Synthesis of ultra-high molecular weight poly(ethylene)-co-(1-hexene) copolymers through high-throughput catalyst screening†

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A family of permethylindenyl titanium constrained geometry complexes, Me₂SB(η⁵-N₃-H*I)TiCl₂ ((η⁵-R-η⁵-C₅Me₅)Me₂Si[H₂])₂, supported on solid polymethylaluminoxane (sMAO) are investigated as slurry-phase catalysts for ethylene/H₂ homopolymerisation and ethylene/1-hexene copolymerisation by high-throughput catalyst screening. Me₂SB(η⁵-N₃-H*I)TiCl₂ supported on sMAO [sMAO-Me₂SB(η⁵-N₃-H*I)TiCl₂] is responsive to small quantities of H₂ (<1.6%), maintaining high polymerisation activities (up to 4900 kgPE mol⁻¹ h⁻¹ bar⁻¹) and yielding polyethylenes with significantly decreased molecular weight (M₅₅) (from 2700 to 41 kDa with 1.6% H₂). In slurry-phase ethylene/1-hexene copolymerisation studies, a decrease in polymerisation activity and polymer molecular weights compared to ethylene homopolymerisation is observed. Compared to many solid supported systems, these complexes all display high 1-hexene incorporation levels up to a maximum incorporation of 14.2 mol% for sMAO-Me₂SB(η⁵-N₃-H*I)TiCl₂. We observe a proportionate increase in 1-hexene incorporation with concentration, highlighting the ability of these catalysts to controllably tune the amount of 1-hexene incorporated into the polymer chain to produce linear low-density polyethylene (LLDPE) materials.

Introduction

The incorporation of longer chain α-olefin monomers into polyethylene chains increases the degree of polymer branching, which lowers the melting point, crystallinity, and density of the polymers.¹ This can lead to significant increases in polymer flexibility, which gives the resultant polymers applications in packaging, foams, elastic fibers, and adhesives.² Metallocene catalysts containing two η⁵-cyclopentadienyl (C₅H₅, Cp) ligands and two α-type ligands (C₅MX₅) have similar reactivities with both ethylene and longer chain α-olefins;³ allowing them to incorporate much larger percentages of higher α-olefins than traditional Ziegler–Natta catalysts.⁴ Unlike the latter, copolymerisation using metallocene catalysts often results in regular comonomer distributions and forms high strength, high clarity polymers.⁵,⁶ Constrained geometry complexes (CGCs), bridged half-metallocenes containing amide ligands, such as the Dow Chemical Co. complexes {[(η⁵-Bu-η⁵-C₅H₅)Me₂Si(η⁵-N₃)]TiMe₂, (Me₂SB(η⁵-N₃)C₆H₄)(η⁵-H*I)TiMe₂, Me₂SB(η⁵-N₃,CP*)(η⁵-H*I)TiMe₂, Me₂SB(η⁵-N,I)TiMe₂, and Me₂SB(η⁵-N₃,OMe)(η⁵-H*I)TiMe₂},⁷ have been shown to be highly efficient ethylene/olefin copolymerisation catalysts, with high levels of olefin incorporated into the polymer chains.⁸,⁹ For example, in the solution phase, α-olefin incorporations of 25.3 mol% have been observed for ethylene/1-octene copolymerisation using Me₂SB(η⁵-N₃,CP*)(η⁵-H*I)TiMe₂/B[NMe₂(C₁₈H₃₇)₂][B(C₆F₅)₄] (20 bar ethylene and 300 g 1-octene),² and incorporations of 69.9% for ethylene/1-hexene copolymerisation using Me₂SB(η⁵-N₃,CP*)(η⁵-H*I)TiCl₂/MAO (1 bar ethylene and 44.5 mmol 1-hexene).¹⁰,¹¹,¹² These CGCs are of industrial interest due to their enhanced ability to copolymerise ethylene and longer chain α-olefins when compared to Cp₂MX₂ metallocene catalysts.²,⁹,¹¹,¹² This has been attributed to the less crowded coordination sphere, decreased tendency to undergo chain transfer reactions, and smaller bite angle (C₅-M-N angle) of CGCs compared to metallocenes (C₅-M-C₅)⁶ by approximately 25–30°.¹³ CGCs are highly tuneable, and variation of the complex components can dramatically influence polymerisation activities.¹³ It has been found that for CGCs containing a substituted indenyl fragment, the addition of electron-donating substituents leads to both increased copolymerisation activity and polymer molecular weights.¹⁴ One advantage of CGCs is their ability to produce polyethylenes with very ultra-high molecular weights, with M₅₅ often in excess of 1000 kDa.¹⁰,¹⁵,¹⁷ The long polymer chains transfer pressure more effectively to the polymer backbone, resulting in very tough materials with the highest impact strength of any thermoplastic currently.

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produced. The extremely low moisture absorption, very low friction coefficient, biological inertness, and self-lubricating nature of UHMWPE have led to their use in fishing lines, joint replacements, and impact-resistant materials in the military.17–19

We recently reported the synthesis and characterisation of a new family of CGCs based on the permethylindenyl ligand (C6Me7, Ind*, I*): [(3-R=–C6Me7)Me2Si(R‘N)]TiX2 (Me2SB(R‘N)3–Y*iPr, and Y‘*Bu; X = Cl, Me, CH3Ph, and CH2SiMe3) (Chart 1).20,21

When immobilised on solid polymeric aluminoxane (sMAO),22 an insoluble form of oligomeric MAO, the CGCs were found to be very active catalysts for slurry-phase ethylene polymerisation, ethylene/1-hexene copolymerisation, and ethylene/styrene copolymerisation with activities up to 7048, 4248, and 2036 kgPE molTi–1 h–1 bar–1, respectively.21 The catalysts showed low levels of 1-hexene and styrene incorporation (1.9–2.4 mol%) and 1-hexene incorporation levels found to increase with increasing copolymerisation temperature.21

Herein, we report a systematic investigation of the polymerisation performance of sMAO supported permethylindenyl titanium constrained geometry complexes for ethylene and ethylene/1-hexene copolymerisation using a high-throughput catalyst screening methodology.

Results and discussion

The CGCs in Chart 1 were immobilised on solid polymeric aluminoxane (sMAO) with an initial aluminium to titanium catalyst loading ([AlsMAO]0/[Ti]0) of 200, using a procedure described in previous work.20 The catalysts were studied under high-throughput conditions for ethylene homopolymerisation with or without dihydrogen (H2), and ethylene/1-hexene copolymerisation. The high-throughput system allowed a large number of parallel experiments to be run simultaneously, enabling the screening of different conditions in a shorter time period.21

Ethylene/H2 homopolymerisation

sMAO supported Me2SB(BuN,I*)TiCl2 (1sMAO), Me2SB(BuN,1*)TiMe2 (2sMAO), Me2SB(BuN,1*)Ti(CH2Ph)2 (3sMAO), Me2SB(BuN,1*)Ti(CH2SiMe3)2 (4sMAO), Me2SB(BuN,1*)Ti(Cl)CH2SiMe3 (5sMAO), and Me2SB(BuN,1*)TiCl2 (6sMAO) were studied for ethylene homopolymerisation and H2 response. High-throughput polymerisation studies were conducted in a parallel pressure reactor (PPR) at 80 °C with 8.3 bar ethylene, 0.8% (0.07 bar) or 1.6% (0.13 bar) H2 supplied by a mixed H2/N2 feed, 5 mL heptane, 10 μmol trisobutylaluminium (TiBA, Al(CH2CH(CH3)2)3) scavenger, and 0.075–0.40 mg pre-catalyst ([AlsMAO]0/[Ti]0 = 200) for 1 hour or until 8.3 bar of ethylene uptake was reached.

Polymerisation activities decreased with the addition of H2, however, the catalysts remained very active; activities of 6700, 5700, and 4800 kgPE molTi–1 h–1 bar–1 for 1sMAO with 0, 0.8, and 1.6% H2 respectively (Fig. 1 and Table 1). The decrease in polymerisation activity with increasing H2 pressure was found to be greater for the alkylated catalysts (2sMAO, 3sMAO, and 4sMAO) than the dichloride (1sMAO and 6sMAO) and mono-chloride (5sMAO) catalysts; with 1.6% H2, activity decreased by 28, 30, 38, and 43% for 2sMAO, 3sMAO, 4sMAO, and 5sMAO respectively, whereas, for 1sMAO and 6sMAO, activity decreased by 8 and 15%, respectively.

Fig. 1 Slurry-phase ethylene polymerisation activity as a function of H2 (%) using sMAO supported Me2SB(BuN,1*)TiCl2 (1sMAO) (black square), Me2SB(BuN,1*)TiMe2 (2sMAO) (red up triangle), Me2SB(BuN,1*)Ti(CH2Ph)2 (3sMAO) (orange circle), Me2SB(BuN,1*)Ti(CH2SiMe3)2 (4sMAO) (blue diamond), Me2SB(BuN,1*)Ti(Cl)CH2SiMe3 (5sMAO) (pink down triangle), and Me2SB(BuN,1*)TiCl2 (6sMAO) (green left triangle) with 0, 0.8, and 1.6% H2. Polymerisation conditions: 8.3 bar ethylene, 0.075–0.40 mg pre-catalyst ([AlsMAO]0/[Ti]0 = 200), 5.0 mL heptane, 10 μmol TiBA, and 80 °C. Reactions quenched at 8.3 bar ethylene uptake or after 60 minutes.
Table 1  Slurry-phase ethylene/H₂ polymerisation using sMAO supported 1⁴ CGCs in a high throughput system

| Catalyst | H₂  | Activity | Mₗ | Mₘ/Mₙ |
|----------|-----|----------|----|-------|
| 1₄MAO   | 0   | 6700     | 2700 | 3.2   |
|          | 0.8 | 5700     | 80  | 2.4   |
|          | 1.6 | 4900     | 41  | 2.9   |
| 2₄MAO   | 0   | 1400     | 1400 | 3.4   |
|          | 0.8 | 570 | 85  | 2.7   |
|          | 1.6 | 640      | 45  | 2.7   |
| 3₄MAO   | 0   | 8400     | 1200 | 3.4   |
|          | 0.8 | 3400     | 84  | 2.8   |
|          | 1.6 | 2900     | 47  | 2.7   |
| 4₄MAO   | 0   | 4400     | 1800 | 3.5   |
|          | 0.8 | 2200     | 82  | 2.6   |
|          | 1.6 | 2500     | 43  | 2.6   |
| 5₄MAO   | 0   | 4700     | 1500 | 3.8   |
|          | 0.8 | 3200     | 73  | 2.7   |
|          | 1.6 | 3300     | 42  | 2.7   |
| 6₄MAO   | 0   | 2600     | 1400 | 3.4   |
|          | 0.8 | 1600     | 80  | 2.8   |
|          | 1.6 | 1500     | 42  | 2.7   |

a Polymerysion conditions: 8.3 bar ethylene, 0.075–0.40 mg pre-catalyst ([Al₉MAO]/[Ti]₀ = 200), 5.0 mL heptane, 10 μmol TiBA, and 80 °C. Reactions quenched at 8.3 bar ethylene uptake or after 60 minutes. b %, c kgPE mol⁻¹ h⁻¹ bar⁻¹, reported to 2 significant figures. d kDa, reported to 2 significant figures.

and 42% for 1₄MAO, 5₄MAO, and 6₄MAO when compared to ethylene homopolymerisation, and by 43, 54 and 65% for 4₄MAO, 2₄MAO, and 3₄MAO. The differences in the relative changes in activities and the absolute activities of sMAO-Me₃SB(⁵⁸⁺N,¹⁺) Ti₂Cl₂ (1₄MAO–⁵₄MAO) catalysts also suggests that the initiator groups remain coordinated to the surface of the support and influence the nature of the active species through a secondary coordination effect. Chlorides initiating group could also block the active sites.

Over the course of the polymerisation runs, the in situ ethylene uptake rate profiles show lower uptake rates for ethylene polymerisation with H₂ compared to without H₂ (Fig. 2 and S1–S3). The lower activities and ethylene uptake rates for ethylene/H₂ polymerisation are attributable to the formation of a metal hydride species from chain transfer to H₂, which requires reactivation by propagation. The lower polymerisation activities may also be due to the formation of dormant bimetallic resting states with a bridging hydride, as has been proposed in the solution phase, that require reactivation to form the cationic methyl species. For 1₄MAO, ethylene polymerisation with 0.8% H₂ initially shows a higher ethylene uptake rate than for polymerisation without H₂; H₂ may activate an alternative site for a short period, which then becomes deactivated as polymerisation progresses (Fig. 2).

Polymer molecular weights (Mₗ) decreased with increased addition of H₂; Mₗ of ~80 and ~45 kDa with 0.8 and 1.6% H₂ respectively for all catalysts (Table 1, Fig. S9 and S11). The narrowing of the molecular weight distributions with increased addition of H₂, (Mₘ/Mₗ of 3.8 and 2.7 for 5₄MAO with 0 and 1.6% H₂) suggests increased control in the reaction. Crystallisation-elution fractionation (CEF) showed that the maximum elution temperature (Tₑₘax) of the polymers decreased slightly in the presence of H₂ (Tₑₘax of 113.3, 112.1, and 111.8 °C with 0, 0.8,

| Catalyst | 1-Hexene | Activity | Mₗ | Mₘ/Mₙ | Incorporation | Tₑₘax |
|----------|----------|----------|----|-------|--------------|-------|
| 1₄MAO   | 0        | 6700     | 2700 | 3.2   | —            | 112.1 |
|          | 125      | 5200     | 270  | 5.6   | 85.1         |
|          | 250      | 3600     | 330  | 6.6   | 73.5         |
| 2₄MAO   | 0        | 1400     | 3400 | 3.4   | —            | 113.3 |
|          | 125      | 380      | 390  | 3.4   | 89.0         |
|          | 250      | 250      | 300  | 6.3   | 70.5         |
| 3₄MAO   | 0        | 8400     | 1200 | 3.4   | —            | 111.4 |
|          | 125      | 2700     | 490  | 3.1   | 89.8         |
|          | 250      | 3000     | 380  | 6.3   | 71.6         |
| 4₄MAO   | 0        | 4400     | 1800 | 3.5   | —            | 113.3 |
|          | 125      | 1100     | 390  | 3.5   | 84.8         |
|          | 250      | 280      | 200  | 7.1   | 69.5         |
| 5₄MAO   | 0        | 4700     | 1500 | 3.8   | —            | 113.3 |
|          | 125      | 2200     | 360  | 3.5   | 88.0         |
|          | 250      | 1500     | 270  | 7.4   | 70.9         |
| 6₄MAO   | 0        | 2600     | 1400 | 4.0   | —            | 113.4 |
|          | 125      | 1700     | 250  | 5.6   | 81.9         |
|          | 250      | 1100     | 220  | 8.4   | 66.0         |
| 7₄MAO   | 0        | 1200     | 1700 | 2.5   | —            | 113.9 |
|          | 125      | 380      | 250  | 6.3   | 98.8         |
| 8₄MAO   | 125      | 490      | 1700 | 6.5   | —            | 80.5  |
|          | 250      | 190      | 360  | 4.7   | —            |

a Polymerysion conditions: 8.3 bar ethylene, 0.075–0.40 mg pre-catalyst ([Al₉MAO]/[Ti]₀ = 200), 5.0 mL heptane, 10 μmol TiBA, and 80 °C. Reactions quenched at 5.5 bar ethylene uptake or after 60 minutes. b %, c kgPE mol⁻¹ h⁻¹ bar⁻¹, reported to 2 significant figures. d kDa, reported to 2 significant figures. e Mol%. f °C.
and 1.6% H₂ respectively for 2sMAO), indicating a slight decrease in melting point and crystallinity (Table S1 and Fig. S18–S20†). The amorphous fraction (AF) increased in the presence of H₂; AF of 0.2, 0.5 and 0.7 with 0, 0.8, and 1.6% H₂ respectively for 2sMAO.

**Ethylene/1-hexene copolymerisation**

sMAO supported Me₂SB(²Bu,N¹)TiCl₂ (1sMAO), Me₂SB(²Bu,N¹)TiMe₂ (2sMAO), Me₂SB(²Bu,N¹)Ti(CH₂Ph)₂ (3sMAO), Me₂SB(²Bu,N¹)Ti(CH₂SiMe₃)₂ (4sMAO), and Me₂SB(²Bu,N¹)Ti(Cl)CH₂SiMe₃ (5sMAO), Me₂SB(²Bu,N,3-Et¹)TiCl₂ (6sMAO), Me₂SB(²Pr,N¹)TiCl₂ (7sMAO), and Me₂SB(²Bu,N¹)TiCl₂ (8sMAO) (Chart 1) were studied as catalysts for ethylene/1-hexene copolymerisation.

Large reductions in activity were observed for ethylene/1-hexene copolymerisation compared to ethylene homopolymerisation (6700 and 3600 kgPE mol⁻¹ h⁻¹ bar⁻¹ for 1sMAO with 0 and 250 µL 1-hexene respectively), indicating that the negative comonomer effects outweigh the positive effects (Table 2, Fig. 3 and S8†). A large decrease in ethylene polymerisation activity is observed with increasing volumes of 1-hexene. For example, a decrease from 4700 to 1500 kgPE mol⁻¹ h⁻¹ bar⁻¹ for 5sMAO with 0 and 250 µL 1-hexene respectively.

Many theories have been proposed for the positive comonomer effect, including fracturing of catalyst particles exposing new sites, the formation of new active species by coordination of α-olefins, and activation of dormant active sites; however, many of these have been refuted for molecular catalyst systems.⁵³ Studies have also shown that the addition of 1-hexene to an alkane reaction mixture leads to a 7–10% increase in ethylene solubility between 70–90 °C,⁴ as well as improved diffusion of ethylene close to the catalytic site, which improves polymerisation activity.⁵ The negative effects of comonomer addition are proposed to be due to competitive binding between ethylene and α-olefins and, if the rate of migratory insertion of the α-olefin is slower than that of ethylene, the rate of chain propagation will decrease leading to a decrease in polymerisation activity.⁵¹ The negative effects of comonomers on ethylene polymerisation activity may also be due to slower rates of insertion; the increased steric bulk of α-olefin comonomers in the polymer chain can lead to reduced rates of ethylene insertion.⁵⁶

Through monitoring changes in temperature during polymerisation, an exothermic temperature spike to approximately 85 °C was observed at the start of the copolymerisation experiments. As the alkyl catalysts (2sMAO, 3sMAO, and 4sMAO) are much more sensitive to polymerisation temperature than the dichloride catalysts (1sMAO, 6sMAO, 7sMAO, and 8sMAO), this thermal spike caused more substantial decreases in polymerisation activities for these catalysts; activity decreases from 6700 to 3600 kgPE mol⁻¹ h⁻¹ bar⁻¹ for 1sMAO from 4400 to 280 kgPE mol⁻¹ h⁻¹ bar⁻¹ for 4sMAO with 0 and 250 µL 1-hexene respectively.

The decreases in polymerisation activity with increasing volumes of 1-hexene are highlighted by the in situ ethylene uptake rate profiles, where sharp decreases in uptake rates with 125 and 250 µL 1-hexene are observed when compared to ethylene homopolymerisation (Fig. 4 and S4–S7†). Polymerisation activity was observed to increase with increasing electron-donating ability of the amido fragment (⁵⁶ Bu > ⁵º Pr > ⁷º Bu; 1sMAO > ⁷sMAO > ⁸sMAO) (Fig. S8†), as observed in previous work.⁶ Kamigaito et al. and Nomura et al. have also observed similar effects when using Me₂SB(²N,Cp*)TiCl₃/MAO (R = ⁵Bu, Ph, and
C6F5; R = 'Bu and Cy)\textsuperscript{38-39} catalysts for solution-phase ethylene/styrene copolymerisation.

Kloosin et al. have previously reported the effects of variation of the indenyl moiety on ethylene/1-octene copolymerisation, finding that increased electron-donating ability led to higher activities and polymer molecular weights.\textsuperscript{14} The opposite effect is observed for these systems, where 6\textsubscript{sMAO} shows a lower ethylene polymerisation activity than 1\textsubscript{sMAO}, attributed to its decreased thermal stability; activities of 1100 and 3600 kgPE mol\textsuperscript{-1} h\textsuperscript{-1} bar\textsuperscript{-1} respectively with 250 mL 1-hexene. The lower polymerisation activity of 3-ethylpentamethylindenyld supported catalysts relative to the permethylindenyld analogs has been observed previously for ethylene polymerisation using 1\textsubscript{sMAO} and 6\textsubscript{sMAO} with 2 bar ethylene and 50 mL solvent at temperatures above 70 °C,\textsuperscript{21} and when using sMAO-Me\textsubscript{2}SB(2,7-flu,3,8\textsuperscript{t})ZrCl\textsubscript{2} catalysts.\textsuperscript{40} 6\textsubscript{sMAO} also shows greater decreases in activities for ethylene/1-hexene copolymerisation compared to ethylene homopolymerisation (35 and 58% decreases for 125 and 250 mL 1-hexene respectively) than 1\textsubscript{sMAO} (22 and 46% decreases respectively). Similar to allylated catalysts (2\textsubscript{sMAO}, 3\textsubscript{sMAO}, and 4\textsubscript{sMAO}), this may be due to the exothermic temperature spike at the beginning of the copolymerisation experiment and the lower thermal stability of 6\textsubscript{sMAO} compared to 1\textsubscript{sMAO}.

The catalysts produced polymers with very high levels of 1-hexene incorporation for supported systems (up to 14.2 mol% for 7\textsubscript{sMAO}), confirming the production of ethylene/1-hexene copolymers. This is a trait commonly observed for CGCs that is attributed to the open metal centre resulting from the strain-inducing ansa-bridge (Table 2).\textsuperscript{22,13}

The incorporation levels observed for these catalysts are lower than for solution-phase ethylene/1-hexene copolymerisation using Me\textsubscript{2}SB(C\textsuperscript{H}N,C\textsuperscript{H}p)\textsuperscript{t}Ti(CH\textsubscript{2}Ph)\textsubscript{3} with an MAO cocatalyst (65-70% 1-hexene incorporation).\textsuperscript{10} However, supported catalysts typically give lower incorporation levels than homogenous catalysts due to mass transfer effects, where both the support and the propagating polymer chain cause diffusional resistance of the comonomer towards the active sites.\textsuperscript{41} The active sites of supported catalysts may also become blocked with polymer more quickly than the same catalysts in solution and therefore become inaccessible.\textsuperscript{42}

It was found that 1\textsubscript{sMAO}, 6\textsubscript{sMAO}, and 7\textsubscript{sMAO} produced polymers with similar incorporation levels with 125 mL 1-hexene (5.6–6.3 mol%). However, 7\textsubscript{sMAO} produced polymers with much higher incorporation levels than 6\textsubscript{sMAO} and 1\textsubscript{sMAO} with 250 mL 1-hexene (14.2, 8.4, and 6.6 mol% respectively). This suggests that higher levels of 1-hexene incorporation accompany reduced steric bulk in the amido substituent, likely due to easier coordination of 1-hexene to the metal centre. Catalysts containing at least one alkyl ligand (2\textsubscript{sMAO}, 3\textsubscript{sMAO}, 4\textsubscript{sMAO}, and 5\textsubscript{sMAO}) produced polymers with similar incorporation levels; 3.1–3.6 and 3.3–7.4 mol% with 125 and 250 mL 1-hexene respectively.

A similar effect was also observed by Chen and Marks for solution-phase ethylene/1-hexene copolymerisation using Me\textsubscript{2}SB(C\textsuperscript{H}N,C\textsuperscript{H}p)\textsuperscript{t}TiMe\textsubscript{2}/[BC\textsubscript{6}F\textsubscript{3}]\textsubscript{3} and Me\textsubscript{2}SB(C\textsuperscript{H}N,C\textsuperscript{H}p)\textsuperscript{t}Ti(CH\textsubscript{2}Ph)\textsubscript{3}/MAO where both alkyl ligand containing catalysts produced polymers with ~70% 1-hexene incorporation.\textsuperscript{10} 8\textsubscript{sMAO} consistently produced polymers with lower incorporation levels (1.6 and 4.7 mol% with 125 and 250 mL 1-hexene respectively), which may be due to the reduced electron donating ability of ‘Bu. A proportionate increase in 1-hexene incorporation was observed for ethylene/1-hexene copolymerisation using 2\textsubscript{sMAO}–7\textsubscript{sMAO} (the amount of 1-hexene incorporated into the polyethylene chain approximately doubled when the amount of 1-hexene in the system was doubled), which gives great potential for these catalysts to controllably tune the amount of 1-hexene incorporated into the polymer chain.

Gel permeation chromatography (GPC) showed that as the amount of 1-hexene added to the system increased, the molecular weights (M\textsubscript{w}) of the polymers significantly decreased; the polymers produced using 1\textsubscript{sMAO} showed an eight-fold decrease in polymer molecular weights on the addition of 250 mL 1-hexene (M\textsubscript{w} of 2700 and 330 kDa with 0 and 250 mL 1-hexene respectively) (Table 2, Fig. S10 and S14–S17). The decrease in polymer molecular weights likely results from frequent chain termination following 1-hexene insertion and chain transfer to 1-hexene monomers, coupled with a decrease in the rate of chain propagation.\textsuperscript{34,44} This effect has been observed and studied for ethylene/olefin polymerisation using other CGC systems, such as Me\textsubscript{2}SB(3,7-flu,3,8-t)Me\textsubscript{2} and Me\textsubscript{2}SB(3,7-flu,3,8-t)EtMe\textsubscript{2}, with work having been undertaken in an attempt to negate the molecular weights decrease by adding heteroatom substituents in the 2- and 3-positions on the indenyl moiety.\textsuperscript{7,14}

The catalysts produced polymers with relatively narrow molecular weight distributions (M\textsubscript{w}/M\textsubscript{n}) of 3.2, 3.0, and 2.7 for 1\textsubscript{sMAO} with 0, 125, and 250 mL 1-hexene. The polymers produced using 8\textsubscript{sMAO} showed wider molecular weight distributions than the polymers produced using the other catalysts (M\textsubscript{w}/M\textsubscript{n} of 6.5, 4.4, and 4.0 with 0, 125, and 250 mL 1-hexene respectively), suggesting the potential for more than one active site (Fig. S17).

CEF showed that the maximum elution temperatures (T\textsubscript{el,max}) of the polymers dramatically decreased with increasing volumes of 1-hexene, indicative of higher levels of 1-hexene incorporation; T\textsubscript{el,max} of 112.1, 85.1, and 73.5 °C for 1\textsubscript{sMAO} with 0, 125, and 250 mL 1-hexene respectively (Table 2 and Fig. S21–S23).

The decreases in T\textsubscript{el,max} are attributable to the weakening of intramolecular forces between the polymer chains with increasing incorporation of 1-hexene and decreasing molecular weights of the polymers.\textsuperscript{44} The amorphous fraction (AF) also increased with increasing 1-hexene concentration; AF of 0.2, 0.7, and 27.2 wt% for 4\textsubscript{sMAO} with 0, 125, and 250 mL 1-hexene respectively (Table S2). This corroborates with the high temperature \textsuperscript{13}C{[\textsuperscript{1}H]} NMR spectra (Fig. S24–S27).

**Conclusions**

A series of eight permethylindenyl constrained geometry titanium complexes (Me\textsubscript{2}SB(C\textsuperscript{H}N,C\textsuperscript{H}p)\textsuperscript{t}TiX\textsubscript{2}) supported on solid polymethylaluminoxane (sMAO) have been studied for ethylene homopolymerisation, H\textsubscript{2} response, and ethylene/1-hexene copolymerisation.
copolymerisation in a high-throughput catalyst screening system.

The catalysts displayed very high ethylene homopolymerisation activities; maximum activity of 8400 kgPE mol⁻¹ h⁻¹ bar⁻¹ for sMAO-Me₂SB(BuN,1)Ti(CH₂Ph)₂, sMAO-Me₂SB(N,N')TiCl₄ displayed the best H₂ response, displaying modest decreases in activity (6700 and 4900 kgPE mol⁻¹ h⁻¹ bar⁻¹ with 0 and 1.6% H₂ respectively), large decreases in polymer molecular weights (Mₚ of 2700 and 41 kDa with 0 and 1.6% H₂ respectively), and narrow molecular weight distributions (Mₚ/Mₙ of 2.4–3.2).

The addition of 1-hexene to the system caused a decrease in polymerisation activity and polymer molecular weights (activities of 6700 and 3600 kgPE mol⁻¹ h⁻¹ bar⁻¹ and Mₚ of 2700 and 330 kDa for sMAO-Me₂SB(N,N')TiCl₄ with 0 and 250 μL 1-hexene respectively), highlighting a negative comonomer effect.

The catalysts displayed high 1-hexene incorporation levels for supported systems with a maximum incorporation of 14.2 mol% for sMAO-Me₂SB(BuN,1)TiCl₄, demonstrating the formation of ethylene/1-hexene copolymers. A proportionate increase in 1-hexene incorporation with 1-hexene concentration was observed, demonstrating the potential capacity of these catalysts to controllably tune the amount of 1-hexene incorporated into the polymer chain to produce industrially relevant linear low-density polyethylene (LLDPE) materials.

Conflicts of interest

There are no conflicts to declare.

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