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Electrically Conducting Poly(undecylbithiophene)s. 1. Regioselective Synthesis and Primary Structure

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ABSTRACT: Poly(undecylbithiophene), formally an alternating copolymer of thiophene and 3-undecylthiophene, has been synthesized via two different protocols. Direct oxidative polymerization of 3-undecyl-2,2′-bithiophene with ferric chloride in nitrobenzene (P3UBT-F) and transition-metal-mediated polymerization of 5-bromo-4-undecyl-5′-iodozincio-2,2′-bithiophene (P4UBT-R) have been carried out. Suprisingly, the two materials have been found to possess similar spectral characteristics (vibrational spectroscopy, ^{1}H NMR) and yet different physical properties. While P4UBT-R has ca. 90% of the head-to-tail motif, the regiochemistry of P3UBT-F could not be established satisfactorily. The former has a higher level of conjugation, but the level of conjugation in P3UBT-F is still comparable to that reported in the literature for *regioregular* poly(3-alkylthiophene)s (P3AT). Preliminary conductivity measurements show that the usually adverse effects of regioirregular structures on conjugation and conductivity can be suppressed substantially by the combination of monosubstitution and “inside” positioning of the pendant group on the bithiophene.

Introduction

Poly(3-alkylthiophene)s (P3ATs) continue to attract considerable interest due to their high electrical conductivity upon doping, environmental stability, and relative transparency. These, as well as an exceptional solubility in organic solvents and good processability, have served to considerably narrow the gap between pure scientific interest and practical applications.[1]

Among successful applications of P3ATs are dye-sensitized titanium dioxide solar cells,[2] field-effect transistors,[3] nonlinear optical materials,[4] electrochromic devices,[5] chemical and optical sensors,[6] optical power limiting devices,[7] and light-emitting diodes.[8] An important aspect of organic conductors is long-range spatial order. Low in most cases, it puts substantial limits on conducting and superconducting properties of polyheterocycles.[9] Current efforts are devoted to improved synthetic strategies, leading to higher molecular weight materials with strictly controlled architecture. Thus, chemical polymerization based upon selective and highly regiospecific reactions has become an important line of research in the field.[10] Unlike electrochemical methods, chemical condensations not only allow for better control of regioselectivity of the polymerization itself but also can tolerate various functionalities which, when attached to the polymer chain, would allow for custom design of its structure and consequent properties. Our interest has been to produce well-defined poly(alkylthiophene)s containing electroactive or pH-sensitive functionalities, which give rise to self-doped (and self-compensated) materials as well as employing groups that by their enhanced affinity toward metallic and nonmetallic surfaces would produce well-organized self-assembled structures.[11]

It has been shown that regioregular polymers surpass their randomly connected counterparts in electrical, optical, and magnetic properties. Because of the lack of symmetry, 3ATs can be incorporated into a polymer chain with two different regioregularities: head-to-tail (HT) and head-to-head (HH). This gives rise to four triad regioisomers in the polymer chain: HT−HT, HT−HH, TT−HH, and TT−HT (see Figure 1).

The steric interaction between aliphatic chains on neighboring rings of HH connections lead to shortening of the effective conjugation in the polymer chain. Two solutions have been presented in the literature: highly regioselective synthetic methods or symmetrically substituted monomers. In our approach, we used derivatives of bithiophene substituted in one ring, which should produce an alternating sequence of P3AT and T structural units when linked in a regioregular fashion. In the event of regiorandom (H−H, T−T) coupling, the alkyl chains will still remain distant enough not to affect the free rotation around the $\alpha-\alpha'$ bond (see Figure 2).

It has also been shown[12] that copolymerization of the long alkyl chain substituted thiophenes with 3-methylthiophene gives soluble, amorphous polymers with higher glass transition temperatures and higher conductivity than the homopolymers. The fact that oxidized P3ATs undergo thermal dedoping readily[13] suggests that the dopant anion can be easily expelled from the polymer matrix, likely due to the steric interference from long alkyl chains and their tendency to self-organize. Thus, “dilution” of the system to the point of retaining its favorable properties (solubility/processability) while forming voids capable of accommodating a dopant should produce more electrically stable systems.[14] The main goal in the present study is to determine whether simple ferric chloride oxidation of 3-undecyl-2,2′-bithiophene can produce polymers with compatible properties to materials obtained via stereocontrolled condensations.[10b,15] Under normal circumstances, chemical oxidative polymerization of 3-alkylthiophenes produces polymers with 70−84% HT−HT regioregularity,[16] although other reports describe oxida-

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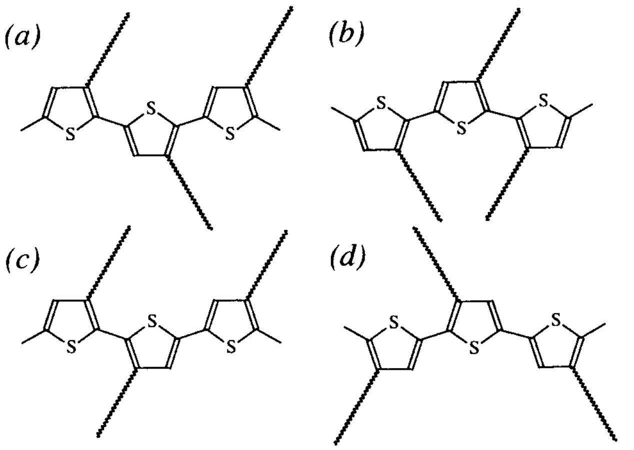


Figure 1. Regiochemistry and connectivities in poly(3-alkylthiophene)s. Possible regioisomeric triads: (a) HT−HT, (b) HT−HH, (c) HH−TT, (d) TH−TT.

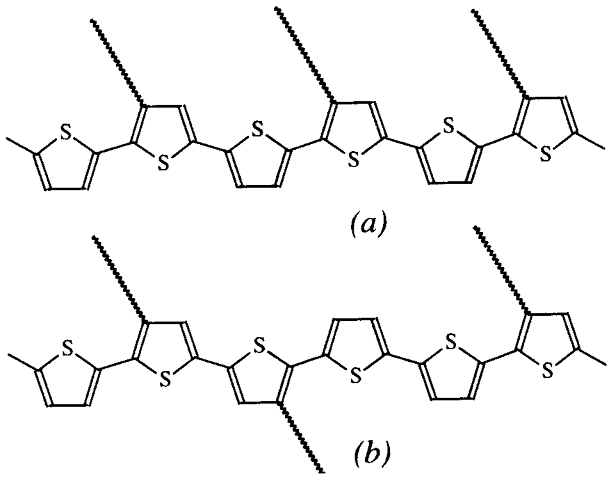


Figure 2. Regiochemistry and connectivities in poly(3-alkylbithiophene)s: (a) regioregular (HT−HT) and (b) regioirregular (HH−TT).

tive polymerization of 3-substituted thiophenes with 88%[10c] and 94%[17] regioregularity.

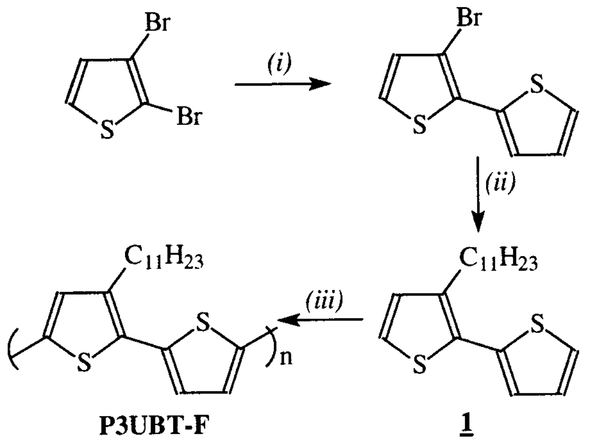
Results and Discussion

Synthesis of Monomers. 3-Undecyl-2,2′-bithiophene (**1**), a starting material for the ferric chloride oxidative polymerization, was synthesized in a two-step process shown in Scheme 1.

Reaction of 2,3-dibromothiophene with excess of 2-thienylmagnesium bromide in the presence of Pd(dppf)Cl_2 was carried out according to the procedure by Carpita and Rossi,[18] producing 3-bromo-2,2′-bithiophene in a good yield. The product was allowed to react with a 1.5-fold excess of 11-undecylmagnesium bromide in the presence of Ni(dppp)Cl_2 to give 3-undecyl-2,2′-bithiophene in 80% yield. The excess of the Grignard reagent was beneficial in this reaction, since the homocoupling to yield docosane ($C_{22}H_{46}$) is a considerable side reaction. A one-pot approach was also tested; upon completion of the first aryl−aryl coupling reaction (monitored by TLC), more solvent and the new catalyst (Ni(dppp)Cl_2) were added followed by 11-undecylmagnesium bromide to afford **1** in ca. 40−50% yield (after distillation).

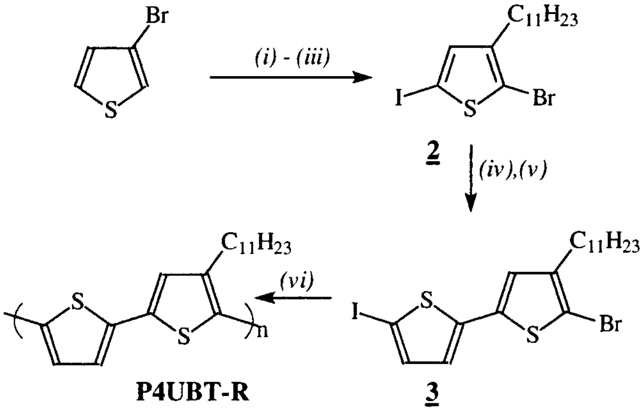
Preparation of 5-bromo-4-undecyl-5′-iodo-2,2′-bithiophene **3**, a monomer for the regiocontrolled Negishi-type homocondensation polymerization, is illustrated in Scheme 2. Nickel-mediated coupling of 11-undecylmagnesium bromide with 3-bromothiophene resulted in a formation of 3-undecylthiophene in 93% yield. Regioselective bromination with NBS in DMF[19] yielded 2-bromo-3-undecylthiophene in 85% isolated yield. The subsequent iodination with iodine in the presence of yellow HgO[18] gave 5-iodo-2-bromo-3-undecylthiophene (**2**) in 92% yield. The Pd(dppf)Cl_2-mediated coupling of **2** with 2-thienylmagnesium bromide produced 5-bromo-4-undecyl-2,2′-bithiophene in 80% yield, which was subsequently iodinated to yield the monomer **3** as a crystalline solid in a high yield (90%).

Scheme 1. Synthesis of P3UBT-F[a]



[a] Reagents and conditions: (i) 2-ThMgBr, Pd(dppf)Cl_2, ether, −20 to 0 °C, 90%; (ii) $C_{11}H_{23}$MgBr, Ni(dppp)Cl_2, ether, r.t., reflux, 80%; (iii) $FeCl_3$/nitrobenzene, 10−15 °C, 24 h, then 4 days at r.t., 72%.

Scheme 2. Synthesis of P4UBT-R[a]



[a] Reagents and conditions: (i) $C_{11}H_{23}$MgBr, Ni(dppp)Cl_2, ether, r.t., reflux, 6 h, 93%; (ii) NBS, DMF, r.t., 85%; (iii) I_2/HgO, PhH, r.t., 92%; (iv) 2-ThMgBr, Pd(dppf)Cl_2, ether, r.t., 12 h, 80%; (v) I_2/HgO, PhH, r.t., 90%; (vi) Zn*, then Ni(dppe)Cl_2, THF, 0 °C−r.t., 5 days, 62%.

Polymerizations. A. Sugimoto-Type Polymerization of 3-Undecyl-2,2′-bithiophene. The most commonly used procedure for Sugimoto-type polymerization [20] of 3-alkylthiophenes involves a reaction of 3ATs with $FeCl_3$ in a chloroform solution (ferric chloride process). The polymers prepared by this method have molecular weights ranging from $M_n = 30\,000$ to 300 000,[16a,21] and the regioregularity, measured by the head-to-tail content, is between 70 and 80%. An improved synthesis affords poly(3-octylthiophene) with 84% HT links.[16b] An interesting approach seemed to be to use solvent other than chloroform, like nitrobenzene,[22] whose higher

Table 1. Molecular Weight (GPC) and λ_{max} (UV−Vis) as a Function of Polymerization Time for P3UBT-F

polymerization time (h)	$\langle M_n \rangle$ (g/mol)	$\langle M_w \rangle$ (g/mol)	λ_{max} (nm) solid film
24	12 100	22 700	506
48	17 600	26 400	514
72	15 900	28 800	505

Table 2. Molecular Weight (GPC) and λ_{max} (UV−Vis) for Extracted Fractions of P3UBT-F (Continuous Extraction)[a]

extraction solvent	$\langle M_n \rangle$ (g/mol)	$\langle M_w \rangle$ (g/mol)	λ_{max} (nm) solid film
acetone	1300	1400	454
hexane	2400	3000	505
methylene chloride	5700	9400	527
THF	10000	26000	530, 498[a]

[a] In diphenyl ether solution.

Table 3. Absorption Maxima of Different Fractions of P4UBT-R from Continuous Extraction

extraction solvent	λ_{max} (nm) solid film	λ_{max} (nm) solution	solvent
acetone	415	399	THF
hexane	512	468	THF
THF	507	456	THF
chloroform	543, 600	554, 603	DPE
diphenyl ether	526, 561, 608	532, 560, 607	DPE

polarity (dielectric constant, $\epsilon_{20°C} = 35.7$ vs 4.8 for $CHCl_3$)[23] seemed better suited for ionic reactions. Thus, our polymerization of 3UBT (**1**) was conducted by a dropwise addition of a 4-fold excess of anhydrous ferric chloride in nitrobenzene to a stirred solution of the monomer in nitrobenzene at 10−15 °C, followed by 4 days at room temperature. Molecular weights and absorption maxima measured during the course of the ferric chloride polymerization are presented in Table 1.

As expected, the molecular weight increased with time. The polymerization was terminated when the number-averaged molecular weight began to drop, accompanied by a significant increase in the polydispersity index. The absorption maxima for the solid films also showed a corresponding increase with the molecular weight, indicating a trend relating λ_{max} and molecular weight.

The crude polymer was subjected to a series of extractions, and the fractions obtained in different solvents were analyzed for their structure and properties. Molecular weight and absorption maxima for the different fractions are presented in Table 2.

The absorption maxima were found in general to increase with molecular weight of the fractions. An interesting feature was the leveling of λ_{max} between the third and fourth fractions, despite a significant increase in molecular weight. This suggests that molecular weight does not significantly affect the conjugation length beyond very low molecular weights. Nevertheless, relatively high molecular weight is required for processability and structural integrity. The THF extract represented as P3UBT-F was used as the final polymer for all subsequent experiments.

B. Negishi-Type Polymerization of 5-Bromo-5′-iodo-4-undecyl-2,2′-bithiophene, P4UBT-R. Rieke et al.[101] have developed an attractive polymerization of 2,5-dihalogeno-3-alkylthiophenes based upon the condensation of the halozincio aromatics with halo aromatics in the presence of Ni catalysts, a method originally developed by Negishi et al.[24] The polymerization of **3** was conducted according to the Rieke et al. procedure. Immediately after addition of the catalyst to the organozincio derivative, the color of the solution changed to deep crimson and the polymer began to precipitate. After quenching, the polymer was fractionated by a routine extraction process. Acetone, hexane, THF, and chloroform helped remove lower molecular weight fractions. However, these solvents extracted very little polymer. Most of the polymer appeared to be of a very high molecular weight and soluble partially in toluene but predominantly only in nitrobenzene and diphenyl ether (DPE) at high temperature (>200 °C). The lack of solubility will be discussed elsewhere.[25] The molecular weight of the final polymer could not be determined due to the insolubility of the final polymer (P4UBT-R) in any of the suitable GPC solvents. UV−vis spectroscopy was used to estimate the effective conjugation of the polymer from different extracts, in solution as well as in solid state, and the corresponding absorption maxima are listed in Table 3.

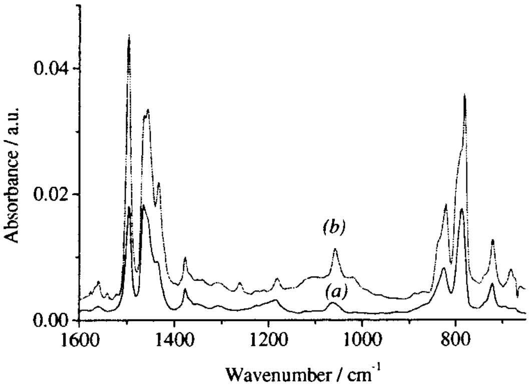


Figure 3. FTIR spectra (selected area) of polymer film: (a) P3UBT-F (from toluene); (b) P4UBT-R (from diphenyl ether) on NaCl plate.

The strong dependence of absorption maxima on the extract again indicates a distinct effect of molecular weight on conjugation. The solution data for the acetone, hexane, and THF extracts were collected in THF, whereas the chloroform and DPE extracts were measured in DPE. The absorption maxima obtained in chloroform solution were found to be 10−20 nm lower than in the solid state and almost identical in the case of the DPE solution (cf. Figure 7). The chloroform extract of the polymer is the first in the sequence of extracts, which begins to exhibit multiple peaks, associated with vibrational fine structure.[26] It is related to the high level of conjugation of the molecules. This aspect, which is more distinct in the DPE extract, is discussed in later sections.

Vibrational Spectroscopy. The FT IR and FT Raman ($\lambda_{exc} = 1064$ nm) spectra of a selected area for polymers P3UBT-F and P4UBT-R are shown in Figure 3, and the comparison with the literature data on polythiophene and poly(3-alkylthiophene), including the vibration assignments, is presented in Table 4. Both polymers were analyzed as films on NaCl plate, and their spectra displayed similar vibrational characteristics. However, the shapes of the peaks and the respective oscillator strengths differ for P3UBT-F and P4UBT-R with the signals being narrower in the case of P4UBT-R. It is also evident that polymers P3UBT-F and P4UBT-R include spectral characteristics of both building blocks: 2,5-disubstituted and 2,3,5-trisubstituted thiophene rings.

Table 4. Selected Spectroscopic Data for P3UBT-F and P4UBT-R; Comparison with the Literature Data for Polythiophene (PT) and Poly(3-alkylthiophene)s (P3AT)[a]

	this paper		literature data	
method	P3UBT-F	P4UBT-R	PT	P3AT
vibration spectroscopy (IR)	1561	1560 (w)		
	1497	1498 (s)	1490 (s) $\mathrm{C{=}C}$ ν(asym)	1510[d] (m) $\mathrm{C{=}C}$ ν(asym)
	1466	1464 (s)		1465 (s) $\mathrm{CH_2}$ and $\mathrm{CH_3}$ δ
	1459 (ssh)	1457 (s)	1457 (w) $\mathrm{C{=}C}$ ν(sym)	
	1437	1434	1440 (w)	
	1377	1377		1377 (m) $\mathrm{CH_2}$ ω
		1260		1208 (vw) $\mathrm{C_2{-}C_{5'}}$ ν
	1185	1181		1186 (vw) C−H bending + $\mathrm{C_2{-}C_{5'}}$ ν
				1182 (w) $\mathrm{C_2{-}C_{5'}}$ ν
	1062	1058		1156 (vw) $\mathrm{C_2{-}C_{5'}}$ ν + C−H bending
				1023 (m) C−S ν
				1021 (m) $\mathrm{C_3{-}C_6}$ ν
	835	835	836 (w) overlap of terminal T (816 and 846) with 2,5-T (856)	850 (w) $\mathrm{CH_3}$ ρ
	826	821		
		791 (sh)		820 (s) $\mathrm{C_\beta{-}H}$ bending
	787	781 (s)	788[b] (s) 786[c] (s) from 2,5-disubst ($\mathrm{C_\beta{-}H}$ bending)	
	721	721		724 (m) $\mathrm{C_\alpha SC_\alpha}$ deformation
		682		721 (m) $\mathrm{CH_2}$ rocking
			695 (w) from 2-monosubst T	661 (vw) ring deformation
Raman spectroscopy			1500 (sh) $\mathrm{C{=}C}$ ν + C−H bending	1512[d] (w) $\mathrm{C{=}C}$ ν asym
			1476 (sh)[e] $\mathrm{C{=}C}$ ν + C−H in-plane bending	
	1451 (s)	1445 (s)	1458 (s) $\mathrm{C{=}C}$ ν	1443 (s) $\mathrm{C{=}C}$ ν sym
	1380 (m)	1382 (m)		1378 (m) $\mathrm{C_3{-}C_4}$ ν
	1206 (w)	1208 (w)		1208 (w) $\mathrm{C_2{-}C_{5'}}$ ν
			1220 (w) C−C ν intercycle	
			1171 (w) $\mathrm{C{=}C}$ def + in-plane C−H bend	1186 (w) C−H bending + $\mathrm{C_2{-}C_{5'}}$ ν
	1058 (m)	1045 (m)	1045 (m) C−H in-plane bending	
				1021 (w) $\mathrm{C_3{-}C_6}$ ν
				1000 (vw) C−S ν
	723 (vw)	721 (w)		724 (m) $\mathrm{C_\alpha SC_\alpha}$ deformation
			741 (w) C−C def	
			647 (w) ring def	681 (w) $\mathrm{C_\alpha SC_\alpha}$ deformation
	$\lambda_{\mathrm{exc}} = 1064$ nm	$\lambda_{\mathrm{exc}} = 1064$ nm	$\lambda_{\mathrm{exc}} = 514.5$ nm	595 (vs) ring deformation
UV−vis spectroscopy	499 (in DPE)	533, 564, 605 (in DPE)	418[b] (s.f.)	447[f] (reg) (in $\mathrm{CHCl_3}$)
	531 (s.f.)	525, 561, 608 (s.f.)		429 (ran) (in $\mathrm{CHCl_3}$)
				526, 558, 606 (s.f., reg)
				435 (s.f., ran)
^{1}H NMR spectroscopy	7.45−7.29	7.45−7.25		6.98 (reg)
	3.08 (in $\mathrm{PhNO_2}$-d_5 120 °C)	3.07 (HT-HT), 2.80−2.70 (HH−HH) (in $\mathrm{PhNO_2}$-d_5 120 °C)		2.80 (reg) in HT−HT regiostructure[f] (in $\mathrm{CDCl_3}$)
^{13}C NMR spectroscopy	140.5, 136.8, 135.1, 135.0, 129.7, 126.6, 126.3, 124.0 (in $\mathrm{CDCl_3}$)	(140.6, 137.1, 134.8, 126.6, 126.4, 124.0)[g]	136.5, 124.8 (solid state)[h]	139.9, 133.7, 130.5, 128.6 (reg) in HT−HT regiostructure[i]

[a] Abbreviations: ran, regiorandom; reg, regioregular, (HT−HT); s, strong; m, medium; w, weak; sh, shoulder; s.f., solid film; DPE, diphenyl ether; ν, stretching; δ, in-plane bending or scissoring; ρ, in-plane rocking or bending; ω, out-of-plane bending or wagging. [b] Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497−1502. [c] Akimoto, M.; Furukawa, Y.; Takeuchi, H.; Harada, I.; Soma, Y.; Soma, M. *Synth. Met.* **1986**, *15*, 353−360. [d] Louarn, G.; Trznadel, M.; Buisson, J. P.; Laska, L., Proń, A.; Łapkowski, M.; Lefrant, S. *J. Phys. Chem.* **1996**, *100*, 12532−12539. [e] Sauvajol, J. L.; Chenouini, D.; Lère-Porte, J. P.; Chorro, C.; Moukala, B.; Petrissans, J. *Synth. Met.* **1990**, *38*, 1−12. [f] Chen, T.-A.; Wu, X. M.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 7, 233−244. [g] Lère-Porte, J. P.; Moreau, J. J. E.; Torilles, C. *Synth. Met.* **1999**, *101*, 588−589. [h] Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W. *Synth. Met.* **1984/85**, *10*, 95−99. [i] Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268−1279.

The 1550−1350 cm^{-1} region is dominated by the $\mathrm{C{=}C}$ stretching, both antisymmetric and symmetric, and the aliphatic C−H in-plane bending or scissoring vibrations due to the presence of the $\mathrm{CH_2}$ and $\mathrm{CH_3}$ groups. For P4UBT-R there are four major signals in that area. A very intense and sharp signal at 1498 cm^{-1} can be attributed to the antisymmetric ν($\mathrm{C{=}C}$) vibration. In regioregular P3ATs it appears at 1510 cm^{-1} [27] and has a medium intensity[27] vs 1490 cm^{-1} [28] in PT (medium intensity).[28] Thus, the absorption at 1498 cm^{-1} in the case of P4UBT-R suggests a combination character of this vibration. A strong, doublet-like signal appears at 1464 and 1457 cm^{-1}. The former does not exist in PT but is common with P3ATs.[27] It can be attributed to the aliphatic C−H in-phase bending vibrations due to the $\mathrm{CH_2}$ group.[27,29] This scissoring band occurs in the spectra of hydrocarbons at a nearly constant position of 1465 cm^{-1} [30] and overlaps with the

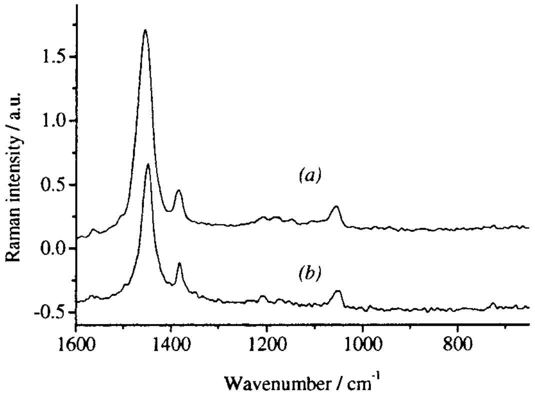


Figure 4. FT Raman spectra of (a) P3UBT-F and (b) P4UBT-R solid films: (a) cast from xylene and (b) molded under pressure; $\lambda_{exc} = 1064$ nm.

asymmetrical bending vibration of the CH_3 group at 1450 cm^{-1} (the complementary symmetrical bending vibration appears at 1375 cm^{-1}).[30] The complementary out-of-phase C−H vibration (absent in PT) shows at 1377 cm^{-1} in P3UBT-F and P4UBT-R as well as in P3ATs. The symmetric ν(C=C) vibration in P3ATs is expected at ca. 1460 cm^{-1} [10l] and at 1440 cm^{-1} in PT.[28] Although a strong signal is present at 1457 cm^{-1}, due to the superimposition of the aliphatic C−H vibrations, it cannot be ascribed unequivocally to the symmetric ν(C=C) vibration.[31a] The absorption at 1434 cm^{-1} coincides with the 1440 cm^{-1} found in PT, and it can be attributed to the symmetric C=C stretching. We were, however, unable to determine whether this was a pure C=C stretching vibration in the 2,5-disubstituted thiophenes or a combination band with the analogous vibration in the 2,3,5-trisubstituted thiophene rings. The complementary FT Raman spectroscopy has revealed strong signals at 1451 cm^{-1} (P3UBT-F) and 1445 cm^{-1} (P4UBT-R) (Figure 4). They can be assigned to the symmetric C=C stretching vibrations.[31b]

These values correlate well with 1458 and 1443 cm^{-1} for the PT and regioregular P3ATs, respectively. Their intensity in the Raman spectrum is obviously in no relation with the possible intensity in the FT IR. Therefore, any conclusions about the degree of the main-chain conjugation may be valid only for the isomeric polymers with an equal contribution of vibrational vectors resulting from the alkyl chain. On this note, by a qualitative inspection of relative intensities of peaks in the 1450 cm^{-1} area vs ca. 1500 cm^{-1}, we suggest that the polymer P4UBT-R has a higher degree of effective conjugation in the solid state than the P3UBT-F counterpart, possibly a result of higher regioregularity. This conclusion finds support in the UV−vis spectroscopy (Figure 7). The spectrum of P3UBT-F in the same spectral area reveals less resolved signals (shoulders) at similar positions (Table 4). This suggests the same vibrational elements are present, but a less regioregular underlying structure of the polymer.

Further structural information can be obtained by examining the 700−900 cm^{-1} spectral region in which the ring C−H out-of-plane vibrations can be found. In addition, a signal at 721 cm^{-1} appears, due to the aliphatic CH_2 rocking transitions. The positions of the out-of-plane vibrations reveal the substitution pattern of the thiophene rings in the polymers. The relationship between peak positions and regioregularity in P3ATs has been established.[10l] A very strong vibration at 786 cm^{-1} (788 cm^{-1}) dominates the spectrum of polythiophene. It has been assigned to the out-of-plane bending of the C_β−H fragment. In P3ATs, where there is only one active vibration of this kind, the position of the signal changes to within the 820−829 cm^{-1} area. The signal position strongly depends on the regioregularity of the polymer,[10l] showing at 822 cm^{-1} for 98.5% HT−HT polymer vs 829 cm^{-1} for the regiorandom counterpart. In P3UBT-F we observe signals at 825 cm^{-1} (C_β−H in 2,3,5-trisubstituted thiophene) and 786 cm^{-1} (C_β−H in 2,5-disubstituted thiophene). These values relate well to the respective vibrations in P3ATs (removed by 3 cm^{-1} from those in regioregular HT−HT polymers) and PT. The signals are relatively broad, unlike in P4UBT-R where the corresponding vibrations appear at 821 and 781 cm^{-1}. These absorptions consist of a very strong and narrow component, which suggests the presence of an organized and well-defined phase superimposed on another one displaying broader signals, like the ones in P3UBT-F.

NMR Spectroscopy. Because of the practical insolubility of the P4UBT-R in common organic solvents, the ^1H NMR spectroscopy of both P3UBT-F and P4UBT-R was done in nitrobenzene-d_5 at 120 °C. (For comparison, chemical shifts for P3UBT-F in $CDCl_3$ are given in Table 4.) The ^{13}C NMR spectrum of P3UBT-F was taken in $CDCl_3$ at 50 °C. (P4UBT-R was insoluble under these conditions.) It is assumed that, in chloroform solution, the poly(alkylthiophene)s will have an unrestricted freedom of rotation; thus, respective chemically equivalent elements will find themselves in randomized magnetic environments. Any nonequivalence of similar protons/carbon nuclei will then be a result of a different regiochemistry (substitution pattern) of the polymer backbone. Proton NMR spectra and peak assignments in regioregular and random P3ATs have been reviewed.[32] Aromatic protons in the 3-position at 6.98 ppm in regioregular P3ATs appear at 7.00 ppm in HT−HH, 7.02 ppm in TT−HT, and 7.05 ppm in TT−HH regiorandom isomers[33] (see Figure 1 for connectivity scheme in P3ATs). Clearly, replacement of an alkyl substitutent with a hydrogen atom in the vicinity of the observed proton causes deshielding and results in a downfield shift of frequency. The spectral area 2.5−3.0 ppm is reserved for the α-methylene protons of the alkyl chain. Because of the shielding effect of the alkyl substituents, the α-protons in the head-to-head linked isomers resonate at a higher field compared to the head-to-tail isomers (2.58 ppm vs 2.80 ppm). Relative integral of these signals has been widely used to determine regioselectivity in the polymerization of 3ATs. The expected spectrum of HT−HT regioisomers of P3UBT-F and P4UBT-R should consist of a singlet at ca. 7.00 ppm and two doublets at ca. 7.00 ppm and at ca. 7.09 ppm. Instead, the ^1H NMR spectrum of P3UBT-F in $CDCl_3$ consists of a complex and broad resonance at 7.18−6.75 ppm, similar in shape to the one in nitrobenzene-d_5. A small paramagnetic shift of the aromatic and α-methylene protons is observed for spectra measured in nitrobenzene-d_5, as compared to $CDCl_3$. It is attributed to the high magnetic anisotropy of nitrobenzene-d_5. Surprisingly, the resonances of the aromatic protons in 90% HT−HT regioregular polymer P4UBT-R are similar to those in potentially random P3UBT-F (Figure 5).

The resonances of the α-methylene protons similar in shape show at 3.06−2.90 ppm for both P3UBT-F and P4UBT-R (2.75 ppm for P3UBT-F in $CDCl_3$). This position favorably compares with 2.80 ppm in regio-

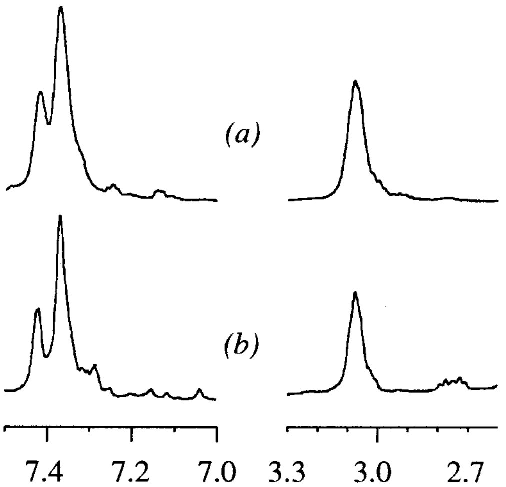


Figure 5. ^{1}H NMR spectra of (a) P3UBT-F and (b) P4UBT-R (aromatic and α-CH_2 region), in nitrobenzene-d_5 solution at 120 °C. δ [ppm] relative to TMS (for nitrobenzene $\delta = 8.1$ ppm).

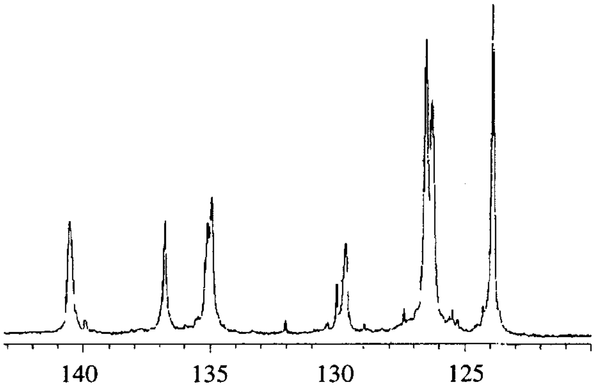


Figure 6. ^{13}C NMR spectrum (aromatic region) of P3UBT-F in $CDCl_3$, room temperature, δ [ppm] relative to TMS.

regular HT-HT P3ATs. In addition, a weak multiplet (two "triplets")[34] appears in P4UBT-R between 2.8 and 2.7 ppm, due to the HH defect. In P3UBT-F there are no signals in that area, suggesting that even in the case of a potentially regioirregular polymer there are no HH interactions leading to a restricted rotation about the C−C inter-ring bond. In P3ATs (and P4UBT-R), on the other hand, the head-to-head couplings produce significant steric interactions between alkyl chains, resulting in a disrupted effective conjugation. In the ^{13}C NMR spectra of regioregular, HT−HT P3ATs four signals are observed (Table 4). In contrast, four possible triads for the regiorandom analogue display all of the 16 magnetically unique carbon atoms.[10l] The differences in their magnetic environments translate to 3−3.5 ppm differences in positions of respective carbon atoms. Unlike P3ATs, P3UBT-F, and P4UBT-R contain eight nonequivalent carbon atoms in a regioregular HT−HT arrangement. An inferior regioselectivity of the polymerization reaction would be expected to result in rather complex ^{13}C NMR spectra of P3UBT-F and P4UBT-R. Surprisingly, the aromatic part of the spectrum of P3UBT-F in $CDCl_3$ consists of eight major resonances[35] (Figure 6). However, it is not clear whether these could be assigned specifically to the eight distinct carbon atoms in the repeat unit.

Since the $\Delta\delta$ difference in chemical shifts of the respective carbon atoms in regioisomeric **P3AT**s is rather large (3−3.5 ppm), it is reasonable to conclude that in P3UBT-F the magnetic environment of the respective carbon atoms remains well-defined, as in highly regioregular structures. Alternatively, the substitution pattern of the polythiophene chain with the undecyl groups in possible regioisomers of P3UBT-F may be nonconsequential for the chemical shifts of the respective carbon nuclei. Incidentally, there has been a recent report on regioregular poly(alkylbithiophene)s,[10b] in which the authors have discussed the NMR spectra of their regioregular HT−HT poly(alkylbithiophene). Remarkably, their ^{13}C spectrum very closely relates to the spectrum of P3UBT-F (see Table 4).

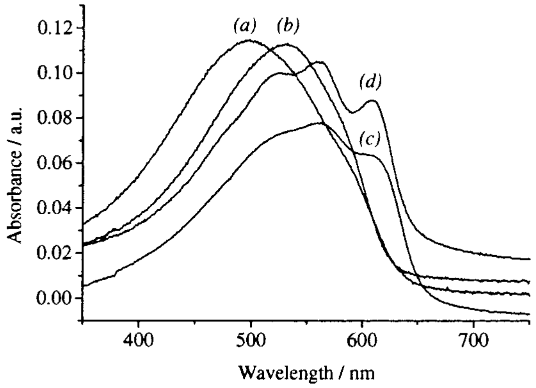


Figure 7. UV−vis spectra of (a) P3UBT-F, solution in diphenyl ether; (b) P3UBT-F, solid film on glass (from toluene); (c) P4UBT-R, solution in diphenyl ether; (d) P4UBT-R, solid film on glass (from diphenyl ether).

UV−vis Spectroscopy. The absorption behavior in conducting polymers is indicative of the effective conjugation in the main chain. Efficient $\pi-\pi$ interactions within the 2,5-bonded polyheterocycles, a prerequisite for an effective conjugation, are more likely to be a result of the order in regioregular structures. Regioregular P3ATs have been found well-suited to self-organize in the condensed phase, a result of the cooperative interaction of aliphatic and polyheterocyclic chains, respectively. This results in the formation of higher-order structures, e.g., lamellas[36] with a high degree of crystallinity as evidenced by the X-ray diffraction studies.[26a,37] Electronically, the band edge of 1.7 eV found for the regular HT−HT P3ATs[10l] approaches theoretical values at 1.71−1.79 eV, as calculated using the valence effective Hamiltonian method.[38] This translates directly to excellent electrical properties with electrical conductivity approaching 2000 S/cm.[39] The UV−vis spectra of P3UBT-F and P4UBT-R are shown in Figure 7, and the results and the literature data are presented in Table 4. The polymers were measured as solid films on glass and as solutions in diphenyl ether. (P4UBT-R was insoluble in other solvents.) The absorption maximum of P3UBT-F at 531 nm (solid state) is higher than that of the regiorandom P3AT (435 nm) and favorably compares to regioregular P3AT**s** (558 nm).[10l] This confirms our original premise, which proposes that, by decreasing the side chain density, fever steric interactions between side chains would occur, leading to the more effectively conjugated molecule. Interestingly, the difference between absorption maxima in P3UBT-F in the solid state and in diphenyl ether solution is only ca. 30 nm (Figure 7a,b). An even more pronounced effect is observed in the case of regioregular P4UBT-R (see Figure 7c,d). The absorption curve for the solid polymer is similar to the one for regioregular P3ATs, with maxima at 521, 561, and 608 nm. The presence of the vibrational fine structure is yet another evidence of a highly regioregular nature of the polymer.[10l,26]

Interestingly, upon dissolving the polymer in DPE, no major changes in the absorption spectrum were observed, with the vibrational structure intact (Figure 7d). The condensed phase conformation of the polymer is apparently maintained in solution. Even though the absorption spectra in polythiophenes arise essentially from the optical response to the primary structures of individual chains, self-organization and aggregation will influence the conjugation in the chains. These phenomena may indeed work hand-in-hand, enhancing each other. The higher structural order in solution may be a good indication of a high degree of regularity at the molecular level.

Electrical Conductivity. The conductivity was measured on thin films of P3UBT-F and P4UBT-R, after exposure to iodine vapors, using a four-point probe connected to a digital multimeter. Thin film (ca. 40K Å) of P3UBT-F was deposited on a glass slide from the xylene solution by a slow evaporation of the solvent, followed by doping with iodine vapor. The measured electrical conductivity of 1470 S/cm compares favorably with the reported values of 1 S/cm for regiorandom and 200 S/cm for regioregular head-to-tail poly(3-octylthiophene)[40] and 1350 S/cm for regioregular poly(3-butylthiophene) and only 5 S/cm for a regiorandom analogue.[39] For a 91% head-to-head poly(3-dodecylthiophene), electrical conductivity was reported at 600 S/cm (average) with 1000 S/cm (maximum conductivity), compared to 10–20 S/cm for the regiorandom analogue.[36a] However, it should be noted that the conductivity of P3UBT-F has been found to be highly variable and is inhomogeneous through the film. This observation is in agreement with the recent literature reports, which discuss the relationship between morphology of the polymer film and conductivity (charge mobility).[9,41] Initial conductivity measurements, with a four-point probe, on thin films of P4UBT-R deposited from DPE showed even higher conductivity of 2500 S/cm; however, this could not be obtained on compression-molded films. It needs to be stressed here that, while the very high conductivity was common with freshly produced polymers, lower conductivity was observed in aged samples. It seems to be supported by other reports in the literature, where conductivity decay in air was observed.[42]

Accurate, uniform, and reproducible measurements of conductivity were obtained using a van der Paaw setup.[43] Figure 8 shows the conductivity of P4UBT-R film during doping. The initial points in this graph correspond to the time before introduction of dopant (iodine crystals) and represent the intrinsic/undoped conductivity of the polymer.

At room temperature (25 °C), both P3UBT-F and P4UBT-R films exhibit conductivity in the range 10^{-7}–10^{-9} S/cm, indicating an intrinsically more conducting nature of this polymer system, as compared to traditional polymers (10^{-12}–10^{-16} S/cm). As doping occurs, conductivity increases rapidly, by more than 6 orders of magnitude, and levels off at a value of 0.5 S/cm in 1000–2000 s of doping. It should be noted that this conductivity has been obtained without optimization of processing to yield the maximum possible conductivity. Figure 9 shows the conductivity as a function of temperature for undoped P4UBT-R and P3UBT-F.

Over the whole temperature range, P4UBT-R possesses a 10-fold higher conductivity compared to that of P3UBT-F. This is probably due to higher regioregularity of P4UBT-R. However, on doping with iodine, both polymers attain comparable levels of conductivity (Figure 8). This aspect will be discussed in detail elsewhere.[25]

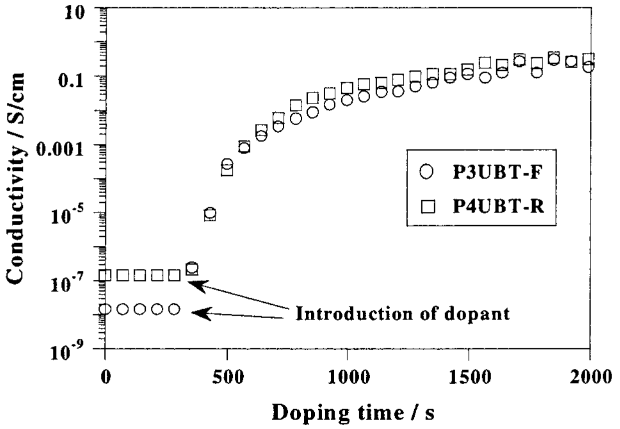


Figure 8. Van der Paaw conductivity of P3UBT-F and P4UBT-R as a function of doping time (in situ doping with iodine).

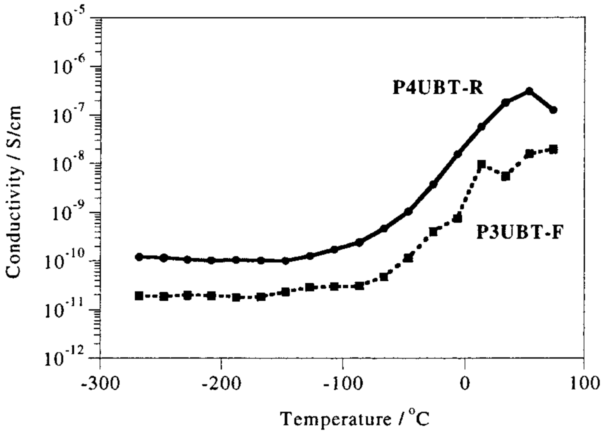


Figure 9. Van der Paaw conductivity of P3UBT-F and P4UBT-R (undoped films) as a function of temperature.

Conclusions

The synthesis of poly(undecylbithiophene), using two different synthetic approaches, has been described. The Negishi-type transition-metal-catalyzed condensation was designed to produce regioregular HT–HT polymer P4UBT-R, while regiorandom polymer P3UBT-F was expected as a result of Sugimoto-type chemical oxidation of 3-undecyl-2,2′-bithiophene with ferric chloride. While the former could be established unambiguously to have a highly regioregular structure, the regioregularity of the latter could not be determined satisfactorily. The solubility, molecular weight, thermal properties, and UV–vis spectra of the two polymers were different, with their characteristics suggesting that P4UBT-R was more regioregular than P3UBT-F. Also, as can be seen from UV–vis and ^{1}H NMR spectroscopy, the "dilution" of the alkyl substituents in the polymer backbone resulted in an extension of effective conjugation in the solid state and in solution of *both* polymers, an apparent result of avoiding the HH interactions that limit effective conjugation in P3ATs. However, it is important to determine the differences, if any, in the solid-state structure and properties of the two polymers and the extent to which they are still retained after doping. The physical states and transitions, the progression of doping, and the consequent changes in structure and properties of P3UBT-F and P4UBT-R will be reported elsewhere.[25]

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Supporting Information Available: Instrumentation, materials, including the procedures for the synthesis of the monomers, and the polymerization reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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