

Functional End-Capped Conducting Poly (3,4-Ethylenedioxythiophene)

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Abstract. Methacrylate-terminated Poly(3,4-Ethylenedioxythiophene) (PEDOT) polymers with controlled degree of polymerization were successfully prepared by direct oxidative polycondensation between Ethylenedioxythiophene (EDOT) and a cross-linkable methacrylate end-capper monomer, obtained via Friedel Crafts acylation starting from EDOT and Methacryloyl chloride. The new polymer was synthesized in order to overcome the well-known technical problems of PEDOT, i.e. difficult processability and patterning, due to its poor solubility in common organic and inorganic solvents. The chemical structure and the degree of polymerization of the end-capped polymers were determined by ¹H NMR spectra. A new synthesis of Methacrylate end-capped PEDOT with controlled degree of polymerization, soluble in common organic and chlorinated solvents and with improved conductivity, 210 S/cm, was performed. This method includes: direct oxidative polycondensation of 3,4-Ethylenedioxythiophene (EDOT) in the presence of a cross-linkable end-capper, i.e. Methacrylate end-capped EDOT prepared via Friedel Crafts acylation with Methacryloyl chloride and oxidant species, i.e. ferric sulfate. Furthermore, the oxidative polycondensation of EDOT monomer and Methacrylate end-capped EDOT in the presence of Sulfonated Polyethersulfone (SPES)- characterized by different degree of Sulfonation (DS)- as dopant agent was performed, leading to functional end-capped conducting PEDOT, easy to process and pattern, with conductivity of 210 S/cm, 50 S/cm higher than the one of commercial PEDOT.

Keywords: conducting polymer, PEDOT, oxidative polycondensation, end-capping monomer, Sulfonated Polyethersulfone.

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INTRODUCTION

Polythiophene and its derivatives have been at the center of considerable scientific interest for their attractive chemical, physical and conductive features for the last years [1]. Among the derivatives of Polythiophene, Poly (3,4-Ethylenedioxythiophene) (PEDOT) is one of the most successful conducting polymers due to its low bandgap, excellent environmental stability, high electrical conductivity and transparency when in the form of thin oxidized films [2].

Since the first synthesis of PEDOT in 1989 [3], several studies on this polymer have been carried out [4] and many applications have been reported for solid electrolytic capacitors, anti-electrostatic agents, transparent electrodes in light emitting diodes, and under layers for the metallization of printed circuit boards [5].

Numerous researches have been made on the synthesis of PEDOT by electrochemical [6] and chemical oxidative [7] polymerization of 3,4-Ethylenedioxythiophene (EDOT), that has been recognized as more suitable for mass production than other possible monomers [8]. In 2005, Lei and others [9] suggested a new technique for PEDOT polymerization: the synthesis is performed by high-concentration emulsion polymerization of EDOT in the presence of sodium salt of 2-naphthalenesulfonic acid as dopant agent and ferric sulfate as oxidant. The conductivity of PEDOT obtained using this polymerization resulted to be 160 S/cm, an excellent value for an organic conducting polymer. Despite the excellent conducting properties, an important drawback of PEDOT is its poor solubility in the common organic and inorganic solvents, which is only partially circumvented in PEDOT-Sulfonated Polystyrene (SPS) composites [10].

In the present work we have developed a synthetic route able to enhance PEDOT solubility and conductivity. Methacrylate-terminated PEDOT polymers with controlled degree of polymerization (n), ranging from 4 to 50, were successfully synthesized via oxidative polymerization of EDOT and cross-linkable Methacrylate end-capped EDOT, with ferric sulfate as oxidant. EDOT end-capping monomer was prepared through Friedel Crafts acylation starting from EDOT and Methacryloyl Chloride. The chemical structure and the degree of polymerization of the end-capped polymers were determined by ^1H NMR spectroscopy. The polymers synthesized have excellent solubility in several organic (dimethylacetamide, dimethylformamide and toluene) and chlorinated solvents (methylene chloride and chloroform). Furthermore, the use of cross-linkable end-caps makes EDOT-based polymers soluble in organic and chlorinated solvents in reversible conditions; the cross-linking of PEDOT film is then possible after UV exposure.

In order to improve PEDOT conductive properties, the dopant agents based on sulfonic groups commonly used with PEDOT are 2-Naphthalenesulfonic acid, para toluene sulfonic acid or others [11]. Besides these molecules, also Sulfonated Polyethersulfone (SPES), obtained as reported in our previous work [12], can be used as dopant agent thanks to the possibility to modulate the moieties of sulfonic groups in the polymeric chains.

In this work, SPESs with different degree of sulfonation (DS) were synthesized via polycondensation using a sulfonated comonomer, 2,5-Dihydroxybenzene-1-sulfonate potassium salt. The oxidative polymerization of EDOT and functional end-capped EDOT monomers with ferric sulfate as oxidant and SPES as dopant was performed; it was found that PEDOT conductive features increase as DS of SPES increases reaching 210 S/cm, a value far higher than the one of commercial PEDOT (160 S/cm).

EXPERIMENTAL

3,4-Ethylenedioxythiophene (EDOT, >97%), Methacryloyl Chloride ($\geq 97\%$), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, >97%), acetone ($\geq 99.9\%$), Dimethylacetamide (DMAc, $\geq 99.5\%$), toluene (99.8% anhydrous), Dimethylformamide (DMF, $\geq 99.5\%$), Methylene chloride (CH_2Cl_2 , $\geq 99.5\%$), Chloroform (CHCl_3 , $\geq 99.5\%$) and Dimethyl sulfoxide- d_6 (DMSO- d_6 , 99.96 atom % D) were supplied by Sigma Aldrich and used without further purification.

Sulfonated Polyethersulfone (SPES) with three different degree of sulfonation (DS) -0.5, 0.75, 1 meq $\text{SO}_3^- \cdot \text{g}^{-1}$ - was synthesized as reported in previous work [12].

DMAc suspension of SPES with 0.5 meq $\text{SO}_3^- \cdot \text{g}^{-1}$ (1.143g in 5ml) was mixed with EDOT (0.50ml, 0.665g) and methacrylate end-capped EDOT (0.555g) on a magnetic stirrer, at room temperature and under air atmosphere. DMAc solution of ferric sulfate (1.638g in 5ml) was added drop-wise by to the suspension. The reaction mixture was stirred for 5 h at room temperature.

The polymerization reaction was repeated changing both SPES DS -0.75, 1 ($\text{SO}_3^- \cdot \text{g}^{-1}$) - and the reaction time: 10 h, 15 h, 20 h and 24 h. The dark-blue deposition obtained was collected by centrifugation with Eppendorf centrifuge, 8000rpm, washed with acetone and dried under vacuum at 30°C and 4 mbar overnight.

The structures of end-capped EDOT monomer and PEDOT copolymers and the degree of polymerization of the resultant polymers were determined by ^1H NMR spectra, collected at 25°C with a BRUKER 400 MHz spectrometer. Samples for the analyses were prepared dissolving 10-15 mg of polymer in 1 ml of DMSO- d_6 . Electrical conductivity of PEDOT was measured employing Metrohm conductivity meter.

RESULTS and DISCUSSION

Methacrylate-terminated PEDOT polymers with controlled degree of polymerization (n), $4 \leq n \leq 50$, were successfully synthesized via oxidative polymerization using ferric sulfate as oxidant species. The degree of polymerization was controlled through the modulation of reaction time -5 h to have $n=4$, 10 h to get $n=20$, 15 h to have $n=30$, 20 h for $n=45$ and 24 h for $n=50$ - and determined by ^1H NMR spectra.

Figure 1 shows the synthetic route for preparing Methacrylate end-capped PEDOT. The end-capper used in this work is a Methacrylate end-capped EDOT monomer, synthesized via Friedel Crafts acylation between EDOT and Methacryloyl Chloride, the latter characterized by the presence of a flexible chain and vinyl cross-linkable group.

The use of cross-linkable end-capped monomers can be an effective way to improve PEDOT processability and patterning: in fact, adding flexible chains promotes the solubility of PEDOT in the common organic and inorganic solvents in reversible conditions and only after UV light exposure, thanks to the presence of cross linkable terminations, it is possible to obtain a stable crosslinked polymeric film.

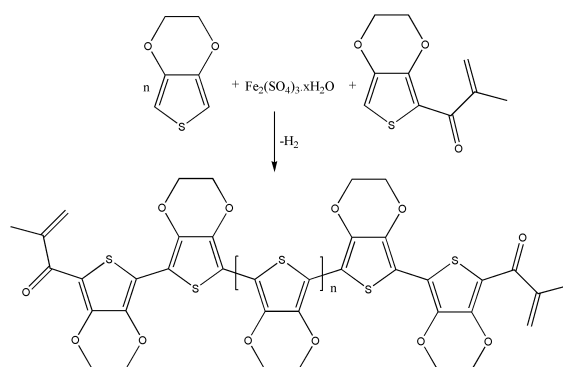


FIGURE 1. Synthetic route for Methacrylate end-capped PEDOT.

The polymers obtained are characterized by excellent solubility in many organic -dimethylacetamide, dimethylformamide and toluene- and chlorinated solvents -methylene chloride and chloroform- for every degree of polymerization considered.

A series of SPES copolymers with three different DS -0.5-0.75-1.0 $\text{meq SO}_3^- \cdot \text{g}^{-1}$ - were successfully synthesized by the aromatic nucleophilic substitution reaction of 4,4'-difluorodiphenylsulfone, 4,4'-dihydroxydiphenyl and a sulfonated comonomer, 2,5-dihydroxybenzene-1-sulfonate potassium salt: these SPES were used as PEDOT dopant agents, thanks to the charge separation deriving from the sulfonated comonomer (Fig. 2). The study related to PEDOT: SPES interaction mechanism is now in progress and will be discussed in subsequent works.

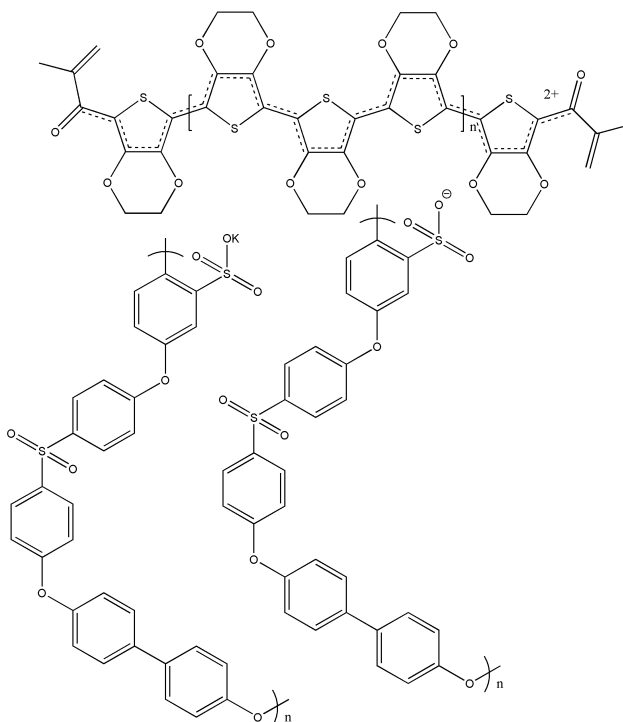


FIGURE 2. SPES as dopant agent for Methacrylate end-capped PEDOT.

The conductive properties of Methacrylate end-capped PEDOT were studied both in function of different PEDOT degrees of polymerization (SPES with DS of 1 $\text{meq SO}_3^- \cdot \text{g}^{-1}$ was used as dopant agent), Fig. 3 (a), and in function of the DS of SPES employed as dopant agents, using Methacrylate end-capped PEDOT with degree of polymerization of 50n, Fig. 3 (b).

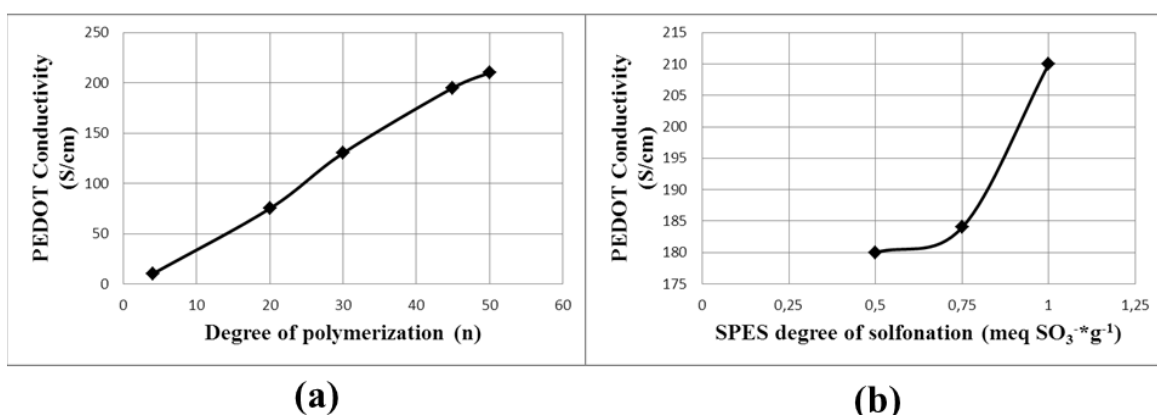


FIGURE 3. (a) PEDOT conductivity vs. PEDOT degree of polymerization (DS of SPES = 1 meq $\text{SO}_3^- \cdot \text{g}^{-1}$); (b) PEDOT conductivity vs. SPES DS (PEDOT degree of polymerization = 50).

Fig. 3 (a) shows that PEDOT conductivity with SPES having DS of 1 meq $\text{SO}_3^- \cdot \text{g}^{-1}$ increases as PEDOT degree of polymerization gets higher: 10 S/cm in the case of 4n, 75 S/cm for 20n, 130 S/cm for 30n, 195 S/cm for 45n and, at last, 210 S/cm in the case of PEDOT characterized by 50n. This last value is 50 S/cm higher than the one of commercial PEDOT. Fig 3b confirms that the higher the DS of SPES used as dopant agent, the higher the conductivity. The results obtained suggest that Methacrylate end-capped PEDOT conductive properties are straightly dependent by both PEDOT degree of polymerization and SPES DS.

CONCLUSIONS

A new synthesis of Methacrylate end-capped Poly (3,4-Ethylenedioxythiophene) (PEDOT) with controlled degree of polymerization, soluble in common organic and chlorinated solvents and with improved conductivity, 210 S/cm, was performed. This method includes: direct oxidative polycondensation of 3,4-Ethylenedioxythiophene (EDOT) in the presence of a cross-linkable end-capper, i.e. Methacrylate end-capped EDOT prepared via Friedel Crafts acylation with Methacryloyl chloride, oxidant species and dopant agent, Sulfonated Polyethersulfone (SPES), characterized by different degree of sulfonation (DS).

It was found that the use of cross-linkable end-caps renders PEDOT soluble in the common organic and chlorinated solvents and only after UV exposure it is possible to obtain a stable crosslinked PEDOT film. Furthermore PEDOT conductive features increase as both PEDOT degree of polymerization increases and SPES DS increases.

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