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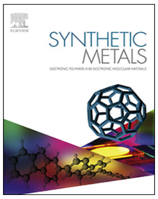

Synthesis and characterization of electroactive PEDOT-TEMPO polymers as potential cathode materials in rechargeable batteries

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ARTICLE INFO

Dedicated to our colleague, friend, and passionate chemist Dr. Günther Götz.

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ABSTRACT

Herein we report a novel series of conjugated polymers bearing stable nitroxide pendant groups for possible applications as cathode-active material in secondary batteries. The polymers comprise a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moiety immobilized on a poly(3,4-ethylenedioxythiophene) (PEDOT) backbone via ester groups (PEDOT-TEMPO **P1** and PEDOT-diTEMPO **P2**). The multistep synthesis of the corresponding monomers and their chemical characterization are described. Furthermore, oxidative electrochemical and chemical polymerization were performed in order to synthesize polymers on gram-scale for battery tests and to investigate their electrochemical behaviour, respectively. In addition, the electrochemical properties of polymer **P1** were studied by potentiodynamic and galvanostatic methods. The results demonstrate that the as-synthesized nitroxide radical polymers showed an electrochemically reversible redox reaction of the TEMPO radicals at 3.5 V vs Li/Li^+. When used as cathode material in galvanostatic cycling tests, **P1** exhibited a moderate initial specific capacity of 47 mA h g^{-1} (62% of the theoretical capacity) which slowly fades to 38 mA h g^{-1} within 50 cycles.

1. Introduction

In the last decade, a great deal of interest has been devoted to the synthesis and investigation of new conjugated oligomers and polymers due to their application in various fields, such as light-emitting diodes (OLED) [1], plastic lasers [2], field-effect transistors [3], photovoltaic devices [4], and more recently as active materials in organic secondary batteries [5]. Although many conducting polymers have been developed so far, poly(3,4-ethylenedioxythiophene), also known as PEDOT [6], is among the most studied conjugated materials from both, fundamental and practical perspectives [7]. PEDOT features versatile organic chemistry, excellent environmental and thermal stability at simultaneous remarkable conductivity [8]. Exceptionally, pristine PEDOT has been used as cathode material in organic batteries with limited success due to moderate specific energy density [9]. To overcome this limitation, it has been reported that PEDOT can be equipped with suitable redox moieties such as anthraquinones [10].

Stable nitroxide radical species have also been shown to be promising candidates for charge storage due to their electrochemically reversible redox properties [11]. One of the best-known stable nitroxide radicals is represented by 2,2,6,6-tetramethyl-1-piperidine-1-oxyl (TEMPO), which offers high charging/discharging rates due to its rapid and stoichiometric reversible redox process at low potentials [12]. TEMPO is reversibly oxidized from the neutral radical to the cation at around 0.3 V vs Fc/Fc^+. The first attempt to use a TEMPO radical as an electrode-active group for organic batteries was published in 2002 by Hasegawa et al. [13] Since then, some examples of TEMPO nitroxide moieties immobilized on aliphatic or conjugated polymer backbones have been reported in the literature [14].

In the course of investigating novel thiophene-based conjugated polymers, we aimed to synthesize TEMPO-substituted PEDOT as possible energy storage material in rechargeable organic batteries. To the best of our knowledge, there have been no examples for TEMPO-decorated PEDOTs as active materials in a secondary battery described so far. Recently, Armand et al. have published a similar approach for the synthesis of EDOT-TEMPO that was investigated as a conductive binder in $LiFePO_4$ electrodes for Li-ion batteries [15]

In this publication, we report synthesis and characterization of conjugated polymers, **P1** and **P2**, which combine a PEDOT backbone with TEMPO moieties as redox-active pendant groups. The connection of the conjugated backbone and the nitroxide radical was realized by using an ester linkage (**M1**). As the theoretical capacity of a battery is

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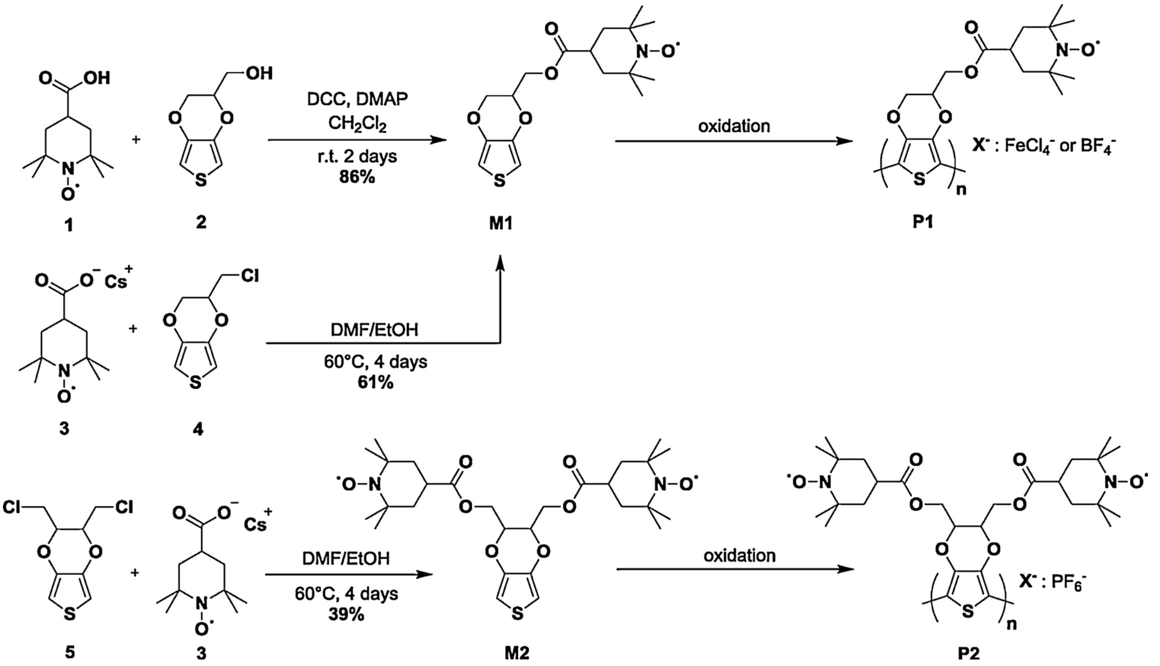

Scheme 1. Synthesis of EDOT-TEMPO monomers **M1** and **M2** and their corresponding polymers **P1** and **P2** (attempted) by oxidative polymerization.

directly connected to the number of redox-active groups in the molecule, we synthesized a second monomer (**M2**) featuring two TEMPO functionalities on each EDOT unit. It allows increasing the theoretical capacity from 76 mA h g^{-1} for **M1** to 95 mA h g^{-1} for **M2**, respectively. Moreover, the electropolymerization of the monomers, as well as the characterization of the corresponding films are described. First investigation on polymer **P1** as active material in batteries is also reported.

2. Results and discussion

2.1. Syntheses and characterizations of the conjugated polymers

The synthetic routes for the synthesis of the EDOT-TEMPO monomers **M1** and **M2** and the corresponding polymers **P1** and **P2** are shown in Scheme 1 and in the electronic supporting information (ESI). EDOT-TEMPO monomer **M1**, which contains an EDOT unit and one TEMPO moiety, which are chemically linked by an ester group, was synthesized via two different synthetic routes. The first one consisted of a nucleophilic substitution reaction of TEMPO carboxylate salt **3** and chloromethyl-EDOT **4**. This reaction permits to isolate the desired monomer after 4 days at 60 °C in a yield of 61%. The long reaction time and the moderate yield are due to the weak nucleophilicity of the TEMPO salt. The second synthesis route consisted of a Steglich esterification reaction [16] of TEMPO-carboxylic acid **1** and hydroxymethyl-EDOT **2** in the presence of activating agent dicyclohexylcarbodiimide (DCC). By using this route, the yield was increased to 86% when the reaction was run at room temperature for two days. Monomer **M2** comprising two TEMPO ester moieties was obtained in moderate yield (39%) by a nucleophilic substitution reaction of TEMPO carboxylate salt **3** and dichloromethyl-EDOT **5** at room temperature after 4 days. After reduction of the TEMPO radical moiety to the corresponding hydroxylamine with ascorbic acid, the structure of both monomers has been characterized by means of NMR spectroscopy, elemental analysis, mass spectroscopy, and IR-spectroscopy (ESI, Fig. S1a).

In order to synthesize the target polymers on larger scale, oxidative chemical polymerization was performed on monomers **M1** and **M2** by using different oxidants. Polymerization of TEMPO-EDOT **M1** took place with iron(III)chloride ($FeCl_3$) as oxidant in a solution of tetrachloromethane/nitromethane (CCl_4/CH_3NO_2) under very mild conditions (0 °C to room temperature, 3 h). According to the mechanism of oxidative polymerization with $FeCl_3$ [17] the oxidized polymer chains are complexed by $FeCl_4^-$-counter anions while growing leading to a reduced solubility of the polymer. Indeed, quick formation of the polymer as $FeCl_4^-$-salt (**P1-FeCl$_4$**) was observed during the first minutes of the polymerization process. If copper(II)tetrafluoroborate Cu$(BF_4)_2$ was used as oxidant [18], polymerization of **M1** was possible in MeCN under more elevated conditions (80 °C, 48 h) whereby complexation occurred with BF_4^--counter anions (**P1-BF$_4$**). This step was followed by a post-polymerization treatment with hydrogen peroxide in methanol in order to retrieve the nitroxide radical moieties, which were partially deactivated during the polymerization process most probably by the formation of hydroxylamine and/or piperidinyloxy copper complexes. With both oxidants, functionalized PEDOT polymers were isolated as dark insoluble solids by centrifugation, washed with several solvents (acetone, $CHCl_3$, MeOH, H_2O, MeCN, Et_2O) and purified by Soxhlet extraction (MeOH, MeCN, $CHCl_3$) to remove all metal salts and oligomers. In this way, the functionalized PEDOTs as $FeCl_4^-$-salt (**P1-FeCl$_4$**) and BF_4^--salt (**P1-BF$_4$**) were obtained in yields of 94% and 21%, respectively (ESI).

Similar conditions were applied to the polymerization of EDOT-diTEMPO monomer **M2**, however, all attempts to form the corresponding polymer **P2** failed (ESI). Despite the oxidation potential of the EDOT unit is in good agreement with the oxidative force of the oxidants, in particular for $FeCl_3$, oxidative chemical polymerization did not occur presumably because the presence of the TEMPO groups immobilized at the EDOT moiety results in a high sterical hindrance, which reduces the accessibility of the oxidant to the reactive α-positions of the EDOT-thiophene.

Due to the complete insolubility of the obtained PEDOT-TEMPO polymers (**P1-FeCl$_4$** and **P1-BF$_4$**) in any common organic solvent, the polymers were characterized in the solid state. In this respect, the thermal stability was investigated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results (ESI, Fig. S2), corresponding to the weight loss over time while the sample is heated, showed a good stability of up to 170 °C (less than 5% mass loss). Between 170 °C and 250 °C, the polymers started to slightly degrade (10% loss) before a complete degradation occurred