

Dioxypyrrole and dioxithiophene based conducting polymers: properties and applications

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Abstract

We have focused recent efforts on developing an understanding of how to optimise the electrical, spectroscopic, electrochemical and physical properties of poly(3,4-alkylenedioxythiophene) (PXDOT) and poly(3,4-alkylenedioxyppyrrrole) (PXDOP) based conjugated polymers. Here we present the results of the temperature dependence of the *dc* and microwave conductivity, as well as magnetic susceptibility and reflectance data, for electrochemically synthesized, free standing, PXDOT and PXDOP films doped with different organic anions. The polymers have properties that are characteristic of disordered materials near the insulator-metal transition (IMT). We also investigate the possibility of applying these polymers as the active layer in visible and IR light emissivity control devices.

Keywords: conductivity, polythiophene and derivatives, polypyrrole and derivatives, switches, transport measurements, UV-Vis-NIR

1. Introduction

A new class of conducting polymers that have variable range band gaps (1.4 to 2.5 eV), as well as other interesting properties, recently has been reported [1]. The polymers are derived from polypyrrole and polythiophene and include poly(3,4-alkylenedioxythiophene) (PXDOT) and poly(3,4-alkylenedioxyppyrrrole) (PXDOP).

These polymers easily electrochemically switch between the p-type, doped state and the neutral state with concurrent changes in absorption spectra. Due to the high contrast ratio between doped and undoped forms, the PXDOT family is a good candidate for use in electrochromic devices such as smart windows [2,3] and IR and microwave shutters [4]. In addition, PXDOPs show outstanding electrochemical stability toward both aqueous and organic media, allowing their use in electrochromic device and in biological applications [5,6]. In order to understand the transport mechanism in this new class of conducting polymers, many studies have been performed in other groups [7] as well as in our labs [8], on highly conducting, free-standing PXDOT and, very recently, PXDOP films. The materials behavior is found to be

typical of highly conducting polymers near the insulator-metal transition (IMT).

2. Experimental

Free-standing films were synthesized by anodic deposition from solutions containing 0.06 M monomer and 0.06 M electrolyte in propylene carbonate [7]. The films were prepared in the constant current mode (0.04 mA/cm²) and the temperature was maintained at –30°C for PEDOT and –7°C for the other films. Film thicknesses were up to 150 μm.

Temperature dependent *dc* conductivity and microwave measurements at 6.5 GHz were performed utilizing the four-probe and cavity perturbation methods, respectively [8b]. Electron paramagnetic resonance (EPR) measurements were performed with a Bruker ESP300E (9.5 GHz) spectrometer and an Oxford ESR900 cryostat under ITC503 temperature control [8a].

Far infrared and mid-infrared region (30 cm^{–1} to 5000 cm^{–1}) measurements were carried out on a Bruker 113v Fourier-transform spectrometer using a 4.2-K bolometer detector (30 cm^{–1} to 600 cm^{–1}) and a DTGS pyroelectric

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detector with KRS-5 window (450 cm^{-1} to 5000 cm^{-1}). An MPM 800 Microscope Photometer with grating

monochromators was used to carry out measurements in the frequency region (4100 cm^{-1} - 45000 cm^{-1}).

Table 1
Transport Properties of PXDOT and PXDOP Films

Doped Polymer	$\sigma_{dc}(S/cm)$ (300K)	$\sigma(10K)/\sigma(300K)$	$\epsilon_{mw}(T)$ (300K)	χ_{Pauli} contribution to $\chi(T)$	ω_{max} for $\sigma(\omega)$, cm^{-1}	W-plot slope	ϵ_{FIR} ($< 25\text{ cm}^{-1}$)
PEDOT-PF ₆	105	0.42	negative	major	1900	positive	negative
PProDOT-PF ₆	16	0.033	positive	noticeable		negative	
PEDOT-CF ₃ SO ₃	95	0.17	negative	major	2100	small positive	negative
PProDOT-CF ₃ SO ₃	38	0.074	positive	noticeable	2300	negative	positive
PEDOP-CF ₃ SO ₃	40	0.12	negative			small negative	
PEDOT-(CF ₃ SO ₂) ₂ N	8.5	0.002	positive			negative	

3. Results and Discussion

3.1. Transport Properties

Studied materials have properties varying from metallic to insulating. Selected transport data are summarised in Table 1.

The most metallic sample, PEDOT-PF₆, has a high room temperature (RT) σ_{dc} , weak T dependence of σ_{dc} along with a positive slope of $W(T) = d\ln(\sigma_{dc}(T))/d\ln(T)$ (reduced activation energy) at low T . RT optical dielectric function obtained through Kramers-Kronig analysis of reflectance data crosses zero three times at $\sim 8000\text{ cm}^{-1}$, $\sim 800\text{ cm}^{-1}$, $\sim 25\text{ cm}^{-1}$ and stays negative at lower frequencies consistent with negative (down to 4 K) 6.5 GHz dielectric response ϵ_{mw} . This behaviour is similar to previously reported data for metallic polyaniline and polypyrrole [8c]. EPR measured magnetic susceptibility $\chi(T)$ has a major contribution from Pauli component χ_{Pauli} associated with delocalized spins.

Stronger T dependence of σ_{dc} for critical regime compositions (PEDOP-CF₃SO₃, PEDOT-CF₃SO₃) results in a small positive or small negative W -plot slope at low T . For PEDOT-CF₃SO₃ ϵ_{RT} at far IR is negative together with $\epsilon_{mw} < 0$ (down to 4 K) demonstrating that this sample is still on the metallic side of IMT. Pauli contribution is less than for PEDOT-PF₆.

PProDOT-CF₃SO₃ and PProDOT-PF₆ show lower σ_{dc} , negative slope of W -plot, positive far IR and microwave dielectric response typical for other dielectric conducting polymers. It is noted that the frequency for maximum of optical conductivity decreases for more metallic samples.

The optical, magnetic and transport studies demonstrate that this family of inhomogeneously disordered (from X-ray diffraction studies) materials spans from dielectric to metal.

3.2. Electrochromic Devices

The high optical contrast ratio and extremely fast switching time between doped and neutral states make PXDOT and PXDOP promising candidates for electrochromic devices.

One objective of this work is both to enhance the lifetime under switching conditions and the contrast of transmissive ECDs, and also to tune the function of the device over the entire visible spectrum. The concept for producing such a device is to use layers of polymers that have different λ_{max} . By overlapping the conducting polymer layers, not only is more of the visible spectrum covered, but the absorbance of the device is also enhanced. This performance was achieved by building a laminated transmissive device based on PEDOP/PProDOT-Me₂ as the cathodically coloring layers and the high-gap N-propyl sulfonate derivative of PProDOP (PProDOP-NPrS) as the anodically coloring polymer. The device switches in about 0.5 seconds from a light blue, transmissive state to a deep dark blue, absorptive state with a change in transmittance of 55% at 577 nm [3].

The other objective of this work is to control the surface emissivity in both visible and IR domains. The construction of a device operating in the reflective mode that has the active top layer PProDOT-Me₂ provides a reflectivity change of the surface of over 90% in the NIR region (1–2 μm). The device switches hundreds of times without any significant degradation of the working electrode [4].

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