# Poly[*trans*-bis(3,4-ethylenedioxythiophene)vinylene]: A Low Band-gap Polymer with Rapid Redox Switching Capabilities between Conducting Transmissive and Insulating Absorptive States

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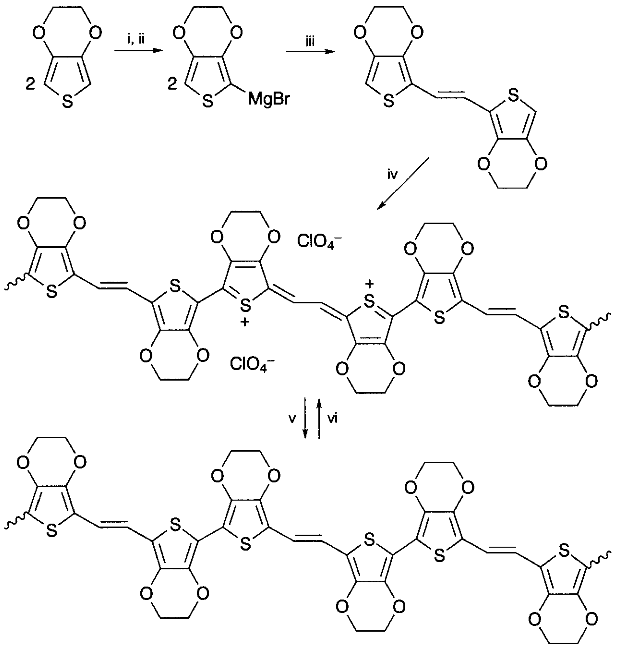
*trans*-Bis(3,4-ethylenedioxythiophene)vinylene is synthesized and electrochemically polymerized to give poly[*trans*-bis(3,4-ethylenedioxythiophene)vinylene] (PBEDOT-V) which exhibits a band gap of 1.4 eV and can be rapidly switched between insulating deep purple absorptive and highly conducting light blue transmissive states.

Poly(arenediylvinylene)s have been the focus of a significant amount of attention recently due to their electro-optical and electrically conductive properties.[1–3] Poly(dithienylethylene) (PDTE) exhibits an absorption edge for the $\pi$–$\pi^*$ transition (the electronic band gap) at 1.74 eV which is significantly lower than that for polythiophene (2.0 eV).[4] The incorporation of alkoxy substituents onto the thiophene rings of poly[thienylenevinylene] (PTV) also lowers the band gap relative to the unsubstituted polymer.[5–7] Motivation for lowering the optical gap in the neutral polymers comes from the fact that the redox-doped and conducting form of the polymers have their $\pi$ absorptions in the near-infrared and a relatively high degree of transmission of visible light. This was illustrated initially for polyisothianaphthene which exhibits a very low band gap of 1 eV.[8,9] One possible use for this class of electroactive conductive polymers is in electrochromic devices. In order for a polymer to be useful for such a device, it has to be able to switch rapidly between the reduced and oxidized states, have a high transmittance contrast ratio between the reduced and oxidized forms, and be able to be switched a high number of times before a significant loss in electroactivity occurs.

3,4-Ethylenedioxythiophene (EDOT) has recently been shown to form a polymer (PEDOT) which is highly electroactive, exhibits a low optical band gap (760–780 nm or 1.6–1.7 eV), and is potentially useful as an antistatic coating and electrochromic material.[10–12] Considering and comparing the properties of PDTE, PTV and PEDOT, we have designed a new EDOT vinylene polymer which provides a highly conducting, low oxidation potential, low band-gap polymer. In this communication, we report the synthesis of *trans*-bis(3,4-ethylenedioxythiophene)vinylene (BEDOT-V), its electrochemical polymerization, optoelectrochemical analysis of the resultant poly[*trans*-bis(3,4-ethylenedioxythiophene)vinylene] (PBEDOT-V), and rapid redox switching capabilities of this polymer.

EDOT was prepared *via* a known five-step procedure.[10] BEDOT-V was synthesized, as outlined in Scheme 1, by first forming the Grignard reagent of EDOT using *n*-butyllithium followed by addition of $MgBr\cdot Et_2O$ at 0 °C. The Grignard reagent was then coupled with *trans*-dichloroethylene utilizing a $[NiCl_2\{Ph_2P(CH_2)_3PPh_2\}]$ catalyst and allowing the reaction to proceed at room temperature for 48 hours. BEDOT-V was crystallized from pentane in a 49% purified yield and subsequently characterized by IR, FAB-HRMS, elemental analysis, $^1H$ NMR and $^{13}C$ NMR spectroscopy.



**Scheme 1** *Reagents and conditions*: i, 2BuLi, THF, −78 °C; ii, $2MgBr_2$, 0 °C, 45 min; iii, *trans*-1,2-dichloroethene, $[NiCl_2\{Ph_2P(CH_2)_3PPh_2\}]$, room temp., 48 h; iv, oxidative polymerization, 0.1 mol dm$^{-3}$ $NBu_4ClO_4$–MeCN; v, electrochemical reduction; vi, electrochemical oxidation

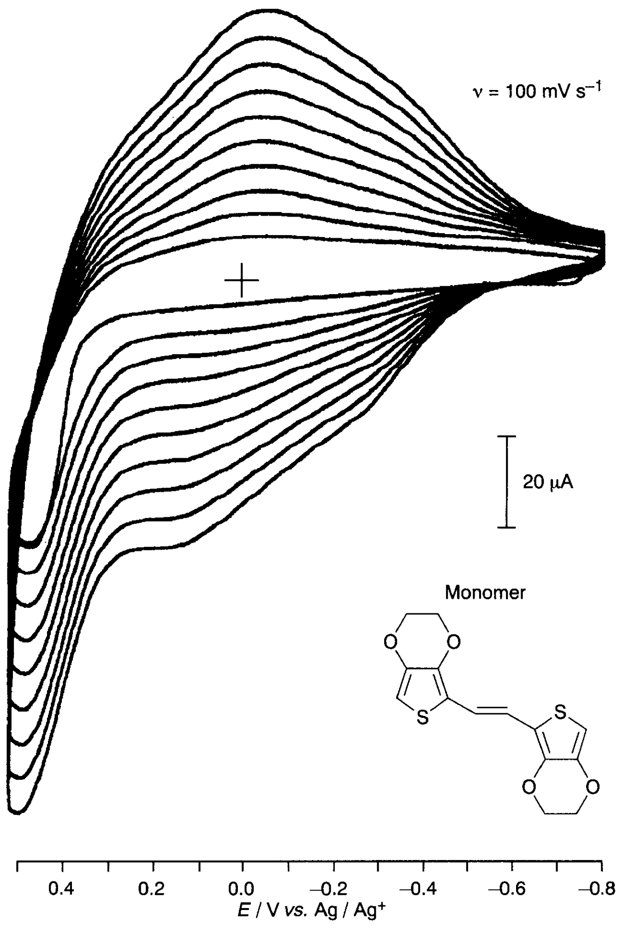


**Fig. 1** Cyclic voltammetric polymerizaton of BEDOT-V carried out in 10 mmol dm$^{-3}$ BEDOT-V–0.1 mol dm$^{-3}$ $NBu_4ClO_4$–MeCN

BEDOT-V was electrochemically polymerized in an argon atmosphere using a 10 mmol dm$^{-3}$ BEDOT-V–0.1 mol dm$^{-3}$ $NBu_4ClO_4$–MeCN solution. Fig. 1 shows the repeated cyclic voltammetric (CV) polymerization of BDOET-V utilizing platinum button working, platinum plate counter, and Ag/Ag$^+$ reference electrodes. The monomer exhibits an onset of oxidation at 0.3 V *vs.* Ag/Ag$^+$ and the redox current of the polymer rapidly grows upon multiple cycling with an $E_{1/2}$ of 0.0 V. The polymer film was washed with acetonitrile and placed in a monomer-free 0.1 mol dm$^{-3}$ $NBu_4ClO_4$–MeCN solution for further electrochemical studies. CV analysis of the polymer shows a linear increase of both the oxidative and reductive peak currents as a function of scan rate which is indicative of an electrode supported electroactive film. The low potentials for both polymerization and redox switching are worth noting. The ease of oxidation of the monomer can be attributed to the extended conjugation of the monomer which allows electropolymerization to occur with a minimum of side reactions. The low potential of the polymer's redox chemistry induces a high degree of stability to the oxidized and conductive state. This is quite similar to polypyrrole which is known as one of the most stable of the conjugated conducting polymers. Additional benefits of the BEDOT-V system are evident in the optical properties as the oxidized conducting form is relatively transparent when compared to the reduced form. This is of importance in considerations for use in conducting transparent antistatic packaging coatings.

In order to determine the band structure of the polymer, a series of UV–VIS–NIR spectra were obtained as a function of applied potential at equilibrium doping. BEDOT-V was polymerized onto an indium tin oxide (ITO) coated glass electrode at a constant potential of +0.45 V *vs.* Ag/Ag$^+$ until a charge density of 12 mC cm$^{-2}$ passed to yield a 200 nm thick film. After washing and placing in monomer-free electrolyte, the band gap ($E_g$) of the polymer in the fully reduced state was determined to be 1.4 eV from the onset of the π–π* transition as shown in Fig. 2. This is significantly lower than the $E_g$ value of 1.6–1.7 eV found for the parent polymer poly(3,4-ethylenedioxythiophene), with a red shift in the onset of absorption of over 100 nm. Upon oxidative doping of PBEDOT-V, the intensity of the π–π* transition decreases while a bipolaronic band appears at 1.1 eV. During oxidation the film is converted from a deep purple absorber to a relatively transmissive light blue in colour. This process was shown to be reversible by repeated doping and undoping of the polymer.

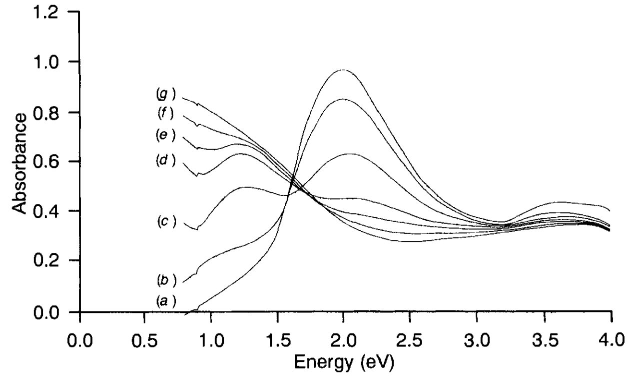


**Fig. 2** Optoelectrochemical analysis of PBEDOT-V; UV–VIS–NIR spectra taken at (*a*) −1.3 (*b*) 0.0 (*c*) 0.1 (*d*) 0.2 (*e*) 0.3 (*f*) 0.4 (*g*) 0.5 V *vs.* Ag/Ag$^+$

In order to test the potential utility of PBEDOT-V for electrochromic devices, a thin film of the polymer (*ca.* 200 nm) was grown potentiostatically onto an ITO coated glass electrode ($E$ = +0.45 V) and the polymer was repeatedly switched every 5 s between oxidized (+0.6 V) and reduced (−0.6 V) forms in 0.1 mol dm$^{-3}$ $NBu_4ClO_4$–MeCN while recording the absorbance at 600 nm ($\lambda_{max}$ for the neutral polymer) and charge passed as a function of time. Monitoring the visible absorbance, this PBEDOT-V film was found to have a switching time (time required to effect 100% of the absorbance change observed) to 500 ms in switching from the oxidized to reduced state. A slightly slower response time of 1.500 ms was observed for switching from the reduced form to the oxidized form. After a total of 400 double potential steps, the polymer retained 52% of its electroactivity, according to coulometry, and 49%, of its absorption contrast. The charge retention directly corresponds to the retention of absorption which indicates an electrochemically efficient electrochromic process.

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