Highly Conjugated Poly(thiophene)s − Synthesis of Regioregular 3-Alkylthiophene Polymers and 3-Alkylthiophene/Thiophene Copolymers

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Tributyltin derivatives of 2-bromo-3-octylthiophene and 5-bromo-4-octyl-2,2′-bi(thiophene) have been selectively prepared. Condensation reactions in the presence of $Pd_2(dba)_3(CHCl_3)/4\ PPh_3$ led to high yields (ca. 90%) of regioregular poly(3-octylthiophene) (M_w = 21.4 $\times 10^4$, M_w/M_n = 1.48) and poly[4-octylbi(thiophene)] (M_w = 3.8 $\times 10^4$, M_w/M_n = 1.1). The regioregularity of the head-to-tail (HT) coupling has been determined by ^1H NMR, which showed HT > 95% for poly(3-octylthiophene) and HT > 90% for the new poly[4-octylbi(thiophene)]. The conjugation properties of these materials have been characterized by FT-IR and UV/Vis spectroscopy. Compared to the corresponding random polymers, the absorption maxima of the new regular polymers are shifted to higher wavelengths (λ_{max} = 448 and 466 nm, respectively). The mean conjugation length increases with increasing regioregularity of the coupling and with fewer substituents along the conjugated chain. The electroactive properties of the materials have also been studied. The new poly[4-octylbi(thiophene)] shows an oxidation peak at a low potential, and, compared to poly(3-octylthiophene), a reduction peak is also observed at a lower potential indicating a higher electron affinity. Both polymers exhibit reversible blue-red electrochromic behavior associated with the reversible redox properties.

Introduction

Since the initial discovery of organic conducting polymers in the late 1970s, very diverse applications of these materials have emerged owing to their remarkable electronic and photonic properties.[1−3] The structure of the conjugated chain is very important in determining the physical properties of the material. Therefore, many efforts are being made to control the macroscopic properties of the polymeric material by a design strategy based on molecular engineering. Polythiophene and its derivatives have been the subject of much attention in this field.[4−7] The difficulty arising from the low processability of the polymers obtained in the early syntheses[8−12] was overcome by the preparation of soluble materials[13−17] using 3-substituted thiophene monomers. The preparation of thiophene-based materials with defined properties and functions requires a selective synthesis as the first step. This involves control of the structure of the chain unit in the monomer and control of the coupling of the chain units leading to the conjugated backbone of the polymer. Additionally, the arrangement of the polymeric chain in the solid is also of great importance, since interchain interactions and dimensionality also play a role in determining the physical properties of the material.

Our ongoing interest in the development of organometallic synthetic routes for controlling the structures of two- and three-dimensional networks containing conjugated organic units[18−25] has led us to explore the use of tin-functionalized monomers. The palladium-catalysed aryltin coupling reaction[26] has also proved useful in polycondensation reactions of arylene and vinylene units.[27−31] Recently, we also reported the synthesis of conjugated polymers with electrochromic or electroluminescent properties using the tin route.[32] Our interest lies in the tuning of the electrical and optical properties of processable polythiophene derivatives. To some extent, these can be controlled by the nature and arrangement of the substituents on the thiophene ring.[33] For example, control of the regiochemistry[34] of the alkyl-substituted polymer backbone or control of the distribution of the alkyl substituent[35] along the conjugated chain can lead to material with enhanced conjugation properties. We wish to report herein on the selective synthesis of well-defined regioregular alkylthiophene polymers and thiophene−alkylthiophene copolymers, as well as on the optical properties of the resulting materials. A portion of this work has been presented as a communication.[36]

Results and Discussion

Regioregular Poly(3-alkylthiophene) and Poly[4-alkyl-2,2′-bi(thiophene)]

Several syntheses of regioregular head-to-tail (HT) coupled poly(3-alkylthiophenes) have been reported. The nickel-catalysed polycondensation of a 3-alkyl-5-bromothienyl Grignard reagent[37] and the related cross-coupling reaction of the corresponding zinc reagent[38] were first reported to give 98−99% HT poly(3-alkylthiophene). The oxidative coupling of bulky or unsymmetrical thiophene derivatives was also found to selectively afford HT polymers.[39,40] We[36] and others[41,42] have recently shown that HT coupling can also be achieved in the palladium-

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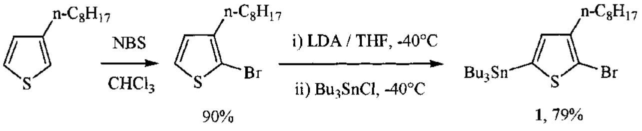
catalysed coupling of tin or boron derivatives of halo-3-alkylthiophenes.

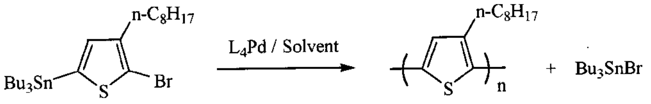
High Molecular Weight Poly(3-alkylthiophene)

Our approach based on the Stille coupling reaction involved the self-condensation of the bromotributylstannyl monomer **1**, which was selectively prepared according to Scheme 1. Its synthesis required selective bromination of 3-alkylthiophene at the 2-position followed by lithiation and stannylation at the 5-position. The monomer **1** was isolated in very good yield.



Scheme 1. Preparation of 2-bromo-3-octyl-5-tributylstannylthiophene (**1**)

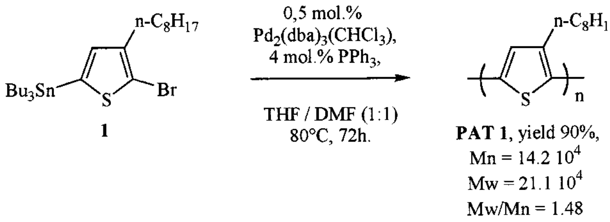
We then studied the polycondensation of **1** in the presence of a zerovalent palladium complex according to Equation (1). The reaction was studied as a function of the solvent, and of the concentration, source, and ligation of the catalyst. The poly(3-alkylthiophene) was isolated after precipitation by the addition of acetone to the reaction mixture. Molecular weights were determined by means of gel permeation chromatography, using THF as the eluent and polystyrene samples as calibration standards.



(1)

The polymerization was first studied using $(PPh_3)_4Pd$ (1 mol-%) at 80 °C for 72 h. The results are shown in Table 1. The choice of solvent was important since it must keep the growing polymer in solution as well as stabilize the zerovalent catalytic species. The catalyst is stable in THF or dioxane, but the solubility of the polymer in these solvents is low. A 1:1 mixture of THF and DMF was found to give poly(3-alkylthiophene) with the highest molecular weight (entry 4). Interestingly, the polymer yield was also much higher than that achieved in a similar polycondensation of an iodo derivative.[41] The optimal catalyst concentration appeared to be 1 mol-%. At a lower concentration, e.g. 0.2 mol-% (entry 5), only oligomers were formed. Higher concentrations, e.g. 1.75 mol-%, did not increase the molecular weight (*cf.* entries 6 and 4).

We also studied the influence of the nature of the catalyst. The results are summarized in Table 2. The use of a Pd^{II} catalyst precursor led only to oligomers (entry 2). The palladium dibenzalacetone complex was rather unstable in the absence of added ligand and gave only a low conversion (entry 3). The effect of the phosphane ligand and of the ligand-to-palladium ratio proved to be critical. This was studied by preparing the catalytic species in situ by mixing $Pd_2(dba)_3(CHCl_3)$ and the appropriate phosphane ligand. A 1:2 Pd to PPh_3 ratio (entry 4) led to a poor yield of polymeric material. This is most likely attributable to instability of the generated catalytic species. Interestingly, with Pd to PPh_3 ratios of 1:4 or greater, a high yield of very high molecular weight poly(3-alkylthiophene) was produced (entries 5 and 6). It is worth noting that the catalytic species generated under these conditions is much more active than $Pd(PPh_3)_4$ (entry 1). When ligands other than PPh_3 were used, e.g. $P(OPh)_3$, $P(p\text{-Tol})_3$, $P(C_6H_{11})_3$, or dppe, the polymer produced had a comparatively low average molecular weight and was often obtained in lower yields (entries 7−10). The best conditions therefore appeared to be those given in Equation (2), which led to a high yield of a high molecular weight poly(3-alkylthiophene) ($M_w \approx 21 \times 10^4$, $M_w/M_n \approx 1.48$).



(2)

Regioregularity of Poly(3-alkylthiophene)

The structure and regiochemistry of poly(3-alkylthiophene) in solution can be determined by means of ^1H and ^{13}C NMR analysis.[5] The coupling of 3-alkylthiophene units can occur with three possible regiochemistries corresponding to head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT) coupling. This leads to four chemically distinct triad regioisomers (Figure 1). Distinct ^1H NMR chemical

Table 1. $Pd(PPh_3)_4$-catalysed polymerization of 2-bromo-3-octyl-5-tributylstannylthiophene **1**

Entry[a]	Solvent	Catalyst (mol-%)	Polymer Yield[b] (%)	M_n[c]	M_w	M_w/M_n
1	THF	1.0	88	4670	8970	1.9
2	Dioxane	1.0	80	4440	5160	1.2
3	DMF	1.0	90	8510	16910	2.0
4	THF/DMF[d]	1.0	84	11640	24610	2.1
5	THF/DMF[d]	0.2	88	2720	3060	1.1
6	THF/DMF[d]	1.75	80	10610	20800	1.9

[a] Reactions performed at 80 °C for 72 h. − [b] Isolated material by precipitation from THF solutions. − [c] Determined by GPC using polystyrene standards. − [d] 1:1 mixtures were used.

Table 2. Influence of the nature of the catalyst in the polymerization of 2-bromo-3-octyl-5-tributylstannylthiophene **1**

Entry[a]	Catalyst	Polymer Yield[b] (%)	M_n[c]	M_w	M_w/M_n
1	$Pd(PPh_3)_4$	84%	11640	24610	2.1
2	$Pd(PPh_3)_2Cl_2$[d]	84%	2330	5670	2.4
3	$Pd_2(dba_3)(CHCl_3)$	10%	3240	4440	1.4
4	$Pd_2(dba_3)(CHCl_3)$, 4 PPh_3	10%	6540	19210	2.9
5	$Pd_2(dba_3)(CHCl_3)$, 8 PPh_3	90%	142020	210910	1.5
6	$Pd_2(dba_3)(CHCl_3)$, 12 PPh_3	83%	138240	223940	1.6
7	$Pd_2(dba_3)(CHCl_3)$, 8 $P(OPh)_3$	90%	5500	10350	1.9
8	$Pd_2(dba_3)(CHCl_3)$, 8 $P(p\text{-Tol})_3$	60%	4010	6440	1.6
9	$Pd_2(dba_3)(CHCl_3)$, 8 $P(C_6H_{11})_3$	70%	7770	15660	2.0
10	$Pd_2(dba_3)(CHCl_3)$, 4 dppe	70%	5260	7520	1.4

[a] The reaction was performed at 80 °C for 72 h in a THF/DMF mixture (1:1) using 1 mol-% of Pd catalyst. – [b] Soluble fractions that were isolated after precipitation with acetone. – [c]Determined by GPC using polystyrene standards. – [d] The oligomer obtained here exhibited poor regioregularity. Head-to-head coupling probably occurs in the initial reduction of the Pd^{II} precursor to form the Pd^0 active catalytic species.

shifts are observed for the protons at the 4-carbon atoms on the central aromatic thiophene rings. Synthesis of the four isomeric trimers allowed unambiguous assignment of the relative chemical shift of each triad,[43] thereby providing a means of evaluating the proportion of HT coupling in a poly(3-alkylthiophene). Additionally, the relative ratio of HT–HT coupling to non-HT–HT coupling can be determined by an analysis of the signals of the α-CH_2 protons of the 3-substituent on the thiophene ring.[44–47]

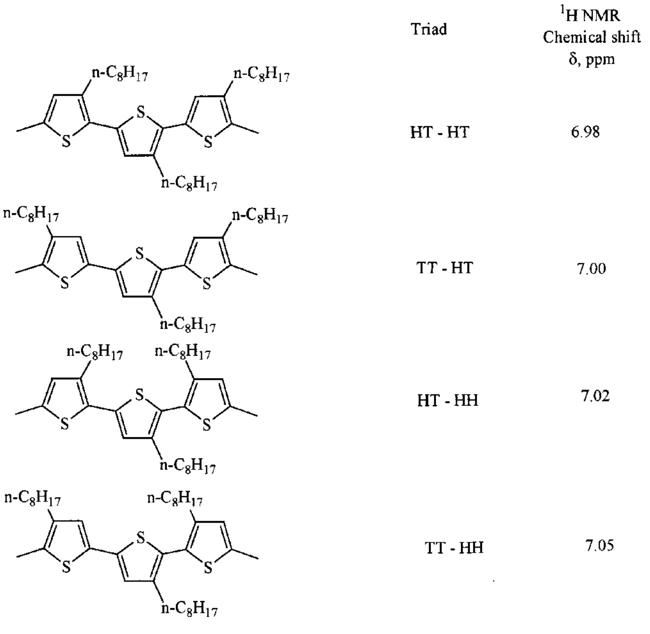


Figure 1. Four possible triad regioisomers in poly(3-octylthiophene) (see ref.[5])

The ¹H NMR spectrum of poly(thiophene) **PAT_1** obtained from the palladium-catalysed polycondensation of **1** [Equation (2)] is shown in Figure 2. **PAT_1** was assigned as having 95% head-to-tail (HT) linkages on the basis of the relative integrals of the relevant resonances. The degree of structural regularity of **PAT_1** is also apparent from its ¹³C NMR spectrum, which shows only four resonances in the aromatic region (δ = 128.6, 130.5, 133.7, and 139.9) (Figure 3). Therefore, the polymerization described by Equation (2) led to regioregular poly(3-octylthiophene) in high yield. Interestingly, the molecular weight determined for **PAT_1** was $M_n \approx 14 \times 10^4$ with a polydispersity $M_w/M_n = 1.48$; these values compare favorably with those of related materials reported previously.[5,37–42]

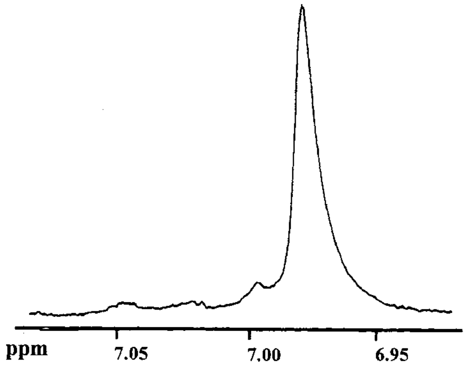


Figure 2. Aromatic region (δ = 6.9–7.1) of the ¹H NMR spectrum of **PAT_1**

Poly[4-octyl-2,2′-bi(thiophene)]

We also studied the preparation of regioregular poly[alkylbi(thiophene)] since, in addition to the regiochemistry of the polymer chain, a reduction in the number of alkyl substituents can lead to an increase in the mean conjugation length of the material.[35] 5-Bromo-4-octyl-5′-tributylstannyl-2,2′-bi(thiophene) **(2)** was obtained according to Scheme 2.

The synthesis involves silylation at the 2-position of 3-alkylthiophene followed by coupling of the 5-lithio derivative with 2-bromothiophene. Despite the use of the silyl derivative, the formation of the cross-coupling product 3-octyl-2-trimethylsilylbi(thiophene) was accompanied by 30% formation of the homo-coupled bis(silyl)bi(thiophene). The desired unsymmetrical bi(thiophene) could nevertheless be isolated in a pure state in about 40% yield. Bromination occurred selectively at the 2-position after desilylation and was followed by lithiation and stannylation at the 5′-position to give pure **2**.

The polymerization of **2** was then effected under the optimal conditions established in the case of **1** [Equation (3)]. The poly[alkylbi(thiophene)] **$PABT_1$** was isolated after pre-

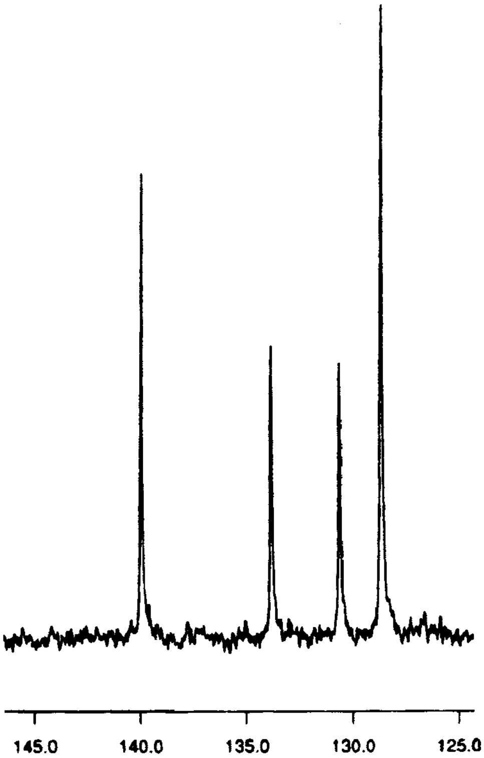
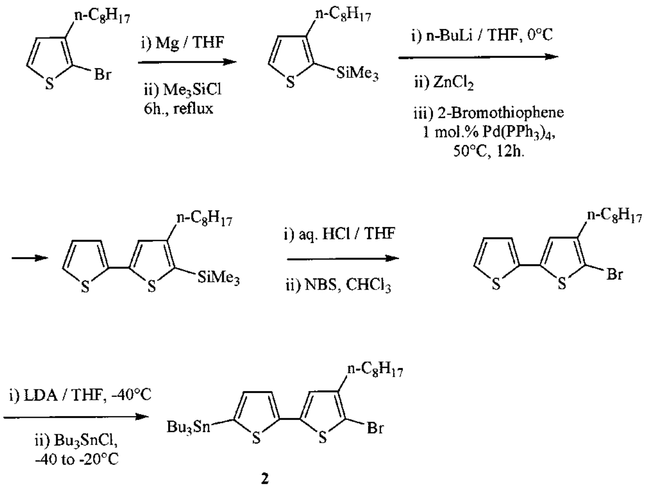
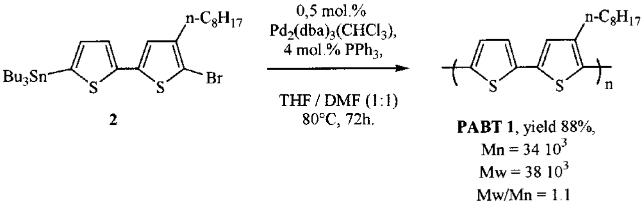


Figure 3. ^{13}C NMR spectrum of $\textbf{PAT}_1$ (in the region δ = 125−145)



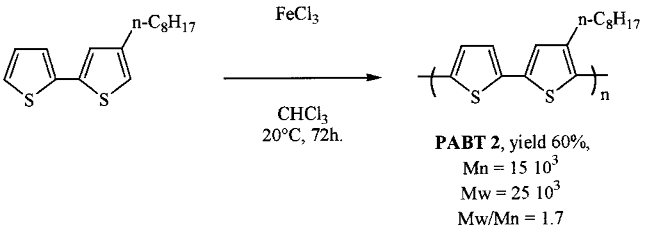
Scheme 2. Preparation of 5-bromo-4-octyl-5′-tributylstannyl-2,2′-bi(thiophene) (**2**)

cipitation with acetone in 88% yield. A high molecular weight material with a low polydispersity was obtained. Its elemental analysis was consistent with the structure presented in Equation (3).



(3)

In order to evaluate the properties of $\textbf{PABT}_1$, for comparison purposes we also prepared a related polymer using the classical chemical oxidation procedure.[39,40] 4-Octyl-2,2′-bi(thiophene) was treated with $FeCl_3$ in $CHCl_3$ to give poly[alkylbi(thiophene)] $\textbf{PABT}_2$ [Equation (4)]. It was isolated in 60% yield upon precipitation with MeOH. Analytical data for $\textbf{PABT}_2$ were consistent with the structure depicted in Equation (4).



(4)

Regioregularity of Poly[4-octyl-2,2′-bi(thiophene)]

The regiochemistry of the coupling of the bi(thiophene) units was studied by NMR analysis of samples of the polymer. The structures were analysed on a similar basis as that discussed for poly(3-alkylthiophene).[34]

The three possible regiochemical couplings, HH, TT, and HT, give rise to three chemically distinct substructures (Figure 4).

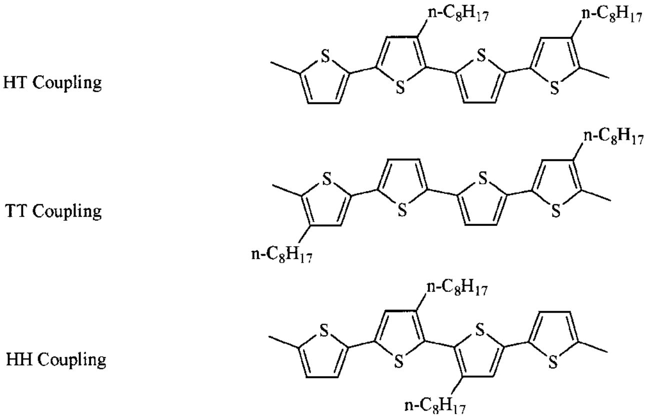


Figure 4. Three possible regioisomer substructures in poly[4-octyl-2,2′-bi(thiophene)]

For a regioregular HT poly[alkylbi(thiophene)], three aromatic proton signals can be expected in the ^1H NMR spectrum. In cases where HH and TT coupling occur, additional signals can be expected. The ^1H NMR spectrum of $\textbf{PABT}_2$ shows five resonances of unequal intensity (δ = 7.025, 7.07, 7.10, 7.16, 7.22), while that of $\textbf{PABT}_1$ also shows several lines with two major resonances at δ = 7.025 and 7.10. However, firm conclusions regarding the regiochemistry could not be drawn from analysis of the aromatic regions of the spectra. Examination of the δ = 1.5−3.0 region was more helpful in this matter. Figure 5 shows the ^1H NMR spectra of $\textbf{PABT}_1$ and $\textbf{PABT}_2$ in this region. By analogy to the resonances observed for poly(3-alkylthiophene),[44−48] the signals at δ = 2.54 and 2.77 can be assigned to the protons of the α-methylene group of the *n*-octyl substituent, while those at $\delta = 1.56$ and 1.69 can be attributed to the adjacent β-methylene protons. The two sets of resonances correspond to the two different diads arising from head-to-tail (HT) and head-to-head (HH) coupling, respectively. The **PABT₂** produced by oxidative coupling of 4-octyl-2,2′-bi(thiophene) [Equation (4)] showed resonance lines with similar intensities (Figure 5). The observed spectrum was consistent with a regiorandom chain structure with an equal distribution of HT and HH linkages, as was expected for $FeCl_3$ oxidation of 4-octyl-2,2′-bi(thiophene), which has similarly reactive 5- and 5′-positions. Interestingly, the spectrum of **PABT₁** was quite different, being dominated by major signals at $\delta = 1.7$ and 2.77. This is in agreement with predominantly HT coupling in the polymerization of **2** [Equation (3)]. Integration of the signals indicated in excess of 90% HT linkages in the chain structure of **PABT₁**. The ^{13}C NMR spectra of the two samples (Figure 6) were also consistent with a regioregular chain structure for **PABT₁** and a regiorandom one for **PABT₂**.

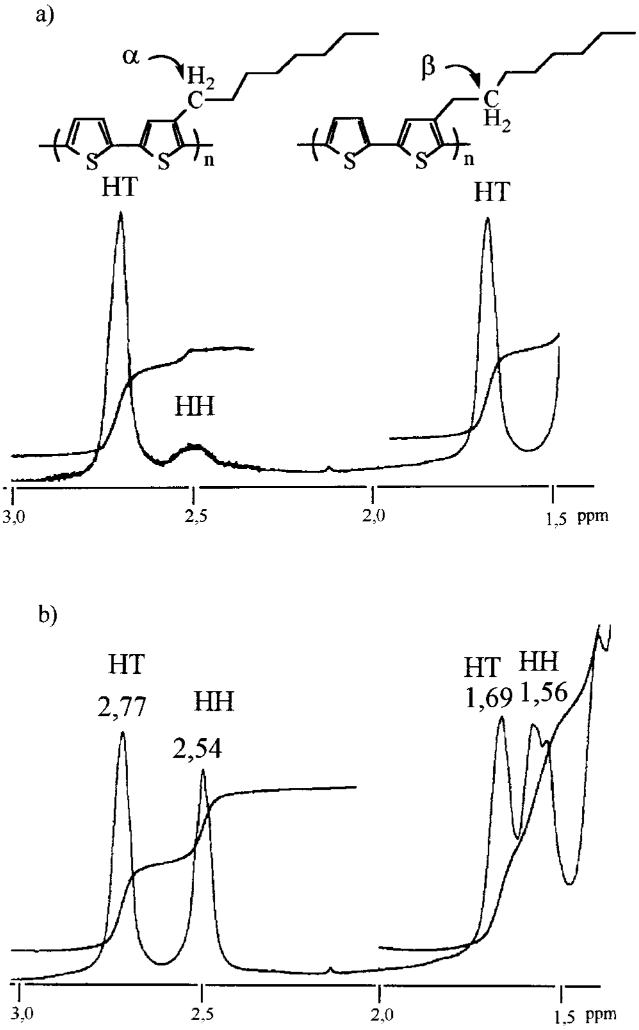


Figure 5. ^1H NMR spectra of **PABT₁** (a) and **PABT₂** (b) (in the region $\delta = 3-1.5$)

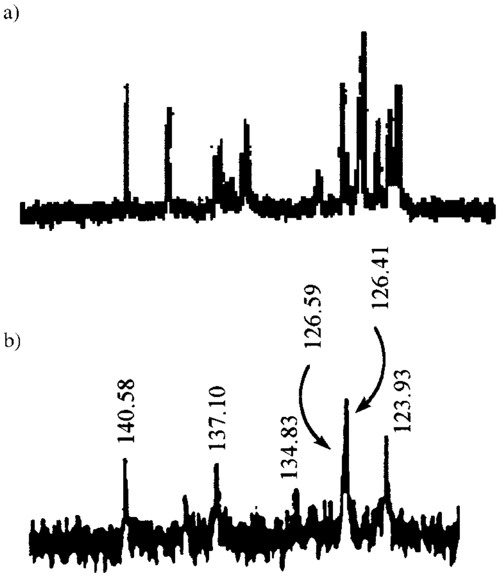


Figure 6. ^{13}C NMR spectra of regiorandom **PABT₂** (a) and regioregular **PABT₁** (b)

Poly(alkylthiophene) and Poly[4-alkylbi(thiophene)]

Infrared Characterization

Poly(thiophene)s can be compared in terms of conjugation length on the basis of the intensity of the infrared absorption associated with the carbon−carbon vibration modes ν(C=C) symmetric (1450 cm^{-1}) and ν(C=C) asymmetric (1490 cm^{-1}). The intensity ratio I_{asym}/I_{sym} increases with the mean conjugation length.[48]

The measured values for poly(3-alkylthiophene) and poly[4-alkylbi(thiophene)] are shown in Table 3. The value of the intensity ratio increases with the regioregularity of the polymer (HT linkages). Thus, much higher values are observed for poly[4-alkylbi(thiophene)]s than for poly(3-alkylthiophene)s. The conjugation length increases with an increase in the degree of HT linkage and with a decrease in the number of alkyl side chains.

Optical Properties

In the case of conjugated polymers, the position of the absorption maximum (λ_{max}) in the visible spectrum corre-

Table 3. Intensity ratios of the infrared asymmetric and symmetric vibrations ν(C=C) in poly(alkylthiophene), recorded in the solid state with samples in KBr pellets

Poly(3-octylthiophene)		Poly[4-alkyl-2,2′-bi(thiophene)]		
	I_{asym}/I_{sym}		I_{asym}/I_{sym}	
PAT_1 (95% HT)	0.76	$PABT_1$	1.00	(90% HT)
PAT [a] (70% HT)	0.60	$PABT_1$	0.94	(50% HT)

[a] This sample (with nonregioselective coupling) was prepared by $FeCl_3$ oxidation of 3-octylthiophene according to Sugimoto et al.[53] for comparison.

sponds to a π-π* electronic transition and depends on the effective conjugation length in the polymeric material. The absorption maximum of a solution of poly(3-alkythiophene) is related to the proportion to TT linkages in the polymer backbone.[34,43] It has been shown that TT linkages of two consecutive 3-alkylthiophene units cause conjugation defects arising from the torsion about the carbon−carbon single bond. This results in a decrease in the effective conjugation length and the absorption maximum (λ_{max}) is shifted towards lower wavelengths. The visible absorption spectra of regioregular poly(alkylthiophene)s are shown in Figure 7.

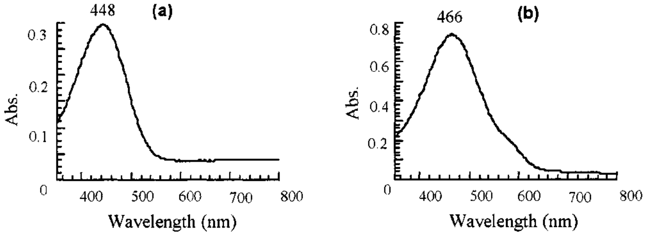


Figure 7. UV/Vis spectra of $CHCl_3$ solutions of $\mathbf{PAT_1}$ (a) and $\mathbf{PABT_1}$ (b)

In $CHCl_3$ solution, a λ_{max} value of 448 nm is observed for regioregular $\mathbf{PAT_1}$. This value is similar to those reported for related regioregular poly(alkylthiophene)s[37−42] and much higher than the λ_{max} values of 428 and 436 nm measured for irregular poly(alkylthiophene)s with 50% and 70% HT linkages of the alkylthiophene units, respectively.[48,49] The λ_{max} values observed for poly[4-alkylbi(thiophene)]s are also much higher in the case of the more regioregular $\mathbf{PABT_1}$ (HT = 90%, λ_{max} = 466 nm). A lower value was found for $\mathbf{PABT_2}$ (HT = 50%, λ_{max} = 458 nm). On the basis of the much higher λ_{max} value, the effective conjugation length appeared to be greater in poly[4-alkylbi(thiophene)] $\mathbf{PABT_1}$ than that in poly(3-alkylthiophene) $\mathbf{PAT_1}$. This arises because of the reduced number of alkyl side chains in the polymer and may be attributed to a decrease in the steric interactions between the sulfur in one thiophene ring and the alkyl substituent on the adjacent ring. Such interactions have been proposed as being responsible for less conjugated conformations of the polymer chain.[50]

When the UV/Vis spectra were recorded in the solid state (Figure 8) using films of $\mathbf{PAT_1}$ and $\mathbf{PABT_1}$, significant bathochromic shifts (67 nm and 109 nm, respectively) were observed. The absorption maxima, λ_{max} = 515 nm and 575 nm, may be attributed to packing effects in the solid state.[51] Better conjugated arrangements of the polymeric chain can be obtained upon casting the material into films. Absorption maximum of λ_{max} = 520−525 nm have been reported for related materials,[49,52] although it is difficult to compare these values since λ_{max} is dependent on the film preparation procedure and on the film thickness.[34]

The emission spectra of $CHCl_3$ solutions of the regioregular $\mathbf{PAT_1}$ and $\mathbf{PABT_1}$ were also recorded (excitation wavelength 450 nm). Emission maxima of λ_{max} = 574 and 569 nm, respectively, were observed. Low quantum yields of 0.1 and 0.2% were found; a similar observation has been made for poly(3-hexylthiophene).[54] The slightly higher value in the case of poly[4-octylbi(thiophene)] may arise from a greater planarity and rigidity of the conjugated π-system. Polymers possessing a high degree of coplanarity and rigidity are less susceptible to deactivation through torsional vibrations.

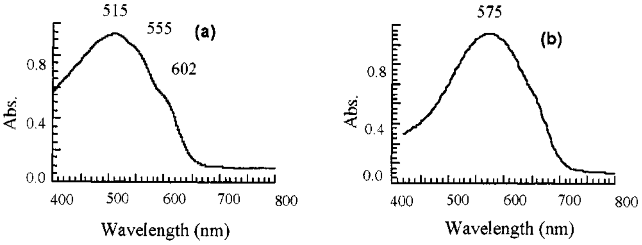


Figure 8. UV/Vis spectra of thick films of $\mathbf{PAT_1}$ (a) and $\mathbf{PABT_1}$ (b) deposited on glass

Electrochemistry

The cyclic voltammetry of thin films of $\mathbf{PAT_1}$ and $\mathbf{PABT_1}$ on a platinum electrode was studied (Figure 9). In the case of $\mathbf{PAT_1}$, the voltammogram showed two reversible oxidation potentials. It exhibited two oxidation peaks at E_{pa} (1) ≈ 0.8 V (vs. SCE) and E_{pa} (2) ≈ 1.05 V (vs. SCE). In the case of irregular poly(3-alkylthiophene), a broad oxidation peak was observed E_{pa} ≈ 1.1 V (vs. SCE). These results can be interpreted in terms of coplanarity of the adjacent thiophene rings.[34] As the system moves towards coplanarity, the increase in molecular orbital overlap will help to stabilize both polaronic (radical cationic) and bipolaronic (dicationic) states. Compared to the case of $\mathbf{PAT_1}$, the voltammogram of $\mathbf{PABT_1}$ exhibits a single oxidation peak at a low potential value (0.84 V vs. SCE). A reduction peak is also observed at a lower potential (−1.84 V vs. SCE; Figure 9), thus indicating a higher electron affinity. A blue-red electrochromism is associated with the redox transfer. Absorption spectra were recorded for films of $\mathbf{PAT_1}$ and $\mathbf{PABT_1}$ deposited on an ITO (indium tin oxide) glass support at potential values ranging from 0.4 to 1.3 V vs. SCE. The change in the absorption spectrum as a function of the applied potential is shown in Figure 10. The spectra of $\mathbf{PAT_1}$ and $\mathbf{PABT_1}$ in the neutral form (before oxidation) show bands at 480 nm. Upon oxidation, the maxima are shifted to 720 nm and 750 nm for $\mathbf{PAT_1}$ and $\mathbf{PABT_1}$, respectively, owing to a π-π* interband transition and the appearance of localized states in the gap. The changes in the spectra as a function of the applied potential are similar in each case. $\mathbf{PABT_1}$ was found to exhibit a well-defined isosbestic point (Figure 10, b), which shows that only the two absorption bands at 480 and 750 nm are involved.

Conclusion

Condensation reactions of tributyltin derivatives of 2-bromo-3-octylthiophene and 5-bromo-4-octyl-2,2′-bi(thiophene) in the presence of palladium catalysts have been

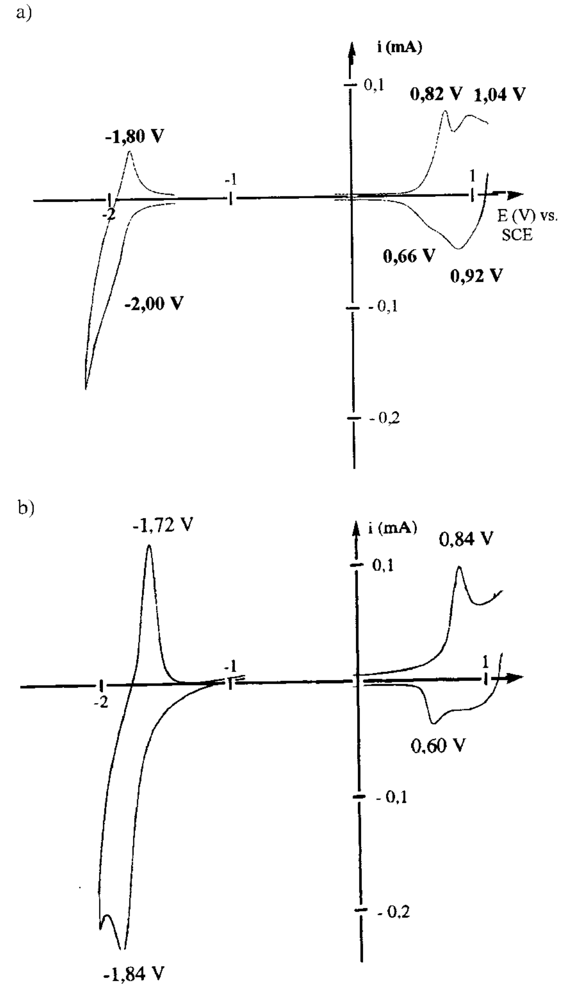


Figure 9. Cyclic voltammograms of **PAT$_1$** (a) and **PABT$_1$** (b) deposited on a Pt electrode from chloroform solutions (scan rate 50 mV/s, electrolytic medium: 0.1 M Bu_4NPF_6 in MeCN)

shown to produce high yields (ca. 90%) of regioregular poly(3-octylthiophene) ($M_w = 21.4 \times 10^4$, $M_w/M_n = 1.48$) and of the new poly[4-octylbi(thiophene)] ($M_w = 3.8 \times 10^4$, $M_w/M_n = 1.1$). The best catalyst precursor proved to be $Pd_2(dba)_3(CHCl_3)$/4 PPh_3, in a 1:1 mixture of THF and DMF as solvent. The average molecular weight of the resulting regioregular poly(3-octylthiophene) was found to be much higher than that of a similar polymer prepared using an iodothiophene derivative.[41] The regioregularity of the head-to-tail coupling was assessed by ^{1}H NMR, which showed HT > 95% for poly(3-octylthiophene) and HT > 90% for the new poly[4-octylbi(thiophene)]. The conjugation properties of these materials have been characterized by FT-IR and UV/Vis spectroscopy. Compared to regiorandom polymers, the absorption maxima of the new regioregular polymers are shifted to higher wavelengths ($\lambda_{max} = 448$ and 466 nm, respectively). Similarly, their emissions appear at higher wavelengths ($\lambda_{max} = 515$ and 575 nm, respectively). The mean conjugation length increases with an increase in the regioregularity of the coupling and with a decrease in the number of octyl substituents along the conjugated chain. This is associated with a reduction in the number of conjugation defects that arise because of steric interactions between the octyl groups along the conjugated chain. The electroactive properties of the materials have also been studied. Both polymers exhibit reversible blue-red electrochromic behavior associated with the reversible redox properties. The new poly[4-octylbi(thiophene)] shows an oxidation peak at a low potential, and, compared to poly(3-octylthiophene), a reduction peak is also observed at a lower potential, indicating a higher electron affinity.

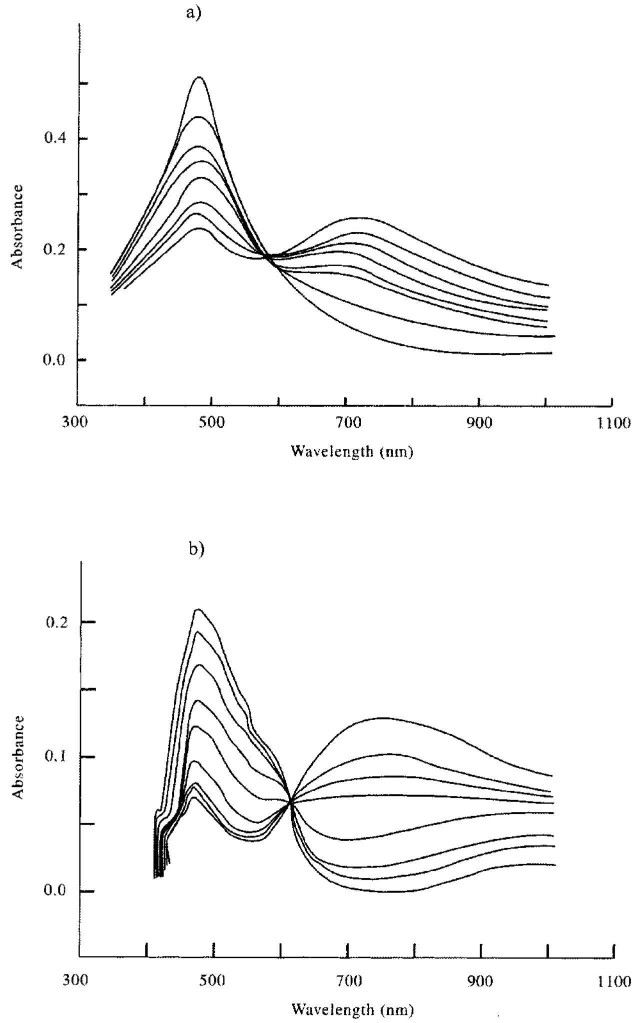


Figure 10. Spectro-electrochemistry of **PAT$_1$** (a) and **PABT$_1$** (b); each spectrum was recorded for E (vs. SCE) from 0.4 V to 1.3 V with an increment of 0.02 V

Experimental Section

General: All experiments were carried out under an inert N_2 atmosphere using Schlenk techniques. $CHCl_3$, THF, DMF, toluene, and hexane (SDS) were dried by distillation over phosphorus pentoxide, sodium benzophenone ketyl, and CaH_2 as appropriate. 2-Bromothiophene, 1-bromooctane, and tributyltin chloride (Aldrich) were used without further purification. $Ni(dppp)Cl_2$ and *n*-butyllithium (2.5 M solution in hexanes) were purchased from Aldrich. The palladium complexes were prepared according to literature procedures: $Pd(PPh_3)_4$,[55] $Pd(PPh_3)_2Cl_2$,[56] $Pd_2(dba)_3(CHCl_3)$.[57] UV/Vis spectra were recorded on an MC^2 Safas spectrometer and emission spectra on an SLM-Aminco MC 200 spectrometer. − Fluorescence quantum yields were measured by the standard procedure.[59] − GPC measurements were made on a Waters chromatograph equipped with HR_2 and HR_3 Styragel columns using THF as the eluent and polystyrene samples as calibration standards. − Cyclic voltammetry was carried out on an EG & G potentiostat connected to a Kipp & Zonen tracer. − Electrochromism measurements were made using a three-electrode (ITO, Pt, Ag) spectroelectrochemical cell connected to an EG & G 362 potentiostat.

3-Octylthiophene: This compound was prepared according to a literature procedure[59] as follows. Ni(dppp)Cl_2 (0.8 g, 2 mmol) was added to a solution of 3-bromothiophene (24.5 g, 0.15 mol) in THF (200 mL) in a 1-dm^3 flask. 1-Octylmagnesium bromide [prepared from magnesium turnings (6.4 g, 0.26 mol) and 1-bromooctane (38 mL, 0.22 mol) in THF (200 mL)] was then slowly added at room temp. Following the addition, the mixture was stirred for 12 h at room temp. Pentane (400 mL) was then added and the resulting mixture was filtered. The filtrate was concentrated in vacuo and distillation of the residue afforded 23 g of 3-octylthiophene (78% yield); b.p. 106 °C/4 Torr. − ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, 3 H, CH_3), 1.30 (m, 10 H, 5 CH_2), 1.64 (m, 2 H, β-CH_2), 2.64 (t, 2 H, α-CH_2), 6.94 (m, 2 H, 2 CH), 7.24 (m, 1 H, CH). − ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3, alkyl), 31.9, 30.6, 30.3, 29.5, 29.4, 29.3, 22.7 (7 CH_2, alkyl), 119.7 (CH, C-2), 125.0 (CH, C-5), 128.3 (CH, C-4), 143.3 (C, C-3). − $C_{12}H_{20}S$ (196.35): calcd. C 73.16, H 10.20, S 16.42; found C 73.48, H 10.24, S 16.30.

2-Bromo-3-octylthiophene: *N*-Bromosuccinimide (NBS) (5.34 g, 0.03 mol) was added to a solution of 3-octylthiophene (5.89 g, 0.03 mol) in $CHCl_3$ (30 mL). The resulting yellow solution was stirred at room temp. for 4 h. It was then refluxed for 4 h, allowed to cool to room temp., and diluted with pentane (50 mL). The mixture was filtered and the filtrate was concentrated in vacuo. The yellow residue was distilled to give 7.4 g (90%) of 2-bromo-3-octylthiophene; b.p. 123 °C (1.1 Torr). − ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (t, 3 H, CH_3), 1.30 (m, 10 H, 5 CH_2), 1.59 (m, 2 H, β-CH_2), 2.58 (t, 2 H, α-CH_2), 2 aromatic H ($\nu_B = 7.18$, $\nu_A = 6.80$, $J = 5.59$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3, alkyl), 31.9, 29.7, 29.4, 29.2, 22.7 (7 CH_2, alkyl), 108.8 (C, C-2), 125.1 (CH, C-5), 128.2 (CH, C-4), 142.0 (C, C-3). − $C_{12}H_{19}BrS$ (275.25): calcd. C 52.36, H 6.90, S 11.63; found C 52.32, H 6.94, S 11.58.

2-Bromo-3-octyl-5-tributylstannylthiophene (1): A solution of 2-bromo-3-octylthiophene (8.5 g, 0.03 mol) in THF (30 mL) was cooled to −40 °C, whereupon LDA (2 N in THF, 15 mL, 0.03 mol.) was added dropwise. The resulting mixture was stirred at −40 °C for 30 min. Then, chlorotributylstannane (9.49 mL, 0.035 mol) was slowly added at the same temperature. The mixture was allowed to warm to room temperature and stirred for 12 h. It was then hydrolysed, the organic layer was extracted with diethyl ether, and the combined ethereal extracts were dried over $MgSO_4$. The solvents were removed in vacuo and the residue was distilled to give crude **1**. The product was further purified by column chromatography on alumina (eluent: $CHCl_3$) to give 13.4 g of pure **1** (yield 79%); b.p. 165 °C (1.5×10^{-2} Torr). − ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, 9 H, 3 CH_3), 1.09 (t, 3 H, CH_3), 1.29 (m, 22 H, 11 CH_2), 1.55 (m, 8 H, 4 CH_2), 2.58 (t, 2 H, α-CH_2), 6.83 (t, 1 H, CH, $J_{H-Sn} = 11.98$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta = 11.06$ (3 CH_3, Bu_3Sn), 13.64, 26.94, 28.91 (9 CH_2, Bu_3Sn), 14.26 (CH_3, alkyl), 31.91, 29.87, 29.34, 29.23, 29.12, 27.24, 22.69 (7 CH_2, alkyl), 113.20 (C, C-2), 136.56 (CH, C-4), 137.00 (C, C-5), 142.92 (C, C-3). − $C_{24}H_{45}BrSSn$ (564.27): calcd. C 51.08, H 8.04, S 5.68; found C 51.10, H 8.07, S 5.66.

3-Octyl-2-trimethylsilylthiophene: A solution of 2-bromo-3-octylthiophene (30 g, 0.14 mol) in THF (150 mL) was added dropwise to magnesium turnings (3.31 g, 0.14 mol) and THF (10 mL). The resulting mixture was refluxed for 2 h and then cooled to room temp., whereupon a solution of chlorotrimethylsilane (15 mL, 0.12 mol) in THF (30 mL) was slowly added. After the addition was complete, the mixture was refluxed for 6 h. It was then poured into cold water. The mixture was extracted with diethyl ether, the combined ethereal extracts were dried over $MgSO_4$, and the solvents were evaporated. Distillation of the residue afforded 28.6 g of 3-octyl-2-trimethylsilylthiophene (76%); b.p. 93 °C (0.5 Torr). − ^{1}H NMR ($CDCl_3$): $\delta = 0.39$ (s, 9 H, $SiMe_3$), 0.92 (t, 3 H, CH_3), 1.32 (m, 10 H, 5 CH_2), 1.64 (m, 2 H, β-CH_2), 2.71 (t, 2 H, α-CH_2), 7.05 (d, 1 H, 4-H, $^{1}J = 4.6$ Hz), 7.45 (d, 1 H, 5-H, $^{1}J = 4.67$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta = 0.4$ (3 CH_3, $SiMe_3$), 14.1 (CH_3, alkyl), 31.9, 31.9, 31.3, 29.8, 29.5, 29.3, 22.7 (7 CH_2, alkyl), 129.3 (CH, C-5), 130.3 (CH, C-4), 132.5 (C, C-2), 150.5 (C, C-3). − ^{29}Si NMR ($CDCl_3$): $\delta = -8.2$ ($SiMe_3$). − $C_{15}H_{28}SSi$ (268.53): calcd. C 67.16, H 10.44, S 11.94; found C 67.12, H 10.39, S 11.92.

4-Octyl-5-trimethylsilyl-2,2′-bi(thiophene): At 0 °C, *n*BuLi (1.6 M solution in diethyl ether, 25.6 mL, 0.041 mol) was added dropwise to a solution of 3-octyl-2-trimethylsilylthiophene (11.0 g, 0.041 mol) in THF (40 mL). The resulting mixture was stirred for 1 h at this temp. and was then allowed to warm to room temp. It was added to a solution of $ZnCl_2$ (6.4 g, 0.041 mol) in THF (40 mL). The resulting organozinc reagent solution was then slowly added to a solution of 2-bromothiophene (6.68 g, 0.041 mol) and $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol) in THF (40 mL). After the addition was complete, the mixture was heated at 50 °C for 12 h. The solvents were then removed in vacuo and the residue was extracted with hexane. Evaporation of the hexane from the extract and distillation of the residue afforded 5.6 g of 4-octyl-5-trimethylsilyl-2,2′-bi(thiophene) (39%); b.p. 150 °C (0.3 Torr). − ^{1}H NMR ($CDCl_3$): $\delta = 0.38$ (s, 9 H, $SiMe_3$), 0.92 (t, 3 H, CH_3), 1.32 (m, 10 H, 5 CH_2), 1.62 (m, 2 H, β-CH_2), 2.65 (t, 2 H, α-CH_2), 7.01 (q, 1 H, 4′-H, $J_{4'3'} = 4.98$ Hz, $J_{4'5'} = 3.68$ Hz), 7.14 (s, 1 H, 3-H), 7.18 (q, 1 H, 5′-H, $J_{5'4'} = 3.68$ Hz, $J_{5'3'} = 1.16$ Hz), 7.20 (q, 1 H, 3′-H, $J_{3'4'} = 4.98$ Hz, $J_{3'5'} = 1.16$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta = 0.42$ (3 CH_3, Me_3Si), 14.15 (CH_3, alkyl), 31.93, 31.78, 31.54, 29.78, 29.56, 29.31, 22.73 (7 CH_2, alkyl), 123.52, 124.14, 127.22, 127.73 (4 CH, C-3, C-3′, C-5′), 132.34, 137.67 (2 C, C-2, C-2′), 140.95 (C, C-5), 151.25 (C, C-4). − ^{29}Si NMR ($CDCl_3$): $\delta = -8.26$ (Me_3Si). − $C_{19}H_{30}S_2Si$ (350.65): calcd. C 65.08, H 8.62, S 18.29; found C 65.16, H 8.50, S 18.31.

4-Octyl-2,2′-bi(thiophene): To a solution of 4-octyl-5-trimethylsilyl-2,2′-bi(thiophene) (1.75 g, 5 mmol) in THF (5 mL) was added 10% aqueous HCl solution (5 mL). The resulting mixture was stirred vigorously for 1 h at room temp. and then extracted with diethyl ether. The combined extracts were dried over $MgSO_4$ and then concentrated in vacuo; distillation of the residue afforded 1.25 g of 4-octyl-2,2′-bi(thiophene) (90% yield); b.p. 120 °C (0.3 Torr). − ^{1}H NMR ($CDCl_3$): $\delta = 0.90$ (t, 3 H, CH_3), 1.29 (m, 10 H, 5 CH_2), 1.60 (m, 2 H, β-CH_2), 2.59 (t, 2 H, α-CH_2), 6.80 (d, 1 H, 5-H, $J_{53} = 0.99$ Hz), 7.01 (q, 1 H, 4′-H, $J_{4'3'} = 5.06$ Hz, $J_{4'5'} = 3.59$ Hz), 7.03 (d, 1 H, 3-H, $J_{3,5} = 0.99$ Hz), 7.15 (q, 1 H, 5′-H, $J_{5'4'} = 3.59$ Hz, $J_{5'3'} = 1.13$ Hz), 7.19 (q, 1 H, 3′-H, $J_{3'4'} = 5.06$ Hz, $J_{3'5'} = 1.13$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta = 14.20$ (CH_3, alkyl), 31.98, 30.59, 30.47, 29.52, 29.41, 29.36, 22.77 (7 CH_2, alkyl), 119.01 (CH, C-5), 123.44, 124.08, 125.17, 127.74 (4 CH, C-3, C-3′, C-4′, C-5′), 137.04, 137.88 (2 C, C-2, C-2′), 144.08 (C, C-4). − $C_{16}H_{22}S_2$ (278.47): calcd. C 69.00, H 7.96, S 23.03; found C 69.01, H 7.97, S 23.01.

5-Bromo-4-octyl-2,2′-bi(thiophene): NBS (0.9 g, 5 mmol) was added to a solution of 4-octyl-2,2′-bi(thiophene) (1.4 g, 5 mmol) in $CHCl_3$ (5 mL). The resulting pale-yellow solution was stirred at room temp. for 4 h. Hexane (20 mL) was then added and the mixture was filtered. The filtrate was concentrated in vacuo and the yellow oily residue was chromatographed on a silica column using hexane as the eluent to furnish 1.43 g of 5-bromo-4-octyl-2,2′-bi(thiophene) (80% yield). − ^1H NMR ($CDCl_3$): $\delta = 0.91$ (t, 3 H, CH_3), 1.30 (m, 10 H, 5 CH_2), 1.61 (m, 2 H, β-CH_2), 2.55 (t, 2 H, α-CH_2), 6.87 (s, 3-H, CH), 7.00 (q, 1 H, 4′-H, $J_{4'3'} = 5.07$ Hz, $J_{4'5'} = 3.57$ Hz), 7.10 (q, 1 H, 5′-H, $J_{5'4'} = 3.57$ Hz, $J_{5'3'} = 1.07$ Hz), 7.21 (q, 1 H, 3′-H, $J_{3'4'} = 5.07$ Hz, $J_{3'5'} = 1.07$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta =$ 14.16 (CH_3, alkyl), 31.92, 29.76, 29.70, 29.62, 29.42, 29.28, 22.72 (7 CH_2, alkyl), 107.60 (C, C-5), 123.71, 124.52, 124.54, 127.82 (4 CH, C-3, C-3′, C-4′, C-5′), 136.84 (C, C-2), 142.89 (C, C-4), 142.98 (C, C-2′). − $C_{16}H_{21}BrS_2$ (357.37): calcd. C 53.77, H 5.92, S 17.94; found C 53.75, H 5.90, S 17.96.

5-Bromo-4-octyl-5′-tributylstannyl-2,2′-bi(thiophene) (2): LDA (2 M solution in THF, 1.89 mL, 3.7 mmol) was added dropwise to a solution of 5-bromo-4-octyl-2,2′-bi(thiophene) (1.23 g, 3.4 mmol) in THF (10 mL) at 40 °C. After stirring for 30 min, chlorotributyltin (1.025 mL, 3.7 mmol) was added and the mixture was allowed to warm to room temp. and stirred for 12 h. The solvent was then evaporated and the residue was extracted with hexane. After evaporation of the hexane from the extract, the oily residue was purified by column chromatography on a short alumina column using hexane and $CHCl_3$ as the eluents to furnish 1.98 g of 5-bromo-4-octyl-5′-tributylstannyl-2,2′-bi(thiophene) **2** (90% yield). − ^1H NMR ($CDCl_3$): $\delta = 0.92$ (t, 9 H, 3 CH_3), 1.13 (t, 3 H, CH_3), 1.31 (m, 22 H, 11 CH_2), 1.60 (m, 8 H, 4 CH_2), 2.54 (t, 2 H, α-CH_2), 6.87 (s, 1 H, CH), 7.05 and 7.22 ($J = 3.38$ Hz). − ^{13}C NMR ($CDCl_3$): $\delta =$ 10.91 (3 CH_3, Bu_3Sn), 13.69, 27.28, 28.97 (9 CH_2, Bu_3Sn), 14.30 (CH_3, alkyl), 31.93, 29.70, 29.62, 29.43, 29.28, 27.28, 22.72 (7 CH_2, alkyl), 107.23 (C, C-5), 124.21 (CH, C-3), 124.89 (CH, C-3′, 2 satellites $J = 17.16$ Hz) , 136.09 (CH, C-4′, 2 satellites $J = 10.87$ Hz) , 136.91, 137.11 (2 C, C-2, C-2′), 142.16 (C, C-5′), 142.79 (C, C-4). − $C_{28}H_{47}BrS_2Sn$ (646.39): calcd. C 52.02, H 7.33, S 9.92; found C 52.04, H 7.37, S 9.90.

Poly(3-octylthiophene)s: Palladium-catalysed polycondensation reactions of **1** were performed according to the same general procedure. The results are given in Table 1. The preparation of **PAT$_1$** is given as an example.

A Schlenk tube was charged with $Pd_2(dba)_3(CHCl_3)$ (10.3 mg, 0.01 mmol) and PPh_3 (21 mg, 0.08 mmol) and a 1:1 mixture of THF and DMF (10 mL). After stirring at room temperature for 15 min, 2-bromo-3-octyl-5-tributylstannylthiophene (**1**) (0.564 g, 1 mmol) was added. The resulting mixture was stirred at 80 °C for 3 days. After cooling to room temperature, the addition of acetone led to the precipitation of the polymer as a deep-red powder. After filtration and washing, 0.17 g (90% yield) of **PAT$_1$** was isolated. − ^1H NMR ($CDCl_3$): $\delta = 6.98$ (s, 1 H, thiophene-H), 2.80 (t, 2 H, CH_2), 1.72 (m, 2 H, CH_2), 1.28 (m, 10 H, 5 CH_2), 0.88 (t, 3 H, CH_3). − ^{13}C NMR ($CDCl_3$): $\delta =$ 139.9, 133.7, 130.5, 128.6, 31.9, 30.5, 29.6, 29.4, 29.3, 22.7, 14.1. − IR (KBr): $\tilde{\nu} = 3056$ cm^{-1}, 2953, 2852, 1510, 1461, 1450, 1374, 824. − UV/Vis: solution $\lambda_{max} =$ 448 nm, solid $\lambda_{max} = 515$ nm (555 nm, 602 nm). − $M_w = 210912$, $M_n = 142021$, $M_w/M_n = 1.48$. − Analysis calcd. for $(C_{12}H_{18}S)_n$: C 74.16, H 9.34, S 16.50; found C 73.73, H 9.23, S 16.43.

Poly[4-octyl-2,2′-bi(thiophene)] (PABT$_1$): The palladium-catalysed polycondensation of monomer **2** was carried out as described above for monomer **1**. Analogous workup led to the isolation of **PABT$_1$** in 88% yield. − ^1H NMR ($CDCl_3$): $\delta = 7.10$ and 7.04 (2 H, thiophene-H), 7.025 (s, 1 H, thiophene-H), 2.77 and 2.54 (m, 2 H, CH_2; HT and HH, respectively), 1.69 and 1.56 (m, 2 H, CH_2; HT and HH, respectively), 1.28 (m, 10 H, 5 CH_2), 0.88 (t, 3 H, CH_3); 90% HT. − ^{13}C NMR ($CDCl_3$): $\delta =$ 140.6, 134.8, 137.2, 129.6, 126.6, 126.4, 123.9, 31.9, 30.5, 29.6, 29.4, 29.3, 22.7, 14.1. − IR (KBr): $\tilde{\nu} = 3056$ cm^{-1}, 2953, 2922, 2852, 1495, 1457, 1435, 1374, 828, 790. − UV/Vis: solution $\lambda_{max} = 466$ nm, solid $\lambda_{max} = 575$ nm. $M_w = 37943$, $M_n = 34027$, $M_w/M_n = 1.11$. Analysis calcd. for $(C_{16}H_{20}S_2)_n$: C 69.51, H 7.29, S 23.19; found C 68.93, H 7.31, S 22.85.

Poly[4-octyl-2,2′-bi(thiophene)] (PABT$_2$): The nonregioregular polymer **PABT$_2$** was obtained as follows. Over a period of 15 min, a solution of 4-octyl-2,2′-bi(thiophene) (2.78 g, 0.01 mol) in $CHCl_3$ (40 mL) was added to a solution of freshly sublimed $FeCl_3$ (4.8 g, 0.03 mol) in $CHCl_3$ (100 mL) in a Schlenk tube. The blue mixture was stirred for 3 days at room temp. and then MeOH (200 mL) was added. Filtration of the reaction mixture allowed the collection of a solid, which was washed with MeOH for 24 h (soxhlet extractor). Thereafter, a red powder (1.68 g) was obtained (60% yield). − ^1H NMR ($CDCl_3$): $\delta = 7.10$ and 7.07 (2 H, thiophene-H), 7.025 (s, 1 H, thiophene-H), 2.77 and 2.54 (m, 2 H, CH_2; HT and HH, respectively), 1.69 and 1.56 (m, 2 H, CH_2; HT and HH, respectively), 1.28 (m, 10 H, 5 CH_2), 0.88 (t, 3 H, CH_3); 56% HT. − UV/Vis: solution $\lambda_{max} = 450$ nm, solid $\lambda_{max} = 596$ nm. $M_w =$ 25326, $M_n = 14898$, $M_w/M_n = 1.70$. Analysis calcd. C 69.51, H 7.29, S 23.19; found C 69.36, H 7.37, S 23.08.

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