

Improvement of optical properties and redox stability of poly(3,4-ethylenedioxythiophene)

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ABSTRACT

In order to improve the optical properties and redox stability of poly(3,4-ethylenedioxythiophene) (PEDOT) without changing its electrochemical and electrochromic behaviour, it was supported with alkyl-substituted polyhedral oligomeric silsesquioxane (POSS) cage. The corresponding copolymers were obtained electrochemically via potentiostatic or potentiodynamic methods and compared to the parent homopolymers. Electrochemical polymerization of EDOT and POSS containing EDOT called EDOT-POSS in various monomer feed ratios was performed in an electrolyte solution of 0.1 M TBAPF₆ dissolved in a mixture of dichloromethane and acetonitrile (1/3: v/v). Just as PEDOT, the copolymers represented the similar band gap (1.61 eV), redox and electrochromic behaviors. On the other hand, when compared to the parent PEDOT, the presence of POSS cages in the copolymer backbone improved the redox stability and optical properties of PEDOT such as higher percent transmittance change (65% at 621 nm), higher transparency at oxidized state, lower switching time (~1.0 s) and higher coloration efficiency (463 cm²/C for 95% switching) as well as higher electrochemical stability (86% of its electroactivity retains after 1750 cycles under ambient conditions).

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) as one of the well-known members of the conjugated polymers has continued to attract the interest of many scientists due to its potential industrial applications like electrochromic displays and devices, organic light-emitting diodes, organic photovoltaic devices, field-effect transistors, capacitors, chemical sensors, etc. [1–9] The extent of this interest can be understood by searching on ‘PEDOT’ in the search engine *Web of Science* (date: May 22, 2017). It can be easily seen that many research papers and patents from academic and industrial areas have been published on the design, synthesis and applications of PEDOT and its derivatives. For example, there have been nearly 9000 published works and they have been cited more than 170,000 times since 1994.

The reasons behind this attraction are its stable and reversible electrochemical and optical properties such as high optical contrast ratio ($\Delta\%T = 52$ at 600 nm), reversible electrochromic behavior (dark blue/violet when neutralized and transparent sky blue when oxidized), low response time (2.0–2.5 s) [10]. When compared to the thiophene analog, the presence of oxygen atoms on 3,4 position results in the rise in the electron density of the aromatic ring and the

polymerization also proceeds through 2,5-coupling due to the blocking of 3,4-position, which causes well-defined and linear polymer backbones. However, the insolubility problem is seen as the biggest barrier for the opto-electronic application of PEDOT. In order to overcome this problem, the parent monomer was substituted with a number of substituents or the polymerization was performed in the presence of comonomer, surfactants and dispersants [1,2,11,12]. Although at the first sight, it seemed that the insolubility problem was overcome, the modified PEDOT materials have several disadvantages including low thermal and electrochemical stability, short life stability at open air, low optical contrast, different optical behavior, long response time, etc. For example, despite the fact that soluble tetradecyl substituted PEDOT was polymerized successfully via oxidative polymerization, it is dark purple in its neutral state unlike the parent PEDOT [12].

Recently, Reynolds and his colleague [13] reported a highly soluble copolymer by using alkoxy-functionalized 3,4-propylenedioxythiophene with unfunctionalized EDOT in varying ratios in order to mimic the electrochemical and optical properties of PEDOT. The obtained copolymers showed highly tunable optical and electronic properties. Also, in our previous work, EDOT was combined with alkyl-substituted polyhedral oligomeric silsesquioxane (POSS) cage to yield a

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soluble PEDOT analogue [14]. Even though the obtained polymer called PEDOT-POSS has a higher positive potential of redox couple when compared to the parent PEDOT, it exhibited higher electrochemical stability and improved optical properties (optical contrast, coloration efficiency, switching time, stability, etc.). Here, the combination of inorganic nano-sized POSS cages which have silicon-oxygen inner center, 1–3 nm variable sizes and modifiable organic functional side group, and conjugated polymer under the same roof led to an improvement in solubility in common solvents. When POSS units were integrated to any conjugated polymer, thermal [15–18], electrochemical [19–21] and mechanical properties [22–24] of the corresponding materials were improved as well. Moreover, it was reported that POSS containing materials exhibited higher performance in optoelectronic applications [15–18,21–27] when compared to their analogues. For example, it is well-known that polyfluorenes have been used as a blue color light source in PLEDs, but they are not thermally stable, which causes undesired green emission (keto effect) [16,24,27]. Chen [28], Shim [24] and their colleagues reported a solution for this problem by integrating POSS cages on polyfluorene. The obtained electroluminescence devices showed much better performance and thermal stability.

Unfortunately, there are few studies on the integration of POSS cages to the electrochromic polymers [19,20]. For instance, polyanilines [19] containing POSS units have better ionic conductivity and 40% higher optical contrast than the parent polyaniline.

In the light of these reports and the encouraging results, we turned our attention to improve the optical properties and redox stability of PEDOT without changing its electrochemical and electrochromic behaviors; therefore, during electropolymerization EDOT-POSS units were incorporated into PEDOT skeleton (Scheme 1). The copolymers were obtained electrochemically in various monomers feed ratios via potentiostatic or potentiodynamic methods. The findings showed that the corresponding polymers have higher redox stability, optical contrast and coloration efficiency as well as shorter switching times when compared to PEDOT.

2. Experimental section

EDOT and tetrabutylammonium hexafluorophosphate (TBAH) and all the solvents were obtained from Sigma Aldrich and used as received. EDOT-POSS was synthesized according to literature reported elsewhere [14].

Electrochemical polymerization and measurements were recorded by using a Gamry PCI4/300 and Gamry Reference 600 potentiostat-galvanostat at room temperature. Spectroelectrochemistry studies and the colorimetric measurements (standard illuminator D65, field of width 10° observer) of the samples were carried out via Specord S600 spectrophotometer. The color space was given by the International Commission of Illumination with L*a*b* color coordinates. Platinum cobalt DIN ISO 621, iodine DIN EN 1557, and Gardner DIN ISO 6430

are the references of colorimetric measurements. The optoelectrochemical spectra of the film were recorded in-situ under applied different potentials by using three-electrode system (an ITO as a working electrode, a platinum wire as a counter electrode and a silver wire as a reference electrode) in a UV cuvette.

Electropolymerization was carried out electrochemically by potentiostatic and potentiodynamic electrolyses on both platinum disc and indium-tin oxide electrodes (ITO, Delta. Tech. 8–12 Ω, 0.7 × 5.0 cm²). For electropolymerization, an electrolyte solution of 0.1 M TBAH dissolved in a mixture of dichloromethane and acetonitrile (1/3: v/v) was used in one compartment cell. In addition, the redox behaviour of the polymer films was studied in 0.1 M TBAH in acetonitrile. Three-electrode system containing a platinum disc (0.0314 cm²), as a working electrode, a platinum wire as a counter electrode and a Ag/AgCl electrode as a reference electrode was used during the electrochemical studies.

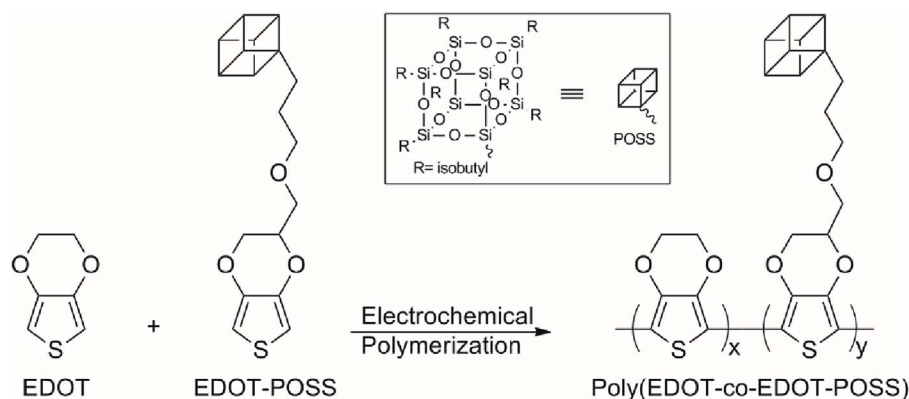
The electrochemical stability and switching behaviour of the polymer films were used to monitor the change in the current intensity and optical percent transmittance, respectively, by using a square wave potential method under applied external constant potentials between the redox states in various time intervals. The electroactivity of the polymer films were compared to their initial values by using cyclic voltammetry. FTIR spectra were recorded on Nicolet 510 FTIR with an attenuated total reflectance (ATR). Also, scanning electron microscope (SEM) images were recorded on Quanta 400 FEI FE-SEM.

3. Results and discussions

First of all, the redox behaviors of EDOT and EDOT-POSS monomers were investigated by using a cyclic voltammetry technique since the oxidation values of the co-monomers must be appropriate to each other in order to get reasonable copolymers via constant potential or potentiodynamic electrolysis. As shown in Fig. 1(a), both monomers exhibited an irreversible oxidation peak at 1.46 V vs Ag/AgCl, which indicates that the electrochemical co-polymerization of EDOT and EDOT-POSS was feasible.

The monomer EDOT-POSS and its corresponding polymers were soluble in dichloromethane and insoluble in acetonitrile, which hinders the electropolymerization on the electrode surface. Therefore, the copolymerization was carried out by using the solvent mixture in order to hinder the solubility of the polymer film formed on the electrode surface by cosolvent effects.

As seen in Fig. 1(b), the cyclic voltammogram obtained after a certain number of potentiodynamic scans looks like a fingerprint of the formation of a conjugated polymer film. The repetitive scans between –0.8 V and 1.6 V resulted in the formation of an insoluble copolymer film called poly(EDOT-co-EDOT-POSS) (CP-n, where n = 1, 5, 10, 15 defines the % of EDOT-POSS in co-monomer mixture) (see Table 1 and Scheme 1) on the electrode surface since upon successive scan a new redox couple appeared between –0.1 V and 1.5 V and intensified as a



Scheme 1. Chemical structures of EDOT, EDOT POSS and their corresponding copolymer poly(EDOT-co-EDOT-POSS).

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