ORIGINAL PAPER

A low-band gap conductive copolymer of bis-3-hexylthiophene substituted 4-*tert*-butylphenyl quinoxaline and 3,4-ethylenedioxythiophene

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Abstract Electrochemical copolymerization of 2,3-bis(4-*tert*-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl)quinoxaline (HTQ) and 3,4-ethylenedioxythiophene (EDOT) was performed to fulfill a strategy in achieving fine-tuned electrochromic properties. The copolymer, P(HTQ-*co*-EDOT) was characterized via detailed studies of cyclic voltammetry and spectroelectrochemistry. Copolymer film has many superior properties compared to the parent homopolymer. E_g of the copolymer was calculated as 1.4 eV, which is substantially lower than the homopolymer's (PHTQ) band gap, which was reported as 1.75 eV. Optical contrast of the resultant copolymer was shown to be 34%, which is nearly 10% higher than the PHTQ. The most striking achievement in the electrochromic properties was in switching times. The copolymer switches very rapidly between its neutral and the oxidized states and achieves a 34% optical contrast in less than 1 s, half of the value for the pristine polymer.

Keywords Electrochemical polymerization ·
Conductive copolymers · Spectroelectrochemistry

Introduction

Conducting polymers (CPs) have aroused a great amount of interest due to their possible applications in automotive industry [1], light-emitting diodes [2], gas sensors [3], organic transistors [4], and electrochromic devices [5].

Electrochromism is related to doping–undoping processes, which modify the polymer electronic structure and produce new electronic states in the band gap causing color changes [6].

Metal oxides such as WO_3 [7], metal complexes [8], and conjugated polymers [9] are presently known as electrochromic materials. However, conducting polymers have received more attention than inorganic materials owing to their advantages over inorganic compounds, such as fast switching ability, high coloration efficiency, fine-tuning of the band gap through chemical structure modification, and multiple colors with the same material [10].

Although conducting polymers have such advantages, they have some limitations, like being insoluble and exhibiting poor mechanical and physical properties [11]. To overcome such disadvantages, soluble oligomers [12,13], soluble precursors [14], or copolymers [15,16] were utilized.

Copolymerization is a major focus in the study of electrochromic materials, since it is an easy method to combine electrochromic properties of comonomers to improve optical properties and also to tune the colors of oxidized and neutral states [17].

For that matter, we synthesized a novel copolymer of 2,3-bis(4-*tert*-butylphenyl)-5,8-bis(4-hexylthiophen-2-yl) quinoxaline (HTQ) wih 3,4-ethylenedioxythiophene (EDOT). EDOT is a popular choice as a comonomer, since it produces a low-band gap polymer with high stability and good conductivity [18]. EDOT can give rise to noncovalent intramolecular interactions with adjacent thiophenic units and thus induce self-rigidification of the π-conjugated system in which it is incorporated [19, 20, 21].

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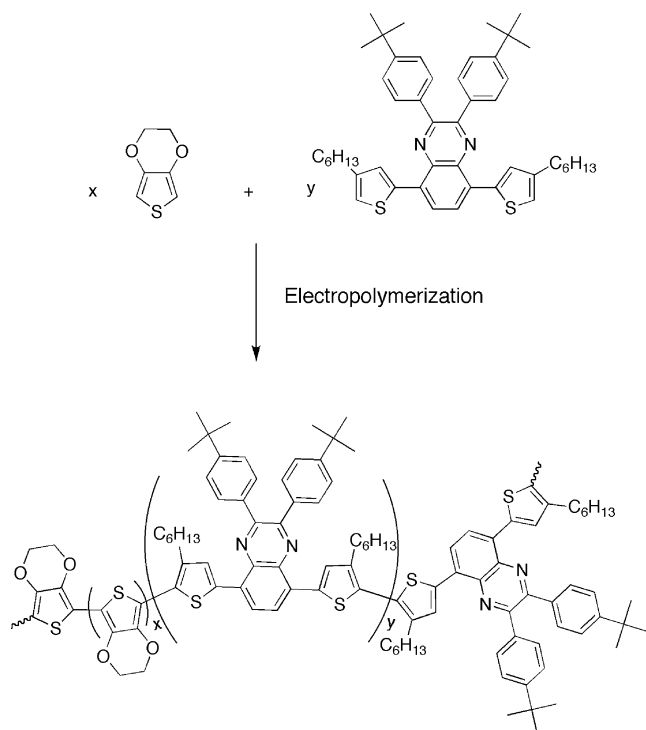
Scheme 1 Schematical representation for the electrochemical copolymerization of HTQ with EDOT

Experimental

Chemicals

Acetonitrile(ACN), dichloromethane(DCM), EDOT, and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) were all purchased from Aldrich. The monomer HTQ was synthesized according to the previously reported method [22].

Equipments

A Voltalab potentiostat was used for all electrochemical studies. Electropolymerization was performed in a three-electrode cell consisting of an indium-tin-oxide-coated glass slide (ITO) as the working electrode, platinum wire as the counter electrode, and Ag wire as the pseudo reference electrode. The Fourier transform infrared (FTIR) spectra were recorded on a Varian FTIR 100 spectrometer. Varian Cary 5000 UV–Vis spectrophotometer was used to perform the spectroelectrochemical studies of the polymer. Colorimetry measurements were done via Minolta CS-100 Spectrophotometer. A system consisting of a potentiostat and a CV cell with ITO as the working, platinum wire as the counter electrodes and a Ag wire pseudo reference electrode was used.

Electrochemistry

The electrochemistry experiments were carried out at room temperature and under nitrogen atmosphere. P(HTQ) was synthesized via cyclic voltammetry by sweeping the potential between -0.5 and 1.3 V, whereas P(HTQ-co-EDOT) and
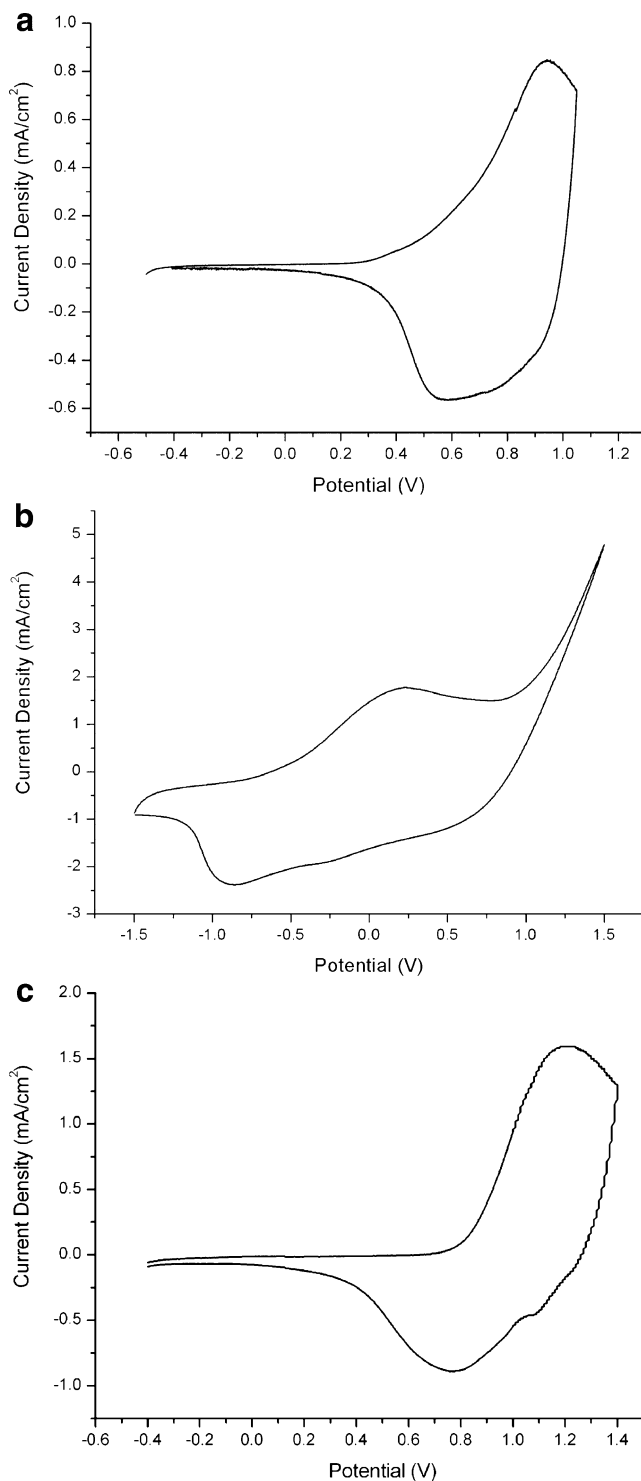

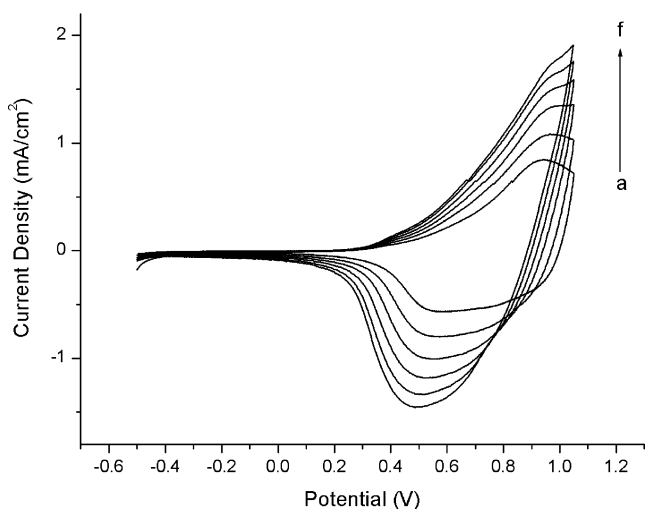Fig. 1 Cyclic voltammograms of a copolymer, b PEDOT, c PHTQ in 0.1 M TBAPF$_6$/ACN/DCM

Fig. 2 Scan rate dependence of copolymer: **a** 100, **b** 150, **c** 200, **d** 250, **e** 300, and **f** 350 mV/s in 0.1 M TBAPF$_6$/CAN/DCM

PEDOT films were prepared by constant potential electrolysis at 1.0 V, since potentiostatic conditions work better for the formation of copolymer film on the electrode.

Synthesis of copolymer

Both EDOT and HTQ were oxidized within the same potential range; hence, the radical cations of both monomers were simultaneously formed at the working electrode surface. The potentiodynamic polymerization of HTQ with EDOT was carried out in a solution containing 4.6×10^{-2} M HTQ and 6.1×10^{-3} M EDOT in TBAPF$_6$ and ACN/DCM (5/95, *v/v*) solvent couple by applying a constant potential of 1.0 V under nitrogen atmosphere. After electrolysis, the film was washed with ACN to remove the supporting electrolyte and the unreacted monomer. When the applied

Fig. 4 Electrochromic switching, optical absorbance change of the copolymer monitored at 345 and 548 nm and 1,799 nm in 0.1 M TBAPF$_6$/ACN

potential was higher than 1.0 V, the product mainly consists of PEDOT as revealed from CV and spectroelectrochemistry studies. At 1.0 V, when the monomer feed ratios are same, the copolymer has characteristics of rather PHTQ as

Fig. 3 Spectroelectrochemistry of copolymer film on an ITO-coated glass slide in a monomer-free, 0.1 M TBAPF$_6$/ACN electrolyte–solvent couple at applied potentials(V): **a** −0.2, **b** 0.5, **c** 0.6, **d** 0.7, **e** 0.75, **f** 0.8, **g** 0.85, **h** 0.9, **i** 0.95, **j** 1.0, **k** 1.05
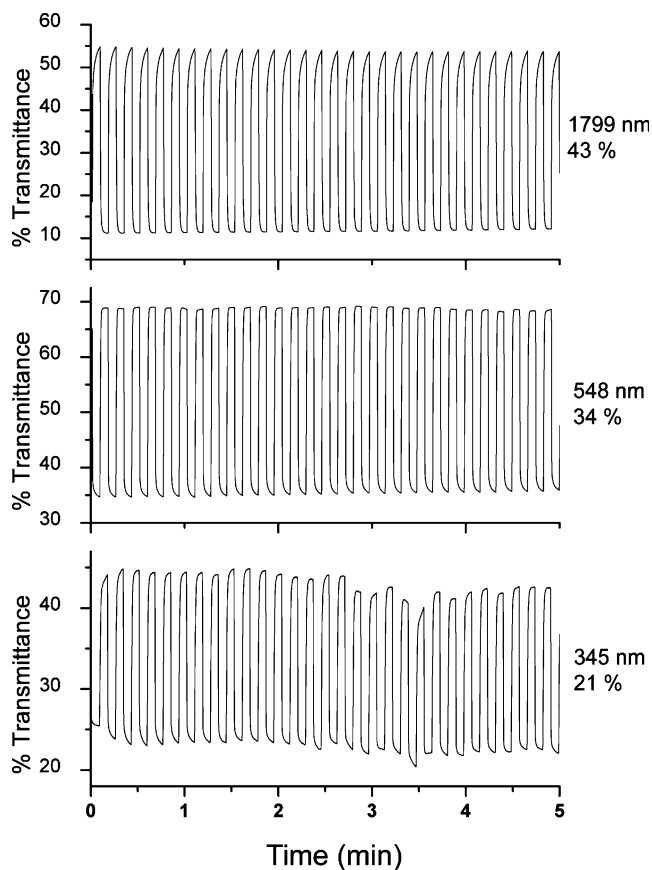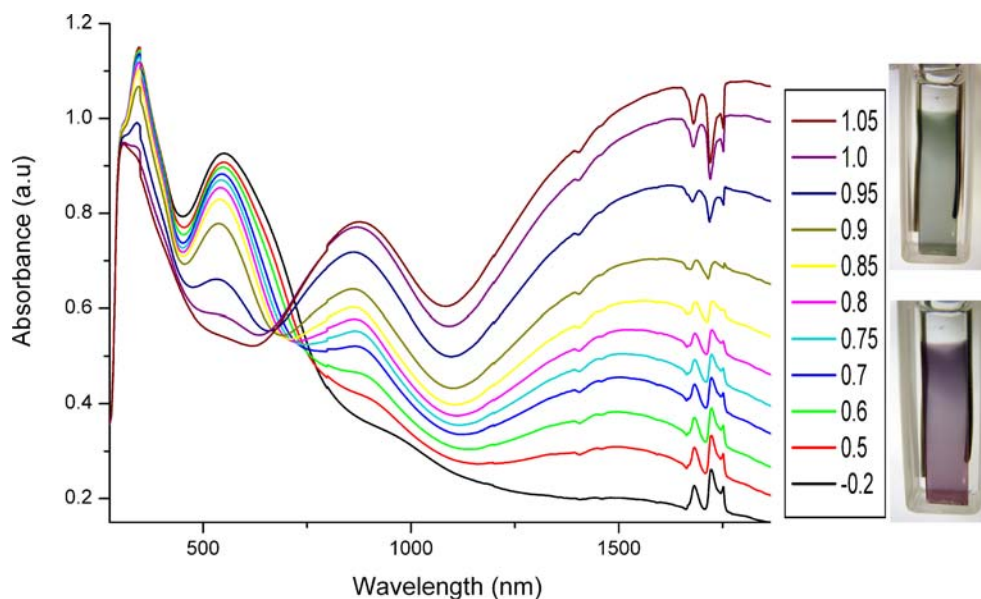
given by its high electroactivity. Hence, 1.0 V was chosen as the electrolysis potential with a monomer feed ratio of 1:8 (HTQ/EDOT) to form the copolymer (Scheme 1).

Results and discussion

Fourier transform infrared

FTIR spectrum of the HTQ shows the following absorption peaks: 3,085 cm^{-1} (aromatic C–H), 3,035 cm^{-1} (C–H$_\alpha$ stretching of thiophene), 1,560–1,340 cm^{-1} (aromatic C=C, C–N stretchings), and 771 cm^{-1} (C – H$_\alpha$ out of plane bending of thiophene). The homopolymer revealed most of the characteristic peaks of the monomer where the peaks related to C – H$_\alpha$ stretching of thiophene disappeared, and the presence of a new peak at around 1,635 cm^{-1} was attributed to polyconjugation. Similar spectra was observed in case of the copolymer where presence of EDOT moieties were signified by the new peaks around 2,850, 2,872 cm^{-1} and 1,148–1,050 cm^{-1} due to the aliphatic and C–O–C stretchings, respectively.

Constant potential electrolysis and cyclic voltammetry

The redox behaviors of PHTQ, PEDOT and the copolymer were examined using the repeated potential method on indium tin oxide electrodes in a solution containing TBAPF$_6$ and ACN/DCM solvent–electrolyte couple. The thickness of the polymer films on ITO electrodes is monitored by the charge passing during polymerization (about 15 mC/μ for thiophene derivatives). The cyclic voltammograms of the homopolymer, PEDOT, and the copolymer are shown in Fig. 1. As seen, the oxidation potential of the copolymer is quite lower than the parent homopolymer and shifted toward the oxidation potential of PEDOT. This is a clear indication of copolymer formation. Additional proofs will be given with spectroelectrochemistry and kinetic studies.

The scan rate dependence of the polymer film was also investigated. A linear relationship was found between the peak current and the scan rate, indicating that the electro-active polymer film was well-adhered and the redox processes were non-diffusion limited (Fig. 2).

Spectroelectrochemistry

Spectroelectrochemistry studies were carried out in order to evaluate electronic transitions upon doping and dedoping of the polymer. Copolymer films were deposited on ITO-coated glass in ACN/TBAPF$_6$. The most convincing evidence of copolymerization was revealed by studying the spectroelectrochemical behavior of the copolymer,

which enables the evaluation of the differences of the spectral signatures of the material compare to those of the pristine homopolymer [23]. PEDOT reveals a π−π* transition centered at 610 nm with a band gap of 1.6 eV, whereas P(HTQ-co-EDOT) has a λ$_{max}$ at 550 nm with a band gap of 1.4 eV. The parent homopolymer has a λ$_{max}$ value at around 538 nm. The λ$_{max}$ value of the copolymer is between the λ$_{max}$ values of the corresponding homopolymers, which is a clear indication of copolymer formation. Due to the unique donor–acceptor nature of the copolymer, a broader absorption band was resulted in a lower band gap value compared to the corresponding homopolymers. The copolymer was purple (Y, 434; x, 0.305; y 0.305) in its neutral state and green (Y, 672; x, 0.302; y, 0.342) in its oxidized state, which are also significant proofs of copolymer formation since PHTQ is red and PEDOT is blue in their neutral states (Fig. 3).

Kinetic studies

A striking enhancement was observed on kinetic properties via copolymerization. The copolymer achieves 34% optical contrast in less than 1 s, where for the parent homopolymer, it took nearly 2 s for a 25% optical contrast. As expected, copolymerization with EDOT improved both the optical contrast and the switching time of the material (Fig. 4).

Conclusion

A novel copolymer, P(HTQ-*co*-EDOT), was electrochemically synthesized, and several improvements were achieved compared to the parent homopolymer. Especially the increase in the optical contrast and a satisfactory decrease in switching time are noteworthy. We believe that this class of donor–acceptor type copolymers will have great contribution to the field of organic electronics. Soluble copolymers may also be synthesized by chemical modification of structures. This may enable their use as active layers in solar cells and light emitting diodes.

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