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# Group-Transfer Polymerization Using Metallocene Catalysts: Propagation Mechanisms and Control of Polymer Stereochemistry[1a]

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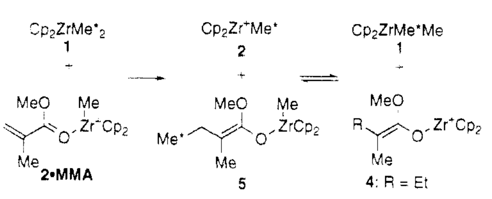
We recently reported that methyl methacrylate (MMA) can be efficiently polymerized using a two-component catalyst system comprised of $Cp_2ZrMe_2$ (1) and $[Cp_2ZrMe(THF)][BPh_4]$ (2).[2] Related studies using organolanthanide catalysts have also been reported.[3]

Our previous work suggested that the mechanism for propagation using the two-component system was similar to that proposed using the isoelectronic lanthanide initiators. Briefly, propagation was envisaged to occur via the intramolecular Michael addition reaction of a cationic enolate complex, generated in situ from 1 and 2, with coordinated monomer.

We report herein that cationic enolate complexes are actually rather ineffective initiators for the polymerization of MMA and the mechanism for propagation involving the two-component catalyst system discovered earlier involves a bimetallic propagation step. Also, the stereochemistry of polymerization can be dramatically affected by choice of catalyst precursor; the use of *rac*-$[C_2H_4(\eta^5\text{-tetrahydroindenyl})]ZrMe_2$ (*rac*-3) and $[nBu_3NH][BPh_4]$ as catalysts led to the production of isotactic poly(methyl methacrylate) (PMMA).[4]

**Results and Discussion.** The polymerization of MMA using a discrete cationic enolate complex of zirconium $[Cp_2ZrOC(OMe)C{=}CMe_2(THF)][BPh_4]$ (4)[5] was investigated, and the results are summarized in Table 1. In contrast to our earlier results (e.g., entries 1 and 2), lower polymer yields and lower MW polymers with a broader MWD were obtained under comparable conditions using catalyst 4 (entries 3 and 4).

We postulated that species analogous to 4 were formed in situ from 1 and 2 as shown in eq 1 on the basis of labeling experiments and some model studies using neutral enolate complexes and metallocene 2.[2] However, based on the above result, it is clear that intermediate 4 (R = Et) cannot be responsible for the rapid and high conversion polymerization of MMA using 1 and 2.



(1)

The key assumption that led us initially to believe that 4 was involved in propagation was that NMR studies indicated that the reaction of 2 with neutral enolate complexes led to the formation of 1 and *kinetically unstable* cationic enolate complexes. However, as complex 4 (R = Me) is reasonably stable in $CH_2Cl_2$, we reinvestigated the reaction depicted in eq 1 by the addition of 1 to a solution of 4 in this solvent. The addition of 1 to 4 resulted in the complete consumption of the latter compound with formation of 2 and $Cp_2ZrMe(OC(OMe){=}CMe_2)$ (see the supplementary material for details). Thus, the equilibrium depicted in eq 1 apparently favors the reactants, cationic methyl complex 2 and neutral enolate complex 5.

It thus seemed clear that the mechanism for propagation did not involve 4 but probably did involve both 2 and enolates analogous to 5. The kinetics of polymerization of MMA using complex 2 and $Cp_2ZrMe(OC(OR){=}CMe_2)$ (5; R = $^t$Bu)[6] were investigated, and the results are depicted in Figure 1. As can be seen from this figure, the rate of polymerization is first order in complex 2, first order in enolate 5, and *zero* order in monomer, up to high conversions. Furthermore, there is no induction period (as observed using 1 and 2)[2] consistent with rapid initiation. As expected, polymer with a narrower MW distribution is formed under similar conditions (compare entries 1 and 2 with, e.g., 5).

A mechanism that is consistent with these observations is depicted in Scheme 1. Propagation is comprised of two steps, the first of which is rate-limiting. It involves an intermolecular Michael addition of the neutral enolate 5 to complexed monomer leading to the formation of a bimetallic intermediate 6. Notice that the metal centers undergo a change in charge following formation of 6. Completion of propagation requires displacement of the cationic zirconium moiety from the polymer chain by, e.g., additional monomer. If this process is fast relative to the first step, one expects zero-order dependence on monomer concentration.[7]

When a chiral initiator system was employed (complex *rac*-3 and $[nBu_3NH][BPh_4]$), slow polymerization of MMA was observed (Table 1, entry 9). Interestingly, the polymer formed was isotactic with a high degree of stereoregularity (Figure 2a). Pentad analysis reveals that an enantiomorphic site control mechanism is operative in this polymerization (i.e., mmmr:mrmm:mrrm = 2:2:1).[8] Furthermore, an identical microstructure was observed when using optically pure [S]-(+)-3 as an initiator (entry 10, Table 1; Figure 2b).

These two findings taken together suggest that the mechanism for propagation using initiator *rac*-3 may be different than that determined for MMA polymerization using 2 and 5. Further studies designed to address these issues are in progress.

**Experimental Section.** MMA monomer was dried over $CaH_2$ and distilled from small quantities of triethylaluminum and stored at −20 °C over activated 4-Å sieves prior to use. Dichloromethane was distilled from $CaH_2$ under nitrogen prior to use. Compounds 1,[9] 2,[10] *rac*-3,[11] [S]-(+)-3,[12] $Cp_2ZrMeCl$,[9] $[nBu_3NH][BPh_4]$,[13] and the lithium enolate of *tert*-butylisobutyrate[14] were prepared by literature methods. The preparation and characterization of complexes 5 (R = $^t$Bu) and 4 (R = Me) is described in the supplementary material.

Polymerizations were conducted in a $CH_2Cl_2$ solution at 0 °C under the conditions reported in Table 1. A general procedure follows: To a solution of MMA (5.0 mL) in $CH_2Cl_2$ (8.0 mL) was added, in sequential fashion via syringe, a solution of compound 1 in $CH_2Cl_2$ (1.0 mL, 0.275 M) and 2 (1.0 mL, 0.100 M) with vigorous stirring. After the indicated time period, the viscous solution was poured into methanol (50 mL), rinsing with additional $CH_2Cl_2$. The solvent was decanted and the polymer rinsed with additional methanol and then dried in vacuo at 60 °C and 0.05 mmHg.

Polymer molecular weight averages were determined using a Waters SEC system equipped with four, 30-cm PL-gel 10-μm columns ($10^5$, $10^3$, 500, and 100 Å) and a guard column maintained at 30 °C. Tetrahydrofuran was

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**Table 1. MMA Polymerization Using Zirconocene Complexes[a]**

| entry | initiator (mM) | catalyst (mM) | MMA (M) | $T$ (°C) | $t$ (min) | % conv[b] | $M_n \times 10^{-3}$ [c] | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|
| 1 | **1** (18.3) | **2** (6.7) | 3.13 | 0 | 30 | 100.0 | 133.0 | 1.38 |
| 2 | **1** (27.6) | **2** (9.0) | 1.16 | 0 | 60 | 100.0 | 63.5 | 1.25 |
| 3 | | **4** (6.8) | 3.13 | 0 | 30 | 21.2 | 20.1 | 1.55 |
| 4 | | **4** (16.8) | 9.39[d] | 0 | 20 | 25.0 | 28.8 | 1.55 |
| 5 | **5** (4.5) | **2** (4.5) | 2.54 | 0 | 30 | 100.0 | 90.5 | 1.16 |
| 6 | **5** (4.5) | **2** (4.5) | 2.54 | 0 | 30 | 96.5 | 93.6 | 1.16 |
| 7 | **5** (4.5) | **2** (4.5) | 2.54 | 0 | 30 | 98.3 | 91.1 | 1.18 |
| 8 | **5** (4.5) | **2** (4.5) | 2.54 | 0 | 30 | 100.0 | 86.8 | 1.15 |
| 9 | **3** (6.1) | *e* | 3.13 | 0 | 30 | 23.4 | 117.0 | 1.53 |
| 10 | [S]-(+)-**3** (5.2) | *e* | 7.05 | 0 | 60 | 30.0 | 393.0 | 1.51 |

[a] All reactions were conducted in an $CH_2Cl_2$ solution unless otherwise noted. [b] Percent conversion = (wt PMMA/wt MMA) × 100. [c] Determined by GPC at 25 °C in a THF solvent at a flow rate of 1.0 mL/min; calibration was achieved using monodisperse PMMA standards. [d] Reaction conducted in neat monomer. [e] $[nBu_3NH][BPh_4]$ (2.6 mM) was employed.

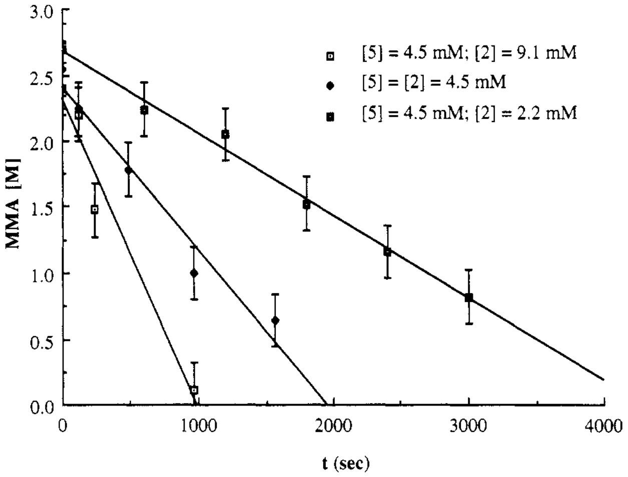
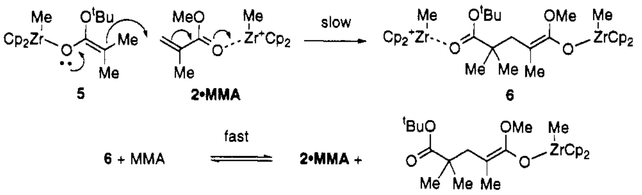


**Figure 1.** Kinetics of MMA polymerization ($CH_2Cl_2$, 0 °C) using complexes **2** and **5**. The estimated error in the concentration data is ±10%.

**Scheme 1**



used as the eluent, and sulfur was used as an internal standard. The columns were calibrated using seven, Polymer Laboratories Ltd., PMMA standards. The standards covered a MW range from 13 900 to 690 000. The polymer concentrations were determined using a DRI detector which was interfaced to a computer for data acquisition at a rate of 1.82 pts/s. All samples were eluted with a flow rate of 1.0 mL/min.

$^{13}C$ NMR spectra of polymers were obtained in a $CDCl_3$ solution at 25 °C at 50.0 MHz. A pulse width of 30°, a relaxation delay of 3.0 s, and broad-band decoupling were employed. A sweep width of 180 ppm was used, and typically 10 000 transients were accumulated.

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**Supplementary Material Available:** Experimental details for the preparation of complexes **5** (R = $^t$Bu) and **4** (R = Me) along with spectroscopic and characterization data, kinetic data, $^1$H-NMR spectra for the reaction of **1** with **4** and a $^{13}C$ NMR spectrum and pentad analysis of isotactic PMMA (8 pages). Ordering information is given on any current masthead page.

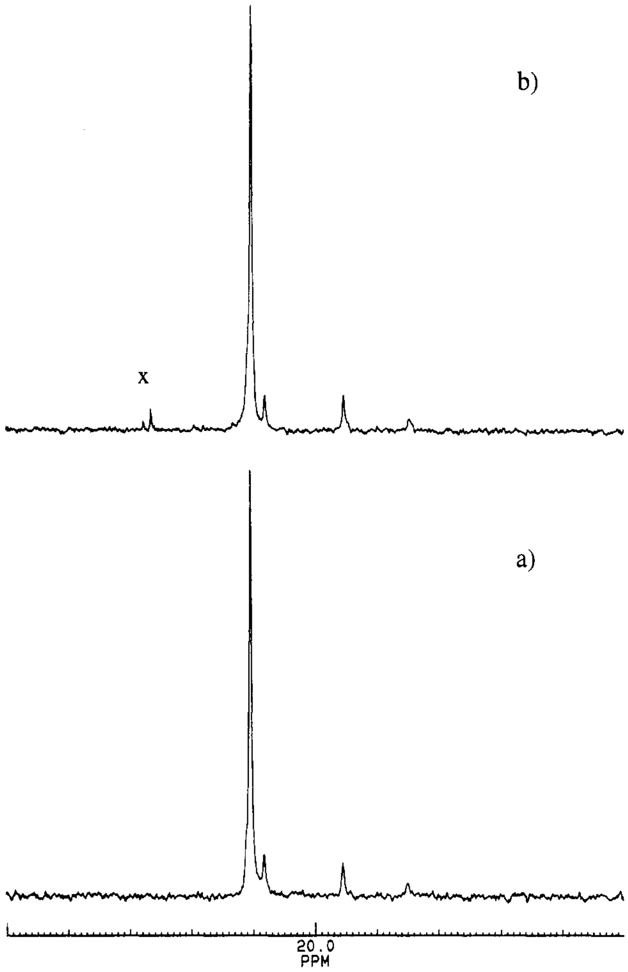

**Figure 2.** $^{13}C$ NMR spectra (10–30 ppm) isotactic PMMA in $CDCl_3$ (25 °C). (a) Prepared using catalyst (±)-**3**. (b) Prepared using catalyst [S]-(+)-**3** (X denotes an impurity). The spectra are scaled so that the main pentad resonance (mmmm) is the same intensity.

## References and Notes

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(4) Isotactic PMMA has been previously prepared at low temperatures using Grignard initiators. See: Hatada, K.; Kityama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189 and references therein.

(5) Compound **4** (R = Me): $^1$H NMR (200 MHz, $CD_2Cl_2$) $\delta$ 7.37 (br m, 8H), 7.06 (br t, $J$ = 7.8 Hz, 8H), 6.91 (br t, $J$ = 7.8 Hz,

4H), 6.42 (s, 10H), 3.68 (br m, 4H), 3.54 (s, 3H), 1.92 (br m, 4H), 1.64 (s, 3H), 1.57 (s, 3H); $^{13}$C NMR (50 MHz, $CD_2Cl_2$) $\delta$ 164.4 (q, $J_{C-B} = 49.2$ Hz), 138.9 ($\mathrm{O\mathbf{C}(OMe){=}CMe_2}$), 136.3 (*o*-C), 128.1 (*m*-C), 122.2 (*p*-C), 116.8 (Cp), 91.0 ($\mathrm{OC(OMe){=}\mathbf{C}Me_2}$), 78.0 (THF), 59.0 ($\mathrm{OC(O\mathbf{Me}){=}CMe_2}$), 28.0 (THF), 17.6 and 16.3 ($\mathrm{OC(OMe){=}C\mathbf{Me}_2}$). Elem. anal. Calcd for $C_{43}H_{47}BO_3Zr$: C, 72.35; H, 6.64. Found: C, 72.57; H, 6.66.

(6) Compound **5** (R = $^t$Bu): $^1$H NMR (200 MHz, $C_6D_6$) $\delta$ 5.82 (s, 10H), 1.81 (s, 3H), 1.61 (s, 3H), 1.26 (s, 9H), 0.38 (s, 3H); $^{13}$C NMR (50 MHz, $CDCl_2$) $\delta$ 160.2 ($\mathrm{O\mathbf{C}(O^tBu){=}CMe_2}$), 111.4 (Cp), 87.0 ($\mathrm{OC(O^tBu){=}\mathbf{C}Me_2}$), 77.4 ($\mathrm{OC(OCMe_3){=}CMe_2}$), 29.53 ($^t$Bu), 24.77 (Zr**Me**), 18.8 and 18.2 ($\mathrm{OC(O^tBu){=}C\mathbf{Me}_2}$); IR (Nujol) 1672, 1270, 108, 1017, 843, 860, 809, 741 cm$^{-1}$; MS (EI) *m/e* 378 ($M^+$). Elem. anal. Calcd for $C_{19}H_{28}O_2Zr$: C, 60.11; H, 7.43. Found: C, 59.86; H, 7.28.

(7) In principle, this should hold until high conversion, at which point first-order behavior should be observed. We are currently trying to address this using an in situ kinetic method.

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