Synthesis and characterization of poly[3-(butylthio)thiophene]: a regioregular head-to-tail polymer

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Poly[3-(butylthio)thiophene] was obtained from 2,5-dibromo-3-(butylthio)thiophene according to the method of Kobayashi. The polymer was characterized as having regioregular head-to-tail (HT) connections with significant extended conjugation length and optical properties, such as solvatochromism and photoluminescence. The polymer is soluble in common organic solvents and can easily form films.

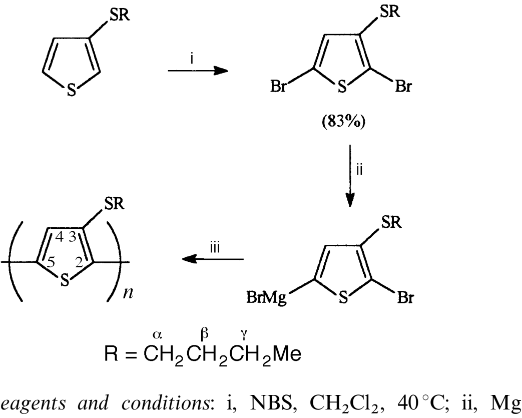
Poly(3-substituted thiophenes)[1–9] with a variety of substituents such as alkyl, alkoxy and alkyl heteroatom-functionalized[10–13] side chains have been extensively investigated. Polythiophenes carrying electron-donating alkylthio groups, on the other hand, are less well documented. Although poly[3-(alkylthio)thiophenes] are generally obtained only by chemical methods,[14,15] papers dealing with the electropolymerization of 3-(methylthio)thiophene[16] and of some (oligothio)thiophenes have appeared.[17] Polymers of 3-(ethylthio)- and 3,4-bis(ethylthio)thiophene have been chemically synthesized and characterized.[14,15] An attempt to polymerize 2,2′:5′,2″-terthiophenes 3′-substituted with the —SR group, where R is a long alkyl chain, has been reported,[18] but with unsatisfactory results. Recently, a paper about the synthesis of a series of regioregular poly[3-(alkylthio)thiophene]s[19] reported the poor solubility and the uncharacterizability of the poly[3-(butylthio)thiophene] obtained.

We here report the polymerization, based on the method of Kobayashi,[14,20] and the characterization of poly[3-(butylthio)thiophene] (PBTT). The polymer is soluble in common organic solvents such as $CHCl_3$, CCl_4, toluene, benzene, THF and CS_2, and shows a highly HT-HT regioregularity.

Experimental

Synthesis and polymerization

Scheme 1 outlines the experimental route from monomer to polymer.



Scheme 1 *Reagents and conditions*: i, NBS, CH_2Cl_2, 40 °C; ii, Mg, 2-MeTHF, reflux; iii, $Ni(dppp)Cl_2$, anisole, 135 °C

3-(Butylthio)thiophene

3-(Butylthio)thiophene[21] was prepared in high yield (96%) according to the method described in the literature.[19]

δ_H 2-H 7.11, 4-H 7.02, 5-H 7.31, $CH_2(\alpha)$ 2.85, $CH_2(\beta)$ 1.63, $CH_2(\gamma)$ 1.43 and CH_3 0.92. δ_C C-2 122.87, C-3 132.35, C-4 129.65, C-5 125.96, $CH_2(\alpha)$ 35.01, $CH_2(\beta)$ 31.48, $CH_2(\gamma)$ 21.81 and CH_3 13.60.

2,5-Dibromo-3-(butylthio)thiophene

Bromination of 3-(butylthio)thiophene was carried out according to the method of Taylor *et al.*[22] A solution of 3-(butylthio)thiophene (5.16 g, 30 mmol) in dichloromethane (55 ml) was stirred while *N*-bromosuccinimide (NBS) (10.7 g, 60 mmol) was added portionwise. The temperature of the reaction mixture was raised to 40 °C and maintained at this temperature for 16 h. The oily crude product was purified by vacuum distillation to give 2,5-dibromo-3-(butylthio)thiophene [7.4 g, 83% yield, bp 112 °C (0.3 torr), n_D^{21} 1.6129].

δ_H 4-H 6.90, $CH_2(\alpha)$ 2.83, $CH_2(\beta)$ 1.57, $CH_2(\gamma)$ 1.43 and CH_3 0.92. δ_C C-2 110.92, C-3 134.05, C-4 132.33, C-5 112.82, $CH_2(\alpha)$ 35.98, $CH_2(\beta)$ 31.57, $CH_2(\gamma)$ 21.68 and CH_3 13.58.

Polymerization

The polymer was prepared by catalysed polymerization of a Grignard reagent according to methods described in the literature.[14,20] Magnesium metal (0.20 g, 8.2 mmol) was reacted, under nitrogen, with 2,5-dibromo-3-(butylthio)thiophene (2.8 g, 8.5 mmol) in dry 2-methyltetrahydrofuran (2MeTHF) (8 ml). After removing nearly all the solvent, dry anisole (7 ml) and nickel(II) bis(diphenylphosphino)propane dichloride [$Ni(dppp)Cl_2$] (0.02 g, 0.04 mmol) were added. The mixture was heated at 135 °C for 80 h and poured into a solution of HCl-acidic methanol (100 ml). The dark precipitate was filtered, washed with HCl-acidic methanol (20 ml) and purified by Soxhlet extraction with methanol (48 h). Extensive (24 h) extraction with dichloromethane afforded 0.6 g (41% yield) of polymer soluble in $CHCl_3$, THF, toluene, benzene and CS_2 at room temp. The polymer was purified by reprecipitation from hexane into toluene.

Measurements

UV–VIS spectra were recorded on a Varian-Cary 3 spectrophotometer. The fluorescence spectrum was recorded on a Jobin-Yvon JY3CS spectrofluorophotometer with $CHCl_3$ solution of polymer. Gel permeation chromatography (GPC) was carried out using an Alltech system equipped with a Shodex KF-804L column and a Shodex RI-71 refractive index detector, with THF as the eluent, at room temperature. The average molecular masses were calculated using a calibration curve of monodisperse polystyrenic standards. ^1H and ^{13}C NMR measurements were performed on a $CDCl_3$ solution of PBTT with a Bruker AMX-400 WB 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 (for ^1H) and 77.0 (for ^{13}C).

HMQC[23] parameters for aromatic and aliphatic region: spectral width $(f_2) = 1–5$ ppm, 2048 complex points; spectral width $(f_1) = 10–50$ ppm, 256 t_1 increments with 16 scans per t_1 value; relaxation and evolution delays = 0.5–1 s and 2.78–4.00 ms, respectively. Zero filling in f_1 and f_2, sine function in f_1 were applied before Fourier transformation.

HMBC[24] parameters: spectral width $(f_2) = 8$ ppm, spectral width $(f_1) = 150$ ppm, 256 t_1 increments with 64 scans per t_1 value; relaxation delay = 0.5 s and delay for long-range coupling constant evolution = 70 ms. Zero filling in f_1 and f_2, sine function in f_1 were applied before Fourier transformation.

DSC (differential scanning calorimeter) was performed with a Perkin-Elmer DCS-4, at a scanning rate of 10 °C min^{-1}.

FTIR: an IR spectrum (KBr disk) was recorded using an Infrared Fourier Spectrometer (Bruker IFS 113 v).

Results

Characterization of the polymer

PBTT was characterized by GPC, UV–VIS and IR and ^1H and ^{13}C NMR spectroscopy. Thermal stability was tested by DSC.

The molecular mass, determined by GPC [relative to a poly(styrene) standard, with THF as eluent, at room temp.] was: weight-average molecular mass $M_w = 5049$ and number-average molecular mass $M_n = 3772$ with a polydispersivity index = 1.34. The M_n of PBTT corresponds to 22 repeating units per chain.

The UV–VIS spectrum, in dilute $CHCl_3$ solution displays an absorption at $\lambda_{max} = 502$ nm.

The IR spectrum of PBTT is characteristic of 2,5-coupled 3-substituted polythiophenes: one aromatic C—H stretching of weak intensity at 3067 cm^{-1}, assignable to the $C—H_\beta$ stretching, and one out-of-plane deformation of aromatic C—H bonds at 818 cm^{-1} (due to the trisubstituted ring) are detected. The butylthio alkyl chain gives rise to stretching vibrations in the region 2954–2854 cm^{-1} and to deformation modes below 1466 cm^{-1}.

Thermal analysis by DSC did not detect any glass transition temperature T_g, but did reveal a decomposition process at T_d of 310 °C.

Regiochemistry assignment of PBTT

The regiochemistry of poly(3-alkylthiophene)s is commonly evaluated from inspection of the aromatic region. In fact, this region provides the distribution of the four configurational triads HT–HT (head to tail-head to tail), HT–HH (head to tail-head to head), TT–HT (tail to tail-head to tail), and HH–TT (head to head-tail to tail), due to all the possible couplings.

The ^1H NMR spectrum of PBTT, in $CDCl_3$, displays (Fig. 1) a major singlet at δ 7.37. This signal is strongly deshielded with respect to the β-protons in 3-(butylthio)thiophene (δ 7.02), in 3,3′-di(butylthio)-2,2′-bithiophene (δ 7.08) and 4,4′-di(butylthio)-2,2′-bithiophene (δ 7.06).[21] Similar behaviour was observed on passing from 3-(methylthio)thiophene (δ 6.97) to 3,4′-di(methylthio)-2,2′-bithiophene (δ 7.20 for 3′-H).[25] Other low intensity signals, whose relative intensities change with the purification procedure, are present in the aromatic region. These signals do not seem indicative of the presence of minor configurational triads but of β- and terminal protons of shorter oligomers. The aliphatic region of the ^1H NMR spectrum displays four groups of signals centred at δ 2.95, 1.65, 1.44 and 0.94 and assigned to $CH_2(\alpha)$, $CH_2(\beta)$, $CH_2(\gamma)$ and CH_3 protons, respectively.

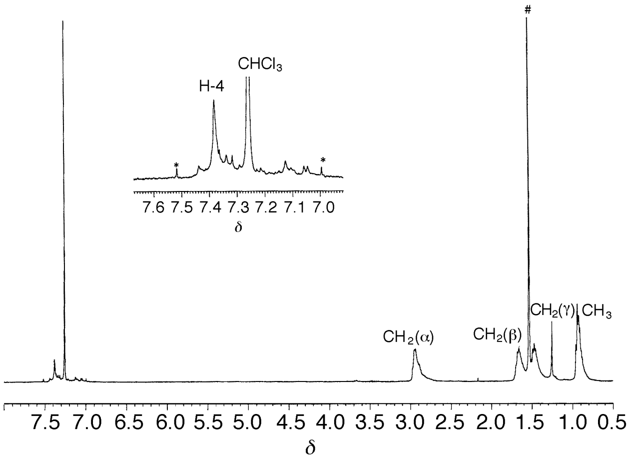


Fig. 1 ^1H NMR spectrum of PBTT. Expanded region corresponds to 4-H proton. The symbols denote $CHCl_3$ satellites (*) and an H_2O signal (#), respectively.

The deshielding of the 4-H and $CH_2(\alpha)$ protons in PBTT with respect to the 3-(butylthio)thiophene (0.35 and 0.10 ppm, respectively) points to the presence of a prevalent HT regiopolymer, in accordance with previous data on dimers of 3-(methylthio)thiophene.[25] The regiochemistry assignment deduced on the basis of the ^1H chemical shifts was confirmed by the ^{13}C NMR data of the aromatic carbons.

The ^{13}C NMR data of PBTT were obtained and assigned through inverse-detected heteronuclear multiple-quantum (HMQC)[23] and multiple-bond (HMBC)[24] correlation experiments, as previously applied to poly(3-alkylthiophenes).[26–28] The HMQC and HMBC spectra are shown in Fig. 2 and 3.

The HMQC spectrum of PBTT shows the presence of a major correlation between 4-H (δ 7.37) and C-4 (δ 130.3) with a coupling constant $^1J_{H,C}$ of 169 Hz, typical of a β-CH thiophene fragment.[29] Another very low-correlation of the same β-H, C-β type, between a minor proton signal at δ 7.30 and a carbon signal at δ 130.4 was found and assigned to a shorter oligomer with the same regiochemistry rather than to a structural defect.

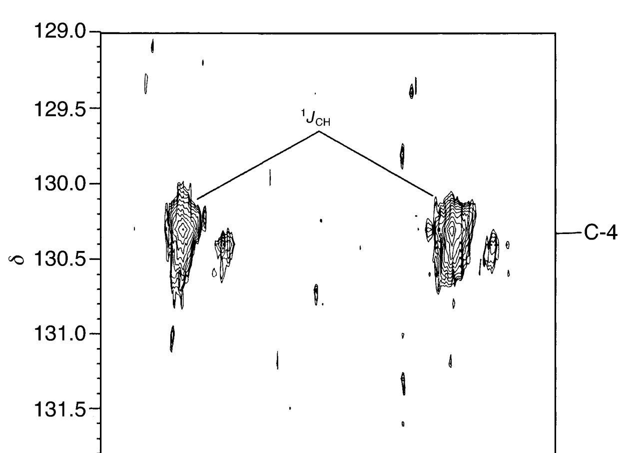


Fig. 2 Coupled HMQC spectrum of the aromatic region of PBTT

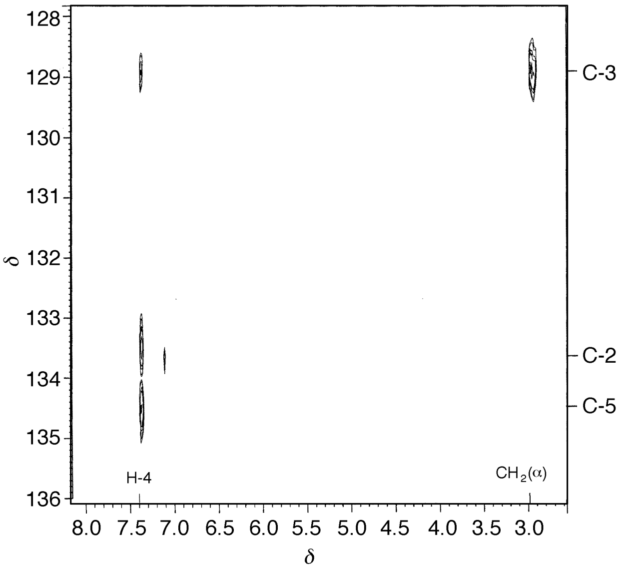


Fig. 3 HMBC spectrum of PBTT performed with an evolution delay of 70 ms. Three carbon signals were detected through the 4-H proton and one of these (C-3) was also detected through the $CH_2(\alpha)$ protons.

Only three aromatic carbon signals at δ 133.5, 129.1 and 134.5 were detected in the HMBC experiment. These are assigned to C-2, C-3 and C-5, respectively, on the basis of the presence of multiple-bond coupling constants with the 4-H proton of the aromatic region and with the $CH_2(\alpha)$ protons. The aliphatic region displays four signals at δ 36.0, 31.7, 21.9 and 13.6 assignable to $CH_2(\alpha)$, $CH_2(\beta)$, $CH_2(\gamma)$ and CH_3 carbons, respectively.

The detection of four aromatic carbon signals, coming from a single triad, is indicative of high regioregularity. In fact, in the case of poly(3-hexylthiophene) (PHT) 85% HT regioregular, almost all the carbons of the four configurational triads were detected in the same conditions.[26] A similar situation was found for poly(3-hexanoyloxyethylthiophene) (PHET) 45% HT regioregular.[28]

The assignment of ^{13}C signals of the four configurational triads of PHT was made by direct comparison with the ^{13}C signals of the central units of the four corresponding trimers.[26] The two sets of data match within 0.5 ppm.

In the case of PHET, it was shown that, if the differences between the ^{13}C chemical shift of the four carbons of a triad and the corresponding carbons of (3-hexanoyloxyethylthiophene) monomer were considered, four sets of data (Δδ), one for each triad, were obtained (Table 1, rows b). These sets were very similar (within 1 ppm) to those derived, in the same way, from the central units of the four configurational trimers of 3-hexylthiophene (Table 1, rows a). The comparison of rows a and rows b of Table 1 enabled the regiochemistry assignment of PHET to be made.[28] This second triad-based[28] approach allows us to overcome the configurational trimers. Only the ^{13}C chemical shifts of the aromatic carbons of the monomer are needed. Its reliability lies in the fact that the four sets of data depend mainly on the different type of adjacent connectivities, the 3-substituent effect being subtracted by using the ^{13}C chemical shifts of the monomer. Regiochemistry assignment of PBTT can be performed by comparing the differences between the ^{13}C chemical shifts of the aromatic carbons of polymer and monomer and the connectivity parameters derived for the trimers of 3-hexylthiophene[26] and the triads of PHET reported in Table 1. As was previously underlined,[28] Δδ(C-3) and Δδ(C-4) are more convenient for the configurational assignment of the polymer, mainly due to their easy detection and assignment.

Table 1 Calculated Δδ values (in ppm) for the carbons of the central unit of each configuration trimers of 3-hexylthiophene (rows **a**) and of the triads of PHET (rows **b**) with respect to the corresponding monomer

a = trimer of PHT **b** = triad of PHET		C-2	C-3	C-4	C-5
HT–HT	**a**	11.0	−3.7	0.4	8.8
	b	10.8	−2.9	1.0	9.1
TT–HT	**a**	10.1	−3.3	−2.0	10.2
	b	9.6	−2.7	−1.5	10.3
HT–HH	**a**	8.9	−0.6	−0.9	10.9
	b	8.1	0.4	−0.4	10.3
TT–HH	**a**	7.8	−0.1	−3.3	12.3
	b	6.6	0.7	−2.8	11.9

The Δδ values found for PBTT [Δδ(C-2) = 10.6 ppm, Δδ(C-3) = −3.3 ppm, Δδ(C-4) = 0.6 ppm and Δδ(C-5) = 8.5 ppm] are very close to those of the HT-HT trimer or triad and furnish a further confirmation of the regiochemistry assignment.

UV–VIS and fluorescence spectroscopy

PBTT displays a strong solvatochromic effect. Fig. 4 shows the UV–VIS spectra of PBTT in mixtures of $CHCl_3$ and CH_3OH. The increased addition of the poor solvent methanol to a chloroform solution shifts the maximum absorption to a longer wavelength, with a change from pink to violet. The maximum shift observed, on passing from $CHCl_3$ solution (100/0) to $CHCl_3$–CH_3OH (20/80), is represented by the presence of a shoulder at 599 nm. When the ratio is further increased, a precipitate of polymer is formed.

The solid-state UV–VIS absorption spectra of the film of PBTT formed by solvent evaporation on glass from $CHCl_3$ and CS_2 solutions are reported in Fig. 5. The film from $CHCl_3$ solution displays absorptions at a longer wavelength (three peaks at 515, 555 and 596 nm) with respect to that obtained from CS_2 solution and the spectrum is similar to that obtained in $CHCl_3$–CH_3OH solution. The changes observed in the UV–VIS absorption spectra of film and of $CHCl_3$/CH_3OH solution are probably due to a more extensive conjugation

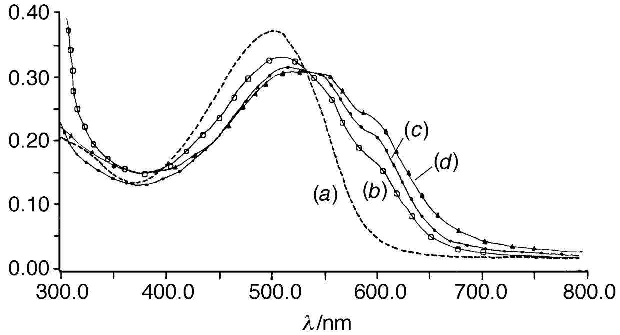


Fig. 4 UV–VIS spectra of PBTT in (*a*) $CHCl_3$, (*b*) $CHCl_3$–MeOH (3:2), (*c*) $CHCl_3$–MeOH (2:3) and (*d*) $CHCl_3$–MeOH (1:4)

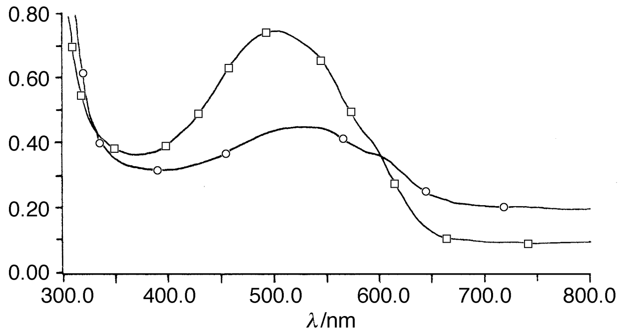


Fig. 5 UV–VIS spectra of PBTT films: (□) from CS_2 solution, (○) from $CHCl_3$ solution

length of the polymer chain or to a more abundant presence of conjugated chains of polymer. The solvatochromic behaviour of PBTT and the UV–VIS spectra are in line with those reported for poly(3-alkylthiophene)s.[30]

The fluorescence spectrum of a chloroform solution of PBTT obtained with an excitation wavelength of 490 nm gives a maximum emission wavelength at 603 nm with a yield Φ_f greater than 10^{-2}.

Conclusions

The polymerization method based on Kobayashi's procedure affords a regioregular HT poly[3-(butylthio)thiophene] soluble in all the common organic solvents. This synthetic route enables a soluble and characterizable polymer to be obtained, and it seems preferable to that proposed by Rieke.

Further studies on the physical properties of PBTT are in progress.

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