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Synthesis, Characterization, and Electropolymerization of Thiophene Derivatives of the Group IV Elements

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A series of thiophene derivatives of the group IV elements was prepared which includes the new compounds 3-(trimethylgermyl)thiophene, 3-germylthiophene, 3-(trimethylplumbyl)thiophene, poly(2,5-(dimethylgermyl)thiophene), and poly(2,5-(dimethylstannyl)thiophene). The compounds were synthesized by reaction of an appropriate electrophile ($M(CH_3)_3X$ or $M(CH_3)_2X_2$; M = group IV element and X = Br, Cl, or I) with 3-lithiothiophene or 2,5-dilithiothiophene. Each compound was characterized by ^1H and ^{13}C NMR, IR, and UV spectroscopy; mass spectrometry was also employed for monomeric species. The compounds were polymerized by electrooxidation at constant potential on indium-doped tin oxide glass (ITO) electrodes in 0.2 M tetrabutylammonium hexafluorophosphate/nitrobenzene solution to yield freestanding polymer films which were electrochromic and electroactive with conductivities in the range 0.05–77 S cm^{-1}. The films obtained from the 3-substituted monomers were shown by EDAX measurements to contain greatly reduced amounts of the group IV element while those obtained from polymers bridged by group IV elements contained no measurable amounts.

Introduction

Oxidative polymerization of five-membered aromatic heterocycles to form electrically conductive thin polymer films is well established and much of the early work has been reviewed.[1-3] The 3-substituted thiophenes have attracted much attention because some of the films have the highest measured conductivities of polymers formed from heterocyclic monomers. Poly(3-alkylthiophene) films have potential for good processability[4] and have been found to be stable for extended periods under a number of conditions.[5] The electroactive and electrochromic properties of the films make them potentially suitable for application as electrode materials[5,6] or in optical display devices.[7] Some success has already been achieved in the production of lightweight storage batteries,[3,5,6] and, more recently, interest has grown in the use of the nonlinear optical properties of conductive polymers.[8]

The generally accepted mechanism for the oxidative polymerization of heterocycles involves oxidation of the monomer to form a radical cation intermediate.[2,3] 3-Substituted thiophenes form highly structured polymers which are assumed to be exclusively linked through the 2- and 5-positions of the thiophene ring by coupling reactions of the radical cation intermediates. These polymers have longer mean conjugated chain lengths and higher conductivities than those observed for the parent polythiophene as a result of the elimination of branching or mislinking of the polymer through the 3- or 4-positions of the thiophene ring.[5] An additional effect of substitution is that an electron-donating substituent in the 3-position is expected to favor oxidation of monomer to a sufficiently stable radical cation intermediate, thereby facilitating oxidative polymerization. An electron-withdrawing substituent, on the other hand, is expected to produce the opposite effect and make polymerization difficult except at very high potentials where breakdown of the solvent becomes competitive.[5] For example, 3-methylthiophene has been found to produce a stable radical cation intermediate relative to unsubstituted thiophene and to yield a better quality polymer film with significantly higher conductivity. Compounds such as 3-thiophenecarboxylic acid, 3-cyanothiophene, and 3-nitrothiophene form radical cations of very low stability, compared to unsubstituted thiophene, which yield no polymer upon oxidation while 3-bromothiophene and 3-iodothiophene form radical cations of low stability which yield only poor-quality polymer films with lower conductivities.[5] Thus, the electrical properties of conductive polymers appear to be directly affected by donation or withdrawal of π-electron density from the aromatic thiophene ring by an appropriate substituent.

Lemaire et al. have shown recently that thiophene can be stereoselectively polymerized when trimethylsilyl substituents are at the 2- and 5-positions of the thiophene ring.[9] The reported disilylation occurs at lower potential than the oxidation potential of unsubstituted thiophene and apparently leads to the formation of polythiophene that contains no trimethylsilyl groups. This polymer showed a significant improvement in conductivity; therefore, it was assumed to be more linearly defined and to have a longer mean conjugated chain length than polythiophene prepared from the unsubstituted thiophene.

We have become interested in the effects of main-group substituents in the 3-position of the ring upon the oxidative polymerization of thiophene. To that end, we have prepared several 3-substituted thiophene monomers that contain group IV elements which include what appears to be the first synthesis of 3-(trimethylgermyl)thiophene,

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3-germylthiophene, and 3-(trimethylplumbyl)thiophene. Studies on the nature of group IV substituent effects have appeared and have involved assessment of the relative electronegativities of the elements ($\chi_C > \chi_{Pb} > \chi_{Ge} > \chi_{Sn} > \chi_{Si}$)[10] and substituent group electronegativities as well.[11-14] Experimental evidence suggests that group IV substituents have a σ-electron-donating effect (+I), and a π-electron-withdrawing effect (−M). The π-electron-withdrawing effect is possible because the group IV elements except carbon possess empty d-orbitals which may be sufficiently low enough in energy to receive electron density from a linear, conjugated molecule or from the delocalized π-system of an aromatic ring. These potential pathways for electron release or withdrawal by a group IV substituent led us to consider that, if conductive polymers can be prepared from substituted thiophenes of the group IV elements, the resultant films could have interesting electrical and mechanical properties. However, the results of Lemaire et al. concerning the facile displacement of trimethylsilyl groups from the thiophene ring suggest that substituents containing group IV elements may also subject the 3-position toward oxidation even though the π-electron density is normally expected to be greater at the 2- and 5-positions.[15] Thus, a competition for the 2- and 3-positions could arise and might result in the formation of a polymer that consists of both thiophene and 3-substituted thiophene units. Accordingly, the oxidative polymerization of 3-substituted thiophenes of the group IV elements was carried out.

Chicart et al. recently prepared a variety of polymers in which thiophene units were linked through the 2- and 5-positions with dimethylsilyl- groups.[16] Their work includes the compound poly(2,5-(dimethylsilyl)thiophene) and compounds in which the number of consecutive thiophene units and consecutive dimethylsilyl groups varies. Earlier reports on thiophene linked with dimethylsilyl groups similar to poly(2,5-(dimethylsilyl)-thiophene) have been published.[17,18] Chicart et al. have shown that these polymers can be chemically doped by $NOBF_4$ to yield polymers with low conductivities (10^{-5}–10^{-1} S cm^{-1}). These thiophene-linked polymers form an interesting new class of conductive materials in which conduction is possible by pπ–dπ conjugation of the polymer chain through the group IV element. There may be, however, some problems associated with the oxidation and doping of polymers formed by linking thiophene units with group IV heteroatoms because the silicon–carbon bond is known to be easily cleaved in electrophilic aromatic substitution and the C–M bonds (M = Si, Ge, Sn) are assumed to be weaker than the C–H bond.[19] This has raised a question about the stability and composition of conductive polymers formed from thiophene derivatives of the group IV elements, and our interest in this has led us to explore the electrochemistry of solutions of some of these chemically prepared polymers. In the course of this work, we achieved what appears to be the first synthesis of poly(2,5-(dimethylgermyl)thiophene) and poly(2,5-(dimethylstannyl)thiophene).

Experimental Section

Materials. GeO_2 (electronic grade 99.999%), KBH_4 (98%), $(CH_3)_3SiCl$ (98%), $(CH_3)_2SiCl_2$ (98%), CH_3I (Gold Label 99.5%), 3-bromothiophene (97%), 2,5-dibromothiophene (95%), diethyl ether (anhydrous, 99+%), methyllithium (1.4 M in diethylether), *n*-butyllithium (2.00 M in cyclohexane), $NOBF_4$, and nitrobenzene (99+%) were obtained from Aldrich. KOH (pellets), glacial acetic acid, and anhydrous diethyl ether (all ACS reagent grade) were obtained from Fisher. $SnCl_4$ (99%, Baker and Adamson), $(CH_3)_3GeBr$, $(CH_3)_2GeCl_2$, and $(CH_3)_2SnBr_2$ (Organometallics, Inc.), $(CH_3)_3SnCl$ and $(CH_3)_3PbCl$ (Johnson Matthey), and tetrabutylammonium hexafluorophosphate (electronic grade, Southwestern Analytical Chemicals) were used as received. Hygroscopic substances were stored in a desiccator.

Methods. Germane, GeH_4, was prepared and characterized by the method of Jolly,[20] and chlorogermane, GeH_3Cl, by that of Cradock.[21] The 3-substituted thiophenes were prepared by variations on the lithiation methods of Gronowitz.[22,23] Preparative-scale gas chromatography was performed on a Gow Mac Series 150 chromatograph with thermal conductivity detector. A 4 ft × $^1/_4$ in. copper column (5% Dexil 400 on 100/120 chromosorb w hp, Ohio Valley) was employed at an oven temperature of 105 °C with helium as the carrier gas at a flow rate of 50 mL min^{-1}. Approximate yields of 3-germylthiophene and 3-(trimethylplumbyl)thiophene were measured by comparison of the peak area of the product to that of unreacted 3-bromothiophene in the gas chromatograms of the crude product mixtures. For the other 3- and 2,5-substituted thiophenes, the yields were determined from the GC peak areas of the product mixtures which were calibrated against the areas produced in the chromatograms of known amounts of pure samples. The retention times (minutes) of some compounds under study were thiophene (0.85), 3-methylthiophene (1.15), 3-germylthiophene (1.63), 3-bromothiophene (2.30), 3-(trimethylsilyl)thiophene (2.45), 3-(trimethylstannyl)thiophene (4.20), 3-(trimethylgermyl)thiophene (4.48), 2,5-bis(trimethylsilyl)thiophene (5.50), and 3-(trimethylplumbyl)thiophene (10.20). The densities of the liquid products were estimated by measurement of the mass contained in a 10-μL pipette. NMR spectra were obtained in $CDCl_3$ (0.03% TMS) with a Varian VXR 200-MHz FT-NMR spectrometer. UV spectra were obtained from 10^{-6} M samples in acetonitrile or dichloromethane (for chemically prepared linked polymers) with a Milton Roy diode-array Spectronic 3000 spectrophotometer. IR spectra were obtained as films on AgCl windows with a Perkin-Elmer 1330 spectrophotometer. The electron-impact mass spectra at 70 eV were obtained from 10^{-4} M samples in anhydrous diethyl ether with an HP 5890 Series II gas chromatograph in tandem with an HP 5989A mass spectrometer. Cyclic voltammetry was performed with a JAS Model JJ 1276 waveform generator and a Southampton potentiostat. Plots were made on a Linseis LY17100 *XY* recorder. All electrochemistry was carried out in 0.2 M $TBAPF_6$ in nitrobenzene using a 4-mL single compartment cell with either a platinum minielectrode (1-mm diameter, Cypress Systems) or indium-doped tin oxide (ITO) glass (Donnelly Corp.) as the working electrode, a platinum wire coil as the secondary electrode, and a silver wire pseudo-reference electrode. The electrochemical cell was rinsed with deionized water and then dried at 150 °C for at least 1 h prior to each use. The electrolyte solution was degassed with dry nitrogen for 15 min prior to use and maintained under nitrogen throughout each experiment. The platinum working electrode was polished before each measurement on 1.0-μm α-alumina (Buehler Corp.) followed by 0.3 and then 0.05 μm. The electrode was subsequently rinsed with deionized water, dried, and sonicated for 30 s in fresh nitrobenzene just prior to use. All electrochemical experiments on the monomers were carried out

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at a scan rate of 100 mV s^{-1}, and monomer concentrations were 0.2 M. The onset potential for polymerization of each monomer, E_a(mon), was measured by extrapolation of the i vs E plot to $i = 0$ at the point of steepest slope. Polymer films were prepared on ITO electrodes at a constant potential of 1.90 V to give thicknesses in the range ~3–11 μm (microscopic measurements). The freshly prepared films were rinsed in anhydrous diethyl ether, deionized water, again in fresh diethyl ether, and dried at room temperature. Conductivity measurements were made approximately 1 h after preparation of each film by a four-point probe method;[24] contacts to the films were made with 0.002-cm copper wire (Omega Engineering) and silver conductive paint (Se 12, Microcircuits Co.). Electrochemistry of polymer-modified platinum electrodes was carried out in monomer-free electrolyte solutions in order to estimate the redox potential of each polymer. EDAX (energy-dispersive X-ray spectroscopy) measurements were made with a Phillips 515 SEM with a PV9800 EDAX attachment. The data were acquired by a standardless, quantitative analytical procedure and were ZAF corrected. The electronic spectra of the as-grown neutral and oxidized polymer films on ITO glass electrodes were recorded on a Cary 219C spectrophotometer in the range ~330–850 nm. A spectral baseline was recorded using ITO glass as reference and sample just prior to deposition of the polymer on the surface of the plate used as the sample. Spectra were then obtained using the same ITO glass reference and the same sample electrode coated with a thin film of the polymer. Atlantic Microlabs performed the elemental analyses.

3-(Trimethylgermyl)thiophene. This procedure is illustrative of our general syntheses of substituted thiophenes. 3-Bromothiophene (1.1 mL, 12 mmol) was introduced by syringe to a two-neck 100-mL round-bottom flask that contained a Teflon-coated stir bar. The reaction vessel was previously dried in an oven at 150 °C for 12 h and then purged with dry nitrogen for 30 min while cooling to ensure an air- and moisture-free environment. Anhydrous diethyl ether (20 mL) was added by syringe as the solvent. The reaction vessel was cooled to −70 °C under nitrogen with a 2-propanol/dry ice bath. *n*-Butyllithium (6.6 mL, 13.2 mmol) was added and produced a clear, faintly colored, yellow-brown solution that was allowed to react for 15 min with stirring. Bromotrimethylgermane, ($(CH_3)_3GeBr$, 1.5 mL, 12 mmol) was added to the reaction vessel by syringe and allowed to react at −70 °C for 2 h. The reaction vessel was then allowed to warm slowly to room temperature while maintaining a nitrogen atmosphere. Over the course of the reaction a small amount of white precipitate was formed (LiBr). Deionized water (5 mL) was added at room temperature to quench the reaction, and the product mixture was extracted with fresh diethyl ether. The ether fraction was washed three times with deionized water; the precipitate was dissolved in the water layer. The water fraction was extracted with fresh diethyl ether, and the ether fractions were combined. The water fraction was a clear red-brown solution that gave a positive flame test for lithium (deep red) and a pale yellow precipitate (AgBr) when a few drops of concentrated $AgNO_3$ were added. The ether fraction was reduced to about 5 mL on a rotary evaporator at room temperature and the product purified by gas chromatography. The product is a colorless liquid, $d^{20} = 1.28$ g cm^{-3}; yield 41% (0.9722 g). Anal. Calcd for $C_7H_{12}SGe$: C, 41.87; H, 6.02; S, 15.97; Ge, 36.14; MW, 200.83. Found: C, 42.09; H, 6.05; S, 15.73; Ge, 36.13 (by difference). ^1H NMR: δ 7.33 d, H_2; 7.14 dd, H_4; 7.40 dd, H_5; 0.38 s, $-CH_3$ (J_{2-4} 0.95 Hz; J_{2-5} 2.74 Hz; J_{4-5} 4.58 Hz). ^{13}C NMR: (δ) 129.33, C_2; 141.5, C_3; 130.90, C_4; 125.42, C_5; −1.06, $-CH_3$ (J_{C2-H2} 185.2 Hz; J_{C4-H4} 168.0 Hz; J_{C5-H5} 186.7 Hz; J_{C-H} ($-CH_3$) 126.9 Hz). IR (cm^{-1}): 3100 vw, 3085 vw, 3058 vw, 2972 m, 2907 m, 2800 vw, 1482 w, 1407 w, 1387 w, 1366 w, 1236 s, 1198 m, 1092 s, 883 vw, 843 m, 823 s, 755 s, 689 m, 599 vs, 569 m. MS (*m/e*, ion, relative %): 187.00, $C_4H_3S^{74}Ge(CH_3)_2^+$, 100.0; 202.00, $C_4H_3S^{74}Ge(CH_3)_3^+$, 13.6; 51.05, $C_4H_3^+$, 11.1; 39.15, $C_3H_3^+$, 10.7; 119.00, $^{74}Ge(CH_3)_3^+$, 5.6%; 45.00, CHS^+, 4.2; 74.00, free $^{74}Ge^+$, 2.5. UV: $\lambda_{max} = 236$ nm, log $\epsilon = 3.47$.

3-Germylthiophene. 3-Bromothiophene (1.9 mL, 20 mmol), *n*-butyllithium (11.2 mL, 22.4 mmol), and chlorogermane, H_3GeCl (1.15 mL, 18.0 mmol) were allowed to react in anhydrous diethyl ether (15 mL) as before. After the addition of 3-bromothiophene and the solvent, the reaction vessel was attached to a vacuum line and the pressure slowly reduced at room temperature to 50 mTorr. The reaction vessel was cooled to −70 °C with a 2-propanol/dry ice bath and the *n*-butyllithium was added by syringe. After 15 min, chlorogermane (bp = 26 °C) was condensed into the reaction vessel and allowed to react under vacuum for 3 h. The reaction mixture was extracted and purified as before. The product is a colorless liquid, $d^{20} = 1.48$ g cm^{-3}. Yield: 90% (GC yield). Anal. Calcd for C_4H_6SGe: C, 30.26; H, 3.81; S, 20.20; Ge, 45.73; MW, 158.75. Found: C, 30.51; H, 3.87; S, 19.96; Ge, 45.66 (by difference). ^1H NMR: (δ) 7.46 d, H_2; 7.16 dd, H_4; 7.42 dd, H_5; 4.23 s, $-CH_3$ (J_{2-4} 0.95 Hz; J_{2-5} 2.69 Hz; J_{4-5} 4.62) Hz. ^{13}C NMR: (δ) 132.54, C_2; 127.89, C_3; 132.59, C_4; 126.03, C_5 (J_{C2-H2} 180.6 Hz; J_{C4-H4} 165.0 Hz; J_{C5-H5} 185.7 Hz). IR (cm^{-1}): 3102 vw, 3088 vw, 3065 vw, 2075 vs, 1483 vw, 1458 w, 1362 w, 1340 w, 1202 w, 1096 w, 1082 w, 871 m, 848 s, 822 vs, 770 s, 693 m, 641 s. MS (*m/e*, ion, relative %): 54.15, $C_4H_6^+$, 100.0; 159.95, $C_4H_3S^{74}GeH_3^+$, 54.1; 85.05, $C_4H_3SH_2^+$, 52.3; 39.15, $C_3H_3^+$, 45.7; 74.00, free $^{74}Ge^+$, 25.8; 45.15, CHS^+, 15.8. UV: $\lambda_{max} = 238$ nm, log $\epsilon = 3.51$.

3-(Trimethylplumbyl)thiophene. A mixture of 3-bromothiophene (0.75 mL, 8.0 mmol), *n*-butyllithium (4.0 mL, 8.0 mmol), and chlorotrimethylplumbane, $(CH_3)_3PbCl$ (1.6483 g, 5.7 mmol) previously dissolved in 7 mL of tetrahydrofuran was allowed to react in anhydrous diethyl ether (10 mL), at −70 °C for 2 h. The product is a colorless liquid, $d^{20} = 2.00$ g cm^{-3}; yield 80% (GC yield). Anal. Calcd for $C_7H_{12}SPb$: C, 25.07; H, 3.61; S, 9.56; Pb, 61.76; MW, 335.44. Found: C, 25.73; H, 3.43; S, 9.85; Pb, 60.99 (by difference). ^1H NMR: (δ) 7.34 d, H_2; 7.22 dd, H_4; 7.46 dd, H_5; 0.99 s, $-CH_3$ (J_{2-5} 2.50 Hz; J_{4-5} 4.64 Hz). ^{13}C NMR: (δ) 130.74, C_2; 143.1, C_3; 133.46, C_4; 125.09, C_5; −1.52, $-CH_3$ (J_{C2-H2} 147.2 Hz; J_{C4-H4} 127.2 Hz; J_{C5-H5} 184.3 Hz; J_{C-H} ($-CH_3$) 127.9 Hz). IR (cm^{-1}): 3090 vw, 3060 w, 3000 m, 2925 m, 1465 w, 1440 w, 1378 m, 1360 m, 1194 m, 1069 m, 869 w, 838 s, 757 vs, 688 s, 600 s, 580 s. MS (*m/e*, ion, relative %): 320.95, $C_4H_3S^{208}Pb(CH_3)_2^+$, 100.0; 290.90, $C_4H_3S^{208}Pb^+$, 63.1; 207.90, free $^{208}Pb^+$, 45.7; 222.95, $^{208}Pb(CH_3)^+$, 15.2; 305.90, $C_4H_3S^{208}Pb(CH_3)^+$, 7.4; 39.05, $C_3H_3^+$, 3.3; 45.10, CHS^+, 1.8; 336.00, $C_4H_3S^{208}Pb(CH_3)_3^+$, 0.5. UV: $\lambda_{max} = 235$ nm, log $\epsilon = 3.71$.

Poly(2,5-(dimethylgermyl)thiophene). 2,5-Dibromothiophene (1.0 mL, 8.6 mmol) and *n*-butyllithium (8.6 mL, 17.2 mmol) were allowed to react in diethyl ether (10 mL) at room temperature for 2 h. $(CH_3)_2GeCl_2$, (1.0 mL, 8.6 mmol) was added, and after an induction period of about 10 s a rapid exothermic reaction occurred and caused the solvent to boil briefly. The reaction was allowed to proceed under a nitrogen atmosphere at room temperature for 1 h. The reaction was accompanied by a solution color change from brown to orange to green. Methyllithium (1.2 mL, 1.7 mmol) was added to terminate the reaction. After an additional 15 min, the reaction mixture was extracted as before. The ether was completely removed on a rotary evaporator at room temperature, and the solid product recrystallized from diethyl ether and methanol to yield initially a light green powder (0.1343 g) which decomposed to a black viscous melt at 120 °C. A different sample of the green solid (synthesized by the same procedure) was dissolved in THF/methanol and reprecipitated as a white solid (0.1303 g). Anal. Calcd for $(C_6H_8SGe)_n$: C, 39.00; H, 4.36; S, 17.35; Ge, 39.28. Found (green material): C, 38.90; H, 4.33; S, 17.27; Ge, 39.50 (by difference). Found (white material): C, 38.90; H, 4.30; S, 17.26; Ge, 39.54 (by difference). The NMR spectra and the S/Ge ratio (EDAX) were the same for both solids. ^1H NMR: (δ) 7.30 s, $H_{3,4}$; 0.74 s, $-CH_3$. ^{13}C NMR: (δ) 134.68, $C_{3,4}$; 143.45, $C_{2,5}$; 0.06, $-CH_3$ ($J_{C3,4-H3,4}$ 165.4 Hz; J_{C-H} ($-CH_3$) 121.6 Hz). IR (cm^{-1}): 3050 vw, 2975 w, 2902 vw, 1487 m, 1400 m, 1379 m, 1265 m, 1235 m, 1198 s, 980 s, 947 w, 830 m, 798 vs, 738 s, 609 s, 580 m, 505 m, 415 vw, 370 m. UV: $\lambda_{max} = 247$ nm, $\epsilon = 62.5$ L g^{-1} cm^{-1}; $\lambda_{sh} = 257$ nm; $\lambda_{max} = 716$ nm, $\epsilon = 0.23$ L g^{-1} cm^{-1}.

Poly(2,5-(dimethylstannyl)thiophene). 2,5-Dibromothiophene (0.53 mL, 4.7 mmol), *n*-butyllithium (4.7 mL, 9.4 mmol), dichlorodimethylstannane, $(CH_3)_2SnCl_2$ (2.0087 g, 4.7 mmol in 5 mL of diethyl ether), and methyllithium (0.67 mL, 0.9 mmol) reacted at room temperature in anhydrous diethyl ether (20 mL) to give initially a dark green solid which decomposed slowly at >200 °C. Upon reprecipitation from THF/methanol, the product did not turn white but remained as a green solid, yield 0.0465 g. Anal. Calcd for $(C_6H_8SSn)_n$: C, 31.21; H, 3.49; S, 13.89; Sn, 51.41.

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Found: C, 30.50; H, 3.20; S, 13.49; Sn, 52.81 (by difference). ^1H NMR: (δ) 7.42 s, $H_{3,4}$; 0.61 s, $-CH_3$. ^{13}C NMR: (δ) 136.70, $C_{3,4}$; 143.5, $C_{2,5}$; −7.22, $-CH_3$ (coupling constants not resolved). IR (cm^{-1}): 3050 w, 2980 w, 2910 w, 1474 m, 1379 m, 1253 m, 1191 m, 948 s, 920 m, 790 s, 760 s, 730 s, 600 m, 520 m, 487 m, 400 vw, 312 m. UV: λ_{max} = 249 nm, ϵ = 40.9 L g^{-1} cm^{-1}; λ_{max} = 719 nm, ϵ = 1.2 L g^{-1} cm^{-1}.

3-Methylthiophene. 3-Bromothiophene (2.0 mL, 21.3 mmol), *n*-butyllithium (15.0 mL, 30.0 mmol), and iodomethane (CH_3I, 4.3 mL, 30.0 mmol) were allowed to react in anhydrous diethyl ether (30 mL) at −70 °C for 3 h. The product is a colorless liquid, d^{20} = 1.52 g cm^{-3}, yield 35% (0.7301 g). The ^1H and ^{13}C NMR, UV, IR, and MS data agree with those reported in the literature.[25,26]

3-(Trimethylsilyl)thiophene. 3-Bromothiophene (3.0 mL, 32.0 mmol), *n*-butyllithium (18.0 mL, 36.0 mmol), and chlorotrimethylsilane ($(CH_3)_3SiCl$, 3.0 mL, 32.2 mmol) were allowed to react in anhydrous diethyl ether (20 mL) at −70 °C for 3 h. The product is a colorless liquid, d^{20} = 1.06 g cm^{-3}, yield 60% (0.7279 g). ^1H NMR: (δ) 7.45 d, H_2; 7.20 dd, H_4; 7.40 dd, H_5; 0.28 s, $-CH_3$ (J_{2-4} 1.03 Hz; J_{2-5} 2.52 Hz; J_{4-5} 4.69 Hz). ^{13}C NMR: (δ) 131.42, C_2; 141.25, C_3; 131.42, C_4; 125.64, C_5; −0.53, $-CH_3$ (J_{C2-H2} 175.0 Hz; J_{C4-H4} 176.0 Hz; J_{C5-H5} 184.4 Hz; J_{C-H} ($-CH_3$) 119.1 Hz). IR (cm^{-1}): 3100 vw, 3093 vw, 3060 w, 2955 vs, 2897 m, 1489 m, 1388 m, 1368 s, 1332 m, 1243 vs, 1198 s, 1102 vs, 1083 m, 899 vs, 835 vs (br), 798 s, 772 s, 750 vs, 693 s, 634 s, 612 m, 602 s, 374 s. MS [156.32] (*m/e*, ion, relative %): 141.00, $C_4H_3S^{28}Si(CH_3)_2^+$, 100.0; 156.00, $C_4H_3S^{28}Si(CH_3)_3^+$, 30.1; 43.00, $^{28}Si(CH_3)^+$, 11.6; 45.10, CHS^+, 10.0; 83.00, $C_4H_3S^+$, 6.8; 39.05, $C_3H_3^+$, 6.2; 73.05, $^{28}Si(CH_3)_3^+$, 5.4. UV: λ_{max} = 238 nm, log ϵ = 3.54. The ^{13}C NMR spectrum is in agreement with that reported in the literature.[27]

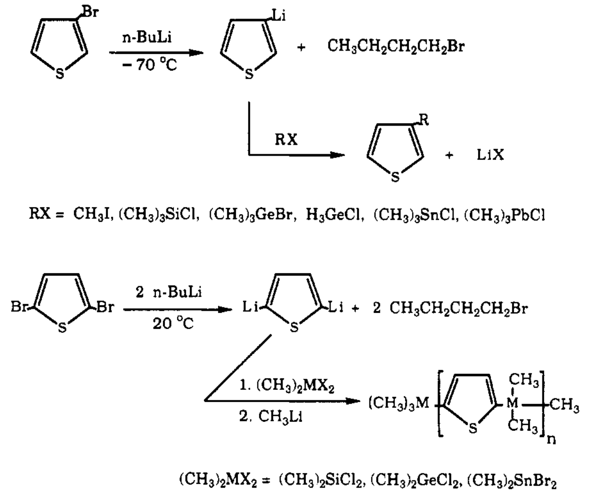
3-(Trimethylstannyl)thiophene. 3-Bromothiophene (2.3 mL, 25.1 mmol), *n*-butyllithium (12.5 mL, 25.0 mmol), and chlorotrimethylstannane ($(CH_3)_3SnCl$, 4.8975 g, 24.6 mmol) in 5 mL of tetrahydrofuran were allowed to react in anhydrous diethyl ether (20 mL) at −70 °C for 3 h. The product is a colorless liquid, d^{20} = 1.48 g cm^{-3}, yield 55% (2.779 g). ^1H NMR: (δ) 7.36 d, H_2; 7.18 dd, H_4; 7.46 dd, H_5; 0.30 s, $-CH_3$ (J_{2-5} 2.46 Hz; J_{4-5} 4.63 Hz). ^{13}C NMR: (δ) 131.33, C_2; 138.45, C_3; 131.67, C_4; 125.27, C_5; 9.01, $-CH_3$ (J_{C2-H2} 186.1 Hz; J_{C4-H4} 166.6 Hz; J_{C5-H5} 184.5 Hz; J_{C-H} ($-CH_3$), 128.9 Hz). IR (cm^{-1}): 3055 w, 2980 m, 2915 m, 1460 w, 1380 w, 1363 w, 1335 w, 1201 m, 1080 m, 842 s, 760 vs, 712 s, 690 s, 600 s, 588 s. MS [246.93] (*m/e*, ion, relative %): 232.90, $C_4H_3S^{120}Sn(CH_3)_2^+$, 100.0; 202.90, $C_4H_3S^{120}Sn^+$, 19.6; 217.90, $C_4H_3S^{120}Sn(CH_3)^+$, 13.7; 134.95, $^{120}Sn(CH_3)^+$, 8.8; 247.95, $C_4H_3S^{120}Sn(CH_3)_3^+$, 7.5; 119.95, free $^{120}Sn^+$, 6.2; 39.05, $C_3H_3^+$, 6.4; 45.05, CHS^+, 2.2. UV: λ_{max} = 207 nm, log ϵ = 3.66; λ_{max} = 235 nm, log ϵ = 3.69. The ^{13}C NMR spectrum is in agreement with that reported in the literature.[28]

2,5-Bis(trimethylsilyl)thiophene. 2,5-Dibromothiophene (0.5 mL, 4.4 mmol), *n*-butyllithium (4.4 mL, 8.8 mmol), and chlorotrimethylsilane ($(CH_3)_3SiCl$, 1.1 mL, 8.8 mmol) reacted in anhydrous diethyl ether (15 mL) at room temperature for 2 h. The product is a colorless liquid, d^{20} = 0.96 g cm^{-3}, yield 80% (1.2767 g). ^1H NMR: (δ) 7.31 s, $H_{3,4}$; 0.31 s, $-CH_3$. ^{13}C NMR: (δ) 135.04, $C_{3,4}$; 145.9, $C_{2,5}$; 0.07, $-CH_3$ ($J_{C3,4-H3,4}$ 164.1 Hz; J_{C-H} ($-CH_3$) 119.6 Hz). IR (cm^{-1}): 3060 w, 2965 s, 2900 m, 1487 m, 1403 m, 1305 w, 1255 s (sh), 1244 vs, 1201 s, 1077 w, 1063 w, 1007 vs, 978 m, 952 m, 834 vs, 803 vs, 753 vs, 693 s, 628 s, 600 s. MS [228.507] (*m/e*, ion, relative %): 213.00, $C_4H_3S^{28}Si_2(CH_3)_5^+$, 100.0; 228.00, $C_4H_3S^{28}Si_2(CH_3)_6^+$, 19.0; 198.00, $C_4H_3S^{28}Si_2(CH_3)_4^+$, 0.04; 183.00, $C_4H_3S^{28}Si_2(CH_3)_3^+$, 0.9; 138.90, $C_4H_3S^{28}Si_2^+$, 2.0; 73.10, $^{28}Si(CH_3)_3^+$, 28.5; 45.05, CHS^+, 13.4; 43.05, $^{28}Si(CH_3)^+$, 7.1; 39.05, $C_3H_3^+$, 1.0. UV: λ_{max} = 242 nm, log ϵ = 3.58.

Poly(2,5-(dimethylsilyl)thiophene). 2,5-Dibromothiophene (1.4 mL, 12.4 mmol), *n*-butyllithium (12.4 mL, 24.8 mmol), dichlorodimethylsilane ($(CH_3)_2SiCl_2$, 1.5 mL, 12.4 mmol), and methyllithium (1.8 mL, 2.5 mmol) were allowed to react in anhydrous diethyl ether (20 mL) at room temperature for 3 h. When precipitated from diethyl ether/methanol, the product appeared initially as a light green solid but was reprecipitated as a white solid from THF/methanol, yield 0.2139 g. ^1H NMR: (δ) 7.36 s, $H_{3,4}$; 0.62 s, $-CH_3$. ^{13}C NMR: (δ) 136.52, $C_{3,4}$; 143.89, $C_{2,5}$; 0.14, $-CH_3$ ($J_{C3,4-H3,4}$ 165.5 Hz; J_{CH-CH3} 119.0 Hz). IR (cm^{-1}): 3050 w, 2955 s, 2898 vw, 1485 s, 1405 m, 1380 w, 1267 vs, 1249 vs, 1200 vs, 1080 m, 1005 vs, 980 s, 800 vs (br), 740 s, 672 s, 522 s, 500 s, 415 w. UV: λ_{max} = 240 nm, ϵ = 16.3 L g-1 cm^{-1}.

Oxidation of Poly(2,5-(dimethylsilyl)thiophene), Poly(2,5-(dimethylgermyl)thiophene), and Poly(2,5′-(dimethylstannyl)thiophene). $NOBF_4$ (0.005 g) was added to the polymer (0.010 g) dissolved in CH_2Cl_2; the solutions immediately turned black. A portion of the solution was placed in a small vial, the solvent was evaporated, and the black film was removed with a spatula. The films were washed with deionized water several times and dried prior to taking measurements by EDAX. Sulfur/M (M = Si, Ge, Sn): 69/1, 43/1, 6/1.

Scheme I



RX = CH_3I, $(CH_3)_3SiCl$, $(CH_3)_3GeBr$, H_3GeCl, $(CH_3)_3SnCl$, $(CH_3)_3PbCl$

$(CH_3)_2MX_2$ = $(CH_3)_2SiCl_2$, $(CH_3)_2GeCl_2$, $(CH_3)_2SnBr_2$

Results and Discussion

Synthesis. The synthesis and characterization of thiophenes have been well documented over the past 50 years with the majority of research compiled in the monographs by Gronowitz[23,25] and by Hartough.[26] Gronowitz was the first to utilize the lithiation reaction of thiophene and bromothiophene as a pathway to prepare substituted thiophenes.[22] This led to the discovery of the temperature dependence of the lithiation of 3-bromothiophene where at room temperature the product is 2-lithiothiophene and at −70 °C, the product is 3-lithiothiophene. Once prepared, the lithiothiophenes have been found to be very useful in the synthesis of a great number of compounds by simple electrophilic displacement of the lithium (Scheme I).

Thiophenes with group IV substituents in the 2-position have been reported in the Russian literature and reviewed in 1982 by Lukevics et al.[17] The synthesis and partial characterization of 3-(trimethylsilyl)thiophene[19,27] and 3-(trimethylstannyl)thiophene[28] have been previously reported. Van Pham et al. have reported the synthesis of some 2,5-dibromothiophene derivatives which are 3-substituted with trimethylsilyl, trimethylgermyl, and trimethylstannyl groups.[29] Polymeric films of these monomers have been prepared by transition-metal-induced polymerization of the bis-Grignard compounds derived from the 2,5-dibromothiophene derivatives.[30] The poly-

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mers showed conductivities as high as 10^2 S cm^{-1}, apparently because of the presence of the transition metal since no redox behavior for the thiophene ring system was observed. Okano et al. recently reported free-standing conductive polymer films prepared from pyrrole that is N-substituted with methyl, trimethylsilyl, and trimethylgermyl groups.[31]

Thiophenes with group IV substituents in the 3-position were prepared by reaction of the appropriate halide with 3-lithiothiophene according to Scheme I. Gas chromatograms of crude product mixtures of the 3-substituted thiophenes in each case confirmed the presence of significant amounts of 1-bromobutane, varied amounts of unreacted 3-bromothiophene, and in some cases a very small amount of thiophene that occurred by hydrolysis of unreacted 3-lithiothiophene when the reactions were quenched. The presence of 1-bromobutane, 3-bromothiophene, and thiophene were confirmed in the ^{1}H NMR of the crude product mixtures. For each reaction, a lithium salt was isolated in the water extract as expected; the identity of the salt was confirmed by a lithium flame test and precipitation of the silver salt of the halide. These results are consistent with the proposed reaction in Scheme I.

Characterization. A collection of ^{1}H and ^{13}C NMR spectral data for 2- and 3-substituted thiophenes has been compiled by Gronowitz.[25] The ^{1}H chemical shifts of the ring hydrogen atoms are deshielded by the delocalized π-electrons of thiophene and characteristically appear near 7 ppm, with some variation noted that is dependent on the electron-releasing or electron-withdrawing nature of the substituent. The ring hydrogen atoms show three distinct resonances that are assigned by resolution of the H–H coupling constants. In general, the ^{13}C NMR spectra of 3-substituted thiophenes show a C_3 resonance of greatly diminished intensity which normally has the largest chemical shift relative to the other ring carbon atoms.

The ^{1}H NMR spectra of the polymers in which the thiophene units are linked by dimethylsilyl, dimethylgermyl, and dimethylstannyl groups show only two resonances, which are consistent with equivalent ring hydrogen atoms in the 3- and 4-positions of thiophene and with equivalent methyl groups on the linking group IV atom. The ^{13}C NMR spectra show two resonances associated with two equivalent pairs of ring carbon atoms and one resonance for the methyl carbon atoms attached to the linking atom.

The ^{1}H and ^{13}C chemical shifts for 2-(trimethylsilyl)thiophene, 2-(trimethylgermyl)thiophene, 2-(trimethylstannyl)thiophene, and 2-(trimethylplumbyl)thiophene have been reported[17] as well as the ^{13}C spectrum of 3-(trimethylsilyl)thiophene[27] and 3-(trimethylstannyl)thiophene.[28] The ^{1}H and ^{13}C NMR spectra for a polymer formed from thiophene linked by two dimethylsilyl groups, poly[2,5-bis(dimethylsilyl)thiophene], have also been reported.[18]

The vibrational spectra of thiophenes have been reviewed,[26] and the 3-substituted thiophenes have several regions of interest: C–H stretching frequencies (2800–3100 cm^{-1}), ring stretching frequencies (1200–1600 cm^{-1}), ring hydrogen in-plane deformation (1070–1098 cm^{-1}), a ring breathing frequency (850–900 cm^{-1}), ring hydrogen out-of-plane deformations (745–855 cm^{-1}), and in-plane ring deformations (590–605 cm^{-1}).[32,33] In addition, M–CH_3 bending (1225–1245 cm^{-1}) and rocking (815–840 cm^{-1}) modes for M = Si, Ge, and Sn have been reported.[34] As expected, these frequencies decrease with increasing mass of the group IV atom.

Ring C–H stretching frequencies for the substituted thiophenes reported here are in the range 3045–3105 cm^{-1}, with the methyl C–H stretching frequencies in the range 2800–2980 cm^{-1}. The Ge–H stretch for 3-germylthiophene appears strongly at 2075 cm^{-1} and is close to those observed for GeH_4 (2094 cm^{-1})[20] and GeH_3Cl (2108 cm^{-1}).[21] 3-Substituted thiophenes are characterized best by the out-of-plane C–H bending frequency which appears for the reported compounds in the range 740–770 cm^{-1}. This mode is absent for 2-substituted thiophenes. The IR spectra of the 2-trimethyl-substituted thiophenes of the group IV elements have been reported,[35] and the data we report are consistent with the known differences between 2- and 3-substituted thiophenes. The M–CH_3 bending mode appears in the range 1237–1247 cm^{-1} and is, of course, absent for 3-methylthiophene and 3-germylthiophene. The M–CH_3 rocking mode appears in nearly the same range as one of the C–H out-of-plane modes, 800–835 cm^{-1}, and in the case of 3-(trimethylsilyl)thiophene, these modes overlap and appear as one broad band. Poly(2,5-(dimethylsilyl)thiophene) and poly(2,5-(dimethylgermyl)thiophene) show two bands near 980 and 945 cm^{-1}. Both appear to be indicative of 2,5-disubstitution in thiophenes and are present at 983 and 948 cm^{-1} in 2,5-dibromothiophene[26] and 978 and 952 cm^{-1} in 2,5-bis(trimethylsilyl)thiophene. These bands occur at slightly lower frequencies (948, 920 cm^{-1}) for poly(2,5-(dimethylstannyl)thiophene).

Mass spectral data for thiophenes are available in the literature.[25,26] Substituted thiophenes under electron impact usually lose an atom or group that is β to the thiophene ring to form the most intense ion in their mass spectra. Other common ions are m/e = 45 (CHS^+), 39 ($C_3H_3^+$), and the ion $C_3H_2R^+$ (R = 3-substituent) which appear from carbon skeletal rearrangements of the thiophene ring. Hydrogen scrambling has been shown to be of minor importance in carbon skeletal rearrangement of thiophenes but can be important in the formation of $C_2H_2S^+$ (m/e = 58).[36] In the case of $(CH_3)_3M$-substituted thiophenes, ions such as $(CH_3)_nM^+$ (M = Si, Ge, Sn, Pb; n = 0–3) are also common.

The mass spectrum of 3-methylthiophene agrees with that reported by Hartough[26] and includes the parent peak ion, the parent peak ion minus one hydrogen atom as the most intense ion, and the ions at m/e = 45 and 39. The mass spectra of the thiophenes substituted with group IV elements other than carbon are complicated by the isotopic distribution of the group IV element but show distinctively the parent peak, with the parent peak minus one methyl group as the most intense ion, and the ions at m/e = 45 and 39. We report only the most abundant of the isotopic ions. The mass spectrum of 2-(trimethylsilyl)thiophene has been reported and is very similar to that observed for 3-(trimethylsilyl)thiophene.[37] The 100% peak for 3-germylthiophene appears unexpectedly at m/e = 54.15; an ion corresponding to this m/e value is $C_4H_6^+$, which is conceivably formed by migration of three hydrogen atoms from the germyl group to the thiophene ring as the mol-

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Table I. Electrochemical Data[a]

	E_a(mon)	$E°$(poly)	$E_{pa} - E_{pc}$	σ, S cm^{-1}
RH	1.86	0.83	0.60	0.8
RCH_3	1.78	0.96	0.09	77
RBr	1.94	1.25	0.23	
$RSi(CH_3)_3$	1.76	1.14	0.44	3.6
$RGe(CH_3)_3$	1.78	1.06	0.24	0.5
$RGeH_3$	1.76	0.93	0.24	0.05
$R'[Si(CH_3)_3]_2$	1.93	1.23	0.34	65
$[R'Si(CH_3)_2]_n$	2.07	1.13	0.15	2.1
$[R'Ge(CH_3)_2]_n$	2.12	0.92	0.12	9.2

[a] R = 3-thiophene; R′ = 2,4-thiophene.

ecule undergoes carbon skeletal rearrangement to cleave both the sulfur and germanium atoms.

Ultraviolet spectra for substituted thiophenes have been reported[25] in which the transitions between the MOs of the aromatic thiophene ring range from 208 to 329 nm with log ϵ from 1.75 to 4.40 depending on the substituent. A study of the UV spectra of thiophene and substituted thiophenes was compared with the results from CNDO/S calculations which indicated that there are two transitions in the UV region.[38] The first is the $\pi_4 \leftarrow \pi_3$ transition with wavelengths on the order of 250–275 nm, and the second transition is a combination of the $\pi_4 \leftarrow \pi_2$ and $\pi_5{}^* \leftarrow \pi_3$ transitions which appears in the range 220–250 nm. Only the most electronegative or electron-withdrawing substituents show the presence of both transitions, with the latter combined transition more prevalent and the only one that appears in most thiophenes reported here.

Hotta et al. have shown by GPC analysis that average molecular weights of soluble poly(3-alkylthiophenes) are about 2.5×10^5 with $n = 1500$.[39] The polymer films prepared here appeared to be insoluble in organic solvents and were stable in concentrated acids as were those previously reported.[5a] End-group analysis of the polymers bridged by group IV elements using ^{1}H NMR provided crude estimates of the molecular weights; comparison of the lower field peak intensities for the dimethyl bridging group with those for the slightly higher field trimethyl end groups gave values of 3800, 20000, and 5800 with n = 26, 105, and 24 for the silicon, germanium, and tin compounds, respectively. Chicart et al. obtained a molecular weight of approximately 4200 (n = 30) for the silicon compound by GPC analysis.[16]

Electrochemistry. The electrochemical properties of the 3-substituted thiophenes were characterized in terms of the oxidation potential of the monomer, the redox properties of the resulting polymer, and the conductivity of a free-standing polymer film. We have included data for thiophene, 3-methylthiophene, and 3-bromothiophene as models for comparison with the electrochemical data for the group IV substituted thiophenes (Table I).

On a scan to positive potential, each monomer solution showed a rapid increase in current and an irreversible oxidation wave characteristic of thiophenes under similar conditions (Figure 1a). To avoid overoxidation,[40] the potential was not allowed to increase to the point that an oxidation peak potential was observed; instead, we report an onset potential for the electropolymerization of each monomer, E_a(mon). The polymer-modified electrodes showed quasi-reversible to irreversible redox behavior in fresh electrolyte solutions as indicated by differences in the anodic and cathodic peak potentials (E_{pa}(poly) − E_{pc}(poly)) in excess of 0.060 V, and, although the contours of the redox waves made it difficult to measure i_p/i_c with confidence, it was clearly less than 1:1 (Figure 1b). Each polymer film exhibited electrochromic behavior, similar to that reported for poly(3-alkylthiophenes),[4,5,41] and changed from red in the reduced state to deep blue in the oxidized state, except polythiophene, which was yellow and blue. Colored solutions (blue near the anode, red near the cathode) were formed in the constant potential polymerization and suggest that either colored oligomers formed or the less likely possibility that the polymers are slightly soluble in nitrobenzene.[42] Each monomer yielded a free-standing film that was conductive. Our measured conductivities for poly(3-methylthiophene) (77 S cm^{-1}) and polythiophene (0.8 cm^{-1}) under the conditions reported here are a factor of about 10–100 times less than those reported for films obtained under optimum conditions [(poly(3-methylthiophene), 250–750 S cm^{-1};[4,9,41] polythiophene, 100 S cm^{-1};[9] poly(3-bromothiophene), 13.5 S cm^{-1})[43]]. The conductivities of the polymers formed from thiophenes substituted with group IV elements are comparable with that of our polythiophene rather than with that of poly(3-methylthiophene). The resultant polymer films for polythiophene and 3-methylthiophene were somewhat difficult to remove from the ITO electrodes while the polymer film obtained from 3-bromothiophene was brittle and could not be removed intact at all. Therefore, a conductivity determination was not possible in the latter case.

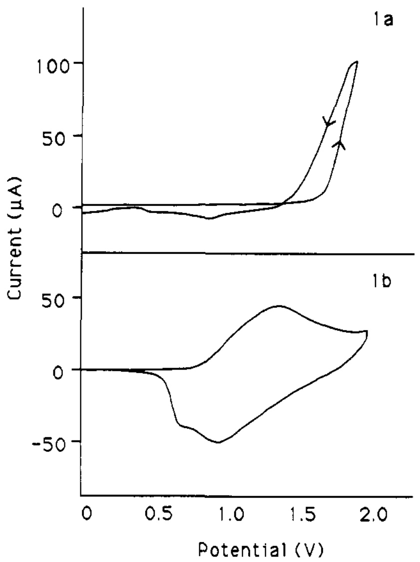

Figure 1. (a) First scan showing nucleation loop and reduction of polymer on Pt electorde for 3-(trimethylsilyl)thiophene (0.2 M) in 0.2 M $TBAPF_6$–nitrobenzene at 100 mV s^{-1}. (b) Oxidation and reduction of polymer formed from 3-(trimethylsilyl)thiophene on Pt electrode in 0.2 M $TBAPF_6$–nitrobenzene at 100 mV s^{-1}.

The onset potentials for thiophenes with group IV substituents in the 3-position are very close to each other but significantly lower than that observed for 3-bromothiophene. This suggests that the electronic effects of the group IV elements are similar, and the same oxidation process is occurring for each monomer. The lower potentials for 3-(trimethylsilyl)thiophene and 3-(trimethylgermyl)thiophene are consistent with the electron-releasing effects of the substituents,[10–14] and the similar potential

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observed for 3-germylthiophene indicates the absence of significant steric effects. No polymer was formed from 3-(trimethylstannyl)thiophene or 3-(trimethylplumbyl)thiophene. Waltman et al. have demonstrated a linear relationship between E_{pa} and the Hammett substituent constant for a number of 3-substituted thiophenes.[5] Their results indicated that the 3-substituted monomers were all oxidized by the same mechanism with little complication from steric effects.

Bredas and Street have discussed the nature of polaron and bipolaron charge states which give rise to optical spectra in oxidized conducting polymers.[44] Removal of an electron from the polymer chain upon oxidation, accompanied by lattice relaxation, generates polaron states in the band gap that result in three allowed transitions. Subsequent removal of electrons may lead to additional polarons, or, if pairing of charges is energetically favorable, bipolarons may be formed. Bipolaron states in the bandgap result in only two allowed transitions. For fully doped polymer films, bipolaron states have been shown to dominate over the polaron states.[44]

Tourillon has noted for polythiophene that the $\pi^* \leftarrow \pi$ bandgap transition is 2.2 eV for the neutral polymer and increases to 2.9 eV for the conducting polymer with a doping level of 25–30%.[45] However, Rughooputh et al. have shown that upon an increase in the doping level from neutral poly(3-hexylthiophene) to a doping level of 22%, the bandgap transition remains constant at about 2.8 eV.[46] The increase in doping level has generally been reported to decrease the intensity of the bandgap transition with a corresponding ingrowth of intensity of the two allowed bipolaron transitions at about 0.6 and 1.6 eV.[45–48] The visible spectra of polythiophene,[49] poly(3-methylthiophene),[50] and poly(3-bromothiophene)[43] have been shown to have absorption maxima near 480 nm for the neutral polymer which are absent or of low intensity for the oxidized, doped polymer. The visible spectra of these doped polymers also show an absorption band of moderate intensity beginning near 650 nm and extending into the infrared region with a maximum occurring between 750 and 800 nm corresponding to the highest energy bipolaron transition.

We observed similar spectral features in the visible spectra of polythiophenes prepared from thiophene, 3-methylthiophene, 3-bromothiophene, and 2,5-bis(trimethylsilyl)thiophene. In each case an absorption maximum was observed between 480 and 495 nm for the neutral polymer films. This absorption band was observed to be greatly reduced in intensity in the oxidized films, and a broad, weak absorption band was observed in each case beginning near 600 nm and extending to about 850 nm with maxima in the region of 670–700 nm. The absorption band in the spectrum of the neutral poly(3-bromothiophene) showed a shoulder at 580 nm similar to that already reported.[43] The spectral features of the polymer films prepared from 3-(trimethylsilyl)thiophene and 3-(trimethylgermyl)thiophene were found to be similar to the polythiophenes noted above. The presence of any silicon or germanium in the polymers prepared from 3-(trimethylsilyl)thiophene, 2,5-bis(trimethylsilyl)thiophene, and 3-(trimethylgermyl)thiophene did not lead to any apparent differences in the visible spectra of these polymers compared with the spectra of polythiophenes which did not contain silicon or germanium. We note that collection of each spectrum from as-grown films on the ITO glass electrodes resulted in the appearance of extraneous absorption bands in the 330–400-nm range even though a spectral baseline was recorded prior to obtaining each spectrum, and a piece of ITO glass was used as a reference. This is not unexpected, however, owing to the known absorption of UV radiation by glass in this spectral region.

Table II. EDAX Measurements

	S/P ratio	doping %	S/M ratio[a]
RH	4.3	19.0	NA[b]
RCH_3	4.1	19.6	NA[b]
RBr	5.5	15.5	1
$RSi(CH_3)_3$	2.3	30.7	27.4
$RGe(CH_3)_3$	2.1	32.7	5.4
$RGeH_3$	6.0	14.2	8.5
$R'[Si(CH_3)_3]_2$[c]	3.8	22.4	28.6
$[R'Si(CH_3)_2]_n$ solid[d]	NA	NA	1.4
$[R'Si(CH_3)_2]_n$ film	4.0	20.2	(M = 0)
$[R'Ge(CH_3)_2]_n$ solid	NA	NA	1.5
$[R'Ge(CH_3)_2]_n$ film	3.6	21.6	(M = 0)
$[R'Sn(CH_3)_2]_n$ solid	NA	NA	1.7

[a] M = Br, Si, Ge, Ge, Si, Si, Ge, and Sn respectively. [b] Not available without a windowless counter. [c] R = 3-thiophene; R′ = 2,5-thiophene. [d] "Solid" is the chemically prepared polymer; "film" is formed by electrooxidation of a solution of the solid.

EDAX Measurements. Because of the ease with which trimethylsilyl groups are cleaved[9] and the similarities in E_a(mon) for the thiophenes substituted with group IV elements and thiophene itself, it was essential to establish the presence (or absence) of the group IV element in the polymer. EDAX measurements (Table II) on the polymeric films revealed that much lower amounts of the group IV elements were incorporated in the films than would be predicted if the monomer retained its integrity during the process. The doping levels for these polymers, measured as phosphorus in PF_6^-, were quite variable, ranging from 14 to 33%. In contrast, polythiophene, poly(3-methylthiophene), and poly(3-bromothiophene) all showed phosphorus (PF_6^-) levels of 15–20%, indicating that there is a positive charge in the polymer for about every five thiophene units. The sulfur/bromine ratio for poly(3-bromothiophene) was 1 which suggests that the integrity of the 3-bromothiophene monomer was retained during the electropolymerization process in that case. The sulfur/phosphorus ratio for the neutral films after constant potential reduction was approximately 20 in each case indicating nearly complete undoping of the oxidized polymers.

All of these results are consistent with the formation of polymers which contain both thiophene and 3-substituted thiophene units probably linked in a random fashion. In addition, there is likely to be significant β-linking of the thiophene units which is known to reduce the mean conjugation length of the polymer and consequently the conductivity.

The known poly(2,5-(dimethylsilyl)thiophene)[16] and the new, solid compounds, poly(2,5-(dimethylgermyl)thiophene) and poly(2,5-(dimethylstannyl)thiophene) are nonconductive in the undoped state, but, when chemically oxidized with $NOBF_4$, they turn black as Chicart et al. observed earlier in the case of poly(2,5-(dimethylsilyl)thiophene).[16] However, EDAX measurements on the washed, black materials indicated that the amount of

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group IV element present had greatly diminished compared with that present before oxidation.

Since chemical oxidation apparently resulted in cleavage of the group IV element, it was anticipated that electrochemical oxidation would produce a similar outcome; this proved to be the case. The solid poly(2,5-(dimethylsilyl)thiophene, poly(2,5-(dimethylgermyl)thiophene and poly(2,5-(dimethylstannyl)thiophene) dissolved in $CHCl_3$ to give nonconductive solutions. With $TBAPF_6$ as supporting electrolyte, cyclic voltammetric scans to as high as 2.8 V failed to produce a film on a Pt electrode. However, in $TBAPF_6$/nitrobenzene, the polymers (except poly(2,5-(dimethylstannyl)thiophene)) underwent electrooxidation, showing a typical nucleation loop similar to that observed for monomeric thiophenes, which resulted in the formation of free-standing films that were easily removed from the ITO electrodes. The electrochemical data are shown in Table I. The electrochromic polymers are red in the reduced state and deep blue in the oxidized state with conductivities in the range of 2.1–9.2 S cm^{-1}. EDAX studies on the films show that there is no measurable Si or Ge present in the oxidized materials in contrast to the original polymers (Table II). These results indicate that the polymer is probably made up of thiophene units only; the measured sulfur/phosphorus ratios are consistent with a doping level of about 20%. On the basis of our experience with thiophenes substituted with groups containing group IV elements and the work of Lemaire et al.[9] in which 2,5-bis(trimethylsilyl)thiophene was used as a precursor for the formation of well-defined polythiophene, these results are not surprising and raise questions concerning the nature of the material prepared by chemical oxidation by $NOBF_4$.[16]

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Registry No. H_3GeCl, 13637-65-5; $(CH_3)_3PbCl$, 1520-78-1; $(CH_3)_3SiCl$, 75-77-4; 3-(trimethylgermyl)thiophene, 100099-21-6; 3-bromothiophene, 872-31-1; bromotrimethylgermane, 1066-37-1; 3-germylthiophene, 141930-56-5; 3-(trimethylplumbyl)thiophene, 141930-57-6; $((CH_3)_2GeCl_2)$(2,5-dibromothiophene) (copolymer), 141930-59-8; $((CH_3)_2GeCl_2)$(2,5-dibromothiophene) (SRU), 141930-65-6; $((CH_3)_2SnCl_2)$(2,5-dibromothiophene) (copolymer), 141930-60-1; $((CH_3)_2SnCl_2)$(2,5-dibromothiophene) (SRU), 141930-66-7; 3-methylthiophene, 616-44-4; iodomethane, 74-88-4; 3-(trimethylsilyl)thiophene, 18245-17-5; 3-(trimethylstannyl)thiophene, 70161-87-4; chlorotrimethylstannane, 1066-45-1; 2,5-bis(trimethylsilyl)thiophene, 17906-71-7; (2,5-dibromothiophene)$((CH_3)_2SiCl_2)$ (copolymer), 141930-61-2; (2,5-dibromothiophene)$((CH_3)_2SiCl_2)$ (SRU), 130904-62-0; thiophene, 110-02-1; thiophene (homopolymer), 25233-34-5; 3-bromothiophene (homopolymer), 84928-93-8; 3-methylthiophene (homopolymer), 84928-92-7; 3-trimethylsilylthiophene (homopolymer), 100099-19-2; 3-trimethylgermylthiophene (homopolymer), 141930-62-3; 3-germylthiophene (homopolymer), 141930-63-4; 2,5-bis(trimethylsilyl)thiophene (homopolymer), 141930-64-5.

Introduction of Functional Groups into Polymer Films via Deep-UV Photolysis or Electron-Beam Lithography: Modification of Polystyrene and Poly(3-octylthiophene) by a Functionalized Perfluorophenyl Azide

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A general method for the covalent attachment of functional groups to polymer films is described. The key step likely involves a C–H bond insertion reaction of a highly reactive nitrene intermediate derived from a functionalized perfluorophenyl azide (PFPA). The nitrene can be generated either by photolysis or during electron-beam lithography. Since a *N*-hydroxysuccinimide (NHS) active ester group is present elsewhere in the nitrene intermediate, this group also becomes attached covalently to the polymer and is capable of further reaction with a variety of reagents containing an amino group by way of amide formation. The methodology is illustrated by the following examples: Photolysis of a polystyrene (PS) or poly(3-octylthiophene) (P3OT) film containing 8–10 wt % of NHS-functionalized PFPA (**1**) resulted in the installment of the NHS groups into the polymers. Reaction of the NHS modified polymer films with amino azide **3** resulted in the introduction of azide groups into the polymers as determined by IR spectroscopy. Alternatively, electron-beam lithography of PS or P3OT films containing **1** resulted in both the introduction of NHS groups and the cross-linking of the polymers in a single step. Micron-size patterns incorporating the NHS functional groups could be produced. Treatment with amino fluorescein **7** resulted in the covalent attachment of fluorescent groups into the polymer structure.

Introduction

Functionalized polymers have been the subject of intensive research, owing to their wide application in chemistry and biology and in technologies involving ion-exchange resins, immobilized enzymes, and electrically conductive polymers.[1] Functionalized polymers can be prepared either by polymerization of functionalized monomers or by modification of polymers. Modification of polymer films or film surfaces with concomitant introduction of functional groups is important for the development of new

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