Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Journal of Organometallic Chemistry 691 (2006) 3490–3497

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis and MMA polymerization of chiral *ansa*-zirconocene ester enolate complexes with C_2- and C_s-ligation

Antonio Rodriguez-Delgado, Wesley R. Mariott, Eugene Y.-X. Chen *

Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, USA

Received 4 February 2006; received in revised form 29 April 2006; accepted 29 April 2006
Available online 5 May 2006

Abstract

A series of chiral *ansa*-zirconocene ester enolate complexes incorporating C_2- or C_s-symmetric ligands, including neutral *rac*-(EBI)ZrCl[OC(O^{i}Pr)=CMe$_2$] (**1**), *rac*-(EBI)Zr(OTf)[OC(O^{i}Pr)=CMe$_2$] (**2**), *rac*-(EBI)Zr(OTf)[OC(OMe)=C(Me)CH$_2$C(Me$_2$)C(O^{i}Pr)=O] (**3**), [Me$_2$C(Cp)(Flu)]ZrMe[OC(O^{i}Pr)=CMe$_2$] (**4**), and cationic [Me$_2$C(Cp)(Flu)]Zr$^+$(THF)[OC(O^{i}Pr)=CMe$_2$][MeB(C$_6$F$_5$)$_3$]$^-$ (**5**), have been synthesized. Within the neutral C_2-ligated zirconocene ester enolate series, the chloride derivative **1** is inactive toward any methyl methacrylate (MMA) additions, the methyl derivative *rac*-(EBI)ZrMe[OC(O^{i}Pr)=CMe$_2$] adds cleanly only 1 equiv. of MMA, and the triflate derivative **2** can add either 1 equiv. of MMA to form the single-MMA-addition product **3** or multiple equivalents of MMA to form P(MMA). Unlike the C_s-ligated methyl cation [Me$_2$C(Cp)(Flu)ZrMe]$^+$, which is inactive for MMA polymerization under various conditions, the C_s-ligated ester enolate cation **5** is moderately active for polymerization of MMA and *N*,*N*-dimethylacrylamide at ambient temperature; the resulting P(MMA) has a high molecular weight of $M_n = 388\,000$ Da but a low syndiotacticity of $[rr] = 64\%$, and the polymerization conforms to a chain-end control mechanism.

Keywords: Metallocene catalysts; Chiral zirconocenes; MMA polymerization; Ester enolates; Chain-end control; Site control

1. Introduction

There has been increasing interest in *controlled* polymerization of methyl methacrylate (MMA) and *N*,*N*-dimethylacrylamide (DMAA) using group 4 metallocene and related *ester or amide enolate* catalysts incorporating metallocene-type achiral C_{2v} [1] and chiral C_2 [2] or C_1 [3] as well as constrained-geometry-type prochiral C_s [4] ligand symmetries. Some of these polymerization systems are living and stereospecific, allowing for a high degree of control over polymer molecular weight, molecular weight distribution, and tacticity as well as for the synthesis of well-defined block and stereoblock copolymers.

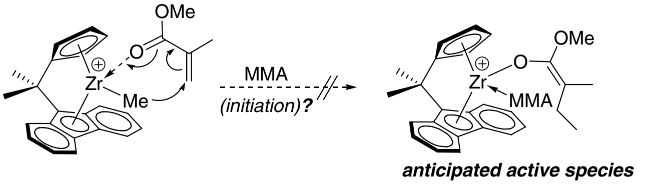
Obviously missing from the above catalyst list is a catalyst system based on the metallocene-type C_s-ligand: [Me$_2$C(Cp)(Flu)] (Cp = η^5-cyclopentadienyl; Flu = η^5- or η^3-fluorenyl). In attempts to produce syndiotactic poly(methyl methacrylate), P(MMA), at least five research groups [5] have investigated the MMA polymerization using the C_s-symmetric zirconocene dimethyl complex [Me$_2$C(Cp)(Flu)]ZrMe$_2$ [6], in combination with borane or borate-based activators; however, they all found no polymerization activity. We reasoned that the inactivity of the derived methyl cation, [Me$_2$C(Cp)(Flu)ZrMe]$^+$, could simply be due to a problem with the initiation step that involves presumably an ineffective Zr–Me transfer to the coordinated monomer; hence, the active cationic ester enolate propagating species cannot be generated (Eq. (1)). In this contribution, we report our efforts to solve this long-standing problem by first, the synthesis of the preformed neutral zirconocene ester enolate complex [Me$_2$C(Cp)(Flu)]ZrMe[OC(O^{i}Pr)=CMe$_2$] and second, the investigation into the MMA polymerization

---

* Tel.: +1 970 491 5609; fax: +1 970 491 1801.
E-mail address: eychen@lamar.colostate.edu (E.Y.-X. Chen).

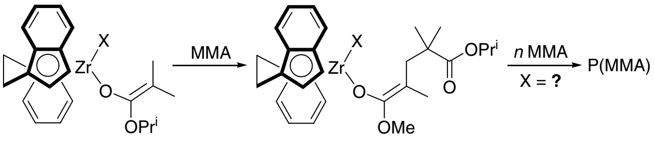
0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.04.036

characteristics using the corresponding cationic complex $[Me_2C(Cp)(Flu)]Zr^+(THF)[OC(O^iPr){=}CMe_2][MeB(C_6F_5)_3]^-$, which models the proposed active propagating species.



(1)

A second, closely related issue that we are addressing in the current contribution pertains to our continued efforts seeking for effective MMA polymerization catalysts based on neutral chiral zirconocene ester enolate complexes. Such neutral catalysts are of interest for the development of an effective catalyst system devoid of any cocatalysts. We previously found that the neutral methyl zirconocene ester enolate complex, *rac*-(EBI)ZrMe$[OC(O^iPr){=}CMe_2]$ $[EBI = C_2H_4(Ind)_2]$ [2c], reacts cleanly with 1 equiv. of MMA in non-coordinating polar solvents such as CH_2Cl_2 at ambient temperature to form the single-MMA-addition product, *rac*-(EBI)ZrMe$[OC(OMe){=}C(Me)CH_2C(Me_2)C(O^iPr){=}O]$ [2b]; no further MMA additions took place, however, in the presence of excess MMA with extended reaction times (24 h). We hypothesized that the size (Cl vs. Me) and lability (OTf vs. Me and Cl) of the X ligand in a neutral zirconocene ester enolate complex series, *rac*-(EBI)ZrX$[OC(O^iPr){=}CMe_2]$ (X = Me, Cl, OTf), should affect the reactivity of these complexes towards possible further MMA additions (Eq. (2)). To seek for appropriate neutral zirconocene ester enolate complexes that can effect further MMA additions to yield P(MMA), we synthesized the other two neutral zirconocene ester enolate derivatives (X = Cl, OTf) to complete the series and subsequently examined their reactivity towards MMA additions.



(2)

2. Experimental

2.1. Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line (typically 10^{-5} to 10^{-7} Torr), or in an argon or nitrogen-filled glovebox (typically <1.0 ppm oxygen and moisture). NMR-scale reactions (typically in a 0.02 mmol scale) were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for THF, Et_2O, and CH_2Cl_2) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene-d_6 and toluene-d_8 were degassed, dried over sodium/potassium alloy, and filtered before use, whereas CD_2Cl_2 was degassed and dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ^1H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) or a Varian Inova 400 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane, whereas ^{19}F NMR spectra were referenced to external $CFCl_3$. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

n-Butyllithium (1.6 M in hexanes), chlorotrimethylsilane, 2-cyclopentadienyl-2-fluorenylpropane, 1,2-dibromoethane, diisopropylamine, 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT-H), indene, isobutyriyl chloride, isopropanol, lithium dimethylamide, triflic acid, trimethyl amine, and zirconium tetrachloride were purchased from Aldrich Chemical Co., trimethylaluminum (neat) from Strem Chemical Co., methyllithium (1.6 M in diethyl ether) from Acros. and trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) from Alfa Aesar. These reagents were used as received, except for the following reagents that were further treated or purified: the amines were degassed using three freeze–pump–thaw cycles and BHT-H was recrystallized from hexanes.

Methyl methacrylate (MMA) and *N*,*N*-dimethylacrylamide (DMAA) were purchased from Aldrich Chemical Co. and TCI America, respectively; they were purified by first degassing and drying over CaH_2 overnight, followed by vacuum distillation; final purification of MMA involved titration with neat tri(*n*-octyl)aluminum to a yellow end point [7] followed by a second vacuum distillation. The purified monomers were stored in brown bottles over activated Davison 4-Å molecular sieves (for DMAA) in a −30 °C freezer inside the glovebox.

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a research gift from Boulder Scientific Co. and further purified by recrystallization from hexanes at −30 °C. The $(C_6F_5)_3B \cdot THF$ adduct was prepared by addition of THF to a toluene solution of the borane followed by removal of the volatiles and drying in vacuo. Alkyl (isopropyl and *tert*-butyl) isobutyrates and their corresponding lithium salts were prepared according to modified literature procedures [8]; the isolated lithium ester enolates were stored in a freezer at −30 °C inside the glovebox. Literature procedures were employed for the preparation of the following zirconium complex precursors: *rac*-(EBI)ZrX_2 (X = NMe_2, Cl, Me) [9], $[Me_2C(Cp)(Flu)]ZrMe_2$ [6], *rac*-(EBI)ZrMe$[OC(O^iPr){=}CMe_2]$ [2c], and *rac*-(EBI)Zr$[OC(O^iPr){=}CMe_2]_2$ [2c].

2.2. Synthesis of *rac-(EBI)ZrCl[$OC(O^iPr){=}CMe_2$]* (**1**)

In an argon-filled glovebox, a 30 mL glass reactor was charged with *rac*-(EBI)$ZrCl_2$ (0.126 g, 0.301 mmol) and 10 mL toluene. To this stirred reactor was added a toluene (5 mL) solution of $LiOC(O^iPr){=}CMe_2$ (0.049 g, 0.361 mmol). The resulting turbid pale yellow mixture was stirred for 24 h at ambient temperature, after which all volatiles were removed in vacuo, giving a yellow oily residue. The residue was extracted with hexanes, and the resulting suspension was filtered twice through a pad of Celite; the filtrate was cooled to −30 °C inside the freezer of the glovebox for about 10 h to afford complex **1** as a bright yellow microcrystalline solid. The combined yield from several crops of recrystallization, after filtration and drying, was 0.12 g (78%). Anal. Calc. for $C_{27}H_{29}O_2ClZr$: C, 63.33; H, 5.71. Found: C, 63.31; H, 5.71%.

^1H NMR (C_6D_6, 23 °C) for **1**: δ 7.32–7.08 (m, 6H), 6.95–6.88 (m, 2H), 6.58 (d, $J = 3.3$ Hz, 1H), 6.28 (d, $J = 3.3$ Hz, 1H), 6.01 (d, $J = 3.3$ Hz, 1H), 5.83 (d, $J = 3.3$ Hz, 1H), 3.99 (sept, $J = 6.3$ Hz, 1H, $OCHMe_2$), 3.14–3.04 (m, 4H, C_2H_4), 1.79 (s, 3H, $=CMe_2$), 1.47 (s, 3H, $=CMe_2$), 1.16 (d, $J = 6.3$ Hz, 3H, $OCHMe_2$), 1.13 (d, $J = 6.3$ Hz, 3H, $OCHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C): δ 154.01 (ZrOC), 130.81, 129.41, 129.30, 126.18, 125.91, 125.46, 125.36, 123.99, 123.08, 123.07, 121.93, 121.24, 120.52, 119.29, 114.33, 114.05, 108.86, 104.93 (18 resonances for indenyl-ring carbons), 85.45 ($=CMe_2$), 68.40 ($OCHMe_2$), 28.89 and 28.57 (CH_2CH_2), 22.88, ($OCHMe_2$), 22.01, ($OCHMe_2$), 17.77 ($=CMe_2$), 17.35 ($=CMe_2$).

2.3. Synthesis of *rac-(EBI)Zr(OTf)[$OC(O^iPr){=}CMe_2$]* (**2**)

In an argon-filled glovebox, a 30 mL glass reactor was charged with *rac*-(EBI)Zr[$OC(O^iPr){=}CMe_2]_2$ (0.100 g, 0.165 mmol) and 10 mL toluene. To this pre-cooled (−30 °C) and stirred yellow solution was added Me_3SiOTf (0.046 g, 0.265 mmol) via pipette. The resulting dark orange solution was stirred for 80 h at ambient temperature, after which all volatiles were removed in vacuo, affording an orange oily residue. The residue was extracted with hexanes, and the resulting suspension was filtered twice through a pad of Celite; the filtrate was cooled to −30 °C inside the freezer of the glovebox for about 16 h to afford 0.092 g (89%) complex **2** as a bright orange microcrystalline solid after filtration and drying. Anal. Calc. for $C_{28}H_{29}O_5F_3SZr$: C, 53.74; H, 4.67. Found: C, 54.37; H, 4.89%.

^1H NMR (CD_2Cl_2, 23 °C) for **2**: δ 7.87–7.82 (m, 2H), 7.82–7.17 (m, 6H), 6.76 (d, $J = 3.3$ Hz, 1H), 6.45 (d, $J = 3.3$ Hz, 1H), 6.42 (d, $J = 3.3$ Hz, 1H), 6.28 (d, $J = 3.3$ Hz, 1H), 3.91–3.88 (m, 4H, C_2H_4), 3.63 (sept, $J = 6.3$ Hz, 1H, $OCHMe_2$), 1.50 (s, 3H, $=CMe_2$), 1.29 (s, 3H, $=CMe_2$), 1.13 (d, $J = 6.3$ Hz, 3H, $OCHMe_2$), 1.06 (d, $J = 6.3$ Hz, 3H, $OCHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C): δ 154.20 (ZrOC), 129.15, 128.96, 126.75, 126.81, 126.20, 125.85, 124.76, 124.59, 123.90, 121.99, 120.71, 120.48, 116.52, 116.09, 114.98, 110.06, 106.87, 106.11 (18 resonances for indenyl-ring carbons), 87.26 ($=CMe_2$), 68.81 ($OCHMe_2$), 29.01 and 28.58 (CH_2CH_2), 21.82, ($OCHMe_2$), 21.57 ($OCHMe_2$), 18.91 (CF_3) 17.68 ($=CMe_2$), 17.38 ($=CMe_2$). ^{19}F NMR (CD_2Cl_2, 23 °C): δ −74.95.

2.4. Isolation of *rac-(EBI)Zr(OTf) [$OC(OMe){=}C(Me)CH_2C(Me_2)C(O^iPr){=}O$]* (**3**): *the single MMA addition product of* **2**

In an argon-filled glovebox, a 20 mL glass vial was charged with **2** (0.080 g, 0.127 mmol) and 10 mL CH_2Cl_2. To this pre-cooled (−30 °C) and stirred yellow solution was added MMA (0.013 g, 0.127 mmol). The resulting solution was stirred for 1 h at ambient temperature, after which an aliquot was taken and dried in vacuo for ^1H and ^{19}F NMR analysis which showed the formation of single MMA addition product **3**. All volatiles of the remaining solution were removed in vacuo, giving a yellow oil. The residue was extracted with hexanes and filtered through a pad of Celite; the filtrate was cooled to −30 °C inside the freezer of the glovebox for about 48 h to afford the product as a bright orange microcrystalline solid. The combined yield from several crops of recrystallization, after filtration and drying, was 0.055 g (60%). Significantly, the isolated complex **3** contains (as shown by NMR) a small amount of oligomers (i.e., higher MMA addition products), indicating that multiple MMA additions can occur and thus a possibility to produce high polymer in the presence of an excess of MMA using neutral zirconocenes either **2** or **3**.

^1H NMR (CD_2Cl_2, 23 °C) for **3**: δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.44–7.17 (m, 6H), 6.76 (s, br, 1H), 6.42 (s, br, 1H), 6.36 (s, br, 1H), 6.27 (s, br, 1H), 4.93 (sept, $J = 6.3$ Hz, 1H, $OCHMe_2$), 3.87 (m, 4H, C_2H_4), 3.12 (s, 3H, OMe), 2.18 (q_{AB}, 2H, CH_2), 1.24 (d, $J = 6.3$ Hz, 3H, $OCHMe_2$), 1.21 (d, $J = 6.3$ Hz, 3H, $OCHMe_2$), 1.12 (s, 3H, $=CMe$), 1.11 and 1.09 (s, 6H, $>CMe_2$). ^{19}F NMR (CD_2Cl_2, 23 °C): δ −75.05.

2.5. Synthesis of *[$Me_2C(Cp)(Flu)$]ZrMe-[$OC(O^iPr){=}CMe_2$]* (**4**)

In an argon-filled glovebox, a 30 mL glass reactor was charged with [$Me_2C(Cp)(Flu)$]$ZrMe_2$ (0.195 g, 0.498 mmol) and 10 mL toluene. To this pre-cooled (−30 °C) and stirred solution was added Me_3SiOTf (0.143 g, 0.647 mmol) via pipette. The resulting dark orange solution was stirred for 24 h at ambient temperature, after which all volatiles were removed in vacuo, affording a red oily solid. The crude product was extracted with hexanes, and the resulting suspension was filtered twice through a pad of Celite; the red filtrate was cooled to −30 °C inside the freezer of the glovebox to afford the spectroscopically pure triflate derivative [$Me_2C(Cp)(Flu)$]Zr(OTf)Me as a red microcrystalline solid. The combined yield from several crops of recrystallization, after filtration and drying, was 0.196 g (75%).

^{1}H NMR (C_6D_6, 23 °C) for [$Me_2C(Cp)(Flu)$]Zr(OTf)Me: δ 7.81 (d, 1H, Flu), 7.58 (d, 1H, Cp), 7.31–6.80 (m, 6H, Flu), 6.18 (q, 1H, Cp), 6.02 (q, 1H, Cp), 5.42 (q, 1H, Cp), 4.74 (q, 1H, Cp), 1.65 (s, 3H, $>\mathrm{C}Me_2$), 1.56 (s, 3H, $>\mathrm{C}Me_2$), −0.77 (Zr–*Me*) ^{19}F NMR (C_6D_6, 23 °C): δ −77.21.

In an argon-filled glovebox, a 30 mL glass reactor was charged with [$Me_2C(Cp)(Flu)$]Zr(OTf)Me (0.100 g, 0.190 mmol) and 10 mL toluene. To this pre-cooled (−30 °C) and stirred red solution was added a toluene (2 mL) solution of $LiOC(O^iPr){=}CMe_2$ (0.033 g, 0.247 mmol). The resulting solution changed from clear red to a turbid orange suspension upon warming to ambient temperature over 20 min with a moderate exotherm being detected. All volatiles were immediately removed in vacuo, the residue extracted with hexanes, and the resulting suspension filtered twice through a pad of Celite. The filtrate was cooled to −30 °C inside the freezer of the glovebox for about 48 h to afford complex **4** as an orange solid. The combined yield from several crops of recrystallization, after filtration and drying, was 0.063 g (65%). The isolated product is spectroscopically pure, as shown by its ^{1}H NMR spectrum (see Fig. 1); however, owing to its thermal instability, this ester enolate complex is not suitable for subject to elemental analysis.

^{1}H NMR (CD_2Cl_2, 23 °C) for **4**: δ 8.11 (d, 1H, Flu), 8.02 (d, 1H, Flu), 7.97 (d, 1H, Flu), 7.44 (t, 1H, Flu), 7.29–7.11 (m, 4H, Flu), 6.18 (q, 1H, Cp), 6.07 (q, 1H, Cp), 5.68 (q, 1H, Cp), 5.60 (q, 1H, Cp), 3.51 (sept, $J = 6.3$ Hz, 1H, $OC\mathit{H}Me_2$), 2.30 (s, 3H, $>\mathrm{C}Me_2$), 2.19 (s, 3H, $>\mathrm{C}Me_2$), 1.32 (s, 3H, $=\mathrm{C}Me_2$), 1.17 (s, 3H, $=\mathrm{C}Me_2$), 1.04 (d, $J = 6.0$ Hz, 3H, $OCH\mathit{Me}_2$), 0.90 (d, $J = 6.3$ Hz, 3H, $OCH\mathit{Me}_2$), −1.28 (Zr–*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 152.49 (ZrO*C*), 127.95, 126.81, 124.49, 124.08, 123.87, 123.22, 122.42, 122.27, 121.72, 121.06, 120.12, 119.36, 119.11, 115.94, 111.58, 102.18, 100.38, 84.15 (18 resonances for Flu and Cp carbons), 84.56 ($=\mathit{C}Me_2$), 67.74 ($O\mathit{C}HMe_2$), 40.89 ($>\mathit{C}Me_2$), 29.11 and 28.90 ($>\mathrm{C}\mathit{Me}_2$), 26.22 (Zr–*Me*), 21.96 and 21.58 ($OCH\mathit{Me}_2$), 16.88 and 16.59 ($=\mathrm{C}\mathit{Me}_2$).

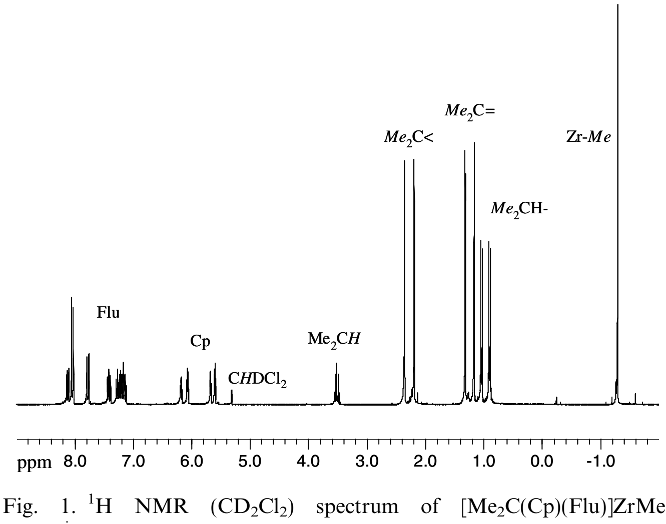


Fig. 1. ^{1}H NMR (CD_2Cl_2) spectrum of [$Me_2C(Cp)(Flu)$]ZrMe[$OC(O^iPr){=}CMe_2$] (**4**).

2.6. In situ generation of ion pair [$Me_2C(Cp)(Flu)$]Zr^+(THF) [$OC(O^iPr){=}CMe_2$][$MeB(C_6F_5)_3$]$^-$ (5)

The cationic ester enolate species **5** can be readily generated by in situ mixing of equimolar amounts of neutral complex **4** and $(C_6F_5)_3B\cdot THF$ in CD_2Cl_2, as shown by NMR. ^{1}H NMR (CD_2Cl_2, 23 °C) for **5**: δ 8.33 (d, 1H, Flu), 8.24 (d, 1H, Flu), 8.05 (t, 2H, Flu), 7.53–7.39 (m, 4H, Flu), 6.60 (q, 1H, Cp), 6.01 (m, 2H, Cp), 5.87 (q, 1H, Cp), 3.56 (sept, $J = 6.3$ Hz, 1H, $OC\mathit{H}Me_2$), 3.58–3.45 (m, 4H, α-$C\mathit{H}_2$, THF), 2.51 (s, 3H, $>\mathrm{C}Me_2$), 2.47 (s, 3H, $>\mathrm{C}Me_2$), 1.87 (m, 2H, β-$C\mathit{H}_2$, THF), 1.76 (m, 2H, β-$C\mathit{H}_2$, THF), 1.38 (s, 3H, $=\mathrm{C}Me_2$), 1.34 (s, 3H, $=\mathrm{C}Me_2$), 1.12 (d, $J = 6.3$ Hz, 3H, $OCH\mathit{Me}_2$), 1.02 (d, $J = 6.3$ Hz, 3H, $OCH\mathit{Me}_2$), 0.48 (s, br, B–Me). ^{19}F NMR (CD_2Cl_2, 23 °C): δ −131.52 (d, $^3J_{F-F} = 20.9$ Hz, 6F, *o*-F), −163.60 (t, $^3J_{F-F} = 20.9$ Hz, 3F, *p*-F), −166.20 (m, 6F, *m*-F).

2.7. General polymerization procedures

Polymerizations were performed in 20-mL glass reactors inside the glovebox at ambient temperature (~23 °C). In a typical procedure for the polymerization using the in situ generated cationic complex **5**, complex **4** (10 mg, 19.8 μmol) and $(C_6F_5)_3B\cdot THF$ (11.5 mg, 19.8 μmol) were dissolved in 1.25 mL CH_2Cl_2 and allowed to stir for 10 min at ambient temperature to cleanly generate the catalyst **5**. To this reactor was quickly added 200 equiv. of MMA (3.96 mmol) via pipette, and the sealed flask was kept with vigorous stirring. After the desired time interval, a 0.2 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4 mL vial containing 0.6 mL of undried "wet" $CDCl_3$ stabilized by 250 ppm of BHT-H. The quenched aliquots were analyzed by ^{1}H NMR to obtain monomer conversion data. The polymerization was immediately quenched after the removal of the aliquot by the addition of 5 mL 5% HCl-acidified methanol. For MMA polymerization, the quenched mixture was precipitated into 100 mL of methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. For DMAA polymerization, the quenched mixture was precipitated into 100 mL of diethyl ether, stirred for 30 min, and the solvent was decanted off. An additional 75 mL of diethyl ether was used to wash the polymer and then decanted; the P(DMAA) product was dried in a vacuum oven at 50 °C to a constant weight.

2.8. Polymer characterizations

Gel permeation chromatography (GPC) analyses of the polymers were carried out at 40 °C and a flow rate of

1.0 mL/min, with $CHCl_3$ as the eluent, on a Waters University 1500 GPC instrument equipped with four 5 μm PL gel columns (Polymer Laboratories) and calibrated using 10 PMMA standards. Chromatograms were processed with Waters Empower software (2002); number-average molecular weight and polydispersity of polymers are given relative to PMMA standards. NMR spectra of the polymers were recorded in $CDCl_3$ and analyzed according to literature procedures [10].

3. Results and discussion

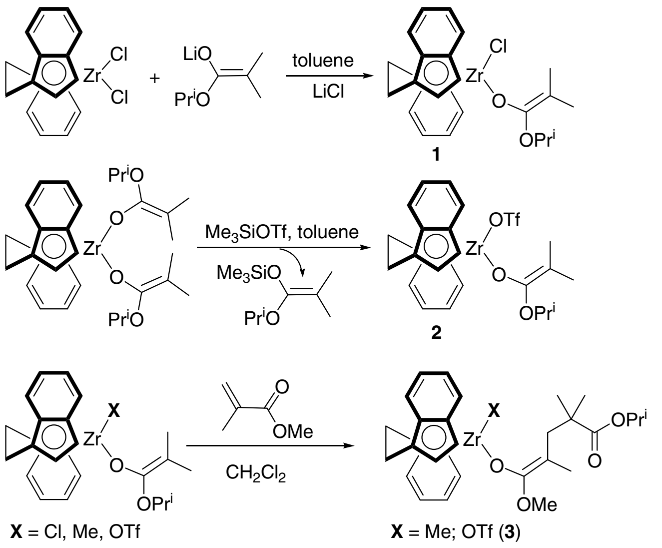
3.1. Neutral zirconocene ester enolate complexes with C_2-ligation

The synthesis of the chloride derivative *rac*-(EBI)ZrCl[OC(O^{i}Pr)=CMe$_2$] (**1**) was accomplished in a straightforward fashion by the reaction of the dichloride zirconocene precursor *rac*-(EBI)ZrCl$_2$ with 1.2 equiv. of LiOC(O^{i}Pr)=CMe$_2$ in toluene (Scheme 1). The NMR spectroscopic characteristics of **1** are nearly identical to those of the known methyl derivative *rac*-(EBI)ZrMe[OC(O^{i}Pr)=CMe$_2$] [2c], except for noticeable down-field shifts of the ^{1}H NMR signals for the methine proton in –C*H*Me$_2$ (by 0.3 ppm) and those for the indenyl C$_5$-ring protons as compared with the methyl derivative. The triflate derivative *rac*-(EBI)Zr(OTf)[OC(O^{i}Pr)=CMe$_2$] (**2**) was conveniently synthesized by the reaction of *rac*-(EBI)Zr[OC(O^{i}Pr)=CMe$_2$]$_2$ [2c] with Me$_3$SiOTf, where the reaction coproduct silyl ketene acetal was removed by extensive vacuum (Scheme 1).

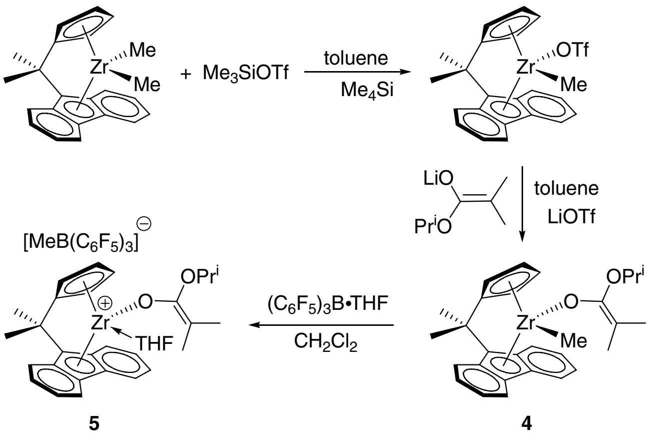
Unlike the methyl derivative, the chloride analog **1** does not react with MMA in CH_2Cl_2 at ambient temperature. On the other hand, the triflate derivate **2** reacts with 1 equiv. of MMA to form the corresponding single-MMA-addition product *rac*-(EBI)Zr(OTf)[OC(OMe)=C(Me)CH$_2$C(Me$_2$)C(O^{i}Pr)=O] (**3**, Scheme 1). However, unlike the methyl derivative, which cleanly affords the single-MMA-addition product in the presence of 1 or more equiv. of MMA [2b], the addition product **3** derived from the reaction of complex **2** with 1 equiv. of MMA is accompanied by the formation of a small amount of higher MMA addition products, thereby suggesting a possibility to produce polymer in the presence of an excess of MMA (vide infra). Nevertheless, both ^{1}H and ^{19}F NMR spectra of **3** feature characteristic signals for a triflate zirconocene ester enolate structure (which differs from that of the precursor **2**) and additionally an isopropyl ester group [–C(O^{i}Pr)=O]. Specifically, the ^{1}H NMR (CD_2Cl_2) signal for the methine proton in –C*H*Me$_2$ (sept, 3.6 ppm) attached to the *enolate ligand* in **2** is substantially down-field shifted by 1.3 ppm to 4.9 ppm (sept) for the methine proton in –C*H*Me$_2$ now attached to the *ester group* in **3**. In agreement with these spectroscopic changes on going from **2** to **3**, the added MMA now becomes a methyl ester enolate ligand [i.e., –OC(OMe)=C(Me)CH$_2$–] bound to Zr in **3**, which can be readily characterized by ^{1}H NMR [δ 3.12 (O*Me*), 2.18 (AB quartet for C*H*$_2$), 1.12 (=C*Me*)]. The triflate ligand in **3** is still covalently bound to Zr, as the ^{19}F NMR for the OTf signal (−75.0 ppm in CD_2Cl_2) remained the same on going from **2** to **3**, whereas the identical chemical shift for the –C*H*Me$_2$ proton of the isopropyl ester group in **3** to that in free isopropyl isobutyrate (4.9 ppm in CD_2Cl_2) suggests that the terminal ester group in **3** is presumably not coordinated to the Zr center. Most significantly, unlike the single-MMA-addition product derived from the methyl derivative, the triflate derivative **3** can undergo further MMA additions to form polymer (vide infra).

3.2. Neutral and cationic zirconocene ester enolate complexes with C_s-ligation

Scheme 2 outlines the procedures for the synthesis of the neutral zirconocene ester enolate complex [Me$_2$C(Cp)(Flu)]ZrMe[OC(O^{i}Pr)=CMe$_2$] (**4**) and the generation of



Scheme 1.



Scheme 2.

the corresponding cationic complex $[Me_2C(Cp)(Flu)]Zr^+(THF)[OC(O^iPr)=CMe_2][MeB(C_6F_5)_3]^-$ (**5**). Thus, treatment of $[Me_2C(Cp)(Flu)]$ $ZrMe_2$ with Me_3SiOTf readily affords the methyl triflate intermediate $[Me_2C(Cp)(Flu)]Zr(OTf)Me$, which subsequently reacts with $LiOC(O^iPr)=CMe_2$ to form the methyl zirconocene ester enolate complex **4**. The ^1H NMR spectrum (Fig. 1) shows C_1-symmetry for **4** in a CD_2Cl_2 solution, featuring an AA′BB′ pattern for the four Cp protons as well as two doublets and two singlets for the two diastereotopic isopropoxy methyl and two bridging isopropylidene methyl groups, respectively.

Clean, instantaneous, and quantitative generation of the THF-stabilized cationic ester enolate complex **5** was accomplished by treatment of the methyl zirconocene ester enolate **4** with $(C_6F_5)_3B \cdot THF$ in CD_2Cl_2 at ambient temperature (Fig. 2). Most characteristically upon formation of the cation, the sharp singlet at −1.28 ppm in ^1H NMR for the Zr–*Me* protons in **4** disappeared and a broad singlet appeared at 0.48 ppm for the B–*Me* protons of the $[MeB(C_6F_5)_3]^-$ anion in **5**. On going from neutral **4** to cation **5**, protons for the rest of the moieties all down-field shifted, consistent with the formation of the more-electron deficient, cationic species **5**. Conversely, on going from $(C_6F_5)_3B \cdot THF$ to $[MeB(C_6F_5)_3]^-$, *para*- and *meta*-fluorines in ^{19}F NMR upfield shifted by 8.7 and 4.1 ppm (see Fig. 2), respectively, consistent with the borate anion formation. These ^1H and ^{19}F NMR observations, coupled with a small chemical shift difference of <3 ppm [Δ (*m*,*p*-F) = 2.6 ppm in **5**] between the *para*- and *meta*-fluorines in the ^{19}F NMR spectrum for the anion, clearly show the formation of the cation **5** paired with the non-coordinating $[MeB(C_6F_5)_3]^-$ anion [11].

3.3. Polymerization of MMA and DMAA

Among the neutral C_2-ligated chiral zirconocene ester enolate complex series, *rac*-(EBI)ZrX$[OC(O^iPr)=CMe_2]$ (X = Me, Cl, OTf), the investigation into their reactivity toward MMA in a non-coordinating polar solvent (CH_2Cl_2) at ambient temperature showed that the chloride derivative **1** is inactive toward any MMA additions, the methyl derivative adds only 1 equiv. of MMA, and the triflate derivative **2** can add either 1 equiv. of MMA to form the single-MMA-addition product **3** or multiple equivalents of MMA to form a polymer product. Monitoring of the reaction between **2** or **3** and 200 equiv. of MMA by ^1H NMR in CD_2Cl_2 clearly showed gradual conversion of MMA to P(MMA), whereas the OTf signal monitored by ^{19}F NMR gradually shifted from −75.0 ppm as a sharp singlet at the beginning of the polymerization to −76.1 ppm as a broad singlet during the course of the polymerization, suggesting that the OTf ligand becomes more partially dissociated from the Zr center as the chain grows.

The preparative scale polymerization in a $[MMA]_0/[\mathbf{3}]_0$ ratio of 200 for 24 h at ambient temperature indeed yielded P(MMA) with $M_n = 10300$ and $M_w/M_n = 1.24$, upon which the monomer conversion reached only 22% (run 1, Table 1), giving an initiator efficiency (I^*) = 49% [$I^* = M_n(\text{calcd.})/M_n(\text{exptl.})$, where $M_n(\text{calcd.}) = MW(MMA) \times [MMA]_0/[\mathbf{3}]_0 \times \text{conversion}\%$]. The low activity (low conversion, long reaction time) of this neutral species is in drastic contrast to that of the cationic zirconocenium ester enolate species, which typically effects quantitative monomer conversions within just a few minutes of reaction time under similar conditions and also produces highly isotactic

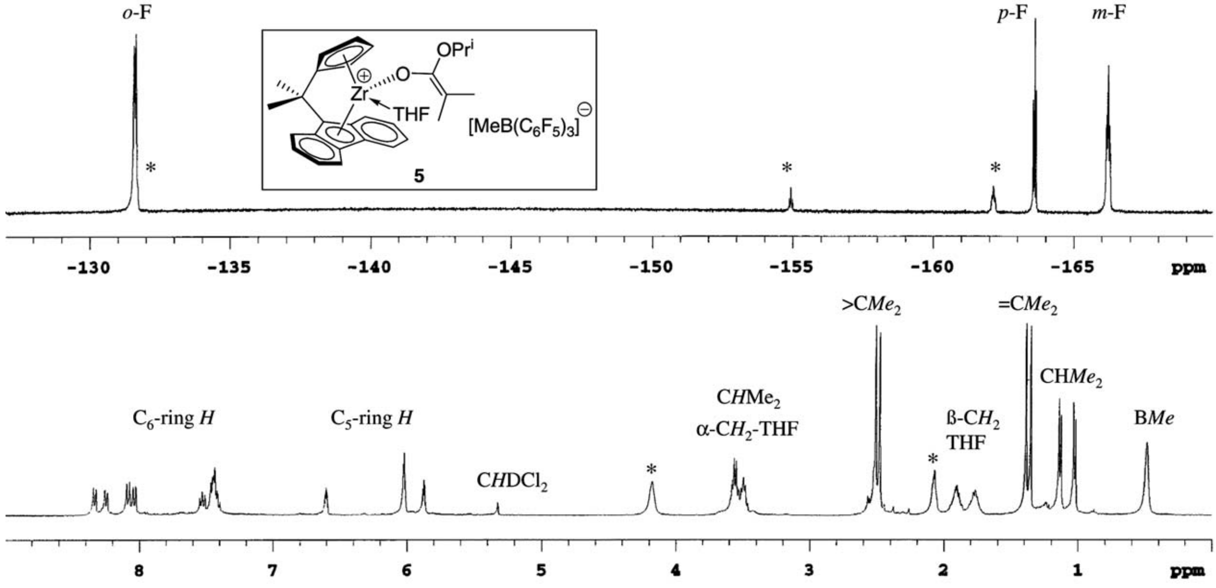


Fig. 2. ^1H (bottom) and ^{19}F NMR (top) spectra of **5** generated in situ by mixing **4** and $(C_6F_5)_3B \cdot THF$ in CD_2Cl_2; peaks marked with ∗ correspond to $(C_6F_5)_3B \cdot THF$ added in excess for comparison.

Table 1
MMA and DMAA polymerization results by zirconocene ester enolate complexes[a]

Run no.	Monomer	Complex	Time (h)	Conv.(%)	10^4 M_n[b] (g/mol)	PDI[b] (M_w/M_n)	[*mm*][c] (%)	[*mr*][c] (%)	[*rr*][c] (%)
1	MMA	**3**	24	25	1.03	1.24	46.5	26.7	26.8
2	MMA	**5**	4	65	38.8	1.57	4.0	32.0	64.0
3	MMA	**4** + **5**	4	55	1.95	1.28	7.0	31.8	61.2
4	DMAA	**5**	1.5	51	>500	Bimodal[d]	n.d.	n.d.	n.d.
5	DMAA	**5**[e]	4	23	>200	Bimodal[d]	n.d.	n.d.	n.d.

[a] Carried out in CH_2Cl_2 at ambient temperature inside a glovebox; $[monomer]_0/[Zr]_0 = 200$.

[b] Number average molecular weight (M_n) and polydispersity index (PDI) determined by GPC relative to PMMA standards.

[c] Methyl triad distribution (tacticity) determined by ^1H NMR spectroscopy.

[d] The reaction mixture gelled at 1.5 h; there exists also a low molecular weight ($M_n = 5.4$ kg/mol for run 4 and 0.8 kg/mol for run 5) fraction on GPC traces.

[e] The solvent volume is increased by 4-fold.

polymer via an enantiomorphic-site control mechanism [2]. Surprisingly, despite its chiral C_2-ligation in neutral **3**, the resulting polymer is not highly isotactic as is the polymer by the cationic species; rather, the polymer produced by neutral **3** shows an unusual tacticity with a methyl triad distribution of $[mm] = 46.5\%$, $[mr] = 26.7\%$, $[rr] = 26.8\%$. This tacticity is presumably a result of double stereo-differentiation, namely the interplay between the enantiomorphic-site control (by the chiral metal center) and chain-end control (by the stereogenic center of the last enchained monomer) mechanisms. To the best of our knowledge, the only other C_2-ligated chiral neutral group 4 metallocene complex that has been found active for MMA polymerization is a zirconocene complex incorporating the chelating isopropylidene-bridged Cp *o*-carboranyl ligand: *rac*-Zr(η^5:η^1-$CpCMe_2CB_{10}H_{10}C)_2$ [12]; this complex, however, polymerizes MMA in polar, coordinating THF (which typically retards or shuts down the coordinative anionic polymerization of MMA by metallocene catalysts) and yields unexpectedly syndio-rich ($[rr] = 65.7\%$) P(MMA) despite its C_2 symmetry. Furthermore, the initiator efficiency I^* based on the polymerization results for 24 h is calculated to be ~510%, indicating considerable chain transfer processes. Hence, the polymerization characteristics of the neutral carboranyl complex are inconsistent with a coordinative anionic mechanism and are also in sharp contrast to those of the neutral ester enolate complex **3**.

As pointed out earlier, the methyl cation $[Me_2C(Cp)(Flu)ZrMe]^+$ is inactive for MMA polymerization under various conditions. Satisfyingly, the ester enolate cation **5** is moderately active for MMA polymerization. Thus, the in situ generated cationic ester enolate **5** polymerizes MMA in CH_2Cl_2 ($[MMA]_0/[\mathbf{5}]_0 = 200$) for 4 h at ambient temperature to high molecular weight P(MMA) with $M_n = 388\,000$ and $M_w/M_n = 1.57$, upon which the monomer conversion reached 65% (run 2, Table 1); this gives a low initiator efficiency (I^*) <4%, implying that the active propagating species is unstable at ambient temperature and that the majority of the active species has been deactivated due to decomposition. The resulting polymer has a low syndiotacticity, with a methyl triad distribution of $[rr] = 64\%$, $[mr] = 32\%$, $[mm] = 4\%$. A triad test using $4[mm][rr]/[mr]^2$ gave 1.0, conforming to a chain-end control mechanism; this result compares well to that observed for the related cationic titanium ester enolate complex bearing the prochiral C_s-constrained geometry ligand, $[Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)]Ti^+(THF)[OC(O^iPr){=}CMe_2][MeB(C_6F_5)_3]^-$ [4a], but it is in sharp contrast to that observed for the isostructural constrained geometry zirconium complex which produces highly isotactic P(MMA) via a site control mechanism at low temperatures [4b]. These results further show the apparent high sensitivity of relative rates of racemization (at the chiral metal center by the process of ligand exchange) and propagation (at the C–C bond formation step by intramolecular Michael addition) to polymerization activity and stereospecificity in the MMA polymerization by the C_s-ligated metallocene system; variations in the type of metal and C_s-ligation can drastically change the polymerization activity and stereocontrol mechanism.

As the unimetallic propagation by the cationic ester enolate **5** is hampered by its low initiator efficiency, we also investigated the MMA polymerization by the bimetallic propagation pathway [1e] with a mixture containing both neutral ester enolate **4** (as initiator) and cationic ester enolate **5** (as catalyst), which is generated in situ by the reaction of 2 equiv. of **4** with 1 equiv. of $(C_6F_5)_3B \cdot THF$. The MMA polymerization by this two-component system produces P(MMA) with significantly lower molecular weight ($M_n = 19\,500$, $M_w/M_n = 1.28$), upon which the monomer conversion reached 55% (run 3, Table 1); this gives a substantially higher initiator efficiency ($I^* = 56\%$), as compared to the polymerization by **5** alone.

Complex **5** is also active for DMAA polymerization (run 4), producing essentially atactic P(DMAA). This polymerization is complicated by gel formation, and the resulting polymer has a bimodal molecular weight distribution consisting of a predominant high molecular weight fraction ($M_n > 5 \times 10^6$) and a low molecular weight fraction ($M_n = 5400$); this behavior can be explained by the substantial catalyst deactivation present in the current catalyst system (vide supra) to form presumably neutral zirconocene species that can also readily initiate the DMAA polymerization but via a radical process [13]. Attempts to avoid the gel formation by increasing the solvent volume by

4-fold (run 5) resulted in similar polymerization characteristics but with much lower activity.

4. Conclusions

In efforts to address the inactivity of MMA polymerization by the zirconocene methyl cation with C_s-ligation, $[Me_2C(Cp)(Flu)ZrMe]^+$, and the neutral methyl zirconocene ester enolate with C_2-ligation, *rac*-(EBI)ZrMe[O-C(O^{i}Pr)=CMe$_2$], we have synthesized a series of neutral and cationic chiral *ansa*-zirconocene ester enolate complexes **1**–**5** with C_2- or C_s-ligation. Within the neutral zirconocene ester enolate complex series, *rac*-(EBI)ZrX-[OC(O^{i}Pr)=CMe$_2$] (X = Cl, Me, OTf), the chloride derivative **1** is inactive toward any MMA additions, the methyl derivative adds cleanly only 1 equiv. of MMA, and the triflate derivative **2** can add either 1 equiv. of MMA to form the single-MMA-addition product **3** or multiple equivalents of MMA to form a polymer product. The relatively high reactivity of the triflate derivative in this series toward MMA additions can be attributed to the lability of the OTf ligand which can gradually and partially dissociate from the metal center to accommodate monomer enchainment as the polymer chain grows.

Unlike the methyl cation $[Me_2C(Cp)(Flu)ZrMe]^+$, which is inactive for MMA polymerization under various conditions, the ester enolate cation **5** having the same ligation, which is derived from the methyl zirconocene ester enolate **4**, is active for polymerization of MMA and DMAA under ambient conditions. The resulting P(MMA) has high molecular weight but low syndiotacticity, and the polymerization conforms to a chain-end control mechanism. These results, coupled with the findings from the titanium and zirconium ester enolate complexes bearing the related prochiral C_s-constrained geometry ligand [4], indicate that current efforts to produce highly syndiotactic P(MMA) using C_s-ligated metallocene catalysts via a site-control mechanism are complicated by the subtle interplay between the relative rates of racemization at the chiral metal center and propagation at the C–C bond formation step. Appropriate site-controlled syndiospecific metallocene catalysts are those that can regulate the relative rates of those events, presumably achievable by variations of the ligand sterics; research toward this direction is currently underway.

Acknowledgments

Funding for this work was provided by the National Science Foundation and Colorado State University. We thank Boulder Scientific Co. for the gift of $B(C_6F_5)_3$.

References

[1] (a) G. Stojcevic, H. Kim, N.J. Taylor, T.B. Marder, S. Collins, Angew. Chem. Int. Ed. 43 (2004) 5523–5526;
(b) M. Ferenz, F. Bandermann, R. Sustmann, W. Sicking, Macromol. Chem. Phys. 205 (2004) 1196–1205;
(c) A.D. Bolig, E.Y.-X. Chen, J. Am. Chem. Soc. 124 (2002) 5612–5613;
(d) F. Bandermann, M. Ferenz, R. Sustmann, W. Sicking, Macromol. Symp. 174 (2001) 247–253;
(e) Y. Li, D.G. Ward, S.S. Reddy, S. Collins, Macromolecules 30 (1997) 1875–1883.

[2] (a) W.R. Mariott, E.Y.-X. Chen, Macromolecules 38 (2005) 6822–6832;
(b) A. Rodriguez-Delgado, E.Y.-X. Chen, Macromolecules 38 (2005) 2587–2594;
(c) A.D. Bolig, E.Y.-X. Chen, J. Am. Chem. Soc. 126 (2004) 4897–4906.

[3] J. Jin, W.R. Mariott, E.Y.-X. Chen, J. Polym. Chem. A 41 (2003) 3132–3142.

[4] (a) A. Rodriguez-Delgado, W.R. Mariott, E.Y.-X. Chen, Macromolecules 37 (2004) 3092–3100;
(b) H. Nguyen, A.P. Jarvis, M.J.G. Lesley, W.M. Kelly, S.S. Reddy, N.J. Taylor, S. Collins, Macromolecules 33 (2000) 1508–1510.

[5] (a) A.D. Bolig, E.Y.-X. Chen, J. Am. Chem. Soc. 123 (2001) 7943–7944;
(b) H. Frauenrath, H. Keul, H. Höcker, Macromolecules 34 (2001) 14–19;
(c) P.A. Cameron, V. Gibson, A.J. Graham, Macromolecules 33 (2000) 4329–4335;
(d) Y.-X. Chen, M.V. Metz, L. Li, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 6287–6305;
(e) K. Soga, H. Deng, T. Yano, T. Shiono, Macromolecules 27 (1994) 7938–7940.

[6] (a) A. Razavi, U. Thewalt, J. Organomet. Chem. 445 (1993) 111–114;
(b) J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255–6256.

[7] R.D. Allen, T.E. Long, J.E. McGrath, Polym. Bull. 15 (1986) 127–134.

[8] Y.-J. Kim, M.P. Bernstein, A.S. Galiano Roth, F.E. Romesberg, P.G. Williard, D.J. Fuller, A.T. Harrison, D.B. Collum, J. Org. Chem. 56 (1991) 4435–4439.

[9] G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024–8033.

[10] (a) A. Bulai, M.L. Jimeno, A.-A.A. de Queiroz, A. Gallardo, J.S. Roman, Macromolecules 29 (1996) 3240–3246;
(b) R.C. Ferguson, D.W. Ovenall, Macromolecules 20 (1987) 1245–1248;
(c) R. Subramanian, R.D. Allen, J.E. McGrath, T.C. Ward, Polym. Prepr. 26 (1985) 238–240.

[11] (a) J. Klosin, G.R. Roof, E.Y.-X. Chen, K.A. Abboud, Organometallics 19 (2000) 4684–4686;
(b) A.D. Horton, J. de With, A.J. van der Linden, H. van de Weg, Organometallics 15 (1996) 2672–2674.

[12] E. Hong, Y. Kim, Y. Do, Organometallics 17 (1998) 2933–2935.

[13] W.R. Mariott, E.Y.-X. Chen, Macromolecules 37 (2004) 4741–4743.