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ARTICLE

Titanium-based phenoxy-imine catalyst for selective ethylene trimerization: effect of temperature on the activity, selectivity and properties of polymeric side product

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Astrid Cordier,^a Pierre-Alain Breuil,^b Typhène Michel,^b Lionel Magna,^b Hélène Olivier-Bourbigou,^b Jean Raynaud,^a Christophe Boisson,^{*a} and Vincent Monteil^{*a}

The reactivity of a phenoxy-imine-ether system (FI)TiCl₃/MAO was studied toward selective ethylene trimerization. This system was shown to either trimerize or polymerize ethylene depending on the reaction temperature. Its selectivity switches from a significant production of the trimerization product, 1-hexene (85 wt %, 520–450 kg_{1-hexene} g_{Ti}⁻¹ h⁻¹) between 30 and 40 °C, to a moderate polyethylene formation (70–80 wt %, 60–70 kg_{polyethylene} g_{Ti}⁻¹ h⁻¹) at higher reaction temperature (T > 60 °C). Polymerization was investigated based on an original “polymer-to-catalyst” strategy aiming at identifying the active species responsible for this side reaction. Using DSC, SEC and high temperature ¹³C NMR analyses, polyethylenes were found to exhibit high molar masses (> 10⁵ g mol⁻¹) and a low 1-hexene content (< 1 mol %) at any temperature. Kinetic studies support that trimerization and polymerization species are generated from the catalyst precursor at 40 °C but a parallel process may occur at higher temperature. The increase dispersity to 4.6 at 80 °C suggests a change from single to multisite catalysis. The poor comonomer incorporation ability of the active species is reminiscent of a molecular Ziegler Natta or a bulky post-metallocene catalyst.

Introduction

Short linear alpha-olefins (LAOs) are crucial intermediates for the production of consumer goods such as lubricants, detergents and mostly polyethylene grades (HDPE, LLDPE). To face the soaring demand in LAOs driven by the global population growth, industrial companies invest continuous efforts for process optimization. Selective ethylene oligomerization processes have emerged to meet the specific requirements of the plastic industry. In the field of selective ethylene trimerization, homogeneous chromium catalysis has been extensively studied and is widely utilized for 1-hexene production.^{1–3}

Among alternative metals, titanium has proven its legitimacy in selective 1-hexene production.^{4,5} In 2001, Hessen *et al.* reported the first hemilabile ancillary systems based on monocyclopentadienyl titanium bearing a pendant aryl group (η⁵-C₅H₄CMe₂C₆H₅)TiCl₃/MAO to be able to produce 1-hexene with unprecedented selectivities (> 75 wt %).⁶ A decade later, Fujita and co-workers shed light on a second family of titanium-based trimerization systems comprising a single phenoxy-imine tridentate ligand (SFI).⁷ Upon activation with 10 000 equivalents of methylaluminoxane (MAO), tridentate phenoxy-imine complex **1** (Fig. 1) yields 1-hexene (92.3 wt %) with an activity close to the performances of the commercial chromium-based

system. 1-hexene selectivity is limited by the formation of higher branched oligomers and polyethylene by-products. Although polymer selectivity seems insignificant (0.4 wt %), its accumulation causes major process issues (e.g. pipe clogging, reactor fouling). Therefore, understanding, controlling and eventually preventing the polymerization is the main challenge for process efficiency improvements and feedstock management.

Most of the reported literature on titanium-based trimerization systems focused on improving and rationalizing the oligomerization reaction, paying little attention to polymerization.^{8–20} On the one hand, applying the ligand-oriented catalyst design strategy, Fujita and coworkers reported the strong dependence between ligand structure and the reactivity of trimerization phenoxy-imine systems.⁹ Indeed, 1-hexene selectivity and activity can be tuned by subtle changes of substituents on specific positions of the phenyl rings. Ishii *et al.* highlighted that the activity and selectivity was modulated by altering the type and position of alkyl substituents.⁹ Nevertheless, any modification of the global framework of the ligand generates polymerization active species.^{8,11,14} On the other hand, efforts were invested on the mechanism and active species involved in the trimerization process. Even though several experimental and calculation studies showed evidences for a metallacycle mechanism, the activation process remains unclear.^{8,11,12} DFT studies reported by Ishii *et al.* support the reduction of cationic Ti^{IV} *via* a β-H transfer followed by reductive elimination to afford cationic Ti^{III} active species.⁹

^a UMR 5265, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Univ. Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France, Fax: (+33)4-7243-1768 Email: monteil@univ-lyon1.fr; boisson@univ-lyon1.fr

^b IFP Energies nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

†Electronic Supplementary Information (ESI) available: details of catalytic tests data and kinetic fitting. See DOI: 10.1039/x0xx00000x

Despite these rigorous studies, no clear identification of polymerization active species is reported. Duchateau and coworkers proposed the formation of a "TiR_x" polymerization species, resulting from the abstraction of the ligand by trimethylaluminum.¹³ Interestingly, they highlighted a decrease in 1-hexene selectivity from 93 wt % at 28 °C to 64 wt % at 58 °C, with a promoted polyethylene selectivity from 1.6 to 35 wt %.

We report herein an original polymer-to-catalyst approach, which consists in gathering information about the polymer to have an insight into the nature of the polymerization active species. For the first time, the influence of temperature on the activity and selectivity was systematically investigated between 30 and 80 °C. From this study, polyethylene properties were analyzed according to reaction temperature, and combined with kinetic studies to propose hypotheses on polymerization active species.

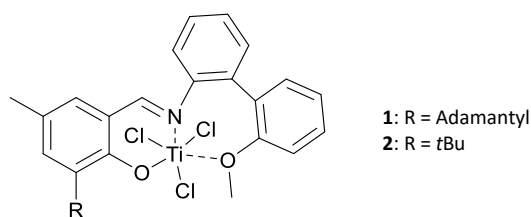


Fig. 1 Titanium-based phenoxy-imine complex for selective trimerization

Results and discussion

Effect of the temperature on the reactivity

Selective trimerization of ethylene was studied with the titanium-based tridentate phenoxy-imine complex **2** (Fig. 1). This SFI complex was selected for its straightforward synthesis and yet similar catalytic performances compared to complex **1**/MAO.^{9,10} Indeed, similar steric hindrance is provided by adamantyl and *tert*-butyl groups at the R position.

Although the temperature-sensitivity of such system is mentioned in the literature, there are only few examples of reactions performed at temperature higher than 30 °C.¹³ To have a clear view of the influence of temperature on the activity and selectivity of the system, a series of 7 experiments were performed from 26 °C to 80 °C (Table 1). All catalytic tests were carried out in a semi-batch mode under 10 bar of ethylene pressure for 30 minutes.

A lower activity reveals the deactivation of the system while increasing temperature. The maximal activities of the system are achieved between 26 and 40 °C (entries 1-3), which is consistent with the observations made in the literature and patents.^{7,21} In fact, Fujita and coworkers reported a high activity at 30 °C for the original complex **1** of 260 kg_{ethylene} g_{Ti}⁻¹ h⁻¹, calculated after extrapolation to 10 bar of ethylene.⁷ Interestingly, the activity drops above 50 °C to reach a minimum at 80 °C (entry 7). This deactivation with the increase of temperature is counter-intuitive regarding pure kinetic considerations and reveals a pronounced sensitivity of the system to temperature. To the best of our knowledge, this

is the first study providing a precise description of the activity decay of a phenoxy-imine titanium-based trimerization systems at higher reaction temperature.

Table 1. Catalytic performance of complex **2**/MAO

Test	T (°C)	t (min)	n _{Ti} (μmol)	Al/Ti	Activity	
					Global ^a	Polym. ^b
1	26	29	2.77	1 640	419	1.3
2	32	35	3.46	1 310	607	5.7
3	42	32	3.78	1 200	537	17.5
4	49	31	3.4	1 330	160	72.3
5	58	31	4.59	1 000	172	84.3
6	68	28	3.19	1 422	97	68
7	80	31	3.85	1 180	78	62.4

Conditions: complex **2**, MAO 30 % in toluene (1 mL), 300 mL toluene, 10 bar of ethylene

^a in kg_{ethylene} g_{Ti}⁻¹ h⁻¹

^b in kg_{polyethylene} g_{Ti}⁻¹ h⁻¹

Along with the activity, the selectivity of this system is temperature-dependent. In the case of low temperature and high activity (Table 1, entries 1-3) 1-hexene is the main product of reaction with more than 85 wt % selectivity (Fig. 2). Low temperatures are therefore necessary to optimize 1-hexene production, which amounts to 520 kg_{1-hexene} g_{Ti}⁻¹ h⁻¹ at 42 °C. In terms of secondary products, about 10 wt % of branched C₁₀H₂₀ oligomers are also formed by co-trimerization of 1-hexene and two ethylene molecules. However, no 1-hexene isomerization is observed. Eventually, ethylene polymerization occurs as minor side reaction. Although this polyethylene production seems insignificant compared to trimerization, it reveals the presence of a polymerization species even at low reaction temperature. Whilst reaction temperature increases, polyethylene production is enhanced but trimerization is highly disfavored. Above 60 °C, the catalytic system mainly polymerizes ethylene (80 wt % selectivity at 80 °C) with a moderate activity (Table 1, entry 7).

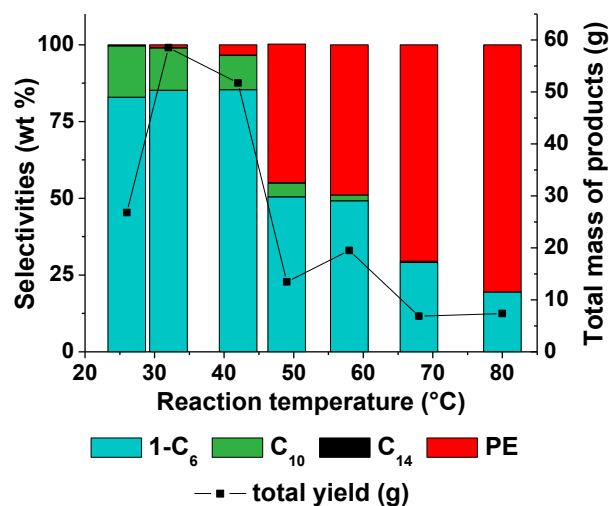


Fig. 2 Evolution of product formation with temperature

The combination of a poorer activity with a higher polymer formation at elevated reaction temperature reveals a new behavior of such systems. Moreover, the omnipresence of polyethylene questions the nature of the active species. As mentioned earlier, the production of polymer increases despite the deactivation of the overall catalytic system above 60 °C. It is still unclear whether the prominence of polyethylene formation at elevated temperature reflects an increase in activity of polymerization catalyst formed during activation and/or the generation of additional active species from trimerization catalyst alteration.

Further investigations support that polymerization catalyst(s) is(are) generated after activation with ethylene rather than from a side reactions during the preactivation step. Indeed, a preheating of the precatalyst/cocatalyst mixture at 80 °C for 30 minutes before running the catalytic test at 30 °C in presence of ethylene has no significant impact on the activity and the selectivity.

Polymer characterization

The investigation of polymer properties is a crucial step for polymerization active species identification. By definition, every catalyst is unique and leaves its fingerprint in the polymer they produce.²² Generally speaking, polyethylenes displaying a large molar mass distribution (MMD) are obtained in the case of multi-site catalysis. In contrast, polymers highly homogeneous in size ($\bar{M}_w \sim 2$) can be produced by single-site metallocenes and post-metallocenes. The amount of short chain branching (SCB) and average molar masses depend on the ability of the species to perform LAO insertion and transfer reactions. These reactions are governed by steric and electronic environments around the metal center. Thus, after the analysis of the polymers obtained in the series, their properties are compared with the ones reported for several classes of catalysts. This strategy allows to have more information about the polymeric side product and also to categorize the unknown active species within a specific family of catalyst.

PE-32 to PE-80 (Table 1, entries 2-7) were characterized in terms of molar mass distribution (MMD) and chemical composition employing high temperature SEC, high temperature ¹³C NMR and DSC techniques. HT-SEC analyses of molar mass distributions reveal a clear evolution of polymer properties upon increase of reaction temperature. All polymers display a high weight average molar mass (M_w) with a decreasing M_w from 15×10^5 to 2×10^5 g mol⁻¹ for PE-32 and PE-80 respectively (Fig. 3, Table 2). It is well known that high molar masses are synonym of disfavored transfer reactions. Moreover, temperature enhances the rate of transfer reactions leading to the decrease of M_w . Under conditions of favored 1-hexene productivity, narrow molar mass distributions are obtained with a low dispersity of about 2. A dispersity around 1.7-1.8 is uncommon in catalytic polymerization except for peculiar pseudo-living bis(phenoxy-imine) systems.²³ Such low values may emerge from a cut-off of the HT-SEC device for ultra-high molar mass hydrocarbon chains ($> 10^6$ g mol⁻¹). It is worth pointing out that the higher the temperature, the broader the MMD since a dispersity of 4.6 was measured for PE-80.

Chemical composition distribution reflects the ability of the catalyst to incorporate comonomers, 1-hexene in this case. By coupling differential scanning calorimetry and high-temperature ¹³C NMR, the length and content of chain branching were evaluated. Only C₄ branching is identified from the incorporation of 1-hexene in the polyethylene backbone. For all polymers produced from 32 °C to 80 °C, 1-hexene content is substantially low (< 1 mol %) and even decreases at higher reaction temperature (Table 2). This trend is explained by the lower amount of 1-hexene produced at $T > 42$ °C (Fig. 2). Noteworthy, high 1-hexene concentration in the reaction media at 32 °C (Table S1) has little impact on the comonomer content in the polymer. Consequently, the polymerization species displays a poor incorporation ability toward short linear alpha-olefins.

Polymer analyses provide valuable information about the polymerization species in the SFI system. First of all, PE-32 to PE-68 are likely produced by one active species as low dispersities are commonly ascribed to single-site catalysis.²⁴⁻²⁶ However, several active sites may be generated at 80 °C given the larger span of PE chain size. To the best of our knowledge, it is the first study reporting the analysis of the polymer produced with such titanium-based phenoxy-imine trimerization systems. Polymers with high molar masses and a low dispersity were also mentioned by Ye *et al.* with a hemi-metallocene ($\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_5$)TiCl₃/MAO.²⁷ In addition, the poor ability for LAOs copolymerization (see a comparison with a metallocene in Fig. S3) and limited transfer reaction are common features for bulky post-metallocenes or ligand-free molecular titanium-based Ziegler-Natta species. On the one hand, the ligands provide a significant steric hindrance close to the metal center, which hampers β -H elimination and LAO coordination. On the other hand, it is typical from ZN species that the PE macromolecules of high molar masses exhibit a low LAO content.²⁸

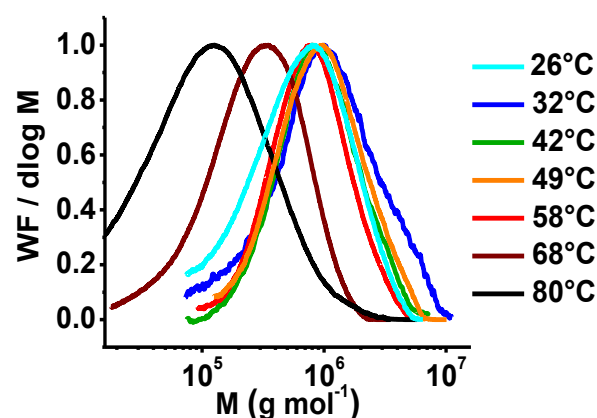


Fig. 3 Molar masses distributions for polymers obtained between 26 and 80 °C.

Table 2. Average molar masses and chemical compositions for polymers obtained between 26 and 80 °C.

Polymer	Reaction temperature (°C)	M_w^a (kg mol ⁻¹)	\bar{D}^a	1-hexene content (mol %) ^b
PE-26	26	910	2.1	NA ^c
PE-32	32	1 550	2.5	0.90
PE-42	42	1 170	1.7	0.60
PE-49	49	1 205	1.8	0.20
PE-58	58	960	1.7	0.08
PE-68	68	380	2.3	0
PE-80	80	190	4.6	0

^adetermined by Size Exclusion Chromatography at 150 °C^bdetermined by High temperature ¹³C NMR at 120 °C^cdissolution issues preventing the analysis

Kinetic studies

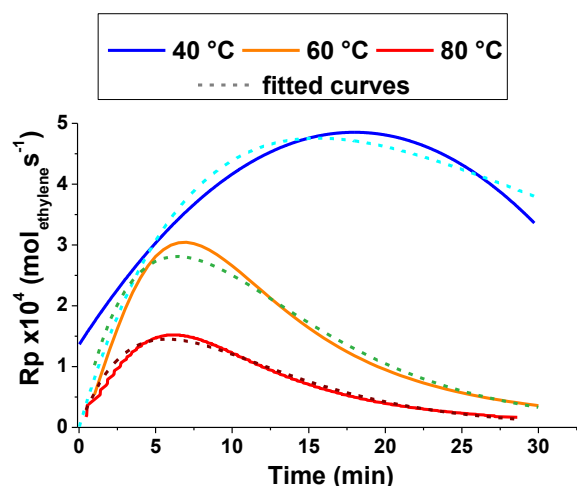
To clarify the relationship between trimerization and polymerization species, kinetic studies were performed at 40, 60 and 80 °C using a medium-throughput automated Chemspeed platform. Catalytic tests were conducted during 5, 10, 20 and 30 minutes in three identical autoclaves.

The kinetic studies reveal that the evolution of ethylene consumption is strongly dependent on the reaction temperature. Fig. 4 shows a clear difference in the reaction rate profile between low and high reaction temperature for experiments carried out for 30 minutes. For all temperatures, activity increases and progressively decreases. The maximum reaction rate of 540 kg_{ethylene} g_{Ti}⁻¹ h⁻¹ at 40 °C is 1.5- and 3-fold of the activity at 60 °C and 80 °C, respectively. Moreover, the system deactivates quicker at higher reaction temperature. The decay in activity is initiated within the first 10 minutes of reaction at 60 and 80 °C while the system starts deactivating after 18 minutes at 40 °C. Average activities for the three experiments (441 kg_{ethylene} g_{Ti}⁻¹ h⁻¹ at 40 °C, 161 kg_{ethylene} g_{Ti}⁻¹ h⁻¹ at 60 °C and 106 kg_{ethylene} g_{Ti}⁻¹ h⁻¹ at 80 °C) are in the same order of magnitude than for the temperature study (Table 1, entries 3, 5 and 7).

A first order dependence of the reaction rate with ethylene concentration was observed (Fig. S6) and a reliable fitting with experimental data was achieved by applying Kissin's kinetic model.²⁹ The model has been applied to oligomerization reaction considering ethylene insertion in the metallacycle as the propagation step. This specific Kissin's model involves a process with initiation (k_i), propagation (k_p) and deactivation (k_d) steps whose reaction rate is described by the following equation:

$$R_p = k_p [C_2][Ti] [\exp(-k_i t) - \exp(-k_d t)] k_i / (k_d - k_i)$$

This model accurately corroborates with experimental data especially in conditions of enhanced polymer productivity, i.e. 60 °C and 80 °C (Fig. 4 and Table 1, entries 5 and 7). Applying Kissin's model at 40 °C is relevant although the fast initial activation could not be fitted. Details regarding data fitting are provided in the supplementary information (Table S5)

**Fig. 4** Evolution of reaction rate from experimental data (solid line) and fitting using Kissin's kinetic model (dashed lines)

As a result, the rate of reaction is governed by an elementary step involving one ethylene molecule in our conditions. Thus, a first order reaction towards ethylene concentration excludes the oxidative coupling as rate determining step of the metallacycle process. DFT calculations reported by Ishii *et al.*, indicate that the insertion of ethylene in the pentacycle is kinetically limiting as it exhibits the highest free energy (122.3 kJ mol⁻¹).⁹

The accurate reproducibility of Chemspeed reactors in polymerization reaction allows to confidently analyze the products formation over time. For each product, the relative yield is calculated by dividing the amount of a product by its final yield, i.e. mass of product obtained after 30 minutes of reaction. From Fig. 5, it is clear that the processes of oligomer and polymer production are different at 40 °C and 80 °C. In conditions of favored trimerization, all products are continuously generated and their relative yields follow the same trend. Indeed, for each compound, about 40 wt % of the overall yield is obtained within the first 5 minutes of reaction (Fig. 5, top). Despite a similar evolution of product formation, the mass of 1-hexene obtained (4.49 g) is significantly greater than the one of polyethylene (0.08 g). In contrast, trimers and polymer production are independent at 80 °C. 1-hexene formation only occurs within the first 5 minutes (0.37 g for 1-hexene) while the quantity of polymer evolves from 1.99 g after 5 minutes to 3.05 g after 30 minutes. Note that the increase of C₁₀H₂₀ oligomers corresponds to the evolution from 0.010 to 0.013 g, which is almost negligible.

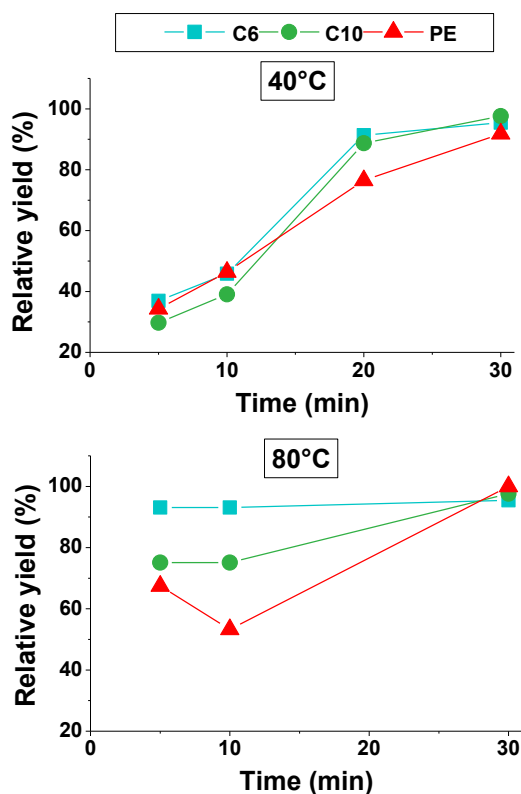


Fig. 5 Evolution of relative yield for oligomers and polymers over time

The kinetics and product studies revealed that the dependence between trimerization and polymerization active species is related to temperature. At 40 °C, the presence of trimers and polymer combined with their continuous formation implies that two catalysts emerged at the beginning of the reaction from the same precatalyst source. While at 80 °C, trimerization catalyst deactivates within the first 5 minutes of reactions and the polymerization catalyst displays an enhanced activity compared to lower temperature conditions. In this case, the polymerization catalyst could be formed either from a degradation of the latter or independently.

The incorporation of 1-hexene in the polymer over time is a reliable indicator of a potential evolution of active species. At 40 °C and 60 °C, 1-hexene content in the polymer (Fig. 6, top) increases owing to the 1-hexene enrichment in the reaction medium (Fig. 5, top). Homopolyethylene is produced at 80 °C due to a negligible amount of 1-hexene produced (Fig. 5, bottom). The relationship between 1-hexene content in the PE and in the reaction media follows the same correlation at 40 °C and 60 °C (Fig. 6, bottom). This similar 1-hexene sensitivity is the characteristic of an identical polymerization catalyst.

These kinetic studies clearly show that the same and unique polymerization catalyst is present between 40 and 60 °C. This species is formed at the early stage of reaction, along with the trimerization catalyst. Besides, as several active species are suspected to polymerize ethylene at 80 °C, trimerization species may be converted into polymerization species.

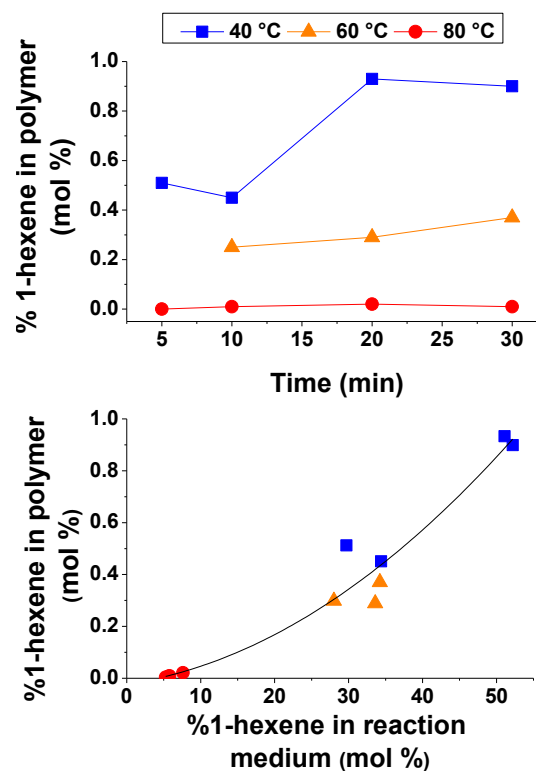


Fig. 6 Evolution of 1-hexene content in the polymer over time (up) and according to the composition of the reaction medium (down)

Based on these conclusions, potential active species hypothesized in the literature exhibit a similar behavior for the production of polymer with such features, i.e. a high molar-mass polyethylenes with a limited amount of SCB. In one case, a "TiR_x" species proposed by Duchateau *et al.*, would result from a ligand abstraction from Ti to Al, probably induced by the TMA contained in MAO. Such homogeneous molecular Ziegler-Natta species would indeed poorly copolymerize LAOs with ethylene.^{30,31} A second assumption results from the identification of Ti^{III} species by Sattler and Talsi *et al.* during catalytic tests with (FI)TiMe₃/B(C₆F₅)₃ and complex 1/MAO, respectively.^{12,18} Even though Ti^{III} formation has been correlated to the deactivation of the system, one cannot exclude this possibility since few homogeneous complexes of Ti^{III} are reported to polymerize ethylene.^{32,33} Eventually, it is also conceivable that a rearrangement or structure alteration of complex 2 would lead to a putative cationic Ti^{IV} species that successively coordinates and inserts ethylene *via* a Cossee-Arlman mechanism. In this case, one could assume that such species bears a bulky phenoxy-imine ligand providing sufficient steric hindrance to disfavor β-H transfer reaction and 1-hexene insertion in the polymer chain.

Conclusion

In this work, the phenoxy-imine titanium-based system for ethylene trimerization has been investigated according to reaction temperature from 26 °C to 80 °C. Unlike most of

previous studies, our focus was oriented towards rationalizing the formation of polymer along with 1-hexene. This study reveals and quantifies a switch of selectivity from 1-hexene to polymer along with a decrease of activity between 26 to 80 °C. An original polymer-to-catalyst strategy revealed that the polymerization catalyst yields polyethylene with high molar masses and poorly incorporates 1-hexene. A joint formation of trimerization and polymerization species at the early stage of reaction is supported by a kinetic study. Further work is in progress to identify the species responsible for the production of polyethylene.

Experimental

General

All air- and moisture-sensitive reactions were performed under an inert argon atmosphere using standard Schlenck and glovebox techniques. Toluene, pentane and dichloromethane were dried from a MBRAUN solvent purification system with activated alumina and copper catalyst columns. Deuterated solvents were stored with molecular sieves in the glovebox. Chemicals were purchased from Sigma-Aldrich, Strem Chemicals, Acros Organics or Tokyo Chemical Industry Co., Ltd. and were used without further purification. Methylaluminoxane 30 wt % in toluene (13.6 wt % of aluminum, 5.24 wt % TMA, 26.2 wt % MAO) was purchased from Albemarle Corporation and stored at -30 °C under inert atmosphere. Ethylene was purified by passing through three columns containing activated molecular sieves, alumina and BASF copper oxide catalyst.

Complex synthesis

Complex **2** was synthesized according to literature procedure.¹⁰ In a 100 mL Schlenk, a solution of titanium tetrachloride 1.0 N in toluene (1.1 mL, 1.1 mmol) was added to a solution of the phenoxy-imine-ether ligand (340.1 g, 0.91 mmol) in 10 mL of toluene at -78 °C. The solution warmed up to room temperature and stirred overnight. 50 mL of pentane was added to precipitate the catalyst. The brown-red particles were washed with 3x10 mL of pentane and dried under vacuum at 40 °C. Yield: 0.38 g, 0.72 mmol, 79 %.

¹H NMR (CD₂Cl₂, 300 MHz): δ (ppm) 8.14 (s, 1H, N=CH), 7.53-7.47 (m, 3H, ArH), 7.41-7.30 (m, 5H, ArH), 7.16 (m, 2H, ArH), 4.34 (s, 3H, O-CH₃), 2.34 (s, 3H, Ar-CH₃), 1.50 (s, 9H, Ar-C(CH₃)₃)
¹³C NMR (CD₂Cl₂, 75 MHz): δ (ppm) 169.23 (CH), 158.39 (C), 151.84 (C), 147.77 (C), 136.48 (C), 136.01 (CH), 134.61 (C), 133.09 (CH), 131.66 (CH), 131.58 (C), 131.02 (C), 130.51 (C), 130.13 (CH), 129.48 (CH), 128.79 (CH), 127.80 (C), 126.15 (C), 123.40 (CH), 72.53 (CH₃), 35.33 (C), 29.87 (3 CH₃), 21.02 (CH₃)
 Anal. calcd (C₂₅H₂₆Cl₃NO₂Ti): C, 57.01; H, 4.98; N, 2.66 %. Found: C, 57.18; H, 5.01; N, 2.61 %.

Catalytic tests

Ethylene oligo/polymerizations were performed in a 1L double-jacketed reactor. A diluted TEA solution in heptane (15 mol L⁻¹) was used to scavenge the reactor at 80 °C prior to catalytic test. A solution of MAO 30 wt % in 290 mL toluene (1.6x10⁻² mol L⁻¹) was introduced in the reactor and heated at desired temperature. 10 mL of precatalyst solution (2.9 mg, 3 μmol) was then injected and ethylene was continuously fed to keep the pressure of 10 bar constant for 30 minutes. Reaction was quenched by 10 mL methanol and the reactor was cooled to 5 °C before depressurization. The liquid phase was treated with a sulfuric acid solution and analyzed by GC using dodecane as internal standard. The polymer was washed with acidified methanol and methanol. Recovered polymers were dried under vacuum at 100 °C for 2 hours.

The kinetic studies were performed on a fully automated Chemspeed homogeneous catalysis platform located at Axel'One Campus, Villeurbanne, France. This unit is included in a Glovebox to guarantee a controlled atmosphere. Catalytic tests were performed in three independent 270 mL-reactors. Toluene (120 mL) and MAO 30 wt % in toluene solution (0.6 mL, 1 500 mmol) were introduced in each reactor. Once the desired temperature was reached, reactors were pressurized to 10 bar of ethylene. Using SWILE© technology, a batch solution of complex **2** (3.2 mg, 6.1 μmol) in toluene (10 mL) from which 3 mL were injected *via* a high pressure pump in each reactors. The reaction was run in a semi-batch mode for the desired reaction time. Ethanol was introduced under pressure to quench the reaction. Reactors were cooled to 5 °C before depressurization. Further treatments of the solid and liquid phase were performed as described previously.

Polymer characterization

High Temperature Size Exclusion Chromatography (HT-SEC)

HT-SEC analyses were performed using a Viscotek system (Malvern Instruments) equipped with three columns (PLgel Olexis 300 mm × 7 mm from Agilent Technologies). Samples volume of 200 μL with concentrations between 1-2 mg mL⁻¹ were eluted in 1,2,4-trichlorobenzene using a flow rate of 1 mL min⁻¹ at 150 °C. The mobile phase was stabilized with 2,6-di(*tert*-butyl)-4-methylphenol (200 mg L⁻¹). Online detection was performed with a differential refractive index detector, a dual light scattering detector (RALS LALS) and a viscometer detector for absolute molar mass measurement.

Differential Scanning Calorimetry (DSC)

Polyethylene melting temperature, crystallization temperature and crystallinity were determined using a Mettler Toledo DSC1. An average of 7 mg of PE was analyzed in a 40 μL aluminum crucible. After a first heating from 25 °C to 180 °C at 20 °C min⁻¹, samples were cooled and heated within the same range of temperature at 5 °C min⁻¹. Only the second heat was considered for melting temperature measurement.

High Temperature Nuclear Magnetic Resonance (HT-NMR)

¹³C NMR analysis were performed with a Bruker Avance II 400 spectrometer operating at 100.6 MHz. Spectra were recorded at 393 K using a PSEX 10 mm probe for ¹³C NMR. A mixture of *o*-dichlorobenzene/*o*-dichlorobenzene-*d*₄ (1/10 v/v) was used as solvent. Samples were prepared as a solution of 100 mg of polymer in 6 mL of solvent after several 150 °C–25 °C cycles.

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