Macromolecules **1999,** *32,* 1321−1324

Molecular Motions in Poly(ferrocenes): Solid-State Deuterium NMR Studies of Poly(ferrocenylsilanes) near Their Glass Transition Temperature

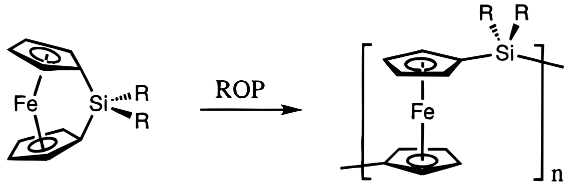
Kevin Kulbaba, Peter M. Macdonald,* and Ian Manners*

Department of Chemistry, University of Toronto,
80 St. George St., Toronto M5S 3H6, Ontario, Canada

Received October 28, 1998
Revised Manuscript Received December 21, 1998

The macroscopic properties of polymeric materials depend on the structure, order, and dynamics of the macromolecular chains.[1] Understanding the motions of polymer chains in a bulk material therefore represents an important scientific challenge and has implications for the observed mechanical properties and possible applications. The incorporation of organometallic moieties with unusual geometries in the polymer main chain is of considerable interest as this should lead to an increase in the range of motions possible in comparison to organic polymer systems.[2]

High molecular weight ($M_w = 10^5{-}10^6$, $M_n > 10^5$) linear poly(ferrocenes) such as the poly(ferrocenylsilane) **2** represent a recently established class of these materials and are readily accessible via the thermal, anionic, or transition-metal-catalyzed ring-opening polymerization (ROP) of strained metallocenophane monomers such as **1**.[3] Recent attention has focused on the interesting physical properties arising from the presence of interacting metal atoms in the main chain and their use as precursors to magnetic materials including nanostructures.[3c,4,5] From the standpoint of molecular motion, ferrocene possesses very facile (almost free) cyclopentadienyl (Cp) ligand rotation. (In fact, the iron atom in a ferrocene unit has been likened to that of a "molecular ball bearing".[6]) On the other hand, the preference for the Cp ligands to remain approximately coplanar might be expected to place significant constraints on chain motions in the solid state.



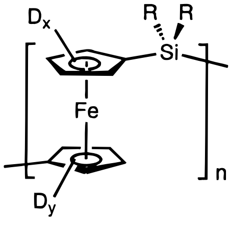
1 **2**

Substantial changes in the mechanical properties of a polymer are observed around the glass transition temperature (T_g), and these can be directly related to molecular motions of the polymer main chain and side groups. Previous studies of the thermal transition behavior of poly(ferrocenes) **2** have shown the T_g to be greatly influenced by side groups, and values from −51 to +150 °C have been determined.[7] To date, very few studies of motion in ferrocene-containing polymers have been reported in the literature.[8,9] Nuyken and coworkers[9] have used Mössbauer absorption spectra to investigate amorphous block copolymers that contain ferrocene and possess a low T_g for temperatures ranging from 4 to 330 K. The decrease in the recoil free fraction at higher temperatures was interpreted as the onset of motion of the ferrocene units with a frequency higher than 10^{10} Hz. The exact nature of these motions was not investigated.

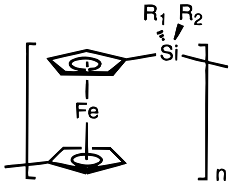
Solid-state deuterium NMR provides a unique probe for the study of molecular motions of organic polymers, including the effects of temperature relative to the glass transition.[10] In this paper we report the deuterium NMR spectra, obtained near room temperature, of three high molecular weight (M_w > 20 000) poly(ferrocenylsilanes) selectively deuterated at either the cyclopentadienyl rings or the side groups of silicon. To our knowledge, this represents the first ^{2}H NMR study of molecular motion in transition-metal-containing polymers.

Selective deuteration of the cyclopentadienyl rings of ferrocene was achieved by the addition of excess D_2O to dilithioferrocene·tetramethylethylenediamine (fcLi$_2$·TMEDA) in THF, which was generated by treatment with ^{n}BuLi in the presence of TMEDA in hexanes.[11] Evaporation to dryness, extraction with CH_2Cl_2, and purification by vacuum sublimation resulted in an isolated yield of 86% (ca. 20% deuteration). Repetition of the lithiation and quenching steps was used in the synthesis of polymers **3b** and **3c** to obtain more significant deuteration (ca. 50%) of the Cp rings. Isolation of the deuterated ferrocene allows for the synthesis of [1]-ferrocenophane monomers and the resulting ring-opened polymers (**3a**, **3b**, and **3c**) by previously reported methods.[3] The monomers were isolated by vacuum sublimation in moderate yields and characterized by ^{1}H NMR and mass spectrometry.[12] Polymers were formed via thermal ROP at 150 °C for **3a** and by transition-metal-catalyzed ROP for **3b** and **3c**. The amounts of deuterium incorporation were found to be approximately 20% for **3a** and 50% for **3b** and **3c** by ^{1}H NMR integration.[12]

To probe side-group motions, two poly(ferrocenes) with selective deuteration at the silicon side groups were also investigated. Polymer **4a** was synthesized via direct halide substitution of poly(ferrocenylmethylchlorosilane) with d_3-MeLi in THF using methods analogous to those reported previously.[13] Analysis of the ^{1}H NMR of the product showed that essentially all of the chlorine substituents on the polymer were replaced with CD_3 groups. Synthesis of **4b** was carried out by the reaction of 2 equiv of d_4-methanol with the $SiCl_2$-bridged monomer followed by ROP via a procedure analogous to that recently reported for the nondeuterated counterpart.[7]



3a: R = CH_3, x+y = 2
3b: R = OCH_3, x+y = 4
3c: R = OC_6H_{13}, x+y = 4



4a: $R_1 = CD_3$, $R_2 = CH_3$
4b: $R_1 = R_2 = OCD_3$

Variable temperature ^{2}H NMR spectra of the deuterated polymers were obtained on a Chemagnetics CMX300

10.1021/ma9816867 CCC: $18.00

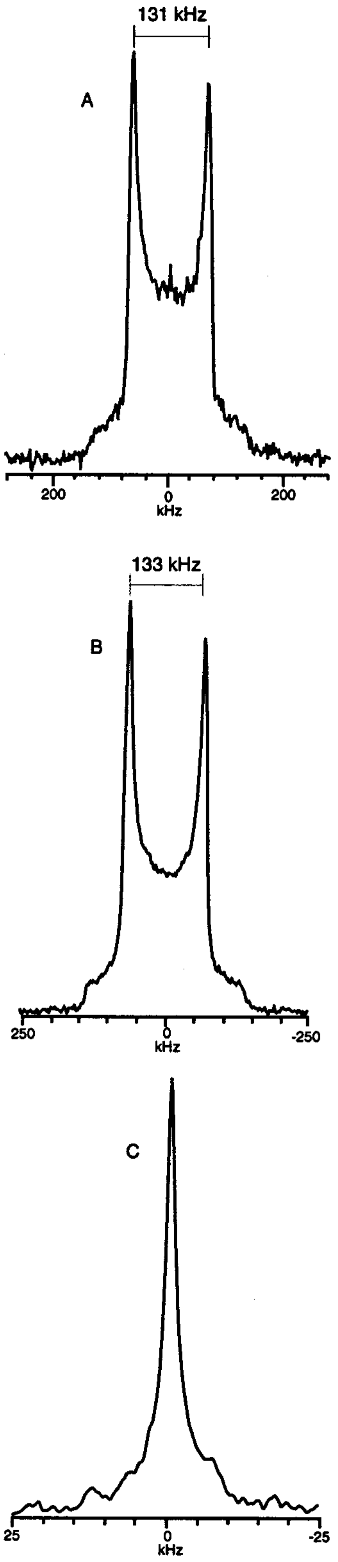


Figure 1. Solid-state ^{2}H NMR spectra at 25 °C with deuteration of the Cp rings of the polymers: (A) polymer **3a** with a quadrupole splitting of 131 kHz, (B) polymer **3b** with a quadrupolar splitting of 133 kHz, and (C) polymer **3c**, a single line which is indicative of an isotropic motion of the Cp ligands.

NMR spectrometer operating at 45.98 MHz for deuterium, using a Chemagnetics static solids probe. The quadrupolar echo pulse sequence was employed[14] with a spectral width of 1 MHz digitized into 1K data points, a 90° pulse width of 2 μs, an interpulse delay of 40 μs, and a recycle delay of 60 s. Typically, between 300 and 600 acquisitions were signal averaged.

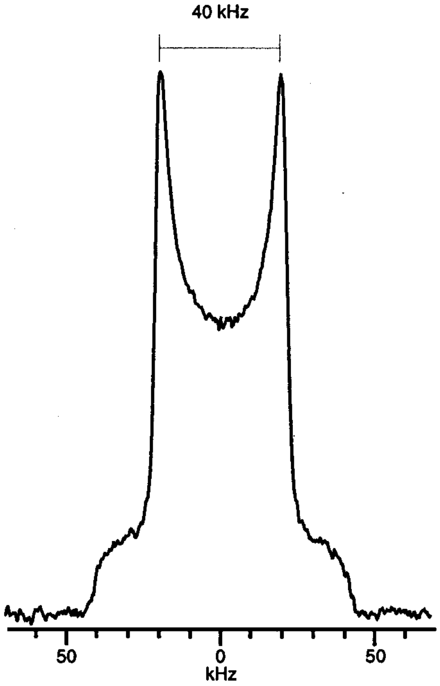


Figure 2. Solid-state ^{2}H NMR spectrum of **4a** at 25 °C showing a quadrupolar splitting of 40 kHz.

The room temperature (25 °C) deuterium NMR spectra of **3a** (T_g = 34 °C) and **3b** (T_g = 19 °C), shown in Figure 1A,B, consist of Pake doublet powder patterns with asymmetry parameters near zero and quadrupole splittings of 131 and 133 kHz, respectively. These values can be compared to the static quadrupole splitting of 145 kHz reported for perdeuterated ferrocene.[15] Thus, the Cp rings of **3a** and **3b** appear to be frozen and immobile at room temperature on the time scale of the experiment. No apparent change in the spectra was observed upon heating to 50 °C. In sharp contrast, the room-temperature deuterium NMR spectrum of **3c** (T_g = −51 °C), shown in Figure 1C, consists of a narrow singlet, indicating virtually isotropic motion of the Cp rings. These polymers therefore appear to exhibit a trend similar to that found for organic polymers in which the NMR T_g is approximately 60−80 °C higher than the mechanical T_g.[10e]

For polymer **4a** (T_g = 34 °C) the deuterium NMR spectrum (Figure 2) consists of a Pake doublet powder pattern with an asymmetry parameter of zero and a quadrupolar splitting of 40 kHz. This is the value expected for methyl rotation about the Si−CD$_3$ bond, so no additional motions of the polymer backbone need to be invoked to explain this finding. It is not surprising, in fact, that poly(ferrocenyldimethylsilane) exhibits only side-group motions and no motion of the polymer backbone since this polymer is known to be crystalline with a melting point in the range of 122−143 °C.[3c] Thus, close packing of the polymer chains should prohibit all but the slowest motions of the ferrocene moieties, and the thermal annealing above T_g would only serve to increase crystallinity.

For polymer **4b** (T_g = 19 °C), which is mainly amorphous, the quadrupolar splitting of 31 kHz observed at 10 °C (Figure 3A) indicates the presence of some motion in addition to methyl rotation about the O−CD$_3$ bond. A likely candidate for this would be some degree of rotation about the Si−O bond. As the temperature is raised to 35 °C (Figure 3B), a second spectral

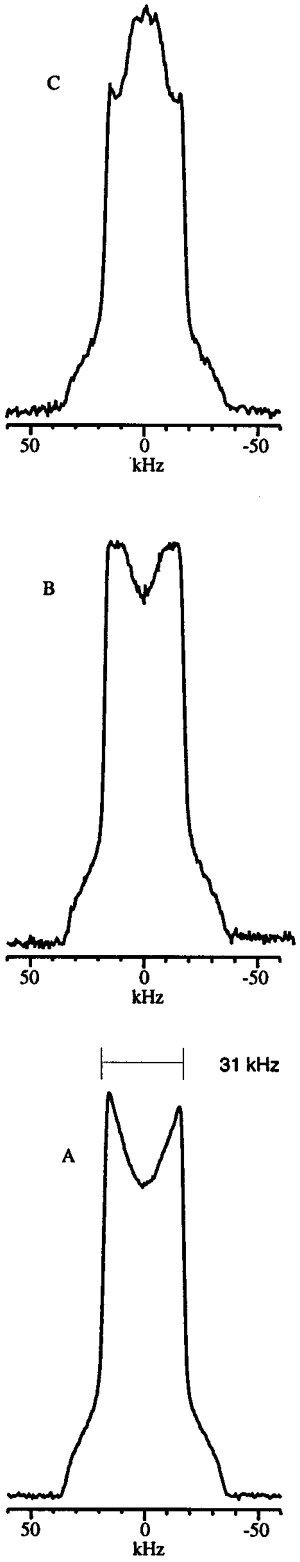


Figure 3. Variable temperature solid-state ^{2}H NMR spectra for **4b** (T_g = 19 °C) at (A) 10, (B) 35, and (C) 50 °C showing a quadrupolar splitting of 31 kHz.

component begins to appear in the central region of the spectrum. This component has a smaller quadrupolar splitting and grows in intensity with increasing temperature. At 50 °C (Figure 3C) the spectrum is clearly a superposition of two spectral components. Evidently, a portion of this polymer sample experiences additional motions not undergone by polymer **4a**. A reasonable explanation for this additional motion would be librations of the polymer backbone.

The results described above indicate that solid-state deuterium NMR provides an excellent probe of the molecular motions of poly(ferrocenes). The lack of motion of the Cp rings for polymers **3a** and **3b** at temperatures near or above the T_g was counterintuitive considering the highly fluxional structure of ferrocene, with the low barrier of rotation about the iron−Cp bonds (3.34 kJ/mol).[16] However, studies of the low-T_g poly(ferrocene) **3c** showed the presence of significant motions at a temperature 75 °C above the T_g of the polymer. Appreciable motion was also detected for **4b** at 50 °C. Since the ^{2}H NMR spectrum of polymer **3b** shows no evidence of these additional motions, they would appear to be localized to the region of the silicon and to not involve the ferrocene units.

Future work in this interesting new area will focus on variable temperature studies of the low-T_g polymer **3c** in addition to deuterium NMR exchange spectroscopy[10e] to better define the nature and time scale of the Cp ring motion.

Acknowledgment. K.K. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Graduate Fellowship. P.M.M. thanks Materials and Manufacturing Ontario (MMO) and NSERC for funding. I.M. also thanks MMO for funding and the Alfred P. Sloan Foundation for a Research Fellowship (1994−1998), NSERC for an E.W.R. Steacie Fellowship (1997−1999), and the University of Toronto for a McLean Fellowship (1997−2003). K.K. thanks Mark J. MacLachlan for helpful discussions and WAXS analysis of the polymers.

References and Notes

(1) See for example: (a) Bernhard, B.; Spiess, H. W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1655. (b) Rushkin, I. L.; Interrante, L. V. *Macromolecules* **1996**, *29*, 3123.
(2) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.
(3) See for example: (a) Manners, I.; Foucher, D. A.; Tang, B. Z. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131. (c) Manners, I. *Can. J. Chem.* **1998**, *76*, 371.
(4) (a) MacLachlan, M. J.; Aroca, P.; Coombs, N.; Manners, I.; Ozin, G. A. *Adv. Mater.* **1998**, *10*, 144. (b) Massey, J.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533. (c) Massey, J.; Power, K. N.; Winnik, M. A.; Manners, I. *Adv. Mater.* **1998**, *10*, 1559.
(5) For the work of others on ring-opened poly(ferrocenes): (a) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (b) Pannell, K. H.; Dementiev, V. V.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A. F. *Organometallics* **1994**, *13*, 3644. (c) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (d) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263. (e) Barlow, S.; Rohl, A. L.; Shi, S.; Freeman, C. M.; O'Hare, D. *J. Am. Chem. Soc.* **1996**, *118*, 7578. (f) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507. (g) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621.
(6) Li, C.; Medina, J. C.; Maguire, G. E. M.; Abel, E.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1997**, *119*, 1609.
(7) Nguyen, P.; Stojcevic, G.; Kulbaba, K.; MacLachlan, M. J.; Liu, X. H.; Lough, A. J.; Manners, I. *Macromolecules* **1998**, *31*, 5977.
(8) See for example: (a) Feyerherm, R.; Litterst, F. J.; Burkhardt, V.; Nuyken, O. *Solid State Commun.* **1992**, *82*, 141. (b) Gahl, A.; Hillberg, M.; Litterst, F. J.; Pöhlmann, T.; Hübsch, C.; Nuyken, O.; Garwe, F.; Beiner, M.; Donth, E. *J. Phys: Condens. Matter.* **1998**, *10*, 961. (c) Litterst, F. J.; Lerf, A.; Nuyken, O.; Alcalá, H. *Hyperfine Interact.* **1982**, *12*, 317. (d) Nienhaus, U. G.; Parak, F. *Hyperfine Interact.* **1994**, *90*,

243. (e) Richter, D.; Zorn, R.; Farago, B.; Frick, B.; Fetters, L. J. *Phys. Rev. Lett.* **1992**, *68*, 71.

(9) Hillberg, M.; Stieler, W.; Litterst, F. J.; Burkhardt, V.; Nuyken, O. *Hyperfine Interact.* **1994**, *88*, 137.

(10) See for example: (a) Spiess, H. W. *Adv. Polym. Sci.* **1985**, *66*, 23. (b) Schmidt-Rohr, K.; Kulik, A. S.; Beckham, H. W.; Ohlemacher, A.; Pawelzik, U.; Boeffel, C.; Spiess, H. W. *Macromolecules* **1994**, *27*, 4733. (c) Shi, J. F.; Inglefield, P. T.; Jones, A. A.; Meadows, M. D. *Macromolecules* **1996**, *29*, 605. (d) Goward, G. R.; Kerr, T. A.; Power, W. P.; Nazar, L. F. *Adv. Mater.* **1998**, *10*, 449. (e) *Multidimensional Solid State NMR and Polymers*; Schmidt-Rohr, K., Spiess, H. W., Eds.; Academic Press: New York, 1994; pp 236−276. (f) Spiess, H. W. *Chem. Rev.* **1991**, *91*, 1321. (g) Havlíček, I.; Ilanvský, M.; Hrouz J. *J. Polym. Sci., Polym Phys. Ed.* **1978**, *16*, 653.

(11) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Marroll, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

(12) **3a:** Monomer, red crystals; yield 79%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.40 (m, 3 H, Cp), 3.94 (m, 3 H, Cp), 0.36 (s, 6H, CH_3) ppm; MS (EI, 70 eV) *m*/*z* (%) 244 (M^+, 100). Polymer **3a**: amber fibrous solid; yield 69%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.27 (m, 3 H, Cp), 4.11 (m, 3 H, Cp), 0.55 (s, 6H, CH_3) ppm; GPC (THF vs polystyrene standards) 512, 000 (M_w), 2.2 (PDI). **3b:** Monomer, red crystals; yield 75%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.40 (m, 2 H, Cp), 4.13 (m, 2 H, Cp), 3.62 (s, 6H, CH_3) ppm; MS (EI, 70 eV) *m*/*z* (%) 278 (M^+, 100). Polymer, amber gum; yield 66%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.54 (m, 2 H, Cp), 4.44 (m, 2 H, Cp), 3.65 (s, 6H, CH_3) ppm; GPC (THF vs polystyrene standards) 422 000 (M_w); 2.9 (PDI). **3c:** Monomer, red liquid; yield 91%; ^{1}H NMR (C_6D_6, 400 MHz) δ 4.44 (m, 2 H, Cp), 4.22 (m, 2 H, Cp), 4.08 (t, 4H, CH_2), 1.71 (m, 4 H, CH_2), 1.42 (m, 4 H, CH_2), 1.27 (m, 8 H, CH_2), 0.89 (t, 6H, CH_3) ppm; MS (EI, 70 eV) *m*/*z* (%) 418 (M^+, 100). Polymer, red gum; yield 96%; ^{1}H NMR (C_6D_6, 300 MHz) δ 4.68 (m, 2 H, Cp), 4.52 (m, 2 H, Cp), 4.05 (t, 4H, CH_2), 1.72 (m, 4 H, CH_2), 1.53 (m, 4 H, CH_2), 1.36 (m, 8 H, CH_2), 0.96 (t, 6H, CH_3) ppm; GPC (THF vs polystyrene standards) 390 000 (M_w), 3.6 (PDI). **4a:** Polymer, amber fibrous solid; yield 74%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.27 (m, 4 H, Cp), 4.10 (m, 4 H, Cp), 0.55 (s, 3H, CH_3) ppm; GPC (THF vs polystyrene standards) 22 000 (M_w), 1.9 (PDI). WAXS showed the material to be moderately crystalline with an approximate degree of crystallinity (ca. 50%) similar to that observed previously. **4b:** Monomer, red crystals; yield 87%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.40 (m, 4 H, Cp), 4.13 (m, 4 H, Cp) ppm. Polymer, amber gum; yield 69%; ^{1}H NMR (C_6D_6, 200 MHz) δ 4.54 (m, 4 H, Cp), 4.43 (m, 4 H, Cp) ppm; GPC (THF vs polystyrene standards) 606 000 (M_w), 1.9 (PDI). WAXS was consistent with the presence of a very small amount of crystallinity.

(13) Zechel, D. L.; Hultzsch, K. C.; Rulkens, R.; Balaishis, D.; Ni, Y.; Pudelski, J.; Lough, A. J.; Manners, I.; Foucher, D. A. *Organometallics* **1996**, *15*, 1972.

(14) Davis, J. H.; Jeffrey, K.; Bloom, M.; Higgs, T. *Chem. Phys. Lett.* **1976**, *42*, 390.

(15) Millar, J. M.; Thayer, A. M.; Zimmermann, H.; Pines, A. *J. Magn. Reson.* **1986**, *69*, 243.

(16) Luke, W. D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3241.

MA9816867