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Conducting polymer “nanogates” – Controllable diffusivities in thin films of novel tether-containing sulfonated polythiophenes

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ABSTRACT

We describe a nanoscale gating effect by an atypical tether-containing polythiophene, [poly(thiophene-3-carboxylic acid 2-(2-(2-(2-ethoxy-ethoxymethyl sulfonate)-ethoxy)-ethoxy)-amide], referred to as poly(TP-OEG-SO_4). Cyclic voltammetry data permitted us to calculate liquid-phase ion diffusivities in the polymer as a function of its oxidation state. Diffusivities are more than 350 times higher in the oxidized state versus the reduced state. As a control, poly 3′,4′-dimethyl-[2,2′;5′,2″] terthiophene (DMPT) was synthesized and characterized. On comparing both polymers in the reduced state, we find diffusivities in poly(TP-OEG-SO_4) to be more than 4500 times lower than in poly(DMPT). To explain this behavior, we propose a model that features a charge-balancing mechanism by the sulfonate tethers in poly(TP-OEG-SO_4), which causes nanoporous regions around the polymer main chains to be opened and closed, leading to the large observed differences in diffusivities. These data suggest that the polymer poly(TP-OEG-SO_4) is evidently able to act as a reversible “nanogate” with an open pore structure when oxidized, and a closed one when reduced.

1. Introduction

Conducting polymers undergo major physical and chemical changes when oxidized (doped) or reduced (dedoped). These changes are accompanied by charge neutralization processes in solution, involving ion movements to and from the polymer main chains. These mass transport processes are often highly complex, with the direction of motion dependent on ion charge, size, and solvation number [1]. Through appropriate molecular design, it may become possible to harness these polymer redox changes and ion transport processes to create a general gating effect on the nanoscale. An investigation involving this approach was reported recently [2], where polypyrrole was synthesized in the presence of anchored, vertically-aligned carbon nanotubes. It exhibited some interesting diffusion gating effects that arose from the swelling/shrinking of the polymer during oxidation/reduction, although the material had a limited ability to undergo repeated cycling. Similar, more cycleable approaches have involved electrochemical gating by poly(vinylpyridine) [3,4].

The concept of “self-doping” in conducting polymers, in which an anionic group (i.e., sulfonate) attached to the polymer main chain provides rapid charge neutralization when the polymer is electrochemically switched between its oxidation states, is well known [5]. We have extended this concept by incorporating unusually long sulfonate-terminated tethers into the conducting polymer polythiophene. We propose that the charged, anchored tethers are able to intramolecularly ion-pair to the polymer when it is in its oxidized state. When the polymer is switched to its reduced state, the freed tethers are then able to “random walk” in the surrounding nanoregions, and thus obstruct movement of liquid or solute. Hence, the tethers serve as “nanogates” that are open when the polymer is oxidized, and closed when the polymer is reduced. The switching of the redox states is reversible, and actuated by the application of small voltages, from 0 to 1.5 V. As is discussed below, we have found that these effects are reversible over at least 10 redox cycles.

2. Experimental

2.1. Materials

Solvents, gold wire, and precursors for the conducting polymers were purchased from Sigma–Aldrich.

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2.2. Chemical synthesis of TP-OEG-SO_4 and DMTP

The monomer thiophene-3-carboxylic acid 2-(2-(2-(2-ethoxy-ethoxymethyl sulfonate)-ethoxy)-ethoxy)-amide (sodium salt), referred to as TP-OEG-SO_4, was synthesized in four steps, using procedures from [6]. The monomer 3′,4′-dimethyl-[2,2′;5′,2″] terthiophene was synthesized as described previously [7].

2.3. Electrochemical synthesis of poly(TP-OEG-SO_4) and poly(DMTP)

Dissolution of 15 mg TP-OEG-SO_4 into 4:1 toluene: acetonitrile (v:v) containing 200 mM *t*-butylammonium hexafluorophosphate (TBA^+HFP^-) was followed by electropolymerization into a thin film onto a 0.2 mm diameter gold coil with a 1 cm^2 immersion area. Polymerization was performed at 1.8 V vs. Ag wire quasi-reference electrode for 90 s, the process being repeated four times. The density of the resulting polymer film was 0.89 g/cm^3 (based on the measured density of the monomer), and the average film thickness was 2.13 μm. The power source was a Model CHI 660C Electrochemical Workstation (CH Instruments, Austin, Texas). By this procedure 0.19 mg poly(TP-OEG-SO_4) were deposited onto the gold coil, as determined by gravimetry and coulometry. In a similar manner, 3′,4′-dimethyl-[2,2′;5′,2″] terthiophene (DMPT) was electropolymerized onto a gold coil, forming a thin film of mass 0.30 mg.

2.4. Transmission electron microscopy

Monomer was electropolymerized onto copper TEM grids in a manner similar to that described above. The grids were washed to remove dried salts, and viewed with a transmission electron microscope (Libra 120, Carl Zeiss SMT, Peabody, MA) at 120 kV. Images were captured on a bottom-mounted digital camera (Olympus SIS, Montvale, NJ).

2.5. Cyclic voltammetry

Studies were performed at 18 °C in a sealed cell using a CHI 660C electrochemical workstation, in the solvent system 4:1 toluene: acetonitrile (v:v) containing concentrations of TBA^+HFP^- in the range of 300–0.1 mM.

3. Results and discussion

We synthesized the novel tether-containing monomer thiophene 3-carboxylic acid-2-(2-(2-(2-ethoxy-ethoxymethyl sulfonate)-ethoxy)-ethoxy)-amide, sodium salt (Fig. 1a). For brevity, we will refer to this compound as thiophene-3-oligoethylene glycol sulfonate, or TP-OEG-SO_4. The structure of its polymerized form, poly(TP-OEG-SO_4), is shown in Fig. 1b. The proposed mechanism of charge balancing through tether movement is also shown in Fig. 1b, which also depicts the resulting effects in the local nanoscale space. Transmission electron microscope (TEM) images of the polymer in the reduced and oxidized states are shown as insets. They clearly indicate that the polymer fine structure changes with oxidation state, with porous regions (lighter areas) becoming significantly larger when the polymer is switched into its oxidized form. If the sulfonate tethers form intramolecular ion-pairs, they would vacate the regions farther away from the polymer main chains and cause the electron density there to drop. Simultaneously, the darker regions (which correspond to polymer-rich regions), would become enlarged. This is, in fact, what is seen in the image. In the oxidized state, the porous regions may be large enough to easily transport solvated electrolyte or tether ions, with

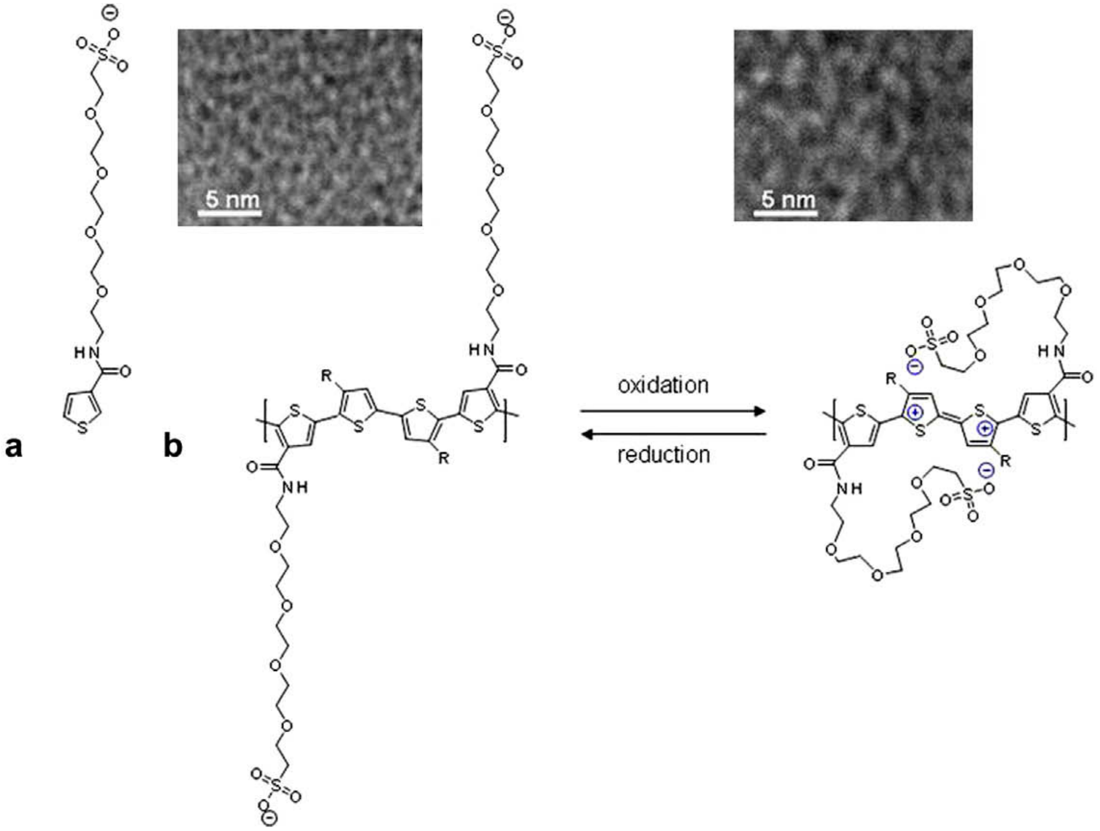

Fig. 1. Monomeric TP-OEG-sulfonate (a) and the proposed charge-balancing mechanism by the sulfonate tethers with polymer TEM images (b). In the central two thiophene residues R denotes the amide tether chains.