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Soluble Alkyl-Substituted Poly(ethylenedioxythiophenes) as Electrochromic Materials

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We report the oxidative solution polymerization and redox doping of soluble tetradecyl-substituted poly(3,4-ethylenedioxythiophene), PEDOT−$C_{14}H_{29}$. This polymer can be oxidatively doped in solution to yield bipolaronic charge carriers and electrochemically switched as cast films on transparent electrodes to provide a new electrochromic material with a high contrast ratio.

Electrochromism is the phenomenon of a persistent color change with the passing of charge.[1] Electrochromic devices (EC) can be constructed by utilizing two complementary electrochromic materials in which one is anodically coloring and the other is cathodically coloring, allowing the two to behave as redox pairs for charge and optical contrast balance. The recent use of conjugated polymers for EC devices is of interest due to the ability to structurally control the electronic band gap, which in turn controls the redox and optical properties of the material.[2−6] In our laboratory, we are investigating the design and synthesis of new monomers with relatively low oxidation potentials to yield polymers with enhanced electroactivity and electrochromic properties.[5,7,8] Recent studies directed toward developing an understanding of the properties of conjugated polymers have encompassed the design and synthesis of 3,4-ethylenedioxythiophene (EDOT) polymers which exhibit low band gaps and high stability relative to other substituted polythiophenes in the oxidatively doped and electrically conducting state.[7,9,10] We have recently shown that electrochemically prepared films of PEDOT−$C_{14}H_{29}$ can be used as the cathodically coloring material in EC devices with optical contrasts of approximately 60%.[11] As electrochemical polymerization is not amenable to the synthesis of large quantities, we set out to develop high-yield syntheses of solution processable and fully characterizable PEDOT−$C_{14}H_{29}$ which retained the electrochromic capability.

Synthesis of the monomer was carried out starting with thiodiglycolic acid, as described previously.[2] Oxidative polymerization to yield a fully soluble polymer which could be isolated in 80% yield was accomplished using 1 equiv of ferric chloride in dry chloroform, as shown by Scheme 1. The as made oxidized polymer was precipitated into methanol, reduced in $CHCl_3$ solution with concentrated aqueous ammonium hydroxide, and precipitated into methanol to yield a red-brown powder which was completely soluble in $CHCl_3$, CH_2Cl_2, $C_2H_2Cl_4$, and THF.[12] Comparison of the ^{1}H-NMR spectrum of the monomer and polymer showed complete disappearance of the singlet at 6.35 ppm, attributable to the lone thienyl proton, indicating a reasonably high molecular weight polymer with no visible end groups. Molecular weight approximations were carried out using GPC (PS standards) with THF as the mobile phase and a weight average molecular weight was approximated to be 10 900. In further polymerizations, we have found that both molecular weight and polymer solubility is sensitive to the $FeCl_3$/monomer ratio used, as shown in Table 1. While there was little change in the molecular weight of the $CHCl_3$ soluble fraction as the ratio of the $FeCl_3$/monomer was increased from 1 to 3, the overall yield of the $CHCl_3$ soluble polymer decreased drastically. The molecular weight of the soluble fraction was found to increase somewhat at $FeCl_3$/monomer = 4, but when $FeCl_3$/monomer = 5, the polymer was found to be completely insoluble in common organic solvents. The insoluble polymer fraction formed at high $FeCl_3$/monomer ratios is likely due to either higher molecular weight or a small amount of cross-linking. The characterization of electronic properties has been carried out on samples prepared with $FeCl_3$/monomer = 1, as the polymer is completely soluble.

Scheme 1

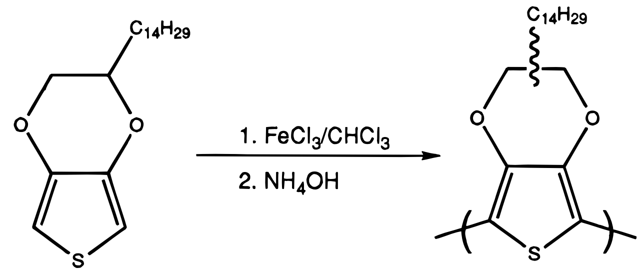

Table 1. Polymerization and Molecular Weight Results for PEDOT−$C_{14}H_{29}$

$FeCl_3$/ monomer	yield (%)	solubility in $CHCl_3$ (%)	M_w[a]	PD
1	80	100	10 900	1.93
2	90	75	11 200	2.00
3	81	30	13 500	2.10
4	85	20	22 500	2.74
5	95	0		

[a] Molecular weight of the chloroform soluble fraction as determined by GPC.

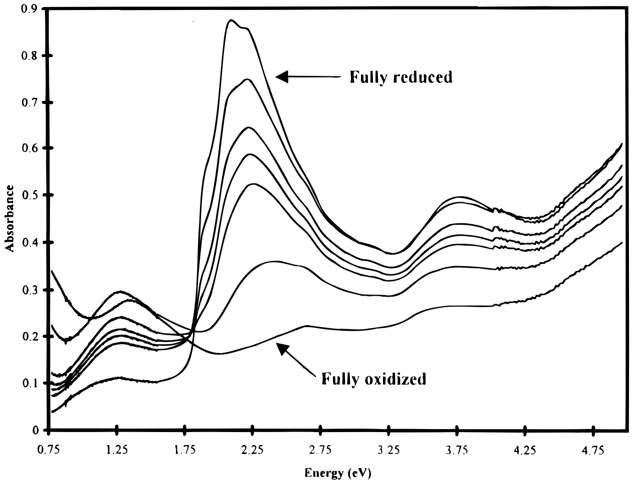

Figure 1. Solution oxidation of PEDOT−$C_{14}H_{29}$ with increasing $SbCl_5$ concentration in $CHCl_3$.

The solution oxidation of PEDOT−$C_{14}H_{29}$ was studied by UV−vis−NIR spectroscopy in $CHCl_3$ as a function of oxidant concentration using $SbCl_5$, as shown in Figure 1. In the reduced, neutral, form the polymer solution exhibited a strong absorbance throughout the visible region (1.75−3.0 eV) and is a deep absorbing purple in color. This absorbance with λ_{max} = 2.15 eV is due to the π to π^* interband transitions of the conjugated

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chain, with the onset used to approximate the electronic band gap (E_g) at 1.78 eV. As the $SbCl_5$ concentration is increased, the visible absorbance decreases to the point that the solution becomes a very pale green and transmissive, as evidenced by the featureless absorption spectrum, when completely oxidized. This loss of absorption throughout the visible region is due to depletion of the states causing the interband transition, while concurrently increasing absorption in the NIR region due to the formation of bipolaronic bands. This gives the polymer a high contrast ratio in the visible region, making it a strong candidate for electrochromic devices. It should be noted that these optical changes are essentially identical to those observed for electrochemically deposited films.[2,4] The polymer could be solution cast and spray (air-brush) cast to yield homogeneous and pinhole free films on glass and ITO-coated glass substrates. Chemical oxidation of these films could be effected by reaction with $SbCl_5$ in CH_3CN. In these experiments, the deep purple film changed instantaneously to transparent light green when exposed to oxidant.

In order to examine the optical changes that occur during electrochemical switching of solution cast films (important for the electrochromic applications) optoelectrochemical analysis was carried out. The PEDOT−$C_{14}H_{29}$-coated ITO glass substrate was used as a working electrode along with Ag wire quasi-reference and platinum counter electrodes in 0.1 M $LiClO_4/CH_3CN$. The reduced deep purple film begins to oxidize at −0.1 V and completely oxidizes to light green transparent at +0.3 V. This redox switching of the polymeric film was found to be reversible over multiple cycles.

In summary, the oxidative solution polymerization of tetradecyl-substituted poly(3,4-ethylenedioxythiophene) results in soluble polymers with optical and redox properties similar to those of electrochemically prepared insoluble films. Current work is in progress to study the contrast ratio, chemical compatability, response time, and long term stability of EC devices prepared using this soluble polymer.

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(12) Elemental analysis results of the soluble PEDOT-$C_{14}H_{29}$: Calcd for ($C_{20}H_{32}O_2S$): C, 71.38; H, 9.58; S, 9.53. Found: C, 70.91; H, 9.38; S, 8.48.

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