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Synthesis, Characterization, Glass Transition Behavior, and the Electronic Structure of High Molecular Weight, Symmetrically Substituted Poly(ferrocenylsilanes) with Alkyl or Aryl Side Groups

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ABSTRACT: A series of high molecular weight, symmetrically substituted poly(ferrocenylsilanes) $[Fe(\eta\text{-}C_5H_4)_2(SiR_2)]_n$ (**2a–e**: **a**, R = Me; **b**, R = Et; **c**, R = Bu; **d**, R = Hex; **e**, R = Ph) have been prepared via the thermal ring-opening polymerization of the corresponding strained cyclic ferrocenylsilane monomers $Fe(\eta\text{-}C_5H_4)_2(SiR_2)$ (**1a–e**). The latter species were prepared via the reaction of dilithioferrocene/TMEDA (TMEDA = tetramethylethylenediamine) with the appropriate symmetrically substituted dichloroorganosilane R_2SiCl_2. Polymers **2a–d** were structurally characterized by ^1H, ^{13}C, and ^{29}Si NMR, UV/visible spectroscopy, and elemental analysis. The molecular weights of polymers **2a–d** were estimated by gel permeation chromatography using polystyrene standards. Polymer **2e** was found to be insoluble in common organic solvents and was characterized by solid-state NMR. In addition, the solution behavior of $[Fe(\eta\text{-}C_5H_4)_2(SiBu_2)]_n$ (**2c**) was investigated by low-angle laser light scattering which yielded an absolute value of $\bar{M}_w = 2.29 \times 10^5$ and a second virial coefficient, $A_2 = 1.3 \times 10^{-4}$ mol cm^2 g^{-2} in THF at 20 °C. The glass transition behavior of the poly(ferrocenylsilanes) **2a–d** was investigated by differential scanning calorimetry and dynamic mechanical analysis. Glass transition temperatures varied with the substituents present and were found in the range of −26 °C (for polymer **2d**) to +33 °C (for polymer **2a**). No evidence for melting transitions was detected for the polymer samples studied. UV/visible spectra of polymers **2a–d** were measured in THF in the 200–800-nm range and were found to be consistent with an essentially localized electronic structure for the polymer backbone.

Introduction

The development and study of new polymer systems containing inorganic elements is an area of growing interest because of their unusual properties and potential applications.[1-7] Silicon-containing polymers such as polysilanes are attracting particular current attention because of their remarkable σ-delocalized main-chain structure and their uses as photoinitiators, photoconductors, photoresists, and precursors to silicon carbide ceramics.[4] In addition, the synthesis of soluble, high molecular weight organometallic polymers which contain skeletal transition-metal atoms is currently under investigation because of their potentially interesting electrical, electrochemical, and optical properties.[5] As part of our studies of new classes of inorganic[6] and organometallic[7] macromolecules, we recently reported the synthesis of the first examples of high molecular weight poly(ferrocenylsilanes).[7a] These polymers, which possess an unusual main chain consisting of alternating ferrocene groups and silicon atoms, were prepared via the thermal ring-opening polymerization of strained cyclic ferrocenylsilanes.[7,8] In this paper we report full details of the synthesis, characterization, and properties of a range of high molecular weight, symmetrically substituted poly(ferrocenylsilanes) with alkyl or aryl side groups which were prepared by this novel ring-opening route.

Experimental Section

Materials. Dialkyl- or diaryldichlorosilanes and tetramethylethylenediamine (TMEDA) were purchased from Huls USA or Aldrich, respectively, and were distilled before use (the latter from calcium hydride). Ferrocene and 1.6 M butyllithium in hexanes were also purchased from Aldrich and were used as received.

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 purification of the polymers **2a–e** which was carried out in air. Solvents were dried by standard methods, distilled, and then stored under nitrogen over activated molecular sieves. The 200- or 400-MHz ^1H NMR spectra and 50.3- or 100.5-MHz ^{13}C NMR spectra were recorded either on a Varian Gemini 200 or a Varian XL 400 spectrometer, respectively. The 39.7-MHz ^{29}Si NMR spectra were recorded on a Varian XL 400 spectrometer utilizing either a normal (proton coupled) or a DEPT pulse sequence (proton decoupled) with a $^2J_{Si-H}$ coupling of 6.7 Hz. All solution NMR spectra were referenced internally to TMS. Solid-state ^{29}Si and ^{13}C NMR spectra were obtained using a Chemagnetics CMX 300 spectrometer equipped with a Chemagnetics magic-angle spinning probe doubly tuned to the resonance frequencies of ^{29}Si (59.7 MHz) or ^{13}C (75.3 MHz). Samples were spun in a 7.5-mm-o.d. zirconium rotor at a spinning rate of 6000 Hz. A single-contact cross-polarization technique was employed with a contact time of 5 ms and proton decoupling during the signal acquisition technique. The proton radial-frequency field strength was 50 kHz. Spectra were acquired using a sweep width of 50 kHz and a data size of 2 Hz and a recycle delay of 5 s. All chemical shifts were referenced to external TMS. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in an electron impact (EI) mode. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, ultrastyragel columns with a pore size between 10^3 and 10^5 Å, and a Waters 410 differential refractometer. A flow rate of 1.0 mL/min was used, and samples were dissolved in a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards were used for calibration purposes. Elemental analyses were performed either by Galbraith, Knoxville, TN, or by the Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. UV/visible spectra were recorded on a Hewlett-Packard 6452A diode array spectrophotometer using a 1-cm quartz cell: the ϵ values quoted have the units L mol^{-1} cm^{-1} and for the polymers are per repeat unit.

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Static light scattering experiments on polymer **2c** 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 (20 °C) using a metal cell 4.93 mm in length. Each solution was filtered a minimum of three times through a Sartorius regenerated cellulose membrane filter with 0.45-μm average pore size and once through a 0.2-μm disposable filter before injection into the sample cell. The value of the refractive index increment dn/dc 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. Prior to LALLS measurements the UV/vis spectrum of the polymer was checked for possible absorption at the wavelength used in the light scattering experiment. The characteristic absorptions of the polymer were well removed from the working wavelength.

A Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a TAC 7 instrument controller was used to study the thermal behavior. The thermograms were calibrated with the melting transitions of decane and indium and were obtained at a heating rate of 10 °C/min under dinitrogen. A Perkin-Elmer DMA 7 instrument operated by a PE 7700 computer was also used. The temperature dependence of the E-modulus and phase angle δ were measured by applying an oscillating uniaxial tensile force on flexible films or an oscillating uniaxial compressive force on gumlike samples or brittle films. In all experiments the frequency of the oscillating force was 1 Hz. The temperature was varied from −60 to +200 °C with a heating rate of 10 °C/min. The tensile experiment was carried out with the film clamp sample holder, for the compressive experiments the 3-mm-diameter and 1-mm-diameter parallel plate sets were used.

Synthesis of the Cycloferrocenylsilane Monomers 1a–e. The dialkyl- and diarylferrocenylsilanes **1a** and **1e** were prepared by the methods reported by Wrighton[9] and Osborne,[10] respectively. Compounds **1b–d** were prepared from dilithioferrocene/TMEDA and the appropriate dichloroorganosilane by analogous procedures. Compound **1b** was purified by high-vacuum sublimation (50 °C, 5×10^{-3} mmHg) and was isolated as a red crystalline material in 60% yield, whereas **1c** and **1d** were isolated at room temperature as semisolids after purification by high-vacuum distillation (130 °C for **1c**, 180 °C for **1d**; 5×10^{-3} mmHg). The yields were 40% for **1c** and ca. 5% for **1d**. The low yield for the latter was due to thermal polymerization during the vacuum distillation step.

For monomer **1a**: Compound **1a** afforded ^{1}H NMR and UV/visible spectra and a melting point which are consistent with those reported in the literature by Wrighton,[9] and these data are included here for comparison: red-orange crystals; mp 81 °C; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −4.6; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 77.7 (Cp), 75.6 (Cp), 33.5 (Cp C–Si), −3.3 ($\mathrm{CH_3}$), ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.41 (dd, $^3J_{\mathrm{HH}}$ = 1.6, 4 H, Cp), 3.95 (dd, $^3J_{\mathrm{HH}}$ = 1.6, 4 H, Cp), 0.36 (s, 6 H, $\mathrm{CH_3}$); MS (EI, 70 eV) m/z (%) 242 (100, $\mathrm{M^+}$), 227 (35, $\mathrm{M^+}$ − Me), 213 (5, $\mathrm{M^+}$ − 2 Me); UV/vis (THF) λ_1 = 470 nm (ϵ_1 = 250 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 284 nm (sh, ϵ_2 = 14 000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 218 nm (ϵ_4 = 31 000 $\mathrm{M^{-1}\,cm^{-1}}$).

For monomer **1b**: red-orange crystals, mp 122 °C; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −1.4, ^{13}C NMR ($\mathrm{C_6D_6}$) δ 77.6 (Cp), 75.9 (Cp), 32.6 (Cp C–Si), 6.7 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_3}$), 3.3 ($\mathrm{-}\mathit{C}\mathrm{H_2CH_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.40 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H), 3.96 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H), 1.14 (t, $^3J_{\mathrm{HH}}$ = 7.7, 6 H, $\mathrm{-CH_2C}\mathit{H}_3$), 0.90 (q, 4 H, $\mathrm{-C}\mathit{H}_2\mathrm{CH_3}$); MS (EI, 70 eV) m/z (%) 270 (100, $\mathrm{M^+}$), 241 (8, $\mathrm{M^+}$ − Et), 213 (41, $\mathrm{M^+}$ − 2 Et); UV/vis (THF) λ_1 = 478 nm (ϵ_1 = 250 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 260 nm (sh, ϵ_2 = 6800 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 216 nm (ϵ_3 = 20 000 $\mathrm{M^{-1}\,cm^{-1}}$).

For monomer **1c**: red-orange semisolid; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −1.5; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 77.6 (Cp), 75.9 (Cp), 32.7 (Cp C–Si), 26.9 ($\mathrm{-CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 25.6 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 14.1 ($\mathrm{-CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 11.6 ($\mathrm{-}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.42 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H, Cp), 4.00 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H, Cp), 1.61 (m, 4 H, $\mathrm{-CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.46 (m, 4 H, $\mathrm{-CH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 0.94 (m, 10 H, $\mathrm{-C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_3$); MS (EI, 70 eV) m/z (%) 326 (100, $\mathrm{M^+}$), 269 (15, $\mathrm{M^+}$ − Bu), 214 (45, $\mathrm{M^+}$ − 2 Bu); UV/vis (THF) λ_1 = 474 nm (ϵ_1 = 280 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 280 nm (sh, ϵ_2 = 8000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 218 nm (ϵ_3 = 18 000 $\mathrm{M^{-1}\,cm^{-1}}$).

For monomer **1d**: red semisolid; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −1.5; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 77.6 (Cp), 76.0 (Cp), 34.3 ($\mathrm{-CH_2CH_2CH_2CH_2CH_2CH_3}$), 33.6 (Cp C–Si), 32.2 ($\mathrm{-CH_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 25.0 ($\mathrm{-CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 23.2 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2CH_2CH_2CH_2CH_3}$), 14.5 ($\mathrm{-CH_2CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 12.0 ($\mathrm{-}\mathit{C}\mathrm{H_2CH_2CH_2CH_2CH_2CH_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.42 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H, Cp), 4.00 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H, Cp), 1.65 (m, 4 H, $\mathrm{-CH_2CH_2CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.46 (m, 8 H, $\mathrm{-CH_2CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.03 (m, 4 H, $\mathrm{-CH_2C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_3}$), 0.94 (m, 10 H, $\mathrm{-C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH_2C}\mathit{H}_3$); MS (EI, 70 eV) m/z (%) 382 (100, $\mathrm{M^+}$), 297 (100, $\mathrm{M^+}$ − Hex), 213 (14, $\mathrm{M^+}$ − Hex − hexene); UV/vis (THF) λ_1 = 470 nm (ϵ_1 = 235 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 286 nm (sh, ϵ_2 = 7000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 220 nm (ϵ_3 = 41 000 $\mathrm{M^{-1}\,cm^{-1}}$).

For monomer **1e**: Compound **1e** afforded ^{1}H and ^{13}C NMR spectra and a melting point which are consistent with those reported in the literature by Osborne,[10] and these data are included here for comparison: red-orange crystals; mp 197 °C; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −11.7; ^{13}C NMR ($\mathrm{CDCl_3}$) δ 134.4 (*ipso*-phenyl), 134.3 (*o*-phenyl), 130.3 (*p*-phenyl), 128.3 (*m*-phenyl), 77.9 (Cp), 76.7 (Cp), 31.0 (Cp C–Si); ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.90–8.10 (m, 4 H, Ph), 7.30–7.60 (m, 6 H, Ph), 4.56 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H, Cp), 4.20 (dd, $^3J_{\mathrm{HH}}$ = 1.7, 4 H, Cp); MS (EI, 70 eV) m/z (%) 366 (100, $\mathrm{M^+}$), 289 (7, $\mathrm{M^+}$ − Ph); UV/vis (THF) λ_1 = 483 nm (ϵ_1 = 270 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 270 nm (sh, ϵ_2 = 13 000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 262 nm (sh, ϵ_3 = 15 000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_4 = 254 nm (sh, ϵ_4 = 12 000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_5 = 218 nm (ϵ_5 = 67 000 $\mathrm{M^{-1}\,cm^{-1}}$).

Ring-Opening Polymerization of 1a–e, Synthesis of the Poly(ferrocenylsilanes) 2a–e. Polymers **2a–e** were prepared similarly, and the general synthesis is illustrated by that of **2c**. A sample of **1c** (2.00 g, 6.13 mmol) was polymerized in an evacuated, sealed Pyrex tube at 130 °C for 1 h. An increase in viscosity was observed, and after 10 min the tube contents were immobile. Heating was then continued for a further 50 min. The polymeric product was dissolved in THF (40 mL) over 4 h and the resulting solution concentrated to 10 mL. This was then added slowly, dropwise to a large excess of hexanes (ca. 300 mL). The polymer was then dried and redissolved in THF (30 mL) and precipitated into methanol (500 mL). The yellow, fibrous product was then dried in vacuo. The yield was 1.80 g (90%).

The yields of purified **2a**, **2b**, **2d**, and **2e** were in the range of 80–95%.

For polymer **2a**: yellow fibrous powder; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −6.4; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 73.6 (Cp), 71.9 (Cp C–Si), 71.8 (Cp), −0.5 ($\mathit{C}\mathrm{H_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.25 (br s, 4 H, Cp), 4.10 (br s, 4 H, Cp), 0.53 (br s, 6 H, $\mathrm{C}\mathit{H}_3$); UV/vis (THF) λ_1 = 430 nm (ϵ_1 = 190 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 258 nm (sh, ϵ_2 = 2300 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 252 nm (sh, ϵ_3 = 2300 $\mathrm{M^{-1}\,cm^{-1}}$), λ_4 = 218 nm (ϵ_4 = 18 000 $\mathrm{M^{-1}\,cm^{-1}}$); GPC $M_{\mathrm{w}} = 5.2 \times 10^5$, $M_{\mathrm{n}} = 3.4 \times 10^5$, polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) = 1.5. Anal. Calcd for C, 59.5; H, 5.8. Found: C, 58.8; H, 5.6.

For polymer **2b**: yellow fibrous powder; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −2.7; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 74.4 (Cp), 72.3 (Cp C–Si), 70.4 (Cp), 8.9 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 6.7 ($\mathit{C}\mathrm{H_2CH_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.31 (br s, 4 H, Cp), 4.10 (br s, 4 H, Cp), 1.24 (br s, 6 H, $\mathrm{-CH_2C}\mathit{H}_3$), 1.10 (br s, 4 H, $\mathrm{-C}\mathit{H}_2\mathrm{CH_3}$); UV/vis (THF) λ_1 = 444 nm (ϵ_1 = 200 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 258 nm (sh, ϵ_2 = 3800 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 252 nm (sh, ϵ_3 = 4000 $\mathrm{M^{-1}\,cm^{-1}}$), λ_4 = 220 nm (ϵ_4 = 35 000 $\mathrm{M^{-1}\,cm^{-1}}$); GPC $M_{\mathrm{w}} = 7.4 \times 10^5$, $M_{\mathrm{n}} = 4.8 \times 10^5$, polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) = 1.6. Anal. Calcd: C, 62.2; H, 6.7. Found: C, 61.5; H, 6.7.

For polymer **2c**: yellow fibrous powder; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −4.9; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 74.1 (Cp), 71.9 (Cp), 70.6 (Cp C–Si), 27.4 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 27.2 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 14.9 ($\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 14.2 ($\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.35 (br s, 4 H, Cp), 4.20 (br s, 4 H, Cp), 1.64–1.53 (m, br, 8 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.13 (m br, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 1.05 (m, br, 6 H, $\mathrm{-CH_2CH_2CH_2C}\mathit{H}_3$); UV/vis (THF) λ_1 = 450 nm (ϵ_1 = 160 $\mathrm{M^{-1}\,cm^{-1}}$); λ_2 = 258 nm (sh, ϵ_2 = 6500 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 252 nm (sh, ϵ_3 = 6900 $\mathrm{M^{-1}\,cm^{-1}}$), λ_4 = 224 nm (ϵ_4 = 21 000 $\mathrm{M^{-1}\,cm^{-1}}$); GPC $M_{\mathrm{w}} = 8.9 \times 10^5$, $M_{\mathrm{n}} = 3.4 \times 10^5$, polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) = 2.6; for sample of polymer used for light scattering $M_{\mathrm{w}} = 1.7 \times 10^5$, $M_{\mathrm{n}} = 9.3 \times 10^4$, polydispersity ($M_{\mathrm{w}}/M_{\mathrm{n}}$) = 1.9. Anal. Calcd: C, 66.4; H, 8.0. Found: C, 65.4; H, 8.1.

For polymer **2d**: amber elastomer; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −2.3; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 74.2 (Cp), 71.9 (Cp C–Si), 70.7 (Cp), 34.4 ($\mathrm{CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 32.7 ($\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 25.1 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 23.3 ($\mathrm{-CH_2}\mathit{C}\mathrm{H_2CH_2CH_2CH_2CH_3}$), 15.4 ($\mathrm{-CH_2CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 14.6 ($\mathit{C}\mathrm{H_2CH_2CH_2CH_2CH_2CH_3}$); ^{1}H NMR ($\mathrm{C_6D_6}$) δ 4.31 (br s, 4 H, Cp), 4.16 (br s, 4 H, Cp), 1.61 (m, 4 H, $\mathrm{CH_2CH_2CH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.46 (m, 8 H, $\mathrm{-CH_2CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2$-

$\mathrm{CH_2CH_3}$), 1.13 (m, 4 H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH_2CH_2CH_2CH_3}$), 0.93 (m, 10 H, $-\mathit{CH_2}\mathrm{CH_2CH_2CH_2CH_2}\mathit{CH_3}$); UV/vis (THF) λ_1 = 450 nm (ϵ_1 = 160 $\mathrm{M^{-1}\,cm^{-1}}$), λ_2 = 258 nm (sh, ϵ_2 = 4200 $\mathrm{M^{-1}\,cm^{-1}}$), λ_3 = 252 nm (sh, ϵ_3 = 4500 $\mathrm{M^{-1}\,cm^{-1}}$), λ_4 = 224 nm (ϵ_4 = 18 000 $\mathrm{M^{-1}\,cm^{-1}}$); GPC $M_w = 1.15 \times 10^5$, $M_n = 7.6 \times 10^4$, polydispersity (M_w/M_n) = 1.5. Anal. Calcd: C, 69.1; H, 8.9. Found: C, 67.5; H, 9.0.

For polymer **2e**: yellow-orange powder; ^{29}Si NMR (solid state) δ −12.9; ^{13}C NMR (solid state) δ 136.3 (*ipso*-phenyl and *o*-phenyl), 128.8 (*p*-phenyl and *m*-phenyl), 75.3 (coincident Cp), 67.8 (Cp C–Si); GPC of a lower molecular weight fraction extracted with hot THF; $M_w = 5.1 \times 10^4$, $M_n = 3.3 \times 10^4$, polydispersity (M_w/M_n) = 1.6. Anal. Calcd: C, 72.1; H, 4.9. Found: C, 70.4; H, 5.3.

Light Scattering Measurements for $[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_4})_2(\mathrm{SiBu_2})]_n$ (2c) in THF. Static light scattering experiments in the low-angle regime were used to determine the weight-average molar mass $\bar{M}_w$ and the second virial coefficient A_2 of a sample of **2c**. The values of $\bar{M}_w$ were obtained from the Rayleigh–Debye relationship, in the limit of low scattering angles, θ:[11]

$$Kc/R_\theta = 1/\bar{M}_w + 2A_2c \qquad (1)$$

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

$$K = [4\pi^2 n^2/(N_0\lambda_0^{\,4})](\mathrm{d}n/\mathrm{d}c)^2 \qquad (2)$$

where n is the refractive index of the solvent, λ_0 is the wavelength of the laser light in vacuum, N_0 is Avogadro's 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 20 °C, and a value of dn/dc = 0.208 ± 0.001 mL/g was obtained.

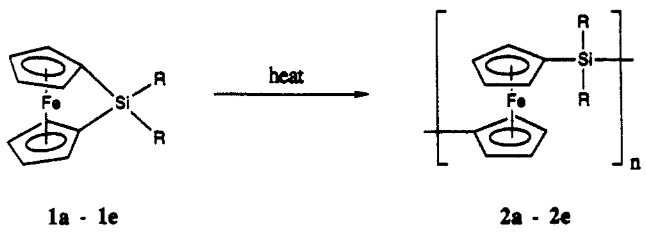
Results and Discussion

Ferrocenyl groups have been introduced into the structure of a wide range of organic polymers and have also been incorporated as side groups in polysilanes.[1c,12–14] However, prior to our preliminary communication[7a] the only previously reported poly(ferrocenylsilanes), which contain ferrocenyl moieties in the polymer main chain, were low molecular weight (1700–7000), relatively poorly characterized materials derived from polycondensation reactions between dilithioferrocene and dichloroorganosilanes.[15] The monomers used for the ring-opening polymerization route to high molecular weight poly(ferrocenylsilanes) are [1]ferrocenophanes containing a single silicon atom in the bridge which we have termed cyclic ferrocenylsilanes.

Synthesis and Characterization of the Cyclic Ferrocenylsilane Monomers 1a–e. Cyclic ferrocenylsilanes have been known since the initial report of **1e** by Osborne and co-workers in 1975, which was prepared via the reaction of dilithioferrocene/TMEDA (TMEDA = tetramethylethylenediamine) with diphenyldichlorosilane.[10] Subsequently several species analogous to **1e** have been prepared by similar methods including the methylated compound **1a**.[9,16] Cyclic ferrocenylsilanes are strained molecules, as indicated by single-crystal X-ray diffraction studies, which show the cyclopentadienyl ligands to be significantly tilted by ca. 19–21° with respect to one another, and by the detection of facile, stoichiometric ring-opening reactions.[16,17] In addition, we have determined the strain energies of **1a** and **1e** to be approximately 80 and 60 kJ $\mathrm{mol^{-1}}$, respectively, by thermochemical methods.[7a]

In the work described in this paper compounds **1a–e** were prepared by the literature method reported for the synthesis of **1a**[9] and **1e**[10] which involved the reaction of dilithioferrocene/TMEDA with the appropriate dialkyl- or diaryldichlorosilane. The compounds were isolated as orange-red, moisture-sensitive materials in ca. 50–60% yield. The structures of the new cyclic ferrocenylsilanes **1b–d** were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and by mass spectrometry. This afforded data similar to that reported for the previously prepared compounds **1a** and **1e**. Thus, the ^{13}C NMR spectra of **1b–d** were consistent with the assigned structures and showed characteristic high-field ^{13}C NMR shifts for the *ipso*-cyclopentadienyl carbon atoms bonded to silicon. Thus, for all of the cyclic ferrocenylsilanes **1a–e** these resonances occur in the region of 31–34 ppm (in $\mathrm{C_6D_6}$). By contrast, in unstrained species such as $\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_4SiPh_3})_2$ in which the bridge between the cyclopentadienyl ligands is absent the corresponding resonance occurs at 66.4 ppm (in $\mathrm{CDCl_3}$).[18] The ^{29}Si NMR spectra of **1a–d** showed singlet resonances in the region of −1 to −5 ppm, whereas for compound **1e**, with phenyl substituents at silicon, the corresponding ^{29}Si NMR resonance was at −11.7 ppm. The ^{1}H NMR spectra for **1b–d** possessed the expected resonances in the correct integrated ratio for the protons of the cyclopentadienyl group and those present in the alkyl or aryl substituents attached to silicon. The mass spectra of **1b–d** showed molecular ion peaks together with peaks assignable to logical fragmentation products. The UV/visible spectra of **1b–d** in the 200–800-nm range contained bands in the visible region at 470–478 nm (ϵ = 235–280 $\mathrm{M^{-1}\,cm^{-1}}$) which showed the characteristic bathochromic shift and increase in intensity relative to the long wavelength band of ferrocene at 440 nm (ϵ = 90 $\mathrm{M^{-1}\,cm^{-1}}$). As discussed previously by Osborne, this is indicative of significant tilting of the cyclopentadienyl rings.[18] Indeed, the angles between the planes of the cyclopentadienyl ligands in **1a** and **1e** have been determined to be 20.8 (5)° and 19.1 (10)°, respectively, by single-crystal X-ray diffraction methods.[7d,16a]

Scheme I



1a - 1e **2a - 2e**

	R
1a, 2a	Me
1b, 2b	Et
1c, 2c	Bu
1d, 2d	Hex
1e, 2e	Ph

Synthesis and Structural Characterization of the Poly(ferrocenylsilanes) 2a–e. Polymerization of **1a–e** (Scheme I) was achieved by heating these species in the melt at elevated temperatures in evacuated, sealed Pyrex tubes. In all cases the tube contents became molten and then rapidly more viscous, and eventually immobile. The polymeric products **2a–d** dissolved slowly, but completely, in THF which indicated that no appreciable cross-linking had taken place. The poly(ferrocenylsilanes) **2a–c** were isolated as yellow, fibrous materials and polymer **2d** was isolated as an amber elastomer by repeated precipitation from THF into nonsolvents such as hexanes, methanol, and in some cases acetone. By contrast, the phenylated polymer **2e** was found to be insoluble in organic solvents

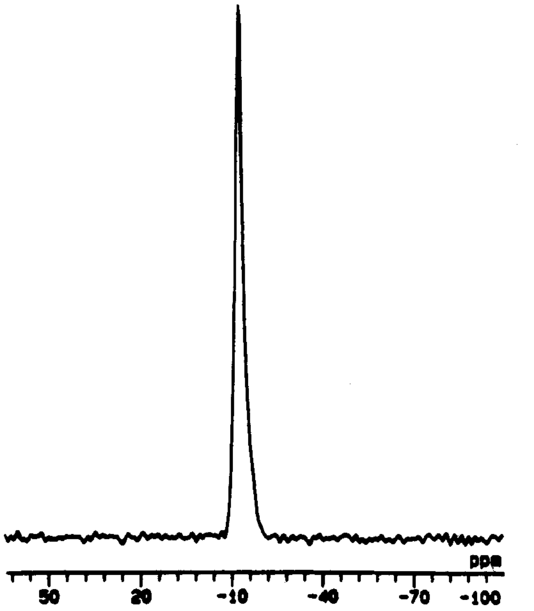


Figure 1. Solid-state ^{29}Si NMR spectrum of polymer **2e**.

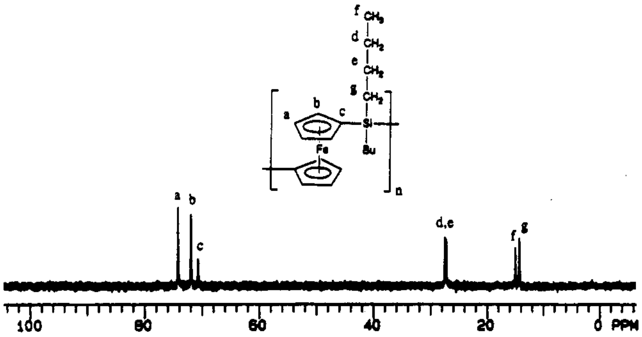


Figure 2. ^{13}C NMR spectrum of polymer **2c** (C_6D_6, 100.5 MHz).

although samples of the material swelled appreciably in *N*-methylpyrrolidone. The yield of the poly(ferrocenylsilanes) **2a–e** was virtually quantitative, and unreacted **1a–e** was not detected.

The poly(ferrocenylsilanes) **2a–e** were structurally characterized by solution (**2a–d**) or solid state (**2e**) multinuclear NMR spectroscopy and elemental analysis. In the cases of the organic solvent soluble polymers **2a–d** solution UV/visible spectra were also obtained and their molecular weight distributions were analyzed by gel permeation chromatography (GPC) and in one case (**2c**), by light scattering (see below). The ^{1}H NMR spectra of **2a–d** (in C_6D_6) showed two broad resonances for the cyclopentadienyl protons at ca. 4.3 and 4.1 ppm and broad resonances assigned to protons in the organic groups attached to silicon. The ratio of these resonances was as expected. The ^{29}Si NMR spectra of **2a–d** consisted of a single, singlet resonance in the range from −2.3 to −6.4 ppm which in each case was slightly shifted to high field compared to that of the corresponding monomers **2a–d** (δ −1.4 to −4.6). In the case of **2e** a broad, singlet ^{29}Si solid-state NMR resonance was detected at −12.9 ppm (Figure 1) compared to the value for the monomer **1e** (in C_6D_6) at −11.7 ppm. The ^{13}C NMR spectra of **2a–e** were also consistent with the assigned structures as is illustrated for the case of **2c** in Figure 2. In particular, the unusual, high field resonances at 31–34 ppm for the cyclopentadienyl carbon attached to silicon in the monomers **1a–e** were shifted to more conventional values of ca. 70–72 ppm. This indicated that the ring tilting present in the strained monomers was absent and that the cyclopentadienyl ligands were approximately parallel. Further evidence for this conclusion came from the UV/visible spectra of polymers **2a–d** in THF (see below). Elemental analysis data for the polymers **2a–e** were found to be in good agreement with the assigned structures for hydrogen, but the values for carbon were found to be slightly low (between 0.7 and 1.7%) even after repeated analyses on spectroscopically pure samples. We attribute the low carbon values to incomplete combustion due to the formation of ceramic products at elevated temperatures.[19] GPC indicated that **2a–d** possessed approximate weight-average molecular weights ($\bar{M}_w$) of 1 × 10^5–9 × 10^5 and number-average molecular weights ($\bar{M}_n$) of 1 × 10^5–4 × 10^5 using polystyrene standards for column calibration (see Table I). The molecular weight distributions for the polymers were quite narrow with polydispersities of 1.5–2.6. Although the poly(ferrocenylsilane) **2e** was found to be insoluble in all common organic solvents at room temperature, relatively low molecular weight fractions ($\bar{M}_w$ = 5.1 × 10^4, $\bar{M}_n$ = 3.2 × 10^4) could be extracted from the solid material using hot THF. In contrast to the situation in polysilanes such as $[SiR_2]_n$ (R = Me or Ph),[1c,4b] the insolubility of **1e** is not attributable to microcrystallinity, as an X-ray powder diffractogram of this polymer was characteristic of an amorphous material.[22] The polymers **2a–e** appear stable to the atmosphere, and amber, free-standing films can be cast from solutions of **2a–c** in organic solvents such as THF or toluene via solvent evaporation.

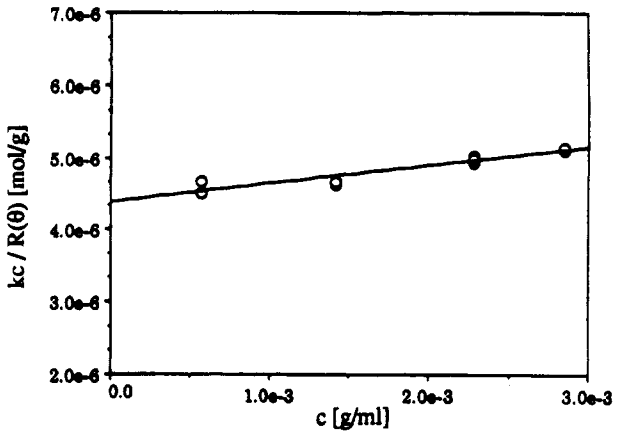


Figure 3. Low-angle laser light scattering data for polymer **2c**.

Light Scattering Measurements for $[Fe(\eta\text{-}C_5H_4)_2(SiBu_2)]_n$ (2c) in THF. In order to investigate the solution properties of poly(ferrocenylsilanes) and to provide an absolute determination of molecular weight, low-angle laser light scattering (LALLS) studies were carried out on THF solutions of polymer **2c** which was selected as a representative example.

Results of LALLS measurements for the polymer **2c** are shown in Figure 3 as a function of the solution concentration. The value of $\bar{M}_w$ was determined from the inverse of the fitted intercept of the straight line in Figure 3 with the *y*-axis where a value of $\bar{M}_w$ = (2.29 ± 0.04) × 10^5 was obtained. There is a significant experimental difference (% error = 26%) between the absolute $\bar{M}_w$ obtained from LALLS and that obtained from GPC measurements. GPC is a size-exclusion chromatographic technique and requires calibration with sharp fractions of known molar mass to determine $\bar{M}_w$.[20] Often a calibration curve for polystyrene is utilized even for polymers with very different structures. In this case, the molar mass obtained by GPC is a relative quantity and is called the "polystyrene effective molar mass". An absolute value for $\bar{M}_w$ can be obtained by GPC if the universal calibration technique is used[20] or if the column is calibrated with the

Table I. Visible Spectroscopic, Molecular Weight, and Glass Transition Data for Poly(ferrocenylsilanes) 2a–e

	R	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	M_w[a]	M_n[a]	PDI	T_g,[d] °C
2a	Me	430 (190)	5.2×10^5	3.4×10^5	1.5	33/25[e]
2b	Et	444 (200)	7.4×10^5	4.8×10^5	1.6	22
2c	Bu	450 (160)	8.9×10^5	3.4×10^5	2.6	3
			1.7×10^5 [b]	9.3×10^4 [b]	1.9	
2d	Hex	450 (160)	1.15×10^5	7.6×10^4	1.5	−26/−27[e]
2e	Ph		5.1×10^4 [c]	3.2×10^4 [c]	1.6[c]	

[a] Determined by GPC. [b] Sample used for light scattering. [c] Soluble polymer fraction extracted with hot THF. [d] T_g values obtained by DMA experiments. [e] T_g values obtained by DSC.

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 $\bar{M}_w$ 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 molar mass of polymer **2c** due to the differences in the coil sizes if polystyrene column calibration is used.

The second virial coefficient, A_2, was determined from the fitted slope of the line in Figure 3, where a value of $A_2 = (1.3 \pm 0.2) \times 10^{-4}$ mol cm^2 g^{-2} was obtained. Polystyrene in THF, a good solvent, with a molecular weight similar to polymer **2c** has an A_2 value about 7 times larger,[21] suggesting that THF is a marginal solvent for the poly(ferrocenylsilane).

Glass Transition Behavior of the Poly(ferrocenylsilanes) 2a–d. In order to obtain information on the conformational flexibility of poly(ferrocenylsilanes), the glass transition behavior of **2a–d** was investigated. Differential scanning calorimetry (DSC) showed no evidence for melting transitions for the polymer samples studied,[22] and glass transitions with very small changes in heat capacity were only detected for **2a** and **2d**. In order to determine the T_g values for **2b** and **2c** and to confirm the values found for **2a** and **2d**, the polymers were analyzed by the more sensitive dynamic mechanical analysis (DMA) technique. The glass transitions determined for **2a–d** are compiled in Table I. The data obtained made physical sense in that polymers **2a–c** were fibrous polymers which could be solution-cast into free-standing amber films whereas polymer **2d** was a gum.

The T_g values for the poly(ferrocenylsilanes) **2a–d** decrease as the length of the organic side group increases. This is a well-established trend for many polymer systems and can be attributed to the generation of additional free volume by pushing the polymer main chains further apart from one another.[23] It is interesting to compare the glass transition data available for polysilanes with those determined for poly(ferrocenylsilanes). The T_g of poly(di-*n*-hexylsilane) has been reported to be −52.5 °C.[4e] This value is significantly less than that for the poly(ferrocenylsilane) analogue **2d** (T_g = −26 to −27 °C; see Figure 4) which indicates that the incorporation of a skeletal ferrocenyl moiety into a polysilane backbone decreases the conformational flexibility. The data for poly(di-*n*-butylsilane) (T_g = −40 °C)[4f] compared to **2c** (T_g = 3 °C) also support this conclusion. It is worth noting that previous work has shown that the incorporation of ferrocenyl groups into the side-group structure of organic polymers such as polyacrylates also leads to a significant increase in the glass transition temperature.[13] This effect can be attributed to the relative steric bulk and rigidity of the ferrocenyl moiety.

Solution UV/Visible Spectra of Poly(ferrocenylsilanes) 2a–d: Implications for the Electronic Structure of the Polymer Backbone. Poly(ferrocenylsilanes) possess an interesting main chain which comprises potentially conjugated σ, pπ, and dπ units. In order to obtain information about the electronic structure of these polymers, UV/visible spectra in the 200–800-nm range were obtained for solutions of **2a–d** in THF. The resulting spectra were found to be similar to that for ferrocene and, in particular, to those for monomeric ferrocenes with organosilicon groups attached to each cyclopentadienyl ring. Ferrocene itself, which possesses a $^1A_{1g}$ ground state that corresponds to an $(e_{2g})^4(a_{1g})^2$ configuration where the e_{2g} and a_{1g} levels are very close in energy and an e_{1g} level is the LUMO, shows several UV/visible absorptions in the 200–800-nm range.[24] The most intense band consists of a UV absorption at λ = 200 nm (ϵ = 51 000 M^{-1} cm^{-1}) which has been assigned to a ligand-to-metal charge-transfer (LMCT) transition. Spin-allowed, predominantly metal d–d HOMO–LUMO type ($e_{2g} \rightarrow e_{1g}$ and $a_{1g} \rightarrow e_{1g}$) one-electron transitions give rise to a much less intense band in the near UV at λ = 324 nm (ϵ = 49 M^{-1} cm^{-1}), which has been assigned to a $^1A_{1g} \rightarrow b^1E_{1g}$ transition, and a second fairly weak band in the visible region at λ = 440 nm (ϵ = 90 M^{-1} cm^{-1}) which has been assigned to overlapping $^1A_{1g} \rightarrow {}^1E_{2g}$ and $^1A_{1g} \rightarrow a^1E_{1g}$ electronic transitions at 416 and 458 nm, respectively.[24] Silylated ferrocenes possess UV/visible spectra which are only slightly different from that of ferrocene. For example, bis(trimethylsilyl)ferrocene, $Fe(\eta\text{-}C_5H_4SiMe_3)_2$, possesses a spectrum in which the high-energy LMCT band shifts slightly to lower energy (λ = 218 nm ϵ = 20 000 M^{-1} cm^{-1}) and the essentially metal-based transitions in the near-UV/visible region show even more slight bathochromic shifts (λ = 332 nm, ϵ = 90 M^{-1} cm^{-1}, and λ = 448 nm, ϵ = 130 M^{-1} cm^{-1}). The essentially unstrained cyclic ferrocenyldisilane $Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2$ shows similar near-UV/visible bands (λ = 324 nm, ϵ = 62 M^{-1} cm^{-1}, and λ = 444 nm, ϵ = 88 M^{-1} cm^{-1}).[7d] The UV/visible spectra of the poly(ferrocenylsilanes) **2a–d** are very similar with intense absorptions in the UV at 218–224 nm (ϵ = 18 000–35 000 M^{-1} cm^{-1}) and visible absorptions at 430–450 nm (ϵ = 160–200 M^{-1} cm^{-1}). The near-UV band detected for ferrocene and small-molecule silylated ferrocenes at 320–330 nm could not be accurately resolved as a shoulder on the intense absorption at ca. 220 nm. This is illustrated by the UV/visible spectrum of **2d** which is shown in Figure 5. By analogy with the UV/visible spectral assignments for ferrocene the absorption in the visible region can be considered to arise from electronic transitions with HOMO–LUMO character. Two significant observations can be made from considerations of these spectra. First, the bands in the visible region are ca. 20–35 nm shifted to higher energy compared to those for the strained, ring-tilted monomers **1a–d** (λ = 470–478 nm, ϵ = 235–280 M^{-1} cm^{-1}). This is indicative of a structure for the polymers in which the cyclopentadienyl rings of the skeletal ferrocenyl units are essentially parallel rather than tilted, as would be expected. Such a conclusion can also be made from considerations of the ^{13}C NMR spectra of the monomers and polymers as discussed previously. Second, the similarity of the λ_{max} for the visible absorption band in the polymers **2a–d** with that for small-molecule species such as ferrocene and silylated ferrocenes indicates that the electronic structure of the polymer main chain can, to at least a first approximation, be considered as localized. By contrast, in polysilanes the λ_{max} of the HOMO–LUMO σ–σ^* transition shifts dramatically to longer wavelength on moving from small-molecule oligosilanes to high molecular weight polysilanes which provides excellent evidence for the delocalization of σ electrons in these

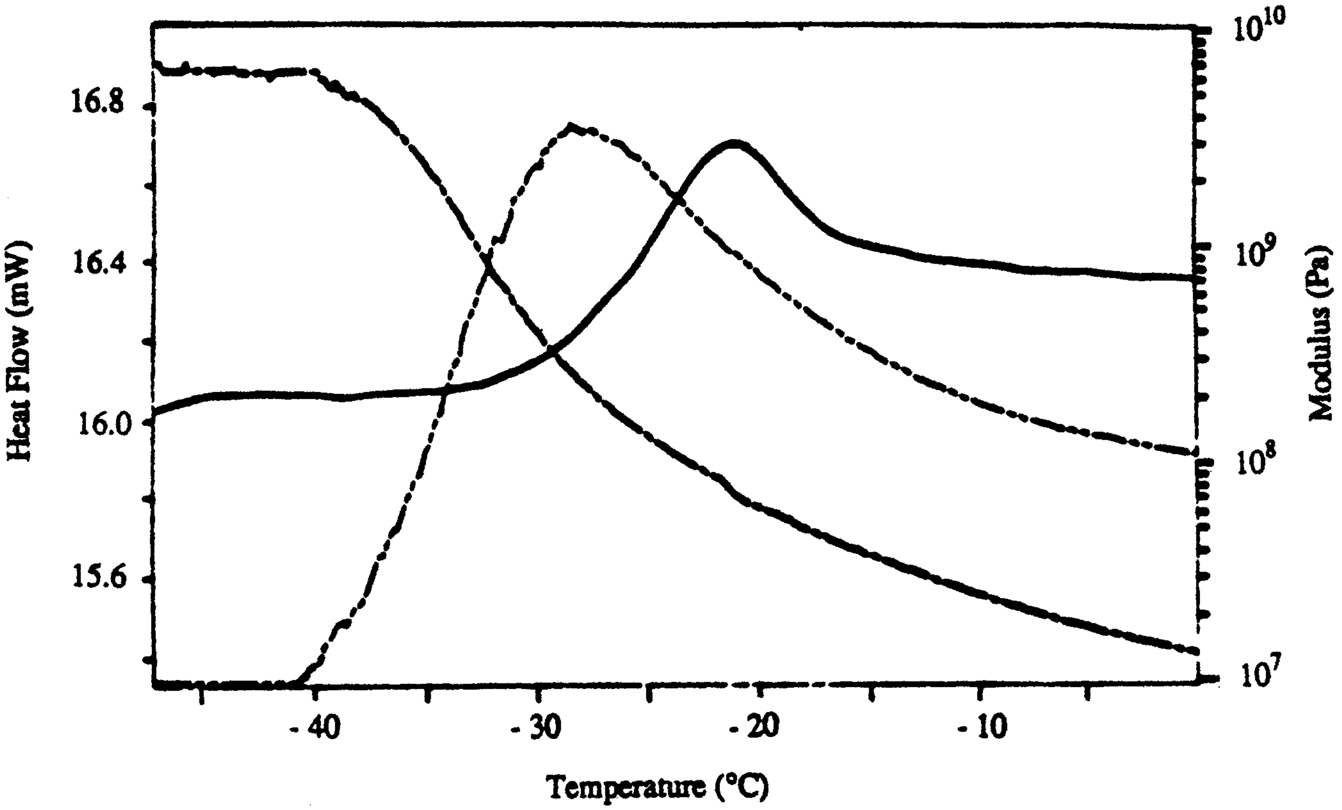


Figure 4. DSC and DMA of the poly(ferrocenylsilane) **2d**: heat capacity (DSC trace) (—); dynamic storage modulus (– • –); mechanical loss factor (tan δ) (– • • • –) as a function of temperature.

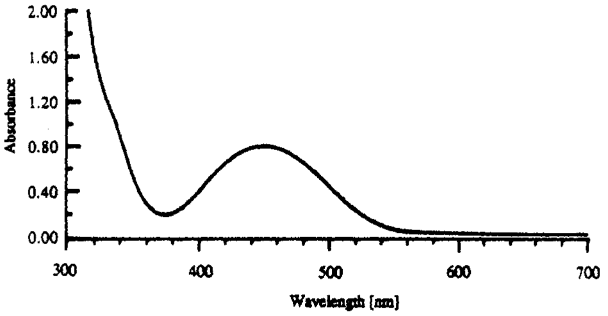


Figure 5. UV/visible spectrum of the poly(ferrocenylsilane) **2d** in THF.

materials. For example, on traversing the series from Me$_3$SiSiMe$_3$ to Me$_3$Si(SiMe$_2$)$_{10}$SiMe$_3$, the $\lambda_{\max}$ of the σ–σ^* transition shifts from ca. 198 nm (ϵ = ca. 8000 M^{-1} cm^{-1}) to 279 nm (ϵ = 42 700 M^{-1} cm^{-1}) and high molecular weight poly(dialkylsilanes) generally absorb in the region from 300–325 nm (ϵ = 5000–10 000 per Si–Si bond).[4a–c,25] Trends similar to these are apparent in the UV/visible spectra of π-conjugated polyenes where the π-electrons are delocalized.

Summary

A series of symmetrically substituted poly(ferrocenylsilanes) have been prepared via the ring-opening polymerization of strained cyclic ferrocenylsilane monomers. By varying the side groups attached to silicon, glassy (**2a–c** and **2e**) or elastomeric (**2d**) polymers were obtained. Glass transition data for **2a–d** indicate that the incorporation of ferrocene groups into the backbone of polysilanes leads to a decrease in skeletal flexibility. The solution UV/visible spectra of poly(ferrocenylsilanes) **2a–d** in the visible region are similar to those for ferrocene and monomeric ferrocene derivatives with organosilicon groups attached to each cyclopentadienyl ring and are indicative of an essentially localized electronic structure. By contrast, in polysilanes the $\lambda_{\max}$ of the σ–σ^* transition shifts to longer wavelength on moving from small-molecule oligosilanes to high molecular weight polysilanes which illustrates the delocalization of σ electrons in the all-silicon backbone present in these materials. Nevertheless, as reported in our initial paper[7a] and elsewhere,[7g] investigations of the electrochemistry of poly(ferrocenylsilanes) by cyclic voltammetry have shown the presence of two oxidation waves which is consistent with the possibility for through-space, electrostatic interactions between iron sites along the polymer chain.[7j] Further detailed studies of the structure and properties of these interesting polymers are in progress and will be reported in the near future.

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