Synthesis and study of poly(3-hexylthiophenes) and poly(3-dodecylthiophenes) containing halogen and sulfur substituents in the ω-position of the side chain

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Dedicated to Professor Henry Shine on the occasion of his 80th birthday

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Abstract

Poly[3-(6-bromohexyl)thiophene] (**1**) and poly[3-(12-bromododecyl)thiophene] (**2**) were synthesized by chemical polymerization of their respective monomers, **3** and **4**, using $FeCl_3$. NMR spectroscopy showed 81% of head-to-tail couplings and GPC showed $\overline{M}_n$ = 51,500 and 91,100 with PDIs of 5.2 and 1.7 for **1** and **2**, respectively. Conductivities of the I_2- and $FeCl_3$-doped **1** were 18 and 7.5 S cm^{-1} and for **2** were 32 and 46 S cm^{-1}, respectively. Poly[3-(6-iodohexyl)thiophene] (**8**) was prepared by S_{N2} displacement (>97%), using NaI, on **1**. Poly[6-(3-thienyl)-1-hexyl *S*-thioacetate] (**10a**) and poly[12-(3-thienyl)-1-dodecyl *S*-thioacetate] (**10b**) were prepared from **1** by post-polymerization S_{N2} reactions. They were insoluble in organic solvents and had ^{13}C CP-MAS NMR spectra consistent with the structures. Reaction of **1** with thiourea followed by basic hydrolysis gave poly[3-(6-mercaptohexyl)thiophene] (**11**). This thiol functionalized polymer was also insoluble in common organic solvents and it, too, had a ^{13}C CP-MAS NMR spectrum consistent with the structure. Polymers **10a** and **11** showed pressed pellet conductivities of 4×10^{-5} and 2.3×10^{-2} S cm^{-1} when doped with $FeCl_3$, respectively and 8×10^{-5} and 0.44 S cm^{-1} when doped with I_2, respectively. TGA of polymers **1**, **8** and **11** showed thermal decomposition in two stages.

Keywords: Poly(ω-haloalkylthiophene), poly[ω-(3-thienyl)-1-alkyl *S*-thioacetate], poly[3-(6-mercaptohexyl)thiophene], ^{13}C CP-MAS NMR

Introduction

Because of their electrical conductivity and electroluminescent properties, polythiophenes have been under intense investigation for many years. A number of 3-substituted polythiophenes, both regiorandom and regioregular, have been prepared by chemical or electrochemical oxidation of appropriately 3-substituted thiophenes.[1-3] In this paper we report on the preparation of poly[3-(6-bromohexyl)thiophene] and poly[3-(12-bromododecyl)thiophene] (**2**) by direct chemical polymerization of the monomers, 3-(6-bromohexyl)thiophene (**3**) and 3-(12-bromododecyl)thiophene (**4**) and on their conversion to other polythiophene derivatives by displacement of the bromine leaving group. This is a follow-up of our preliminary report describing the preparation of these two polymers **1** and **2** using ferric chloride oxidative polymerization of monomers **3** and **4**.[4,5] About the same time as our initial preliminary report[4] Iraqi et al. reported on the preparation of head-to-tail regioregular polymer **1**.[6] The following year Ng et al. reported on the synthesis of three poly[3-(□-bromoalkyl)thiophene] polymers[7] using our reported methodology but failed to cite the prior publications.[4-6]

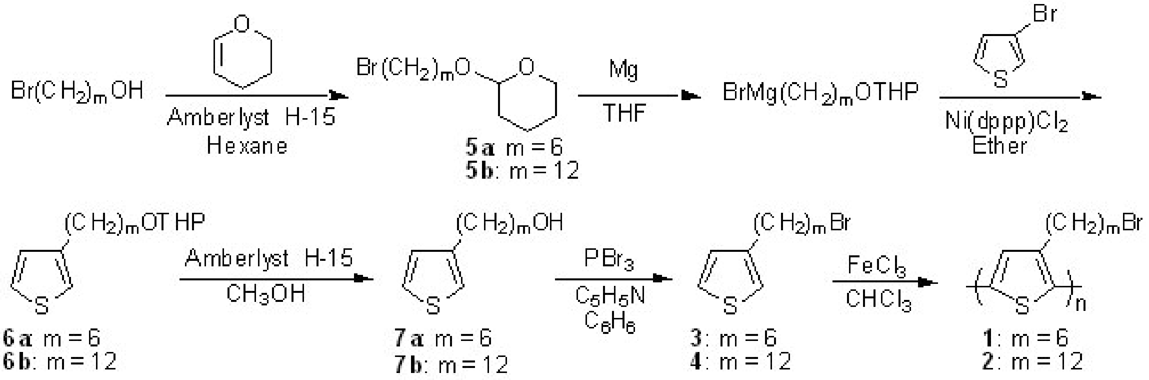
Very recently a paper appeared reporting on head-to-tail regioregular polymer **1** and on several other polymers derived from **1** by post-polymerization reactions where the bromine acts as a leaving group.[8]

Results and Discussion

Bromine and iodine containing polymers

The monomers, (6-bromohexyl)thiophene (**3**) and 3-(12-bromododecyl)thiophene (**4**), were prepared as shown in Scheme 1 using a modification of the synthesis reported by Bäuerle.[9] The synthetic steps we employed were similar to those of Bäuerle except for the alcohol protecting group. We used the tetrahydropyranyl (THP) protecting group whereas Bäuerle used the *p*-methoxyphenyl group. 1-Bromo-6-(2-tetrahydropyranyloxy)hexane and 1-bromo-12-(2-tetrahydropyranyloxy)dodecane were prepared by a modification of the literature procedure from the corresponding ω-bromo-1-alkanol.[10,11] Amberlyst H-15,[12] an ion exchange resin containing strongly acidic –SO_3H groups, was used and yields of 90% and 97% of **5a** and **5b**, respectively, were obtained. Coupling of the Grignard reagents obtained from **5a** and **5b** with 3-bromothiophene using Ni(dppp)Cl_2 [dppp=1,2-bis(diphenylphosphino)propane] as catalyst gave compounds **6a** and **6b**. Methanolysis, using Amberlyst H-15, produced 6-(3-thienyl)-1-hexanol (**7a**) and 12-(3-thienyl)-1-dodecanol (**7b**) and conversion of –OH to –Br to give **3** and **4** was carried out using PBr_3 following the procedure of Smith,[13] and also with HBr in the case of **7b**. For the oxidative polymerization, 4 equivalents of anhydrous $FeCl_3$ were used to give polymers **1** and **2** (Scheme 1) after dedoping with NH_4OH. **1** and **2** were soluble in common organic solvents such as chloroform, toluene, THF, DMF and DMSO.

The chemical structures and degrees of regioregularity of **1** and **2** were studied by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra show two resonances at δ 2.83 and 2.60 for **1** and δ 2.81 and 2.60 for **2**. On the basis of the shielding effect of the thiophene ring and comparison with the spectrum of poly(3-hexylthiophene)[14] and poly(3-dodecylthiophene)[15] the peaks

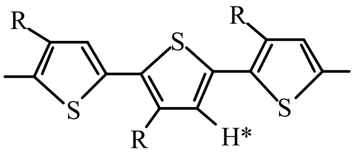
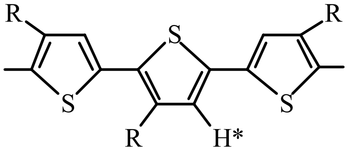
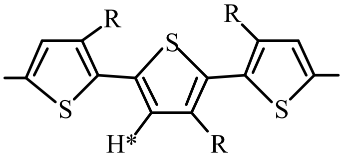
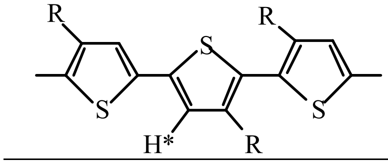


Scheme 1

at δ 2.60 and δ 2.83/2.81 were assigned to the CH_2 groups adjacent to the thiophene ring for the head-to-head (HH) and head-to-tail (HT) configurations, respectively. Furthermore, the intensity ratio of these two peaks suggests that both **1** and **2** consist of 81% HT dyads and 19% HH dyads. Analysis of the spectral region at δ 6.98-7.06 provides additional configurational and regiochemical information on the polymers. The four resonances for **1**/**2** at δ 6.98, 7.01, 7.03 and 7.06/7.05 are assigned to HT-HT, HT-TT, HT-HH, TT-HH triad configurations, respectively.[14,15] It should be noted that the HT-HT peak at δ 6.98 compares quite favorably with the value of δ 6.98 reported by Iraqi, et al.[6] and δ 6.95 reported recently by Zhai, et al. for the HT-regioregular version of **1**.[8] In addition, the peaks reported by Ng, et al. agree with those we observed and, while in our hands the HT dyad is 81% of the polymer, they report that their polymer **1** has only 68-73% HT dyads.[7] The reasons for their lower regioregularity is not clear. The relative percentage of triad configurations and ^{1}H NMR data for polymers **1** and **2** are shown in Table 1. The signal for the methylene protons linked to the -Br group are at δ 3.43 for **1** and 3.39 for **2**. There is, in addition, a fairly small (<5%) broad peak centered at δ 0.86 ppm for both **1** and **2** which corresponds to a terminal methyl group which must have been produced by reduction of the ω-CH_2Br in one of the synthetic steps. The structure of the polymers was also revealed in part by the ^{13}C NMR spectra. The signals at δ 139.6 and 139.8 are assigned to the carbons in position 3 of the thiophene rings containing the alkyl substituents in **1** and **2**, respectively, the signals at δ 133.7 and 133.6 to the carbon in position 5, those at δ 130.6 and 130.4 to the carbons in position 2 and those at δ 128.7 and 128.6 to the unsubstituted carbons at position 4, analogous to the assignments that have been made for poly(alkylthiophenes) by Hotta, et al.[16]

Table 1. Relative percentage and ^{1}H NMR spectral data for triads of polymers **1/2**

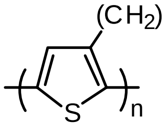
	Triad Config.	$\delta_{^1H}$	Rel. %

	HT-HT	6.98/6.98	58/59
	HT-TT	7.01/7.01	15/15
	HT-HH	7.03/7.03	11/13
	TT-HH	7.06/7.05	16/13

Number-average molecular weights, $\overline{M}_n$, obtained by gel permeation chromatography (GPC) using polystyrene standards, for **1** and **2** were 51,500 and 91,100 with polydispersities of 5.2 and 1.7, respectively. This is to be compared with the significantly lower number average molecular weights of 12,300-23,400 obtained by Ng, et al. for **1** also using $FeCl_3$ polymerization.[7] Films of **1** and **2** were deep red/burgundy in color with very similar UV-vis absorption maxima at 492 nm and 505 nm, respectively, and THF solutions of these two polymers also showed similar absorption spectra with λ_{max} of 436 and 438 nm, respectively, all close to the values reported for poly(3-hexylthiophene)[17-19] and poly(3-dodecylthiophene)[19] prepared using $FeCl_3$. The fluorescence properties of **1** and **2** were also examined. THF solutions of **1** and **2** showed emission maxima at 573 and 576 nm while films cast from THF showed maxima at 670 and 680 nm, respectively. The UV-vis maxima reported by Ng, et al. was 434 nm in $CHCl_3$ solution and 488 nm for the film while the fluorescence maximum reported was 558 nm for a film of **1**.[7] These values show that the polymers prepared here have significantly greater conjugation lengths than those prepared by Ng.

The deep red/burgundy polymer films of **1** and **2** turned dark blue upon doping with iodine and 0.05 M $FeCl_3$ in dry nitromethane. Doping of **1** with I_2 gave a 4-point probe electrical conductivity of $\sigma = 18$ Scm^{-1} while the $FeCl_3$-doped polymer showed $\sigma = 7.5$ Scm^{-1}. Films of **2** gave somewhat higher conductivities. With I_2 doping $\sigma = 32$ Scm^{-1} and with $FeCl_3$ doping $\sigma = 46$ Scm^{-1}. Ng, et al. reported iodine doped conductivities for **1** of 7.9-8.2 Scm^{-1}.[7]

In order to investigate the effectiveness of S_{N2} type displacements on these bromo polymers we examined the displacement of bromide by iodide using polymer **1**. Since the polymer was soluble in $CHCl_3$ but insoluble in acetone and the displacement reaction (Finkelstein reaction)[20] is generally run in acetone where NaI is soluble, but it is insoluble $CHCl_3$, it was determined that a 3.8:1 (v/v) mixture of $CHCl_3$ and acetone would keep the reactants in solution. In order to see if the displacement reaction went to completion and produced poly[3-(6-iodohexyl)thiophene] (**8**) ^{1}H NMR spectra were examined. The peak in **1** at δ 3.43 was replaced by a peak at δ 3.21 due to the hydrogen atoms on the carbon α- to the halogen. Integration of the peak at δ 3.21 vs the area around δ 3.43 showed that the displacement



8

had occurred to at least 97% completion. Figure 1 shows the ^{1}H NMR spectra of **1** and **8**. This 97% displacement is larger than the 87% reported by Iraqi et al.[6] in displacement on the HT-regioregular version of **1** with a carboxylate nucleophile and is similar to the report of Zhai, et al.[8]

Sulfur containing polymers

Approaches to the synthesis of sulfur containing polymers included attempted polymerization of sulfur containing monomers and displacement reactions on the bromoalkyl substituted polythiophenes. Initially we prepared 6-(3-thienyl)-1-hexyl *S*-thioacetate (**9a**) and 12-(3-thienyl)-1-dodecyl *S*-thioacetate (**9b**) by displacement on bromoalkyl monomers **3** and **4** using potassium thioacetate in ethanol.

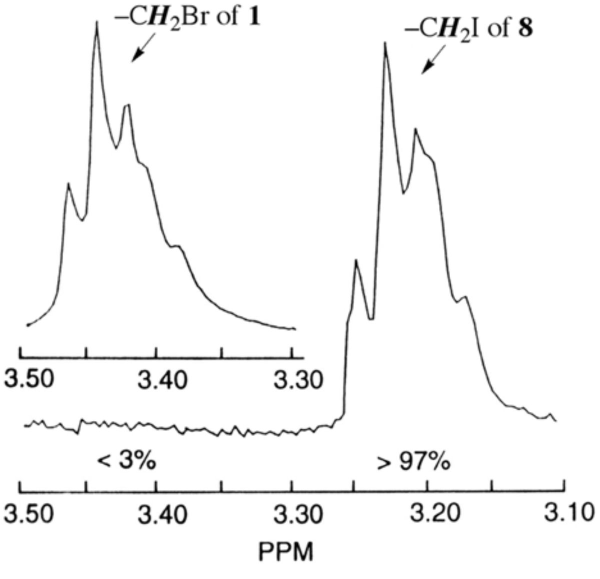
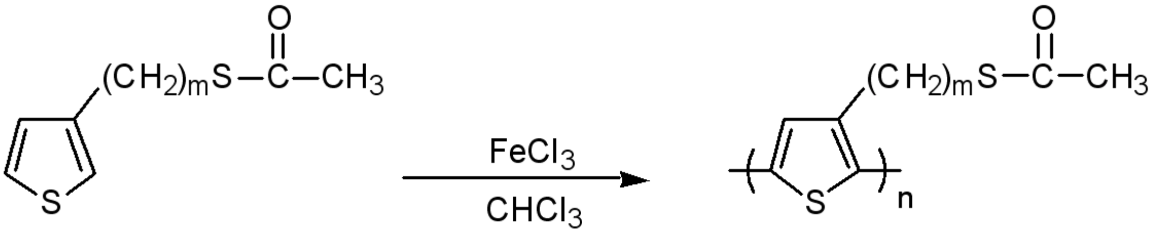


Figure 1. ^{1}H NMR spectra of **1** and **8**.

Polymerization was carried out using 4 equivalents of anhydrous $FeCl_3$ in $CHCl_3$ (Scheme 2). The polymers precipitated and were washed with MeOH and dedoped with NH_4OH or hydrazine to give red-orange solids of **10a** and **10b**. Surprisingly, it was found that both ω-$SCOCH_3$ functionalized polyalkylthiophenes **10a** and **10b** were insoluble in $CHCl_3$, THF, DMSO, CH_3OH, toluene, *o*- dichlorobenzene and tetramethylene sulfone, and only very slightly soluble in boiling thiophene (84 °C). The reasons for the insolubility of these polymers is unknown. However, since Zhai, et al. report that HT-regioregular **10a** is soluble in organic solvents, the insolubility of the samples we prepared by $FeCl_3$ oxidation may be due to a higher molecular weight. As discussed above, the number average molecular weights of **1** and **2** were 51,500 and 91,100 respectively whereas that reported for the HT-regioregular **1** was 15,000-18,000 using a lower monomer concentration or 25,000-30,000 using a higher monomer concentration.[8] Thus, our molecular weight was at least double those reported by Zhai, et al.[8] for **1** and are 3-4 times that for polymer **2**. Polymers **10a** and **10b** were characterized by IR and ^{13}C CP-MAS NMR spectroscopy along with elemental analysis. Thus, for example, **10a** showed the ring C–H stretch at 3058 cm^{-1}, the aliphatic C–H stretching at 2852 and 2926 cm^{-1} and the carbonyl stretch at 1688 cm^{-1}. The ^{13}C CP-MAS spectra of **10a** and **10b** are shown in Figure 2. The spectra are consistent with the structures in that the integrated ratios of the aromatic peaks (at $\delta \approx 120$-145) to aliphatic peaks (at $\delta \approx 20$-45) are 0.54:1.00 for **10a** and 0.26:1.00 (including spinning side-bands) for **10b**. The theoretical integrated ratios should be 0.57:1.00 and 0.31:1.00 for **10a** and **10b** respectively. The pressed pellet conductivities for polymer **10a** were $\sigma = 4 \times 10^{-5}$ Scm^{-1} doped with $FeCl_3$ and $\sigma = 8 \times 10^{-5}$ Scm^{-1} doped with I_2.



9a: m = 6
9b: m = 12

10a: m = 6
10b: m = 12

Scheme 2

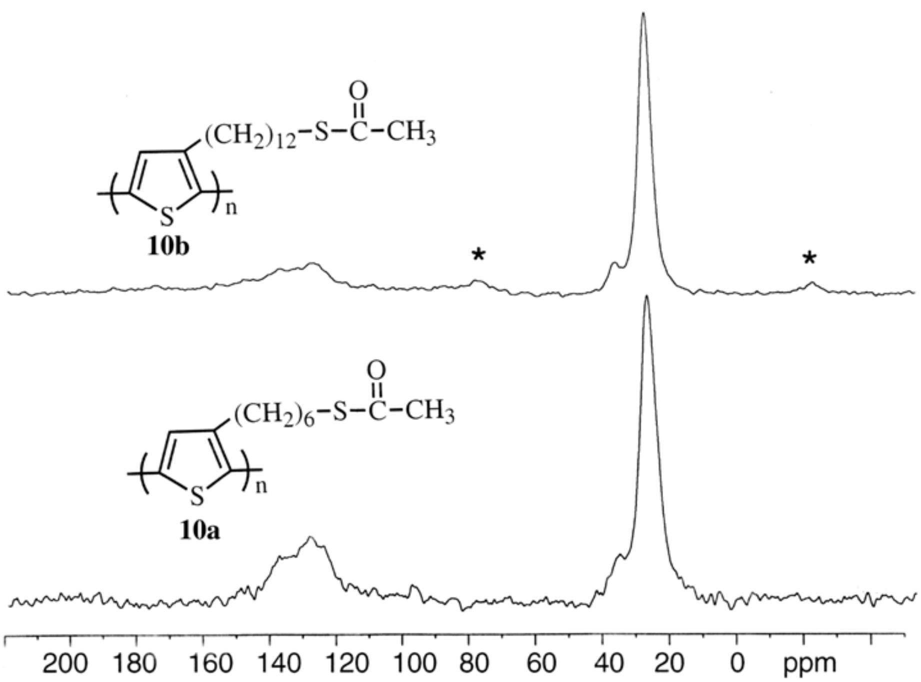
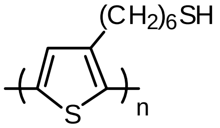


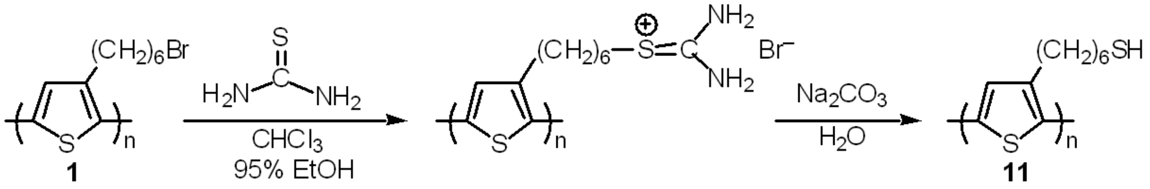
Figure 2. ^{13}C CP-MAS NMR spectra of **10a** and **10b**. The peaks marked with * are spinning sidebands.

Since we also wanted the thiol containing polymer we attempted to convert the thioacetate polymer **10a** to the thiol **11** by several different reactions. Stirring with KOH/EtOH for 13 hours under argon at room temperature, refluxing with KOH/H_2O/CH_2Cl_2 for 32 hours under argon, refluxing with KOH/H_2O/CH_2Cl_2/$NaBH_4$ for 48 hours under argon and stirring with KOH/EtOH/$NaBH_4$ under argon at room temperature all failed to give any thiol product. The IR spectrum of the product was identical to that of the reactant in all cases. The lack of reaction is no doubt due to the insolubility of the polymer.



11

The next approach to poly[3-(6-mercaptohexyl)thiophene] (**11**) involved post-polymerization substitution of bromo-polymer **1**. A standard method for preparing thiols from a halide is by S_{N2} reaction with thiourea to produce an isothiouronium salt, which, in turn, can be hydrolyzed with aqueous Na_2CO_3[21,22] to produce a thiol.[23] Scheme 3 shows this sequence of reactions as applied to polymer **1**. Polymer **11** was produced as a red powder which was insoluble in standard organic solvents



Scheme 3

such as $CHCl_3$, THF, DMF, DMSO, toluene, xylene and *o*-dichlorobenzene but was very slightly soluble in refluxing thiophene.

Zhai, et al.[8] report that the HT-regioregular version of **11** is soluble in common organic solvents. Once again, the lack of solubility may be the result of the **11** which we have prepared from **1** being about twice the molecular weight of the HT-regioregular **11** prepared by Zhai, et al. Our structure proof rests on the IR and 13C CP-MAS spectra as well as elemental analysis. The thiophene and aliphatic C–H stretching frequencies were at 3059, 2853 and 2927 cm^{-1}. Unfortunately there was not an obvious S–H stretching band in the range 2550-2600 cm^{-1} but because it is characteristically rather weak it may go undetected in thin films or in dilute solutions.[24] The ^{13}C CP-MAS spectrum of **11** is shown in Figure 3. The integrated ratio of the aromatic peaks (at $\delta \approx 120\text{-}145$) to aliphatic peaks (at $\delta \approx 20\text{-}45$) is 0.58 (including spinning side-bands):1.00 whereas the required ratio for **11** is 0.67:1.00. The pressed pellet conductivities for polymer **11** were $\sigma = 2.3 \times 10^{-2}$ Scm^{-1} doped with $FeCl_3$ and $\sigma = 0.44$ Scm^{-1} doped with I_2.

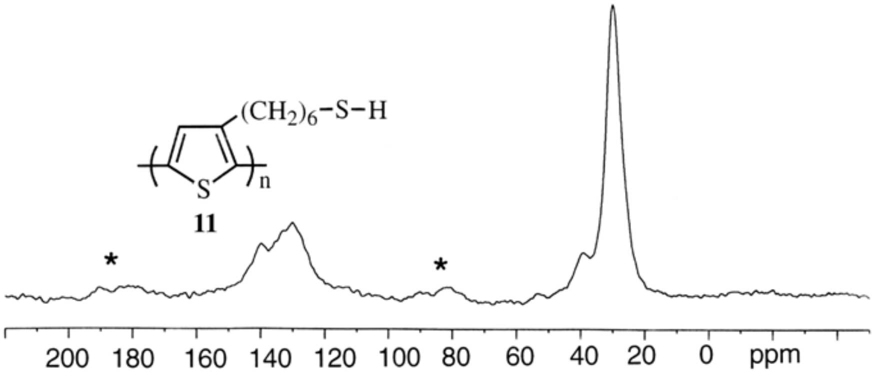
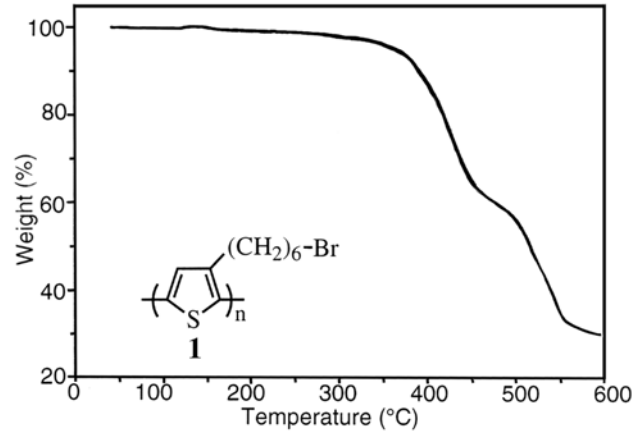
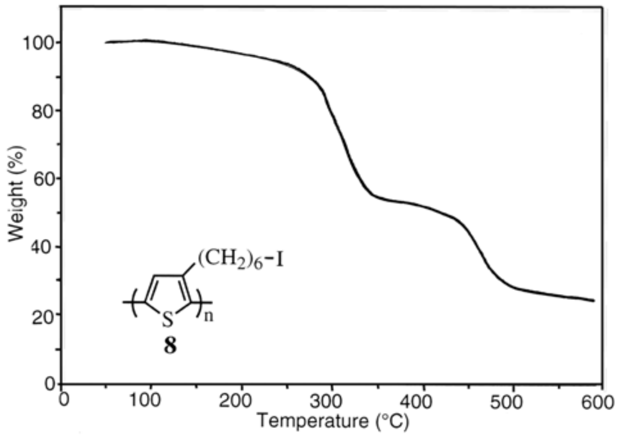


Figure 3. ^{13}C CP-MAS NMR spectrum of **11**. The peaks marked with * are spinning sidebands.

Thermogravimetric analysis

Thermogravimetric analyses (TGA) were run on polymers **1**, **8**, and **11** to examine their thermal stabilities. All three showed two stage weight losses (Figure 4). For **1**, decomposition began at about 330 °C, and the second step began at about 470 °C and ended at about 580 °C. For **8**, which was less stable than **1**, decomposition began slowly at about 150 °C and the second step began at about 370 °C and ended at about 510 °C. For **11**, decomposition began at about 210 °C and the second step began at about 360 °C and ended at about 520 °C which makes this polymer of intermediate stability. From the weight loss it appears that the first step in each case is loss of HBr, HI and H_2S respectively. For polymer **1** the first weight loss is about 36% and loss of HBr requires 33%, for polymer **8** the first weight loss is about 41-45% and loss of HI requires 44% while for polymer **11** the first weight loss is about 26% and loss of H_2S requires 17%. The second weight loss is most likely due to side chain loss.





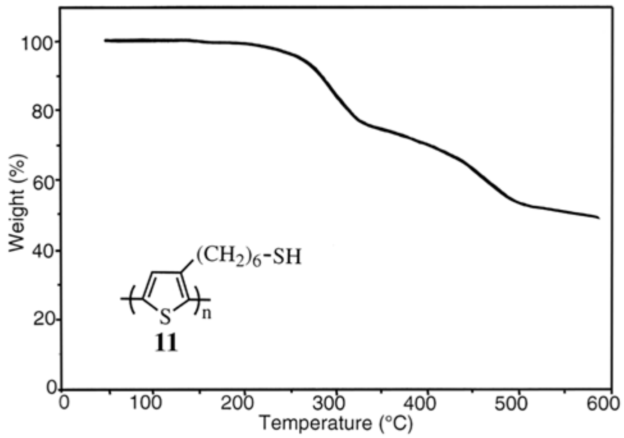


Figure 4. TGA curves of polymers **1**, **8** and **11**.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were obtained on either a Bruker MSL 300 spectrometer operating at 300.13 MHz for ^{1}H and 75.97 MHz for ^{13}C or on a JEOL Eclipse 500 spectrometer operating at 500.16 MHz for ^{1}H and 125.78 MHz for ^{13}C. $CDCl_3$ was used as the solvent with TMS ($\delta = 0.00$ ppm) and $CDCl_3$ ($\delta = 77.0$ ppm) used as internal reference for ^{1}H and ^{13}C spectra, respectively. CP-MAS ^{13}C NMR spectra were taken on a Bruker Avance 400 instrument operating at 100.63 MHz by Bruker Instruments, Billerica, MA. FT-IR spectra were obtained on a Biorad-Digilab FTS-40 or a Bruker VECTOR22 FT-IR instrument using powdered samples (approximately 1-2 weight %) with KBr in a diffuse reflectance unit or liquid samples between NaCl plates. Gel permeation chromatography (GPC) was carried out on a Waters GPC system, using a Waters Model 510 HPLC pump, a Model 490 multiwavelength detector $\lambda = 254$ nm), Millennium 2010 Software, a serial combination of 10^3, 10^4, and 10^5 Å Ultrastyragel columns and THF with a flow rate of 1.0 mL/min. The calibration curve was established by use of polystyrene standards with a molecular weight range of 800 to $9\text{x}10^5$ g/mol. HPLC was performed on a Waters HPLC system, using a Waters Model 501 HPLC pump, a Lambda-Max Model 481 LC UV-vis detector (254 nm), Maxima 820 Chromatography Software, and an Econosil C18 10U (10 µm) reverse phase column (250 mm x 4.6 mm). Methanol was used as the eluent with a flow rate of 1.0 mL/min. UV-vis-NIR spectra were recorded on a Cary 5E UV-vis-NIR spectrophotometer using tetrahydrofuran solutions and polymer thin films cast onto quartz cuvettes from polymer-THF solutions. Fluorescence spectra were measured on a Perkin-Elmer Model 204 fluorescence spectrophotometer using a Perkin-Elmer 150 Xenon power supply. Samples were either polymer-THF solutions or polymer thin films on glass substrates. TGA was carried out on a DuPont model 9900 Thermal Analysis system fitted with a Model 951 Thermogravimetric Analyzer, under nitrogen with a heating rate of 10 °C/min. Elemental analyses were obtained either on a Perkin-Elmer 2400 CHN analyzer or determined by Texas Analytical Laboratories, Stafford, Texas. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. EI mass spectra were obtained at 70 eV on a Finnigan MAT TSQ-70 instrument. The electrical conductivity of doped polymer films was measured using the standard four-in-line probe method.[25,26] The thickness of polymer films was determined with an Alpha-Step 200 profilometer or Mitutoyo Digimatic Digital Micrometer.

12-Bromododecan-1-ol.[10] 12-Bromododecan-1-ol was prepared essentially according to the literature procedure.[10] 20.2 g (0.100 mol) of 1,12-dodecanediol, 100 mL of heptane and 40 mL of 48% aq. HBr were put into a 250 mL 3-necked flask equipped with a magnetic stirrer. The mixture was stirred under reflux for 25 h and the organic layer was extracted with ethyl ether (3x100 mL). The combined organic extract was washed with deionized water (3x100 mL), followed by 5% Na_2CO_3 solution (2x100 mL) and 150 mL of saturated NaCl solution, dried ($MgSO_4$) and the solvent was removed in vacuum. The crude product was purified by silica gel flash column chromatography using hexane/ethyl acetate (5:1 v/v) as eluent. 16.0 g of the 12-bromododecane-1-ol was obtained as white crystals (60% yield). mp 31.5-32.5 °C (Lit.[27] 31-32 °C) ^{1}H NMR δ: 1.20-1.50 (m, 17 H), 1.57 (quintet, 2 H, *J* = 7 Hz), 1.85 (quintet, 2 H, *J* = 7 Hz), 3.40 (t, 2 H, *J* = 7 Hz), 3.64 (t, 2H, *J* = 7 Hz).

1-Bromo-6-(2-tetrahydropyranyloxy)hexane (5a).[11] In a modification of the literature procedure[11] a solution of 6-bromohexane-1-ol (18.1 g, 0.100 mol) and 3,4-dihydro-2H-pyran (11.0 g, 0.130 mol) in 60 mL of hexane was slowly added to a suspension of Amberlyst H-15 (1.00 g, 20-60 mesh) in 20 mL of hexane. The mixture was stirred at 0 °C for 3 h, and an additional 1.5 h at room temperature. The resin was filtered and the solvent was removed in vacuo. The residue was purified by silica gel flash column chromatography eluting with hexane/ethyl acetate (10:1.4 v/v). 22.0 g (90%) of **5a** was obtained as a clear, colorless liquid. ^{1}H NMR δ: 1.35-1.90 (m, 14 H), 3.32-3.39 (m, 3 H), 3.42-3.51 (m, 1 H), 3.66-3.73 (m, 1 H), 3.80-3.88 (m, 1 H), 4.56 (dd, 1 H); ^{13}C NMR δ: 67.4, 62.4, 33.9, 32.8, 30.8, 29.6, 28.1, 25.5_6, 25.5_4, 19.6. IR (neat, cm^{-1}) 2939, 2864, 1440, 1351, 1261, 1201, 1134, 1077, 1032, 987, 905, 869, 814, 729, 645, 563. Anal. Calcd. for $C_{11}H_{21}O_2Br$: C, 49.82; H, 7.98. Found: C, 50.19; H, 7.78. MS [m/z (% rel. int.)]: 266.1 (11, M+3), 265.1 (90, M+2), 264.1 (10, M+1), 263.1 (88, M+), 193.1 (23), 191.1 (23), 165.1 (58), 163.1 (70), 123.0 (26), 121.0 (28), 115.2 (82), 101.1 (100).

1-Bromo-12-(2-tetrahydropyranyloxy)dodecane (5b).[10] 4.70 g of 12-bromo-1-dodecanol was used employing the literature procedure.[10] The crude product was purified by silica gel flash column chromatography, eluting with hexane/ethyl acetate (25:1 v/v), to give 6.00 g (97%) of **5b** as a colorless liquid. ^{1}H NMR δ: 1.20-1.59 (m, 22 H), 1.62-1.88 (m, 4 H), 3.30-3.40 (m, 3 H), 3.44-3.52 (m, 1 H), 3.70 (dt, 1 H), 3.81-3.90 (m, 1 H), 4.55 (t, 1 H); ^{13}C NMR δ: 98.8, 67.6, 62.2, 33.9, 32.8, 30.7, 29.7, 29.5_1, 29.4_9, 29.4_6, 29.4_2, 29.3_7, 28.7, 28.1, 26.2, 25.5, 19.6. Anal. Calcd. for $C_{17}H_{23}O_2Br$: C, 58.45; H, 9.52. Found: C, 58.46; H, 9.46.

3-[6-(2-Tetrahydropyranyloxy)hexyl]thiophene (6a).[28] Into a 100 mL, three-necked flask equipped with a magnetic stirrer, a pressure-equalizing dropping funnel, and a reflux condenser attached to an argon gas inlet was put 0.85 g (35 mg-atom) of magnesium turnings. A solution of 1.00 g of 1-bromo-6-(2-tetrahydropyranyloxy)hexane (**5a**; 3.80 mmol) in 20 mL of dry THF was added rapidly and an exothermic reaction occurred. Then an additional 7.08 g (total = 8.08 g; 30.0 mmol) of **5a** in 50 mL of dry THF was added over ca. 1.5 h at room temperature. The mixture was stirred at room temperature for 2 h, then heated at about 45 °C with stirring for 1 h. Then, into a 100 mL three-necked flask, equipped in the same manner as above, was put 4.20 g (26.0 mmol) of 3-bromothiophene, 20 mL of dry ether and 20 mg of $Ni(dppp)Cl_2$ [$Ni(Ph_2P(CH_2)_3 PPh_2Cl_2$]. The Grignard reagent prepared above was transferred to a dropping funnel and added over 2 h with stirring to the mixture cooled in an ice bath. After the addition was complete, stirring was continued for an additional 3 h at the ice bath temperature. A white precipitate formed and the resulting mixture was allowed to warm to room temperature. Stirring was continued for another 18 h and then the mixture was heated with stirring at 50 °C for 1 h. The mixture was cooled to room temperature and poured into 100 mL of 1 M NaOH solution. This was extracted with diethyl ether (2x50 mL) and the combined ether extracts were washed with water (4x60 mL) and dried ($MgSO_4$). After filtration, the ether was removed in vacuum to give a crude brown product which was purified by silica gel flash column chromatography using hexane/ethyl acetate (33:1 v/v) as eluent. 4.80 g (70%) of **6a** was obtained as a clear, colorless liquid with a purity >98% (HPLC area percent, $t_R = 4.22$ min.). ^{1}H NMR δ: 1.30-1.85 (m, 14 H), 2.61 (t, 2 H, $J = 7$ Hz), 3.30-3.60 (m, 2 H), 3.65-3.90 (m, 2 H), 4.56 (br, m, 1 H), 6.84-6.95 (m, 2 H), 7.10-7.24 (m, 1 H). ^{13}C NMR δ: 19.6, 25.4, 26.0, 29.1, 29.6, 30.1, 30.4, 30.7, 62.2, 67.5, 98.8, 119.8, 125.1, 128.3, 143.1. IR (neat, cm^{-1}): 3101, 3050, 2935, 2857, 1537, 1454, 1440, 1352, 1260, 1200, 1136, 1120, 1077, 1033, 868, 814, 773, 684, 633. Anal. Calcd. for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01. Found: C, 67.48; H, 9.07.

3-[12-(2-Tetrahydropyranyloxy)dodecyl]thiophene (6b).[28] was made in the same way as **6a**. The crude product was purified by silica gel flash column chromatography using hexane/ethyl acetate (50:1 v/v) as eluent to give 35-39% of the colorless liquid product with a purity >98% (HPLC area percent, $t_R = 7.53$ min.). The product became solid on standing a few h at room temperature. mp: 29.0-34.0 °C. ^{1}H NMR δ: 1.26-1.80 (m, 26 H), 2.61 (t, 2 H, $J = 8$ Hz), 3.30-3.55 (m, 2 H), 3.68-3.90 (m, 2 H), 4.57 (t, 1 H, $J = 8$ Hz), 6.85-6.94 (m, 2 H), 7.12-7.22 (m, 1 H). ^{13}C NMR δ: 19.7, 25.5, 26.3, 29.4, 29.5, 29.5, 29.6 (br), 29.6, 29.8, 30.3, 30.5, 30.8, 62.3, 67.7, 98.8, 119.7, 125.0, 128.3, 143.2. IR (KBr, cm^{-1}): 3102, 3050, 2925, 2853, 1537, 1465, 1440, 1352, 1323, 1260, 1200, 1136, 1121, 1078, 1034, 986, 905, 898, 834, 815, 771, 723, 683. Anal. Calcd. for $C_{21}H_{36}O_2S$: C, 71.54; H, 10.29. Found: C, 71.88; H, 10.60.

6-(3-Thienyl)-1-hexanol (7a).[28] A solution of **6a** (1.08 g, 4.00 mmol) in methanol (20 mL) was added to Amberlyst H-15 (0.20 g, 20-60 mesh) in 10 mL of methanol, the mixture was stirred for 4 h at room temperature and then heated at 45 °C for 1 h. The resin was filtered and the solvent was removed in vacuum. Silica gel column chromatography using hexane/ethyl acetate (10:3 v/v) as eluent gave 0.76 g (98%) of **7a** as a clear colorless liquid with a purity >99% (HPLC, $t_R =$ 3.3 min). UV-vis (hexane): λ_{max} 235 nm (e = 4.58 x 10^3). ^{1}H NMR δ: 1.30-1.40 (m, 4 H), 1.45-1.68 (m, 4 H), 2.59 (t, 2 H, $J = 8$ Hz), 3.25 (s, 1 H), 3.54 (t, 2 H, $J = 7$ Hz), 6.84-6.92 (m, 2 H), 7.10-7.24 (m, 1 H). ^{13}C NMR δ: 25.4, 28.9, 30.0, 30.3, 32.4, 62.4, 119.6, 124.9, 128.0, 142.8. IR (neat, cm^{-1}): 3333, 3104, 3077, 2931, 2857, 1537, 1459, 1439, 1411, 1239, 1074, 1155, 1055, 1033, 966, 911, 856, 834, 773, 684, 633. Anal. Calcd. for $C_{10}H_{16}OS$: C, 65.17; H, 8.75. Found: C, 65.11; H, 8.47.

12-(3-Thienyl)-1-dodecanol (7b).[28] was made in the same manner as 6-(3-thienyl)-1-hexanol (**7a**). The product was obtained as white crystals with purity >98% (HPLC, $t_R = 4.26$ min.). Yield: 89%. mp: 47.5-48.5 °C. UV-vis (hexane): λ_{max} 235 nm (ε = 4.47 x 103). ^{1}H NMR δ: 1.21-1.44 (m, 17 H), 1.50-1.70 (m, 4 H), 2.62 (t, 2 H, $J = 8$ Hz), 3.64 (t, 2 H, $J = 7$ Hz), 6.90-6.95 (m, 2 H), 7.20-7.25 (m, 1 H). ^{13}C NMR δ: 25.7, 29.3, 29.4, 29.6 (br), 30.3, 30.6, 32.8, 63.1, 119.7, 125.0, 128.3, 143.3. IR (neat, cm^{-1}): 3426, 3365, 3099, 3053, 2923, 2850, 1564, 1559, 1462, 1438, 1365, 1344, 1300, 1155, 1079, 1063, 1003, 975, 864, 833, 770, 756, 726, 683, 622, 582. Anal. Calcd. for $C_{16}H_{28}OS$: C, 71.59; H, 10.51. Found: C, 71.47; H, 10.37.

6-(3-Thienyl)-1-bromohexane (3).[9] In a 50 mL three-necked flask fitted with a pressure equalizing dropping funnel, and a condenser capped with a drying tube was placed 0.540 g (2.00 mmol) of PBr_3 and 20 mL of freshly distilled benzene. A mixture of 0.10 mL of dry pyridine and 2 mL of the benzene was added dropwise via syringe with stirring over a period of 10 minutes. The flask was then placed in an ice-salt bath, and the contents cooled to –10 °C. A mixture of 1.00 g of **7a** (5.43 mmol) and pyridine (0.10 mL) in 5 mL of benzene was added slowly over a period of 1 h keeping the temperature between –10 °C and –5 °C. Stirring was continued for 1 additional h in the cooling bath and then the mixture was allowed to warm to room temperature and stirred for 46 h. The mixture was poured into 100 mL of saturated $NaHCO_3$ solution and two small portions of benzene were used to rinse the flask (2x20 mL). The combined extracts were washed with water (4x60 mL) and dried ($MgSO_4$). After filtration, the benzene was removed in vacuum giving a crude product which was purified by silica gel column chromatography, eluting with hexane/ethyl acetate (10:1 v/v). The yield of **3** was 0.66 g (49%; HPLC purity >99%, t_R = 4.17 min). UV-vis (hexane): λ_{max} 234 nm (e = 6.98 x 10^3). ^{1}H NMR δ: 1.28-1.48 (m, 4 H), 1.61 (quintet, 2 H), 1.82 (quintet, 2 H), 2.60 (t, 2 H, *J* = 8 Hz), 3.35 (t, 2 H, *J* = 7 Hz), 6.86-6.92 (m, 2 H), 7.10-7.24 (m, 1 H). ^{13}C NMR δ: 27.9, 28.3, 30.1, 30.3, 32.7, 33.9, 119.9, 125.1, 128.2, 142.8. IR (neat, cm^{-1}): 3103, 3050, 3004, 2931, 2855, 1537, 1460, 1438, 1410, 1258, 1238, 1153, 1080, 860, 834, 773, 685, 635, 561. Anal. Calcd. for $C_{10}H_{15}BrS$: C, 48.59; H, 6.12. Found: C, 48.74; H, 6.33.

12-(3-Thienyl)-1-bromododecane (4). In a 100 mL three-necked flask fitted with a pressure equalizing dropping funnel, and a condenser capped with a drying tube was placed 0.490 g (1.80 mmol) of PBr_3 and 20 mL of freshly distilled benzene. A mixture of 0.10 mL of dry pyridine and 2 mL of benzene was added dropwise via syringe with stirring over a period of 10 minutes. The flask was placed in an ice-salt bath, the contents were cooled to –10 °C and a mixture of 1.32 g of **7b** (4.92 mmol) and pyridine (0.10 mL) in 5 mL of benzene was added slowly over a period of 1 h keeping the temperature between –10 °C and –5 °C. Stirring was continued for 1 additional h in the cooling bath and then the mixture was allowed to warm to room temperature and stirred for 46 h. The product was purified by silica gel flash column chromatography using hexane/ethyl acetate (100:1 v/v) as eluent to give 0.47 g (29%) of the colorless liquid product **4**. 48% HBr was also used in place of PBr_3 with benzene as solvent. The reaction was carried out for 6 h under reflux. 1.50 g of **7b**, 13 mL of 48% HBr, and 15 mL of benzene were placed in a 100 mL round bottomed flask under argon. The reaction was run for 6 h under reflux and gave 37% (0.66 g) of **4**. The chief advantages of this latter method for preparing **4** were that not only did it give improved yields (to 37-46%) but also that 35-47% of unreacted **7b** could be completely recovered from the reaction mixture for reuse. UV-vis (hexane): λ_{max} 235 nm (ε = 4.71 x 10^3). ^{1}H NMRδ: 1.25-1.50 (m, 16 H), 1.51-1.70 (quintet, 2 H), 1.83 (quintet, 2 H, *J* = 7 Hz), 2.61 (t, 2 H, *J* = 8 Hz), 3.38 (t, 2 H, *J* = 7 Hz), 6.86-7.00 (m, 2 H), 7.10-7.23 (m, 1 H). ^{13}C NMR δ: 28.1, 28.7, 29.3, 29.4, 29.5 (br), 30.2, 30.5, 32.8, 33.9, 119.7, 124.9, 128.2, 143.1. IR (neat, cm^{-1}): 3104, 3050, 2926, 2853, 1536, 1463, 1439, 1409, 1387, 1247, 1079, 857, 834, 772, 722, 683, 636. Anal. Calcd. for $C_{16}H_{27}BrS$: C, 58.00; H, 8.21. Found: C, 58.07; H, 8.25.

Poly[3-(6-bromohexyl)thiophene] (1). 6-(3-Thienyl)-1-bromohexane (**3**) 0.350g (1.42 mmol) in 5 mL of freshly distilled $CHCl_3$ was added to a stirred solution of 0.920 g of anhydrous $FeCl_3$ (5.68 mmol) in 30 mL of freshly distilled $CHCl_3$. The reaction vessel was purged with nitrogen and stirred for 2 h at room temperature. The black precipitate which formed was filtered, washed with methanol and then added to 200 mL of $CHCl_3$ and 10 mL of conc. aqueous ammonia and stirred for 15 min. at room temperature. Some insoluble red-orange material was filtered. The $CHCl_3$ solution was washed several times with water and dried ($MgSO_4$). The solvent was removed in vacuo to give dark red **1**. Low molecular weight products were removed by adding a concentrated $CHCl_3$ solution of **1** into 50 mL of methanol. The product then was filtered and dried under vacuum at room temperature for 12 h to give 0.215 g (61%) of **1**. ^1H NMR δ: 6.99 (br m, 1 H), 3.43 (br t, 2 H), 2.82 and 2.60 (br m, 2 H), 1.90-1.20 (br m, 8 H), 0.90-0.85 (br, small peaks, about 3-5%). ^{13}C NMR δ: 139.6, 133.7, 130.6, 128.7, 33.9, 32.7, 30.3, 29.3, 28.6, 28.0. IR (KBr, cm^{-1}): 3054, 2929, 2854, 1647, 1509, 1458, 1437, 1258, 1235, 1103, 830, 726, 669, 645, 561. UV-vis (THF) λ_{max} 436 nm, band edge 520 nm (2.39 eV); Film (cast from THF) λ_{max} 492 nm, band edge 630 nm (1.97 eV). Fluorescence: THF solution $\lambda_{Emission\ max}$ = 573 nm and film (cast from THF) $\lambda_{Emission\ max}$ = 670 nm at excitation wavelengths of 506 nm and 400 nm, respectively. GPC analysis: $\overline{M}_n$ = 51,500 (PDI = 5.2). Anal. Calcd. for $(C_{10}H_{13}SBr)_n$: C, 48.99; H, 5.34; Br, 32.59. Found: C, 48.87; H, 5.38; Br, 32.68.

Poly[3-(12-bromododecyl)thiophene] (2). The polymerization was carried out as described above for **1** except the reaction time was 2.5 h. 12-(3-Thienyl)-1-bromododecane (**4**) (0.300 g; 0.906 mmol) in 5 mL of freshly distilled $CHCl_3$ was added to a stirred solution of anhydrous $FeCl_3$ (0.591 g; 3.63 mmol) in 20 mL of freshly distilled $CHCl_3$ **2** was obtained as a dark red powder (0.236 g; 80%). ^1H NMR δ: 6.98 (br, 1 H), 3.39 (t, 2 H), 2.81 and 2.60 (br, 2 H), 1.88-1.28 (br, 20 H), 0.85 (br, small peaks, about 2%). ^{13}C NMR δ: 139.9, 133.7, 130.5, 128.6, 33.9, 32.8, 30.5, 29.5_5 (br), 29.4_6 (br), 28.8, 28.2. IR (KBr, cm^{-1}): 3053, 2922, 2851, 1511, 1462, 1262, 1097, 1021, 822, 803, 721, 645, 563. UV-vis (THF) λ_{max} 438 nm, band edge 530 nm; Film (cast from THF) λ_{max} 505, 570 (sh), 610 (sh) nm, band edge 670 nm. GPC analysis: $\overline{M}_n$ = 91,100 (PDI = 1.7). Fluorescence: THF solution $\lambda_{Emission\ max}$ = 576 nm and film (cast from THF) $\lambda_{Emission\ max}$ = 680 at excitation wavelengths of 530 nm and 400 nm, respectively. Anal. Calcd. for $(C_{16}H_{25}SBr)_n$: C, 58.35; H, 7.65; Br, 24.26. Found: C, 57.98; H, 7.76; Br, 24.10; Fe, 0.03%.

Doping of 1 and **2.** Thin films, deep red-burgundy in color, of the polymers **1** and **2** were cast onto glass slides from a dilute solution of the polymer in xylene. They were then oxidized into their electronically conductive form, which was dark blue in color, by two methods. 1) The polymer/substrate was immersed into a nitromethane solution containing 0.05 M anhydrous $FeCl_3$ for 50 min, rinsed with nitromethane and dried in vacuum before the electrical conductivity measurement. 2) The polymer/substrate was exposed to I_2 vapor for 24 h at room temperature, then excess iodine was removed under vacuum for 5-10 min. Doping of a 3.1 μm thick film of polymer **1** with $FeCl_3$ gave σ = 7.5 S cm^{-1} and of a 2.7 μm thick film with I_2 gave σ

= 18 S cm^{-1}. Doping of a 4.0 μm thick film of polymer **2** with $FeCl_3$ gave σ = 46 S cm^{-1} and of a 2.5 □m thick film with I_2 gave σ = 32 S cm^{-1}.

Poly[3-(6-iodohexyl)thiophene] (8). Poly[3-(6-iodohexyl)thiophene] (**8**) was obtained by a modification of the Finkelstein reaction[9] from **1.** The solvent selection was critical for the completion of substitution of bromine by iodide**.** A solubility study showed that **1** was completely soluble in $CHCl_3$ and insoluble in acetone, while sodium iodide was soluble in acetone and insoluble in $CHCl_3$. However, both **1** and NaI were soluble in a mixture of $CHCl_3$ and acetone in the ratio of 3.8 to 1. Poly[3-(6-bromohexyl)thiophene] (**1**; 30.0 mg; 0.120 mmol) and $CHCl_3$ (25 mL) were placed in a 100 mL three-necked round bottomed flask equipped with magnetic stirrer, and nitrogen inlet. A solution of NaI (0.18 g, 1.22 mmol) in acetone (6.50 mL) was prepared in a small vial. The $CHCl_3$ and acetone were dried over 4 Å molecular sieves before they were used. To the flask containing **1**/$CHCl_3$ was added the NaI/Me_2CO solution via syringe. The mixture was heated at 65 °C for 22 h, then 3 mL of acetone was added and the mixture was heated for an additional 24 h at 65 °C. The solvent was removed in vacuum and 50 mL of $CHCl_3$ was added. The solution was washed four times with water, dried ($MgSO_4$) and the solvent was removed in vacuum to give dark red poly[3-(6-iodohexyl)thiophene] (**8**). Further purification was done by adding a concentrated $CHCl_3$ solution of **8** to 40 mL of methanol from which 32.9 mg (92%) of **8** was obtained. ^{1}H NMR δ: 6.98 (m, 1 H), 3.43 (m, about 2-3%, this peak belongs to –CH_2Br of **1**), 3.21 (m, 2 H), 2.51-2.89 (br m, 2 H), 1.20-1.92 (m, 8 H). Integration of the peaks at δ 3.43 (-CH_2Br) and δ 3.21 (-CH_2I) indicated >97% of the bromine had been displaced by iodide. ^{13}C NMR δ: 7.3, 28.5, 29.4, 29.8, 30.4, 33.5, 128.7, 130.7, 133.8, 139.7. IR (KBr), cm^{-1}) 3398, 2924, 2853, 1740, 1607, 1515, 1460, 1393, 1365, 1311, 1249, 1162, 1099, 823, 755, 721, 651, 589. UV-vis (THF) λ_{max} 430 nm; Film (cast from THF) λ_{max} 478 nm. Anal. Calcd. for $C_{10}H_{13}IS$: C, 41.11; H, 4.48. Found: C, 44.96; H, 4.94.[29]

6-(3-Thienyl)-1-hexyl *S*-thioacetate (9a). Potassium thioacetate (0.420 g, 3.66 mmol) and absolute ethanol (20 mL) were put into a 50 mL three-necked round bottomed flask equipped with a magnetic stirrer, and nitrogen inlet. To the flask was added 0.650 g (2.60 mmol) of 6-(3-thienyl)-1-bromohexane (**3**), the mixture was stirred for 5 h under reflux and then cooled to ambient temperature. The product was extracted with diethyl ether (4x50 mL), the combined extracts were washed with water (4x5 mL) and dried ($MgSO_4$). After filtration, the ether was removed in vacuum and the light yellow crude product was purified by silica gel flash column chromatography using hexane/ethyl acetate (33:1 v/v) as eluent. The yield of 6-(3-thienyl)-1-hexyl *S*-thioacetate (**9a**) was 0.400 g (70%) as a colorless liquid (HPLC purity >98%, t_R= 4.09 min). ^{1}H NMR δ: 1.30-1.50 (m, 4 H), 1.50-1.70 (m, 4H), 2.32 (s, 3 H), 2.62 (t, 2 H, J = 8 Hz), 2.86 (t, 2 H, J = 8 Hz), 6.87-6.95 (m, 2 H), 7.20-7.24 (m, 1 H). ^{13}C NMR δ: 28.6, 28.7, 29.1, 29.4, 30.1, 30.3, 30.6, 120.1, 125.3, 128.4, 143.2, 196.2. IR (neat, cm^{-1}): 3103, 3054, 2929, 2855, 1691, 1536, 1458, 1354, 1298, 1239, 1134, 954, 859, 834, 773, 628, 530. Anal. Calcd. for $C_{12}H_{18}OS_2$: C, 59.46; H, 7.48. Found: C, 59.07; H, 7.53.

12-(3-Thienyl)-1-dodecyl *S*-thioacetate (9b). Potassium thioacetate (0.420 g, 3.66 mmol) and absolute ethanol (20 mL) were put into a 50 mL three-necked round bottomed flask equipped with a magnetic stirrer, and nitrogen inlet. To the flask was added 0.880 g (2.66 mmol) of 12-(3-thienyl)-1-bromododecane (**4**). The product was obtained in the same manner as described for **9a**, as a colorless liquid (HPLC purity >97%, t_R = 6.69 min). The crude product was purified by silica gel flash column chromatography using hexane/ethyl acetate (100:1 v/v) as eluent to yield 0.444 g (51%) of **9b**. ^{1}H NMR δ: 1.20-30 (m, 16 H), 1.50-1.65 (m, 4H), 2.30 (s, 3 H), 2.61 (t, 2 H, *J* = 8 Hz), 2.85 (t, 2 H, *J* = 8 Hz), 6.85-6.93 (m, 2 H), 7.10-7.23 (m, 1H). ^{13}C NMR δ: 28.8, 29.1_0, 29.1_4, 29.3, 29.4_4, 29.4_8, 29.5_3, 29.5_5, 29.5_8, 30.3, 30.5, 30.6, 119.7, 125.0, 128.3, 143.2, 196.0. IR (neat, cm^{-1}): 3104, 3051, 2925, 2853, 1693, 1536, 1460, 1410, 1352, 1134, 1108, 953, 857, 834, 773, 722, 627. Anal. Calcd. for $C_{18}H_{30}OS_2$: C, 66.21; H, 9.26. Found: C, 65.84; H, 9.53.

Poly[6-(3-thienyl)-1-hexyl *S*-thioacetate] (10a). Was prepared by a method similar to that used for the preparation of poly[3-(6-bromohexyl)thiophene] (**1**). 0.180 g of 6-(3-thienyl)-1-hexyl *S*-thioacetate (**9a**; 0.740 mmol) in 3 mL of freshly distilled $CHCl_3$ was added to a stirred solution of anhydrous $FeCl_3$ (0.480 g; 2.96 mmol) in 15 mL of freshly distilled $CHCl_3$ The reaction was carried out for 1.75 h at ambient temperature. The brown precipitate of **10a** was washed with methanol several times then put into 100 mL of $CHCl_3$ and 3 mL of 30% ammonium hydroxide was added. The brown **10a** changed to a red-orange color immediately upon ammonium hydroxide addition. The polymer was dried under vacuum for 24 h and yielded 0.109 g (61%) of **10a** which was insoluble in $CHCl_3$, THF, DMSO, CH_3OH, toluene, *o*-dichlorobenzene or tetramethylene sulfone, and very slightly soluble in refluxing thiophene (84 °C). ^{13}C CP-MAS NMR (10 kHz spinning speed): δ 20-45 (br), 120-145 (br). IR (KBr, cm^{-1}): 3058, 2926, 2852, 1688, 1518, 1457, 1351, 1264, 1186, 1132, 951, 833, 726, 627. Anal. Calcd. for $C_{12}H_{16}OS_2$: C, 59.96; H, 6.71; S, 26.67. Found: C, 59.73; H, 6.78; S, 26.54. The pressed pellet conductivities for polymer **10a**, obtained as described for polymers **1** and **2**, but on pellets pressed in a KBr IR die, were $\sigma = 4 \times 10^{-5}$ Scm^{-1} doped with $FeCl_3$ and $\sigma = 8 \times 10^{-5}$ Scm^{-1} doped with I_2.

Poly[12-(3-thienyl)-1-dodecyl *S*-thioacetate] (10b). Was prepared by a method similar to that used for the preparation of **10a**. 0.040 g of 12-(3-thienyl)-1-dodecyl *S*-thioacetate (**9b**; 0.123 mmol) in 2.5 mL of freshly distilled $CHCl_3$ was added to a stirred solution of anhydrous $FeCl_3$ (0.080 g; 0.490 mmol) in 5 mL of freshly distilled $CHCl_3$ The reaction was carried out for 1.75 h at ambient temperature. The dark purple-brown mixture was poured into 100 mL of methanol. The solid product was filtered and washed with methanol several times, then 150 mL of $CHCl_3$ was added followed by 0.20 mL of anhydrous hydrazine. The green-brown color changed to a red-orange color immediately upon NH_2NH_2 addition. The polymer **10b** was dried under vacuum for 24 h and yielded 0.020 g (50%) of **10b** which was insoluble in $CHCl_3$, THF, DMSO, CH_3OH, acetone, toluene, *o*-dichlorobenzene and tetramethylene sulfone, and very slightly soluble in refluxing thiophene (84 °C). ^{13}C CP-MAS NMR (5 kHz spinning speed): δ 20-45 (br), 120-145 (br). IR (KBr, cm^{-1}): 2922, 2850, 1639, 1459, 1090, 1169, 831, 721. Anal. Calcd. for $C_{18}H_{28}OS_2$: C, 66.62; H, 8.70; S, 19.76. Found: C, 66.12; H, 8.81; S, 19.57.

Poly[3-(6-mercaptohexylthiophene)] (11). Was synthesized by using a post-polymerization process. 80.0 mg (0.330 mmol) of poly[3-(6-bromohexylthiophene)] **1** was dissolved in 20 mL of

$CHCl_3$. 40.0 mg (0.520 mmol) of thiourea was dissolved in 10 mL of EtOH and both solutions were combined in a 50 mL three-necked flask equipped with a magnetic stirring bar, condenser capped with a drying tube and nitrogen inlet. The reaction mixture was stirred for 24 h under reflux, cooled to room temperature and the solvent was removed in vacuo. 20 mL of $CHCl_3$ and 6 mL of saturated Na_2CO_3 were added and the mixture was stirred under nitrogen at room temperature for 24 h. The product **11** was separated and washed with an aqueous HCl solution (pH = 4.00), methanol and dried under vacuum. The red powder of **11** was insoluble in $CHCl_3$, THF, DMF, DMSO, toluene, xylene, *o*-dichlorobenzene and very slightly soluble in refluxing thiophene (84 °C). ^{13}C CP-MAS NMR (5 kHz spinning speed): δ 20-45 (br), 120-145 (br). IR (KBr, cm^{-1}): 3059, 2927, 2853, 1711, 1519, 1459, 1367, 1261, 1195, 1129, 1039, 833, 724, 667, 603. Anal. Calcd. for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11; S, 32.33. Found: C, 60.23; H, 7.28; S, 31.94. The pressed pellet conductivities for polymer **11**, obtained as described for polymers **1** and **2**, but on pellets pressed in a KBr IR die, were $\sigma = 2.3 \times 10^{-2}$ Scm^{-1} doped with $FeCl_3$ and $\sigma = 0.44$ Scm^{-1} doped with I_2.

Attempted hydrolysis of 10a. 0.02 g (0.083 mmol) of poly[6-(3-thienyl)-1-hexyl *S*-thioacetate] **10a**, 5 mL of 2M KOH solution and 10 mL of CH_2Cl_2 were placed in a 50 mL three-necked round bottomed flask equipped with a magnetic stirrer and nitrogen inlet. The mixture was refluxed for 32 h and the solid material did not go into solution during this time. After hydrolysis, the solid was filtered and its IR spectrum was identical to that of the starting material **10a**. Another hydrolysis experiment was performed using 0.5 g $NaBH_4$ in 5 mL of 1M KOH and 10 mL of C_2H_5OH. This reaction was carried out for 48 h under reflux. The solid material **10a** did not go into solution during the hydrolysis process and after hydrolysis, the product again was shown to be the starting material **10a** by IR spectroscopy.

Summary

We have prepared poly[3-(6-bromohexyl)thiophene] (**1**) and poly[3-(12-bromododecyl)thiophene] (**2**) by $FeCl_3$ polymerization of the corresponding monomers and they show 81% head-to-head regioregularity. Poly[3-(6-iodohexyl)thiophene] (**8**) was prepared by S_{N2} displacement on **1**. Conductivities, up to 46 Scm^{-1}, of the doped polymers were measured for **1** and **2**. The S_{N2} displacement reaction was >97% complete as shown by NMR spectroscopy. Further, S_{N2} reactions provided polymers with sulfur substituted in the ω-position of the alkyl groups, namely poly[6-(3-thienyl)-1-hexyl *S*-thioacetate] (**10a**), poly[12-(3-thienyl)-1-dodecyl *S*-thioacetate] (**10b**) and poly[3-(6-mercaptohexylthiophene)] (**11**). These were insoluble in organic solvents, possibly due to their relatively high molecular weights. The ^{13}C CP-MAS spectra were obtained along with pressed pellet conductivities of up to 0.44 Scm^{-1} for the doped polymers. TGA was obtained for several of these polymers and they show thermal decomposition in two stages.

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References and Notes

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