

Biocompatible Ionic Liquid-Derived Conducting
Polymers

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A significant and frequently encountered challenge when making an electrical connection to a protein is that its electron-transfer sites are buried within the polypeptide matrix and thus, are not readily accessible to bulk metal electrodes.[1,2] A further complicating factor is that inorganic (i.e., metallic) electrodes are often incompatible with biological samples. These obstacles might be overcome by the use of conducting oligomers and / or polymers, which are flexible, offering a means to access remote redox centers. These oligomers can be readily modified to include chemical moieties that can connect covalently to sites near redox centers. In addition, conducting polymers can be made to be environmentally responsive (dynamic), processable (conformal coating, soluble) and mechanically durable, thus enabling them to function as an electrical conduit (wire or electrode) to biomolecules. In this work, we describe the design, synthesis and electrochemical properties of thiophene-based ionic liquid monomers, such as 1-(10-thien-3-yl)decyl-3-methylimidazolium nitrate, and its bulk polymerization by chemical oxidation to yield a cationic, aqueous-soluble polymer. Both a bromide and nitrate salt of the amphiphilic thiophene IL have been shown to self-assemble in water and the nanostructures have been characterized using polarized optical microscopy and small and wide angle X-ray scattering (SAXS and WAXS). The SAXS and WAXS studies showed that the self-assembled nanostructures adopt well ordered columnar mesophases. More specifically, at low water content the IL – water binary mixtures forms liquid crystalline mesophases possessing significant short-range ordering due to strong pi-pi interactions between adjacent thiophene moieties. At higher water content the short-range ordering is lost, but long-range ordering persists up to ca. 45 % (w/w) water. The chemical oxidative coupling of the nitrate monomer yields a highly water-soluble polymer. The electrochemical properties of an aqueous solution of the IL polymer have been carried out (Figure 1) and show that the polymer possesses a high oxidation potential (1.95 V) and thus, is resistant to chemical doping. In dilute aqueous solution, electronic absorption

spectroscopy and X-ray scattering show the polymer adopts a random, coil-like conformational state. Slight improvement in the polymer conformation can be achieved by exchange of the counter anion. The solution structure and electrochemical properties are compared to those determined for thin films of the solvent cast polymers. Preliminary studies have been carried out evaluating the compatibility of electroactive proteins with the cationic polythiophene.

References:

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2. Reiss, B. D.; Hanson, D. K.; Firestone, M. A., "Evaluation of the photosynthetic reaction center protein as a bioelectronic circuit element", *Biotechnol. Prog.* (2007) **23**, 985-987.

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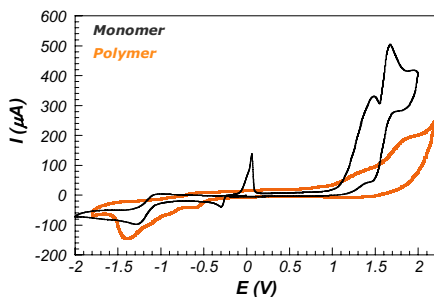


Figure 1. Cyclic voltammograms of [ThienylC₁₀mim⁺][NO₃⁻] in a solution of 0.1 M (Me)₄N⁺PF₆⁻ in acetonitrile, at 50 mV / s and poly[ThienylC₁₀mim⁺][SO₄²⁻] in water added to 0.1 M (Me)₄N⁺PF₆⁻ in acetonitrile, at 50 mV / s.