

## Stability of poly(3-alkylthiophene) doped with copper(II)perchlorate

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### Abstract

Poly(3-dodecyl-2,2'-bithiophene)(PDBT), Poly(3-dodecylthiophene)(PDT), and poly(3,4-dibutoxythiophene)(PDBOT) were chemically prepared and doped with copper(II) perchlorate. The conductivity, stability and spectral change of the doped polymers during storage in air were compared. The results suggest that copper(II) perchlorate is an effective oxidant.

*keywords:* Coupling reactions, UV-Vis-NIR absorption, Polythiophene and derivatives

### 1. Introduction

Since poly(3-alkylthiophene) was shown to be soluble and conducting, many soluble substituted polythiophenes were prepared [1-3]. Although poly(3-alkylthiophene) was the first soluble polythiophene to be reported, its doped states are labile. This is a large disadvantage for not only industrial application but also scientific investigation of solution properties. Previously, PDBT was electrochemically prepared and shown to be more stable in a doped state [4]. Thus, PDBT was chemically prepared. It was found that chemically prepared PDBT in doped states was more stable in organic solvents than electrochemically prepared PDBT. In this paper, PDBT, PDT and PDBOT were chemically prepared and doped or redoped with copper(II) perchlorate. The conductivity, stability and spectral change of the doped polymers during storage in air were compared. In order to estimate the stability of the doped states, the solution spectra of the doped polymers in dichloromethane (DCM) were measured after various durations of storage in air.

### 2. Results and discussion

The chemical polymerization of 3-dodecyl-2,2'-bithiophene (DBT) was carried out in acetonitrile with various kinds of metallic salts. The chemical polymerization of 3-dodecyl-thiophene (DT) was performed in chloroform using iron(III) chloride as an oxidant. The redoping for PDT was carried out in acetonitrile containing 0.1 mol/l oxidant with stirring after the chemical polymerization. 3,4-Dibutoxythiophene (DBOT) was coupled with oxidants in acetonitrile in an argon atmosphere. The products were washed with acetonitrile and dried in vacuo. The conductivity was measured for

pressed pellets.

Table 1 shows the conductivity results. The conductivity of poly(2,2'-bithiophene)(PBT) was 17 S/cm. PDBT has long side chains, but its conductivity is almost equivalent to that of PBT. In the case of PDT, iron(III) perchlorate could not be doped. However, copper(II) ions were good. Since the oxidation potential of DBOT was low due to the electron-donative substituents, perchlorates and tetrafluoroborate of copper(II) and iron(III) were effective for their oxidative coupling. The conductivity of PDBOT was very low, but it was soluble in such less polar solvents as chloroform, tetrahydrofuran (THF) and DCM. The salts of copper(II) ions were effective oxidants for chemical polymerization.

PDBT prepared chemically was almost soluble in pyridine and N-methylpyrrolidone, and less soluble in chloroform, THF and DCM. The degree of polymerization (DP) was measured for the part dissolved in THF by using GPC.

Table 1  
Conductivity results (S/cm)

Oxidant	PDBT	PDT	PDBOT
Cu(ClO <sub>4</sub> ) <sub>2</sub>	16	10 <sup>a</sup>	1.5 × 10 <sup>-4</sup>
Fe(ClO <sub>4</sub> ) <sub>3</sub>	6		8.5 × 10 <sup>-5</sup>
Cu(BF <sub>4</sub> ) <sub>2</sub>	11	4 <sup>a</sup>	1.9 × 10 <sup>-4</sup>
FeCl <sub>3</sub>	2		

a: Redoping after chemical polymerization

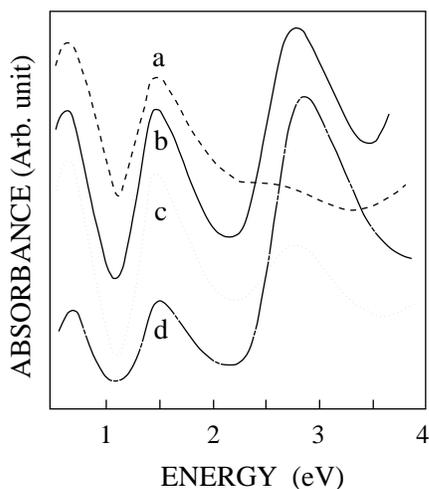


Figure 1. Absorption spectra of PDBT in DCM. Oxidant: a;  $\text{Cu}(\text{ClO}_4)_2$ , b;  $\text{Fe}(\text{ClO}_4)_3$ , c;  $\text{Cu}(\text{BF}_4)_2$ , d;  $\text{FeCl}_3$ .

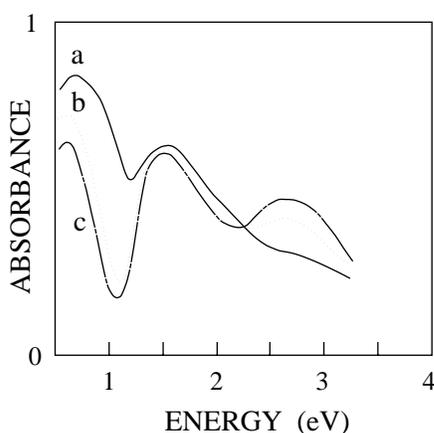


Figure 2. Spectral change of PDBT doped with copper(II) perchlorate in DCM. a; as-prepared, b; after 10 days, c; after 40 days.

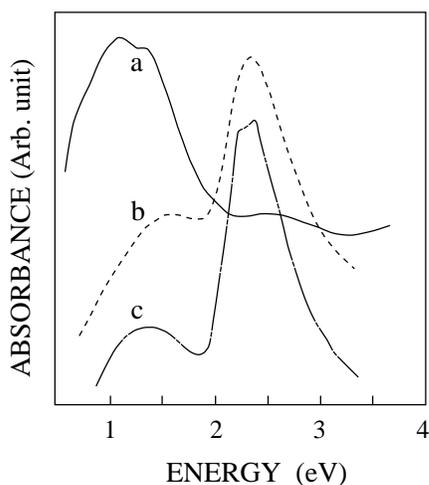


Figure 3. Absorption spectra of PDBOT in DCM. Oxidant: a;  $\text{Cu}(\text{ClO}_4)_2$ , b;  $\text{Fe}(\text{ClO}_4)_3$ , c;  $\text{Cu}(\text{BF}_4)_2$ .

DPn was found to be 37 and DPw was 67. For PDBOT, DPn=18 and DPw = 48.

The solution spectra were measured in DCM, chloroform and carbon tetrachloride. The stability of various solvent/oxidant combinations was investigated. The solvent effect increased in the order: carbon tetrachloride < chloroform < DCM. DCM was found to be the best solvent.

Figure 1 shows the solution spectra of PDBT prepared with various kinds of metallic salts. Each spectrum has three peaks at nearly the same energy. Spectrum(a) has two large peaks below 2 eV due to the bipolaron and one shoulder around 2.7 eV due to the interband transition. These features indicate this polymer to be in highly doped states. In spectrum(c), the bipolaron bands are much larger than the interband transition peak, indicating this polymer to be in moderately doped states. On the other hand, the interband transition peaks are larger than the bipolaron peaks in spectra(b) and (d), indicating these polymers to be undoped to a large extent. This indicates that perchlorate and tetrafluoroborate of copper(II) were effective oxidants, and these ions were more stable than iron ones.

The spectral change of PDBT in DCM is shown in Figure 2. In the spectrum of the as-prepared solution(a), two peaks appeared corresponding to the transition from the valence band to the two bipolaron bands and a slight shoulder due to the interband transition. Even after 40 days(c), the bipolaron peaks were larger than the interband peak, indicating the doped states to be stable to a large extent.

The solution spectrum of PDT redoped with copper(II) perchlorate has three peaks, two large peaks at 0.8 and 1.7 eV due to the bipolaron and one small peak at 3.2 eV due to the interband transition. This indicates that PDT is in highly doped states. However, after 15 days, the bipolaron peaks were smaller than the interband peak, indicating the doped states to be unstable in comparison with PDBT.

The absorption spectra of PDBOT is in highly doped states in chloroform and DCM and these doped states were very stable, but in an almost undoped state in THF solution.

Figure 3 shows absorption spectra of PDBOT in DCM. In spectrum(a), the bipolaron bands are much larger than the interband transition peak, indicating this polymer to be in highly doped states. Even after 50 days, the absorption spectrum was little changed. On the other hand, in spectra(b) and (c), the interband transition peaks are larger than the bipolaron peaks, indicating these polymers to be undoped to a large extent. The combination of copper(II) perchlorate and DCM contributed well to the stability in doped states.

These results suggest that PDBT and PDBOT doped with copper(II) perchlorate are stable in doped states in DCM.

## References

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