

## Synthesis and polymerization of new monomers derived from 3,4-ethylenedioxythiophene

P. Schottland, O. Stéphan, P.-Y. Le Gall and C. Chevrot\*

*Université de Cergy-Pontoise, Laboratoire de Recherche sur les Polymères et les Matériaux Électroactifs, 5 mail Gay-Lussac, 95031 Cergy-Pontoise cedex, France*

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\* Correspondence and reprints.

### RÉSUMÉ

Nous présentons ici la synthèse et certaines propriétés optiques de polymères solubles dérivés du 3,4-éthylènedioxythiophène. A partir d'un monomère 3,4-éthylènedioxythiophène fonctionnalisé par un groupement hydroxyméthyl, nous avons synthétisé des composés possédant des groupes latéraux de natures différentes. Nous avons examiné l'influence de la longueur de la chaîne d'un substituant alkyl sur la solubilité du polymère correspondant obtenu par oxydation chimique. D'autre part, les propriétés optiques de certains matériaux obtenus chimiquement sont également abordées.

**Mots-clés :** 3,4-éthylènedioxythiophene, monomère fonctionnalisé, polymère soluble.

### ABSTRACT

We report here the results of the synthesis of soluble polymers derived from 3,4-ethylenedioxythiophene. Starting from a 3,4-ethylenedioxythiophene monomer functionalized by an hydroxymethyl group, we synthesized several monomers bearing different side groups. The influence of alkyl chain length of side groups was studied in order to improve the solubility of the resulting polymer obtained by chemical oxydation. The optical properties of some chemically polymerized materials are also reported.

**Keywords :** 3,4-ethylenedioxythiophene, functionalized monomer, soluble polymer.

### INTRODUCTION

Poly(3,4-ethylenedioxythiophene), usually called PEDT, has attracted a great interest in the past few years. The commercial availability of the monomer (EDT) and the

outstanding properties of the resulting polymer are certainly the origin of its success. Despite its improved conductivity and stability compared to other polyheterocycles such as polypyrroles or polythiophenes [1, 2], PEDT has a main drawback : its processability. In fact, PEDT is not soluble but only dispersible at low concentrations in aqueous solutions. In order to yield soluble derivatives of PEDT, we decided to synthesize functionalized EDT monomers. We choosed therefore to synthesize as a starting material an EDT bearing an hydroxymethyl side group (EDTM). This monomer was of particular interest because of the versatility of the alcohol function.

## EXPERIMENTAL

### *Monomer synthesis*

The detailed synthesis of a 3,4-ethylenedioxythiophene (EDT) bearing an hydroxymethyl group (called EDTM) was previously described by us [3]. The EDTM is first obtained as a 90:10 mixture of 3,4-ethylenedioxythiophene and 1,3-propylenedioxythiophene derivatives. Contrary to what was observed by Ng and co-workers [4], EDTM could be isolated from the mixture by column chromatography using diethyloxide/cyclohexane (95:5). After reaction with an halogenated compound with a long alkyl chain, we obtain the desired alkoxy substituted 3,4-ethylenedioxythiophene monomers (see Fig. 1). Each compound was checked by  $^1\text{H}$  NMR (JEOL 270 MHz) by comparing to the theoretical spectra predicted with H-NMR version 2.5 from ACD-Software, available on line at <http://www.acdlabs.com>.

### *Chemical polymerization*

The obtained monomers were polymerized chemically in  $\text{CHCl}_3$  with anhydrous  $\text{FeCl}_3$  under dry nitrogen atmosphere following the procedure described by Jarvinen [5] for poly(3-octylthiophene) leading to a doped insoluble material in an average yield of 90%. The dedoping process was carried out in a 10%  $\text{NH}_4\text{OH}$  aqueous solution during 72 hours under a vigorous magnetic stirring. The polymers were then obtained by extraction using  $\text{CH}_2\text{Cl}_2$ .

## RESULTS

We synthesized several alkoxy substituted 3,4-ethylenedioxythiophene with different alkyl chain length (from  $n\text{-C}_6\text{H}_{13}$  to  $n\text{-C}_{16}\text{H}_{33}$ ) as shown on figure 1.

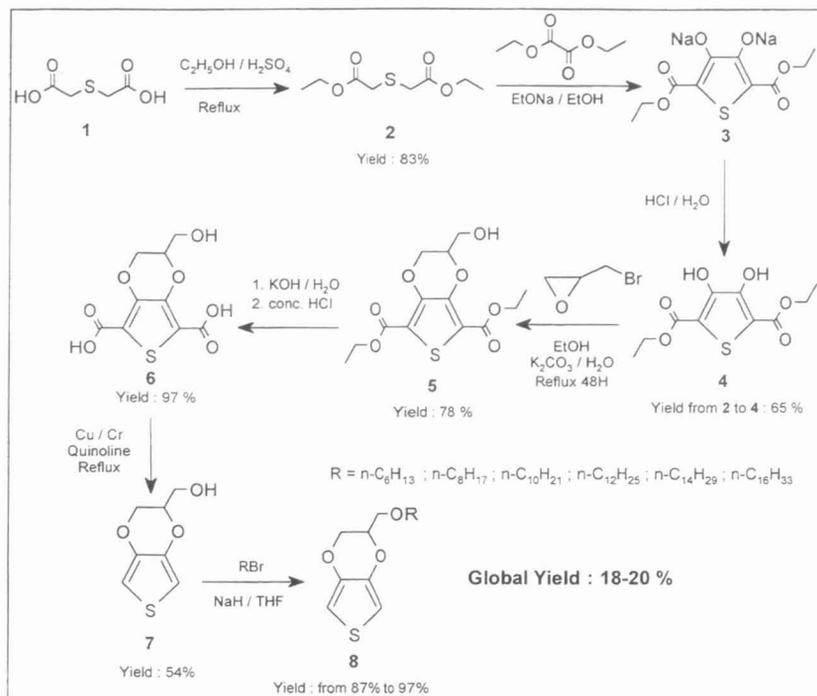


Figure 1 : The different steps of monomer synthesis

As previously noted by Reynolds [6] on similar compounds (alkyl substituted), the soluble fraction depends both on the alkyl chain length and on the amount of  $\text{FeCl}_3$  used for polymerization. The length of the side chain is more important because there is no soluble part for smaller chains than  $n\text{-C}_{12}\text{H}_{25}$ . The optimum conditions were for a  $n\text{-C}_{14}\text{H}_{29}$  and  $n\text{-C}_{16}\text{H}_{33}$  polymerized with 1.5 equivalents of  $\text{FeCl}_3$ . The respective soluble parts of polymers in  $\text{CH}_2\text{Cl}_2$  were 65% and 68%. The polymers called PEDT- $\text{C}_{14}$  and PEDT- $\text{C}_{16}$  gave approximately the same GPC results ( $M_w$ : 12.900 and 14.300

with a polydispersity of 1.45 and 1.65). Nevertheless, we should mention that THF doesn't seem to be the most accurate solvent because it causes the precipitation of a non negligible part of the  $\text{CH}_2\text{Cl}_2$  soluble polymer. As a consequence, the average molecular weights are probably underestimated. Improvements in the dedoping process are under investigations in order to solubilize a greater amount of polymer with a higher molecular weight.

To illustrate the electrochromic contrast of these polymers, we spray coated a glass window of  $8 \text{ cm}^2$  with a 0.5% solution of PEDT- $\text{C}_{16}$  in  $\text{CH}_2\text{Cl}_2$ . We recorded the visible absorption spectrum of this coated substrate before and after soaking 8 hours in a 5% solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in nitromethan (doping). We can note on figure 2 the strong difference between reduced and oxidized states of the polymer. These interesting optical properties open a wide range of applications to these materials.

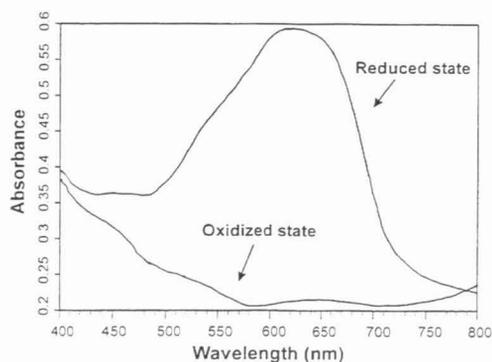


Figure 2 : Absorption spectra of PEDT- $\text{C}_{16}$  for oxidized and reduced forms

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