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On the Polymerization of Methyl Methacrylate by Group 4 Metallocenes

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ABSTRACT: Dimethylzirconocene precatalysts are shown to initiate the polymerization of methyl methacrylate (MMA) when activated by a Lewis acidic methyl abstractor in the absence of any $ZnEt_2$ additive. The order of addition of the various components is crucial to forming a well-defined active species. Conversion of the precatalysts Cp_2ZrMe_2 (**1a**), *rac*-$\{C_2H_4(\eta^5\text{-}C_9H_6)_2\}ZrMe_2$ (**2a**), $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)\}ZrMe_2$ (**3a**), $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}ZrMe_2$ (**4a**), $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}2\text{-}MeC_9H_5)\}ZrMe_2$ (**5a**), and (Cp)(Cp*)$ZrMe_2$ (**6a**) to their cationic methylzirconocene derivatives (**2b**−**6b**) followed by addition of methyl methacrylate results in controlled polymerization to poly(methyl methacrylate) with the exception of **3b** which is inactive.

Introduction

The group 4 metallocenes have found commercially significant applications as well-defined, single-site catalysts for the polymerization of hydrocarbon olefins.[1−7] Despite the oxophilicity of tetravalent group 4 metal centers, zirconocenes have also been used to polymerize polar monomers such as alkyl acrylates in a reasonably controlled fashion. One of the first reports was by Collins and co-workers,[8] who showed that a combination of neutral Cp_2ZrMe_2 and the cationic zirconocene $Cp_2ZrMe(THF)^+BPh_4^-$ affords syndiotactic-rich poly(methyl methacrylate) (poly(MMA), 80% r dyads) by a propagation step that is chain-end-controlled. The poly(MMA) product is of high molecular weight but with a comparatively narrow molecular weight distribution ($M_w/M_n \approx 1.2{-}1.4$). Further work by the same group[9,10] has indicated that the polymerization proceeds via a neutral zirconocene enolate species.

Subsequently, Soga and co-workers[11−14] demonstrated the use of dimethylzirconocenes in conjunction with $B(C_6F_5)_3$ or $Ph_3C^+B(C_6F_5)_4^-$ activators. They found that the MMA is first required to be preaged with $ZnEt_2$ for polymerization to occur. In comparison to the Collins system, these polymerizations are rather slow, typically taking ca. 24 h, as opposed to 1 h for an analogous polymerization using the Collins protocol.

In related work on the lanthanides, Yasuda and coworkers[15,16] reported that highly syndiotactic (up to 95% rr triads), high molecular weight (M_n > 100 000) poly(MMA) with a very narrow molecular weight distribution (M_w/M_n < 1.05) can be obtained using initiators such as $[Cp^*_2SmH]_2$ and $Cp^*_2LnMe(THF)$ [Ln = Sm, Yb, or Lu]. The postulated oxygen-bound enolate intermediate was confirmed by the isolation of the species arising from the insertion of two monomer units into $[Cp^*_2SmH]$ and its characterization by X-ray crystallography. It has proved possible to influence the tacticity of the resultant poly(MMA) through modifications to the metallocene ligand environment. Marks and co-workers[17] have investigated chiral *ansa*-bridged lanthanocenes of the form $\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R^*)\}LnR$ [R* = (+)-neomenthyl: R = $CH(SiMe_3)_2$, Ln = Y; R = H, Ln = Y; R = $N(SiMe_3)_2$, Ln = La. R* = (−)-menthyl: R = $CH(SiMe_3)_2$, Ln = Sm; R = $N(SiMe_3)_2$, Ln = Lu]. Complexes where R* = (+)-neomenthyl form highly isotactic (ca. 95% m dyads) poly(MMA), whereas syndiotactic biased polymerization (rr triads ≈ 70%) is obtained for R* = (−)-menthyl.

The isoelectronic and isolobal relationship that exists between the neutral trivalent alkylmetallocenes of the lanthanides and cationic tetravalent alkylzirconocenes suggested that a well-defined cationic zirconocene ought to be capable of polymerizing alkyl acrylates in a controlled fashion similar to their lanthanide relatives, yet the reports of Collins and Soga seemed to indicate a number of complications. Inspection of the experimental conditions employed in these earlier studies reveals that the zirconocene catalyst system may not have been evaluated under ideal circumstances, for example the presence of THF and the use of the relatively coordinating tetraphenylborate counteranion in the Collins protocol and preageing of monomer with a large excess of $ZnEt_2$ in the Soga methodology.

With a view to gaining additional insight into the polymerization of alkyl acrylates by zirconocenes, we therefore decided to undertake a further investigation into zirconocene-initiated MMA polymerization in which the cationic methylzirconocenes bearing fluoroarylborate counteranions are preformed in solution before addition of monomer (Scheme 1). A series of zirconocene precatalysts **1a**−**6a**, embracing both C_2 and C_s ligand symmetries, were chosen to allow the influence of the ligand environment on tacticity to be probed and to allow comparisons with the results of other workers.

Results and Discussion

Initiator Formation. Since Collins and co-workers had previously shown that a combination of neutral Cp_2ZrMe_2 (**1a**) and the cationic zirconocene $Cp_2ZrMe(THF)^+BPh_4^-$ is capable of polymerizing MMA, for the purposes of this study it is essential that all of the dimethylzirconocene precatalyst is first converted to the cationic methylzirconocene. Figure 1 shows that clean conversion of **1a** (Figure 1a) to $[Cp_2ZrMe][MeB(C_6F_5)_3]$ (**1b**, Figure 1b) occurs upon treatment with 1 equiv of $B(C_6F_5)_3$. The changes observed in the ^{19}F NMR spectra (Figure 1c,d) are also consistent with the transformation of the neutral three-coordinate borane into the four-coordinate $[MeB(C_6F_5)_3]^-$ counteranion. A slight (ca. 1−2%) excess of borane is typically added to the di-

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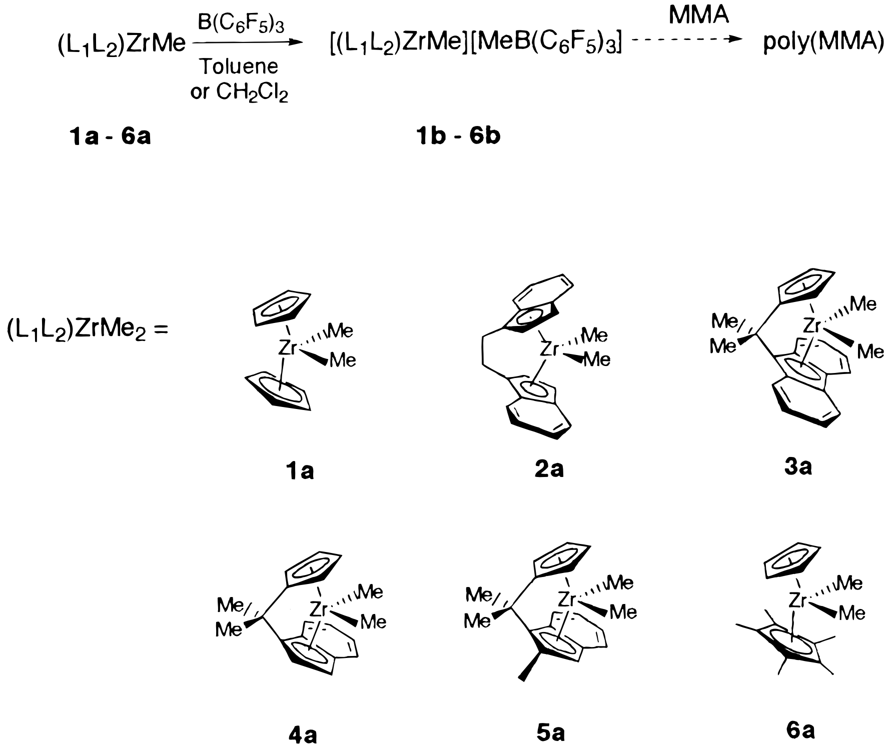
Scheme 1. Formation of Catalysts 1b to 6b from Precatalysts 1a to 6a



methylzirconocene to ensure complete conversion. Similar experiments were carried out on the other zirconocene precatalysts in order to ensure that complete conversion to the cationic alkyl had occurred prior to addition of monomer.

In the procedure reported by Soga and co-workers, the zirconocene is added to the monomer in toluene *followed* by addition of the $B(C_6F_5)_3$ activator.[11] Under these conditions, it seemed likely that the borane would form a strong interaction with the Lewis basic carbonyl oxygen of the monomer and that this may prevent the borane activating the zirconium center. This would then explain why a large excess of another Lewis acid ($ZnEt_2$) is required to release the borane from the monomer so that it is then available to activate the dimethylzirconocene. To confirm that an adduct is formed between MMA and $B(C_6F_5)_3$, an NMR study was carried out in C_6D_6 on a 1:1 mixture of the monomer and the borane. Little shift from the frequencies found for free MMA was observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra, but the $^{11}B\{^1H\}$ and ^{19}F spectra indicated unambiguously that adduct formation had occurred. In particular, the ^{19}F NMR spectrum revealed three new resonances at δ -167.26, -158.91, and -138.58 ppm consistent with the presence of $L{\cdot}B(C_6F_5)_3$, and the $^{11}B\{^1H\}$ NMR spectrum showed a relatively sharp resonance at δ 6.7 ppm, also characteristic of four-coordinate boron. Addition of **1a** to this sample resulted in only a small fraction (ca. 5%) of the metallocene being converted to **1b** (by ^{19}F NMR spectroscopy).

A similar experiment was carried out with $Ph_3C^+B(C_6F_5)_4^-$ and MMA since it seemed less likely that the monomer should interact unfavorably with $Ph_3C^+B(C_6F_5)_4^-$. ^1H and ^{19}F NMR spectra obtained on a 1:1 mixture of MMA and trityl borate in CD_2Cl_2 revealed no significant shifts in the resonances observed in separate spectra of the monomer and borate. This implies no interaction between the two species, and indeed, addition of **1a** to the sample results in formation of **1b** (by ^1H NMR spectroscopy) and initiation of polymerization, as evidenced by disappearance of the signals due to monomer in the ^1H NMR spectrum. Repetition of this experiment on a bulk scale resulted in controlled PMMA formation. This finding contrasts with the observations of Soga,[11] who observed no polymerization under similar circumstances. Last, it is observed by ^{19}F NMR spectroscopy that addition of $B(C_6F_5)_3$ to an equimolar mixture of **1a** and MMA results in quantitative formation of **1b**.

Polymerization Studies. In the modified protocol adopted in this study, the cationic methylzirconocene **1b** is *preformed* in methylene chloride or toluene solution by addition of 1 equiv of $B(C_6F_5)_3$ to the dimethylzirconocene, and monomer is then added as a solution in the same solvent. This results in an immediate color change from yellow to colorless and rapid evolution of heat. The reaction is terminated after 1 h, though in reality for some of the zirconocene initiators studied, **1b** and **2b** especially, the monomer is consumed within 1−2 min, affording a virtually quantitative yield of poly(MMA).[18] Contrastingly, addition of **1a** to a solution of $B(C_6F_5)_3$ *after* addition of the monomer resulted only in a low yield of poly(MMA) (after 1 h), consistent with Soga's observations.

The results of polymerizations with various alkyl abstracting reagents are collected in Table 1. The polymerizations proceed in methylene chloride or toluene to a virtually quantitative yield of poly(MMA) with reasonably narrow molecular weight distributions (entries 1 and 2). Contrastingly, in THF solvent (entry 3) the yield is dramatically reduced, and the resultant poly(MMA) is very high molecular weight and with a broad molecular weight distribution. The anilinium borate activator $[C_6H_5NMe_2H][B(C_6F_5)_4]$ also gives a controlled polymerization (entry 4), unlike $[Et_3NH][BPh_4]$ (entry 5) which afforded only trace amounts of

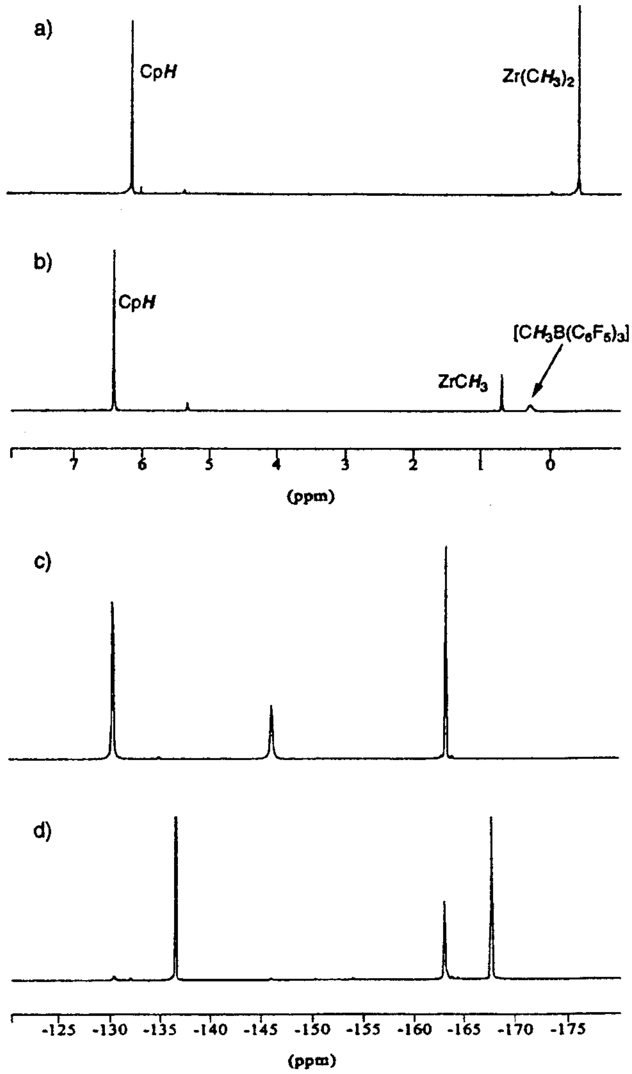


Figure 1. ^{1}H NMR spectra of (a) **1a** and (b) **1b**; ^{19}F NMR spectra of (c) $B(C_6F_5)_3$ and (d) **1b**.

poly(MMA). The latter observation may possibly be due to the presence of the noninnocent tetraphenylborate counteranion or the Et_3N byproduct binding to the active site.

Polymerization results for the other metallocene precatalysts (**2a**−**6a**) are collected in Table 2. The C_2-symmetric precatalyst *rac*-$\{C_2H_4(\eta^5\text{-}C_9H_6)_2\}ZrMe_2$ (**2a**) was found to produce highly isotactic poly(MMA) rapidly (minutes) and in virtually quantitative yield. The resultant tacticity accords with Soga's results,[11] though the polymerization rate is substantially faster and molecular weight control significantly improved in the present case. The C_s-symmetric precatalyst $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)\}ZrMe_2$ (**3a**)[19] is found not to polymerize MMA using the modified activation methodology; this observation is consistent with Soga's findings. Formation of $[\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)\}ZrMe][MeB(C_6F_5)_3]$ (**3b**) was confirmed by ^{1}H NMR spectroscopy, and although a color change from dark red to pink was observed upon monomer addition to this catalyst, no polymerization occurred in either methylene chloride or toluene even after 20 h. It is postulated that this color change represents the first product of conjugate monomer addition, subsequent attack being blocked by the bulky fluorenyl ligand. Attempts to characterize this product have proved unsuccessful to date.

The inability of the fluorenylzirconocene precatalyst **3a** to polymerize MMA led us to investigate the less hindered indenyl derivative $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}ZrMe_2$ (**4a**).[20] In this case, polymerization occurs smoothly over a period of 1 h to give isotactic-rich poly(MMA) in 74−77% yield. Introducing a methyl substituent at the 2-position on the indenyl ring, precatalyst **5a**,[21] gave a catalyst of similar activity, but the resultant poly(MMA) has a much lower isotactic content and a significant proportion of syndiotactic dyads. The presence of the methyl substituent does not appear to prevent the binding and insertion of MMA. A significant contrast to the findings of Soga and co-workers is found for precatalyst (Cp)(Cp*)$ZrMe_2$ (**6a**).[22] This is not active using the Soga protocol[14] but here is found to give a slow, controlled formation of syndiotactic-rich poly(MMA). The polymerization is 30−40% complete after 1 h and takes ca. 6 h for all of the monomer to be consumed. The tacticity of the resultant polymer differs appreciably depending on whether the reaction solvent is toluene or dichloromethane. As yet we have no satisfactory explanation for this phenomenon although the differing coordinative abilities of these two solvents may be relevant.

In all cases, the experimentally determined M_n values are approximately double what might be expected on the basis of monomer-to-initiator ratios, a difference which seemed too large to be explained simply by the errors involved in calibrating poly(MMA) samples against polystyrene standards. Indeed, a sample calibrated separately against poly(MMA) and polystyrene standards gave similar M_n values (to within 10%), confirming a real doubling of molecular weight. This may be interpreted as providing evidence for a bimolecular mechanism in which the polymerization occurs at a cationic zirconocene enolate site with monomer being carried to this center via a zirconocene cation; cf. Collins' mechanism which involves polymerization at a neutral zirconocene enolate with monomer being carried to the site by a zirconocene cation.[9]

A number of experiments have been conducted to determine the degree of control attainable using these metallocene precatalysts under the modified conditions. The linear relationship between M_n(observed) and $[M]_0/[I]_0$ for **1b** (Figure 2) and the narrow molecular weight distribution across the molecular weight range indicates a well-controlled polymerization. However, the exceedingly rapid consumption of monomer using **1b** or **2b** precluded a plot of M_n versus conversion.

Therefore, as further probes of the polymerization behavior of **1b**, reinitiation experiments and a block copolymerization with *n*-butyl methacrylate (BMA) were investigated. First, the polymerization of MMA was followed in an NMR scale reaction, with progress being monitored by comparing the integrals of the −OMe peaks for monomer and polymer in the ^{1}H NMR spectrum. Once all the monomer had been consumed, a further charge of MMA was added, and this was observed to polymerize at a rate comparable to the polymerization of the first charge. This implies that a species capable of initiating polymerization is generated after all monomer has been consumed, and the observed propagation rate is suggestive of a propagating species of similar activity. A preparative scale reinitiation reaction was carried out by adding 200 equiv of MMA to **1b** in CH_2Cl_2 solution and stirring for 1 h followed by removal of a sample for GPC analysis. A further

Table 1. Polymerization Results for MMA Using Cp_2ZrMe_2 (1A) Pre-catalyst[a]

entry	alkyl abstractor	solvent	% yield[b]	M_n[c]	M_w/M_n[c]	% rr[d]	% mm[d]	% mr[d]
1	$B(C_6F_5)_3$	CH_2Cl_2	96	39 900	1.62	63	4	33
2	$B(C_6F_5)_3$	toluene	92	45 200	1.24	67	4	29
3	$B(C_6F_5)_3$	THF	13	$>10^6$	3.16	70	3	27
4	$C_6H_5NMe_2H^+ B(C_6F_5)_4^-$	CH_2Cl_2	98	51 000	1.34	62	4	34
5	$Et_3NH^+ BPh_4^-$	CH_2Cl_2	trace	n/a	n/a	n/a	n/a	n/a

[a] Polymerization conditions: Zr:alkyl abstractor:MMA = 0.05 mmol:0.05 mmol:10 mmol; [MMA] = 3.26 M; 1 h polymerization time. [b] Yield defined as mass of dry polymer recovered after precipitation/mass of monomer used. [c] Measured by gel permeation chromatography (GPC) in $CHCl_3$ calibrated with polystyrene standards. [d] Determined by ^1H NMR spectroscopy.

Table 2. Polymerization Results with Precatalysts 2a to 6a[a]

entry	precatalyst	solvent	% yield[b]	M_n[c]	M_w/M_n[c]	% rr[d]	% mm[d]	% mr[d]
1	**2a**	CH_2Cl_2	98	48 700	1.20	1	95	4
2	**3a**	CH_2Cl_2 or toluene	0	n/a	n/a	n/a	n/a	n/a
3	**4a**	toluene	77	33 400	1.49	8	81	11
4	**4a**	CH_2Cl_2	74	33 200	1.32	8	81	11
5	**5a**	toluene	85	25 000	1.51	23	54	23
6	**6a**	CH_2Cl_2	33	21 300	1.06	67	5	28
7	**6a**	toluene	42	30 800	1.15	44	15	41

[a] Polymerization conditions: Zr:alkyl abstractor:MMA = 0.05 mmol:0.05 mmol:10 mmol; [MMA] = 3.26 M; 1 h polymerization time. [b] Yield defined as mass of dry polymer recovered after precipitation/mass of monomer used. [c] Measured by gel permeation chromatography (GPC) in $CHCl_3$ calibrated with polystyrene standards. [d] Determined by ^1H NMR spectroscopy.

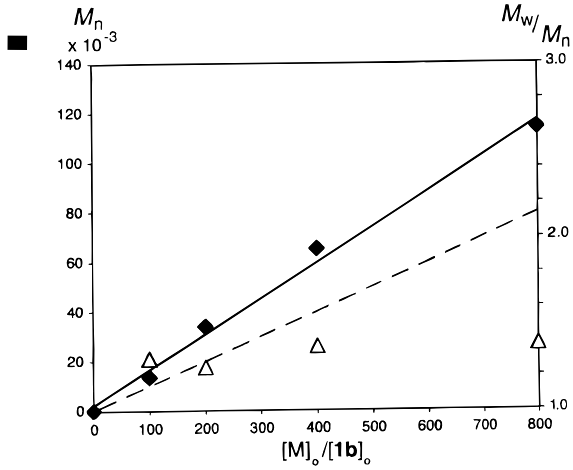


Figure 2. Plot of M_n (◆) and M_w/M_n (Δ) vs $[M]_0/[\mathbf{1b}]_0$ for polymerization using precatalyst **1a**. [MMA] = 3.26 M, 1 h polymerization time. M_n and M_w/M_n values obtained from GPC data in $CHCl_3$ calibrated with polystyrene standards (- - -, calcd M_n).

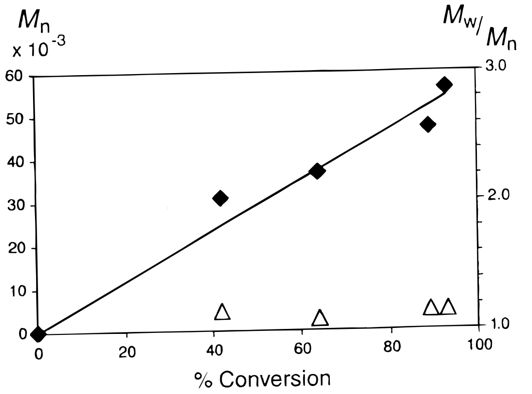


Figure 3. Plot of M_n (◆) and M_w/M_n (Δ) vs percentage conversion for polymerization using precatalyst **6a**. [MMA] = 3.26 M, between 1 and 6 h polymerization time. M_n and M_w/M_n values obtained from GPC data in $CHCl_3$ calibrated with standard polystyrene samples.

aliquot of monomer (200 equiv) was added, and after stirring for 2 h, the final product was isolated and analyzed. The molecular weights of the first and second fractions were identical to within experimental error, 44 400 and 42 900, indicating that although reinitiation occurs (as demonstrated in the NMR experiment), the polymerization is not living. Further confirmation of the nonliving behavior was provided by attempts to prepare a block copolymer of poly(MMA) and poly(*n*-butyl methacrylate) (PBMA). Treatment of **1b** with 200 equiv of MMA followed, after complete consumption of monomer, by 200 equiv of BMA gave a mixture of the two homopolymers (by ^1H NMR spectroscopy and GPC). These results imply that, upon consumption of monomer, chain termination occurs; however, the zirconocene species so formed is still capable of initiating and propagating polymerization at a comparable rate to **1b**.

The slower rate of propagation for **6b** allowed a plot of M_n vs conversion to be obtained (Figure 3). This reveals that the molecular weight increases smoothly with conversion as would be expected for a well-controlled polymerization system. Additionally, the molecular weight distribution of the resultant poly(MMA) remains low and relatively constant throughout the measured range. These features are believed to hold true for the other precatalysts used; however, **6b** is the only one for which such an experiment is feasible since the others polymerize MMA too rapidly. A plot of M_n(obs) vs consumed monomer/initiator ratio was also obtained for **6b** (Figure 4) and displays similar characteristics to that for **1b** (vide supra).

Reinitiation experiments similar to those described for **1b** were also performed on **6b**. Once again, the initiator is stable in the absence of monomer; however, reinitiation of growth on the same polymer chain was not observed, indicating that the system is not “living”. Attempts to prepare a block copolymer of poly(MMA) and poly(*n*-butyl methacrylate) (poly(BMA)) were similarly unsuccessful, again affording a mixture of homopolymers.

Finally, in a separate experiment we found that preageing of monomer with Et_2Zn inhibits the polymerization of MMA by **6b**, presumably either as a result of deactivation of the olefin or due to the effective increase in size of the MMA monomer when bound to Et_2Zn.

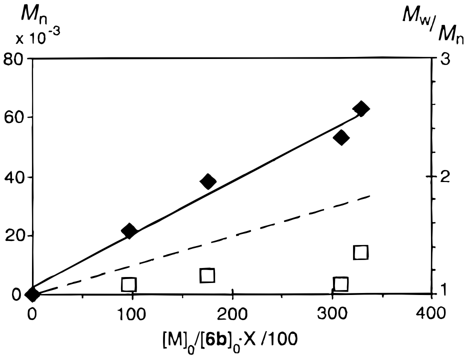


Figure 4. Plot of M_n (obs) (◆) and M_w/M_n (Δ) vs $[M]_0/[\mathbf{6b}]_0X/100$ (where X = % conversion) for polymerization using precatalyst **6a**. [MMA] = 3.26 M, between 6 and 20 h polymerization time. M_n and M_w/M_n values obtained from GPC data in $CHCl_3$ calibrated with polystyrene standards (- - -, calcd M_n).

Table 3. Triad Test Results for PMMA Produced by Precatalysts 2a, 4a, and 5a

precatalyst	% mm[a]	% mr[a]	% rr[a]	$4[rr][mm]/[mr]^2$	$2[rr]/[mr]$
2a[b]	94.7	3.7	1.6	44.2	0.86
4a[c]	85.3	10.9	3.8	10.9	0.70
5a[d]	55.0	33.0	12.0	2.4	0.73

[a] Triad percentages obtained from pentad analysis of CO region of $^{13}C\{^1H\}$ NMR spectra. [b] Sample obtained under the conditions described in Table 2 (entry 1). [c] Sample obtained under the conditions described in Table 2 (entry 4). [d] Sample obtained under the conditions described in Table 2 (entry 5).

Triad tests may be used to differentiate between enantiomorphic site control and chain-end control.[23] In the latter case, $4[rr][mm]/[mr]^2$ should equal one, and in the former, $2[rr]/[mr]$ is theoretically unity. Data for precatalysts **2a**, **4a**, and **5a** are given in Table 3. It may be seen that all three precatalysts yield polymers that can best be described as having been formed under conditions of enantiomorphic site control, although the case of **5a** is less clear.

Experimental Section

General Procedures. All air- and/or moisture-sensitive materials were prepared and manipulated under an atmosphere of oxygen-free, dry dinitrogen either in a glovebox or using standard Schlenk-line techniques. Solvents were predried over activated 4 Å molecular sieves (CH_2Cl_2) or sodium wire (diethyl ether and THF) before being distilled from CaH_2 (CH_2Cl_2) or sodium (diethyl ether and THF) under a slow continuous stream of dinitrogen. Toluene and petroleum ether (bp 40−60 °C) were dried by passage through a column containing alumina and Q5 catalyst. All solvents were deoxygenated before use either by bubbling dinitrogen through them for 15 min or by repeated evacuation followed by admission of dinitrogen. Deuterated solvents for NMR spectroscopy were dried before use over activated 4 Å molecular sieves and deoxygenated by three freeze−pump−thaw cycles.

NMR spectra were recorded on a Bruker AC250 spectrometer (^1H, ^{13}C, and ^{19}F spectra were recorded at 250.13, 62.90, and 235.34 MHz, respectively; distortionless enhancement by polarization transfer (DEPT) was performed using a standard 90° or 135° pulse sequence) or a Bruker DRX400 spectrometer (^1H, ^{11}B, and ^{13}C spectra were recorded at 400.13, 128.34, and 100.58 MHz, respectively; $^1H-^1H$ and $^{13}C-^1H$ correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) were performed using standard pulse sequences). The spectra were referenced internally using the residual protio-solvent (^1H) and solvent (^{13}C) resonances and measured relative to tetramethylsilane (δ 0 ppm) or referenced externally to $BF_3 \cdot Et_2O$ (^{11}B, δ 0 ppm) or $CFCl_3$ (^{19}F, δ 0 ppm). Chemical shifts are quoted in δ (ppm) and given as (multiplicity, integral, coupling constants in hertz, assignment).

Gel permeation chromatography (GPC) was performed using Viscotek Trisec software connected to a Knauer differential refractometer. Samples were injected onto two linear 10 μm columns using chloroform as elutant (conventionally calibrated prior to use, using polystyrene standards (PSS Mainz)) at a flow rate of 1.0 cm^3 min^{-1}.

Methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) were supplied by ICI Acrylics and dried over CaH_2, vacuum distilled, and deoxygenated by three freeze−pump−thaw cycles prior to use. $ZnEt_2$ (15% w/w solution in toluene) and MeMgBr (3.0 M solution in diethyl ether) were purchased from Aldrich. $B(C_6F_5)_3$,[24,25] Cp_2ZrMe_2, **1a**,[26,27] *rac*-$\{C_2H_4(\eta^5\text{-}C_9H_6)_2\}ZrMe_2$, **2a**,[28] $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)\}ZrMe_2$, **3a**,[19] $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_9H_6)\}ZrMe_2$, **4a**,[20] and (Cp)(Cp*)$ZrMe_2$, **6a**,[22] were prepared according to literature procedures. $\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}2\text{-}MeC_9H_5)\}ZrX_2$ [X = Me, **5a**, or Cl, **5c**] have been reported in the literature[21] but not fully characterized. Details of the preparation of **5a** and NMR characterizing data for **5a** and **5c** are therefore included here.

General Polymerization Procedure. Polymerizations were performed in a dinitrogen-filled glovebox using oven-dried sample vials. In a typical procedure, $B(C_6F_5)_3$ (26.0 mg, 0.051 mmol) in the specified reaction solvent (1 cm^3) was added to a solution of the appropriate dimethylzirconocene (0.05 mmol) in the same solvent (1 cm^3). A color change was observed from colorless or pale yellow to dark yellow (**1a** and **6a**), bright orange (**2a**), red (**3a**), or red-brown (**4a** and **5a**). MMA (1.00 g, 10.0 mmol) was added, causing the catalyst solution to become pale in color once again and heat to be evolved. The reaction was stirred for the specified period (usually 1 h) before being removed from the glovebox, terminated by the addition of a few drops of methanol, and then precipitated by being added dropwise to acidified methanol (300 cm^3 of a 1% v/v solution of HCl). The polymer was then isolated by filtration and washed with a little methanol before drying overnight at ca. 40 °C.

All polymer samples were analyzed by GPC in $CHCl_3$ and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in $CDCl_3$; relevant data are given in Tables 1, 2, and 3.

Polymerization Procedure with $ZnEt_2$ Additive. These polymerizations were performed identically to the above except that $ZnEt_2$ (9.0 cm^3 of a 15% v/v (1.1 M) solution in toluene, 9.9 mmol) was added to the MMA 1 h before it was added to the catalyst.

Reinitiation and Block Copolymerization Experiments. The above general procedure was used for a double-scale polymerization (i.e., 20.0 mmol of MMA, 0.1 mmol of **1a** or **6a**, and 0.102 mmol of $B(C_6F_5)_3$ in 4 cm^3 of CH_2Cl_2). After 1 h, exactly one-half of the reaction mixture (by weight) was removed, terminated, and precipitated as above and analyzed by GPC. To the remainder of the reaction was added 10.0 mmol of monomer, either MMA (reinitiation experiment) or BMA (block copolymerization experiment) in dichloromethane (2 cm^3). After 2 h, the remainder of the reaction was precipitated in the normal manner and subjected to analysis by GPC:

Reinitiation experiment using **1a**: first block M_n 44 400, M_w/M_n 1.34; final block M_n 42 900, M_w/M_n 1.39.

Block copolymerization using **1a**: first block M_n 45 800, M_w/M_n 1.63; final block M_n 50 000, M_w/M_n 1.60.

Reinitiation experiment using **6a**: first block M_n 61 200, M_w/M_n 1.12; final block M_n 60 900, M_w/M_n 1.14.

Block copolymerization using **6a**: first block M_n 67 400, M_w/M_n 1.24; final block M_n 64 400, M_w/M_n 1.49.

In all cases, recovered yields of polymer were ca. 80−90% based on the amount of monomer initially added to sample (i.e., 1 g for first block and 2 g for final block).

Observation of $MMA \cdot B(C_6F_5)_3$ via NMR Spectroscopy. To a solution of $B(C_6F_5)_3$ (25.6 mg, 0.05 mmol) in C_6D_6 (0.7 cm^3) was added MMA (10.0 mg, 0.10 mmol); the sample was then analyzed by NMR spectroscopy.

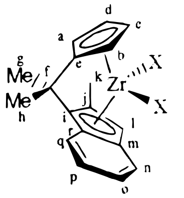
NMR data (C_6D_6): ^1H [400.13 MHz, 298 K] 1.72 (dd, 3H, $^4J_{HH}$ = 1,1, 1,5, vinylic Me), 3.33 (s, 3H, OMe), 5.12 and 6.00 (m, 1H each, olefinic H); $^{11}B\{^1H\}$ [128.34 MHz, 298 K] 6.7 (s);

^{13}C{^{1}H} [100.58 MHz, 298 K] 18.28 (s, vinylic Me), 51.93 (s, OMe), 117.0 (br s, C_6F_5, C_{ipso}), 125.83 and 136.24 (s, olefinic C), 137.60 (dt, $^1J_{CF} = 234$, $^2J_{CF} = 3.2$, C_6F_5, C_{meta}), 141.08 (dm, $^1J_{CF} = 253$, C_6F_5, C_{para}), 148.08, (dm, $^1J_{CF} = 240$, C_6F_5, C_{ortho}), 168.49 (s, CO); ^{19}F [235.34 MHz, 298 K] −167.26 (dd, 2F, $^3J_{FF}$ = 17.9, 20.7, C_6F_5, F_{meta}), −158.91 (t, 1F $^3J_{FF} = 20.7$, C_6F_5, F_{para}), −138.58 (d, 2F $^3J_{FF} = 17.9$, C_6F_5, F_{ortho}).

1a (8.0 mg, 0.03 mmol) was then added to the sample, and further ^{19}F NMR spectroscopic analysis showed that less than 5% of it had become converted to **1b**.

Preparation of {$Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}2\text{-}MeC_9H_5)$}$ZrMe_2$, 5a. To a cold (−78 °C) solution of {$Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}2\text{-}MeC_9H_5)$}$ZrCl_2$, **5c** (0.356 g, 0.898 mmol), in diethyl ether (35 cm^3) was added dropwise MeMgBr (0.66 cm^3 of a 3.0 M solution in diethyl ether, 1.98 mmol). The solution was allowed to stir for 1 h while it warmed to ambient temperature and then for a further 4 h, resulting in a pale-yellow solution with an off-white precipitate. Volatiles were removed in vacuo and the residues extracted into petroleum ether (bp 40−60 °C) (2 × 40 cm^3). The filtrate was reduced in volume to ca. 10 cm^3 and cooled to −30 °C overnight to yield the yellow product which was isolated by filtration and dried under vacuum for 4 h. Yield: 0.229 g (71%).

Characterization of {$Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}2\text{-}MeC_9H_5)$}$ZrX_2$ [X = Cl, 5c or Me, 5a] by 2-Dimensional NMR Spectroscopy. Samples of **5c** and **5a** were analyzed by DEPT, COSY, and NOE NMR techniques. Almost full assignments of both ^{1}H and ^{13}C{^{1}H} NMR spectra were possible for both compounds. A guide to the labeling system employed is given below:



NMR data for **5c** (CD_2Cl_2): ^{1}H [400.13 MHz, 298 K] 2.12 (s, 3H, Me_g), 2.25 (s, 3H, Me_h), 2.37 (s, 3H, Me_k), 5.83 (2 overlapping d, 2H, $^3J_{HH}$ = 2.8, 2.8, H_a and H_b), 6.48 (2 overlapping dd, 2H, $^3J_{HH}$ = 2.8, 3.5, 2.9, 3.4, H_c and H_d), 6.62 (s, 1H, H_l), 6.98 (dd, 1H, $^3J_{HH}$ = 6.7, 7.9, H_p), 7.30 (dd, 1H, $^3J_{HH}$ = 6.7, 8.5, H_o), 7.54 (d, 1H, $^3J_{HH} = 8.5$, H_n), 7.76 (d, 1H, $^3J_{HH} = 7.9$, H_q); ^{13}C{^{1}H} [100.58 MHz, 298 K] 20.93 (s, C_k), 27.85 (s, C_g), 28.62 (s, C_h), 41.48 (s, C_f), 98.04 (s, C_e), 103.12 and 106.81 (s, C_a and C_b), 116.67 (s, C_l), 119.83 and 120.17 (s, C_i and C_j), 121.71 and 121.76 (s, C_c and C_d), 124.32 (s, C_q), 125.57 (s, C_n), 125.96 (s, C_p), 126.19 (s, C_o), 129.84 and 130.25 (s, C_m and C_r).

NMR data for **5a** (C_6D_6): ^{1}H [400.13 MHz, 298 K] −1.01 and 0.07 (s, 3H each, Zr−CH_3), 1.47 (s, 3H, Me_g), 1.62 (s, 3H, Me_h), 1.87 (s, 3H, Me_k), 5.24 (2 overlapping d, 2H, $^3J_{HH}$ = 3.1, 5.4, H_a and H_b), 6.20 (dd, 1H, $^3J_{HH}$ = 3.1, 5.4, H_c or H_d), 6.27 (dd, 1H, $^3J_{HH}$ = 3.1, 5.4, H_c or H_d), 6.34 (s, 1H, H_l), 6.70 (ddd, 1H, $^3J_{HH}$ = 6.6, 8.4, $^4J_{HH} = 0.8$, H_p), 7.08 (ddd, 1H, $^3J_{HH}$ = 6.6, 9.0, $^4J_{HH} = 0.9$, H_o), 7.29 (dd, 1H, $^3J_{HH} = 9.0$, $^4J_{HH} = 0.8$, H_n), 7.38 (dd, 1H, $^3J_{HH} = 8.4$, $^4J_{HH} = 0.9$, H_q); ^{13}C{^{1}H} [100.58 MHz, 298 K] 19.60 (s, C_k), 27.47 (s, C_g), 28.04 (s, C_h), 29.79 and 34.31 (s, Zr-Me), 40.01 (s, C_f), 92.57 (s, C_e), 101.76 and 103.91 (s, C_a and C_b), 109.07 (C_l), 112.84 (s, C_m, C_r, C_i or C_j), 113.64 and 114.47 (s, C_c and C_d), 120.15 (s, C_m, C_r, C_i or C_j), 122.92 (s, C_p), 123.27 (C_n), 123.74 (s, C_o), 124.87 (s, C_q), 125.32 (s, C_m, C_r, C_i or C_j), remaining resonance hidden by C_6D_6 solvent peak.

Summary and Conclusions

In summary, we have demonstrated that MMA can be polymerized by a simple zirconocene system, a cationic alkyl analogue of Yasuda's rare earth initiator, and by a closely related methodology to that used for the polymerization of simple α-olefins. Previous work either has utilized a mixture of dimethylzirconocene and a solvated metallocene methyl cation where the drawback may be partly due to the moderately coordinating BPh_4^- counterion, and in part due to the presence of a strong donor ligand (THF), or has required treatment of the monomer with $ZnEt_2$ prior to polymerization where the additive appears to interfere with the generation of an active intiator and suppresses the rate of propagation. We have demonstrated that the two-component system of a dimethylzirconocene and Lewis acid activator (usually $B(C_6F_5)_3$) can initiate controlled and rapid formation of poly(MMA) as long as the active species is formed before monomer addition. If this is not the case, then the Lewis basic monomer binds to the alkyl abstractor, rendering it ineffective. This has been demonstrated by the observation and characterization of the adduct MMA·$B(C_6F_5)_3$ by NMR spectroscopy and its failure to react subsequently with dimethylzirconocene. The modified protocol described here offers a straightforward, highly efficient, and well-controlled approach to the synthesis of poly(MMA) using metallocene catalysts, the only exception being {$Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)$}$ZrMe_2$ which is believed to be too crowded to initiate polymerization of the relatively bulky 1,1-disubstituted MMA olefin. Although a useful degree of control over molecular weight and molecular weight distribution is obtained, the system is nonliving as demonstrated by reinitiation studies and attempts to prepare block copolymers.

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