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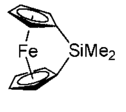
Ring-Opening Polymerization of a Galla[1]ferrocenophane: A Gallium-Bridged Polyferrocene with Observable Tacticity

Bidraha Bagh,† Joe B. Gilroy,‡ Anne Staubitz,‡ and Jens Müller*,†

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan S7N 5C9, Canada, and School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom

Received December 17, 2009; E-mail: jens.mueller@usask.ca

Since Manners et al. reported that thermal ring-opening polymerization (ROP) of dimethylsila[1]ferrocenophane (**1**) yields high-molecular-weight poly(ferrocenyldimethylsilane) (**2**),[1a] the tool box for ROP of strained sandwich compounds has been developed significantly.[1] To date, in addition to thermal ROP, transition metal catalyzed-, anionic-, and photocontrolled ROP of metallacyclophanes are described in the literature.[1c] The latter two methods are of particular interest as they can be performed as living polymerizations, which give access to block copolymers.



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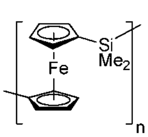

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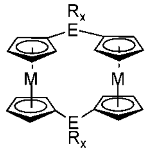

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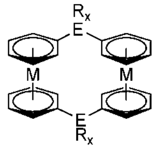

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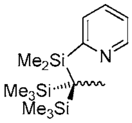
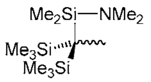
Poly(ferrocenylsilanes) are functional materials applicable as plasma-etch resists for nanopatterning,[2] precursors to ceramics,[3] a tunable component of photonic crystals displays (photonic ink),[4] redox-tunable surfaces,[5] and polyelectrolyte capsules with redox-dependable permeability.[6] Block copolymers in block-selective solvents allow control of different micelle morphologies, and poly(ferrocenyldimethylsilane) (**2**) containing block copolymers, which form cylindrical micelles with semicrystalline cores,[7] show significant promise for future applications in nanotechnology.[8]

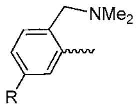
Despite these recent advances, the number of well-defined metallopolymers is still quite restricted. Recently, we synthesized strained sandwich compounds with aluminum or gallium in bridging positions with the aim of developing new polymeric materials through ROP.[9] In this paper, we describe the first, well-characterized polyferrocene with gallium in bridging positions.[10] In depth NMR spectroscopy studies reveal that this air-stable organometallic polymer shows a surprising sensitivity toward the stereochemistry of the polymer backbone.



Pytsi

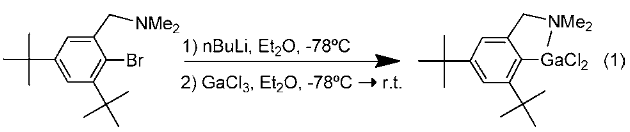


Me$_2$Ntsi



R = H (**Ar′**), *t*Bu (**p-*t*BuAr′**)

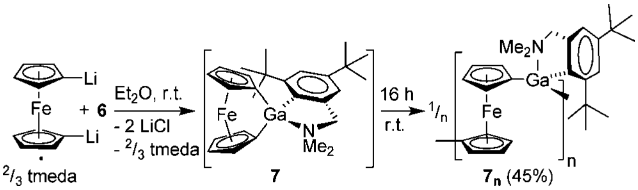
All known strained Al- or Ga-bridged [1]metallacyclophanes[9] were equipped with the bulky, intramolecularly coordinating, *trisyl*-based ligands **Pytsi** or **Me$_2$Ntsi**. However, ROP attempts with these [1]ferrocenophanes and [1]ruthenocenophanes either failed or resulted in sluggish polymerizations.[9e] On the other hand, employing the "one-armed phenyl" ligand **Ar′** or **p-*t*BuAr′** gave [1.1]metallacyclophanes as the only isolatable products [**3** (M = Fe) and **4** (M = Cr, Mo)].[11] Obviously, the bulkiness of the group-13 bound ligand has a major effect on the outcome of reactions between a dilithiated sandwich species and an aluminum or gallium dihalide. Within this paper, we report on results obtained using a new "one-armed phenyl" ligand designed to incorporate steric bulk.



5 **6** (79%)

Starting from commercially available 3,5-di-*tert*-butyl-toluene, the known amine **5**[12] was prepared in three steps (eq 1), from which the gallium dichloride **6** was obtained as an analytically pure solid (see Supporting Information (SI) for details). Species **6** reacted readily with dilithioferrocene to form the targeted galla[1]ferrocenophane **7** as an intermediate (Scheme 1).

Scheme 1. Synthesis of Intermediate **7** and Polymer **7$_\mathrm{n}$**



Attempts to isolate this new strained sandwich compound **7** gave an orange powder, which was characterized as the poly(ferrocenylgallane) **7$_\mathrm{n}$**. The formation of species **7** was confirmed by ^{1}H NMR spectroscopy studies. If the Et$_2$O from an aliquot of the reaction mixture, taken after ca. 15 min, was quickly replaced by C$_6$D$_6$, intermediate **7** was observed by ^{1}H NMR spectroscopy with resonances in the typical Cp range at δ 4.69 (4 β-H), 4.56 (2 α-H), and 4.01 (2 α-H). This pattern and the chemical shifts match very well with other gallium-bridged [1]ferrocenophanes we have characterized previously [bridging moiety Ga(Pytsi):[9b] δ 4.65 (2 β-H), 4.61 (2 β-H), 4.45 (2 α-H), 4.08 (2 α-H); or Ga(Me$_2$Ntsi):[9c] δ 4.54 (4 β-H), 4.24 (2 α-H), 3.90 (2 α-H)].

Polymer **7$_\mathrm{n}$** was purified by precipitation into MeOH (45% isolated yield) and characterized by elemental analysis, GPC, DLS, WAXS, DSC, TGA, CV, UV/vis, ^{1}H and ^{13}C NMR spectroscopy (SI). Material **7$_\mathrm{n}$** is an amorphous polymer with a glass transition at 205 °C. The polymer is thermally robust as it retained 98% of its mass at 340 °C; further heating to 600 °C gave a nonmagnetic char with a low yield of 14% (TGA). Electrochemical studies (cyclic voltammetry) revealed two poorly resolved oxidation waves and one broad reduction wave. The midpoint between the main redox waves was found at −0.047 V versus the couple FeCp$_2$/FeCp$_2^+$.

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† University of Saskatchewan.
‡ University of Bristol.

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GPC analysis showed a broad peak corresponding to an M_w of 48 kDa ($DP_w = 96$, PDI = 3.3) with respect to polystyrene. Dynamic light scattering of $\mathbf{7_n}$ resulted in a hydrodynamic radius of 2.99 ± 0.36 nm. Assuming that $\mathbf{7_n}$ can be described as a random coil, with CH_2Cl_2 being a good solvent, this R_h value gives a radius of gyration of 6.13 ± 0.74 nm ($R_g/R_h = 2.05$),[13] which translates into an M_w of 36 kDa ($DP_w = 72$) with respect to poly(ferrocenyldimethylsilane).[14]

^{1}H NMR spectra of $\mathbf{7_n}$ showed broad peaks relative to those of the monomer **7**, with some peaks exhibiting a rich fine structure. For example, the *t*Bu group *para* to gallium appears as a singlet (δ 1.32), whereas the *t*Bu group *ortho* to gallium is split into 10 signals (centered at δ 1.53). This *ortho*-*t*Bu group is oriented toward the polymer backbone and acts as a fine sensor for the tacticity of $\mathbf{7_n}$. As shown in Figure 1, the 10 peaks can be sorted into three groups with 3, 4, and 3 singlets, respectively (see A, B, and C in Figure 1). Every Ga atom in polymer $\mathbf{7_n}$ is a stereogenic center, and neighboring Ga atoms could have either the same or a different chirality, leading to *racemo* or *meso* diads. For three repeat units, three different arrangements are possible, which are illustrated in Figure 1. The splitting of the signal of the *ortho*-*t*Bu group into the three groups A, B, and C is due to a triad sensitivity. The approximate intensity ratio between those three groups is 1:2:1, indicating that $\mathbf{7_n}$ is a polymer with a statistical distribution of stereogenic centers; hence, signal B can be assigned to heterotactic triads *mr* and *rm*. The fine structure in A, B, and C can be explained by a further sensitivity toward pentads.

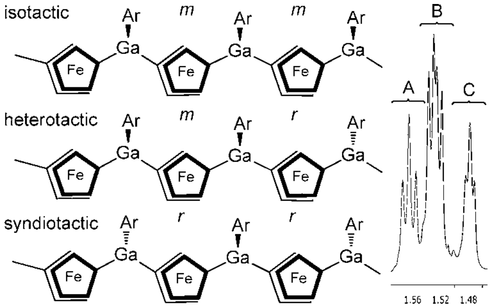

Figure 1. Illustration of different triads in $\mathbf{7_n}$ (the NMe_2 group at the aryl ligand is omitted for clarity). ^{1}H NMR signal of the *ortho*-*t*Bu group of $\mathbf{7_n}$ exhibiting pentad resolution (intensity ratio A/B/C $\approx$ 1:2:1).

An extension from three to five repeat units results in 16 possible pentads, from which 10 are distinguishable.[15] In case of a polymer with a statistical distribution of stereogenic centers, isotactic and syndiotactic triads both result in four pentads from which three are distinguishable giving a distribution ratio of 1:2:1 (A and C in Figure 1). In contrast, the heterotactic triad results in eight pentads with four being distinguishable giving a distribution ratio of 2:2:2:2 (B in Figure 1). Expectedly, the signal pattern of the ferrocene units is more complex than that of the *ortho*-*t*Bu group. The Cp protons could show a diad or tetrad sensitivity, with the latter being the pendant to the pentad sensitivity of the *t*Bu group. A diad sensitivity in the form of two sets of four Cp signals in an approximately 1:1 intensity ratio can be clearly seen in ^{1}H NMR spectra of $\mathbf{7_n}$. Some of the individual peaks show an additional fine structure, but a full resolution into tetrads was not observed. The $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{7_n}$ is similarly complex as the proton spectrum. For example, while the tertiary carbon atom of the *para*-*t*Bu group gives one resonance only, that of the *ortho*-*t*Bu group gives three signals (triad resolution).

In summary, all attempts to synthesize the strained [1]ferrocenophane **7** resulted in the isolation of the air-stable poly(ferrocenylgallane) $\mathbf{7_n}$. However, ^{1}H NMR spectroscopy revealed that the targeted monomer is first formed and one can assume that a spontaneous ROP results in $\mathbf{7_n}$. This behavior is reminiscent of the chemistry of phospha- and stanna[1]ferrocenophanes.[1b,c,16] Interestingly, one of the two *t*Bu groups of the ligand points toward the polymer backbone and serves as a very sensitive probe of the polymer stereochemistry.[17] Polymer $\mathbf{7_n}$ is thermally robust and can be purified and handled under ambient conditions, making it an ideal candidate for incorporation into polymer based materials offering an alternative to existing polyferrocenes. Future work will focus on the isolation of monomers such as **7**, toward the realization of well-defined poly(ferrocenylgallanes) via living ROP methodologies.

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Supporting Information Available: Experimental section for **5**, **6**, and $\mathbf{7_n}$; ^{1}H NMR spectrum of **7**; spectra and diagrams for $\mathbf{7_n}$ (NMR, GPC, DLS, WAXS, DSC, TGA, CV). This material is available free of charge via the Internet at http://pubs.acs.org.

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