Synthesis of a Ferrocene-Based Polymer via Ring-Opening Polymerization

Yizeng Ni and Ian Manners
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 3H6, O N, Canada

John B. Sheridan
Department of Chemistry, Rutgers, The State University of New Jersey, University Heights, Newark, NJ 07102

Richard T. Oakley
Department of Chemistry and Biochemistry, University of Guelph, Guelph N1G 2W1, O N, Canada

The widespread use of synthetic organic polymers in everyday life has led to the development of a range of practical experiments designed for undergraduate laboratories. Although polymers based on inorganic elements are of growing interest (1, 2), apart from the synthesis of poly(dimethylsiloxane) as “silly putty”, easily implemented experiments on these materials are extremely rare. This laboratory experiment involves the synthesis of an unusual organometallic ferrocene-containing monomer and the subsequent ring-opening polymerization (ROP) of this species to afford a high molecular weight organometallic polymer, a poly(ferrocenylsilane), which can be easily handled in air (see Scheme) (3). The ROP can be carried out using transition metal catalysis or, alternatively, thermally (3-6).

The first step involves the lithiation of ferrocene (to give 1) using two equivalents of n-butyl lithium in the presence of tetramethylethylene diamine (TMEDA), which functions as a catalyst, breaking up the less reactive aggregated structures by coordinating to lithium (7). Reaction of 1 with dimethyl dichlorosilane yields the red crystalline [1]ferrocenophane 2 (8). This species has a strained structure in which the cyclopentadienyl ligands are tilted with respect to one another by about 21° (6, 9). Indeed, the strain energy of 2 has been measured to be 80 kJ mol⁻¹ (3). In contrast to 2, ferrocene has cyclopentadienyl ligands that are parallel to one another. The monomer 2 can be isolated as a red-orange crystalline solid or subjected to ROP directly. Transition metal catalyzed polymerization of unpurified 2 to yield the amber-colored poly(ferrocenylsilane) 3 can be performed at 25-80 °C during 2-24 h in solution by the addition of very small amounts of a catalyst such as PtcI₂. Alternatively, the monomer can be isolated and then polymerized by heating to ca. 140 °C under N₂ in an oil bath. The polymer 3 can be isolated by precipitation from toluene or THF into an antisolvent such as hexanes and can be cast into freestanding films again from toluene or THF. After drying, characterization of the poly(ferrocenylsilane) 3 can be achieved by 'H NMR spectroscopy. If available, other techniques such as gel permeation chromatography and differential scanning calorimetry can be used to characterize the molecular weight distribution and the thermal transition behavior of the polymer, respectively. The iron centers of 3 can be readily oxidized by dipping a film of the material into a solution of iodine in hexanes; this leads to a blue coloration, as the material is electrochromic. Reduction of the oxidized films to the neutral amber state can be achieved by dipping the film into a solution of a reducing agent such as methanolic hydrazine. If the equipment is available, cyclic voltammetry gives insight into one of the most interesting characteristics of these polymers. Two reversible oxidation waves are detected, as the iron centers are redox coupled (oxidation of one center makes the neighboring iron centers more difficult to oxidize owing to Fe⁻⁻ Fe interactions) (3, 6).

Most early syntheses of ferrocene-backbone polymers gave very low-molecular-weight products (2, 6). This is a result of the condensation routes used to prepare the materials where an exact 1:1 reaction stoichiometry of difunctional reactants, a necessary condition for the production of high molecular weights, was very difficult to achieve. Indeed, the synthesis of the poly(ferrocenylsilane) 3 via a condensation polymerization of dilitioferrocene-TMEDA with Me₂SiCl₂ in polar solvents such as THF has been reported (10). However, the molecular weight of the product is extremely low (<2,000), which means that the chains are not long enough to take advantage of the processability characteristics of high-molecular-weight polymers (11). When purified 2 is used, the ROP route provides molecular weights of up to 4,000,000. This is an example of a chain-growth type of polymerization that leads to high-molecular-weight polymers much more readily than polycondensation, a step-growth route (11). The mechanisms of the ROP reactions are not known with certainty, but the different possibilities have recently been considered (11). It is also noteworthy that this type of ROP route can be applied to a wide range of strained ferrocenophanes and other strained organometallic monomers (6, 12, 13).

In summary, the experiment illustrates a combination of organometallic and polymer chemistry and a useful principle of polymer synthesis, that chain-growth polymerizations provide easier access to high-molecular-weight polymers than polycondensations.
Experimental Procedure

Ferrocene, n-BuLi, tetramethylethylenediamine (TMEDA), M_2SiCl_2, and PtCl_2 were purchased from Aldrich and used without further purification. The catalyst platinum-divinyltetramethyldisiloxane complex (3–3.5% Pt in vinyl-terminated polydimethylsiloxane) was purchased from Glest Inc., Tullytown, PA. All solvents were used without drying or purification. The reactions were run under N_2, but the polymer can be worked up in air. The dry solid adduct of dilithioferrocene can be reduced to ferrocene with TMEDA, which is pyrophoric in air and we do not recommend its isolation. The use of a vacuum line can be replaced by the use of a water aspirator equipped with a CaCl_2 drying tube.

(a) Dilithiation of Ferrocene: Synthesis of 1

Weigh 2.0 g (11 mmol) of ferrocene and place it in a dry 24/40 round-bottom flask equipped with a side arm. The flask should be predried in a hot (120–150 °C) oven for at least 30 min prior to use. Add 75 mL of hexanes (reagent grade) to the flask from a measuring cylinder followed by 1.6 mL of TMEDA from a plastic disposable 2-mL syringe. Flush the flask with nitrogen gas for 5 min and then place a rubber septum in the 24/40 joint. Using a 20-mL disposable syringe and a 12" (30 cm) syringe needle, measure out 13.5 mL of a 1.6 M butyllithium solution in hexanes and add it quickly to the flask through the septum. The syringe needle should now be rinsed with t-butanol to destroy unreacted n-BuLi, in order to prevent clogging of the needle. The reaction mixture is now left for 12–24 h, during which time the initially cloudy orange solution turns clear red before the precipitation of orange dilithioferrocene. Close the stopcock and ensure that the flask is sealed under a nitrogen atmosphere during the reaction. Note: Excess BuLi must be avoided. Titration of commercial samples may be necessary.

(b) Synthesis of Silaferrocenophane 2

Under a flow of N_2, replace the septum on the flask with a small addition funnel and purge the system with nitrogen gas for 5 min. Caution: Dry flakes of dilithioferrocene may be blown out of the flask and will ignite; ensure that no flammable materials are near the flask. Prepare a solution of dichlorodimethylsilane (1.4 mL) in hexanes (20 mL) and place it in the addition funnel. Cool the flask to ca. 10 °C using an ice/salt bath and slowly add the dimethyldichlorosilane to the orange precipitate over a period of about 20 min with stirring. Continue stirring the reaction at 0 °C for ca. 30 min and then allow the flask to warm to room temperature and stir for a further 30 min. The resulting solution should be red after allowing the LiCl precipitate to settle. (If isolation of 2 is intended, see option 1 below to work up half of the solution.) Remove the solvent in vacuo and dry under vacuum for 30 min. Separation of the solution from the LiCl precipitate is not necessary. At this stage, the product can be left under N_2 for 24 h to 1 week in a freezer.

(c) Platinum-Catalyzed ROP of [1]Silaferrocenophane 2: Synthesis of Poly(ferrocenylsilane) 3

Add 15 mL of toluene to the red residue from (b) above and stir the solution to ensure all of the red oil has dissolved. (Note: insoluble LiCl will still be present). Using a spatula add a few milligrams of PtCl_2 or (preferably) 1 drop of Pt catalyst and place the flask in an oil bath maintained at 80–90 °C on a hot-plate. Ensure that the temperature does not exceed 90 °C, because this leads to poor yields of the polymer. Stir the solution vigorously at this temperature for ca. 2 h, during which time the red suspension fades to orange-amber. Allow the flask to cool to room temperature and proceed immediately with the isolation of the polymer 3.

(d) Isolation of Poly(ferrocenylsilane) 3

Filter the suspension through filter paper on a Buchner funnel. (If the paper becomes clogged, decant the suspension from the funnel, replace the filter paper, and continue filtering.) Rinse the reaction flask and residues on the paper with toluene (5 mL) and add this to the turbid filtrate. Discard the paper and residues and add the filtrate dropwise by pipet to a beaker of hexanes (300 mL) with rapid stirring. The filtrate should be added slowly to dropwise to the edge of the vortex of the vigorously stirred nonsolvent. An orange precipitate of polymer should form. Continue stirring for 10 min and then filter off the polymer on a filter paper (the clear red filtrate contains unreacted ferrocenophane 2 and ferrocene, and can be discarded). Redissolve the polymer in a minimum amount of THF, filter if needed, and precipitate into hexanes (300 mL). Filter off the polymer again, wash the polymer on the filter paper with hexanes (20 mL), and suck air through the orange powder for 10 min to dry it. Weigh the polymer and record your yield (typically 0.5–1.0 g, 20–40% based on ferrocene).

1H NMR data for 3 (dry CDCl_3): 0.51 (s, 6H, Me), 4.08 (t, J_H-H = 1.7 Hz, 4H, Cp), 4.23 (t, J_H-H = 1.7 Hz, 4H, Cp) ppm.

DSC: T_g = 34 °C, T_m = 122–143 °C (not observed for all samples).

GPC (THF vs polystyrene) M_w = 15,000–20,000; M_n typically ca. 10,000.

Cyclic Voltammetry: two reversible oxidation waves at 0.00 and 0.24 V vs ferrocene/ferrocenium in CH_2Cl_2 due to redox coupling between iron atoms.

Option 1: Isolation of [1]Ferrocenophane 2

This can be performed at the same time as part (c). After allowing the LiCl to settle, remove about half of the red hexane solution by cannula (a pipet can be used but a cannula is preferred) to a 250-mL Schlenk flask. Evaporate the solution in vacuo at 25 °C and dry under vacuum for 30 min. Replace the glass stopper with a sublimator or a water-cooled cold finger and heat the flask under vacuum at ca. 50 °C for 10 min. Admit N_2 to the flask, remove the finger, and then wash off the orange ferrocene using hexanes from a wash bottle. Dry the cold finger and replace it in the flask. Continue heating at 70 °C under vacuum for 2 h. Red crystals of the ferrocenophane 2 form on the cold finger. These can be removed and stored in a vial under N_2, preferably in a glove bag. The crystals are moisture sensitive. Note: care should be taken not to heat the sublimation flask above 70 °C because this may melt the material in the flask under N_2 in an oil bath at 140 °C. The material melts at ca. 75 °C and changes from red to orange. The melt becomes first highly viscous and then immobile as polymerization proceeds. Polymer 3 can be dissolved...
in THF and precipitated into hexanes without filtration, using the methodology described in (c). Generally, the lower the purity of \( \mathbf{2} \), the more easily thermal ROP will take place and the lower the molecular weight of the product \( \mathbf{3} \) will be.

**Option 3: Oxidation of Films of Poly(ferrocenylsilane) \( \mathbf{3} \)**

Freestanding amber films of poly(ferrocenylsilane) \( \mathbf{3} \) can be cast on glass in a large Petri dish by thinly spreading a concentrated solution in THF or toluene (ca. 0.4 g of \( \mathbf{3} \) in 1 mL of solvent) and allowing the solvent to evaporate for 2–24 h. The amber films are then dipped in a hexane solution of \( \mathbf{I}_2 \) and the blue-black films are washed with hexanes from a wash bottle. (Care is needed, as oxidation makes the polymer films much more brittle.) The films change color as a result of oxidation of the Fe\( ^{II} \) sites to Fe\( ^{III} \). Reduction back to the amber form can be achieved by dipping the films in a solution of hydrazine in methanol. Alternatively, the redox reactions can be performed with the polymer film attached to a microscope slide, which can be dipped in the solutions.

**Suggested Time Frame**

The experiments in parts (a) to (d) can be run during three successive 3–4-h lab periods, reactions or products being left overnight (or longer) between labs.

Part (a): 3–4-h lab; ca. 45 min work, then leave reaction to form \( \mathbf{1} \) overnight. Part (b): 3–4–h lab; leave dry product \( \mathbf{2} \) overnight. Parts (c, d): 3–4 h lab; leave dry product \( \mathbf{3} \).

**Option 1:** the isolation of \( \mathbf{2} \) can be performed at the same time as part (c). Options 2 and/or 3 and spectral characterization of \( \mathbf{2} \) and \( \mathbf{3} \) could be a 3–4-h lab.

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**Literature Cited**