Copolymerization of Styrene and Ethylene at High Temperature with Titanocenes Containing a Pendant Amine Donor

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ABSTRACT: The copolymerization of ethylene and styrene at 120 °C was investigated with a series of titanocenes: Cp′$TiCl_2$L [**1**, **2**: Cp′ = cyclopentadienyl (Cp) versus **3**, **4**: Cp′ = {2-(dimethylamino)ethyl}cyclopentadienyl (Cp^N); **1**, **3**: L = Cl versus **2**, **4**: L = 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)], in combination with methylaluminoxane (MAO). At 120 °C, titanocenes bearing a pendant amine ligand (**3** and **4**) are effective catalysts for the ethylene-styrene (ES) copolymerization, whereas complexes lacking the pendant group (**1** and **2**) afford only mixtures of polyethylene (PE) and atactic polystyrene (aPS). At these temperatures, copolymerization with complexes **3** and **4** yields mixtures of ES copolymers and atactic polystyrene that are not readily separated by solvent extraction or gel permeation chromatography as both components of the mixture exhibit similar molecular weights and solubility in THF and acetone. The source of the atactic polystyrene was the autopolymerization of styrene as deduced by carrying out the copolymerization in the presence of a catalytic chain transfer agent, cobalt tetraphenylporphyrin (Co(tpp)). The addition of Co(tpp) caused a decrease in the molecular weight of the atactic polystyrene but had no effect on the molecular weight of the ES copolymer.

Introduction

Coordination catalysis by well-defined organometallic complexes has opened up new opportunities for the generation of polyolefin materials with tailored structures and properties.[1−13] Syndiotactic polystyrene (sPS)[14,15] and random ethylene-styrene (ES) copolymers[12,16−20] are two examples of polymers with unique properties that are inaccessible with traditional Ziegler−Natta catalysts. Historically, styrene and ethylene were viewed as incompatible monomers, as attempts to copolymerize these two monomers with many coordination catalysts yielded mixtures of homopolymers.[21−34] New families of coordination complexes of Ti[13,22,35] and the lanthanides[25,36−38] have been shown to copolymerize ethylene and styrene to generate ES copolymers with a range of compositions and sequence distributions.[22] In particular, monocyclopentadienyl-amido "constrained geometry catalysts" exhibit high activity for ES copolymerization at 90−100 °C to generate pseudorandom ES copolymers of high molecular weight.[17] Reports in the patent literature indicated that monocyclopentadienyl titanium complexes with pendant neutral amine donors[39−44] were active for ES copolymerization at elevated temperatures,[39] whereas monocyclopentadienyl titanium complexes (active for syndiospecific styrene polymerization)[14,45] typically give mixtures of polystyrene (PS) and polyethylene (PE) in ES copolymerization.[22−34]

The requirements for a successful ES copolymerization catalyst are severe and include high activity, high comonomer incorporation, the ability to generate high molecular weights, and the ability to operate at the high temperatures (80−120 °C), compatible with most commercial polymerization processes.[17] For ES copolymerization, one of the additional challenges is the suppression of styrene autopolymerization at these elevated temperatures.

Herein we report the copolymerization of ethylene and styrene at 120 °C with a variety of monocyclopentadienyl Ti complexes **1**−**4**[41,46,47] (Figure 1) containing pendant amine donors[39−44] and hydroxylaminato[46−51] ancillary ligands. Comparative investigations of complexes **1**−**4** were carried out to explore the role of both the pendant amine as well as the hydroxylaminato ligand on the ES copolymerization behavior. We have demonstrated that Ti complexes bearing a hydroxylaminato ligand have weak and tunable Ti−O bond strengths that can undergo Ti−O bond homolysis to generate Ti(III) and the nitroxyl radical.[46,49,50] Titanium complexes containing both hydroxylaminato ligands as well as pendant amines have particularly low Ti−O bond energies.[46] One of the objectives of our comparative study of complexes **1**−**4** in ES copolymerization at 120 °C was to assess whether the liberation of the hydroxyl radical from such systems might mitigate the autopolymerization of styrene[52] via facile trapping of polystyryl radicals growing by radical autopolymerization of styrene.[53]

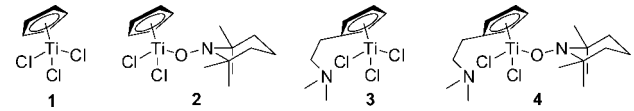

Figure 1. Mono-Cp titanium complexes used for ethylene−styrene copolymerization.

Results and Discussion

Copolymerization of Ethylene and Styrene. To investigate the role of both the TEMPO ligand (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) and the pendant amine on the polymerization behavior, copolymerizations of ethylene and styrene were conducted with complexes **1**−**4**/methylaluminoxane (MAO) at 120 °C. A constant overpressure of ethylene was applied from 20−80 psig to generate a range of compositions (Table 1). Fractionation of the resultant polymer was carried out[26,31,32,54] to assess the amount of ES copolymer relative to atactic polystyrene (aPS) or polyethylene (PE) homopolymer. The crude polymer products were first extracted with boiling acetone to remove aPS, and the acetone-insoluble fraction was extracted with boiling THF to separate the THF-soluble ES copolymer from ethylene homopolymer.[26,31,32,54] The composition, thermal properties, and molecular weights of the THF-soluble fractions are summarized in Table 1.

The copolymerization of ethylene and styrene with catalysts **1** and **2** in the presence of MAO at 120 °C afforded mixtures of syndiotactic polystyrene (sPS) and polyethylene (PE). These observations are consistent with previous reports on the at-

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Table 1. Ethylene−Styrene Copolymerization at 120 °C in Toluene[a]

entry	Ti catalyst	P_E (psig)	yield[b] (g)	prod[b,c]	wt %	styrene mol %[d]	T_g[e] (°C)	T_m[e] (°C)	M_n[g]	PDI[g]
1	**1**	20	1.11	35	80[h]	93	100	224	bm[j]	bm[j]
2	**2**	20	3.74	117	28[h]	92	100	228	bm[j]	bm[j]
3	**3**	20	1.25	39	82[i]	82	97	n.o.[f]	57 K	1.7
4	**4**	20	0.78	24	40[i]	97	103	n.o.[f]	60 K	1.8
5	**1**	50	3.37	105	63[h]	76	90	224	bm[j]	bm[j]
6	**2**	50	6.28	196	40[h]	79	90	225	bm[j]	bm[j]
7	**3**	50	1.22	38	78[i]	40	−15; 101	n.o.[f]	43 K	2.1
8	**4**	50	1.21	38	23[i]	48	−10; 105	n.o.[f]	38 K	1.9
9	**1**	80	1.54	48	63[h]	56	100	211	bm[j]	bm[j]
10	**2**	80	2.00	63	45[h]	67	96	206	bm[j]	bm[j]
11	**3**	80	2.15	67		22	−17; 101	n.o.[f]	47 K	1.9
12	**4**	80	1.48	46		29	−18; 107	n.o.[f]	53 K	2.1

[a] All polymerizations were performed with 8 μmol catalyst, 10 g of styrene, and 232 mg MAO in a toluene solution (total volume of 50 mL) for 4 h. Al/Ti = 500. [b] Yield and productivity before solvent fractionation. [c] Productivity in kg P·(mol Ti)$^{-1}$ h^{-1}. [d] Styrene content (mol %) in polymer after acetone (and THF) fractionation, estimated by ^{13}C NMR. [e] Determined by DSC. T_g: glass transition. T_m: melting point. [f] Not observed. [g] GPC (gel permeation chromatography) data of THF-soluble fraction in THF vs polystyrene standards. M_n: number-average molecular weight. PDI: polydispersity index (molecular weight distribution). [h] Weight percent of acetone-insoluble fraction. [i] Weight percent of acetone-insoluble, THF-soluble fraction. [j] Bimodal distribution.

tempted ES copolymerization with complex **1**.[21,22,30] Differences in polymerization behavior between **1** and **2** are modest; nevertheless, it is noteworthy that polymers generated by the hydroxylaminato complex **2** contain more aPS than those by complex **1**, as evidenced by a higher weight fraction of acetone-soluble material from **2** relative to **1**. These trends suggest that the hydroxylaminato ligand is ineffective for suppressing styrene homopolymerization under the activation conditions (MAO) employed.

In contrast to the behavior observed with **1** and **2**, complexes **3** and **4** are active for ES copolymerization upon activation with MAO at 120 °C and generate high molecular weight ES copolymers (M_n = 38000−60000). These results illustrate the critical role of the pendant amine on the ES copolymerization behavior. Chien had reported that **3** (P = 270 kg PS·(mol Ti)$^{-1}$ [S]$^{-1}$ h^{-1}) had significantly lower activity than **1** (P = 14000 kg PS·(mol Ti)$^{-1}$ [S]$^{-1}$ h^{-1}) for styrene homopolymerization at 20 °C, but higher activity for ethylene polymerization (P = 4900 vs 60 kg PE·(mol Ti)$^{-1}$ [E]$^{-1}$ h^{-1}, respectively).[40,41] At the polymerization temperature of 120 °C, the productivities in ES copolymerizations (averaged over 4 h) with **3** and **4** (P = 25−70 kg PS·(mol Ti)$^{-1}$ h^{-1}) are lower than that reported for ethylene polymerization at 20 °C; nevertheless, the ability of **3** and **4** to efficiently copolymerize ethylene and styrene at 120 °C attests to the thermal stability of the Cp^{N}Ti catalysts. The crude products afforded with **4** consist of higher weight percentage of aPS compared to those produced with **3**, consistent with the behavior observed for **1** and **2**.

Fractionation and Analysis of ES Copolymers Derived from 3 and 4. The copolymerization of ethylene and styrene with **3** and **4** at 120 °C generates mixtures of aPS and ES copolymers. The THF-soluble fractions of polymers derived from complexes **3** and **4** exhibited molecular weights of 38000−60000, monomodal molecular weight distributions and polydispersities of 1.7−2.1, indicating that the ES copolymers generated are reasonably monodisperse.

^{13}C NMR analysis of the THF-soluble fractions derived from **3** and **4** provides clear evidence for the formation of ES copolymers. Aliphatic regions of representative ^{13}C NMR spectra (entries 8 and 12) of copolymers derived from **4** are shown in Figure 2. The spectra of the ES copolymers derived from **3** and **4** clearly reveal resonances attributable to head-to-tail styrene−styrene sequences (SSS; $T_{\beta\beta}$, $S_{\alpha\alpha}$), methylene sequences (EEE; $S_{\delta\delta}$), and ES sequences ($T_{\delta\delta}$, $S_{\alpha\delta}$). Signals for tail-to-tail or head-to-head styrene sequences[27,55] were not observed. Significantly, the intensities of the $T_{\beta\beta}$ and $S_{\alpha\alpha}$ resonances, characteristic for SSS sequences, and the $S_{\delta\delta}$ resonances, characteristic of EEE sequences, are intense compared to $T_{\delta\delta}$ or $S_{\alpha\delta}$, characteristic for the ethylene−styrene sequences.

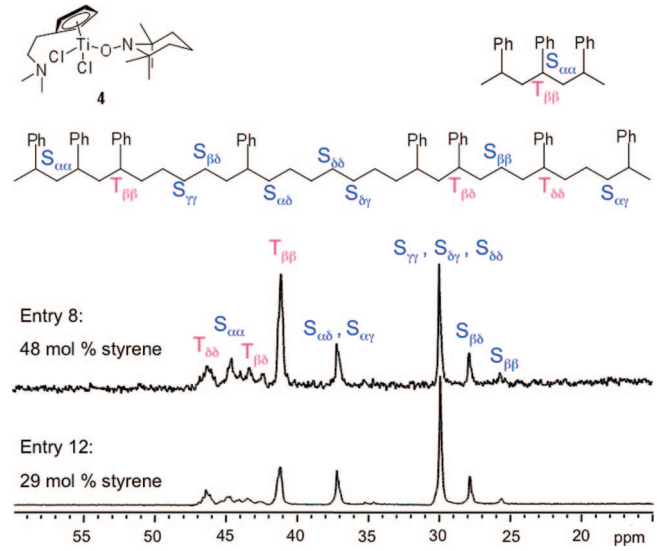

Figure 2. Aliphatic regions of ^{13}C NMR spectra (1,2-dichlorobenzene/benzene-d_6) and peak assignments of ethylene-styrene copolymers (THF-soluble fractions) prepared by Cp^{N}TiCl$_2$(TEMPO) (**4**)/MAO under different ethylene pressure (entries 8 and 12 in Table 1).

Compared to previously described ES copolymers with similar or even lower styrene content,[17,19,27,28,32,56,57] the observation of a high intensity of styrene repeat units ($T_{\beta\beta}$) is unusual. As depicted in Figure 3, the fraction of [$T_{\beta\beta}$]/[T_{total}] in the ES copolymers derived from complexes **3** and **4** is compared to that predicted by Bernoullian statistics and that observed by Nomura for the complex Cp′Ti(OAr)Cl$_2$ (OAr = *O*-2,6-^{i}Pr$_2$C$_6$H$_3$).[27] This plot clearly indicates that the fraction of SSS sequences in the THF-soluble fraction of copolymers derived from **3** and **4** are much higher than that predicted by Bernoullian statistics and are indicative of either a poly[(ethylene-*co*-styrene)-*b*-styrene] or a blend of ES copolymer and PS. The fact that the molecular weight distributions of the THF-soluble fractions are monomodal and reasonably narrow (PDI of 1.7−2.1) is consistent with a blocky microstructure, but does not rule out a blend of ES copolymer and PS if the components of the blend were to have similar molecular weights and solubility in acetone and THF.

Thermal analysis of the THF-soluble fractions by differential scanning calorimetry (DSC) showed two glass transition temperatures for samples with styrene contents below 50%. These two T_gs can be reasonably assigned to ES sequences (T_g = −18 to −10 °C) and styrene homosequences (T_g = 101−107 °C).

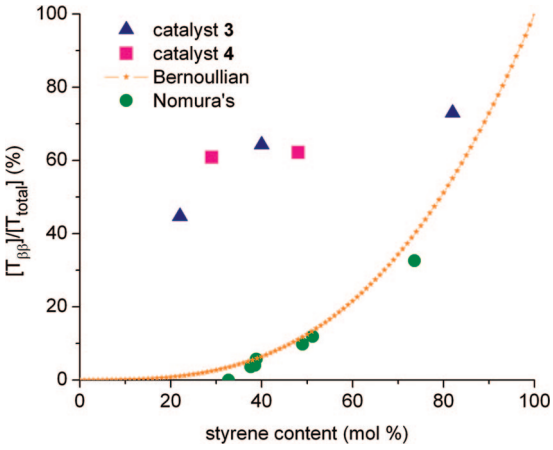

Figure 3. Plots of $[T_{\beta\beta}]/[T_{total}]$ ratio determined by ^{13}C NMR spectra as a function of styrene content in copolymers produced by **3** (triangles), **4** (squares), and Nomura et al.'s catalyst[27] (circles) vs styrene content in copolymers determined by ^{13}C NMR spectra. $[T_{\beta\beta}]/[T_{total}]$ value (%) based on Bernoullian statistics was calculated as [styrene content]^3 × 100.

The lack of melting endotherms attributable to syndiotactic SSS sequences and the broadening of the ^{13}C NMR resonances from 40−47 ppm indicate that the SSS sequences in these samples are atactic.

Role of Styrene Radical Polymerization on the Copolymerization Behavior. A most likely source of the aPS observed in ES copolymerizations at 120 °C is the radical autopolymerization of styrene (or the cationic polymerization of styrene initiated from cationic Ti complexes[58] or MAO). Even after extraction of aPS with acetone, the resulting THF-soluble ES copolymers contained significant amounts of atactic polystyrene (SSS) sequences. The narrow polydispersities of these THF-soluble fractions are suggestive of a blocky poly[(ethylene-*co*-styrene)-*b*-styrene]. In this case, the origin of the SSS sequences could be a consequence of a copolymerization mechanism where the styrene and ethylene reactivity ratios favor the homopropagation over cross-propagation of the two monomers ($r_e r_s > 1$).[59−61] Alternatively, a blocky structure might derive from a mechanism where polystyryl radicals combine with the Ti centers[62] to mediate a combined coordination/radical polymerization. To evaluate the latter possibility, we investigated ES copolymerizations in the presence of both AIBN initiator and catalytic chain-transfer agents (CCT),[63−65] and analyzed the compositions of the THF-soluble fractions to assess the influence of these additives on the ES copolymer microstructure. If the THF-soluble fractions are ES block copolymers generated by a single-site copolymerization process with $r_e r_s > 1$, the addition of AIBN or CCT agents should have no effect on the composition of the resulting ES copolymers. On the other hand, if the THF-soluble fractions are ES block copolymers generated by a combined radical/coordination mechanism, the addition of AIBN would be expected to increase the SSS sequence lengths and a CCT agent would be expected to decrease the SSS sequence lengths. Finally, if the THF-soluble fractions are blends of ES copolymers and styrene homopolymers that have similar molecular weights and solubility in acetone and THF, then addition of a CCT agent should decrease the molecular weight of the styrene homopolymer, but have no effect on the molecular weight of the ES copolymer.

To assess the degree to which radical polymerization of styrene is contributing to the microstructure of the polymers we observe, we carried out ES copolymerizations with **3**/MAO in the presence of AIBN (Table 2).

The addition of AIBN results in an increase in the amount of acetone-soluble fraction in the raw polymer, but also increases the amount of styrene in the acetone-insoluble, THF-soluble fraction. With increasing amounts of AIBN, the styrene content in the resulting THF-soluble fraction increases. Moreover, the fraction of SSS sequences also increases (entries 13−15) as evidenced by the higher ratio of $[T_{\beta\beta}]/[T_{total}]$ in the THF-soluble fractions. The narrow polydispersities of the THF-soluble fractions and the increase in styrene contents and fraction of SSS sequences are suggestive of a tandem radical/coordination mechanism to give a blocky poly[(ethylene-*co*-styrene)-*b*-styrene], where the addition of AIBN results in a higher contribution of a radical polymerization mechanism. However, these results could also be consistent with a parallel radical/coordination mechanism to give blends of atactic styrene homopolymer and ES copolymers if the radical polymerization of styrene under these conditions fortuitously generated similar molecular weights to that of the ES copolymer and both components of the blend exhibited similar solubility profiles in acetone and THF.

To distinguish between these two possibilities, we investigated the influence of the CCT agent, cobalt tetraphenylporphyrin [Co(tpp)],[63−65] on the ES copolymerization behavior at 120 °C in the presence of AIBN. Three sets of experiments were carried out: (1) in the absence of Ti, MAO and Co(tpp) (Table 3, entry 16), (2) in the absence of Ti and the presence of Co(tpp) with and without MAO (Table 3, entries 17 and 18), (3) in the presence Ti, MAO and Co(tpp) (Table 3, entry 19).

In the absence of Ti, MAO, and Co(tpp), the AIBN-initiated polymerization of styrene yielded aPS with a molecular weight $M_n = 75000$ (PDI = 2.4), very similar to that observed with AIBN in the presence of **3**/MAO (entry 16 vs 14). The addition of Co(tpp) resulted in a significant decrease in the molecular weight of the aPS ($M_n = 75000$ vs 6500, entry 16 vs 17); the addition of MAO led to similar behavior indicating that MAO has little influence of the behavior of the CCT agent (entry 18). When Co(tpp) is added to the ES copolymerization initiated by both **3**/MAO and AIBN (entry 19), the resulting polymer exhibited a bimodal molecular weight distribution (Figure 4a), which was easily separated by Soxhlet extraction using boiling acetone. Fractionation of this sample with acetone (entry 19, Table 4) yielded 55 wt % of an acetone-soluble fraction of $M_n = 6600$, which is aPS, as determined by ^{13}C NMR (Figure 5b). The higher molecular weight THF-soluble fraction (38 wt %, $M_n = 45000$) was shown by ^{13}C NMR to be an ES copolymer of approximately 20% styrene. These results clearly indicate that the copolymerization of styrene and ethylene in the presence of both

Table 2. Influence of AIBN on ES Copolymerization with Cp^NTiCl_3 (3)[a]

entry	AIBN (μmol)	Cp^NTiCl_3 (μmol)	P_E (psig)	yield (g)[b]	St mol % raw[b,d]	St mol % THF-sol[c,d]	M_n[c,e]	PDI[c,e]	$[T_{\beta\beta}]/[T_{total}]$ (%)[c]
11	0	8	80	2.15	26	22	47K	1.91	47
13	8	8	80	1.47	41	39	55K	2.08	62
14	16	8	80	1.24	46	50	74K	2.15	69
7	0	8	50	1.22	48	40	43K	2.09	64
15	16	8	50	0.87	89	86	73K	2.09	72

[a] All polymerizations were performed with 8 μmol catalyst, 10 g of styrene, and 232 mg MAO in a toluene solution (total volume of 50 mL) for 4 h. Al/Ti = 500. [b] Before solvent fractionation. [c] After solvent fractionation. [d] Styrene content (mol %) in polymer estimated by ^{13}C NMR. [e] GPC (gel permeation chromatography) data in THF vs polystyrene standards.

Table 3. Crude Product of ES Copolymerization in the Presence of Co(tpp)[a]

entry	Ti catalyst	MAO (mmol)	Co(tpp) (μmol)	AIBN (μmol)	yield (g)	styrene mol %[b]	M_n[c]	M_w[c]	PDI[c]
14	**3**	4		16	1.24	46	74 K	159 K	2.15
16				16	1.35	100	75 K	183 K	2.44
17			8	16	1.32	100	6.5 K	11 K	1.73
18		4	8	16	1.11	100	6.0 K	10 K	1.73
19	**3**	4	8	16	1.85	34	bimodal	bimodal	bimodal
20	**3**	4	8		1.43	38	bimodal	bimodal	bimodal
21		4			0.76	100	28 K	104 K	3.76

[a] All polymerizations were performed with 10 g of styrene, 80 psig ethylene in a toluene solution (total volume of 50 mL) for 4 h. Al/Ti = 500. [b] Styrene content (mol %) before solvent fractionation. [c] GPC (gel permeation chromatography) data in THF vs polystyrene standards.

Table 4. Fractionated Polymer Properties

entry	fraction	wt %[a]	styrene mol %[b]	polymer type	M_n[c]	M_w[c]	PDI[c]
19	acetone-soluble	55	100	aPS	6.6K	13 K	1.92
	acetone-insoluble and THF-soluble	38	20	E-*co*-S[d]	45 K	107K	2.36
20	acetone-soluble	47	100	aPS	5 K	8.2 K	1.63
	acetone-insoluble and THF-soluble	45	20	E-*co*-S[d]	57 K	116K	2.03

[a] Weight percent of each fraction. [b] Styrene content (mol %) in each fraction estimated by ^{13}C NMR. [c] GPC (gel permeation chromatography) data of THF-soluble fraction in THF vs polystyrene standards. M_w: weight-average molecular weight. [d] E-*co*-S: ES copolymer.

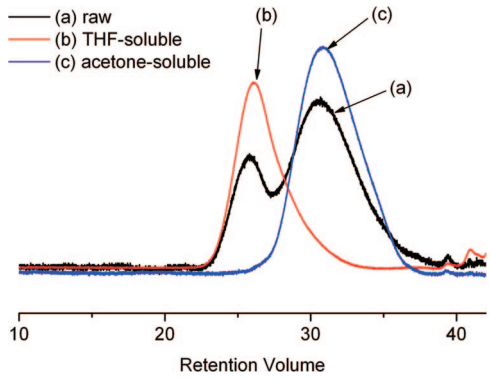

Figure 4. Gel permeation chromatograms (GPC) of (a) raw polymer, (b) THF-soluble fraction, and (c) acetone-soluble fraction of entry 19, Tables 3 and 4.

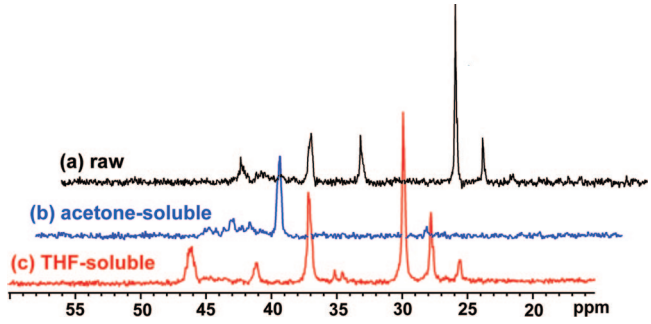

Figure 5. Aliphatic regions of ^{13}C NMR spectra (1,2-dichlorobenzene/benzene-d_6) of (a) raw polymer, (b) acetone-soluble fraction, and (c) THF-soluble fraction of entry 19, Tables 3 and 4.

3/MAO and AIBN generate blends of aPS and ES copolymers, which exhibit similar molecular weights and similar solubility in both THF and acetone. Similar results were obtained for ES copolymerizations with **3**/MAO and Co(tpp) in the absence of AIBN (entry 20, Tables 3 and 4), illustrating that at 120 °C competitive radical polymerization generates atactic polystyrene along with the ES copolymer. We conclude that solvent extraction alone is not a reliable method for a complete separation of ES copolymer from other byproducts such as self-initiated polystyrene of $M_n > 30000$. In this case, addition of a proper chain transfer reagent facilitates identification of the atactic polystyrene homopolymer by decreasing the molecular weight of polystyrene generated by a radical process.

Conclusion

We have prepared a series of monocyclopentadienyl titanium complexes containing pendant donor ligands in an effort to asses the role of the pendant donor group on the Ti−O bond energy and the role of the potentially labile TEMPO ligand on the ES copolymerization behavior. At elevated temperatures (120 °C), the titanocene complexes with a pendant amine group are active for ES copolymerization to generate mixtures of high molecular weight ES copolymers along with aPS. Under these conditions, the molecular weight of the ES copolymers produced by a coordination mechanism is coincident with that of the aPS produced by a radical mechanism. The addition of a catalytic chain-transfer agent, Co(tpp), decreases the molecular weight of the radically produced polystyrene, facilitating separation of the aPS from the ES copolymer. These studies illustrate the liabilities of solvent fractionation as a sole measure of single-site polymerization behavior, particularly when the components of a polymer sample contain compatible fractions. We conclude that (1) the pendant amine group has a significant effect on incorporation of ethylene into polystyrene chains to afford ES copolymer, (2) complexes with TEMPO ligand afford more aPS during the ES polymerizations, and (3) the addition of the catalytic chain-transfer reagent can provide a useful test for competitive radical polymerization processes in coordination polymerization.

Experimental Section

General Considerations. All reactions and polymerizations were performed in a drybox or with standard Schlenk techniques under nitrogen. The catalyst **1** was purchased from Strem Chemicals, Inc., and the catalysts **2**−**4** were prepared according to the literature procedures.[41,46,47] Ethylene (Matheson, polymerization grade) and argon (supplied by Praxair) were purified by passage through columns of Alltech Oxy-trap and Alltech gas drier. PMAO was supplied as a toluene solution by Akzo Nobel and dried under vacuum to remove solvent and residual trimethylaluminum prior to use. Toluene and benzene-d_6 were dried over metallic sodium/benzophenone solutions and distilled under reduced pressure before use. Styrene was purified by distillation under reduced pressure over CaH_2 and stored in the freezer.

Polymerizations were carried out in a 300 mL stainless steel reactor equipped with a mechanical stirrer. Temperature control was maintained using a heating mantle in combination with an ethylene glycol cooling loop. Prior to the polymerization the Parr reactor was evacuated on a vacuum line and then filled and flushed three times with desired overpressure of ethylene.

Representative Procedure for Preparation of Ethylene−Styrene Copolymer. A total volume of 45 mL of toluene suspension containing 232 mg PMAO and 10 g styrene was loaded into a double-ended injection tube. The suspension was injected into the reactor and allowed to equilibrate at the appropriate temperature while stirring under a constant ethylene pressure. The reaction was started by injection of the titanium complexes (8 μmol in 5 mL of toluene) and terminated after 4 h by addition of 10 mL of methanol. The resulting polymer was precipitated in 300 mL of acidified methanol, filtered, washed with additional methanol, and dried in a vacuum oven at 60 °C for at least 6 h.

Polymer Fractionation. Selective solvent fractionation to remove homopolymers was carried out using a Soxhlet extractor. Crude copolymer was placed in a Whatman cellulose thimble and extracted with boiling acetone for at least 12 h to remove atactic polystyrene. The acetone-insoluble fraction in a Whatman thimble was placed in a Soxhlet extractor and treated with boiling THF for at least 12 h to remove homopolymers. The THF-soluble extracts were isolated by filtering, dried under vacuum, and analyzed by NMR, DSC, and GPC. The amount of THF-insoluble fractions was negligible.

Polymer Analysis. ^{13}C NMR spectra were recorded at 75 MHz on Varian Inova 300 spectrometer at 95 °C in a 80:20 v/v solution of 1,2-dichlorobenzene/benzene-d_6 with in the presence of chromium(III) acetylacetonate (1 mM) to reduce the relaxation time of the aliphatic carbons (acquisition time = 1.8 s, pulse width = 3 μs.) By using the areas of the peaks, the comonomer composition can be evaluated by means of the following equation

$$x_s = \{A(S_{\alpha\gamma+}) + A(S_{\alpha\beta}) + 2 \cdot A(S_{\alpha\alpha})\} / \{A(S_{\gamma+\gamma+}) + A(S_{\beta\beta}) + A(S_{\beta\delta}) + 1.5 \cdot A(S_{\alpha\gamma+}) + 1.5 \cdot A(S_{\alpha\beta}) + 2 \cdot A(S_{\alpha\alpha})\} \quad (1)$$

This formula is adopted from Oliva et al.[66,67] and modified to be valid for different copolymer types. The formula is derived from the frequency of secondary carbons related to tertiary carbons. If $S_{\alpha\alpha}$ is not taken into consideration the formula is only valid for ES copolymer containing isolated styrene units. By including $S_{\alpha\alpha}$, it is valid for all polymer distributions.

Gel permeation chromatography (GPC) analysis was performed in THF at a flow rate of 1 mL/min on a Waters chromatograph equipped with four 5 μm Waters columns connected in series with increasing pore size (10, 100, 1000, 10^5, 10^6 Å). This system was calibrated using monodisperse polystyrene standards. Viscotek refractive index and UV detectors were used.

Differential scanning calorimetry (DSC) was performed using TA Instruments Q100 differential scanning calorimeter. Melting and glass transition temperatures were determined at a heating and cooling rate of 5 °C/min. The instrument was calibrated by measurement of the melting point of indium. Thermal history in the copolymer was eliminated by recording the second DSC scan.

Peak Assignment in ^{13}C NMR. The tacticity and distribution of the polymer as well as the styrene content were calculated from the ^{13}C NMR spectra. The peak assignments of the ^{13}C NMR spectra of the copolymers were made by comparing the spectra of ES copolymers in the literature.[17,19,27,31,36]

S represents a secondary carbon, whereas T represents a tertiary carbon. The Greek letters (α, β, γ, and δ) show the distance to the next tertiary carbon atom to each side, where α equals one, β equals two, γ equals three, and δ equals four or more carbon atom distance.

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Supporting Information Available: Figures showing representative GPC and DSC curves and selected ^{13}C NMR spectra of ethylene−styrene copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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