Homogeneous Catalysis

Methacrylate Polymerization using a Dinuclear Zirconocene Initiator: A New Approach for the Controlled Synthesis of Methacrylate Polymers**

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There has been renewed interest in the controlled polymerization of acrylates and other susceptible monomers using Group 4 metallocene initiators during the past five years. These complexes have been applied to the synthesis of polyacrylates and polymethacrylates, where control over molecular weight (M_W), comonomer sequence distribution, and polymer tacticity is possible in some cases.[1]

Over 10 years ago we reported that a two-component initiator system comprising [Cp_2ZrMe_2] ($Cp = C_5H_5$) and [$Cp_2ZrMe(L)$][X], either preformed ($X = BPh_4$, L = THF)[2a] or generated in situ ($X = MeB(C_6F_5)_3$, $B(C_6F_5)_4$, L = methyl methacrylate (MMA))[2b,c] was competent for MMA polymerization. Mechanistic work revealed that propagation involved the rate-limiting, intermolecular Michael addition of zirconocene enolate **1** (formed in situ from complex **2** and [Cp_2ZrMe_2]) to MMA, activated by complexation to **2** (Scheme 1).[3]

We based this mechanism on the observed polymerization kinetics using preformed neutral enolates **1** in combination with **2** (independently first order in both and zero order in [MMA])[2c,3] and on the observation that **2** or even a discrete cationic zirconium enolate complex, [$Cp_2Zr\{OC(OMe)=CMe_2\}(thf)$][$BPh_4$][3] were much less competent initiators.

It occurred to us that a covalently linked, dinuclear enolate initiator might function analogously to the two-component systems studied earlier and could represent a new strategy[4] for the controlled polymerization of methacrylates and other susceptible monomers.

We concentrated on the use of dinuclear zirconocene complexes featuring the μ-oxo linkage as this unit is robust.[5,6] The dinuclear ion-pair [$(Cp_2Zr)_2(\mu\text{-}Me)(\mu\text{-}O)$][$MeB(C_6F_5)_3$][7]

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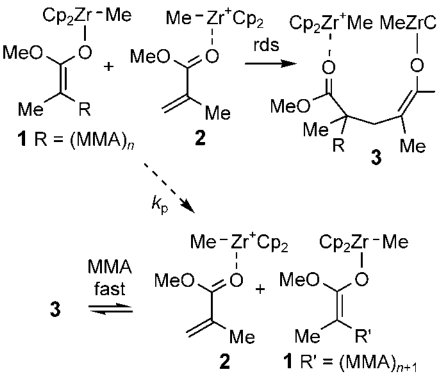


Scheme 1. Mechanism of MMA Polymerization using **1** and **2**; rds = rate determining step.

formed in situ from $[\{Cp_2Zr(Me)\}_2O]$[6] and $B(C_6F_5)_3$ was inactive in MMA polymerization, and as enolate complexes often prove to be effective initiators when the corresponding alkyls do not (e.g. ref. [1a] vs. ref. [4]), attention was thus focused on the synthesis of dinuclear bis(enolate) complexes **6**.

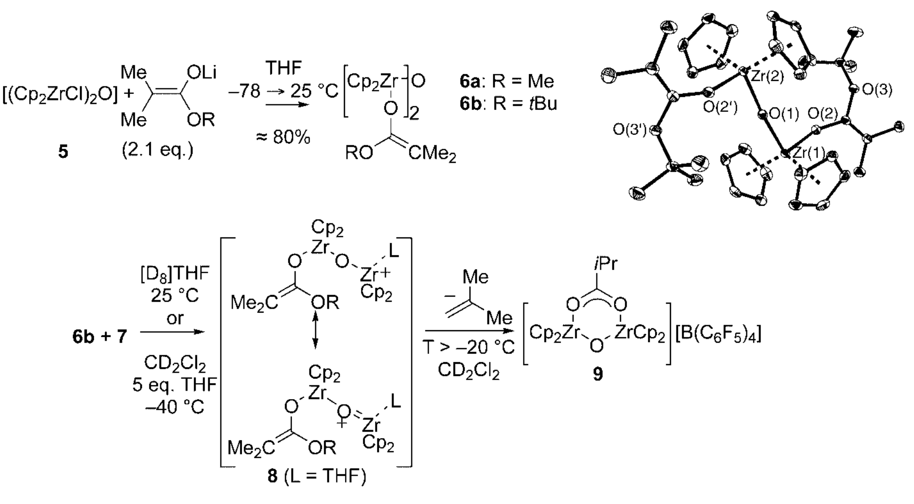
These complexes can be prepared from μ-oxo dichloride complex **5**[5] and two equivalents of a lithium enolate, either preformed (R = *t*Bu) or generated in situ (R = Me, Scheme 2). Complexes **6** are obtained as air-sensitive solids in about 80% yield following crystallization and the molecular structure of **6b** appears in Scheme 2.[8,9] Despite the presence of two electron-rich enolate moieties, the Zr-O-Zr bridge is approximately linear at O with Zr(1)-O(1)-Zr(2) = 174.9(1)° and with short Zr–O bonds lengths of Zr(1)–O(1) 1.966(1) and Zr(2)–O(1) 1.972(1) Å. These features have been attributed to partial π character to the Zr–O bonds in this class of compounds.[5,6]

A cationic enolate complex (**8**)[8] can be generated from bis(enolate) complex **6b** using 1.1 equivalents of $[PhNHMe_2][B(C_6F_5)_4]$ (**7**) in THF solution at 25°C (Scheme 2) but is inactive for MMA polymerization in this solvent. Attempted isolation of this compound leads to the formation of *iso*-butene and cationic carboxylate complex **9**.[8] Complex **8** can also be generated from **6b** and **7** in the presence of approximately five equivalents of THF in CH_2Cl_2 solution and is stable at temperatures below −20°C in this solvent.

Table 1: Polymerization of MMA using zirconocene initiators (In).

Entry	In ([In] [mM])	[MMA] [M]	T [°C]	t [min]	Conv. [%]	rr [%]	$\bar{M}_n$ [K]	PDI	f [%][a]
1[b]	**6b** (3)	2.81	−40	30	20	83	29.8	1.03	64
2[b]	**6b** (6)	2.81	−40	30	41	83	24.4	1.05	78
3[b]	**6b** (3)	2.73	−20	25	75	80	79.2	1.03	88
4[b]	**6b** (6)	2.73	−20	10	74	80	49.8	1.04	62
5[b]	**6b** (9)	2.73	−20	10	86	80	35.0	1.05	59
6[c]	**6b** (10)	1.06	≥25	<5	99	66	22.1	1.27	39
7[c]	**6b** (10)	1.06	0	30	100	74	24.8	1.15	35
8[c]	**6b** (12)	1.33	−20	30	80	80	20.6	1.10	43
9[c]	**6b** (12)	1.33	−40	60	61	83	8.57	1.10	78
10[c]	**6b** (12)	1.33	−80	240	10	86	1.44	1.10	77
11	**10** (24)	1.33	−20	30	20	–	33.2[d]	≈1.1	2.4
12[e]	**10** (24)	1.33	−20	30	100	79	5.80	1.07	64[f]
13[e]	**10** (12)	1.33	−20	30	100	77	9.29[d]	≈1.1	71[f]

[a] Initiator efficiency $f = 100(M_n^\circ/M_n)$ where $M_n^\circ = ([MMA]_o/[In]_o)$ (Conv./100). [b] Complex **8** was generated from **6b** and **7** in CH_2Cl_2 solution containing THF (5 equiv) at −40°C and then added to a solution of MMA in CH_2Cl_2 at the temperature (T) indicated. Reactions were quenched with MeOH at the time (t) indicated. [c] A solution of **6b** or **10** in toluene was added to a solution of **7** (1.1 equiv) in toluene containing MMA at the T indicated. [d] Bimodal MWD—only data for the major component (>75%) is reported. [e] Two equivalents of **10** were added to 1.0 equivalent of **7**. [f] Initiator efficiency calculated on the basis of three chains per mole of **7**.



Scheme 2. Synthesis and structure of bis(enolate) **6b**[9] and its conversion to cationic enolate **8**.

Fortunately, complex **8** is an effective initiator of MMA polymerization under these conditions. As shown in Table 1, entries 1–5, partially syndiotactic PMMA (s-PMMA) is formed (by a chain-end control mechanism) with a very narrow molecular weight distribution (MWD) at moderate to high conversion below −20°C. Kinetic studies, using complex **8** generated at −40°C from **6b** and **7**, at various [**8**] and [MMA] at −20°C, have revealed that propagation is zero order in MMA and first order in [**8**] (Figure 1), consistent with the mechanism shown in Scheme 1, where rate-determining formation of an intermediate analogous to **3** is unimolecular owing to the strong μ-oxo linkage between the two zirconocene moieties. Under these conditions, MW linearly increases with [MMA]:[**8**] ratios (with $f >$ 50% at −40°C) and with conversion with PDI = 1.05, characteristics of a living polymerization.[8] MALDI-TOF mass spectra were in agreement with chains being initi-

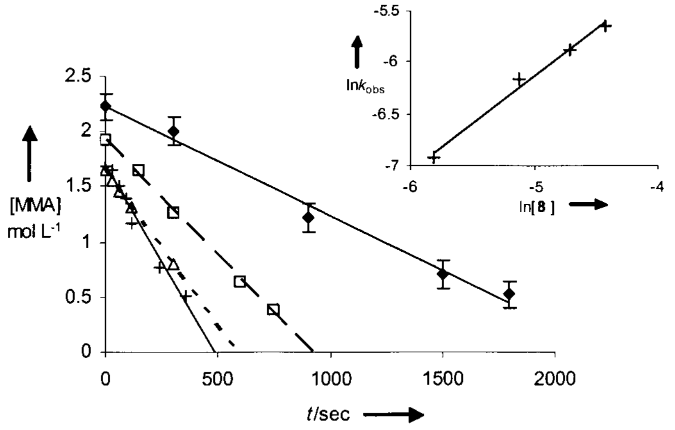


Figure 1. Plot of [MMA] versus time for polymerization initiated by $[\mathbf{8}]_o = 3.0$ (◆), 6.0 (□), 9.0 (△), and 12.0 mM (+) at −20 °C in CH_2Cl_2. Inset: Plot of $\ln(k_{obs})$ versus ln[**8**] where k_{obs} is the slope of the [MMA] versus time plots—the kinetic order with respect to [**8**] is given by the slope = 0.91 ± 0.10.

ated by **8** and chain growth being quenched by MeOH during work-up.[8]

Complex **8** can also be conveniently generated in situ from **6b** and **7** in toluene solution in the presence of monomer (Table 1, entries 6–10). As might be expected from the foregoing, initiator efficiencies increase and polymer MWD narrows at lower temperature as the thermal stability of species **8** improves.

We wished to compare the performance of this dinuclear initiator to a mononuclear, cationic zirconocene enolate, partnered with the $B(C_6F_5)_4$ counteranion, either alone or in combination with a neutral zirconocene enolate initiator. In situ formation of a cationic zirconium enolate from $[Cp_2Zr\{OC(OtBu){=}CMe_2\}_2]$ (**10**)[2,3] and **7** (1.1 equiv) in toluene was much less effective for polymerization at −20 °C (entry 11 vs. 8) while use of 2:1 ratio of **10**:**7** gave quantitative conversion to polymer (entries 12, 13).

The PMMA formed with **10**:**7** features a bimodal MWD with a major and minor component. As shown in Figure 2, a higher MW component predominates (low elution volume) when using a 1:1 ratio of **10**:**7** while only a lower MW component is evident at a 2:1 ratio and the same [Zr]. As the initiator is diluted, more of the higher MW component is produced at a 2:1 stoichiometry. This behavior suggests independent formation of polymer by both a unimolecular process involving a cationic enolate and a competing pathway involving a neutral enolate analogous to that shown in Scheme 1.

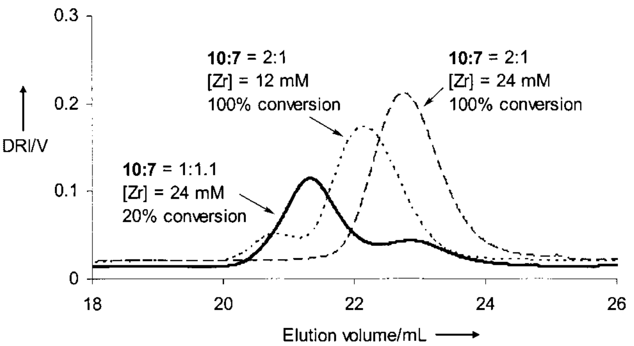


Figure 2. Differential refractive index (DRI) response [V] versus elution volume [mL] for PMMA samples prepared using mixtures of bis(enolate) **10** and activator **7**. For conditions see Table 1, entries 11–13.

However, at high [Zr] and a 2:1 stoichiometry, the calculated initiator efficiencies exceed 100 % unless it is assumed that all enolate moieties (i.e. 3.0 equivalents per-equivalent of **7**) are competent for chain growth (Table 1, entries 12, 13). An explanation for this behavior is that the species involved in propagation using a 2:1 ratio of **10** to **7** is in fact dinuclear (i.e. $[\{Cp_2ZrOC(OMe){=}CMe(MMA)_n\}_2\{\mu\text{-}OC(OMe){=}CMe(MMA)_n\}]$ but additional work is needed in support of this hypothesis.

It can be seen from comparing entry 8 with 13 in Table 1 that the reactivity of **6b**/**7** is marginally lower than **10**/**7**. We suspect the lower reactivity of **8** reflects interaction between the two metal centers through the μ-oxo bridge (Scheme 2). On the other hand, when partnered with a weakly coordinating counterion, initiation using complex **8** is uncomplicated by the formation of PMMA through a competing pathway which would result in a bimodal MWD as with **10** and **7** (see above).

It is clear that **8** is an effective initiator of MMA polymerization. Also, the bimetallic pathway (Scheme 1) is more competitive than a unimolecular process involving a cationic enolate at least in the parent $[Cp_2Zr]$ system.[2,3] Future work will concentrate on the application of initiators such as **8** to the polymerization of other susceptible monomers.

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[8] See Supporting Information for synthesis and characterization of complexes **6**, **8**, and **9**, additional polymerization experiments, and MALDI-TOF mass spectral data.

[9] Molecular structure of **6b** with thermal ellipsoids set at 30% probability depicted in Scheme 2. CCDC-239734 (**6b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).