Copolymerizations of ethylene and α-olefins with supported piano-stool catalysts

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Abstract

Recent developments in single-site catalysis (SSC) have led to many interesting discoveries in ethylene and α-olefin copolymerizations. Here, we report the synthesis of, and polymerizations with, supported piano-stool catalysts and their related analogues. $CpTiCl_3$, $Cp*TiCl_3$, $TMSCpTiCl_3$, and $(TMS)_2CpTiCl_3$ were covalently bound to a poly(styrene-r-4-hydroxystyrene) copolymer, affording macroligated catalysts. Ethylene/1-octene and ethylene/styrene copolymerizations with each of these supported catalysts were attempted with cocatalysts including methyl aluminoxane, $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$, and $[PhN(CH_3)_2H][B(C_6F_5)_4]$. To determine the effects that the macroligand and the substituents on the cyclopentadienyl ring have on polymer yield and activity, comonomer incorporation, polymer composition, molecular weight, polydispersity index, melting point, and crystallization behavior were investigated.

We discovered that the catalysts have vastly different, yet interesting, effects on ethylene/1-octene (EO) and ethylene/styrene (ES) copolymerizations. For ethylene/1-octene copolymers, the activity of the supported catalysts and the amount of 1-octene incorporated into the copolymer is dependent upon the substituents on the cyclopentadienyl ring. The formation of EO copolymers using supported aryloxy-based cyclopentadienyl complexes can also be used as additional evidence for the presence of the tethered aryloxy moiety. The copolymer composition and the thermal properties of these copolymers were also studied.

Ethylene/styrene copolymerizations produced polymers with varying characteristics specific to the catalyst employed for the polymerizations. Polymers synthesized with the supported $CpTiCl_3$ and $TMSCpTiCl_3$ displayed both polyethylene and syndiotactic polystyrene melting points. Conversely, polymers synthesized with the supported $Cp*TiCl_3$ displayed only a polyethylene melting point, while polymers prepared with the supported $(TMS)_2CpTiCl_3$ displayed only a syndiotactic polystyrene melting point. These findings suggest that copolymerization of ethylene and styrene is not possible with these catalysts. Analysis of the homopolymerizations of styrene and ethylene with $Cp*TiCl_3$ and $(TMS)_2CpTiCl_3$, respectively, shows significantly lower activities, leading to preferential polymerization of the more active monomer during copolymerization.
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1. Introduction

The copolymerization of ethylene and various comonomers (1-butene, 1-hexene, 1-octene, and styrene) is made possible by the discovery of new single-site cata-lytic (SSC) architectures [1–6]. For example, ethylene/α-olefin copolymers (LLDPE) or ethylene/styrene (ES) copolymers are produced using piano-stool and modified piano stool complexes, with uniform comonomer incorporation, high molecular weight, and good activity. These copolymers with alkyl or aryl branches have better melt-flow properties, toughness and optical properties compared to high-density polyethylene (HDPE) [7]. The introduction of aromatic groups in the ES

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copolymer results in significant increase in viscoelastic, mechanical properties and compatibility of ES copolymers with LLDPE [7]. Additionally, ES copolymers contain syndiotactic styrene dyads, which enhance the thermal properties, as syndiotactic polystyrene is known to have a T_m of 273 °C.

Other discoveries put forth regarding piano-stool catalysts include the effect that substitution of alkyl groups on the cyclopentadienyl ring and of the halides on the titanium catalyst center for various substituents has on the copolymerization of ethylene and α-olefins. Most significant to this work are Nomura's publications on the aryloxy substituted CpTi(R)₂OAr complexes [8–13]. The authors found that by substituting one of the halide groups on the Ti catalyst center with an aryloxy group, polyethylene, poly(ethylene-*co*-1-butene), and poly(ethylene-*co*-styrene) could be obtained with reasonable activity, molecular weight, polydispersity, and comonomer distribution [8–13].

There is a significant commercial drive to combine the inherent advantages of SSC catalysts (high activity, control over monomer reactivity and polymer structure control) with the attributes of supported catalyst technology (morphology and high bulk density control) [14]. With this in mind, piano-stool catalysts have been supported on a variety of substrates including, but not limited to, lightly cross-linked polystyrene beads [15], alumina or MgCl₂ [14], butyl ethylmagnesium treated silica [14], mesoporous silica [16], and (4-hydroxystyrene)-styrene (HPS) copolymers [17].

In this work, various piano-stool catalysts were reacted with a (4-hydroxystyrene) styrene copolymer (HPS), in essence creating bulky aryloxy substituents (macroligand). We have previously shown that the presence of the macroligand is vital for the production of butyl branched polyethylene produced during ethylene homopolymerization [18]. More importantly, the support should be regarded as a part of the ligand–metal environment. Hence, chemical and structural changes to the support affect the overall performance of the piano-stool complex bound to the HPS support [18]. In this paper, the use of macroligated catalysts for the copolymerization of ethylene with 1-octene and styrene has been explored. The effect of using the macroligated catalysts with appropriate cocatalysts for ethylene/α-olefin copolymerization on the molecular weight, branch content, melting temperature, degree of crystallinity, and copolymer microstructure has been analyzed in detail.

2. Experimental

2.1. Reagents and general techniques

All reactions were performed under nitrogen in Schlenk glassware or in an inert atmosphere dry box. All solvents used were obtained from a solvent manifold [19]. Titanium tetrachloride, bis(trimethylsilyl)cyclopentadiene, 2,5,5-tris(trimethylsilyl)-1,3-cyclopentadiene, cyclopentadienyltitanium trichloride, pentamethyl-cyclopentadienyltitanium trichloride, styrene, 4-acetoxy styrene, AIBN, tetrahydrofuran, and hydrazine hydrate were obtained from Aldrich. AIBN was recrystallized from acetone, and styrene was distilled over calcium hydride. Methyl aluminoxane (MAO, 30 wt% (4.7 M) in toluene) was generously supplied by Albemarle. The copolymerizations were performed using heavy-walled glass reactors and a polymerization manifold [20]. The styrene-*co*-hydroxy styrene (HPS, macroligand) and the supported aryloxy cyclopentadienyltitanium trichloride complexes were synthesized as previously reported [18].

2.2. Instrumentation

^{13}C NMR spectra of the polyolefins in tetrachlorethylene-d_2 were recorded at 150 MHz on an Avance DPX 600 using a quantitative pulse program for solution NMR at 135 °C. Gel permeation chromatography (GPC) of the polyolefins was performed with a Polymer Laboratories PL-220 high temperature GPC equipped with a Wyatt MiniDawn (620 nm diode laser) high temperature light scattering detector and refractive index detector. Experiments were performed at 135 °C using 1,2,4-trichlorobenzene as solvent, and results were based on calibration with polystyrene standards. The dn/dc value for polyethylene used was −0.11. Thermal analyses were performed using a TA differential scanning calorimeter (DSC) 2910 equipped with liquid nitrogen cooling accessory unit. Experiments were performed under a continuous nitrogen purge (50 mL/min) with a heating and cooling scan rate of 10 °C/min.

3. General procedure for supported catalyst preparation (HPS-Ti-1 to -4)

Synthesis of the support matrix poly(styrene-*r*-4-hydroxystyrene (HPS)) and subsequent assembly of the aryloxy piano stool complex on HPS was carried out in the glovebox using precursor catalysts (**1**–**4**) as previously reported [18,21]. The support contains 0.3 mol% hydroxystyrene, as determined by ^{1}H NMR. The supported catalysts were analyzed via elemental analysis in order to determine the weight percent of Ti, as well as the ratio of Cl:Ti. For all cases, it was determined that the Cl:Ti ratio was between 1 and 2, meaning that the most prevalent forms of the supported catalysts were Form A and Form B (Fig. 1). Although a Form C (containing three bonds to the macroligand) is not ruled out, the authors believe that this form would be sterically hindered. The reaction of the homogeneous
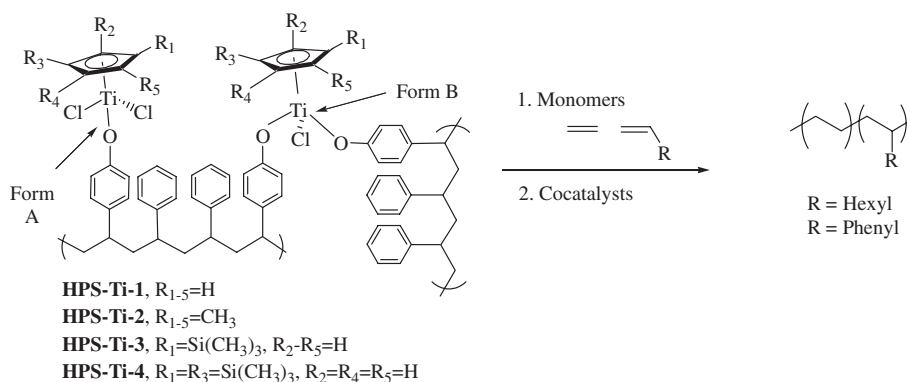
Fig. 1. Synthesis of ethylene/α-olefin random copolymers using supported aryloxy piano stool complexes.

catalysts with the support was observed to form a gel, which further supports the crosslinked structure outlined in Fig. 1. Independent confirmation of the proposed supported structure was obtained via ^{1}H and ^{13}C NMR. The ^{1}H NMR displays a downfield shift for the trimethylsilyl protons from δ 0.2 for the precursor of **HPS-Ti-4** to δ 0.4 ppm for **HPS-Ti-4**. Further confirmation of the presence of Forms A and B was obtained from the ^{13}C NMR of **HPS-Ti-4**, which displays two peaks in the trimethylsilyl region at δ −0.1 (Form A) and δ 1.5 ppm (Form B).

4. Synthesis of mono(phenoxy)(trimethylsilylcyclopentadienyl) titanium(IV) dichloride (5)

To a mixture of 10.0 mL of dichoromethane and (trimethylsilyl)cyclopentadienyltitanium trichloride (**3**, 102 mg, 0.34 mmol), phenol (32 mg, 0.35 mmol) was added slowly with constant stirring, The reaction was allowed to proceed at room temperature for a period of 12 h. The solvent was removed in vacuo, affording an orange solid (110 mg, 82% yield).

^{1}H NMR (CDCl$_3$): 0.4 (s, 9H, Si(CH$_3$)$_3$), 6.8 (t, 2H), 7.1 (t, 2H), 7.0–7.4 (m, 5H, C$_6$H$_5$).

^{13}C NMR (CDCl$_3$, CPD): −0.2, 118.8, 124.6, 123.9, 126.9, 128.6, 129.8, 137.5, 168.3.

5. Synthesis of bis(phenoxy)(trimethylsilyl-(cyclopentadienyl)) titanium(IV) chloride (6)

To a solution of 10.0 mL of toluene and (trimethylsilyl)cyclopentadienyltitanium trichloride (**3**, 102 mg, 0.34 mmol), phenol (75 mg, 0.7 mmol) was added slowly with constant stirring, and the reaction mixture was refluxed for a period of 1 day. The solvent was removed in vacuo, affording a red solid in 90% yield.

^{1}H NMR (CDCl$_3$): 0.3 (s, 9H, Si(CH$_3$)$_3$), 6.6–7.4 (m,14H, C$_6$H$_5$, C$_5$H$_4$).

^{13}C NMR (CDCl$_3$, CPD): 0.0, 115.7, 118.9, 121.5, 123.2, 126.3, 130.1, 133.7, 167.6.

6. Copolymerization of ethylene and 1-octene

To a mixture of 10.0 mL of toluene and 1.7 mL of 30 wt% of MAO in toluene in a polymerization reactor, 38.2 mg of **HPS-Ti-1** was added. To this system, 1-octene (5 mL) was added, and ethylene (60 psig) was supplied for 15 min with stirring. The ethylene supply was stopped and the reactor was vented to remove excess ethylene, the reaction mixture was quenched with 10% hydrochloric acid–methanol mixture and the polymer was collected by filtration and dried in vacuo overnight resulting in ethylene/1-octene copolymer (Table 1,

Table 1
Ethylene/1-octene copolymerization using macroligated catalysts in conjunction with MAO

Entry	Catalysts	Al:Ti	Activity (kg/mol Ti h atm)	$T_m{}^a$ (°C)	1-Octene incorporation (mol%)[a,b]	$M_w{}^c$ (×10⁻³)	PDI[c]
1	**HPS-Ti-1**	511	48	116.4	2.5	268	broad
2	**HPS-Ti-2**	665	17	119.8	2.5	177	2.4
3	**HPS-Ti-3**	1710	42	105.1	3.8	407	2.2
4	**HPS-Ti-4**	1613	10	123.3	2.0	501	broad
5	**3**[d]	660	5	134.9		n.d	n.d.
6	**5**	780	60	114.1	3.0	400	2.0
7	**6**	765	71	115.3	3.0	110	1.9

[a] DSC *first* scan.
[b] Calculated from depression in melting point [26] and ^{13}C NMR measurements.
[c] Determined through GPC at 135 °C in TCB using light scattering detectors calibrated with PS standards.
[d] (Trimethylsilyl)cyclopentadienyltitanium(IV) chloride.

entry 1). For copolymerizations catalyzed with an unsupported catalyst, conditions were identical to the supported catalyst systems, however, only 3–5 mg of the catalyst were used (Table 1, entries 5–7).

7. Homopolymerization of styrene

To 50 mL round bottom flasks equipped with magnetic stirbars, 10.5 mL of distilled toluene, 25–30 mg of the supported catalyst, and 1.7 mL of MAO were added. (Al:Ti ratios for **HPS-Ti-1** and **HPS-Ti-2** were 600, while **HPS-Ti-3** was 1000 and **HPS-Ti-4** was 1400. The amount of MAO was increased for **HPS-Ti-3** and **-4**, as we knew that the homogeneous precursors were much less active.) After sealing with septa, the charged flasks were removed from the glovebox and placed on magnetic stirrers. At zero minutes reaction time, 3.0 mL (0.026 mol) of distilled styrene (which had been loaded in syringes in the glovebox) were added to each flask. If gelation did not occur within a few minutes, the reaction was allowed to proceed for 50–60 min. The reaction mixture was quenched with 10% hydrochloric acid–methanol mixture, and the polymer was collected by filtration and dried in vacuo overnight.

8. Copolymerization of ethylene and styrene

To a 12 fluid ounce glass reactor, 75 mL of distilled toluene, 25–30 mg of supported catalyst, and 1.7 mL of MAO were added. (Al:Ti ratios were the same as for the styrene polymerization.) The reactor was then fitted with the mechanical stirring apparatus and reactor head. To a 25 mL side-port on the reactor head, 21.5 mL (0.188 mol) of distilled styrene were added. The entire closed system was then removed from the glove box and attached to a medium pressure line and mechanical stirrer [20]. After flushing the system, the reactor was pressurized to 60 psig with ethylene gas. At this point, the styrene was added by back-pressuring the side port of the reactor with nitrogen. The nitrogen line was then detached from the reactor, and the excess nitrogen in the reactor was vented out of the side port. The reactor was then repressurized with ethylene, and the reaction was allowed to proceed for 1.5 h. The reaction mixture was quenched with 10% hydrochloric acid–methanol mixture and the polymer was collected by filtration and dried in vacuo overnight.

9. Results and discussions

We have designed synthetic schemes to tether piano-stool complexes on hydroxy-functionalized polystyrene supports (HPS) in order to study the influence of the

Table 2
Homopolymerization of styrene

Entry	Catalyst	Activity (kg/mol Ti h)	T_m[a] (°C)	ΔH (J/g)	M_w ($\times 10^{-3}$)	PDI
8	**HPS-Ti-1**	962	261	15	17	[b]
9	**HPS-Ti-2**	6	260 271	1.5 14	132	2.31
10	**HPS-Ti-3**	1946	260 271	2.1 9.2	135	2.34
11	**HPS-Ti-4**	114	260 271	4.0 17	52	2.35

[a] Second scan.
[b] Chromatogram is multimodal.

Table 3
Copolymerization of ethylene and styrene results

Entry	Catalyst	Activity (kg/mol Ti h atm)	T_m[a] (°C)	ΔH (J/g)	M_w ($\times 10^{-3}$)	PDI
12	**HPS-Ti-1**	26.6	114 247	30.4 2.2	412	2.10[b]
13	**HPS-Ti-2**	18.0	117	38.7	341	2.42[b]
14	**HPS-Ti-3**	4.6	128 255	24.8 6.2	478	2.22[c]
15	**HPS-Ti-4**	2.7	259 270	2.2 11.3	340	1.95[c]

[a] Second scan.
[b] Chromatogram is multimodal.
[c] Chromatogram contains a low molecular weight shoulder.

support matrix on the catalyst performance and the properties of the resulting polyolefin [18]. Additionally, we studied how the substituents on the cyclopentadienyl ring affect both the amount of comonomer incorporated into the copolymer and also the microstructure of the copolymer. These effects on polymer yield, activity, weight average molecular weight (M_w), polydispersity index (PDI), melting point (T_m), and percent comonomer incorporation are outlined in Tables 1–3.

9.1. Ethylene/1-octene copolymers

During ethylene homopolymerizations, the supported aryloxy complexes (**HPS-Ti-1** to **-4**), in conjunction with different cocatalysts (MAO, tris(pentafluorophenyl)borane, dimethylanilinium borate, trityl borate), afford linear or branched polyethylenes from an ethylene only feed. The production of butyl branched polyethylene from an ethylene only feed has been attributed to 1-hexene produced from an ethylene trimerization process triggered by the use of macroligated catalysts [18]. In order to determine the effect of the macroligand on the properties of LLDPE, ethylene and 1-octene copolymerizations were performed using the macroligated catalysts (**HPS-Ti-1–4**) and MAO as the cocatalyst. It was

observed that for the ethylene/1-octene copolymers, **HPS-Ti-3** and **HPS-Ti-1** show higher activity than **HPS-Ti-2** and **HPS-Ti-4**. Also, **HPS-Ti-3** affords higher levels of 1-octene incorporation compared to the other three macroligated catalysts. The copolymers synthesized from these supported catalysts are of moderately high molecular weights (Table 1, entries 1–4).

For 1-octene incorporation, the trend followed **HPS-Ti-3** > **HPS-Ti-2** > **HPS-Ti-4**. The trend in the molecular weight of the ethylene/1-octene copolymer was found to be **HPS-Ti-4** > **HPS-Ti-3** > **HPS-Ti-1** > **HPS-Ti-2**. The trends observed in the activity and the molecular weight of the copolymer produced from the macroligated catalysts agree well with the results obtained by Nomura and co-workers. These authors have shown that in the case of non-bridged cyclopentadienyl aryloxy titanium species like ^tBuCp, $(CH_3)_5Cp$, and $(^tBu)_2Cp$, the Cp–Ti–O bond angle changes from 117.6°, 120.5° and 119.3° [9,22,23]. For 1-hexene incorporation, the activity of the substituents has been shown to follow the trend: $^tBu\ Cp > (CH_3)_5Cp > (^tBu)_2Cp$. On the other hand, the molecular weight for the copolymer is highest for $(^tBu)_2Cp$ followed by the ^tBu and the $(CH_3)_5Cp$ analogues. Nomura and co-workers [9,22,23] have attributed the observed trends in activity and molecular weight of the ethylene/hexene copolymer produced to the rotational flexibility of the substituents on the cyclopentadienyl ring.

Another interesting feature is that the formation of ethylene/octene-based copolymers using supported aryloxy-based cyclopentadienyl complexes can also be used as additional evidence for the presence of the tethered aryloxy moiety. A previous control polymerization performed with complex **3**, MAO as the cocatalyst, and ethylene and 1-octene in the monomer feed produced HDPE (Table 2, entry 5). On the other hand, the use of small molecular analogues **5** and **6** with MAO resulted in the formation of ethylene/1-octene copolymers (LLDPE) from ethylene and 1-octene copolymerization (Table 1, entries 6 and 7, respectively).

9.2. Copolymer microstructure analysis of ethylene/octene copolymers obtained from macroligated catalysts

In order to determine the copolymer composition of the copolymers synthesized, ^{13}C NMR of the copolymers was performed at 135 °C. The ^{13}C NMR resonances of the copolymer synthesized from complex **HPS-Ti-1** were analyzed. The spectrum is similar to that reported by Cavagna [24,25], and hence low level of octene incorporations were expected. The nomenclature for carbon assignments, monomer sequence distribution and equations relating signal intensity to the sequences as reported by Randall were used to identify the branches in ^{13}C NMR of the polyolefin [25]. The ^{13}C peak resonances were assigned as 14.19 ($1s + 1B_6$, CH_3, $EOE + EOO + OOE + OOO$), 22.85 ($2s + 2B_6$,
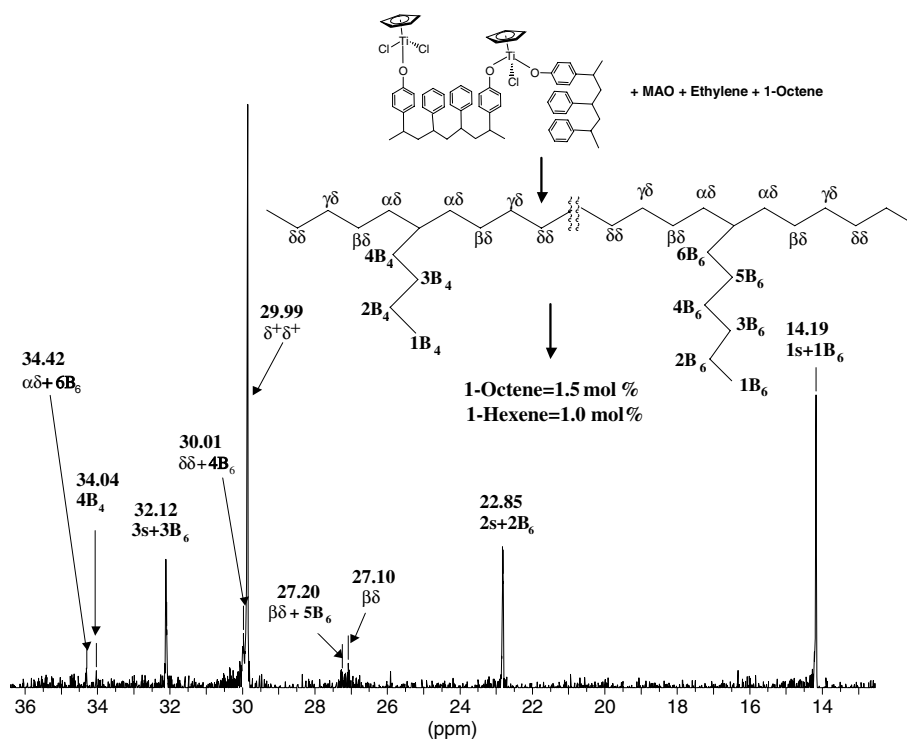

Fig. 2. ^{13}C NMR composite pulse decoupling (CPD) spectrum of ethylene/octene copolymer synthesized from complex **HPS-Ti-1** with MAO as the cocatalyst.

EOE + EOO + OOE + OOO), 27.10 (βδ, OOEE + EEOO), 27.20 (βδ + 5B$_6$, EOE), 29.99 (δδ, EEE), 30.01 (δδ + 4B$_6$, EEE), 32.12 (3s + 3B$_6$, EOE), 34.04 (4B$_4$, EHE), 34.42 (αδ + 6B$_6$, EOEE + EEOE), and 38.01 (CH, EOO + OOE, methine), as shown in Fig. 2. A quantitative relationship between signal intensity to monomer sequences was established to quantify the 1-octene incorporated in the copolymer [25]. The 1-octene content, calculated from the ratio of the sum of the octene-centered sequences to that of all the sequences, was determined to be 1.5 mol%. The presence of a 4B$_4$ branch (butyl branch) was also observed. This can be attributed to the 1-hexene formed by ethylene trimerization and further incorporation of 1-hexene into the copolymer. The resonances 4B$_4$ and (αδ + 6B$_6$) were used to quantify the ratio of hexene (1.0 mol%) and octene (1.5 mol%) incorporated into the ethylene chain.

The microstructure of ethylene/octene copolymer obtained from complexes **HPS-Ti-2** and **HPS-Ti-3** were also analyzed and assigned as δ 14.22 (1s + 1B$_6$, EOE + EOO + OOE + OOO), 22.87 (2s + 2B$_6$, EOE + EOO + OOE + OOO), 26.95 (βδ, OOEE + EEOO), 27.05 (βδ + 5B$_6$, EOE), 29.97 (δδ, EEE), 32.21 (3s + 3B$_6$, EOE), 34.51 (αδ + 6B$_6$, EOEE + EEOE), and 38.04 (CH, methine). The α-olefin incorporation in the copolymers obtained from **HPS-Ti-2** and **HPS-Ti-3** were estimated to be 2.5 and 3.8 mol%, respectively, as established by ^{13}C NMR. These values are corroborated by the observed depression in melting point. The microstructure of ethylene/octene copolymers from the macroligated catalysts (**HPS-Ti-1** to **3**) is similar to the microstructure of copolymers obtained from non-bridged cyclopentadienyl aryloxy complexes [23].

9.3. Ethylene/styrene copolymers

Homopolymerizations of styrene with the supported catalysts **HPS-Ti-1** to **-4** and assorted cocatalysts (MAO, tris(pentafluorophenyl)borane, dimethylanilinium borate, trityl borate) were performed in order to determine any differences between the catalysts and to discern if they would yield syndiotactic polystyrene as do the unsupported analogues. Table 2 shows that these polymerizations did indeed yield syndiotactic polystyrene with varying activities, molecular weights and polydispersities. Overall, polymerizations cocatalyzed with MAO display higher yields than those polymerized with a borane as the cocatalyst. The DSC results show that runs with **HPS-Ti-2**, **-3**, and **-4** contain the expected melting temperature at 270 °C, which is associated with syndiotactic polystyrene. The polystyrene obtained with **HPS-Ti-1**, however, lacks the melting transition around 270 °C. Also, the GPC data indicates significantly lower molecular weight and a multimodal distribution. The data indicate that the polystyrene produced with catalyst **HPS-Ti-1** is neither completely syndiotactic nor

does it have uniform molecular weight. This may be due to leaching of the precursor catalyst from the supported catalyst, **HPS-Ti-1**. As the precursor to this supported catalyst (CpTiCl$_3$) is known to produce syndiotactic polystyrene in high yield and purity, the macroligand form of the catalyst displays an obvious and significant effect on the polymer properties.

Xu et al. [17] reported similar styrene polymerization results with CpTiCl$_3$, which had been supported onto a polystyrene terpolymer containing hydroxy and methoxy moieties. While our reaction conditions are comparable, it is apparent that the melting point data that we obtained for entry 8 corresponds to the production of polystyrene with higher syndiotactic content. This further supports our argument that the use of macroligated catalysts is an additional tuning parameter in dictating the characteristics of the resulting polymer.

Additionally, entry 9 displays that the polystyrene produced with **HPS-Ti-2** was obtained with activity that was two to three orders of magnitude lower than the rest of the catalysts. It is widely known and accepted that the precursor, Cp*TiCl$_3$, produces syndiotactic polystyrene in high yield and activity. This phenomenon further illustrates the effect that the macroligand imparts on the catalyst's ability to polymerize styrene. Polymerizations with the borane cocatalyst system produced very similar results with respect to catalyst activity, polymer yield, and melting behavior, thereby ensuring this result is neither an anomaly nor dependent upon the cocatalyst system employed.

Polymerization of ethylene and styrene with the supported catalysts **HPS-Ti-1** to **-4** and MAO catalyst system produced very interesting results, Table 3. As with the styrene homopolymerization, very similar results were obtained with the borane cocatalyst system. It is evident that activity shows a marked decrease with the introduction of the ethylene comonomer. Although no trend is evident from yield and activity results with respect to cyclopentyl substituents, it is apparent from the DSC analysis that each supported catalyst produced very different polymers. In entries 12 and 14, the data is consistent with the presence of a reactor blend of polyethylene and syndiotactic polystyrene. Entry 13, however, suggests that only polyethylene is produced. A degree of crystallinity of 13.4% was calculated by dividing the heat of fusion value for the polyethylene melting by the total heat of fusion for a perfect polyethylene crystal (293 J/g) [26]. Finally, data in entry 15 suggest that only syndiotactic polystyrene is produced. This can also be seen in the DSC chromatogram (Fig. 3).

Analysis of the homopolymerizations of ethylene and styrene sheds some light on the polymer composition of entries 13 and 15. For the homopolymerization of styrene, **HPS-Ti-2** is clearly a poor performer, as the activity of this polymerization is two to three orders lower
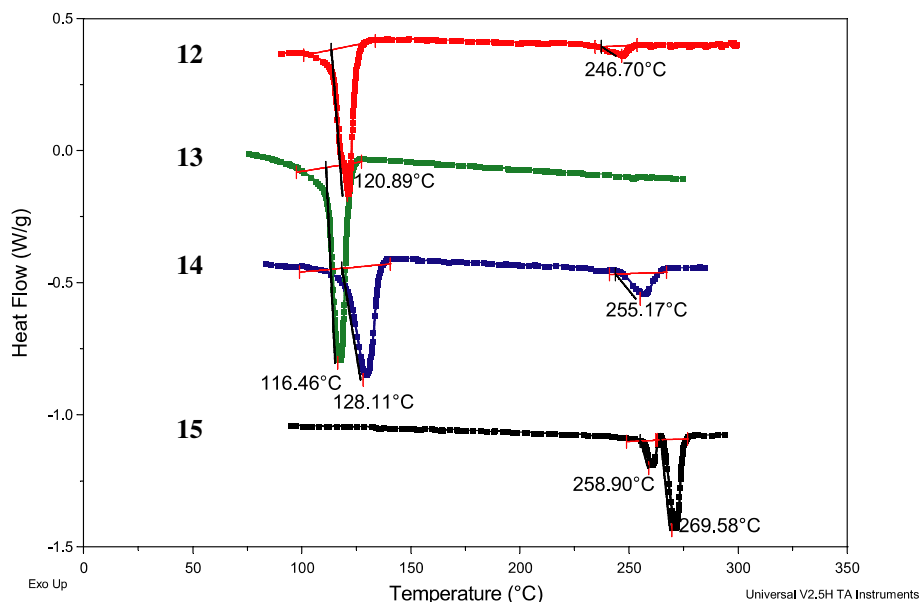
Fig. 3. Differential scanning calorimetry chromatograms of entries 12–15 (before extraction).

than that of the other catalysts employed. For this reason, it is expected that **HPS-Ti-2** would preferentially polymerize ethylene in copolymerization conditions with styrene. Indeed, the DSC chromatogram of the polymer obtained with **HPS-Ti-2** in the presence of ethylene and styrene monomers is consistent with the production of polyethylene.

Similarly, **HPS-Ti-4** displays a remarkably lower activity for the homopolymerization of ethylene than the other catalysts employed in this study [18]. Using this information in conjunction with the styrene homo-

polymerization results from Table 2, it is possible to predict that **HPS-Ti-4** would only polymerize styrene in copolymerization conditions with ethylene. As predicted, the entry 15 data and the DSC chromatogram display a preferential polymerization of styrene.

HPS-Ti-1 and **HPS-Ti-3** display sufficiently high activities in homopolymerizations of ethylene and styrene, and therefore it is conceivable that they would produce either a copolymer or a reactor blend of two homopolymers. Evidence of such a blend of homopolymers was detected through DSC and NMR analyses.
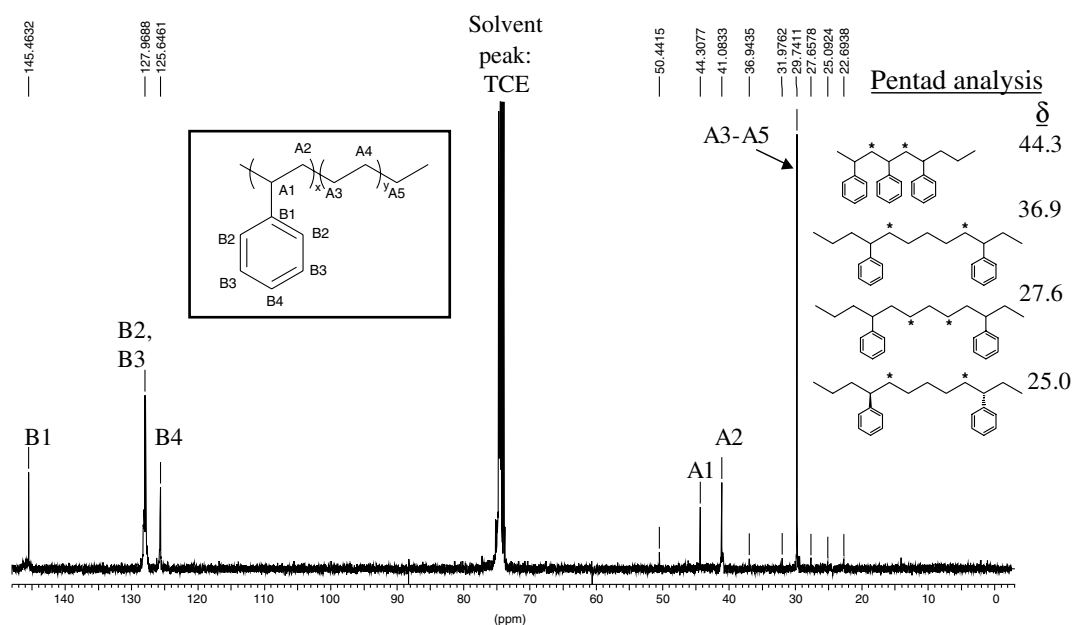

Fig. 4. ^{13}C NMR of entry 14.

Sequential Soxhlet extractions in methyl ethyl ketone (MEK) and tetrahydrofuran (THF) were performed on the entry 12 sample, in order to determine the relative amounts of atactic polystyrene, random ethylene/styrene copolymer, and polyethylene that were present. These results indicate that there is a significant amount of atactic polystyrene (MEK-soluble, >50%), random ES copolymer (THF-soluble, 11%), and polyethylene (THF-insoluble, 32%, $T_m = 132$ °C). Entry 14 was analyzed via ^{13}C NMR, as insufficient yield did not allow for Soxhlet extraction. As shown in Fig. 4, significant resonances in the NMR were consistent with syndiotactic polystyrene and polyethylene. Peaks consistent with the presence of an ES copolymer are of very low intensity, suggesting that an insignificant amount of the sample consists of random ES copolymer. The NMR and DSC data of entry 14 indicate the presence of two homopolymers: syndiotactic polystyrene and polyethylene.

Due to insufficient yield quantities, Soxhlet extractions could not be performed on entries 13 or 15. While DSC results of entry 15 are consistent with syndiotactic polystyrene, DSC results of entry 13 cannot conclusively determine whether or not a significant portion of the sample contains atactic polystyrene.

In summary, there seems to be a notable macroligand effect on the homopolymerization of styrene and the copolymerization of ethylene and styrene. This is clearly demonstrated in the decrease of the melting temperatures for the polystyrene. For the copolymerizations, it is evident that although the variety of substituents on the cyclopentadienyl ring does not have a correlation with the polymer composition, there is clearly another effect that causes these catalysts to produce different copolymer compositions. This effect is demonstrated through the supported catalysts behavior in homopolymerizations of styrene and ethylene. As the results are mirrored with the borane cocatalyst system, we believe that they are true results and not merely anomalies.

10. Conclusions

In order to study the influence of the support matrix on the catalyst performance and the properties of the resulting polyolefin, macroligated aryloxy titanium complexes (**HPS-Ti**) were prepared. In this paper, the effect of the macroligand on ethylene and α-olefin (1-octene or styrene) copolymerization using aryloxycyclopentadienyl macroligated catalysts were studied.

LLDPE has been synthesized from ethylene and 1-octene feed using supported aryloxycyclopentadienyltitanium complexes. The activity of the supported catalysts for copolymerization and the amount of 1-octene incorporated into the copolymer is dependent upon the substituents on the cyclopentadienyl ring. The microstructure of the copolymers was determined using ^{13}C NMR and shows random incorporation of the octene comonomer. The formation of ethylene/1-octene copolymers using supported aryloxy-based cyclopentadienyl complexes can also be used as additional evidence for the presence of the tethered aryloxy moiety, since the precursor piano-stool complex affords HDPE during attempted copolymerization. (Due to the incorporation of the comonomer, the melting points (T_m) and the enthalpy of fusion (ΔH) of the copolymers is depressed as determined by DSC.)

We have also explored the effect of supported single-site catalysts on styrene and ethylene/styrene polymerizations. Polymerizations with each of the supported catalysts, (**HPS-Ti-1** to **-4**) were carried out with MAO and borane cocatalysts. The MAO and borane cocatalyst systems produced very similar results.

DSC analysis displayed that **HPS-Ti-1** produced polystyrene with lower syndiotactic content than the precursor catalyst, indicating the presence of a strong macroligand effect. DSC analysis also showed that polymer composition varies greatly with the specific supported catalyst. Polymerizations of ethylene and styrene via **HPS-Ti-1** and **HPS-Ti-3** display both polyethylene and syndiotactic polystyrene melting behavior, while polymerizations of ethylene and styrene via **HPS-Ti-2** and **HPS-Ti-4** produce melting temperatures consistent with polyethylene or syndiotactic polystyrene, respectively. Based on homopolymerization data with styrene and ethylene, the phenomenon of different catalysts producing vastly different polymer compositions in copolymerization conditions was proscribed to the fact that certain supported catalysts preferentially polymerize ethylene or styrene.

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