

Selective ethylene trimerization: A study into the mechanism and the reduction of PE formation

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Abstract

In the present study, the titanium-catalyzed ethylene trimerization in general, and more specifically, the concomitant PE formation have been studied. The polymer formation is undesirable as it not only will lead to lower 1-hexene yields, but it can cause reactor fouling under the applied conditions (30–80 °C, toluene solvent). It is, therefore, important to know which factors are involved in the formation of polymeric products and how their formation can be reduced or even prevented. The PE formation turns out to be catalyzed by at least two different species. A significant amount of PE is formed in the early stages of the reaction, caused by the presence of partly alkylated titanium species. The PE formation during later stages of the reaction is due to degraded catalyst species, which means that polymer formation is an inherent property of this catalyst system. The polymer output can be reduced largely by premixing Cp^{*}TiCl₃ and methyl aluminoxane (MAO) prior to injection into the reactor. It was also demonstrated that the type of MAO activator/impurity scavenger is of great importance. For a low yield of PE it is essential to use an MAO that does not contain and/or is not able to generate aluminum hydride species. In the end the best results with respect to both productivity and selectivity were obtained by starting from trimethyl titanium compounds.

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1. Introduction

Linear low-density polyethylene (LLDPE) is produced by the copolymerization of ethylene with lower α -olefins, especially, 1-hexene and 1-octene. The market for LLDPE is predicted to have an annual growth of 6% and as a consequence there is also an increasing demand for lower α -olefins. Currently, the most important process for the production of such α -olefins is the catalytic oligomerization of ethylene to give a C₄–C₂₀ range of linear α -olefins. Even though there is an increasing demand for the lower α -olefins (C₄–C₈), producers are reluctant to invest in new production units as they are faced with a much lower growth for the higher α -olefins. Clearly, a need for more selective α -olefin production processes exists.

A commercially attractive route to 1-hexene is the selective trimerization of ethylene [1]. The only commercial process capable of performing this conversion is based on a chromium catalyst. It is being practiced in a facility in Qatar, which is owned by a joint venture of the Chevron Phillips Chemical Company (CPCChem) and Qatar Petroleum.

A titanium-based, highly active and highly selective catalyst system for this conversion was discovered by Hessen and coworkers [2]. The catalytic ethylene trimerization with the titanium catalyst/methyl aluminoxane (MAO) system is a highly efficient and very selective process, resulting in more than 90 wt% of C₆ product from the converted ethylene, with an excellent 1-hexene selectivity of more than 99%. The basic catalyst system as published is [(η^5 -C₅H₄CMe₂Ph)TiCl₃]/MAO in toluene. Exploratory variations of the basic system indicated that a CR₂-bridge between the Cp and arene moieties is essential for the trimerization selectivity, while substitutions on the Cp-group can enhance the catalyst activity [2a].

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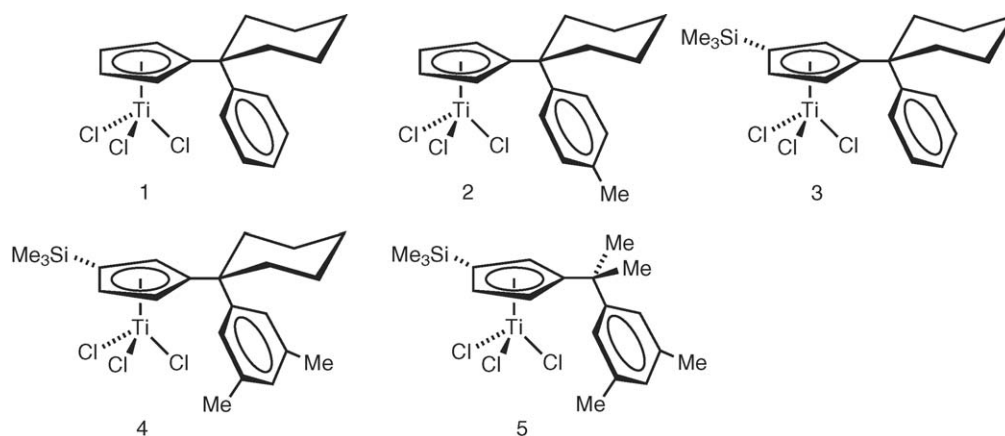


Fig. 1. Catalysts structures and their numbering.

The catalysts used in the present investigations are depicted in Fig. 1.

This selectivity of the titanium-based system is higher than for most of the other trimerization processes [3,4]. However, like all other trimerization catalysts, the present one has a similar disadvantage, i.e., the production of 2–5 wt% of high molecular weight polyethylene. Not only will this lead to lower yields, but the presence of high molecular weight PE in the reaction mixture can cause reactor fouling. This is especially true for the titanium-based process, which currently runs at lower temperatures than the chromium-based systems (30–80 °C versus 110–125 °C for the CPChem process [5]). It is, therefore, highly desirable to know which factors are involved in the formation of polymeric products and how the formation of these products can be reduced or prevented. Here we report the results of our investigations.

2. Experimentals

2.1. General considerations

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Toluene, hexane and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al₂O₃ (Fluka) and over molecular sieves (Aldrich, 4 Å). All solvents were degassed before use. Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4 Å). PMAO (4.9 wt% Al in toluene, Akzo Nobel), PMAO-IP (13.4 wt% Al in toluene, Akzo Nobel), MMAO-3A (2.03 wt% Al in isopar, Akzo Nobel), TIBA (Witco), DIBAH (2.0 M in toluene, Aldrich) and AlMe₃ (2.0 M in toluene, Aldrich) were used as received.

The compounds 6,6-pentamethylenefulvene [6], B(C₆F₅)₃ [7] and catalysts **1**, **3** and **5** [2b] were prepared according to literature procedures. *p*-Tolyl- and 3,5-dimethylphenyl lithium were synthesized according to standard procedures starting from *p*-tolyl- or 3,5-dimethylphenylbromide by reaction with BuLi in diethylether.

NMR spectra were recorded on a Varian Gemini 200 (¹H: 200 MHz, ¹³C: 50.3 MHz) or a Varian VXR-300 (¹H: 300 MHz, ¹³C: 75.4 MHz) spectrometer. The ¹H and ¹³C NMR spectra, measured at 25 °C, were referenced internally using the residual solvent resonances, and the chemical shifts (δ) are reported in ppm. Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph at 135 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (*M*_w = 50,000 g/mol) and polystyrene (*M*_w = 100,000–500,000 g/mol) standards.

2.2. Electrospray ionization mass spectrometry

Electrospray ionization mass spectrometry (ES-MS) experiments were conducted on a Nermag R3010 triple quadrupole MS system with a custom-built IonSpray (pneumatically assisted electrospray) source equipped with a gas curtain, comprised in a closed chamber which can be evacuated, flushed and maintained under nitrogen. Samples were taken up into a 500 μL syringe (Model 1750 RNR, Hamilton) and electrosprayed via a syringe pump operating at 10 μL/min. The capillary voltage was 3.5 kV. Mass spectra were recorded from *m/z* 200 to 900 at 10 s per scan under control of the Nermag Sidar data system. The sampling orifice (nozzle) was increased from +40 to +160 V to generate ion fragmentation. The skimmer located behind the sampling orifice was at +25 V in all experiments. In a typical experiment, 2.7 mg (10 μmol) of **1a** was dissolved in a mixture of 50 μL α-olefin (1-hexene, 1-heptene or 1-octene) in 1 mL toluene. After addition of 5.1 mg (10 μmol) B(C₆F₅)₃, the sample was shaken for 5 min and diluted 10 times with toluene generating a 10⁻³ M solution. Details of the electrospray experiments can be found in the supplementary information.

2.3. NMR tube experiments

All NMR tube experiments were prepared under a nitrogen atmosphere in a glove box at room temperature and measured

in Young-valve sealed NMR tubes. The mixtures were also analyzed by GC–MS. Details of the NMR tube experiments can be found in the supplementary information.

2.4. General description of trimerization experiments

The catalytic ethylene trimerization reactions were performed in a stainless steel 1 L autoclave (Medimex) in batch or semi-batch mode. The reactor was temperature and pressure controlled and in case of semi-batch experiments the pressure was kept constant to within 0.2 bar of the initial pressure by addition of ethylene. After the desired reaction time the reactor was vented and residual MAO was destroyed by addition of 20 mL of ethanol. Polymeric product was collected, stirred for 90 min in acidified ethanol and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried on air and subsequently in vacuum at 80 °C. Details of the trimerization experiments can be found in the supplementary information.

2.5. Synthesis of [1-(4-methylphenyl)cyclohexyl]-cyclopentadienyl titanium trichloride (**2**)

0.98 g (0.010 mol) *p*-tolyl lithium was dissolved in 50 mL of ice-cooled diethyl ether before 1.46 g (0.010 mol) 6,6-pentamethylenefulvene was added. The mixture was allowed to warm up to room temperature and stirred for 12 h. The suspension was filtered, the residue washed with neat diethyl ether and dried under reduced pressure. After dissolving the pale yellow powder in 20 mL ice-cooled THF, trimethylsilyl chloride (1.20 g, 0.011 mol) was added. The mixture was stirred at room temperature for 2 h before all volatiles were removed under reduced pressure. The residue was suspended in 20 mL CH₂Cl₂ and filtered through silica. Removal of the solvent leaves the 3-[1-(4-methylphenyl)cyclohexyl]trimethylsilylcyclopentadiene as yellow oil, which was used without further purification.

The yellow oil was dissolved in 30 mL neat CH₂Cl₂ and cooled to –20 °C before 1.5 g (0.008 mol) TiCl₄ was added. The mixture was allowed to warm up to room temperature and stirred for 12 h. After removal of all volatiles the residue was continuously extracted with 30 mL of hexane. Cooling of the hexane extract to –30 °C gave 1.60 g of pure **2** as bright orange crystals in 38% overall yield.

3-[(4-MeC₆H₄)C₆H₁₀]C₅H₄SiMe₃: ¹H-NMR (δ, CDCl₃): –0.06 (s, 9H), 1.40–1.60 (m, 6H), 2.10 (m, 4H), 2.29 (s, 3H), 3.22 (s, 1H), 6.10 (s, 1H), 6.38 (m, 2H), 7.07 (d, 2H, ³J_{HH} = 8.0 Hz), 7.22 (d, 2H, ³J_{HH} = 8.0 Hz).

2: ¹H-NMR (δ, CDCl₃): 1.20–1.50 (m, 6H), 1.89 (t, br, 2H), 2.12 (s, 3H), 2.52 (d, br, 2H), 5.94 (t, br, 2H), 6.34 (t, br, 2H), 6.67 (d, 2H, ³J_{HH} = 8.0 Hz), 7.22 (d, 2H, ³J_{HH} = 8.0 Hz).

2.6. Synthesis of 3-[1-(3,5-dimethylphenyl)cyclohexyl]-trimethylsilylcyclopentadienyl titanium trichloride (**4**)

1.12 g (0.010 mol) 3,5-dimethylphenyl lithium was dissolved in 50 mL of ice-cooled diethyl ether before 1.46 g (0.010 mol) 6,6-pentamethylenefulvene was added. The mix-

ture was allowed to warm up to room temperature and stirred for the next 12 h. The suspension was filtered, the residue washed with neat diethyl ether and dried under reduced pressure. After dissolving the pale yellow powder in 40 mL ice-cooled ether/THF (5:1, v/v), 1.08 g (0.010 mol) trimethylsilyl chloride was added. The white suspension was stirred at RT for 2 h before it was cooled to 0 °C and 4.8 mL of 2.5 M (0.012 mol) BuLi in hexane was added. After stirring for 5 h, 1.52 g (0.014 mol) trimethylsilyl chloride was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed and the residue was three times extracted with 15 mL CH₂Cl₂. The combined extracts were filtered through silica before the solvent was removed, leaving the 3-[1-(3,5-dimethylphenyl)cyclohexyl]-bistrimethylsilylcyclopentadiene as orange oil, which was used without further purification.

The oil was dissolved in 30 mL neat CH₂Cl₂ and cooled to –20 °C before 1.5 g (0.008 mol) TiCl₄ was added. The mixture was allowed to warm up to room temperature and stirred for 12 h. After removal of all volatiles the residue was continuously extracted with 30 mL of hexane. Cooling of the hexane extract to –30 °C gave 1.10 g of pure **4** as red crystals in 23% overall yield.

¹H-NMR (δ, C₆D₆): 0.10 (s, 9H), 1.20–1.50 (m, 6H), 1.78–2.10 (m, 2H), 2.10 (s, 6H), 2.64 (m, 2H), 6.41 (t, 1H, ³J_{HH} = 3.1 Hz), 6.47 (t, 1H, ³J_{HH} = 3.1 Hz), 6.64 (br, 1H), 6.96 (br, 1H), 7.12 (br, 2H).

2.7. Synthesis of 1-phenylcyclohex-1-yl-cyclopentadienyl trimethyl titanium (**1a**)

0.4 g (1.9 mmol) of 1-phenylcyclohex-1-yl-cyclopentadienyl titanium trichloride (**1**) was dissolved in 20 mL ice-cooled THF and 1.2 mL of a 3.0 M solution of MeMgCl in THF was added. After stirring the suspension for 4 h, all volatiles were removed under reduced pressure. The residue was extracted with 20 mL of pentane. The pentane solution was filtered and the solvent was pumped off to give a colorless solid which was re-crystallized from 5 mL neat pentane to give 250 mg white crystals of 1-phenylcyclohex-1-yl-cyclopentadienyl trimethyl titanium (**1a**) in 73% yield.

¹H-NMR (δ, C₆D₆): 1.10–1.40 (m, 6H), 1.23 (s, 9H), 1.64 (dt, 2H, ³J_{HH} = 12.5 Hz, ³J_{HH} = 3.3 Hz), 2.40 (³J_{HH} = 12.5 Hz), 5.75 (t, 2H, ³J_{HH} = 2.8 Hz), 5.84 (t, 2H, ³J_{HH} = 2.8 Hz), 7.10–7.26 (m, 5H).

2.8. Synthesis of 3-[2-(3,5-dimethylphenyl)prop-2-yl]-trimethylsilylcyclopentadienyl trimethyl titanium (**5a**)

3-[2-(3,5-Dimethylphenyl)prop-2-yl]-trimethylsilylcyclopentadienyl titanium trichloride (**5**) (0.3 g, 0.69 mmol) was dissolved in ice-cooled diethyl ether/THF (20 mL, 50/50 vol%) and MeMgCl (0.69 mL, 3.0 M in THF) was added. After stirring the suspension for 4 h all volatiles were removed under reduced pressure. The residue was extracted with 20 mL of pentane. The pentane solution was filtered and the solvent was pumped off to give a colorless oil of 3-[2-(3,5-dimethylphenyl)prop-2-yl]-trimethylsilylcyclopentadienyl trimethyl titanium (**5a**) in

almost quantitative yield. After standing for a few weeks at 0 °C the oil became crystalline.

¹H-NMR (δ , C₆D₆): 0.11 (s, 9H), 1.34 (s, 9H), 1.48 (s, 3H), 1.51 (s, 3H), 2.16 (s, 6H), 6.12 (m, 1H), 6.19 (m, 1H), 6.24 (m, 1H), 6.69 (s, 1H), 6.93 (s, 1H).

2.9. Premix experiments

2.9.1. Reaction of **1** with MAO

19 mg (50 μ mol) of **1** was added to 2.8 g (500 μ mol) MAO (4.9 wt% Al in toluene) in 2 mL of toluene. The sample was shaken and allowed to settle. After a few minutes a blue solid was formed, which turned into a blue oil after an additional 5 min. The MAO/toluene solution was decanted off before 2 mL neat toluene and 0.5 mL methanol were added. After filtration over silica the sample was analyzed by GC–MS.

GC–MS (min[M^{•+}]): 11.01 (160, cyclohexyl-benzene), 11.55 (158, 1-phenyl-cyclohexene), 13.95 [224, C₅H₅C(Ph)C₅H₁₀].

2.9.2. Reactions of **1** with MAO in presence of an olefin

3.8 mg (10 μ mol) of **1** was added to a mixture of 1.375 g (250 μ mol) MAO (4.9 wt% Al in toluene) and 2 mL of toluene containing (a) 0.05 mL 1-hexene, (b) 0.05 mL ENB, (c) 0.05 mL ENB and 0.05 mL 1-heptene or (d) 0.05 mL ENB and 0.05 mL 1-octene. The samples were shaken for 5 min before 0.5 mL of methanol was added. After filtration over silica, the sample was analyzed by GC–MS.

(a) GC–MS (min[M^{•+}]): 3.17 [98, 2-methyl-1-hexene], 3.40 [98, Z-3-heptene], 3.48 [98, 2-methyl-2-hexene], 9.42 [166], 9.86 [168], 9.99 [168, Z-2-dodecene], 10.03 [168], 10.33 [168], 11.51 (158, 1-phenyl-cyclohexene), 12.57 [252], 12.77 [252], 13.30 [250], 13.40 [252], 13.90 [224, C₅H₅C(Ph)C₅H₁₀].

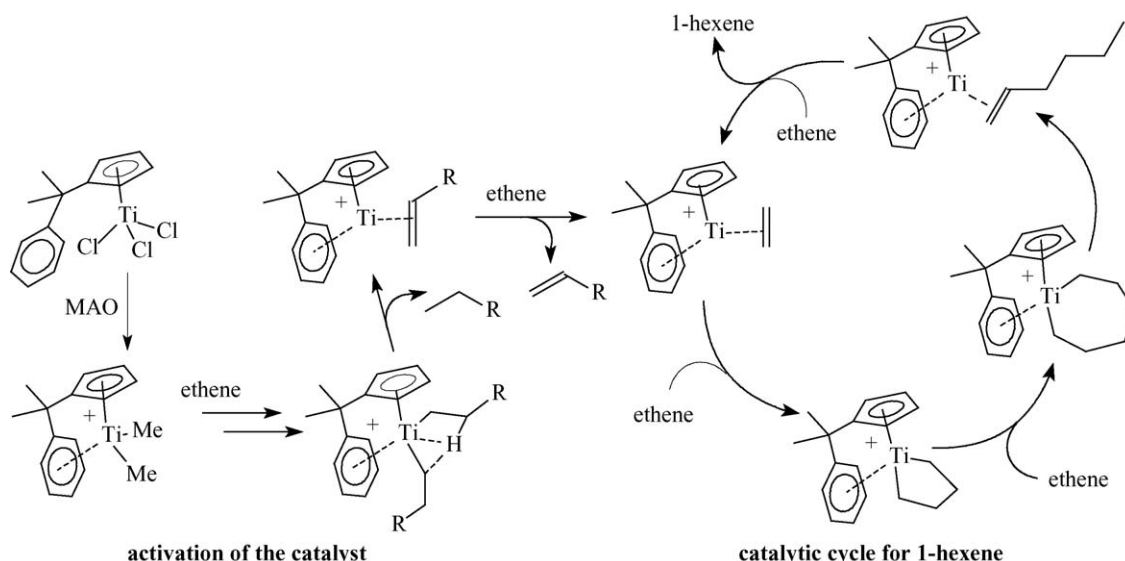
(b) GC–MS (min[M^{•+}]): 7.36 [120, ENB], 7.42 [120, ENB], 8.30 [136], 13.90 [224, C₅H₅C(Ph)C₅H₁₀], 14.40 [256].

(c) GC–MS (min[M^{•+}]): 7.33 [120, ENB], 7.40 [120, ENB], 8.2.5 [136], 13.42 [248], 13.53 [248], 13.70 [246], 13.90 [224, C₅H₅C(Ph)C₅H₁₀], 14.40 [256], 14.46 [256], 17.08 [352].

(d) GC–MS (min[M^{•+}]): 7.33 [120, ENB], 7.40 [120, ENB], 8.2.5 [136], 12.86 [234], 12.97 [234], 13.12 [232], 13.22 [232], 13.90 [224, C₅H₅C(Ph)C₅H₁₀], 14.40 [256], 14.46 [256], 14.53 [256], 16.61 [338], 16.63 [338].

3. Results and discussion

The trimerization catalysis is thought to start with a titanium(IV) catalyst precursor that upon activation with methyl aluminoxane forms a cationic dimethyl complex. In this complex, the arene moiety of the ligand coordinates to the metal center. The dimethyl species can undergo ethylene insertions to produce a bis(*n*-alkyl) compound. Supposedly, this type of complex is in equilibrium with alkyl–olefin–hydride species, which would have the arene moiety detached. Displacement of the olefin by ethylene, which rapidly inserts into the M–H bond, would be identical to the normal chain transfer process of catalytic ethylene polymerization. However, the olefin can also be displaced by the pendant arene moiety to yield an alkyl–hydride complex, which then can undergo reductive elimination to give an alkene and a Ti²⁺ species. The latter reaction has been proposed as the key step for the switch from a polymerization to a trimerization catalyst. Coordination and coupling of two molecules of ethylene gives a titana(IV) cyclopentane. Migratory insertion of a third molecule of ethylene results in the formation of a titana(IV) cycloheptane. Subsequent reductive elimination and displacement steps similar to those occurring in the dialkyl species as discussed above, give back the titanium(II) intermediate (see Scheme 1) [2a,2b,8].



Scheme 1. Proposed reaction mechanism for the catalyst activation and ethylene trimerization.

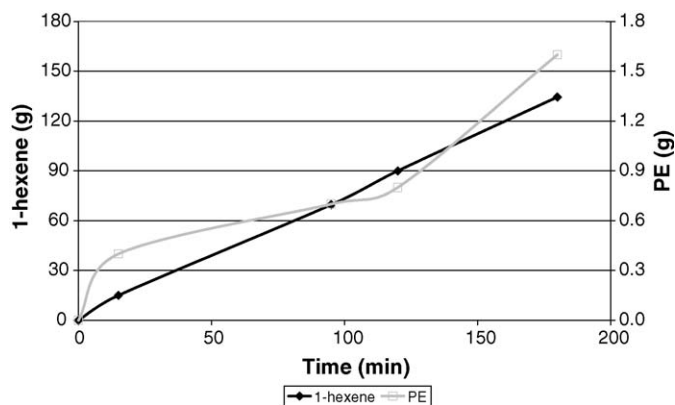


Fig. 2. 1-Hexene and PE formation as a function of time for **4**/MAO (3 μ mol catalyst, 260 mL toluene, 15 bar ethylene, Ti:Al= 1:500 (m/m), 30 °C). Lines are intended for illustrative purposes only.

During the trimerization experiments always the formation of about 2–5 wt% of linear high-density polyethylene was observed [2a]. To gain more insight into the reason of the polyethylene formation, the 1-hexene and PE formation profiles were determined for catalyst **4**/MAO (see Fig. 2). At 30 °C and 15 bar of ethylene pressure this catalyst does not show any significant deactivation over a 3-h period. As shown in Fig. 2, it is possible to identify three phases in the polymer formation process, i.e., (1) a short initial activation period, during which the polymer formation rate is high, (2) a long period, with a moderate growth of polymeric product and (3) a final period with an increased rate in polymerization activity. From the shape of the profile for this stable trimerization catalyst we can conclude, that there are at least two, but perhaps three catalyst species that give polymeric products. This can also be concluded from the GPC analyses of the polyethylene formed during the trimerization reactions. Typically, M_w is in the range of 500,000–1,000,000 g/mol with molecular weight distributions (MWD) of around 40. For a single-site polymerization catalyst under constant conditions (temperature and ethylene concentration), the MWD would have Flory's theoretical value of 2. The fact that the MWDs are much broader proofs that multiple species are active.

3.1. Polymer formation in the activation period

As can be seen in Fig. 2 a significant part of the polymer is formed in an early stage of the reaction. Originally, we assumed that a source of PE is the intermediate dialkyl titanium(IV) cationic species (see Scheme 1). Prior to the changeover to the titanium(II) trimerization catalyst, such a species could catalyze the polymerization of ethylene to PE. However, when considering the results of the DFT calculations by Blok and Budzelaar [8a], one could question the validity of this mechanism. These authors showed that for a diethyl titanium cation the direct hydrogen transfer is already favored over the next ethylene insertion, which means that polymer formation is unlikely. The outcome of these calculations was supported by NMR tube experiments. After adding $B(C_6F_5)_3$ to a mixture of a trimethyl cyclopentadienyl titanium species and a few equivalents of 1-hexene or 1-octene in an aromatic solvent, spontaneous evolution of

methane was observed, while in the residue predominantly either 2-methyl-1-hexene together with traces of methyl-dodecene or 2-methyl-1-octene was detected. Apparently, the presence of one alkyl with β -hydrogens and one methyl group at the cationic titanium(IV) center results in a fast β -hydrogen transfer, which should lead to the generation of the active trimerization catalyst. Even though it cannot be excluded that during the activation at high ethylene pressures PE is formed during the activation step, it is very likely that the majority of the initial polymer originates from other species.

The original reaction mechanism (Scheme 1) stated that the titanium trichloride precatalysts react with MAO to form the corresponding dimethyl titanium cations [2a,2b]. It has always been assumed that this reaction is fast and quantitative. In order to investigate if this is actually the case, the alkylation of cyclopentadienyl titanium trichlorides with aluminum alkyls was studied by means of NMR tube experiments. Reacting Cp^*TiCl_3 with 2–5 eq. of $AlMe_3$ in deuterobenzene yielded only the monomethyl complex $Cp^*TiMeCl_2$. This result is in agreement with the earlier reported synthesis of $Cp^*TiMeCl_2$, which was done by using $AlMe_3$ as a selective mono-alkylating agent [9]. The reaction with 10–30 eq. of $AlMe_3$ gave the dimethyl derivative Cp^*TiMe_2Cl . Both the mono- and dimethyl compounds $Cp^*TiMeCl_2$ and Cp^*TiMe_2Cl were found to be stable for at least 24 h at room temperature in aromatic solvents containing $AlMe_3$. Similar observations were made for the reactions of Cp^*TiCl_3 with 2–30 eq. of MAO. In all cases, the presence of trimethyl titanium complexes could not be detected.

Reacting Cp^*TiCl_3 with 50 eq. of $AlMe_3$ in C_6D_6 resulted in the immediate formation of the dimethyl complex, which slowly reacted further to form a violet-colored solid with the concomitant release of methane. The nature of violet-colored solid is unclear, but based on the color it is presumably a titanium(III) species. The intermediate compound, from which the titanium(III) species is formed, is probably the trimethyl titanium(IV) complex as an NMR tube experiment demonstrated that in absence of an olefin, but in the presence of $AlMe_3$ the trimethyl titanium complex Cp^*TiMe_3 (**1a**) is not stable and decomposes while releasing a gas (most likely methane).

The conventional procedure for starting a trimerization experiments is injection of the trichloro titanium species, Cp^*TiCl_3 , into the reactor loaded with solvent, ethylene and MAO. The slow reaction of Cp^*TiMe_2Cl to Cp^*TiMe_3 makes it likely that the partly alkylated compound is present in the presence of both ethylene and excess of MAO. Methyl or chloride abstraction from this compound will then generate either the dimethyl titanium cation or the cationic methyl titaniumchloride species. Whereas the former, according to the proposed reaction mechanism (see Scheme 1), will react to the titanium(II) trimerization species, the latter species is an active ethylene polymerization catalyst [9,10]. When present such a species will result in the formation of polymer during in the early stages of the reaction.

3.2. Polymer formation in the second and third period

As mentioned before, after the rapid polymer formation at the beginning of a run, a slow but continuous polymer for-

Table 1
Influence of co-catalyst type on productivity and selectivity^a

Co-catalyst	C ₆ (g)	PE (g)	Productivity (10 ³ kg C ₆ mol ⁻¹ Ti h ⁻¹)	C ₆ /PE ratio (g/g)
PMAO	54.0	1.3	11.4	42
d-MAO	52.9	1.2	11.1	44
PMAO + TIBA	35.9	2.1	7.6	17
PMAO + DIBAH	31.1	2.2	6.5	14
PMAO-IP	33.9	3.4	7.1	10
MMAO-3A	35.7	1.6	7.5	22

^a Batch mode, 3 μmol catalyst **5**, Ti:Al = 1:500 (m/m), 360 mL toluene, 50 °C, 30 bar ethylene, 95 min run time.

mation is observed. Such slow processes are not easily interpreted. For example it is not possible to distinguish between very small amounts of highly active short-living catalysts or slow but continuously active ones. Nevertheless, several catalyst transformation pathways can be envisaged with as the most important one the degradation of the ligand system. Evidence for this route came from a number of experiments with pre-mixed catalyst–olefin systems (vide infra). After hydrolysis of such a mixture containing catalyst **1**, MAO and 1-hexene not only the expected 2-methylhexene, and free ligand were found, but in addition 1-phenylcyclohexene was detected as well. The latter is a fragmentation product of the substituted cyclopentadienyl ligand. Loss of the aryl-bearing substituent (instrumental in achieving good trimerization selectivity) will leave an unsubstituted cyclopentadienyl titanium species, which is likely to be active as an ethylene polymerization catalyst.

To evaluate the influence of the type of MAO activator on polymer formation trimerization reactions were carried out in batch mode with different kinds of commercially available MAOs (Akzo Nobel [11]) and with mixtures of MAO and alkyl aluminum compounds:

- PMAO in toluene (Akzo Nobel [11])
 - 4.9 wt% Al, 25 wt% free AlMe₃.
 - Composition of hydrolysis gas: 98.7 mol% CH₄, 0.0 mol% H₂.
- Vacuum-dried PMAO (d-MAO) [12].
- PMAO (450 eq.) + triisobutyl aluminum (TIBA) (50 eq.).
- PMAO (450 eq.) + diisobutyl aluminum hydride (DIBAH) (50 eq.).
- PMAO-IP in toluene (Akzo Nobel [11])
 - 13.4 wt% Al, 14.0 wt% free AlMe₃.
 - Composition of hydrolysis gas: 99.6 mol% CH₄, 0.2 mol% H₂.
- MMAO-3A in isopar (Akzo Nobel [11])
 - 2.1 wt% Al, ~40 wt% free AlR₃.
 - Composition of hydrolysis gas: ~70 mol% CH₄, 30 mol% isobutane, 1.5 mol% H₂.

As presented in Table 1, the C₆ productivity and C₆/PE ratio were found to be highly sensitive for the type of MAO activator used. Whereas PMAO and d-MAO performed equally well with respect to productivity and selectivity, the use of the other MAOs resulted in both a lower productivity and an

increase in the quantity of polyethylene. PMAO and d-MAO differ only in the amount of free AlMe₃ and based on the similarity in results, it is justified to conclude that the trimerization behavior is relatively independent on the amount of free AlMe₃ [13]. What makes these two activators different from the others is the absence of aluminium hydrides. It appears that the use of MAOs, which either contain aluminum hydride species (MMAO-3A, PMAO-IP, PMAO + DIBAH) or are able to generate them (PMAO + TIBA), affects both productivity and selectivity. This behavior might be the consequence of a stronger coordinating ability of the hydride containing anions versus the methyl containing ones [14]. As a stronger coordination means more blocking of the active sites a lower productivity will be observed. In this context it is notable that both Arndt et al. [14] and Muhoro and Hartwig [15] were able to get X-ray structure determinations of a bis(cyclopentadienyl)titanium(II) complexes with a coordinated hydroborane or diisobutyl aluminum hydride, respectively.

The decrease in selectivity probably has its origin in the alkylating power of the various MAOs. As demonstrated above partially alkylated titanium(IV) species, such as Cp'/TiMe₂Cl, are thought to be one of the main reasons for polymer formation (at least in the earlier stages of the reaction). If a certain type of MAO is less active in the alkylating reaction, this will lead to an increase in PE formation. In addition, it will also lead to a lower production of 1-hexene as the absolute number of species active in trimerization is less. The difference in activity in the alkylation reaction can also explain why PMAO-IP performs so much worse than PMAO. With respect to its composition it differs from PMAO that it has less free AlMe₃, and that it contains some hydrides. Based on the results for d-MAO, the lower free AlMe₃ content should not make a substantial difference. Also, the hydride content is quite low (about 15% of MMAO-3A), which makes the reasoning that hydride coordination alone is causing its low productivity unsatisfactory. A very distinct difference between PMAO and PMAO-IP resides in the synthetic procedure. Contrary to PMAO, PMAO-IP is prepared via a non-hydrolytic route [16]. As a consequence of this different synthetic route, PMAO-IP has an other cage-structure resulting in a higher storage stability. Unlike PMAO it does not form a precipitate with time, but it gives solutions with increased viscosities. The precipitate in the case of PMAO is an aluminium oxide-like structure, resulting from AlMe₃ liberation from the cages. It is quite possible that this difference in stability is translated into a difference in reactivity in the alkylation reaction.

3.3. Premixing

As discussed above partially alkylated titanium species are assumed to be responsible for the formation of polymer. By using catalysts that have been alkylated prior to their addition to the reactor, it should be possible to avoid the polymer formation by these species. The best way of doing this, is, of course, the synthesis of trimethyl titanium species, Cp'/TiMe₃. However, the synthesis and isolation of these compounds is not always straightforward. Another approach would be the reaction of

Table 2
Effect of premixing step on productivity and selectivity^a

Catalyst	Method ^b	C ₆ (g)	C ₁₀ (g)	PE (g)	Productivity (10 ³ kg C ₆ mol ⁻¹ Ti h ⁻¹)	C ₆ /PE ratio (g/g)
1	Standard	13.4	0.5	1.1	5.3	13
	Premix	17.6	0.8	0.7	7.1	25
2	Standard	2.0	0.0	0.4	1.2	8
	Premix	3.0	0.0	0.3	1.2	11
3	Standard	9.1	0.1	0.4	12.1	23
	Premix	19.5	0.5	0.3	26.0	65
4	Standard	10.2	0.1	0.2	13.7	57
	Premix	11.8	0.1	0.1	15.8	84
5	Standard	15.3	0.5	0.5	20.4	31
	Premix	19.2	0.8	0.5	25.5	38

^a Semi-batch mode, 260 mL toluene solvent, 30 °C, 10 bar ethylene, 15 min run time, 10 μmol for catalysts **1** and **2**, 3 μmol for catalysts **3**, **4** and **5**, Ti:total Al = 1:500 (m/m).

^b 15 min premix time.

trichloro titanium species, Cp'TiCl₃, with MAO outside the reactor, and this procedure has been used to test the hypothesis. The results have been listed in Table 2. To eliminate other variables than pre-alkylation (e.g., decomposition, ethylene/1-hexene co-trimerization, temperature) on the catalyst performance a short run time of 15 min and a low ethylene pressure (10 bar) were chosen.

From the results in Table 2, it is clear that the pre-activation of the catalysts in all cases had a beneficial influence on the 1-hexene/PE ratio. An increase in the 1-hexene productivity was observed, while the PE formation was somewhat reduced or at the most equal. Both results indicate that by premixing more trimerization catalyst species are formed in the activation step at the expense of the number of polymerization catalyst species.

The increase in productivity upon premixing with MAO is strongly related to the catalyst structure. Catalysts with substituted pendant aryl groups showed only a low (**2**) or a moderate (**4** and **5**) increase in productivity after pre-mixing, while for

the catalyst with an unsubstituted aryl group (**1** and **3**) a >70% increase in productivity was observed.

The decrease in productivity by using longer premix times (15 min instead of 1 min) clearly shows that the titanium alkyls are not very stable under the conditions used and that the premix time should be short.

Instead of using MAO as the alkylating agent in the premix step, it is also possible to use AlMe₃. By injecting catalyst solutions, which were prepared by pre-mixing the cyclopentadienyl titanium trichlorides with 50 eq. of AlMe₃, into toluene solutions containing MAO (250 or 450 eq.), a reduction of the PE formation was observed in comparison to the standard procedure (cf. catalyst **1** – premix, Table 2 with entry 1, Table 3). Under inverted conditions, i.e., a catalyst premixed with 250 eq. of MAO and 50 eq. of TMA as a scavenger (entry 2), very similar results were observed. In the latter case a lower 1-hexene productivity was observed than for the MAO-only case. The reason for this behavior is most likely the lower amount of impurity scavenger present during these runs in comparison to the baseline run. Similar effects can be observed by looking at results for a standard run with less MAO (300 eq. versus 500 eq., entry 3, lower productivity) or a premix run with more MAO in the reactor (450 eq. versus 250 eq., entry 4, higher productivity). Also when using a different catalyst, **3**, increasing the amount of MAO improves the efficiency while the amount of PE formed remains more or less the same (entries 5 and 6).

The importance of the alkylation level was further proven by trimerization experiments that were started with titanium species having different degrees of alkylation (see Table 4). By using the trimethyl versions of catalysts **1** and **5** (**1a** and **5a**), the catalytic productivity was almost doubled, while the selectivity was doubled (**5**) or even almost quadrupled (**1**).

From the aforementioned results, it is clear that a large part of the polyethylene formation can be suppressed by activating the pre-catalyst in the absence of ethylene. The premix time should be short as prolonged exposure of the catalyst to the alkylating agent without ethylene present reduces the productivity, even though the polymer formation itself is reduced as well and the C₆/PE ratio is improved. The extent of the decrease in productivity is much larger than the one observed normally during trimerization experiments. This suggests that the species active in ethylene trimerization is not stable in the absence of ethylene. One way to achieve the advantage of the premixing without this loss of productivity could be premixing of pre-catalyst and MAO

Table 3
Effect of type and amount of co-catalyst and method of addition on productivity and selectivity^a

Entry	Premix (eq.)	Reactor (eq.)	C ₆ (g)	C ₁₀ (g)	PE (g)	Productivity ^c	C ₆ /PE ratio (g/g)
1	AlMe ₃ (50)	MAO (250)	13.4	0.4	0.6	5.4	22
2	MAO (250)	AlMe ₃ (50)	12.9	0.3	0.6	5.2	22
3	–	MAO (300)	10.0	0.3	0.7	4.0	13
4	AlMe ₃ (50)	MAO (450)	15.5	0.7	0.6	6.2	26
5 ^b	MAO (250)	MAO (250)	19.5	0.5	0.3	26.0	65
6 ^b	MAO (750)	MAO (750)	27.8	1.2	0.4	37.1	70

^a Semi-batch mode, catalyst **1** (10 μmol), 260 mL toluene solvent, 30 °C, 10 bar ethylene, 15 min run time, 1 min premix time.

^b Catalyst **3** (3 μmol).

^c Productivity in 10³ kg C₆ mol⁻¹ Ti h⁻¹.

Table 4
Effect of the alkylation stage of added catalyst on productivity and selectivity^a

Catalyst	C ₆ (g)	C ₁₀ (g)	PE (g)	Productivity (10 ³ kg C ₆ mol ⁻¹ Ti h ⁻¹)	C ₆ /PE ratio (g/g)
Cp ⁺ /TiCl ₃ (1)	13.1	0.5	1.0	5.2	13
Cp ⁺ /TiMe ₂ Cl ^b	15.5	0.7	0.6	6.2	26
Cp ⁺ /TiMe ₃ (1a)	23.1	0.9	0.5	9.2	46
Cp ⁺ /TiCl ₃ (5)	15.3	0.5	0.5	20.4	31
Cp ⁺ /TiMe ₃ (5a) ^c	31.9	2.0	0.5	42.3	60

^a Semi-batch mode, 260 mL toluene solvent, 30 °C, 10 bar ethylene, 15 min run time, catalyst amount: 10 μmol (**1**), 3 μmol (**5**), Ti:Al = 1:500 (m/m).

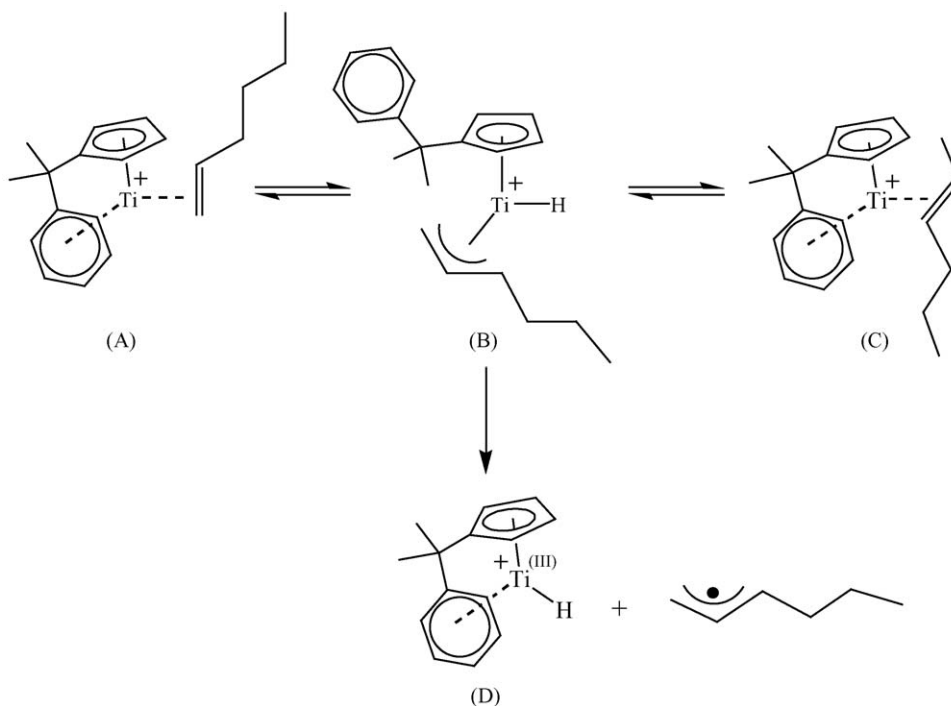
^b Cp⁺/TiCl₃ (**1**) was pre-mixed with 50 eq. of AlMe₃ for 1 min, total Ti:Al = 1:500 (m/m).

^c Activated with 1.1 eq. of [R₃N][B(C₆F₅)₃], MAO (Ti:Al = 1:20 (m/m) present as impurity scavenger).

in the presence of alkenes other than ethylene. Such alkenes, e.g., 1-hexene, would have the same stabilizing effect on the active catalyst, but even if polymerization would occur during the activation, a soluble polymer (e.g., poly-1-hexene) would be formed. In order to check the hypothesis a number of olefins were tested by premixing a catalyst with 250 eq. of MAO activator in the presence of an olefin (a complete overview of all results is given in the supplementary information). In all cases, norbornene and its derivatives enhance productivity, while a good selectivity is maintained. For other olefins there is no systematic change, as in some cases the presence of olefins has hardly any influence, while in others cases a strong decrease in both productivity and selectivity was observed. This striking difference between 2-norbornene or one of its analogs and the other olefins is very interesting and gives possible clues about the underlying reasons for polymer formation during the trimerization process.

To investigate the reactions taking place during the preactivation in the presence of an olefin, a mixture containing 1-hexene was hydrolyzed and analyzed with GC-MS. In addition to the

expected methane and 2-methylhexene, also the hexene isomers 2- and 3-hexene were observed. This shows that in the absence of ethylene the titanium trimerization catalysts are olefin isomerization catalysts. The isomerization of 1- to 2-hexene (or identically from 2- to 3-hexene) will most likely proceed via a mechanism involving titanium allyl hydride species (Scheme 2, **B**) and oxidative addition/reductive elimination reactions. The 1-hexene side-on coordinated species (Scheme 2, **A**) is identical to the complex formed in the last step of the catalytic circle of the trimerization reaction (see Scheme 1). If the life-time of this complex is sufficiently long, i.e., if the exchange with ethylene is not immediate, γ -hydrogen abstraction of the 1-hexene results in the formation of an allyl-hydride complex with the potential of forming a titanium(III) hydride species (**D**), which is known as an active polymerization catalyst [17]. This mechanism was supported by the results from electrospray ionization mass spectroscopy (ESI-MS) analyses [18]. For our investigations solutions of **1a** in aromatic solvents were reacted with 1.1 eq. of B(C₆F₅)₃ or 20 eq. of MAO in the presence of 10 eq. of an α -



Scheme 2. Possible reactions for 1-hexene coordinated Ti-species.

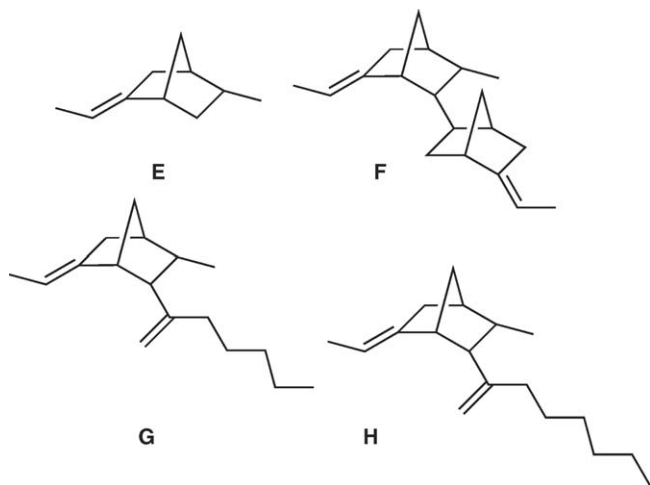


Fig. 3. Saturated and unsaturated hydrolysis products of preactivation mixtures containing ENB.

olefin. By using a mixture of 1-hexene, 1-heptene or 1-octene as olefins, mass peaks corresponding to the $[(C_5H_4CMe_2Ph)TiH]^+$ and $\{(C_5H_4CMe_2Ph)Ti(1-alkene)-H\}^+$ cations (Scheme 2, **D** and **B**) were observed [19]. An important conclusion from this is, is that, fundamentally, it will be impossible to reduce the polymer formation completely.

The reason that the preactivation in the presence of norbornene or one of its derivatives never leads to poorer results is caused by the difference in the activation mechanism. Similarly to the other olefins, 2-norbornene and its analogs can insert in the Ti–Me bond. The second step, the direct hydrogen transfer, is however disfavored due to steric reasons and the titanium complex will remain in the 4+ oxidation state. This was confirmed by GC–MS analysis of hydrolyzed mixtures of **1**/MAO/ENB, which showed only compounds with saturated end-groups, such as 2-methyl-5-ethylidene-norbornane (**E**, Fig. 3) or 2-methyl-3-(5-ethylidene-norborn-2-yl)-5-ethylidene-norbornane (**F**). The formation of titanium(II) species will only occur after an insertion of an ethylene (or an α -olefin) as was demonstrated by similar GC–MS analyzes of mixtures of **1**/MAO/ENB and an α -olefin (1-heptene, 1-octene). In addition to compounds **E** and **F** the compounds 2-methyl-3-(hepten-2-yl)-5-ethylidene-norbornane (**G**) and 2-methyl-3-(octen-2-yl)-5-ethylidene-norbornane (**H**) were found. The latter, which both have an additional unsaturation, derive from species that have undergone an initial insertion of ENB into the titanium methyl bond, followed by an insertion of the α -olefin and subsequent hydrogen transfer. This confirms that the Ti catalyst activated in the presence of 2-norbornene or ENB remains in the 4+ oxidation state, while in case of other olefins after the insertion of the olefin it reacts further to titanium(II). After an insertion of ethylene, which in the case of preactivation will happen in the reactor, the titanium(IV) precatalyst will be transformed to the actual titanium(II) catalyst species. Therefore, there is no possibility to rearrange to a titanium(III) compound with the accompanying increase in PE formation.

It was noted that in the trimerization experiments with catalysts premixed in the presence of ENB, 2-norbornene or

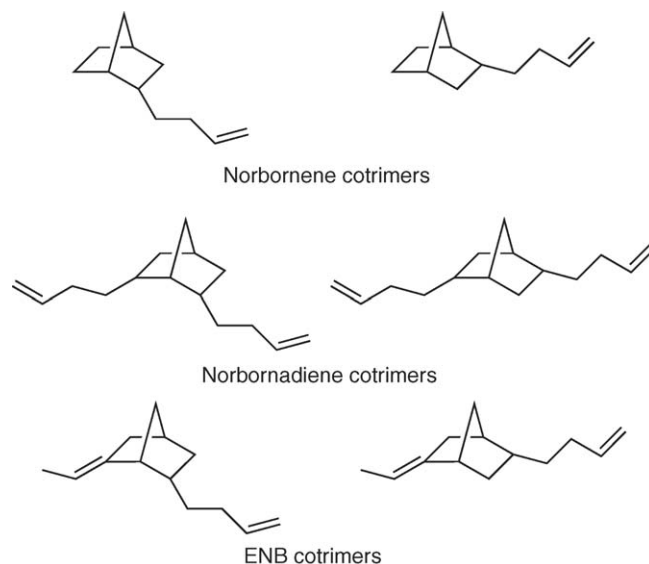


Fig. 4. Co-trimerization products for norbornene derivatives.

2,5-norbornadiene, a rather long (0.05 mL: 10–15 s, 0.5 mL: 3–4 min) initiation period (the time between catalyst injection and observed reactor exotherm) is present. This phenomenon can be explained by the assumption that the ethylene trimerization to 1-hexene does not start until all of the norbornene derivatives have been converted into the corresponding co-trimer. The presence of an olefin, which binds stronger to the titanium metal center than ethylene, will induce a selective co-trimerization that is preferred over ethylene trimerization. Interestingly, this means that the titanium ethylene trimerization catalyst may be useful for the preparation of some unique α -olefins, such as 4-norbornyl-1-butene and related compounds (see Fig. 4) [20]. A comparable selective co-trimerization process of ethylene and styrene was also observed by Pellechia et al. [21] for the $(C_5Me_5)TiMe_3/B(C_6F_5)_3$ catalyst in toluene during their attempts to copolymerize these olefins.

From the present study it has become clear that the polymer formation can be reduced drastically to less than 1 wt%. Unfortunately, the remaining small amount of high-molecular weight polymer could still lead to issues, e.g., reactor fouling. One way to reduce the disadvantageous effects of the polymeric products is, instead of preventing the polymerization itself, lowering of the molecular weight of the polyethylene formed. From the ethylene trimerization reactions catalyzed by chromium-based systems it is known that addition of hydrogen can reduce the molecular weight of the polymer to such an extent, that it will stay in solution under the applied temperature of about 100 °C [3d,4,22]. In order to evaluate the influence of hydrogen on the present system, the trimerization reaction was carried out for two catalysts under a partial hydrogen pressure of 3 bar (see Table 5). However, no positive effect on the polymer formation/solubility was observed. The molecular weight of the PE remained the same, pointing to a very low H_2 response of the catalysts. Obviously, the productivity decreased as the ethylene partial pressure, and thus the ethylene concentration in solution, was lower.

Table 5
Hydrogen influence on the titanium catalyst trimerization^a

Catalyst (μmol)	H ₂ (bar) ^b	C ₆ (g)	C ₁₀ (g)	PE (g)	Productivity ($10^3 \text{ kg C}_6 \text{ mol}^{-1} \text{ Ti h}^{-1}$)
1	–	55.1	4.1	4.6	2.3
(15)	3	44.7	3.3	3.8	1.9
5	–	98.7	11.9	1.9	20.8
(3)	3	82.9	8.4	2.4	17.5

^a Semi-batch mode, 30 °C, 260 mL toluene, 15 bar total pressure, 95 min run time, Ti:Al = 1:500 (m/m).

^b Partial pressure.

4. Conclusions

The catalytic ethylene trimerization with the titanium catalyst/MAO system is a highly efficient and very selective process, resulting in more than 90 wt% of C₆ product from the converted ethylene, with an excellent C₆ selectivity of more than 99% towards 1-hexene. This selectivity is higher than for most of the other trimerization processes. However, as all other trimerization catalysts, the present one has the same disadvantage, i.e., the production of 2–5 wt% of high molecular weight polyethylene. Not only will this lead to lower yields, but the presence of high molecular weight PE in the reaction mixture can cause reactor fouling. This is especially true for the titanium-based process, which currently runs at lower temperatures than the chromium-based systems (30–80 °C versus 110–125 °C for the CPCChem process). It is, therefore, highly desirable to know which factors are involved in the formation of polymeric products and how their formation can be reduced or prevented.

We have identified that the PE formation turns out to be catalyzed by at least two different species/processes. A significant amount is formed in early stage of the reaction and it is most likely caused by the presence of partly alkylated titanium species, which may act as polymerization catalysts. The PE formation during later stages of the reaction is due to degraded catalyst species, which means that polymer formation is an inherent property of this catalyst system.

It has been shown that the PE formation in beginning of the reaction can be greatly reduced by premixing the Cp^{*}TiCl₃ and MAO prior to injection into the reactor. This went hand in hand with a significant increase in productivity. We also demonstrated that the type of MAO activator/impurity scavenger is of great importance. For a high productivity and a low yield of PE it is essential to use MAOs that do not contain and/or are not able to generate aluminum hydride species. The best results with respect to both productivity and selectivity were obtained by starting from trimethyl titanium compounds.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.12.030.

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