Living anionic polymerization of phosphorus-bridged, [1]ferrocenophanes: synthesis and characterization of poly(ferrocenylphosphine) homopolymers and block copolymers

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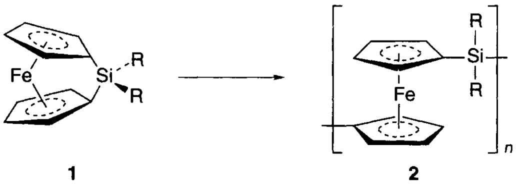
The phosphorus-bridged [1]ferrocenophane Fe(η-C_5H_4)$_2$-PPh undergoes living anionic ring-opening polymerization at 25 °C in THF using Bu^{n}Li as initiator to yield monodisperse poly(ferrocenylphosphines) of controlled molecular mass and novel block copolymers with potentially coordinating phosphorus atoms in one segment.

The development of new synthetic routes to transition-metal-based polymers is attracting significant attention because of the potentially attractive physical and chemical properties associated with these materials.[1,2] With this in mind, we have recently reported the thermal ring-opening polymerization (ROP) of strained, ring-tilted silicon-bridged [1]ferrocenophanes (*e.g.* **1**) to yield high molecular mass (M_n > 10^5) poly(ferrocenylsilanes) (*e.g.* **2**).[3] Subsequent publications have focussed on detailed studies of the electrochemical, magnetic, morphological, and conformational properties of these interesting polymers.[4–11]

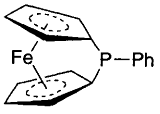
Further work has also led to the extension of the thermal ROP route to other strained [1]- and [2]-metallocenophanes[8,12–14] including phosphorus-bridged [1]ferrocenophanes (*e.g.* **3**[15]) which yield poly(ferrocenylphosphines) **4**.[14] Recently we have reported that silicon-bridged [1]ferrocenophanes such as **1** undergo living anionic ROP which allows access to polymers with controlled molecular masses, end-group structures and block copolymers.[16]

The phosphorus-bridged [1]ferrocenophane **3** can be prepared *via* the reaction of dilithioferrocene·tmeda and $PhPCl_2$ at low temperature in non-polar solvents such as hexanes. Previous attempts to initiate the ROP of **3** using anionic initiators were unsuccessful.† However, low to high molecular mass poly(ferrocenylphosphines) **4** were prepared by Seyferth *et al. via* a reported condensation polymerization of dilithioferrocene, tmeda and $PhPCl_2$ in hexanes at ambient temperature or in ethereal solvents.[17] The formation (in some cases) of high molecular mass materials despite the lack of stoichiometric balance of reactants together with the hindsight provided by the recent discovery that silicon-bridged [1]ferrocenophanes successfully undergo anionic ROP suggested to us that the poly(ferrocenylphosphines) with substantial molecular mass are more likely to result from a chain-growth process, namely the anionic ROP of the [1]ferrocenophane **3** which is generated *in situ* under the reaction conditions used.[18] Here, we report that the anionic ROP of the phosphorus-bridged [1]ferrocenophane **3** can indeed be achieved. Moreover, under carefully controlled conditions we have found that the anionic polymerization is living and allows access to poly(ferrocenylphosphines) with well defined and controlled architectures.

Red, crystalline **3** was prepared according to the literature method[15] and was carefully purified by multiple recrystallizations from hexanes until completely pure by ^{1}H and ^{13}C NMR. Reaction of **3** with various amounts of Bu^{n}Li in THF at 25 °C for 30 min followed by quenching of the living polymer **5** by the addition of H_2O yielded a variety of poly(ferrocenylphosphines) **6** of different chain lengths. As has been noted previously by Seyferth *et al.*[17] and subsequently by us,[14] poly(ferrocenylphosphine) homopolymers do not elute from a styragel gel permeation chromatograph (GPC) column using THF as elution solvent. However, we have previously shown that these polymers can be analysed by GPC after conversion to the corresponding phosphine sulfides *via* reaction with S_8.[14] Thus, samples of all the homopolymers were sulfurized to give poly(ferrocenylphosphine sulfides) **7**. The molecular masses of the polymers could be controlled from $M_n = 2.4 \times 10^3$ to 3.6×10^4 with narrow polydispersities (M_w/M_n = 1.08–1.25) by varying the Bu^{n}Li : **3** ratio from 1 : 11 to 1 : 100 (Table 1). The polymer products **6** and **7** gave ^{31}P, ^{1}H and ^{13}C NMR spectra which were consistent with those previously reported from **4** formed by thermal ROP. The ^{31}P NMR signal at δ −31.7 was attributed to the P^{III} centres in the polymer main chain and is consistent with the literature value.[17] A resonance for the Bu^{n}P(Ph)fc end group can be observed at δ −28.8 while we have attributed the resonance at δ −31.1 to the fcPPhFc terminus [fc = Fe(η-C_5H_4)$_2$, Fc = Fe(η-C_5H_4)(η-C_5H_5)]. The ^{31}P NMR integration for these resonances in runs 1–4 was consistent with the original initiator : monomer ratio in each case.‡



1 **2**



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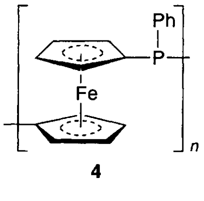

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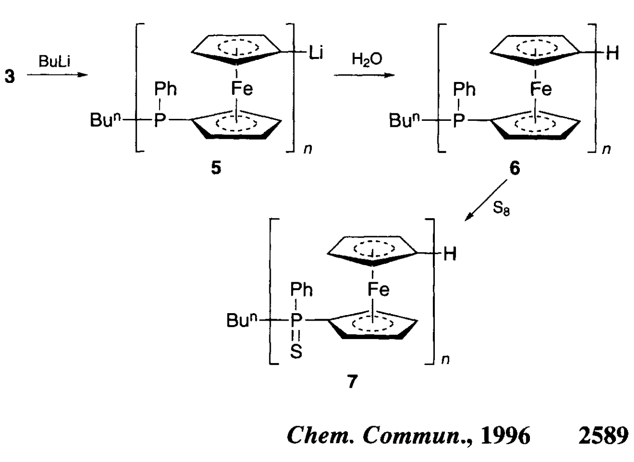

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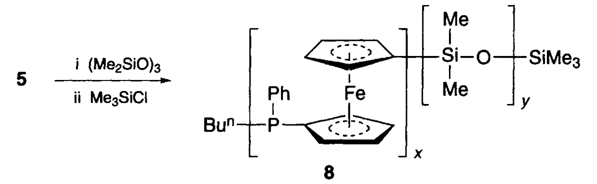
It was also possible to utilize the active end of the living polymer **5** to synthesize novel block copolymers with either poly(dimethylsiloxane) **8** or poly(ferrocenylsilane) **9** segments. The resulting block copolymers were isolated as amber-coloured materials; copolymer **8** was soluble in hexanes whereas **9** was insoluble. Each was analysable by GPC in THF without sulfurization (Table 1). This is probably a consequence of the improved solubility characteristics induced by the presence of the siloxane and ferrocenylsilane blocks.

Block copolymers **8** and **9** were characterized by ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR and all spectra were consistent with the assigned structures. For example, the ^{1}H NMR of **8** showed resonances for the phenyl group (δ 7.0–7.6) and the cyclopentadienyl group (δ 3.9–4.4) of the poly(ferrocenylphosphine) segment as well as a silicon methyl resonance (δ 0.28) for the dimethylsiloxane block. In the ^{29}Si NMR spectrum an intense resonance at δ −21.4 was detected which was assigned to the poly(siloxane) segment as well as small peaks due to the crossover group (fcSiMe$_2$O at δ 0.7) and the end group (OSiMe$_3$ at δ 7.6). The ^{31}P NMR spectrum was consistent with the presence of a poly(ferrocenylphosphine) block consisting of 11 repeat units. The molecular mass distributions of **8** and **9** were monomodal and narrow (Table 1).

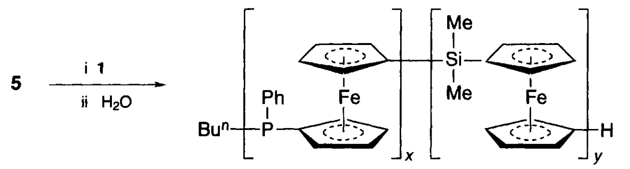
In summary, living anionic ROP of phosphorus-bridged, [1]ferrocenophanes has been achieved and permits access to poly(ferrocenylphosphine) homopolymers and novel block copolymers with segments containing coordinating phosphorus atoms. Further investigations of the properties of these and related materials are in progress and will be reported in due course.



8

$x = 11$

$y = 64$



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$x = 11$

$y = 11$

Table 1 Molecular mass data for sulfurized poly(ferrocenylphosphine) homopolymers and block copolymers from the living anionic ROP of **3**[a]

Polymer	Mole ratio Bu^{n}Li : **3** : x	M_n Calc.	M_n Found	M_w/M_n[b]
7 (run 1)	1 : 11 : —	3.2×10^3	2.4×10^3	1.08
7 (run 2)	1 : 20 : —	5.8×10^3	3.9×10^3	1.08
7 (run 3)	1 : 55 : —	1.6×10^4	1.3×10^4	1.11
7 (run 4)	1 : 100 : —	2.9×10^4	3.6×10^4	1.25
8	1 : 11 : 27[c]	9.2×10^3	8.7×10^3	1.10
9	1 : 11 : 11[d]	5.9×10^3	3.2×10^3	1.08

[a] Polymerizations were run in dry THF at 25 °C under N$_2$. The living ends of the polymers were terminated either *via* the addition of water (polymers **6** and **9**) and precipitation into hexanes or *via* the addition of Me$_3$SiCl (polymer **8**) and precipitation into methanol. [b] Polymer molecular masses were determined by GPC in THF using polystyrene standards for styragel column calibration. For the samples of homopolymer **6**, all polymers were sulfurized to yield **7** before GPC analysis. [c] x = (Me$_2$SiO)$_3$. [d] x = **1** (R = Me).

We would like to thank the Ontario Centre for Materials Research for financial support. We also thank the Natural Sciences and Engineering Research Council of Canada for a postgraduate scholarship for T. J. P.

Footnotes

† The reaction of **3** with anionic initiators yielded oligomers with between 2 and 5 repeat units. No increase in chain length was reported when lower concentrations of anionic initiator were used (see ref. 17).

‡ The resonances in the ^{31}P NMR spectra consist of multiple peaks which we attribute to tacticity effects as the phosphorus atoms are stereocentres. Similar effects have been seen in the ^{29}Si NMR spectra of certain poly(ferrocenylsilane) (see ref. 19).

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Received, 26th June 1996; Com. 6/04449B