

Model Studies of Methacrylate Chain Transfer Polymerization Mediated by Cationic Zirconocene *tert*-Butyl Enolate

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Enolizable ketones and thiols have been investigated as potential transfer agents for methyl methacrylate (MMA) polymerization mediated by the $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system. Addition of 1–10 equiv of acetophenone, acetone, or thiophenols inhibits polymerization, while the system tolerates the presence of *tert*-butylthiol (*t*BuSH). In this case, a moderate decrease in the molecular weight of the PMMAs is observed. The stoichiometric reactivity of these organic acids toward the cationic ester enolate complex $[\text{Cp}_2\text{Zr}(\text{THF})(\text{O}(\text{tBuO})\text{C}=\text{CMe}_2)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1**), which models the active species for MMA polymerization, has been investigated. Ketones undergo aldolization reactions with **1** to generate species that are inactive in MMA polymerization. Thiols readily cleave the Zr–O bond of **1** to give $[\text{Cp}_2\text{Zr}(\text{SR})(\text{THF})]^+$ cations ($\text{R} = \text{tBu}$, **4**; $\text{SC}_6\text{H}_4\text{-}p\text{-Cl}$, **6**; $\text{SC}_6\text{H}_4\text{-}o\text{-OMe}$, **7**). The crystal structure of **7** has been determined. In the presence of a *tert*-butyl ester $\text{R}'\text{CO}_2\text{tBu}$, thiolato complexes **4**, **6**, and **7** smoothly decompose into the corresponding cationic carboxylato complex $[\text{Cp}_2\text{Zr}(\text{THF})(\text{O}_2\text{CR}')^+]^+$ ($\text{R}' = i\text{Pr}$, **5**; CH_3 , **9**) and thiol RSH, with release of isobutene. *tert*-Butylthiolato complex **4** and the in situ combination $\text{Cp}_2\text{Zr}(\text{StBu})\text{Me}/\text{B}(\text{C}_6\text{F}_5)_3$ polymerized quantitatively MMA in toluene to yield PMMAs with narrow dispersity ($M_n/M_w = 1.26\text{--}1.48$), but with molecular weight much higher than the expected M_n values, consistent with poor initiation efficiency and/or instability.

Introduction

Zirconocene-mediated polymerization of methacrylates has attracted much attention in recent years.^{1–4} Detailed studies by the groups of Collins, Chen, and others established either bimetallic or monometallic mechanisms, involving the rate-limiting intramolecular Michael addition of a neutral or cationic zirconocene enolate to activated or nonactivated methyl methacrylate monomer (MMA), respectively.^{1b,d,2f,4g} For this purpose, a variety of neutral and cationic zirconocene

ester enolate complexes that model the propagating species, e.g., $\text{Cp}_2\text{ZrMe}[\text{O}(\text{OtBu})\text{C}=\text{CMe}_2]$,⁵ $\text{Cp}_2\text{Zr}^+(\text{THF})[\text{O}(\text{OtBu})\text{C}=\text{CMe}_2][\text{Me}(\text{B}(\text{C}_6\text{F}_5)_3)]^-$,⁴ⁿ and $(\text{rac-EBI})\text{Zr}^+(\text{THF})[\text{O}(\text{OiPr})\text{C}=\text{CMe}_2][\text{Me}(\text{B}(\text{C}_6\text{F}_5)_3)]^-$,^{2f} were prepared and their reactivity was fully investigated. A major interest of these zirconocenes, when used in a suitable initiating form, is the high degree of control they exhibit over polymerization, i.e., the livingness and stereochemistry of polymerization. The use of a *stoichiometric* amount of metal complex per macromolecular chain

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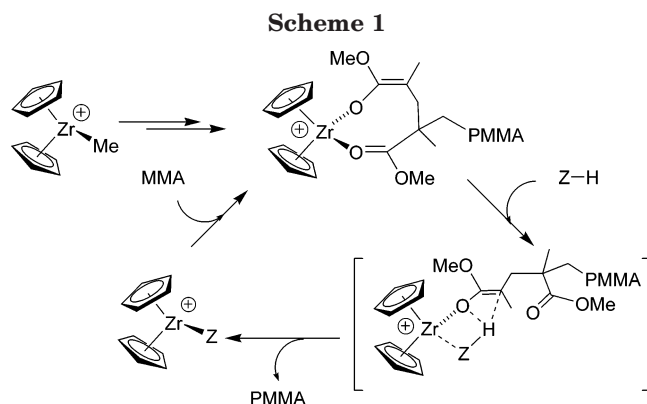


Table 1. MMA Polymerization Promoted by $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ in the Presence of Organic Acids^a

entry	organic acid	org acid/Zr	yield (%)	$M_{n,\text{calc}}^b$ (g·mol ⁻¹)	$M_{n,\text{exp}}^c$ (g·mol ⁻¹)	M_w/M_n^c
1	none		98	38 800	54 500	1.97
2	PhCOMe	1	<1			
3	PhCOMe	5	<1			
4	<i>t</i> BuSH	5	97	3880	29 900	2.85
5	<i>t</i> BuSH	10	48	960	19 800	1.38
6	<i>t</i> BuSH	20	43	430	15 700	2.21
7	<i>p</i> -ClC ₆ H ₄ SH	5	<1			
8	<i>o</i> -MeOC ₆ H ₄ SH	5	<1			

^a Reaction time = 3 h, $T = 20^\circ\text{C}$, solvent = toluene (2 mL); MMA/Zr/B = 200:1:1; Zr = 0.050 mmol. ^b Calculated $M_{n,\text{calc}}$ values considering a bimetallic initiator (in the absence of organic acid) or one polymer chain per organic acid. ^c Experimental M_n and M_w/M_n values as determined by GPC in THF vs PMMA standards.

remains, however, a major limitation of initiating polymerization systems. To transform zirconocenes from *initiators* into true *catalysts*, the search for effective chain transfer agents (CTAs) is of high industrial relevance. In this process, two essential objectives must be achieved: (i) CTAs must cleave the growing PMMA chain, and (ii) the resulting new cationic species must reinitiate polymerization of MMA (Scheme 1). Such an approach that employs organic acids has been recently reported for lanthanidocenes,⁶ which are isoelectronic counterparts of cationic zirconocenes. In this note, we report our preliminary studies on the use of various organic acids as potential CTAs for zirconocene-mediated polymerization of MMA. Polymerization data and results from stoichiometric studies of model complexes are described.

Results and Discussion

The ubiquitous $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system³ was selected for this preliminary study. The effectiveness of several organic acids⁷ that were found suitable for monocomponent lanthanidocene systems,⁶ such as enolizable ketones and thiols, was first screened in MMA polymerization. Representative results obtained with PhCOMe, *t*-BuSH, *p*-ClC₆H₄SH, and *o*-MeOC₆H₄SH are summarized in Table 1. In contrast to group 3 metal initiators, poor performances were observed. Only 1 equiv of acetophenone suffices to inhibit completely

polymerization (entries 2, 3); similar poisoning was also observed with acetone and thiophenols (entries 7, 8). With *t*BuSH, the polymerization was not inhibited for *t*BuSH/Zr up to 5 equiv, but a significant although not complete decrease in conversion was observed in the presence of 10 and 20 equiv (entries 4–6). Promisingly, the molecular weight of the obtained PMMAs ($M_{n,\text{exp}}$) was roughly half that in the absence of thiol, but still much higher than the calculated molecular weight ($M_{n,\text{calc}}$). Two possibilities can account for this decrease of the $M_{n,\text{exp}}$ values: (i) *t*BuSH may modify the mechanism to monometallic species, which promote MMA polymerization still with moderate initiation efficiency ($f = 49$ –67% for entries 4–6 in this hypothesis vs $f = 73\%$ in entry 1); (ii) *t*BuSH acts as a transfer agent with moderate chain transfer efficiency.

To get a better insight in the reactions that actually take place in the above polymerizations, we investigated in more detail the stoichiometric reactivity of these organic acids toward a model complex that mimics the propagating species of the methacrylate polymerization by the $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system. The cationic ester enolate complex $[\text{Cp}_2\text{Zr}(\text{THF})(\text{O}(\text{tBu})\text{C}=\text{CMe}_2)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1**) that we reported recently⁴ⁿ was selected for this purpose.

Reactivity of Zr-Ester Enolate Cationic Species 1 toward Organic Acids. Complex **1-d₈** reacts with 1 equiv of acetophenone in THF-*d*₈ at room temperature within a few minutes to give quantitatively the Zr-aldol **2** (Scheme 2). Cationic complex **2** was fully characterized in solution by 1D and 2D NMR analyses. Key ¹H NMR resonances include a singlet for the equivalent Cp protons (δ 6.46), a singlet for the Me at the chiral (racemic) center (δ 1.78), and two singlets for the diastereotopic C(CH₃)₂ (δ 1.19 and 1.07).⁸ This reactivity evidences that acetophenone does not behave as an organic acid toward **1-d₈** in THF solution as anticipated, but rather as an electrophile.⁹ In a separate experiment, the Zr-aldol complex **2** was found not to initiate MMA polymerization (THF or toluene, 20 °C, MMA/**2** = 200), as expected for an alkoxy complex.^{6a} These observations are in direct line with the inhibition effect of 1–5 equiv of acetophenone in the polymerization of MMA initiated by the $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system in toluene (vide supra). Complex **2** is not stable in THF-*d*₈ at room temperature and transforms over 5 days (52%, based on *t*Bu resonances) with release of isobutene (not polymerized), to give a complex that could not be fully characterized thus far.¹⁰

The reaction of complex **1-d₈** with 1 equiv of acetone in THF-*d*₈ at room temperature proceeds similarly as for acetophenone, giving quantitatively within a few minutes the Zr-aldol **3** (Scheme 2).⁸ Complex **3** was characterized in solution by 1D and 2D ¹H and ¹³C NMR. It also decomposes in THF solution at room

(8) ¹H NMR in CD₂Cl₂ of complexes **2** and **3** generated in THF solution instead of THF-*d*₈ established that no THF molecule coordinates the metal center in those species.

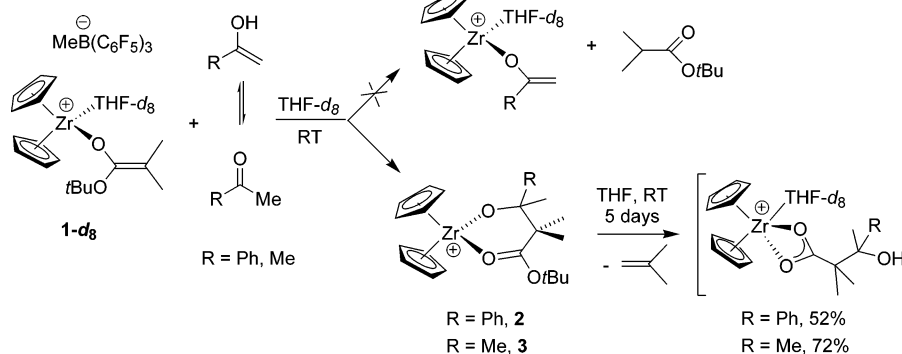
(9) Aldolization reactions between acetophenone derivatives and neutral enolate complexes $[\{\text{Ph}_2\text{N}(\text{CHR})\text{O}\}\text{ZrCp}_2\text{Cl}]$ (R = H, Me) have been described: Cozzi, P. G.; Veya, P.; Floriani, C.; Rotzinger, F. P.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4092–4100.

(10) Based on our previous decomposition studies of Zr-*tert*-butyl enolate,⁴ⁿ the latter can be tentatively formulated $[\text{Cp}_2\text{Zr}(\mu^2\text{-O}_2\text{CCMe}_2\text{-CMe}(\text{R})\text{OH})]^+$.

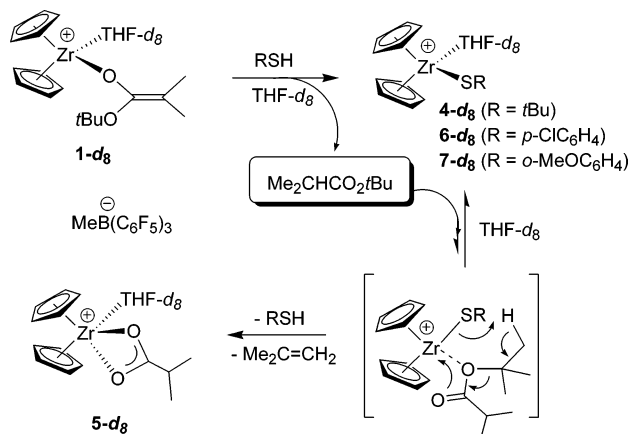
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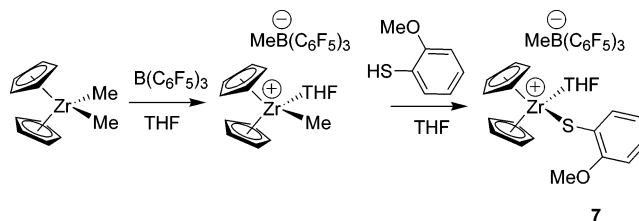
Scheme 2



Scheme 3



Scheme 4



temperature with release of isobutene, somewhat faster than the Zr-aldol **2** (72% based on *t*Bu resonances after 5 days).

On the other hand, complex **1-d₈** reacts in THF-*d*₈ at room temperature with *t*BuSH via protonolysis of the Zr–O(enolate) bond to yield the thiolato complex **4-d₈** with concomitant release of *tert*-butyl isobutyrate (Scheme 3). This is the pathway expected to take place while using *t*BuSH as a transfer agent in the polymerization of MMA. However, species **4-d₈** is not stable under those conditions and decomposes to give isobutyrate complex **5-d₈**, with release of isobutene and regeneration of *t*BuSH.^{11,12} A ¹H NMR monitoring of the reaction of complex **1-d₈** and 3 equiv of *t*BuSH showed complete conversion of **1-d₈** after 1 h to give a 70:30 mixture of **4-d₈** and **5-d₈**.¹³ Complete conversion of **4-d₈** to **5-d₈** was observed after 8 h; at the same time, the resonances for *tert*-butyl isobutyrate disappeared concomitantly with the appearance of those for isobutene and increase of the singlet for *t*BuSH.

The reactions in THF-*d*₈ of **1-d₈** with 1 equiv of *p*-ClC₆H₄SH and *o*-MeOC₆H₄SH, which differ in acidity⁷

and potential coordinating abilities thanks to the substituents on the aryl ring, were also investigated. A ¹H NMR monitoring showed that **1-d₈** was consumed within 10 min to give a 56:44 mixture of **5-d₈** and the thiophenato complexes **6-d₈** and **7-d₈**, respectively. Conversion of **6/7-d₈** to **5-d₈** was completed within 30 min, concomitant with the release of 1 equiv of isobutene and the corresponding thiophenol (*p*-ClC₆H₄SH and *o*-MeOC₆H₄SH, respectively) (Scheme 3). Thus, the more acidic the thiol (i.e., thiophenols vs alkylthiol), the faster the kinetics for both protonolysis of the enolato-Zr complex **1-d₈** and, more surprisingly, subsequent transformation of the thiolato complex (**4-d₈**, **6-d₈**, and **7-d₈**).

The cationic species **7** was independently synthesized by the reaction of Cp₂ZrMe₂ with B(C₆F₅)₃ in THF, followed by the addition of *o*-MeOC₆H₄SH (Scheme 4). This species is stable in THF solution for several weeks at room temperature. Crystals of **7** suitable for an X-ray

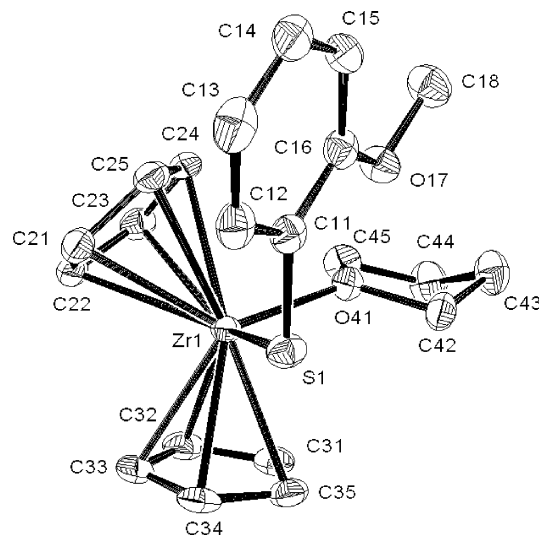


Figure 1. Molecular structure of the cation [Cp₂Zr(THF)(SC₆H₄-*o*-OMe)]⁺ of **7**.

(11) The analogous complexes **4** and **5** were independently generated in nondeuterated THF. ¹H NMR spectroscopy in CD₂Cl₂ established the coordination of one THF molecule in both complexes (see Experimental Section).

(12) Slow decomposition of the parent complex [Cp₂Zr(*St*Bu)](BPh₄) at 20 °C in THF solution to the sulfide-bridged dimer [Cp₂ZrS]₂ and organic products, presumably arising from the decomposition of putative [Me₃C][BPh₄], i.e., Me₃C=CH₂, Me₃CH, B(C₆H₅)₃, and C₆H₆, has been reported. This process (formation of [Cp₂ZrS]₂) was not observed under our conditions. See: Piers, W. E.; Koch, L.; Ridge, D. S.; MacGillivray, L. R.; Zaworotko, M. *Organometallics* **1992**, *11*, 3148–3152.

(13) Reactions of **1-d₈** with 1 or 2 equiv of *t*BuSH were found to proceed more slowly with the same selectivity.

Table 2. Crystal Data and Structure Refinement for 7

empirical formula	C ₄₀ H ₂₈ BF ₁₅ O ₂ SZr
fw	959.72 g·mol ⁻¹
temperature/K	100
wavelength/Å	0.71073
cryst syst	monoclinic
space group	P2 ₁ /n (no. 14)
a/Å	12.9296(2)
b/Å	12.9776(2)
c/Å	22.9040(3)
α/deg	90
β/deg	105.3940(10)
γ/deg	90
volume/Å ³	3705.30(9)
Z	4
density (calcd) Mg·m ⁻³	1.720
absorp coeff/mm ⁻¹	0.467
F(000)	1920
cryst size/mm ³	0.04 × 0.04 × 0.02
θ range for data collection/deg	3.14 to 26.40
index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28
reflins collected	56 591
indep reflins	7565 [R _{int} = 0.0678]
reflins with I > 2σ(I)	5675
completeness to θ = 26.40°	99.6%
absorp correction	semiempirical from equivalents
refinement method	full-matrix least-squares on F ²
data/restraints/params	7565/0/543
goodness-of-fit on F ²	1.015
final R indices [I > 2σ(I)]	R ₁ = 0.0349 wR ₂ = 0.0623
R indices (all data)	R ₁ = 0.0603 wR ₂ = 0.0697
largest diff peak and hole/e Å ⁻³	0.368 and -0.352

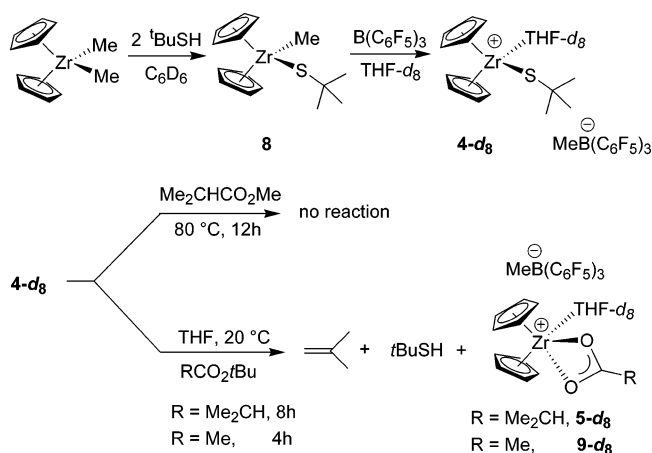
Table 3. Selected Bond Lengths (Å) and Angles (deg) for 7

Zr(1)–O(41)	2.2207(16)	Zr(1)–C(33)	2.470(2)
Zr(1)–S(1)	2.4726(6)	Zr(1)–C(32)	2.477(2)
Zr(1)–C(22)	2.499(2)	Zr(1)–C(21)	2.503(2)
Zr(1)–C(23)	2.503(2)	Zr(1)–C(34)	2.510(2)
Zr(1)–C(25)	2.523(2)	Zr(1)–C(24)	2.527(2)
Zr(1)–C(31)	2.528(2)	Zr(1)–C(35)	2.528(2)
C(11)–S(1)–Zr(1)	113.19(8)	C(12)–C(11)–S(1)	119.02(19)
C(16)–C(11)–S(1)	121.88(19)	O(17)–C(16)–C(11)	115.9(2)
C(16)–O(17)–C(18)	117.38(19)	Cp(cent)–Zr–Cp'(cent) ^a	130.54

^a Cp(cent) = centroid of C(21)–C(25), Cp'(cent) = centroid of C(31)–C(35).

diffraction study were grown from a THF/toluene mixture. The solid-state structure of **7** features a dissociated ion pair with a normal MeB(C₆F₅)₃⁻ anion and a tetragonal 16-electron cationic center with a coordinated THF molecule and an uncoordinated methoxy group (Figure 1). Important crystallographic data and bond distances and angles are listed in Tables 2 and 3. The Zr(1)–S(1) (2.4726(6) Å) and Zr(1)–O(41) (2.2207(16) Å) bond distances are in agreement with those reported for a related *tert*-butylthiolato-zirconocene cation (Zr–S, 2.4618(13) Å; Zr–O, 2.2150(25) Å).¹²

In light of these observations, we assumed that decomposition of the thiolato complexes **4-d₈**, **6-d₈**, and **7-d₈** to **5-d₈** proceeds by reaction with the released *tert*-butyl isobutyrate (Scheme 3). To support this hypothesis, the reaction of the latter ester with **4-d₈** in the absence of *t*BuSH was investigated in a separate experiment. The cationic thiolato complex **4-d₈** was cleanly

Scheme 5

generated in a two-step one-pot procedure: the reaction of Cp₂ZrMe₂ with *t*BuSH (1 or 2 equiv) in benzene affords Cp₂Zr(StBu)Me (**8**), which was further reacted with 1 equiv of B(C₆F₅)₃ in THF-*d*₈ at room temperature to yield **4-d₈**. This species is as such stable at least for 2 days at room temperature; however, **4-d₈** readily reacts indeed with 1 equiv of *tert*-butyl isobutyrate (Scheme 5). A ¹H NMR monitoring revealed that complex **4-d₈** was consumed over 8 h to form selectively complex **5-d₈** with release of 1 equiv of *t*BuSH and isobutene (Figure 2).

The reaction of **4-d₈** with *tert*-butyl acetate proceeds similarly to give the cationic Zr-acetato complex **9-d₈** with release of 1 equiv of *t*BuSH and isobutene (Scheme 5). The kinetics is significantly increased as compared with *tert*-butyl isobutyrate (complete conversion within 4 h), presumably because of the lower bulkiness of this ester.¹⁴ More importantly, no reaction between **4-d₈** and Me₂CHCO₂Me takes place, even for 12 h at 80 °C, indicating this process is specific to *tert*-butyl esters^{1e,4n,15} and not relevant to MMA polymerization.

MMA Polymerization Initiated by Isolated [Cp₂Zr(SR)(THF)][MeB(C₆F₅)₃] Complexes and in Situ Cp₂Zr(StBu)Me/Activator Systems. The abilities for MMA polymerization of the isolated [Cp₂Zr(SR)(THF)]-[MeB(C₆F₅)₃] complexes **4** and **7** were next evaluated (MMA/Zr = 200:1). Because polymerizations are usually conducted in an apolar solvent such as toluene, the activity of [Cp₂Zr(StBu)]⁺, i.e., the THF-free species putatively generated by protonolysis of the polymergrowing-chain zirconium intermediate by *t*BuSH (Scheme 1), was also investigated using in situ combinations of the precursor Cp₂Zr(StBu)Me (**8**) with a discrete methyl abstractor. Representative results are summarized in Table 4.

The thiophenato complex **7** does not show any significant activity (Table 4, entry 1), consistent with the

(14) When the reaction of **4** with *tert*-butyl isobutyrate (1:1) was carried out in CD₂Cl₂ instead of THF-*d*₈, complete conversion to **5** with release of 1 equiv of isobutene and HStBu was reached within 10 min (vs 8 h in the THF-*d*₈ solution). Increase of kinetics in a weakly coordinating solvent such as CD₂Cl₂ is consistent with a decomposition pathway involving a "base-free" cationic Zr species, as proposed in Scheme 3; see refs 4n and 12.

(15) For examples of cationic zirconium complexes having a reactive *tert*-butoxy group see: (a) Nguyen, H.; Jarvis, A. P.; Lesley, M. J. G.; Kelly, W. M.; Reddy, S. S.; Taylor, N. J.; Collins, S. *Macromolecules* **2000**, *33*, 1508–1510. (b) Stoebe, E. J., III; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 3222–3223.

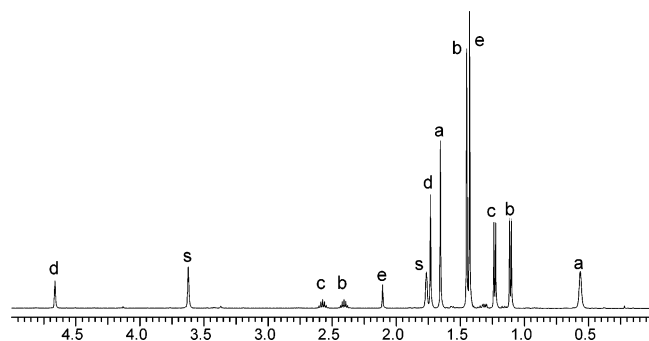


Figure 2. ^1H NMR monitoring (500 MHz, 20 °C, $\text{THF-}d_8$) of the 1:1 reaction of **4-d₈** with $\text{Me}_2\text{CHCO}_2t\text{Bu}$ [after 3.5 h at 20 °C]. Descriptors a, b, c, d, e, and s refer respectively to **4-d₈**, $\text{Me}_2\text{CHCO}_2t\text{Bu}$, **5-d₈**, $\text{Me}_2\text{C}=\text{CH}$, $t\text{BuSH}$, and residual solvent resonances.

Table 4. MMA Polymerization Promoted by Isolated $[\text{Cp}_2\text{Zr}(\text{SR})(\text{THF})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ Complexes and in Situ $\text{Cp}_2\text{Zr}(\text{StBu})\text{Me}$ (8**)/Activator Systems^a**

entry	initiator	yield (%)	$M_{n,\text{calc}}^b$ ($\text{g}\cdot\text{mol}^{-1}$)	$M_{n,\text{exp}}^c$ ($\text{g}\cdot\text{mol}^{-1}$)	M_w/M_n^c
1	7	2	400	25 400	2.55
2	4-d₈	98	19 600	373 200 ^d	1.42 ^d
3	8 / $\text{B}(\text{C}_6\text{F}_5)_3$	95	19 000	234 000	1.26
4	8 /[HNMe_2Ph][$\text{B}(\text{C}_6\text{F}_5)_4$]	11	2200	15 000	1.48
5	8 /[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$]	<1			

^a Reaction time = 1 h, $T = 20$ °C, solvent = toluene (2 mL); MMA/Zr/B = 200:1:1; Zr = 0.050 mmol. ^b Calculated $M_{n,\text{calc}}$ values considering one polymer chain per Zr. ^c Experimental M_n and M_w/M_n values as determined by GPC in THF vs PMMA standards. ^d A second distribution that accounts for ca. 5% of the sample was observed with $M_n = 12\,300$ and $M_w/M_n = 1.36$.

mentioned inhibition effect of 1–5 equiv of $p\text{-ClC}_6\text{H}_4\text{SH}$ and $o\text{-MeOC}_6\text{H}_4\text{SH}$ in the MMA polymerization initiated by the $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system in toluene (Table 1). This can be reasonably explained on the basis of the poor nucleophilicity of the thiophenato moiety. Conversely, complex **4**, which has a relatively more nucleophilic $t\text{BuS}$ reactive group, and the in situ combination of **8** and $\text{B}(\text{C}_6\text{F}_5)_3$ gave quantitative conversions of MMA (entries 2, 3). Although the resulting PMMAs have relatively narrow molecular weight distribution ($M_w/M_n = 1.26\text{--}1.48$), the average number molecular weights are ca. 1 order of magnitude higher than the theoretical values. These results suggest that both the THF adduct **4** and the corresponding base-free cationic Zr-thiolato species are active in MMA polymerization, but have poor initiation efficiency. Alternatively, they may also be unstable in toluene solution at room temperature and decompose to some extent¹² before MMA polymerization takes place. The very poor and low MMA conversions obtained when using the virtually noncoordinating activator $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and the weakly stabilizing activator $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ ¹⁶ (as compared to the stabilization effect of the coordinating anion $\text{MeB}(\text{C}_6\text{F}_5)_3^-$, respectively (entries 4, 5)), are in line with this hypothesis.¹⁷

Conclusion

Using the cationic zirconocene ester enolate complex $[\text{Cp}_2\text{Zr}(\text{THF})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**1**), which mimics the propagating species of methacrylate polymerization by cationic zirconocene complexes, we have

shown that thiols, in contrast to enolizable ketones, are valuable candidates as chain transfer agents in these polymerizations. *tert*-Butyl mercaptan and thiophenols readily cleave under stoichiometric conditions the Zr–O(enolate) bond of **1** to generate a cationic zirconocene-thiolato species (**4**, **6**, **7**). The latter are stable at room temperature in THF, except in the presence of *tert*-butyl esters, which promote the formation of zirconocene-carboxylato species. Of zirconocene-thiolato species **4**, **6**, and **7**, only the *tert*-butyl thiolato complex **4** proved able to reinitiate the polymerization of MMA. Cationic complexes **6** and **7**, which contain a thiophenato group, are likely not nucleophilic enough for this purpose. As revealed by the modest initiation efficiency of **4** and the limited transfer efficiency of the $t\text{BuSH}/\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system in MMA polymerization, other organic acids are still required to achieve effective chain transfer and eventually render the polymerization process catalytic; research toward this goal is currently underway.

Experimental Section

General Procedures. All experiments were carried out under argon using standard Schlenk techniques or a high-performance glovebox (<1 ppm O_2 , 5 ppm H_2O). Toluene and pentane were distilled from Na/K alloy, THF was distilled from Na/benzophenone, dichloromethane was distilled from calcium hydride under nitrogen, and all were degassed by freeze–thaw–vacuum cycles prior to use. Deuterated solvents were purchased from Eurisotop and distilled over appropriate drying agents before use. Methyl methacrylate (MMA, Acros) was distilled twice under argon over CaH_2 . *tert*-Butylmercaptan ($t\text{BuSH}$, Aldrich) was distilled before use. Thiophenols $p\text{-ClC}_6\text{H}_4\text{SH}$ (Acros) and $o\text{-MeOC}_6\text{H}_4\text{SH}$ (Acros), Cp_2ZrMe_2 (Aldrich), $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Boulder), and $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Boulder Scientific Co.) were used as received. $\text{B}(\text{C}_6\text{F}_5)_3$ (Boulder) was sublimed twice before use. Complexes $\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)^5$ and $[\text{Cp}_2\text{Zr}(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ ⁴ⁿ were synthesized as previously reported.

NMR spectra were recorded on Bruker AC-200, AC-300, and AM-500 spectrometers in Teflon-valved NMR tubes at 20 °C unless otherwise stated. ^1H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported vs TMS. ^{19}F and ^{11}B NMR chemical shifts are referenced to external CFCl_3 and external $\text{BF}_3\cdot\text{Et}_2\text{O}$, respectively. Assignment of signals was made from $^1\text{H}\text{--}^1\text{H}$ COSY, $^1\text{H}\text{--}^{13}\text{C}$ HMQC, and $^1\text{H}\text{--}^{13}\text{C}$ HMBC 2D NMR experiments. Coupling constants are given in hertz. Cationic Zr complexes containing $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ are totally dissociated in $\text{THF-}d_8$ or CD_2Cl_2 solution, and the NMR resonances for this anion are almost identical (see below). Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations. Molecular weights of PMMA were determined by gel permeation chromatography (GPC) at room temperature on a Waters apparatus equipped with five PL gel columns (Polymer Laboratories Ltd), a Waters WISP 717 autosampler, and a Shimadzu RID 6A differential refractometer. THF was used as eluent at a flow rate of $1.0\text{ mL}\cdot\text{min}^{-1}$. PMMA standards were used for molecular weight calibration.

(16) Although NMR data of $[\text{Cp}_2\text{Zr}(\text{StBu})]^+$ in $\text{THF-}d_8$ indicated that NMe_2Ph is free and does not coordinate to the metal center, such a coordination of NMe_2Ph to $[\text{Cp}_2\text{Zr}(\text{StBu})]^+$ is much more likely in a weakly coordinating solvent such as toluene.

(17) Very similar results were obtained by using these combinations in methylene chloride, confirming that these poor results reflect more the instability of the produced species rather than their poor solubility in toluene; **8**/[HNMe_2Ph][$\text{B}(\text{C}_6\text{F}_5)_4$]: 18% yield, $M_{n,\text{exp}} = 68\,000$, $M_w/M_n = 1.17$; **8**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$]: <1% yield (all other conditions as stated in Table 4). We thank a reviewer for suggesting these experiments.

NMR Data for the Free Anion $\text{MeB}(\text{C}_6\text{F}_5)_3^-$. ^1H NMR (THF- d_8): δ 0.50 (br s, 3H, BCH_3). ^1H NMR (CD_2Cl_2): δ 0.54 (br s, 3H, BCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 148.5 (dm, $J_{\text{C-F}} = 252$, $o\text{-C}_6\text{F}_5$), 137.4 (dm, $J_{\text{C-F}} = 247$, $p\text{-C}_6\text{F}_5$), 136.2 (dm, $J_{\text{C-F}} = 229$, $m\text{-C}_6\text{F}_5$), 129.7 (C_{ipso}), 9.7 (br, BCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 148.3 (dm, $J_{\text{C-F}} = 238$, $o\text{-C}_6\text{F}_5$), 137.4 (dm, $J_{\text{C-F}} = 257$, $p\text{-C}_6\text{F}_5$), 136.4 (dm, $J_{\text{C-F}} = 245$, $m\text{-C}_6\text{F}_5$), 128.9 (C_{ipso}), 9.9 (br, BCH_3). ^{11}B NMR (THF- d_8): δ -14.8 (s, BCH_3). ^{11}B NMR (CD_2Cl_2): δ -14.9 (s, BCH_3). ^{19}F NMR (THF- d_8): δ -134.5 (d, $^3J_{\text{F-F}} = 21$, 6F, $o\text{-F}$), -168.5 (t, $^3J_{\text{F-F}} = 21$, 3F, $p\text{-F}$), -170.6 (m, $^3J_{\text{F-F}} = 18$, 6F, $m\text{-F}$). ^{19}F NMR (CD_2Cl_2): δ -133.6 (d, $^3J_{\text{F-F}} = 18$, 6F, $o\text{-F}$), -165.6 (t, $^3J_{\text{F-F}} = 22$, 3F, $p\text{-F}$), -168.2 (t, $^3J_{\text{F-F}} = 22$, 6F, $m\text{-F}$).

Reaction of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (1- d_8) with PhCOCH_3 in THF- d_8 . Generation of $[\text{Cp}_2\text{Zr}(\text{OC}(\text{Me})_2(\text{C}(\text{Me})_2\text{CO}_2t\text{Bu}))][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (2). To a solution of $\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)$ (21 mg, 0.055 mmol) in THF- d_8 (ca. 0.5 mL) in a Teflon-valved NMR tube was added at room temperature $\text{B}(\text{C}_6\text{F}_5)_3$ (28 mg, 0.055 mmol). The solution was left for 10 min at 20 °C to ensure the complete formation of 1- d_8 , then PhCOMe (6.6 mg, 0.055 mmol) was added via a microsyringe. Immediately, the pale brown solution changed to a colorless solution, and NMR spectra were recorded. The conversion of 1- d_8 to 2 was virtually quantitative after 2 min. ^1H NMR (THF- d_8): δ 7.46 (m, 2H, Ph), 7.31 (m, 2H, Ph), 7.22 (m, 1H, Ph), 6.46 (s, 10H, Cp), 1.78 (s, 3H, $\text{ZrOC}(\text{CH}_3)(\text{Ph})$), 1.69 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.19 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.07 (s, 3H, $\text{C}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 183.0 ($\text{CO}(\text{O}t\text{Bu})$), 142.8 (Ph- C_1), 128.0 (Ph), 127.5 (Ph), 127.2 (Ph), 114.8 (Cp), 87.2 ($\text{C}(\text{CH}_3)_3$), 85.3 ($\text{ZrOC}(\text{Me})(\text{Ph})$), 49.1 ($\text{C}(\text{Me})_2$), 27.5 ($\text{C}(\text{CH}_3)_3$), 26.1 ($\text{ZrOC}(\text{CH}_3)(\text{Ph})$), 22.5 ($\text{C}(\text{CH}_3)_2$), 20.8 ($\text{C}(\text{CH}_3)_2$). Over 5 days, decomposition of 2 (52%, based on $t\text{Bu}$ resonances) ensues with formation of isobutene and a thus far unidentified compound, tentatively formulated $[\text{Cp}_2\text{Zr}(\mu^2\text{-O}_2\text{-CCMe}_2\text{CMe}(\text{Ph})\text{OH})]^+$, which has the following key ^1H NMR resonances (THF- d_8): δ 7.53–7.22 (m, Ph), 6.50 (s, 10H, Cp), 1.61 (s, 3H, $\text{CCH}_3(\text{Ph})\text{OH}$), 1.25 (s, 3H, $\text{C}(\text{CH}_3)_2$), 1.05 (s, 3H, $\text{C}(\text{CH}_3)_2$). NMR data for isobutene: ^1H NMR (THF- d_8): δ 4.62 (m, $^4J = 1.0$, 2H, $\text{CH}_2=$), 1.69 (t, $^4J = 1.0$, 6H, $=\text{C}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 142.0 ($=\text{C}(\text{CH}_3)_2$), 110.4 ($\text{CH}_2=$), 23.6 ($=\text{C}(\text{CH}_3)_2$).

Reaction of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (1- d_8) with Acetone in THF- d_8 . Generation of $[\text{Cp}_2\text{Zr}(\text{OC}(\text{Me})_2(\text{C}(\text{Me})_2\text{CO}_2t\text{Bu}))][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (3). This reaction was conducted as described above starting from $\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)$ (17.8 mg, 0.047 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (24 mg, 0.047 mmol), and CH_3COCH_3 (2.7 mg, 0.047 mmol). The conversion of 1- d_8 to 3 was virtually quantitative after 2 min. ^1H NMR (THF- d_8): δ 6.38 (s, 10H, Cp), 1.66 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.27 (s, 6H, $\text{C}(\text{CH}_3)_2\text{CO}_2t\text{Bu}$), 1.23 (s, 6H, $(\text{CH}_3)_2\text{COZr}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 182.8 ($\text{CO}(\text{O}t\text{Bu})$), 114.5 (Cp), 86.5 ($\text{C}(\text{CH}_3)_3$), 82.3 ($\text{ZrOC}(\text{Me})_2$), 48.8 ($\text{C}(\text{Me})_2\text{CO}_2t\text{Bu}$), 27.4 ($\text{C}(\text{CH}_3)_3$), 26.2 ($\text{ZrOC}(\text{CH}_3)_2$), 21.1 ($\text{C}(\text{CH}_3)_2\text{CO}_2t\text{Bu}$). Over 5 days at room temperature, 74% of compound 3 decomposed (based on $t\text{Bu}$ resonances) with release of isobutene and formation of a thus far unidentified compound, tentatively formulated $[\text{Cp}_2\text{Zr}(\mu^2\text{-O}_2\text{CCMe}_2\text{CMe}_2\text{OH})]^+$, which has the following key ^1H NMR resonances (THF- d_8): δ 6.50 (s, 10H, Cp), 1.19 (s, 3H, $\text{O}_2\text{CC}(\text{CH}_3)_2$), 1.15 (s, 3H, $\text{C}(\text{CH}_3)_2\text{OH}$).

Reaction of $[\text{Cp}_2\text{Zr}(\text{THF})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (1-THF) with Acetone. Synthesis of $[\text{Cp}_2\text{Zr}(\text{OC}(\text{Me})_2(\text{C}(\text{Me})_2\text{CO}_2t\text{Bu}))][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (3). This reaction was conducted as described above starting from $\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)$ (36 mg, 0.094 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (48 mg, 0.094

mmol), and CH_3COCH_3 (5.5 mg, 0.094 mmol) in THF (1.0 mL). The solvent was removed in a vacuum, and the residue was washed with pentane (2×1 mL) and dried under vacuum, leaving 3 as a yellow solid (46 mg, 52%). ^1H NMR in THF- d_8 was as reported above. Anal. Calcd for $\text{C}_{40}\text{H}_{34}\text{BF}_{15}\text{O}_5\text{Zr}$ (949.71): C, 50.59; H, 3.61. Found: C, 51.16; H, 3.73. ^1H NMR (CD_2Cl_2): δ 6.36 (s, 10H, Cp), 1.67 (s, 9H, $\text{OC}(\text{CH}_3)_3$), 1.30 (s, 6H, $\text{C}(\text{CH}_3)_2\text{CO}_2t\text{Bu}$), 1.26 (s, 6H, $(\text{CH}_3)_2\text{COZr}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 184.9 ($\text{CO}(\text{O}t\text{Bu})$), 115.0 (Cp), 90.7 ($\text{C}(\text{CH}_3)_3$), 83.2 ($\text{ZrOC}(\text{Me})_2$), 48.9 ($\text{C}(\text{Me})_2\text{CO}_2t\text{Bu}$), 28.1 ($\text{C}(\text{CH}_3)_3\text{CO}_2t\text{Bu}$), 27.3 ($\text{ZrOC}(\text{CH}_3)_2$), 21.6 ($\text{C}(\text{CH}_3)_2\text{CO}_2t\text{Bu}$). The NMR data for the free anion $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ were the same as those described above. Compound 3 also decomposes at room temperature in CD_2Cl_2 solution with release of isobutene and formation of a thus far unidentified compound, tentatively formulated $[\text{Cp}_2\text{Zr}(\mu^2\text{-O}_2\text{CCMe}_2\text{CMe}_2\text{OH})]^+$, which has the following key NMR resonances: ^1H NMR (CD_2Cl_2): δ 6.62 (s, Cp), 1.24 (s, $\text{O}_2\text{CC}(\text{CH}_3)_2$), 1.13 (s, $\text{C}(\text{CH}_3)_2\text{OH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 188.2 ($\text{O}_2\text{CC}(\text{CH}_3)_2$), 115.7 (Cp), 82.8 ($\text{C}(\text{CH}_3)_2\text{OH}$), 48.7 ($\text{O}_2\text{CC}(\text{CH}_3)_2$), 26.5 ($\text{C}(\text{CH}_3)_2\text{OH}$), 21.4 ($\text{O}_2\text{CC}(\text{CH}_3)_2$).

Reaction of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (1- d_8) with $t\text{BuSH}$ in THF- d_8 : Generation of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{StBu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (4- d_8). $\text{B}(\text{C}_6\text{F}_5)_3$ (25.8 mg, 0.05 mmol) was added at room temperature to a solution of $\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)$ (19.1 mg, 0.05 mmol) in THF- d_8 (ca. 0.5 mL) in a Teflon-valved NMR tube. The solution was left for 10 min at room temperature to ensure complete formation of 1- d_8 , and then $t\text{BuSH}$ (4.5 mg, 0.05 mmol) was added via a microsyringe. No color change of the pale brown solution was noticed. ^1H NMR spectra were periodically recorded and revealed that the reaction was finished within 1.5 h to give 4- d_8 in 95% NMR yield. Over 8 h, the complex 4- d_8 transformed cleanly to complex 5- d_8 (98% NMR yield). NMR data for 4- d_8 : ^1H NMR (THF- d_8): δ 6.68 (s, 10H, Cp), 1.61 (s, 9H, $t\text{Bu}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 114.5 (Cp), 53.9 ($\text{C}(\text{CH}_3)_3$), 35.8 ($\text{C}(\text{CH}_3)_3$). NMR data for *tert*-butyl isobutyrate: ^1H NMR (THF- d_8): δ 2.43 (sept, $J = 6.0$, 1H, $\text{CH}(\text{CH}_3)_2$), 1.45 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.11 (d, $J = 6.0$, 6H, $\text{CH}(\text{CH}_3)_2$). NMR data for the cation 5- d_8 : ^1H NMR (THF- d_8): δ 6.50 (s, 10H, Cp), 2.53 (m, $^3J = 7.0$, 1H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $^3J = 7.0$, 6H, $\text{CH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 192.4 (O_2C), 116.4 (Cp), 35.2 ($\text{CH}(\text{CH}_3)_2$), 16.7 ($\text{CH}(\text{CH}_3)_2$). The reactions of 1- d_8 with 2 and 3 equiv of $t\text{BuSH}$ were also investigated and found to proceed somewhat faster with the same selectivity.

Reaction of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (1- d_8) with $p\text{-ClC}_6\text{H}_4\text{SH}$ in THF- d_8 : Generation of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{SC}_6\text{H}_4\text{-}p\text{-Cl})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (6- d_8). This reaction was conducted as described above starting from $[\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)]$ (20.9 mg, 0.055 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (28.2 mg, 0.055 mmol), and $p\text{-ClC}_6\text{H}_4\text{SH}$ (8.0 mg, 0.055 mmol). The color changed from pale brown to bright yellow upon addition of the thiophenol. ^1H NMR spectra were periodically recorded and revealed that the reaction was finished within 10 min to give 6- d_8 in 95% NMR yield. NMR data for 6- d_8 : ^1H NMR (THF- d_8): δ 7.49–7.21 (m, 4H, Ph), 6.56 (s, 10H, Cp). Over 30 min, complex 6- d_8 decomposed cleanly to complex 5- d_8 (98% NMR yield), isobutene, and $p\text{-ClC}_6\text{H}_4\text{SH}$. NMR data for $p\text{-ClC}_6\text{H}_4\text{SH}$: ^1H NMR (THF- d_8): δ 7.49–7.21 (m, 4H, Ph), 4.41 (s, 1H, SH). The NMR data for 5- d_8 and isobutene were the same as those described above.

Reaction of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (1- d_8) with $o\text{-MeOC}_6\text{H}_4\text{SH}$ in THF- d_8 : Generation of $[\text{Cp}_2\text{Zr}(\text{THF-}d_8)(\text{SC}_6\text{H}_4\text{-}o\text{-Me})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (7- d_8). This reaction was conducted as described above starting from $\text{Cp}_2\text{Zr}(\text{Me})(\text{O}(t\text{BuO})\text{C}=\text{CMe}_2)$ (20.9 mg, 0.055 mmol), $\text{B}(\text{C}_6\text{F}_5)_3$ (28.2 mg, 0.055 mmol), and $o\text{-MeOC}_6\text{H}_4\text{SH}$ (7.8 mg, 0.055 mmol). The color changed from pale brown to bright yellow upon addition of the thiophenol. ^1H NMR spectra were periodically recorded and revealed that the reaction was finished within 10 min to give 7- d_8 in 95% NMR yield. NMR

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data for **7-d₈**: ¹H NMR (THF-*d*₈): δ 7.28 (t, *J* = 6, 1H, Ph), 7.20 (d, *J* = 6, 1H, Ph), 7.12 (d, *J* = 6, 1H, Ph), 6.98 (t, *J* = 6, 1H, Ph), 6.51 (s, 10H, Cp), 3.85 (s, 3H, OCH₃). ¹³C{¹H} NMR (THF-*d*₈): δ 156.3 (Ph), 132.7 (Ph), 128.6 (Ph), 120.8 (Ph), 115.2 (Cp), 111.5 (Ph), 55.1 (OCH₃). Over 30 min, complex **7-d₈** transformed cleanly to complex **5-d₈** (98% NMR yield), isobutene, and *o*-MeOPhSH. NMR data for *o*-MeOPhSH: ¹H NMR (THF-*d*₈): δ 7.19 (d, *J* = 5, 1H, Ph), 7.04 (t, *J* = 5, 1H, Ph), 6.88 (d, *J* = 5, 1H, Ph), 6.77 (t, *J* = 5, 1H, Ph), 4.05 (s, 1H, SH), 3.83 (s, 3H, OCH₃). ¹³C{¹H} NMR (THF-*d*₈): δ 153.7 (Ph), 127.3 (Ph), 124.0 (Ph), 118.9 (Ph), 108.8 (Cp), 52.7 (OCH₃). The NMR data for the free anion MeB(C₆F₅)₃[−], **5-d₈**, and isobutene were the same as those described above.

Synthesis of [Cp₂Zr(THF)(SC₆H₄-*o*-OMe)][MeB(C₆F₅)₃] (7). In the glovebox, a flask was charged with Cp₂ZrMe₂ (65 mg, 0.26 mmol) and B(C₆F₅)₃ (132 mg, 0.26 mmol). THF (5 mL) and *o*-MeOC₆H₄SH (37 mg, 0.26 mmol) were added sequentially at room temperature. Evaporation of volatiles in vacuo left a yellow powder that was recrystallized from toluene/THF (3:1) at −34 °C to give yellow crystals of **7** (230 mg, 92%). A suitable crystal was selected for X-ray diffraction analysis. Anal. Calcd for C₄₀H₂₈BF₁₅O₂SZr (959.72): C, 50.06; H, 2.94. Found: C, 50.94; H, 2.68.

Generation of Cp₂Zr(Me)(StBu) (8). Cp₂ZrMe₂ (18.3 mg, 0.074 mmol) and *t*BuSH (13.3 mg, 0.15 mmol, 2 equiv) were charged in a Teflon-valved NMR tube, and C₆D₆ (ca. 0.5 mL) was vacuum transferred. The tube was sealed and kept at 80 °C for 6 h. NMR was recorded which revealed the quantitative formation of **8**, together with excess (1 equiv) *t*BuSH. ¹H NMR (C₆D₆): δ 5.80 (s, 10H, Cp), 1.51 (s, 9H, C(CH₃)₃), 0.13 (s, 3H, ZrCH₃). ¹H NMR (THF-*d*₈): δ 6.13 (s, 10H, Cp), 1.38 (s, 9H, C(CH₃)₃), −0.15 (s, 3H, ZrCH₃). ¹³C{¹H} NMR (C₆D₆): δ 110.0 (Cp), 47.1 (C(CH₃)₃), 36.2 (C(CH₃)₃), 26.9 (ZrCH₃).

Reaction of Cp₂Zr(Me)(StBu) (8) and B(C₆F₅)₃ in THF. Synthesis of [Cp₂Zr(THF)(StBu)][MeB(C₆F₅)₃] (4). A C₆D₆ solution of **8** was prepared as described above starting from Cp₂ZrMe₂ (51 mg, 0.203 mmol) and *t*BuSH (36 mg, 0.41 mmol, 2 equiv). After monitoring by ¹H NMR to ensure completion of the reaction, the solution was concentrated under vacuum to remove excess *t*BuSH and THF (1.0 mL) was added. In the glovebox, B(C₆F₅)₃ (104 mg, 0.205 mmol) was added and the solution was stirred for 15 min at room temperature. Volatiles were removed under vacuum, and the residue was washed with pentane (3 × 1 mL) and dried under vacuum to leave **4** as a yellow powder (150 mg, 81%). The NMR data for **4** were the same as those described above. Anal. Calcd for C₃₇H₃₀BF₁₅OSZr (909.71): C, 48.85; H, 3.32. Found: C, 49.24; H, 3.42.

Reaction of [Cp₂Zr(THF-*d*₈)(StBu)][MeB(C₆F₅)₃] (4-d₈) with (CH₃)₂CHCO₂*t*Bu in THF-*d*₈. Generation of [Cp₂Zr(THF-*d*₈)(O₂CiPr)][MeB(C₆F₅)₃] (5-d₈). To the above NMR tube (freshly prepared), (CH₃)₂CHCO₂*t*Bu (10.1 mg, 0.074 mmol) was added via microsyringe. The tube was sealed and ¹H NMR was recorded periodically. Complete conversion of **4-d₈** to **5-d₈** and release of 1 equiv of isobutene and *t*BuSH was observed over 8 h. The NMR data for **5-d₈** were the same as those described above.

Reaction of [Cp₂Zr(THF-*d*₈)(StBu)][MeB(C₆F₅)₃] (4-d₈) with CH₃CO₂*t*Bu in THF-*d*₈. Generation of [Cp₂Zr(THF-*d*₈)(O₂CCH₃)][MeB(C₆F₅)₃] (9-d₈). To an NMR tube containing a solution of **4-d₈** in THF-*d*₈ (generated from Cp₂ZrMe₂ (16.8 mg, 0.067 mmol), *t*BuSH (12 mg, 0.13 mmol), and B(C₆F₅)₃ (34 mg, 0.067 mmol)) was added CH₃CO₂*t*Bu (7.7 mg, 0.067 mmol) via microsyringe. The tube was sealed and ¹H NMR was recorded periodically. Complete conversion of **4-d₈** to [Cp₂Zr(THF-*d*₈)(O₂CCH₃)][MeB(C₆F₅)₃] and release of 1 equiv of isobutene and *t*BuSH was observed over 4 h. NMR data for **9-d₈**: ¹H NMR (THF-*d*₈): δ 6.50 (s, 10H, Cp), 2.07 (s, 3H, CH₃). ¹³C{¹H} NMR (THF-*d*₈): δ 185.9 (CH₃CO₂), 114.5 (Cp), 20.0 (CH₃). The NMR data for the free anion MeB(C₆F₅)₃[−] and isobutene were the same as those described above.

Reaction of [Cp₂Zr(THF)(StBu)][MeB(C₆F₅)₃] (4) with (CH₃)₂CHCO₂*t*Bu in CD₂Cl₂. Generation of [Cp₂Zr(THF)(O₂CiPr)][MeB(C₆F₅)₃] (5). An NMR tube containing a solution of **4** in THF (generated from Cp₂ZrMe₂ (21.2 mg, 0.084 mmol), *t*BuSH (15.2 mg, 0.17 mmol), and B(C₆F₅)₃ (43 mg, 0.084 mmol)) was dried in a vacuum, and CD₂Cl₂ (ca. 0.5 mL) was vacuum transferred. Then, (CH₃)₂CHCO₂*t*Bu (12.2 mg, 0.084 mmol) was added via microsyringe. ¹H NMR revealed complete conversion of **4** to **5** within 10 min and release of 1 equiv of isobutene and *t*BuSH. NMR data for the cation of **4**: ¹H NMR (CD₂Cl₂): δ 6.60 (s, 10H, Cp), 3.83 (m, 8H, OCH₂-CH₂), 1.94 (m, 8H, OCH₂CH₂), 1.66 (s, 9H, ⁴Bu). NMR data for *t*BuSH: ¹H NMR (CD₂Cl₂): δ 1.66 (s, 1H, SH), 1.46 (s, 9H, C(CH₃)₃). ¹H NMR for the cation of **5** (CD₂Cl₂): δ 6.42 (s, 10H, Cp), 4.10 (m, 4H, OCH₂CH₂), 2.58 (m, ³*J* = 7.0, 1H, CH(CH₃)₂), 2.17 (m, 4H, OCH₂CH₂), 1.24 (d, ³*J* = 7.0, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 193.0 (O₂C), 116.1 (Cp), 75.3 (OCH₂-CH₂), 35.4 (CH(CH₃)₂), 25.2 (OCH₂CH₂), 17.2 (CH(CH₃)₂). The NMR data for the free anion MeB(C₆F₅)₃[−] were the same as those described above.

Crystal Structure Determination of Complex 7. A suitable single crystal of **7** was mounted onto glass fibers using the “oil-drop” method. Diffraction data were collected at 100 K using a NONIUS Kappa CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A combination of ω- and φ-scans was carried out to obtain at least a unique data set. Crystal structures were solved by means of the Patterson method, and remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on *F*² (programs SHELXS-97 and SHELXL-97).¹⁹ Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement are given in Table 2. Crystallographic data for **7** are also available as a cif file (see Supporting Information).

Typical Procedure for MMA Polymerization. In the glovebox, to a 10 mL vial equipped with a magnetic stirrer and containing a solution of the Zr catalyst (0.05 mmol) in toluene or THF (1.0 mL), was added the activator (B(C₆F₅)₃, [HNMe₂Ph][B(C₆F₅)₄], or [Ph₃C][B(C₆F₅)₄] (0.05 mmol) in toluene or THF (1.0 mL). The solution was stirred, and MMA (10.0 mmol) (or a mixture of MMA and CTA) was added by syringe within 20 s. The polymerization was carried out for 1–3 h at 20 °C and quenched by addition of acidified methanol (3% HCl, 200 mL). The polymer was filtered and dried overnight under vacuum at 60 °C. The microstructure of the PMMAs was determined by ¹H NMR in CDCl₃ and found in all cases to be in the range 63–65% *rr*, 5–8% *mm*, and 29–33% *mr*.

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Supporting Information Available: Crystallographic data for **7** as a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>

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