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Synthesis, characterization and optical properties of a regioregular and soluble poly[3-(10-hydroxydecyl)-2,5-thienylene]

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Abstract

The preparation of a regioregular trimethylsilanyloxydecyl 3-substituted polythiophene and its conversion to the corresponding hydroxydecyl polymer, which is soluble in common organic solvents, is described both in solution and in film. The chromic behaviour of the hydroxy functionalized polymer was investigated by UV–vis spectroscopy in different solvent/non-solvent mixtures and in the solid state by exposing the polymer adsorbed on hydroxylic matrices to methanol vapours.

Keywords: Polyhydroxyalkylthiophene; Regioregularity; Post-functionalization

1. Introduction

Intrinsically conductive polymers (ICP) have been studied for many years now for their interesting electric and electronic properties [1]. In the field of polymers, these materials are indeed of considerable importance and of great scientific and industrial interest as testified to by the Nobel Prize for Chemistry having been awarded to Heeger, McDiarmid and Shirakawa in 2000 for their studies on electroconductive polymers.[1]

In addition to the typical properties of ICPs, polyalkylthiophenes (PATs) also possess other specific characteristics such as good solubility and processability [2]. The type of substituent most commonly found in polythiophenes is the linear alkylic one in the 3-position of the aromatic ring. The possibility of introducing a functionalization in the side chain has, however, afforded the opportunity of modulating the final properties of the polymeric material.

Hydroxy-functionalized polythiophenes prepared through the post-functionalization of soluble precursor polymers have been recently studied by the authors [3–5]. This method has permitted not only to overcome the reduced solubility typical of these materials when they are directly derived from the monomer through oxidative polymerization but also to underscore their peculiar properties, thus making their full characterization possible.

The possibility of forming hydrogen bonds between the side chains reduces the rotational mobility of the polythiophenic backbone while favouring states which are conformationally better ordered [6,7].

The present work sets out to synthesize a poly[3-(10-hydroxydecyl)-2,5-thienylene] (PHDT) (Fig. 1) with high regioregularity, the purpose being to determine whether the –OH functionality levels off the configurational differences giving comparable chromic effects among different PHDT samples as already hypothesized [3]. Another objective of this study was to investigate the behaviour of PHDT in the solid state by supporting the polymer on different types of hydroxylated solid matrices and studying the chromic effects of exposure of the samples to methanol vapours. PHDT was synthesized starting from the corresponding 2,5-dibrominated monomer with the hydroxy group protected by means of the trimethylsilanyloxy group. The transformation from the precursor polymer to PHDT was performed both in solution and directly on the film.

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[1] For further information link to http://www.kva.se

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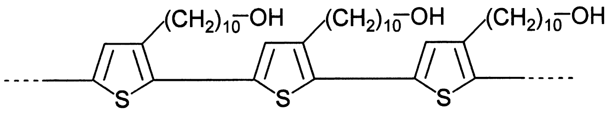


PHDT

Fig. 1. Regioregular poly[3-(10-hydroxydecyl)-2,5-thienylene].

2. Experimental part

2.1. Monomer synthesis

2.1.1. 3-(10-hexanoyloxydecyl)thiophene (T10Es)

4.28 g (14 mmol) of 3-(10-bromodecyl)thiophene (T10B, synthesized according to Refs. [8,9]) are reacted with 3.90 g (28 mmol) of sodium hexanoate in 42 ml of anhydrous *N*,*N*-dimethylformamide (DMF) under stirring at 90 °C for 2 h. The reaction mixture is poured into 750 ml of water and extracted with 5 × 200 ml of heptane. The organic phase is dried with $MgSO_4$ and concentrated to give 4.29 g (90% yield) of crude T10Es which is purified by column chromatography (SiO_2/heptane–diethyl ether 95:5) giving 4.09 g of a colourless oil (86% yield).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.24$ (dd, 1H); 6.91 (m, 2H); 4.05 (t, 2H); 2.62 (t, 2H); 2.28 (t, 2H); 1.60 (m, 6H); 1.30 (m, 16H); 0.89 (t, 3H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 173.60$, 139.54, 133.90, 125.40, 123.29, 65.10, 34.70, 31.10, 29.90, 29.70, 29.48, 29.30, 28.60, 28.20, 27.50, 26.10, 24.50, 22.30, 13.95.

IR (KBr, cm^{-1}): 3105, 3052, 2928, 2855, 1737, 1537, 1466, 1173, 773, 738.

Elemental analysis: calcd for $C_{20}H_{34}O_2S$: C, 70.95%; H, 10.12%; S, 9.47%. Found: C, 70.94%; H, 10.11%; S, 9.44%.

2.1.2. 3-(10-hydroxydecyl)thiophene (T10OH)

4.07 g (12 mmol) of T10Es are reacted with 2.11 g of KOH in 100 ml of CH_3OH for 1 h under reflux. The reaction mixture is poured into 700 ml of H_2O, added with aqueous H_2SO_4 (2.90 ml, 5%) and extracted with diethyl ether (4 × 175 ml). The organic phase is washed several times with water, dried with Na_2SO_4 and concentrated to give 2.83 g (98% yield) of T10OH.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.24$ (dd, 1H); 6.92 (m, 2H); 3.65 (t, 2H); 2.65 (t, 2H); 1.70–1.28 (m, 17H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 139.55$, 134.11, 125.50, 123.20, 62.75, 32.39, 29.90, 29.75, 29.50, 29.30, 28.25, 27.75, 26.45.

IR (KBr, cm^{-1}): 3306, 3106, 3055, 2926, 2854, 1538, 1465, 1057, 775, 730.

Elemental analysis: calcd for $C_{14}H_{24}OS$: C, 69.94%; H, 10.06%; S, 13.34%. Found: C, 69.97%; H, 10.04%; S, 13.39%.

2.1.3. 3-(10-hydroxydecyl)-2,5-dibromothiophene [2,5 BT10OH] (from T10OH)

A solution of 0.33 g (1.84 mmol) of *N*-bromosuccinimide (NBS) in 1 ml of DMF is added to a solution of 0.22 g (0.92 mmol) of 3-(10-hydroxydecyl)thiophene in 1 ml of DMF. After stirring for 36 h at room temperature and under nitrogen, the reaction mixture is poured into 20 ml of distilled water and extracted with 5 × 10 ml of $CHCl_3$. The organic phase is washed again with water (5 × 10 ml), dried with $MgSO_4$ and concentrated to give 0.33 g (0.83 mmol) of crude 2,5 BT10OH. The product is purified by a chromatographic column (SiO_2/heptane–diethyl ether 4:1) to give 0.07 g (0.17 mmol; 18% yield) of 2,5 BT10OH.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.78$ (s, 1H); 3.64 (t, 2H); 2.62 (t, 2H); 1.71–1.54 (m, 4H); 1.43 (s, 1H); 1.30 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 144.80$, 135.60, 114.30, 111.90, 62.79, 32.90, 30.82, 29.62, 29.45, 28.72, 28.30, 27.80, 26.50.

IR (KBr, cm^{-1}): 3340, 3084, 2926, 2854, 1542, 1463, 1057, 1004, 825, 722, 474.

Elemental analysis: calcd for $C_{14}H_{22}Br_2OS$: C, 42.23%; H, 5.57%; Br, 40.13%, S, 8.05%. Found: C, 43.02%; H, 5.69%; Br, 38.93%, S, 8.25%.

2.1.4. 3-[(10-trimethylsilanyloxy)decyl]thiophene [T10OSi]

0.55 g (2.5 mmol) of 1,3-bis(trimethylsilyl)urea are added to a solution of 1.20 g (5.0 mmol) of 3-(10-hydroxydecyl)thiophene in 5 ml of anhydrous CH_2Cl_2 and the reaction mixture is refluxed, under stirring, for 3 h. After filtration, the solution is concentrated to give 1.54 g (4.9 mmol) of crude product. 80 ml of *n*-pentane and 0.200 g of neutral Al_2O_3 are then added to crude T10OSi and the suspension is stirred for 1 h. After filtration and evaporation of the solvent, 1.41 g (4.51 mmol; 90% yield) of T10OSi are obtained.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.23$ (dd, 1H); 6.91 (m, 2H); 3.55 (t, 2H); 2.50 (t, 2H); 1.68–1.20 (bm, 16H); 0.12 (s, 9H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 139.50$, 134.05, 125.40, 123.30, 61.52, 30.93, 29.91, 29.25, 28.20, 27.80, 27.25, -0.41.

IR (KBr, cm^{-1}): 3106, 3086, 2928, 2855, 1541, 1462, 1250, 1186, 840, 773, 723.

Elemental analysis: calcd for $C_{17}H_{32}OSSi$: C, 65.32%; H, 10.32%; S, 10.26%. Found: C, 65.37%; H, 10.30%; S, 10.31%.

2.1.5. 3-[(10-trimethylsilanyloxy)decyl]-2,5-dibromothiophene [2,5 BT10OSi] (from 2,5 BT10OH)

0.386 g (1.74 mmol) of 1,3-bis(trimethylsilyl)urea are added to a solution of 1.43 g (3.91 mmol) of 2,5 BT10OH in 4 ml of anhydrous CH_2Cl_2. The reaction mixture is refluxed for 3 h under stirring and under a flow of dry nitrogen, and then filtered and dried under vacuum to give 1.69 g (3.59 mmol; 92% yield) of 2,5 BT10OSi in >99% purity (GC–MS, t_r 18.63 min).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.78$ (s, 1H); 3.55 (t, 2H), 2.50 (t, 2H); 1.68–1.20 (bm, 16H), 0.12 (s, 9H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 144.78, 135.74, 114.35, 111.80, 61.52, 30.82, 29.44, 28.75, 28.30, 27.80, 27.21, -0.39$.

IR (KBr, cm^{-1}): 3085, 2927, 2855, 1542, 1462, 1250, 1186, 1004, 840, 750, 473.

Elemental analysis: calcd for $C_{17}H_{30}Br_2OSSi$: C, 43.41%; H, 6.43%; Br 33.97%, S, 6.82%. Found: C, 43.44%; H, 6.39%; Br 33.94%, S, 6.85%.

Mass spectrometry (m/e, % relative intensity): 470 (6, M^+), 391 (12, $C_{17}H_{31}BrOSSi^+$), 255 (25, $C_5H_3Br_2S^+$), 177 (19, $C_5H_5BrS^+$).

2.1.6. 3-[(10-trimethylsilanyloxy)decyl]-2,5-dibromothiophene [2,5 BT10OSi] (from T10OSi)

A solution of 0.56 g (3.2 mmol) of NBS in 4 ml of DMF is added to a solution of 0.5 g (1.6 mmol) of T10OSi in 4 ml of DMF. After stirring for 30 h at room temperature and under a flow of dry nitrogen, the reaction mixture is poured into 60 ml of distilled water and extracted with 5 × 10 ml of CH_2Cl_2. The organic phase is washed again with water (5 × 10 ml), dried with $MgSO_4$, and concentrated to give 0.68 g (1.44 mmol) of crude 2,5 BT10OSi, which is purified by chromatography (Al_2O_3/heptane–diethyl ether 9:1) to give 0.12 g (0.26 mmol; 16% yield) of the desired product in >97% purity (GC–MS, t_r 18.62 min).

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.78$ (s, 1H); 3.55 (t, 2H), 2.50 (t, 2H); 1.68–1.20 (bm, 16H), 0.12 (s, 9H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 144.78, 135.74, 114.35, 111.80, 61.52, 30.82, 29.44, 28.75, 28.30, 27.80, 27.21, -0.39$.

IR (KBr, cm^{-1}): 3085, 2927, 2855, 1542, 1462, 1250, 1186, 1004, 840, 750, 473.

Elemental analysis: calcd for $C_{17}H_{30}Br_2OSSi$: C, 43.41%; H, 6.43%; Br 33.97%, S, 6.82%. Found: C, 43.36%; H, 6.37%; Br 34.24%, S, 6.87%.

Mass spectrometry (m/e, % relative intensity): 470 (4, M^+), 391 (12, $C_{17}H_{31}BrOSSi^+$), 255 (24, $C_5H_3Br_2S^+$), 177 (18, $C_5H_5BrS^+$).

2.1.7. 3-[(10-bromo)decyl]-2,5-dibromothiophene [2,5 BT10B]

A solution of 0.356 g (2.0 mmol) of NBS in 2 ml of DMF is added dropwise to a solution of 0.607 g (2.0 mmol) of 3-[(10-bromo)decyl]thiophene (T10B, prepared as in Ref. [3]) in 2 ml of DMF. After stirring for 6 h at 20 °C under a flux of dry nitrogen, a solution of 0.534 g (3.0 mmol) of NBS in 3 ml of DMF is added dropwise to the reaction mixture. The resulting mixture is stirred at room temperature for 24 h under nitrogen and then poured into 70 ml of distilled water and extracted with 5 × 20 ml of diethyl ether. The organic phase is washed with 5 × 20 ml of distilled water, dried with Na_2SO_4, and concentrated to give 0.82 g (1.78 mmol) of crude 2,5 BT10B. Finally, 10 ml of pentane and 0.6 g of SiO_2 are added to the product and the suspension is stirred for 1 h. After filtration and evaporation of the solvent, 0.67 g (1.45 mmol; 73% yield) of 2,5 BT10B are obtained.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.78$ (s, 1H); 3.40 (t, 2H); 2.50 (t, 2H); 1.95–1.20 (bm, 16H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 144.75, 135.91, 114.50, 111.63, 34.10, 33.25, 30.02, 29.35, 28.74, 28.24, 27.78, 27.25$.

IR (KBr, cm^{-1}): 3083, 2925, 2854, 1542, 1466, 1002, 825, 722, 645, 562, 474.

Elemental analysis: calcd for $C_{14}H_{21}Br_3S$: C, 36.47%; H, 4.59%; Br, 51.99%, S, 6.95%. Found: C, 36.55%; H, 4.43%; Br, 51.78%, S, 7.03%.

2.1.8. 3-[10-(hexanoyloxy)decyl]-2,5-dibromothiophene [2,5 BT10Es]

1.01 g (7.33 mmol) of sodium hexanoate are added under stirring to a solution of 1.69 g (3.7 mmol) of 2,5 BT10B in 10 ml of DMF. The reaction mixture is stirred at 90 °C for 2 h and then poured into 200 ml of distilled water, extracted with heptane (5 × 50 ml), and washed again with water (5 × 50 ml). After anhydrification and evaporation of the solvent, 1.58 g (3.2 mmol; 86% yield) of 2,5 BT10Es are obtained.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.78$ (s, 1H), 4.05 (t, 2H), 2.62 (t, 2H); 2.28 (t, 2H); 1.60 (m, 6H); 1.30 (m, 16H); 0.89 (t, 3H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 173.62, 144.81, 135.80, 114.40, 111.80, 64.25, 34.75, 31.30, 30.80, 29.45, 28.75, 28.24, 27.80, 26.20, 24.60, 22.32, 13.95$.

IR (KBr, cm^{-1}): 3089, 2953, 2925, 2854, 1735, 1541, 1466, 1173, 1001, 825, 722, 474.

Elemental analysis: calcd for $C_{20}H_{32}Br_2O_2S$: C, 48.40%; H, 6.50%; Br, 32.20%, S, 6.46%. Found: C, 48.52%; H, 6.39%; Br, 32.23%, S, 6.60%.

2.1.9. 3-(10-hydroxydecyl)-2,5-dibromothiophene [2,5 BT10OH] (from 2,5 BT10Es)

0.083 g (1.48 mmol) of KOH are added to a solution of 0.57 g (1.15 mmol) of 2,5 BT10Es in 4 ml of methanol and stirred for 2 h at 40 °C. The reaction mixture is then poured into 70 ml of distilled water, added with 0.2 ml of 5% aqueous H_2SO_4 and extracted with diethyl ether (4 × 20 ml), dried with $MgSO_4$ and concentrated to give 0.44 g (1.10 mmol; 96% yield) of 2,5 BT10OH.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.78$ (s, 1H); 3.64 (t, 2H); 2.62 (t, 2H); 1.71–1.54 (m, 4H); 1.43 (s, 1H); 1.30 (m, 12H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 144.80, 135.60, 114.30, 111.90, 62.79, 32.90, 30.82, 29.62, 29.45, 28.72, 28.30, 27.80, 26.50$.

IR (KBr, cm^{-1}): 3340, 3084, 2926, 2854, 1542, 1463, 1057, 1004, 825, 722, 474.

Elemental analysis: calcd for $C_{14}H_{22}Br_2OS$: C, 42.23%; H, 5.57%; Br, 40.13%, S, 8.05%. Found: C, 42.26%; H, 5.54%; Br, 40.10%, S, 8.07%.

2.2. Polymer synthesis

2.2.1. Poly[3-(10-trimethylsilanyloxydecyl)-2,5-thienylene [PT10OSi]

1.50 ml (1.5 mmol) of a 1 M solution of methylmagnesiumbromide in di-*n*-butylether are added to a solution of 0.7 g (1.5 mmol) of 2,5 BT10OSi in 9 ml of anhydrous THF. The reaction mixture is refluxed for 1 h under stirring and under a flow of nitrogen; 0.0084 g (0.016 mmol) of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2) are then added and the mixture is refluxed again for 2 h. The mixture, cooled down to room temperature, is poured slowly into 80 ml of MeOH and filtered. The precipitated polymer is washed with methanol (3 × 20 ml) and with hexane (3 × 20 ml) to give 0.193 g (0.62 mmol; 42% yield) of PT10OSi.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.07$, 7.04, 7.01, 6.98 (4s, 1H); 3.68–3.50 (bm, 2H); 2.82, 2.55 (2bm, 2H); 1.80–1.10 (bm, 16H); 0.10 (s, 9H).

^{13}C NMR ($CDCl_3$, ppm): $\delta = 140.27$, 134.26, 130.66, 128.75, 62.53, 31.75, 30.25, 29.80, 29.35, 28.91, 27.80, 27.21, -0.40.

IR (KBr, cm^{-1}): 3056, 2924, 2853, 1512, 1462, 1251, 1186, 840, 722.

Elemental analysis: calcd for $(C_{17}H_{30}OSSi)_n$: C, 65.74%; H, 9.74%; S, 10.33%. Found: C, 65.59%; H, 9.69%; Br, 0.23%, S, 10.28%.

2.2.2. Poly[3-(10-hydroxydecyl)-2,5-thienylene] [PHDT96]

10 ml of HCl 0.2 M in methanol are added dropwise in 5 h to a solution of 0.16 g (0.51 mmol) of PT10OSi in 15 ml of THF. The mixture is stirred at room temperature for 5 h, then neutralized with several drops of a solution of KOH 5% in methanol, added with 15 ml of MeOH, and finally filtered on a Teflon septum (0.45 μm pore size). The precipitated polymer is washed with methanol giving 0.12 g (0.50 mmol; 99% yield) of PHDT96.

^{1}H NMR ($CDCl_3/CD_3OD$; 0.28 CD_3OD m.f., ppm): $\delta =$ 7.08, 7.05, 7.00 (3s, 1H); 3.55 (t, 2H); 2.90–2.50 (2bm, 2H); 1.80–1.10 (bm, 16H).

^{13}C NMR ($CDCl_3/CD_3OD$; 0.28 CD_3OD m.f., ppm): $\delta =$ 139.97, 133.84, 130.59, 128.77, 62.69, 32.70, 30.72, 29.78, 29.67, 29.38, 29.26, 25.95.

IR (KBr, cm^{-1}): 3370, 3056, 2923, 2852, 1511, 1463, 1057, 821, 721.

Elemental analysis: calcd for $(C_{14}H_{22}OS)_n$: C, 70.54%; H, 9.30%; S, 13.45%. Found: C, 70.32%; H, 9.27%; Br, 0.30%, S, 13.40%.

2.3. Analyses

^{1}H and ^{13}C NMR spectra were run on a Varian Gemini 300 FT–NMR spectrometer (300 MHz) using TMS as reference. IR spectra of the monomers (pure liquids) were carried out on KBr disks and polymers (films) on KBr or Si disks using a Perkin Elmer 1750 FT–IR spectrophotometer.

Elemental analyses were performed using a ThermoQuest Flash 1112 Series EA. Mass spectrometry (m.s.) was carried out on a VG 7070E spectrometer at 70 eV. GC–MS was performed on a Carlo Erba QMD 1000 using a Quadrex 007-5 (5% phenyl)methylpolysiloxane fused silica capillary column, temperature program 75–280 °C, 15 °C/min, carrier gas He. The molecular weights were determined by gel permeation chromatography (GPC) (relative to polystyrene standards) on a HPLC Lab Flow 2000 apparatus equipped with a PL gel 10^4 column and a Linear Instrument (model UVIS-200) UV–vis detector working at 263 nm, with THF being used as an eluent. The UV–vis spectra of the films on glass substrate or of the solutions at 18 °C were recorded with a Perkin Elmer Lambda 19. The solutions were prepared using spectroquality solvents stored over molecular sieves keeping the polymer concentration constant at ca. 7×10^5 mol l^{-1} (moles of polymer repeat unit per litre). UV–vis spectra in the solid state (powder of the pristine polymer or adsorbed on solid substrates or in film on a silicon disk) were carried out at 18 °C on a Perkin Elmer Lambda 19 spectrophotometer equipped with an integrating sphere (Perkin Elmer code number C6951014).

The solid substrates employed for the PHDT96 adsorption were: (a) silica gel, high purity grade, 70–230 mesh, 60 Å, BET surface area ~500 $m^2\,g^{-1}$, pore volume 0.75 $cm^3\,g^{-1}$; (b) microcrystalline cellulose, 20–100 μm; (c) poly(vinyl alcohol), 99% hydrolysed, $M_w = 85.000 \div 146.000$. 1 ml of the chloroform solution employed for the solvatochromism experiments was adsorbed on 100 mg of the support and then the sample dried under vacuum.

X-ray diffraction (x.r.d.) data were collected at room temperature using a Cu Kα radiation ($\lambda = 1.5406$ 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 THF solution.

3. Results and discussion

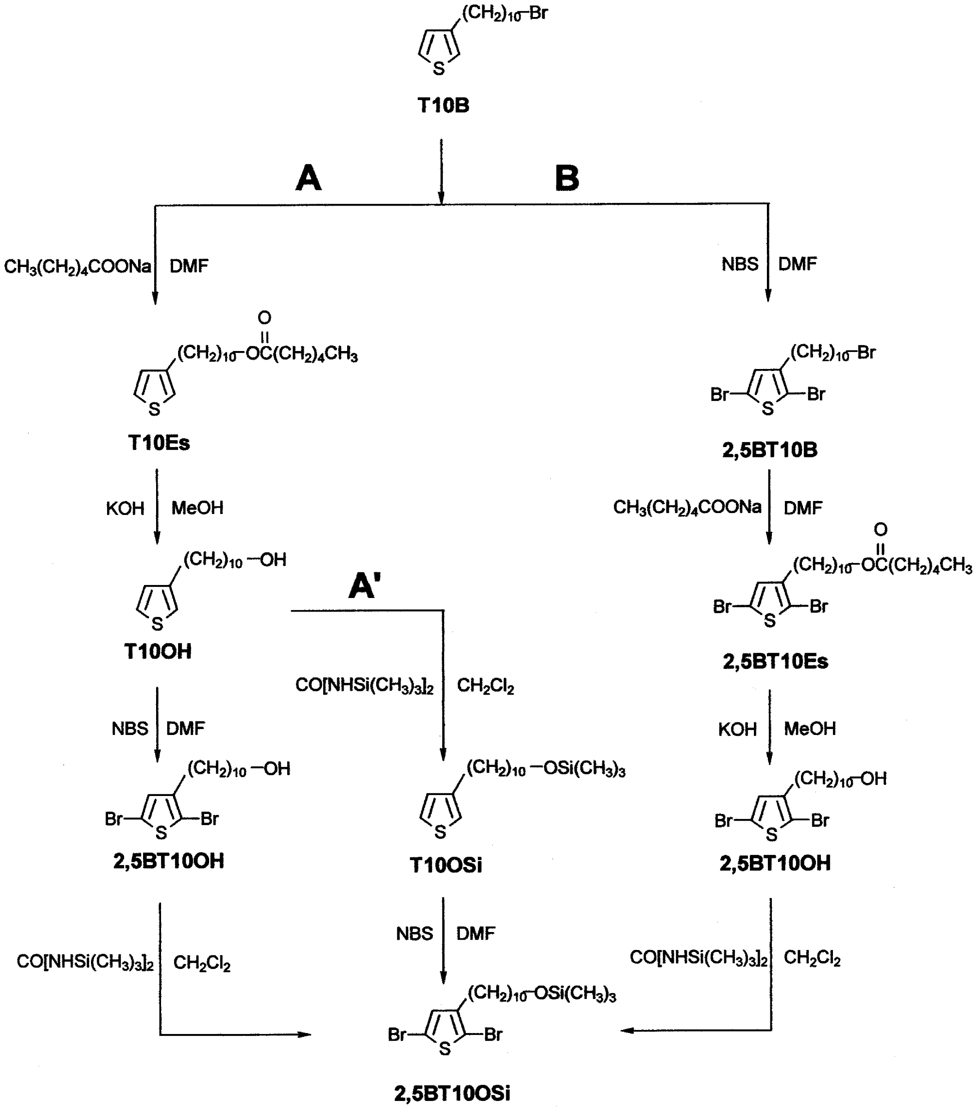
3.1. Synthesis of the 2,5 BT10OSi monomer

The methods of synthesis for obtaining polythiophenes with reduced configurational defects reported in the literature and which mostly exploit the nickel-catalysed coupling of organometallic derivatives [10–12] work well on thiophenes substituted with alkylic groups but are incompatible with the hydroxyfunctionalized monomer. In view of the foregoing, recourse must be made to a group for the protection of hydroxy functionality. For this purpose, a trimethylsilanyloxy derivative was employed as a precursor of the hydroxylic group, thus permitting the synthesis of 3-

(10trimethylsilanyloxy)decyl]-2,5-dibromothiophene (2,5 BT10OSi). The use of this protection group made it possible to obtain, with a good yield, a regioregular poly(hydroxyalkylthiophene) that is soluble in common organic solvents. Such a result would not have been possible with the methods of synthesis reported in the literature for similar polymers as these methods yield materials that are poorly soluble except in special amidic solvents [13,14].

A first attempt to synthesize 2,5 BT10OSi was made using 3-(10-hydroxydecyl)thiophene (T10OH) that was synthesized by means of the alkaline methanolysis of 3-(10-hexanoyloxydecyl)thiophene (T10Es) obtained from the reaction of 3-(10-bromodecyl)thiophene (T10B, synthesized according to Refs. [8,9]) with sodium hexanoate in anhydrous DMF (Scheme 1, pathway A). This synthetic route entails the direct dibromination of the hydroxy-functionalized monomer and its subsequent conversion to a silanyloxy derivative, while its variant A′ first entails protecting the hydroxy functionality before dibromination.

Poor results were obtained from pathway A as far as the transformation of T10OH into 2,5 BT10OH. A poor yield (18%) was in fact reported as the crude material resulting from this reaction was found to contain not only 2,5 BT10OH but also a rather considerable quantity of mono and tribromination by-products even after attempts at optimizing the reaction conditions by varying times and temperatures. Moreover, the purification of 2,5 BT10OH was found to be difficult, the presence of the highly polar hydroxy group tending to level out the retardation factors (Rf) of the variously brominated intermediates, thus making the chromatographic pathway complex. Even distillation did not make for improved results. The subsequent step (from 2,5 BT10OH to 2,5 BT10OSi), however, was not



Scheme 1. Synthesis of 2,5 BT10OSi.

found to be difficult (92% yield). The overall yield in 2,5 BT10OSi, starting from T10B, obtained by pathway A is 14%.

The first step of pathway A′ (from T10OH to T10OSi) resulted in a high yield (90%) while problems deriving from partial desilylation of the ether group were encountered during the second step (from T10OSi to 2,5 BT10OSi), giving rise to a reaction mixture more complex than the previous one. In fact, bromination products of both T10OSi and T10OH were found to be present, thus adversely affecting the yield in 2,5 BT10OSi (16%), corresponding to an overall yield of 12% starting from T10B.

In view of the drawbacks encountered for the previous two pathways, dibromination on T10B was attempted as shown in Scheme 1, pathway B. A high conversion rate of the initial product with a high selectivity in 2,5 BT10B was obtained by using this way. Moreover, no tribromination product was found to be present in this case and the desired product proved easy to separate from the traces of reaction by-products by chromatography (73% yield). After esterification with sodium hexanoate followed by alkaline hydrolysis, the halogen in the end position of the side chain was easily converted to hydroxy functionality. The functionality was then protected by means of 1,3-bis(trimethylsilyl)urea thus yielding 2,5 BT10OSi (92% conversion yield, corresponding to an overall yield of 55%, starting from T10B). Pathway B is therefore more advantageous with respect to A and A′, leading not only to a greater overall yield, but also to easier and more effective purification procedure of the intermediates and to a final product that, thanks to its high degree of purity (99% GC–MS), could thus be used directly for the subsequent regiospecific polymerizations.

3.2. Synthesis of the PHDT96 polymer

Poly[3-(10-hydroxydecyl)-2,5-thienylene] (PHDT96) was obtained by a post-functionalization reaction based on the acid hydrolysis of the precursor polymer PT10OSi as shown in Scheme 2. PT10OSi was synthesized by refluxing the 2,5 BT10OSi monomer with one equivalent of methylmagnesium bromide in anhydrous THF [12]. The actual reactive monomer is the organometallic intermediate which gives rise to the final polymer by a coupling catalysed by [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl_2).

A quenching test was performed by adding a solution of HCl 0.1 M in THF to a mixture of methylmagnesium bromide and 3-decyl-2,5-dibromothiophene in anhydrous THF. This experiment was conducted at the same concentration and temperature conditions (1 h under reflux) as those adopted for the synthesis of PT10OSi and under continuous heating. A 2:1 molar ratio between the isomer containing magnesium in the 2-position and that in the 5-position of the aromatic ring was found by NMR. Despite the regioselectivity of the metathesis reaction, the degree of regioregularity of the obtained polymer was found to be considerably higher (96% HT). This finding may be ascribable to the different reactivity of the organometallic intermediates with respect to the polymerization reaction as borne out by the non-total polymer yield (42%). The polymer was in the form of a fine purple–black powder (see characteristics in Table 1) that was found to be well soluble in common organic solvents.

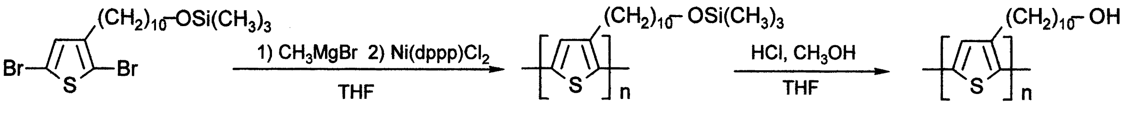
The acid hydrolysis reaction of PT10OSi easily leads to PHDT96 that quickly starts to precipitate. At the end of the reaction, precipitation was completed by adding methanol and the hydroxy-functionalized polymer was recovered by filtration with high yield (99%); the complete transformation of the functional group was confirmed by the NMR, IR and elemental analyses. PHDT96 features a colour similar to that of its precursor but with metallic lusters. Table 1 shows its regiostructural and ponderal characteristics.

As discussed further on, PHDT96 is more soluble in the chloroform/methanol mixture having a MeOH molar fraction (m.f.) of 0.28 than in pure chloroform or tetrahydrofuran. In view of this, the ^{1}H and ^{13}C NMR microstructural characterization of the aforementioned polymer was made in $CDCl_3/CD_3OD$ with the composition described above.

Fig. 2 shows the ^{1}H NMR spectrum of PHDT96. The degree of regioregularity (96% HT) was evaluated on the basis of the intensity ratio of the two signals in the 2.90–2.50 ppm range ascribable to the methylenic protons in α to the thiophenic ring. The signal in the lower fields is assigned to the HT diads while the one observable in the higher fields, of lower intensity, is assigned to the HH and TT diads.

In the aromatic region, the absorption of the proton in β on the thiophenic ring is shown as a prevailing singlet at 7.00 ppm ascribable to the HT–HT triad, and as very weak signals ascribable to the other types of junctions.

The inset on Fig. 2 shows the expansion of the ^{13}C NMR spectrum with reference to the aromatic region which confirms the almost exclusive presence of the signals



2,5BT10OSi **PT10OSi** **PHDT96**

Scheme 2. Synthesis of PT10OSi and PHDT96.

Table 1
Characteristics of the polymers

Polymer	Yield (%)	HT (%)[a]	$\bar{M}_n$[b] (g/mol)	$\bar{M}_w/\bar{M}_n$[b]	$\overline{DPn}$[b]
PT10OSi	42	96	14,000	1.6	45
PHDT96	99	96	11,000	1.6	45
PHDT78	99[c]	78	11,500	1.5	48

[a] Regioregularity expressed as head-to-tail diads determined by ^{1}H NMR.

[b] Number average molecular weight $\bar{M}_n$, polydispersity index $\overline{M}w/\overline{M}n$ and number average degree of polymerization $\overline{DPn}$ determined by GPC using polystyrene standards.

[c] Conversion yield from the fractionated precursor polymer poly[3-(10-hexanoyloxydecyl)-2,5-thienylene].

ascribable to thiophenic carbons in a HT configuration [10,11].

3.3. Solvatochromism

The solvatochromism of PHDT96 was investigated in the dimethylpropyleneurea (DMPU)/methanol solvent/non-solvent system (Fig. 3A) and compared with that of a poly[3-(10-hydroxydecyl)-2,5-thienylene] at 78% HT couplings (PHDT78, Fig. 3B). The latter has been obtained by alkaline methanolysis of a sample of poly[3-(10-hexanoyloxydecyl)-2,5-thienylene] prepared according to Ref. [6]. The precursor polymer had been subjected to an accurate fractionation procedure (dissolution in $CHCl_3$ and reprecipitation with methanol several times) to isolate a fraction having $\overline{DP}$n and a polydispersity index comparable to those of PHDT96 (see Table 1).

In pure DMPU the polymer with greatest regioregularity exhibits a maximum absorption (λ_{max}) at 451 nm (curve 1, Fig. 3A), while the maximum absorption of PHDT78 was found to be at 442 nm (curve 1, Fig. 3B). The addition of methanol gave rise to a more conjugated polymer conformation with a spectrum profile, where the vibronic structure appeared to be particularly resolved. At the highest non-solvent molar fraction, λ_{max} is located on the second vibronic quantum at 556 nm in the case of PHDT96 (curve 5, Fig. 3A), while in that of PHDT78 it is situated at 544 nm (curve 5, Fig. 3B).

Already at particularly low molar fractions of MeOH, PHDT96 was found to exhibit a tendency to generate considerable quantities of highly conjugated forms. The absorbance of the pure electronic transition E_{0-0} ($\lambda =$ 598 nm) is proportional to the concentration of the more conjugated polymeric form present in the solution; when the absorbance is considered as a function of the non-solvent molar fraction (see insets in Fig. 3), a quicker transformation of the less conjugated form to the more conjugated one may be observed for PHDT96. This finding may be ascribed to the greater regioregularity of PHDT96 that could favour the setting up of highly cooperative phenomena for the transformation.

Anomalous solvatochromism in chloroform/methanol mixtures [6] was observed for PHDT96 (Fig. 4A) and for PHDT78 (Fig. 4B); in fact, the solutions in pure chloroform exhibit the simultaneous presence of two forms with different mean conjugation lengths. Moreover, unlike what is usually observed for PATs with the chloroform/methanol couple, the initial addition of a non-solvent gives rise to a marked blue-shift caused by the reduction of the concentration of the more conjugated form pre-existing in the pure solvent. The more conjugated form of the polymer was observed to re-appear after the addition of methanol beyond a certain threshold value as shown by the typical structured profile at high wavelengths. In such a mixture, the chromism of the two polymers was seen to exhibit similar spectrum profiles especially at high non-solvent molar fractions (see, for example, curves 7 in Fig. 4A and B).

The molar fraction of methanol corresponding to the lowest absorbance of the more planar conformation was found to be slightly less for PHDT96, that is 0.28 vs. 0.40

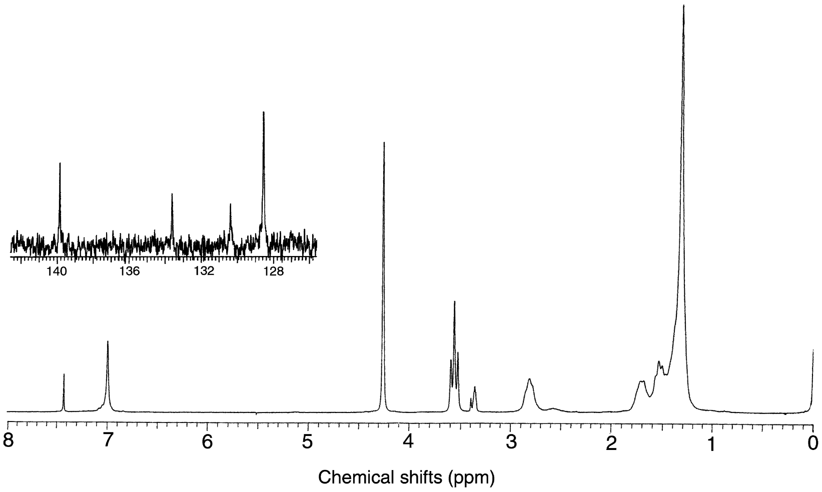


Fig. 2. ^{1}H NMR spectrum of PHDT96 in $CDCl_3/CD_3OD$ (0.28 CD_3OD m.f.); signals at 7.41 ($CHCl_3$), 4.25 and 3.35 (CH_3OH) are due to the non-deuterated solvents. Inset: expanded ^{13}C NMR aromatic region of PHDT96.

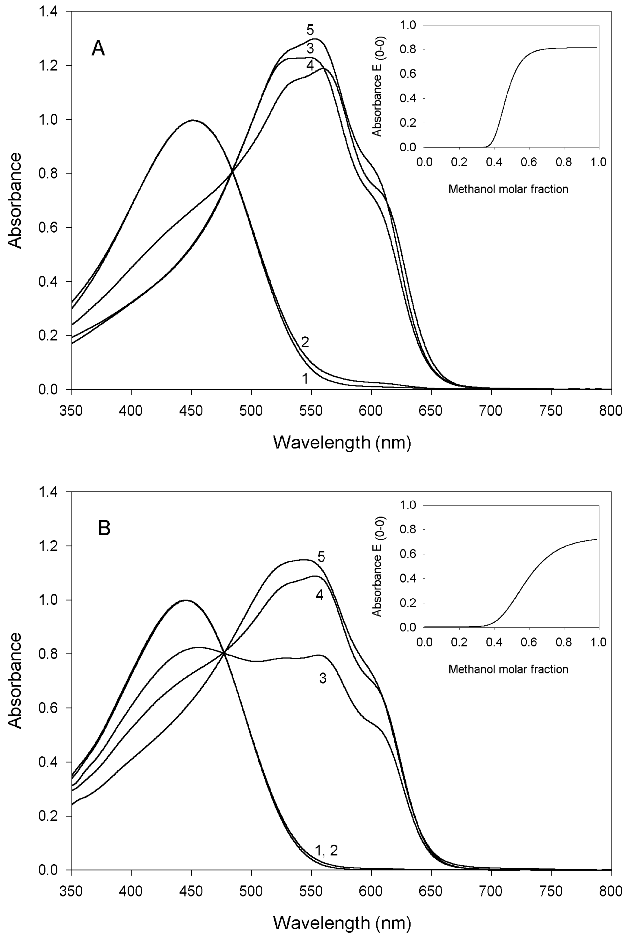


Fig. 3. UV–vis absorption spectra of (A) PHDT96 and (B) PHDT78 in DMPU solutions at 18 °C with different m.f. of MeOH: (1) 0.00; (2) 0.37; (3) 0.60; (4) 0.75; (5) 0.99. Insets: absorbance of the 0–0 band vs. methanol molar fraction.

MeOH m.f. (see insets in Fig. 4). Moreover, even with the $CHCl_3$/MeOH mixture, a quicker conformational transformation in the transition from the more conjugated to the less conjugated form, and vice versa, was observed for PHDT96. It should be emphasized, at the end of this comparative study, that the solvatochromic properties of the two PHDT samples are very similar. The main driving force of the solvatochromic transformation, that is the desolvation of the polymeric backbones [15], is probably strongly assisted by the formation of intramolecular hydrogen bonds, that can help overcome the energy barrier to the chain planarization, by controlling the mobility and the rotational freedom of the side chains. This assistance seems prescind from the configurational characteristics of the two polymers, giving rise, in both cases, to the same chromophoric unit for the more conjugated conformation induced by the solvatochromic effect.

3.4. Conversion of PT10OSi in film

An effective method for obtaining a good film of PHDT96 is through the acid hydrolysis of a film of the

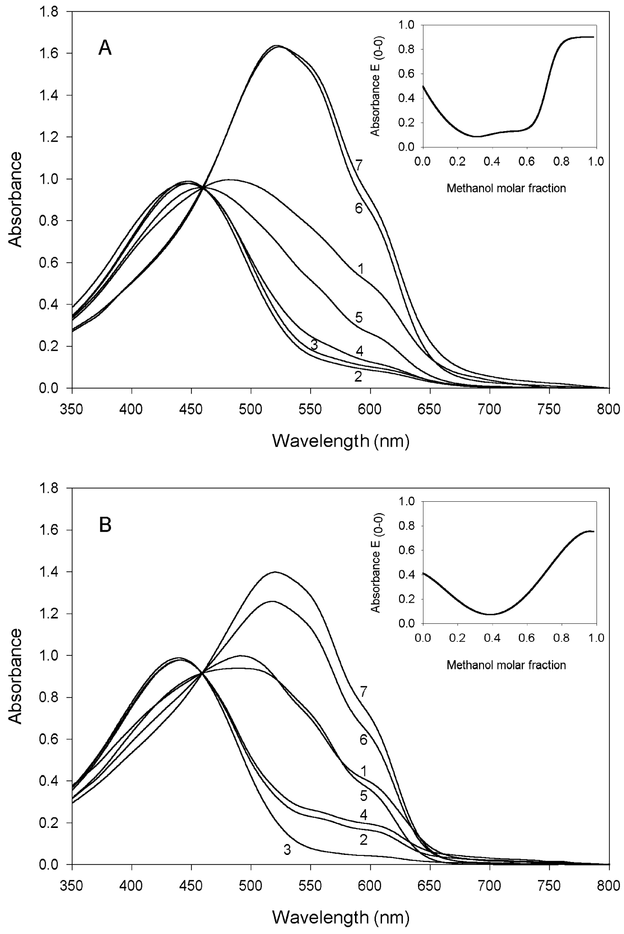


Fig. 4. UV–vis absorption spectra of (A) PHDT96 and (B) PHDT78 in $CHCl_3$ solutions at 18 °C with different m.f. of MeOH: (1) 0.00; (2) 0.28; (3) 0.39; (4) 0.50; (5) 0.66; (6) 0.80; (7) 0.98. Insets: absorbance of the 0–0 band vs. methanol molar fraction.

PT10OSi precursor polymer. A film of PT10OSi on a silicon disk, obtained by evaporation of a solution in THF, was hence subjected to acid hydrolysis with HCl 2% in methanol for 2 h at room temperature. Transformation was confirmed by the disappearance at the IR of the three strong bands ascribable to silylether at 1253 ($\delta_{\mathrm{Si-CH_3}}$), 1098 ($\nu_{\mathrm{Si-O-C}}$) and 842 ($\nu_{\mathrm{Si-CH_3}}$) cm^{-1} as well as by the appearance of the two bands, typical of hydroxy functionality, at 3375 ($\nu_{\mathrm{O-H}}$) and 1057 ($\nu_{\mathrm{C-O-H}}$) cm^{1} (Fig. 5A).

The UV–vis spectrum in diffuse reflectance of PHDT96 in film on silicon and that of its precursor under the same conditions (Fig. 5B) exhibited a similar spectrum profile, with $\lambda_{\max}$ around 558 nm in proximity to the second vibronic quantum. On the other hand, the spectrum of the PHDT96 as a film cast directly from the chloroform/methanol solution (0.28 MeOH m.f.) exhibited a maximum on the third vibronic quantum (see Fig. 6, curve 1), blue-shifted by 25 nm (from 558 to 533 nm) and with a relative intensity of the pure electronic transition markedly lower ($I_{E_{0-0}}/I_{\lambda_{\max}}$ at 0.66 vs. 0.83) than that of the film of the same polymer obtained by acid methanolysis of the film of PT10OSi (Fig. 5B, curve 2). Thus the direct acid hydrolysis

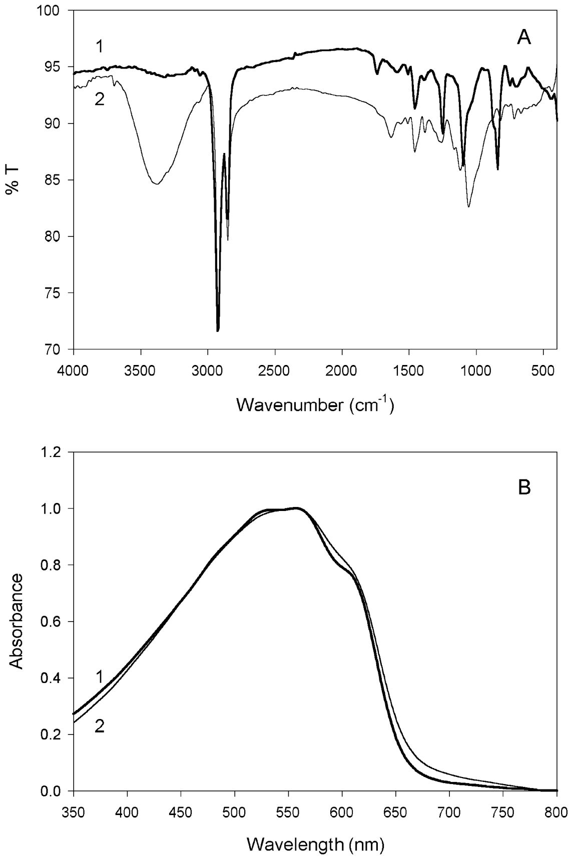


Fig. 5. (A) FT–IR and (B) UV–vis spectra of PT10OSi (film on Si disk) before (1) and after (2) hydrolysis.

reaction of a film of the precursor polymer was found to be a convenient method to obtain a more conjugated film of PHDT96.

3.5. Chromism in solid matrices

The chromism of PHDT96 was also investigated by adsorbing solutions of the polymer on solid matrices characterized by the presence of hydroxy groups in their structure. The adsorbents employed were silica gel, microcrystalline cellulose and polyvinyl alcohol (see Section 2).

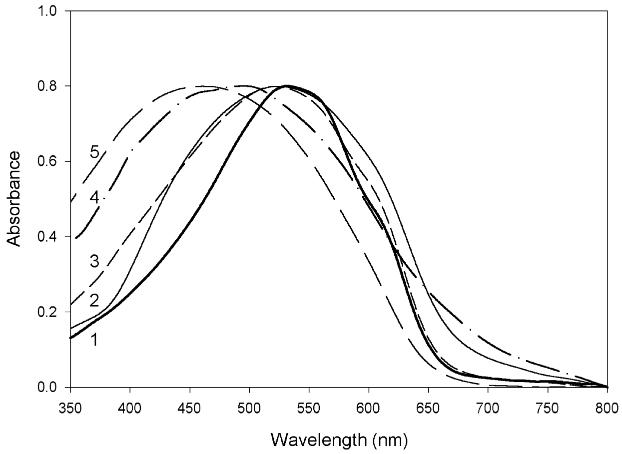


Fig. 6. UV–vis absorption spectra of PHDT96 as: (1) film on glass; (2) adsorbed on PVA; (3) adsorbed on microcrystalline cellulose; (4) pristine powder; (5) adsorbed on SiO_2.

The spectral behaviour of the polymer on substrates with a higher content of hydroxy groups (polyvinyl alcohol and cellulose, curve 2 and 3 of Fig. 6) was found to be much more similar to that of the film (curve 1, Fig. 6) than to that of the pristine polymer powder (curve 4 in Fig. 6). The existence of markedly ordered conformations may therefore be assumed in these cases.

The PHDT96 samples on cellulose and silica exposed to methanol vapours exhibited in both cases an appreciable red-shift of the absorption maximum, namely 36 nm in cellulose (Fig. 7A, with a noteworthy λ_{max} of 558 nm being reached) and 50 nm in SiO_2 (Fig. 7B). Elimination of MeOH by evaporation under vacuum results in the initial values of λ_{max} being restored. The bathochromic shift may be probably ascribable to the fact that methanol, by interacting with the active sites of the substrate, leaves the polymer free to take on states with a more extended conjugation and a more ordered conformation. Moreover, the elimination of methanol reactivates the hydrogen-bond

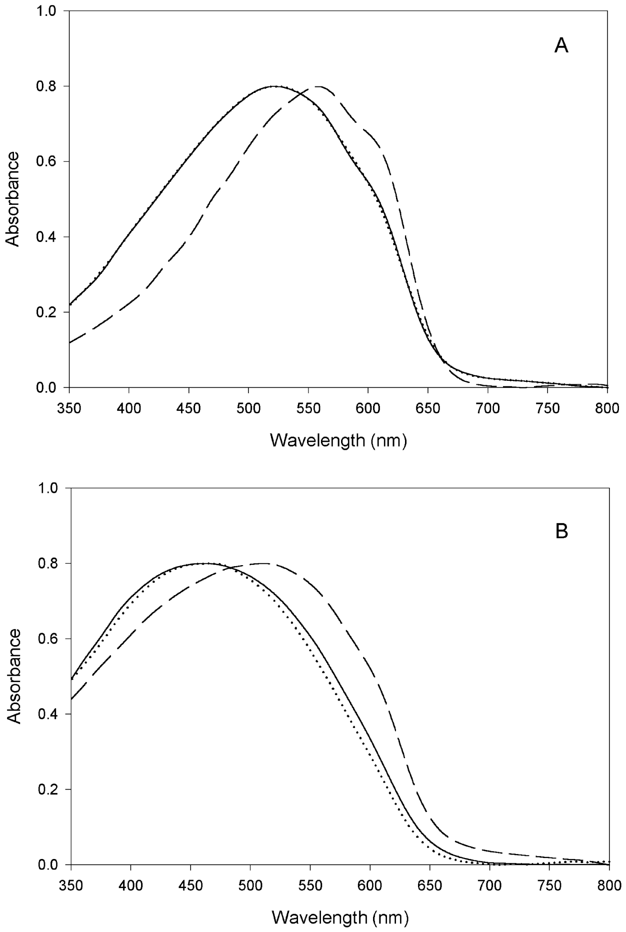


Fig. 7. UV–vis absorption spectra of PHDT96 (A) on microcrystalline cellulose and (B) on SiO_2 before (solid line), after (dashed line) exposure to methanol vapours. Dotted line: after methanol desorption.

interactions between the hydroxy groups of the polymer and those of the substrate, thus causing the initial conditions to be restored. PHDT96 adsorbed on PVA does not present any chromic effect when exposed to MeOH vapours.

Further investigations are underway with other types of solvents for the purpose of evaluating the possibility of using PHDT96 as a chromic sensor.

3.6. X-ray diffraction measurements

The room temperature X-ray determinations of PHDT samples are shown in Fig. 8A (96% HT) and Fig. 8B (78% HT). They revealed the intense low-angle reflections at 25.4 Å ($2\theta = 3.50$) and 26.4 Å ($2\theta = 3.34$) and the broad high-angle halos centred at 3.04 Å ($2\theta = 29.0$) and 3.70 Å ($2\theta = 24.0$) for PHDT96 and PHDT78, respectively.

The first reflections correspond to the double length of a fully extended lateral chain (lateral packing) which means that the side-chains are not interdigitated. This situation is in agreement with the spacing of about 22 Å found in poly(3-decylthiophene) [16] considering the presence of the hydroxy group at the end of the lateral chains and its possibility to give hydrogen bonds.

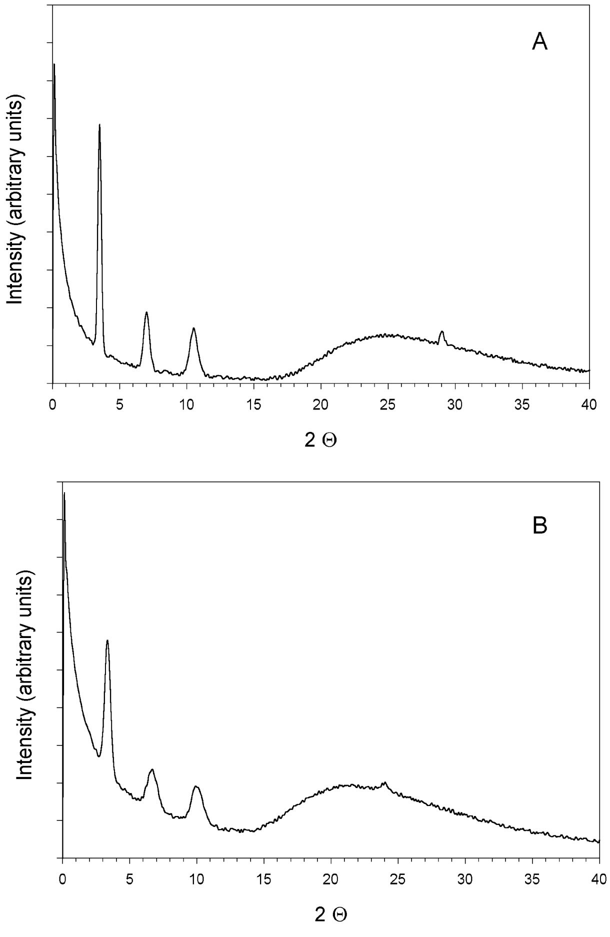


Fig. 8. X-ray diffraction patterns of (A) PHDT96 and (B) PHDT78.

The second reflections may be referred to a more disordered superposition of parallel chains (π-stacking). Moreover, it should be noticed that the crystalline peak found in PHDT96 is sharper and more intense than in PHDT78, suggesting that for the polymer with higher regioregularity the ordered domains are bigger.

Finally, the presence of the second- and third-order reflections (at $2\theta = 7.00$ and 10.5 for PHDT96 and at $2\theta = 6.70$ and 10.0 for PHDT78) relative to the polythiophenes interchains distances [17,18] indicates an high degree of regularity in the lateral packing distance for both the PHDT samples.

4. Conclusions

A regioregular poly[3-(10-hydroxydecyl)-2,5-thienylene] (PHDT96) that is soluble in common organic solvents was obtained by optimizing the methods for the synthesis of the 3-[(10-trimethylsilanyloxydecyl)-2,5-dibromothiophene] monomer and for its subsequent polymerization and post-functionalization. It was hence possible to fully characterize PHDT96 from a chemical and structural point of view and to investigate the chromism of this polymer in solution and in film, as well as in different types of solid matrices containing hydroxy groups.

The influence of the hydroxy group at the end of the side chains was, once again, very important in controlling the conformational order of the polymer both in solution and in the solid state. In fact, the UV–vis spectra of the PHDT samples exhibited characteristics which are similar apart from regioregularity; moreover X-ray diffraction shown a single crystalline phase only, with a crystalline structure of PHDT96 closely resembling those of PHDT78.

PHDT96 proved to be very interesting both as far as its synthesis is concerned, as it can be easily obtained from its precursor even through direct conversion in film, as well as for its application potential. In fact, its high sensitivity to solvents, both in solution and on solid matrices, makes it potentially suitable for use as a chromic sensor in systems based on chemorecognition principles.

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