



# A new carborane based polymeric electrochrome



Emine Gul Cansu-Ergun, Atilla Cihaner\*

Atilim University, Department of Chemical Engineering and Applied Chemistry, Atilim Optoelectronic Materials and Solar Energy Laboratory (ATOMSEL), TR-06836 Ankara, Turkey

## ARTICLE INFO

### Article history:

Received 9 July 2013

Received in revised form 20 August 2013

Accepted 26 August 2013

Available online 31 August 2013

### Keywords:

Electropolymerization

Electrochromics

Carborane

Thiophene

EDOT

## ABSTRACT

New electrochromic copolymers of 3,4-ethylenedioxythiophene and di(m-carboranyl thiophene) were synthesized, characterized and their electro-optical properties were reported. The copolymers were successfully prepared from various monomer feed ratios using electrochemical polymerization technique. It can be conjectured that electrochemical and optical properties of the copolymers can be adjusted by playing with monomer feed ratios. For example, the maximum wavelength of poly(3,4-ethylenedioxythiophene) at 600 nm can be shifted to lower values (i.e., 522 nm) by increasing the ratio of di(m-carboranyl thiophene) in the monomer mixture. The copolymer films also have low band gap values between 1.69 and 1.82 eV and showed electrochromic properties; purple when neutralized and transparent sky blue when oxidized. Also, during redox switching the films exhibited a percent transmittance change between 32% and 46% with a switching time between 1.0 s and 1.3 s.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

According to the application areas, the electro-optical and chemical properties of conjugated polymers can be tuned by modifying the starting monomers. For example, the substitution of luminol as a chemiluminescent unit to a conjugated dithienylpyrrole monomer can be used as a sensor to detect reactive oxygen species and blood, which makes it a promising candidate for use in forensic application [1]. However, it is not easy to use the conjugated polymers in technological applications such as light emitting diodes (LEDs) [2–4] and solar cells [5,6] due to their chemical and thermal instabilities. In order to improve their robustness, hybrid monomers consisting of organic and inorganic units combined into the same pot can be one of the promising ways. Here, the incorporation of inorganic unit can be unresponsive towards chemical and thermal factors. For this aim, the combination of carborane units into the polymer backbones may be one of the good attempts since carboranes have low nucleophilicity, chemical inertness, high hydrophobicity, high electron deficient nature, large molecule volume, high electrochemical and thermal stabilities [7,8]. In the light of this information, it can be easily concluded that these properties can be transferred to the hybrid monomers and their polymers. For instance, the electrochemical stability of polypyrrole was improved by the substitution of carborane to the pyrrole unit [9–12]. Inspired by these studies, Fabre and his colleagues extended these approach to thiophene combined with carborane clusters (*ortho*-, *meta*-, *para*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) [13,14]. When compared

to naked polythiophene, the corresponding polymers were found to be thermally more stable. For example, polythiophene bearing carborane cage exhibited less than 10% of weight loss up to 800 °C, whereas polythiophene showed a loss in mass (about 80%) up to 600 °C. Based on these findings, the researchers began to use carborane based conjugated polymers in advanced technological applications. For instance, Carter and his colleagues firstly incorporated carborane clusters into polyfluorene backbone to surmount the stability problems of blue emitting color [15–21]. Polyfluorene bearing carborane cages resulted in a stable blue emission with a suppression of the green emission even after heating to 180 °C.

Examples of conjugated polymers with carborane cages in industrial applications have still been rare and newer ones are welcome. For instance, to the best of our knowledge, no reports exist on electrochromic polymers with carborane cages in electrochromic device. In order to be amenable for use, it is need to increase the spectroelectrochemical properties of carborane supported by conjugated polymers. For this aim, the copolymer formation can be one of the good approaches and 3,4-ethylenedioxythiophene (EDOT) will be a good candidate. In this study, we reported the first copolymer formation containing di(2-thiophenyl)carborane (1) and EDOT units (Scheme 1).

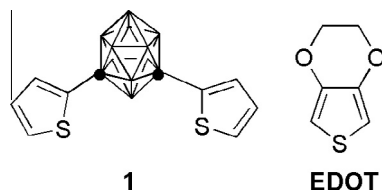
## 2. Experimental

### 2.1. Materials

All chemicals, except for m-carborane (KatChem), were purchased from Aldrich Chemical and used as received unless other-

\* Corresponding author. Tel.: +90 3125868304x8528; fax: +90 3125868091.

E-mail address: [cihaner@atilim.edu.tr](mailto:cihaner@atilim.edu.tr) (A. Cihaner).



Scheme 1. Chemical structures of monomers.

wise noted. The synthesis of monomer **1** is reported elsewhere [13]. For electrochemical synthesis and analysis, acetonitrile (ACN) as a solvent and tetrabutylammonium hexafluorophosphate (TBAH) (Fluka,  $\geq 98\%$ ) as a supporting electrolyte were used. ACN was dried and distilled on  $\text{CaH}_2$  (Acros,  $\geq 99\%$ ) prior to use. A platinum disc ( $0.02 \text{ cm}^2$ ) as a working electrode, a platinum wire as a counter electrode and a Ag/AgCl electrode in 3 M NaCl (aq) solution as a reference electrode were used. 1.5 mM solution of ferrocene exhibits an onset potential of oxidation at 0.36 V vs. Ag/AgCl. *In situ* optical properties were investigated using an indium-tin oxide (ITO, Delta. Tech. 8–12  $\Omega$ ,  $0.7 \text{ cm} \times 5 \text{ cm}$ ) electrode in a UV cuvette. A platinum wire and a Ag wire electrodes were used as a counter electrode and a pseudo-reference electrode, respectively. In order to obtain repeatable results, the polymer films coated on ITO had been switched between its redox states several times in order to break-in the polymer film in a monomer-free electrolyte solution prior to electro-optical experiments. Electroanalytical measurements were performed using a Gamry PCI4/300 potentiostat-galvanostat and the electro-optical spectra were monitored on a Specord S600 spectrometer.

### 3. Results and discussion

One of the most important parameters is the compliance of the oxidation peaks of the monomers used to obtain the copolymer. After the determination of oxidation peaks of comonomers, copolymers can be prepared by both potentiodynamic or potentiostatic methods. The oxidation potential of co-monomers were determined by cyclic voltammetry and the resulting cyclic voltammograms are shown in Fig. 1. As seen from Fig. 1, both EDOT and

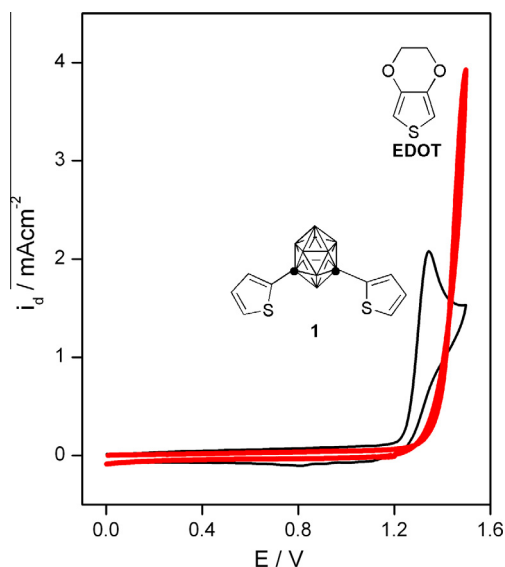


Fig. 1. Cyclic voltammograms of monomer **1** ( $1.25 \times 10^{-2} \text{ M}$ ) and EDOT ( $1.25 \times 10^{-2} \text{ M}$ ) on Pt electrode ( $0.02 \text{ cm}^2$ ) in 0.1 M TBAH electrolyte solution in ACN at a scan rate of 100 mV/s vs. Ag/AgCl.

monomer **1** exhibit an irreversible oxidation peak at 1.48 V and 1.34 V vs. Ag/AgCl, respectively. This proximity between oxidation potential values makes them a good candidate for the synthesis of a copolymer. Also, the systematic potential increasing results in different copolymer formation upon moving from 1.34 V to 1.48 V due to the incorporation of various amount of comonomers depending on the applied external potential.

As shown in Fig. 2, electropolymerization was carried out via cyclic voltammetry between  $-0.7 \text{ V}$  and  $1.5 \text{ V}$  vs. Ag/AgCl. Fig. 2a and f demonstrate the homopolymerization of monomer **1** and EDOT, respectively. By increasing the amount of EDOT in the comonomer mixture, the cyclic voltammogram of monomer **1** expectedly starts to resemble that of EDOT. The similar behavior was observed for the redox behaviors of the homopolymers and their copolymers obtained from various monomer feed ratios. Table 1 summarized the oxidation and reduction potentials of related polymers.

Upon moving from the cyclic voltammograms of monomer **1** and its polymers P1 to EDOT and PEDOT, the changes in the electrochemical behaviors of the copolymers were shown in Fig. 2. The intensities of the redox couples of homopolymers are lower than those of copolymers since the total amount of monomers used for the formation of copolymer is higher than homopolymers and therefore, more monomers are oxidized to get polymer on the electrode surface in spite of the same repetitive cycles (see Fig. 3a). On the other hand, the copolymer film starts to oxidize easily by increasing the amount of EDOT in monomer feed ratio.

Also, the redox behaviours of the homopolymers and copolymers can be followed by preparing the polymer film with the same polymerization charge on the same electrode surface via constant potential electrolysis. As shown in Fig. 3b, the polymer films exhibited nearly the same current intensity of redox couple. The change in monomer feed ratio directly affected the voltammograms of the films as observed in potentiodynamic polymerization on foregoing results.

In order to investigate the electrochemical properties of the copolymer (C-3) obtained from 10:3 monomer **1** and EDOT monomer feed ratio, respectively, the current intensity of redox couple was followed using cyclic voltammetry as a function of scan rate between  $-0.9 \text{ V}$  and  $1.2 \text{ V}$  (Fig. 4a). As shown in Fig. 4b, anodic and cathodic current peaks increase by increasing scan rate and it is absolutely linear as a function of scan rate, which indicates that the redox behaviour is non-diffusion controlled.

On the other hand, if the potential range was limited between 0.0 V and 1.1 V, the copolymer C-3 film exhibited an ideal fingerprint signature of a capacitor bearing a rectangular voltammogram due to the fast charging and discharging upon moving from lower potential to higher potential (Fig. 5a). The rectangular shape of voltammogram did not change even at higher scan rates in a potential window of 1.1 V. Charging/discharging current intensity increases linearly with scan rates, which confirms that the copolymer film was firmly attached on the electrode surface and electron loss and electron gain process occurred mainly both at lower and higher scan rates (Fig. 5b).

Based on the foregoing results, it can be easily concluded that the copolymer films absolutely exhibit different redox behaviour when compared to its homopolymers. Similar effects can be expected from the optical properties. In order to test this expectation, the homopolymers and the copolymers were coated on the ITO working electrode by using the same amount of charge and all polymeric films were reduced at  $-1.0 \text{ V}$  to get them in the neutral form, which allows to calculate the band gap of the films. Fig. 6 undoubtedly demonstrated the changes in optical behavior of the polymers upon moving from P1 to the copolymers and finally to PEDOT. The broad absorption band between 380 and 650 nm indicated  $\pi-\pi^*$  transition. While the band gap of P1 with a maximum

Download English Version:

<https://daneshyari.com/en/article/6662814>

Download Persian Version:

<https://daneshyari.com/article/6662814>

[Daneshyari.com](https://daneshyari.com)