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Unusual chromic and doping behavior of ether substituted polythiophenes

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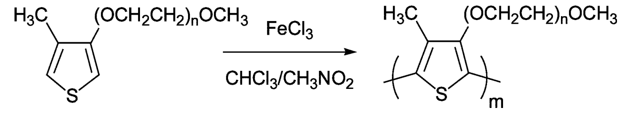
Poly[3-(oligoethylene oxide)-4-methylthiophene] is doped by HCl in aqueous solution in the absence of oxygen and undergoes dramatic solvatochromism in water–ethanol mixtures.

The ability to convert conjugated polymers to a conductive state was discovered more than twenty years ago,[1] creating a new field of research on the boundary between chemistry and physics.[2] Conducting polymers can undergo redox doping, photo-doping, charge-injection doping and protonic acid doping.[3] However, protonic acid doping has been largely limited to polyaniline and poly(heteroaromatic vinylenes).[4] Acid doping has been reported for alkyl, alkoxy, and sulfonic and phosphonic acid substituted polythiophenes.[5] However, these reports either utilize very strong acids or mild acids in the presence of oxygen.[6] Doping of polythiophenes under mild acidic anaerobic conditions has not been reported.[7] Another interesting property of polythiophenes is solvatochromism. A change in color is observed for many substituted polythiophenes upon changing from a "good" to a "poor" solvent.[8] While the mechanism of the solvatochromic transitions in polythiophenes is not fully understood, it is generally attributed to a change in polymer conformation[9] or aggregation[10,11] upon variation of the solvent. Polythiophenes typically have shorter wavelength absorptions in good solvents and longer wavelength absorptions in poor solvents.

In this paper we report on an improved synthesis along with the unusual protonic acid doping and solvatochromic properties of poly[3-(oligoethylene oxide)-4-methylthiophene]s (**1**). The synthesis of **1** is conducted *via* a modified literature procedure (Scheme 1).[12] Oxidative coupling of 3-(oligoethylene oxide)-4-methylthiophene by $FeCl_3$ in CH_3NO_2 or 1 : 9 CH_3NO_2–$CHCl_3$ provides **1a** and **1b** in 65 and 90% yield respectively.† Polymer **1** prepared *via* oxidative polymerization is largely regioregular with > 95% head-to-tail content.[12]‡ While the molecular weight of **1** polymerized in the presence of CH_3NO_2 is lower than that prepared in pure $CHCl_3$ the yield of soluble polymer is noticeably improved. Oligomer **1a** (M_n = 1400, PDI = 7.3, THF *vs.* polystyrene) is soluble in water while **1b** (M_n = 7000, PDI = 5.4, THF *vs.* polystyrene) is soluble in water–ethanol mixtures.



Scheme 1 Synthesis of poly[3-(oligoethylene oxide)-4-methylthiophene] (**1**).

Protonic acid doping of **1a** under anaerobic conditions is supported by UV-Visible spectroscopy (Fig. 1). The addition of dilute aqueous solutions of HCl to **1a** provides a systematic shift of the optical absorption spectra with increasing concentrations of HCl. The absorptions of neutral **1a** at 400, 560, and 595 nm gradually disappear while absorptions centered at 350, 800, and 1300 nm steadily appear consistent with the formation of delocalized radical cationic fragments. Similar doping is observed in the presence of atmospheric oxygen at lower concentrations of acid. The shift in the optical absorption spectra under air can be observed at about 0.42 M HCl compared with about 0.92 M HCl under nitrogen. This agrees with previous observations for poly(dimethoxyphenylene vinylene).[4] Oxygen can be ruled out as being a necessary component of protonic acid doping. However our results suggest that oxygen can act cooperatively with protonic acids to assist doping under more mild conditions.

Many substituted polythiophenes are solvatochromic.[8,9,11] The change in color is attributed to changes in conformation of the polythiophene chain. Upon dissolving substituted polythiophenes in good solvents, THF or $CHCl_3$, the polythiophene chain obtains a disordered conformation resulting in minimal electronic delocalization along the polythiophene chain and a shorter wavelength optical absorption. Alternatively, dissolving substituted polythiophenes into poor solvents, MeOH or EtOH, results in an ordered backbone conformation with more extensive delocalization of the π-electrons and a longer wavelength optical absorption. Interestingly we observe a solvatochromic transition for **1a** and **1b** in mixtures of two poor solvents, water and EtOH.

Dissolving oligomer **1a** in water or ethanol results in deep purple solutions with absorption maxima at 510, 540 and 595 nm, consistent with dissolution in "poor" solvents. However, in water–ethanol mixtures the solutions are yellow with an absorption maximum at 420 nm. The systematic preparation of solutions of **1b** with varying concentrations of water in ethanol results in a dramatic solvatochromic shift in the optical absorption spectrum (Fig. 2a). Absorptions at 510, 540, and 595 nm completely disappear, to be replaced by an absorption at 420 nm upon addition of 11% water. Continued addition of water results in a reversal of the solvatochromism back to the original longer wavelength absorptions upon the addition of 61% water (Fig. 2b). The presence of a well defined isosbestic point in both series of spectra suggests a two phase transition: an ordered phase with long wavelength optical absorptions and a disordered phase with short wavelength optical absorptions. A concentration dependence is observed for the solvatochromism. At high concentrations of **1b** (1.0×10^{-5} M) the disordered phase is dominant between 11 and 30% water in ethanol, while lower concentrations of **1b** (1.0×10^{-6} M) increase this range to between 9 and 42%. The concentration dependence suggests that the solvatochromism is an intermolecular transition

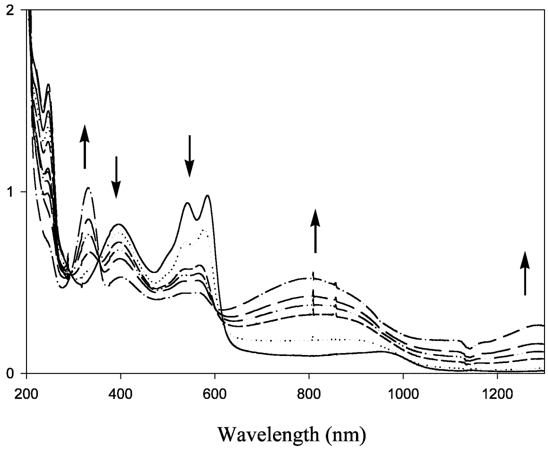


Fig. 1 Absorption spectra of **1a** (1.4×10^{-4} M) under nitrogen (all solutions were purged for more than 1 h before use): HCl concentration (a) 0.0 M, (b) 0.46 M, (c) 0.92 M, (d) 1.4 M, (e) 1.8 M, (f) 2.8 M.

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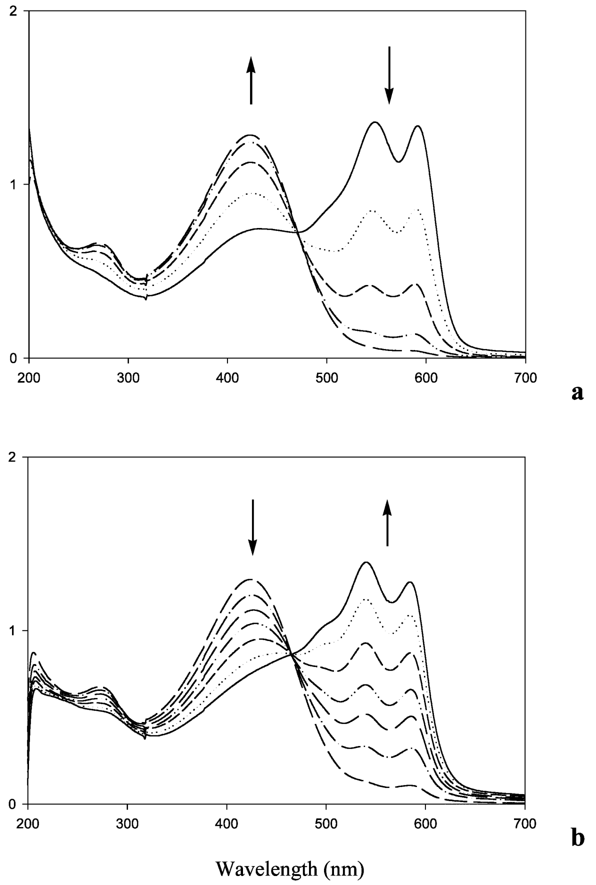

Fig. 2 Absorption spectra of **1b** (1.0×10^{-5} M) in water–ethanol. **a:** percent water 0, 3, 6, 9, 11. **b:** percent water 30, 42, 48, 51, 56, 61, 67.

consistent with an aggregated ordered phase and a deaggregated disordered phase.[11] Similar solvatochromic transitions are observed for isopropanol–water and *t*-butanol–water mixtures, but are not observed for mixtures of methanol and water.

The unusual solvation phenomenon is related to the solubility properties of many carboxylic acids, glycol ethers, and pharmaceuticals and is typically attributed to increases in the entropy in the solvent.[13] The addition of ethanol to water results in a decrease in the order of the solvent favoring the interactions between the solvent and the solute over solvent–solvent interactions. The hydrogen bonding of the oligoethylene oxide sidechains of **1** with the disordered solvent mixture is strong enough to break apart the strong π-stacking interactions of the ordered polythiophene aggregates. We will continue to investigate the source of this unusual solvatochromic behavior and the role of aggregation in the solvatochromic and thermochromic properties of polythiophenes.

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Notes and references

† Under a positive atmosphere of nitrogen, 2.0 g (4.5 mmol) 3-(oligoethylene oxide)-4-methylthiophene (n = 7.2) in 25 mL of $CHCl_3$–CH_3NO_2 (w/w = 9 : 1) was added to 3.0 g (18.5 mmol) $FeCl_3$ in 25 ml of $CHCl_3$–CH_3NO_2 (w/w = 9 : 1) at 0 °C. The mixture was then allowed to stir overnight at room temperature. To this reaction mixture was added 10 mL methanol to stop the reaction followed by 50 mL $CHCl_3$. The reaction mixture was washed with water (3 × 25 mL) followed by removal of solvent by evacuation to yield **1b** (1.8 g, 90%).

‡ Due to the low molecular weight and high concentration of end groups the regioregularities of polymers **1a** and **1b** were not determined.

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