Macromolecules **2008,** *41,* 539−547

Articles

Soluble Poly(ferrocenylenevinylene) with *t*-Butyl Substituents on the Cyclopentadienyl Ligands via Ring-Opening Metathesis Polymerization

Georgeta Masson,[†] Alan J. Lough,[†] and Ian Manners*[,†,‡]

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada, and School of Chemistry, University of Bristol, Bristol BS8 1TS, England

Received May 7, 2007; Revised Manuscript Received October 2, 2007

ABSTRACT: Soluble poly(ferrocenylenevinylene) (PFV) **6** was synthesized via ring-opening metathesis polymerization (ROMP) of *ansa*-(vinylene)ferrocene $Fe(\eta\text{-}C_5H_3{}^tBu)_2C_2H_2$ (**5**) with ^{t}Bu substituents on the cyclopentadienyl (Cp) ligands. Monomer **5** was obtained through intramolecular dicarbonyl coupling of the corresponding ferrocene-dicarbaldehyde, 1,1′-di-*t*-butyl-3,3′-dicarbaldehyde, $Fe(\eta\text{-}C_5H_3{}^tBu)(CHO)_2$ (**4**) in the presence of the McMurry reagent. Both monomer precursor **4** and monomer **5** were structurally characterized by ^{1}H and ^{13}C NMR spectroscopy, X-ray crystallography, mass spectrometry, and elemental analysis. ROMP of **5** was investigated using molybdenum-based (Schrock-type) and ruthenium-based (Grubbs-type) initiators under various conditions and was monitored by ^{1}H NMR spectroscopy. Soluble polymers with low or high molecular weight were obtained and completely characterized. Photolytic and thermal ring-opening polymerizations of **5** were also attempted, but only unreacted monomer was isolated under these conditions. The electronic structure of polymer **6** was explored using UV−vis spectroscopy, and evidence for moderate rather than extensive electron delocalization was revealed. Redox reversibility was probed by cyclic voltammetry (CV) for both monomer **5** and polymer **6**. The electron-donating effect of the ^{t}Bu groups substituted to the Cp ligands was signaled by the negative shift of the oxidation potentials, and the electronic interaction between the iron centers in the polymer backbone was also evaluated using CV.

Introduction

Since the discovery of the electrical conductivity of polyacetylene films upon chemical doping with oxidizing or reducing agents,[1] conjugated polymers have been extensively studied in both academic and industrial settings. These materials have a vast number of areas of application such as organic light-emitting diodes, nonlinear optics, or charge dissipation films.[2] More recently, driven by the possibility of coupling the characteristics of metal centers with those of delocalized organic materials and, consequently, providing additional functionality such as luminescence, redox, or catalytic activity, an important class of new materials has been developed by introducing metals into conjugated polymers. A considerable number of metal-containing conjugated polymers has been synthesized and reported to date, and they can be classified on the basis of the possible arrangements of metal centers relative to the polymer backbone. Thus, the metal centers can be located in the side chain linked to the polymer backbone or integrated directly in the main chain.[3] Although side chain metal-containing polymers are sufficient for some applications, incorporation of the metal atoms in polymer main chain leads to the most profound influence on properties and affords materials with characteristics arising from electronic interactions between the metal centers and the conjugated organic spacer.[3a]

The main synthetic protocols used to prepare conjugated polymers containing metal centers in a polymer backbone are either step-growth polycondensation,[4] chain-growth ring-opening polymerization (ROP),[3b] or electropolymerization.[5] While condensation routes generally lead to low molecular weight materials and electropolymerization is restricted to a certain class of monomers, ROP has been proven to be a versatile method permitting the access to well-characterized high molecular weight polymers with skeletal metal atoms. ROP of strained metallocenophanes has been most intensively studied. This research area initially involved studies of silicon-bridged [1]-ferrocenophane monomers in the early 1990s[6] and later was further expanded to monomers containing other bridging elements, transition metals, or π-hydrocarbon rings[7,8] as well as to controlled polymerization methodologies such as living anionic[9] and transition metal-catalyzed ROP.[10,11]

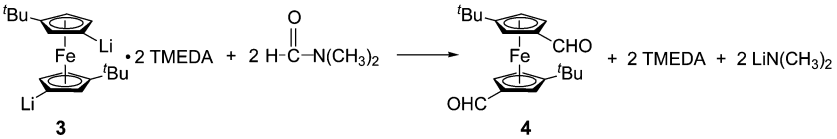
Transition metal-catalyzed ROMP generates polymers in which the double bonds present in the monomer are formally preserved upon conversion into macromolecular chains. Also, ROMP permits the synthesis of polymers with controlled molecular weights and the preparation of well-defined block copolymers as well as the incorporation of chemical functionalities.[12] In an effort to develop conjugated organometallic polymers by ROMP, unsaturated ferrocenophanes are attractive targets[11,13] due to the convenient air and thermal stability of ferrocene derivatives[14] that would be expected to make the resultant materials easy to handle. In addition, ferrocene can

---

* Corresponding author. E-mail: Ian.Manners@Bris.ac.uk.
[†] University of Toronto.
[‡] University of Bristol.

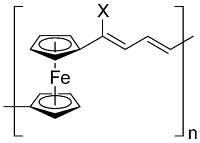
10.1021/ma071034v CCC: $40.75

Scheme 1



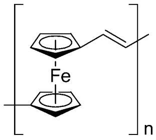
be relatively easily functionalized[15] and offers a wide range of interesting properties including redox activity.[16]

To date, several examples of conjugated ferrocene-based polymers synthesized by ROMP of vinylene-bridged [2]ferrocenophanes and diene-bridged [4]ferrocenophanes have been reported, but only in the case of the latter were soluble polymers with high molecular weight obtained.[11a,17] Early work using this synthetic approach involved the preparation of poly(ferrocenylenedivinylene) (PFDV) **1a** that was either insoluble or impossible to characterize due to the hydrolysis of the vinyl ether group.[18] The first soluble high molecular weight conjugated polymer-containing ferrocene units in the main chain were reported by Lee et al.[11a] when 1,1′-(1-*t*-butyl-1,3-butadienylene)ferrocene was polymerized in the presence of a tungsten-based metathesis initiator. To enhance the electrical conductivity of this class of polymers, the same group successfully prepared other high molecular weight soluble PFDV derivatives in which the solubilizing *t*-butyl group was replaced by aromatic substituents such as phenyl or mesityl (**1b**).[17] However, the groups on the bridging elements do not affect the redox properties of ferrocene units. ROMP of a vinylene-bridged [2]ferrocenophane in the presence of a molybdenum-based initiator gave poly(ferrocenylenevinylene) (PFV) **2** as an insoluble orange powder.[11b] Moderate solubility was achieved by incorporating *ansa*-(vinylene)ferrocene as a second block in a block copolymer with norbornene, allowing characterization by NMR spectroscopy, GPC, and cyclic voltammetry (CV).[11b] However, studies of high molecular weight PFV were limited by the poor solubility.



1a, X = H, OCH$_3$

1b, X = ^{t}Bu, Ph, Mes



2

In the present work, we report on the synthesis and characterization of an analogous soluble electron-rich PFV. We have addressed the solubility limitations of PFV by introducing *t*-butyl groups on the Cp ligands of *ansa*-(vinylene)ferrocene followed by ROMP. At the same time, the presence of the electron-donating *t*-butyl groups on the Cp rings was expected to affect the electrochemical properties of both monomer and polymer. Therefore, to probe the electron delocalization and electron-donating effect of the *t*-butyl groups, we also report on the properties of both the monomer and resulting polymer investigated by UV−vis spectroscopy and CV.

Results and Discussion

Synthesis and Characterization of Fe(η-C$_5$H$_3$^{t}Bu)$_2$C$_2$H$_2$. The synthesis of an *ansa*-(vinylene)ferrocene with ^{t}Bu substitutents on Cp ligands (**5**) was achieved through a titanium-induced dicarbonyl coupling reaction[19] of the corresponding ^{t}Bu substituted ferrocene-dicarbaldehyde. Therefore, 1,1′-di-*t*-butyl-3,3′-dicarbaldehyde (**4**) was first prepared following a similar procedure to that reported by Balavoine et al.[20] and was obtained from 1,1′-di-*t*-butyl-3,3′-dilithioferrocene chelated with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), Fe(η-C$_5$H$_3$^{t}BuLi)$_2$•2TMEDA (**3**) in a reaction with *N*,*N*-dimethylformamide (DMF) in diethyl ether followed by hydrolysis and extraction with dichloromethane. The pure product was obtained as a red solid in 75% yield after drying the organic phase resulting from extraction over MgSO$_4$ and crystallization from cyclohexane (Scheme 1).

We used ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis to confirm the chemical structure of **4**. The ^{1}H NMR spectrum displayed Cp, ^{t}Bu, and carbaldehyde protons at expected chemical shifts in correct integration ratios. The ^{13}C NMR spectrum showed the characteristic downfield resonance for the carbonyl group at 192.2 ppm, five distinct resonances for Cp ligands, and two other resonances for ^{t}Bu carbons. A typical downfield resonance of *ipso*-Cp carbon atoms attached to the ^{t}Bu groups[21] relative to the conventional values of chemical shifts for Cp carbons (60−80 ppm) appeared at 107.8 ppm.

The molecular structure of **4** was also confirmed by a single-crystal X-ray analysis (Figure 1). In contrast to the non-alkylated analogue, 1,1′-ferrocene-dicarbaldehyde, which adopts two conformations with different torsional angles,[22] a single geometry was found for **4** having parallel eclipsed Cp rings with an anti arrangement for the ^{t}Bu substituents (torsional angle 140°) and a syn arrangement for the CHO groups (torsional angle 68.3°) so that the steric hindrance was minimized. Bond parameters were found in the expected ranges. One molecule of cyclohexane per two molecules of **4** was found in the crystal lattice representing the difference in the molecular weight found by mass spectrometry (see Experimental Procedures) and that reported by X-ray analysis (Table 3).

The ^{t}Bu substituted *ansa*-(vinylene)ferrocene **5** was synthesized by intramolecular coupling of carbonyl groups of **4** in the presence of the McMurry reagent[19] (Scheme 2) following a similar procedure to that reported by Tilley and Buretea.[11b] As the intermolecular dicarbonyl coupling leading to formation of oligomers is a competitive reaction,[19a] high dilution was essential to maximize the yield of the intramolecular coupling product. Both intra- and intermolecular coupling products were isolated. When the reaction was completed, the solvent was removed under vacuum, and the dark brown solid material was redispersed in hexane. The product was separated from the coupling reagent by filtration through a Florisil column and further purified by sublimation under vacuum at 45−50 °C. The *ansa*-(vinylene)ferrocene **5** was obtained in moderate yields varying from 35 to 47% as air-stable red crystals.

The oligomeric byproduct resulted from competitive intermolecular titanium-induced coupling was isolated by dissolving the red−brown involatile residue remaining from the vacuum sublimation of **5** in CH$_2$Cl$_2$ followed by precipitation in methanol. The resulting red solid was characterized by NMR spectroscopy and GPC. These results are discussed in the next section.

The presence of the olefin bridge in ferrocenophane **5** was confirmed by ^{1}H and ^{13}C NMR spectroscopy. In addition to resonances attributed to Cp and ^{t}Bu protons, the ^{1}H NMR spectrum showed a singlet at 6.13 ppm characteristic of olefinic

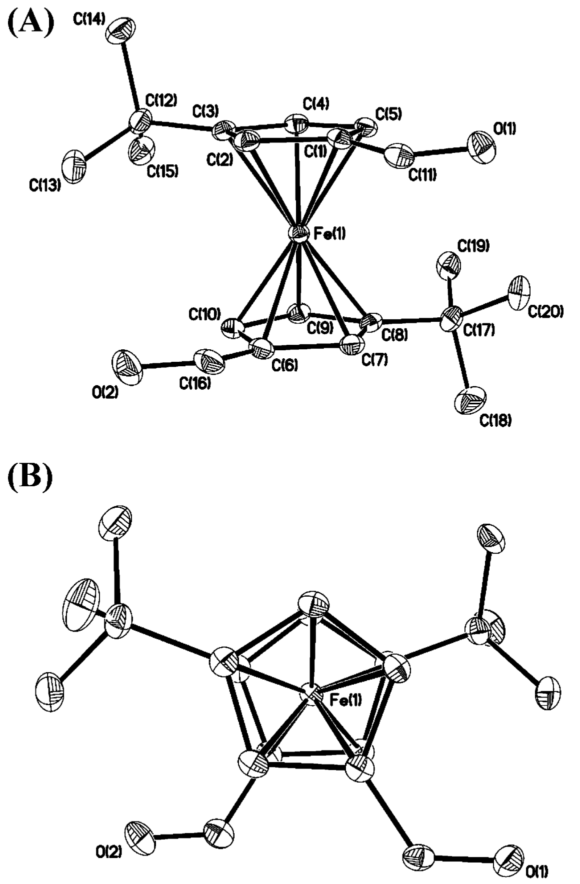
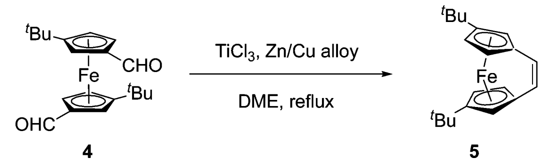


Figure 1. Side (A) and top (B) ORTEP views of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Scheme 2



protons. The ^{13}C NMR spectrum consisted of eight distinct signals, and the olefin carbons gave rise to a peak at 135.7 ppm. Similar to the case of the ferrocene-dicarbaldehyde precursor, the downfield resonance at 101.7 ppm was attributed to the Cp carbons substituted with ^{t}Bu groups. As compared to the typical Cp carbons resonances (60−80 ppm), the resonance for the *ipso*-Cp carbons attached to the bridge was slightly shifted downfield to 88.4 ppm.

An X-ray crystallographic analysis confirmed the bent-sandwich geometry with expected atom connectivity (Figure 2). No significant changes were observed in the structural features of **5** as compared to the non-alkylated homologue. The dihedral angle between the Cp ligands (tilt angle, α) was found to be 23.4° (0.31), which is close to the values previously reported by Aggarwal et al. (22.6°)[23] and Tilley and Buretea (23°)[11b] for the analogous unsaturated ferrocenophane without ^{t}Bu substituents on the Cp ligands. This indicates considerable ring strain in **5** and, therefore, suggests a driving force for ROMP.[24] In Figure 2B, the top view Oak Ridge Thermal Ellipsoid Plot (ORTEP) shows a partially eclipsed syn arrangement of ^{t}Bu groups (torsional angle 74.1°).

When **5** was heated under an inert atmosphere (N_2) at a rate of 10 °C min^{-1}, the DSC trace showed a melting transition at 65 °C represented by a sharp endothermic peak. TGA experiments indicated a rapid weight loss with the onset point around 150 °C leading to zero residue at 225 °C. Since ferrocene-based materials generate ceramics upon heating,[25] this is indicative of an evaporation process rather than a pyrolysis reaction. No exothermic transition associated with thermal ring-opening polymerization was observed up to this temperature by DSC.

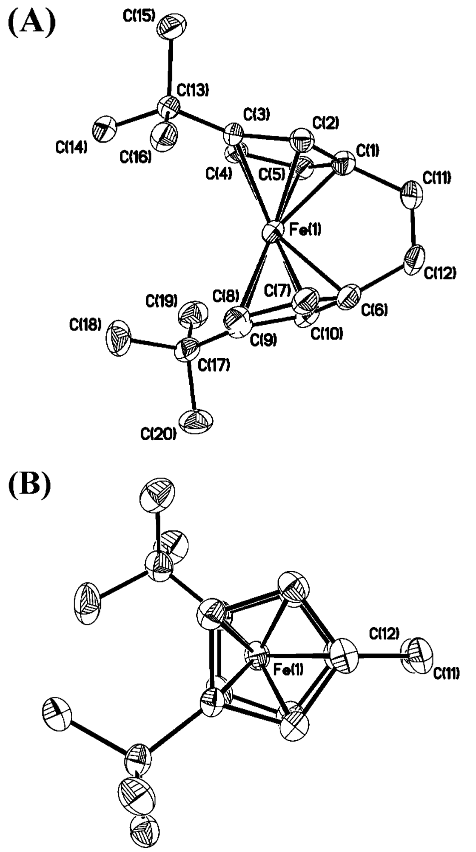
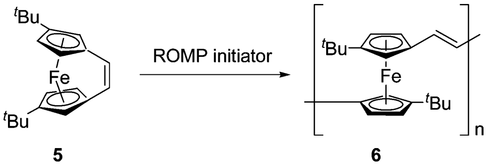


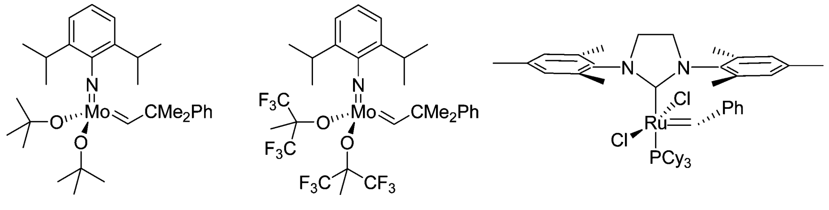
Figure 2. Side (A) and top (B) ORTEP views of **5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Scheme 3



Synthesis and Characterization of Soluble Poly(ferrocenylenevinylene). Ring-Opening Metathesis Polymerization of 5. As reported previously,[11b] ROMP of *ansa*-(vinylene)-ferrocene leads to an insoluble polymer. In contrast, ROMP of **5** generates a polymer (**6**) with a good solubility in organic solvents such as toluene, THF, benzene, dichloromethane, and chloroform imparted by the presence of the ^{t}Bu groups in the polymer chain (Scheme 3).

All reactions were carried out at room temperature and were monitored by ^{1}H NMR spectroscopy, and the resulting polymers were analyzed by GPC. Molybdenum-based (Schrock-type) and ruthenium-based (Grubbs-type) initiators were used in ROMP of **5** (Figure 3). The polymers were isolated as a red−orange powder by precipitation into methanol after termination with benzaldehyde when a molybdenum-based initiator was used or with ethyl vinyl ether when a ruthenium-based initiator was involved. For comparison purposes, the oligomers resulting as



I II III

Figure 3. Initiators used in ROMP of **5**.

Table 1. Ring-Opening Metathesis Polymerization of 5

run	initiator	concn of **5** (mol L^{-1})	solvent	M/I	$M_{n,calcd}$^{a}	$M_{n,exptl}$	PDI	observations
a	**I**	0.04	d_6-benzene	10:1	3220			no reaction
b	**II**	0.10	d_6-benzene	10:1	3220	5940	1.30	after 4 h
c	**II**	0.10	d_6-benzene	10:1	3220	7100	1.43	after 4 days
d	**II**	0.10	toluene	10:1	3220	5700	2.40	after 4 h
e	**II**	0.20	toluene	20:1	6440	7700	2.34	after 4 h
f	**II**	0.10	THF	50:1	6440			no reaction
g	**III**	0.06	d_6-benzene	20:1	6440	102000	1.81	after 4 h
h	**III**	0.12	DCM	20:1	6440	91400	2.23	after 2 h
i	**III**	0.12	DCM	100:1	32200	109000	2.17	after 2 h

[a] End groups are not included.

byproducts from the synthesis of **5**, which would be expected to have the same structure as polymer **6**, were also investigated. The possibility to synthesize polymer **6** with controlled molecular weight and a low polydispersity index (PDI) was explored in a series of experiments where the monomer to initiator ratio (M/I), type of initiator, monomer concentration, and solvent were varied. The non-living nature of the ROMP of **5** is supported by both GPC analysis and NMR spectroscopic data.

GPC. GPC data for polymer **6** synthesized under various conditions are listed in Table 1. No polymer was isolated from the reaction initiated by **I** (run a), but soluble polymers with a low or high molecular weight were obtained from ROMP initiated by **II** and **III**. Apparently, the activity of the initiator **II** depends on the nature of the solvent (runs b, d, and f), but the monomer concentration does not affect the polymerizability of **5** (runs d and e), which is expected for strained cyclic monomers.[24a] In addition, while no polymerization occurred in the presence of complex **I**, a high molecular weight polymer was isolated for a similar initial concentration of the monomer **5** when complex **III** was used as the initiator (run a vs run g).

ROMP of **5** using **II** as the initiator in deuterated benzene (runs b and c) yielded polymers with experimental molecular weights ($M_{n,exptl}$) higher than calculated molecular weights ($M_{n,calcd}$) and a large PDI indicating the non-living character of the ROMP of monomer **5**. In addition, polydispersity increased with longer reaction times (run c vs run b), presumably due to side reactions such as cis–trans isomerization or chain transfer. Nevertheless, this behavior is not surprising for ROMP in presence of complex **II**, which is also active for the metathesis of acyclic olefins. In addition, a slow initiation may be a contributing factor to the non-living character of ROMP of **5**. The PDI values are even higher when toluene is used as a solvent (run b vs runs d and e). As previously demonstrated for norbornene, the kinetics of the ROMP varied considerably with solvent,[26] and the rate of propagation was drastically reduced in coordinating solvents such as THF. Thus, in the attempt to lower the k_p/k_i ratio in ROMP of **5**, THF was also used as a solvent, but the activity of **II** was completely inhibited (run f).

GPC analysis of polymers prepared by ROMP using **III** as the initiator indicated that the molecular weights were not controlled by the M/I ratio under any of the experimental conditions (runs g–i). Much higher molecular weights than calculated values and large PDIs were found in all cases and suggest that a slow initiation step is followed by very fast propagation.

^{1}H and ^{13}C NMR Spectroscopy. Since the molybdenum complex **I** is known to be inactive in the metathesis of acyclic olefins and is able to produce a living system in the case of the ROMP of norbornene and other cyclic olefins,[27] the first attempt to obtain polymer **6** involved polymerization of **5** in the presence of this initiator. Unfortunately, no reaction was observed by ^{1}H NMR spectroscopy over 2 days. Instead, the initiator alkylidene proton (H_α) at 11.33 ppm was considerably diminished presumably due to decomposition in a reductive process.[28]

Further investigations were performed on the NMR scale with 10 equiv of **5** added to the molybdenum complex **II** in deuterated benzene, and the reaction progress was monitored by ^{1}H NMR spectroscopy over 4 days (runs b and c in Table 1). Within the first 30 min, in addition to the initiator alkylidene proton resonance (H_α) at 12.13 ppm, a new signal appeared as a doublet at 13.13 ppm characteristic of alkylidene protons at the end of the growing chain ($H_{\alpha'}$).[27,29] Moreover, the presence of the growing chain was confirmed by the appearance of new broad ^{1}H NMR resonances, and after 4 h, monomer **5** was completely converted into the polymer. At the end of reaction, $H_{\alpha'}$ appeared as a doublet of multiplets,[30] and the initial alkylidene signal was still present in a ratio $H_{\alpha'}/H_\alpha$ of 2:1. This is an indicative of a higher rate of propagation (k_p) than the rate of initiation (k_i) and suggests that the molybdenum complex **II** is less reactive than the first insertion product **6a** (Scheme 4).[31]

The olefin protons in polymer **6** appeared as two new broad multiplets slightly shifted downfield relative to those of monomer **5**, and they are ascribed to trans (6.59 ppm) and cis (6.33 ppm) protons of the double bond.[32] The trans content increases to 24% during the first 4 h of reaction and to a maximum of 40% over the next days (Figure 4A) as a consequence of secondary metathesis of C=C bonds in the polymer backbone catalyzed by **II**.[27] Consequently, a slight increase in the molecular weight and PDI values was observed for polymer isolated after 4 days of reaction (run c vs run b in Table 1).

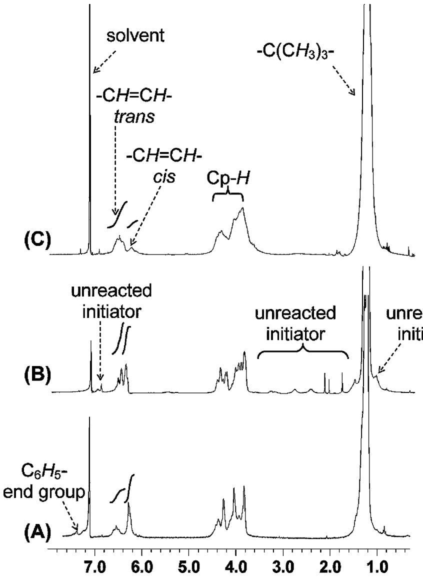
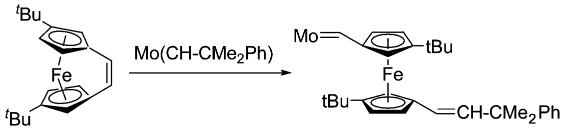


Figure 4. ^{1}H NMR spectra in C_6D_6 acquired for polymers obtained by ROMP of **5** using initiator **II** (A) and **III** (B). For comparison purposes, the spectrum of the oligomeric byproduct resulting from the titanium-induced intermolecular dicarbonyl coupling reaction is also given (C).

Scheme 4



5 **6a**

Ruthenium complexes were used previously for the ROMP of ferrocenophanes with an unsaturated bridge when the first generation of Grubbs catalyst was employed as the initiator in the polymerization of 1,1′-(1-propane-1,3-diyl)-ferrocene as reported by Barlow et al.[33] In the case of ferrocenophane **5**, ROMP was initiated by complex **III** and monitored by NMR spectroscopy in deuterated benzene over 4 h (run g in Table 1). The monomer was consumed in less than 2 h, but, similar to the case of the ROMP initiated by **II**, unreacted initiator was detected at the end of reaction. The polymeric olefin protons gave rise to two broad multiple resonances at 6.58 and 6.39 ppm, indicating that both trans and cis double bond conformations are adopted in the polymer chain with a trans content of 65% (Figure 4B).

The ^{1}H NMR spectrum of the oligomeric byproduct (M_n = 3500; PDI = 2.53) resulting from the titanium-induced intermolecular dicarbonyl coupling reaction used for the synthesis of **5** was found to be identical to that observed for polymer **6** obtained by ROMP, except for the trans content, which was 85% (Figure 4C).

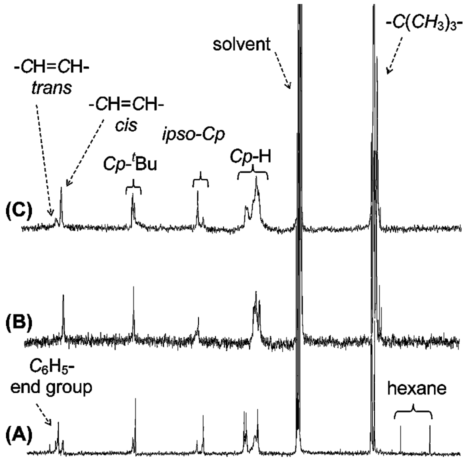


Figure 5. ^{13}C NMR spectra in CD_2Cl_2 acquired for polymers obtained by ROMP of **5** using initiator **II** (A) and **III** (B). For comparison purposes, the spectrum of the oligomeric byproduct resulting from the titanium-induced intermolecular dicarbonyl coupling reaction is also given (C).

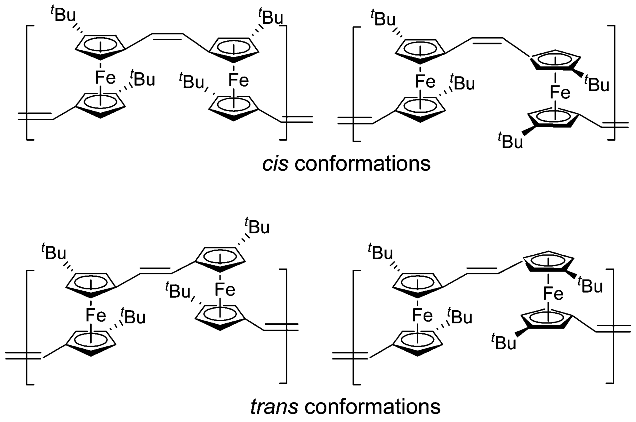


Figure 6. Four possible primary structures for the monomer repeating units in PFV **6**.

The ^{13}C NMR spectra of polymers **6** isolated from ROMP reactions were acquired in CD_2Cl_2 to avoid possible overlapping of olefin or end group signals with solvent resonances. Both low molecular weight polymer (M_n = 7100) from ROMP initiated by **II** and high molecular weight polymer (M_n = 102 000) obtained using **III** gave rise to broad resonances consistent with their proposed structure, and their spectra are almost identical. However, notable differences were found in the ^{13}C NMR spectra: while pairs of broad signals are observed for the olefin carbons, trans (126.4 ppm) and cis (124.9 ppm) carbons,[32] *ipso*-Cp carbons (84.0 and 82.1 ppm), and ^{t}Bu substituted Cp carbons (103.4 and 102.6 ppm) in low molecular weight polymers, only one broad signal for each of these types of carbon nuclei is detected in the high molecular weight polymer (Figure 5A,B, respectively). In addition, pairs of resonances for olefin, *ipso*-Cp, and ^{t}Bu substituted Cp carbons were present in the ^{13}C NMR spectrum of the oligomeric byproduct isolated from the titanium-induced dicarbonyl coupling reaction (Figure 5C). These pairs of signals are ascribed to cis and trans conformations of the double bond further affected by the position of the neighboring ferrocene units. Similar to the case of the polymers obtained by ROMP of the 2,3-difunctional norbornadiene,[30] four primary structures are possible for the repeat units in polymer **6** as schematically represented in Figure 6. The ^{1}H and ^{13}C NMR spectroscopy data indicate that none of the investigated polymerizations was stereoselective.

Thermal Analysis. Thermal analysis of polymer **6** was performed under inert atmosphere (N_2) with a heating rate of 10 °C min^{-1}. DSC experiments were performed for polymers **6** with low and high molecular weights (M_n = 7100 and 102 000, respectively), and different values of glass transition temperature were found. The low molecular weight polymer displayed a T_g at 165 °C, whereas the high molecular weight polymer had a T_g at 223 °C. Independent of the molecular weight, TGA analysis indicated that polymer **6** is stable to weight loss up to 370 °C. Above this temperature, weight loss is observed in two stages: a fast degradation up to 570 °C with a weight change

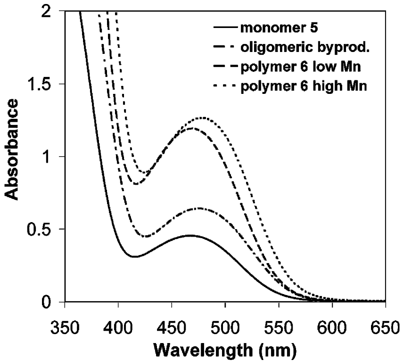


Figure 7. UV−vis spectra of monomer **5** (solid line) and polymer **6** with low molecular weight (dashed line) and high molecular weight (dotted line) in THF. The spectrum of the oligomeric byproduct (interrupted line) resulting from the titanium-induced intermolecular dicarbonyl coupling reaction is also given.

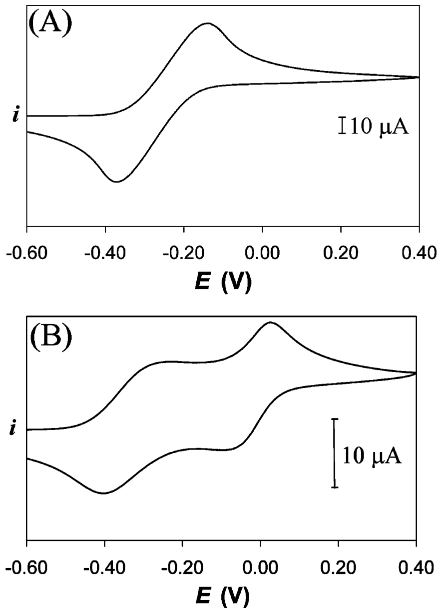


Figure 8. Cyclic voltammogram of monomer **5** (A) and polymer **6** (B) in CH_2Cl_2 vs ferrocene/ferrocenium ion couple at a scan rate of 100 mV/s.

of 68% followed by a much slower degradation up to 780 °C. The ceramic yield at 1000 °C was ca. 15%.

Attempted Photolytic Anionic Ring-Opening Polymerization of 5. Recently, our group reported a new living ROP mechanism for sila-[1]ferrocenophanes that proceeds through nucleophilic attack of initiators such as $M[C_5H_4R]$ (where M = Li or Na and R = ^{t}Bu, Me, or H) at the iron center of photoexcited monomers followed by selective Fe−Cp bond cleavage.[9b] This approach might represent an alternative to ROMP of **5** to afford monodisperse polymer **6**. Unfortunately, as indicated by ^{1}H NMR spectroscopy, no reaction occurred by irradiation with UV light of a THF solution of **5** in the presence of either CpNa or the more basic nucleophile ^{t}BuCpLi. Similar results have been previously reported in our group for an electron-rich sila-[1]ferrocenophane, $Fe(\eta\text{-}C_5H_3{}^tBu)_2Ph_2$.[21] Therefore, on the basis of all these considerations, it is consistent with our initial assertion that the increased electron density on Cp ligands endowed by the ^{t}Bu substituents strengthens the Fe−Cp bond and is also less favorable for an anionic mechanism that involves a buildup of negative charge on the Cp rings.[9]

Attempted Thermal Ring-Opening Polymerization of 5. When ferrocenophane **5** was sealed in an evacuated, thermally resistant glass tube and heated at 350 °C, only unreacted monomer was detected by ^{1}H NMR spectroscopy after 4 h. As indicated by thermal analysis, polymer **6** is stable up to 370 °C, and for this reason, 350 °C was chosen as an upper limit temperature for which **5** was expected to undergo ROP without degradation of any ring-opened polymer product. As compared to [2]ferrocenophanes with a saturated hydrocarbon bridge (e.g., $Fe(\eta\text{-}C_5H_4)_2C_2H_4$) that undergo polymerization at 300 °C,[34] monomer **5** seems to be more thermally robust. One explanation may consider the differences in the dissociation enthalpy of a C=C double bond (612 kJ mol^{-1}) and a C−C single bond (348 kJ mol^{-1}).[35] This tentatively suggests that ROP of hydrocarbon-bridged [2]ferrocenophanes may occur via cleavage of the C−C bond in the hydrocarbon bridge rather than the cleavage of C−C$_{ipso}$ bond, in contrast to sila-[1]ferrocenophanes for which the thermal ROP proceeds through Si−C$_{ipso}$ bond cleavage.[36]

Table 2. Uv−vis Data for Monomer 5 and Polymer 6

	monomer (**3**)	oligomeric byproduct (**6**)[a]	polymer (**6**)	
DP_n		10	25[b]	340[c]
trans content (%)		85	40	65
λ_{max} (nm)	465	477	470	478
ϵ (L^{-1} mol cm^{-1})	600	820	1200	1600

[a] Formed as a byproduct in the synthesis of monomer **5**. [b] Synthesized with complex **II** (run e, Table 1). [c] Synthesized with complex **III** (run i, Table 1).

UV−vis Analysis of Monomer 5 and Polymer 6. The UV−vis spectra of ferrocene and its derivatives have been studied extensively[37] and have led to the detection of six low energy bands. Most studies of ferrocene-containing species have focused on the spin-allowed but Laporte forbidden d−d HOMO−LUMO transition with a λ_{max} at 440 nm because it is the most intense band in the visible region and is well-resolved. In order to explore the degree of electron delocalization in polymer **6**, UV−vis spectra were acquired for monomer **5** and polymer **6** with low and high molecular weights (M_n = 7700 and 109 000, respectively) and the oligomeric byproduct (**6**) that resulted from the synthesis of **5** (Figure 7). All measurements were performed in THF solution with a concentration of 7.8×10^{-4} M in a monomer or a monomer repeating unit. UV−vis analysis of **5** in THF solution revealed a maximum absorption at 465 nm with a moderate intensity (ϵ = 600 L^{-1} mol cm^{-1}) but significantly higher than that of ferrocene, sila-[1]ferrocenophanes, and their derivatives.[38] When strained sila-[1]-ferrocenophanes are polymerized, a hypsochromic shift (blue shift) to values closer to that of ferrocene is observed for the low energy d−d band of the resulting polymers. In contrast to this, but similar to butadiene-bridged ferrocenophanes[11a,17] upon ROMP, a bathochromic shift (red shift) of the maximum of this band with a hyperchromic effect was observed when **5** was converted into **6** to values consistent with a small degree of conjugation for the corresponding polymers (see Table 2). Comparing the UV−vis spectra of polymeric samples, stronger absorptions were observed for higher DP_n values whereas λ_{max} was red shifted with an increasing trans content up to a limiting value.

CV of Monomer 5 and Polymer 6. The electrochemical properties of monomer **5** and polymer **6** were probed using CV. The voltammogram obtained in a CH_2Cl_2 solution of **5** at a scan rate of 100 mV/s showed a reversible one-electron redox wave with a half-wave potential, $E_{1/2}$, of −0.25 V versus the ferrocene/ferrocenium ion couple with i_{red}/i_{ox} = 0.99. The more negative value of the half oxidation potential as compared to that of

Table 3. Crystal Data and Structure Refinement for 4 and 5

	4	**5**
empirical formula	$C_{23}H_{32}O_2$	$C_{20}H_{26}Fe$
Fw	396.34	322.26
temp (K)	150(1)	150(1)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	orthorhombic
space group	$P21/c$	Pbca
a (Å)	10.9521(2)	17.7080(8)
b (Å)	22.8780(8)	6.990(3)
c (Å)	8.1682(3)	27.097(3)
α (deg)	90	90
β (deg)	109.4230(18)	90
γ (deg)	90	90
Z	4	8
ρ_{calcd} (g cm^{-1})	1.364	1.276
μ (Mo Kα) (mm^{-1})	0.796	0.891
F(000)	848	1376
cryst size (mm^3)	0.30 × 0.20 × 0.10	0.22 × 0.06 × 0.02
θ range (deg)	2.79−27.46	2.75−25.33
reflns collected	13037	12433
independent reflns	4411 ($R_{int} = 0.0390$)	3025 ($R_{int} = 0.1566$)
abs correction	semiempirical from equivalents	semiempirical from equivalents
max and min trans coeff	0.925 and 0.784	1.031 and 0.431
GOF on F^2	1.073	0.989
R1[a] ($I > 2\sigma(I)$)	0.0391	0.0613
wR2[b] (all data)	0.0928	0.1541
peak and hole (e Å^{-3})	0.426 and −0.481	0.500 and −0.548

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

ferrocene or other non-alkylated ferrocenophanes is a consequence of the electron-donating effect of the ^{t}Bu groups transmitted to the iron center.[21] Moreover, these results significantly differ from those reported by Lee and co-workers[11a] for 1,1′-(1,3-butadienylene)ferrocenes of which the oxidation potential is very close to that of ferrocene, indicating that the presence of a ^{t}Bu group on the divinylene bridge does not affect the electrochemical properties of the metal center.

The CV of polymer **6** revealed two reversible waves with oxidation potentials $^1E_{1/2} = -0.24$ V and $^2E_{1/2} = 0.02$ V relative to the ferrocene/ferrocenium ion couple (Figure 8). The two-wave cyclic voltammogram is characteristic of chains possessing interacting metal centers with a magnitude given by the separation of the waves $\Delta E_{1/2} = {}^2E_{1/2} - {}^1E_{1/2}$.[16b,39] As is the case of monomer **5**, the presence of the electron-donating ^{t}Bu groups on the Cp ligands determines the negative shift of the first oxidation potential observed for polymer **6** when compared to that of ferrocene or ferrocene-containing polymers with non-alkylated Cp ligands. However, the redox coupling, $\Delta E_{1/2}$, of 0.26 V indicates a smaller extent of interaction between the iron centers than that exhibited in polyferrocenylsilane with ^{t}Bu substituents on the Cp ligands reported recently by our group ($\Delta E_{1/2} = 0.33$ V)[21] but is close to that reported by Tilley and Buretea for the block copolymer of ferrocenylenevinylene with norbornene ($\Delta E_{1/2} = 0.25$ V).[11b] For further comparison, the $\Delta E_{1/2}$ value in the ferrocenylenedivinylene-based polymers reported by Lee et al.[16] varies from 0.21 to 0.26 V depending on the side group attached to the divinylene bridge.

Conclusion

The *ansa*-(vinylene)ferrocene with ^{t}Bu substituents on Cp ligands, $Fe(\eta\text{-}C_5H_3{}^tBu)_2C_2H_2$ (**5**), was successfully synthesized and characterized. ROMP of **5** in the presence of molybdenum- or ruthenium-based initiators yielded highly soluble poly(ferrocenylenevinylene) (**6**) with low and high molecular weights. On the basis of GPC and ^{1}H NMR spectroscopy data, it was found that under the studied reaction conditions, the synthesis of monodisperse, well-defined polymers by ROMP of **5** could not be achieved. By introducing *t*-butyl groups on the Cp ligands, we not only addressed the insolubility problem for this class of organometallic polymers but also altered their electrochemical properties. CV experiments revealed a negative shift of the first oxidation potential of polymer **6** relative to that of ferrocene, which is a consequence of the electron-donating effect of the *t*-butyl groups transmitted to the iron center. Also, the presence of appreciable Fe···Fe interactions along the polymer backbone was demonstrated by a two-wave CV pattern with a separation, $\Delta E_{1/2}$, of 0.26 V. UV−vis analysis of monomer **5** and polymer **6** indicated a bathochromic shift accompanied by a hyperchromic effect for the HOMO−LUMO transition upon polymerization consistent with a moderate degree of conjugation in polymer **6**.

Experimental Procedures

Materials. All reactions were carried out under an atmosphere of prepurified nitrogen gas (BOC) using common Schlenk techniques or an inert atmosphere glove box (M-Braun). Solvents were dried using a Grubbs-type solvent system[40] or standard methods followed by distillation.[41] The materials were purchased from Aldrich except molybdenum-based catalysts purchased from Strem Chemicals Inc. Zn/Cu alloy[19a] and $Fe(\eta\text{-}C_5H_3{}^tBuLi)_2\cdot 2TMEDA$[21] were prepared as previously reported.

Equipment and Procedures. ^{1}H (300 MHz), and ^{13}C (75.4 MHz) NMR spectra were recorded on a Mercury 300 spectrometer. ^{1}H and ^{13}C resonances were referenced internally to the deuterated solvent resonances. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Elemental analysis (EA) was performed on a PerkinElmer 2400 series C/H/N Analyzer. Photolysis was performed with a Philips 125 W high pressure mercury arc lamp. A Pyrex filter was placed inside the quartz immersion wall to filter out wavelengths below 310 nm. Molecular weights were determined by gel permeation chromatography (GPC) using a Viscotek GPC MAX liquid chromatograph equipped with a Viscotek triple detector array. The triple detector array consists of a deflection refractometer, a four-capillary differential viscometer, and a right angle laser light scattering detector ($\lambda_0 = 670$ nm). GPC columns were calibrated versus polystyrene standards (American Polymer Standards). A flow rate of 1.0 mL/min was used with ACS grade THF as the eluent. UV−vis spectra were recorded using a PerkinElmer Lambda 900 UV−vis-NIR spectrometer. Polymer molar absorptivity was quoted per monomer repeating unit and was determined from analysis of at least three different concentrations. Thermal analysis was performed on a TA Instruments simultaneous DSC-TGA Q600 at a heating/cooling rate of 10 °C min^{-1} under N_2. CV was performed using an Epsilon EC instrument equipped with an Au electrode and an Ag/AgCl reference electrode. The working electrode, Au, was used in conjunction with a Pt wire as a counter electrode. Data were obtained by analysis at 22 °C of CH_2Cl_2 solutions with a concentration of 5×10^{-3} M in monomer or monomer repeating unit and 0.1 M in $[NBu_4][PF_6]$ at a scan rate of 100 mV/s. In each case, the CV data were acquired for two independent samples, and no significant changes were observed in the reversible pattern of CV curves or the ratio of the peak currents upon multiple sweeps of the same sample in a single-cycle method. CH_2Cl_2 was dried over CaH_2 and distilled prior to use. $[NBu_4][PF_6]$ was previously recrystallized from ethanol and vacuum-dried. Ferrocene, purified by sublimation, was used as internal standard, and potentials were reported versus the ferrocene/ferrocenium ($E = 0.00$ V) couple.

Synthesis of 4. This procedure was adapted from that of Balavoine et al.[20] To a suspension of 5.70 g of $Fe(\eta\text{-}C_5H_3{}^tBuLi)_2\cdot 2TMEDA$ (10.5 mmol) in ca. 200 mL of dry diethyl ether, a solution of distilled DMF (1.80 mL, 23.2 mmol, 2.2 equiv) in 20.0 mL of dry ether was added via syringe at −78 °C. The reaction was continued for 2 h and then hydrolyzed at −78 °C. The organic phase was extracted with CH_2Cl_2 and dried over $MgSO_4$ for 24 h.

Then, the solution was decanted, and the solvent was removed under vacuum. A total of 2.80 g of highly pure product was obtained by repeated crystallization from cyclohexane as red crystals in 75% yield.

^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ 9.79 (s, 2 H, -C*H*O), 4.49 (m, 2H, Cp-*H*), 4.33 (m, 2H, Cp-*H*), 4.87 (m, 2H, Cp-*H*), 1.03 (s, 18H, CC*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 25 °C) δ 192.2 (s, Cp*C*HO), 107.8 (*Cp*^{t}Bu), 78.8 (*Cp*CHO), 70.1, 70.1, 68.3 (*Cp*H), 30.9 (C*C*H$_3$), 30.4 (*C*CH$_3$); MS (70 eV, EI) *m/z* (%): 356 (6) [M + 2]$^+$, 355 (31) [M + 1]$^+$, 354 (100) [M]$^+$, 339 (5) [M − CH$_3$]$^+$; Anal. calcd for $C_{20}H_{26}O_2{}^{56}Fe$: C, 67.80; H, 7.34, Found: C, 67.63; H, 7.37; mp 109 °C (by DSC).

Synthesis of 5 and Oligomers 6. This synthesis follows the procedure reported by Tilley and Buretea[11b] with a few modifications. High dilution is essential to maximize the yield of the intramolecular dicarbonyl coupling product. Therefore, ca. 250 mL of dimethoxyethane was added via cannula to a mixture of $TiCl_3$ (3.50 g, 22.7 mmol) and Zn/Cu alloy (3.42 g, 51.6 mmol) and resulted in a suspension heated to reflux for 12 h. To the refluxing dark-green suspension, a solution of **4** (0.73 g, 2.06 mmol) in 20.0 mL of dimethoxyethane was added via syringe driven by a mechanical pump through a septum at the top of the condenser at a delivery rate of 1.0 mL/h (0.1 mmol/h). When the addition was completed, the reaction mixture was refluxed for another 12 h. The red−brown suspension was cooled to room temperature, and the solvent was removed under vacuum. The remaining solid was redispersed in hexane and filtered through a 3−5 cm column of 100−200 mesh Florisil. The dark-red oily product resulting from solvent removal was warmed to 45−50 °C under vacuum (0.01 mmHg), and a red solid was collected on a cold finger at the temperature of the cold tap water. The viscous red−brown material remaining from vacuum sublimation was investigated by ^{1}H NMR. If the monomer was still present, a second filtration through Florisil was performed and, after solvent removal, **5** was separated under the same conditions as described previously. The combined fractions gave 0.30 g of pure **5** (45% yield). The red−brown material remaining from vacuum sublimation, free of monomer **5**, was redissolved in CH_2Cl_2, and an oligomeric byproduct resulting from intermolecular titanium-induced coupling was separated by precipitation in methanol and isolated as a red powder (0.33 g; 50% yield). This was further investigated by NMR and GPC.

Monomer 5. ^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ 6.13 (s, 2 H, C*H*═C*H*), 4.63, 4.62 (m, 4H, Cp-*H*), 3.74 (m, 2H, Cp-*H*), 1.20 (s, 18H, CC*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 25 °C) δ 135.7 (*C*H═*C*H), 101.7 (*Cp*^{t}Bu), 88.5 (*ipso-Cp*), 73.9, 73.3, 65.4 (*Cp*H), 32.1 (C*C*H$_3$), 29.7 (*C*CH$_3$); MS (70 eV, EI) *m/z* (%) 323 (23) [M + 1]$^+$, 322 (100) [M]$^+$, 307 (48) [M − CH$_3$]$^+$, 250 (42) [M − CH$_3$ − C(CH$_3$)$_3$]$^+$; Anal. calcd for $C_{20}H_{26}{}^{56}Fe$: C, 74.53; H, 8.07, Found: C, 74.45; H, 8.36; mp 65 °C (by DSC); UV−vis (25 °C, THF): λ_{max} = 465 nm, ϵ = 600 L^{-1} mol cm^{-1}.

Oligomeric Byproduct 6. ^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ 6.53 (br m, 2 H, C*H*═C*H* trans), 6.27 (br m, 2 H, C*H*═C*H* cis), 4.43−3.93 (br m, 6H, Cp-*H*), 1.40−1.23 (br m, 18H, CC*H*$_3$); ^{13}C-{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 25 °C) δ 126.5 (br m, *C*H═*C*H trans), 124.2 (br m, *C*H═*C*H cis), 103.2, 102.6 (br m, *Cp*^{t}Bu), 83.9, 82.0 (br m, *ipso-Cp*), 69.9−68.9, 67.5−65.9 (br m, *Cp*H), 31.8 (br m, C*C*H$_3$), 30.7 (br m, *C*CH$_3$); trans content: 85%. GPC (polystyrene standards): M_n = 3500, PDI = 2.53; UV−vis (25 °C, THF): λ_{max} = 475 nm, ϵ = 820 L^{-1} mol cm^{-1}.

Ring-Opening Metathesis Polymerization of 5. The following NMR scale procedure is typical. A solution of 0.033 g (0.10 mmol, 10 equiv) of monomer **5** in 0.75 mL of C_6D_6 was added to a solution of 0.008 g (0.01 mmol; 1 equiv) of molybdenum-based initiator **II** in 0.25 mL of C_6D_6 under vigorous stirring. The reaction was carried out at room temperature and monitored by ^{1}H NMR until the monomer was completely consumed. After the monomer was completely converted in the polymer, an aliquot was taken, and after quenching with benzaldehyde, the polymer was isolated by precipitation into methanol, dried under vacuum, and analyzed by GPC. The reaction mixture was further monitored by ^{1}H NMR for the next 4 days. The polymer was isolated as described for an aliquot and GPC data were acquired. Ethyl vinyl ether was used to quench the polymerization reaction initiated by **III**.

Polymer 5 from ROMP Initiated by II. ^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ 7.43−7.31 (br m, 10H, -*Ph*, end groups), 6.59 (br m, 2 H, C*H*═C*H* trans), 6.33 (br m, 2 H, C*H*═C*H* cis), 4.48−3.86 (br m, 6H, Cp-*H*), 1.38−1.25 (br m, 18H, CC*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 25 °C) δ 128.2, 126.5 (s, *Ph* end groups), 126.4 (br m, *C*H═*C*H trans), 124.9 (br m, *C*H═*C*H cis), 103.4, 102.6 (br m, *Cp*^{t}Bu), 84.0, 82.1 (br m, *ipso-Cp*), 69.9−69.2, 66.6−65.8 (br m, *Cp*H), 34.8 (s, *C*(CH$_3$)$_2$Ph, end group), 31.8 (br m, C*C*H$_3$), 30.7 (br m, *C*CH$_3$), 25.4 (s, C(*C*H$_3$)$_2$Ph, end group); trans content: 40%. GPC (polystyrene standards): first fraction, after 4 h of reaction: M_n = 5940, PDI = 1.30; second fraction, after 4 days: M_n = 7100, PDI = 1.43; UV−vis (25 °C, THF): λ_{max} = 470 nm, ϵ = 1200 L^{-1} mol cm^{-1}.

Polymer 6 from ROMP Initiated by III. ^{1}H NMR (C_6D_6, 300 MHz, 25 °C) 6.52 (br m, 2 H, C*H*═C*H* trans), 6.39 (br m, 2 H, C*H*═C*H* cis), 4.48−3.91 (br m, 6H, Cp-*H*), 1.37−1.28 (br m, 18H, CC*H*$_3$); ^{13}C{^{1}H} NMR (75.4 MHz, CD_2Cl_2, 25 °C) δ 124.0 (br m, *C*H═*C*H), 102.8 (br m, *Cp*^{t}Bu), 83.5 (br m, *ipso-Cp*), 67.2−65.3 (br m, *Cp*H), 31.6 (br m, C*C*H$_3$), 30.5 (br m, *C*CH$_3$); trans content: 65%. GPC (polystyrene standards): M_n = 102 000, PDI = 1.81; UV−vis (25 °C, THF): λ_{max} = 478 nm, ϵ = 1600 L^{-1} mol cm^{-1}.

Attempted Photolytic Ring-Opening Polymerization of 5. A total of 5 μL of 2.0 M CpNa in THF was added under vigorous stirring to 0.033 g (0.10 mmol, 10 equiv) of **5** in 1 mL of THF in the absence of light. The reaction mixture was irradiated for 4 h with UV light at 5 °C under stirring and quenched with few drops of degassed methanol. After solvent removal, the ^{1}H NMR spectrum of the isolated red solid indicated that no reaction occurred since only resonances of unreacted monomer were observed. The same results were obtained for reactions carried out in the presence of ^{t}BuCpLi as the initiator.

Attempted Thermal Ring-Opening Polymerization of 5. Monomer **5** (0.070 g, 0.22 mmol) was sealed in an evacuated thermal resistant glass tube and heated for 4 h at 350 °C. As indicated by ^{1}H NMR spectrometry no polymerization reaction occurred as only unreacted monomer was detected.

X-ray Crystallography. Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer and monochromated Mo Kα radiation (λ = 0.71073 Å) and were measured using a combination of ϕ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package.[42] The structure was solved and refined using SHELXTL V6.1[43] for full-matrix least-squares refinement that was based on F^2. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation. Selected data for investigated compounds **4** and **5** are given in Table 3.

Acknowledgment. We thank Dave Rider, Hai Wang, and Yishan Wang for collecting GPC data. I.M. thanks the EU for a Marie Curie Chair and the Royal Society of Chemistry for a Wolfson Research Merit Award.

References and Notes

(1) (a) Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098. (b) Heeger, A. J. *Rev. Mod. Phys.* **2001**, *73*, 681.

(2) (a) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1998. (b) Nalwa, H. S. *Handbook of Advanced Electronic and Photonic Materials and Devices, Volume 8: Conducting Polymers*; 2001.

(3) (a) Manners, I. *Synthetic Metal-Containing Polymers*; Wiley-VCH: Weinheim, Germany, 2004. (b) Nguyen, P.; Gomez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515. (c) Abd-El-Aziz, A. S.; Carraher, C. E., Jr.; Pittman, C. U., Jr.; Sheats, J. E.; Zeldin, M. *Macromolecules Containing Metal and Metal-Like Elements, Vols. 1−7*; John Wiley and Sons Inc.: New York, 2003−2005. (d) Holliday, B. J.; Swager, T. M. *Chem. Commun. (Cambridge, U.K.)* **2005**, 23. (e) Kingsborough,

R. P.; Swager, T. M. *Prog. Inorg. Chem.* **1999**, *48*, 123. (f) Whittell, G. R.; Manners, I. *Adv. Mater.* **2007**, *19*, 3439.

(4) Selected examples: (a) Knapp, R.; Velten, U.; Rehahn, M. *Polymer* **1998**, *39*, 5827. (b) Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379. (c) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromolecules* **1977**, *10*, 879. (d) Bochmann, M.; Lu, J.; Cannon, R. D. *J. Organomet. Chem.* **1996**, *518*, 97. (e) Leung, A. C. W.; Chong, J. H.; MacLachlan, M. J. *Macromol. Symp.* **2003**, *196*, 229. (f) Wong, W-Y.; Lu, G.-L.; Choi, K.-H.; Shi, J.-X. *Macromolecules* **2002**, *35*, 3506. (g) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496. (h) Kurashina, M.; Murata, M.; Watanabe, T.; Nishihara, H. *J. Am. Chem. Soc.* **2003**, *125*, 12420. (i) Hirao, T.; Kurashina, M.; Aramaki, K.; Nishihara, H. *Dalton Trans.* **1996**, 2929. (j) Sicard, S.; Berube, J.-F.; Samar, D.; Messaoudi, A.; Fortin, D.; Lebrun, F.; Fortin, J.-F.; Decken, A.; Harvey, P. D. *Inorg. Chem.* **2004**, *43*, 5321. (k) Fournier, E.; Lebrun, F.; Drouin, M.; Decken, A.; Harvey, P. D. *Inorg. Chem.* **2004**, *43*, 3127.

(5) Wolf, M. O. *J. Inorg. Organomet. Polym. Mater.* **2006**, *16*, 189.

(6) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(7) (a) Vogel, U.; Lough, A. J.; Manners, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 3321. (b) Berenbaum, A.; Manners, I. *Dalton Trans.* **2004**, *14*, 2057. (c) Resendes, R.; Nelson, J. M.; Fischer, A.; Jäkle, F.; Bartole, A.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2001**, *123*, 2116. (d) Berenbaum, A.; Braunschweig, H.; Dirk, R.; Englert, U.; Green, J. C.; Jäkle, F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 5765. (e) Rulkens, R.; Gates, D. P.; Balaishis, D.; Pudelski, J. K.; McIntosh, D. F.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1997**, *119*, 10976. (f) Jakle, F.; Rulkens, R.; Zech, G.; Foucher, D. A.; Lough, A. J.; Manners, I. *Chem.—Eur. J.* **1998**, *4*, 2117. (g) Sharma, S.; Caballero, N.; Li, H.; Pannell, K. H. *Organometallics* **1999**, *18*, 2855. (h) Foucher, D. A.; Manners, I. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 63. (i) Schachner, J. A.; Tockner, S.; Lund, C. L.; Quail, J. W.; Rehahn, M.; Müller, J. *Organometallics* **2007**, *26*, 4658.

(8) (a) Tamm, M.; Kunst, A.; Bannenberg, T.; Herdtweck, E.; Sirsch, P.; Elsevier, C. J.; Ernsting, J. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5530. (b) Mochida, K.; Shibayama, N.; Goto, M. *Chem. Lett.* **1998**, 339. (c) Mizuta, T.; Onishi, M.; Miyoshi, K. *Organometallics* **2000**, *19*, 5005. (d) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367. (e) Bartole-Scott, A.; Braunschweig, H.; Kupfer, T.; Lutz, M.; Manners, I.; Nguyen, T. L.; Radacki, K.; Seeler, F. *Chem.—Eur. J.* **2006**, *12*, 1266.

(9) (a) Ni, Y. Z.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102. (b) Tanabe, M.; Vandermeulen, G. W. M.; Chan, W. Y.; Cyr, P. W.; Vanderark, L.; Rider, D. A.; Manners, I. *Nat. Mater.* **2006**, *5*, 467.

(10) (a) Ni, Y. Z.; Rulkens, R.; Pudelski, J. K.; Manners, I. *Macromol. Rapid Commun.* **1995**, *16*, 637. (b) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263.

(11) (a) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621. (b) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507.

(12) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Grubbs, R. H.; Tumas, W. *Science (Washington, DC)* **1989**, *243*, 907.

(13) Finckh, W.; Tang, B. Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904. (b) Pudelski, J. K.; Callstrom, M. *Organometallics* **1992**, *11*, 2757. (c) Pudelski, J. K.; Callstrom, M. *Organometallics* **1994**, *13*, 3095.

(14) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemistry II*; Elsevier Science Ltd.: Amsterdam, 1995; Vol. 7, p 185.

(15) Togni, A.; Hayashi, T. *Ferrocenes*; Wiley-VCH: Weinheim, Germany, 1995. (b) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon Press Ltd.: Elmsford, NY, 1982; Vol. 4, p 475 and Vol. 8, Ch. 59.

(16) (a) Nelson, J. M.; Nguyen, P.; Petersen, R.; Rengel, H.; MacDonald, P. M.; Lough, A. J.; Manners, I.; Raju, N. P.; Greedan, J. E.; Barlow, S.; O'Hare, D. *Chem.—Eur. J.* **1997**, *3*, 573. (b) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683.

(17) Heo, R. W.; Park, J. S.; Lee, T. R. *Macromolecules* **2005**, *38*, 2564.

(18) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713.

(19) (a) McMurry, J. E.; Lectka, T.; Rico, J. G. *J. Org. Chem.* **1989**, *54*, 3748. (b) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.

(20) Balavoine, G. G. A.; Doisneau, G.; Fillebeenkhan, T. *J. Organomet. Chem.* **1991**, *412*, 381.

(21) Masson, G.; Beyer, P.; Cyr, P. W.; Lough, A. J.; Manners, I. *Macromolecules* **2006**, *39*, 3720.

(22) MacGillivray, L. R.; Spinney, H. A.; Reid, J. L.; Ripmeester, J. A. *J. Chem. Crystallogr.* **1999**, *29*, 865.

(23) Aggarwal, V. K.; Jones, D.; Turner, M. L.; Adams, H. *J. Organomet. Chem.* **1996**, *524*, 263.

(24) (a) Ivin, K. J.; Saegusa, T. *Ring-Opening Polymerization*; Elsevier Applied Science: Amsterdam, 1984; p 7. (b) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley and Sons: New York, 1991; p 591.

(25) (a) MacLachlan, M. J.; Ginzburg, M.; Coombs, N.; Raju, N. P.; Greedan, J. E.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 3878. (b) Ginzburg, M.; MacLachlan, M. J.; Yang, S. M.; Coombs, N.; Coyle, T. W.; Raju, N. P.; Greedan, J. E.; Herber, R. H.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 2625. (c) Sun, Q. H.; Lam, J. W. Y.; Xu, K. T.; Xu, H. Y.; Cha, J. A. K.; Wong, P. C. L.; Wen, G. H.; Zhang, X. X.; Jing, X. B.; Wang, F. S.; Tang, B. Z. *Chem. Mater.* **2000**, *12*, 2617.

(26) Cazalis, C.; Heroguez, V.; Fontanille, M. *Macromol. Chem. Phys.* **2000**, *201*, 869.

(27) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

(28) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.

(29) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.

(30) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; Oregan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

(31) It has been shown that a molybdenum-based complex having a ferrocenyl (Fc) substituent at the methylidene carbon, Mo(CH-Fc)-(NAr)[OCMe(CF$_3$)$_2$]$_2$, has a considerable lower k_p/k_i value than that of the parent initiator with alkyl substituent, Mo(CH-^{t}Bu)(NAr)[OCMe-(CF$_3$)$_2$]$_2$: Albagli, D.; Bazan, G.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150.

(32) Cis and trans resonances were assigned by comparison of olefin resonances in polymer **6** to those of low molecular weight compounds as well as polymers containing internal olefin —CH═CH— groups. This method is often used in structure determination of polymers: Koenig, J. L. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1992; p 150. According to the textbooks on NMR spectroscopy, *cis*-CH═CH— group signals in small molecule compounds appear upfield from those of *trans*-CH═CH—: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley and Sons, Inc.: New York, 1991; p 237. Identical trends are observed in organic macromolecular compounds containing —CH═CH— units (see ref 29 and Feast, J. W.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157) and also ferrocene-based polymers (see ref 11b).

(33) Arisandy, C.; Cowley, A. R.; Barlow, S. *J. Organomet. Chem.* **2004**, *689*, 775.

(34) Nelson, J. M.; Rengel, H.; Manners, I. *J. Am. Chem. Soc.* **1993**, *115*, 7035.

(35) McMurry, J. *Organic Chemistry*, 4th ed.; Brooks/Cole Publishing Company: 1995, p 28.

(36) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; MacDonald, M. P.; Manners, I.; Barlow, S.; O'Hare, D. *Macromolecules* **1996**, *29*, 1894.

(37) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(38) Pudelski, J. K.; Foucher, D. A.; Honeyman, C. H.; Lough, A. J.; Manners, I.; Barlow, S.; O'Hare, D. *Organometallics* **1995**, *14*, 2470.

(39) (a) Jones, S. C.; Barlow, S.; O'Hare, D. *Chem.—Eur. J.* **2005**, *11*, 4473. (b) Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262. (c) Southard, G. E.; Curtis, D. M. *Organometallics* **2001**, *20*, 508. (d) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; LeVanda, C.; Kaufman, F.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506.

(40) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(41) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Elsevier: Amsterdam, 2003.

(42) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(43) Sheldrick, G. M. *SHELXTL/PC*, version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1997.

MA071034V