Soluble Conjugated Polymers That Contain Ferrocenylene Units in the Backbone

Richard W. Heo, Fernando B. Somoza, and T. Randall Lee*

Department of Chemistry, University of Houston
Houston, Texas 77204-5641

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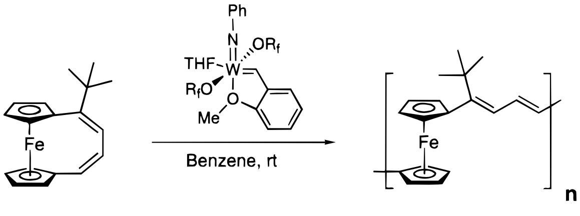
We report the synthesis of a new ferrocenophane, 1,1′-(1-*tert*-butyl-1,3-butadienylene)ferrocene (**1**), and its successful polymerization to yield the first soluble conjugated polymer that contains repeat units of ferrocenylene *in the backbone*. Conjugated polymers that contain transition metals in the backbone have been targeted since the late 1950s because of their potential use as conducting, semiconducting, and/or optoelectronic materials.[1−9] Previous synthetic efforts have led, however, either to oligomeric materials that have poor electrical properties or to polymeric materials that are insoluble and intractable.[10−12] Oligomeric materials are less likely to exhibit the mechanical properties displayed by high molecular weight polymers,[13] and insoluble polymers cannot be readily processed because of difficulties in casting the materials into useful shapes and films. The approach reported here provides convenient solutions to both of these problems.

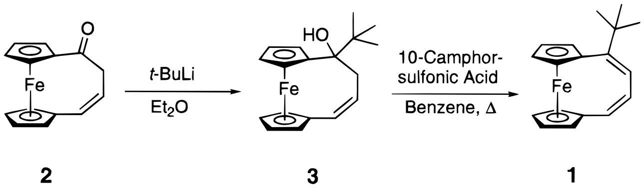
Scheme 1 shows the synthesis of ferrocenophane **1** in two steps from 1,1′-(4-oxo-1-butenylene)ferrocene[14] (**2**). Alkylation of **2** with *tert*-butyllithium followed by dehydration afforded **1** in 43% overall yield.[14] Purification by column chromatography followed by recrystallization from hexane gave large red needles of **1** that are stable in air and soluble in common organic solvents such as benzene, hexane, CH_2Cl_2, and THF.

Ring-opening metathesis polymerization (ROMP)[16] of ferrocenophane **1** by the tungsten-based metathesis catalyst W(=NPh)(=CHPh(2-OMe))($OC(CF_3)_2(CH_3))_2$)(THF)[17] readily generated the conjugated polymer **4** (eq 1).[18] During the polymerizations, the initially red solutions became noticeably darker and more viscous. The resultant deep red polymers are soluble in common organic solvents such as benzene, CH_2Cl_2, and THF. These polymers are stable to the atmosphere and can be stored for long periods of time under ambient conditions without detectable degradation. Polymers having $M_w \leq 100\,000$ are brittle and amorphous, while those with $M_w \geq 300\,000$ are flexible and can be readily peeled from glass slides.[19] Thermogravimetric analysis (TGA) of a high molecular weight sample ($M_w \approx 240\,000$) showed the onset of degradation at ca. 300 °C with substantial mass loss occurring above 550 °C (see the Supporting Information), which suggests remarkably high thermal stabilities for this new class of materials.[11]



1 **4** (1)

Scheme 1. Synthesis of Ferrocenophane **1** from 1,1′-(4-Oxo-1-butenylene)ferrocene **2**[14,15]



We attempted to vary the molecular weight of polymer **4** by adjusting the ratio of monomer to catalyst in a series of polymerizations. Figure 1 shows that the molecular weights increased qualitatively as we increased the ratio; the values of PDI ranged from 1.6 to 2.3.[19] These preliminary results demonstrate that a moderate degree of control over the molecular weight can be achieved. More importantly, the high molecular weights obtained here are unprecedented for soluble conjugated materials with ferrocenylene units in the backbone.

We measured the UV/vis spectra of both **1** and **4** in the range 200−900 nm in an effort to explore the degree of electron delocalization in polymer **4**. For monomer **1**, the π-orbitals of

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(15) Standard procedure for the synthesis **3**: 0.50 g (2.0 mmol) of **2**[14] was placed in a 100-mL Schlenk flask that was thoroughly dried, flushed with argon, and equipped with a magnetic stirbar. To this reaction flask was transferred 60 mL of dry diethyl ether. Upon cooling to 0 °C, 1.7 mL (2.6 mmol) of a solution of *tert*-butyllithium (1.5 M pentane) was transferred dropwise. The reaction flask was slowly allowed to reach room temperature and stirred for an additional 2 h. The ether layer was washed with saturated NH_4Cl and brine to give the crude oily product **3**. Chromatography on silica gel using 5% Et_2O/hexanes ($R_f = 0.25$) gave fine yellow crystals of **3** (0.35 g, 56% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 6.37 (dd, $J = 1.6, 11.2$ Hz, 1 H), 5.76 (ddd, $J = 6.9, 9.1, 11.2$ Hz, 1 H), 3.91−4.26 (m, 8 H), 2.73 (dd, $J = 9.1, 13.0$ Hz, 1 H), 2.56 (ddd, $J = 1.6, 6.9, 13.0$ Hz, 1 H), 1.86 (s, 1 H), 0.89 (s, 9 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 129.0, 128.4, 92.7, 81.1, 71.8, 70.3, 68.9, 68.6, 68.5, 68.2, 67.8, 67.7, 67.0, 38.4, 33.9, 25.3. Standard procedure for the synthesis of **1**: 0.35 g (1.1 mmol) of **3** was dissolved in 20 mL of benzene. In a 200-mL round-bottomed flask equipped with a magnetic stirbar and a reflux condenser were added 130 mL of benzene and 0.46 g (2.0 mmol) of 10-camphorsulfonic acid. To this round-bottomed flask was added dropwise the mixture of **3** in benzene. After the addition was completed, the mixture was refluxed for 2 h, concentrated to 50 mL, and dissolved in 100 mL of hexanes. The solution was washed with saturated NH_4Cl and brine to give a dark solid material. Chromatography on silica gel using hexanes ($R_f = 0.42$) gave fine orange needles of **1** (0.25 g, 76% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 6.28 (d, $J = 12.1$ Hz, 1 H), 5.83 (d, $J = 8.4$ Hz, 1 H), 5.76 (dd, $J = 8.4, 12.1$ Hz, 1 H), 4.05−4.19 (m, 8 H), 0.99 (s, 9 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 150.3, 127.5, 126.2, 117.8, 82.8, 81.1, 70.2, 69.3, 68.9, 68.4, 38.8, 30.4. Anal. Calcd for $C_{18}H_{20}Fe$: C, 73.99; H, 6.90. Found: C, 74.22; H, 6.62.

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S0002-7863(97)02871-0 CCC: $15.00

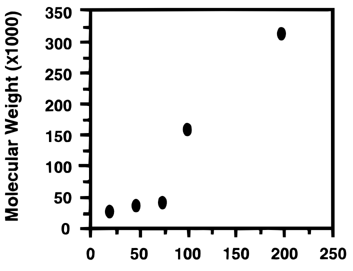

Figure 1. Molecular weights of the polymer can be adjusted by varying the ratio of monomer to catalyst.

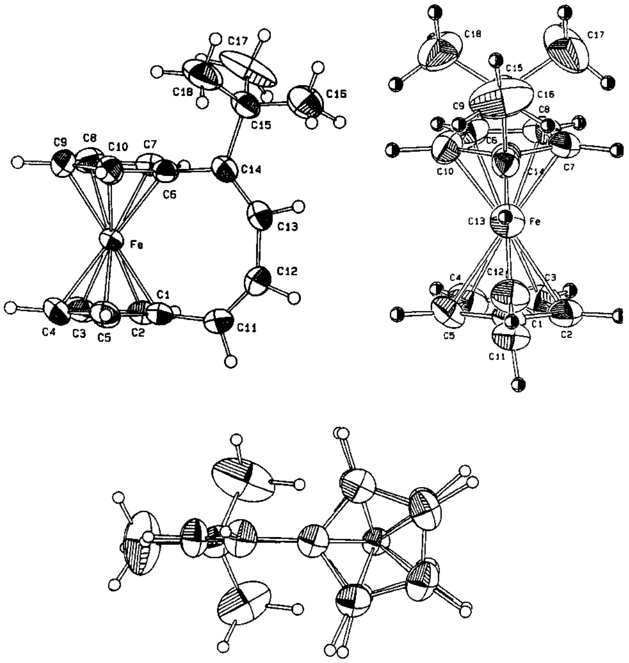

Figure 2. ORTEP drawings (40% probability level) for **1**.

the olefinic groups are perpendicular to those of the Cp groups (see Figure 2); thus, extended overlap is not possible. For polymer **4**, however, these two sets of π-orbitals have the potential to be coplanar; thus, extended overlap is possible. Analysis of the UV/vis spectra for **1** and **4** revealed a bathochromic shift of $\lambda_{\max}$ upon polymerization: $\lambda_{\max}$ for **1** = 240 nm; $\lambda_{\max}$ for **4** = 320 nm (see the Supporting Information). Furthermore, while the monomer exhibited moderately intense absorptions ($\epsilon = 4.5 \times 10^3$ M^{-1} cm^{-1}), the polymeric samples showed stronger absorptions ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}). These results are consistent with a moderate degree of conjugation for polymer **4**.[20] The spectra for **1** and **4** also revealed broad absorptions near 360 and 470 nm resulting from symmetry-forbidden excitations of electrons from the d orbitals of iron. These absorptions, which are red-shifted relative to those of ferrocene, are characteristic of conjugated ferrocenyl moieties.[21]

We characterized the structure of **1** by single-crystal X-ray diffraction.[22] As expected, the *tert*-butyl group stands adjacent to one of the Cp groups (Figure 2). Interestingly, the Cp groups are eclipsed with respect to each other and only slightly tilted (i.e., nearly planar parallel to each other). In the X-ray structure of the parent unsubstituted 1,4-(1,1′-ferrocenediyl)-1,3-butadiene,[23] the Cp groups are staggered and substantially more tilted with respect to each other. Accordingly, the torsion angle of the butadiene bridge in **1** is ca. 2°, while that of the parent compound is substantially larger (ca. 42°).

The strained geometry in **1** likely results from the steric bulk of the *tert*-butyl group, which forces the molecule to adopt a rigid conformation. Support for this hypothesis is provided from the X-ray analysis of 1,1′-(1-methoxy-1,3-butadienylene)ferrocene,[15] which, like **1**, is unsaturated with a sole substituent adjacent to one of the Cp groups. In this derivative, however, the Cp rings are staggered and the torsion angle of the butadiene bridge is similar to that of the parent unsubstituted ferrocenophane. The relatively small size of the methoxy substituent apparently allows this unsaturated ferrocenophane to adopt a more relaxed conformation than that which we observe for **1**.

The apparent strain in **1** coupled with the increased solubility afforded by the incorporation of the *tert*-butyl group[24] permits the generation of conjugated polymers having remarkably high molecular weights. We are currently further exploring the thermal, mechanical, electrical, and structural properties of this promising new class of materials.

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Supporting Information Available: TGA data for **4**, UV/vis and IR spectra for **1** and **4**, and X-ray data for **1** including a summary of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, and bond distances and angles (13 pages). See any current masthead page for ordering and Web access instructions.

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(19) Molecular weights were determined by gel permeation chromatography (GPC) performed on a Waters GPC system equipped with two Waters Styragel HR columns and a 410 differential refractometer. THF was used as the eluant at a flow rate of 1.0 mL/min. Molecular weights were calculated from a calibration curve of narrow molecular weight polystyrene standards purchased from Polysciences. GPC samples (3−5 mg/mL) were filtered through a 0.5-μm filter prior to injection into the chromatograph. Standard procedure for small-scale polymerizations of **1**: These polymerizations were carried out in NMR tubes with monomer and catalyst dissolved in deuterated solvent (C_6D_6 or CD_2Cl_2). To allow complete mixing of the monomer and catalyst, the contents of the tube were gently agitated. The extent of polymerization was monitored by ^{1}H NMR spectroscopy. Polymerization was confirmed by the shifting and broadening of the resonances attributable to the monomer. Polymerizations were terminated with 1−2 drops of benzaldehyde. Standard procedure for bulk polymerizations of **1**: These polymerizations were carried out in 1-dram vials by combining monomer and catalyst dissolved in either CH_2Cl_2 or benzene. Polymerizations were monitored by color and viscosity changes in the solution. Termination of the polymerizations was accomplished by the addition of a few drops of benzaldehyde. Sample polymerization: 3 mg of the tungsten catalyst[17] was dissolved in 1 mL of CH_2Cl_2. To this solution was added 0.21 g of **1** dissolved in a minimum amount of CH_2Cl_2 (ca. 2.5 mL). This mixture was allowed to stir under nitrogen for 24 h and then terminated by the addition of benzaldehyde. 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 four precipitations into hexanes). Removal of the solvent gave a dark rubbery polymer. ^{1}H NMR (300 MHz, C_6H_6): δ 6.35−6.39 (br, 1 H), 5.73−5.90 (br, 2 H), 4.01−4.53 (br, 8 H), 1.02 (br, 9 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 145.8, 144.3, 131.4, 128.8, 127.2, 125.4, 125.1, 85.4, 85.2, 85.0, 72.5, 71.5, 70.1, 70.5, 69.4, 68.1, 67.3, 37.3, 37.5, 31.3, 31.0. Anal. Calcd for $(C_{18}H_{20}Fe)_n$: C, 73.99; H, 6.90. Found: C, 73.76; H, 7.41.

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