

## Synthesis of poly(3-alkoxymethylthiophenes)

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### Abstract

The reaction of 3-lithiothiophene with alkyl chloromethyl ether yielded 3-alkoxymethylthiophenes, which were electrochemically polymerized to give conducting polymer films. The conductivity of poly(3-ethoxymethylthiophene) was higher than that of poly(3-methoxymethylthiophene), indicated that a longer side chain homologue exceptionally shows higher conductivity.

*Keywords:* Electrochemical polymerization, UV-Vis-NIR absorption, Polythiophene and derivatives

### 1. Introduction

Since poly(3-alkylthiophenes) were shown to be soluble and conducting [1], many substituted polythiophenes were prepared. It is still important to find new polymers showing more desirable properties. We have been studying the preparation and properties of new conducting polymers. Previously, 3-alkoxymethylthiophene were prepared by the reaction of 3-bromomethylthiophene with sodium alcoholates [2]. Since 3-bromomethylthiophene was unstable and its preparation was laborious, in this work we prepared 3-methoxymethylthiophene (MOMT) and 3-ethoxymethylthiophene (EOMT) by the new route reaction and investigated the electrochemical polymerization of these monomers.

### 2. Results and discussion

EOMT was prepared by the reaction of 3-lithiothiophene with chloromethyl ethyl ether (b. p. 94 - 95 °C / 38 mm Hg), and identified by elemental analysis, IR and NMR. MOMT was synthesized using a similar procedure. The electrochemical polymerization with various kinds of tetrabutylammonium salts was carried out using the same procedure as previously described [3]. The products were washed with acetonitrile and dried in vacuo. The conductivity was measured according to the four-probe method for films. The electrochemical polymerization of these monomers yielded high-quality films on the surface of the anode. Table 1 shows the conductivity results. The conductivity of PMOMT was 1.8 S/cm, one order of magnitude higher than that reported by Bryce et al. [4]. The conductivity of PEOMT was 26 S/cm for tetrabutylammonium hexafluorophosphate at -20 °C in propylene carbonate, showing PEOMT to be more highly conducting than PMOMT.

The current density was changed in the range 0.1 to 3 mA/cm<sup>2</sup>. A free-standing film was obtained at 1 mA/cm<sup>2</sup>. These results suggest that the electrochemical polymerization conditions for film formation are limited. For poly(3-alkylthiophenes) and poly(3-alkoxythiophenes), their conductivity decreases with an increase in the alkyl chain length. Although poly(3-methoxythiophene) is soluble in polar solvents, these polymers were insoluble in organic solvents. The characteristic IR bands of C-O-C stretching vibration of the ether groups of PEOMT and PMOMT did not deteriorate during the polymerization. The IR bands were observed at 1097 cm<sup>-1</sup> (PEOMT) and 1094 cm<sup>-1</sup> (PMOMT), respectively.

Fig. 1 shows absorption spectra of PEOMT film. The as-grown film (a) had three peaks at 0.88, 1.57 and 2.88 eV. The peak at 2.88 eV is due to the interband transition. The shapes of the spectra

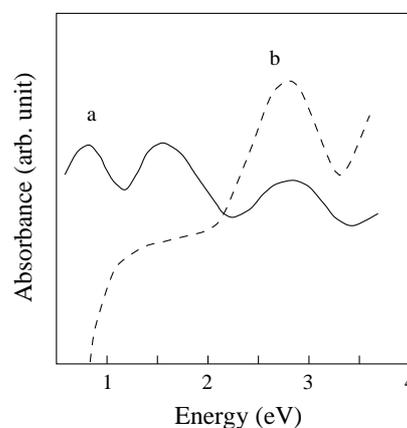


Fig. 1. Absorption spectra of PEOMT film prepared with Bu<sub>4</sub>NPF<sub>6</sub> (a): As grown film, (b): Neutral film

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Table 1  
Electrochemical polymerization of MOMT and EOMT

Monomer	Electrolyte	Temperature ( $^{\circ}C$ )	Current density ( $\text{mA}/\text{cm}^2$ )	Conductivity ( $\text{S}/\text{cm}$ )
MOMT	$\text{Bu}_4\text{NPF}_6$	0	1	0.14
MOMT	$\text{Bu}_4\text{NPF}_6$	-10	1	0.88
MOMT	$\text{Bu}_4\text{NPF}_6$	-20	1	1.9
MOMT	$\text{Bu}_4\text{NBF}_4$	-20	1	3.5
MOMT	$\text{Bu}_4\text{NClO}_4$	-20	1	0.03
EOMT	$\text{Bu}_4\text{NPF}_6$	-15	1	8
EOMT	$\text{Bu}_4\text{NPF}_6$	-20	1	26
EOMT	$\text{Bu}_4\text{NBF}_4$	-20	1	10
EOMT	$\text{Bu}_4\text{NClO}_4$	-20	1	$\text{H}^a$

a: products were heterogeneous film

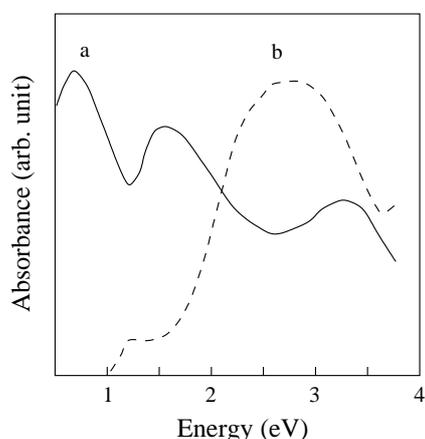


Fig. 2. Absorption spectra of PMOMT film prepared with  $\text{Bu}_4\text{NBF}_4$ . (a): As-grown film, (b): Neutral film.

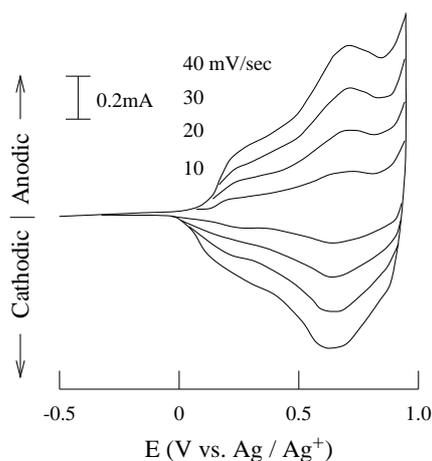


Fig. 3. Cyclic voltammograms of PEOMT film prepared with  $\text{Bu}_4\text{NPF}_6$ .

were independent of dopants. Although the neutral film(b) showed the peak due to the interband transition at 2.8 eV, the dopant could not be completely removed. In the case of PMOMT (Fig. 2), the as-grown film(a) had three peaks at 0.70, 1.57 and 3.30 eV. The neutral film(b) showed a peak due to the interband transition at 2.85 eV. Spectra of PMOMT and PEOMT were very similar to those of poly(3-nonylthiophene)(PNOT) and poly(3-undecylthiophene)(PUDT). Fig. 3 shows cyclic voltammograms (CV) of PEOMT. There were two anodic peaks at 0.23 and 0.72 V and two cathodic peaks at 0.2 and 0.68 V, respectively. In the case of PMOMT, there were two anodic peaks at 0.23 and 0.72 V and two cathodic peaks at 0.2 and 0.68 V, respectively. These values and shape of CV were very similar to those of PEOMT, PNOT and PUDT.

It is known that the locations and number of oxygen atoms in the side chain have significant effects on the optical and electrochemical properties of the substituted polythiophene [5]. The results of electrical and optical data for PMOMT and PEOMT indicate that one methylene group is enough to interrupt the electron-donating effect of the alkoxy group. Although PMOMT and PEOMT were expected to show advantageous properties of poly(3-alkylthiophene) and poly(3-alkoxythiophene), they are very similar to poly(3-alkylthiophene).

### 3. References

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