4232 *Macromolecules* **1999,** *32,* 4232−4239

Synthesis and Oxidative Polymerization of Semifluoroalkyl-Substituted Thiophenes

Xiaoyong Hong, J. Cameron Tyson, Jennifer S. Middlecoff, and David M. Collard*

School of Chemistry and Biochemistry and the Polymer Education and Research Center,
Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received January 5, 1999; Revised Manuscript Received April 27, 1999

ABSTRACT: A series of semifluorinated 3-alkylthiophenes ((3-thienyl-$(CH_2)_m$-$CF_2)_nF$, **Th-*m,n***) were prepared by addition of perfluoroalkyl iodides to 3-(ω-alken-1-yl)thiophenes followed by treatment with $NaBH_4$. Chemical and electrochemical oxidation gave the corresponding substituted polythiophenes. The fluorinated side chains have dramatic effects on the conjugation of the polythiophene backbone and thermal phase bahavior. Since the perfluoroalkyl parts of the side chains are approximately the same size as alkyl parts, and the electron-withdrawing effect of the fluorine atoms is insulated from the thiophene ring by a hydrocarbon spacer, these effects are ascribed to interactions between side chains. Microsegregation arising from the immiscibility of fluorocarbon and hydrocarbon segments of semifluorinated alkyl-substituted polymers provides for control of supermolecular architecture. The new 3-(semifluorinated alkyl)thiophenes will serve as comonomers in the design of self-organizing conjugated polymers.

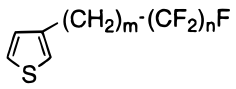
Introduction

Polythiophenes prepared from 3-alkylthiophenes have many interesting and potentially useful properties as a result of extended conjugation along the polymer backbone.[1] However, steric interactions associated with head-to-head linkages (i.e., between 2-positions) cause twisting around the backbone and limit the conjugation length. This twisting has been lowered by synthesizing polymers consisting of head-to-tail (2,5-) couplings.[2,3] Assembly of the side chains of these polymers leads to planar conjugated chains which organize into lamellae in the solid state.[4] A detailed study of poly(3-dodecylthiophene) revealed a shear-induced birefringent phase but no evidence for thermotropic mesomorphism.[5] Besides side chain organization of simple poly(3-alkylthiophene)s, other attempts to prepare self-assembled conjugated polymers include the substitution of the backbones with side chain mesogens,[6] preparation of amphiphilic monomers,[7] and polymerization in organized media (e.g., liquid crystals,[8] surfactant solutions[9]). However, these approaches introduce structural features that are incommensurate with the structure of the polymer backbone (i.e., side chain mesogens and surfactant counterions are large compared to the single heterocylic ring in the backbone repeat unit). To explore the properties of ordered conjugated polymers, we have undertaken a study of polythiophenes substituted with semifluorinated alkyl side chains which have the potential to self-organize.

Fluorinated polymers have attracted attention because of their unusual properties which are a consequence of the hydrophobicity, rigidity, thermal stability, chemical and oxidative resistance, and self-organization of perfluoroalkyl chains.[10] Molecules consisting of both hydrocarbon and fluorocarbon segments of six or more carbons (i.e., $H(CH_2)_m(CF_2)_nF$, where m, $n \geq 6$) form assemblies such as lyotropic mesophases[11] and smectic-like structures[12] owing to microsegregation arising from the immiscibility of fluorocarbons and hydrocarbons. Semifluorinated alkyl side chains have been attached to a variety of polymers to control molecular architecture, including poly(methyl methacrylate)s,[13] ionenes,[14] norbornenes,[15] and styrene−butadiene[16] and styrene−isoprene[17] block copolymers. The microphase segregation of perfluorinated alkyl chains also gives rise to layered structures in thin films of adsorbed polymers.[18]

A number of methylene units (1−3) between a fluorocarbon chain and a thiophene ring (i.e., in 3-thienyl-$(CH_2)_m(CF_2)_nF$, **Th-*m,n***)[19] and other spacers (e.g., in 3-perfluoroalkylmethyloxythiophenes, 3-thienyl-OCH_2-$(CF_2)_nF$)[20] remove the effect of the electron-withdrawing fluorine atoms and lower the oxidation potential of the ring. With a three-carbon spacer, the perfluoroalkyl-substituted thiophenes have electronic properties similar to 3-alkylthiophenes. Fluoroalkyl-substituted polythiophenes prepared by polymerization of 3′-perfluoroalkyl-2,2′:5,2″-terthiophene, perfluoroalkoxythiophene, and 3-perfluoroalkoxy-4-methylthiophene[21] have electronic and optical properties similar to those of the hydrocarbon analogues. However, thermochromic transitions occur at higher temperatures for the fluorinated derivatives, consistent with the rigidity of the perfluoroalkyl chains.

Our previous attempts to study poly(2-(3-thienyl)ethyl perfluoroalkanoate)s were hindered by the facile hydrolysis of the ester.[22] Here we report the efficient synthesis and polymerization of a series of semifluorinated 3-alkylthiophenes, **Th-*m,n***, which will serve as comonomers in the design of self-organizing polymers.



m = 3, n = 4	**Th-3,4**
m = 3, n = 6	**Th-3,6**
m = 5, n = 4	**Th-5,4**
m = 7, n = 2	**Th-7,2**
m = 7, n = 4	**Th-7,4**
m = 5, n = 8	**Th-5,8**
m = 11, n = 4	**Th-11,4**
m = 11, n = 8	**Th-11,8**
3-nonylthiophene	**Th-9,0**

10.1021/ma9900030 CCC: $18.00

Experimental Section

General Methods. All reagents were obtained from commercial sources and used without further purification unless stated otherwise. Column chromatography was performed on silica gel (40 mesh, 60 Å, Baker). Thin-layer chromatography was performed on 5 × 5 cm plates of silica gel (0.2 mm thick, 60 F_{254}) on an aluminum support (EM Separations). All ^1H NMR spectra were recorded on a Varian Gemini 300 MHz instrument using $CDCl_3$ as the solvent unless otherwise specified. Chemical shifts are reported relative to tetramethylsilane. ^{13}C NMR spectra were obtained at 75.5 MHz. IR analysis was performed on a Nicolet 520 FTIR spectrometer. UV−vis analysis was performed with a Perkin-Elmer Lambda 19 spectrometer. Electron ionization or chemical ionization mass spectra were obtained using a VG Analytical 70-SE instrument with a L-250J data system analyzer. Elemental analysis was performed by Atlantic Microlab Inc. (Atlanta, GA).

Polymeric films were spin-coated onto glass slides using a Specialty Coating Systems P-6000 spin coater. Film thickness were measured by a Tencor Alpha-step 100 surface profilometer. Spin-coated polymeric films were doped with I_2 vapor for 12 h, and conductivity measurements were made using a four-point probe.[23] Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7. Gel permeation chromatography was performed on a Waters 510.

Electrochemical experiments were performed using a BAS 100B electrochemical analyzer in a three-electrode cell equipped with a 2.0 mm^2 platinum disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE).

3-(2-Bromoethyl)thiophene, 3. Triphenylphosphine (53.5 g, 204 mmol) was added to a solution of 2-(3-thienyl)ethanol (7.88 g, 61.5 mmol) and carbon tetrabromide (36.5 g, 110 mmol) in CH_2Cl_2 (340 mL) at 0 °C, and the mixture was stirred for 2 h. The volume was reduced to approximately 25 mL under reduced pressure, and the solution was poured onto silica gel in a glass fritted funnel. The silica gel was washed with petroleum ether until TLC analysis revealed no further elution of product. The filtrate was collected, and the solvent was removed under reduced pressure to give crude product. Column chromatography (silica gel/petroleum ether) was performed to obtain **3** as a colorless liquid (10.2 g, 86%). ^1H NMR ($CDCl_3$): δ 3.20 (t, J = 7 Hz, C1−CH_2), 3.57 (t, J = 7 Hz, C2−CH_2), 6.97 (dd, J = 1, 3 Hz, Ar−H2), 7.07 (dd, J = 1, 5 Hz, Ar−H4), 7.29 (dd, J = 3, 5 Hz, Ar−H5). ^{13}C NMR ($CDCl_3$): δ 139.3, 127.9, 125.9, 121.9, 33.7, 32.2. IR (neat): 3105 (ArH stretch), 2966 (asymmetric CH_2 stretch), 2855 (symmetric CH_2 stretch), 1433 (CH bend), 861 (CH out-of-plane vibration), 775 cm^{-1} (CH_2 rock).

3-(ω-Alkenyl)thiophenes, 4. *Method A: 3-(2-Propenyl)thiophene, **4(n = 3)**.* A solution of 3-bromothiophene (19.6 g, 120 mmol) in anhydrous Et_2O was added slowly into a mixture of *n*-butyllithium in hexane (2.5 M, 50 mL, 125 mmol) and anhydrous Et_2O under N_2 at −78 °C. The mixture was stirred at −78 °C for 1 h, and a solution of allyl bromide (12.1 g, 100 mmol) in anhydrous Et_2O was added dropwise into the mixture at −78 °C under N_2. The mixture was allowed to warm to room temperature slowly. Ice/water was added to the mixture followed by 10 mL of 5% HCl. The mixture was extracted with petroleum ether (3 × 30 mL), and the organic layers were combined and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford crude product which was purified by column chromatography (silica gel/petroleum ether) to afford 3-(2-propenyl)thiophene as a colorless liquid (10.5 g, 85%). ^1H NMR ($CDCl_3$): δ 3.38 (d, J = 7 Hz, 2H, CH_2), 5.50 (m, 2H, $=CH_2$), 5.95 (m, 1H, CH=), 6.95 (m, 2H, Ar−H2, Ar−H4), 7.24 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR ($CDCl_3$): δ 140.1, 136.8, 128.3, 125.5, 120.7, 115.8, 34.6. IR (neat): 3079 (Ar−H stretch), 3004, (Ar−H stretch), 2961 (CH_2 stretch), 2905 (CH_2 stretch), 1641 (C=C stretch), 1434 (CH bend), 995 (CH out-of-plane vibration), 909 (CH out-of-plane), 774 cm^{-1} (CH_2 rock).

*Method B: 3-(4-Pentenyl)thiophene, **4(n=5)***. A solution of 3-(2-bromoethyl)thiophene (5.42 g, 28.4 mmol) in anhydrous Et_2O (30 mL) was added dropwise to Mg (779 mg, 32.0 mmol) in dry THF (45 mL) under N_2, and the mixture was sonicated for 1 h. The solution of Grignard reagent was added dropwise to a solution of allyl bromide (4.89 g, 40.0 mmol) and Li_2CuCl_4 (4 mL of a 0.1 M solution in THF, 1.4 mol %) in dry THF (30 mL) at 0 °C. The solution was stirred for 6 h and allowed to warm to room temperature. Water (200 mL) was added, and the mixture was extracted with petroleum ether (2 × 200 mL). The organic extracts were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure to give crude product. Column chromatography (silica gel/petroleum ether) gave 3-(4-pentenyl)thiophene[24] as a colorless liquid (3.65 g, 85%). ^1H NMR ($CDCl_3$): δ 1.75 (p, J = 7 Hz, 2H, C2−CH_2), 2.11 (q, J = 7 Hz, 2H, C3−CH_2), 2.67 (t, J = 7 Hz, 2H, C1−CH_2), 4.98−5.09 (m, 2H, $=CH_2$), 5.87 (ddt, J = 11, 18, 7 Hz, 1H, CH=), 6.96 (dd, J = 1, 3 Hz, 1H, Ar−H2), 6.97 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.26 (dd, J = 3, 5 Hz, 1 H, Ar−H5). ^{13}C NMR ($CDCl_3$): δ 142.8, 138.6, 128.3, 125.2, 120.0, 114.8, 33.2, 29.6, 29.5. IR (neat): 3079 (ArH stretch), 2980 (asymmetric CH_2 stretch), 2861 (symmetric CH_2 stretch), 1644 (C=C stretch), 1446 (CH bend), 992 (CH out-of-plane vibration), 775 cm^{-1} (CH_2 rock). MS (EI) 152 (M^+).

*3-(6-Heptenyl)thiophene, **4(n=7)*** (method B, 73% yield). ^1H NMR ($CDCl_3$): δ 1.3−1.4 (m, 4H, $(CH_2)_2$), 1.75 (p, J = 7 Hz, 2H, C2−CH_2), 2.11 (q, J = 7 Hz, 2H, C5−CH_2), 2.67 (t, J = 7 Hz, 2H, C1−CH_2), 4.98−5.09 (m, 2H, $=CH_2$), 5.87 (ddt, J = 11, 18, 7 Hz, 1H, CH=), 6.96 (dd, J = 1, 3 Hz, 1H, Ar−H2), 6.97 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.26 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR ($CDCl_3$): δ 143.2, 139.1, 128.3, 125.1, 119.9, 114.3, 33.6, 30.3, 30.1, 38.7, 28.6. IR (neat): 3079 (ArH stretch), 2934 (asymmetric CH_2 stretch), 2855 (symmetric CH_2 stretch), 1644 (C=C stretch), 999 (CH out-of-plane vibration), 775 cm^{-1} (CH_2 rock). MS (EI): 180 (M^+). Elemental analysis ($C_{11}H_{16}S$). Calcd: C, 73.28; H, 8.94. Found: C, 73.35; H, 8.91.

*Method C: 3-(10-Undecenyl)thiophene, **4(n=11)***. A solution of 11-bromo-1-undecene (15.2 g, 65 mmol) in anhydrous Et_2O (30 mL) was added dropwise to Mg (1.70 g, 70 mmol) in anhydrous Et_2O (15 mL) under N_2 at room temperature, and the mixture was sonicated for 1 h. The solution of Grignard reagent was added dropwise to a mixture of 3-bromothiophene (6.5 g, 40 mmol) and Ni(dppp)Cl_2 (0.43 g, 0.8 mmol) in anhydrous Et_2O (30 mL) at 0 °C under N_2. The mixture was allowed to warm to room temperature and then heated at reflux overnight. Ice/water was added, and the mixture was extracted by petroleum ether (3 × 50 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to give crude product. Column chromatography (silica gel/petroleum ether) gave a mixture of 3-(10-undecenyl)thiophene[25] and ca. 5% of internal alkene (determined by ^1H NMR spectroscopy) as colorless liquid (7.7 g, 81%). ^1H NMR ($CDCl_3$): δ 1.27 (m, 12H, $(CH_2)_6$), 1.57 (p, J = 6 Hz, 2H, C2−CH_2), 2.10 (q, J = 7 Hz, 2H, C9−CH_2), 2.60 (t, J = 7 Hz, 2H, C1−CH_2), 6.90 (m, 2H, Ar−H2, Ar−H4), 7.21 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR ($CDCl_3$): δ 143.3, 139.3, 128.3, 125.1, 119.8, 114.2, 33.73, 30.47, 30.18, 29.43, 29.39, 29.36, 29.24, 29.04, 28.84. IR (neat): 3105 (ArH stretch), 3076 (ArH stretch), 2923 (CH_2 stretch), 2853 (CH_2 stretch), 1641 (C=C stretch), 1464 (CH bend), 992 (CH out-of-plane), 910 (CH out-of-plane) 771 cm^{-1} (CH_2 rock).

3-(Iodo-semifluorinated alkyl)thiophenes, 5. *3-(2-Iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiophene, **5-(m=3,n=6)***. A mixture of 3-(2-propenyl)thiophene (6.1 g, 49.1 mmol), perfluorohexyl iodide (25 g, 56 mmol), and AIBN (0.92 g, 5.6 mmol) was stirred at 70 °C under N_2 for 48 h. The crude mixture was subjected to column chromatography (silica gel/petroleum ether) to give 3-(2-iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiophene (11.5 g, 41%) as colorless clear liquid. ^1H NMR ($CDCl_3$): δ 2.80 (m, 2H, C3−CH_2), 3.29 (d, J = 7 Hz, 2H, C1−CH_2), 4.47 (p, J = 7 Hz, 1H, CHI), 6.97 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.09 (dd, J = 1, 3 Hz, 1H, Ar−H2), 7.29 (dd, J = 3, 5 Hz, 1H, Ar−H5).

*3-(2-Iodo-4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophene, **5-(m=3,n=4)***. Colorless liquid, yield 41%. ^1H NMR ($CDCl_3$): δ

2.81 (m, 2H, C3−CH$_2$), 3.29 (d, J = 7 Hz, 2H, C1−CH$_2$), 4.47 (p, J = 7 Hz, 1H, C2−CHI), 6.97 (d, J = 6 Hz, 1H, Ar−H4), 7.10 (dd, 1H, Ar−H2), 7.30 (dd, J = 3, 5 Hz, 1H, Ar−H5).

3-(4-Iodo-6,6,7,7,8,8,9,9,9-nonafluorononyl)thiophene, ***5-(m=5,n=4)***. Colorless liquid, 35% yield. ^{1}H NMR (CDCl$_3$): δ 1.8−2.0 (m, 4H, (CH$_2$)$_2$), 2.7 (m, 4H, C1−CH$_2$, C5−CH$_2$), 4.32 (p, J = 7 Hz, 1H, C4−CH), 6.94 (dd, J = 1, 3 Hz, 1H, Ar−H2), 6.96 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.27 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 141.8, 128.1, 125.6, 120.4, 41.5, 39.7, 30.4, 29.0, 20.0. IR (neat): 3105 (ArH stretch), 2947 (asymmetric CH$_2$ stretch), 2868 (symmetric CH$_2$ stretch), 1236 (CF stretch), 887 (CH out-of-plane vibration), 782 cm^{-1} (CH$_2$ rock).

3-(6-Iodo-8,8,9,9,9-pentafluorononyl)thiophene, ***5(m=7,n=2)***. Colorless liquid, 21% yield. ^{1}H NMR (CDCl$_3$): δ 1.2−2.0 (m, 8H, (CH$_2$)$_4$), 2.7−2.8 (m, 4H, C1−CH$_2$, C7−CH$_2$), 4.32 (p, J = 7 Hz, 1H, C6−CH), 6.94 (dd, J = 1, 3 Hz, 1H, Ar−H2), 6.96 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.27 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 142.8, 128.3, 125.3, 120.0, 41.4, 40.0, 30.1, 30.0, 29.3, 28.0, 20.6. IR (neat): 3112 (ArH stretch), 2940 (asymmetric CH$_2$ stretch), 2861 (symmetric CH$_2$ stretch), 1210 (CF stretch), 841 (CH out-of-plane vibration), 781 cm^{-1} (CH$_2$ rock).

3-(6-Iodo-8,8,9,9,10,10,11,11,11-nonafluoroundecyl)thiophene, ***5(m=7,n=4)***. Colorless liquid, 46% yield. ^{1}H NMR (CDCl$_3$): δ 1.35 (m, 4H, (CH$_2$)$_2$), 1.61 (m, 2H, C2−CH$_2$), 1.78 (m, 2H, C5−CH$_2$), 2.62 (t, J = 7 Hz, 2H, C1−CH$_2$), 2.81 (m, 2H, C7−CH$_2$), 4.29 (m, 1H, C6−CH$_2$), 6.91 (m, 2H, Ar−H2, Ar−H4), 7.23 (dd, J = 3, 5 Hz, 1H, Ar−H5).

3-(4-Iodo-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecyl)thiophene, ***5(m=5,n=8)***. White solid, yield 51%. ^{1}H NMR (CDCl$_3$): δ 1.8 (m, 4H, (CH2)$_2$), 2.6−2.9(m, 4H, C1−CH$_2$, C5−CH$_2$), 4.31 (m, 1H, C4−CHI), 6.92 (m, 2H, Ar−H2, Ar−H4), 7.23 (dd, J = 3, 5 Hz, 1H, Ar−H5).

3-(10-Iodo-12,12,13,13,14,14,15,15,15-nonafluoropentadecyl)-thiophene, ***5(m=11,n=4)***. Colorless liquid, 52% yield. ^{1}H NMR (CDCl$_3$): δ 1.27 (m, 12H, (CH$_2$)$_6$), 1.57 (m, 2H, C2−CH$_2$), 1.77 (m, 2H, C9−CH$_2$), 2.60 (t, J = 7 Hz, 2H, C1−CH$_2$), 2.81 (m, 2H, C11−CH$_2$), 4.30 (m, 1H, C10−CHI), 6.91 (m, 2H, Ar−H2, Ar−H4), 7.23 (dd, J = 3, 5 Hz, 1H, Ar−H5).

3-(10-Iodo-12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,-19-heptadecafluorooctadec-yl)thiophene, ***5(m=11,n=8)***. White solid, 78% yield. ^{1}H NMR (CDCl$_3$): δ 1.26 (m, 12H, (CH$_2$)$_6$), 1.54 (m, 2H, C9−CH$_2$), 1.77 (m, 2H, C2−CH$_2$), 2.60 (t, J = 7 Hz, 2H, C1−CH$_2$), 2.81 (m, 2H, C11−CH$_2$), 4.30 (m, 1H, C10−CHI), 6.91 (m, 2H, Ar−H2, Ar−H4), 7.23 (dd, J = 3, 5 Hz, 1H, Ar−H5).

3-(Semifluorinated alkyl)thiophenes, Th-*m,n*. *3-(6,6,7,7,8,8,9,9,9-Nonafluorononyl)thiophene*, ***Th-5,4***. A mixture of 3-(4-iodo-6,6,7,7,8,8,9,9,9-nonafluorononyl)thiophene (1.05 g, 2.11 mmol) and NaBH$_4$ (350 mg, 9.26 mmol) in dry DMSO (10 mL) was heated to 80 °C for 3 h. The solution was cooled to room temperature. Water (50 mL) was added, and the mixture was extracted with petroleum ether (2 × 200 mL). The combined organic extracts were dried over MgSO$_4$, and the solvent was removed under reduced pressure to give crude product. Column chromatography (silica gel/petroleum ether) gave 3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)thiophene as a colorless liquid (526 mg, 67%). ^{1}H NMR (CDCl$_3$): δ 1.35 (p, J = 7 Hz, 2H, C-3 CH$_2$), 1.5−1.7 (m, 4H, C-2 and C-4 CH$_2$), 2.05 (t of t, J = 7, 14 Hz, C-5 CH$_2$), 2.66 (t, J = 7 Hz, 2H, C-1 CH$_2$), 6.94 (dd, J = 1, 3 Hz, 1H, Ar−H2), 6.96 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.27 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 142.6, 128.2, 125.4, 120.1, 30.6, 30.1, 29.9, 28.6, 19.9. IR (neat): 3105 (ArH stretch), 2934 (asymmetric CH$_2$ stretch), 2868 (symmetric CH$_2$ stretch), 1236 (CF stretch), 880 (CH out-of-plane vibration), 775 cm^{-1} (CH$_2$ rock). MS (CI) 372 (M + H). Elemental analysis ($C_{13}H_{13}F_9S$). Calcd: C, 41.44; H, 3.52. Found: C, 41.24; H, 3.26.

3-(4,4,5,5,6,6,7,7,7-Nonafluoroheptyl)thiophene, ***Th-3,4***. Colorless clear liquid, 78% yield. ^{1}H NMR (CDCl$_3$): δ 1.93 (m, 2H, C2−CH$_2$), 2.07 (m, 2H, C3−CH$_2$), 2.72 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.92 (dd, J = 1, 5 Hz, 1H, Ar−H4), 6.95 (dd, J = 1, 3 Hz, 1H, Ar−H2), 7.26 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$) δ 141.0, 127.9, 125.9, 120.8, 30.12 (t, J = 23 Hz), 29.33, 21.00. IR (neat): 3105 (ArH stretch), 3056 (ArH stretch), 2953 (CH$_2$ stretch), 2863 (CH$_2$ stretch), 1460 (ring breathing), 1236 (CF stretch), 881 (CH out-of-plane), 772 cm^{-1} (CH$_2$ rock). Elemental analysis ($C_{11}H_9F_9S$). Calcd: C, 38.38; H, 2.64. Found: C, 38.54; H, 2.69.

3-(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl)thiophene, ***Th-3,6***. Colorless liquid, 79% yield. ^{1}H NMR (CDCl$_3$): δ 1.9−2.2 (m, 4H, (CH$_2$)$_2$), 2.75 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.96 (dd, J = 1, 5 Hz, 1H, Ar−H4), 6.98 (dd, J = 1, 3 Hz, 1H, Ar−H2), 7.30 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 141.0, 127.9, 125.9, 120.8, 30.2, 29.3, 21.0. IR (neat): 2953 (asymmetric CH$_2$ stretch), 1210 cm^{-1} (CF stretch). MS (EI): 444 (M+). Elemental analysis ($C_{13}H_9F_{13}S$). Calcd: C, 35.15; H, 2.04. Found: C, 35.24; H, 2.02.

3-(8,8,9,9,9-Pentafluorononyl)thiophene, ***Th-7,2***. Colorless liquid, 59% yield. ^{1}H NMR (CDCl$_3$): δ 1.2−1.3 (m, 6H, (CH$_2$)$_3$), 1.5−1.7 (m, 4H, C3−CH$_2$, C6−CH$_2$), 2.05 (t of t, J = 7, 14 Hz, 2H, C7−CH$_2$), 2.66 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.94 (dd, J = 1, 3 Hz, 1H, Ar−H2), 6.96 (dd, J = 1, 5 Hz, 1H, Ar−H4), 7.27 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 143.1, 128.3, 125.2, 119.9, 30.8, 30.5, 30.3, 30.2, 30.1, 28.9, 20.1. IR (neat): 3105 (ArH stretch), 2934 (asymmetric CH$_2$ stretch), 2868 (symmetric CH$_2$ stretch), 1203 (CF stretch), 861 (CH out-of-plane vibration), 782 cm^{-1} (CH$_2$ rock). MS (EI): 300 (M+). Elemental analysis ($C_{13}H_{17}F_5S$). Calcd: C, 51.99; H, 5.71. Found: C, 52.08; H, 5.74.

3-(8,8,9,9,10,10,11,11,11-Nonafluoroundecyl)thiophene, ***Th-7,4***. Colorless liquid, 88% yield. ^{1}H NMR (CDCl$_3$): δ 1.34 (m, 8H, (CH$_2$)$_2$), 1.58 (m, 2H, C2−CH$_2$), 2.01 (m, 2H, CH$_2$−CF$_2$), 2.61 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.90 (m, 2H, Ar−H2, Ar−H4), 7.22 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 143.1, 128.3, 125.2, 119.9, 30.68 (t, J = 23 Hz), 30.36, 30.12, 28.95, 19.95. IR (neat): 3104 (Ar−H stretch), 3052 (Ar−H stretch), 2932 (CH$_2$ stretch), 2859 (CH$_2$ stretch), 1463 (ring breathing), 1240 (CF stretch) 879 (CH out-of-plane), 771 cm^{-1} (CH$_2$ rock). Elemental analysis ($C_{15}H_{17}F_9S$). Calcd: C, 45.00; H, 4.28. Found: C, 45.23; H, 4.35.

3-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heptadecafluorotridecyl)thiophene, ***Th-5,8***. White solid, mp = 40−41 °C, 88% yield. ^{1}H NMR (CDCl$_3$): δ 1.42 (m, 2H, C3−CH$_2$), 1.63 (m, 4H, C2−CH$_2$, C4−CH$_2$), 2.03 (m, 2H, CH$_2$−CF$_2$), 2.62 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.91 (m, 2H, Ar−H2, Ar−H4), 7.24 (dd, J = 3, 5 Hz, 1H, Ar−H5).^{13}C NMR (CDCl$_3$): δ 142.7, 128.2, 125.4, 120.1, 30.77 (t, J = 23 Hz), 30.10, 29.90, 28.64, 19.89. IR (neat): 3100 (Ar−H stretch), 3054 (Ar−H stretch), 2944 (CH$_2$ stretch), 2860 (CH$_2$ stretch), 1467 (ring breathing), 1217 (CF stretch), 773 cm^{-1} (CH$_2$ rock). Elemental analysis ($C_{17}H_{13}F_{19}S$): Calcd: C, 35.68; H, 2.29. Found: C, 35.85; H, 2.30.

3-(12,12,13,13,14,14,15,15,15-Nonafluoropentadecyl)thiophene, ***Th-11,4***. Colorless liquid, yield 82%. ^{1}H NMR (CDCl$_3$): δ 1.25 (m, 16H, (CH$_2$)$_2$), 1.58 (m, 2H, C2−CH$_2$), 2.01 (m, 2H, CH$_2$−CF$_2$), 2.60 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.90 (m, 2H, Ar−H2, Ar−H4), 7.22 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 143.4, 128.4, 125.1, 119.8, 30.69 (t, J = 23 Hz), 30.50, 30.21, 29.46, 29.37, 29.30, 29.25, 29.15, 29.02, 19.96. IR (neat): 3105 (Ar−H stretch), 3051 (Ar−H stretch), 2929 (CH$_2$ stretch), 2857 (CH$_2$ stretch), 1462 (ring breathing), 1238 (CF stretch), 770 cm^{-1} (CH$_2$ rock). Elemental analysis ($C_{19}H_{25}F_9S$). Calcd: C, 50.00; H, 5.52. Found: C, 50.63; H, 5.67.

3-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluorooctadecyl)thiophene, ***Th-11,8***. White solid, mp = 56−57 °C, yield 72%. ^{1}H NMR (CDCl$_3$): δ 1.24 (m, 16H, (CH$_2$)$_8$), 1.54 (m, 2H, C2−CH$_2$), 2.01 (m, 2H, CH$_2$−CF$_2$), 2.62 (t, J = 7 Hz, 2H, C1−CH$_2$), 6.91 (m, 2H, Ar−H2, Ar−H4), 7.21 (dd, J = 3, 5 Hz, 1H, Ar−H5). ^{13}C NMR (CDCl$_3$): δ 143.4, 128.4, 125.1, 119.8, 31.12, 30.83, 30.54, 30.24, 29.52, 29.43, 29.36, 29.31, 29.22, 29.08, 20.00. IR (neat): 3097 (Ar−H stretch), 2920 (CH$_2$ stretch), 2850 (CH$_2$ stretch), 1466 (ring breathing), 1212 (CF stretch), 749 cm^{-1} (CH$_2$ rock). Elemental analysis ($C_{23}H_{25}F_{17}S$). Calcd: C, 42.08; H, 3.85. Found: C, 42.31; H, 3.87.

Polymerization of 3-Perfluoroalkylthiophenes Th-*m,n* and 3-Nonylthiophene, Th-9,0. FeCl$_3$ (4.2 mmol) was added to a solution of 3-(pefluoroalkyl)thiophene (1 mmol) in dry

Table 1. Yields of p(Th-*n,m*) Isolated by Extraction in Soxhlet Extractor[a]

polymer	% extracted in solvent[b] acetone	hexane	chloroform	insoluble
p(Th-3,4)	10	7	22	59
p(Th-3,6)	<1	<1	<1	91
p(Th-5,4)	10	46	31	<1
p(Th-7,2)	8	82	16	<1
p(Th-9,0)	<1	22	65	<1
p(Th-7,4)	4	96	<1	<1
p(Th-5,8)	<1	<1	<1	90
p(Th-11,4)	2	90	<1	<1
p(Th-11,8)	<1	<1	15	68

[a] Polymerization reaction mixtures were poured into methanol to precipitate product and then extracted in a Soxhlet extractor with methanol, acetone, hexane, and chloroform. [b] Numbers do not sum to 100% because of incomplete precipitation of polymer in methanol.

CHCl$_3$ (2 mL) and stirred for 24 h under nitrogen. MeOH (20 mL) was added to precipitate the polymer. The mixture was filtered and extracted in a Soxhlet extractor with methanol, acetone, hexane, and CHCl$_3$ (Table 1).

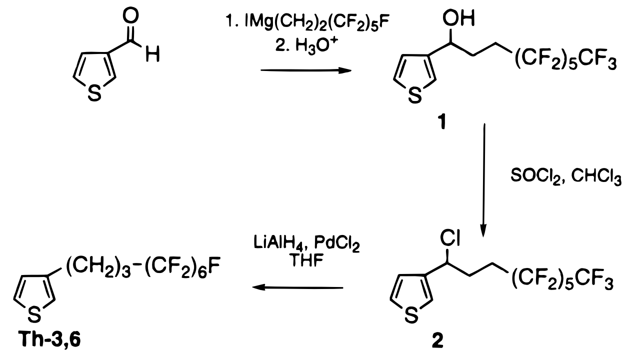
Representative spectral data for *poly(3-(4,4,5,5,6,6,7,7,8,8,-9,9,9-tridecafluorononyl-thiophene),* ***p(Th-3,6)***: ^{1}H NMR (octafluorotoluene): δ 1.7−1.9 (m, 14H, (CH$_2$)$_2$), 2.4−2.6 (m, 2H, C1−CH$_2$), 6.6−6.9 (m, 1H, ArH). IR (neat): 2914 (asymmetric CH stretch), 2848 (symmetric CH stretch), 1203 cm^{-1} (CF stretch).

Results and Discussion

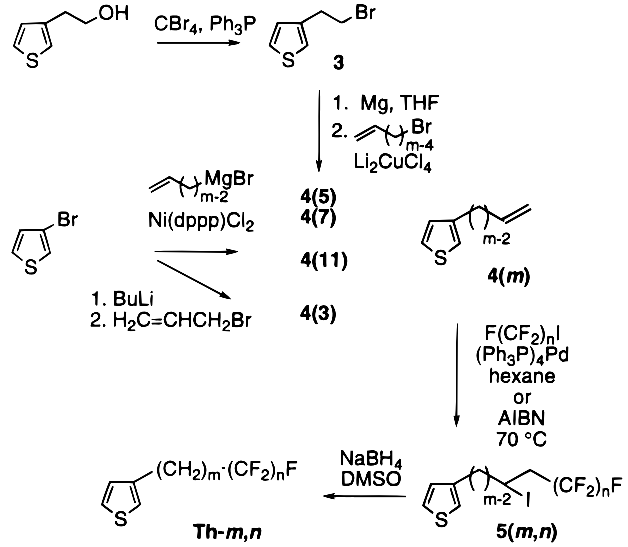
Synthesis of 3-(Semifluorinated alkyl)thiophenes Th-*m,n*. Whereas 3-alkylthiophenes (e.g., 3-nonylthiophene, **Th-9,0**) can be prepared by the Ni(II)-catalyzed coupling of Grignard reagents with 3-bromothiophene (i.e., Kumada coupling),[26] the corresponding perfluoroalkyl compounds are not available by this route owing to the anomalous reactivity of perfluorinated Grignard reagents. Perfluoroalkyl substitution of 3-bromothiophene with perfluoroalkyl iodides promoted by copper[27] affords a mixture of the 2- and 3-regioisomers.[28] Although the 3-trifluoromethyl derivative can be purified, along with the difluoromethyl[29] analogue, mixtures of 2- and 3-isomers of longer homologues are inseparable. Other perfluoroalkylating reagents (e.g., perfluoroalkanoyl peroxides,[30] perfluoroalkanesulfonyl chlorides,[31] sodium perfluoroalkanoates[32]) substitute preferentially at the 2,5-positions of thiophene.

Grignard reagents F(CF$_2$)$_n$(CH$_2$)$_m$−MgBr, where m = 1 or 2, also have anomalous reactivity[33] and do not provide the corresponding 3-(semifluoriated alkyl)thiophenes upon reaction with 3-bromothiophene under Kumada coupling conditions. 3-(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl)thiophene (**Th-3,6**) was synthesized by a published procedure.[34] Reaction of the Grignard reagent derived from 1,1,1,2,2,3,3,4,4,5,5,6,6-trideca-fluoro-8-iodooctane with 3-thiophenecarboxaldehyde in dry Et$_2$O gave 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-1-(3-thienyl)-1-nonanol **1** (Scheme 1). The alcohol was converted to the corresponding chloride, **2**, by reaction with thionyl chloride. Reduction of the chloride with lithium aluminum hydride required an excess of palladium(II) chloride to afford **Th-3,6** without the formation of products arising from base-catalyzed dehydrochlorination of **2**. Generation of the 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-1-magnesium iodide for the first reaction in this sequence gave as much as 20% of the homocoupled semifluorinated alkane, C$_6$F$_{13}$(CH$_2$)$_4$C$_6$F$_{13}$.[35] Attempts to avoid homocoupling were unsuccessful. Another problem in generating 2-(perfluoroalkyl)ethyl-1-magnesium iodide reagents was the limited range of solvents that could be used. Whereas solutions of alkylmagnesium iodides can be generated in Et$_2$O or THF, (perfluoroalkyl)ethyl iodides do not react with Mg in THF even with further activation (addition of I$_2$, sonication, entrainment with ethylene bromide, exposure of clean surfaces of Mg, heating).

Scheme 1



Scheme 2



A more general route to semifluorinated alkylthiophenes was sought which avoids these problems. Monomers **Th-*n,m*** were successfully prepared by addition of perfluoroalkyl iodides to 3-(ω-alkenyl)thiophenes in the presence of catalytic palladium(0)[36] or azobis(isobutyronitrile) (AIBN),[37] followed by reductive deiodination (Scheme 2).

3-(2-Propenyl)thiophene, **4**(m=3), was prepared by reaction of 3-lithiothiophene (generated by addition of butyllithium to 3-bromothiophene at −78 °C) with allyl bromide. Longer chain 3-(ω-alken-1-yl)thiophenes, **4**(m=5, 7, 9, or 11) were prepared by one of two methods: Kumada coupling of 3-bromothiophene and ω-alkenyl-1-magnesium bromides or coupling of 2-(3-thienyl)ethyl-1-magnesium bromide and ω-bromo-1-alkenes in the presence of catalytic lithium copper chloride.[38]

3-(ω-Alken-1-yl)thiophenes **4** react with perfluoroalkyl iodides in the presence (Ph$_3$P)$_4$Pd or AIBN to give 3-(iodo-semifluorinated alkyl)thiophenes **5**. Although catalytic amounts (0.5 mol %) of (Ph$_3$P)$_4$Pd have been used to perform the addition of perfluoroalkyl iodides

Table 2. Molecular Weights of p(Th-*n*,*m*) Determined by Gel Permeation Chromatography[a]

polymer	M_n	M_w	X_n	PDI[b]
p(Th-5,4) ($CHCl_3$ soluble)	43 600	216 600	129	5.0
p(Th-5,4) (hexane soluble)	28 200	213 400	83	7.6
p(Th-7,2) (hexane soluble)	15 600	80 200	59	5.1
p(Th-9,0) ($CHCl_3$ soluble)	17 600	95 100	100	5.4
p(Th-7,4) (hexane soluble)	57 900	278 800	158	4.8
p(Th-11,4) (hexane soluble)	38 500	183 600	91	4.8

[a] Tetrahydrofuran, 25 °C; relative to polystyrene standards. [b] Polydispersity index.

to terminal alkenes in high yield,[36] only low yields of products were obtained using 3-(ω-alkenyl)thiophenes (e.g., 30% yield when using 30 mol % of the expensive catalyst). We ascribe this observation to the ligation of the palladium by the thiophene ring. However, use of AIBN in place of $(Ph_3P)_4Pd$ led to high yields of the desired addition product. Samples of 3-(10-undecenyl)-thiophene prepared by Kumada coupling of 3-bromothiophene and 10-undecen-1-magnesium bromide contained approximately 5% of internal alkenes (determined by ^1H NMR spectroscopy).[39] However, internal alkenes are unreactive in the subsequent addition step and could be separated from the desired product.

Attempts to reduce iodides **5** with lithium aluminum hydride gave as much as 25% of products arising from dehydroiodination, as shown by mass spectrometry and ^1H NMR spectroscopy of crude reaction products. Reduction of the iodides with sodium borohydride in dry DMSO gave 3-(semifluorinated alkyl)thiophenes **Th-*m*,*n*** in high yields.

Polymerizations. The 3-(semifluorated alkyl)thiophenes **Th-*m*,*n*** were oxidatively polymerized using anhydrous $FeCl_3$ in $CHCl_3$.[40] The reaction mixtures were poured into methanol to precipitate the polymers, which were then extracted in a Soxhlet extractor with methanol, acetone, hexane, and chloroform. The yields of polymers extracted into acetone, hexane, and chloroform are listed in Table 1. In general, polymers with a high degree of fluorine substitution are sparingly soluble in these solvents. However, $CHCl_3$-insoluble fractions of **p(Th-3,4)**, **p(Th-3,6)**, **p(Th-5,8),** and **p(Th-11,8)** are soluble in hot octafluorotoluene and hot 1,1,2-trichlorotrifluoroethane. ^1H NMR spectroscopy showed that all of the polymers are regiorandom, as shown by the appearance of different peaks between 2 and 3 ppm corresponding to the C-1 methylene protons for diads with different regiochemistries (i.e., head-to-head, head-to-tail, and tail-to-tail). A peak at 2.6 ppm has been assigned to head-to-tail couplings in poly(3-alkylthiophene)s, whereas a peak at 2.4 ppm is assigned to head-to-head couplings. The spectra of these polymers are in accord with the those for regiorandom poly(3-alkylthiophene)s published elsewhere.[2b,41] Analysis of the aromatic region of the ^1H NMR spectrum of the polymers revealed four broad peaks corresponding to different triad regiochemistries. Comparison of the IR spectra of the polymers and corresponding monomers reveals the disappearance of the α-CH vibration of the thiophene ring of the monomer (3100 cm^{-1}) upon polymerization, consistent with the formation of 2,5-couplings (the β-CH vibration at 3060 cm^{-1} remains).

The number-average molecular weights of polymers measured by GPC (for those polymers soluble in THF) are given in Table 2. The average degree of polymerization (X_n) is in the range 60−100, and as expected the samples are polydisperse. GPC indicates that the hexane-soluble fraction of **Th-5,4** has a lower molecular weight than the $CHCl_3$-soluble sample.

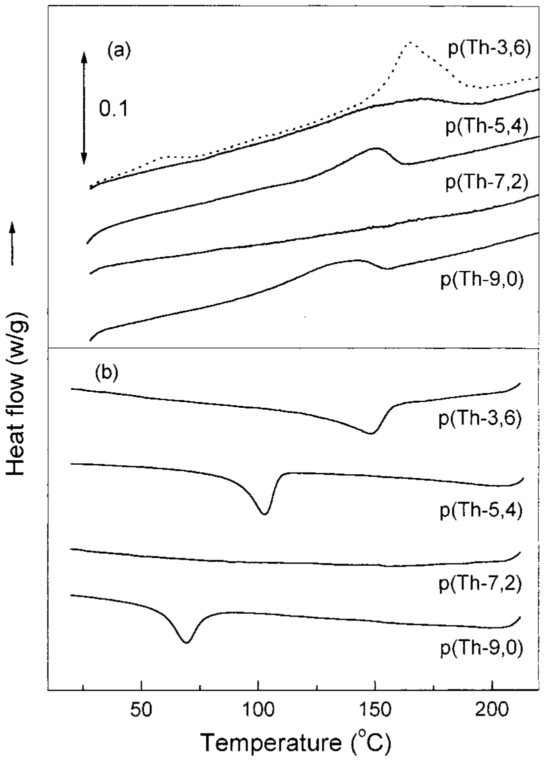


Figure 1. Differential scanning calorimetry thermograms for **p(Th-*m*,*n*)**, where $n + m = 9$: A, heating; B, cooling. Thermograms were obtained on second heating at 10 °C/min. For **p(Th-3,6)** the endotherm on the first heating was much more distinct (dashed line).

Differential Scanning Calorimetry. DSC thermograms of polymers derived from **Th-*m*,*n*** are shown in Figures 1 and 2 and summarized in Table 3. For most of the polymers, a single endothermic peak was observed between 110 and 180 °C on heating, along with a corresponding exotherm on cooling. Transitions in this temperature range for polyalkylthiophenes have been ascribed to melting points, although a transition in this range for amorphous poly(3-alkoxy-3-methylthiophene)s has been assigned to a rod-to-coil transition of the backbone.[42] For the series of poly(3-semifluorononylthiophene)s **p(Th-*m*,*n*)** where $m + n = 9$, as the proportion of fluorocarbon increases (i.e., n/m), the melting point increases (Figures 1 and 2).

In the case of **p(Th-7,2)** there is no melting or crystallization peak in the DSC thermogram, even after annealing at 80 °C. The short perfluoroalkyl group at the end of the side chain appears to disturb the crystalline packing and promotes formation of an amorphous phase. Observations of UV−vis spectra also support this suggestion (see below).

For the series of polymers bearing a nonafluorobutyl chain (i.e., **P(Th-*m*,4)**) or heptadecafluorooctyl chain (i.e., **p(Th-*m*,8)**) the melting points decrease upon increasing the length of the hydrocarbon spacer (increasing *m*). This is consistent with the effect of side chain lengths of poly(3-alkylthiophene)s on the melting point.[43] However, for **p(Th-11,4)** there are two endothermic peaks (87 and 128 °C). The nature of these transitions is under continued investigation. We note that this polymer, which has a low-temperature transition, has a low *n*/*m* ratio in common with **p(Th-7,2)** in which a crystallinity is absent.

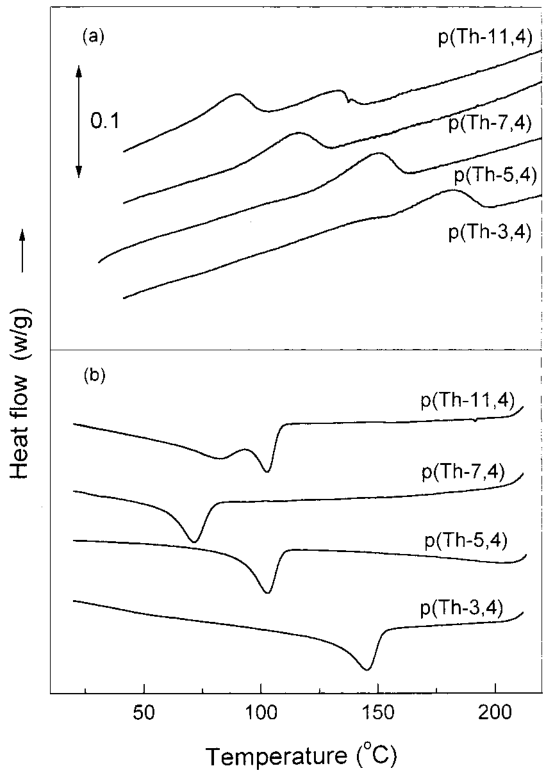


Figure 2. Differential scanning calorimetry thermograms for **p(Th-*m*,4)**: A, heating; B, cooling; 10 °C/min.

Table 3. Thermal Transitions of p(Th-*n*,*m*)[a]

	heating endotherm(s)[b]		cooling exotherm
polymer	T_{onset}/°C	T_{peak}/°C	T_{peak}/°C
p(Th-3,4) (insoluble)	154	180	145
p(Th-3,6) (insoluble)	152[c]	164[c]	149
p(Th-5,4) ($CHCl_3$ soluble)	131	148	103
p(Th-7,2) ($CHCl_3$ soluble)			
p(Th-9,0) ($CHCl_3$ soluble)	101	134	69
p(Th-7,4) (hexane soluble)	100	112	71
p(Th-11,4) (hexane soluble)	58	87, 128	103
p(Th-5,8) (insoluble)	153	175	152
p(Th-11,8) (insoluble)	116	133	125
p(Th-9,0-*co*-Th-3,6)[d] ($CHCl_3$ soluble)	154	177	154
p(Th-9,0-*co*-Th-5,4)[d] ($CHCl_3$ soluble)	91	116	72

[a] From differential scanning calorimetry. [b] Second heating unless noted otherwise. [c] First heating (second heating gave a broad peak with $T_{peak} = 131$ °C). [d] 1:1 random copolymers.

Random Copolymerization. Random copolymers of semifluorinated monomers (**Th-3,6** or **Th-5,4**) and nonylthiophene (**Th-9,0**) were prepared by chemical polymerization of an equimolar mixture of the two monomers. Whereas **p(Th-3,6)** is a powdery solid which is insoluble in hot $CHCl_3$, poly(**Th-9,0**-*co*-**Th-3,6**) is soluble in $CHCl_3$ and forms high-quality free-standing films by evaporation of the solvent. ^1H NMR spectroscopy reveals that the composition of the copolymer corresponds to the monomer feed ratio. Differential scanning calorimetry indicates that the copolymer has a higher melting point (177 °C) than either of the homopolymers (**p(Th-3,6)**, 164 °C; **p(Th-9,0)**, 134 °C). We ascribe this to the higher molecular weight of the copolymer which retains solubility during polymerization. The polymer derived from **Th-3,6** is insoluble in $CHCl_3$ and precipitates from the polymerization reaction mixture, thereby limiting the molecular weight. Although the molecular weight **p(Th-3,6)** was not determined (it is insoluble in THF used for GPC), it shows a very small difference in T_m and T_c ($\Delta T = 15$ °C) which might be a consequence of a low molecular weight. The soluble copolymers display larger values of ΔT. Both **p(Th-5,8)** and **p(Th-11,8)**, which also show limited solubility in chloroform, display low values of ΔT, possibly due to a low molecular weight. In contrast, the copolymer of **p(Th-9,0)** and **p(Th-5,4)** has a lower melting point than either of the homopolymers.

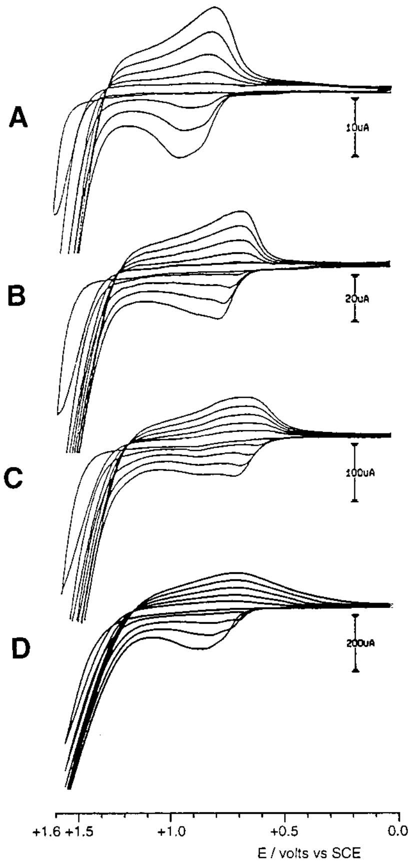


Figure 3. Cyclic voltammograms of **Th-*m*,*n***: A, **Th-3,6**; B, **Th-5,4**; C, **Th-7,2**; D, **Th-9,0**; 100 mV/s. Parts A and B in 0.1 M Bu_4NPF_6/propylene carbonate; parts C and D in 0.1 M $LiClO_4$/acetonitrile.

Electrochemistry. Cyclic voltammetry was performed on semifluorinated 3-nonylthiophenes **Th-3,6**, **Th,-5,4**, and **Th-7,2** and 3-nonylthiophene, **Th-9,0**. The different solubilities of these derivatives restricted choice of solvents for electrochemical polymerization. Cyclic voltammetry of **Th-3,6** and **Th-5,4** was performed in propylene carbonate containing tetrabutylammonium hexafluorophosphate, whereas **Th-7,2** and **Th-9,0** were analyzed in acetonitrile containing lithium perchlorate. Cyclic voltammograms of the fluorinated monomers revealed an oxidation wave with an onset at approximately +1.4 V (versus SCE) (Figure 3A−C), comparable to the onset of oxidation for 3-nonylthiophene (Figure 3D). Repetitive cycling to a switching potential of +1.6 V resulted in the deposition polymers which undergo redox switching at approximately +0.8 V. The difference in potential for the peaks associated with oxidation and reduction of the polymer continues to increase upon repeated potential cycling as more polymer is deposited and presents a barrier to diffusion of counterion in and out of the film. As the fluorocarbon content of the side chains increases, the rate of anodic

Table 4. Ultraviolet−Visible Spectra of p(Th-*m*,*n*)

polymer	λ_{max} ($CHCl_3$ solution)/nm	λ_{max}(film)/nm	$\Delta\lambda$/nm
p(Th-3,4) ($CHCl_3$ soluble)	421 (415)[a]	482	61
p(Th-3,6) ($CHCl_3$ soluble)	395 (410)[a]	469	74
p(Th-5,4) (hexane soluble)	428	481	53
p(Th-5,4) ($CHCl_3$ soluble)	428	462	34
p(Th-7,2) (hexane soluble)	426	443	17
p(Th-7,2) ($CHCl_3$ soluble)	428	448	20
p(Th-9,0) (hexane soluble)	428	506	78
p(Th-9,0) ($CHCl_3$ soluble)	435	501	66
p(Th-7,4) (hexane soluble)	434	466	32
P(Th-11,4) (hexane soluble)	441	516	75
P(Th-11,8) ($CHCl_3$ soluble)	440, 510 (521, 600[a])[b]	518, 600[a]	

[a] Shoulder. [b] In octafluorotoluene.

oxidation decreases (as indicated by the current at +1.6 V in Figure 3), as does the rate of deposition of polymer on the electrode. This is consistent with the more rigid fluorocarbon segments decreasing the diffusion constant for the monomer in the electrolyte solution.

Attempts to potentiostatically deposit polymers by electrolysis of monomers at +1.6 V gave rise to polymers with different adhesion to gold electrodes. Monomers **Th-3,6** and **Th-5,4** gave powdery black solids with poor adhesion to the surface, whereas **Th-7,2** and **Th-9,0** were deposited as continuous dark red films.

Ultraviolet−Visible Absorption Spectra. UV−vis analysis of **p(Th-*m*,*n*)** was performed to relate λ_{max} to the conjugation length along the polymer backbone. In general, the difference in λ_{max} between the spectra obtained from thin films versus those obtained on solutions has been related to assembly of the polymers and the planarity of the backbone. For the series of semifluorinated poly(3-nonylthiophene)s, increasing the fluorine content of the side chain gives rise to a decrease in the absorption maximum for both solutions and films (Table 4). In the case of **p(Th-7,2)**, the difference in absorption maximum, $\Delta\lambda_{max}$, between the polymer film and $CHCl_3$ solution ($\Delta\lambda_{max} = \lambda_{max}$ (film) − λ_{max}(solution)) is much lower than for the other polymers (ca. 20 nm). If the solution spectra relates to a disordered, less conjugated conformation, these data suggest that **p(Th-7,2)** also adopts a less conjugated conformation in the solid state, consistent with the DSC observation that this polymer is completely amorphous.

For **p(Th-3,4)** and **p(Th-3,6)**, which have limited solubility in $CHCl_3$, the UV−vis spectra consist of a broad absorption, suggesting a range of conformations leading to segments with a wide variety of conjugation lengths. Spectra obtained from solutions of these polymers in 1,1,2-trichlorotrifluoroethane show much narrower absorption bands with peaks blue-shifted relative to the spectra obtained in $CHCl_3$.

The UV−visible spectrum of **p(Th-11,8)** in $CHCl_3$ solution consists of two peaks at 440 and 510 nm (Figure 4). In contrast, the spectra obtained on both a thin film and in octafluorotoluene solution consist of a single peak at 520 nm with a shoulder at approximately 600 nm. Thus, in $CHCl_3$, a poor solvent, the polymer consists of more and less conjugated segments. In films or in octafluorotoluene, only the more conjugated conformation is observed. The formation of highly conjugated conformations in octafluorotoluene solution might be explained by lack of solvation of the long hydrocarbon spacer between the polythiophene backbone and fluoroalkyl segments, with the retention of an ordered, planar conformation. The appearance of the spectra of octafluorotoluene solutions of **p(Th-11,8)** is independent of the concentration, suggesting that assembly takes place even in dilute solution, indicating intramolecular assembly of side chains attached to the same polymer chain rather than intermolecular assembly of polymer chains. Thermochromism and solvachromism were observed for all polymers, and detailed studies will be reported elsewhere.

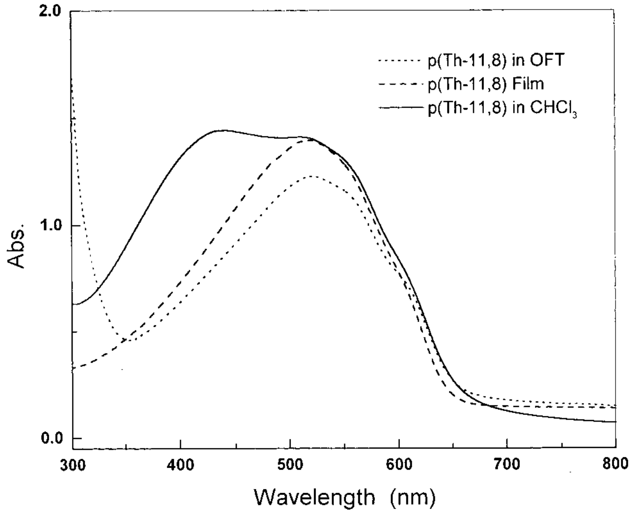


Figure 4. Ultraviolet−visible spectra of **p(Th-11,8)**.

Table 5. Contact Angles of p(Th-*m*,*n*)

polymer	contact angles (deg) dodecane	contact angles (deg) perfluorohexane
p(Th-3,6)	82	21
p(Th-5,4)	71	36
p(Th-7,2)	40	64
p(Th-9,0)	36	83
polyethylene	20	83
Teflon	87	14

Contact Angle Measurements. The oleophilicity and fluorophilicity of the semifluorinated polymers were assessed by contact angle measurements with dodecane and perfluorohexane, respectively. Polymer films of **p-(Th-*m*,*n*)** where $m + n = 9$ were spin-coated from various halogenated solvents. Measurements of poly(ethylene) and Teflon were included for comparison. Contact angles of the polymer films varied according to the ratio of hydrocarbon and fluorocarbon in the side chains. Using dodecane, the angle measurements showed the expected trend of decreasing as hydrocarbon content increased. At the two extremes, the advancing contact angle of dodecane on **p(Th-3,6)** and poly(3-nonylthiophene) are 87° and 36°, respectively. The opposite trend was observed using perfluorohexane, where poly(3-nonylthiophene) (**27**) has the largest measurement of 81°. A complete list of contact angle measurements is given in Table 5.

Electrical Conductivity. Conductivity measurements were made on thin films of polymer that were doped with iodine. The unusual viscosity of solutions of **p(Th-7,2)** did not allow for formation of a thin film using the spin-coating technique so films of this polymer were generated using electrochemical polymerization of 3-(8,8,9,9,9-pentafluorononyl)thiophene. Conductivities for semifluorinated alkylthiophenes were obtained in the range 0.1−10 S/cm, similar to conductivities found for regiorandom poly(3-nonylthiophene).

Conclusions. A general synthetic approach for the synthesis of semifluorinated 3-alkylthiophenes, **Th-*m*,*n***, was developed. Chemical and electrochemical oxidative polymerization gave the corresponding polymers. The limited solubility of the fluorine-rich polymers presents some difficulty in processing and characterization. The fluorinated side chains clearly have some dramatic effects on the conjugation of the polythiophene backbone. Since the perfluoroalkyl parts of the side chain are approximately the same size as hydrocarbon parts, and the electron-withdrawing effects of the fluorines are insulated from the thiophene ring by a hydrocarbon spacer, these effects must be ascribed to interactions between side chains. Further studies to investigate the nature of these interchain interactions (i.e., inter- or intrapolymer chain) and to exploit the amphiphilic nature of semifluorinated alkyl side chains on the self-organization of polythiophenes are underway.

Acknowledgment. We thank the National Science Foundation for support in the form of a CAREER Award (to D.M.C.) and the contributors to the Georgia Tech Polymer Associates Program which provided partial funding of graduate studentships (to J.C.T. and J.S.M.). We thank Dr. Xiaogun Wu for assistance with gel permeation chromatography.

References and Notes

(1) Roncali, J. *Chem. Rev.* **1992**, *92*, 711. Kanatzidis, M. G. *Chem. Eng. News* **1990**, *68*, 36. *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1991; Vol. 1; pp 297−350. *Conjugated Polymers*; Bredas, J. L., Silbey, R.; Eds.; Kluwer: Dordrecht, 1991; pp 472−486.

(2) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (c) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Ewbank, P. C.; Anderson, D. L. *Synth. Met.* **1993**, *55*, 1198. (d) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (e) McCullough, R. D.; Jayaraman, M. *J. Chem. Soc., Chem. Commun.* **1995**, 135. (f) McCullough, R. D.; Ewbank, P. C.; Lowe, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 633.

(3) Chen, T. A.; Rieke, R. D. *Synth. Met.* **1993**, *60*, 175. Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

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

(5) Levon, K.; Park, K. C.; Pashkovski., E. *Plast. Eng. (N.Y.)* **1998**, *45*, 137. Levon, K.; Park, K. C.; Cai, C. *Synth. Met.* **1997**, *84*, 335. Park, K. C.; Levon, K. *Macromolecules* **1997**, *30*, 3175.

(6) Chen, S. H.; Conger, B. M.; Mastrangelo, J. C.; Kende, A. S.; Kim, D. U. *Macromolecules* **1998**, *31*, 8051. Kijima, M.; Akagi, K.; Shirakawa, H. *Synth. Met.* **1997**, *84*, 237. Melamed, D.; Nuckols, C.; Fox, M. A. *Tetrahedron Lett.* **1994**, *35*, 8329.

(7) Stoakes, M. S.; Collard, D. M. *Chem. Mater.* **1994**, *6*, 850.

(8) Torres, W.; Fox, M. A. *Chem. Mater.* **1992**, *4*, 583.

(9) Barr, G. E.; Sayre, C. N.; Connor, D. M.; Collard, D. M. *Langmuir* **1996**, *12*, 1395. Peres, R. C. D.; Juliano, V. F.; De Paoli, M.-A. Panero, S.; Scrosati, B. *Electrochim. Acta* **1993**, *38*, 869. Warren, L. F.; Anderson, D. P. *J. Electrochem. Soc.* **1987**, *134*, 101.

(10) Schmiegel, W. W. *Chemistry of Organic Fluorine Compounds II: A Critical Review*; Hudlicky, M., Pavlath, A. E., Eds.; ACS Monograph 187; American Chemical Society: Washington, DC, 1995; p 1101. Feiring, A. E. *J. Macromol. Sci. Pure Appl. Chem.* **1994**, *A31*, 1657.

(11) Kuwahara, H.; Hamada, M.; Ishikawa, Y.; Kunitake, T. *J. Am. Chem. Soc.* **1993**, *115*, 3002. Giulieri, F.; Krafft, M.-P.; Riess, J. G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1514.

(12) Mahler, W. P.; Guillon, D.; Skoulios, A. *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *2*, 111. Hopken, J.; Pugh, C.; Richtering, W.; Möller, M. *Makromol. Chem.* **1988**, *189*, 911.

(13) Jariwala, C. P.; Mathias, L. J. *Macromolecules* **1993**, *26*, 5129. Johansson, G.; Percec, V.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 646.

(14) Wang, J.; Ober, C. K. *Macromolecules* **1997**, *30*, 7560.

(15) Arehart, S. V.; Pugh, C. *J. Am. Chem. Soc.* **1997**, *119*, 3027.

(16) Ober, C. K.; Wang, J. G.; Mao, G. P. *Macromol. Symp.* **1997**, *118*, 701.

(17) Wang, J. G.; Mao, G. P.; Ober, C. K.; Krammer, E. J. *Macromolecules* **1997**, *30*, 1906.

(18) Sun, F.; Castner, D. G.; Mao, G.; Wang, W.; McKeown, P.; Grainger, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 1856. Sun, F.; Mao, G.; Grainger, D. W.; Castner, D. G. *Thin Solid Films* **1994**, *242*, 106.

(19) Büchner, W.; Garreau, R.; Lemaire, M.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1990**, *277*, 355. Lemaire, M.; Büchner, W.; Garreau, R.; Guetté J.-P.; Cotton, J.-P. *New J. Chem.* **1992**, *16*, 1009.

(20) El Kassmi, A.; Büchner, W.; Fache, F.; Lemaire, M. *J. Electroanal. Chem.* **1992**, *326*, 357.

(21) Robitaille, L.; Leclerc, M. *Macromolecules*, **1994**, *27*, 1847. Robitaille, L.; Bergeron, J.-Y.; D'Aprano, G.; Leclerc, M.; Callender, C. L. *Thin Solid Films* **1994**, *244*, 728.

(22) Middlecoff, J. S.; Collard, D. M. *Synth. Met.* **1997**, *84*, 221.

(23) Smits, F. M. *Bell System Tech. J.* **1958**, 711.

(24) Murray, K. A.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1996**, *76*, 161.

(25) Murray, K. A.; Moratti, S. C.; Baigent, D. R.; Greenham, N. C.; Pichler, K.; Holmes, A. B.; Friend, R. H. *Synth. Met.* **1995**, *69*, 395.

(26) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958. Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, K.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.

(27) Chen, G. J.; Tamborski, C. *J. Fluorine Chem.* **1990**, *46*, 137.

(28) Leroy, J.; Rubinstein, M.; Wakselman, C. *J. Fluorine Chem.* **1985**, *27*, 291.

(29) Noftle, R. E.; Odian, M. A.; Ritter, S. K. *J. Fluorine Chem.* **1995**, *71*, 177. Ritter, S. K.; Noftle, R. E.; Ward, A. E. *Chem. Mater.* **1993**, *5*, 752.

(30) Sawada, H.; Yoshida, M.; Hagh, H.; Aoshima, K.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 215.

(31) Kamigata, N.; Ohtsuka, T.; Fukushima, T.; Yoshida, M.; Shimizu, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1339.

(32) Carr, G. E.; Chambers, R. D.; Holmes, T. F.; Parker, D. G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 921.

(33) Haszeldine, R. N. *J. Chem. Soc.* **1952**, 3423. McBee, E. T.; Hass, H. B.; Bitterbender, W. A.; Weesner, W. E.; Frost, L. W. *Ind. Eng. Chem.* **1947**, 39.

(34) Büchner, W.; Garreau, R.; Roncali, J.; Lemaire, M. *J. Fluorine Chem.* **1992**, *59*, 301.

(35) Boutevin, B.; Pietrasanta, F. G.; Ratsimihety, A.; Caporiccio, G. *J. Fluorine Chem.* **1995**, *70*, 53. Boutevin, B.; Pietrasanta, F. G.; Ratsimihety, A.; Caporiccio, G.; Gronowicz, G. *J. Fluorine Chem.* **1993**, *60*, 211. Von Werner, K.; Blank, H.; Gisser, A.; Manhart, E. *J. Fluorine Chem.* **1980**, *16*, 193.

(36) Ishihara, T.; Kuroboshi, M.; Okada, Y. *Chem. Lett.* **1986**, 1895. Chen, Q. Y.; Yang, Z. Y.; Zhao, C. X.; Qin, Z. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 563.

(37) Feiring, A. E. *J. Org. Chem.* **1985**, *50*, 3269. Kitazume, T.; Ikeya, Y. *J. Org. Chem.* **1988**, *53*, 2350.

(38) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303.

(39) Inaoka, S.; Collard, D. M. *Langmuir*, in press.

(40) Sugimoto, R.; Takeda, S. Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.

(41) Robitaille, L.; Leclerc, M. *Macromolecules* **1994**, *27*, 1847.

(42) Claudine, R.; Leclerc, M. *Macromolecules* **1992**, *25*, 2141.

(43) Ho, K.-S.; Bartus, J.; Levon, K.; Mao, J.; Zheng, W.-Y. *Synth. Met.* **1993**, *55*−*57*, 384.

MA9900030