

## Preparation and properties of polythiophene derivatives

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### Abstract

Chemically prepared poly(3-alkyl-2,2'-bithiophene)s (poly-ArBT) are found to be highly soluble and electrochemically prepared ones less soluble. The salts of copper (II) and iron (III) ions are found to be effective oxidants for the chemical polymerization of poly-ArBT, due to the low oxidation potential of the bithiophene derivatives. The conductivities of electrochemically prepared polymers are found to be lower than those of chemically prepared polymers and near to the conductivity of poly(2,2'-bithiophene).

*keywords:* Electrochemical polymerization, Oxidative coupling, UV-Vis-Nir absorption, Polythiophene and derivatives

### 1. Introduction

Since poly(3-alkylthiophene)s (poly-ArT) were first reported to be soluble and conducting [1], soluble polythiophenes with flexible side chains have attracted considerable attention. It is still important to find new polymers showing more desirable properties. We have been studying the preparation and properties of polythiophene derivatives. The polymerization of substituted 2,2'-bithiophene has been studied by several authors[2-7]. Previously, poly(3-hexyl-2,2'-bithiophene) (poly-HBT) and poly(3-dodecyl-2,2'-bithiophene)(poly-DBT) were electrochemically prepared and shown to be more stable in doped states[8]. In this paper we focus on the chemical and electrochemical polymerization of HBT, DBT and 3-eicosyl-2,2'-bithiophene (EBT) and these results are compared with the characteristics of poly-ArT.

### 2. Results and discussion

HBT, DBT and EBT were prepared by the reaction of 3-bromo-2,2'-bithiophene with the corresponding alkylmagnesium bromides in the presence of a nickel catalyst. The chemical polymerization was carried out in acetonitrile or acetonitrile/nitrobenzene with a

few kinds of metallic salts. The results of the chemical and the electrochemical polymerization are summarized in Table 1. The salts of copper (II) and iron (III) ions were effective oxidants for the chemical polymerization of HBT, DBT and EBT, due to the low oxidation potential of the bithiophene derivatives.

The conductivities of poly-HBT, poly-DBT and poly-EBT are 14, 16 and 0.1 S/cm, respectively. Although the present polymers have long side chains, these values

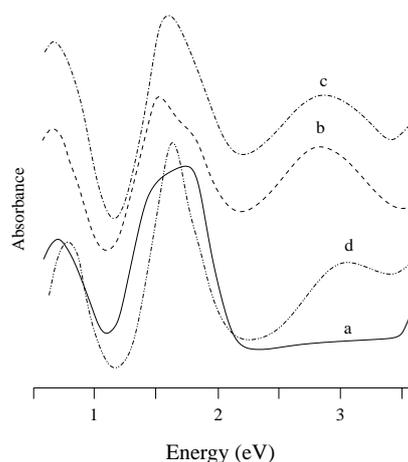


Fig. 1. Absorption spectra of chemically prepared poly-EBT in DCM solution. Oxidant : a;  $\text{Cu}(\text{ClO}_4)_2$ , b;  $\text{Cu}(\text{BF}_4)_2$ , c;  $\text{Fe}(\text{ClO}_4)_3$ , d;  $\text{FeCl}_3$ .

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Table 1  
Conductivity results

Nos.	Monomer	Oxidant / Electrolyte	Solvent	Conductivity (S/cm)
C1	EBT	Cu(ClO <sub>4</sub> ) <sub>2</sub>	CH <sub>3</sub> CN/C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.18
C2	EBT	Cu(BF <sub>4</sub> ) <sub>2</sub>	CH <sub>3</sub> CN/C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.0 x 10 <sup>-2</sup>
C3	EBT	Fe(ClO <sub>4</sub> ) <sub>3</sub>	CH <sub>3</sub> CN/C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.2 x 10 <sup>-3</sup>
C4	EBT	FeCl <sub>3</sub>	CH <sub>3</sub> CN/C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	6.2 x 10 <sup>-4</sup>
E1	EBT	Et <sub>4</sub> NBF <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	0.1
C5	DBT	Cu(ClO <sub>4</sub> ) <sub>2</sub>	CH <sub>3</sub> CN	16
E2	DBT	Bu <sub>4</sub> NBF <sub>4</sub>	CH <sub>3</sub> CN	1.3
C6	HBT	Cu(ClO <sub>4</sub> ) <sub>2</sub>	CH <sub>3</sub> CN	14
E3	HBT	Bu <sub>4</sub> NBF <sub>4</sub>	CH <sub>3</sub> CN	1.4

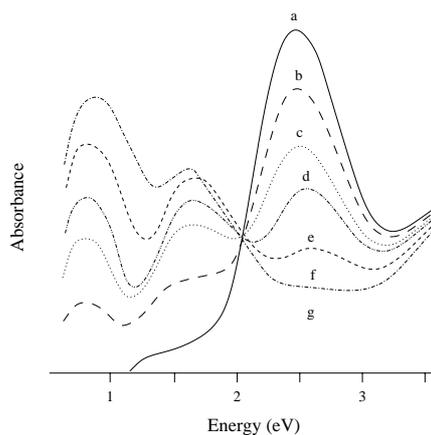


Fig. 2. Spectral change of a poly-EBT film during electrochemical BF<sub>4</sub>-doping. Applied potential a; -0.2V, b; 0.1V, c; 0.3V, d; 0.4V, e; 0.6V, f; 0.7V, g; 0.8V.

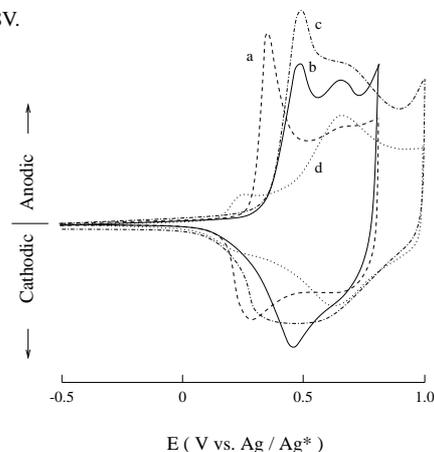


Fig 3. Cyclic voltammograms of polythiophene derivatives. a; poly-HBT, b; poly-DBT, c; poly-EBT, d; poly-NOT.

except for poly-EBT are almost equivalent to the conductivity of poly-BT(2,2'-bithiophene) (poly-BT)[4,5]. These polymers were well soluble in N-methylpyrrolidone and pyridine, and soluble in dichloromethane (DCM) after undoping. The conductivities of electrochemically prepared polymers were 0.1-1.4 S/cm. These values were lower than those of chemically prepared polymers and near to the conductivity of poly-BT [6]. These polymers were less soluble than chemically prepared ones.

Although these polymers were only slightly soluble in DCM, their solution spectra showed well defined features of the bipolaron, as shown in Fig. 1. In particular, the C1 polymer (a) showed two bipolaron peaks and the interband transition peak was very small.

Fig. 2 shows the spectral change of a poly-EBT film during electrochemical BF<sub>4</sub><sup>-</sup>-doping. The spectrum of a neutral film (a) had a peak at 2.45 eV and onset at 1.88 eV. These values are lower than those of poly-ArT. When the applied potential increased to +0.8 V (g), the interband transition peak disappeared and the two peaks remained at 0.9 and around 1.6 eV (shoulder), showing the film to be in a fully doped state.

Fig. 3 shows the comparison of the cyclic voltammograms (CV) of poly-HBT, poly-DBT, poly-EBT, and poly(3-nonylthiophene) (poly-NOT). While the CV of poly-BT had one anodic peak at 0.65 V, poly-HBT, poly-DBT and poly-EBT showed two peaks. Their higher potential peaks were located at almost the same position as the peak of poly-BT and poly-NOT.

Chemically prepared poly-ArBT was found to be highly soluble and electrochemically prepared ones were found to be less soluble. The salts of copper (II) and iron (III) ions were effective oxidants for the chemical polymerization of poly-ArBT, due to the low oxidation potential of the bithiophene derivatives. The conductivities of electrochemically prepared polymers were lower than those of chemically prepared polymers and near to the conductivity of poly-BT.

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