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Regioregular poly(thiophene-3-alkanoic acid)s: water soluble conducting polymers suitable for chromatic chemosensing in solution and solid state

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Abstract—Regioregular polythiophenes with pendant carboxylic acid functionality, poly(thiophene-3-propionic acid) (PTPA, **3**) and poly(thiophene-3-octanoic acid) (PTOA, **4**), were prepared as water soluble conducting polymers and their chemosensory response was studied. Treatment with aqueous base generated intensely colored water soluble conducting polymer salts, with the color varying both as a function of counter ion size and length of the carboxyalkyl substituent. PTPA showed a different colorimetric response to each of the alkali earth metals whereas the longer chain PTOA was only sensitive to ions larger than Et_4N^+. Distinct color changes were also noted in studies of divalent cations known to selectively bind carboxylates, such as Zn^{2+}, Mn^{2+}, and Cd^{2+}. Cast films of PTPA have been found to act as sensors to acid vapor ($\Delta\lambda_{max}$ of up to 132 nm). IR shows that the polymer self-assembles upon HCl vapor exposure, and that the process is completely reversible, leading to a good solid-state sensor for acids. This work demonstrates that regioregular polythiophenes containing acid side-chains have tremendous potential in the development of new sensors.
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1. Introduction

Due to their excellent electrical properties, regioregular poly(3-alkylthiophene)s are rapidly being developed into new products with applications such as field effect transistors, sensors, solar cells and new electrostatic dissipative coatings and materials.[1–8] Their high conductivities and low band gaps are a consequence of their ability to self-assemble into π-stacked, planar aggregates.[9–11] Previous work in our lab has shown that both conformational order and solid state organization in regioregular polythiophene derivatives are remarkably sensitive to the placement and nature of the substituent chains.[12,13] This sensitivity provides the opportunity to design new conducting polymers in which self-assembly (and hence the color) is controlled by environmental factors. Changes in conformation of conjugated systems are readily detected not only by conductivity changes, but also by optical absorption changes. Various polythiophene derivatives are known to show striking chromatic responses, such as piezochromism (changes in pressure),[6,14,15] photochromism (changes in light),[6,16,17] electrochromism (changes in electrical potential),[18–20] thermochromism (changes in temperature),[6,21–25] ionochromism (changes in chemical moieties),[12,26–30] biochromism,[6,31–35] and affinity chromism.[36] Chromatic responses are particularly useful since discernable changes are generally apparent to the human eye, obviating the need for expensive instrumentation and really represent an opportunity for chemists to develop new sensors.[6,37,38] We are particularly interested in developing sensors based on head-to-tail regioregular polythiophenes (rr-PTs).[10] These polymers do not have coupling defects, have a tendency to form elongated supermolecular structures with optimal orbital overlap and small HOMO–LUMO gaps,[39–41] and should exhibit a very wide response range between the minimally and maximally perturbed states, providing for excellent sensitivity. Of rr-PTs, the water soluble salts of carboxylic acid functionalized regioregular polythiophenes demonstrate one of the largest optical shifts in response to ions.[26] Here, we study the ionochromism of these polymers with the intent to understand the underlying mechanism of chromatic changes. Two representative polymers with differing substituent lengths were selected: head-to-tail coupled poly(thiophene-3-propionic acid) (PTPA) and head-to-tail coupled poly(thiophene-3-octanic acid) (PTOA). The synthesis, characterization, and studies of ion binding by UV–vis and IR spectroscopy are reported.

Keywords: Conducting polymers; Polythiophenes; Sensors.
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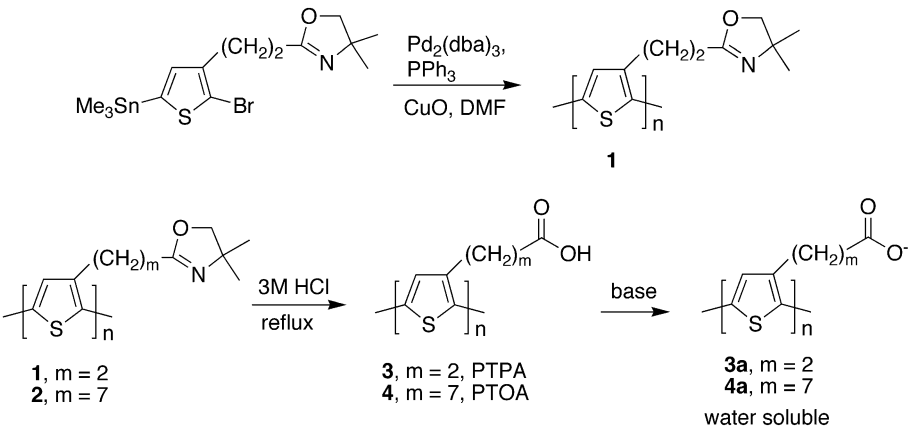

Scheme 1. Synthesis of the water soluble regioregular polythiophenes.

Table 1. UV/vis λ_{max} (nm) of PTPA and PTOA in water with 1 equiv of base (R^+OH^-) per carboxylic acid residue

Polymer	NH_4^+	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Li^+	Na^+	K^+	Cs^+
PTPA (**3**)	550	486	476	446	426	546	532	512	506
PTOA (**4**)	—	556	554	534	513	556	554	554	—

2. Results and discussion

2.1. Synthesis

Regioregular (rr) head-to-tail (HT) poly(thiophene-3-propionic acid) (PTPA, **3**) was synthesized by Stille/CuO polymerization of an oxazoline protected monomer followed by acid hydrolysis to afford a violet solid in yield of greater than 80%.[26] Regioregular head-to-tail poly(thiophene-3-octanoic acid) (PTOA, **4**), was prepared as previously described.[42] Although the polymers were not very soluble in common organic solvents, they were both soluble in aqueous base (species **3a** and **4a**) (Scheme 1).

2.2. Spectroscopic behavior in solution

Intensely colored solutions were formed when PTPA (**3**) or PTOA (**4**) reacted with 1 equiv alkali metal hydroxide or tetraalkylammonium hydroxide per carboxylic acid group, with colors ranging from violet to yellow depending on the size of the counter ion (Table 1). For PTPA, the observed λ_{max} varied over a range of ~124 nm when the size of the ammonium counterion increased from NH_4^+ to Bu_4N^+, and over a range of ~40 nm when the alkali metal size increased from Li^+ to Cs^+. For PTOA, on the other hand, the observed λ_{max} did not deviate much from 556 nm (violet color) until the ion size exceeded Et_4N^+. Even with the larger Bu_4N^+, the λ_{max} blue shifted by only 43 nm.

These results are explained as follows. Varying the size of the counterion in the carboxylate polymer changes the effective steric bulk of the substituent. Small cations favor a planar, π-stacked purple phase while large cations can prevent planarity and self-assembly to give a twisted, isolated yellow phase (Fig. 1). When a longer alkyl side chain was used, such as in PTOA, the chemoselectivity was limited to the larger cations (Pr_4N^+ and Bu_4N^+) because longer chains can more easily accommodate the steric bulk of the substituent without compromising the π-stacked structure of the polymer.

The following results further support the role of steric bulk in the observed ionochromism. (1) All the solutions (in Table 1) became yellow when treated with a vast excess of base. (2) In a separate experiment, the yellow phase was also obtained by titrating a solution of PTPA and 1 equiv KOH (per carboxylic acid residue) with 18-Crown-6. This effectively changes the steric bulk of the cation (by complexation) without changing the ionic strength of the solution. A twisted, yellow phase became more pronounced as the concentration of crown ether increased, while the absorption at longer wavelength decreased. A clear isosbestic point was observed around 420 nm.

All the solutions described in Table 1 were stable, except for NH_4^+. For solutions of PTPA with 1 equiv of NH_4OH, the polymer tended to precipitate when the solutions were left undisturbed for several hours. This indicates that the polymer forms large aggregates. We believe that the

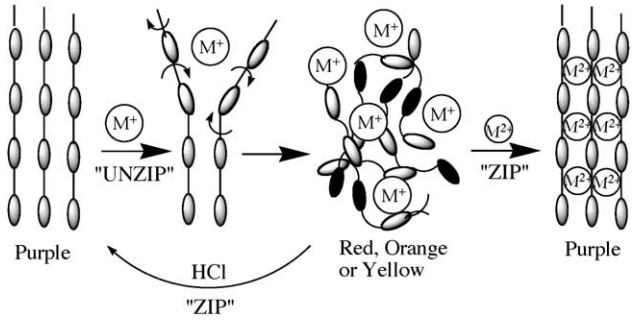

Figure 1. Polythiophene zipper sensors: analyte driven disassembly and self-assembly.

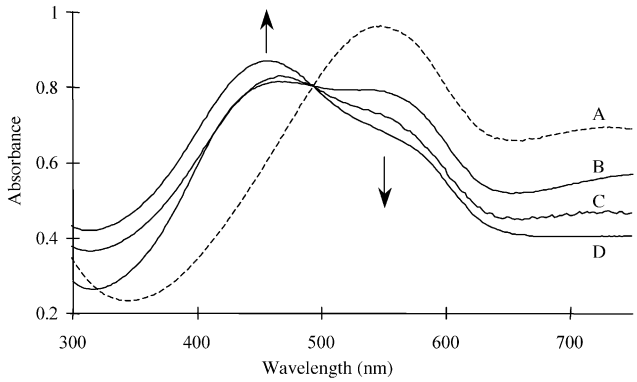

Figure 2. UV/vis of PTPA in water as a function of added NH_4OH. (A) 1 equiv; (B) 10 equiv; (C) 15 equiv; (D) 25 equiv of base per carboxylate group.

quite strong and could be used as a qualitative sensor to detect the presence of divalent cations.

In an effort to better understand the self-assembly by divalent cations, we attempted to get X-ray spectra of the filtered solids (for the samples in Table 2). While the X-ray study revealed several peaks in all cases, we could not easily discern structural order in any of the powder samples. Alternatively, we also tried to study the aggregation by UV–vis in solution, but this tended to be difficult due to the formation and precipitation of coordination polymers at very low cation concentrations. We were able to titrate a solution of PTOA in DMF with small quantities of aqueous $CdCl_2$ without precipitation (up to 0.4 equiv). The UV–vis spectra are shown in Figure 3. Aggregation was promoted, as indicated by the increasing absorption at 610 nm, while

Table 2. Summary of results obtained when we added divalent metals to a red solution of PTPA and Et_4NOH

Divalent metal added	Observations
Mn^{2+}, Mg^{2+}, Fe^{2+}	Solutions turned purple, formation of a purple precipitate
Cd^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}	Solutions were red to purple, formation of magenta to brown solids

ammonium cation is involved in the assembly of this ordered, aggregated phase, for example, by hydrogen bonding or salt pairing, as indicated by IR experiments (discussed later). One could argue that the NH_4^+ cation is not large enough to disrupt the ordered phase. However, solutions of PTPA with Li^+, a smaller cation than NH_4^+, are quite stable.

The aggregates of PTPA with NH_4^+ can disassemble when large excess of base are added to the solution. For example, solutions that contain a large excess of NH_4OH ($\sim$10 equiv or greater) did not precipitate and solutions remained homogeneous indefinitely. This suggests that at higher concentrations of NH_4OH, steric or ionic repulsive interactions overcame some of the attractive inter-chain interactions and allowed for the rapid solvation in water. This is quite similar to deaggregation of proteins in water. Figure 2 shows the titration of an aqueous solution of PTPA with NH_4OH. Upon addition of excess ammonium hydroxide, the ordered purple phase is depleted and a higher energy non-aggregated and/or twisted (coiled) phase is produced. The conformational change from planar to twisted appears to occur via a cooperative mechanism, as shown by the presence of a clear isosbestic point. The UV–vis spectra of PTPA with NH_4OH also showed a significant absorption past 800 nm, which slowly decreased with increasing NH_4OH concentration. The origin of this absorption band was not studied, but suggests the presence of self-doping in the aggregated phase.

We found that divalent metal cations can 'zip up' the disordered solvated polymers back into an ordered phase (Fig. 1). When divalent cations were added to an aqueous basic solution of PTPA (or PTOA), a precipitate was formed, indicating aggregation (Table 2). Divalent metal cations can form coordination complexes with the polymers by binding to two carboxylate groups either intra- or intermolecularly, and the latter is expected to drive self-assembly. The inter-chain attractive force is therefore the proportion of disordered phase decreased. Polymer PTOA could therefore be a potential candidate for semiquantitative sensing of, for example, dangerous divalent cations in drinking water.

2.3. Spectroscopic behavior in the solid state

Thin films of PTPA and PTOA with ammonium hydroxide and with tetraalkylammonium hydroxide were prepared on quartz and the UV–vis spectra were examined (Table 3). Colors were similar to the parent solution, with larger ions yielding a larger hypsochromic shift. We can therefore conclude that the polymer structure in the films is similar to that in solution.

In order to gain more information about the polymer structure and the nature of chromatic changes discussed earlier, we analyzed films of PTPA with the ammonium salts by IR spectroscopy. In the case of tetraalkylammonium salts of PTPA, the IR spectra (Fig. 4) showed the presence of a carboxylate anion (1575 cm^{-1}) and the absence of

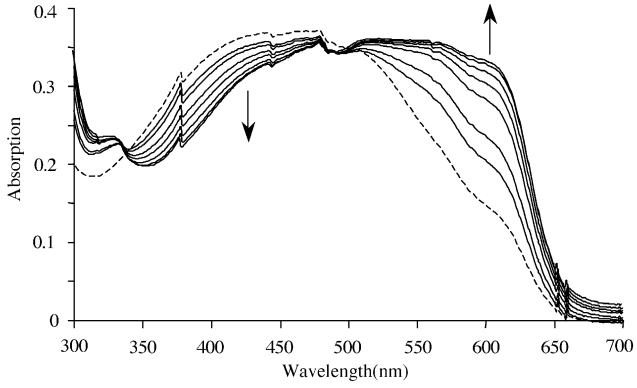

Figure 3. Titration of a 10 μM solution of PTOA in DMF with a 0.5 μM aqueous solution of $CdCl_2$. The amounts of added Cd_2Cl_2 went from 0.05 (- - -) to 0.4 equiv of Cd_2Cl_2. At 0.45 equiv of $CdCl_2$, a precipitate was formed.

Table 3. UV/vis λ_{max} (nm) of PTPA and PTOA thin films[a]

Polymer	H_4N^+	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+
PTPA (**3**)	531	504	489	450	428
PTOA (**4**)	[b]	550	550	530	499

[a] Cast from solutions in water with 1 equiv of base (R^+OH^-) per carboxylic acid group.
[b] Not measured. We expect a value around 550 nm.

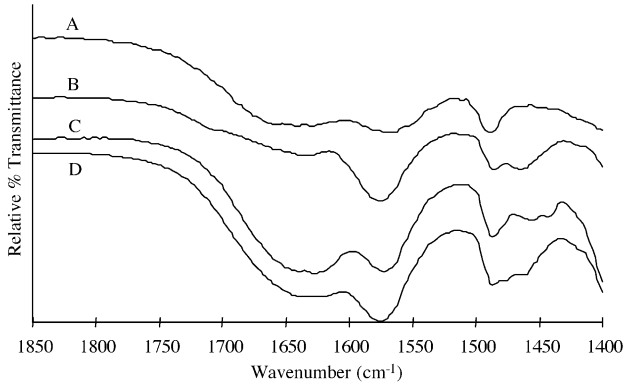

Figure 4. IR spectra of films of PTPA with 1 equiv of (A) Me_4NOH; (B) Et_4NOH; (C) Bu_4NOH; and (D) Pr_4NOH.

hydrogen bonded carboxylic acid (1710 cm^{-1}). These results indicate that these films are completely deprotonated and that hydrogen bonding does not play a significant role in the structure.

We then exposed these disordered films to HCl vapor to see if carboxylic acid groups would form hydrogen bonds and cause the polymers to self-assemble. To our amazement, all four films quickly changed from red, orange or yellow (depending on the cation) to purple upon exposure to HCl vapor, even though the polymers were in the solid state (Fig. 5). Furthermore, IR showed that the carboxylate stretch (1565 cm^{-1}) disappeared and that the hydrogen-bonded carbonyl stretch ($\sim$1725 cm^{-1}) appeared upon exposure to HCl (Fig. 6). Protonation of the carboxylate groups therefore allowed the polymer chains to relax from a twisted conformation to a violet π-stacked conformation with H-bonding, essentially zipping the polymer up into an ordered phase (Fig. 1). When the films were left in air, they reverted back to their original color and IR characteristics due to HCl desorption. Films could be cycled several times through this color change ($\Delta\lambda_{max}$ up to 130 nm) without noticeable degradation of the spectrum. This reversible self-assembly and disassembly could provide a reliable, cheap method for optical detection of acidic vapors.

In contrast, films made from a solution of PTPA with 1 equiv NH_4OH were purple (ordered phase). Analysis of the IR spectra revealed the presence of both hydrogen bonded carboxylic acid (1709 cm^{-1}) and carboxylate anion (1550 cm^{-1}) (Fig. 7A). Significant hydrogen bonding is therefore present at equilibrium and influences the molecular ordering.

To see if we could disassemble the ordered state with excess base, dried films cast from the 1:1 solution of PTPA/NH_4OH were exposed to ammonia vapor. Exposing the films to NH_3 vapor essentially temporarily adds more NH_4^+ into the film. The IR spectra obtained showed that the carboxylate stretch at 1550 cm^{-1} intensified while the carbonyl stretch at 1709 cm^{-1} was suppressed (Fig. 7B). These films reverted

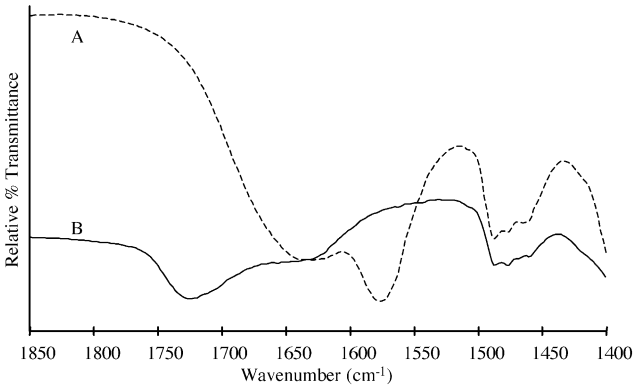

Figure 6. IR spectra of **3** with Bu_4NOH (A) before and (B) after exposure to HCl.

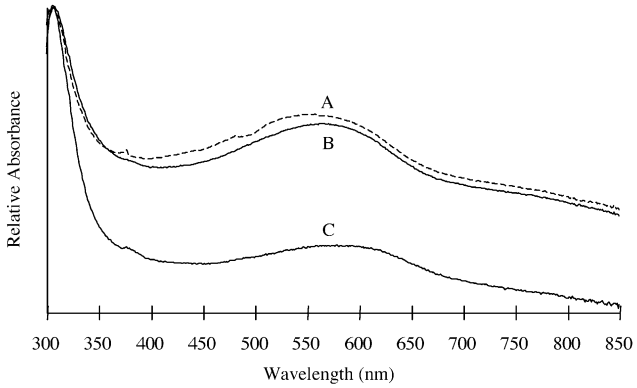

Figure 5. UV–vis spectra of films of alkylammonium hydroxides after exposure to HCl vapor. (A) Bu_4NOH; (B) Pr_4NOH; (C) Et_4NOH.

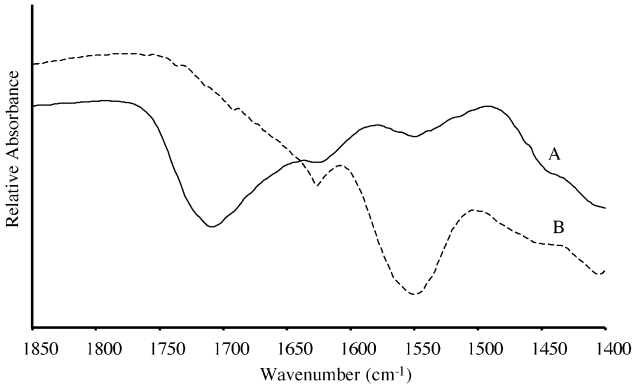

Figure 7. IR spectra of PTPA with NH_4OH (A) before and (B) after exposure to NH_3.

to their original IR characteristics upon standing, due to NH_3 desorption. Exposure to ammonia therefore removed the H-bonds. However, the film color did not change, suggesting that the ordered phase was not affected. We surmise that salt-pairing through the ammonium cation might play a role in the ordered phase. The absence of a chromatic change in this experiment is quite unlike the behavior of aqueous solutions treated with excess NH_4OH (Fig. 2). This suggests that a change in solvation of the polymer system is important in the disassembly process in solution.

2.4. X-ray of PTPA and PTOA

Bao and Lovinger have previously reported PTPA to be amorphous, though slight crystallinity could be obtained by slow evaporation of a DMSO solution.[43] They observed a weak peak at 11.5 Å, attributed to the lateral separation of polymer chains by substituents. We have found that crystalline X-ray can be observed upon careful preparation of the films, however most samples do not form good films as the acid polymer. The X-ray spectra of a thin film of PTOA (**4**) drop cast from DMF is shown in Figure 8. Three peaks were observed in the 2θ scan of the polymer. The broad reflection, corresponding to 3.7 Å distance, is assigned to the π–π stacking distance between the polythiophene chains. Although this is smaller than the 3.8 Å reported for HT-PAT,[44] the resolution is too poor to draw any definitive conclusions. The two sharp reflections correspond to the lamellar interlayer spacing of the polymer chains. The observed distance of 20.5 ± 0.2 Å compares favorably with 20.8 Å previously reported for HT-poly(3-octylthiophene).[44]

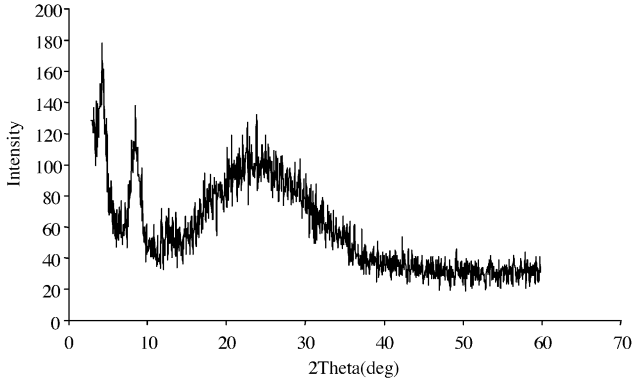

Figure 8. X-ray spectrum of PTOA drop cast from DMF.

3. Conclusions

In this work, we have explored the sensing properties of PTPA and PTOA in both basic solutions and thin films. In addition to ionochromism in basic solution with monovalent cations, these polymers are also quite sensitive to the presence of divalent metal cations. Furthermore, films cast from a solution of PTPA and 1 equiv Bu_4NOH underwent a dramatic visual color change from yellow to purple upon HCl vapor exposure. We expect that other detection methods such as fluorescence, conductivity and FET sensing could be used with these materials. Regioregular polythiophene containing acid side-chains therefore show tremendous potential for the development of new sensors.

4. Experimental

4.1. General

All reactions were performed under prepurified nitrogen, using dry glassware. Glassware was either dried in an oven overnight or flame dried and then cooled under a stream of nitrogen. Tetrahydrofuran was dried over Na benzophenone ketyl radical and freshly distilled prior to use. Diisopropylamine was dried over CaH_2 and distilled prior to use.

All UV–vis spectra were recorded using a Perkin–Elmer Lamda 900 UV/vis/near-IR spectrometer. NMR spectra were recorded on an IBM Bruker FT300 spectrometer. Infrared spectra were obtained using a Nicolet 7199 FTIR. The thin films of PTPA salts (**3a**) were prepared by casting a solution of PTPA with 1 equiv of NH_4OH per carboxylic acid group onto 3M Teflon IR cards and dried overnight in air. The GPC measurements were carried out on a Waters 2690 separation module with two 5 μm Phenogel columns connected in series (guard, 1000 and 100 Å), and a Waters 2487 dual λ absorbance UV detector. Analyses were performed at 30 °C using chloroform as the eluent and the flow rate was 1.0 μL/min. The calibration was based on polystyrene standards (Polymer Standards Service). GC–MS analysis was performed on a Hewlett–Packard 59970 GC–MS workstation with a HP fused silica capillary column cross-linked with 5% phenyl-methylsilicone as the stationary phase. The X-ray diffraction spectra were obtained with a Rigaku θ/θ X-ray diffractometer utilizing Cu Kα source operating at 35 kV and 25 mA, a curved graphite diffracted beam monochromator and a NaI scintillation detector. Data was gathered from 3 to 60°, with steps of 0.05° and 2 s. Elemental Analysis was performed by Midwest Microlab, Indianapolis, IN.

4.2. Synthesis

The synthesis of HT-poly(3-(7-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)heptyl)thiophene) (**1**), and HT-poly(thiophene-3-octanoic acid) (**3**) are reported in the literature.[42]

4.2.1. 2-Bromo-3-(bromomethyl)thiophene. Caution! Repugnant, lachrymatory compound. This compound has been described previously.[45] This procedure has been adapted to utilize benzene rather than CCl_4 as the solvent. NBS (75.85 g, 427 mmol) was suspended in anhydrous benzene (250 mL) and heated to reflux. 2-Bromo-3-methylthiophene (75.0 g, 424 mmol) and AIBN (0.97 g, 5.9 mmol) were added, and the suspension was heated to reflux for 45 min. The crude reaction mixture was cooled to −40 °C to precipitate some of the succinimide, and this was filtered off. The solvent was removed from the filtrate, causing more succinimide to precipitate. This crude oil was redissolved in excess hexanes and filtered through a pad of silica using hexanes as the eluent to remove remaining succinimide. The solvent was removed and the crude oil was distilled (64 °C, 0.5 T) to recover the product in 80% yield (86.8 g, 339 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.46

(s, 2H), 7.00 (d, 1H) 7.26 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 113.0, 126.4, 128.2, 136.9.

4.2.2. 2-(2-(2-Bromothiophen-3-yl)ethyl)-4,5-dihydro-4,4-dimethyloxazole. 2,4,4-Trimethyl-2-oxazoline (7.0 mL, 54.7 mmol) was dissolved in THF (50 mL) and cooled to −70 °C. Butyllithium (2.62 M, 20 mL, 52.4 mmol) was added dropwise over a 10 min period while maintaining a temperature below −50 °C. After the mixture was stirred for 15 min, 2-bromo-3-(bromomethyl)thiophene (14.37 g, 56.11 mmol) was added precipitously. The reaction was extremely exothermic, heating to 25 °C despite the cooling bath. The color varied from red to yellow. The cooling bath was removed and the reaction mixture was stirred for 20 min. The reaction was quenched with H_2O and the solvent was removed. The crude oil was poured into hexanes, the precipitated solids were filtered off, and the filtrate was filtered through silica using hexanes as the eluent. When TLC indicated no further elution of precursor 2-bromo-3-(bromomethyl)thiophene, the column was flushed with EtOAc to recover the product. (*Note*: unreacted 2-bromo-3-(bromomethyl)thiophene catalyses ring opening of the oxazoline upon heating.) The solvent was removed and the remaining oil was distilled (80 °C, 0.01 T) to recover the product in 77% yield (12.15 g, 42.20 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 6H), 2.52 (t, 2H, J=8.2 Hz), 2.89 (t, 2H, J=8.1 Hz), 3.91 (s, 2H), 6.84 (d, 1H, $J_{4,5}$=5.6 Hz), 7.19 (d, 1H, $J_{4,5}$=5.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.9, 28.1, 28.3, 66.9, 79.0, 109.6, 125.4, 128.1, 139.7, 164.5. Anal. Calcd: C, 45.83; H, 4.86; N, 4.86. Found: C, 45.80; H, 4.84; N, 4.79.

4.2.3. 2-(2-(2-Bromo-5-(trimethylstannyl)thiophen-3-yl)ethyl)-4,5-dihydro-4,4-dimethyloxazole. 2-(2-(2-Bromothiophen-3-yl)ethyl)-4,5-dihydro-4,4-dimethyloxazole (4.885 g, 16.96 mmol) was dissolved in THF (40 mL) and cooled to −70 °C. LDA was prepared in a separate flask from diisopropylamine (2.50 mL, 17.8 mmol) and butyllithium (2.79 M, 6.10 mL, 17.0 mmol) in THF (10 mL). This was added while maintaining a solution temperature below −60 °C, and the reaction mixture was stirred at −70 °C for 1 h. Trimethylstannyl chloride (1.0 M, 26.74 mL, 26.7 mmol) was added dropwise, maintaining the temperature below −62 °C. The solution was stirred for 1 h, poured into 75 mL of aqueous KF and stirred for 20 min, then was partitioned between H_2O and ether. The organic layer was dried over $MgSO_4$ and the solvent was removed. The remaining oil was distilled (110–118 °C, 0.04 T) to recover the product (5.952 g, 13.20 mmol) in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.32 (t, 9H, J_{Sn}= 28.5 Hz), 1.23 (s, 6H), 2.51 (t, 2H, J=8.2 Hz), 2.90 (t, 2H, J=8.8 Hz) Hz, 3.89 (s, 2H), 6.89 (t, 1H, J= 13.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ −8.4, 25.7, 28.2, 28.3, 67.0, 79.1, 114.2, 136.2 (t, J_{Sn}=52.1 Hz), 138.3, 140.9, 164.8. Anal. Calcd: C, 37.28; H, 4.92; N, 3.11. Found: C, 37.32; H, 4.95; N, 3.23.

4.2.4. HT-2,5-poly(3-(2-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)ethyl)thiophene) (1). Polymerization was done using Gronowitz conditions for the formation of dimers.[46] 2-(2-(2-Bromo-5-(trimethylstannyl)thiophen-3-yl)ethyl)-4,5-dihydro-4,4-dimethyloxazole (3.09 g, 6.86 mmol) was dissolved in DMF (80 mL). Tris(dibenzylidene acetone)dipalladium(0) (336 mg, 0.05 equiv) was added, followed quickly by copper(II)oxide (367 mg, 1.0 equiv), and triphenylphosphine (570 mg, 0.20 equiv). The solution was warmed to 100 °C and allowed to stir for 2 days. The reaction was quenched by pouring into methanol. The resulting solid was filtered and transferred into a Soxhlet thimble. The sample was extracted with methanol until the eluent was colorless, then was recovered by extraction with chloroform. The solvent was removed and the resulting purple solid was dried under vacuum overnight to recover the polymer (1.075 g, 5.19 mmol) in 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 6H), 2.75 (t, 2H), 3.19 (t, 2H), 3.94 (s, 2H), 7.11 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.4; 29.2; 29.6; 68.0; 80.0; 129.8; 132.4; 134.4; 138.4; 166.7. M_n=8K, PDI=1.2 (by GPC).

4.2.5. HT-2,5-poly(thiophene-3-propionic acid) (3). A sample of **1** (404.4 mg) was dissolved in 3 N HCl (90 mL) and heated to reflux for 12 h. The solution consisted of a dark purple suspension at this point. The solid was filtered, rinsed with H_2O, and dried to recover the product in 82% yield (248.4 mg). As prepared, most polymer samples submitted for elemental analysis contained large amounts of ash (10–15%). This suggests the presence of copper (II) salts and other impurities, though this has not been confirmed. A drastic reduction in the ash content was achieved by dissolving polymer PTPA (**3**) in aqueous base, re-precipitating it upon acidification, and recovering it by filtration. Re-precipitating two to three times eliminated the ash, giving elemental analysis results in reasonable agreement with the theoretical composition of this polymer. ^{1}H NMR (300 MHz, CD_3OD) (characterized as its cesium salt by adding CsOH): δ 7.05 (s, 1H); 3.92 (t, 2H); 2.35 (t, 2H). Anal. Calcd: C, 54.54; H, 4.08. Found: C, 52.64; H, 4.08.

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