Isotactic Polymerization of Methyl Methacrylate Using a Prochiral, Zirconium Enolate Initiator

Hoa Nguyen, Adam P. Jarvis, M. J. G. Lesley, W. Mark Kelly, Srinivasa S. Reddy, Nicholas J. Taylor, and Scott Collins*

Department of Chemistry, University of Waterloo, 200 University Ave. W.; Waterloo, Ontario Canada N2L 3G1

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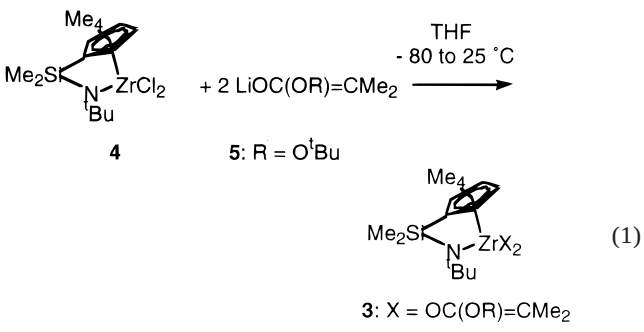
There is considerable interest in the use of metallocene or lanthanocene complexes as initiators of polymerization of acrylate-based monomers.[1] We and others have demonstrated that C_2-symmetric, dialkyl zirconocene initiators—e.g. *rac*-en$(H_4Ind)_2ZrX_2$ (**1**, X = Me)—polymerize methyl methacrylate to isotactic poly(methyl methacrylate) (i-PMMA) by an enantiomorphic, site-control mechanism.[2] While syndiotactic PMMA can be prepared using sterically encumbered, lanthanocene initiators at low temperatures,[1a,c,d,g] attempts to use C_s-symmetric, dialkyl zirconocene initiators—i.e., Me_2C(Cp)(Flu)ZrX_2 (**2**, X = Me)—for this purpose have been unsuccessful.[2b,c]

As we have shown elsewhere, either cationic enolate or neutral enolate complexes of zirconium (the latter in concert with metallocenium activators) may serve as initiators of acrylate polymerization.[1h] Mechanistic studies can be simplified using such compounds, as formation of these species in situ (from, e.g., metallocene dialkyls, ionic activators, and acrylates) can be slow and/or inefficient.

We have attempted to prepare bis(enolate) complexes of **1** or **2** in the hope of studying isospecific or syndiospecific MMA polymerization using cationic enolates derived from such species. These synthetic studies have met with very limited success; in one case the bis(enolate) complex **1** could be prepared [X = OC(Me)=CH_2] but this compound failed to effect polymerization of MMA in the presence of $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, or $[PhNHMe_2][B(C_6F_5)_4]$.[3]

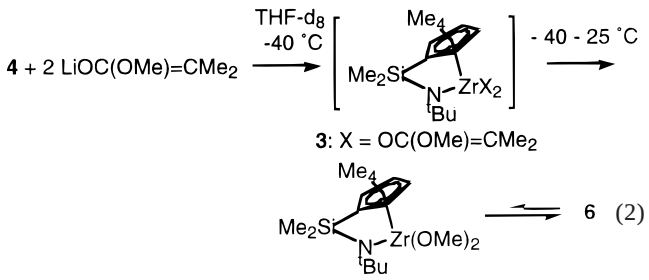
More recently, we have focused our attention on linked, Cp−amido complexes of zirconium, as these compounds are less sterically encumbered than their metallocene "analogues", a feature which facilitates the synthesis of bis(enolate) complexes. We report here our observations using this class of initiators for MMA polymerization.

The prototypical complex **4**[4] reacts cleanly with 2 equiv of stable, lithium enolate **5** (R = O^{t}Bu)[5] to provide bis(enolate) complex **3** as a crystalline, white solid (eq 1).[6]



(1)

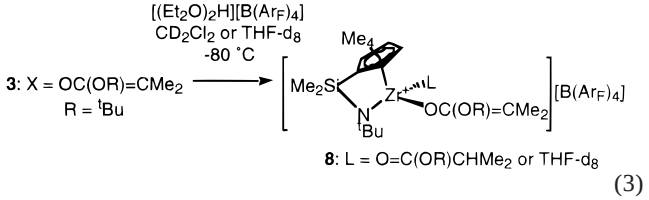
Attempts to isolate the analogous complex **3** (R = OMe) using the corresponding lithium enolate **5** (formed in situ from methyl isobutyrate and LDA) and **4** were unsuccessful. Monitoring of this reaction by NMR spectroscopy revealed that complex **3** (R = OMe) was formed at −40 °C;[7] on warming to room temperature, this species decomposed to form, inter alia, bis(methoxide) complex **6**, which could be isolated and purified by crystallization from hexane (eq 2).



(2)

The X-ray structure[8] (Figure 1) reveals that complex **6** is a dimer in the solid state[9] with approximate 2-fold symmetry, with each Zr adopting a distorted, four-legged piano-stool geometry. The terminal OMe groups bonded to each Zr feature short Zr−O bonds and near linear angles at the methoxide oxygen (Figure 1). The oxygen atoms of the μ-OMe groups feature distinctly different bond lengths to each Zr and each is somewhat pyramidal. The Zr(μ-OMe)$_2$Zr subunit is not planar with a hinge angle at the μ-OMe oxygens of 20.6(1)°.

Treatment of complex **3** (R = O^{t}Bu) in CD_2Cl_2 or THF-d_8 solution at −80 °C with 1 equiv of the strong acid $[(Et_2O)_2H][B(Ar_F)_4]$ (**7**: Ar_F = 3,5-$(CF_3)_2C_6H_3$−)[10] leads to formation of species **8**, whose spectral characteristics are consistent with that of a cationic enolate complex,[11] along with 1 equiv of *tert*-butyl isobutyrate (eq 3). This species is stable in solution for extended periods of time below ca. −40 °C; on warming, decomposition ensues with formation of isobutene (detected by ^{1}H and ^{13}C NMR spectroscopy).[12]



(3)

Polymerization of MMA Using Complex 8. When complex **8** is generated in a small volume of CH_2Cl_2 at −80 °C, and MMA is subsequently added, slow polymerization is observed at low temperatures (Table 1). For example, 90% conversion of monomer (as determined by GC of quenched aliquots) is observed after 18 h at −40 °C with initial MMA:Zr ratios of 190:1 (Table 1, entry 2). The polymer formed under these conditions is highly isotactic (% mm > 95) and the triad distribution is consistent with a site-control mechanism (2rr/mr = 1.05). Despite the thermal instability of complex **8** under these conditions,[13] the polymer features M_n = 20.1 K with M_w/M_n = 1.18, suggesting quasi-living behavior with an initiator efficiency (f) = 86%.

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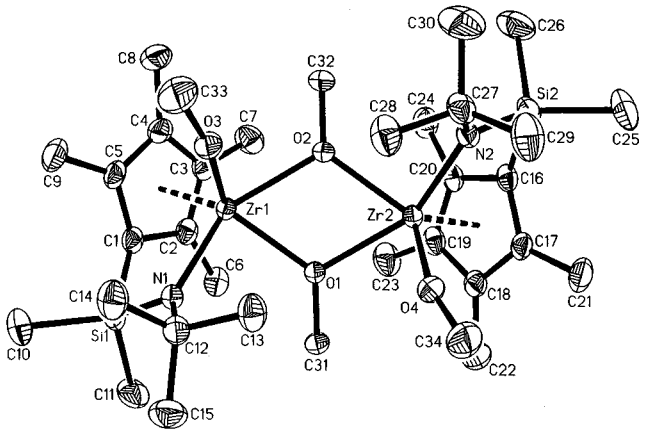


Figure 1. Molecular structure plot of compound **6** with 50% thermal probability ellipsoids depicted and H atoms removed for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: Zr(1)−O(1) 2.171(1), Zr(1)−O(2) 2.240(1), Zr(1)−O(3) 1.946(1), Zr(1)−Cn 2.238(1); Zr(1)−O(3)−C(33) 165.7(1), O(2)−Zr(1)−O(1) 65.8-(1), O(2)−Zr(1)−O(1)−Zr(2) 20.6(1).

Table 1. Polymerization of Methyl Methacrylate Using Cationic Enolate Complex 8[a]

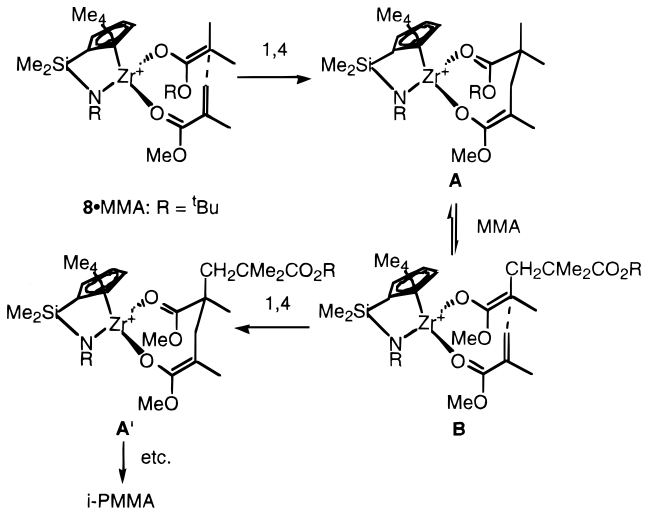
entry	T (°C)	t (h)	% convn	mm[b]	mr[b]	rr[b]	$10^{-3}M_n$[c]	PDI[c]
1	−60	18	31	95.5	3.1	1.4	19.6	1.10
2	−40	18	90	95.5	3.0	1.5	20.1	1.18
3[d]	−40	18	23	79.6	13.3	7.1	17.3	1.20
4	−20	18	56	80.5[e]	9.2[e]	10.3[e]	16.5	1.72
5[f]	−20	18	25	70.9[g]	11.7[g]	17.4[g]	13.7	1.48

[a] General procedure: To a solution of bis(enolate) **3** (50 mg, 0.08 mmol) in toluene (0.25 mL) at −80 °C was added a precooled solution of oxonium acid **7** (78 mg, 0.08 mmol) in CH_2Cl_2 (0.25 mL). After 30 min at −80 °C, cold, freshly distilled MMA (1.50 g, 15.0 mmol) and *n*-decane (0.30 g) were added in one portion by syringe at the indicated temperature. The conversion of monomer (in %) was estimated by GC analyses of a quenched aliquot at the time indicated by comparison to *n*-decane, added as an internal standard.[1h] The polymer was isolated, after quenching with MeOH, by precipitation from MeOH, followed by drying in vacuo to constant weight at 100 °C and 0.01 mmHg. [b] Determined from the ^{1}H NMR spectrum in $CDCl_3$. [c] Absolute MWD determined by GPC in THF at 25 °C, calibrated using PS standards. [d] THF (10.0 equiv with respect to **3**) was added at −80 °C, prior to monomer addition at −40 °C. [e] A small quantity (11.3 wt %) of partially s-PMMA was present as was evident from integration of the CH_2 signals at δ 1.7 vs 2.10 and 1.48 ppm; the triad distribution is consistent with a mixed, enantiomorphic site ($\beta = 0.97$, $w_I = 0.89$) and chain-end control ($P = 0.81$, $w_S = 0.11$) models. [f] Two equivelants of bis(enolate) **3** and 1 equiv of oxonium acid **7** were used. [g] The PMMA was a mixture of isotactic (ca. 76.3 wt %) and partially syndiotactic (ca. 23.7 wt %) material; the triad distribution is consistent with a mixed, enantiomorphic site ($\beta = 0.97$, $w_I = 0.76$) and chain-end control ($P = 0.81$, $w_S = 0.24$) models.

Interestingly, the addition of small quantities of THF (10 equiv) to enolate complex **8**, prior to addition of the monomer, significantly decreases both the rate of polymerization and the tacticity of the PMMA formed (entry 3), but does not affect the triad distribution (i.e., 2rr/mr = 1.07). The ^{13}C NMR spectrum of the polymer formed under these conditions (see Supporting Information) was also consistent with an enantiomorphic site control mechanism (i.e., mmmr:mmrr:mrrm = 2:2.1:1.5).

At lower or higher temperatures, conversion of MMA is lower (Table 1, entries 1 and 4, respectively). In the former case, the polymer properties are comparable to those observed at −40 °C (Table 1, entry 1 vs 2) whereas at higher temperatures, the MWD is significantly broader and the polymer less isotactic (entry 4).[14] At higher temperatures, the lower conversion, in combination with the broader MWD, suggests limited thermal stability of the propagating centers. Importantly, if addition of MMA is delayed at −20 °C for a period corresponding to complete decomposition of **8**, no polymer is produced.

Scheme 1



Cationic enolate complex **8** is chiral at Zr (eq 3). While the spectroscopic properties of **8** are consistent with this in CD_2Cl_2 solution,[11a,15] the spectra are consistent with time-averaged, 2-fold symmetry in donor solvents (THF-d_8),[11b] suggesting rapid, racemization by exchange of free and bound, neutral donor ligand L. If racemization at Zr, by the process of ligand exchange, was rapid compared to the rate of propagation, i-PMMA would not be formed by a enantiomorphic site control mechanism using chiral initiator **8**.

The formation of i-PPMA can be explained if C−C bond formation occurs predominantly via the conformation depicted for **B** (Scheme 1).[16] That is, enolate stereochemistry (i.e., [Z]) must be preserved during the Michael addition, while the lateral coordination site for MMA must be the same (compare **B** vs **8**·MMA). This requires that dissociation of the terminal ester group from **A** or **A′** is slow relative to (associative) displacement by MMA (with inversion at Zr) and that Michael addition from **B** is faster than racemization at Zr (by exchange of free and bound MMA in **B**). The effect of added THF would seem to involve (partial) racemization during polymerization by displacement of the chain end from the metal prior to monomer coordination.

In hindsight, it seems clear that attempts to form s-PMMA using metallocene catalysts that form s-poly(propylene) (e.g., **2**) may be complicated by slow interconversion of enantiomeric, catalyst−monomer complexes during chain growth as reported here for a topologically similar complex. Future work will concentrate on the generality of these findings as well as studies concerned with the mechanism for this polymerization process.[17]

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Supporting Information Available: Tables of crystallographic and refinement data, atomic coordinates and isotro-

pic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters for compound **6**, ^{1}H and ^{13}C NMR spectra for compounds **3** and **8** and isotactic PMMA. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(3) In particular, reaction of **1** [X = OC(Me)=CH_2] with 1 equiv of [PhNHMe_2][B(C_6F_5)$_4$] led to formation of a cationic, aldolate complex arising from intramolecular reaction of coordinated acetone with the remaining enolate moiety: Reddy, S. S. Unpublished results. For studies involving reactions of zirconocene enolate complexes with B(C_6F_5)$_3$ and their involvement in methyl vinyl ketone polymerization see: Spaether, W.; Klass, K.; Erker, G.; Zippel, F.; Frohlich, R. *Chem.—Eur. J.* **1998**, *4*, 1411.

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(6) Compound **3**: ^{1}H NMR (300 MHz, C_6D_6) δ 2.26 (s, 6H, C_5-Me_4) 2.01 (s, 6H, C_5Me_4) 1.80 (s, 6 H, =CMe_2) 1.78 (s, 6H, =CMe_2) 1.40 (s, 9H, N^{t}Bu) 1.34 (s, 18H, O^{t}Bu) 0.63 (s, 6H, $SiMe_2$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 153.3 (ZrO**C**(OR)=CMe_2) 130.0 (**C$_5$**Me_4) 128.2 (**C$_5$**Me_4) 103.7 (Me_2Si**C$_5$**Me_4) 91.0 (ZrOC(OR)=**C**Me_2) 78.2 (ZrOC(O**C**Me_3)=CMe_2) 55.4 (N**C**-Me_3) 34.1 (NC**Me**$_3$) 29.6 (ZrOC(OC**Me**$_3$)=CMe_2) 19.7 (ZrOC-(OR)=C**Me**$_2$) 19.3 (ZrOC(OR)=C**Me**$_2$) 14.3 (C$_5$**Me**$_4$) 10.4 (C$_5$**Me**$_4$) 7.2 (Si**Me**$_2$).

(7) ^{1}H NMR (300 MHz, toluene-d_8, 233 K): δ 3.41 (s, 6H, OMe) 2.16 (s, 6H, C_5Me_4) 1.95 (s, 6 H, C_5Me_4) 1.85 (s, 6H, =CMe_2) 1.76 (s, 6H, =CMe_2) 1.31 (s, 9H, N^{t}Bu) 0.59 (s, 6H, $SiMe_2$).

(8) Complex **6**: Triclinic, space group $P\bar{1}$, a = 10.026(1) Å, b = 10.465(1) Å, c = 21.400(2) Å, α = 83.740(5)°, β = 80.133-(5)°, γ = 64.176(6)°. V = 1989.8(4) Å^3, Z = 2, 7497 observed reflections with $F > 6\sigma(F)$. data-to-parameter ratio 16.2:1, GOF = 2.31, R = 2.59%, and R_w = 3.83%.

(9) In solution, this material is a mixture of two complexes, one of which appears to be monomeric and the other dimeric, based on the ^{1}H NMR spectra. Complex **6** (dimer): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.80 (s, 6H, OMe) 3.69 (s, 6H, μ-OMe) 2.19 (s, 6H, C_5Me_4) 2.14 (s, 6H, C_5Me_4) 2.13 (s, 6H, C_5Me_4) 2.00 (s, 6H, C_5Me_4) 1.18 (s, 18H, N^{t}Bu) 0.52 (s, 6H, $SiMe_2$) 0.49 (s, 6H, $SiMe_2$). Complex **6** (monomer): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.74 (s, 6H, OMe) 2.09 (s, 6H, C_5Me_4) 2.06 (s, 6H, C_5Me_4) 1.17 (s, 9H, N^{t}Bu) 0.50 (s, 6H, $SiMe_2$).

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(11) (a) Complex **8**: ^{1}H NMR (300 MHz, CD_2Cl_2:toluene-d_8 1:1, 233 K) δ 7.99 [br s, 8H, B(Ar_F)$_4$] 7.53 [br s, 4H, B(Ar_F)$_4$] 2.07 [br m, 1H, Zr- -O=C(O^{t}Bu)**CH**Me_2] 1.85 (s, 3H, C_5**Me$_4$**) 1.80 (s, 3H, C_5**Me$_4$**) 1.76 (s, 3H, C_5**Me$_4$**) 1.56 (s, 3H, C_5**Me$_4$**) 1.47 (s, 3 H, =C**Me$_2$**) 1.33 (s, 3 H, =C**Me$_2$**) 1.07 [br s, 9H, N**^{t}Bu**] 1.06 [s, 9H, Zr- -O=C(O**^{t}Bu**)CHMe_2] 1.01 [br s, 9H, ZrOC(O**^{t}Bu**)=CMe_2] 0.84 [two overlapping d, total 6H, Zr- -O=C(O^{t}Bu)CH**Me$_2$**] 0.40 (s, 3H, Si**Me$_2$**) 0.39 (s, 3H, Si**Me$_2$**). (b) Complex **8**: ^{1}H NMR (300 MHz, THF-d_8, 233 K) δ 7.86 [br s, 8H, B(Ar_F)$_4$] 7.67 [br s, 4H, B(Ar_F)$_4$] 2.23 (s, 6H, C_5**Me$_4$**) 2.21 (s, 6H, C_5**Me$_4$**) 1.68 (br s, 3 H, =C**Me$_2$**) 1.60 (br s, 3 H, =C**Me$_2$**) 1.38 (s, 9H, N**^{t}Bu**) 1.28 [s, 9H, ZrOC(O**^{t}Bu**)=CMe_2] 0.74 (s, 6H, Si**Me$_2$**); ^{13}C{^{1}H} NMR (75 MHz, THF-d_8, 233 K) δ 162.8 [1:1:1:1 q, J_{CB} = Hz, *i*-C, B(Ar_F)$_4$] 153.5 (ZrO**C**(OR)=CMe_2) 135.9 (**C$_5$**Me_4) 135.4 [br s, o−C, B(Ar_F)$_4$] 132.3 (**C$_5$**Me_4) 129.9 [q, J_{CF} = 47 Hz, m−C, B(Ar_F)$_4$] 125.4 [q, J_{CF} = 272 Hz, CF_3, B(Ar_F)$_4$] 118.3 [br s, p−C, B(Ar_F)$_4$] 106.0 (Me_2Si**C$_5$**Me_4) 94.9 (ZrOC(OR)=**C**Me_2) 79.7 (ZrOC-(O**C**Me_3)=CMe_2) 59.3 (N**C**Me_3) 33.6 (ZrOC(OC**Me**$_3$)=CMe_2) 29.6 (NC**Me**$_3$) 19.5 (ZrOC(OR)=C**Me**$_2$) 19.4 (ZrOC(OR)=C**Me**$_2$) 14.5 (C$_5$**Me**$_4$) 11.3 (C$_5$**Me**$_4$) 6.3 (Si**Me**$_2$).

(12) Preliminary results suggest that the major, Zr product is a cationic, carboxylate complex.

(13) Complex **8** is more thermally stable in THF-d_8, decomposing at temperatures above −20 °C. Presumably it is also more thermally stable in MMA solution.

(14) A small amount of partially s-PMMA is formed under these conditions (entry 4). We suspect this arises from stoichiometric imbalance of **3** and **7** as deliberate use of excess **3** also leads to (increased) formation of s-PMMA (Table 1, entry 5).

(15) The ^{1}H NMR spectrum of complex **8** in CD_2Cl_2 solution is complex and temperature dependent suggestive of exchange between coordinated *tert*-butyl isobutyrate and Et_2O derived from oxonium acid **7**.

(16) This mechanism is similar to that invoked by Yasuda and co-workers to account for the formation of s-PMMA using [Cp*$_2$SmH]$_2$ as initiator; in that case, alternating insertion of MMA was proposed—see ref 1d.

(17) Preliminary evidence suggests that a bimetallic propagation step, analogous to that observed using simple zirconocene initiators,[1h] is also observed using this system at a 2:1 stoichiometry of enolate **3** to [(Et_2O)$_2$H][B(Ar_F)$_4$] as s-PMMA is partially formed in addition to i-PMMA under these conditions (Table 1, entry 5).

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