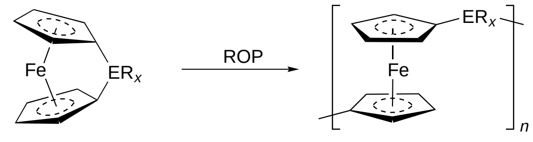
Synthesis, structure and cationic ring-opening polymerization (ROP) of a strained [2]carbathioferrocenophane

Rui Resendes, Paul Nguyen, Alan J. Lough and Ian Manners*†

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

The synthesis and cationic ring-opening polymerization of a novel [2]carbothiaferrocenophane is reported; the polymerization represents the first cationic ring-opening polymerization of a metal-containing ring.

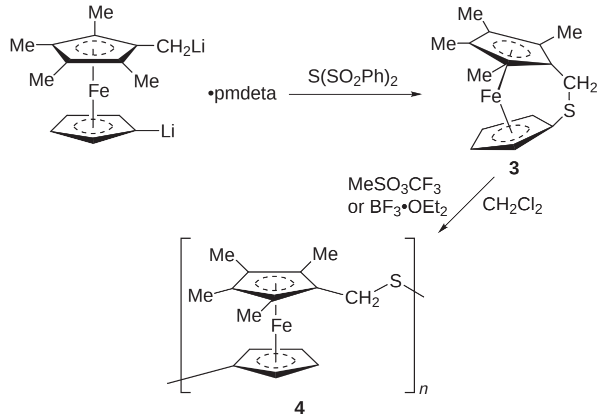
Macromolecules containing transition metal atoms in the main chain are attracting growing attention as a result of their combination of processability and interesting physical properties.[1–3] Until recently, the development of this area has been hindered by the lack of viable synthetic routes to these materials.[2] The recent discovery of a thermal ring-opening polymerization (ROP) route to poly(ferrocenes) from strained [1]- and [2]-metallocenophanes **1** provided facile access to high molecular mass metallocene-based polymers **2** with interacting metal atoms.[4–6] Subsequently, examples of anionic and transition metal-catalyzed ROP of [1]ferrocenophanes have also been reported which afford routes to polymers with controlled architectures including block and graft copolymers.[7–10] Recent attention has focused on detailed studies of the interesting properties of the resulting poly(metallocenes) including their electrochemical, charge transport, electrochromic and morphological (*e.g.* liquid crystalline) properties and their potential function as precursors to spin-aligned magnetic materials *via* oxidation or pyrolysis.[5,11–15]



1 **2**

Cationic polymerization provides an important, well established methodology for the preparation of organic polymers which complements other synthetic routes.[16,17] However, to date, cationic ROP of a metal-containing ring has not been reported. In this paper we report the synthesis of a novel [2]ferrocenophane which undergoes the first example of such a cationic ROP process.

Few examples of unsymmetrically bridged [2]ferrocenophanes have been reported.[18] We found that the reaction of the pmdeta (pmdeta = 1,1,4,7,7-pentamethyldiethylenetriamine) adduct of $(C_5Me_4CH_2Li)(C_5H_4Li)Fe$ in Et_2O at −78 °C with 1 equiv. of $S(SO_2Ph)_2$ afforded **3** in 30% yield as deep red crystals after purification by vacuum sublimation. The identity of **3** was confirmed by ^1H and ^{13}C NMR and GC–MS.[19] The ^1H NMR spectrum revealed the α and β protons of the Cp ring at δ 4.69 and 3.64, respectively. The large separation of the Cp proton resonances is indicative of the ring strain present in **3**. Of note, is the bridging CH_2 resonance which occurs quite downfield at δ 4.17, indicating a deshielded environment. The ^{13}C NMR shows the C_{ipso} resonances of the Cp′ (tetramethyl-Cp) and Cp rings occurring at δ 83.8 and 93.7, respectively. This is, again, consistent with the proposed structure of **3**. An X-ray diffraction analysis of a suitable single crystal was also performed.[20] The molecular structure of **3** is shown in Fig. 1; of note is the 18.5(1)° angle between the planes of the Cp′ and Cp rings. This suggests that **3** possesses significant ring strain and may be a suitable candidate for ROP.



Scheme 1

DSC analysis of **3** revealed an endotherm associated with the melting point at 68 °C and an exotherm due to ROP at 210 °C. When a sample of **3** was heated at 215 °C in a sealed, evacuated Pyrex tube, a yellow fibrous material which was insoluble in common organic solvents was obtained. A small fraction, which was soluble in C_6D_6, was shown to be the ring-opened poly(carbothiaferrocene) **4** by ^1H NMR (see below). GPC analysis of this soluble fraction (in THF) revealed a M_w of *ca.* 6000 with a PDI value of 1.1.

Samples of **3** in C_6D_6 did not undergo ROP under the influence of anionic initiators such as Bu^nLi. However, treatment of both CH_2Cl_2 and C_6D_6 solutions of **3** with methyl triflate, $MeSO_3CF_3$, resulted in a color change from bright red to light orange, followed by the precipitation of a fine yellow powder. ^1H NMR analysis of the soluble fraction demonstrated

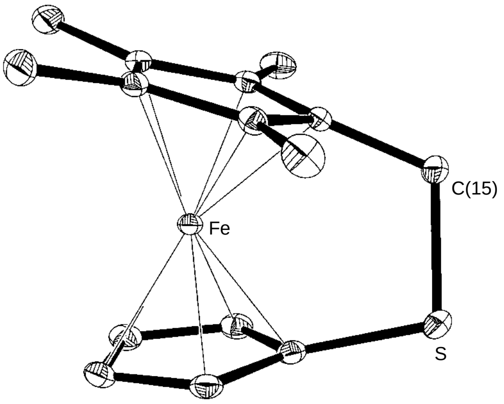


Fig. 1 X-Ray crystal structure of **3**, showing 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe–$Cp_{centroid}$ 1.82(2), C(15)–S 1.844(2), Cp_{ipso}–S 1.783(2), Cp'_{ipso}–C(15) 1.513(3); α (angle between Cp planes) 18.51(14), β_1 [angle between Cp plane and Cp_{ipso}–S bond) 10.9(2), β_2 [angle between Cp′ plane and Cp'_{ipso}–C(15) bond] 9.5(2).

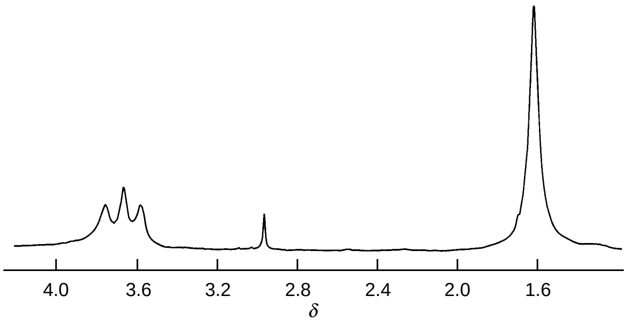


Fig. 2 400 MHz ^{1}H NMR (C_6D_6) of **4** (soluble fraction)

that ROP to yield **4** had indeed occurred (Fig. 2).[21] Of note in the ^{1}H NMR spectrum of **4** is the broad multiplet centered at δ 3.65 which arises from both the Cp and bridging methylene protons as well as the broad resonance centered at δ 1.61 corresponding to the Cp′ methyl protons.

A side reaction of the MeOTf initiated polymerization involved oxidation of the resulting material. In an attempt to circumvent this, initiation of ROP was attempted with the alternative Lewis acid, $BF_3\cdot OEt_2$. Indeed, when a toluene solution of **3** was treated with 0.02 equiv. of $BF_3\cdot OEt_2$, ROP did occur, as evidenced by ^{1}H NMR, the immediate color change of the solution, and the precipitation of **4**. However, unlike the MeOTf initiated polymerization, no oxidation of the polymer was apparent. ^{1}H NMR analysis of the soluble fraction and CP MAS ^{13}C NMR[22] analysis of the bulk material confirmed the presence of **4** and is consistent with the proposed structure. In addition, analysis by mass spectrometry revealed peaks which could be assigned to species possessing oligomeric $[(\eta\text{-}C_5Me_4)Fe(\eta\text{-}C_5H_4)CH_2S]_x$ units where x = 1–3. This again is consistent with the proposed polymeric structure of **4**.

In summary, we have shown that the novel [2]ferrocenophane **3** successfully undergoes both thermal and cationic initiated ROP to afford the polymer **4**, the high molecular mass fraction of which is insoluble in common organic solvents. Future work in this area will involve studies of the ROP mechanism and copolymerization of **4** with other heterocycles in an effort to obtain soluble, high molecular mass materials.

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Notes and References

† E-mail: imanners@alchemy.chem.utoronto.ca

‡ *Crystallographic data* for **3**: $C_{15}H_{18}FeS$, M_w = 286.2, monoclinic, space group $P2_1/c$, a = 8.0787(6), b = 24.179(3), c = 7.5462(10) Å, β = 117.553(7)°, U = 1306.9(2) Å^3, Z = 4, D_c = 1.455 g cm^{-3}, μ = 12.87 cm^{-1}, R_1 (wR_2) = 0.0365(0.975). CCDC 182/807

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19. For **3**: ^{1}H NMR (400 MHz, C_6D_6): δ 4.69 (m, 2 H, η-C_5H_4), 4.17 (s, 2 H, CH_2S), 3.64 (m, 2 H, η-C_5H_4), 2.41 (s, 6 H, η-C_5Me_4), 1.65 (s, 6 H, η-C_5Me_4); ^{13}C NMR (400 MHz, C_6D_6, room temp.): δ 93.7 (Cp$_{ipso}$), 84.7 (η-C_5Me_4), 84.6 (η-C_5H_4), 83.8 (Cp′$_{ipso}$), 81.2 (η-C_5Me_4), 71.2 (η-C_5H_4), 42.6 (CH_2S), 12.3 (η-C_5Me_4), 11.2 (η-C_5Me_4); GC–MS (70 eV): *m/z* (%) 286 (100) [M$^+$], 194 (8) [M$^+$ − 4CH$_3$ − S], 126 (11) [M$^+$ − 4CH$_3$ − CH$_2$ − S − Fe].
20. A crystal of **3** suitable for X-ray diffraction analysis was obtained from a recrystallization in minimal hexanes at −30 °C.
21. For **4**: ^{1}H NMR (400 MHz, C_6D_6): δ 3.65 (br, m, 6 H, η-C_5H_4, CH_2S), 2.95 (br, s, CH_3OTf), 1.61 (br, s, 12 H η-C_5Me_4).
22. For **4**: ^{13}C CP MAS NMR (400 MHz, 8 kHz spin rate): δ 83.6–72.1 (br, m, η-C_5Me_4, η-C_5H_4), 35.9 (br, s, CH_2), 10.4 (br, s, C_5Me_4).

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