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Titanium-Mediated Syndiospecific Styrene Polymerizations: Role of Oxidation State

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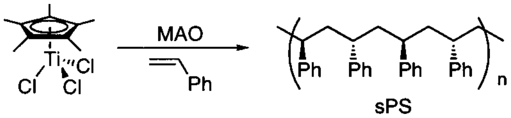
Homogeneous polymerization catalysts have provided a selective means of polymerizing olefin, conjugated diene, and styrene monomers to produce a wide variety of polymer microstructures.[1] Syndiotactic polystyrene (sPS) is an interesting new polymeric material due to its high melting point (T_m = 270 °C), high crystallinity, low density, low dielectric constant, and high chemical resistance to organic solvents at ambient temperatures.[2] Of the compounds identified as effective catalyst precursors for the synthesis of sPS,[2,3] the most active are based upon monocyclopentadienyl titanium complexes such as Cp^*TiCl_3 activated with methylaluminoxane (MAO),[2−4] $Cp^*TiMe_3/B(C_6F_5)_3$, or $Cp^*Ti(CH_2Ph)_3/[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$.[5]



Although sPS has many desirable materials properties, it possesses a high glass transition temperature (T_g = 100 °C) and is brittle at room temperature. Attempts to improve the toughness of sPS through copolymerization of styrene with nonconjugated olefins have largely been unsuccessful, although recent reports show that conjugated dienes can be copolymerized with styrene.[6] Copolymerizations of ethylene and styrene with Cp^*TiR_3 (R = halide, Me, CH_2Ph, etc.) in the presence of various activators yield mixtures of homopolyethylene, syndiotactic polystyrene (sPS), and varying amounts of ethylene/styrene copolymers containing less than 50 mol % styrene with no regioregular styrene−styrene sequences.[7] These results suggest that activation of $CpTiR_3$ precursors generates a family of active catalysts,[4b] some which produce polyethylene, others that produce sPS, and others that produce ethylene−styrene copolymers.[5c,d] Several studies have been carried out in an attempt to identify the nature of these active species. The oxidation state of the species responsible for ethylene polymerization is proposed to be Ti(IV).[8] The oxidation state of the active catalysts as well as the mechanism of the syndiospecific polymerization of styrene continue to be matter of considerable research.[2−10] Efforts to assign the oxidation state of the active metal catalyst with use of EPR and NMR studies have implicated Ti(II),[9,10] Ti(III),[4b,5c,10] and Ti(IV)[9] as possible active species for styrene polymerization. Among these reports, spectroscopic evidence supports Ti(III) as an active valence state.[5c] Furthermore, dimeric Ti(III) compounds activated with MAO were reported to be slightly more productive sPS catalysts than those derived from Ti(IV) precursors.[11]

Herein we describe the catalytic activity of the well-defined monomeric Ti(III) precursor $Cp^*Ti(C_3H_5)_2$ (**1**)[12] for the syndiospecific polymerization of styrene. The published synthesis of complex **1** involves the reaction of $TiCl_3{-}THF_3$ with Cp*Li followed by treatment with C_3H_5MgCl (Scheme 1).[12] We have found that this highly oxygen, water, and light sensitive compound **1** can be obtained in higher yields with simpler product isolation by the reaction of Cp^*TiCl_3 with Mn powder to generate $Cp^*TiCl_2(THF)$,[7] followed by allylation as previously described.[12] Elemental analysis, ^1H NMR, and EPR spectra of **1** synthesized by both methods are identical. Surprisingly, attempts to activate **1** in the presence of either Akzo Type IV modified MAO ([Al]/[Ti] = 500/1) or $B(C_6F_5)_3$ at 22 °C yielded no observable polymerization activity! In contrast, introduction of a toluene solution of **1** into a styrene solution containing a stoichiometric amount of $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (AFPB) in the absence of alkylaluminum reagents generated a very active styrene polymerization catalyst that yields sPS along with a small amount of atactic polystyrene (M_n = 19 840, PDI = 1.80) (Table 1).[13,14] High productivities for the formation of sPS were also obtained from an equimolar mixture of $[Ph_3C][B(C_6F_5)_4]$ (TFPB) and **1**.[15] These data indicate that catalysts derived from Ti(III) precursors are competent for syndiospecific styrene polymerization.

During the course of our investigation, we noted that the presence or absence of light greatly influenced the productivities of catalysts derived from Ti(IV) precursors.[9] In ambient light at room temperature, $Cp^*Ti(CH_2C_6H_5)_3$/AFPB catalyzed the polymerization of styrene to sPS. In contrast, polymerizations with this Ti(IV) catalyst precursor carried out the in dark at 22 °C yielded only traces of atactic PS.[16] Similar molecular weights (M_n) were observed for the polystyrenes produced with Ti(III) (dark) and Ti(IV) (light) complexes, implicating similar catalytically active species. In the light, the Ti(III) precursors produce sPS

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Scheme 1

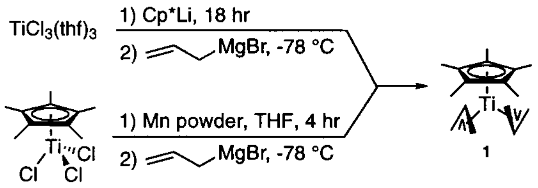

Table 1. Polymerization of Styrene with Ti(III) and Ti(IV) Precursors[f]

catalyst[a]	light[b]	SY (%)[c]	productivity[d] (kg sPS/mol Ti·h)	M_n[e] (×10^{-3})	PDI
1/AFPB	dark	94	1480	503	2.89
1/AFPB	light	92	770	95.5	2.50
1/TFPB	dark	85	1827	n.d.	
2/AFPB	dark		Trace	n.d.	
2/AFPB	light	66	405	476	1.96

[a] [B]/[Ti] = 1/1, AFPB = $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$, TFPB = $[Ph_3C][B(C_6F_5)_4]$. [b] Dark reactions were wrapped in a black bag to prevent exposure to light. [c] Weight % sPS in the isolated polymer. [d] Methyl ethyl ketone insoluble fraction possessing [*rrrr*] > 95% by ^{13}C NMR. [e] Determined by GPC-LS. [f] Polymerization conditions: 10 mL of toluene; 20 mL of styrene; $T_p = 22$ °C; polymerization time $t_p = 5$ min; [Ti] = 390 μM.

with substantially lower molecular weights (Table 1). The origin of this behavior is unclear, but may be related to the photolytic instability of **1**.[12]

The competence of Ti(IV) for syndiospecific styrene polymerization was studied by copolymerizing mixtures of styrene and propylene in the presence of the Ti(IV) precursor **2**. Activation of **2** at room temperature in the dark with the anilinium salt AFPB yielded propylene/styrene oligomers[17] in low yields and a substantial fraction of atactic PS; no sPS is produced under these conditions.[18] This result suggests that, in the absence of light, species derived from Ti(IV) precursors are incompetent for syndiospecific styrene polymerization. In addition, the much lower productivity for this polymerization compared to that for propylene homopolymerization with the same catalyst (Table 2) suggests that styrene inhibits propylene polymerization by Ti(IV) precursors.

Table 2. Copolymerization with Ti(III) and Ti(IV) Precursors (Dark)[d]

catalyst	feed[a]	product [b]	productivity (kg/molTi h)	M_n[c] (× 10^{-3})	PDI
2/AFPB	P	aPP	830	87.4	2.67
2/AFPB	P/S	aPS + P/S oligomers	263	n.d.	
1/AFPB	P	aPP	236	61.0	3.04
1/AFPB	P/S	sPS + aPS (8%)	895	269	3.58

[a] 12 psi of propylene (P), S = styrene. [b] Determined by ^{13}C NMR. [c] Determined by GPC-LS. [d] Polymerization conditions: 10 mL of toluene; 20 mL of styrene or toluene (total volume of 30 mL); $T_p = 22$ °C; polymerization time $t_p = 5$ min; [Ti] = 390 μM.

Polymerization of styrene/propylene mixtures under similar conditions with the Ti(III) complex **1**/AFPB produced only sPS and aPS (Table 2) and no observable polypropylene or propylene–styrene copolymers. The lower molecular weight observed for the polystyrene thus obtained (Table 2) suggests that propylene may serve as a chain-transfer agent; further studies are in progress to test this hypothesis. The absence of any observed polypropylene in the copolymerization experiments suggests that catalysts derived from the Ti(III) precursor **1** are inactive for propylene polymerization in the presence of styrene;[19] nevertheless, homopolymerization of propylene with the Ti(III) precursor **1**/AFPB yields atactic polypropylene, albeit with a productivity lower than that of **2**/AFPB.[16] The propylene polymerization behavior of **1**/AFPB in the absence of styrene may possibly arise from the disproportionation of Ti(III) into Ti(II) and Ti(IV), the latter of which can polymerize α-olefins. Pellecchia and co-workers have implicated a similar disproportionation in $Cp^*TiMe_3/B(C_6F_5)_3/AlMe_3$ mediated ethylene polymerizations which yield ethylene/hexene copolymers.[20]

In summary, Ti(III) complexes are active catalyst precursors for the syndiospecific polymerization of styrene, whereas analogous Ti(IV) precursors are inactive in the dark. In the presence of styrene/α-olefin mixtures, catalysts derived from Ti(III) complexes exhibit high chemoselectivity for styrene homopolymerization, while those from Ti(IV) precursors demonstrate complementary selectivity for α-olefin polymerization (albeit with the incorporation of some styrene comonomer). These results imply that the formation of polyethylene, syndiotactic polystyrene (sPS), and ethylene/styrene copolymers in styrene/ethylene copolymerization systems derived from Ti(IV) precursors[7] is a consequence of the incomplete reduction of a Ti(IV) precursor to give mixtures of Ti(III) and Ti(IV), which catalyze the polymerization of styrene and ethylene, respectively.

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