Enhanced Electrical Conductivity in Regioselectively Synthesized Poly(3-alkylthiophenes)

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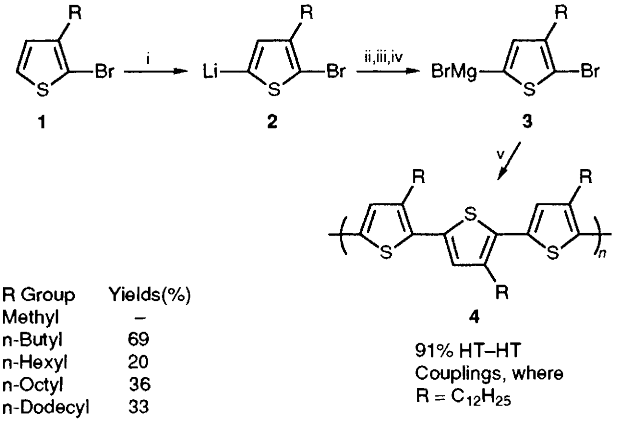
A regioselective synthetic method to poly(3-alkylthiophenes) provides structurally homogeneous poly(3-dodecylthiophene), which upon oxidation with I_2 leads to polymers with average conductivities of 600 S cm^{-1} and maximum conductivities of 1000 S cm^{-1}.

Over the past few years it has become clear that structure plays a key role in determining the physical properties of conducting polymers.[1] The most striking conclusion is that control of the regularity and order in the polymeric structure leads to remarkable enhancements in the electrical properties of these novel materials.[2,3] However, there are almost no examples of 3-substituted polythiophenes or polypyrroles that possess the structural order needed for a large improvement in their electrical conductivity.[3] Although the synthesis of new conducting polymers[4,5] and new polymer synthetic methods[2,6] have provided the greatest advancements in the field, methods to synthesize polymers of 3-substituted thiophenes and pyrroles with regular structures have been lacking. The major problem is that the standard synthetic methods that yield

Table 1 A comparison of PDDT made by various methods

	Preparation type		
	Present method yield (%)	w/$FeCl_3$ yield (%)	Electro-chemical yield (%)
HT–HT	91	54[a]	54[b]
HT–HH	5	13	17
TT–HT	2	18	13
TT–HH	2	15	16
UV–VIS (λ_{max})[c]/nm	450	436	428
Avg conductivity[d] σ_{RT}/S cm^{-1}	600	10	[e]
Max conductivity σ_{RT}/S cm^{-1}	1 000	20	[e]

[a] Prepared by the method of Sugimoto in our lab (see ref. 13). The %'s are approximate. [b] Data taken from ref. 7. [c] Spectroscopic and conductivity data were measured on the polymeric mixtures prepared by the above method. UV–VIS data were obtained from $CHCl_3$ solutions. [d] Four-probe measurements of polymer films cast from $CHCl_3$ or PhMe. Average of six samples of varying thicknesses. Exact film thicknesses were determined by SEM analysis and ranged from 5–12 μm. [e] We did not make PDDT–I_3 by the electrochemical method, however, for comparison PDDT–PF_6 has a maximum conductivity of 70 S cm^{-1}.



R Group	Yields(%)
Methyl	–
n-Butyl	69
n-Hexyl	20
n-Octyl	36
n-Dodecyl	33

Scheme 1 *Reagents and conditions*: i, LDA, THF, −40 °C; ii, $MgBr_2{\cdot}OEt_2$, −60 °C; iii, −40 °C; iv, −10 °C; v, $Ni(dppp)Cl_2$, −5–25 °C; LDA - lithium diisopropylamide; THF = tetrahydrofuran; dppp = 1,3-bis(diphenylphosphino)propane

mono-functionalized polythiophenes and polypyrroles lead to couplings at the 2,5 positions with random regiospecificity, which provides a mixture of polymeric structures.[7] These polymers contain a number of defects, which in turn reduces the electrical conductivity of the polymer. We herein describe a regioselective synthesis of poly(3-alkylthiophenes), which provides highly ordered poly(3-dodecylthiophene) (PDDT) containing almost exclusively head-to-tail (HT) couplings. The oxidation of PDDT with I_2 leads to polymer samples with average conductivities of 600 S cm^{-1} and maximum conductivities of 1000 S cm^{-1}.

Poly(3-alkylthiophenes) **4** were synthesized from 2-bromo-3-alkylthiophenes[8] in a one-pot reaction as shown in Scheme 1. Compound **3** was generated and then polymerized through the use of a nickel catalysed cross-coupling reaction[9] to yield poly(3-alkylthiophenes) **4** in 20 to 69% yields. The primary advantage of cross-coupling catalysis is that essentially only HT poly(3-alkylthiophenes) are produced. The resultant polymers were identified by IR, NMR and UV–VIS spectroscopy, and GPC (gel-permeation chromatography), and in some cases, elemental analysis. GPC and NMR analysis of PDDT gave $\overline{M}_w$ of 11 600 (46 repeat units) and 16 000 (64 repeat units), respectively. Although we have polymerized monomers with other alkyl groups (R = methyl, butyl, hexyl and octyl), we will present the physical properties of only PDDT **4**, where R = $C_{12}H_{25}$.

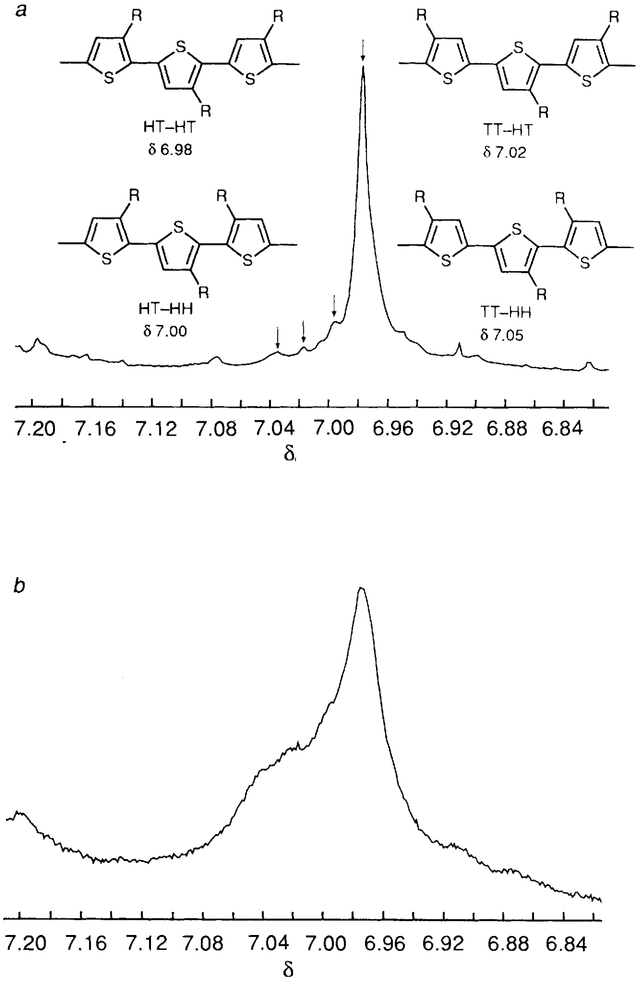


Fig. 1 NMR spectra of (*a*) PDDT synthesized by our method and (*b*) PDDT made by the $FeCl_3$ method. The structures in (*a*) represent the different types of couplings and the literature assignments of each. The arrows in (*a*) indicate our assignments of these representative couplings. An NMR spectrum of electrochemically prepared PDDT can be found in ref. 7.

Conducting polymers with regular structures (as in polymer **4**) are expected to be highly ordered and therefore exhibit improved electrical conductivities. As seen in Table 1, our PDDT shows a greater effective conjugation length as indicated from the UV–VIS data and the I_2 doped polymers exhibit an average conductivity of 600 S cm^{-1}. These conductivity values are 50- to 60-fold higher than PDDT polymers synthesized by the usual chemical or electrochemical methods. Although doped PDDT is expected to have a relatively low conductivity, our samples have exhibited conductivities as high as 1000 S cm^{-1}, which is a very large value for an unoriented conducting polymer. We expect that oxidized PDDT will have the lowest conductivity in the alkyl series due to the large alkyl substituents blocking interchain transport and sterically inhibiting intrachain carrier mobility. In fact, our preliminary conductivity results on poly(3-butylthiophene) and poly(3-hexylthiophene) indicate this to be the case.[10]

The lowest conductivity measured for any of our PDDT–I_2 films was 340 S cm^{-1} and examination of the polymer morphology by SEM (scanning electron microscopy) showed the film to be very porous. However, all of the samples having smooth and uniform morphologies exhibited conductivity values of 700 S cm^{-1} or higher. Also, in stark contrast to previously prepared samples of neutral PDDT, our polymer is thermally stable to 370 °C (as determined by DSC–TGA analysis) (DSC = differential scanning calorimetry; TGA = thermogravimetric analysis) and does not exhibit melting behaviour.[11] One interpretation of these data is an increase in crystallinity of our material relative to the PDDT prepared by other methods.[12]

The structural regularity of the PDDT prepared by this method was examined by ^1H NMR spectroscopy. Recent 2-D NMR spectroscopic work by Sato and Morii[7] has shown that four singlets in the aromatic region can be clearly attributed to the four-protons with each peak representing the different types of trimeric sequences (shown in Fig. 1) of HT–HT (δ 6.98), HT–HH (δ 7.00), TT–HT (δ 7.02) and TT–HH (δ 7.05) linked thiophene rings. Fig. 1 shows the NMR spectra of PDDT as synthesized by our method and by the standard $FeCl_3$ polymerization method.[13] The percentages of each type of triad sequence, as obtained from NMR integration (Table 1), shows that we have been able to gain an additional 35–40% of HT–HT couplings over standard methods for the synthesis of PDDT, yielding 91% of HT–HT couplings *vs.* the usual 54%.

In conclusion, we have presented a method for the synthesis of structurally homogeneous 3-alkyl substituted polythiophenes, which results in a large improvement in the electrical conductivity of PDDT. The trends in the physical properties of the conducting polymers prepared by this method are proving to have strikingly different physical properties than those polymers synthesized by the standard methods.[10]

We gratefully acknowledge Professor Krzystof Matyjaszewski for use of the GPC and DSC instruments and Jeffrey Hrkach and Michael White for technical assistance. We also thank the donors of The Petroleum Research Fund, administered by the American Chemical Society for partial support and the Howard Hughes Foundation for providing an undergraduate research fellowship for R. L.

Received, 23rd September 1991; Com. 1/04897J

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