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Synthesis and Characterization of a Highly Soluble Poly[3-(10-hydroxydecyl)thiophene]

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Summary: The preparation of a regioregular HH-TT linked poly[3-(10-hexanoyloxy)decyl]thiophene and its conversion to the corresponding hydroxy-functionalized polymer is described and discussed. The hydroxydecyl polymer, highly soluble in common organic solvents, has been characterized via NMR, FT-IR, DSC and X-ray diffractometry.

Keywords: conjugated polymer; differential scanning calorimetry (DSC); functionalization of polymers; polythiophenes; regioregular polymers

Introduction

Polythiophene and its functionalized derivatives have been widely investigated because of their interesting optical and electro-optical properties, good environmental stability and easy synthesis.[1] Polyalkylthiophenes (PATs) also possess other characteristics such as good solubility and processability.[2] The introduction of a functional group at the end of the side chain makes it possible to tune the final properties of the polymer, which in some cases leads to the formation of a truly multifunctional material.[3] The features of these systems are influenced mainly by the nature of the monomers and by the degree of functionalization, but chain micro-structure also plays a role. In this regard many works in the literature discuss the preparation of highly regioregular PATs.[4] Hydroxy-functionalized polyalkylthiophenes synthesized via a post-polymerization functionalization technique have been recently studied by the authors.[5,6] The polymers thus obtained exhibited a strong tendency to self-assemble thanks to hydrogen bonds

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among the lateral chains[7] but had a reduced solubility in common organic solvents. The aim of this work was to synthesize a new poly[3-(10-hydroxydecyl)thiophene] completely free from HT linkages so as to assess to what extent polymer regiochemistry affects the macroscopic properties of the material, especially its solubility.

Experimental

Materials and instruments

All the solvents and reagents used for the synthesis were purchased from Aldrich Chemical Company. ^{1}H and ^{13}C NMR spectra were run on a Varian Gemini 300 FT-NMR spectrometer (300MHz), using TMS as reference. IR spectra were carried out using a Perkin Elmer 1750 FT-IR spectrophotometer. The molecular weights were determined by size exclusion chromatography (SEC), relative to polystyrene standards, on a HPLC Lab Flow 2000 apparatus equipped with a Phenogel mixed MXL column and a Linear Instrument (model UVIS-200) UV-Vis detector working at 263 nm, with THF being used as an eluent, at a flow rate of 1.0 mL/min. Thermal analysis was performed on a TA Instruments DSC 2920 and the heating rate was 10°C/min. X-ray diffraction (x.r.d.) data were collected at room temperature using Cu Kα radiation (λ = 1.5406 Å) and Bragg-Brentano powder diffractometer (Philips PW1050/81-PW1710) equipped with a graphite monochromator in the diffracted beam. A 2Θ range between 2.0 and 40.0° was scanned by steps of 0.2° 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 a film of the polymer, which was cast from THF solution.

Dimer synthesis

2-bromo-3-[10-(p-methoxyphenoxy)decyl]thiophene (2)

A solution of 3.63 g (20.39 mmol) of NBS in 26.25 ml of N,N-DMF is added in 4 h in the dark at –20 °C to a solution of 5.90 g (17.02 mmol) of 3-[10-(p-methoxyphenoxy)decyl]thiophene (**1**, prepared as in Ref [8]) in 34.50 ml of N,N-DMF. After stirring for 15 h at room temperature, the mixture is poured into 900 ml of distilled water and extracted with 6 × 300 ml of n-pentane. The organic phase is dried with Na_2SO_4 and concentrated to give 7.05 g (16.57 mmol) of crude **2** which is purified by chromatography (SiO_2/n-pentane-diethyl ether 9:1) giving 6.66 g (15.65 mmol; 92% yield) of the desired product. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.18 (d, 1H); 6.83 (s, 4H);

6.79 (d, 1H); 3.90 (t, 2H); 3.78 (s, 3H); 2.56 (t, 2H); 1.85-1.11 (m, 16H); ^{13}C-NMR ($CDCl_3$, ppm): δ 156.8, 154.8, 139.1, 126.9, 124.0, 115.9, 115.1, 109.1, 68.2, 55.5, 31.6, 29.7, 29.5, 28.8, 28.1, 27.8, 25.7; FT-IR (KBr, cm^{-1}): 3104, 3045, 2995, 2922, 2853, 1507, 1465, 1440, 1409, 1392, 1288, 1229, 1180, 1106, 1040, 991, 822, 741, 719, 636, 521.

3,3'-di[10-(p-methoxyphenoxy)decyl]-2,2'-bithiophene (3)

37 ml of anhydrous THF are added under Ar atmosphere to a mixture of 14.64 g (34.41 mmol) of product **2** and 0.65 g (26.74 mmol) of magnesium turnings and then refluxed for 7 h. The mixture is subsequently transferred via cannula to a second apparatus and added dropwise to 0.34 g (0.63 mmol) of [1,3-bis(diphenylphosphino)propane]nikel(II) chloride ($NiDPPPCl_2$) with the temperature being kept at –6 °C. The reaction mixture is refluxed for 20 h and afterwards hydrolyzed with 300 ml of 2% HCl. The aqueous phase is extracted with 4 × 100 ml of diethyl ether and the combined organic phases are washed to neutrality, dried with Na_2SO_4 and concentrated to give 10.86 g (15.71 mmol) of crude **3**, which is then purified by chromatography (SiO_2/n-heptane-diethyl ether 8:2) to give 3.31 g (4.79 mmol; 28% yield) of the desired product. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.27 (d, 2H); 6.95 (d, 2H); 6.82 (s, 8H); 4.88 (t, 4H); 4.76 (s, 6H); 2.49 (t, 4H); 1.81-1.17 (m, 32H); ^{13}C-NMR ($CDCl_3$, ppm): δ 153.9, 153.5, 142.5, 128.9, 128.7, 125.4, 115.6, 114.8, 68.8, 55.9, 30.9, 29.7, 29.6, 29.5, 29.0, 26.2; FT-IR (KBr, cm^{-1}): 3107, 3047, 3009, 2932, 2917, 2850, 1512, 1475, 1465, 1441, 1395, 1292, 1240, 1181, 1112, 1037, 826, 743, 718, 685, 532.

3,3'-di(10-bromodecyl)-2,2'-bithiophene (4)

A mixture of 7.36 ml of 48% HBr and 10.01 ml of acetic anhydride is added under N_2 atmosphere to 2.49 g (3.60 mmol) of **3** and 0.094 g (0.18 mmol) of hexadecyltributylphosphonium bromide. The reaction mixture is heated at 90°C for 24 h. After dilution with 200 ml of distilled water and ice, the mixture is extracted with 3 × 75 ml of diethyl ether. The organic phase is washed to neutrality with saturated $NaHCO_3$, dried with $CaSO_4$, and concentrated. The residuum is diluted with 500 ml of n-pentane and filtered. 2.5 g of SiO_2 are added to the solution and the mixture is then stirred for 30 min. After filtration the solvent is removed in vacuo to give 1.60 g (2.65 mmol; 74 % yield) of crude **4** which is used without further purification. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.29 (d, 2H); 6.96 (d, 2H); 3.20 (t, 4H); 2.48 (t, 4H); 1.84 (m, 4H); 1.61-1.17 (m, 28H); ^{13}C-NMR ($CDCl_3$, ppm): δ 141.3, 129.8, 125.3, 122.9, 34.1, 33.3, 30.1, 29.4, 28.5, 28.1, 27.9, 27.3; FT-IR (KBr, cm^{-1}): 3102, 3060, 3001, 2925, 2853, 1462, 1439, 1409, 1371, 1255, 1235, 1090, 877, 831, 721, 694, 646, 562.

*3,3'-di(10-hexanoyloxydecyl)-2,2'-bithiophene (**D1**)*

A solution of 1.82 g (3.01 mmol) of **4** in 4 ml of N,N-DMF is added in 4 h at 105°C to a solution of 1.66 g (12.02 mmol) of sodium hexanoate in 33 ml of N,N-DMF, and stirred at 105°C for 3 h and at room temperature for 15 h. The reaction mixture is then poured into 500 ml of distilled water and extracted with 6 × 150 ml of n-pentane. The organic phase is washed with water, dried with $CaSO_4$, and concentrated to give 1.85 g (2.74 mmol) of crude **D1** which is purified by chromatography (SiO_2/n-heptane-THF 85:15) to give 0.46 g (0.68 mmol; 23 % yield) of the desired product. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.28 (d, 2H); 6.96 (d, 2H); 4.05 (t, 4H); 2.46 (t, 4H); 2.30 (t, 4H); 1.77-1.18 (m, 44H); 0.94 (t, 6H); ^{13}C-NMR ($CDCl_3$, ppm): δ 174.4, 142.3, 129.5, 125.2, 122.8, 64.9, 34.9, 31.8, 30.0, 29.8, 29.6, 29.1, 28.9, 26.7, 25.3, 23.2, 14.8; FT-IR (KBr, cm^{-1}): 2927, 2855, 1737, 1465, 1417, 1356, 1316, 1245, 1173, 1098, 877, 832, 723, 694, 654.

Polymer synthesis

*Poly{3,3'-di(10-hexanoyloxydecyl)-2,2'-bithiophene} (**P1**)*

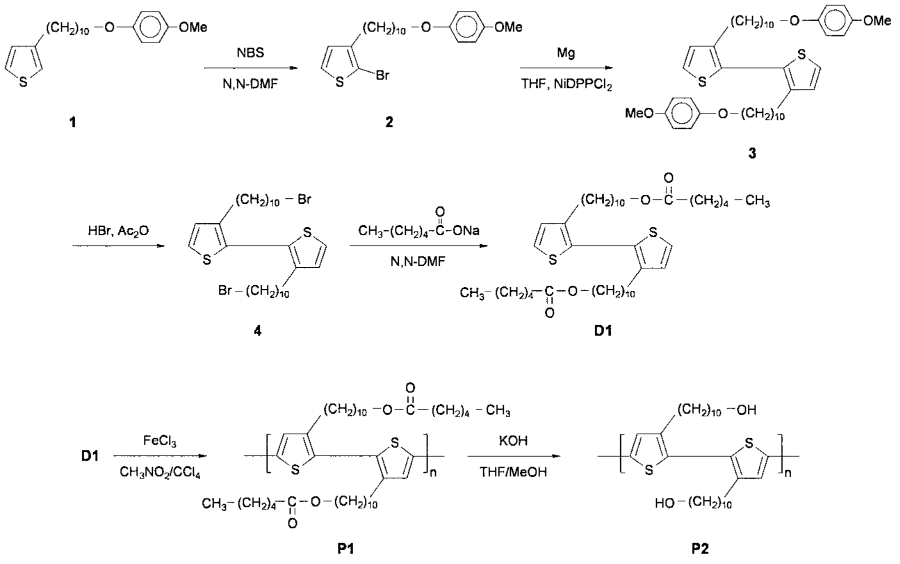
A solution of 0.69 g (4.25 mmol) of anhydrous $FeCl_3$ in 5.23 ml of CH_3NO_2 is added dropwise over 40 min to a solution of 0.72 g (1.07 mmol) of **D1** in 10.67 ml of CCl_4. After stirring for 140 min at 20 °C under a flux of dry argon, 15 ml of freshly distilled THF, 30 ml of a solution of HCl in CH_3OH (5%) and 130 ml of $CHCl_3$ are added to the reaction mixture. The solution is then washed with 2% HCl and with water to neutrality, dried over $CaSO_4$ and concentrated. The product is dissolved in 6 ml of $CHCl_3$ and re-precipitated by adding 60 ml of MeOH. After the elimination of the solution the procedure is repeated using 5 ml of $CHCl_3$ and 15 ml of MeOH to give 0.65 g (0.96 mmol; 90% yield) of fractionated **P1**. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.02 (s, 2H); 4.05 (t, 4H); 2.45 (bm, 4H); 2.30 (t, 4H); 1.75-1.20 (m, 44H); 0.95 (t, 6H); ^{13}C-NMR ($CDCl_3$, ppm): δ 174.6, 144.1, 137.7, 128.0, 125.8, 65.1, 35.1, 32.0, 31.4, 30.2, 30.1, 29.9, 29.7, 29.3, 26.6, 25.4, 23.0, 14.6; FT-IR (KBr, cm^{-1}): 3055, 2926, 2855, 1736, 1519, 1465, 1420, 1245, 1172, 1099, 828, 724.

*Poly{3,3'-di(10-hydroxydecyl)-2,2'-bithiophene} (**P2**)*

30 ml of a solution of KOH in MeOH (6%) are added dropwise over 1 h to a solution of 0.40 g (0.594 mmol) of **P1** in 30 ml of freshly distilled THF. The reaction mixture is refluxed for 3 h and

cooled at room temperature, after which 100 ml of CH_3OH are added. The mixture is then neutralized by adding several drops of formic acid and the precipitated polymer is recovered by centrifugation (4000 rpm for 20'). The product is washed with CH_3OH and centrifugated again for several times to give 0.28 g (0.587 mmol; yield 99%) of **P2**. ^{1}H-NMR (d_8THF, ppm): δ 7.10 (s, 2H); 3.45 (bm, 4H); 2.50 (bm, 4H); 1.75-1.20 (m, 32H); ^{13}C-NMR (d_8THF, ppm): δ 144.5, 138.0, 128.2, 126.2, 62.6, 34.1, 31.5, 30.7, 30.5, 30.4, 30.3, 29.9, 26.9; FT-IR (KBr, cm^{-1}): 3343, 3054, 2922, 2851, 1517, 1462, 1057, 823, 721.

Results and Discussion



Scheme 1. Dimeric unit and polymer synthesis.

Product **2** was obtained with a very good yield (92%) via the bromination of **1** (Scheme 1) in the 2 position of the thiophenic ring. Thanks to the controlled reaction conditions the bromination of the remaining thiophenic ring positions and of the side-chain aromatic ring was avoided. The subsequent reaction was carried out with the organometallic reactive of **2** synthesized using magnesium in anhydrous THF and $NiDPPPCl_2$ as catalytic agent. Dimer **3** was obtained with

28% yield after purification and then subjected to the ether cleavage reaction with HBr in acetic anhydride to obtain, with a good yield (74%), the intermediate **4** that was used without further purification. Dimer **D1** was synthesized from **4** using the nucleophilic substitution of the –Br groups with the hexanoyloxy groups in N,N-DMF. Despite the quantity of sodium hexanoate used in excess and the high temperature (105 °C) adopted, only a 23% yield was achieved. It may be presumed that the regiochemistry of the bithiophenic dimer determines a reciprocal steric hindrance of the alkylic chains, hence making reactions based on this molecule difficult. This hypothesis can be supported taking into account that 3-(10-bromodecyl)thiophene can be converted in the hexanoyloxy derivative with very high yield[9] using analogous experimental conditions. The yield in **D1** could be improved employing the iodinated derivative of **4** or crown ethers to increase the carboxylate nucleofilicity.

Dimer **D1** was then polymerized (Scheme 1) via oxidative polymerization with $FeCl_3$ in the CH_3NO_2/CCl_4 mixture that permits a good control of molecular weight[10] to give **P1** with a high yield (90% after the fractionation procedure). **P1** was converted into the analogous ω-hydroxy functionalized polymer **P2** (Scheme 1) with a post-polymerization functionalization procedure through the alkaline hydrolysis of the ester group.[6] Several characteristics of the synthesized polymers are reported in Table 1.

Table 1. Characteristics of **P1** and **P2**.

Polymer	Yield %	M_n^*	M_w/M_n^*	Dp_n^*
P1	90	23600	1.7	35
P2	99	17100	1.7	35

* Number average molecular weight M_n, polydispersity index M_w/M_n, degree of polymerization DP_n.

Unlike other previously synthesized poly[3-(10-hydroxydecyl)thiophene]s,[11] **P2** was found to be fully soluble in many organic solvents and even partially soluble in solvents normally classified as non-solvents for products of this kind (see Table 2).

Table 2. **P2** solubility.

Solvent	THF	DMPU	$CHCl_3$	MeOH	Et_2O	n-C_5	H_2O
Solubility mg/ml	50	20	10	<1	<1	<1	<1

The presence of two doublets with the same intensity at 7.25 and 6.96 ppm in the **D1** ^{1}H NMR spectrum (see experimental part) confirms the exclusive HH linkage of the thiophenic units. The disappearance, even if not complete, of the first signal ascribable to 5 and 5' thiophenic protons is observable in the **P1** ^{1}H NMR spectrum. It proves that polymerization took place only through α and α' positions, while the residual signal assigned to the terminal protons is presumably ascribable to moderate molecular weight. The presence of a single peak at 2.55 ppm, ascribable to methylene protons in α to the thiophene ring, points to the existence of HH (TT) linked diads, and the singlet at 7.02 ppm, assigned to the thiophenic β proton, confirms the sole presence of the HH-TT triad. Being derived from **P1** by a post-polymerization functionalization reaction, **P2** also exhibits regular linkage. The conversion of hexanoyloxy into hydroxy functionality was complete, as confirmed by the complete disappearance in the **P2** spectrum of the signals at 4.05 (-C$\underline{H}_2$-OCO-), 2.27 (-CO-C$\underline{H}_2$-) and 0.95 (-C$\underline{H}_3$) ppm, ascribable to the ester group, and by the appearance of the 3.50 ppm peak assignable to methylene protons in α to the hydroxy functionality.

Table 3 shows the frequencies and assignments of the characteristic FT-IR bands of dimer **D1** and of polymers **P1** and **P2**.

Table 3. Characteristic FT-IR frequencies (cm^{-1}) for **D1**, **P1** and **P2**.

D1	**P1**	**P2**	Assignment
-	-	3343	O-H stretching
3103	-	-	C-H stretching (aromatic, α-hydrogen)
3061	3055	3054	C-H stretching (aromatic, β-hydrogen)
2927	2926	2922	C-H antisymmetric stretching (methylenes)
2855	2855	2851	C-H symmetric stretching (methylenes)
1737	1736	-	C=O stretching
Not resolved	1519	1517	thiophene ring antisymmetric stretching
1465	1465	1462	thiophene ring symmetric stretching
1173	1172	-	C-O-C antisymmetric stretching
-	-	1057	C-OH stretching
831, 694	-	-	aromatic C-H out-of-plane bending in 2,3-di-substituted thiophene
-	828	823	aromatic C-H out-of-plane bending in 2,3,5-tri-substituted thiophene
723	724	721	methylene rocking

The presence of the absorptions at 831 and 694 cm^{-1} for **D1** confirms the obtainment of a 2,2'-bithiophenic structure. A comparison of the **P1** bands with those of the corresponding **D1** monomer makes for some interesting considerations on the polymerization process undergone. The presence of the 3055 cm^{-1} signal in the **P1** spectrum is evidence of the 5,5' linkage of the thiophenic units, while the absence of the 3103 cm^{-1} band confirms that there is no structural irregularity due to β-linkages. The absorption ascribable to aromatic C-H out-of-plane bending in 2,3-di-substituted thiophene is substituted in **P1** FT-IR by the 2,3,5-tri-substituted thiophene generated band, hence further confirming that polymerization had occurred. Disappearance of the strong band characteristic of the hexanoyloxy group and onset of the bands typical of hydroxy functionality provide evidence of the total conversion of **P1** into **P2**. **P2** was also obtained by dipping a film cast from a solution of its precursor in a solution of KOH in MeOH. After 24 h the film was washed with MeOH, thoroughly dried, and analyzed via FT-IR. Figure 1 shows film spectra before and after alkaline treatment. A comparison of the two spectra reveals that full conversion may even occur in a solid state.

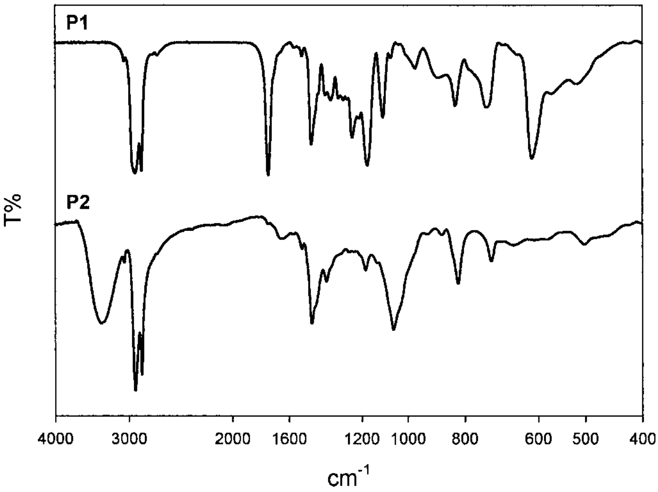


Figure 1. **P1** and **P2** FT-IR spectra on Si disk.

Figure 2 shows the thermograms of **P1** and **P2** during the heating process. **P1** and **P2** glass transition temperatures (6 and 9 °C, respectively) and those of alkylic side chain fusion (22 and

27 °C, respectively) may be observed. An endothermic peak is also recorded for **P2** at 130 °C ascribable to the polymeric backbone fusion. It appears evident that the substitution of the ester group with the hydroxy one, probably owing to the formation of hydrogen bonds and a reduced steric hindrance in lateral chains, leads to a stiffening and stacking of the system thus allowing **P2** to assume ordered conformational states higher than those of **P1**.

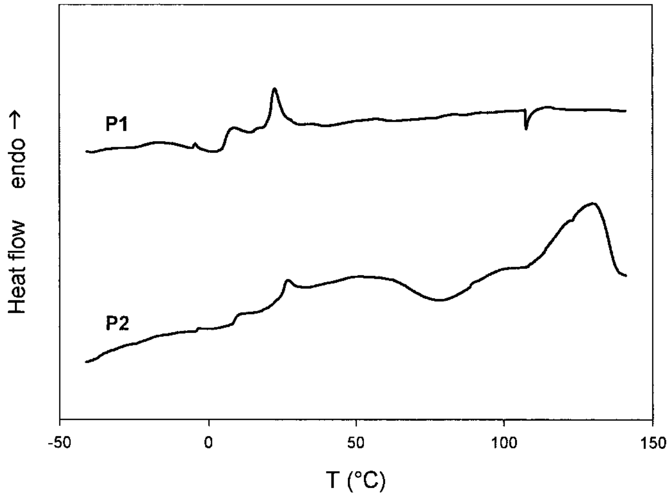


Figure 2. **P1** and **P2** DSC (heating rate 10 °C/min).

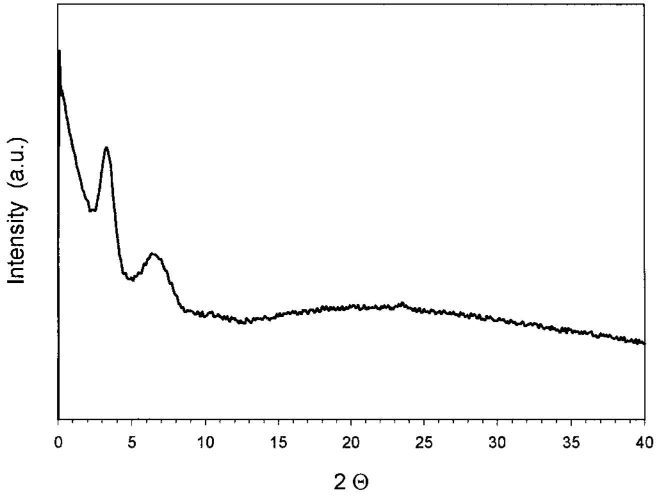


Figure 3. **P2** XRD.

The room temperature X-ray determination of **P2** is shown in Figure 3. It exhibits an intense low-angle reflection at 26.2 Å ($2\Theta=3.38$) and a broad high-angle halo with a peak at 3.78 Å ($2\Theta=23.50$). The first reflection corresponds to the double length of a fully extended lateral chain, which means that the side-chains are not interdigitated.[12] The second reflection may be referred to the superposition of parallel chains (π-stacking). The presence of a partially crystalline structure is in agreement with DSC data and confirms the fact that HH-TT linkages do not hinder the formation of ordered domains.

Conclusions

A new synthetic strategy for obtaining a poly[3-(10-hydroxydecyl)thiophene] with 100% of HH-TT linkages was developed. Despite the non-regiospecific procedure adopted, namely oxidative polymerization via $FeCl_3$, a regioregular polymer was obtained thanks to the symmetry of the starting dimeric unit. The configurational regularity of **P2** makes it highly soluble, far more than what has so far been observed for other poly[3-(10-hydroxydecyl)thiophene]s. Moreover, polymer thermal behaviour and micro-structural characteristics were not observed to be adversely affected.

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