Organosilane Effects on Organotitanium-Catalyzed Styrene Polymerization

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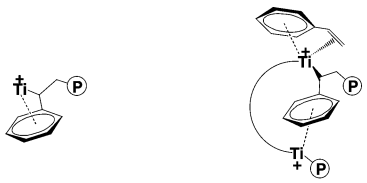
Received January 10, 2007

Summary: Organosilane reagents are introduced into organotitanium-mediated styrene polymerizations to produce atactic polystyrene with high activities (up to 10^6 g polymer/(mol Ti·h)) and narrow polydispersities. Previously recognized CGCTiMe$_2$ systems having marginal styrene homopolymerization activity are shown to be up to 3 orders of magnitude more active for styrene homopolymerization upon addition of organosilane.

Polystyrenes have a multitude of useful applications such as anticorrosion coatings, thermoplastics, and foams.[1] Over the past decade, methods to produce, control, and understand single-site styrene polymerization processes have been widely explored.[2] Although many advances have been made in understanding the polymerization mechanism(s), only a relatively restricted class of catalysts is known to efficiently mediate styrene polymerization.[3] While Cp′TiXYZ-derived catalysts (Cp′ = substituted or unsubstituted cyclopentadienyl; X, Y, Z = Cl, alkyl, alkoxy, etc., ligand) are among the most effective,[4] the active species are not well-defined and there is debate concerning how many and what the active species may be.[5] In contrast, *ansa*-amido monocyclopentadienyl Ti constrained geometry catalysts (CGCs) are known to be virtually inactive for styrene homopolymerization.[5d,6] It is thought that this inertness is a consequence of catalyst inactivation/binding by the phenyl ring π-system of a 2,1-inserted monomer unit (e.g., **A**).[5d,6] Previous work from this laboratory showed that increasing the CGC catalyst nuclearity can significantly overcome these constraints by a process that is thought to involve preferential binding of the last inserted (inactivating) styrene to the adjacent Ti-center (e.g., **B**).[7] These observations raise the intriguing question of whether a similar polymerization rate effect could be achieved via addition of a weakly basic reagent instead of altering the catalyst nuclearity, to weaken the competing π-complexation. We report here that alkenyl-, aryl-, and alkysilane addition to mononuclear CGCTiMe$_2$-mediated polymerization processes results in very large activity increases for styrene homopolymerization.



A **B**

All polymerizations were carried out under rigorously anhydrous/anaerobic conditions using procedures minimizing mass transport effects,[8] with pseudo-zero-order [styrene] and [organosilane]. A typical styrene + organosilane copolymerization proceeds by charging a polymerization reactor, which has been dried overnight at 160 °C, with 50 mL of dry toluene. The reactor is next attached to a high-vacuum line and the toluene is freeze−thaw−degassed. Styrene (10.0 mL) is vacuum-transferred into the flask immediately prior to polymerization, followed by introduction of argon (1.0 atm) with rapid stirring. Next, organosilane (6.0 mmol) is injected into the reactor with rapid stirring and positive Ar pressure. In the glovebox, the active catalyst solution is prepared with 3.5 mg (0.011 mmol) of Me$_2$Si(Me$_4$C$_5$)(^{t}BuN)TiMe$_2$, 9.22 mg (0.010 mmol) of

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10.1021/om0700260 CCC: $37.00
Publication on Web 05/15/2007

Table 1. CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-Mediated Styrene Homopolymerization

entry	organosilane/comonomer	[organosilane] (mM)	activity[c] ($\times 10^4$)	M_n[d]	M_w/M_n[d]	T (°C)	T_g (°C)	tacticity[e]
1			0.10	5500	1.9	25	104	atactic
2	allylsilane	100	18.0	5200	2.0	25	100	atactic
3	3-butenylsilane	100	1.00	8100	2.3	23	85	atactic
4	5-hexenylsilane	200	120	5600	3.3	30	100	atactic
5	7-octenylsilane	100	100	4400	1.8	32	98	atactic
6	*n*-hexylsilane	50	5.20	4100	1.8	28	100	atactic
7	*n*-hexylsilane	100	10.0	4500	1.6	26	95	atactic
8	*n*-hexylsilane	200	11.0	3700	1.8	24	95	atactic
9	*n*-hexylsilane	400	11.0	3700	1.7	23	97	atactic
10	di-*n*-hexylsilane	100	10.0	3900	2.0	23	95	atactic
11	tri-*n*-hexylsilane	100	13.0	10 500	2.3	23	98	atactic
12	tetramethysilane	100	0.10	3800	2.0	24	102	atactic
13	phenylsilane	100	30.0	9600	2.4	25	95	atactic
14	tetraphenylsilane	100	0			23		
15	1-hexene		0.38	3000	2.0	24	110	atactic

[a] CGC = Me$_2$Si(Me$_4$C$_5$)(N^{t}Bu); polymerization conditions: 50 mL of toluene, 60 min. [b]Cocatalyst = 10 μmol of Ph$_3$CB(C$_6$F$_5$)$_4$; catalyst = 10 μmol. [c]Units = g/(mol Ti·hr). [d]By GPC in 1,2,4-trichlorobenzene vs polystyrene standards. [e]Tacticity based on ^{13}C NMR spectra.

Table 2. EBICGCTi$_2$Me$_4$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-Mediated Styrene Homopolymerization

entry	organosilane/comonomer	[organosilane] (mM)	activity[c] ($\times 10^4$)	M_n[d]	M_w/M_n[d]	T (°C)	T_g (°C)	tacticity[e]
1			5.87	4800	2.1	27	83	atactic
2	allylsilane	100	28.6	4100	1.9	26	76	atactic
3	3-butenylsilane	100	1.90	6200	1.9	22	105	atactic
4	5-hexenylsilane	200	1.00	3900	1.7	25	97	atactic
5	7-octenylsilane	100	1.00	7000	1.5	25	98	atactic
6	*n*-hexylsilane	200	2.00	4600	1.9	27	101	atactic

[a] CGC = Me$_2$Si(Me$_4$C$_5$)(N^{t}Bu); EBI = ethylene-bridged bis(indenyl); polymerization conditions: 50 mL of toluene, 60 min. [b]Cocatalyst = 10 μmol of Ph$_3$CB(C$_6$F$_5$)$_4$; catalyst 10 μmol. [c]Units = g/(mol Ti·hr). [d]By GPC in 1,2,4-trichlorobenzene vs polystyrene standards. [e]Tacticity based on ^{13}C NMR spectra.

Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$, and 4 mL of toluene. The catalyst solution is rapidly syringed through a septum-sealed sidearm into the rapidly stirring reactor. After 60 min, methanol (5 mL) is injected to quench the reaction. Excess methanol (~500 mL) is then used to precipitate the polymer. The polymer is collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h. Polymeric products were characterized by ^{1}H/^{13}C NMR, GPC, and DSC; data are compiled in Tables 1 and 2.

The results of the CGCTiMe$_2$-mediated styrene homopolymerization experiments (Table 1) reveal a dramatic increase in polymerization activity upon organosilane addition. Under identical conditions, CGCTiMe$_2$-mediated styrene homopolymerization activities are up to 3 orders of magnitude greater in the presence of alkenyl-, aryl-, or alkylsilanes than styrene homopolymerization in the absence of silane. All product polymers exhibit a single endothermic DSC feature between 80 and 105 °C, the characteristic glass transition temperature (T_g) region for atactic polystyrene (Table 1, entries 1−9).[9] ^{1}H and ^{13}C NMR spectra exhibit characteristic broad resonances at δ 2.2 and 145 ppm, respectively, also indicating atactic polystyrene (Figure 1). Furthermore, monomodal GPC traces with polydispersities of ~2.0 argue that these homopolymers are produced exclusively via a coordinative/insertive single-site pathway and that silane addition has little effect on product M_n. In accord with this latter observation, there is insignificant incorporation of alkenylsilane into the polymer chain as a comonomer under these conditions as well as insignificant polystyrene end-capping via silanolytic chain transfer,[10] as judged by NMR spectroscopy (Figure 1). Although radical polymerization processes typically result in very broad product polydispersities, under certain conditions such polymerizations

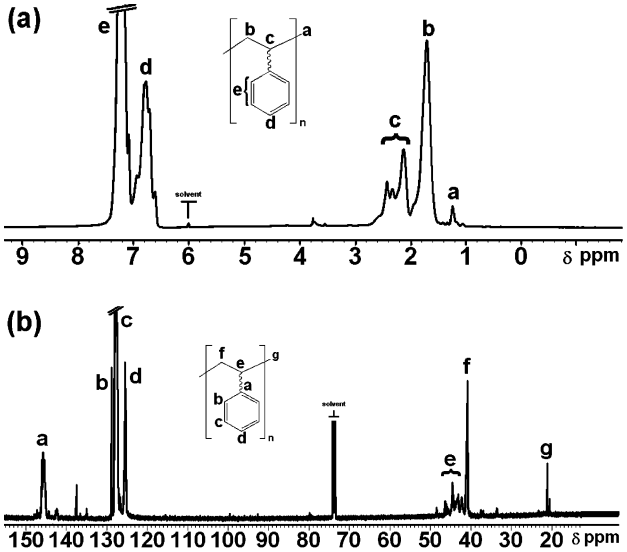

Figure 1. (a) ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$) spectrum and (b) ^{13}C NMR (100 MHz, C$_2$D$_2$Cl$_4$) spectrum of the styrene homopolymer produced by CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ in the presence of an organosilane.

can also afford narrow polydispersities.[11] To eliminate the possibility of radically initiated polymerization, control polymerizations were performed with AIBN and 5-hexenylsilane and are discussed in detail below. In addition, note that radically initiated styrene polymerizations typically result in product polymers devoid of vinyl end-groups.[11] In the present polymerization systems, the polymer products contain styrenic vinyl

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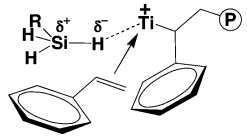
resonances, as verified by ^{1}H NMR spectroscopy (Figure S3).[8] In addition, known styrene + ethylene copolymerizations were performed in the presence of organosilanes and these yield copolymer products in agreement with the literature.[7b,10b,c] Under similar conditions, radical copolymerizations inititiated with AIBN do not yield styrene + ethylene copolymers, whereas styrene + ethylene copolymerizations mediated by CGC catalysts in the presence of organosilane evidence up to 50 mol % styrene incorporation into the polyethylene chain, consistent with a coordinative/insertive pathway.[7b,10b,c]

To minimize the possibility of cationic polymerization pathways,[2f,12] a slight excess of catalyst:cocatalyst is always used to ensure complete $Ph_3C^+B(C_6F_5)_4^-$ consumption.[7b] The homopolymers produced in the presence of organosilanes have three significant regiochemical signatures, the relative abundances of which are consistent with a coordinative/insertive pathway (Figure 1b).[13,14] Thus, ^{13}C NMR end-group analysis reveals three polystyrene microstructures. The resonance at δ 21.2 ppm indicates 2,1-insertion followed by a second 2,1-insertion of styrene monomer,[16] while the resonance at δ 21.8 ppm results from a 2,1-insertion followed by a 1,2-insertion of styrene monomer.[16] Finally, the resonance at δ 34 ppm indicates a 1,2-insertion followed by a second 1,2-insertion of monomer.[7,14] The relative intensities indicate that 2,1-insertion regiochemistry predominates.[15,16]

The present low activity of the control $CGCTiMe_2$-mediated styrene homopolymerizations in the absence of organosilane is in agreement with previous results.[5f,7] As noted above, the modest activity has been ascribed to inactivation via intramolecular coordination of a 2,1-insertion product (e.g., **A**).[6] In contrast to this scenario, we suggest that weakly Lewis basic Si−H groups[17] compete with the "back-biting" of the last inserted styrene and facilitate incoming monomer coordination and enchainment, hence accelerate chain propagation (e.g., **C**).[17,18] This would involve interaction between the weakly Lewis basic $-SiH_3$ group and the electrophilic Ti-center.[17,18]



C

To assess whether any changes in the fundamental catalyst structure are involved in this process (e.g., CGCTi−N bond scission[19]), control experiments were performed using stoichiometric organosilane additions to $CGCTiMe_2$ and $CGCTiMe_2$/$Ph_3C^+B(C_6F_5)_4^-$ solutions in C_7D_8.[8] Upon organosilane addition to $CGCTiMe_2$ at room temperature, no reaction occurs over the course of 3 h, as judged by ^{1}H NMR spectroscopy. However, upon addition of stoichiometric alkenylsilane to $CGCTiMe_2$/$Ph_3C^+B(C_6F_5)_4^-$, rapid Ti−C/Si−H transposition[20,21] and olefin coordination are observed at −80 °C. Olefin coordination[22] is presumably followed by Ti−C/Si−H transposition, indicated by the gradual disappearance of the δ 3.6 ($-SiH_3$) resonance. Furthermore, upon addition of excess alkenylsilane to $CGCTiMe_2$/$Ph_3C^+B(C_6F_5)_4^-$ at room temperature, alkenylsilane homopolymerization occurs.[8] Additionally, there are no detectable changes in the *ansa*-amido ligand NMR parameters. Therefore, there is no evidence that catalyst "CGC" ligation changes upon organosilane addition, but rather the expected Ti−C/Si−H transposition and olefin coordination processes occur.

To eliminate the possibility of silyl radical-initiated styrene polymerization,[11] the possible reaction of 5-hexenylsilane with a solution of styrene in C_7D_8 was investigated, and no reaction was observed over a period of 3 h by ^{1}H NMR spectroscopy. However, upon addition of $CGCTiMe_2/Ph_3C^+B(C_6F_5)_4^-$ to this solution, rapid styrene polymerization occurs as observed by ^{1}H NMR spectroscopy. Furthermore, upon addition of AIBN to the unreactive styrene/5-hexenysilane solution, rapid styrene polymerization again occurs as observed by ^{1}H NMR spectroscopy. Importantly, the atactic polystyrene produced by AIBN initiation is devoid of vinyl resonances as assessed by ^{1}H NMR spectroscopy.

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To better evaluate the role of the Si−H functionality, control polymerizations were also performed with tetramethylsilane and tetraphenylsilane (Table 1, entries 12 and 14, respectively). Importantly, these polymerizations exhibit marginal activity and produce negligible amounts of product polymer. This result further supports the requirement for the weakly basic Si−H to disrupt the styrene "back-biting" (**A**). Tetramethylsilane was used here to ensure that the sterics associated with tetraphenylsilane are not the sole reason for the low polymerization activity and lack of "back-biting" interference. In addition, the importance of the Si−H group was investigated by performing polymerizations in the presence of di- and trisubstituted organosilanes (Table 1, entries 10, 11). As seen from the high polymerization activities and atactic polymer microstructures, secondary and tertiary organosilanes have a very similar effect on styrene homopolymerization processes.

To further scrutinize the role of the Si−H functionality with respect to polymerization rate enhancement, a series of EBICGCTi$_2$Me$_4$-mediated styrene polymerization experiments was also conducted (Table 2). Interestingly, for EBICGCTi$_2$Me$_4$-mediated systems, there is *modest to negligible* change in styrene homopolymerization activity in the presence of organosilane. These results are consistent with the observation that catalyst deactivation by the last inserted styrene is not known to occur in these systems.[7,10] Intriguingly, the CGCTiMe$_2$- and EBICGCTi$_2$Me$_4$-derived systems do not significantly participate in organosilane chain transfer processes during styrene homopolymerization as judged from the consistency of polymer M_n even in the presence of large organosilane concentrations (up to 400 mM; Tables 1 and 2; Figure 1). This is consistent with the retention of fundamental CGC ligation structure in these catalysts. Preliminary experiments also reveal that these same organosilanes have little effect on the activity of Cp*TiMe$_3$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ styrene polymerization catalysts.[10b,d]

The present results show that organosilanes (alkyl-, alkenyl-, and arylsilanes) have the capability to activate otherwise marginally active CGCTiMe$_2$-derived catalysts for rapid styrene homopolymerization. Organosilanes also exhibit diverse chain transfer efficiencies, depending on the catalyst architecture. Further studies of the proposed mechanism are in progress.

Acknowledgment. Financial support by the NSF (Grant CHE-04157407) is gratefully acknowledged. We thank Z. Dance for helpful discussions. We thank Dr. E. Szuromi and Prof. R. F. Jordan for generous assistance with GPC measurements.

Supporting Information Available: Detailed experimental procedures are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0700260