

A New Polythiophene Prepared by the Electropolymerization of a Branched Sexithienyl

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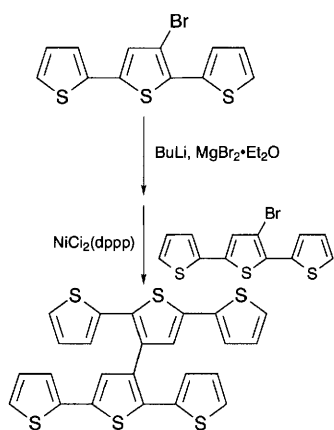
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A new polythiophene film prepared by the electrochemical polymerization of a branched sexithienyl, 3',3'-bis(2,2':5',2''-terthiophene), has a highly developed conjugated system and shows electroactivity.

Polythiophenes have recently received increasing attention because of their large field of application such as energy storage and electrochromic devices.¹⁻⁴ Among thiophene-derived polymers, poly(3-methylthiophene) exhibited the highest electrical conductivity,⁵ indicating that the presence of the methyl group reduces the possibility of β -coupling between thiophene units.⁶ Using thiophene oligomers instead of thiophene monomer as starting materials for the electropolymerization is another possible way to enhance the selectivity of α -coupling. However, contrary to what was expected, the use of oligomers as starting substrate led to polymers with shorter conjugation lengths.⁷ In an attempt to improve the regularity of polythiophene, Roncali *et al.* have chemically synthesized 2,2'-bithiophene and 2,2':5',2''-terthiophene, and carried out a comparative study of the resulting polymers. Their experimental results based on the analysis of the electrical, electrochemical and spectroscopic behaviour of the three polymers showed that the conjugation length and conductivities of the polymers decreased steadily with increasing chain length of the starting oligomers. It thus appeared that using highly conjugated systems as starting molecules was not a convenient way to increase the degree of conjugation.

In this communication, we report the first electropolymerization of a branched thiophene. We show that 3',3'-bis(2,2':5',2''-terthiophene) (BTT), synthesized by dehalogenation condensation of 3'-bromo-2,2':5',2''-terthiophene with magnesium, gave a film with an absorption maximum at 480 nm, and it was found to be highly anode-active as well as cathode-active. These results are in marked contrast with those reported for the electropolymerization of 2,2':5',2''-terthiophene (TT),^{7,8} and indicates that using the highly conjugated bis(terthiophene) as a starting molecule is a convenient way to increase the degree of conjugation in such films.

The monomeric BTT was prepared by dehalogenation condensation of 3'-bromo-2,2':5',2''-terthiophene⁹ with magnesium according to the literature procedure (Scheme 1).¹⁰ The structure of the monomer was confirmed by IR and NMR spectroscopy and elemental analysis. The monomer was



Scheme 1

polymerized electrochemically in a one-compartment cell equipped with three electrodes and an argon inlet. A platinum plate and a silver wire were used as counter and reference electrodes, respectively. The working electrode was a platinum plate or indium-tin oxide glass. Electrodeposition was performed by the cyclic potential sweep method, scanning the potential range 0–1.2 V at a scan rate of 100 mV s⁻¹. The solvent and electrolyte were propylene carbonate (PC) and Bu₄NBF₄, respectively. The monomer and electrolyte concentrations were 10⁻³ and 10⁻¹ mol dm⁻³, respectively. Cyclic voltammograms were measured in 0.1 mol dm⁻³ Bu₄NBF₄ solution in MeCN. PC was dried over 4 Å molecular sieves and distilled *in vacuo* under argon. Bu₄NBF₄ was dried *in vacuo* at 100 °C for 1 h. MeCN was dried from calcium hydride. VIS-near IR and NMR spectra were measured on a Shimadzu UV-3100PC spectrometer and a Varian Model 300BB spectrometer, respectively. FTIR spectra and CVs were recorded as described previously.¹¹

From the CV of BTT, the monomer oxidation wave showed a shoulder at 0.85 V, which is almost the same oxidation potential as seen for TT. The cyclic potential sweep of BTT gave a smooth and uniform film on the surface of the working electrode, although the potentiostatic polymerization at 1.2 V gave a powdery product in addition to a small quantity of soluble polymer. The cyclic potential sweep method was effective in obtaining a high-quality film. On the other hand, both the cyclic potential sweep method and potentiostatic polymerization of TT gave a soluble product and powdery deposit on the electrode. For obtaining a film, it was necessary to use BTT instead of TT, which may be explained by the fact that a radical cation derived from BTT has more resonance structures than that derived from TT because the 3'-(2,2':5',2''-terthiophene) group behaves as an electron donor. Therefore,

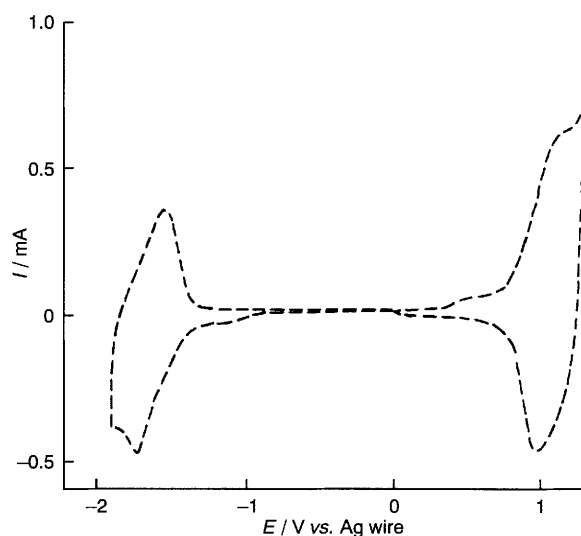


Fig. 1 CV of poly(BTT). Sweep rate: 100 mV s⁻¹; electrolyte: Bu₄NBF₄

using BTT as a starting material enhances the selectivity of α -coupling between thiophene units.

A FTIR spectrum of poly(BTT) showed three bands at 697, 793, and 834 cm^{-1} , assignable to the C–H deformation vibration of 2-substituted, 2,5-disubstituted and 2,3,5-trisubstituted thiophene rings,^{12,13} respectively. No band was detected at 730 cm^{-1} , due to the C–H deformation vibration of 2,4-disubstituted thiophene rings.¹³ These results indicate that only α -coupling between thiophene units occurred and consequently suggest that a highly conjugated system is formed.

A VIS–near IR spectrum of poly(BTT) showed a π – π^* transition at 480 nm in addition to a shoulder at 375 nm. The π – π^* transition band at 400 nm of poly(TT) reported by Roncali *et al.* is located at a wavelength shorter by 80 nm than the present value and thus the present polymer may have a greater conjugation length. Fig. 1 shows the CV of poly(BTT). The polymer showed an anode-activity at applied voltages lower than 0 V as well as a cathode-activity at those higher than 0 V. On the sweep ranging from 0 to 1.5 V, an anodic peak was observed at 1.2 V and a cathodic peak at 1.0 V. The film was blue above the oxidation potential and brown–yellow below the reduction potential. On another sweep ranging from 0 to –1.9 V, a cathodic peak was found at –1.7 V and an anodic peak at –1.6 V. The film was brown–yellow in the neutral state and

blue below the reduction potential. The details of electrochromism will be reported elsewhere.

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