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Synthesis, Characterization, and Properties of High Molecular Weight Poly(ferrocenylgermanes) and Poly(ferrocenylsilane)−Poly(ferrocenylgermane) Random Copolymers

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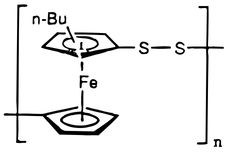
ABSTRACT: A series of high molecular weight poly(ferrocenylgermanes) $[Fe(\eta\text{-}C_5H_3X)_2GeR_2]_n$ **5a**−**d** (X = H; **a**, R = Me; **b**, R = Et; **c**, R = *n*-Bu; **d**, R = Ph) and **7** (X = $SiMe_3$, R = Me) were synthesized via the thermal ring-opening polymerization of the corresponding germanium-bridged [1]ferrocenophanes **4a**−**d** and **6**. Poly(ferrocenyldimethylsilane)−poly(ferrocenyldimethylgermane) random copolymer **8** was obtained by the thermal and transition metal-catalyzed ring-opening polymerization of a mixture of the [1]germaferrocenophane $[Fe(\eta\text{-}C_5H_4)_2GeMe_2]$ (**4a**) and the corresponding [1]silaferrocenophane $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]$ (**2a**). The molecular weights for the homo- and copolymers were estimated by gel permeation chromatography in THF versus polystyrene standards and were found to be in the range of $M_w = 5.0 \times 10^4−2.0 \times 10^6$ and with polydispersities in the range of $M_w/M_n = 1.2−2.4$. A low-angle laser light scattering study of **5a** in THF gave an absolute value of M_w of 3.3×10^6, which was significantly greater than the GPC estimate ($M_w = 8.2 \times 10^5$). Polymer thermal transition behavior and morphology were investigated by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). Glass transitions (T_g) for the polymers were in the range of −7 to +128 °C and were found to be strongly dependent on the size and nature of the substituents attached to germanium and the substitution of the cyclopentadienyl rings. The semicrystalline nature of the poly(ferrocenyldialkylgermanes) **5a**−**c** and the copolymer **8** was apparent from the appearance of several fairly sharp diffraction peaks in the WAXS profiles of these polymers and the presence of melt transitions (T_m) in the DSC thermograms. In contrast, polymers **5d** and **7** were found to be amorphous. Cyclic voltammetry of the polymers showed the presence of two oxidation waves, which is consistent with the presence of redox coupling arising from significant interactions between the iron centers. UV/visible spectra of polymers **5a**−**c**, **7**, and **8** were measured in THF in the 350−800 nm range and were found to be consistent with an essentially localized electronic structure for the polymer backbone.

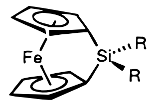
Introduction

High molecular weight transition metal-based polymers have received considerable recent attention.[1−5] These materials are expected to possess a range of attractive and useful attributes such as high thermal stability, tunable redox characteristics, and possibly novel magnetic and charge transport properties which are often difficult or impossible to achieve with organic polymers.

In 1992, ring-opening polymerization (ROP) was first reported as a method for successfully obtaining high molecular weight polymers with ferrocene in the main chain. A novel atom abstraction route was used by Rauchfuss et al.[3,6] to prepare poly(ferrocenylpersulfides) **1** from trithia[3]ferrocenophanes, while we described the use of thermal ring-opening polymerization (TROP) of strained, ring-tilted silicon-bridged [1]ferrocenophanes **2** to obtain high molecular weight, poly(ferrocenylsilanes) **3**.[7]

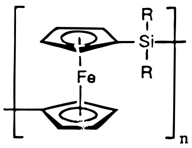


1



2

a (R = Me)
b (R = Et)
c (R = n-Bu)
d (R = Ph)
e (R = n-Hex)



3

a (R = Me)
b (R = Et)
c (R = n-Bu)
d (R = Ph)
e (R = n-Hex)

We have since employed a similar TROP methodology to prepare high molecular weight polymers from other strained [1]- and [2]ferrocenophanes.[8−14] In addition, random copolymers are accessible via thermal copolymerization of **2a** with different silicon-bridged ferrocenophane monomers, with the cyclotetrasilane $[SiMePh]_4$, or with silicon-bridged bis(arene)chromium complexes ([1]silachromarenophanes).[15−17] We also found that living ROP of silicon-bridged [1]ferrocenophanes can also be achieved in solution at room temperature in the presence of anionic initiators.[18,19] This has provided access to poly(ferrocenylsilanes) with controlled molecular weights as well as block copolymers.[19] More recently, we reported the ROP of [1]silaferrocenophanes in solution at room temperature using transition metal catalysts.[20]

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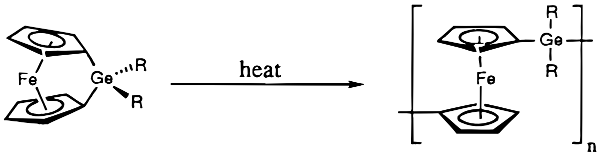
As part of our efforts to extend the scope of the ROP route to poly(metallocenes), we previously reported the synthesis of a series of germanium-bridged [1]ferrocenophanes **4a**,**b**,**d** and their thermal ROP to yield poly(ferrocenylgermanes) **5a**,**b**,**d**.[8,9] In this paper as a follow-up to this work and our brief previous reports[21] of the electrochemistry and thermal transition behavior of these poly(ferrocenylgermanes), we report the full details of our studies of the properties of these and some other related new materials.



4

a (R = Me)
b (R = Et)
c (R = *n*-Bu)
d (R = Ph)

5

a (R = Me)
b (R = Et)
c (R = *n*-Bu)
d (R = Ph)

Experimental Section

Materials. Ferrocene, 1.6 M butylithium in hexanes, and tetramethylethylenediamine (tmeda) were purchased from Aldrich. Dimethyldichlorogermane, diethyldichlorogermane, di(*n*-butyl)dichlorogermane, diphenyldichlorogermane, and trimethylchlorogermane were purchased from Gelest and were distilled prior to use. The synthesis of dilithio-1,1′-bis-(trimethylsilyl)ferrocene·tmeda was reported elsewhere.[11,22,23] Compounds **10b**, **10c**, and **11** were synthesized using modifications of literature procedures.[22]

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the polymers for which manipulations were carried out in air. Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves. Spectra (200 or 400 MHz ^{1}H NMR and 50.3 or 100.5 MHz ^{13}C NMR) were recorded either on a Varian Gemini 200 or Varian Unity 400 spectrometer. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in either an electron impact (EI) or fast atom bombardment (FAB) mode. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Model 510 HPLC pump, a Model U6K injector, Ultrastyragel columns with pore sizes of 10^3−10^5 Å, and a differential refractometer. A flow rate of 1.0 mL/min was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards purchased from American Polymer Standards were used for calibration purposes. Retention time (min)/M_w/PDI: 11.89/1.75 × 10^6/1.06, 12.06/6.00 × 10^5/1.10, 12.78/2.00 × 10^5/1.06, 13.54/1.11 × 10^5/1.06, 14.19/6.30 × 10^4/1.03, 15.55/2.00 × 10^4/1.10, 16.72/9.00 × 10^3/1.04, 17.6/4.00 × 10^3/1.10, and 19.24/1.00 × 10^3/1.10. Static light scattering experiments were carried out by utilizing the low-angle laser light scattering (LALLS) technique, using a Chromatix KMX-6 instrument at a wavelength of 632.8 nm, and a scattering angle of 6−7°. Measurements were carried out at room temperature (23 °C) using a metal cell 4.93 mm in length. Each solution was filtered twice through a Gelman Science arcodisk filter with a 0.2 μm average pore size before injection into the sample cell. The value of the refractive index increment, d*n*/d*c*, of the polymer solutions was obtained by using a Chromatix KMX-16 differential refractometer operating at a wavelength of 632.8 nm. The instrument was calibrated with NaCl solutions.

Glass transition temperatures and melting points were obtained with an E. I. DuPont 910 differential scanning calorimeter operating at a heating rate of 10 °C/min under N_2. UV/visible spectra were recorded in anhydrous THF on a Hewlett-Packard 6452A diode array instrument using a 1 cm cell. Elemental analyses were performed by either Canadian Microanalytical Services, Delta, BC, Canada or Quantitative Technologies Inc., Whitehouse, NJ.

Electrochemical experiments were carried out using a PAR Model 273 potentiostat with a Pt working electrode, a W secondary electrode, and an Ag wire reference electrode in a Luggin capillary. Polymer solutions were 5×10^{-3} M in CH_2Cl_2 with 0.1 M [Bu_4N][PF_6] as a supporting electrolyte. Peak currents were found to be proportional to the square root of the scan rate over the range studied (25−1000 mV/s^{-1}), which indicated that charge transfer is similar to a semiinfinite linear diffusion process.

Powder X-ray diffraction studies were perfomed by Dr. Srebri Petrov from the Powder X-ray Diffraction Service at the University of Toronto. Powder diffraction data were obtained on a Siemens D5000 diffractometer using Ni-filtered Cu Kα (λ = 1.541 78 Å) radiation. The sample were scanned at step widths of 0.02° with 1.0 s per step in the range of 3−40° 2θ. Samples were prepared by spreading the finely ground polymer on grooved glass slides.

Synthesis of [1]Di(*n*-butyl)germaferrocenophane (4c). To dilithioferrocene·tmeda (1.00 g, 3.62 mmol) in ether (100 mL) at −78 °C was added neat *n*-Bu_2GeCl_2 (1.22 g, 5.62 mmol). The reaction mixture was slowly allowed to warm to −10 °C over 3 h. The solvent was then removed while the temperature was maintained at −10 °C. Residual tmeda was then removed under vacuum (25 °C, 0.005 mmHg). LiCl was removed by dissolution of the product in hexanes and filtration through a frit. The product was then recrystallized from hexanes to yield orange-red crystals: yield 0.41 g (31%).

For monomer **4c**: Fe(η-C_5H_4)$_2$Ge(*n*-Bu)$_2$ orange-red crystals; ^{13}C NMR (C_6D_6) δ 76.8 (Cp), 76.4 (Cp), 30.0 (GeCp$_{\mathrm{ipso}}$), 27.3 ($CH_2CH_2CH_2CH_3$), 26.4 ($CH_2CH_2CH_2CH_3$), 14.0 ($CH_2CH_2CH_2$-CH_3), 13.5 ($CH_2CH_2CH_2CH_3$) ppm; ^{1}H NMR (C_6D_6) δ 4.41 (pseudo tr, 4 H, Cp), 4.11 (pseudo tr, 4 H, Cp), 1.60 (t, 4 H, $CH_2CH_2CH_2CH_3$), 1.27 (m, 8 H, $CH_2CH_2CH_2CH_3$), 0.87 (t, 6 H, $CH_2CH_2CH_2CH_3$) ppm; MS (EI, 70 eV) *m/z* (%) 372 (63, M$^+$), 315 (21, M$^+$ − C_4H_9), 259 (100, M$^+$ − C_4H_9 − C_4H_8).

Characterization Data for the Poly(ferrocenylgermanes) 5a,b,d. The synthesis and characterization of **4a**,**b**,**d** and the corresponding polymers **5a**,**b**,**d** were reported previously.[9] The NMR characterization data for **5a** are repeated here for comparison purposes with respect to the copolymer **8**. The molecular weight data for the polymer samples studied in this work are also given. The molecular weights of the polymers formed in the thermal polymerization reactions were found to vary slightly from experiment to experiment as reported previously for **4a**.[8,9] In general, the molecular weights were higher with higher purity monomer and the polymerization times were found to be dependent on the temperature used.

For polymer **5a**: [Fe(η-C_5H_4)$_2$GeMe$_2$]$_n$, yellow fibrous powder; ^{13}C NMR (in C_6D_6) δ 74.6 (Cp$_{\mathrm{ipso}}$), 72.9 (Cp), 71.0 (Cp), −1.1 ppm (GeMe$_2$); ^{1}H NMR (in C_6D_6) δ 4.25 (pseudo tr, $^{3}J_{HH}$ = 1.6 Hz, 4 H, Cp), 4.11 (pseudo tr, $^{3}J_{HH}$ = 1.6 Hz, 4 H, Cp), 0.64 (s, 6 H, GeMe$_2$) ppm; GPC, sample for light scattering study M_w = 8.2 × 10^5, M_n = 2.9 × 10^5 polydispersity (M_w/M_n) = 2.8, sample for all other studies M_w = 2.0 × 10^6, M_n = 8.5 × 10^5 polydispersity (M_w/M_n) = 2.4; LALLS M_w = 3.3 × 10^6; WAXS *d* = 6.58 Å.

For polymer **5b**: [Fe(η-C_5H_4)$_2$GeEt$_2$]$_n$, yellow fibrous powder; GPC M_w = 1.0 × 10^6, M_n = 8.1 × 10^5 polydispersity (M_w/M_n) = 1.2; WAXS *d* = 6.68 Å.

For polymer **5d**: [Fe(η-C_5H_4)$_2$GePh$_2$]$_n$, yellow powder; GPC M_w = 1.0 × 10^6; M_n = 8.2 × 10^5 polydispersity (M_w/M_n) = 1.2; WAXS *d* = 8.11, 4.72, 3.10 Å.

Synthesis of the Poly(ferrocenyldi(n-butyl)germane) 5c. A sample of **4c** (0.50 g, 1.32 mmol) was sealed in an evacuated, Pyrex tube and heated at 180 °C for 2 h. The polymer was then dissolved in THF and precipitated by dropwise addition to methanol: yield 0.27 g (54%).

For polymer **5c**: [Fe(η-C_5H_4)$_2$Ge(*n*-Bu$_2$)]$_n$, yellow fibrous powder; ^{13}C NMR (in C_6D_6) δ 73.6 (GeCp$_{\mathrm{ipso}}$), 73.4 (Cp), 71.2

(Cp), 28.3 ($CH_2CH_2CH_2CH_3$), 27.1 ($CH_2CH_2CH_2CH_3$), 15.5 ($CH_2CH_2CH_2CH_3$), 14.2 ($CH_2CH_2CH_2CH_3$); ^{1}H NMR (in C_6D_6) δ 4.36 (s br, 4 H, Cp), 4.21 (s br, 4 H, Cp), 1.71 (m br, 4 H, $CH_2CH_2CH_2CH_3$), 1.54 (m br, 4 H, $CH_2CH_2CH_2CH_3$), 1.35 (m br, 4 H, $CH_2CH_2CH_2CH_3$), 1.05 (m br, 6 H, $CH_2CH_2CH_2CH_3$) ppm. Anal. Calcd: C, 58.30; H, 7.07. Found: C, 57.75; H, 7.15. GPC $M_w = 5.0 \times 10^4$, $M_n = 3.5 \times 10^4$ polydispersity (M_w/M_n) = 1.4; WAXS d = 10.94, 8.33, 6.29, 4.90, 2.83 Å.

Synthesis of the Trimethylsilylated [1]Germaferrocenophane 6 and the Isolation of the Poly(ferrocenylgermane) 7. Freshly distilled Me_2GeCl_2 (0.94 mL, 8.1 mmol) was added dropwise to a stirred solution of dilithio-1,1′-bis(trimethylsilyl)ferrocene·tmeda (3.69 g, 8.1 mmol) in 300 mL of hexanes at −78 °C. The product was filtered to remove LiCl and then purified by vacuum distillation (150 °C, 0.05 mmHg). Yield of **6** after distillation 1.20 g (35%). The distillation residue was dissolved in THF and filtered. The filtrate was then precipitated dropwise into methanol to yield **7** (1.82 g, 53%).

For monomer **6**: $Fe(\eta\text{-}C_5H_3SiMe_3)_2GeMe_2$, red liquid; ^{29}Si NMR ($CDCl_3$) δ −4.1 (s, $SiMe_3$, 2 Si) ppm; ^{13}C NMR ($CDCl_3$) δ 81.9 (Cp, $CSiMe_3$), 81.8 (η-C_5H_3), 80.3 (η-C_5H_3), 77.2 (η-C_5H_3), 33.4 (Cp CGe), 0.13 ($SiMe_3$), −2.9 ($-GeMe_2$) ppm; ^{1}H NMR ($CDCl_3$) δ 4.3 (two ps q, 4 H, Cp), 4.0 (ps tr, 2 H, Cp), 0.71 (s, 6 H, $GeMe_2$), 0.21 (s, 18 H, $SiMe_3$) ppm; MS (EI, 70 eV) m/z (%) 432 (100, M^+), 417 (38, $M^+ - CH_3$), 403 (12, $M^+ - CH_3, - CH_2$).

For polymer **7**: $[Fe(\eta\text{-}C_5H_3SiMe_3)_2GeMe_2]_n$, red-orange powder; ^{29}Si NMR (C_6D_6) δ −2.6 (br s, $SiMe_3$, 2 Si) ppm; ^{13}C NMR (C_6D_6) δ 78.1 (br s, Cp), 77.9 (br s, Cp), 75.3 (br s, Cp), 74.9 (br s, Cp), 74.3 (Cp), 1.1 ($GeMe_2$), 0.8 ($SiMe_3$) ppm; ^{1}H NMR (C_6D_6) δ 4.03 (br s, 2 H, Cp), 3.95 (br s, 2 H, Cp), 3.47 (s, 2 H, Cp), 0.75 (br s, 6 H, $GeMe_2$), 0.17 (br s, 18 H, $SiMe_3$) ppm. Anal. Calcd: C, 50.0; H, 6.99. Found: C, 50.7; H, 6.91. GPC $M_w = 5.8 \times 10^4$, $M_n = 2.7 \times 10^4$, polydispersity (M_w/M_n) = 2.1; WAXS d = 9.55 Å.

Low-Angle Laser Light Scattering Measurements for 5a. Static light scattering experiments in the low-angle regime were used to determine the weight-average molecular weight M_w of a sample of **5a**. The values of M_w were obtained from the Rayleigh−Debye relationship, in the limit of low scattering angles, θ:[24]

$$Kc/R_\theta = 1/M_w + 2A_2c \qquad (1)$$

where c is the concentration of the polymer, R_θ is the measured Rayleigh ratio, A_2 is the second virial coefficient, and K is an optical constant defined as

$$K = [4\pi^2n^2/(N_0\lambda_0^{\ 4})](dn/dc)^2 \qquad (2)$$

where n is the refractive index of the solvent, λ_0 is the wavelength of the laser light in vacuum, N_0 is the Avogadro number, and dn/dc is the refractive index increment of the polymer solution. Refractive index increment measurements were performed at five different concentrations in THF at 23 °C and a value of dn/dc = (0.1674 ± 0.0001) mL/g was obtained.

Transition Metal-Catalyzed Polymerization of 4a. To a C_6D_6 solution of **4a** (0.10 g, 0.35 mmol) was added 0.05 equiv of $PtCl_2$. The solution was allowed to stir over 4 h at 25 °C by which time the polymerization was judged to be >90% complete by ^{1}H NMR. The solvent was removed under high vacuum. The polymer was redissolved in THF and precipitated into hexanes: yield 0.092 g (92%). The ^{1}H NMR data were consistent with the assigned structure:[9] GPC $M_w = 3.2 \times 10^5$, $M_n = 1.4 \times 10^5$ polydispersity (M_w/M_n) = 2.3.

Synthesis of the Copolymer 8. (a) By Thermal Copolymerization of 4a and 2a. A 1:2 mole ratio of the two solid monomers **4a** (0.14 g, 0.49 mmol, mp 90 °C) and **2a** (R = Me) (0.28 g, 1.17 mmol, mp 78 °C) was sealed in an evacuated, Pyrex tube and heated at 90 °C for 10 min. The contents of the tube were then dissolved in THF, filtered, and precipitated dropwise into hexanes to yield **8**: yield 0.35 g (83%); GPC monomodal, $M_w = 3.2 \times 10^5$, $M_n = 2.1 \times 10^5$ polydispersity (M_w/M_n) = 1.5.

(b) By Transition Metal-Catalyzed Copolymerization of 4a and 2a. To a C_6D_6 solution of **2a** (46 mg, 0.19 mmol) and **4a** (50 mg, 0.17 mmol) in a 5 mm NMR tube was added 0.05 equiv of $PtCl_2$. The contents of the tube were shaken, and ^{1}H NMR spectra were taken every 30 min over a period of 3 h. The polymerization at this point was found to be 69% complete. After a total of 10 h, the reaction was found to be >90% complete. All ^{1}H NMR spectra were consistent with literature values for the presence of only **2a**, **4a**, and **8**, and the rates of depletion of **2a** and **4a** were found to be the same within the limits of ^{1}H NMR integration.[9,25] The solvent was removed under high vacuum. The polymer was then redissolved in THF and precipitated into hexanes: yield 0.085 g (89%); GPC monomodal, $M_w = 3.6 \times 10^5$, $M_n = 1.2 \times 10^5$ polydispersity (M_w/M_n) = 3.0.

The characterization data for **8** formed by thermal ROP and by transition metal-catalyzed ROP showed the copolymers to be identical except for a higher proportion of $SiMe_2$ groups in the thermally generated copolymer due to the composition of the monomer mixture.

For copolymer **8**: yellow fibrous powder; ^{29}Si NMR (C_6D_6) δ −6.38, −6.40, −6.41 ($SiMe_2$) ppm; ^{13}C NMR (in C_6D_6) δ 74.59, 74.57, 74.53, 74.50 ($GeCp_{ipso}$), 73.64, 73.59 (SiCp), 72.93, 72.87 (GeCp), 71.86, 71.84, 71.80 ($SiCp_{ipso}$), 71.77, 71.61 (SiCp), 71.18, 71.01 (GeCp), −0.42, −0.44, −0.47 ($SiMe_2$), −1.09, −1.11, −1.13 ($GeMe_2$) ppm; ^{1}H NMR (in C_6D_6) δ 4.26 (s, 4 H, Cp), 4.10 (s, 4 H, Cp), 0.64 (s, 6 H, $GeMe_2$), 0.55 (s, 6H, $SiMe_2$) ppm; MS of hexanes soluble extract of the product formed by the TROP of **2a** and **4a**. m/z <1300 (%) 1152 (33, Ge_4), 1060 (17, Si_2Ge_2), 818 (17, $SiGe_2$), 576 (33, Ge_2), 484 (100, Si_2). Pyrolysis-mass spectrometry (in situ) (errors of up to 2 m/z are likely above m/z 1000) m/z 1720 (Ge_6), 1674 ($SiGe_5$), 1584 (Si_3Ge_3), 1542 (Si_4Ge_2), 1496 (Si_5Ge), 1432 (Ge_5), 1388 ($SiGe_4$), 1343 (Si_2Ge_3), 1299 (Si_3Ge_2), 1255 (Si_4Ge), 1209 (Si_5), 1145 (Ge_4), 1101 ($SiGe_3$), 1057 (Si_2Ge_2), 1013 (Si_3Ge), 967 (Si_4), 859 (Ge_3), 815 ($SiGe_2$), 771 (Si_2Ge), 725 (Si_3), 573 (Ge_2), 483 (Si_2), 287 (Ge), 242 (Si). Note Si = $\{Fe(\eta\text{-}C_5H_4)_2SiMe_2\}$ and Ge = $\{Fe(\eta\text{-}C_5H_4)_2GeMe_2\}$; WAXS d = 6.37 Å.

Synthesis of the Model Compound 10c. Freshly distilled Me_3GeCl (1.0 mL, 8.2 mmol) was added to a suspension of dilithioferrocene·tmeda (1.00 g, 3.2 mmol) in ether (100 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stir overnight. The solvent was removed under high vacuum. The product was dissolved in hexanes and filtered through a frit. The hexanes were removed under high vacuum, and any residual ferrocene or tmeda was removed by leaving the product under high vacuum overnight. The product was purified by vacuum distillation (0.005 mmHg, 83 °C): yield 0.84 g (63%). For **10c**: ^{13}C NMR (C_6D_6) δ 74.8 ($GeCp_{ipso}$), 72.4 (Cp), 70.7 (Cp), −0.7 ($GeMe_3$) ppm; ^{1}H NMR (C_6D_6) δ 4.20 (m, 4 H, Cp), 4.01 (m, 4 H, Cp), 0.35 (s, 18 H, $GeMe_3$) ppm; low-resolution MS (EI, 70 eV) m/z (%) 420 (100, M^+), 405 (30, $M^+ - CH_3$); 288 (68, $M^+ - GeMe_3, -$ Me); high-resolution MS $C_{16}H_{26}{}^{74}Ge_2{}^{56}Fe$ calcd 421.9822, found 421.9807.

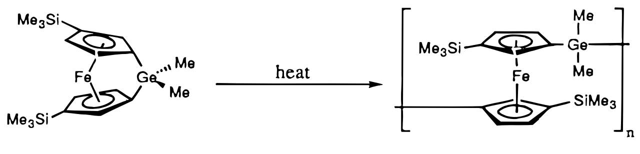
Results and Discussion

Synthesis and Characterization of the Germanium-Bridged [1]Ferrocenophanes 4c and 6. The synthesis and structural characterization of monomers **4a**, **4b**, and **4d** and their respective polymers **5a**, **5b**, and **5d** have been reported previously.[8,9] The preparation of these monomers was achieved using the method previously described by Osborne and co-workers.[26] The germanium-bridged [1]ferrocenophane **4c** was similarly prepared by the reaction of n-Bu_2GeCl_2 and dilithioferrocene·tmeda in Et_2O at −78 °C. The product was isolated as orange-red, moisture-sensitive crystals.

The synthesis of 3,3′-bis(trimethylsilyl)-1,1′-dimethyl-[1]germaferrocenophane (**6**) was accomplished by using a modification[23] of the method outlined by Silver and co-workers to prepare regio- and stereospecifically substituted bis(trimethylsilyl)ferrocenes.[22] First, dilithio-1,1′-bis(trimethylsilyl)ferrocene·tmeda was prepared by addition of 2 equiv of Me_3SiCl at −78 °C to dilithioferrocene·tmeda in Et_2O followed by metalation of the isolated 1,1′-bis(trimethylsilyl)ferrocene with 2 equiv of BuLi and 2 equiv of tmeda. Addition of Me_2GeCl_2 to dilithio-1,1′-bis(trimethylsilyl)ferrocene·tmeda in hexanes at −78 °C and subsequent warming to room temperature resulted in the formation of **6** which was isolated as a dark red liquid by vacuum distillation.

Characterization of the monomers **4c** and **6** was achieved by ^1H and ^{13}C NMR spectroscopy, and by mass spectrometry, which provided data consistent with the assigned structures. As has been found with other silicon- and germanium-bridged [1]ferrocenophanes, the cyclopentadienyl bridging C_{ipso} signals were shifted significantly upfield by ∼30−40 ppm compared to the other Cp carbons, which resonated at ∼76−82 ppm. This is indicative of significant strain and distortion from a planar geometry at the cyclopentadienyl ipso carbon attached to the bridge in these molecules. In the case of **4c**, there was also a relatively large separation (∼0.4 ppm) between the ^1H NMR signals for the cyclopentadienyl protons α and β in comparison to unbridged, substituted ferrocenes in which separations of ∼0.2 ppm are found. The ^1H NMR spectrum of **6** revealed two pseudoquartets and a pseudotriplet in the cyclopentadienyl region, characteristic of an $A_2B_2C_2$ spin system. A similar pattern was observed with the analogous silicon-bridged [1]ferrocenophane.[23]

Synthesis and Characterization of the Poly(ferrocenylgermanes) 5c and 7. Polymer **5c** was obtained by heating **4c** at 180 °C for 2 h in a sealed, evacuated Pyrex tube. The polymer was purified by dissolution in THF and precipitation into methanol, and was then dried under high vacuum to give a yellow fibrous material. The temperature required for this ROP was significantly higher than was found for the ROP of either **4a** or **4b** (90 °C) but less than that of **4d** (230 °C). Polymer **7** was obtained from the distillation residue of **6** and was purified in a manner similar to **5c**. The polymers were found to be of high molecular weight with $M_w = 5.0 \times 10^4$ ($M_w/M_n = 1.4$) for **5c** and 5.8×10^4 ($M_w/M_n = 2.1$) for **7** by GPC in THF using polystyrene standards. ^1H and ^{13}C NMR and elemental analysis data were consistent with the assigned structures. In the case of **5c**, the downfield position of the Cp C_{ipso} ^{13}C NMR resonance (73.6 ppm) relative to that for the monomer (33.0 ppm) illustrates the relief of strain on ring opening these germanium-bridged [1]ferrocenophanes. Similar changes in the chemical shift have been found for the Cp C_{ipso} resonances in the analogous silicon compounds.[25,28] For **7**, the ^{13}C NMR spectrum showed five broad peaks in the cyclopentadienyl region and these could not be specifically assigned. The ^1H NMR spectra also showed two broad peaks in the cyclopentadienyl region for **5c** and three broad peaks for **7**. In both cases, the separation between these signals was considerably less than had been observed in the respective monomers.



6 **7**

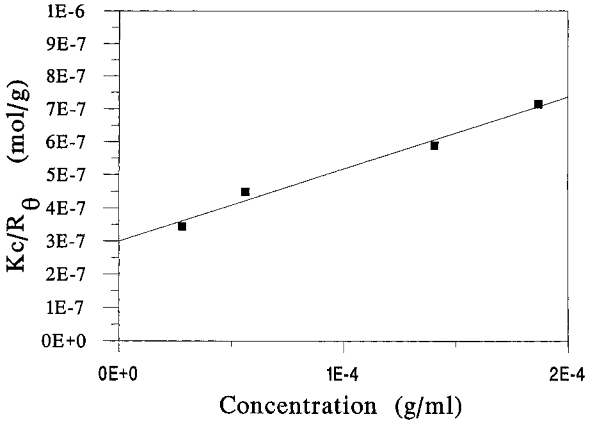


Figure 1. Low-angle laser light scattering results for **5a**.

Light Scattering Measurements for 5a in THF. In order to investigate the solution properties of poly(ferrocenylgermanes) and to provide an absolute determination of molecular weight, LALLS studies were carried out on THF solutions of polymer **5a**, which was selected as a representative example.

Results of LALLS measurements for the polymer **5a** are shown in Figure 1 as a function of the solution concentration. The value of M_w was determined from the fitted intercept of the straight line in Figure 1 with the y axis, and $M_w = 3.3 \times 10^6$ was obtained. To our knowledge this is the highest absolute molecular weight ever reported for a polymer containing a transition metal in the main chain. There is a difference between the absolute M_w obtained from LALLS and that obtained from GPC measurements, $M_w = 8.2 \times 10^5$. GPC is a size exclusion chromatographic technique and requires calibration with sharp fractions of known molecular weight to determine M_w. Often a calibration curve for polystyrene is utilized even for polymers with very different structures. In this case, the molecular weight value obtained by GPC is a relative, but useful quantity called the "polystyrene effective molecular weight". An absolute value for M_w can be obtained by GPC if the universal calibration technique is used[27] or if the column is calibrated with the polymer being studied. GPC separation is based on the effective hydrodynamic size, where the effective hydrodynamic size of a polystyrene random coil of a given M_w in a given solvent is not expected to be the same as a coil of a different polymer under the same conditions. Thus GPC underestimates the molecular weight of polymer **5a** due to the differences in the coil sizes if polystyrene column calibration is used. This was also found to be the case for poly(ferrocenylsilanes) studied by LALLS.[28,30]

Synthesis and Characterization of the Poly(ferrocenylsilane)−Poly(ferrocenylgermane) Copolymer 8. Thermal- and transition metal-catalyzed copolymerization reactions between the [1]germaferrocenophane **4a** and [1]silaferrocenophane **2a** were also attempted. For the thermal reaction, these two monomers were viewed as promising candidates for copolymerization because they homopolymerize at similarly low temperatures (**4a** at 90 °C, **2a** at 125 °C) to give THF-soluble polymeric products. When a ∼1:2 mole ratio of the monomers **4a** and **2a** was heated at 90 °C for 10 min, the contents of the tube became viscous and then immobile. The relatively low polymerization temperature, which is coincident with the ROP temperature of **4a**, suggests that ring-opened germanium species may

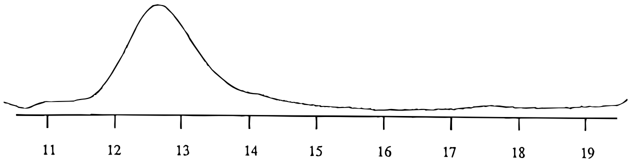


Figure 2. Gel permeation chromatogram of **8** (produced via thermal ROP): retention time (RT) = 11.89 min, $M_w = 10^6$; RT = 13.73 min, $M_{10} = 10^5$.

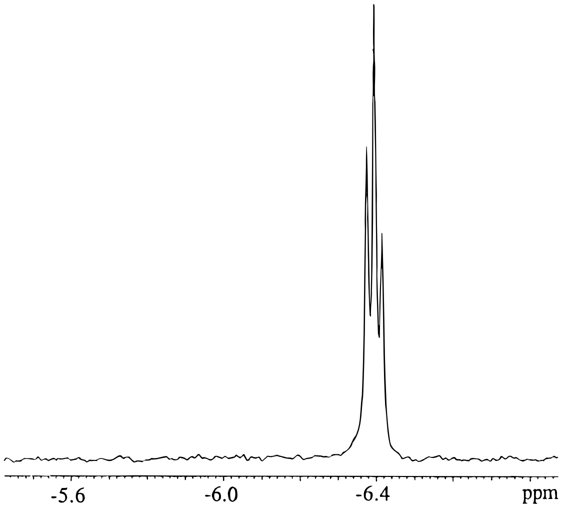


Figure 3. ^{29}Si NMR (79.5 MHz) spectrum of **8** (produced via transition metal-catalyzed ROP) in C_6D_6.

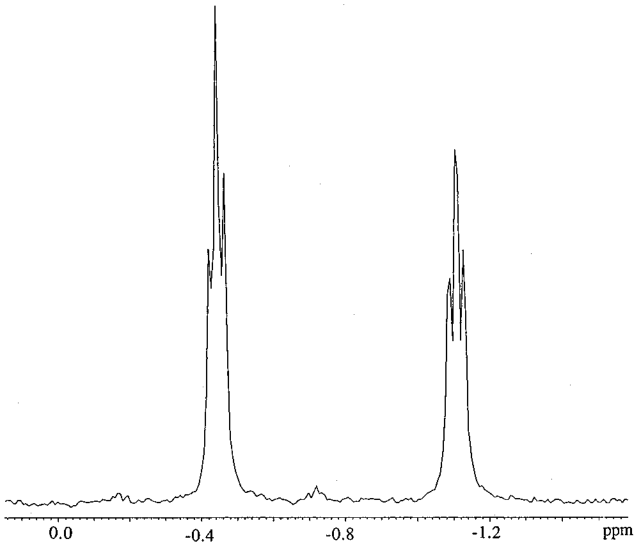


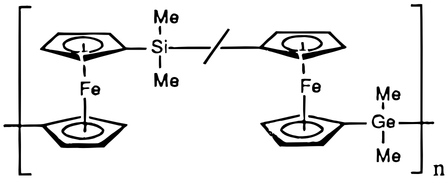
Figure 4. ^{13}C NMR (100.5 MHz) spectrum of **8** (produced via transition metal-catalyzed ROP) in C_6D_6 in the methyl region.

Table 1. Thermal Transition Data for Selected Polymers

polymer	M_w	M_n	T_g (°C)	T_m (°C)	ref
3a	5.2×10^5	3.4×10^5	33	120	5
5a	2.0×10^6	8.5×10^5	28	125	*a*
5b	1.0×10^6	8.1×10^5	12	79	*a*
5c	5.0×10^4	3.5×10^4	−7	74, 111	*a*
5d	1.0×10^6	8.2×10^5	114		*a*
7	5.8×10^4	2.7×10^4	128		*a*
8	3.2×10^5	2.1×10^5	30	81, 117	*a*
9	1.4×10^5	8.4×10^4	128		23

[a] This work.

have initiated the polymerization of the mixture. The products were dissolved in THF, and polymer **8** was then precipitated from hexanes as a fibrous, bright yellow material. GPC analysis revealed that the product was a high molecular weight polymer ($M_w = 3.2 \times 10^5$, $M_n = 2.1 \times 10^5$) with a monomodal weight distribution (Figure 2), which suggested the formation of a copolymer rather than a mixture of two homopolymers. Transition metal-catalyzed ROP of a mixture of **4a** and **2a** with 5 mol % of $PtCl_2$ in C_6D_6 also yielded a similar, amber polymeric material with a monomodal molecular weight distribution by GPC. Analysis of polymer products of the thermal- and transition metal-catalyzed reactions by NMR confirmed that they possess the random copolymer structure **8**. For example, ^{29}Si NMR showed the presence of three resonances (Figure 3) assigned to Si environments neighboring two fcSi, two fcGe, or both fcSi and fcGe monomer units (fc = Fe(η-$C_5H_4)_2$). Similarly, new resonances were apparent in the ^{13}C NMR spectrum of **8** which are not present in the spectra of the corresponding homopolymers **3a** and **5a**. This is illustrated for the $SiMe_2$ (at ∼−0.4 ppm) and $GeMe_2$ (at ∼−1.1 ppm) regions in Figure 4, where the presence of three resonances again arises from the presence of three possible permutations of neighboring monomer units. Further evidence for copolymerization was provided by analysis of the oligomeric residue recovered from the initial precipitation of the polymer. This was found to contain hexane-soluble cyclic oligomeric species which were identified by mass spectrometry. In addition to peaks that were assigned to homosilane and germane cyclic oligomers, molecular ions were detected that corresponded to large ferrocene-containing rings with one or two bridging Si and two bridging Ge atoms (1 Si, 2 Ge $M^+ = 818$ *m/z*; 2 Si, 2 Ge $M^+ = 1060$ *m/z*). Pyrolysis-mass spectrometry analysis of the polymer **8** led to the detection of similar species and also supported a random copolymer structure.



8

Thermal Transition Behavior and Polymer Morphology. The thermal transition behavior of **5a**−**d**, **7**, and **8** was studied by DSC. The glass and melt transitions for the alkyl and aryl poly(ferrocenylgermanes) (**5a**−**d**, **7**) and the poly(ferrocenylsilane)−poly(ferrocenylgermane) copolymer **8** are reported in Table 1. For the poly(ferrocenyldialkylgermanes), lower glass transition temperatures were observed upon increasing the length of the substituent attached to germanium. A similar trend was previously observed for the analogous poly(ferrocenydialkylsilanes).[28] Interestingly, the T_g for **8** (30 °C) falls in between those of the two homopolymers (33 °C for **3a** and 28 °C for **5a**). The presence of bulky trimethylsilyl substitutents on the cyclopentadienyl rings is expected to cause a decrease in the conformational flexibility, which explains the high T_g value (128 °C) detected for **7**. Similarly, increasing the number of methyl substitutents on the cyclopentadienyl rings of poly(ferrocenyldimethylsilane) leads to higher T_g values.[29] The high T_g (114 °C) for **5d** in comparison to **5a** is probably a consequence of the more rigid and bulky phenyl substituents at germanium. High glass transition temperatures have also been detected for poly(ferrocenylsilanes) bearing aryl substituents at silicon,[28,30] as well as for organic polymers

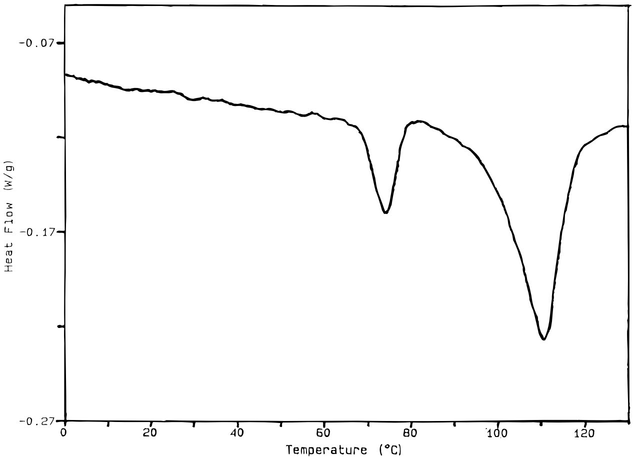


Figure 5. DSC thermogram of **5c** (first scan).

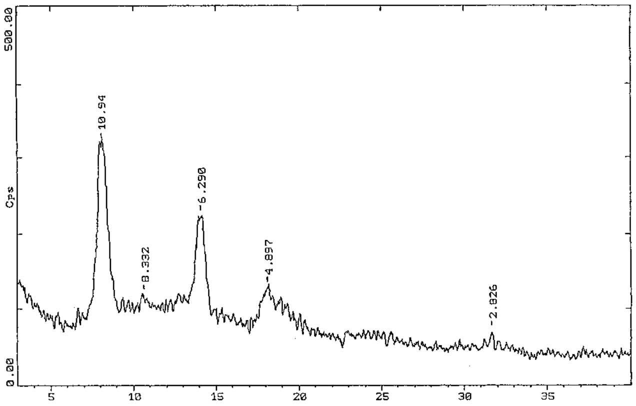


Figure 6. WAXS pattern of **5c**.

where ferrocenyl groups have been introduced into the side-chain structure.[31]

DSC melt transitions were detected for polymers **5a**−**c** and **8**, and their values are listed in Table 1. In all cases, samples that were annealed for 36 h at 60 °C showed considerably more intense melt endotherms (i.e., higher degrees of crystallinity) in comparison to the unannealed polymers. In the case of **5c** (Figure 5), two well-separated melt transitions were observed in the first DSC scan at 74 and 111 °C. A subsequent DSC run on the same sample showed only a single melt transition at 111 °C. Two distinct melt transitions were observed during the first DSC scan for the copolymer **8** at 81 and 117 °C while no melt transitions were seen on subsequent runs. No obvious melt transitions were observed in the case of polymers **5d** or **7**, consistent with the results for the poly(ferrocenylsilanes) with the same substituents.[23,28]

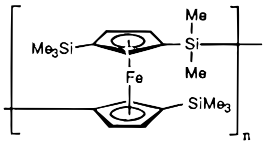
Further morphological information on the polymers was provided by wide angle X-ray scattering (WAXS). The WAXS patterns for the poly(ferrocenylgermanes) also revealed significant structural ordering for **5a**−**c** as well as for the copolymer **8**. The di-*n*-butyl-substituted polymer **5c** (Figure 6) displayed highly ordered and crystalline features with several strong diffraction peaks in contrast to **7**, which showed only a single broad amorphous halo. The maximum *d* spacings for **5a** at 6.58 Å and **5c** at 10.94 Å are in accordance with the increasing size of the substituent attached to germanium. This was also observed for the analogous poly(ferrocenylsilanes) **3a** and **3c**, where the maximum *d* spacings are 6.34 and 11.06 Å, respectively.[32−35] Although less crystalline than either **5a** or **5c**, **5d** showed three resolved but broad peaks with a maximum *d* spacing of 8.11 Å. This value is intermediate to those for **5a** and **5c** and thus also appears to be a function of the side group size. The amorphous character of **7** may be related to irregular structure of the polymer backbone as a consequence of the bulky trimethylsilyl substituents. A single sharp diffraction peak superimposed upon an amorphous halo in the WAXS pattern for the copolymer **8** with a *d* spacing of 6.37 Å is similar to the value found for the silicon homopolymer **3a** (6.3 Å).

Table 2. Electronic and Electrochemical Data for Selected Polymers and Model Systems

polymer	$^1E_{1/2}$ (V)	$^2E_{1/2}$ (V)	ΔE (V)	λ_{max} (nm)	ϵ (L mol^{-1} cm^{-1})	ref
3a	−0.04	0.17	0.21	442	230	7
5a	−0.06	0.12	0.18	448	179	10, *a*
5b	−0.09	0.18	0.27	448	188	*a*
5c	−0.03	0.23	0.26	448	125	*a*
7	−0.04	0.14, 0.19	0.18, 0.23	474	228	*a*
8	−0.01	0.16	0.17	446	189	*a*
9	0.00	0.25	0.25	476	215	*a*
10a	0.00			440	90	25
10b	0.05			448	132	*a*
10c	−0.03			444	160	*a*
11	−0.01			484	187	*a*

[a] This work.

Electronic and Electrochemical Properties. In order to obtain information concerning the electronic structure of these polymers, UV/visible spectra in the 350−800 nm region were obtained for solutions of **5a**−**c**, **7**, and **8** in THF. The λ_{max} values for the bands in the visible region are reported for these polymers, poly(ferrocenylsilane) **9** (the Si analogue of polymer **7**), and several small molecule models **10a**−**c** and **11** in Table 2. By analogy with UV/visible spectral assignments for ferrocene (**10a**), the lowest energy absorption in the visible region for poly(ferrocenylgermanes) can be considered to arise from HOMO−LUMO electronic transitions, which are essentially d−d in character. All of the poly(ferrocenylgermanes) show weak bands with λ_{max} = 448 nm, with the exception of **7**, where the transition occurs 474 nm. The values for **5a**−**c** are similar to those for ferrocene (λ_{max} = 440 nm) and bis(trimethylgermylferrocene) **10c** (λ_{max} = 444 nm). As found with poly(ferrocenylsilanes), the lack of formation of a band structure is indictative of an essentially localized electronic structure for the backbone of these polymers.[5]



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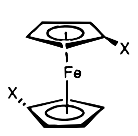

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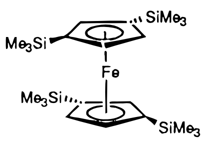

11

a (X = H)
b (X= SiMe$_3$)
c (X = GeMe$_3$)

The λ_{max} value for the copolymer **8** is close to the corresponding value for the homopolymer **5a**. The significantly lower energy transition for the trimethylsilyl-substituted polymer **7** compared to those for **5a**−**c** is interesting. The poly(ferrocenylsilane) analogue of **7**, polymer **9**, possesses a similarly red-shifted transition (λ_{max} = 476 nm) relative to polymer **3a**. In order to

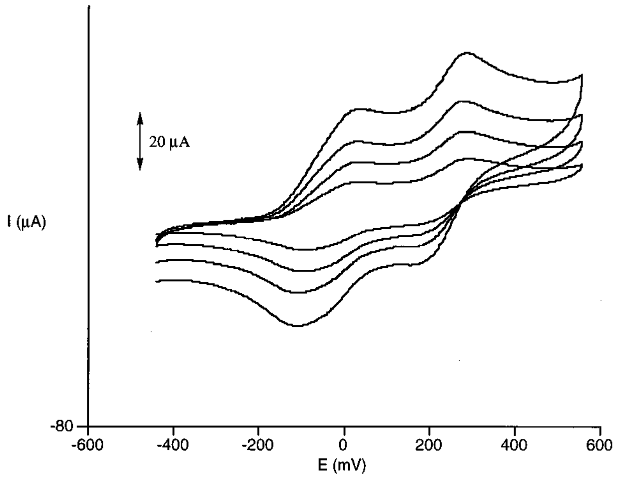

Figure 7. Cyclic voltammograms of a 5 × 10^{-3} M CH_2Cl_2 solution of **5c** at scan rates of 100, 250, 500, and 1000 mV/s at 25 °C. The *x* axis is referenced to the ferrocene/ferrocenium ion couple at $E = 0.0$ mV.

examine the effect of the introduction of additional trimethylsilyl groups at the small-molecule level, we compared the UV/visible spectrum of bis(trimethylsilyl)ferrocene **10b** ($\lambda_{max} = 448$ nm) with that of tetrakis(trimethylsilyl)ferrocene **11**. For the latter species, $\lambda_{max} = 484$ nm and so the cause of the bathochromic shift of polymer **7** relative to **5a** and polymer **9** relative to **3a** also operates in small-molecule models of the polymer repeat units. Perhaps significantly, a single-crystal X-ray study of **11** by Okuda and Herdtweck[36] has revealed that the cyclopentadienyl rings are tilted with respect to one another (tilt angle 6°) due to the steric interactions between the bulky trimethylsilyl substituents. In contrast, ferrocene and its disubstituted derivatives possess cyclopentadienyl rings that are parallel (or almost parallel) to one another.[37] It therefore seems possible that the red-shifted band for **11** and perhaps that for polymers **7** and **9** are related to a weakening of the iron−cyclopentadienyl bond which decreases the HOMO−LUMO energy difference and leads to a consequent increase in λ_{max}. We recently found that poly(ferrocenylsilanes) with methylated cyclopentadienyl rings show similar bathochromic shifts for the lowest energy visible absorption band,[29] and further work aimed at investigating this phenomenon in more detail in these and related materials with substituted cyclopentadienyl rings is in progress.

Cyclic voltammetry experiments were performed on **5a**−**c**, **7**, and **8**, and the half-wave potentials ($^1E_{1/2}$ and $^2E_{1/2}$) and the peak-to-peak separation values (ΔE) are reported in Table 2. The shapes of the cyclic voltammograms for several of these polymers are significantly modified by electrode adsorption effects. As was previously found for a series of symmetrically and unsymmetrically substituted poly(ferrocenylsilanes),[5,10] the cyclic voltammograms in CH_2Cl_2 show two reversible redox waves corresponding to oxidation of essentially half the iron centers with the first wave and subsequent oxidation of the remaining iron centers with the second wave, as shown in Figure 7 for **5c**. The peak-to-peak separation values or redox couplings (ΔE) of the first and second oxidation waves for these polymers fall in the range between 0.17 and 0.27 V and provide a useful measure of the interaction between the skeletal transition metal centers. A comparison of the ΔE values for a series of group 14 bridged poly(ferrocenes), $[Fe(\eta\text{-}C_5H_4)_2X(n\text{-}Bu)_2]_n$ (X(ΔE) = Si (0.29 V), Ge (0.26 V), Sn (0.24 V)), reveals a decreasing electronic interaction between neighboring iron centers with the increasing size of the bridging atom.[10] The cyclic voltammogram for copolymer **8** is essentially the same as those for the two homopolymers **3a** and **5a**. Additional peaks were observed for the higher potential reduction wave for **7** which might be related to conformational effects as the polymer backbone is particularly rigid in this case.

Summary

A series of symmetrically substituted poly(ferrocenylgermanes) have been prepared via the ring-opening polymerization of strained, germanium-bridged [1]ferrocenophanes. In addition, a poly(ferrocenylsilane)−poly(ferrocenylgermane) random copolymer has been synthesized. Glass transition temperatures of the polymers were found to be dependent upon the size of the substituents on germanium as well as those attached to the cyclopentadienyl rings. The poly(ferrocenylgermanes) **5a**−**c** and the copolymer **8** were found to be semicrystalline according to the WAXS analysis and the presence of melt transitions in the DSC thermograms. In contrast, polymers **5d** and **7** were found to be amorphous. Cyclic voltammetry of polymers **5a**−**c** and **7** showed two oxidation waves, consistent with significant electronic interactions between iron centers. Similar behavior was previously found for poly(ferrocenylsilanes).[5] No distinguishable features, such as additional peaks in the cyclic voltammograms, were found for the cyclic voltammetric behavior of the random copolymer **8**. The solution UV/visible spectra of polymers **5a**−**c** were similar to those of ferrocene and the analogous poly(ferrocenylsilanes). The HOMO−LUMO transition in the UV/visible spectrum of polymer **7**, which has bulky trimethylsilyl substitutents on the cyclopentadienyl rings, is considerably red-shifted relative to that for the other poly(ferrocenylgermanes) and may be a consequence of weaker Fe−cyclopentadienyl bonding arising from unfavorable steric interactions between the $SiMe_3$ substitutents.

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(21) (a) A preliminary account of some of the work reported in this paper has been published: see refs 9, 10, and 33. (b) After this manuscript was submitted, the synthesis of copolymer **8** using different transition metal catalysts was reported independently by Tanaka and co-workers (Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263) and studies of the poly(ferrocenylgermanes) **5a**−**c** were described by Pannell and co-workers (Kapoor, R. N.; Crawford, G. M.; Mahmoud, J.; Dementiev, V. V.; Nguyen, M. T.; Diaz, A. F.; Pannell, K. H. *Organometallics* **1995**, *14*, 4944). In the latter case, the polymers were prepared by a thermal ROP route similar to that described previously by us (refs 8 and 9) except that the [1]ferrocenophane monomers were not purified, which resulted in lower molecular weights on thermal treatment.

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