Synthesis and Mechanism of Formation of Syndiotactic Polystyrene Using a (*tert*-Butylcyclopentadienyl)titanium Complex

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ABSTRACT: Polymerization of styrene in the presence of [Ti(η^5-$C_5H_4{}^tBu$)Cl_3]-methylaluminoxane has been investigated. The resultant polymer is essentially 100% syndiotactic polystyrene (SPS; by NMR and differential scanning calorimetry measurements) and of narrow polydispersity (*ca.* 2.0−2.2). Analysis of SPS using matrix-assisted laser/desorption ionization time-of-flight mass spectrometry demonstrates that polymer chains have both methyl and ethyl end groups, indicating that the SPS is formed by both "Ti^+-H" and "Ti^+-Me" initiators. These mass spectral data, together with NMR data, confirm that the major mode of chain growth termination is *via* β-H transfer. The polymer molecular weight is dependent on the temperature of polymerization: at 0 °C, $M_n = 26 \times 10^3$ (by NMR and size exclusion chromatography), whereas at 65 °C, $M_n = 4 \times 10^3$. Semilogarithmic plots of consumption of styrene with time are linear over the initial part of the polymerization, indicating that the number of active titanium centers remains constant during this time. Increasing the quantity of styrene results in an identical conversion (percentage), suggesting that propagation is favored over termination processes.

Introduction

Since the first report describing the room-temperature synthesis of syndiotactic polystyrene (SPS) by Ishihara *et al.* in 1986,[1] there has been great interest in the identification of homogeneous organometallic complexes capable of efficient and stereoregular polymerization of styrenes. SPS is a crystalline material with far superior heat and chemical resistance properties than atactic PS, and as such it has potential for a range of applications in the electronics and engineering industries.[2] Recent advances have identified mono(η^5-cyclopentadienyl) complexes of the group 4 metals as efficient styrene polymerization catalysts and have shown that, while [Zr(η^5-C_5H_5)]-based systems are often poorly syndioselective, related titanium complexes are effective at promoting polymer stereocontrol.[3] The pentamethylcyclopentadienyl complex [Ti(η^5-C_5Me_5)Me_3], when activated by $B(C_6F_5)_3$, is active for the polymerization of various hydrocarbon monomers, including styrene.[4] In a recent study, Pellecchia *et al.* presented good evidence that syndiospecific polymerization of styrene by [Ti(η^5-C_5Me_5)Me_3] occurs via a coordination−2,1-insertion mechanism.[5]

As part of our studies directed at the synthesis of chiral-at-metal titanium complexes, we have developed an efficient synthesis of the *tert*-butylcyclopentadienyl complex [Ti(η^5-$C_5H_4{}^tBu$)Cl_3] (**1**).[6] In this paper, we report results that demonstrate that **1**, in conjunction with methylaluminoxane (MAO), is an extremely active, homogeneous polymerization catalyst which produces highly syndiotactic (>99%) polystyrene at ambient temperature with relatively narrow polydispersity (2.0−2.2), in good yield (*ca.* 90%). We also present definitive mass spectrometric evidence showing that styrene polymerization is initiated by both "Ti^+-Me" and "Ti^+-H" species, which requires the principal chain growth termination step to be a unimolecular β-hydrogen transfer reaction.

Experimental Section

General Methods and Materials. All reactions were carried out using standard Schlenk and glovebox techniques under atmospheres of nitrogen or argon. Toluene was distilled under nitrogen from molten sodium. Styrene was distilled from calcium hydride under reduced pressure and stored at 5 °C under nitrogen in the dark. [Ti(η^5-$C_5H_4{}^tBu$)Cl_3] and methylaluminoxane (MAO) were prepared as described previously.[6,7]

Polymer samples were characterized by high-temperature SEC (140 °C) measurements using a Waters 150C instrument. Two Polymer Laboratories PLgel 10 μm mixed-B columns (300 mm) were employed and calibrated with atactic polystyrene standards. Analysis was carried out using 1,2-dichlorobenzene as eluant at 1 mL/min. DSC measurements were carried out using a Netzsch 404 calorimeter.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry was carried out using a Kratos Kompact III spectrometer in reflection mode. Samples were prepared as follows: two 0.4 mL aliquots of 9-nitroanthracene in acetone/water (1×10^{-3} M $C_{14}H_9NO_2$ in 80:20 v/v solution), doped with 1×10^{-3} M $AgSO_3CF_3$, were deposited on a sample slide and dried. Two 0.4 μL aliquots of SPS solution (1 mg mL^{-1} in tetrachloroethane) were subsequently added to the sample slide and dried. MALDI-TOF-MS analysis of such samples results in each polystyrene macromolecule being observed as an Ag^+ adduct at M + 108 Da. The spectrometer was calibrated using bovine insulin (5734), Na (23.99), and K (39.10) ions. The widths of the polymer peaks were approximately 5 Da at half-peak height.

Polymerizations. Styrene polymerization reactions were carried out in 500 mL Schlenk tubes equipped with a magnetic stirrer. In a typical experiment, toluene (100 mL), styrene (5 mL, 43.6 mmol), MAO (1.33 g, 23 mmol), and **1** (10 mg, 36 μmol) were added sequentially. During the reaction, some polymer was seen to precipitate from solution. After the reaction was complete, polymerization was terminated by the addition of *ca.* 30 mL of 5% HCl in methanol, which caused the precipitation of more product. The precipitated polymer was washed with methanol and dried *in vacuo* at 60 °C to constant mass. The mass of polymer produced was reproducible to ±5%. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 7.07 (m, 3H, *meta-* and *para*-H), 6.59 (m, 2H, *ortho*-H), 1.89 (m, 1H, CH), 1.38 ppm (m, 2H, CH_2). ^{13}C NMR (100.6 MHz, $C_2D_2Cl_4$): δ 144.9 (C_{ipso} of Ph), 127.4, 127.3 (*ortho-* and *meta*-CH of Ph), 125.0 (*para*-CH of Ph), 43.7 (CH), 40.5 ppm (CH_2). Combustion

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† Principal author, deceased.

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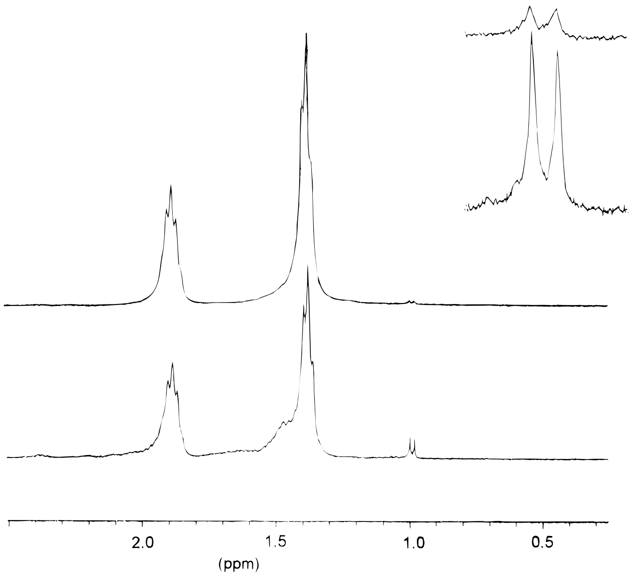
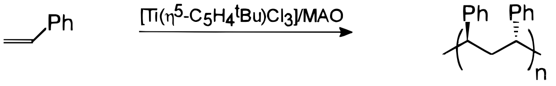


Figure 1. Part of the ^1H NMR spectra of SPS prepared at 0 °C (top) and 65 °C (bottom). The major resonances at δ 1.89 and 1.38 ppm are due to the CH and CH_2 groups of the SPS backbone. The resonance at δ 0.99 ppm, assigned to the methyl end group, is also shown expanded.

analysis indicated polystyrene samples to be analytically pure. Anal. Calcd: C, 92.26; H, 7.74. Found: C, 91.60; H, 7.72.

Results

Mixtures of $[Ti(\eta^5\text{-}C_5H_4{}^tBu)Cl_3]$ (**1**) and methylaluminoxane are active catalysts for the polymerization of styrene, eq 1. In our standard experiment, 5 mL of



(1)

styrene is converted to 3.78 g of PS over a period of hours (typically 5 h, giving 84% yield) using 10 mg of **1** and *ca.* 500 mol equiv of MAO; we have found that 10 mL of styrene, under identical conditions, yields 7.79 g (86% yield) of PS. The polymer so produced is insoluble in ketones (greater than 96% of polymer was recovered after extraction with boiling acetone) but soluble in 1,1,2,2-tetrachloroethane at elevated temperatures, indicating the PS to be highly stereoregular and of relatively high molecular weight. ^1H and ^{13}C NMR spectra ($C_2D_2Cl_4$ solution at 373 K, Figure 1) confirm this, clearly showing the polymer to be essentially 100% syndiotactic in nature.[8] Thus, complex **1** has an important role in determining polymer stereochemistry.

Mass averages of SPS prepared using **1**/MAO, measured using size exclusion chromatography, are presented in Table 1. The molecular weight of polymer so produced is temperature-dependent; thus, performing the polymerization reaction at higher temperatures yields SPS of lower molecular weight and slightly narrower polydispersity. These M_n data indicate that the rate of chain transfer, R_{CT}, increases more rapidly than the rate of propagation, R_p, as the temperature is raised. The fairly narrow polydispersities, in the range 2.0–2.6, are consistent with homogeneous, single-site catalysis.

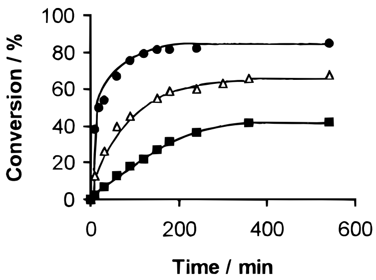


Figure 2. Increase in SPS yield with time of polymerization, at 0 °C (■), 25 °C (△), and 65 °C (●).

The ^1H NMR spectra of SPS prepared at 25 and 65 °C contain a small doublet at 0.98 ppm ($J_{HH} = 6.9$ Hz), which we assign to the methyl end group (Figure 1). Analysis of the relative intensities of this resonance compared with the methine resonance at 1.89 ppm (*ca.* 1:250 and 1:36, respectively) provides alternative estimates of number-average molecular weights of polymer samples; calculated values of 26×10^3 and 4×10^3 are in excellent agreement with SEC data ($M_n = 26.3 \times 10^3$ and 4.5×10^3, respectively).

We have investigated the rate of conversion of styrene to SPS with time at different temperatures. Figure 2 presents time–conversion plots which show that (i) the polymer yield increases with increasing temperature; (ii) the initial polymerization rate increases with increasing temperature; and (iii) the polymerization rate at a particular temperature decreases over time, suggesting relatively slow deactivation of the active titanium species during the course of the reaction. The polydispersity of SPS is essentially independent of conversion but does vary somewhat according to the temperature of polymerization.

The molecular weight dependence of the SPS is illustrated in Figure 3. Number-average molecular weights are clearly dependent on the temperature at which the polymerization is carried out (Figure 3a). Thus, the M_n of SPS produced at high temperatures very rapidly reaches a maximum at *ca.* 5×10^3 and thereafter decreases slightly as the styrene is consumed. In contrast, SPS produced at 0 °C shows gradually increasing M_n throughout the time the polymerization system is active (Figure 3). These SEC data are broadly similar to those reported for the unsubstituted analogue. The molecular weights of SPS samples are somewhat smaller, which may be a reflection of the more crowded titanium center (see Discussion). While the catalyst activation processes are complicated, radiolabeling studies on related systems show that active species are formed rapidly,[3e] and as such we assume that rapid activation occurs here. Thus, these data are consistent with a chain transfer step that becomes progressively more important as the temperature is increased. The semilogarithmic plot shown in Figure 4 (for SPS pro-

Table 1. Styrene Polymerization Results Using 1/MAO

run	temp (°C)	styrene (mL)	yield (g)/ conversion (%)	M_n (SEC)	M_n (NMR)	M_w/M_n	T_m (°C)[a]	% insoluble in boiling acetone
1	0	5	2.62/54	38 900		2.6	269	>96
2	25	5	3.78/84	26 300	26 000	2.2	265	>96
3	25	10	7.79/86					
4	65	5	4.32/39	4500	4000	2.1	244	70

[a] First melt. DSC traces show additional features very similar to those previously reported for SPS.[3e]

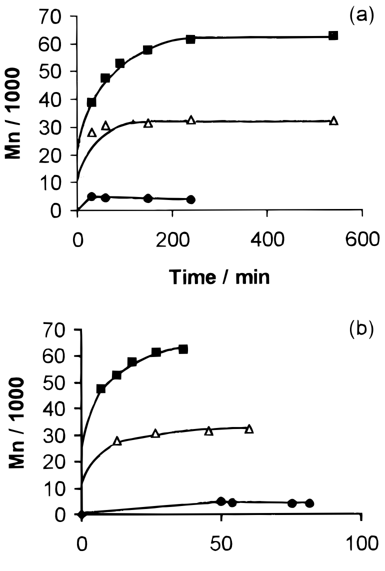


Figure 3. Variation of M_n with (a) time of polymerization and (b) conversion, at 0 °C (■), 25 °C (△), and 65 °C (●).

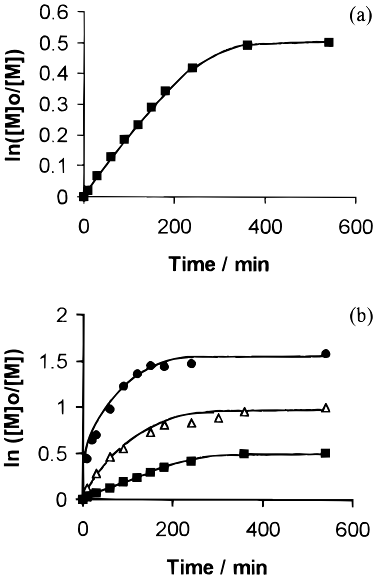


Figure 4. Semilogariathmic plot showing consumption of styrene with time, at (a) 0 °C and (b) 0 °C (■), 25 °C (△), and 65 °C (●).

duced at 0 °C) is initially linear but tails off with time; the linear (*i.e.*, pseudo-first-order) behavior indicates that the concentration of active titanium centers is constant for most of the time the system is active.[9] However, decomposition processes slowly remove the active titanium centers, and thus the rate of polymerization eventually falls away as the reaction progresses. This pattern of behavior is also seen at higher temperatures, Figure 4b. At 65 °C, the polymerization remains first-order in titanium at styrene conversions in excess of 80%.

Thermal analysis by differential scanning calorimetry of SPS prepared at different temperatures (Table 1) indicates that the melting points decrease as the temperature of polymerization increases. Thus, while the melting point of SPS prepared at 0 °C is 269 °C (cf. Ishihara's report of 272 °C[10]), the melting point is lowered to 244 °C when SPS is produced at 65 °C. NMR spectra show evidence for a loss of stereocontrol by **1**/MAO at higher temperatures, which might account for the lower T_m.[3e]

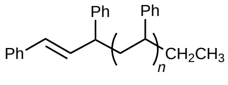
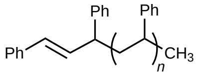
The low-molecular-weight polymer produced at 65 °C ($M_n \approx 4000$) is suitable for matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analysis.[11] The mass spectrum shown in Figure 5 shows two series of peaks characterising low-molecular-weight SPS, with regular peak-to-peak separations of 104.26 ± 0.73 Da (molecular mass of styrene = 104.15 Da). The major and minor series, beginning at 838 and 853 Da, respectively, are separated by 14–15 Da (average 14.8 ± 1.2 Da), which is consistent with an extra methylene group in the higher molecular weight polymer. Table 2 presents plausible macromolecular structures that might be produced by **1**/MAO and styrene. It is clear that the major polymer series present in the SPS sample was formed by a "Ti$^+$-H"-based initiator and that the minor polymer series was formed by a "Ti$^+$-Me"-based initiator. Given that the full width at half-maximum height of each peak of *ca.* 4.5 Da, the agreement between observed and calculated molecular masses is satisfactory. We are unable to distinguish between saturated and unsaturated end groups using these spectra due to the resolution limitation. However, ^{1}H and ^{13}C NMR spectra clearly demonstrate the presence of vinylic end groups in the polymer samples, with a weak resonance at 6.07 ppm (^{1}H NMR spectrum), together with weak resonances at 128.6 and 133.3 ppm (^{13}C NMR spectrum) being good evidence for unsaturated groups.[12] The ^{1}H NMR spectra also support the presence of methyl end groups in the majority of SPS chains *(vide supra).*

MALDI-TOF-MS of polymers can be mass-sensitive, especially where $M_w/M_n > 1.2$.[13–15] The mass spectrum of SPS does not necessarily show the complete envelope of the mass distribution but is probably biased toward low-mass macromolecules.[13] However, the spectrum in Figure 5 clearly shows the macromolecular structure over a wide range of degree of polymerization. Thus, we are confident that the mass spectrum, the first reported for SPS, gives a true representation of the polymer structure over the entire mass range.

Discussion

The role of half-sandwich titanium complexes in styrene polymerization has been of considerable interest recently.[3] The η^5-cyclopentadienyl ligand is believed to be retained by the titanium during the reaction. The

Table 2. Structures and Molecular Masses of SPS

			obsd (calcd) molecular masses (Da)	
initiator	polymer formula	MW of Ag$^+$ complex	$n = 6$	$n = 7$
Ti$^+$-Me		n(104.15) + 330.20	956.5 (955.1)	1061.4 (1059.3)
Ti$^+$-H		n(104.15) + 316.20	942.0 (941.1)	1046.4 (1045.3)

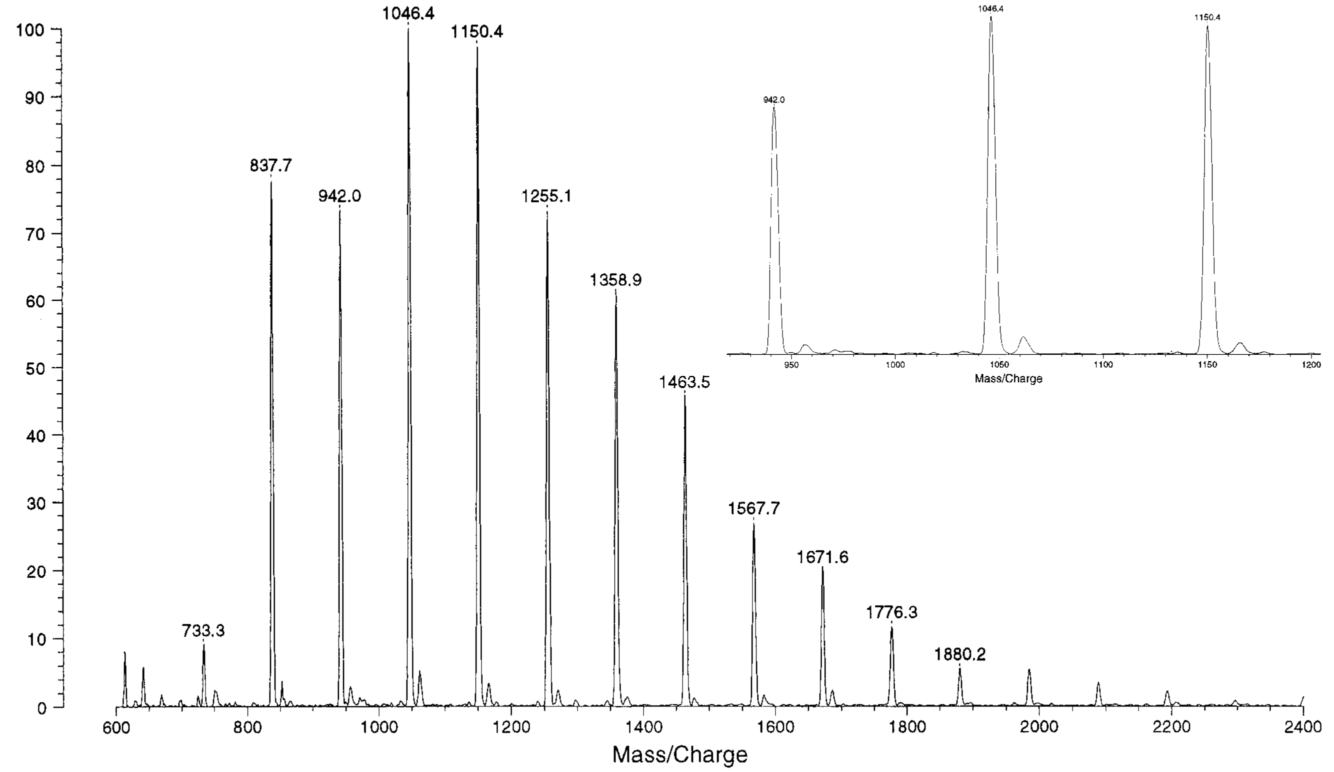
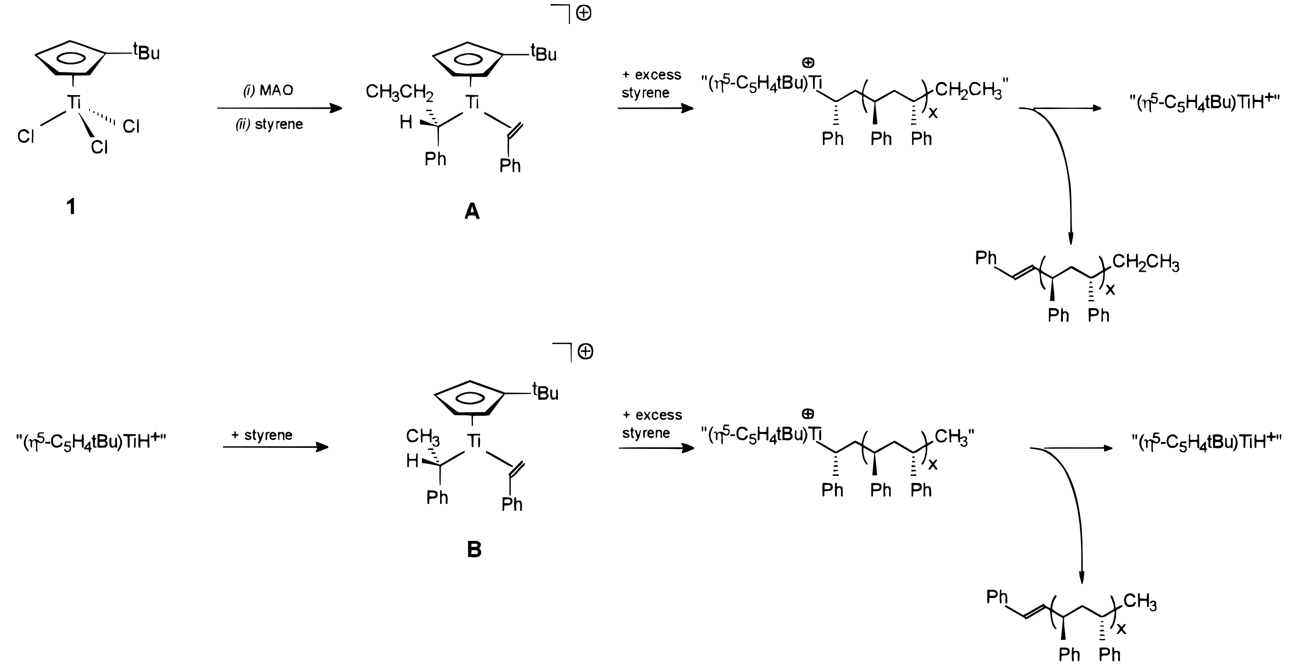


Figure 5. MALDI-TOF spectrum of low-molecular-weight SPS showing polymer chains initiated by "Ti$^+$-Me" (minor series beginning at 751 Da) and "Ti$^+$-H" (major series beginning at 733 Da) species. All macromolecules are detected as Ag$^+$ adducts.

Scheme 1



consensus is that the active titanium species is a cationic titanium(III)alkyl complex, as demonstrated by EPR spectroscopy.[16] It has been suggested that Ti(III)-alkyl complexes polymerize styrene syndiospecifically, whereas the Ti(IV) precursor produces atactic polymer.[17]

Propagation occurs *via* secondary insertion of styrene into the titanium−alkyl bond, as shown in Scheme 1.[5] The intermediates proposed in the scheme have not been identified but are invoked to account for the polymer structures observed. As such, their detailed nature remains unknown. The first insertion product, **A**, may be stabilized by an η^2-benzyl interaction, well-known in early transition-metal benzyl complexes, or by agostic interactions.[18] The suggestion that addition of MAO to **1** leads to the reduction of the Ti(IV) precursor to the active Ti(III) species is consistent with the observation that solutions of **1** and MAO in toluene become dark green. However, at this stage, we have no data to establish the degree of reduction. The orientation of the styrene monomer is governed by the ^{t}Bu group such that the phenyl group of the coordinated monomer is "down", such that it is oriented as far from the $C_5H_4{}^tBu$ ligand as possible. In principle, coordination of the prochiral styrene to the titanium leads to the formation of diastereomers, since the α-carbon is chiral; however, the stereoregularity of the SPS product suggests that the titanium selects only one face of the incoming monomer. In this respect, the bulky *tert*-butylcyclopentadienyl ligand is expected to provide enhanced control of polymer tacticity, compared with the unsubstituted η^5-C_5H_5 analogue, as observed.[19] However, the selectivity is somewhat diminished at higher temperatures. Our and other reported[12] NMR data show that one end group of the product polymer is unsaturated, indicating that the major mode of chain growth termination is *via* a β-hydrogen transfer mechanism, leading to the formation of a cationic titanium(III) hydride. The first SPS chain so formed has an ethyl group as the second end group. Subsequent initiation of a second chain occurs by a complex of form **B**, which acts in a manner similar to **A**. SPS chains formed in this way have methyl end groups. MALDI mass spectra do, in fact, show the presence of both methyl and ethyl end groups in SPS samples. Assuming that each active titanium center is responsible for up to several hundred SPS chains on average, SPS chains with methyl end groups are expected to form the major component of the polymer sample. This is demonstrated by our mass spectral data.

The existence of mononuclear titanium(III) hydride complexes is demonstrated by the recent structural characterization of the first example, $[Ti(\eta^5\text{-}C_5Me_4Ph)_2H]$, which is stabilized by the bulky peralkylated cyclopentadienyl ligands.[20] The decreasing rate of polymerization by **1**/MAO (Figure 2) may be interpreted as the slow deactivation of the "$[Ti(\eta^5\text{-}C_5H_4{}^tBu)H]^+$" cation, which is presumably sterically somewhat more accessible than related bis-cyclopentadienyl complexes and, therefore, more susceptible to associative attack. However, given that doubling the quantity of monomer in polymerization reactions at 25 °C results in an essentially identical percentage yield of SPS, we infer that trapping "$[Ti(\eta^5\text{-}C_5H_4{}^tBu)H]^+$" by styrene is an extremely competitive reaction compared with deactivation and, indeed, much the favored process at higher temperatures.

Conclusion

Mixtures of $[Ti(\eta^5\text{-}C_5H_4{}^tBu)Cl_3]$ and MAO are active for the syndiospecific polymerization of styrene. The molecular weight and polydispersity of the SPS so formed may be controlled by varying the temperature. DSC measurements indicate that polymerizations carried out at higher temperatures result in poorer control over styrene orientation. MALDI-TOF-MS data show that SPS samples contain both methyl and ethyl end groups, indicating that the major mechanism of chain termination is *via* β-hydrogen transfer, and that the resultant Ti^+-H species initiates further chain growth. Further support for such conclusions is provided by NMR spectroscopy. Experiments concerning the reactivity of Ti(III) species for olefin polymerization are under way.

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