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Polymerization of Methyl Methacrylate Using Zirconocene Initiators: Polymerization Mechanisms and Applications

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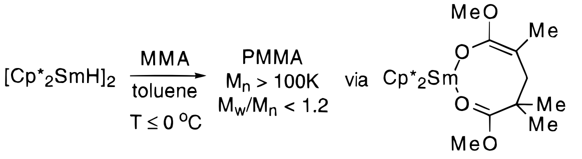
ABSTRACT: The polymerization of methyl methacrylate (MMA), initiated by zirconocene complexes Cp_2ZrMe_2 (**1**) and $[Cp_2ZrMe(THF)][BPh_4]$ (**2**), provides partially syndiotactic poly(methyl methacrylate) (PMMA) in high yield and with a narrow molecular weight distribution (MWD). The kinetics of this process were studied and reveal that in this system, the rate of initiation is much slower than that of propagation. Initiation appears to involve the rate-limiting reaction of complex **2** with monomer to generate a cationic enolate complex (**3**). The latter compounds also initiate polymerization of MMA, albeit at a much slower rate than that observed using initiators **1** and **2**. The mechanism for propagation in polymerizations initiated by complexes **1** and **2** has a rate-limiting step involving the reaction of neutral zirconium enolate species (**4**), produced in situ from **3** and **1**, with monomer, activated by coordination to complex **2**. Neutral enolate complexes **4** and complex **2** function as effective initiators of MMA polymerization in which the rate of initiation is greater than or equal to the rate of propagation. Under these conditions, PMMA can be produced with very narrow MWD and the polymerization process is living at or below 0 °C. The rate of this process is highly sensitive to the presence of impurities and thus the degree of polymerization is practically limited by initiator concentration. The polymerization of MMA, using initiators **4** and **2**, in the presence of trialkylaluminum compounds was studied with a view to overcoming these limitations. Alkylaluminum compounds appear to act as chain transfer/termination reagents in these polymerizations, although the rate of this process is much slower than the rate of propagation. In particular, triisobutylaluminum can be used to purify monomer and solvent and allows production of PMMA with a narrow MWD at high conversion. The polymerization of *n*-butyl acrylate (BuA), initiated by complexes **4** and **2**, was studied. Poly(*n*-butyl acrylate) (P(BuA)) can be prepared in high yield at low temperatures with a narrow MWD. This process is not living and the principal termination process involves back-biting cyclization as revealed by MALDI-TOF mass spectra of low-MW polymer. At higher temperatures, the growing chains are deactivated by this process and also by competitive α-hydrogen transfer, such that high monomer conversions are not obtained.

Introduction

In 1992, we reported that methyl methacrylate (MMA) could be efficiently polymerized (i.e. monomer conversions approaching 100%) using a two-component catalyst system comprised of Cp_2ZrMe_2 (**1**) and $[Cp_2ZrMe(THF)][BPh_4]$ (**2**) at or below room temperature (eq 1).[1] The poly(methyl methacrylate) (PMMA) produced was partially syndiotactic (ca. 80% r diads at 0 °C), high molecular weight ($M_n > 100K$) and had a narrow molecular weight distribution (MWD; $M_w/M_n < 1.4$). At the time of its discovery, this process was somewhat unprecedented,[2] and therefore of mechanistic as well as practical interest.

$$\underset{\mathbf{1}}{Cp_2ZrMe_2} + \underset{\mathbf{2}}{[Cp_2ZrMe(THF)][BPh_4]} \xrightarrow[\substack{CH_2Cl_2 \\ T \le 25\,^{\circ}C}]{MMA} \begin{array}{c} PMMA \\ (ca.\ 100\%) \\ 80\%\ r\ dyads \\ M_n\ 50-200K \\ M_w/M_n\ 1.2-1.4 \end{array} \tag*{1)}$$

At about the same time, Yasuda and co-workers independently reported that MMA could also be polymerized using lanthanocene initiators under similar conditions (eq 2).[3] They were able to demonstrate that a neutral enolate complex, formed in situ from the initiator and MMA, was responsible for propagation. Since that time, this group has reported elegant applications of this chemistry to the homo- and copolymerization of methacrylates and acrylates and the synthesis of block copolymers.[4]



2)

More recently, Soga and co-workers have reported that MMA can be polymerized using dialkylzirconocene complexes in combination with stoichiometric amounts of activators such as $B(C_6F_5)_3$, in the presence of a large excess of e.g. diethylzinc.[5] The rate of this polymerization process is very slow compared with that reported previously.[1] Some kinetic studies concerning this process have been reported, but the nature of the propagating species has not been conclusively demonstrated.

Finally, a number of groups have independently reported that isotactic PMMA can be produced using chiral group 4 or lanthanide initiators.[6] The microstructure of the polymer is consistent with enantiomorphic site control (mmmr:mrmm:mrrm = 2:2:1) of stereochemistry. Although definitive mechanistic studies on this process have not appeared, it seems plausible that intermediates analogous to those implicated in MMA polymerization using achiral initiators are involved.

In this paper, we report full details concerning the mechanism of polymerization, initiated by complexes **1** and **2**, and the development of more effective initiators for living polymerization of MMA. In addition, the use

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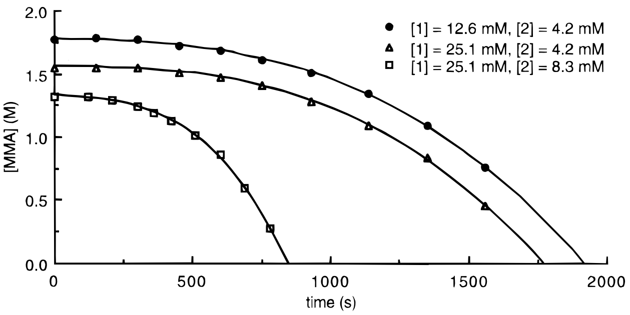


Figure 1. Kinetics of MMA polymerization using complexes **1** and **2** (data and conditions in Table 8;- see Experimental Section).

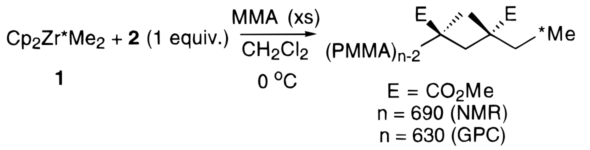
of trialkylaluminum compounds as in-situ scrubbing reagents was studied and applications to polymerization of *n*-butyl acrylate (BuA) are described.

Results and Discussion

Polymerization of MMA Using Initiators 1 and 2. The kinetics of polymerization of MMA were studied by monitoring the disappearance of monomer with time, and some typical results are plotted in Figure 1. The polymerization process is characterized by a pronounced induction period followed by a rapid and constant rate of polymerization; conversions approaching 100%, as revealed by GC, are typical. Experiments at different concentrations of initiators **1** and **2** reveal that the length induction period is only sensitive to the concentration of **2** (Figure 1). The rate of polymerization, following the induction period, also appears to depend only on the concentration of complex **2** and is roughly first order in the concentration of this complex. Moreover, the degree of polymerization (as measured by GPC; vide infra), at constant conversion, appears to be largely unaffected by the concentration of **1** but is sensitive to the initial concentration of complex **2**. Overall, the kinetics of this process are consistent with a polymerization mechanism in which initiation is much slower than propagation.

Control experiments using either complex revealed that neither, by itself, was an effective initiator for MMA polymerization, although *slow* formation of PMMA was observed (by NMR) in mixtures of monomer and complex **2**. Thus, although the kinetics and degree of polymerization suggest that the initiation and propagation steps depend only on complex **2**, the rapid propagation rates observed in the presence of both are inconsistent with a process analogous to that discovered by Yasuda (i.e. eq 2).[3]

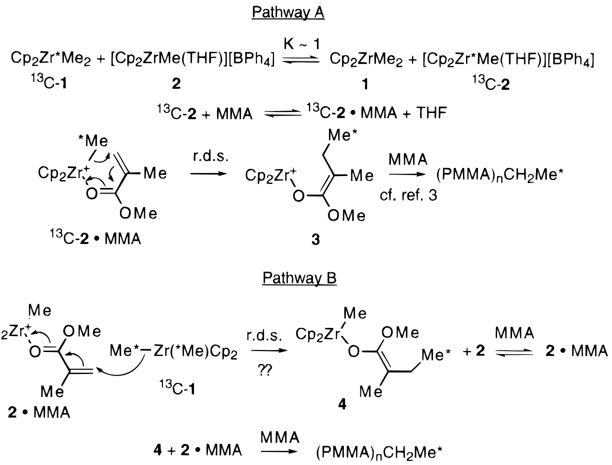
Earlier work, which involved the polymerization of MMA using a mixture of ^{13}C-labeled complex **1** and unlabeled complex **2**, revealed that the label was incorporated into the polymer chain at the position indicated in eq 3.[1] Control experiments revealed that the label was rapidly scrambled between complexes **2** and **1** under these conditions, and thus, although *all* polymer chains incorporated the label, this could have arisen from either complex or both.



3)

Two possible mechanisms that are consistent with incorporation of the label at the position indicated are outlined in Scheme 1. The first of these (Pathway A) involves transfer of a methyl group from complex **2** to the β-carbon of coordinated MMA[7] and is analogous to the initiation step in MMA polymerization mediated by lanthanocene complexes.[3] The product of this reaction is a cationic enolate complex **3**. As this species is isoelectronic with the neutral lanthanide enolate complex reported by Yasuda, one might expect that it is capable of effecting polymerization of MMA. While this mechanism nicely accounts for the fact that the rate of polymerization, following the induction period, and the degree of polymerization are only affected by the concentration of **2**, it does not explain the rapid rates of polymerization observed in the presence of **1** and the (much) slower rates observed in the presence of only complex **2**. The second initiation mechanism invokes transfer of a methyl group from complex **1** to monomer, activated by complex **2**. The product of this reaction is a neutral zirconium enolate complex **4** which might participate in propagation. While this mechanism does provide a role for complex **1** in these polymerizations, one would expect that the rate of initiation (and hence the degree of polymerization) should depend on the concentration of both complexes, contrary to what is observed. We will postpone further discussion of initiation until our studies concerning the mechanism of propagation have been presented.

Scheme 1



Propagation Mechanisms and Model Studies. Enolate complexes **3** and **4** are invoked as possible intermediates in this polymerization. If either species was responsible for propagation, independent preparation of complexes **3** and **4** would facilitate studies concerning the mechanism of propagation, assuming the rate of their formation is rate-limiting in polymerizations involving initiators **1** and **2**.

Neutral zirconocene enolates had been prepared by a number of routes. Initially, we prepared the aldehyde enolate complex **5**, reported by Curtis and co-workers.[8] In the presence of complex **2**, rapid consumption of monomer was observed with formation of high-MW PMMA (eq 4a). This was the first indication that polymer might be formed by Pathway B outlined in Scheme 1. However, NMR experiments revealed that methyl exchange between complex **5** and **2** was rapid under these conditions and gave rise to complex **1** and an *unstable* species, presumed to be **6** (eq 4b). Thus, one could not exclude Pathway A from consideration as a mechanism for propagation, as **3** might be formed in situ from **4** and **2** by analogy (i.e. eq 4c).

$$\underset{\mathbf{5}}{Cp_2ZrMe(OCH{=}CMe_2)} + \mathbf{2} \xrightarrow[\substack{CH_2Cl_2 \\ 0\ ^\circ C}]{MMA} PMMA \quad \begin{array}{l} 96\ \%\ \text{conversion} \\ M_n = 170\ K \\ M_w/M_n = 1.2 \end{array} \qquad \text{4a)}$$

$$\mathbf{5} + \mathbf{2} \xrightarrow{CD_2Cl_2} \underset{\mathbf{6}\ \text{(decomp.)}}{[Cp_2Zr^+(OCH{=}CMe_2)]} + \underset{\mathbf{1}}{Cp_2ZrMe_2} \qquad \text{4b)}$$

$$\underset{\text{(Scheme 1)}}{\mathbf{4} + \mathbf{2}} \xrightarrow{??} \underset{\mathbf{3}}{Cp_2Zr^+(OC(OMe){=}CR_2)} \xrightarrow{MMA} PMMA \qquad \text{4c)}$$

Clearly, resolution of this dichotomy required independent synthesis of complexes analogous to **3**. Of the various routes investigated, protonolysis of the bis(enolate) complex **7** provided access to cationic complex **3** in moderate yields (eq 5a).[9] Complex **3** was much less effective as an initiator for MMA polymerization compared with either **1** and **2** or **5** and **2**; conversions were lower under equivalent conditions and the MWD distribution of the polymer was broader (eq 5b).[10] Furthermore, NMR experiments revealed that mixtures of **3** and **1** were transformed, essentially irreversibly, into the neutral enolate **4** and complex **2** (eq 5c).

$$\underset{\mathbf{7}}{Cp_2ZrR_2} \xrightarrow[\substack{THF,\ -78\ -\ 0\ ^\circ C \\ 50\text{-}60\%}]{[Et_3NH][BPh_4]} \underset{\mathbf{3}}{[Cp_2Zr(THF)R][BPh_4]} \qquad \text{5a)}$$

$$R = -OC(OMe){=}CMe_2$$

$$\mathbf{3}\ (\sim 10\ mM) \xrightarrow[\substack{CH_2Cl_2 \\ 0\ ^\circ C}]{MMA\ (ca.\ 2.0\ M)} \begin{array}{c} PMMA \\ 20\ \%\ \text{conversion after 60 min.} \\ M_n = 20\ K \\ M_w/M_n = 1.55 \end{array} \qquad \text{5b)}$$

$$Cp_2ZrMe_2 + \mathbf{3} \xrightarrow[\substack{25\ ^\circ C \\ \text{fast}}]{CD_2Cl_2} \mathbf{2} + \underset{\mathbf{4}}{Cp_2Zr(Me)OC(OMe){=}CMe_2} \qquad \text{5c)}$$

From these results, it was clear that the reaction depicted in eq 4b was misleading as far as the mechanisms of both initiation and propagation were concerned. That is, formation of **1** (and **6**) was evidently driven by the instability of the latter compound under these conditions. Furthermore, propagation via complex **3** seemed unlikely from two perspectives; independently synthesized material was less active (eq 5b) and if it was present during initiation, would be converted into complex **4** by reaction with zirconocene **1** (eq 5c).

Thus, these experiments revealed that, in all likelihood, propagation occurred via Pathway B, Scheme 1. However, the kinetic work was more consistent with initiation occurring via Pathway A. The observation that the product of initiation via Pathway A (i.e. **3**) was converted into **4** by reaction with **1** (eq 5c) would be consistent with the kinetic studies if the latter process were not rate-limiting. That is, chains are formed at a rate that is governed solely by the concentration of **2** and propagation occurs rapidly via **4** (and **2**) formed in situ from **3** and **1** (Scheme 2).

Polymerization of Methyl Methacrylate Using Enolate Initiator 4 and Catalyst 2. The results obtained from both kinetic studies and model experiments suggested that the mechanism outlined in Scheme 2 was responsible for initiation and propagation. Clearly, if the former process is rate-limiting, formation of narrower MWD PMMA is precluded using initiators **1** and **2**. However, the use of enolate initiators analogous to **4**, in combination with **2**, should bypass this initiation process and might result in narrow-MWD polymers. Although this concept had been demonstrated in the case of aldehyde enolate initiator **5** (eq 4a), the instability of this compound under the polymerization conditions (eq 4b) suggested an alternate approach. In view of the result depicted in eq 5c, it seemed clear that use of an enolate complex **4** (derived from an ester) might obviate this latter problem.

Scheme 2

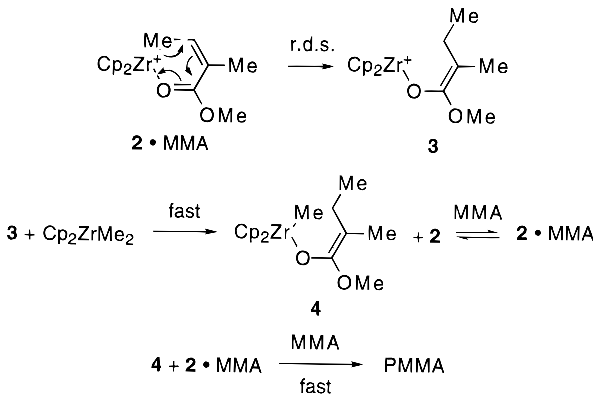


Table 1. MMA Polymerization Catalyzed by Enolate 4 and Cation 2[a]

[**4**] (mM)	[**2**] (mM)	[MMA] (M)	time (s)	% conv	M_n (K)	M_w/M_n
10.0	5.0	1.84	0	0	0	
10.0	5.0	1.03	90	44	16.8	1.10
10.0	5.0	0.72	150	61	28.3	1.07
10.0	5.0	0.02	240	99	34.6	1.10
10.0	5.0			100[b]	36.4	1.08
5.0	5.0	2.09	0	0	0	
5.0	5.0	1.84	60	12		
5.0	5.0	1.63	120	22	21.7	1.07
5.0	5.0	0.97	240	54	46.6	1.09
5.0	5.0	0.59	360	72	52.2	1.15
5.0	5.0	0.44	480	79		
5.0	5.0			100[b]	72.3	1.13
5.0	2.5	2.22	0	0	0	
5.0	2.5	1.73	240	22		
5.0	2.5	1.26	480	43	32.9	1.12
5.0	2.5	0.75	720	66	43.3	1.12
5.0	2.5	0.12	960	94	59.3	1.14
5.0	2.5			100[b]	63.7	1.11

[a] All polymerizations were performed with MMA that was distilled from $AlEt_3$ prior to use[13] and in CH_2Cl_2 that had been distilled from P_2O_5 (see text). [b] Characterization data for the bulk polymer obtained on quenching after the end of the kinetic run.

Neutral enolate complex **4** could be cleanly prepared from $Cp_2ZrMeCl$ as outlined in eq 6. Control experiments revealed that this complex was stable in the presence of cationic zirconocene **2** and that it was ineffective, in the absence of **2**, in the polymerization of MMA. However, this new two-component catalyst system was much more effective than **1** and **2**, and the results of a series of polymerizations employing **4** and **2** are summarized in Table 1 and in Figures 2 and 3.

$$\begin{array}{c} Cp_2ZrMeCl \\ + \\ Li[OC(O^tBu){=}CMe_2] \end{array} \xrightarrow[\substack{-78\ -\ 0\ ^\circ C \\ 80\text{-}90\%}]{THF} \underset{\mathbf{4}}{Cp_2ZrMe[OC(O^tBu){=}CMe_2]} \qquad \text{6)}$$

As can be seen from the results in Figure 2, there is no induction period observed and the rate of polymerization is independent of monomer concentration, even at high conversion.[11] Furthermore, the rate of polymerization is first order in both initiators. These findings are consistent with the mechanism proposed in Scheme

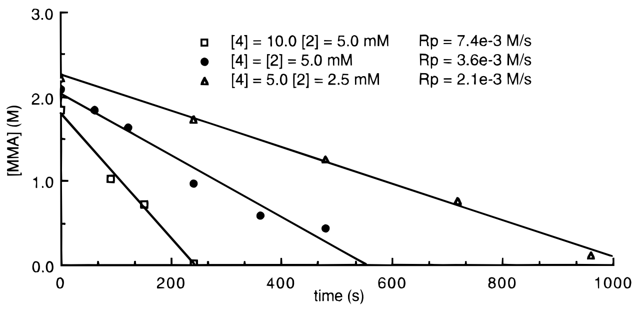


Figure 2. Kinetics of MMA polymerization employing complexes **2** and **4** (data and conditions in Table 1).

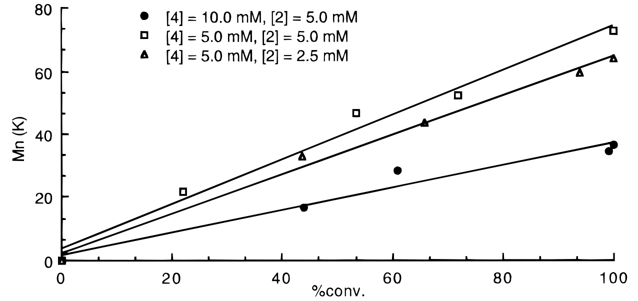
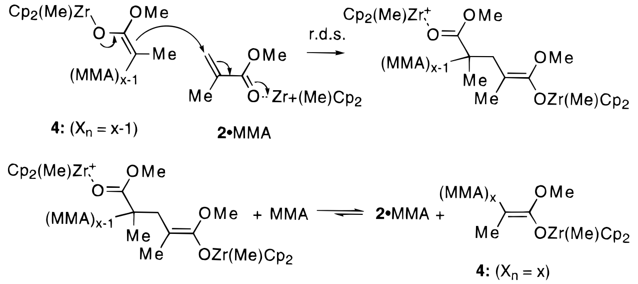


Figure 3. Molecular weight of PMMA, prepared using complexes **2** and **4**, vs percent conversion (data and conditions in Table 1).

Scheme 3



3. If the rate-limiting step in propagation involves intermolecular Michael addition of the polymeric enolate **4** to activated monomer (**2**·MMA), application of the steady-state approximation to the bimetallic intermediate formed in this first step results in a rate expression that is independent of monomer concentration.

Note that the first step in propagation converts **2**·MMA into a neutral enolate complex with concomitant transformation of **4** into a cationic zirconocene complex; the two metals are interchanged as a result of propagation. We originally suggested that this polymerization was somewhat reminiscent of group-transfer polymerization; a more apt name, in view of the proposed mechanism of propagation, would be polymer-transfer polymerization as it is the polymer chain that is transferred between the two metals during propagation.

As shown in Figure 3, the MW of PMMA produced using this initiator system is a linear function of conversion (or time in this specific case) and the MWD remains narrow at all times ($M_w/M_n < 1.2$). These features are characteristic of living polymerization processes; it should be noted, however, that the catalytic efficiency of this system rarely exceeds 70% as a result of adventitious deactivation of catalyst (vide infra). Furthermore, the degree of polymerization is *solely* related to the concentration of neutral enolate initially present. This finding is also consistent with the mechanism depicted in Scheme 3 in which the growing chains are ultimately derived from the enolate initiator and the principal function of the cationic metallocene is to activate monomer toward nucleophilic attack. Thus, the rate of polymerization is affected by the concentration of **2** but not the ultimate degree of polymerization.

Table 2. Sequential Polymerization of MMA[a]

entry	$[MMA]_0/[\mathbf{4}]$	% conv	Δt (min)[b]	M_n (K)	M_w/M_n	% eff[c]
1	110	100		14.1	1.05	78.5
2	220	100	1.0	29.8	1.06	94.6
3	114	95		15.2	1.05	71.3
4	228	100	2.0	32.7	1.08	92.9
5	110	96		14.8	1.07	72.1
6	220	100	4.0	32.7	1.09	90.5
7	110	100		15.4	1.09	72.0
8	220	100	8.0	33.0	1.10	93.3

[a] All polymerizations were performed with MMA that was distilled from $AlEt_3$ prior to use[13] and in CH_2Cl_2 that had been distilled from P_2O_5 (see text) with $[\mathbf{4}]_0 = [\mathbf{2}]_0 = 7.5$ mM. [b] Time interval between the second addition of monomer and completion of the previous polymerization (as determined from GC of a quenched aliquot). [c] Catalyst efficiency determined from ($[MMA]_0 \times$ % conv)/$[\mathbf{4}] = M_n$(theor), with % eff $= M_n$(theor)/M_n(obs) $\times$ 100. For the second-stage polymerization, % eff is calculated based on the expected increase in M_n.

To conclusively demonstrate the living character of this polymerization process, sequential polymerization of MMA was carried out. As shown in Table 2, the chains are living for at least 8 min at 0 °C in the absence of monomer. Moreover, the living chains appear to be less susceptible to adventitious quenching than enolate initiator (compare the calculated efficiencies in the second stage vs first stage polymerization). From a practical perspective, however, the polymerization process is not immortal; catalyst **2** is known to be unstable in chlorinated solvents[12] and although this, in and of itself, will not necessarily lead to chain termination, the rate of propagation (i.e. chain growth) will be dramatically reduced as the concentration of **2** is lowered through reaction with solvent under these conditions.

Polymerization of MMA Using Initiators 1 and 2—Initiation Revisited. The above experiments reveal that polymerization of MMA using catalysts **1** and **2** likely involves the propagation sequence depicted in Scheme 3. What remains to be addressed is whether chains are initiated in the manner depicted in Scheme 2. For a polymerization process that proceeds without (kinetically significant) termination, the degree of polymerization at any time is related to monomer and growing chain concentration through eq 7. As both the time dependence of [MMA] and MW are known for this system, the concentration of growing chains can be estimated from eq 7.

$$\bar{X}_n(t) = \frac{[MMA]_0 - [MMA]}{[Zr^*]} \qquad 7)$$

This data is summarized in Table 3 and plotted in Figure 4; the rate of formation of [Zr*] is dependent only on the concentration of **2** and in the region where significant formation of chains is occurring, the dependence on [**2**] is approximately first order, consistent with the mechanism depicted in Scheme 2. In hindsight, the function of complex **1** is clearly secondary; its only serves to convert complex **3** into **4**, which, under the conditions studied, is rapid and irreversible. Once formed, propagation involving **4** occurs rapidly via the mechanism depicted in Scheme 3. As the rate of the latter process depends on both the concentration of **2** and the concen-

Table 3. Time Dependence of X_n and [Zr*] in MMA Polymerization Using Complexes 1 and 2[a]

entry	time (s)	$[M]_0 - [M]$ (M)	M_n (K)	X_n	[Zr*] (mM)[b]
1	600	0.092	48.7	487	0.19
2	750	0.131	61.0	610	0.27
3	930	0.268	78.5	785	0.34
4	1140	0.435	74.4	744	0.59
5	1350	0.687	86.3	863	0.80
6	1560	1.012	100.7	1007	1.00
7	600	0.078	50.9	509	0.15
8	750	0.138	65.5	655	0.21
9	930	0.269	81.7	817	0.33
10	1140	0.460	75.4	754	0.61
11	1350	0.723	96.1	961	0.75
12	1560	1.091	126.2	1262	0.86
13	210	0.032	26.8	268	0.12
14	300	0.087	39.4	394	0.22
15	360	0.136	50.5	505	0.27
16	420	0.192	60.7	607	0.32
17	510	0.309	72.9	729	0.42
18	600	0.465	70.6	706	0.66
19	690	0.805	93.8	938	0.77
20	780	1.040	106.8	1068	0.96

[a] All polymerizations were performed with MMA that was distilled from $AlEt_3$ prior to use[13] and in CH_2Cl_2 that had been distilled from P_2O_5 (see text). Entries 1−6: [**1**] = 12.6 mM, [**2**] = 4.2 mM. Entries 7−12: [**1**] = 25.1 mM, [**2**] = 4.2 mM. Entries 13−20: [**1**] = 25.1 mM, [**2**] = 8.3 mM. Monomer concentrations are given in Table 8 (see Experimental Section). [b] Calculated from eq 7.

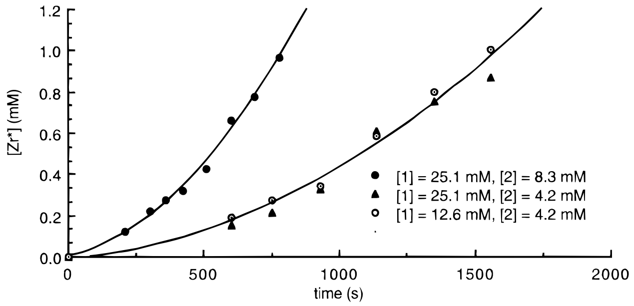


Figure 4. [Zr*] (active center concentration) vs time for polymerization of MMA with complexes **1** and **2** (data and conditions in Table 3).

tration of growing chains (which are ultimately derived from **2**), the invariance of both the rate and degree of polymerization on the concentration of **1** is clearly expected.

Polymerization of MMA in the Presence of Trialkylaluminum Compounds. As the results in Table 1 demonstrate, the MW of PMMA produced using initiators **4** and **2** is lower than that obtained using **1** and **2** under similar conditions (cf. Table 3). A slow rate of initiation in the latter case ensures that only a small fraction of added initiator is converted into (rapidly) growing chains and thus high-MW polymer can be easily produced. Attempts to produce high-MW polymer with **4** and **2** immediately revealed the sensitivity of this system to catalyst dilution; at concentrations below 5 mM (of either component), the rate of polymerization was either extremely slow or no polymer was obtained. As shown in Table 4, part of this problem is undoubtedly due to adventitious quenching of initiators. Scrupulous purification of both monomer and solvent results in significant increases in the rate of polymerization, other conditions being equal. Because of the bimetallic nature of the propagation step, this polymerization system is far more sensitive to the presence of impurities than that reported by Yasuda. All of the results reported earlier (Tables 1−3) were conducted under the conditions reported in Table 4, entry 6.

Table 4. Polymerization of MMA under Various Conditions Using Enolate 4 and Cation 2[a]

entry[b]	[**4**] (mM)	[**2**] (mM)	[MMA] (M)	k_p (M^{-1} s^{-1})
1	10.0	5.0	2.10	121.0
2	5.0	5.0	2.10	*c*
3	5.0	2.5	2.10	*c*
4	5.0	5.0	1.56	95.0
5	5.0	5.0	1.56	97.5
6	5.0	5.0	2.09	150 ± 20[d]

[a] All polymerizations were performed in CH_2Cl_2 solution at 0 °C; monomer disappearance was monitored using GC analysis of quenched aliquots with *n*-decane as an internal standard. [b] Entries 1−3, MMA and solvent were distilled from CaH_2. Entries 4 and 5, MMA was distilled from $AlEt_3$. Entry 6, MMA was distilled from $AlEt_3$ and CH_2Cl_2 was distilled from P_2O_5. [c] No polymer was produced. [d] Average of six trials.

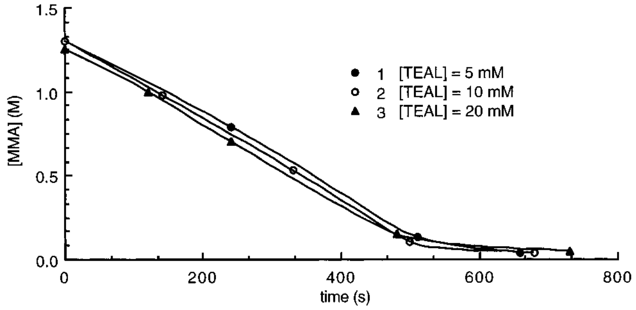


Figure 5. [MMA] vs time in the presence of low concentrations of [TEAL] (data in Table 9).

The sensitivity of this two-component initiator system to impurities in monomer and solvent suggested that development of a scrubbing agent that could be used, in situ, to purify them would be attractive. To this end, we elected to study the polymerization of MMA using **4** and **2** in the presence of trialkylaluminum compounds; these reagents are typically used to purify acrylate and methacrylate monomers for use in e.g. anionic polymerization.[13]

Some control experiments revealed that neither complex **4** nor complex **2**, in the presence of $AlEt_3$ (TEAL), would effect rapid polymerization of MMA. However, titration of a solution of monomer in CH_2Cl_2 to the characteristic yellow end point of the MMA·$AlEt_3$ complex[13] followed by the addition of **4** and **2** led to extremely rapid polymerization of monomer.

As shown in Figure 5, at low [TEAL], the kinetics are largely unaffected by the presence of this additive; the rate constant for propagation under these conditions (ca. 420 ± 20 M^{-1} s^{-1}) is much larger than that observed previously (ca. 150 ± 20 M^{-1} s^{-1}) and may be indicative of the effective scrubbing action of TEAL. However, as shown in Figure 5, these polymerizations were not quantitative; small quantities of unreacted monomer remained even after extended periods of time. This latter effect is more pronounced at higher [TEAL] (i.e. $>$20 mM); not only that, the rate of polymerization was dependent on monomer concentration (ca. first order in monomer for [TEAL] $>$ 50 mM). With reference to Scheme 3, these effects may be partly rationalized in terms of a reduction in the concentration of uncomplexed monomer. Propagation will be independent of monomer concentration only if the first step is rate-limiting with respect to the first; at high conversion, one expects this assumption to break down. Alternatively, a reduction in [MMA] by complexation to TEAL would

Table 5. Molecular Weight and Weight Distribution of PMMA in the Presence of TEAL

[**4**] (mM)	[**2**] (mM)	[TEAL] (mM)	[MMA] (M)	% conv	M_n (K)	M_w/M_n	% eff[a]
2.5	2.5	10	1.30	24	14.5	1.08	82.7
2.5	2.5	10	1.30	66	35.2	1.09	97.8
2.5	2.5	10	1.30	89	42.5	1.11	109
2.5	2.4	20	1.25	16	12.0	1.09	67.4
2.5	2.4	20	1.25	52	24.6	1.09	92.7
2.5	2.4	20	1.25	72	40.6	1.13	109.6
2.5	2.4	20	1.25	90	45.4	1.13	107.0
2.5	2.4	47	1.20	52	26.3	1.22	96.0
2.5	2.4	47	1.20	72	35.0	1.27	100.0
2.5	2.4	47	1.20	90	40.3	1.27	109.0
2.4	2.3	83	1.15	47	27.5	1.50	81.9
2.4	2.3	83	1.15	72	32.0	1.60	109.0
2.4	2.3	83	1.15	85	33.5	1.47	121.0

[a] Initiator efficiency determined from ([MMA]$_o$ x % conv)/[**4**] = M_n(theor) with % eff = M_n(theor)/M_n(obs) × 100.

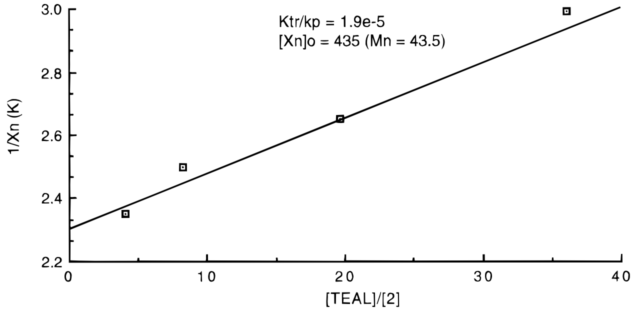


Figure 6. $1/X_n$ vs [TEAL]/[**2**] at constant conversion of MMA (data from Table 5, last entry for each run).

have the same effect, provided the latter were effectively irreversible.

Having said that, the effect of TEAL is not as innocuous as implied by the above analysis. As can be clearly seen from the results in Table 5, the MWDs of PMMA are broader in the presence of TEAL, particularly at high concentrations, and the catalyst efficiencies exceed 100%. This behavior is consistent with TEAL functioning as a chain-transfer agent in these polymerizations. The degree of polymerization will be regulated by both the concentration of TEAL and [**2**] as shown in eq 8a–c; if chain transfer is first order in both TEAL and growing chains, the relationship between the degree of polymerization in the presence of chain transfer and these variables is shown in eq 8c. This relationship is plotted out in Figure 6 for [TEAL] < 100 mM and at constant conversions of MMA (data from Table 5). A linear correlation is observed, and from the slope and $k_p = 420 \pm 20\ \mathrm{M^{-1}\ s^{-1}}$ (estimated from the linear portion of the time–conversion curves (Figure 5)), one can obtain an estimate for k_{tr} ($(8.0 \pm 1.0) \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$). Thus, TEAL is not a particularly effective chain-transfer agent, which explains the lack of significant effects on the MWD at low [TEAL].

$$R_p = \frac{-\partial[\mathrm{MMA}]}{\partial t} = k_p[\mathrm{Zr}^*][\mathbf{2}]_o \qquad 8a)$$

$$R_{tr} = \frac{-\partial[\mathrm{Zr}^*]}{\partial t} = k_{tr}[\mathrm{Zr}^*][\mathrm{TEAL}]_o \qquad 8b)$$

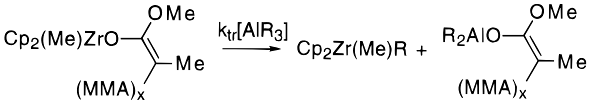
$$\frac{1}{\overline{X}_n} = \frac{1}{(\overline{X}_n)_o} + \frac{k_{tr}[\mathrm{TEAL}]_o}{k_p[\mathbf{2}]_o} \qquad 8c)$$

In view of this, it seemed likely that even more effective scrubbing agents could be developed, particularly ones that would be less likely to engage in chain-transfer reactions. If chain transfer involves ligand exchange between a zirconium enolate and the alkylaluminum (e.g. eq 9), the rate of this process will be affected by, inter alia, the steric bulk of the trialkylaluminum compound.

Table 6. Effect of Triisobutylaluminum (TIBAL) on MMA Polymerization[a]

[TIBAL] (mM)	time (s)	[MMA] (M)	M_n (K)	M_w/M_n	% eff[a]
20	0	1.25	0		
20	360	0.35	44.6	1.19	80.8
20	600	0.05	65.9	1.10	75.2
40	0	1.2	0		
40	360	0.22	55.7	1.22	78.8
40	600	0.07	63.4	1.13	75
80	0	1.05	0		
80	420	0.10	44.4	1.16	83.4
80	540	0.06	52.1	1.11	80.0

[a] TIBAL was added to a solution of MMA in CH_2Cl_2 at 0 °C, and initiators **4** and **2** were then added sequentially; [**4**] = [**2**] = 2.5 mM. [b] Initiator efficiency determined from ([MMA]$_0$ × % conv)/[**4**] = M_n(theor), with % eff = M_n(theor)/M_n(obs) × 100.



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With this in mind, the use of Al^iBu_3 (TIBAL) was investigated as a scrubbing agent. As shown in Table 6, the use of TIBAL gives rise to similar phenomena as observed using TEAL. In particular, high rates of propagation are accompanied by high conversion of monomer at low [TIBAL]. At equivalent concentrations of alkylaluminum, the use of TIBAL provides access to PMMA with a narrower MWD ($M_w/M_n < 1.2$) compared with TEAL ($M_w/M_n > 1.2$) at high conversion. Although this suggests that TIBAL is less effective than TEAL in chain transfer, this conclusion must be prefaced by the observation that at lower conversions, the polymer possessed a bimodal MWD. It is possible that this phenomenon arises from reversible chain transfer or an independent propagation process; in any event, at high conversion, the polymer possessed a unimodal MWD with a degree of polymerization that was dependent on enolate concentration in the usual fashion.

Polymerization of *n*-Butyl Acrylate Using Initiators 2 and 4. In view of the high-conversion, living polymerization of MMA using initiators **2** and **4**, the polymerization of unhindered acrylate monomers was of obvious interest.[3,14] Initial experiments using *n*-butyl acrylate (BuA) conducted under the same conditions as used for MMA ([**2**] = [**4**] = 5 mM; 0 °C, CH_2Cl_2) were disappointing; little or no polymer was obtained under these conditions. Subsequent work revealed that at lower temperatures (−78 °C), high conversions were obtained at higher catalyst loadings (Table 7) and poly(BuA) with a narrow MWD ($M_w/M_n < 1.3$) was produced. At higher temperatures, conversions were lower and the MWD of the polymer was considerably broadened.

This behavior is consistent with a polymerization process involving not only termination of growing polymer chains but also catalyst deactivation. In an attempt to identify the mode(s) of termination, polymerization of BuA was investigated at higher catalyst concentrations at −78 and 0 °C and the low-MW poly(BuA) produced was characterized by MALDI-TOF mass spectrometry (see Experimental Section for details). As shown in Figure 7a, the mass spectrum of poly(BuA)

Scheme 4

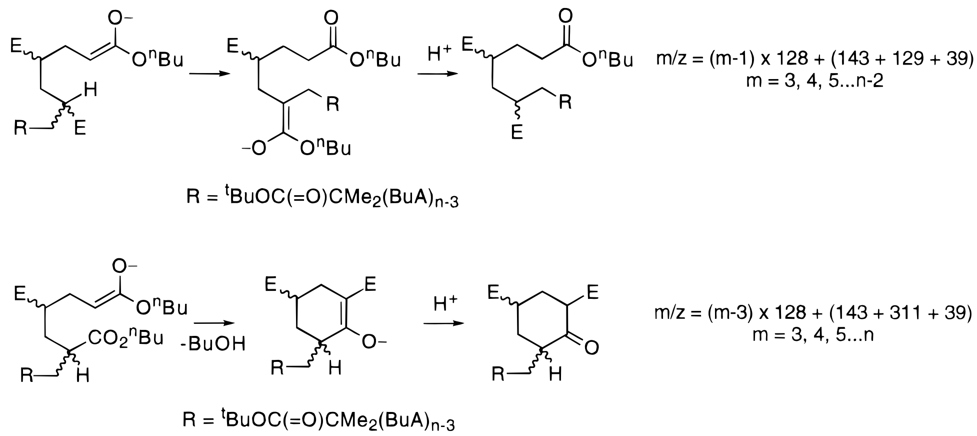


Table 7. Polymerization of BuA Catalyzed by Zirconocene Complexes[a]

entry	[**4**][b]	[**2**][b]	[BuA][c]	*T* (°C)	time (h)	% conv	M_n (K)	M_w/M_n	% eff[d]
1	12.1	13.3	1.16	−78	1	100	21.0	1.24	59
2	10.0	5.0	1.10	−78	1	100	35.0	1.27	40
3	10.0	5.0	1.05	−42	2	90	26.0	1.65	46
4	9.9	5.0	1.05	−23	1.5	65	20.0	1.91	49
5	9.9	5.0	1.05	0	1.5	55	15.0	2.02	50

[a] All polymerizations were conducted in CH_2Cl_2 with monomer distilled from $AlEt_3$ prior to use.[13] [b] Concentration in mM. [c] Concentration in M. [d] Initiator efficiency determined from M_n(theor)/M_n(obs) × 100 = % eff, with M_n(theor) = ([BuA]$_0$ × % conv/[**4**]$_0$ × 100)M_{BuA}, where M_{BuA} is the MW of the repeat unit.

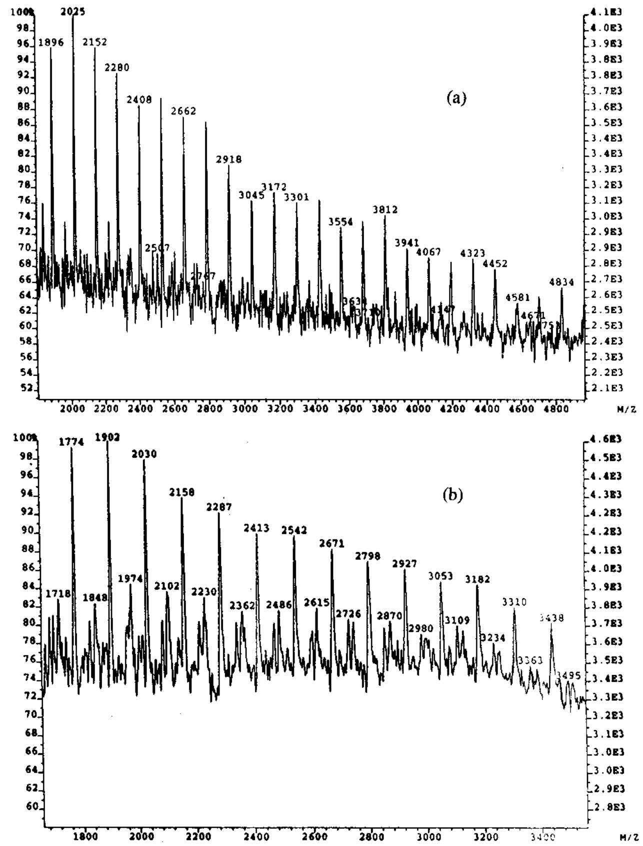


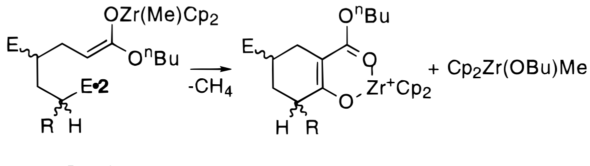
Figure 7. Matrix-assisted laser desorption ionization (MALDI) mass spectra of poly(butyl acrylate) prepared with **2** and **4** at (a) −78 and (b) 0 °C. Only a portion of the mass spectra is shown.

produced at low temperatures consists of a single series of mass ions separated by the repeat unit of the monomer (*m*/*z* = 128). In contrast, the mass spectrum of material produced at 0 °C was comprised of two series of mass ions, the more predominant of which was the same as that produced at lower temperature. Clearly, there are two possible modes of termination and/or initiation.

Proton and ^{13}C NMR spectra of these polymers revealed the presence of a *tert*-butyl group (singlets at δ 1.15 and 28.6 ppm, respectively) arising from initiator **4**. The M_n calculated from the ^{13}C NMR spectrum of the polymer formed at −78 °C, assuming one such group per chain, was in excellent agreement with that independently measured by GPC (5.7 vs 5.8 K, respectively). With this information, the mass spectra of the polymers can be properly analyzed with respect to the mode(s) of termination.

Two principal pathways for termination in e.g. anionic acrylate polymerization have been identified. One involves proton transfer from the polymer chain and the other involves "back-biting" cyclization (Scheme 4). In the present case, the former process should result in a series of mass ions at *m*/*z* = 567, 695, 823, 951, etc. and the latter should result in a series of ions at *m*/*z* = 493, 621, 749, 877, etc. after taking into account of the mass of the cation used in the MALDI process (K^+) and the mass fragments arising from the initiator and the end group (Scheme 4).

As can be appreciated from Figure 7a, the latter process is dominant at low temperature whereas both processes are competitive at higher temperatures (Figure 7b). Proton transfer may not be accompanied by catalyst deactivation (i.e. the product would still be a zirconium enolate) but the rate of further chain growth may be much slower from the internal enolate formed. However, it is expected that cyclization will result in termination of chain growth and also catalyst deactivation, perhaps through the formation of a stable "acac"-type complex of zirconium (eq 10). This process, in particular, probably accounts for the lower conversions observed at higher temperatures—presumably, most of the enolate initiator added is consumed via this process prior to complete depletion of monomer.



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Conclusions

The polymerization of MMA using two-component zirconocene initiators **1** and **2** proceeds via the intermediacy of neutral enolate complexes **4** which, in concert with **2**·MMA, are responsible for propagation. Initiation of polymerization is a slow and rather complex process involving transient, rate-limiting formation of a cationic enolate complex **3** from **2**·MMA and transformation of the former into **4** by reaction with dimethylzirconocene (**1**). By use of preformed enolate initiators and complex **2**, PMMA can be produced with a narrow MWD and the polymer chains are living for short periods of time at 0 °C. Trialkylaluminum compounds can be used, in situ, to purify monomer and solvent prior to polymerization; under these conditions, the rate of polymerization is extremely fast and if a bulky R_3Al (i.e. TIBAL) is employed, high-MW PMMA with a narrow MWD can be obtained at high conversion. Finally, the polymerization of BuA, initiated by **4** and **2**, is complicated by termination processes, the most important of which is back-biting cyclization; at higher temperatures, incomplete conversion of monomer is observed and the polymer has a broad MWD.

Experimental Section

All chemicals and solvents were reagent grade and were purified as required. Diethyl ether, THF, toluene, and hexanes were dried and distilled from potassium and benzophenone. Dichloromethane was dried by distillation from CaH_2 followed by distillation from P_2O_5.

Methyl methacrylate and butyl acrylate were predried by stirring over and distillation from CaH_2 under reduced pressure. Final purification involved titration with a toluene solution of $AlEt_3$ at 0 °C until a yellow end point was obtained, followed by distillation under reduced pressure (50 and 5 mmHg, respectively); in the case of *n*-butyl acrylate, this distillation must be performed carefully to avoid contamination of the distillate with $AlEt_3$, which results in subsequent polymerization. In both cases, the distillate was contaminated with small quantities of toluene, the amounts of which were estimated by ^1H NMR spectroscopy prior to polymerization.

Routine ^1H and ^{13}C NMR spectra were recorded on either a Bruker AC-200 or AM-250 spectrometer and spectra are referenced to residual protonated solvent or deuterated solvent, respectively. IR spectra were recorded using a Bomem MB-100 FTIR spectrometer at 4.0 cm^{-1} resolution. Routine mass spectra were obtained using a Kratos MS-890 instrument at the University of Guelph or a VG70/70 SE instrument at Waterloo, while elemental analyses were performed by M.H.W. Ltd. (Phoenix, AZ). GC analyses were conducted using a HP 5890 chromatograph equipped with a Supelco SE-30 column [50 m × 0.25 mm; 50 °C (2.0 min) to 200 °C (10 min) at 20 °C/min] and an FID detector. GPC analyses were performed using a Waters chromatograph equipped with four PL-gel 10 μM columns (10^5, 10^3, 500, and 100 Å) and a guard column maintained at 30 °C, a Waters DRI and UV detectors, and a Viscotek differential viscometer detector. THF was used as the eluent at a flow rate of 1.0 mL/min and the system was calibrated using monodisperse PMMA standards obtained from PL-Sciences Ltd. Polymer solutions for analysis were prepared by weight (ca. 2.5−3.5% in THF) or in the case of samples obtained at very low conversions, polymer concentrations were calculated from the area of the (baseline resolved) GPC trace after adding a known quantity of a high-MW PMMA standard.

MALDI-TOF mass spectra were recorded using a Fizons/VG Instrument, operating in a linear mode, in which samples were irradiated with a nitrogen laser (wavelength 337 nm; 4 ns pulse) under high vacuum. Satisfactory results were obtained by preparing a solution of the matrix (2,4-dihydroxybenzoic acid recrystallized from ethanol/H_2O) and the polymer (ca. 10:1 w/w) in $CHCl_3$ (10 mL) and vigorously stirring this with a solution of KCl in MeOH/H_2O (0.1 mL). An aliquot was then withdrawn and the solvent evaporated under a stream of nitrogen prior to introduction into the laser desorption chamber. The production of singly charged ions was verified by conducting these measurements at different salt concentrations. Raw spectra were calibrated using known procedures.[15]

Table 8. Kinetic Studies of MMA Polymerization Involving Cp_2ZrMe_2 (1) and $[Cp_2ZrMe][BPh_4]$ (2)[a]

[MMA][b] (M)	time (s)	[MMA][c] (M)	time (s)	[MMA][d] (M)	time (s)
1.77	0	1.55	0	1.52	0
1.78	150	1.55	150	1.32	120
1.77	300	1.55	300	1.29	210
1.72	450	1.51	450	1.24	300
1.68	600	1.47	600	1.19	360
1.61	750	1.41	750	1.13	420
1.51	930	1.28	930	1.01	510
1.34	1140	1.09	1140	0.86	600
1.09	1350	0.83	1350	0.58	690
0.76	1560	0.46	1560	0.28	780

[a] All polymerizations were performed in a CH_2Cl_2 solution at 0 °C with monomer distilled from $AlEt_3$ prior to use.[13] [b] [**1**] = 12.6 mM, [**2**] = 4.2 mM. [c] [**1**] = 25.1 mM, [**2**] = 4.2 mM. [d] [**1**] = 25.1 mM, [**2**] = 8.3 mM.

Table 9. Kinetics of MMA Polymerization in the Presence of Triethylaluminum (TEAL)[a]

[**4**] (mM)	[**2**] (mM)	[TEAL] (mM)	time (s)	[MMA] (M)
2.5	2.5	5	0	1.30
2.5	2.5	5	240	0.79
2.5	2.5	5	510	0.13
2.5	2.5	5	660	0.04
2.5	2.5	10	0	1.30
2.5	2.5	10	140	0.98
2.5	2.5	10	330	0.43
2.5	2.5	10	500	0.14
2.5	2.5	10	680	0.04
2.5	2.5	20	0	1.25
2.5	2.5	20	120	1.05
2.5	2.5	20	240	0.70
2.5	2.5	20	480	0.15
2.5	2.5	20	730	0.06

[a] TEAL was added to a solution of MMA in CH_2Cl_2 at 0 °C; solutions of initiators **4** and **2** were then added sequentially.

Polymerizations of MMA were conducted in dry CH_2Cl_2 solution using the following general procedure:

A solution of MMA and *n*-decane (as an internal GC standard: RRF = 2.01) in CH_2Cl_2 was prepared (ca. 1.5 −3.0 M in monomer and ca. 0.2 M in *n*-decane) under nitrogen and aliquots were removed by syringe and transferred to reaction flasks. Solutions of initiator **1** (or **4**) and cation **2** in CH_2Cl_2 (ca. 0.1 M each) were separately prepared, initially at −78 °C followed by warming to 0 °C. A fixed amount of the initiator solution was added to each reaction flask at the reaction temperature, followed by a known quantity of the cation solution with vigorous stirring. Aliquots (ca. 0.1 mL) were withdrawn by disposable syringe and quenched into wet hexanes to precipitate both polymer and catalyst residues. The supernatant was analyzed by GC for residual monomer and the polymer formed was analyzed by GPC.

Typical experimental results are summarized in Table 8 (for **1** and **2**; see Figure 1) and in Table 9 (for **2** and **4** in the presence of TEAL; see Figure 5).

Preparation and Characterization of Initiators and Catalysts. The compounds Cp_2ZrMe_2,[16] $Cp_2ZrMeCl$,[17] $[Cp_2ZrMe(THF)][BPh_4]$,[12] $[Et_3NH][BPh_4]$,[18] and $Cp_2ZrMe(OCH{=}CMe_2)$[8] were prepared by literature procedures. *tert*-Butyl 2-methylpropanoate was prepared by reaction of 2-methylpropanoyl chloride with potassium *tert*-butoxide in THF solution. The lithium enolate of this ester was prepared and isolated as described by Collum and co-workers.[19]

Preparation of $Cp_2ZrMe(OC(O^tBu){=}CMe_2)$ (4). A solution of $LiOC(O^tBu){=}CMe_2$ in THF (1.005 g, 6.69 mmol in 10 mL) was prepared at −78 °C. A solution of $Cp_2ZrMeCl$ in THF (1.84 g, 6.78 mmol in 15 mL) was prepared and added to the former solution by cannula with stirring at this temperature. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed in vacuo and the residue slurried in dry hexanes (20 mL). The mixture was concentrated to dryness in vacuo and resuspended in dry hexanes (20 mL). The mixture was filtered under nitrogen washing with dry hexanes (2 × 10 mL) and the filtrate was concentrated to dryness in vacuo to provide the title compound as a viscous, pale yellow oil (1.88 g, 74%). ^{1}H NMR (250 MHz, C_6D_6) δ 5.82 (s, 10H), 1.81 (s, 3H), 1.61 (s, 3H), 1.26 (s, 9H), 0.38 (s, 3H). ^{13}C NMR (62.5 MHz, C_6D_6) δ 155.71 $[\mathrm{O}\mathbf{C}(\mathrm{O^tBu})\text{-}\mathrm{CMe_2}]$, 111.44 (Cp), 87.0 $[\mathrm{OC(O^tBu)}\mathbf{C}\mathrm{Me_2}]$, 77.36 $[\mathrm{O}\mathbf{C}\mathrm{(Me)_3}]$, 29.53 $[\mathrm{OC}(\mathbf{CH_3})_3]$, 24.77 (Zr**Me**), 18.77 and 18.16 $[\mathrm{OC(OMe)}\text{-}\mathrm{C}\mathbf{Me}_2]$. Anal. Calcd for $C_{19}H_{28}O_2Zr$: C, 60.11; H, 7.43. Found: C, 59.86; H, 7.28.

Preparation of $\mathbf{Cp_2Zr(OC(OMe){=}CMe_2)_2}$ (7). A solution of LDA in THF was prepared from diisopropylamine (3 mL, 21.4 mmol) in THF (20 mL) and a solution of *n*-butyllithium in hexanes (9 mL, 2.5 M, 22.5 mmol) at 0 °C under nitrogen. The solution was cooled to −78 °C and methyl 2-methylpropanoate (2.5 mL, 22 mmol distilled from $MgSO_4$) was added dropwise via syringe at this temperature with vigorous stirring. The solution was warmed to 0 °C and was then recooled to −78 °C. The solution was transferred by cannula to a suspension of Cp_2ZrCl_2 in THF (3.18 g, 10.9 mmol in 30 mL). The mixture was allowed to warm to room temperature and stirred for 3 h. The solvents were removed in vacuo and the residue dried under high vacuum (10^{-3} mmHg). The residue was suspended in dry isooctane (20 mL) and this process repeated. Finally, the residue was suspended in dry hexane (20 mL) and the mixture was filtered, washing with hexanes (20 mL). The filtrate was concentrated in vacuo to provide the title compound as a yellow, waxy solid (3.8 g, 82%) which could be crystallized from hexanes at −90 °C. ^{1}H NMR (250 MHz, C_6D_6) δ 6.32 (s, 10H), 3.46 (s, 3H), 1.60 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (62.5 MHz, C_6D_6) δ 159.08 $[\mathrm{O}\mathbf{C}\mathrm{(OMe)CMe_2}]$, 113.87 (Cp), 82.7 $[\mathrm{OC(OMe)}\mathbf{C}\mathrm{Me_2}]$, 55.83 (OMe), 17.66 and 17.02 $[\mathrm{OC(OMe)C}\mathbf{Me}_2]$. High-resolution mass spectrum calcd for $C_{20}H_{28}O_4{}^{90}Zr$: 422.10345. Found (EI): 422.10019.

Preparation of $\mathbf{[Cp_2Zr(OC(OMe){=}CMe_2)THF][BPh_4]}$ (3). A solution of $Cp_2Zr(OC(OMe){=}CMe_2)_2$ in THF (1.58 g, 3.73 mmol in 20 mL) was added via cannula to a suspension of $[Et_3NH][BPh_4]$ in THF (1.54 g, 3.65 mmol in 20 mL) at −78 °C. The mixture was warmed to 0 °C and kept at this temperature for 5 h. The solvent was then concentrated to ca. 20 mL in vacuo and diluted with 20 mL of dry hexanes with vigorous stirring. A yellow solid precipitated and was filtered off and washed with dry hexanes (20 mL). The crude product (1.36 g, 70%) could be further purified by repeating this procedure using a minimal volume of THF to dissolve it at 0 °C. ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.37 (br m, 8H), 7.06 (br t, $J = 8$ Hz, 8H), 6.91 (br t, $J = 8$ Hz, 4H), 6.40 (s, 10H), 3.68 (m, 4H), 3.54 (s, 3H), 1.92 (m, 4H), 1.64 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (50 MHz, CD_2Cl_2) δ 164.4 (q, $J_{CB} = 49.2$ Hz, ipso-C), 138.9 $[\mathrm{O}\mathbf{C}\mathrm{(OMe){=}CMe_2}]$, 136.3 (*o*-C), 128.1 (*m*-C), 122.2 (*p*-C), 116.8 (Cp), 91.0 $[\mathrm{OC(OMe){=}}\mathbf{C}\mathrm{Me_2}]$, 78.0 ($\alpha$-C, THF), 59.0 $[\mathrm{OC}\text{-}(\mathrm{O}\mathbf{Me}){=}\mathrm{CMe_2}]$, 28.0 ($\beta$-C, THF), 17.6 and 16.3 $[\mathrm{OC}\text{-}(\mathrm{OMe{=}C}\mathbf{Me}_2]$. Anal. Calcd for $C_{43}H_{47}BO_3Zr$: C, 72.35; H, 6.64. Found: C, 72.57; H, 6.66.

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