, a reduced thermochromic blue shift in the neutral state and, correspondingly, an improved thermal stability in the doped state should be expected for the novel polymers compared to the conventional PATs. The latter expectation is even reinforced by the fact that, contrary to the conventional PATs having an alkyl substituent per thiophene ring, in PDHBT and PDDBT one-half of the thiophene rings are not alkylated and therefore more space is left available to accommodate the dopant close to the backbone. The relevance of this space in order to overcome the thermal instability of the doped conventional PATs was stressed by different authors [41–43,94,95], especially by synthesizing β-substituted polythiophenes bearing dilutely attached long flexible side chains. Indeed, the conductivity stability was improved to some extent, but the higher the conductivity stability, the lower the processibility was found, due to the lower average substitution density of these polymers compared to the conventional PATs. On the contrary, PDHBT and PDDBT, as a result of the same substitution density of the conventional PATs, are able to show very high solution and melt tractability, while providing space close to the backbone. In order to confirm our expectations and shed more light on the interesting material properties of PDHBT and PDDBT, future work will focus on solvatochromism, thermochromism and thermal undoping of these easily accessible novel polyalkylthiophenes.

Acknowledgements

The financial support by MURST (Fondi 60%) is gratefully acknowledged.

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