

Self-Assembly and Disassembly of Regioregular, Water Soluble Polythiophenes: Chemoselective Ionchromatic Sensing in Water

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The development of polythiophene (PT) derivatives with essentially 100% head-to-tail (HT) couplings^{1,2} has led to the discovery of materials that self-assemble both in solution and in the solid state. Light-scattering studies on regioregular, HT-poly(3-dodecylthiophene) (HT-PDDT) show that a supramolecular organization occurs via intermolecular aggregation.³ This solution aggregation is precursive to a microcrystalline, self-assembled structure which has been characterized by X-ray studies.^{1,2,4} Polythiophenes possessing this metastable organization evidence high electrical conductivities^{1,2,5–8} and very small bandgaps. Previous work in our lab has shown that both conformational order and solid state organization in regioregular PT derivatives are remarkably sensitive to the placement and nature of the substituent chains.^{1,6,7,9} This sensitivity provides the opportunity to design new conducting polymers in which self-assembly is controlled by environmental factors. One remarkable example is HT-2,5-poly(thiophene-3-propionic acid) (**3**, PTPA). This polymer was designed such that upon deprotonation, water soluble polythiophene salts are formed.¹⁰ Both **3** and its partially deprotonated derivative **5** undergo protein-like hydrophobic assembly, with subsequent H-bond stabilization, to generate a self-assembled conducting polymer aggregate. Varying the size of the counterion in the carboxylate polymer changes the effective steric bulk of the substituent. Small cations favor a self-assembled (purple) state and large cations can completely disrupt the aggregated phase. In fact, a remarkable chemoselective counterion size-dependent chromaticity (Figure 1) is observed for polymer **5**. The UV-vis λ_{max} can be varied over a 130 nm range (from purple to yellow) simply by changing the countercation.

Initially, we prepared the carboxylate precursor polymer **2** using the Ni(dppp)Cl₂ cross-coupling method for the synthesis of HT polythiophenes.^{5,6,9} This method leads to low molecular weights ($M_n = 1.5\text{--}3.0$ K), low yields (<5%), and polymers that show variable ionic chromaticity. However, the regioregular oxazoline polythiophene (**2**) ($M_n = 8$ K, PDI = 1.2) is prepared (Scheme 1) from monomer **1** in high yields (84%)

(1) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.

(2) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(3) Yue, S.; Berry, G. C.; McCullough, R. D. *Macromolecules* **1996**, *29*, 933.

(4) Prosa, T.; Winokur, M.; McCullough, R. D. *Macromolecules* **1996**, *29*, 3654.

(5) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608.

(6) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.

(7) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Ewbank, P. C.; Anderson, D. L.; Tristram-Nagle, S. *Synth. Met.* **1993**, *55*, 1198.

(8) (a) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.

(b) Chen, T.-A.; Rieke, R. D. *Synth. Met.* **1993**, *60*, 175.

(9) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

(10) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. *J. Am. Chem. Soc.* **1987**, *109*, 1858.

(11) Monomer **1** and polymers **2**, **4**, and **5** have been characterized by ¹H and ¹³C NMR and in some cases IR and elemental analysis (see Supporting Information).

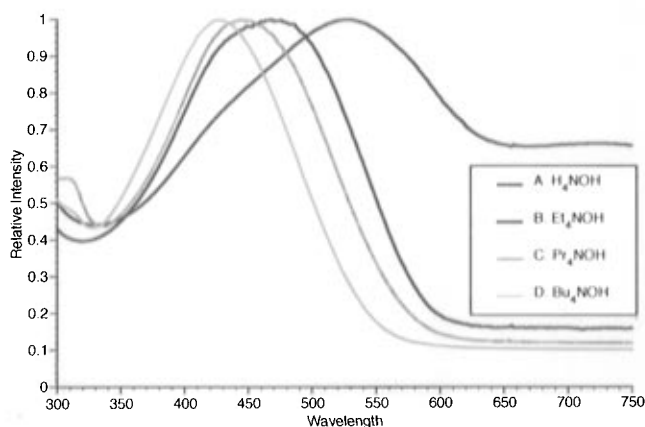
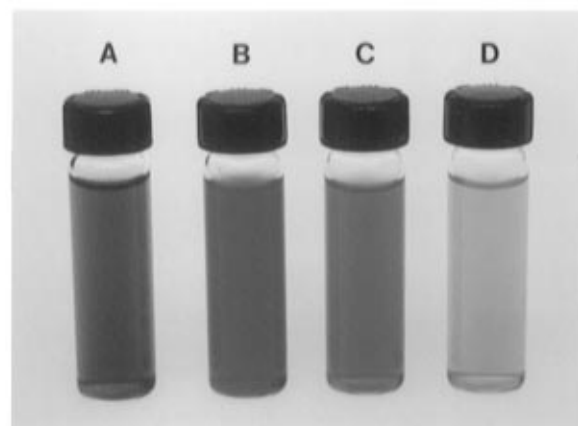
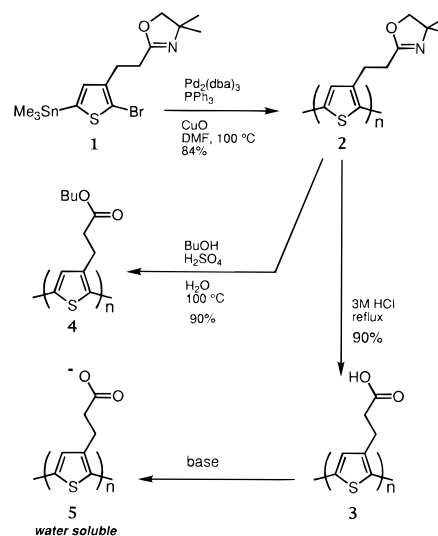


Figure 1. Vials of polymer **3** with added base (top): (A) **3** + H₂NOH; (B) **3** + Et₄NOH; (C) **3** + Pr₄NOH; (D) **3** + Bu₄NOH. UV-vis spectra of the above solutions **A**, **B**, **C**, and **D** (bottom).

Scheme 1. Synthesis of Regioregular, Head-to-Tail Polythiophenes



by using a CuO-modified Stille coupling route that has been adapted from work described by Gronowitz.¹² Polymer **2** is readily soluble in CHCl₃ and is easily purified to obtain the product as a lustrous red solid. Polymer **2** carries a carboxylic acid masked as an oxazoline and is easily modified by a post-polymerization hydrolysis reaction to give PTPA (**3**) (90%) as a dark purple solid, which can be filtered and used without

(12) Gronowitz, S.; Bjork, P.; Malm, J.; Hornfeldt, A.-B. *J. Organomet. Chem.* **1993**, *460*, 127.

further purification. Although **3** is not very soluble, we have found that after treatment of **3** with CsCO_3 its cesium salt, **5**, is soluble in CD_3OD and the polymer can be characterized by ^1H NMR. The ester derivative **4** has also been prepared by this method and analysis of both **4** and **5** by NMR indicated that the oxazoline group is cleanly removed and that the polymers are regioregular with $\sim 100\%$ HT couplings.

Water soluble ammonium salts of **5** are prepared by dissolution of **3** in aqueous base. For solutions containing approximately 1 equiv of base for each carboxylic acid residue, the cation size-dependent chromaticity^{5,13} is readily apparent (Figure 1). The UV-vis λ_{max} of **5** can be varied over approximately a 130 nm range simply by changing the size of the ammonium counterion (Figure 1). When PTPA (**3**) was treated with NH_4OH , purple solutions of **5** with a λ_{max} of 540 nm and a significant absorption past 800 nm are observed (Figure 1). If a slightly larger base such as Me_4NOH is added to **3**, a magenta solution results (not shown). More sterically encumbered bases such as Et_4NOH and Pr_4NOH give red and orange solutions for **5**, respectively. The largest bases, such as Bu_4NOH , lead to yellow solutions. Regioregular polymer **5** gives a chemoselective color response to a various analytes including alkali metal bases. As the size of the counterion varies from Li^+ (0.60 Å) to Cs^+ (1.69 Å), a 40 nm shift in the λ_{max} is seen. In addition, purple solutions (**3** + $\text{NH}_4\text{OH}(\text{aq})$) can be treated with Bu_4NOH (e.g., to give a yellow color response). Yellow solutions (**3** + $\text{Bu}_4\text{NOH}(\text{aq})$) can be treated with "assembly cations" such as Zn^{2+} , Cd^{2+} , Mn^{2+} , etc., which promote aggregation and lead to purple solids. While a number of organic bases have been tested, the ammonium base series provides a clear size-dependent tuning of the colorimetric response of the conjugated polymer.

We hypothesize that the purple phase observed in aqueous NH_4OH solutions of **5** occurs by a hydrophobic supramolecular assembly of the polythiophene backbone, with subsequent order being determined by hydrogen bonds and/or salt-pairing of the side chains.¹⁴ Infrared spectra of neutral **3** exhibit a peak at 1710 cm^{-1} which corresponds to a hydrogen-bonded carboxylic acid dimer carbonyl stretching frequency. Upon exposure of **3** to NH_3 vapor, a new carboxylate carbonyl appears at 1550 cm^{-1} and the 1710 cm^{-1} absorption is 3 times weaker.¹⁵ This indicates that the carboxylate is formed; however, significant hydrogen bonds remain and hold the assembled structure together. In addition, absorption occurring beyond 800 nm in UV-vis indicates ordering by aggregation, as we have observed in HT-PDDT by UV-vis and light scattering. At the other extreme, in the yellow phase (**3** + $\text{Bu}_4\text{NOH}(\text{aq})$), the polymer is found to be solvated as single chains, twisted out of conjugation. This phase can be obtained by incorporating bulky

Bu_4N^+ cations that prevent or break up aggregational self-assembly. The purple and yellow phase are two distinct phases. Support of these arguments are found in the well-known thermochromism phenomena found in polythiophene solutions,^{3,16} where rotational transitions and aggregation can occur from a conformationally disordered coil-like phase in order to form an ordered rodlike phase as the temperature is reduced. The ionochromism found is thought to be an analogous chemically induced self-assembly by small cations to give an aggregated rodlike phase or a disassembly of **5** to give a coil-like phase. The difference here is that the hydrophobic packing, hydrogen bonds, and/or salt-pairing drive structural order instead of the temperature effects inducing the phase ordering.

We have also found that we could switch between purple and yellow phases by increasing the amount of NH_4OH in solutions of **5**. At 1 equiv of NH_4OH , we have an absorption at 560 nm only with a significant absorption tailing out beyond 800 nm. Upon addition of 5 equiv, we observe a growth of a new absorption at 420 nm, in addition to the 560 nm peak. Further increasing the concentration of base suppresses, then virtually eliminates the 560 nm absorption, with simultaneous growth of the 420 nm peak. A clean isosbestic point is observed, further supporting that a rod-coil type phase transition, usually observed in thermochromism, is *ionically induced*. It appears that excess NH_4OH removes any H-bonds that direct aggregational ordering and consequently breaks up the aggregate.

Self-assembly in conjugated polymers is highly desirable in order to generate conducting polymers with high electrical conductivities and large nonlinear optical responses. In addition, chemoselective ionochromic sensing and assembly in water can provide opportunities to make conducting polymer sensors^{5,13,17} and nanowire assemblies. It remains to be seen if side chain induced self-assembly can be used in other conducting polymers, such as polyanilines, poly(*p*-phenylenes), and polypyrroles with well-defined structures. However, it is clear that regioregularity in poly(3-substitutedthiophenes) continues to provide new conjugated polymers with very interesting properties.

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Supporting Information Available: Spectroscopic data for **1**, **2**, **4**, and **5** (12 pages). See any current masthead page for ordering and Internet access instructions.

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(16) (a) Rughpooth, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, 25, 1071. (b) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, 88, 183. (c) Inganas, O.; Salaneck, J. E.; Osterholm, J.; Laakso, J. *Synth. Met.* **1988**, 22, 395. (d) Roux, C.; Leclerc, M. *Macromolecules* **1992**, 25, 2141.

(17) (a) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, 28, C341 (b) Roncali, J. *Chem. Rev.* **1992**, 92, 711. (c) Marsella, M. J.; Carroll, P. J.; Swager, T. J. *J. Am. Chem. Soc.* **1995**, 117, 9832. (d) Levesque, I.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2293.

(13) Marsella, M. J.; Swager, T. J. *J. Am. Chem. Soc.* **1993**, 115, 12214.

(14) Herzfeld, J. *Acc. Chem. Res.* **1996**, 29, 31.

(15) Infrared spectra of solid **3** before and after treatment with NH_3 vapor is found in the Supporting Information.