Rings and Chains: Synthesis and Characterization of Polyferrocenylmethylene

Tamara Winter, Wasim Haider, Alexander Schießer, Volker Presser, Markus Gallei,* and André Schäfer*

The synthesis and characterization of polyferrocenylmethylene (PFM) starting from dilithium 2,2-bis(cyclopentadienide)propane and a Me2C[1]magnesocenephane is reported. Molecular weights of up to \( M_w = 11700 \text{ g mol}^{-1} \) featuring a dispersity, \( D \), of 1.40 can be achieved. The material is studied by different methods comprising nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectrometry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) measurements elucidating the molecular structure and thermal properties of these novel polymers. Moreover, cyclic voltammetry (CV) reveals quasi-reversible oxidation and reduction behavior and communication between the iron centers. Also, the crystal structure of a related cyclic hexamer is presented.

1. Introduction

In the recent past a unique class of smart and functional materials, so-called metallolpolymers, centered scientific studies for a manifold of applications. The key features of these materials are their fascinating redox-responsive (opto)electronic as well as catalytic switching capabilities. Moreover, as part of more complex polymer architectures such as block copolymers or dendritic polymers also their excellent structure formation and separation characteristic have been shown.[1–8] Within this context, one of the most significant representative in this emerging field is the ferrocene/ferrocenium redox couple. The latter provides a highly reversible (electro)chemical addressability between a rather hydrophobic ferrocene and a more hydrophilic ferrocenium ion.[9–13]

In general, the incorporation of the transition metal into the polymer architecture can occur upon functionalization of the polymer backbone or the redox-active moiety can be laterally bonded to the polymer chains.

A fundamental breakthrough with respect to the synthesis of switchable ferrocene-containing main-chain polymers was the ring-opening polymerization (ROP) of strained metalloacenophanes invented by Manners and co-workers.[2,4,14–16] On the other hand, also side-chain ferrocene-containing polymers attracted enormous attention for many interesting applications. Reviews in these fields are given by Zhou et al.,[2] the Tang's group,[17–19] and other authors.[20,21] Among such ferrocene-containing macromolecules, polyferrocylnilsilanes are a very popular class of compounds.[4,22] They are generally prepared via ring-opening polymerization starting from the corresponding ring-strained Si[1]ferrocenophanes. Although this synthetic route facilitates diverse substituents on the silicon atom and can also be applied to some other ferrocenophanes, it does not allow for the synthesis of a methylene-bridged polyferrocylnaphane, since a C[1]ferrocenophane is unknown and believed to be unstable due to its large ring-strain.[23] To circumvent this difficulty, we explored using s-block metal-based precursors for transmetalation reactions since Cp compounds of s-block metals are versatile Cp transfer reagents.

In this study, we synthesized polyferrocenylmethylene, 1, by transmetalation of dilithium 2,2-bis(cyclopentadienide)propane or Me2C[1]magnesocenephane with iron(II)-bromide and iron(II)-chloride. The obtained materials were fully...
characterized by nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography (SEC), multi-angle light scattering detection (MALLS), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and cyclic voltammetry (CV).

2. Results and Discussion

The synthesis of polyferrocenylmethylene (PFM) 1 was carried out via two different routes, starting either from a C[1]magnesocenophane or the dilithiated 2,2-bis(cyclopentadienide)propane analog and iron(II)-chloride and iron(II)-bromide (Scheme 1).

The reaction was carried out at room temperature to give PFM 1 as a yellow and air-stable solid after workup. The product was soluble in THF and chloroform and insoluble in water, similar to polyferrocenylsilanes. The 1H-NMR spectrum exhibits two signals at $\delta^{1H} = 1.74$ and 4.12 ppm corresponding to the methyl groups and Cp protons, respectively, the latter coinciding with a singlet, similar to what has been observed for the silicon analog poly(ferrocenyldimethylsilane), PFS.[14]

The materials were additionally characterized by size exclusion chromatography (SEC) in THF versus polystyrene standards. The corresponding molecular weight distribution is given in Figure 1, and the obtained data for all samples are compiled in Table 1. From the SEC measurements, it can be concluded that a polyferrocenylmethylene was achieved. Based on both applied synthetic protocols, differences in the obtained molar masses were observed; that is, the cyclopentadiene precursor has a significant influence on the resulting polymers' molecular weight. While the usage of dilithium 2,2-bis(cyclopentadienide)propane lead to molar masses around 2200 g mol$^{-1}$ the corresponding C[1]magnesocenophane yielded higher molar masses in the range of 4000–8000 g mol$^{-1}$ (vs. PS as standard). Comparing the synthesis of batch three and four, as the only difference between both is the usage of the iron precursor, we see that using FeBr$_2$ leads to a lower dispersity of PFM, indicating better control over the reaction.

The 13C-NMR spectrum shows two resonances for the aliphatic carbon atoms at $\delta^{13C} = 30.7$ and 33.5 ppm, and three resonances at $\delta^{13C} = 66.4, 67.7$, and 101.2 ppm corresponding to the aromatic carbon atoms of the Cp groups.

The molar mass distribution of polymers derived via the Me$_2$C[1]Cp$_2$Mg$^+$FeCl$_2$ route revealed a more pronounced second molar mass distribution shifted to lower molar masses. This might result from different mechanisms, which, in the

![Scheme 1. Synthetic routes for the preparation of polyferrocenylmethylen (PFM) 1 (X = Cl and Br).](image)

![Figure 1. A) 1H-NMR spectrum of PFM, 1, in CDCl$_3$; B) Molar mass distribution obtained by size exclusion chromatography (SEC) in THF versus PS standards using different precursors: Me$_2$C[1]Cp$_2$Li$_2$ + FeCl$_2$ (black line), Me$_2$C[1]Cp$_2$Li$_2$ + FeBr$_2$ (blue line), Me$_2$C[1]Cp$_2$Mg + FeCl$_2$ (green line) and Me$_2$C[1]Cp$_2$Mg + FeBr$_2$ (red line).](image)

Table 1. Molar masses and dispersity indices of the synthesized polyferrocenylmethylenes using different cyclopentadienide and iron precursors.

| Precursor            | FeX$_2$ | $M_n$ [g mol$^{-1}$] | $M_w$ [g mol$^{-1}$] | Đ   |
|----------------------|---------|----------------------|----------------------|-----|
| 1 Me$_2$C[1]Cp$_2$Li$_2$ FeCl$_2$ | 2200    | 3000                 | 1.36                 |
| 2 Me$_2$C[1]Cp$_2$Li$_2$ FeBr$_2$ | 2400    | 3400                 | 1.37                 |
| 3 Me$_2$C[1]Cp$_2$Mg FeCl$_2$ | 4300    | 9000                 | 2.09                 |
| 4 Me$_2$C[1]Cp$_2$Mg FeBr$_2$ | 8300    | 11 700               | 1.40                 |

$^a$Determined by size exclusion chromatography in THF versus polystyrene standards.
lithium precursor, promote backbiting and give cyclic oligomers rather than long-chain polymers.

In summary, the molar masses' resulting data vary between 2200–8300 g mol\(^{-1}\), and the dispersity, \(D\), was determined to be in a range of 1.36–2.09. Overall, the reaction of Me\(_2\)C[1]magnesocenophane with iron(II)-bromide gave PFM with the highest molar masses (\(M_n = 8300; M_w = 11700\)). In general, apparent molar masses for metallopolymers by relative methods can strongly deviate from their absolute molar masses.\(^{[24–26]}\) We also expect a difference in the hydrodynamic volume of PFM in THF compared to the values obtained for PS standards. For this purpose, the obtained PFM from the Me\(_2\)C[1]Cp\(_2\)Mg + FeBr\(_2\) reaction was additionally analyzed via SEC MALLS to gain more insights into the absolute molar mass. A corresponding molar mass of \(M_w = 13100\) g mol\(^{-1}\) was obtained. Therefore, it can be concluded that the hydrodynamic volumes of the samples and the PS standards are quite similar, and the SEC measurements are in good agreement.

To further investigate the molecular structure of PFM 1, we performed MALDI-ToF mass spectroscopy. The MALDI-ToF spectrum shows two different domains of cyclic and non-cyclic oligomers, with mass differences of two times the repeating unit (Figure 2).

The material contains at least some cyclic compounds besides the expected linear PFM chains. By extracting 1 with hexane, we separated a batch from which we could grow single crystals suitable for X-ray diffraction analysis. The resulting crystal structure indicates a cyclic hexamer (Figure 3), which has also been observed in the corresponding MALDI-ToF mass spectrum before.

The bonding situation of the ferrocene units in this hexameric macrocycle resembles unsubstituted ferrocene,\(^{[27–29]}\) with Fe-C\(_{\text{cent}}\) bond lengths of 165.5 pm, Fe-C\(_{\text{Cp}}\) bond length of 204.5–207.2 pm, and a C\(_{\text{cent}}\)-Fe-C\(_{\text{cent}}\) angle of 178.1°. A hexameric macrocycle of ferrocene moieties directly linked together has been reported by Albrecht and Long et al. in 2016 and shares similar bonding properties.\(^{[30]}\)

Moreover, metal-containing polymers can be used as preceramic materials, paving the way for a manifold of applications.\(^{[31–33]}\) Thus, the herein presented iron-containing polymers were further analyzed regarding their thermal properties and the residues after ceramization by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The corresponding TGA curves of the PFM under synthetic air (10% O\(_2\) and 90% N\(_2\)) and under a nitrogen atmosphere in a temperature range of 30 to 600 °C and the DSC thermogram are given in Figure S1 (Supporting Information). As seen from the
In the presence of oxygen, degradation starts at around 285 °C and at 350 °C in a nitrogen atmosphere (340 °C). In nitrogen, we also see a more distinct weight loss of up to 460 °C. At the end of the measurement, no further decomposition was observed, and the residual weight reached a constant value at higher temperatures for the synthetic air (410 °C) and the sample treated in a nitrogen atmosphere (480 °C).

A relatively high ceramic yield (compared to other linear ferrocene-containing polymers) was obtained under both conditions,[38-40] resulting in a final residue of ≈29 wt% (N2) and 35 wt% (synthetic air). While the oxygen treated sample changed from an initial orange to a more red-brownish powder, the sample treated under a nitrogen atmosphere presents a black material, presumably due to carbon. Both samples showed a magnetic response, as demonstrated by tracking the obtained powder with a magnet.

To give more insights into these materials' chemical structure and composition, X-ray diffraction (XRD) measurements of the obtained residues were carried out after thermal treatment (Figure S2, Supporting Information). The XRD pattern of the oxygen treated sample indicates the transformation into α-Fe2O3 (hematite), showing a trigonal crystal system with a corresponding hR3c space group and lattice parameters of a = 5.03 Å and c = 13.74 Å. Compared to this, the samples treated under a nitrogen atmosphere leads to a combination of elemental iron (sharp reflections at 45°, 65°, and 82° 2θ) and iron carbide. Besides the TGA, the pristine polymer's DSC thermogram revealed a glass transition temperature (Tg) at 60.5 °C.

In previous studies on different PFS structures, the Manners group showed that the Tg of the corresponding polymer depends on the appropriate substituents located at the silicon atom in the polymer main chain.[22] They demonstrated in detail that a relatively high Tg (above room temperature) is observed for methyl substituents due to the ferrocene moieties' static behavior or rather the cyclopentadiene rings. Compared to these findings, the obtained glass transition temperature of the herein presented polyferrocenylmethylene is in good agreement with expectations.

The metal atom within the PFM structure renders these materials to a functional material with redox-mediated switching capabilities. Therefore, the redox-responsiveness of the herein synthesized PFM was investigated by electrochemical means. For this purpose, the mixture containing linear polymer chains of PFM as well as cyclic components were analyzed by cyclic voltammetry (CV) measurements using a 0.1 M solution of tetraethylammonium hexafluorophosphate as the electrolyte in either acetonitrile (ACN) or THF in the potential range of −0.1 to +1.3 V versus Ag/AgCl and referenced by using the solvent signals.[37] Elemental analysis was performed on an Elementaranalysator vario MICRO cube. Single crystal X-ray diffraction analysis was carried out at low temperatures on a Bruker AXS D8 Venture diffractometer. Structure solution and refinement were performed using SHELXL[38].

Cyclic voltammetry (CV) measurements were carried out on a Et3Al3+ potentiostat (Belttec) using PStrace 5.5 as software to collect the data. All measurements were acquired using an Ag/AgCl reference electrode, a platinum counter electrode, and a glassy carbon working electrode with an inner diameter of 5 mm. The scan rate was varied at 25–50 mV s⁻¹ in a range of −0.1 to +1.3 V for oxidation and reduction experiments and calibrated versus ferrocene. For CV measurements,
a five-necked round-bottom flask was used with a solution of tetra n-butyl ammonium hexafluorophosphate ((nBu₄N)PF₆) (0.1 M) in degassed tetrahydrofuran or acetonitrile as an electrolyte. Matrix-assisted laser desorption/ionization (MALDI) spectra were recorded with a Bruker Daltonik Autoflex speed TOF/TOF. The analyzer was a time-of-flight mass spectrometer. For the matrix the nonpolar, aprotic 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) and AgTFA were used.

For evaluating the thermal properties, thermogravimetric analysis (TGA) was applied by using a Netzsch TGA 209 F1 Libra with a heating rate of 20 K min⁻¹ in a range of 30–600 °C in nitrogen or synthetic air (10% O₂ and 90% N₂) atmosphere. Differential scanning calorimetry (DSC) measurements were carried out with a Netzsch Polyma DSC 214 from −160 to +300 °C.

Standard size exclusion chromatography (SEC) was performed with a system composed of a 1260 Infinity II (Agilent Technologies), a 1260 UV detector (G7114A) at 260 nm (Agilent Technologies), and a 1260 RI detector (G7162A) at 35 °C (Agilent Technologies), THF as the mobile phase (flow rate 1 mL min⁻¹) on a SDV column set from polymer standard service (PSS) (SDV 10⁴ Å, SDV 10⁵ Å, and SDV 10⁶ Å). Calibration was carried out using PS standards from PSS. X-ray diffraction of the final residues after the thermogravimetric analysis was acquired with a D8 Discover diffractometer (Bruker AXS) using a copper source (Cu-Kα, 40 kV, 40 mA), a Göbel mirror, and a 0.5 mm point focus. Data were collected with a 2D VANTEC-500 detector covering an angle range of 20° to 80°. Four frames were recorded at 5° positions of 20°, 40°, 60°, and 80° using a measurement time of 2500 s for each frame.

**Synthesis of Polyferrocenylmethylene (PFM) 1**

The synthesis was carried out under an argon 5.0 inert gas atmosphere using dry solvent. **Method A:** Dilithium 2,2-bis(cyclopentadienide)propane (Me₂C[1]Cp₂Li₂) (1.0 g, 5.43 mmol) and iron(II)-chloride (0.7 g, 5.43 mmol) or iron(II)-bromide (1.2 g, 5.43 mmol) were charged into a Schlenk flask. 100 mL of THF were added, and the resulting mixture was stirred overnight under an inert gas atmosphere at ambient temperature, turning from yellow to red/brown. Subsequently, the reaction mixture was poured into 200 mL of an ice-cold hexane/methanol/water mixture (10:9:1 by volume), resulting in the precipitation of the product collected by filtration, washed several times with water, and vacuum-dried. After drying in vacuum at 80 °C for 3 h a pale-yellow powder was observed (Yield: from FeCl₂: 12 mg; from FeBr₂: 115 mg).

**Method B:** Me₂C[1]Magnesocenophane (Me₂C[1]Cp₂Mg) (1.5 g, 7.88 mmol) and iron(II)-chloride (1.0 g, 5.43 mmol)
or iron(II)-bromide (1.0 g, 4.63 mmol) were charged into a Schlenk flask. 100 mL of THF were added, and the resulting mixture was stirred overnight under an inert gas atmosphere at ambient temperature, turning from yellow to red/brown. Isolation and workup were identical to what is described in Method A (Yield: from FeCl₃: 100 mg; from FeBr₂: 396 mg).

Elemental analysis for C₃H₁₃Fe: calculated: 69.06 at% C, 6.24 at% H; found: 66.18 at% C, 6.09 at% H (low-carbon values were repeatedly and reproducibly observed upon analysis of different samples and have been described before in case of polyferrocenylsilanes[10,11].

1H NMR (400.13 MHz, CDCl₃, δ): 4.12 (br s, 8H, Cp-H), 1.74 (br s, 6H, CH₃).

13C NMR (100.62 MHz, CDCl₃, δ): 101.2 (Cp), 67.7 (Cp), 66.4 (Cp), 33.5 (C(CH₃)₂).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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