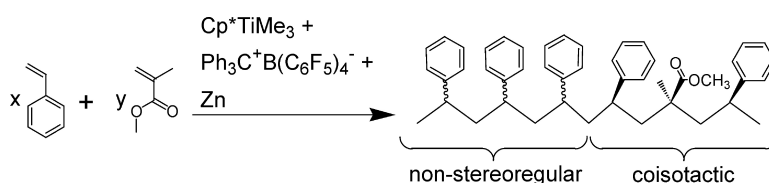


Organotitanium-Mediated Stereoselective Coordinative/Insertive Homopolymerizations and Copolymerizations of Styrene and Methyl Methacrylate

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Organotitanium-Mediated Stereoselective Coordinative/ Insertive Homopolymerizations and Copolymerizations of Styrene and Methyl Methacrylate

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Abstract: This contribution describes coordinative/insertive stereoregular homopolymerizations and copolymerizations of styrene and methyl methacrylate (MMA) mediated by a highly active single-site organotitanium catalyst. The catalyst system used to effect these polymerizations of nonpolar and polar olefinic monomers is prepared by in situ Zn reduction of the precursor derived from the reaction $(\text{Me}_5\text{Cp})\text{-TiMe}_3 + \text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$. The resulting catalyst produces polystyrene (>95% syndiotactic, 170 000 g/mol molecular weight; *s*-PS) by the established coordinative/insertive pathway. The same catalyst mediates polymerization of MMA to poly(methyl methacrylate) (>65% syndiotactic, >70 000 g/mol molecular weight; *s*-PMMA) by a group transfer protocol-like (GTP-like) pathway (1,4 insertion mechanism). Under optimal conditions, this catalyst also mediates the copolymerization of MMA + styrene (1:19 ratio) at 50 °C to yield random ~80% coisotactic poly[styrene-*co*-(methyl methacrylate)] (*coiso*-PSMMA) which contains ~4% MMA. Control experiments argue that a single-site Ti catalyst is the active species for the copolymerization. The catalyst formation process is quite general, and a variety of reducing agents can be substituted for Zn and still effect copolymerization. Control experiments also indicate that known noncoordination copolymerization mechanisms (i.e., ionic or radical) cannot explain this copolymerization. We suggest a new mechanism involving sequential conjugate addition steps to explain these copolymerization results.

Introduction

Single-site early-transition metal metallocenium and related single-site catalysts have been extensively investigated for the coordinative/insertive polymerization of nonpolar olefins.¹ Such catalysts are of great fundamental scientific and technological importance, and a broad understanding of catalyst–cocatalyst structure–activity–selectivity relationships has recently emerged. A major question currently concerns the scope of such polymerization processes and, in particular, the scope of olefinic monomers that are amenable to polymerization by these catalysts. The picture emerging is that, as a consequence of their

extreme oxophilic/halophilic/Lewis acidic nature, such catalysts have generally proven incompatible with functionalized vinyl monomers in achieving single-site controlled insertive polymerization of olefins bearing polar functional groups (“polar olefins”) or copolymerization of polar and nonpolar olefins.² The ability to enchain polar olefins is expected to enhance polyolefin properties such as adhesion, barrier properties, biocompatibility, miscibility with other polymers, toughness, solvent resistance, surface properties (paintability, printability, etc.), and rheological properties.³ Although late-transition metal catalysts, especially palladium and nickel, have demonstrated greater versatility in this regard, high levels of polar comonomer incorporation are generally not possible, and polymerization activity drops substantially at higher concentrations of polar comonomer.^{1,2d,4} There have also been limited disclosures of early-transition metal-mediated polymerizations with “masked” polar monomers in which polar groups are suitably protected or remote from the olefinic functionality.⁵

The reports of methyl methacrylate (MMA) homopolymerization using early-transition metal single-site catalysts represent

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one of the major advances in polar monomer polymerization by early-transition metal single-site catalysts. Poly(methyl methacrylate) (PMMA) has been known and produced in large-scale commercial quantities for almost half a century.⁶ MMA can be polymerized via radical,⁷ anionic,⁸ or group transfer protocol (GTP)⁹ type pathways. A great deal has been reported on the synthesis, characterization, and stereoregularity-dependent properties of PMMA. High tacticity can often be achieved at low temperatures via radical and ionic techniques as demonstrated by Hatada in the synthesis of isotactic,¹⁰ syndiotactic,¹¹ and heterotactic¹² PMMA. Because the highly active single-site homogeneous polymerization catalysts mentioned above can effect impressive control over product polymer microstructure, comonomer incorporation, stereoregularity, and molecular weight characteristics, there was great interest when almost simultaneously Farnham, et al.,¹³ Collins, et al.,¹⁴ and Yasuda, et al.¹⁵ reported that single-site d^0/f^0 catalysts can be applied to the homogeneous polymerization of MMA.

Collins and co-workers showed that a two-component catalytic system comprising a cationic zirconocene and a neutral zirconocene which act in concert can mediate MMA homopolymerization to high molecular weight PMMA with a syndiotactic microstructure via a bimetallic GTP-like insertion mechanism (Figure 1).¹⁴ Yasuda and co-workers showed that organolanthanocenes Cp^*_2LnR ($R =$ hydride or alkyl group) are competent to produce syndiotactic PMMA with narrow

polydispersity via a monometallic GTP-like insertion sequence (Figure 1).¹⁵ Marks and co-workers then used a C_1 -symmetric lanthanocene catalyst to produce isotactic PMMA,¹⁶ while Soga and co-workers developed a system for producing PMMA by prereacting MMA with Et_2Zn and then introducing a zirconocenium ion pair.¹⁷ Novak and co-workers produced PMMA using bimetallic initiators, formed either in situ from oxidation of a Sm^{2+} precursor or via direct synthesis of the bimetallic initiator, in the latter case to form a "link functionalized" PMMA with a 1,3-butadiene group incorporated at the chain center.¹⁸ Recently, Gibson, et al. and Höcker, et al. showed that cationic group 4 metallocenes are capable of producing high molecular weight syndiotactic PMMA via a mononuclear pathway without an exogenous Lewis acid (similar to the lanthanocene-catalyzed process).^{19,20} Thus, to date, it has been demonstrated that cationic group 4 metallocene and related catalysts can mediate MMA polymerization to syndio- or isotactic high molecular weight PMMA with narrow polydispersity via both mono- and bimetallic pathways (Figure 1). The fundamental factors that determine whether a catalyst will traverse the mono- or bimetallic pathway are not well understood.

Homogeneous single-site early-transition metal polymerization catalysts are not limited in scope to α -olefins or MMA polymerizations. They also exhibit activity for the polymerization of conjugated olefins, with an important and excellent example being the syndiospecific polymerization of styrene first reported by Ishihara and co-workers.²¹ Since the initial report,²¹ syndiotactic polystyrene (*s*-PS) has been the subject of intense investigation because of useful properties that include a high melting point (270 °C) and a low specific gravity, in addition to general resistance to water and organic solvents at ambient temperature.²² Of the complexes identified as effective catalyst precursors for *s*-PS synthesis, the most effective are based upon monocyclopentadienyl Ti complexes such as Cp^*TiR_3 ($R =$ halide, Me, CH_2Ph , etc.) activated with methylaluminoxane (MAO), $B(C_6F_5)_3$, $C_6H_5NH(CH_3)_2^+B(C_6F_5)_4^-$, or $Ph_3C^+B(C_6F_5)_4^-$.²² While relatively few complexes of transition metals other than Ti have been found to initiate styrene polymerization to *s*-PS,²³ efforts to assign the Ti oxidation state through EPR and NMR studies have variously implicated Ti(II),^{23,24} Ti(III),²⁵ and Ti(IV)^{24c} as possible active species for styrene polymeri-

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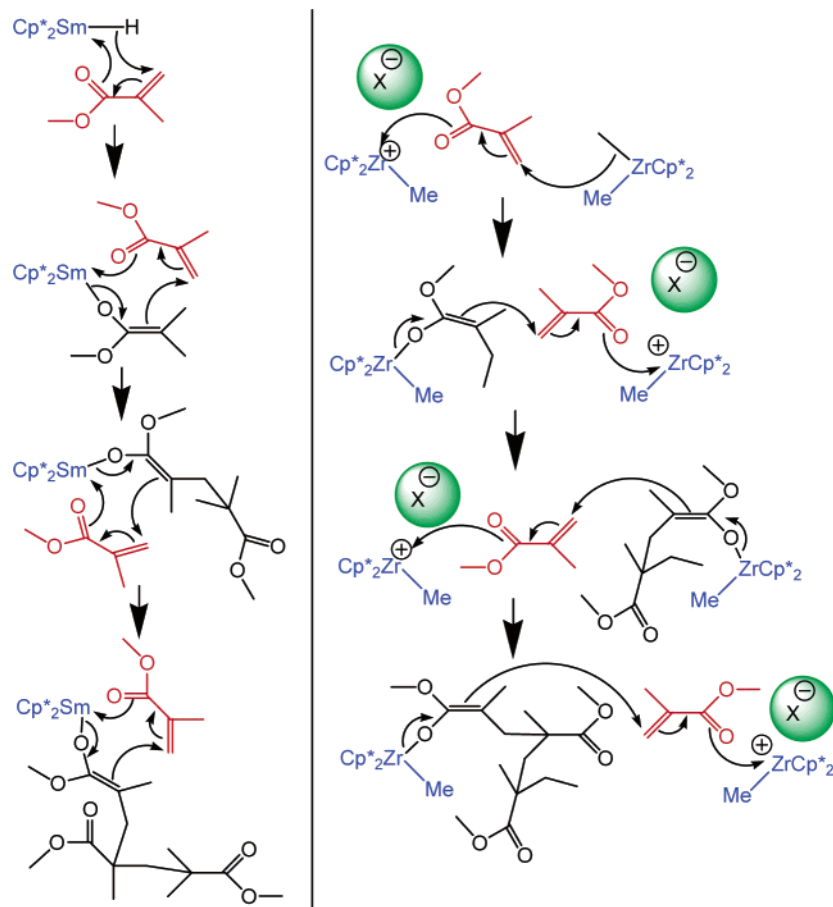
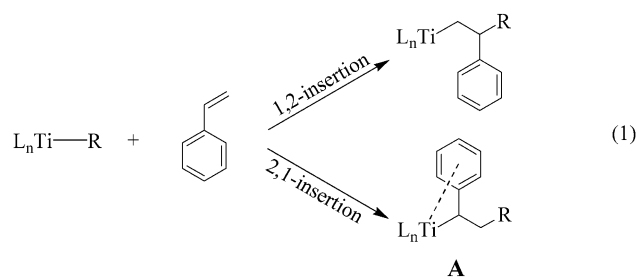


Figure 1. The monometallic (left) and bimetallic (right) GTP-like methyl methacrylate polymerization pathways traversed by single-site early-transition metal catalysts.

zation.²² Although there is still debate concerning the exact nature of the species active in *s*-PS polymerization,^{24c,25a,b,26} many characteristics of the polymerization mechanism are understood. NMR experiments clearly indicate that polymerization occurs through a Ziegler–Natta type single-site insertion mechanism. The regiochemistry of styrene insertion is secondary (2,1-insertion, eq 1) as established by polymer end-group analysis.²⁷ That tacticity is chain-end controlled and not enantiomorphic site-controlled is argued by $4[rr][mm]/[mr]^2 \approx 1$.^{23,28}

Thus, although extensive research has been conducted both on single-site homogeneous MMA polymerization (by a GTP-like mechanism) and on styrene polymerization (2,1-insertion into the M–R bond), to our knowledge, the copolymerization of MMA and styrene by a single-site homogeneous catalyst has not been achieved. In contrast, MMA + styrene copolymerizations (including alternating, block, and random copolymers) have been achieved by ionic and radical processes or combinations

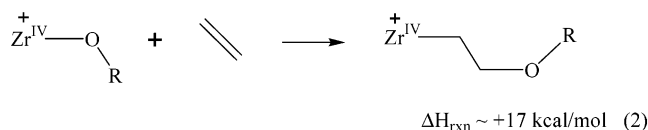


thereof.²⁹ Studies of MMA + styrene copolymers benefit greatly from the extensive high-resolution NMR studies that have been performed on this system.^{29d,30}

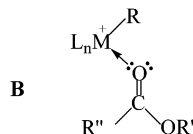
The goal of the present study was to investigate a means of effecting the single-site copolymerization of MMA and styrene. Bonding energetic considerations argue that the pronounced endothermicity (and likely endoergicity) of olefin insertion into group 4 d⁰ M–OR bonds, likely strengthened by ligand-to-metal π donation³¹ (e.g., eq 2),^{15,32} and olefin enchainment-impeding

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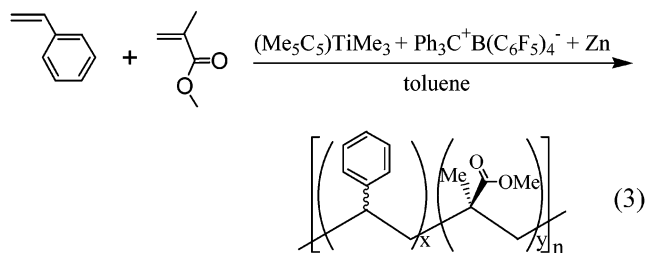


Lewis acid–base interactions (e.g., **B**) would likely present thermodynamic impediments and kinetic barriers, respectively.



These considerations raise the intriguing question of whether it might be possible to produce a group 4 system more competent for polar comonomer polymerization via (1) decreasing $D(L_nM-O)-D(L_nM-C)$ and catalyst Lewis acidity by lowering the metal oxidation state (e.g., this quantity decreases by ~ 15 kcal/mol for $d^0 \rightarrow d^2$ metallocenes);^{33,34} and (2) assisting competing nonpolar monomer activation/enchainment via multihapto substrate coordination (e.g., **A** in eq 1). We report here one embodiment of this strategy in the polymerizations of styrene and MMA to produce stereoregular, high molecular weight homopolymers and, most interestingly, random styrene–MMA copolymers.³⁵

To achieve these ends, we sought to modify the properties of the established $(\text{Me}_5\text{Cp})\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**1**) catalyst, which, as noted above, is a highly effective catalyst for syndiospecific styrene polymerization.^{25a,b,36} In the present study, a lower-valent Ti catalyst is generated in situ from **1** via reaction of $(\text{Me}_5\text{Cp})\text{TiMe}_3$ with $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ and a stoichiometric excess of Zn powder (eq 3), $(\text{Me}_5\text{Cp})\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (**2**). We report here that the new catalyst system, **2**, is more efficient than **1** for the homopolymerizations of styrene and MMA. Most interesting, however, is that **2** is competent to mediate the random copolymerization of styrene and MMA to produce a coisospesific copolymer. A variety of control experiments eliminate the possibility that this copolymerization is either ionic or radical in character. Rather, a new single-site polymerization pathway is proposed to explain this copolymerization process.



Experimental Section

General Procedures (See Supporting Information for Full Details). All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried glassware on a high vacuum-line (10^{-6} Torr), or in either a nitrogen-filled Vacuum Atmospheres or a Mbraun glovebox with a high capacity recirculator (<1 ppm of O_2). Argon (Matheson, PP) was purified by passage through a MnO oxygen-removal column and a Davison 4A molecular sieve column. All hydrocarbon solvents were predried and distilled under dry nitrogen from appropriate drying agents (sodium benzophenone ketyl, metal hydrides, Na/K alloy) and were subsequently stored over Na/K alloy. The reagents $(\text{Me}_5\text{Cp})\text{TiMe}_3$ ³⁷ and metallic Zn powder³⁸ were synthesized/activated according to literature procedures. The reducing agents, Mn, Mg, Sm, and Sn powders, were purchased from Aldrich and were transferred to a storage tube inside the glovebox, and they were dried under high-vacuum overnight before use. $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ was either obtained from Asahi Glass Co. or synthesized by literature procedure,³⁹ and 2,2'-azobisisobutyronitrile (AIBN) was purchased from Aldrich and purified by recrystallization from methanol. Styrene was freeze–thaw degassed three times, dried over calcium hydride, and then stored over calcium hydride in a -20 °C freezer. It was then freshly distilled just prior to use. MMA was freeze–thaw degassed three times, dried over calcium hydride, and then vacuum-transferred onto and stirred with AlEt_3 (Aldrich product) to remove protonic sources.⁴⁰ It was then vacuum-transferred from AlEt_3 and stored over calcium hydride in a -20 °C freezer. It was freshly distilled immediately prior to use.

Representative Copolymerization. Styrene with MMA Catalyzed by $(\text{Me}_5\text{Cp})\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (Styrene:MMA = 19:1). In the glovebox, styrene (19.0 g, 0.18 mol) and 50 mL of toluene were transferred to a 250 mL reaction flask having two side outlets (one fitted with a rubber septum and the other with an in situ thermocouple probe) and equipped with a magnetic stirring bar. The flask was attached to the high-vacuum line, and MMA (1 mL, 0.0093 mol) was added by syringe. The flask was then placed in a 20 °C water bath. Next, a 100 mL two-neck flask was charged with $(\text{Me}_5\text{Cp})\text{TiMe}_3$ (7.0 mg, 31 μmol), $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (26.0 mg, 29 μmol), and Zn (15 mg, 225 μmol) in the glovebox. On the vacuum line, toluene (1.0 mL) was vacuum-transferred into mixture, followed by stirring for 1.5 h to allow the reagents to undergo reaction. Over this time period, the solution changed from an orange color to dark brownish-green. The supernatant was then injected into the rapidly stirring solution of styrene and MMA via cannula. After being vigorously stirred at 20 °C for 240 min, the reaction was quenched by addition of MeOH (20 mL) to precipitate the polymeric product. The white polymeric material was triturated with MeOH (100 mL) by vigorously stirring for 12 h. The resulting solid was collected by filtration, washed with MeOH (3×10 mL), and dried under vacuum at 80 °C for 12 h to give a white polymeric solid (12.1 g).

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Table 1. Styrene and MMA Homopolymerization Data^a

entry	MMA (mL)	styrene (g)	toluene (mL)	polym. time (min)	polymer yield (g)	activity ^b	M_n^c (M_w/M_n)	tacticity ^d (rr %)
1	2	0	0	5	0.06	23	27 (1.8)	66
2	2	0	0	10	0.12	23	35 (2.2)	69
3	2	0	0	20	0.23	22	54 (2.4)	67
4	2	0	0	30	0.36	23	79 (2.0)	66
5	2	0	0	40	0.40	19	76 (1.9)	72
6	2	0	0	50	0.36	14	76 (1.8)	72
7	0	2	50	5	1.40	542	170 (2.1)	95

^a Polymerizations were carried out with Cp*TiMe₃ (7 mg, 31 μmol), Ph₃C⁺B(C₆F₅)₄⁻ (26 mg, 29 μmol), and Zn (15 mg, 225 μmol) as the catalyst at 103 °C (temperature monitored by in situ thermocouple probe; temperatures were constant except entry 7 in which the temperature change was <5 °C). ^b 10³ g of polymer/(mol of catalyst × h). ^c 10³ g/mol. ^d By ¹H NMR.

Results

The goal of this research was to investigate the possibility of creating a single-site homogeneous catalyst capable of polymerizing polar and nonpolar olefins. After some brief comments on the nature of the catalyst, in the first section we discuss the homopolymerization of MMA mediated by catalyst **2**, (Me₅Cp)TiMe₃ + Ph₃C⁺B(C₆F₅)₄⁻ + Zn. The next section will discuss the homopolymerization of styrene mediated by catalyst **2**. This will be followed by a presentation of results on the catalyst **2**-mediated copolymerization of MMA and styrene. Next, results as a function of reducing agent are discussed. Finally, a number of control experiments are conducted to gain further insight into the copolymerization pathway. The Discussion section will bring together a complete picture of this new polymerization system, and we propose a possible new mechanism to explain the results.

Although much research has been devoted to the characterization of monocyclopentadienyl titanium polymerization catalysts,²² there exists considerable uncertainty concerning the oxidation state(s) of the active Ti species in the syndiotactic styrene polymerization systems.^{25a,b,26} It is agreed that addition of cocatalyst to Cp*TiR₃ complexes results in a complex mixture of species containing several titanium oxidation states (the exact percentages of each species and their respective activities are still debated).^{25,26} The goal of the present study was to lower the Ti oxidation state to potentially weaken the Ti–O bonding and to reduce the Lewis acidity. To accomplish this, a reducing agent (Zn) was added to the known, highly active and selective catalytic system, Cp*TiMe₃ + Ph₃C⁺B(C₆F₅)₄⁻. The order of addition of reagents to produce catalyst **2** was found to be inconsequential. Equivalent activity can be achieved by adding toluene to Cp*TiMe₃ + Ph₃C⁺B(C₆F₅)₄⁻ and then transferring the solution onto Zn powder and stirring for 90 min, or by adding toluene to the three admixed solid reagents, Cp*TiMe₃ + Ph₃C⁺B(C₆F₅)₄⁻ + Zn, at once and stirring for 90 min. Note that it is generally accepted that a mixture of titanium oxidation states results during the formation of catalyst **1**, Cp*TiMe₃ + Ph₃C⁺B(C₆F₅)₄⁻;^{25,26} therefore, even without a reducing agent, low-valent Ti species are present, and we find that some of the activity reported here can be observed even in the absence of a reducing agent. However, it will also be seen that catalyst **2** is well optimized for the transformations of interest.⁴¹

MMA Homopolymerizations Mediated by Catalyst 2. The new catalyst system **2** effects the rapid polymerization of MMA with modest syndiotacticity. The polymerization results are shown in Table 1. A ¹H NMR spectrum of the syndiotactic PMMA product is shown in Figure 2A. To gain insight into

the polymerization mechanism, a time-dependent study of the polymerization was conducted (results are plotted in Figure 3). Figure 3 shows that polymer yield increases linearly for the first 30 min of the polymerization and then activity declines.

Presumably, the catalyst undergoes deactivation in ~30 min. In parallel, the polymer molecular weight increases linearly over the first 30 min before leveling off (as catalytic activity declines). This observation argues that the polymerization process is living over the first ~30 min prior to catalyst deactivation. Admittedly, the polydispersity of the polymer is somewhat large for a living system ($M_w/M_n > 1.5$). However, the fact that the catalyst is undergoing deactivation as the polymerization proceeds is expected to broaden the polydispersity, and initiation is probably slow relative to propagation (indicated by the fact that the polydispersity is high even at the initiation of polymerization), which should further increase the polydispersity.^{42,43} Consistent with a living polymerization model, the catalyst produces less than 1.0 polymer chains per Ti (for Table 1, entry 4: yield/ M_n = 0.36 g/79 000 g mol⁻¹ = 4.6 μmol of polymer; 4.6 μmol of polymer/31 μmol of Cp*TiMe₃ = 15% active Ti). Thus, in the present MMA homopolymerization process, ~15% of the Ti centers of catalyst **2** are productive.

The mechanistic observables in the **2**-mediated MMA polymerization are consistent with known GTP-like (1,4-insertion or Michael addition) pathways which other metallocene catalysts have been shown to traverse (Figure 1). To our knowledge, the **2**-mediated process is the first example of MMA polymerization via a GTP-like mechanism mediated by a monocyclopentadienyl Ti catalyst.⁴⁴ The polymerization follows a chain-end control-

- (41) EPR spectroscopy has previously been used to detect Ti^{III} species in the reaction of Cp*TiMe₃ + Ph₃C⁺B(C₆F₅)₄⁻, and signals assignable to Ti^{III} were observed in the present study. However, it is conceivable that Ti^{III} would be silent in a tightly coupled dimer. This situation is somewhat more complicated in the present system because the catalyst solubility in toluene is low (previous studies used CH₂Cl₂ or C₆H₅Cl) and an oil/solid inevitably forms on the bottom of the tube. We nevertheless carried out EPR experiments on our Zn-reduced system **2** (in toluene at 25 °C) and observed signals assignable to Ti^{III} (a sharp singlet at $g = 1.984$ and a broad singlet at $g = 1.960$). However, spin-counting experiments with TEMPO as an external standard showed <1% of the total Ti precursor is observed in the EPR spectrum of catalyst **2**.
- (42) Slow initiation relative to propagation has been observed in these types of systems before. See ref 12.
- (43) That the line in Figure 3 does not strictly pass through the origin is likely due to slow initiation. Calibration of the M_n data relative to polystyrene standards may slightly overestimate the actual values.
- (44) It has been reported that an *ansa*-titanocene imido complex can initiate the GTP-like polymerization of MMA (Jin, J.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 13–15). There is also a report that Cp₂TiCl₂ + excess AlEt₃ mediates MMA polymerization to low yield with high polydispersity; the polymerization mechanism is not clear (Benedek, I.; Simionescu, C.; Asandei, N.; Ungureanu, C. *Eur. Polym. J.* **1969**, *5*, 449–462). We were also unsuccessful in implementing a bimetallic metallocene mechanism to mediate MMA polymerization with [(CGCTiMe₂)(*μ*-Me)]⁺MePBB⁻ (Chen, Y. X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287–6305).

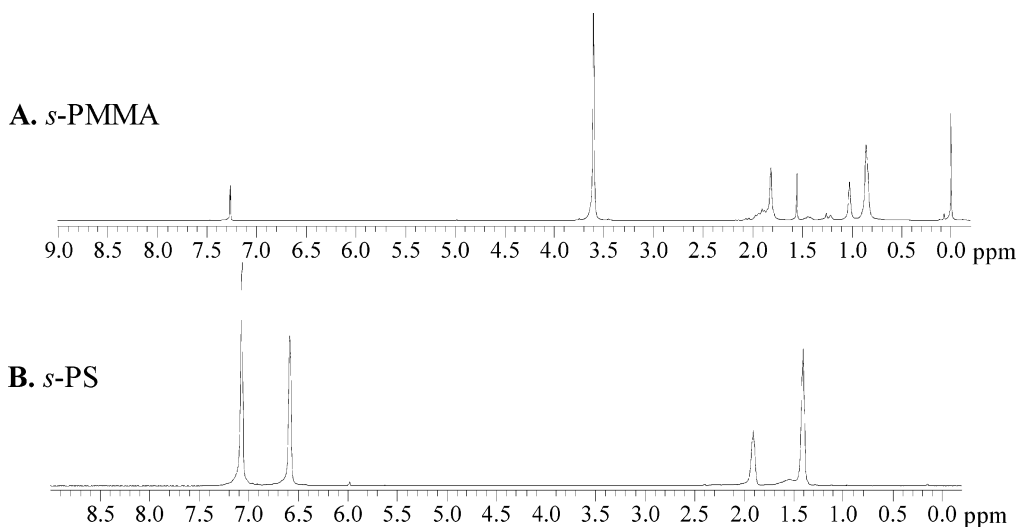


Figure 2. The 500 MHz ^1H NMR spectra of (A) syndiotactic-poly(methyl methacrylate) in CDCl_3 + TMS at 25 °C and (B) syndiotactic-polystyrene in $\text{C}_2\text{D}_2\text{Cl}_4$ at 125 °C. Both polymerizations were mediated by $(\text{Me}_5\text{C}_5)\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (**2**).

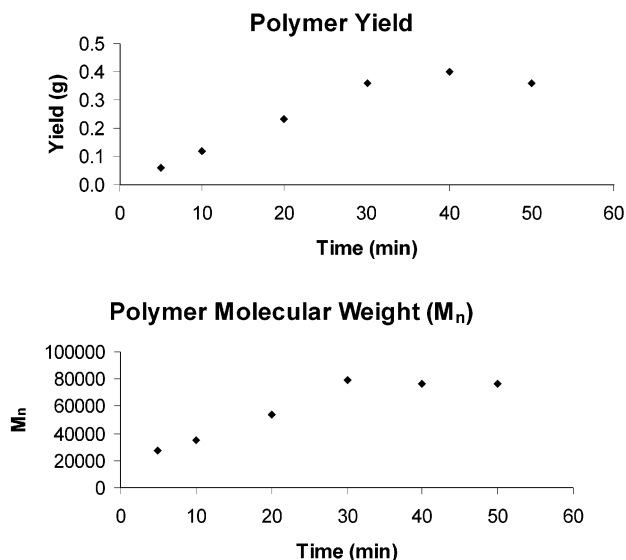


Figure 3. Homopolymerizations of MMA mediated by $(\text{Me}_5\text{C}_5)\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (**2**) as a function of polymerization time. See Experimental Section and text for details.

like pathway with $4[rr][mm]/[mr]^2 \approx 1.45$. The observed molecular weights ($M_n > 75\,000$) are also consistent with previous reports of metallocene-mediated MMA polymerization through a GTP-like mechanism, while the molecular weights are high for known ionic or radical processes.¹⁵ With the data at hand, the actual active metal oxidation state and catalytic nuclearity cannot be unambiguously defined. Certainly this system is no less complex than the case of syndiotactic styrene polymerization catalysts, for which the Ti oxidation state has not been conclusively resolved.^{25a,b,26} In many ways, the present system, potentially, is significantly more complex than the styrene system because the active catalyst oxidation state and the nuclearity of the mechanism (mono- or bimetallic) are intimately intertwined (e.g., the zirconocene-catalyzed polymerization of MMA is known to proceed via both mono- and bimetallic pathways,^{14,19,20} Figure 1). With the zirconocene systems, distinguishing between the mono- and bimetallic pathways is

(45) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173–182.

straightforwardly determined by changing the catalyst:cocatalyst ratio. This is only possible because one-electron zirconocene reduction has little precedent.⁴⁶ In the present case, addition of 1.0 equiv of cocatalyst to 1.0 equiv of Cp^*TiMe_3 results in products with a mixture of Ti oxidation states;^{24–26} one can reasonably assume that manipulation of the catalyst:cocatalyst ratio will alter the distribution of Ti oxidation states and it will likely not be in a straightforward fashion.^{47,48}

Although the preparation of catalyst **2** uses Zn metal, this MMA polymerization system is almost certainly not the same as the system used by Soga and co-workers.^{17,49} First, in that system, very large excesses of Et_2Zn are employed (0.25 equiv relative to MMA; >500 equiv relative to Ti). In the present system, Zn(0) is used so at most 1.5 equiv of Me_2Zn relative to Ti could be formed in the reduction of Cp^*TiMe_3 . Second, the order of Et_2Zn addition is very important in the Soga system, with no activity observed if MMA is not prereacted with Et_2Zn prior to catalyst injection. Obviously, in the present system, any Me_2Zn formed would be injected simultaneously with the catalyst. Third, the Et_2Zn system is reported to exhibit essentially no activity if Me_2Zn is substituted for Et_2Zn .^{17a} And last, under approximately the same reaction conditions, the Et_2Zn system exhibits ~2% of the activity as catalyst **2**.

Efforts to effect MMA polymerization using $\text{Cp}^*\text{TiMe}_3 + \text{B}(\text{C}_6\text{F}_5)_3$ under conditions similar to those employed for catalyst **2** were similarly successful (see Experimental Section for details). Note that for highest activity, these polymerizations must be carried out in neat monomer. Both $\text{Cp}^*\text{TiMe}_3 + \text{B}(\text{C}_6\text{F}_5)_3$ and **2** yield no *s*-PMMA under more dilute conditions (1:5 ratio of MMA:toluene). Interestingly, the known metal-

(46) Ryan, E. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Lappert, M. F., Volume Ed.; Pergamon: Oxford, New York, 1995; Vol. 4, Chapter 8.

(47) One pathway for Ti reduction has been shown to proceed through a bimetallic mechanism: Chien, J. C. W. *J. Am. Chem. Soc.* **1959**, *81*, 86–92.

(48) We cannot conclusively rule out the possibility that there are multiple active Ti species present. The high polydispersity indices ($1.5 < M_w/M_n < 2.5$) observed could conceivably be the result of multiple active species. However, the linear increase in polymer M_n with time and the monomodal GPC traces (M_w/M_n is large for a living system; however, the peak is monomodal) are strong evidence for the predominance of a single active species.

(49) Deng, H.; Shiono, T.; Soga, K. *Macromol. Chem. Phys.* **1995**, *196*, 1971–1980.

Table 2. Styrene + MMA Copolymerization Data^a

entry	styrene (g)	MMA (mL)	polym. temp (°C) ^b	toluene (mL)	polym. time (min)	polymer yield (g)	activity ^c	M_n^d (M_w/M_n)	MMA incorp. (%) ^e
1	10	10.2	20	1	30	0.02	0.1	3.7 (1.6)	<i>f</i>
2	10	10.2	20	50	30	0.76	4.9	3.5 (2.0)	<i>f</i>
3	10	10.2	50	1	15	0.11	1.4	14.7 (1.8)	<i>f</i>
4	9	1	20	50	10	2.5	48.4	9.8 (3.2)	2.5
5	19	1	20	1	30	5.1	32.9	16.3 (2.6)	1
6	19	1	20	50	240	12.1	9.8	5.5 (2.04)	1
7	19	1	50	1	3	17.1	1103.2	3.4 (3.1)	4

^a Polymerization was carried out with Cp*TiMe₃ (7.0 mg, 31 μmol), Ph₃C⁺B(C₆F₅)₄⁻ (26 mg, 29 μmol), and Zn (15 mg, 225 μmol) as the catalyst. ^b Temperature was monitored by in situ thermocouple probe; temperature changes throughout polymerization changed <2 °C except in entry 7 which had a large initial exotherm of ~30 °C. ^c The activity units: 10⁴ g mol⁻¹ h⁻¹. ^d $M_w \times 10^3$. ^e MMA monomer content (mol %) based on NMR integration. ^f Only atactic PS homopolymers are observed.

locene catalyst systems for GTP-like polymerization of MMA (e.g., zirconocene) are generally quite stable under typical polymerization conditions. It is not yet obvious why catalyst **2** is unstable (with activity ceasing after ~30 min) or what the pathway of deactivation is.

Homopolymerization of Styrene Mediated by Catalyst 2. Catalyst **2** is competent to efficiently polymerize styrene in a syndiospecific manner (Table 1, entry 8). The ¹H NMR spectrum of the product is shown in Figure 2B. Metallic Zn appears to accelerate Ti^{IV} reduction, and the resulting catalyst is found to be more active in the stereoregular styrene homopolymerizations than is catalyst **1**,⁵⁰ without Zn activation. Styrene polymerizations mediated by **2** exhibit high activities, and the resulting polymers have substantial molecular weights (>170 × 10³ g mol⁻¹) with relatively narrow monomodal polydispersities ($M_w/M_n = 2.1-2.2$), suggesting a single-site catalyst. As noted above, the exact nature of the active species in typical Cp*TiR₃-mediated styrene polymerizations is still unclear. The polystyrene produced by catalyst **2** exhibits molecular weight characteristics and syndiotacticity similar to those of previous systems.²² Therefore, it seems likely that the active species in these two systems is the same or very similar. The enhanced activity observed with catalyst **2** is likely the result of more efficient formation of the active species and not the generation of a new active species in these polymerizations. Thus, our results implicate a low-valent Ti complex as the active species because addition of a reducing agent increases activity. Presumably, mechanistic knowledge pertaining to catalyst **1** is applicable to catalyst **2** as well (polymerization via a Ziegler–Natta insertion pathway with primarily 2,1 regiochemistry).

Copolymerization of Styrene and MMA. The most interesting observation in the present study is that catalyst **2** is competent to copolymerize MMA and styrene to poly(styrene-co-MMA). The polymerization process functions at a variety of temperatures. Optimal conditions are at 50 °C, with neat monomers in a 1:19 stoichiometric ratio (MMA:styrene) to produce, with high activity (>10⁶ g of polym/(mol of cat × h)), random ~80% coisotactic poly(MMA-co-styrene) which contains 4% MMA (~96% atactic-PS; Table 2). The fraction of styrene in the copolymer, F_{sty} , was determined using the equation:

$$F_{sty} = \frac{3A_{\text{phenyl}}}{3A_{\text{phenyl}} + 5A_{\alpha\text{-methyl}}} \quad (4)$$

(50) Grassi, A.; Lamberti, C.; Zambelli, A.; Mingozzi, I. *Macromolecules* **1997**, *30*, 1884–1889.

where A_{phenyl} is the area of the styrene phenyl proton resonances (δ 7.5–6.2 ppm) and $A_{\alpha\text{-methyl}}$ is the area of the MMA α -methyl proton resonances (δ 0.9–0.2 ppm) in the ¹H NMR spectrum.³⁰

Copolymerization reactions mediated by **2** were carried out with varying MMA:styrene feed ratios (Table 2). Generally, copolymerization activities and molecular weights are lower than those from the analogous homopolymerizations. Polymer yields increase with decreasing MMA:styrene monomer ratios. The polymeric products generally exhibit $M_w/M_n \approx 2$, suggesting a single-site process. As expected,¹ activity increases and polymer molecular weights decrease with increasing temperature. Activity also increases in neat monomer solutions (higher concentrations), consistent with the rate law being first-order in monomer.¹ For 1:1 MMA:styrene feed ratios,⁵¹ the atactic-PS homopolymer is obtained in low yield (Table 2, entries 1–3), while a 9:1 styrene:MMA ratio produces the copolymer. Lowering the quantity of MMA relative to styrene while increasing the temperature results in greater incorporation of MMA into the copolymer.

Relative to the corresponding homopolymerizations, activities in the copolymerization process are depressed, as are the product polymer molecular weights. The tacticity is modified as well. While the homopolymers are highly syndiotactic, the copolymer contains atactic polystyrene with coisotactically enchaind MMA units and thus is distinctly different from typical radical⁵² and anionic⁵³ styrene + MMA copolymerizations that usually afford nonstereoregular random copolymers.⁵⁴ Thus, the 500 MHz ¹H NMR spectrum of the present styrene–MMA copolymers (Figure 4) reveals the enchaind MMA methoxy units in the region δ 3.6–2.2 ppm, with the most intense peak observed at δ 2.3 ppm (integrating as ~80% of the δ 2.5–2.2 ppm region), indicating that this copolymer is enriched ~80% coisotactic.⁵⁵ A HETCOR NMR spectrum⁵⁶ confirms that these methoxy units have the appropriate cross-peak with resonances δ ~50 ppm in the ¹³C NMR spectrum. The α -methyl group of MMA appears in the ¹H NMR in the δ 0.9–0.2 ppm region.

(51) At a MMA:styrene ratio of 95:5, only PMMA homopolymer is formed (with no styrene incorporation).

(52) (a) Bataille, P.; Grossetete, P. *Chem. Eng. Commun.* **1987**, *51*, 167–178.

(b) Hirai, H.; Tanabe, T.; Koizumi, H. *J. Polym. Sci.* **1979**, *17*, 843–857.

(53) Furukawa, J.; Tsuruta, T.; Inoue, S.; Kawasaki, A.; Kawabata, N. *J. Polym. Sci.* **1959**, *128*, 268–271.

(54) (a) Bovey, F. A. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 1, p 339. (b) Heffner, S. A.; Bovey, F. A.; Verge, L. A.; Mirau, P. A.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 1628–1634. (c) Katritzky, A. R.; Weiss, D. E. *J. Chem. Soc., Perkin Trans. II* **1974**, 1547–1554.

(55) For determination of coisotacticity, see: Yokota, K.; Hirabayashi, T. *J. Polym. Sci.* **1976**, *14*, 57–71.

(56) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Organic Structural Spectroscopy*; Prentice Hall: Upper Saddle River, 1998; p 132.

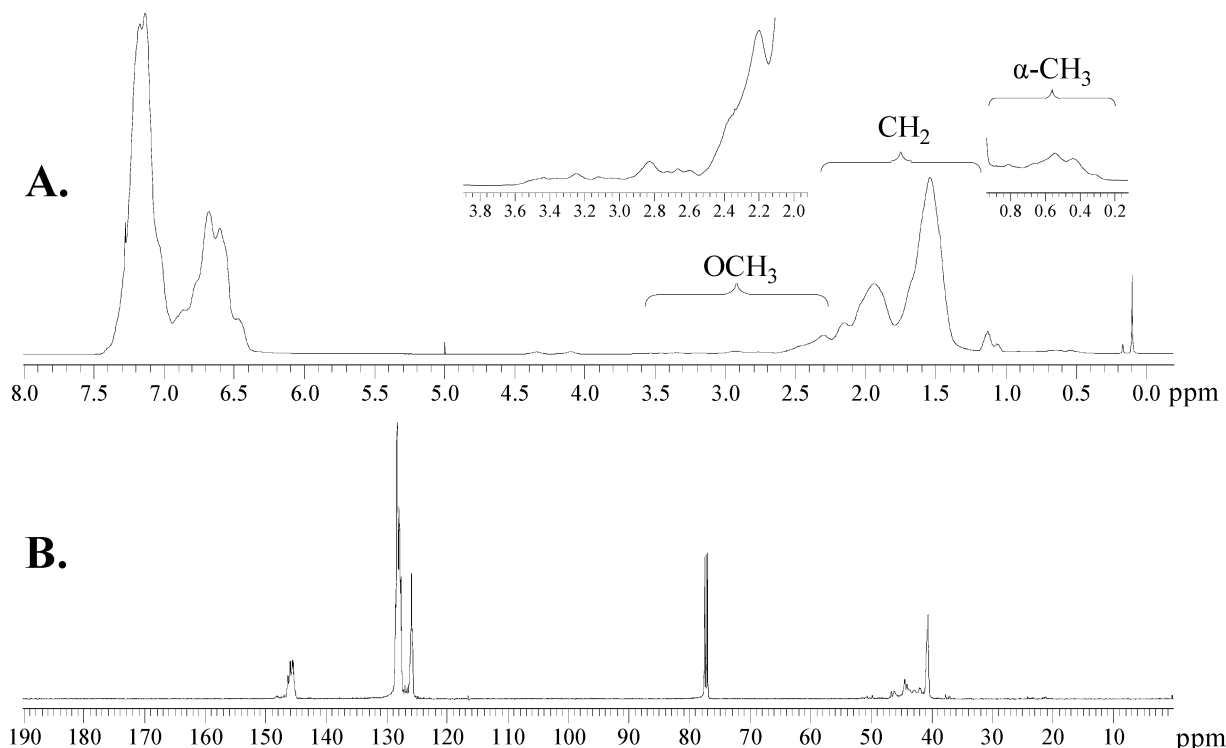
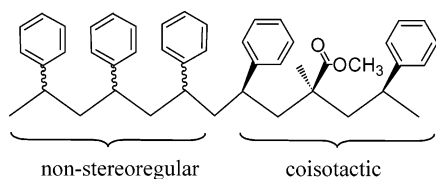


Figure 4. (A) ^1H (500 MHz) and (B) ^{13}C NMR (125 MHz) spectra of an MMA + styrene copolymer (Table 2, entry 7) produced by $(\text{Me}_5\text{C}_5)\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (**2**) (spectrum taken in CDCl_3 at 25 °C).



IR spectroscopy is a standard technique used to identify styrene and MMA homo- and copolymers.⁵⁷ Unfortunately, the FTIR spectrum of polystyrene has small absorptions at the characteristic carbonyl stretching region of PMMA (1730 cm^{-1}), rendering FTIR data of limited value for quantifying MMA incorporation systems such as the present one.⁵⁸

A time-dependent copolymerization study was conducted under conditions similar to Table 2, entry 6, and the results are shown in Figure 5. The polymer yield increases over time, but the polymer molecular weight, MMA incorporation level, and PDI remain approximately constant. These data are consistent with a standard single-site insertive polymerization pathway.¹ The $\text{PDI} \approx 2$ over the course of the polymerization suggests a single species as the active catalyst. Further evidence that this polymerization is not living can be obtained from a calculation showing that the polymerization generates >70 polymer chains per Ti (Table 2, entry 6: $12.1\text{ g of polym}/5500\text{ g mol}^{-1} = 2.2\text{ mmol}/31\text{ }\mu\text{mol of Ti} = 71$), assuming 100% of the Ti sites are active. Final monomer consumption (by styrene) is greater than 80%. Moreover, all evidence argues that the copolymer is not a simple mixture of homopolymers. Thus, the ^1H NMR spectra indicate that this copolymer does not contain homo-PMMA

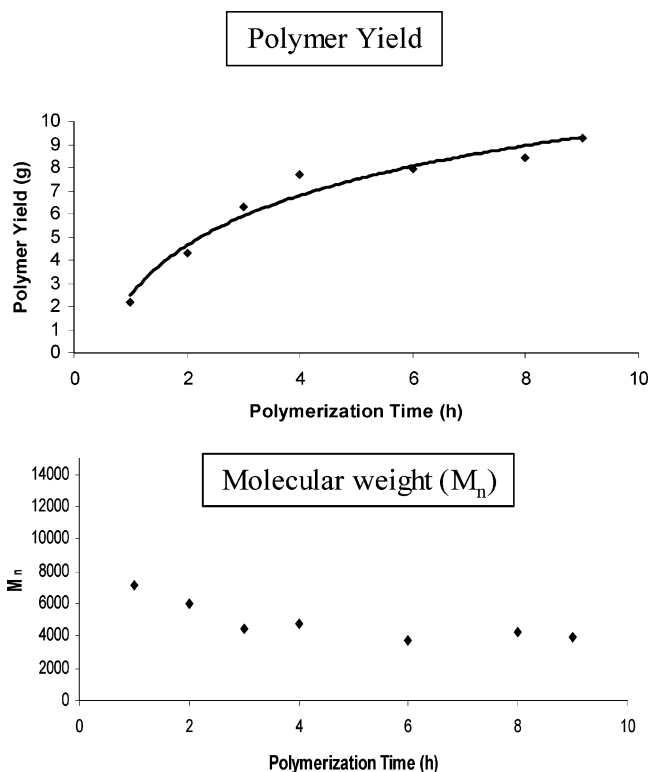


Figure 5. Time-dependent copolymerization data for MMA + styrene mediated by $(\text{Me}_5\text{C}_5)\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$.

(regardless of tacticity, the methoxy protons of homo-PMMA appear as a sharp singlet at δ 3.6 ppm). Note in Figure 4 that the δ 3.65–3.58 ppm region is featureless. This result is consistent with the aforementioned observation that the homo-polymerization of MMA is negligible under dilute conditions. A priori, the isolated polymer could be inferred to be a mixture

(57) Kuptsov, A. H.; Zhizhin, G. N. *Handbook of Fourier Transform Raman and Infrared Spectra of Polymers*; Elsevier: New York, 1998.

(58) An increase in the absorption at 1730 cm^{-1} in the copolymer is observed. However, this assay is not as convincing as the NMR data because there would be nonnegligible absorption at 1730 cm^{-1} in the absence of MMA incorporation.

Table 3. Control Experiments for Copolymerization of MMA + Styrene

entry	catalyst	amount (μmol)	monomer	temp ($^{\circ}\text{C}$)	time (h)	yield (g)	
1	$\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + Zn	41 122	MMA (0.4 mL)	21	72		no rxn
2	Me_2Zn	200	S (19 mL) + MMA (1 mL)	21	12	0.4	a-PS
3	$\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + Me_2Zn	28 200	S (19 mL) + MMA (1 mL)	21	12	1.1	~2.5% MMA incorporation
4	$\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + Me_2Zn	28 200	MMA (2 mL)	21	12		no rxn

Table 4. Examination of Various Reducing Agents for the Copolymerization of Styrene and MMA^a

entry	reducing agent	reducing agent mg (μmol)	styrene (g)	MMA (mL)	toluene (mL)	polymerization time (min)	polymer yield (g)	activity ^b
1	Mn	12.6 (230)	9.3	0.5	25	720	8.0	2.15
2	Zn	15 (230)	9.3	0.5	25	720	8.6	2.31
3	Mg	5.6 (230)	9.3	0.5	25	720	8.3	2.23
4	Sn	27.3 (230)	9.3	0.5	25	720	8.5	2.28
5	Sm	34.5 (230)	9.3	0.5	25	720	8.2	2.20

^a All polymerizations were carried out with Cp^*TiMe_3 (7 mg, 31 μmol) and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (26 mg, 29 μmol) and the reducing agent indicated at 20 $^{\circ}\text{C}$ (temperature monitored by in situ thermocouple probe; temperature change was $<2^{\circ}\text{C}$). ^b 10^4 g of polymer/(mol of catalyst \times h).

of atactic PS homopolymer and poly(styrene-*co*-MMA) having a higher MMA content than that reported in Table 2. Admittedly, in some examples this must be true. For example, in entry 6, Table 2, the copolymer has $M_n = 5500$, which corresponds to a number average degree of polymerization of ~ 55 , while the copolymer contains only 1% MMA. As such, there is insufficient MMA to place one MMA unit in each polymer chain, and this polymer must necessarily be a mixture of homopolystyrene and copolymer. However, it still seems unlikely that the polymer is a mixture of substantially higher MMA content copolymer and homopolystyrene because by GPC the polymer samples are generally monodisperse ($\text{PDI} \approx 2$, Table 2). An alternative explanation of polymer microstructure based on the observed low MMA incorporation levels is that the MMA is simply capping the atactic polystyrene chain. We do not believe this to be the case and will expound on this issue more fully at the end of the Discussion section.

Mechanistic Control Experiments. Random styrene and MMA copolymerizations have been known for well over 50 years,^{29d} with a variety of mechanisms demonstrated to be operative, including ionic and free radical.⁵⁹ A series of control experiments were carried out in the present study to probe if any of these previously reported mechanisms were operative. First, a series of control experiments designed to identify possible non-Ti catalytic species were performed with various combinations of metallic Zn, ZnMe_2 , and $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$, which might conceivably initiate radical, anionic, or cationic pathways. Attempted styrene + MMA copolymerizations with these reagents revealed very little or no catalytic activity as compared to the above Ti catalyst **2** (Table 3). This suggests that an organotitanium species is the active polymerization catalyst, although this does not rigorously rule out formation and activity of a cluster or bimetallic species (as proposed in the GTP polymerization of MMA with some zirconocene catalysts, Figure 1).

(59) Matyjaszewski, K.; Pugh, C. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 67–82.

There is one report of a catalyst system that effects MMA + styrene copolymerization with a zinc-based catalyst, the synthesis of which vaguely is reminiscent of the present system.⁶⁰ A calcium–zinc tetraethyl complex⁶¹ is formed via reaction of Et_2Zn and calcium powder in benzene at 110 $^{\circ}\text{C}$ (to produce a thick brownish-black suspension).⁶⁰ However, this system is very different from catalyst **2** in many respects. First, it is orders of magnitude less active than catalyst **2**, and, probably more importantly, the reported reactivity ratios are consistent with an anionic polymerization (with styrene as monomer 1; $r_1 = 0.31$ and $r_2 = 17.1$).⁶⁰ These ratios require a copolymer produced from a 9:1 styrene:MMA feed ratio to contain only $\sim 12\%$ styrene, clearly very different from catalyst **2** (Table 2, entry 4, a 9:1 styrene:MMA ratio yields a polymer containing 97.5% styrene).

To further eliminate any possibility that a Zn compound alone serves as the catalyst and to broaden the flexibility of catalyst synthesis, a series of experiments were carried out using four non-Zn reducing agents (Mn, Mg, Sn, and Sm). Results are summarized in Table 4. Clearly, catalysts prepared using all five reducing agents (including Zn) have the same functional characteristics within experimental error. Therefore, Zn is not an essential catalyst component of **2** for activity and selectivity, and other reducing agents yield similar results.

As shown above, reactivity ratios for the present system are inconsistent with an anionic polymerization mechanism.⁶² The inability to effect the present copolymerization process over a wide range of monomer ratios (MMA:styrene must be <1) is

(60) Furukawa, J.; Tsuruta, T.; Inoue, S.; Kawasaki, A.; Kawabata, N. *J. Polym. Sci.* **1959**, *35*, 268–271.

(61) Formed according to the method of: Gilman, H.; Meals, R. N.; O'Donnell, G.; Woods, L. A. *J. Am. Chem. Soc.* **1943**, *65*, 268–270.

(62) True-anionically derived random copolymers of MMA and styrene are not possible because the methyl methacrylate anion does not efficiently attack styrene (see: Graham, R. K.; Dunkelberger, D. L.; Goode, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 400–403); however, copolymers produced by anionic initiation have been reported (see: Landler, I. *J. Polym. Sci.* **1952**, *8*, 63–72 and O'Driscoll, K. F.; Tobolsky, A. V. *J. Polym. Sci.* **1959**, *37*, 363–368). For a more complete discussion of this topic, see: Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983; pp 140–142.

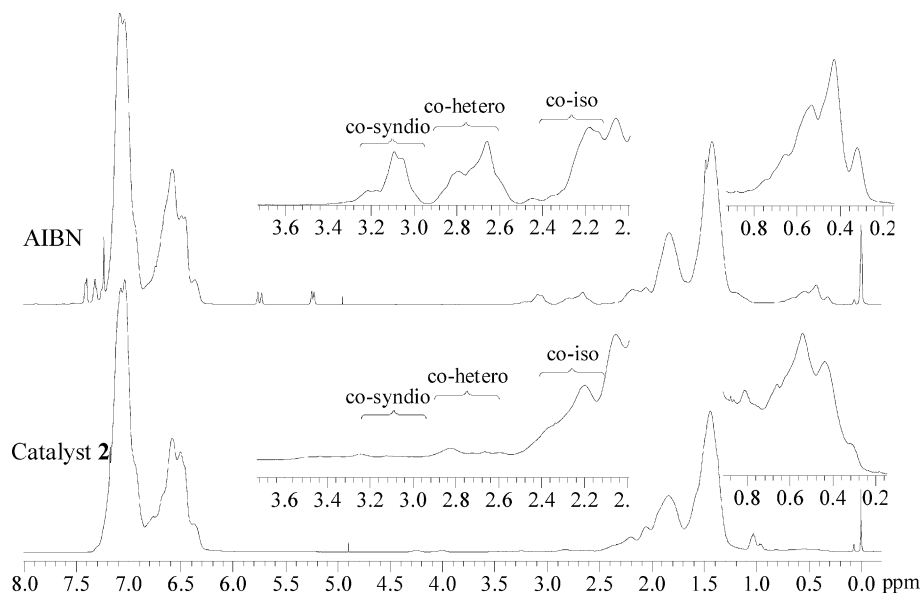
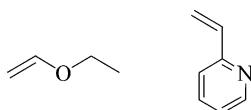


Figure 6. Comparison of the 500 MHz ^1H NMR spectra of styrene + MMA copolymers produced by AIBN initiation (top) and by $\text{Cp}^*\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (bottom).

not characteristic of typical reactivity ratios for radical or ionic systems. That said, known reactivity ratio patterns can be applied to the present feed ratios to determine if the results are mechanistically consistent with a particular copolymerization pathway. To conclusively eliminate the possibility that this polymerization proceeds via a cationic polymerization mechanism, polymerizations with catalyst **2** were carried out in the presence of classic substrates known to be extremely active for cationic polymerizations.⁶³ Two examples are shown below.



The present Ti catalyst system exhibits negligible polymerization activity with respect to these substrates that are typically very reactive in cationic polymerizations.⁶³ This inability to effect the polymerization of known cationic monomers argues that no significant quantities of a cationic active center are generated which can initiate cationic MMA + styrene copolymerization.

Copolymerization of MMA and styrene via radical initiation produces a copolymer, the structure of which is inconsistent with the copolymer produced by catalyst **2**. Thus, an AIBN-initiated 19:1 styrene:MMA copolymerization in toluene yields a product of greatly different comonomer content, ~11% MMA incorporation (consistent with reported reactivity ratios⁶⁴), and macromolecule microstructure. The copolymer produced by AIBN initiation is ~38% coisotactic (Figure 6). Comparison of the ^1H NMR (Figure 6) and ^{13}C NMR data (Figure 7) for the AIBN- and **2**-derived copolymers makes this abundantly clear. Note in Figure 6 that the methoxy and α -methyl regions (the expanded regions in Figure 6) are substantially different.

Radical-initiated polymerization of vinyl chloride by Cp^*TiX_3 + MAO ($\text{X} = \text{Cl}$ or OCH_3 ; MAO = methylaluminumoxane) has

recently been reported.^{2b,65} For optimal performance, the polymerization must be carried out with CH_2Cl_2 as the solvent (toluene affords very low conversions) and with low concentrations of MAO. If the vinyl chloride polymerization is carried out with Cp^*TiMe_3 + MAO (high Al/Ti ratio) in benzene at 80 °C, the only product observed is the coordinative/insertive (coupled with β -chloride elimination) product, atactic oligo-propylene, and negligible poly(vinyl chloride) is detected. Therefore, even though radical polymerizations have been initiated by catalyst systems similar in some respects to catalyst **2**, the present copolymerization conditions (in toluene at 25–50 °C) do not, according to the previous reports,^{2,65} yield significant radical-initiated product.

The foregoing control experiments strongly argue that known styrene and MMA polymerization pathways are not consistent with the characteristics of the **2**-based copolymerization system. Thus, anionic polymerization has reactivity ratios that are inconsistent with those of the present polymerization. The inability of catalyst **2** to effect polymerization of known cationically active monomers is compelling evidence that catalyst **2** does not operate, under the present conditions, in a conventional cationic polymerization mode. Radical polymerizations display reactivity ratios that are close to, but not quantitatively consistent with, those observed here. However, the strongest argument against a radical pathway is the observation of ~80% coisotactic poly(MMA-*co*-styrene), whereas a radical-initiated polymerization under identical conditions yields ~38% coisotactic poly(MMA-*co*-styrene). As a final argument, all of the known mechanisms function properly in polymerizations of MMA and styrene in a 1:1 ratio; however, the present system is only marginally active under these conditions (low activity, exclusive homopolymer formation).

Discussion

The goal of this project was to discover and understand single-site homogeneous catalysts capable of copolymerizing polar and

(63) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111–172.

(64) Allcock, H. R.; Lampe, F. W., Eds. *Contemporary Polymer Chemistry*; Prentice Hall: New York, 1981; pp 48, 271.

(65) (a) Endo, K.; Saitoh, M. *Polym. J.* **2000**, *32*, 300–302. (b) Endo, K.; Kaneda, N.; Waku, H.; Saitoh, M.; Emori, N. *J. Vinyl Addit. Technol.* **2001**, *7*, 177–183.

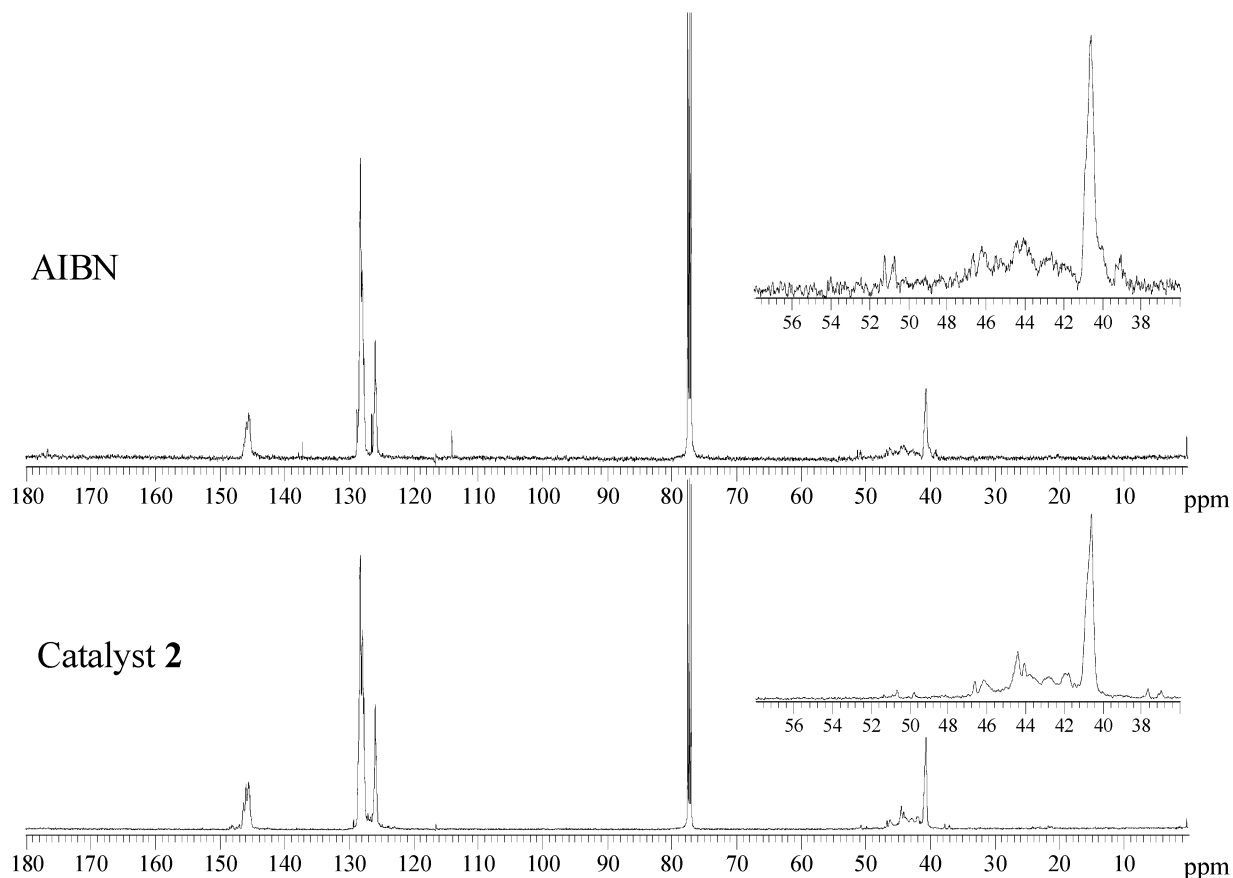


Figure 7. The ^{13}C NMR spectra (CDCl_3 at 25°C) of the styrene + MMA copolymers produced by AIBN initiation (top) and by $\text{Cp}^*\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}^-(\text{C}_6\text{F}_5)_4^-/\text{Zn}$ (bottom).

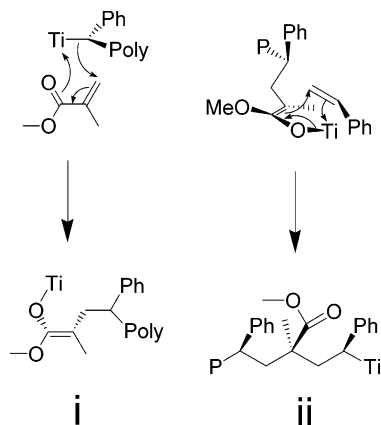
nonpolar olefins. In this section, we first discuss known polymerization pathways for the homo- and copolymerization of MMA and styrene and evaluate their applicability to catalyst **2** phenomenology. Finally, we speculate on possible reaction mechanisms to explain the present findings.

Known Copolymerization Mechanisms of MMA and Styrene. The MMA and styrene copolymerization results with catalyst **2** are inconsistent with known copolymerization mechanisms for these monomers. Anionic copolymerizations of MMA and styrene have been thoroughly documented,^{8,62} and it is well established that in anionic systems, relative MMA:styrene reactivities are far greater than that exhibited by catalyst **2**. Cationic polymerizations have also been extensively studied,⁶³ and the complete inability of catalyst **2** to effect the polymerization of representative, highly reactive cationic monomers is inconsistent with classic cationic reactivity patterns. Radical copolymerization of MMA + styrene is also well documented, and considerable research has been reported on the topic.²⁹ There are two principal reasons why a radical mechanism is incompatible with the present copolymerization phenomenology. First, the difference in product coisotacticity is pronounced, and, equally important, the inability of catalyst **2** to function efficiently at high MMA concentrations relative to styrene is strikingly at variance with typical radical processes. While the MMA incorporation percentages of the radical versus catalyst **2** polymerization in a 1:19 MMA:styrene polymerization (11% vs 4% respectively) are reasonably similar, it is important to note that the two pathways display opposite monomer preferences. When the monomer feed is 5% MMA, the radical process

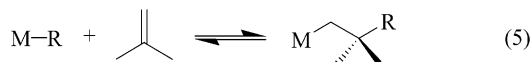
produces a polymer with greater than 5% MMA in the product, while catalyst **2**, in contrast, produces a copolymer with a lower MMA ratio than in the feed. Radical polymerizations typically function across all concentration ratios of MMA and styrene.²⁹

Proposed Mechanism. The control experiments discussed above argue strongly that the present **2**-mediated polymerization pathway is not classical. Known mechanisms are not consistent with the results; however, the observed homopolymerizations of styrene and MMA are readily understood in terms of well-documented pathways (a single-site 2,1-insertion pathway for styrene, and a GTP-like pathway for MMA). Thus, it is attractive to rationalize the copolymerization process discussed here by combining the above homopolymerization mechanisms to yield what is essentially a new pathway. The mechanism of styrene incorporation in the copolymer is not that difficult to rationalize and likely proceeds similarly to the known single-site homopolymerization process (a 2,1-insertion mechanism). The loss of syndiospecific stereocontrol is likely due to the presence of polar coordinating species. In systems such as this, stereocontrol is thought to occur via a chain end control mechanism in which a “multihapto” interaction (**A**, eq 1) is involved with the phenyl π system of the last inserted monomer. If the presence of a polar monomer disrupts this “multihapto” interaction, stereocontrol is likely to be compromised. To test this hypothesis, a styrene homopolymerization with catalyst **2** was carried out in the presence of a 20-fold stoichiometric excess of THF (relative to Ti). In this case, polystyrene is formed with depressed activity and complete loss of stereocontrol; atactic polystyrene is now produced.

Scheme 1. (i) The 1,4-Insertion Mechanism of MMA into a Ti–R Bond,¹⁴ and (ii) the Proposed Insertion Mechanism of Styrene into the Ti–MMA Bond To Form Coisotactic Poly(styrene-co-MMA)



The insertion of MMA into a Ti–R bond has ample literature precedent (Scheme 1, step i)^{14,15} and probably occurs via a 1,4-insertion conjugate addition mechanism (GTP-like, Figure 1); however, this process could, in principle, occur via a 2,1 olefinic insertion. These two possibilities are shown in Figure 8, steps A and B. After MMA insertion into the Ti–styrene bond, enol–keto equilibration can interconvert the products of the two aforementioned insertion processes. As stated earlier, catalyst **2** can mediate MMA homopolymerization via a GTP-like pathway. We suggest that any adjacent MMA units in the copolymer backbone are incorporated this way. The fact that the polymer is ~80% coisotactic means that at least 80% of all MMA insertion events are followed immediately by styrene insertion. This is the next step depicted in Figure 8, steps C and D. Styrene 2,1-insertion into the Ti–MMA bond (keto form; Figure 8, step C) would result in the observed polymer microstructure. We also show the two 2,1-insertions (Figure 8, steps A and C) because they are in principle possible. However, they are unlikely because step A has little precedent. To our knowledge, 1,2-insertion of an α,α -disubstituted olefin at a mononuclear single-site center (eq 5) is rare,⁶⁶ although there is considerable precedent for the microscopic reverse.⁶⁷ Similarly, step C (Figure 8) appears to be unprecedented. We are aware of no reports of α -olefin insertion (either 1,2- or 2,1-) into a metal–tertiary carbon bond.



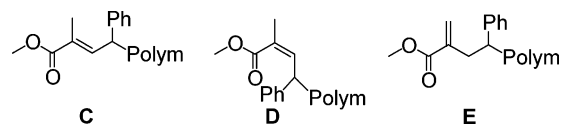
Therefore, we strongly favor step B (Figure 8) as the likely insertion pathway for MMA in the copolymerization process. Step B (Figure 8) is similar to the initiation of all metallocene-catalyzed GTP-like polymerizations of MMA.^{14–20} Note also that 1,2-insertion of MMA is microstructurally inconsistent with the copolymer observed.⁶⁸

The unusual pathway suggested by the present work is shown in step D (Figure 8). First, this process should be exothermic, with ΔH estimated to be ~ -43 kcal/mol + $\{D(\text{Ti}-\text{O})-D(\text{Ti}-\text{C})\}$.³³ The value of $\{D(\text{Ti}-\text{O})-D(\text{Ti}-\text{C})\}$ for Ti^{4+} is $\sim +36.8$

kcal/mol.^{33b} As discussed earlier, one expects $\{D(\text{Ti}^{4+}-\text{O})-D(\text{Ti}^{4+}-\text{C})\} > \{D(\text{Ti}^{<4+}-\text{O})-D(\text{Ti}^{<4+}-\text{C})\}$. Therefore, as an upper limit for step D (Figure 8), $\Delta H < -6.2$ kcal/mol. Moreover, this step is not without precedent. The formation of β -lactams from reaction of Ti enolates with arylimines represents a close analogy (Scheme 2).⁶⁹ Interestingly, it should be noted that the aforementioned reaction proceeds with a high degree of diastereofacial selectivity. This not only provides precedent for step D in Figure 8 but also serves to suggest how coisotacticity is imparted in the copolymerization of MMA and styrene (Scheme 1, step ii).

We suggest that steps B and D (Figure 8) are the most likely propagation steps for this new copolymerization process. They are reasonable as compared to steps A and C (Figure 8) and, importantly, explain the observed coisotacticity and why the copolymerization rate slows at increasing MMA concentrations. At low MMA concentrations, styrene likely competes favorably for Ti coordination/activation, which is then followed by step D (Figure 8). At higher MMA concentrations, the Ti center is likely mostly bound by MMA. While not all mechanistic aspects have been defined, MMA homopolymerization is unstable, with catalyst deactivation within ~ 30 min. Note that MMA homopolymerization is also negligible under dilute conditions. These two factors suggest that once a critical point is reached, and the Ti center is heavily coordinated by MMA, it can no longer efficiently enchain styrene, yet MMA polymerization under these relatively dilute conditions is also sluggish, resulting ultimately in low activity and catalyst deactivation. This is essentially what is observed at 1:1 MMA:styrene ratios.

Let us return to the discussion of whether the MMA incorporated into the copolymer may be simply capped at the polymer terminus.⁷⁰ Any process envisioned for this must be catalytic (>70 polymer chains are produced per Ti). One reasonable way to achieve this would be to propose that after MMA insertion, no further styrene insertion can occur (steps C and D in Figure 8 are prohibited), and eventually β -hydride elimination from the keto form (Figure 8) occurs. There are three possible structures that could result from this β -hydride elimination (**C**, **D**, and **E**). Small molecule analogues of **C** and **D** are known.⁷¹



In the ¹H NMR spectrum, the olefinic proton of **C** should occur at $\delta \sim 5.95$ ppm (the olefinic proton of **D** at $\delta 6.88$ ppm would be obscured by the polystyrene phenyl resonance) and is clearly not visible in the copolymer spectrum (Figure 4). More importantly, the methoxy resonances of both **C** and **D** appear at $\delta 3.60$ ppm, and such features are not present in the copolymer ¹H NMR spectrum (Figure 4). Additionally, the

(66) (a) Li, H.; Li, L.; Marks, T. J.; Liable-Sands, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10788–10789. (b) Shaffer, T. D.; Canich, J. A. M.; Squire, K. R. *Macromolecules* **1998**, *31*, 5145–5147.

(67) (a) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358–10370. (b) Horton, A. D. *Organometallics* **1996**, *15*, 2675–2677.

(68) If 1,2-insertion of MMA occurred, it would place the MMA tertiary carbon adjacent to the phenyl-bearing carbon derived from styrene. This would shift the α -methyl resonance of MMA downfield to $\delta \sim 1.5$ ppm (for a model complex of this structure and ¹H NMR data, see: Dyllick-Brenzinger, R. A.; Patel, V.; Rampersad, M. B.; Stothers, J. B.; Thomas, S. E. *Can. J. Chem.* **1990**, *68*, 1106–1115). Because the integrals of the methoxy and α -methyl regions of MMA are similar, this means that $>95\%$ of MMA insertion cannot be 1,2-insertion.

(69) Fujisawa, T.; Ukaji, Y.; Noro, T.; Date, K.; Shimizu, M. *Tetrahedron Lett.* **1991**, *32*, 7563–7566.

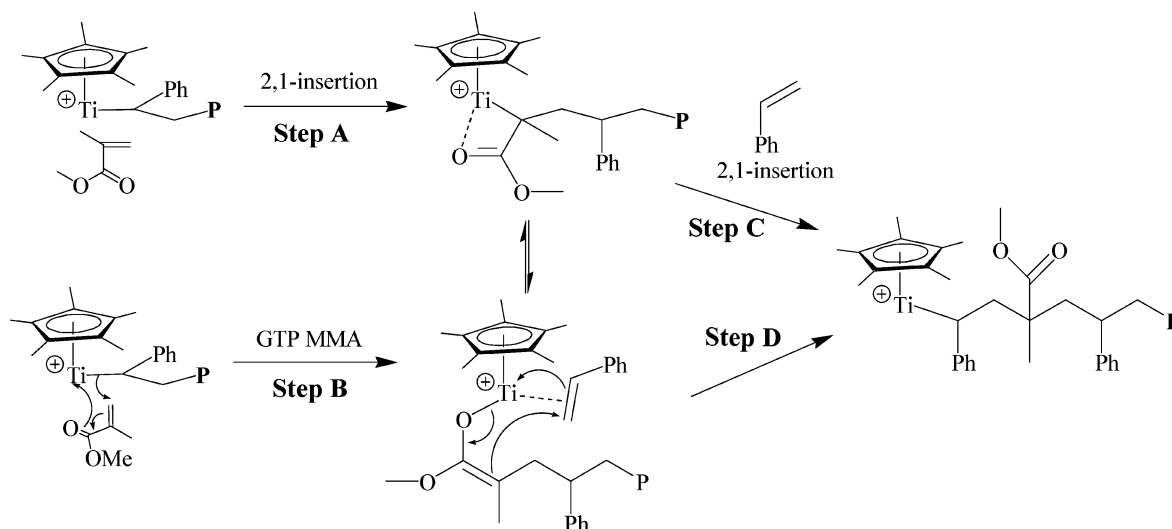
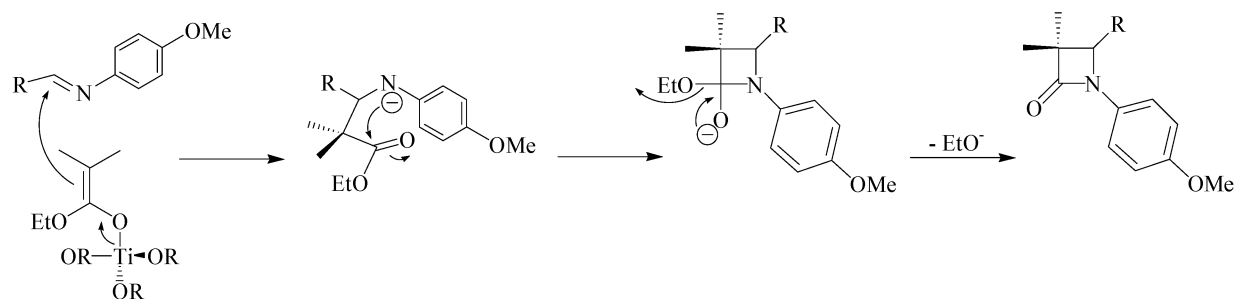


Figure 8. Proposed pathway for MMA insertion into a Ti-styryl bond and subsequent insertion of styrene into a Ti-MMA bond.

Scheme 2. Proposed Pathway for β -Lactam Formation from the Reaction of a Titanium Enolate and an Aryl Imine⁶⁹



α -methyl resonances of **C** and **D** are both downfield of δ 1.2 ppm. While the ^1H NMR spectrum of a small molecule analogue of **E** has not been reported, it seems reasonable to assume that the methoxy peak will be at $\delta \sim 3.60$ ppm, similar to **C** and **D**, and the α -methylene signal will be downfield of δ 1.0 ppm. In sum, the ^1H NMR spectrum of the copolymer appears quite inconsistent with an MMA-capped polystyrene chain, whereas it is in good agreement with the published spectra of random MMA and styrene copolymers.^{29d,30} Therefore, the MMA unit is primarily located in the interior of the copolymer chain and not at the terminus.

Summary

A new single-site organotitanium catalyst has been developed which efficiently mediates the polymerization of styrene and MMA to the corresponding high molecular weight syndiotactic homopolymers as well as the copolymerization of styrene and MMA to a coispecific random sequence macromolecule. The homopolymerizations are consistent with the established GTP-like polymerization pathway for MMA and with the well-

documented stereospecific 2,1-insertion pathway for styrene. Control experiments argue that known copolymerization mechanisms of MMA and styrene cannot explain the copolymerization results. Rather, a new polymerization mechanism is proposed to explain the characteristics of the copolymer formation. This new mechanism involving sequential conjugate addition steps explains the stereospecificity of the catalyst system as well as the general reactivity patterns. Further extending the scope of such polar + nonpolar olefin copolymerization processes depends on two elements: (1) a nonpolar monomer that competes relatively well with the polar monomer in the activation/enchainment process, and (2) that $\{D(L_nM-O)-D(L_nM-C)\}$ be sufficiently small to allow nonpolar monomer insertion. Note that for Zr^{4+} , step D of Figure 8 is approximately thermoneutral. Following these guidelines may lead to new and interesting catalytic systems as well as completely new macromolecules.

Acknowledgment. We thank DOE(86ER13511) and BP Chemicals for support of this research. We thank Drs. A. E. Ernst, N. Kaminskaya, L. R. Satek, and L. S. Tee of BP Chemicals for helpful discussions.

Supporting Information Available: Complete experimental procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(70) The vinyl end groups of polystyrene ($\delta \sim 6.4$ ppm) are obscured by the phenyl region in the ^1H NMR. The peaks at $\delta \sim 4.1$ and ~ 4.35 ppm are unrelated to MMA; they are also observed in homo styrene polymerizations. The $\delta \sim 4.1$ ppm resonance was shown to arise from a contaminant, 1,1-diphenylethane. For the above assignments, see: Charleux, B.; Rives, A.; Vairon, J.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 5777–5783.

(71) Etemad-Moghadam, G.; Seyden-Penne, J. *Tetrahedron* **1984**, *40*, 5153–5166.