# Lithium ion and electronic conductivity in 3-(oligoethylene oxide)thiophene comb-like polymers

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## Abstract

The Li-ion and electronic conductivities of a series of p-doped poly(thiophene)s with oligo-ethylene oxide side chains have been determined at room temperature as functions of side-chain length and concentration of LiOTf dissolved in the polymers in order to assess their utility as binders in Li-ion batteries. The lithium triflate concentration was varied from 0.23 to 2.26 mmol LiOTf/g $-C_2H_4O-$ (100 O:Li to 10 O:Li), and the concentration of dissociated $Li^+$ was determined from the IR spectra of the polymer solutions. The greatest ionic conductivity, $2 \times 10^{-4}$ S cm$^{-1}$, was attained with intermediate concentrations of added salt that corresponded with the greatest degree of LiOTf dissociation. Li-ion mobilities of $5 \times 10^{-7}$ cm$^2$ (Vs)$^{-1}$ were measured for poly(thiophene)s (PT) with short oligo(ethylene oxide) side-chains ($E_n$), PE$_2$T and PE$_3$T, whereas the polymers with longer side chains, PE$_7$T and PE$_{15}$T, had Li-ion mobilities about an order of magnitude greater, $5 \times 10^{-6}$ cm$^2$ (Vs)$^{-1}$. The electronic conductivity of the polymers heavily doped with NOBF$_4$ was near 0.1 S cm$^{-1}$ for PE$_2$T and PE$_3$T, but was orders of magnitude smaller for the polymers with longer side-chains. Addition of LiOTf caused the electronic conductivity of PE$_2$T and PE$_3$T to drop to that of the longer chain polymers whose conductivities were insensitive to the LiOTf concentration.
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## 1. Introduction

In order to achieve high power densities, a battery must be capable of rapid discharge, and this capability requires the electrode structure to have a high electron mobility and that the interface of the electrode with the electrolyte have a high ionic mobility. In the present generation of Li-ion batteries, the electroactive cathode material, e.g., $Li_{(1-x)}CoO_2$, is typically bonded to the current collector plate with a glue, e.g., EPDM, which is an insulator. Thus, some portion of the powdered $Li_{(1-x)}CoO_2$ is isolated from the current collector with resulting loss of capacity. Furthermore, some of the active surface area of the $Li_{(1-x)}CoO_2$ particles is covered by the EPDM, thereby limiting the transport of Li-ions and decreasing the rate of discharge. Therefore, the development of a binder material that can conduct both electrons and Li-ions would appear desirable as a means to improve both the capacity and power density of Li-ion batteries.

Materials that combine the electronic conductivity of conjugated polymers with ion-receptive groups have been studied primarily for use as ion sensors [1–6]. In these applications, ions interact with the ion-coordinating components of the material, leading to changes in the electronic nature of the conjugated polymer backbone. These changes can manifest themselves as differences in the physical properties of the material. Color, fluorescence, electrochemical potential, and conductivity have been used to monitor the concentration of the desired ion in these systems.

Less than 30 years have passed since Wright performed preliminary work on poly(ethylene oxide) (PEO) as an alkali

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metal ion conductor [7–9]. The conductivity of PEO-salt solutions is quite temperature dependent. Ionic conduction is facilitated by segmental motion of the flexible PEO chains. Above the melting point, $T_m \approx 65\,°C$, values near $10^{-4}\,S\,cm^{-1}$ are observed; but at ambient temperature, the conductivity of these systems is considerably lower. The room temperature conductivity of PEO has been improved through the use of small-molecule plasticizers and the development of less crystalline polymers with PEO side chains (comb polymers) [10–23]. In this work, a series of poly(thiophene)-based comb polymers featuring oligo(ethylene oxide) side chains of various lengths were synthesized, and the conductivities of polymer-salt solutions with several different concentrations of lithium triflate were measured. Ionic conductivity values as great as $2 \times 10^{-4}\,S\,cm^{-1}$ were obtained for the neutral polymer/salt blends. The ionic conductivity of these materials was found to be strongly dependent on the concentration of lithium triflate. The electronic conductivities of the $NOBF_4$-doped polymers were determined also as a function of the LiOTf concentration. Electronic conductivity was observed to drop by several orders of magnitude upon addition of lithium salt.

## 2. Experimental

All materials used were obtained from Aldrich, Acros, or Fluka and purified according to accepted procedures before use. Standard Schlenk techniques were utilized when air exclusion was necessary. NMR spectra were recorded using a Varian 400 MHz spectrometer. Chemical shifts were referenced to residual solvent.

The monomers, 3-(2,5-dioxahex-1-yl)thiophene (E$_1$T) and 3-(2,5,8-trioxanon-1-yl)thiophene (E$_2$T), and their 2-bromo derivatives were synthesized as reported previously [24a,25]. The monomers with longer side chains were synthesized similarly.

*Syntheses of 2-bromo-3-(2,5,8,11-tetraoxadodecyl)thiophene (BE$_3$T), 2-bromo-3-(methoxy(ethoxy)$_{7.5}$)methylthiophene (BE$_7$T), and 2-bromo-3-(methoxy(ethoxy)$_{15.5}$)methylthiophene (BE$_{15}$T).* These monomers were synthesized in the same manner as for the bromination of E$_1$T [25]. Distillation of the BE$_3$T product at 0.02 Torr gave a clear liquid boiling from $136 - 139\,°C$. Yield: 83%. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 (d, $J = 5.8$ Hz, 1H), 6.98 (d, $J = 5.5$ Hz, 1H), 4.45 (s, 2H), 3.59 (m, 10H), 3.32 (s, 3H). BE$_7$T: this product was purified by flash column chromatography. The stationary phase was neutral alumina and the eluent was ethyl acetate. Volatile contaminants were removed by heating at $100\,°C$ in vacuo for 24 h. Yield: 73%. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 (d, $J = 5.7$ Hz, 1H), 6.95 (d, $J = 5.5$ Hz, 1H), 4.46 (s, 2H), 3.59 (m, 28H), 3.49 (m, 2H), 3.32 (s, 3H). BE$_{15}$T: this product was also purified by flash chromatography with neutral alumina as the stationary phase and ethyl acetate as the eluent. Volatile contaminants

were removed by heating at $100\,°C$ in vacuo for 24 h. Yield: 76%. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J = 6.0$ Hz, 1H), 6.92 (d, $J = 5.5$ Hz, 1H), 4.49 (s, 2H), 3.64 (m, 50H), 3.52 (m, 2H), 3.37 (s, 3H).

The polymers were prepared by McCullough's GriM method with only minor changes to the reported syntheses for PE$_n$T ($n = 1,2$) [24,26]: Regioregular poly(3-(2,5,8,11-tetraoxadodecyl)thiophene) (PE$_3$T). Yield: 29%. ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 (s, 1H), 4.58 (s, 2H), 3.64 (m, 10H), 3.49 (m, 2H), 3.31 (s, 3H). Regioregular poly(3-(methoxy(ethoxy)$_{7.5}$)methylthiophene) (PE$_7$T). The fraction of the product soluble in methanol was recovered and purified by precipitation with hexanes. Yield: 42%. ^{1}H NMR (400 MHz, MeOH-$d^4$) $\delta$ 7.25 (s, 1H), 4.65 (s, 2H), 3.68 (m, 28H), 3.54 (m, 2H), 3.33 (s, 3H). Regioregular poly(3-(methoxy(ethoxy)$_{15.5}$)methylthiophene) (PE$_{15}$T). The fraction of the product soluble in methanol was recovered and purified by precipitation with hexanes. Yield: 40%. ^{1}H NMR (400 MHz, MeOH-$d^4$) $\delta$ 7.21 (s, 1H), 4.61 (s, 2H), 3.62 (m, 50H), 3.50 (m, 2H), 3.29 (s, 3H). No signals due to H-atoms at the ends of the chains were detected above the noise level ($\leq 1/20$ of the peak height for the ring H-atom) for any of the polymers reported here, indicating the degree of polymerization, DP $\geq$ 20.

All current/voltage measurements were performed using a Perkin-Elmer model 273A potentiostat in conjunction with a PC interface for data acquisition. Film thickness was measured by profilometry using a Dektak [3] profilometer. DSC scans were performed with a Perkin-Elmer DSC 7 calorimeter at $5\,°C\,min^{-1}$.

### 2.1. Infrared spectra

IR spectra were obtained from KBr pellets using a Perkin-Elmer Spectrum BX spectrometer. Deconvolution of infrared peaks was accomplished with GRAMS/32 software. The peaks were assumed to be of Lorentzian shape. The area of the signal corresponding to the symmetric sulfur–oxygen stretch of the triflate ion was normalized by referencing it to the area of the peak for the carbon–hydrogen stretching mode observed near $3000\,cm^{-1}$. In order to relate the area of each component peak to the concentration of the ionic species it represents, the spectra of the most dilute PE$_n$T/LiOTf blends were considered. In these cases, essentially all of the lithium triflate was dissociated, as indicated by curve-fitting. So, the ratio of the area of the observed peak to the total salt concentration was indicative of the oscillator strength of the free triflate ion. This ratio was then applied to samples with intermediate LiOTf concentrations which showed free ions and ion pairs. The peak area corresponding to free ions was converted to concentration and then subtracted from the total salt concentration. In this way, the ratio of peak area to ion pair concentration was determined. The procedure was then repeated for the spectra of the most concentrated samples, allowing for the concentration of multiple-ion aggregates to be determined.