

Ring-Opening Metathesis Polymerization (ROMP) of an Unsaturated Ferrocenophane Yields Soluble Conjugated Polymers that Contain Ferrocenylene Units in the Backbone

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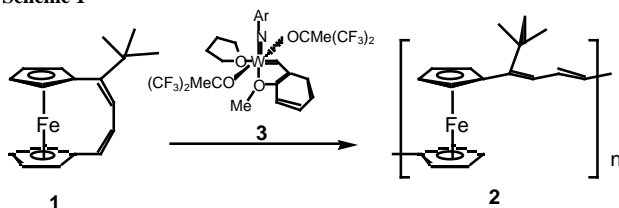
Introduction

Interest in conducting polymers heightened with the discovery that doped polyacetylene can give electrical conductivities as high as some metals.¹ Polyacetylene, however, possesses a number of shortcomings: it is insoluble in most organic solvents and it is unstable to air, heat and light. These shortcomings have spurred the search for new materials that mimic polyacetylene's attractive electrical properties, but with greater solubilities and stabilities.

Conjugated polymers that contain transition metal backbones are a promising class of new materials.² These polymers are expected to combine the electrical conductivity of metals with the strength, flexibility and processability of organic polymers to create new lightweight electronic materials.³ Previous attempts, however, to synthesize these materials has yielded poorly conducting, poorly soluble oligomers (rather than polymers) with limited potential for use as electronic materials.⁴

As a result of these considerations, we are targeting the synthesis of new organometallic polymers that will exhibit good electrical properties yet still be soluble in common organic solvents. We wish to report the successful ring-opening metathesis polymerization (ROMP)^{5,6} of a specifically functionalized ferrocene-containing monomer,⁷ which yields the desired new materials (Scheme 1).

Scheme 1



Results and Discussion

ROMP of 1,1'-((1-*tert*-butyl)1,3-butadienyloxy)ferrocene **1**⁷ yielded soluble high molecular weight polymer **2** having ferrocenylene units in the backbone. We attempted to vary the molecular weights of the polymer by varying the ratio of monomer to catalyst. The results in Table 1 show that we were able to qualitatively adjust the molecular weights of the resulting polymers by changing this ratio. These polymers are stable to air and light, and can be stored without degradation under ambient conditions. Thermogravimetric analysis (TGA) of high molecular weight polymer **2** (M_w 240,000) showed remarkably high thermal stabilities for this new class of materials. The initial onset of degradation occurred at *ca.* 300 °C with substantial mass loss occurring above 550 °C (data not shown).

Table 1. Molecular Weight as a Function of Monomer/Catalyst Ratio

Monomer/Catalyst Ratio	Molecular Weight (M_w)	PDI
20:1	24,474	1.57
50:1	32,566	1.67
75:1	35,555	1.88
100:1	152,247	1.65
200:1	308,550	2.34

The UV/VIS spectra for **1** and **2** revealed a bathochromic shift of λ_{max} upon polymerization (Figure 1). The λ_{max} for monomer **1** and polymer **2** were 240 nm and 320 nm, respectively. Polymer **2** ($\epsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) also absorbed more intensely than monomer **1** ($\epsilon = 4.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). These results suggest that polymer **2** is more highly conjugated than monomer **1**. Conjugation is not possible for monomer **1** because the plane of the olefinic bridge lies perpendicular to the Cp rings. Conjugation is, however, possible for polymer **2**, where the π -orbitals of the olefinic groups have the potential for overlap with those of the Cp rings.

Conclusions

The results reported here demonstrate the synthesis of the first soluble fully conjugated polymers that contain ferrocenylene units in the backbone. Polymer **2** is readily soluble in common organic solvents, which is unprecedented for fully conjugated high molecular weight polymers with ferrocenylene units in the backbone. The polymers are thermally stable and their molecular weight can be controlled by adjusting the ratio of monomer to catalyst. Taken together, these properties suggest a wide range of applications for this new class of materials.

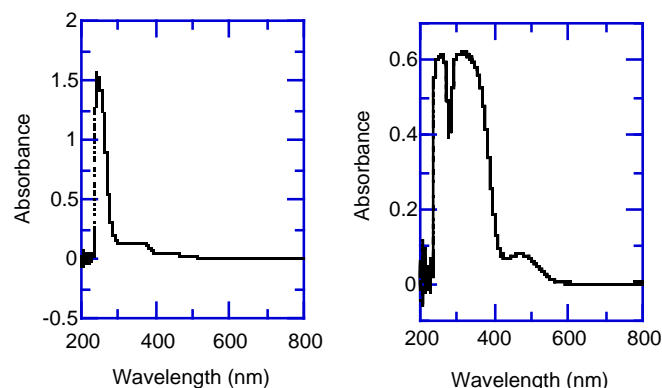


Figure 1. UV/VIS spectra of monomer **1** (left) and polymer **2** (right).

Experimental Section

Polymerization of Monomer 1. Polymerizations were performed under nitrogen in a glove box. A sample (0.21 g) of **1** was placed into a 1 dram vial, and dissolved in a minimum amount of CH_2Cl_2 (*ca.* 2.5 mL). A sample (3 mg) of the tungsten catalyst **3**⁸ dissolved in 1 mL of CH_2Cl_2 was added to this solution. The mixture was allowed to stir at rt for 24 h. Upon consumption of the monomer, the polymerization was terminated with the addition of a few drops of benzaldehyde. For purification, the polymer was first precipitated into methanol and then repeatedly into hexanes from CH_2Cl_2 until the solution containing the precipitate became clear (typically 4 precipitations into hexanes). Removal of the solvent gave a dark rubbery polymer.

Characterization of Polymer 2. Molecular weights were measured using a Waters Gel Permeation Chromatography (GPC) system equipped with two Waters Styragel HR columns and a 410 differential refractometer. GPC samples (3–5 mg/mL) were filtered through a 0.5 μm filter prior to injection into the chromatograph. THF was used as the eluant at a flow rate of 1.0 mL/min. Polystyrene standards purchased from Polysciences were used to calculate a calibration curve of narrow molecular weights from which the molecular weights of the polymers were determined. UV/VIS spectra were obtained on a Varian Cary 3-Bio UV-Visible Spectrophotometer. Spectra were measured for both **1** and **2** in THF over the range of 200–900 nm. The thermal stability of the polymer **2** was examined using a TA Instrument Hi-Res TGA 2950 Thermogravimetric Analyzer. A 12 mg sample of polymer **2** was heated at 0.5 °C/min under a flow of N_2 gas.

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