TUNING THE BANDGAP FOR POLYMERIC SMART WINDOWS AND DISPLAYS

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(Received 6 April 1995)

Abstract—The band gap, and thus the optical properties, of polythiophene can be tuned for use in electrochromic applications by attaching substituents to the monomers before polymerization. Electron donating substituents lower the bandgap, while steric interaction of side groups on adjacent thiophene rings forces the conjugated backbone to twist and increases the band gap. By choosing the right combination, a polymer with specific optical properties can be designed.

Properties of interest for electrochromic applications, like oxidation potential, ionic conductivity and thermal stability, can also be improved by substitution. Poly(ethylenedioxythiophene) (PEDOT) has shown to have interesting optical properties, increased ionic conductivity and a high thermal stability.

Key words: electrochromism, conjugated polymer, polymer electrolyte, optical spectroscopy, Substituted polythiophene.

1. INTRODUCTION

A class of materials with electrochromic properties, that have been studied for use in solid state smart windows are the electroactive conductive polymers[1-8]. If these materials are to be used as electrochromic material in real applications they need to have good stability and useful optical properties. They should be tunable between one transparent and one opaque state. To achieve this, there are two possibilities:

(1) A polymer with a bandgap in the visible range, being transparent in its neutral state. Upon doping new electronic states are formed in the bandgap and absorption of light with lower energies, ie in the visible range, occurs. Thus, the polymer becomes opaque, or heavily colored, upon doping.

(2) A polymer with the bandgap in the middle of the visible range. Upon doping absorption at lower energies, ie in the near-infrared region outside the visible range, will occur and the material becomes transparent.

The conjugated polymers may be designed for a particular band gap energy depending on the molecular architecture. For instance, by attaching electron donating substituents the band gap of the polymer is lowered. When both the 3- and 4-positions are substituted, the steric hindrance between side groups on adjacent thiophene rings results in twisting of the conjugated backbones, reducing the conjugation length and widening the band gap. The substituent can also influence properties like solubility, thermal stability, oxidation potential, electronic structure and conductivity of the polymer[9-17].

We have studied the optical absorbance of four polymers of the polythiophene family: I. poly[3-(4-octyl-phenyl)-thiophene] (POPT), II. poly[3-(4-octyl-phenyl)-2,2'-bithiophene] (PTOPT), III. poly[3-cyclohexylthiophene] (PCHT) and IV. poly[3,4-ethylenedioxythiophene] (PEDOT) (Fig. 1). For polymers I, II and IV, a solid state electrochemical cell comprising one polymer layer on ITO coated glass, a solid polymer electrolyte [poly(oxymethylene-oligo(oxyethylene)) (POMOE) complexed with LiClO₄][18], and one lithium intercalating vanadium oxide [Li₂VO₄][19] layer on ITO coated glass was built. Due to the large difference in coulombic capacity and coloration efficiency, only the optical changes of the conjugated polymer will be detectable; the vanadium oxide can be considered as optical passive during the experiments[5].

The electrode reactions can be written as

P⁰ + ClO₄⁻ → P⁺ClO₄⁻ + e⁻   (1a)
PEDOT⁰PSS⁻Li⁺ → PEDOT⁺PSS⁻ + Li⁺ + e⁻   (1b)
VO₄⁻ + Li⁺ + e⁻ → VO₄⁻(Li⁺)   (2)

where P stands for polymer I-III.

During the electrochemical synthesis of PEDOT we used the sodium salt of polystyrene sulfonate (PSS) as supporting electrolyte. The conjugated
3. RESULTS AND DISCUSSION

Figure 2 shows the optical absorbance of polymer I–III. The peak is related to the only absorption in the neutral state, the band gap absorption. Obviously, the band gap is strongly correlated to the attached substituents; the stronger the steric hindrance due to the substituent, the larger band gap of the polymer. It should be noted that the spectra have been normalized to better show the shift in peak position.

The optical absorptions peaks of the polymers are in the visible range in both the neutral and the doped state. POPT changes colour from reddish purple in the neutral state, to bluish purple in the doped state, PTOPT changes from red to sky blue and PCHT changes from yellow to light green upon doping. Optical spectra of cells with polymer I–II at different applied voltages are shown in Fig. 3.

Figure 4 shows the change in optical absorbance with increasing applied potential, i.e., higher doping level of the polymer, of the PEDOT cell. PEDOT, being dark purple/blue in the neutral state due to a band gap in the middle of the visible range, is an example of a polymer of type 2 state above. Upon doping the absorbance is moved to lower energies, outside the visible range, and the polymer becomes transparent with a light sky-blue colour. The switching time from fully coloured to almost transparent is about 4 s [23], a much shorter switching time than for other polythiophenes. A hypothetical explanation of this could be that the oxyethylene ring of the EDOT monomers, which has a structure similar to chain segments of polyethers, known to be good ionic conductors, contributes to cation transport in the material.

A solid state electrochromic cell with one PEDOT electrode and one vanadium oxide electrode has been cycled in room conditions for about 10⁵ times, with only slight decrease, about 10%, of the current density and optical switching ability. After about 1000 cycles more, the cell eventually stops working, and its seems to be a photoconversion of the vanadium oxide that causes the disfunction of the cell. Also the thermal stability of the doped state is much better for PEDOT than for other conjugated polymers. A thin film in the doped state can be kept at room temperature.
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[Graph showing optical absorbance for solid state electrochemical cells for different applied voltages.]

110°C for more than 70 h with only a slight loss of doping [22]. A recent paper [24] also shows that PEDOT can reach a very high doping level, around 75 mol%, which makes it interesting for use as electrode material in polymeric batteries.

The combination of thermal and electrochemical stability, the desirable optical absorption properties and the high coloration efficiency points to PEDOT as the most attractive electrochromic conjugated polymer at present.

4. CONCLUSIONS

By attaching suitable substituents on the monomers before polymerization, the band gap of the polymer can be tuned for use in electrochromic windows and displays. The side groups also influence some properties of the polymer, like ionic conductivity and thermal stability.

Acknowledgements—We thank Dr. G. Zuccarello for preparing the ethylenedioxothiophene monomer.

REFERENCES