Regioregular Poly[2,5-bis(3-butyl-2-thienyl)tellurophene]: Synthesis and Characterization Aspects

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This work reports on a novel, facile synthetic methodology into the tellurophene nucleus, which was applied in particular to the synthesis of the centrosymmetrical 2, 5-bis(3-butyl-2-thienyl)tellurophene. Thereafter, oxidative polymerization of the monomer using iron (III) chloride afforded the regioregular poly[2,5–bis(3–butyl–2–thienyl)tellurophene]. Preliminary characterization aspects of the polymer are reported.

Whilst polythiophenes[1] have generated enormous interests on account of their high electrical conductivity in the oxidized doped state, facile synthetic generation as well as their fast and large nonlinear optical response in the neutral state, the chemistry of polytellurophene prepared from tellurophene, the heaviest analogue of the series of chalcophenes, has received little attentive from the stand point of electrically conducting polymers.

An early paper[2] reported the electrical conductivity of I_2 doped polytellurophene **1** to be around 10^{-6} S cm^{-1} at room temperature. A subsequent patent[3] claimed the synthesis of polymer **2** from fused-ring tellurophene, but no properties were reported. Further efforts[4,5] on the electrochemical polymerization of bi- and tertellurophene to polymers **3** and **4** showed that the conductivity remained little changed at *ca* 10^{-6} S cm^{-1} (Figure. 1).

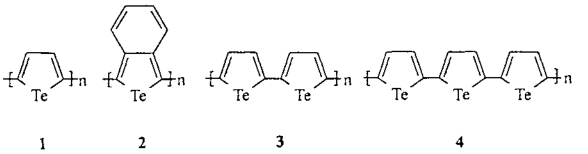
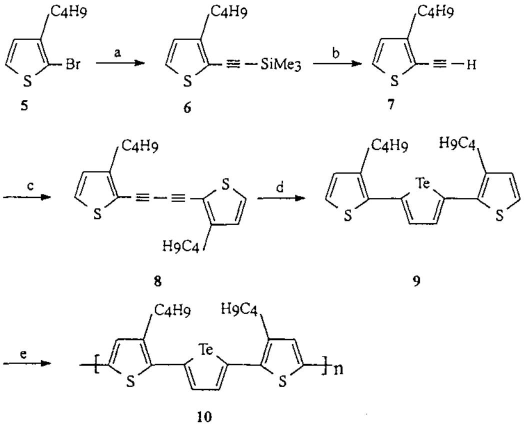


Figure 1.

Meanwhile, polymerization of centrosymmetrical monomers of thiophene,[6] such as -3,3”-dihexy-2,2’: 5’,2”-terthiophene, was shown to have not only overcome the lack of regiospecificity of general polymerization methods, but also improved doping stability of the corresponding polymers. With regard to the advantages of these regioregular alkyl-substituted polythiophenes which can be readily generated from centrosymmetrical monomers and in keeping with our ongoing interests[7-10] in the structure-property correlation studies of functional polymers, we synthesized a centrosymmetrical monomer, from which regioregular polymer comprising alternating tellurophene and symmetrically substituted bithiophene units can be generated from chemical polymerization using $FeCl_3$. Apart from deriving a novel facile entry into the tellurophene nucleus reported herein, preliminary studies show the derived polymer to possess improved electric properties, processability and stability.

The key monomer, 2,5-bis(3-butyl-2-thienyl)tellurophene **9**, was prepared in 6 steps (Scheme 1) with an overall yield of 23%. The starting material, **5** was prepared as reported in the literature.[11] **6** was obtained in 85% yield from **5**, using an improved procedure[12] for palladium-catalyzed coupling of terminal alkynes with bromothiophene. The precursor diacetylene **8** was prepared in 60% yield by homo coupling of **7**, which was obtained *in situ* from **6** after deprotection. The monomer **9** was thereafter prepared in 65% yield, using a novel methodology to form the tellurophene ring, by simply reacting **8** with Te powder in an aqueous-ethanol solution of $NaBH_4$ and NaOH.[13]The current methodology into the tellurophene nucleus is extremely facile and represents a definite improvement over existing methodologies which invariably required the use of liquid ammonia techniques and/ or the use of relatively labile/ not readily accessible/ expensive reaction intermediates.[14-17]



Scheme 1. Regents and conditions: a. HC≡CSiMe$_3$ / Pd(PPh$_3$)$_2$Cl$_2$ / CuI / PPh$_3$ / THF; b. K$_2$CO$_3$ / MeOH; c. O$_2$ / CuCl / Pyridine / E:OH / MeOH; d. Te / NaOH / NaBH$_4$ / MeOH/ reflux; e. FeCl$_3$ / CHCl$_3$.

Chemical polymerization of the monomer was carried out by stirring with $FeCl_3$[18] and then removing oligomeric contaminants from the polymer by soxhlet extraction in turn with methanol and THF. The polymer was obtained in 70% yield and was slightly soluble in $CHCl_3$. The ^1H NMR of polymer showed two singlets at δ 7.60 and 6.98 ppm corresponding respectively to the β-Hs of the tellurienyl moiety and the β-H on C4 of the 3-alkythienyl moiety. These are suggestive of good regioregularity in this polymer.

The number-averaged molecular weights (Mn) for the polymer as determined by GPC using THF as eluent is 2970, having a polydispersity index of 1.21. The GPC results indicated there are *ca* 7 repeating monomer units (ie 21 chalocophene moieties) in the polymer chain. The polymer has

λ_{max} at 484 and 493 nm respectively in $CHCl_3$ solution and film phase, in contrast to that for the monomer at 279 nm ($CHCl_3$ solution). The polymer has a bandgap energy of 1.71 eV as determined by extrapolation of the low energy absorption edge to zero from plot of $(\alpha h\nu)^2$ vs $h\nu$.[19] This is comparatively lower than that of polythiophene (2.20 eV) and poly(3-alkylthiophenes)[20] (2.40 eV).

As depicted in figure 2 the disappearance of the characteristic vibration of the thienylene α-H in 730 cm^{-1} and the presence of 2 strong intensity peaks observed at 824 and 871 cm^{-1} corresponding to β-H of thiophene in the polymer were indicative of a predominant α–α coupling mode during polymerization.

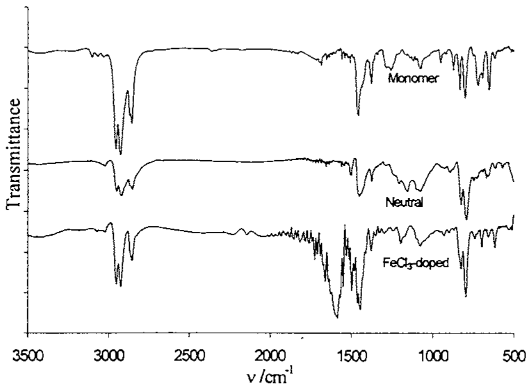


Figure 2. FTIR of monomer, neutral and $FeCl_3$ doped polymer.

TGA results (in air) showed the doped polymers decomposed faster than the neutral polymers and the maximum degradation rates occur at 294, 347 and 395 °C for the $FeCl_3$-doped, I_2-doped and neutral polymers, respectively. However, the doping stability of the $FeCl_3$ doped polymer was improved as compared to polythiophene. When heated at 110 °C, the polymer showed no obvious FT-IR intensity decrease for the characteristic doping bands at 1000-1500 cm^{-1}, while the latter showed a marked intensity decrease.

The maximum conductivity of the I_2-doped polymer was attained at 0.42 S cm^{-1} when the I_2 intake is approximately 120 wt %. These results are of importance from the view point of future structural optimization of conductivity and processability.

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13 Typical procedure into the tellurophene nucleus: A mixture of **8** (0.95 g, 2.9 mmol), Te (0.377 g, 2.9 mmol), NaOH (0.116 g, 2.9 mmol) and $NaBH_4$ (0.264 g, 7.0 mmol) in ethanol (20 ml) and H_2O (10 ml) was refluxed for 20 h. The crude product was extracted with ether and purified by chromatography to give 0.62g (63%) of **9** as pale yellow liquid. Analytical data for **9**: IR (KBr) 3100, 3064, 2955, 2856, 1656, 1546, 1461, 1377, 1299, 1169, 1084 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (t, 2H, J= 4.92 Hz), 7.10 (d, 2H, J= 5.22 Hz), 6.90 (d, 2H, J= 5.22 Hz), 2.7 (t, 4H), 1.65 (m, 4H), 1.45 (m, 4H), 0.95 (t, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.29, 137.54, 135.09, 130.14, 123.19, 63.14, 32.70, 29.16, 16.69, 13.83, 12.05; HREIMS: m/z Calcd. for: 458.03818, found: 458.03855.

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