ELECTRICAL PROPERTIES OF HIGHLY CONDUCTIVE EDOT BASED COPOLYMERS

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Introduction

The discovery of electrical conductivity in conjugated polymers has inspired a tremendous amount of research focused on the development of practical conducting plastics. In the field of conducting polymers, polythiophenes (PTs) continue to be one of the most versatile and extensively studied conjugated polymer systems due to their exceptional spectroscopic and electronic properties, in addition to the ease of synthesis of PTs derivatives. Practical and potential applications of PT derivatives such as poly(alkylenedioxythiophene) [PXDOT] include electrochromic devices (ECDs), antistatic coatings, hole conducting material in organic/polymer-based light-emitting diodes (OLEDs/PLEDs),[1a-d] chemical and optical sensors.[1e-f]

Here we report electrical and spectroscopic properties of alternating copolymers of 3-alkyl/alkoxy-substituted-thiophenes and 3,4-ethylene-dioxythiophene (EDOT) such as poly(2,5-(3-dodecyl-3,4-ethylenedioxy)bithiophene) [poly(2,5-(3-DD-3,4-EDO)bithiophene)] and oligo(2,5-(3-(2-(2-methoxyethoxy)ethoxy)-3,4-ethylenedioxy)bithiophene) [oligo(2,5-(3-MEE-3,4-EDO)bithiophene)], where the former was synthesized via the Grignard Metathesis (GRIM) method[2] and the later through autopolymerization via radical mechanism.[3] These copolymers exhibit a variety of favorable properties, which include a reduced band gap and low oxidation potential for the conversion to the highly stable conducting state. UV-vis-NIR spectroscopic studies and conductivity measurements revealed that these copolymers possess higher conductivities in the solid state and are readily oxidized in an oxygen atmosphere. Further oxidation (doping) with I_2 increases conductivity and prolongs the stability of the doped state. Furthermore, these copolymers in their undoped state are very soluble in organic solvents and possess excellent film-forming abilities. The films of oligo(2,5-(3-MEE-3,4-EDO)bithiophene remain in the doped state for a length of time that is unprecedented.

Experimental

Materials. All polymerization reactions were performed under prepurified nitrogen, using either flame-dried or oven-dried glassware. Commercial chemicals, purchased from Aldrich Chemical Co., Inc., were used without further purification unless noted otherwise. All solvents were freshly distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium/potassium benzophenone ketyl. Titration of the Grignard reagents was performed following the procedure described by Love.[4]

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz and 500 MHz spectrometer. All NMR spectra were recorded in deuteriochloroform ($CDCl_3$) as solvent containing 0.003% TMS as an internal reference. The amount of head-to-tail coupling was determined by NMR integration of the small peaks near 7.0 ppm using the Sato and Morii analysis and the peaks near 2.5 ppm using the method of Elsenbaumer *et. al*.[5] All UV/Vis spectra were taken on either polymer solutions in chloroform or polymer thin films cast onto cover glass 22 mm sq. using a Perkin-Elmer Lambda 900 UV/Vis NIR spectrometer and are reported in λ in nm. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. Gel Permeation Chromatography (GPC) spectra were recorded on a Waters 2690 Separations Module apparatus and a Waters 2487 Dual λ Absorbance Detector with chloroform as the eluent (flow rate 1.0 ml/min, 35°C) with a series of three Styragel columns (10^5, 10^3, 100 Å; Polymer Standard Services). Calibration based on polystyrene standards was applied for determination of molecular weights of polymers. Conductivity was measured for thin films of the alternating copolymers oxidized with I_2 for various time periods by the 4-probe technique. The film thickness was measured by Scanning Electron Microscopy (SEM) and the conductivity calculated according to the following equation:

$$\sigma = 1 \div (4.53 * R * l)$$

were R is the resistance ($R = V/I$) and l is the film thickness.

Synthesis of 2,5-(3-MEE-3,4-EDO)bithiophene oligomers. In a typical experiment, a dry 100 mL three-neck flask was charged with 2,5-(3-MEE-3,4-EDO)bithiophene (0.50 g, 1.5 mmol) and anhydrous THF (25 mL) under N_2. The reaction flask was cooled to -78 °C (acetone/dry ice bath) followed by addition of 1,3-dibromo-5,5-dimethylhydantoin (0.21 g, 0.73 mmol). The reaction mixture was stirred for 1 h at -76 °C. The cooling bath was removed, and the reaction was allowed to proceed for 2 h at RT. As soon as the solvent was removed under reduced pressure, deep blue colored solid formed. The solid was collected and dried under vacuum yielding 90% of the oligomeric material.

Results and Discussion

Poly(2,5-(3-dodecyl-3,4-ethylenedioxy)bithiophene). The polymer was synthesized via the Grignard Metathesis (GRIM)[4a] method as depicted in **Figure 1**. This method involves treatment of aryl dibromide species with a Grignard reagent R′MgBr in THF in order to generate a mixture of Grignard intermediates (*e.g*., 2-bromo-5-bromomagnesio-3-alkylthiophene and 2-bromomagnesio-5-bromo-3-alkylthiophene), followed by addition of $Ni(dppp)Cl_2$ to produce HT-coupled regioregular polymers. This methodology was expanded to include 3/3,4-substituted bithiophene derivatives such as 2,5-(3-DD-3,4-EDO)bithiophene and 2,5-(3-MEE-3,4-EDO)bithiophene, which resulted in poly(2,5-(3-DD-3,4-EDO)bithiophene) (**Figure 1**).

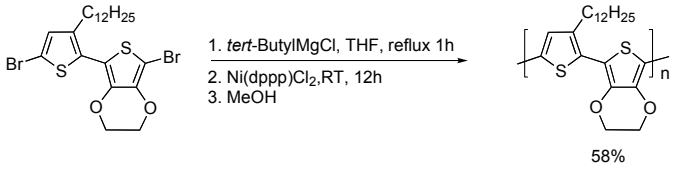


Figure 1. Synthesis of poly(2,5-(3-dodecyl-3,4-ethylenedioxy)bithiophene) via the Grignard Metathesis (GRIM) method.

Oligo(2,5-(3-(2-(2-methoxyethoxy)ethoxy)-3,4-ethylenedioxy) bithiophene). Monobrominated (or dibrominated) derivatives of 2,5-(3-MEE-3,4-EDO)bithiophene have been prepared by direct bromination according to known procedure.[6] The oligomerization of 2,5-(3-MEE-3,4-EDO)bithiophene was a result of a work up of brominated species. The yellow liquid that remained after removing the solvent under reduced pressure, transformed into a dark blue solid as depicted in **Figure 2**. The obtained material was readily soluble in common organic solvents, especially *N,N*-dimethylformamide (DMF), with pronounced solvatochromism properties. The observed transformation of such halogeneted species into oligomers is similar to the one reported by Meng *et. al*. for polymerization of bromine-doped PEDOT.[3]

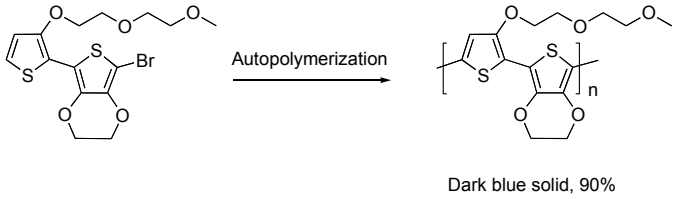


Figure 2. Synthesis of oligo(2,5-(3-MEE-3,4-EDO)bithiophene).

The films of oligo(2,5-(3-MEE-3,4-EDO)bithiophene were drop cast from DMF and upon further doping with iodine showed surprisingly high conductivities. The changes in conductivity were monitored over a period of time and an increase of conductivity with time was observed.[7]
The corresponding molecular weights and electrical conductivity for the synthesized co-poly/oligomers are depicted in **Figure 3**.

Conclusions

We have synthesized ethylenedioxythiophene based co-poly/oligomers which exhibit a variety of favorable properties. UV-Vis-NIR spectroscopic studies and conductivity measurements revealed that these novel copolymers/oligomers are readily oxidized in an oxygen atmosphere, due to

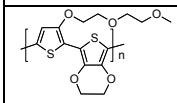
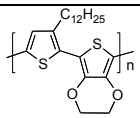
Structure	Conductivity, σ (S/cm)			M_n (GPC)
	Air doped	2 min doped w/I_2	24 h doped w/I_2	
	*l* = 5μm **0.26** 1day later **0.54** 30days	*l* = 420nm **0.78** - RA **1.97** 1day later **4.95** 30days	*l* = 3.36μm **0.71** - RA **10.3** 1day later **23.4** 30days	2,000
	 **6.0x10^{-4}** 1 day **0** 30days	*l* = 2.41μm **0.08** 1day later **0.02** 30days	*l* = 42.2μm **1.57x10^{-3}** RA **6.86x10^{-3}** 1day later	11,000

Figure 3. Electrical conductivity of EDOT based copolymers.

the reduced band gap, and possess high conductivities in the solid state that can be further promoted with iodine doping. The fully undoped co-poly/oligo-mers are soluble in common organic solvents and possess excellent film-forming properties. Furthermore, films of oligo(2,5-(3-MEE-3,4-EDO)bithiophene remain in the doped state for a long time and their conductivity increases.

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(7) The films were doped with I_2 and then exposed to air.