3750 *Macromolecules* **1998,** *31,* 3750−3752

Low Band Gap Cyanovinylene Polymers Based on Ethylenedioxythiophene

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Received August 26, 1997

Revised Manuscript Received February 13, 1998

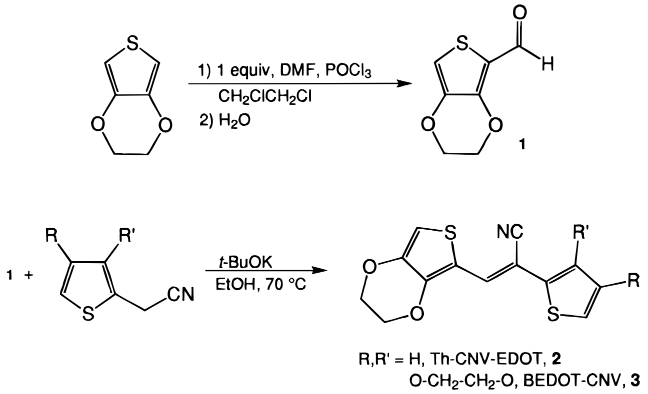
Low band gap (E_g) conjugated polymers[1] have attracted attention due to their high visible light transmissivity in the conducting form (important for static charge dissipation applications) and their ability to be both p- and n-type doped (allowing their use in all-polymer-based batteries, supercapacitors, and dual-polymer electrochromic devices[2] as both the cathodic and anodic materials). Within this family of polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) stands out for its optical properties ($E_g = 1.6$ eV), high stability in the conducting state, and propensity to multiple redox switches due to its ease of oxidation.[3] This last property can be attributed to the high effective HOMO energy level for the backbone.

Previously, we and others have reported the synthesis and facile electrochemical polymerization of *trans*-1,2-bis(3,4-ethylenedioxythienyl))vinylene (BEDOT-V).[4] Poly(BEDOT-V) was found to exhibit a low half-wave redox potential ($E_{1/2,p}$) of ca. 0.0 V, making it a stable p-dopable conductor, and a reduced E_g relative to PEDOT of 1.4 eV. Unfortunately, the n-doping process for both PEDOT and poly(BEDOT-V) is particularly unstable. It has been shown that the incorporation of a cyano group onto the vinylene unit of electron rich poly(bis(heterocycle)vinylene) systems affords polymers with low E_g values.[5,6]

Here we communicate the synthesis and electrochemical polymerization of 1-cyano-2-(2-(3,4-ethylenedioxythienyl))-1-(2-thienyl)vinylene (Th-CNV-EDOT) and 1-cyano-1,2-bis(2-(3,4-ethylenedioxythienyl))vinylene (BEDOT-CNV). By using EDOT as the terminal polymerizable moiety, facile oxidative polymerization occurs to yield stable p-type dopable polymers exhibiting the lowest E_g values for the family of poly(1,2-bis(2-thienyl)-vinylene)'s.[1,5] In addition, the band structure as determined via spectroelectrochemistry is distinct and free from defects, suggestive of a highly efficient polymerization process.

Scheme 1 depicts the synthesis of Th-CNV-EDOT and BEDOT-CNV. The first step entailed the Vilsmeier formylation of EDOT to afford 2-(3,4-ethylenedioxythienyl)carboxaldehyde, **1**, in a ca. 90% yield. Knoevenagel condensation of **1** with 2-thienylacetonitrile or 2-(3,4-ethylenedioxythienyl)acetonitrile[7] afforded either Th-CNV-EDOT or BEDOT-CNV in yields of 93% or 80%, respectively. Both Th-CNV-EDOT and BEDOT-CNV were characterized by FAB-HRMS and ^{1}H and ^{13}C NMR. Furthermore, Th-CNV-EDOT was characterized by X-ray crystal structure analysis.

Scheme 1. Synthesis of Th-CNV-EDOT and BEDOT-CNV



The X-ray crystal structure of Th-CNV-EDOT was determined at −125 °C. It crystallizes in the monoclinic space group $P2_1/n$ with a single molecule in the asymmetric unit. The structure determination confirms the cis relationship of the cyano and EDOT substituents. The conformations of the two thiophene rings are such that their sulfur atoms are cisoid to the carbon−carbon double bond, as shown by the structure in Scheme 1. Most significantly, the molecule is close to planar. Specifically, the plane of the double bond is inclined to the plane of the EDOT thiophene ring at an angle of 6.6(3)° and to the plane of the other thiophene ring at an angle of 8.7(3)°, while the planes of the two thiophene rings make an angle of only 2.8(3)°. The structure of the monomer in the solid state may be correlated to the structure of the polymer repeat unit in the neutral form. We have previously shown that the EDOT−EDOT linkage is planar by the crystal structure of the bis-TMS derivative of 2,2′-bis(3,4-ethylenedioxy)thiophene (BiEDOT-TMS$_2$).[8] Since the monomer is able to attain a nearly planar conformation, the repeat unit of the polymer should also be able to achieve this conformation. The more planar the repeat of the polymer, the lower the energy required to stabilize the charged state upon oxidation of the polymer and the higher the possibility of interchain electron transport occurring.

Poly(Th-CNV-EDOT) and poly(BEDOT-CNV) films were synthesized by utilizing repeated potential scan electrochemical polymerization in 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (ACN) using a platinum button working electrode and a Ag/Ag$^+$ reference electrode.[9] A peak for monomer oxidation ($E_{p,m}$) of 0.80 V was obtained for Th-CNV-EDOT. Due to the increased electron density of the bis-EDOT derivative BEDOT-CNV, the $E_{p,m}$ shifts to a lower value of 0.72 V. These polymerizations were very efficient, as indicated by a high peak current response for the cathodic process ($i_{p,c}$, charge neutralization) obtained during the course of polymerization. After three scans, the $i_{p,c}$ value for the electrochemical polymerization was 30 and 37 μA for Th-CNV-EDOT and BEDOT-CNV, respectively. In comparison, EDOT and BEDOT-V exhibit $i_{p,c}$ values of 26 and 31 μA, respectively under the same electrochemical conditions.

Figure 1 shows a cyclic voltammogram (CV) of poly-(Th-CNV-EDOT) in 0.1 M TBAP/ACN solution containing 10 mg of LiH at a scan rate of 100 mV/s. The

S0024-9297(97)01290-4 CCC: $15.00

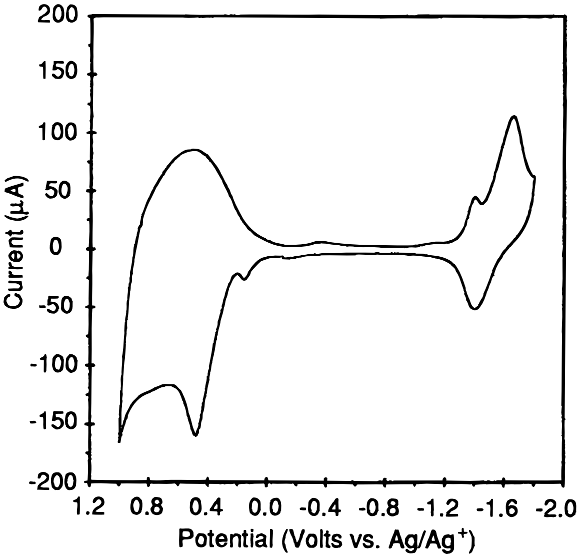


Figure 1. Cyclic voltammetry (third scan) of poly(Th-CNV-EDOT) on a Pt button in 0.1 M TBAP/ACN at a scan rate of 100 mV/s.

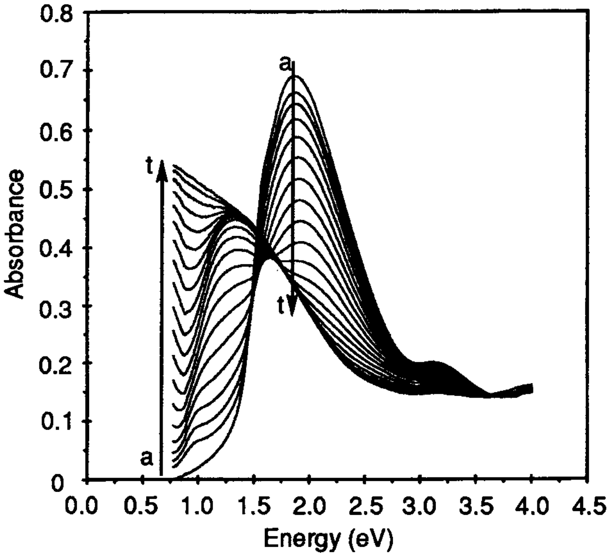


Figure 2. Optoelectrochemical analysis of poly(Th-CNV-EDOT) in 0.1 M TBAP/ACN at applied potentials of (a) −0.6 V, (b) 0.10 V, (c) 0.15 V, (d) 0.20 V, (e) 0.25 V, (f) 0.30 V, (g) 0.35 V, (h) 0.40 V, (i) 0.45 V, (j) 0.50 V, (k) 0.55 V, (l) 0.60 V, (m) 0.65 V, (n) 0.70 V, (o) 0.75 V, (p) 0.80 V, (q) 0.85 V, (r) 0.90 V, (s) 0.95 V, and (t) 1.00 V vs Ag/Ag$^+$.

addition of LiH was necessary in order to ensure the exclusion of water from the electrolytic medium since water would interfere with the reduction process of the polymer. By scanning between −1.8 V and +1.0 V, two major redox processes are observed along with a set of prepeaks. The anodic process, with an $E_{1/2}$ occurring at +0.6 V is attributed to the p-doping ($E_{1/2,\mathrm{po}}$) of the polymer, while the redox process with an $E_{1/2}$ at ca. −1.5 V is due to reduction ($E_{1/2,\mathrm{pr}}$) of the polymer. An electrochemical band gap (E_g) of 1.3 eV can be taken as the difference between the onset potentials of these two processes. Poly(BEDOT-CNV) was found to exhibit an $E_{1/2,\mathrm{po}}$ at −0.1 V, an $E_{1/2,\mathrm{pr}}$ value of −1.6 V, and an electrochemically measured E_g of 1.1 eV. The redox stability of poly(Th-CNV-EDOT) was tested by cycling the polymer on a Pt button over 10 times in 0.1 M TBAP/ACN between −1.8 and +1.0 V under anaerobic conditions. No change was observed in the current response for either polymer oxidation (oxidized to neutral) or polymer reduction (reduced to neutral) redox processes.

The E_g values for the polymers obtained by CV were further confirmed by in situ spectroelectrochemical analysis, as shown for poly(Th-CNV-EDOT) in Figure 2. At an applied potential of −0.6 V, at which the polymer is in its fully neutral form, the onset for the π to π^* transition (E_g) is 1.3 eV with a $\lambda_{\max}$ at 1.8 eV. Relative to other polymers of this type, this transition is narrow and distinct with a difference between the onset for the π to π^* transition and $\lambda_{\max}$ of only 0.5 eV. This is attributed to the efficient polymerization process of the EDOT-containing monomers and is suggestive of a regular, defect-free stucture. Upon oxidation of the polymer to +0.10 V, a new lower energy (valence to bipolaron) transition becomes apparent at ca. 1.0 eV. Sequential oxidation of the polymer in 50 mV steps results in a decrease in the absorbance of the π to π^* transition and an increase in the intensity of the lower energy transitions, which can be attributed to bipolaron charge carriers. It should be noted that, during the evolution of the spectra, the higher energy valence to bipolaron transition shifts to 1.25 eV, while at an applied potential of +0.30 V the transition edge for the lower energy valence to bipolaron transition could be detected. These two transitions coalesce into one broad absorption at an applied potential of +1.00 V, possibly indicating metallic behavior.

The in situ spectroelectrochemical behavior of poly(BEDOT-CNV) was very similar to that of poly(Th-CNV-EDOT) in that the lowering of intensity for the π to π^* transition and increased intensity for the lower energy transitions occurred during successive oxidations. Poly(BEDOT-CNV), held at an applied potential of −1.00 V, has an E_g at 1.1 eV with the higher energy valence to bipolaron transition shifted to an energy of 1.1 eV at 0.65 V. Again upon full oxidation of the polymer at 0.85 V, there is only one broad transition observed, much like that of poly(Th-CNV-EDOT).

In conclusion, both Th-CNV-EDOT and BEDOT-CNV undergo facile electrochemical polymerization to provide two new low gap conducting polymers that are able to be both p-doped and reversibly reduced. Poly(Th-CNV-EDOT) and poly(BEDOT-CNV) exhibit E_g values of 1.3 and 1.1 eV, respectively, making them the lowest gap polymers in this family, while simultaneously providing quite stable oxidative doping to the conductive form.

Acknowledgment. We acknowledge support from the Naval Air Warfare Center, the Air Force Office of Scientific Research (F49620-96-1-0067, F49620-97-1-0232), and the National Science Foundation (CHE-9629854).

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MA971290F