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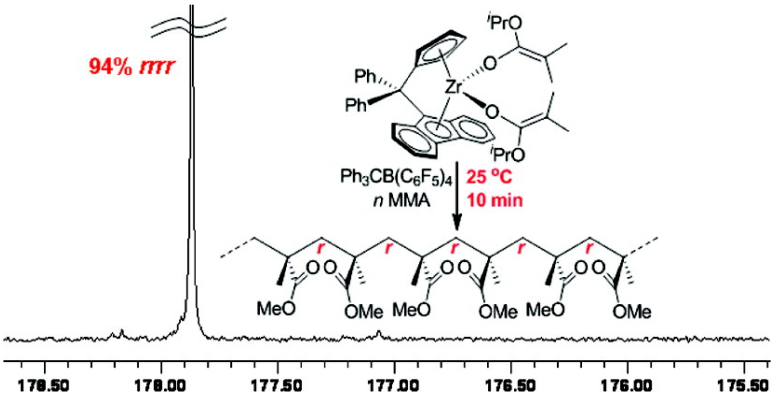

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Metallocene-Catalyzed Polymerization of Methacrylates to Highly Syndiotactic Polymers at High Temperatures

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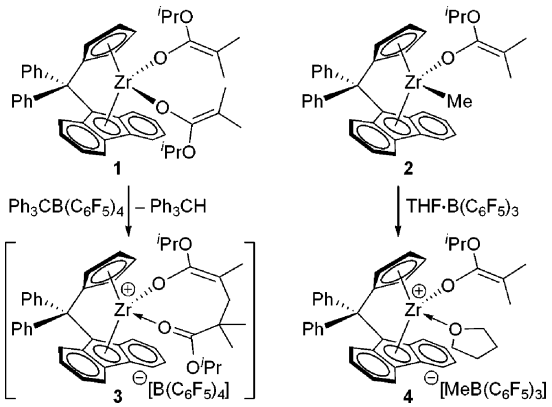
Technologically important, readily accessible, and remarkably tunable chiral metallocene catalysts, especially those of cationic group 4 complexes,[1] have been widely employed to precisely control the stereomicrostructure (tacticity) of polyolefins through their catalyzed homogeneous, single-site, stereospecific polymerization of *nonpolar* α-olefins.[2] In comparison, the polymerization of *polar* functionalized alkenes with such highly electron-deficient group 4 metallocene and related complexes has been investigated to a much less extent.[3] Nonetheless, there is increasing interest in the latter area,[4] already achieving the synthesis of highly isotactic poly(methacrylate)s (≥95% *mm*)[5] and poly(acrylamide)s (>99% *mm*)[6] using chiral C_2-ligated zirconocenium complexes at ambient temperature. This initial success seemed to indicate that the catalyst symmetry−polymer stereomicrostructure relationship already established for the polymerization of nonpolar α-olefins may be readily applied to the polymerization of polar functionalized alkenes, despite their differences in the chain-growth mechanism (i.e., migratory insertion[2] vs conjugate addition[3]). To further test this hypothesis, over the past decade, at least five research groups[7] have attempted the synthesis of syndiotactic poly(methyl methacrylate), PMMA, using a C_s-ligated cationic zirconocene methyl complex, $[Me_2C(Cp)(Flu)ZrMe]^+$ (Cp = η^5-cyclopentadienyl; Flu = η^5-fluorenyl)—which is known for its ability to catalyze syndiospecific polymerization of propylene[8]—but none observed any activity for polymerization of methyl methacrylate (MMA). Although we[9] recently solved this inactivity issue using an ester enolate derivative, $\{Me_2C(Cp)(Flu)Zr(THF)[OC(O^iPr)=CMe_2]\}^+$, the resulting PMMA is essentially a syndio-biased atactic polymer (64% *rr*, 32% *mr*, 4.0% *mm*) via a chain-end control mechanism. Another C_s-ligated zirconium ester enolate complex $CGCZr(L)[OC(O^tBu)=CMe_2]^+$ [L = neutral donor ligand, CGC = $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)$] affords highly isotactic PMMA via a site-control mechanism at low temperatures,[10] whereas the isostructural titanium CGC complex produces syndiotactic PMMA (up to 82% *rr*) by a chain-end control mechanism.[11] Isoelectronic neutral lanthanocenes supported by C_s-symmetric, $Me_2C<$ and $Ph_2C<$ bridged (Cp)(Flu) ligands also produce syndio-rich atactic (*rr* ∼ 60%) PMMA.[12] In short, there exhibited no strict analogy between olefin insertion and MMA addition polymerizations catalyzed by C_s-ligated complexes because of their significant differences revealed in stereoselection[4d] and fundamental chain-growth events[10,11b] between those two processes, and the synthesis of highly syndiotactic PMMA by a site-control mechanism remained a challenge.

Intense research efforts have been directed at development of a polymerization system that can lead to the efficient production of highly syndiotactic PMMA, due to the fact that the glass transition temperature (T_g)—an important materials property parameter—of PMMA rises as an increase in the polymer syndiotacticity. It has been shown that PMMA exhibits a wide range of the T_g values as a function of its stereomicrostructure: ca. 55,[13] 87, [13] 110, [13] 130,[11b] and 140 °C[7a] for highly isotactic (96% *mm*), isotactic-*b*-syndiotactic (46% *mm*, 46% *rr*), syndio-biased atactic (60% *rr*), syndiotactic (81% *rr*), and highly syndiotactic (95% *rr*) PMMA, respectively. Several initiator systems have been developed to produce highly syndiotactic PMMA, *but all require low to extremely low polymerization temperatures* (T_p; Table 1). The syndioselectivity of such non-site-control systems typically erodes to a moderate to low level of *rr* ≤ 80% when T_p reaches 25 °C. Our work communicated herein describes a highly active polymerization system based on C_s-ligated *ansa*-zirconocene bis(ester enolate) **1** and mono(ester enolate) **2**—which, upon activation with appropriate activators, generate the corresponding chiral cationic catalysts **3** and **4** (Scheme 1)—that produces highly syndiotactic PMMA at ambient or higher temperatures (Table 1).

Table 1. Polymerization Systems Producing Highly Syndiotactic PMMA

catalyst or initiator	T_p (°C)	*rr* (%)	T_g (°C)	ref no.
m-$(CH_2{=}CH)C_6H_4CH_2MgCl$/THF	−98	94		14
$[Cp^*_2SmH]_2$	−95	95		15
^{t}BuLi/3Al(^{n}Oct)$_3$	−93	96		16
$Ph_3P/AlEt_3$	−93	95	135	17
$Me_2C{=}C(OMe)OLi/2Al(C_6F_5)_3$	−78	94	138	7a
$Cp^*_2YbAlH_3{\cdot}NEt_3$	−40	93		18
$[HC(C(Me){=}N\text{-}2,6{-}{}^iPr_2C_6H_3)_2Mg(\mu{-}OC(=CH_2){-}2,4,6{-}Me_3C_6H_2)]_2$	−30	92	135	19
1/$Ph_3CB(C_6F_5)_4$ (i.e., **3**)	25	94	139	this work
2/THF·$B(C_6F_5)_3$ (i.e., **4**)	25	95	139	this work
1/$Ph_3CB(C_6F_5)_4$ (i.e., **3**)	50	93	136	this work

Scheme 1



Zirconocene bis(ester enolate) **1** was conveniently synthesized by the reaction of the corresponding dichloride precursor[20] with $Me_2C{=}C(O^iPr)OLi$ in 92% yield.[21] The synthesis of mono(ester enolate) **2** involved three steps: methylation of the dichloride precursor with MeMgBr to yield the dimethyl derivative (96% yield), treatment of the dimethyl with Me_3SiOTf to give the methyl triflate complex (>99% yield), and reaction of the triflate with $Me_2C{=}C(O^iPr)OLi$ to afford **2** in 75% yield.[21] Activation of the

methyl ester enolate complex **2** with THF•$B(C_6F_5)_3$ in CH_2Cl_2 at room temperature generated cleanly the corresponding chiral cationic species **4**; the same activation approach has been well-established for C_2- and C_s-ligated zirconocene methyl ester enolate complexes.[5a,b,9] For the activation of the bis(ester enolate) complex **1**, we employed a unique activation process that we recently developed for oxidative activation of the silyl ketene acetal initiator $Me_2C{=}C(OMe)OSiMe_3$ with a catalytic amount of $Ph_3CB(C_6F_5)_4$ to a highly active propagating species structure containing both nucleophilic [R(Me)C═C(OMe)OSiMe$_3$] and electrophilic (Me_3Si^+) catalyst sites.[22] Accordingly, we reasoned that the reaction of **1** with 1 equiv of $Ph_3CB(C_6F_5)_4$ should occur in the similar fashion: H^- abstraction from the methyl group within the enolate [OC(O^{i}Pr)═CMe$_2$] moiety[23] by Ph_3C^+ forms Ph_3CH and the resulting isopropyl methacrylate coordinated to Zr, and subsequent nucleophilic addition of another enolate ligand to this activated methacrylate monomer gives the cationic eight-membered ring chelate **3** (a catalyst resting state).[24] Indeed, the formation of Ph_3CH was observed at temperature as low as −60 °C (5.55 ppm, C*H*, CD_2Cl_2); however, unlike **4**, complex **3** is unstable in the absence of monomer.

Significantly, the activated species promote rapid and controlled MMA polymerizations with high syndiospecificity at ambient temperature (ca. 25 °C). The polymerization by the bis(ester enolate) **1** was carried out in a in-reactor activation mode, that is, addition of a premixed solution of 100 equiv of MMA with 1 equiv of $Ph_3CB(C_6F_5)_4$ to a CH_2Cl_2 solution of **1**. A 92% monomer conversion (ρ) was reached within 14 min of the reaction, and a linear increase of M_n (number-average molecular weight) versus ρ was observed with PDI (polydispersity index) ranging from 1.10 at low ρ (M_n = 4.51×10^3) to 1.37 at high ρ ($M_n = 2.09 \times 10^4$).[21] *Most remarkably, the resulting polymer shows rr = 94.4% and T_g = 139 °C!* The triad-level stereomicrostructure of the PMMA (*mr* = 4.0%, *mm* = 1.6%) is more characteristic of site control than chain-end control, but the test result of 2[*mm*]/[*mr*] = 0.8 somewhat deviates from unity, which may suggest that it does not conform to a pure site-control mechanism. Furthermore, this high level of syndiotacticity is not markedly altered by changing the [MMA]/[**1**] ratio (400, *rr* = 93.5%; 800, *rr* = 93.2%), solvent (400 MMA, toluene, *rr* = 93.7%), temperature (400 MMA, T_p = 50 °C in toluene, *rr* = 92.8%, T_g = 136 °C; 400 MMA, T_p = 0 °C in CH_2Cl_2, *rr* = 96.0%, T_g = 140 °C), and addition sequence (preactivation mode, i.e., premixing **1** with $Ph_3CB(C_6F_5)_4$ for 10 min before addition of 400 MMA, *rr* = 94.5%, *mr* = 3.7%, *mm* = 1.8%, T_g = 139 °C). However, the use of the borane $B(C_6F_5)_3$ as activator for bis(ester enolate) **1** resulted in the formation of PMMA with substantially lower syndiotacticity (*rr* = 76.4%, *mr* = 20.6%, *mm* = 3.0%); this observation is attributable to a combination of a different activation pathway involving $B(C_6F_5)_3$ (which undergoes electrophilic addition to the ester enolate α-carbon forming an adduct analogous to the structure previously characterized for the C_2-symmetric metallocene derivative[24]) with a competing bimetallic pathway as a result of the slow and reversible activation process using $B(C_6F_5)_3$ (i.e., coexistence of both neutral and cationic species under this activation condition).

The mono(ester enolate) **2** is instantaneously activated using THF•$B(C_6F_5)_3$ (in situ mixing or isolation of **4**), $B(C_6F_5)_3$ (in-reactor activation), or $Ph_3CB(C_6F_5)_4$, all leading to highly active (a 95% monomer conversion is typically achieved in 7 min) and highly syndiospecific (94% *rr*) polymerization of MMA at ambient temperature. Kinetic profiling of the MMA polymerization in a [MMA]/[**2**] ratio of 100 at 25 °C in CH_2Cl_2 gives a first-order rate dependence in [MMA] (Figure 1) and a linear increase of M_n versus

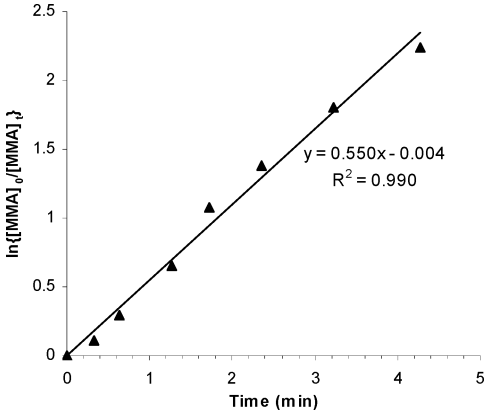


Figure 1. First-order kinetic plot of ln{$[MMA]_0/[MMA]_t$} versus time for the MMA polymerization in CH_2Cl_2 at 25 °C: $[MMA]_0$ = 0.468 M, $[\mathbf{2}]_0 = [B(C_6F_5)_3]_0$ = 4.68 mM.

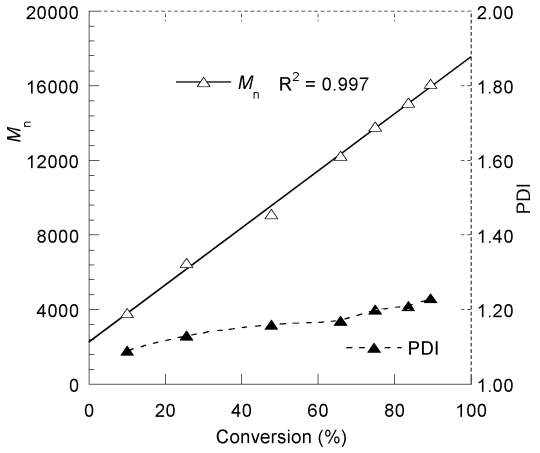


Figure 2. Plots of M_n and PDI of PMMA versus MMA conversion in CH_2Cl_2 at 25 °C: $[MMA]_0$ = 0.468 M, $[\mathbf{2}]_0 = [B(C_6F_5)_3]_0$ = 4.68 mM.

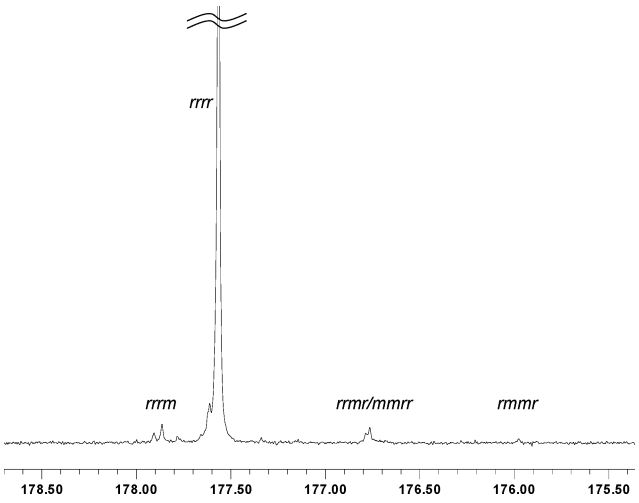
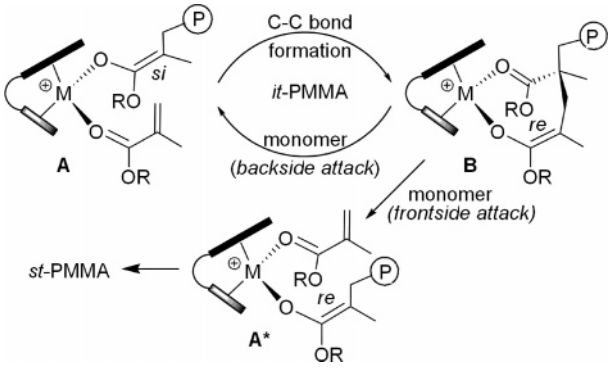


Figure 3. ^{13}C NMR (125 MHz) spectrum showing the C═O pentad region of the PMMA produced by **4** in CH_2Cl_2 at 25 °C: *rrrr* = 93.1%.

ρ with a nonzero intercept and small PDI values in the range of 1.09−1.23 (Figure 2). The PMMA produced by **4** derived from **2** + THF•$B(C_6F_5)_3$ + 400 MMA exhibits *rr* = 94.9% (^1H NMR, 500 MHz), *rrrr* = 93.1% (^{13}C NMR, 125 MHz, Figure 3), and T_g = 139 °C. Polymerization of 200 equiv of *n*-butyl methacrylate by this system also affords highly syndiotactic poly(*n*-butyl methacrylate): ρ = 90% (1 h), $M_n = 3.47 \times 10^4$, PDI = 1.30, *rr* = 94.1%, *mr* = 3.9%, *mm* = 2.0%.

Scheme 2



C_s-Ligated catalyst structure **A** (Scheme 2) is chiral at metal and exhibits two enantiotopic lateral coordination sites. Isotactic PMMA is formed by a site-control mechanism when the reaction follows a **A**→**B**→**A** cycle in which stereoselective C−C bond formation occurs predominantly through the same preserved structure **A**, and the lateral coordination site for MMA is also the same due to monomer *backside* attack (relative to the coordinated ester leaving group) following each bond formation step.[10] On the other hand, syndiotactic PMMA is formed by a site-control mechanism if both lateral sites are alternately utilized for stereoselective monomer enchainment via a **A**→**B**→**A*** cycle (* denotes an enantiomer) requiring *frontside* attack of the incoming monomer at the resting cyclic intermediate **B** following each C−C bond formation step. For both site-control cases, the rate of MMA-assisted site epimerization must be slow relative to Michael addition. No site epimerization was observed for **3** and **4** in CD_2Cl_2 or in the presence of 10 or 20 equiv of THF. Consistently, addition of 10 or 20 equiv of THF decreased the syndiotacticity of the PMMA produced by **3** or **4** in CH_2Cl_2 by only ∼1.0%, suggesting little to no site epimerization during polymerization by displacement of the coordinated chain end from the metal prior to monomer coordination. Hence, the observed differences in reactivity and stereoselectivity between the $Me_2C<$ and $Ph_2C<$ bridged Zr systems may be explained by their different Thorpe−Ingold effect[25] in terms of relative rates of ring closing (Michael addition step) and ring opening as compared to the rate of MMA-assisted site epimerization. In the event of fast site epimerization relative to propagation, syndiotactic PMMA would not be formed by a site-control mechanism using C_s-ligated catalysts.

In summary, we have developed a highly active catalyst system based on the C_s-ligated *ansa*-zirconocene bis- and mono(ester enolate) complexes **1** and **2**, leading to the production of highly syndiotactic poly(methacrylate)s at industrially convenient temperatures, thus accomplishing a long-standing scientific goal of the field. However, a fundamental understanding of the unique features that the current system possesses and further development of possibly even better systems based on this understanding require much further work, which will be a focus of our ongoing studies.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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