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Synthesis and Optical Properties of Group 14 Element–Thienyl Polymers

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The syntheses of several types of polymers containing silicon, germanium and tin in the main chain are described. Optical studies show that they exhibit absorption in the far-ultraviolet region of the spectrum (200–400 nm). Electrical studies show that these polymers behave as insulators. Preliminary studies indicate, that depending on the chemical structure of the backbone, it is possible to dope some of the polymers via partial oxidation in solution. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Although the electronic properties of main-chain polysilanes have previously been studied,[1–10] there is little or no information available regarding tin and germanium polymers in which the metal centres are connected by conjugated organic fragments.

Such polymers are of interest in optics due to their high transparency in the visible region and the possibility that d_π–p_π interaction may render them polarizable.[11] The studies conducted here aim to provide preliminary information regarding the electronic properties of polymers containing Group 14 elements in which there could be d_π–p_π conjugation along the polymer backbone. One of the aims of this study was to identify any possible element-dependent trends in these properties.

EXPERIMENTAL

General methods

All of the reactions were performed under a dry argon atmosphere using standard Schlenk techniques. The compounds were characterized by the usual analytical techniques and the following instruments: ^{1}H NMR, AC 80 Bruker; ^{13}C NMR, AC 200 Bruker; IR, Perkin-Elmer 1600 FT; mass spectra, Ribermag R 1010 (CI, CH_4) and HP 5989 A. Elemental analysis were done by the Centre de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse. The new Group 14 metal compounds and polymers obtained are listed in Fig. 1.

Preparation of 1a

To a solution of 2-thienylmagnesium bromide [prepared from 2-bromothiophene (5.80 g, 35.6 mmol) and magnesium (1.10 g, 45.5 mmol) in 40 ml of THF] was added Bu_2GeCl_2 (3.7 g, 14.3 mmol). The mixture was refluxed for 2 h, then hydrolysed. Extraction with petroleum ether followed by drying with Na_2SO_4 yielded **1a**: 4.87 g (96%); b.p. 93 °C/0.025 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.82–1.02 (m, 6H, CH_3); 1.18–1.55 (m, 12H, CH_2); 7.15–7.26 (m, 4H, C_4H_3S); 7.57–7.64 (m, 2H, C_4H_3S) ppm. ^{13}C NMR ($CDCl_3$): δ 13.70 (CH_3), 15.84 (CH_2CH_3), 26.22 and 27.09 (CH_2), 127.92, 130.34, 134.38; 136.24 (C_4H_3S). Mass spectrum: *m/z* (M^+) 354 (2),

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(M − Bu) 297 (67). Analysis: Calcd for $C_{16}H_{24}GeS_2$: C, 54.42; H, 6.85. Found: C, 54.14; H, 6.86%.

Preparation of 1b

Using the conditions described above (except that extraction was with CH_2Cl_2), 63 mmol of 2-bromothiophene and Ph_2GeCl_2 (7.2 g, 24 mmol) led, after sublimation (180 °C/ 0.02 mmHg) to **1b**: 8.95 g (95%); m.p. 166 °C. ^1H NMR ($CDCl_3$): δ 7.18–7.78 (m, C_6H_5,C_4H_3S). ^{13}C NMR ($CDCl_3$): δ 128.20, 131.66, 135.73, 136.39 (C_4H_3S); 128.48, 129.73, 133.85, 134.79 (C_6H_5). Mass spectrum: *m/z* (M^+) 394 (51), (M − C_6H_5) 317 (100). Analysis: Calcd for $C_{20}H_{16}GeS$: C, 61.11; H,4.10. Found: C, 60.58; H, 4.01%.

Preparation of 3a

BuLi (5.8 mmol) 1.6 M in hexane) was added dropwise to a solution of **1a** (0.82 g, 2.3 mmol) in 10 ml of THF. An exothermic reaction was observed. After 15 min at boiling solvent temperature, the mixture was cooled to − 10 °C. Me_3SiCl (0.76 ml, 6 mmol) was added. The mixture was warmed up to room temperature and stirred at 20 °C for 1 h. After concentration under vacuum, the residue was extracted with petroleum ether, and the resulting solution was concentrated and distilled leading to **3a**: 0.98 g

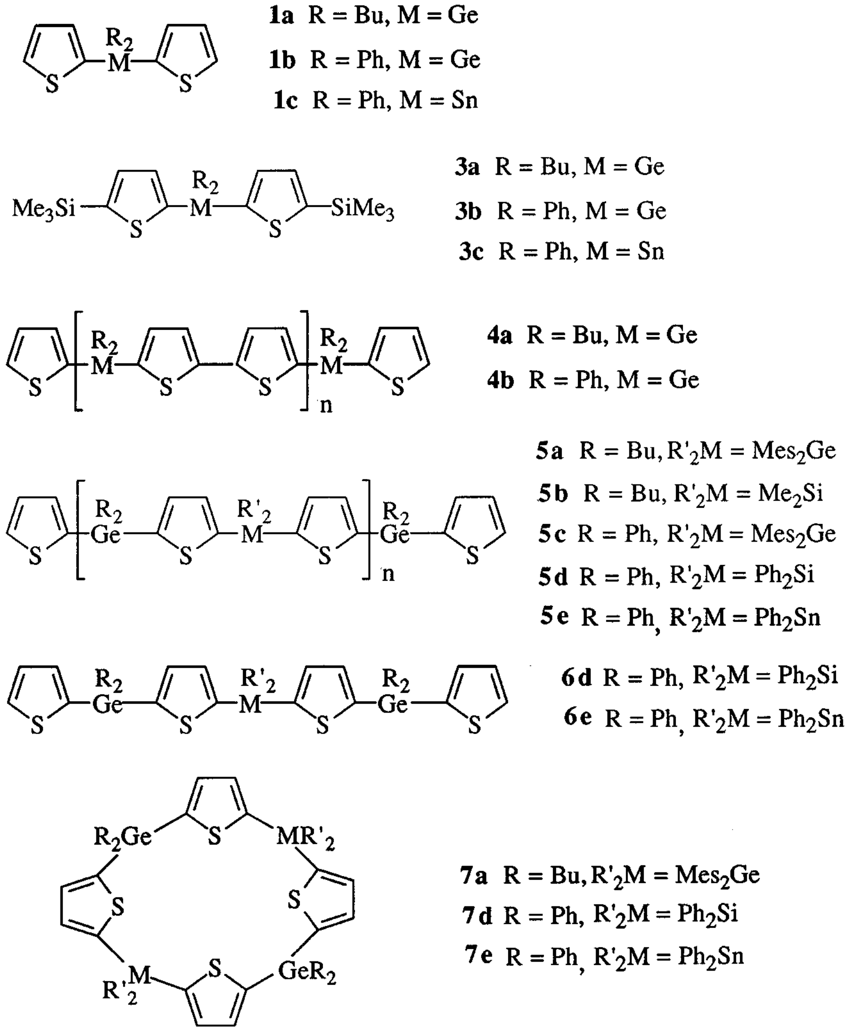


Figure 1 Group 14 element compounds and polymers. (Mes:mesityl)

(86%); b.p. 170 °C/0.03 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.38 (s, 18H, $SiMe_3$), 0.84–1.60 (m, 18H, Bu), 7.33 and 7.37 ppm (AB System, $J = 3.2$ Hz, 4H, C_4H_2S) ^{13}C NMR ($CDCl_3$): δ 0.21 ($SiMe_3$); 13.72 (CH_3); 16.06 ($\underline{C}H_2CH_3$), 26.30 and 27.13 (CH_2); 134.83, 135.42, 142.09, 145.65 (C_4H_2S). Mass spectrum: *m/z* (M^+) 498 (1), ($M-CH_3$) 483 (2), ($M-Bu$) 441 (18), ($M-2Bu$) 385 (14). Analysis: Calcd for $C_{22}H_{40}GeS_2Si_2$: C, 53.12; H, 8.10. Found: C, 53.92; H, 8.33%.

Preparation of 3b

A solution of BuLi (3 mmol) (1.6 M in hexane) was added to a solution of **1b** (0.52 g, 1.3 mmol) in 10 ml of THF. The mixture was warmed at reflux for 30 min, then cooled to −30 °C. Me_3SiCl (0.5 ml, 4 mmol) was then added. After 1 h at 20 °C and concentration, the residue was extracted with CH_2Cl_2. After concentration, pentane was added. After filtration upon silica gel, the pentane solution was partially concentrated and then cooled to −30 °C leading to the formation of white crystals of **3b** which were isolated after filtration and drying: 0.63 g (93%); m.p. 96–102 °C. ^{1}H NMR ($CDCl_3$): δ 0.33 (s, 18H, $SiMe_3$), 7.34–7.68 (m, 14H, C_6H_5 et C_4H_2S). ^{13}C NMR ($CDCl_3$) δ 0.17 ($SiCH_3$); 128.38, 129.56, 134.82, 136.14 (C_6H_5); 134.93, 137.26, 139.38, 147.14 (C_4H_2S). Mass spectrum: *m/z* (M+) 538 (20), ($M-CH_3$) 523 (10), ($M-C_6H_5$) 461 (38). Analysis: Calcd for $C_{26}H_{32}GeS_2Si_2$: C, 58.10; H, 6.00. Found: C, 58.10; H, 5.99%.

Preparation of 3c

To a solution of **1c** (0.20 g, 0.46 mmol) in 10 ml of THF and 2 ml of TMEDA (tetramethylethylenediamine) was added t-BuLi (1.14 mmol) 1.7 M in pentane) at −95 °C. The mixture was stirred for 45 min, warmed up to −60 °C and treated with Me_3SiCl (0.2 ml, 1.6 mmol). The mixture was warmed up to room temperature and refluxed for 5 min. After concentration, the residue was extracted with pentane and filtered on silica gel. Recrystallization from pentane–isopropyl alcohol led to white crystals of **3c**: 0.23 g (85%); m.p. 78 °C. ^{1}H NMR ($CDCl_3$): δ 0.40 (s, 18H, $SiMe_3$), 7.35–7.80 (m, 14H, C_6H_5 and C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 0.33 ($SiMe_3$); 128.95, 129.59, 136.98, 137.48 (C_6H_5Sn); 135.20, 137.58, 138.49, 147.95 (C_4H_2S). Mass spectrum: *m/z* (M+) 584 (2), ($M-CH_3$) 569 (2), ($M-SiMe_3$) 511 (3), ($M-C_6H_5$) 507 (15). Analysis: Calcd for $C_{26}H_{32}S_2Si_2Sn$:C, 53.51; H, 5.52. Found: C, 53.01; H, 4.80%.

Preparation of 4a

Two procedures have been used.

(a) To a solution of **2a** (2.18 mmol) (see above) was added $CuCl_2$ (0.88 g, 6.5 mmol) at −60 °C. The mixture was slowly warmed to room temperature (1.5 h). After 30 min at 20 °C, followed by concentration under vacuum, the residue was extracted with pentane (5 × 50 ml). The brown solution was then filtered on silica gel, concentrated under vacuum and gave **4a** as a dark yellow oil: 0.30 g (39%). ^{1}H NMR ($CDCl_3$): δ 0.63–1.65 (m, 18H, nBu), 7.19 and 7.33, 7.20 and 7.32 (AB System, $J = 3.46$ Hz, 4H, C_4H_2S), 7.63 (dd, $J = 2.4$ Hz, $J = 1.6$ Hz, 2H, terminal C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 13.46 (CH_3), 15.61 (CH_2Ge), 26.30 and 27.15 (CH_2), 125.02, 135.42, 135.81, 142.62 (C_4H_2S); 126.06, 130.54, 134.55, 136.14 (terminal C_4H_3S). Analysis: Calcd for $C_{16}H_{22}GeS_2$: C, 54.74; H, 6.31. Found: C, 54.38; H, 6.55%.

(b) A mixture of **2a** (2.6 mmol) and $CuCl_2$ (1.06 g, 7.9 mmol) (prepared as above) was stirred for 12 h at 20 °C. After concentration under vaccum, the residue was extracted with petroleum ether, then filtered on silica gel. Extraction with CH_2Cl_2 gave **4a** as a brown oil: 0.45 g (48%). ^{1}H NMR ($CDCl_3$): δ 0.63–1.69 (m, 18H, nBu); 7.16 and 7.29 (AB system, $J = 3.5$ Hz, 4H), 7.63 (dd, $J = 2.4$ Hz, $J = 1.6$ Hz, 2H, terminal C_4H_3S).

These two procedures led to the same polymer **4a** but these products have different molecular weights (cf. Table 1).

Preparation of 4b

A mixture of **2b** (1.97 mmol) (see above) and $CuCl_2$ (0.54 g, 4 mmol) was stirred for 2 h at 20 °C, then refluxed for 30 min. After hydrolysis (4 M HCl) and extraction with THF, the ethereal phase was washed with a saturated solution of NH_4Cl and dried with Na_2SO_4. After concentration, the residue was recrystallized from a mixture of THF–MeOH leading to the formation of a brown powder which was isolated after filtration and drying, i.e. **4b**: 0.30 g (39%); m.p. 95–105 °C. ^{1}H NMR ($CDCl_3$): δ 6.70–7.90 (m,

Table 1. Molecular weights of the polymers **4a** and **4b** determined experimentally

Compound	Yield (%)	Reaction time (h)	M_n	M_w	M_{calc}[a]	I[b]
4a (yellow oil)	39%	2 h	836	3526	4209	4.2
4a (brown oil)	48%	20 h	763	6218	5962	8.1
4b (brown solid)	39%	2h30	484	2574	—	5.3

[a] M_{calc}, molecular weight calculated from ^{1}H NMR spectra.
[b] I, polydispersity (M_w/M_n).

14H, C_6H_5, C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 128.61, 129.87, 134.77, 135.12 (C_6H_5); 125.39, 133.56, 137.30, 143.54 (C_4H_2S). Analysis: Calcd for $C_{20}H_{14}S_2Ge$: C, 61.53, H, 3.60. Found: C, 60.20; H, 3.53%.

Reaction of 2a with Mes_2GeCl_2

To a solution of **2a** (2.29 mmol) (see above) was added Mes_2GeCl_2 (0.87 g, 2.29 mmol). The reaction was exothermic. The mixture was stirred for 12 h at 20°C, then refluxed for 1 h. After concentration, the residue was extracted with 30 ml of pentane, filtered on silica gel and concentrated. The viscous yellow oil was dissolved in a mixture of CH_2Cl_2–iPrOH and then concentrated. The semi-solid was treated with 10 ml of pentane and filtered, resulting in a white powder identified as **7a**: 0.14 g (9%); m.p. 107–110 °C. ^{1}H NMR ($CDCl_3$): δ 0.75–1.50 (m, 36H, nBu); 2.08 (s, 24H, *o*-CH_3); 2.24 (s, 12H, *p*-CH_3); 6.75 (s, 8H, C_6H_2); 7.16 and 7.33 (AB system, $J=3.3$ Hz, 8H, C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 13.76 (CH_3); 15.96 (CH_2CH_3); 21.06 (*p*-CH_3); 24.89 (*o*-CH_3); 26.08 and 27.16 (CH_2); 129.40, 135.39, 138.51, 143.58 (C_6H_2); 134.81, 137.41, 143.09, 145.97 (C_4H_2S). Mass spectrum: (CI, CH_4) (M+1) 1325 (55); (M−Bu) 1267 (25); (M−Mes) 1205 (48). Analysis: Calcd for $C_{68}H_{88}Ge_4S_4$: C, 61.68; H, 6.69. Found: C, 60.51; H, 6.73%.

The last filtrate was concentrated leading to a light-yellow viscous oil, **5a**: 1.25 g (74%). ^{1}H NMR ($CDCl_3$): δ 0.80–1.85 (m, 18H, nBu); 2.24 (s, 12H, *o*-CH_3); 2.35 (s, 6H, *p*-CH_3); 6.69 (s, 4H, C_6H_2); 7.22–7.38 (m, 4H, C_4H_2S); 7.50–7.90 (m, 2H, terminal C_4H_2S). ^{13}C NMR ($CDCl_3$); δ 13.90 (CH_3); 16.10 ($\underline{C}H_2CH_3$); 21.19 (*p*-CH_3); 24.89 (*o*-CH_3); 26.23 and 27.31 (CH_2); 129.56, 135.50, 138.62, 143.67 (C_6H_2); 134.95, 137.55, 143.19, 146.16 (C_4H_2S).

Reaction of 2a with Me_2SiCl_2

To a solution of **2a** (2.12 mmol) (see above) was added Me_2SiCl_2 (0.25 ml, 2.12 mmol) at 0 °C. The mixture was stirred at 20 °C for 1 h, then treated with MeLi (1.1 mmol) (1.5 M in ether). After stirring for 30 min and concentration, the mixture was extracted with petroleum ether, filtered on silica gel and concentrated, leading to a colourless viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.64 (s, 6H, CH_3Si); 0.80–1.50 (m, 18H, nBu); 7.29 and 7.39 (AB System, $J=3.2$ Hz, 4H, C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 0.34 ($SiCH_3$); 13.71 (CH_3); 16.00 (CH_2CH_3); 26.23 and 27.08 (CH_2); 135.53, 136.28, 142.98 (C_4H_2S).

Another procedure, without the use of MeLi, was also performed: Me_2SiCl_2 (0.24 ml, 1.98 mmol) was added to a solution of **2a** (4.55 mmol) at −10 °C. The mixture was slowly warmed to 20 °C (30 min), then refluxed for 30 min. Using the same procedure as described above, 0.73 g (90%) of a colourless oil was isolated. The ^{13}C NMR analysis shows the presence of residual **1a**. Further treatments by a mixture of pentane–iPrOH did not eliminate **1a** completely. The polymer **5b** is always obtained with traces (5–10%) of **1a**. **5a**: ^{1}H NMR ($CDCl_3$): δ 0.65 (s, 6H, CH_3Si); 0.85–1.45 (m, 18H, nBu); 7.25–7.42 (m, 4H, C_4H_2S), 7.60 (m, 2H, terminal C_4H_3S).

Reaction of 2b with Mes_2GeCl_2

To a solution of **2b** (1.52 mmol) (see above) was added Mes_2GeCl_2 (0.58 g, 1.52 mmol) at −30 °C. The mixture was warmed up to 20 °C, stirred for 12 h at 20 °C and refluxed for 2 h. After hydrolysis, extraction with CH_2Cl_2, drying on $CaCl_2$ and concentration under vacuum, the residue was extracted with CH_2Cl_2 and filtered on silica gel. After concentration, recrystallization of the residue from a THF–CH_3OH mixture led to a white solid identified as **5c**: 0.74 g

(70%); m.p. 152–163 °C. ^{1}H NMR ($CDCl_3$): δ 2.07 (sl, 12H, *o*-CH_3); 2.22 (sl, 6H, *p*-CH_3); 6.73 (sl, 4H, C_6H_2); 7.24–7.52 (m, 12H, C_6H_5, C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 21.06 (*p*-CH_3); 24.93 (*o*-CH_3); 129.47, 134.96, 138.65, 143.57 (C_6H_2); 128.29, 129.47, 134.74, 136.05 (C_6H_5); 136.82, 137.49, 140.03, 147.62 (C_4H_2S). Analysis: Calcd for $C_{38}H_{36}Ge_2S_2$: C, 65.01; H, 5.17. Found: C, 66.02; H, 5.31%.

Reaction of 2b with Ph_2SiCl_2

To a solution of **2b** (1.35 mmol) (see above) was added, at − 60 °C, Ph_2SiCl_2 (0.32 g, 1.26 mmol). After stirring for 12 h at 20 °C, a yellow powder precipitated which was isolated after hydrolysis by filtration. **5d**: 0.45 g (59%); m.p. 235–248 °C, insoluble in the usual solvents. Analysis: Calcd for $C_{32}H_{24}GeS_2Si$: C, 67.04; H, 4.22. Found: C, 66.58; H, 4.19%.

The filtrate was concentrated; the residue was extracted with 150 ml of CH_2Cl_2. This solution was filtered on silica gel, then concentrated. Recrystallization with toluene led to a white powder (0.18 g). After washing with $CHCl_3$, 0.13 g of a white solid was obtained. Analysis by mass spectroscopy shows the predominant formation of **6d** (17%): (M+) *m/z* 966 (CI, CH_4). The $CHCl_3$ solution was then concentrated. The residue was analysed showing the presence of macrocycle **7d** (7%) and traces of **6d**. **7d** ^{1}H NMR ($CDCl_3$): δ 7.35–7.70 (m, C_6H_5, C_4H_2S). ^{13}C NMR: δ (ppm) 128.04, 130.16, 135.63, 139.95 (C_6H_5Si); 128.49, 129.72, 134.03, 134.82 (C_6H_5Ge); 137.57, 139.43, 140.45, 142.03 (C_4H_2S). Mass spectrum (CI, CH_4) (M+1) 1147 (23); (M − C_6H_5) 1069 (46).

Reaction of 2b with Ph_2SnCl_2

A solution of Ph_2SnCl_2 (0.62 g, 1.8 mmol) in 5 ml of THF was added to a solution of **2b** (1.9 mmol) (see above) at − 60 °C. After stirring for 20 h at 20 °C, hydrolysis, extraction with THF, drying on Na_2SO_4 and concentration, the residue was recrystallized with a mixture of THF–iPrOH leading to **5e**: 0.53 g (44%); m.p. 330 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 6.95–7.75 (m, C_6H_5, C_4H_2S), 7.85–8.10 (m, 2H, terminal C_4H_2S). ^{13}C NMR ($CDCl_3$): δ 128.44, 129.65, 134.82, 133.90 (C_6H_5Ge); 128.44, 128.87, 136.89, 137.17 (C_6H_5Sn); 136.89, 137.73, 139.06, 141.56 (C_4H_2S). Analysis: Calcd for $C_{32}H_{24}GeS_2Sn$: C, 57.89 H, 3.64. Found: C, 57.59; H, 3.63%. Analysis by mass spectroscopy (CI, CH_4) of the concentrated filtrate shows the formation of **6e**: (M+1) 1057, (M − Ph) 979; as well as **7e**: (M+1) 1329, (M − Ph) 1251.

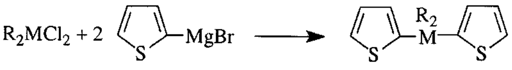
RESULTS AND DISCUSSION

Synthesis of poly(organometal$_{14}$)thiophene

Many polymers containing a regular alternating arrangement of organosilicon groups and π-electron systems (e.g. phenylene,[6–10] diethynylene[12–14] and thienylene[15,16]) have been prepared.

Only a few thiophene derivatives with germanium groups in the 2-position[17] and 3-position[18] have been reported. More recently a poly(2,5-dimethylgermyl)thiophene has been isolated[19] with a low yield. We report here the synthesis and characterization of a new variety of polymer in which thiophene units are linked through the 2- and 5-positions with Group 14 organometallic groups (M = Si, Ge, Sn).

The dithienyl diorganogermanes **1a** and **1b** or stannane[20] **1c** were prepared by reaction of the appropriate organometallic halide with 2-thienylmagnesium bromide (cf. Eqn [1]).

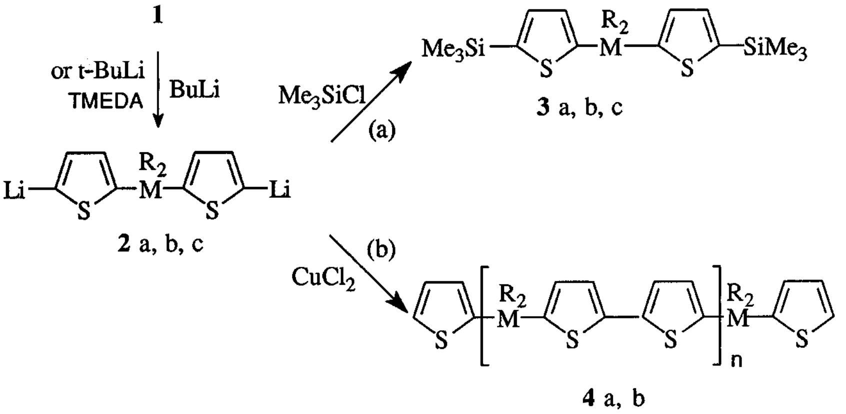


1a, b, c

Reaction of **1a** and **1b** with two equivalents of nBuLi at ambient temperature in THF gave the dimetallated derivatives **2a** and **2b** respectively. Dilithiation of the organostannane **1c** only occurs with tBuLi in a TMEDA–THF mixture (Scheme 1).

Silylation of **2** with Me_3SiCl then afforded the disilylated derivatives **3** with high yield and regioselectivity: only metallation in the α-position of the thienyl groups was observed. All these new metallated thiophene compounds have been isolated and characterized by ^{1}H and ^{13}C NMR and by mass spectroscopy (cf. the Experimental section).

Polymeric chains **4** have been prepared by oxidative polymerization of the lithiated compounds **2a** and **2b** with $CuCl_2$ at low temperature [Scheme 1, route (b)]. These compounds **4** are stable materials (a yellow or brown viscous oil for **4a**, or a coloured solid for **4b**), soluble in common organic solvents such as THF, chlorinated and aromatic solvents but insoluble in



Scheme 1

alcohols. Their molecular weights were determined by gel permeation chromatography (GPC) in THF by UV detection using polystyrene standards for calibration and are listed in Table 1.

These first results show that the degree of polycondensation depends on the nature of the substituents around the germanium centre and the time of reaction. The highest molecular mass was obtained with alkyl (butyl) substituents (**4a**) when the reaction was performed during 20 h. In all cases, we have the alternating sequence of one diorganogermyl and two thiophene units in the main chain.

The ^{1}H NMR spectra show an AB system or a multiplet which is consistent with non-equivalent ring hydrogen atoms in the 3- and 4-positions (3′ and 4′ respectively) of the dithiophene. The ^{13}C NMR spectra confirm these results, showing also two different resonances for the C_3 and C_4 (C'_3 and C'_4 respectively) atoms of dithiophene and for the two quaternary carbons in the 2- and 5- (2′- and 5′- respectively) positions.

In the proton NMR spectra of **4a** we also observed the presence of terminal thiophene groups which permitted us to calculate approximately the molecular weights of these polymers. The calculated values were close to those obtained by GPC (cf. Table 1).

The reaction of **2c** with $CuCl_2$ led to an oxidative coupling and to a cleavage of the thiophenic tin bond. In this case, mass spectra and ^{13}C NMR spectra of the crude deep-coloured product show a mixture of oligo- and polythiophenes with some inserted diphenylstannylene units.

The dilithiated compounds **2** also react with organometallic dihalide R'_2MCl_2 (M = Si, Ge, Sn) leading to a mixture of linear and cyclic polymer chains (cf. Scheme 2).

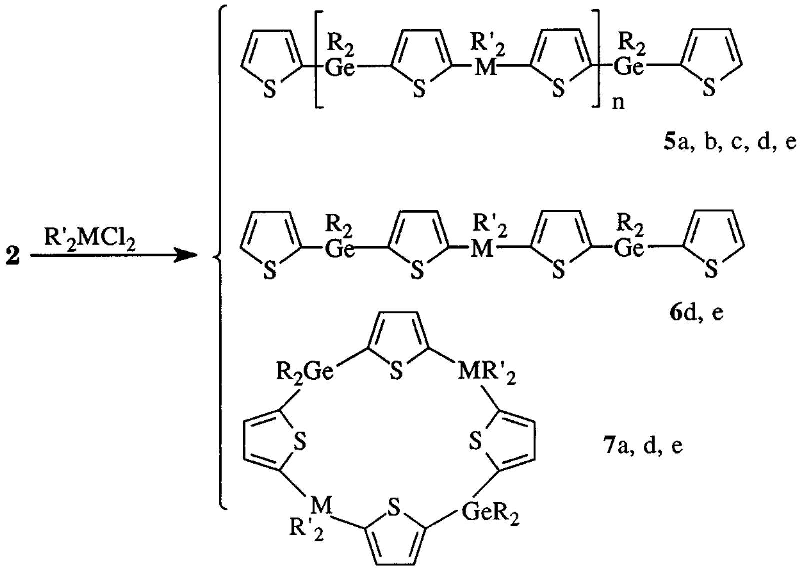
The synthesis results for copolymers **5, 6** and **7** are listed in Table 2. In these reactions, we generally observe the preponderant formation of linear polymer **5** with a terminal thiophene unit. These compounds are soluble in organic solvents (only **5c** was insoluble). The molecular weights (cf. Table 3) were determined to be $M_w = 2893$ for **5a**, 5809 for **5b** and 1063 for **5e**. This last small value can be explained by the presence of large tin atoms in the chain. Phenyl groups around the metal$_{14}$ centre also induce sufficient stabilization to allow the formation of short linear chains **6e** and **6d** identified by mass spectroscopy.

However, more steric hindrance around the germanium atom is necessary to form stable macrocycles **7**. When R′ = mesityl, we could isolate a new germa-calixarene **7a**, but the macrocycles **7d** and **7e** could only be detected in low yields.

Electronic spectra and electrical properties of the polymers

The UV/visible absorption spectra of solutions of the **4** and **5** family of polymers were recorded in THF. The spectral features are summarized in Table 4.

Clearly polymers **4a** and **4b** exhibit slightly lower-energy optical gaps than polymers **5a, 5c** and **5e**. This observation agrees with Kunai *et al.*,[21] who stated that when the metals in such polymers are separated by longer conjugated segments, the optical gap decreases. This is thought to be due primarily to an increased degree of π-character within the thiophene rings when the number of connected rings increases.



Scheme 2

Table 2. Synthesis results of the copolymerization reactions

Reagents	Products and yields
2a/Mes_2GeCl_2	**5a** 74%; **7a** 9%
2a/Me_2SiCl_2	**5b** 56%
2b/Mes_2GeCl_2	**5c** 70%
2b/Ph_2SiCl_2	**5d** 59%; **6d** 17%; **7d** 7%
2b/Ph_2SnCl_2	**5e** 44%; **6e** and **7e** (traces)

Table 3. Molecular weights of polymetallated polymers **5b**

Polymer	M_n	M_w	I
5a	1161	2893	2.5
5b	1496	5809	3.9
5e	559	1063	1.9

Table 4. Physical properties of polymeric chains

Sample	Conductivity (S cm^{-1})	λ_{max}(nm)	Solvent
4a	$<10^{-13}$	328	Tetrahydrofuran (THF)
4b	8.6×10^{-14}	322	THF
5a	$<10^{-13}$	248	THF
5c	1.0×10^{-14}	248	THF
5d	3.0×10^{-15}		Not soluble
5e	4.1×10^{-15}	248	THF

Comparison of λ_{max} for **4a** and **4b** reveals that there is a marginal influence on the optical gap from the polymer side groups. It appears that the less electron-withdrawing butyl side groups employed in **4a** give rise to a slightly smaller optical gap than **4b**, where more electron-withdrawing phenyl groups are present.

There appears to be little difference in the electronic properties of polymers containing germanium atoms (**5a** and **5c**) and those containing a regular alternation of germanium and tin (**5e**). This tends to suggest that there is little or no electronic interaction between the metal centres in these polymers.

Pressed pellets of the polymers included in Table 4 were tested for electrical conductivity using a standard two-point probe technique. In all cases, the polymers were found to be insulating in accordance with studies performed previously on similar silicon-containing polymers.[14,21] Interestingly, the previous studies found that oxidative ‘doping’ dramatically increased the conductivity in a similar manner to the doping of conjugated organic polymers.

Preliminary doping studies

In order to study the effect of oxidation on the optical properties of the polymers, toluene solutions of the polymers included in Table 4 were treated with varying amounts of nitrosonium

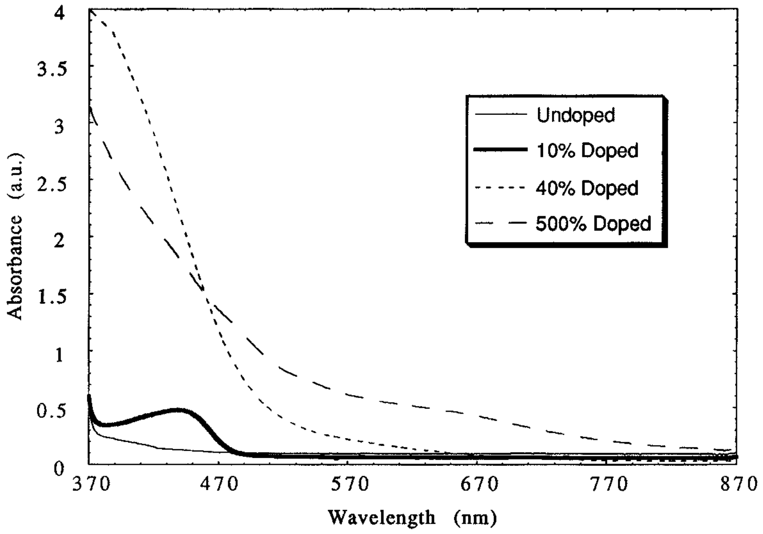


Figure 2 Visible spectrum for different doping levels in **4b**.

tetrafluoroborate. It was found that only polymers **4a** and **4b** were readily oxidized, while the others either did not react at all or reacted far more slowly.

Treatment of practically colourless solutions of **4a** and **4b** with a less than quantitative amount of $NOBF_4$ gave rise to an orange coloration and the evolution of gas (presumably nitrous oxide). Figure 2 shows the dependence of the degree of doping on the optical spectrum for solutions of **4b** in toluene.

At low doping levels, a small peak centred at around 450 nm was observed. As the degree of doping increased, so the intensity of this peak increased up to a limit (*ca* 40%), above which the peak diminished in intensity and a weak, ill-defined shoulder appeared at around 630 nm. This behaviour is somewhat similar to that observed for solution doping of conjugated organic polymers[22] and is thought to arise from formation of intra-gap polaron states at low doping levels which are replaced by bipolaron states as the level of doping increases. Further studies of the dependence of doping level on electrical properties are currently in progress and will serve to characterize further the nature of the states formed by doping.

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REFERENCES

1. P. Chicart, R. J. P. Corriu, J. M. Moreau, F. Garnier and A. Yasser, *Chem. Mater.* **3**, 8 (1991).
2. G. Magnani, A. Krâme, G. Pucetti, I. Ledoux, G. Soula, J. Zyss and R. Meyrueix, *Organometallics* **9**, 2460 (1990).
3. M. Ishikawa, *Pure Appl. Chem.* **63**, 851 (1991).
4. K. S. Wong, S. G. Han, Z. V. Vardeny, J. Shinar, Y. Pang, S. Ijadi Maghshoodi, T. J. Barton, S. Grigoras and B. Parbhoo, *Appl. Phys. Lett.* **58**, 1695 (1991).
5. J. Ohshita, D. Kanaya, M. Ishikawa, T. Kocke and T. Yamanaka, *Macromolecules* **24**, 2106 (1991).
6. S. Yajima, *Am. Ceram. Soc. Bull.* **62**, 893 (1983).
7. M. Zeldin, K. J. Wynne, and H. K. Allcock (eds), *Inorganic and Organometallics Polymers: Macromolecules Containing Silicon, Phosphorous and Other Inorganic Elements,* ACS Symposium Series No. 360, American Chemical Society Washington, DC, 1988.
8. J. M. Zeigler and F. W. G. Fearon (eds), *Silicon-based Polymer Science,* Advances in Chemistry Series No. 224, American Chemical Society, Washington, DC, 1990.
9. R. West, *J. Organomet. Chem.* **300**, 327 (1986).
10. D. Seyferth, *Actual. Chim. Fr.* 71 (1986).
11. F. Kazjar, J. Messier and C. Rosilio, *J. Appl. Phys.* **60**, 3040 (1986).
12. M. Ishikawa, Y. Hasegawa, A. Kunai and T. Yamanaka, *J. Organomet. Chem.* **381**, C57 (1990).
13. S. Ijadi-Maghshoodi and T. J. Barton, *Macromolecules* **23**, 4485 (1990).
14. J. L. Breford, R. J. P. Corriu, P. Gerbier, C. Guerin, B. Henner, A. Jean, T. Kuhlmann, F. Garnier and A. Yasser, *Organometallics* **11**, 2500 (1992).
15. S. Hu and W. P. Weber, *Polym. Bull.* **21**, 133 (1989).

16. J. Ohshita, D. Kanaya, M. Ishikawa, T. Koike and T. Yamanaka, *Macromolecules* **24**, 2106 (1991).
17. E. Lukevics, A. E. Skorova and O. A. Pudova, *Sulfur Rep.* **2**, 177 (1982).
18. C. Van Pham, R. S. Macomber, H. B. Mark and H. Zimmer, *J. Org. Chem.* **49**, 5250 (1984).
19. S. K. Ritter and R. E. Noftle, *Chem. Mater.* **4**, 872 (1992).
20. H. E. Ramsden (Metal et Thermit. Corp.) British Patent 825 039 (9 Dec. 1959).
21. A. Kunai, M. Takafumi, H. Katsuhiro, E. Toyoda, I. Nagamoto, J. Oshita, M. Ishikawa and K. Tanaka, *Organometallics* **15**, 2000 (1996).
22. T. Sommer, Diplome Arbeit, Karlsruhe University, Germany (1994).