IPPI

Polyolefins Journal, Vol. 4, No. 1 (2017)
DOI: 10.22063/poj.2016.1395

ORIGINAL PAPER

# Polymerization of sterically hindered α-olefins with single-site group 4 metal catalyst precursors

Gabriel Theurkauff [1], Katty Den Dauw[2], Olivier Miserque[2], Aurélien Vantomme[2], Jean-Michel Brusson[3], Jean-François Carpentier[1,*] and Evgueni Kirillov[1,*]

[1] Organometallics, Materials and Catalysis Laboratories, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, F-35042 Rennes, France

[2] Total Raffinage Chimie, Zone Industrielle Feluy C, B-7181 Seneffe, Belgium

[3] Total S.A., Corporate Science, Tour Michelet A, 24 Cours Michelet – La Défense 10, F-92069 Paris La Défense Cedex, France

Received: 13 August 2016, Accepted: 25 September 2016

## ABSTRACT

A variety of group 4 metal catalytic systems ($C_2$-symmetric {EBTHI}-, {SBI}-type zirconocene complexes (**$C_2$-1–4**); $C_1$-symmetric (**$C_1$-5–8**) and Cs-symmetric (**$C_s$-9**) {Cp/Flu}-type zirconocene complexes; $Cp^*_2ZrCl_2$ (**$Cp^*_2$-10**)), half-metallocene complexes ($CpTiCl_3$, **HM-11**), constrained-geometry (**CGC-12**) titanium catalysts) and post-metallocene catalysts (Dow's ortho-metallated amido-pyridino hafnium complex (**PM-13**)) have been screened in the polymerization of the sterically demanding 3-methylbut-1-ene (3MB1) and vinylcyclohexane (VCH). All systems proved to be sluggishly active under regular conditions (toluene, 20°C; MAO as cocatalyst) towards 3MB1, with productivities in the range 0–15 $kg.mol^{-1}.h^{-1}$. Higher productivities (up to 75 $kg.mol^{-1}.h^{-1}$) were obtained in the polymerization of VCH with $C_1$-symmetric metallocene catalysts under the same conditions, while Cs-symmetric systems were found to be completely inactive. For both 3MB1 and VCH, under all conditions tested, the most productive catalyst appeared to be Dow's post-metallocene system **PM-13**/MAO. Optimization of the polymerization conditions led to a significant enhancement of the productivities of this catalyst system towards both 3MB1 and VCH up to 390 and 760 $kg.mol^{-1}.h^{-1}$, respectively ($T_{polym}$ = 70°C). $^{13}C$ NMR spectroscopy studies revealed that all isolated P(3MB1) and P(VCH) polymers were isotactic, regardless the nature/symmetry of the (pre)catalyst used. The nature of the chain-end groups in P(3MB1) is consistent with two different chain-termination mechanisms, namely β-H elimination/transfer-to-monomer for **$C_2$-1**/MAO and chain-transfer to $Me_3Al$ for **PM-13**/MAO systems, respectively. For polymerization of VCH with **PM-13**/MAO at 70°C, β-H elimination / transfer-to-monomer appeared to be the main chain termination reaction. **Polyolefins J (2017) 4: 123-136**

**Keywords**: 3-methylbut-1-ene ; vinylcyclohexane ; catalysis; polymerization; NMR analysis.

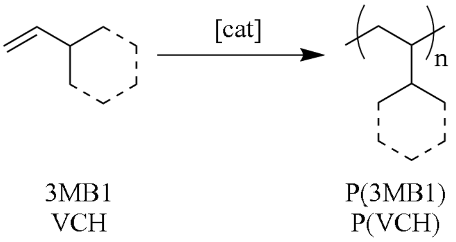
## INTRODUCTION

Elaboration of new, high performance thermoplastic materials based on readily available, inexpensive olefins is a challenging area of modern polymer chemistry [1,2]. Along with conventional stereoregular poly(α-olefins) (polypropylene, polystyrene, etc), homopolymers of sterically hindered monomers like 3-methylbut-1-ene (3MB1) and vinylcyclohexane (VCH) are potentially attractive materials in light of their specific properties such as high crystallinity and unusually high melting temperature (Tm up to 300 [3] and 380°C [4], respectively). Yet, P(3MB1) and P(VCH) (Scheme 1) are quite few documented and studied in the literature. A possible reason for such lack of information is the low catalytic productivities (0.1–220 $kg.mol^{-1}.h^{-1}$ at -40 – +80°C) typically achieved in the preparation of P(3MB1) with all heterogeneous[5,6] and homoge-

---

* Corresponding Authors - E-mail: J.F.Carpentier (jean-francois.carpentier@univ-rennes1.fr) and Evgueni Kirillov (evgueni.kirillov@univ-rennes1.fr); Fax: +33 (0)223236938

neous [4,6,7] catalytic systems thus far explored. In fact, among homogeneous systems, only a few $C_2$- and $C_s$- symmetric group 4 metallocenes have been studied in the polymerization of 3MB1 [4,6,7]. Although the very first sample of P(VCH) has been synthesized by hydrogenation of polystyrene [8], the homopolymer can be obtained directly by polymerization of VCH with either heterogeneous Ziegler-Natta [8,9,10,11] or homogeneous group 4 metallocene [6, ] or post-metallocene [4,13,14,15] catalysts. An additional hurdle in the study of P(3MB1), highlighted in the literature, is its very poor solubility in organic solvents that makes problematic examination of its microstructure by regular analytical methods [4,16]. All $^{13}C$ NMR spectroscopic analyses reported in the literature, conducted both in solution and in the solid/molten state, suggest that the vast majority of P(3MB1)s produced, both with catalysts that are isoselective and syndioselective towards propylene, are actually isotactic polymers. [4,5,7] Also, polymerization of VCH with all utilized metallocene catalysts resulted in the production of isotactic P(VCH). In all cases, the origin of the observed isoselective behavior has been tentatively attributed to a chain-end stereocontrol mechanism. On the other hand, synthesis of syndiotactic P(VCH) has been achieved with a heterogeneous catalyst [10], while polymerization of VCH with group 4 metal amino-bis(phenolate) catalytic systems {ONON}$MBn_2$/$B(C_6F_5)_3$ (M = Ti, Zr) afforded an atactic material [14]. Herein, we report on the studies of a variety of group 4 metallocene and related post-metallocene catalytic systems in the polymerization of 3MB1 and VCH. The objectives of these investigations were to explore the catalytic outcome (productivity, stereoselectivity and molecular weight properties) under homogeneous conditions in order to identify specific structure-activity relationships. Additionally, we aimed at determining optimal conditions for achieving high catalytic performance with the above systems.



Scheme 1. P(3MB1) and P(VCH) homopolymers obtained by coordination/insertion polymerization.

## EXPERIMENTAL

### Materials

Complexes **$C_2$-1–4** [17,18] were generously provided by Total Raffinage Chimie (Feluy research center). Complexes **$C_1$-5–8** [19], $C_s$-9 [20] and PM-13 [21] were synthesized following published procedures. Precursors **$Cp^*_2$-10**, **HM-11** and **CGC-12** were purchased from Boulder Scientific Co., while $CpTiCl_3$ and $(C_5Me_5)_2ZrCl_2$ were purchased from Strem Chemicals. Monomers 3M1B and VCH were purchased from TCI Chemicals.

### Purification of 3M1B and VCH monomers

Commercial 3M1B contains up to 5 mol% of acetone and thus requires exhaustive purification prior to polymerization. Due to its low boiling point (bp = 25°C), fractional distillation of 3M1B was not efficient. Therefore, 3M1B was distilled from $CaH_2$ and kept over activated 4Å and 13X molecular sieves as the 2 mol.$L^{-1}$ solution in dry toluene. VCH (bp = 128°C) was distilled over $CaH_2$ and then stored over activated 4Å molecular sieves.

### 3-Methyl-1-butene polymerization at room temperature

An argon-purged Schlenk flask was charged with 3MB1 (15 mL of a 2.0 M solution in toluene, 0.030 mol, 2.1 g) and MAO (0.5 mL of a 30 wt% solution in toluene, 2.25 mmol). After 30 min of stirring, a precatalyst solution was introduced (1.0 mg of catalyst in 1.0 mL of toluene) and the flask was sealed for the desired polymerization time. The polymerization was quenched with a 10 wt% solution of aqueous HCl in methanol (ca. 3 mL). The polymer was precipitated in methanol (ca. 100 mL) and 37 wt% aqueous HCl (ca. 1 mL) was added to dissolve inorganic residues.

### 3-Methyl-1-butene polymerization at 40 and 70°C

An argon-purged 50 mL glass pressure vessel was charged with 3MB1 (15 mL of a 2.0 M solution in toluene, 0.030 mol, 2.1 g) and MAO (0.5 mL of 30 wt% in toluene, 2.25 mmol). After 30 min of stirring, a precatalyst solution was introduced (1.0 mg of catalyst in 1.0 mL of toluene), the vessel was sealed and put in a preheated water bath for the desired polymerization time. The vessel was then vented and the reaction was quenched with a 10 wt% solution of aqueous HCl in methanol (ca. 3 mL). The polymer was precipitated in methanol (ca. 100 mL) and 37 wt% aqueous HCl (ca. 1 mL) was added to dissolve inorganic residues.

### Vinylcyclohexane polymerization

An argon-purged Schlenk flask was charged with toluene (15 mL), VCH (2.5 mL, 2.0 g, 18 mmol) and MAO (0.50 mL of a 30 wt% solution in toluene, 2.3 mmol). After 30 min of stirring, a precatalyst solution was introduced (1.0 mg of catalyst in 1.0 mL of toluene) and the flask was sealed for the desired polymerization time and eventually put in a preheated water bath. The polymerization was quenched with a 10 wt% solution of aqueous HCl in methanol (ca. 3 mL). The polymer was precipitated in methanol (ca. 100 mL) and 37 wt% aqueous HCl (ca. 1 mL) was added to dissolve inorganic residues.

## RESULTS AND DISCUSSION

### General Trends

In this study, we set out to investigate comprehensively VCH and 3MB1 polymerization reactions upon varying different parameters: nature of catalyst precursor and activation mode, and temperature and duration of polymerization reaction. Different group 4 metal complexes from classical series, which have demonstrated different outcomes in terms of stereoselectivity (isospecific, syndiospecific and non-specific) in polymerizations of α-olefins (typically propylene) and also arylalkenes (styrene), were selected (Scheme 2): (a) $C_2$-symmetric {EBTHI}- and {SBI}-based ansa-zirconocene complexes **$C_2$-1–4** [7] and (b) metallocene catalysts **$C_1$-5–8** from C1-symmetric {Cp/Flu}-based series, which are all highly isoselective towards propylene [19,22,23 ]; (c) zirconocene catalyst **$C_s$-9** that is syndioselective towards propylene but previously reported to afford isotactic P(3MB1) presumably by a chain-end control mechanism [4,5,7]; (d) non-stereoselective zirconocene complex **$Cp^*_2$-10**; (e) half-titanocene complex HM-11 known as precursor for syndioselective polymerization of styrene by a chain-end control mechanism [24]; (f) constrained-geometry complex **CGC-12** known for its high productivity towards α-olefins and ability to copolymerize α-olefins with ethylene [25]; and (g) Dow's post-metallocene complex **PM-13** known for its high productivity and isoselectivity in propylene polymerization [21, 26].

In order to avoid possible rapid degradation of active species and also to allow catalysts with lower productivities or with longer induction time periods to produce enough material for further characterization, all experiments were first run at room temperature and over long polymerization times. Details of the polymerization experiments are summarized in Table 1.

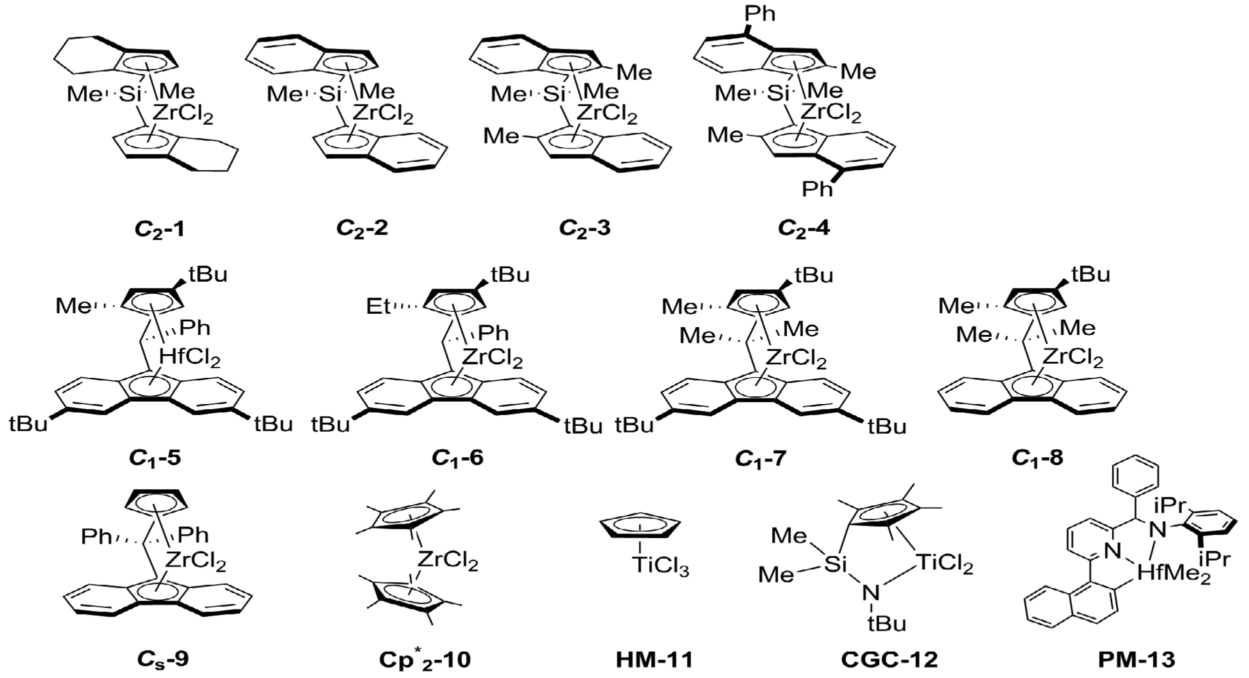
In 3MB1 polymerization, all metallocene-based catalysts showed productivities similar or very close to those reported in the literature under the same conditions (Figure 1) [4,6,7]. In fact, despite significant differences in terms of symmetry, sterics and electronics, precatalysts from various ansa-zirconocene catalyst families, namely **$C_2$-1–4**, **$C_1$-5,6** and **$C_s$-9**, showed close productivities ranging from 6.8 to 15 $kg.mol^{-1}.h^{-1}$ (entries 1, 3, 5, 7, 9, 11 and 15, respectively). Surprisingly, a comparable productivity of 6.4 $kg.mol^{-1}.h^{-1}$ was achieved with **CGC-12** (entry 19), while even poorer values were obtained with catalysts **$Cp^*_2$-10** and **HM-11** (0 and 2.1 $kg.mol^{-1}.h^{-1}$, entries 17 and 18, respectively). The most effective catalyst system within the whole series appeared to be that based on Dow's hafnium pyridino-amide complex **PM-13** with a productivity (46 $kg.mol^{-1}.h^{-1}$, entry 21) about one order of magnitude higher than those observed with all other precatalysts.

In VCH polymerization tests, carried out under identical conditions to those for 3MB1, the productivities were found generally higher. Moreover, a few catalyst systems clearly perform much better than the other ones (Figure 2). Again, complex **PM-13** was found the most productive (98 $kg.mol^{-1}.h^{-1}$, entry 22) within the whole series, although its superiority was not as large as that for 3MB1. Surprisingly, complexes **$C_s$-9** and **CGC-12** appeared completely inactive. Obviously, the observed productivity trend is very dissimilar to that observed in 3MB1 polymerization experi-

**Table** 1. Polymerizations of 3MB1 and VCH conducted at room temperature with various precatalyst/MAO combinations.[a]

| Entry | Precatalyst | $[M]_0$ (μmol·L$^{-1}$) | $[MAO]/[M]_0$ | Monomer | Momomer weight (g) | Polymer weight (g) | Yield (%) | Productivity (kg·mol$^{-1}$·h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | $C_2$-1 | 142 | 1000 | 3MB1 | 2.60 | 0.53 | 20 | 15 |
| 2 | | 121 | 1000 | VCH | 2.00 | 0.19 | 10 | 5.3 |
| 3 | $C_2$-2 | 135 | 1000 | 3MB1 | 2.60 | 0.29 | 11 | 8.8 |
| 4 | | 116 | 1000 | VCH | 2.00 | 1.17 | 59 | 35 |
| 5 | $C_2$-3 | 127 | 1000 | 3MB1 | 2.60 | 0.31 | 12 | 10 |
| 6 | | 110 | 1000 | VCH | 2.00 | 0.73 | 4 | 23 |
| 7 | $C_2$-4 | 96 | 1400 | 3MB1 | 2.20 | 0.23 | 10 | 9.4 |
| 8 | | 84 | 1400 | VCH | 2.40 | 0.09 | 4 | 3.9 |
| 9 | $C_1$-5 | 236 | 1200 | 3MB1 | 2.20 | 0.55 | 25 | 9.4 |
| 10 | | 84 | 1400 | VCH | 2.40 | 0.14 | 6 | 5.9 |
| 11 | $C_1$-6 | 90 | 1500 | 3MB1 | 2.60 | 0.17 | 6 | 7.5 |
| 12 | | 78 | 1300 | VCH | 2.40 | 1.90 | 79 | 75 |
| 13 | $C_1$-7 | 84 | 1400 | VCH | 2.00 | 0.56 | 28 | 23 |
| 14 | $C_1$-8 | 95 | 1200 | VCH | 2.00 | 1.63 | 82 | 60 |
| 15 | $C_s$-9 | 109 | 1200 | 3MB1 | 2.60 | 0.18 | 7 | 6.8 |
| 16 | | 95 | 1200 | VCH | 2.00 | 0.00 | 0 | 0.0 |
| 17 | $Cp^*_2$-10 | 139 | 1000 | 3MB1 | 2.20 | 0.00 | 0 | 0.0 |
| 18 | HM-11 | 276 | 300 | 3MB1 | 2.20 | 0.14 | 6 | 2.1 |
| 19 | CGC-12 | 165 | 800 | 3MB1 | 2.60 | 0.26 | 10 | 6.4 |
| 20 | | 142 | 800 | VCH | 2.40 | 0.00 | 0 | 0.0 |
| 21 | PM-13 | 89 | 1500 | 3MB1 | 2.60 | 1.08 | 41 | 46 |
| 22 | | 79 | 1500 | VCH | 2.40 | 2.21 | 92 | 98 |

[a] Polymerization conditions: 100 mL-Schlenk flask reactor, solvent: toluene (15 mL), Tpolym = 20°C, time = 15 h. Each polymerization experiment was duplicated under the same conditions, revealing good reproducibility in terms of productivity (polymer yield).



**Scheme** 2. Structures of group 4 metal precatalysts investigated in 3MB1 and VCH homopolymerizations.

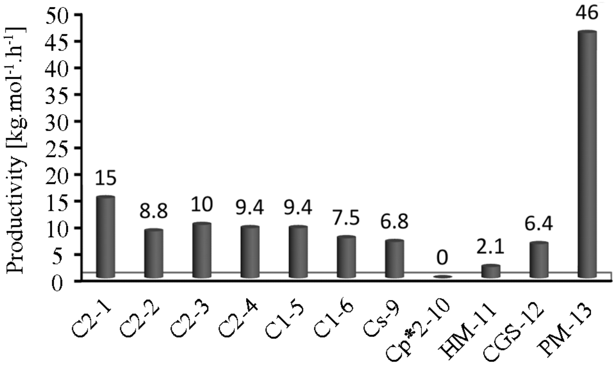


**Figure 1**. Overall productivities of different catalyst systems in 3MB1 polymerization at 20°C over 15 h reaction.

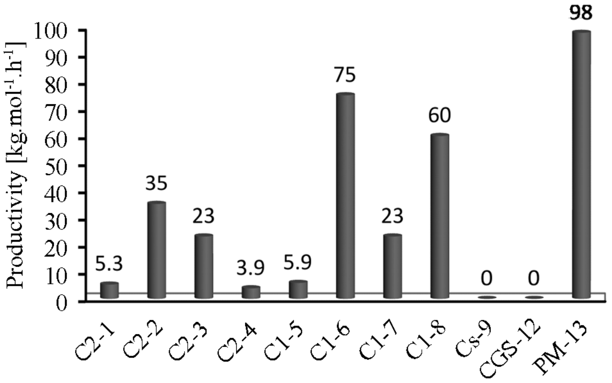


**Figure 2.** Overall productivities of different catalytic systems in VCH polymerization at 20°C over 15 h reaction.

ments; it is clearly not related directly to either the steric or electronic situation in the precatalysts.

Given the remarkably low catalytic performances found for the above catalytic systems in polymerization of bulky 3MB1 and VCH, the corresponding productivity values can be benchmarked against those observed in polymerization of propylene under homogeneous conditions. Thus, the following trend of productivity values (in kg.mol$^{-1}$.h$^{-1}$) was established from the literature: **$C_2$-1** (4750 at 20°C) [17], **$C_2$-2–4** (99000–755000 at 70°C) [18], **$C_1$-5** (260 at 40°C) [22], $C_1$-6–8 (1710–14330 at 60°C) [23], **$C_s$-9** (28800 at 65°C) [27], **$Cp^*_2$-10** (1400 at 20°C) [28], **HM-11** (40 at –60°C) [29], **CGC-12** (820 at 30°C) [30], and **PM-13** (4400 at 60°C) [31]. This trend clearly demonstrates that diminished steric requirements for non-bulky propylene lie at the basis of the more rapid growth of the polymeric chain onto metal centers of different geometry.

While productivities of the hafnium-based metallocene catalysts are generally at least one order of magnitude lower than those of the zirconium-based analogues [32], the beneficial productivity bias found for hafnium post-metallocene catalyst **PM-13** in polymerization of both 3MB1 and VCH is consistent with the one disclosed for polymerization of propylene with this system [31].

### Influence of operational conditions: (1) activation, (2) temperature, and (3) duration of polymerization

Studies on the influence of polymerization conditions were conducted with the most active catalysts, namely post-metallocene catalyst **PM-13** and ansa-zirconocene catalysts **$C_2$-1**, **$C_1$-6** and **$C_s$-9**.

1) The nature of activator plays obviously a crucial role on the activity/productivity of catalyst. This is much likely in close relation with the concentration and stability of active cationic species that are generated, and also their propensity to reversibly convert into “dormant” species. It is indeed known that, for example, a commercial-grade MAO “naturally” containing ca. 10 mol% of $AlMe_3$, when used for activation in large amounts with respect to precatalyst, can lead to both beneficial and deleterious effects [33,34]. Thus, the productivity of **PM-13** in 3MB1 polymerization increased as the [MAO]/[Hf]0 ratio is increased (Table 2, entries 1−3), while polymerization tests performed with $AlMe_3$-depleted versions of MAO, that is “dried” MAO and BHT-modified MAO, showed somewhat reduced productivities (46 vs. 32 and 35 kg.mol$^{-1}$.h$^{-1}$; compare entries 2 vs. 4 and 6, respectively). On the other hand, deliberate introduction of excess $AlMe_3$ (340 equiv vs. Hf) to a “dried” MAO resulted in a quasi-complete loss of productivity (1.2 kg.mol$^{-1}$.h$^{-1}$, entry 5).

For VCH polymerization, increase of the MAO quantity resulted in a decrease of the productivity (compare entries 7 and 8), probably due to deactivation induced by $AlMe_3$ [33]. Yet, utilization of BHT-modified MAO resulted only in marginal increase of productivity (entry 9). In direct line with the above-mentioned results for 3MB1, deliberate addition of $AlMe_3$ significantly lowered the productivity of the catalytic system (entry 10).

Activation using molecular cocatalysts ($B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $[PhMe_2NH]^+[B(C_6F_5)_4]^-$) was

**Table 2**. Influence of the quantity of MAO and $AlMe_3$ on 3MB1 and VCH polymerizations with PM-13.[(a)]

| Entry | Monomer | $[Hf]_0$ (µmol·L$^{-1}$) | $n_{MAO}$ (µmol) | $n_{AlMe_3}$ $^{(b)}$ (µmol) | $n_{BHT}$ $^{(c)}$ (µmol) | [Al]/ $[Hf]_0$ | Polymer weight (g) | Productivity (kg·mol$^{-1}$·h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| **1** | 3MB1 | 91 | 675 | - | - | 500 | 0.85 | 39 |
| **2** | | 89 | 2250 | - | - | 1500 | 1.08 | 46 |
| **3** | | 84 | 6750 | - | - | 4500 | 1.26 | 57 |
| **4** | | 89 | 2210$^d$ | 0 | - | 1500 | 0.71 | 32 |
| **5** | | 89 | 2210$^d$ | 340 | - | 1700 | 0.03 | 1.2 |
| **6** | | 89 | 2250 | - | 1000 | 1500 | 0.78 | 35 |
| **7** | VCH | 79 | 2250 | - | - | 1500 | 2.21 | 98 |
| **8** | | 74 | 6750 | - | - | 4500 | 1.23 | 55 |
| **9** | | 77 | 2250 | - | 900 | 1500 | 2.28 | 102 |
| **10** | | 77 | 2250 | 1000 | - | 2200 | 0.05 | 2.2 |

(a)Polymerization conditions: 100 mL-Schlenk flask reactor, solvent: toluene (15 mL), Tpolym = 20°C; polymerization time = 15 h, monomer: 3MB1 (2.20 g) or VCH (2.40 g). Each polymerization experiment was duplicated, revealing good reproducibility in terms of productivity (polymer yield). (b) Amount of added $AlMe_3$ vs [Hf]0. (c) Amount of added 2,6-di-tert-butyl-4-methylphenol (BHT). (d) AlMe3-free dry MAO ("DMAO").

studied (Table 3); $Al(iBu)_3$ (TIBAL) was then used as scavenger. Unexpectedly, all experiments with such systems resulted in negligible productivities (entries 2−4 and 6, 7). This behavior may be a result of several factors: very short lifespan of active species generated under these conditions, high sensitivity towards possible impurities present in monomers, secondary reactivity with respect to TIBAL [35].

2) Several experiments were conducted in the temperature range 20–70°C (Table 4). With the **PM-13**/MAO system, a 8-fold productivity increase was observed both in 3MB1 and VCH polymerizations (entries 1−3 and 6−8, respectively). For zirconocene complexes **$C_2$-1** and **$C_1$-6**, a similar, however less pronounced, productivity increase was observed (entries 4, 5 and 9, 10, respectively). This result likely reflects different temperature robustness of these various catalytic systems. Also, precatalyst **$C_s$-9** appeared to be inactive in the whole temperature range (entries 11 and 12).

3) Experiments were conducted over longer polymerization times to improve the polymer yield with poorly active catalytic systems as well as to evaluate the robustness of catalysts against deactivation (Table 5). For polymerization of 3MB1 with the **PM-13**/MAO catalytic system, deactivation over time was clearly evidenced: (i) at 20°C, multiplying of the polymerization time by 4, from 15 to 60 min, led to a

**Table** 3. Influence of the nature of activator on 3MB1 and VCH polymerizations.[(a)]

| Entry | Monomer | Precatalyst | $[M]_0$ (µmol·L$^{-1}$) | $[Al]/[M]_0$ (equiv) | Cocatalyst (1 equiv) | Polymer weight (g) | Productivity (kg·mol$^{-1}$·h$^{-1}$) |
|---|---|---|---|---|---|---|---|
| **1** | 3MB1 | **PM-13** | 89 | MAO (1500) | - | 1.08 | 46 |
| **2** | | | 89 | TIBAl (500) | $[PhNMe_2H]^+ [B(C_6F_5)_4]^-$ | 0.12 | 5.1 |
| **3** | | | 89 | TIBAl (500) | $B(C_6F_5)_3$ | 0.00 | 0.0 |
| **4** | | | 89 | TIBAl (500) | $[Ph_3C]^+ [B(C_6F_5)_4]^-$ | 0.07 | 3.1 |
| **5** | VCH | ***$C_1$*-6** | 78 | MAO (1300) | - | 1.90 | 75 |
| **6** | | | 78 | TIBAl (300) | $B(C_6F_5)_3$ | 0.09 | 3.6 |
| **7** | | | 78 | TIBAl (300) | $[Ph_3C]^+ [B(C_6F_5)_4]^-$ | 0.40 | 17 |

(a) Polymerization conditions: 100 mL-Schlenk flask reactor, solvent: toluene (15 mL), Tpolym = 20°C; polymerization time = 15 h, monomer: 3MB1 (2.20 g) or VCH (2.40 g). Each polymerization experiment was duplicated, revealing good reproducibility in terms of productivity (polymer yield).

**Table** 4. Influence of temperature on polymerization of 3MB1 and VCH.[(a)]

| Entry | Monomer | Catalyst | $[Zr]_0$ (μmol·$L^{-1}$) | $[MAO]/[Zr]_0$ (equiv) | Temp (°C) | Time (h) | Polymer weight (g) | Productivity (kg·$mol^{-1}$·$h^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| **1** | 3MB1 | PM-13 | 89 | 1500 | 20 | 15 | 1.08 | 46 |
| **2** | | PM-13 | 89 | 1500 | 40 | 1 | 0.15 | 100 |
| **3** | | PM-13 | 89 | 1500 | 70 | 1 | 0.54 | 390 |
| **4** | | $C_2$-1 | 142 | 1000 | 20 | 15 | 0.53 | 15 |
| **5** | | $C_2$-1 | 142 | 1000 | 70 | 1 | 0.24 | 52 |
| **6** | VCH | PM-13 | 79 | 1500 | 20 | 15 | 2.21 | 98 |
| **7** | | PM-13 | 79 | 1500 | 40 | 1 | 0.47 | 310 |
| **8** | | PM-13 | 79 | 1500 | 70 | 1 | 1.14 | 760 |
| **9** | | $C_1$-6 | 78 | 1300 | 20 | 15 | 1.90 | 75 |
| **10** | | $C_1$-6 | 78 | 1300 | 70 | 1 | 0.73 | 430 |
| **11** | | $C_s$-9 | 95 | 1200 | 20 | 15 | 0.00 | 0 |
| **12** | | $C_s$-9 | 95 | 1200 | 70 | 1 | 0.00 | 0 |

[(a)] Polymerization conditions: 100 mL-Schlenk flask reactor, solvent: toluene (15 mL); monomer: 3MB1 (2.20 g) or VCH (2.40 g). Each polymerization experiment was duplicated, revealing good reproducibility in terms of productivity (polymer yield).

decrease of the productivity by a factor of 3 (entries 1 and 2); (ii) at 70°C, short polymerization times (0.5−1 h) led to a nearly steady productivity (entries 3 and 4), however, a longer polymerization time (2 h) resulted in the drop of productivity (entry 5).

The performances of two the **PM-13**/ and **$C_1$-6**/MAO catalytic systems over time were assessed in VCH polymerization as well. Short polymerization times with **PM-13** (3 vs. 15 h) led to decreased productivity (compare entries 6 and 7, respectively). This result was unexpected and may be accounted for by a necessary induction period for formation of active species. For given catalytic system, the reported induction periods are due to slow processes of generation of an active form of catalyst [36,37]. On the other hand, the **$C_1$-6**/MAO system showed a steady productivity over relatively short polymerization times (1−5 h), and a drop in productivity was noticed after 5 h (Figure 3, entries 8−12), likely reflecting deactivation of the active species.

Hence, the productivities of some catalytic systems have been eventually improved as compared to what

**Table 5**. Influence of reaction time on 3MB1 and VCH polymerization.[(a)]

| Entry | Monomer | Precatalyst | $[Mr]_0$ (μmol·$L^{-1}$) | $[MAO]/[Zr]_0$ (equiv) | Temp (°C) | Time (h) | Polymer weight (g) | Productivity (kg.$mol^{-1}$.$h^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| **1** | 3MB1 | PM-13 | 89 | 1500 | 20 | 0.25 | 1.08 | 46 |
| **2** | | PM-13 | 89 | 1500 | 20 | 1 | 1.67 | 18 |
| **3** | | PM-13 | 89 | 1500 | 70 | 0.5 | 0.26 | 360 |
| **4** | | PM-13 | 89 | 1500 | 70 | 1 | 0.54 | 390 |
| **5** | | PM-13 | 89 | 1500 | 70 | 2 | 0.63 | 210 |
| **6** | VCH | PM-13 | 79 | 1500 | 20 | 3 | 0.14 | 31 |
| **7** | | PM-13 | 79 | 1500 | 20 | 15 | 2.21 | 98 |
| **8** | | $C_1$-6 | 78 | 1300 | 20 | 1 | 0.29 | 190 |
| **9** | | $C_1$-6 | 78 | 1300 | 20 | 2 | 0.41 | 140 |
| **10** | | $C_1$-6 | 78 | 1300 | 20 | 3 | 0.88 | 200 |
| **11** | | $C_1$-6 | 78 | 1300 | 20 | 5 | 1.45 | 200 |
| **12** | | $C_1$-6 | 78 | 1300 | 20 | 15 | 1.90 | 75 |

[(a)] Polymerization conditions: 100 mL-Schlenk flask reactor, solvent: toluene (15 mL); monomer: 3MB1 (2.20 g) or VCH (2.40 g). Each polymerization experiment was duplicated, revealing good reproducibility in terms of productivity (polymer yield).

was reported in the literature by increasing polymerization temperature, and could be further improved by optimizing reaction times and MAO grades. The productivity of the **PM-13**/MAO catalytic system towards 3MB1 (up to 390 kg.mol$^{-1}$.h$^{-1}$ at 70°C) compares favorably to that of rac-Me$_2$Si{2-Me-benz[e]-1-indenyl}2ZrCl$_2$/MAO (220 kg.mol$^{-1}$.h$^{-1}$ at 60°C in benzene over 4 h) [7]. On the other hand, the best performance of this system towards VCH (up to 790 kg.mol$^{-1}$.h$^{-1}$ at 70°C) remains inferior to that achieved in bulk conditions with the salan-based {ONNO}ZrBn$_2$/B(C$_6$F$_5$)$_3$ (3600 kg.mol$^{-1}$.h$^{-1}$ at 20°C over 3.5 min) [4], although it is difficult to compare solution and neat conditions.

## Microstructural NMR analysis of P(3MB1) and P(VCH) polymers

1) The P(3MB1) polymers produced by the two most productive catalysts **C$_2$-1** and **PM-13** and also those obtained with **CGS-12** were analyzed by $^{13}$C NMR spectroscopy. All those polymer samples were found to be sparingly soluble in trichlorobenzene/C$_6$D$_6$ mixture even at 135°C, and the recorded NMR data corresponded to the soluble fraction. The solubility of the polymer varied from a sample to another and, in some cases, $^{13}$C NMR spectroscopic analysis was just not possible. Melt-state $^{13}$C MAS NMR spectroscopy has been used for analyzing otherwise insoluble in organic solvents P(3MB1) polymers [4]. Our attempts to use solid/melt-state MAS NMR analysis of P(3MB1)s at high temperature failed to give exploitable results.

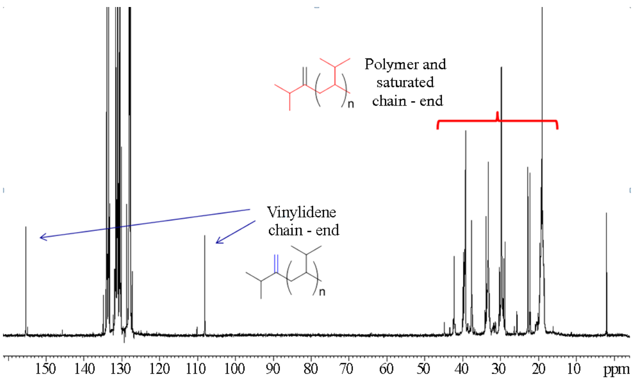


**Figure 4**. $^{13}$C{$^1$H} NMR spectrum (125 MHz, trichlorobenzene/C$_6$D$_6$ (4:1), 135°C) of a P(3MB1) produced with **C$_2$-1**/MAO at 70°C (Table 4, entry 5).

The polymer produced by **C$_2$-1** showed a series of signals in the aliphatic region at δ 15.0–45.0 ppm for the saturated main-chain and saturated chain-ends as well as two distinct resonances from unsaturated chain-ends at δ 108.0 and 155.0 ppm that were assigned to vinylidene moieties (Figure 4) [23]. For the polymer produced with **PM-13**, only the signals in the aliphatic region were observed (Figure 5), suggesting either the absence of unsaturated chain ends or very high molecular weight of the polymer. The former hypothesis seems much more realistic in light of the relative intensities of the carbons of the saturated chain-end groups vs. those of the main-chain signals in the aliphatic region (vide infra).

Close inspection of the aliphatic region of the $^{13}$C{$^1$H} NMR spectra of P(3MB1)s obtained with **C$_2$-1** and **PM-13** (Figure 6a) showed two series of signals corresponding respectively to the four sets of signals of the main-chain carbons. The chemical shifts of the observed signals matched those previously reported in the literature [4,6,7].

Signals from the saturated chain-end groups were unequivocally identified (Figure. 6b). These resonanc-

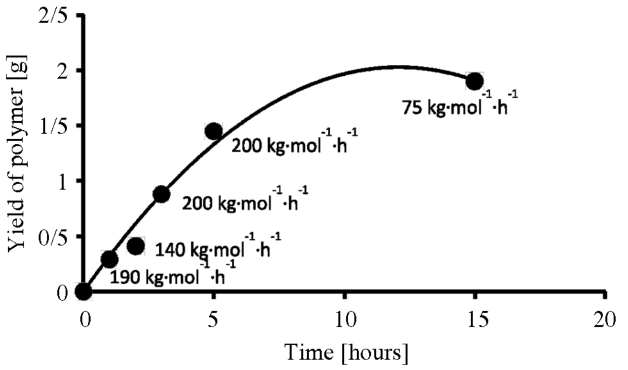


**Figure 3**. Yield of P(VCH) as a function of time for the **C$_1$-6**/MAO catalytic system (20°C).

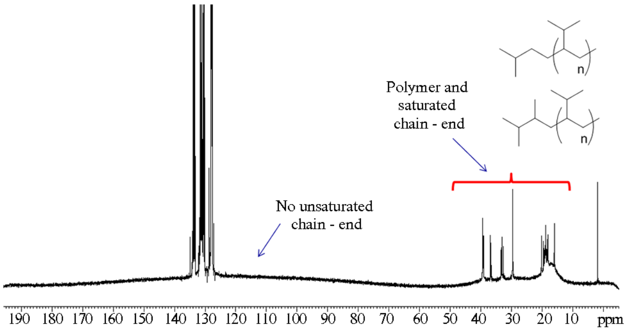


**Figure 5**. $^{13}$C{$^1$H} NMR spectrum (125 MHz, trichlorobenzene/C$_6$D$_6$ (4:1), 135°C) of a P(3MB1) produced with **PM-13**/MAO at 20°C (Table 1, entry 21).

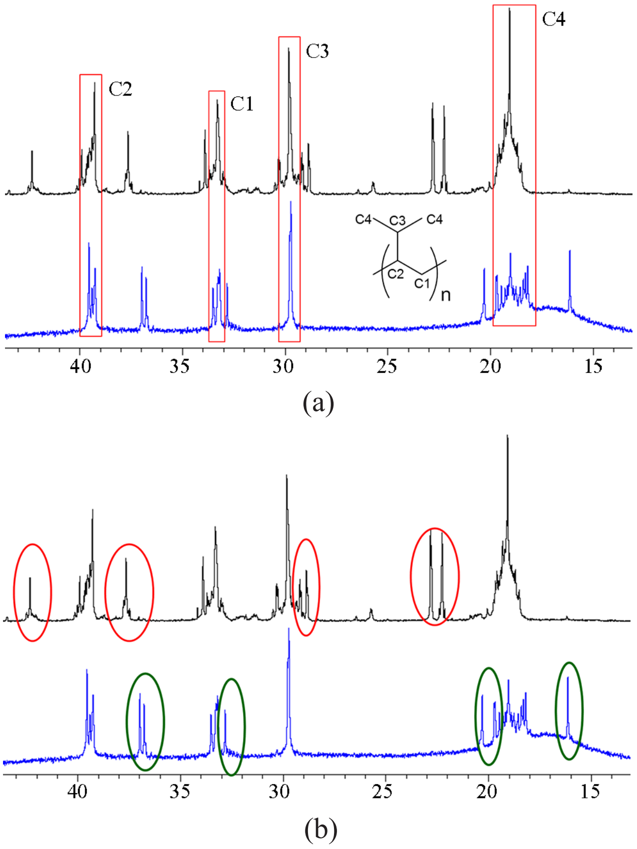
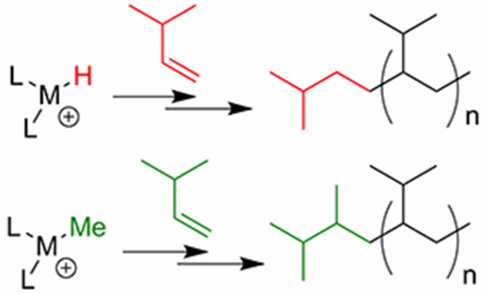


**Figure 6**. Details of the aliphatic region of the $^{13}C\{1H\}$ NMR spectra (125 MHz, trichlorobenzene/$C_6D_6$ (4:1), 135°C) of a P(3MB1) produced: (a) by **$C_2$-1**/MAO at 70°C (Table 4, entry 5); and (b) by **PM-13**/MAO at 20°C (Table 1, entry 21).

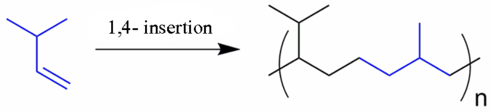


**Scheme 3**. Formation of the saturated iso-butyl and 2,3-dimethylbutyl chain-ends in P(3MB1) by insertion of monomer into the M–H (top) and in the M–Me (bottom) bonds.

es assigned by Busico et al. [7] correspond to the iso-butyl and 2,3-dimethylbutyl end-groups arising from the first primary (1,2-) insertions of a monomer into the M–H or M–Me bonds, respectively, during the initiation step (Scheme 3) and to the iPr-vinylidene end-groups resulted from β-H elimination/transfer-to-monomer. In addition, a series of resonances of lower intensity arising not from chain-end groups but rather from “1,4-insertions” (Scheme 4) [7] were also observed in the spectra of P(3MB1)s obtained with **$C_2$-1**.

For polymers prepared with **$C_2$-1**, the relative proportion of the different chain-end signals appeared to be temperature dependent, as judged from the direct comparison of the aliphatic region of the corresponding $^{13}C\{^1H\}$ NMR spectra (Figure. S2). For example, the $^{13}C\{^1H\}$ NMR spectrum of P(3MB1) obtained at 20°C showed only the signals from the iBu and iPr-vinylidene end-groups present, while for the polymer obtained at 70°C, the corresponding spectrum also displayed resonances from the 2,3-dimethylbutyl groups. On the other hand, in the NMR spectra of the P(3MB1)s obtained with **PM-13** at 20°C and 70°C, signals from the iBu chain-end groups were observed in both cases (Figure S1). The above data suggest that the two catalytic systems actually operate via two different chain-termination mechanisms, namely β-H elimination/transfer-to-monomer for **$C_2$-1** and chain-transfer to $ALMe_3$ for **PM-13** [38], respectively. The $^{13}C\{^1H\}$ NMR spectrum of the soluble part of the polymer produced with **CGC-12** at 20°C (Figure S3) showed resonances of regiodefects arising from 1,4-insertions along with other signals from saturated chain-ends, which nature could not be unambiguously identified.

Determination of the microstructure of P(3MB1) samples at the triad level was performed by integration of the C3 region of the $^{13}C\{^1H\}$ NMR spectra using a standard deconvolution method (Figure 7) [7,16]. All P(3MB1)s obtained with **$C_2$-1**, **PM-13** and **CGC-12** systems appeared to be isotactic-enriched, with mm triad contents ranging from 68 to 98% (Table 6, entries 1−4). The formation of highly isotactic P(3MB1) (98% mm) with the **PM-13**/MAO system at high temperature (70°C) is remarkable (entry 4). The apparent drop of isoselectivity observed with **$C_2$-1** at 70°C is possibly due to the differences in solubility of the two samples (entries 1 and 2, respectively). The formation of an isotactic-enriched polymer with usually non-stereoselective **CGC-12** (entry 5) is in line



**Scheme 4**. Regiodefect generated by the 1,4-insertion of 3MB1 monomer.

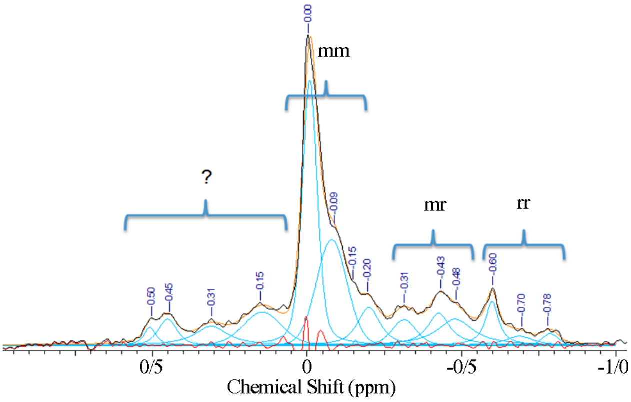


**Figure 7**. Deconvolution of the C3 region of the $^{13}C\{^1H\}$ NMR spectrum (125 MHz, trichlorobenzene/C6D6 (4:1), 135°C) of a P(3MB1) produced with **CGC-12**/MAO (Table 1, entry 19).

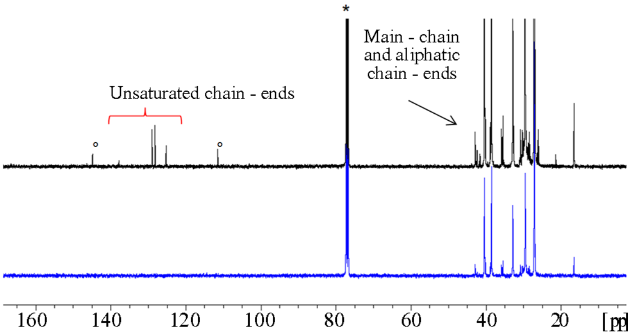


**Figure 8**. $^{13}C\{^1H\}$ NMR spectrum (100 MHz, $CDCl_3$, 25°C) of a P(VCH) sample produced with **PM-13**/MAO at 70°C (Table 4, entry 8, top black trace) and at 20°C (Table 1, entry 22, bottom blue trace); * stands for solvent signal; ° stands for residual monomer.

with previous reports on other catalysts typically non-stereoselective towards α-olefins (propylene) [7] and has been accounted for by a chain-end stereocontrol mechanism.

2) In striking contrast to P(3MB1)s, all P(VCH)s produced with **$C_1$-2**, **$C_2$-4** and **PM-13**/MAO are soluble in some organic solvents and their characterization by $^{13}C$ NMR spectroscopy was eventually carried out in $CDCl_3$. A representative $^{13}C\{^1H\}$ NMR spectrum of a P(VCH) obtained with **PM-13** is depicted in Figure 8; it shows the signals from the main-chain groups in the high field aliphatic region and a set of resonances from unsaturated chain-end groups in the downfield region. These signals are identical to those previously reported by Sita et al. [13] and Kol et al. [15] for P(VCH)s obtained with different catalytic systems isoselective towards propylene.

Interestingly, in contrast with 3MB1 polymerization, the catalytic system **PM-13**/MAO enables β-H elimination/transfer-to-monomer reaction at higher polymerization temperature (70°C); this is evidenced from the observation of resonances at δ 120.0–140.0 ppm from vinylidenic groups in the $^{13}C$ NMR spectrum.

In the aliphatic region of the $^{13}C\{^1H\}$ NMR spectrum (Figure 9), the low intensity resonances observed at δ 31.0, 36.0 and 43.0 ppm were assigned to the saturated chain-ends. The general pattern of single, sharp resonances from the main-chain groups in P(VCH) samples derived from **$C_2$-4**, **$C_1$-6** and **PM-13** is diagnostic of the highly isotactic nature ($[m]^4$ > 95%) [13,14,15].

## Molecular weights determination

Very few data about molecular weights of P(3MB1) polymers are reported in the literature, which is obviously related to their very poor solubility. Also, all attempts to study the thermal properties of the P(3MB1) and P(VCH) polymers by DSC failed due to decomposition of samples at high temperatures, even under inert atmosphere. The partial solubility of P(3MB1) samples in regular solvents used for SEC (THF, $CHCl_3$, trichlorobenzene), even at high temperature, prevented exhaustive analysis of molecular weights and distributions by this technique. Therefore, an estimation of the $M_n$ values was carried out by $^{13}C\{^1H\}$ NMR spectroscopy, from integration of the chain-end

**Table** 6. Triad distributions for P(3MB1) polymers obtained with **$C_2$-1**, **PM-13** and **CGC-12**.[(a)]

| Entry | Catalyst | $T_{polym}$ (°C) | *mm* (%) | *mr* (%) | *rr* (%) | *m* (%) | Table, entry |
|---|---|---|---|---|---|---|---|
| **1** | $C_2$-1 | 20 | 89 | 7 | 4 | 92 | 1, 1 |
| **2** | $C_2$-1 | 70 | 71 | 15 | 14 | 78 | 4, 5 |
| **3** | PM-13 | 20 | 90 | 7 | 3 | 94 | 1, 21 |
| **4** | PM-13 | 70 | 96 | 3 | 1 | 98 | 4, 3 |
| **5** | CGC-12 | 20 | 68 | 23 | 9 | 79 | 1, 19 |

(a)Determined by $^{13}C$ NMR spectroscopy.

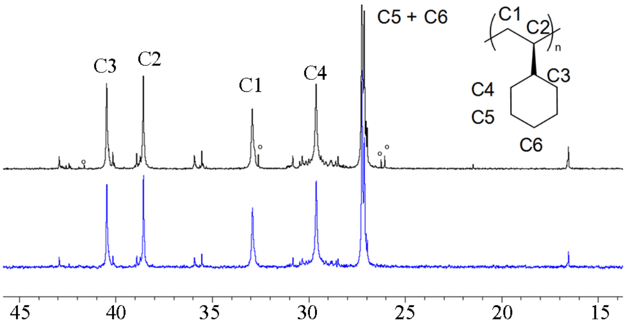


**Figure 9**. Details of the aliphatic region of the $^{13}C\{^1H\}$ NMR spectra (100 MHz, $CDCl_3$, 25°C) of P(VCH) samples produced with PM-13/MAO at 70°C (Table 4, entry 8, top black trace) and at 20°C (Table 1, entry 22, bottom blue trace). ° stands for resonances of residual monomer.

and main-chain signals (Table 7). The soluble part of P(3MB1) consists of oligomers with $DP_n$ in the range 6-30, which is in agreement with previous reports using the same technique [7]. However, as long as the insoluble part of the polymer apparently consists of macromolecules of higher mass, it is difficult to establish any relationship between either the nature of catalyst or the polymerization conditions and molecular weight of the produced polymer.

For **PM-13**, the effect of temperature on molecular weights of P(VCH)s is limited: samples produced at 40 and 70°C had molecular weights comparable to those obtained at 20°C (compare entries 2–4), again resulting in bimodal molecular weight distributions (Figure S6); only at 70°C, a slight decrease in the dispersity and $M_w$ values is noted. Lower molecular weight polymers were produced at shorter polymerization time at 20°C (compare entries 1 and 2, after 3 h and 15 h, respectively) (Figure 10). The bimodal molecular weight distributions, typically observed with **PM-13**/MAO, indicate that several different active species are operative, possibly resulting from generation during precatalyst activation and/or different evolution of active species during catalysis. This observation is in line with previous results reported for this catalytic system with other α-olefins [21,39].

**Table 7**. Degree of polymerization and average number molecular weight of the soluble part of P(3MB1) samples as determined by $^{13}C$ NMR spectroscopy.

| Entry | Catalyst | $T_{polym}$ (°C) | $DP_n$ | $M_n$ ($g \cdot mol^{-1}$) | Table, entry |
|---|---|---|---|---|---|
| **1** | PM-13 | 20 | 6 | 420 | 1, 21 |
| **2** | PM-13 | 70 | 10 | 700 | 4, 3 |
| **3** | $C_2$-1 | 20 | 30 | 2100 | 1, 1 |
| **4** | $C_2$-1 | 70 | 6 | 420 | 4, 5 |

[a] Determined by $^{13}C$ NMR spectroscopy. Being readily soluble in THF, many P(VCH) samples were analyzed by SEC at 35°C (Table 8). All P(VCH)s obtained with PM-13 displayed bimodal distributions (DM = 4.8−6.0, entries 1−4, Figure 10); contrastingly, P(VCH) samples produced by metallocene catalysts featured narrow monomodal distributions (DM = 1.5−2.2, entries 5−14, Figure S5).

No clear trend between structure, productivity and molecular weight characteristics could be found for P(VCH)s produced with metallocene catalysts from the {Cp/Flu}-, {EBTHI}- and {SBI}-based series. For **$C_1$-6**, rising the polymerization temperature from 20 to 70°C resulted in polymers with molecular weights one order of magnitude lower ($M_w$ = 104 vs. 10.6 kg.mol$^{-1}$, compare entries 5 and 6, respectively), as anticipated from enhanced β-H elimination and transfer processes at higher temperatures. Also, the polymerization time has a limited effect on both the molecular weights and distributions of the polymers produced with **$C_1$-6** (compare entries 5 and 8). Within the {Cp/Flu}-based series, the most productive precursors **$C_1$-6** and **$C_1$-8** afforded higher molecular weight polymers (entries 8 and 10, respectively). The same phenomenon can be seen for the **$C_2$-2** and **$C_2$-3** systems of the {SBI}-based congeners (entries 12 and 13, respectively).

## CONCLUSION

Polymerization of the bulky α-olefins 3MB1 and VCH was investigated under different conditions using a broad series of group 4 catalytic systems. Dow's

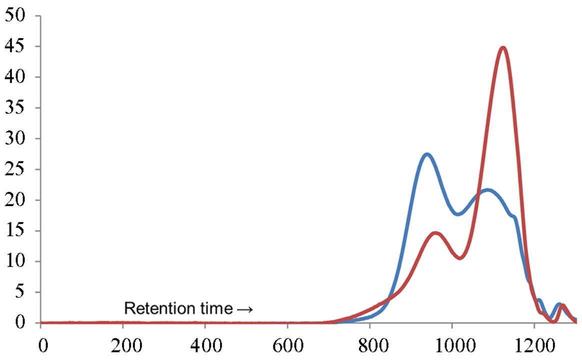


**Figure 10**. GPC traces of P(VCH) samples produced with PM-13/MAO at 20°C after 3 and 15 h (Table 8, entries 1 and 2: red and blue traces, respectively).

**Table 8**. Molecular weights and polydispersities of P(VCH) samples determined by SEC analysis.

| Entry | Precatalyst | Time (h) | $T_{polym}$ (°C) | Productivity ($kg·mol^{-1}·h^{-1}$) | $M_w$$^{(a)}$ ($kg·mol^{-1}$) | $Đ_M$$^{(a)}$ | Table, entry |
|---|---|---|---|---|---|---|---|
| **1** | PM-13 | 3 | 20 | 31 | 10.6 | 6.0 | 5, 6 |
| **2** | PM-13 | 15 | 20 | 98 | 16.8 | 5.5 | 1, 22 |
| **3** | PM-13 | 1 | 40 | 310 | 17.4 | 6.1 | 4, 7 |
| **4** | PM-13 | 1 | 70 | 760 | 12.4 | 4.8 | 4, 8 |
| **5** | $C_1$-6 | 3 | 20 | 200 | 104 | 1.7 | 5, 10 |
| **6** | $C_1$-6 | 1 | 70 | 430 | 10.6 | 2.2 | 4, 10 |
| **7** | $C_1$-5 | 15 | 20 | 5.9 | 101 | 1.5 | 1, 10 |
| **8** | $C_1$-6 | 15 | 20 | 75 | 117 | 1.9 | 1, 12 |
| **9** | $C_1$-7 | 15 | 20 | 23 | 67.6 | 1.6 | 1, 13 |
| **10** | $C_1$-8 | 15 | 20 | 60 | 117 | 2.1 | 1, 14 |
| **11** | $C_2$-1 | 15 | 20 | 5.3 | 4.4 | 1.8 | 1, 2 |
| **12** | $C_2$-2 | 15 | 20 | 35 | 97.8 | 1.8 | 1, 4 |
| **13** | $C_2$-3 | 15 | 20 | 23 | 78.2 | 1.6 | 1, 6 |
| **14** | $C_2$-4 | 15 | 20 | 3.9 | 7.4 | 2.0 | 1, 8 |

(a) In THF at 35°C vs. polystyrene standards.

ortho-metallated amido-pyridino hafnium complex **PM-13** was found to be the most efficient for both monomers, affording productivities of 46 and 98 $kg.mol^{-1}.h^{-1}$, respectively, at 20°C. Optimization of the polymerization conditions with this catalyst system led to improved productivities up to 390 and 760 $kg.mol^{-1}.h^{-1}$ at 70°C, respectively. These values are slightly higher than or comparable to those previously reported for these two monomers, though direct comparison is always delicate because of the various polymerization conditions documented in the literature. Yet, these productivities remain far from those relevant to industrial applications. Also, straightforward relationships between the precatalyst structures and their performances could not be established unambiguously. It appears grossly that catalysts with a more open coordination sphere are more productive, however, this trend is valid only for a few systems and a significant, puzzling exception is the very poor performance of the ubiquitous constrained geometry Ti catalyst **CGC-12**, famous for its propensity, in principle, to (co)polymerize effectively α-olefins.

The isotactic nature of the P(3MB1) polymers, even of those produced with a priori syndioselective catalysts (i.e., syndioselective catalysts towards propylene), was confirmed, suggesting that a chain-end control is likely the principal stereocontrol mechanism operative for 3MB1 polymerization. However, conclusions on the general trends for the polymerization of 3MB1 are limited by the sole analysis of the soluble fractions of polymer samples. Likewise, all the obtained P(VCH)s proved to be isotactic. For catalysts that are syndioselective towards propylene, their inactivity in polymerization of VCH might be attributed to a possible conflict between the geometry of the active site and the stereocontrol mechanism.

**Supporting Information Available**

Additional $^{13}C$ NMR spectra and GPC traces of polymers.

## REFERENCES

1. Vasile C (2000) Handbook of polyolefins, 2nd Edition (Plastics Engineering). CRC Press, 1-1032
2. Fink JK (2010) Handbook of engineering and specialty thermoplastics, Vol. 1, Polyolefins and

styrenics, Wiley-Scrivener, 1-400

3. Wei H, Hagihara H, Miyoshi T (2007) Microstructure and thermal property of isotactic poly(3-methyl-1-butene) obtained using the $C_2$-symmetrical zirconocene/MAO catalyst system. Macromolecules 40: 1763-1766
4. Segal S, Yeori A, Shuster M, Rosenberg Y, Kol M (2008) Isospecific polymerization of vinylcyclohexane by zirconium complexes of salan ligands. Macromolecules 41: 1612−1617
5. Asakura T, Nakayama N (1991) Carbon-13 nuclear magnetic resonance analysis of poly(3-methyl-1-butene). Polym Commun 32 : 213-216
6. Rishina LA, Galashina NM, Nedorezova PM, Klyamkina AN, Aladyshev AM, Tsvetkova VI, Kleiner VI (2006) Homo-and copolymerization of vinylcyclohexane with α-olefins in the presence of heterogeneous and homogeneous catalytic systems. J Polym Sci Pol Chem 48: 18-25
7. Borriello A, Busico V, Cipullo R, Chadwick JC, Sudmeijer O (1996) Polymerization of 3-methyl-1-butene promoted by metallocene catalysts. Macromol Rapid Commun 17: 589-597
8. Ammendola P, Tancredi T, Zambelli A (1986) Isotactic polymerization of styrene and vinylcyclohexane in the presence of carbon-13-enriched Ziegler-Natta catalyst: Regioselectivity and enantioselectivity of the insertion into metal-methyl bonds. Macromolecules 19: 307-310
9. Endo K, Fujii K, Otsu T (1991) Steric effects of substituents on polymerization activity of branched 1-olefins with titanium trichloride-triethylaluminum catalyst. J Polym Sci Pol Chem 29: 1991-1993
10. Endo K, Otsu T (1992) Polymerization of vinylcyclohexane with Ziegler-Natta catalyst. J Polym Sci Pol Chem 30: 679−683
11. Soga K, Nakatani H, Shiono T (1989) Polymerization of vinylcyclohexane with Ziegler-Natta catalyst. Macromolecules 22: 1499-1500
12. Grisi F, Pragliola S, Costabile C, Longo P (2006) Polymerizations of vinyl-cyclohexane in the presence of $C_2$, $C_{2v}$, and $C_s$ zirconocene-based catalysts. Polymer 47: 1930-1934
13. Keaton RJ, Jarayatne KC, Henningsen DA, Koterwas LA, Sita LR (2001) Dramatic enhancement of activities for living Ziegler-Natta polymerizations mediated by "Exposed" zirconium acetamidinate initiators: The isospecific living polymerization of vinylcyclohexane. J Am Chem Soc 123: 6197-6198
14. Tsurugi H, Ohnishi R, Kaneko H, Panda TK, Mashima K (2009) Controlled benzylation of α-diimine ligands bound to zirconium and hafnium: An alternative method for preparing mono- and bis(amido)M(CH2Ph)n (n = 2, 3) complexes as catalyst precursors for isospecific polymerization of α-olefins. Organometallics 28: 680-687
15. Gendler S, Groysman S, Goldschmidt Z, Shuster M, Kol M (2006) Polymerization of 4-methylpentene and vinylcyclohexane by amine bis(phenolate) titanium and zirconium complexes. J Polym Sci Pol Chem 44: 1136-1146
16. Miyoshi T, Wei H, Hagihara H (2007) Microstructure and thermal property of isotactic poly(3-methyl-1-butene) obtained using the $C_2$-symmetrical zirconocene/MAO catalyst system. Macromolecules 40: 6789-6792
17. Kaminsky W, Kulper K, Brintzinger HH, Wild FRWP (1985) Polymerisation von propen end buten mit einem chiralen zirconocen und methylaluminoxan als cokatalysator. Angew Chem 97: 507-508
18. Spaleck W, Kuber F, Winter A, Rohrmann J, Bachmann B, Antberg M, Dolle V, Paulus EF (1994) The influence of aromatic substituents on the polymerization behavior of bridged zirconocene catalysts. Organometallics 13: 954-963
19. Kirillov E, Marquet N, Razavi A, Belia V, Hampel F, Roisnel T, Gladysz JA, Carpentier JF (2010) New $C_1$-symmetric $Ph_2C$-bridged multisubstituted ansa-zirconocenes for highly isospecific propylene polymerization: Synthetic approach via activated fulvenes. Organometallics 29: 5073-5082
20. Razavi A, Peters L, Nafpliotis L (1997) Geometric flexibility, ligand and transition metal electronic effects on stereoselective polymerization of propylene in homogeneous catalysis. J Mol Catal A-Chem 115: 129-154
21. Boussie TR, Diamond GM, Goh C, Hall KA, LaPointe AM, Leclerc MK, Murphy V, Shoemaker JAW, Turner H, Rosen RK, Stevens JC, Alfano F, Busico V, Cipullo R, Talarico G (2006) Nonconventional catalysts for isotactic propene polymerization in solution developed by using

high-throughput-screening technologies. Angew Chem Int Ed 45: 3278-3283

22. Kirillov E, Marquet N, Bader M, Razavi A, Belia V, Hampel F, Roisnel T, Gladysz JA, Carpentier JF (2011) Chiral-at-ansa-bridged Group 4 metallocene complexes {($R^1R^2$C)-(3,6-$tBu_2$Flu)(3-$R^3$-5-Me-$C_5H_2$)}$MCl_2$: Synthesis, structure, stereochemistry, and use in highly isoselective propylene polymerization. Organometallics 30: 263-272
23. Bader M, Marquet N, Kirillov E, Roisnel T, Razavi A, Lhost O, Carpentier JF (2012) Old and new C1-symmetric Group 4 metallocenes {($R^1R^2$C)-($R^{2'}R^{3'}R^{6'}R^{7'}$-Flu)(3-$R^3$-5-$R^4$-$C_5H_2$)}$ZrCl_2$: From highly isotactic polypropylenes to vinyl end-capped isotactic-enriched oligomers. Organometallics 32: 8375-8387
24. Rodriguez AS, Kirillov E, Carpentier JF (2008) Group 3 and 4 single-site catalysts for stereospecific polymerization of styrene. Coord Chem Rev 252: 2115-2136
25. Delferro M, Marks TJ (2011) Multinuclear olefin polymerization catalysts. Chem Rev 111: 2450-2485
26. Arriola DJ, Carnahan EM, Hustad PD, Kuhlman RL, Wenzel TT (2006) Catalytic production of olefin block copolymers via chain shuttling polymerization. Science 312: 714-719
27. Theurkauff G, Roisnel T, Waassenaar J, Carpentier JF, Kirillov E (2014) iPP-sPP stereoblocks or blends ? studies on the synthesis of isotactic-syndiotactic polypropylene using single $C_1$-symmetric {$Ph_2$C-(Flu)(3-$Me_3$Si-Cp)}$ZrR_2$ metallocene precatalyst. Macromol Chem Phys 215: 2035-2047
28. Kaminsky W, Kulper K, Niedoba S (1986) Olefin polymerization with Highly Active Soluble zirconium compounds using aluminoxane as cocatalyst. Macromol Chem Macromol Symp 3: 377-387
29. Csok Z, Liguori D, Sessa I, Zannoni C, Zambelli A (2004) Stereochemical structure of polypropylene obtained in the presence of half-sandwich titanium complexes. Macromol Chem Phys 205: 1231-1237
30. McKnight AL, Masood MA, Waymouth RM (1997) Selectivity in propylene polymerization with group 4 Cp-amido catalysts. Organometallics 16: 2879-2885
31. Frazier KA, Froese RD, He Y, Klozin J, Theriault CN, Vosejkka PC, Zhou Z (2011) Pyridylamido hafnium and zirconium complexes: Synthesis, dynamic behavior, and ethylene/1-octene and propylene polymerization reactions. Organometallics 30: 3318-3329
32. Kaminsky W (1998) Highly active metallocene catalysts for olefin polymerization. J Chem Soc Dalton Trans: 1413-1418
33. Busico V, Cipullo R, Pellechia R, Talarico G, Razavi A (2009) Hafnocenes and MAO: Beware of trimethylaluminum. Macromolecules 42: 1789-1791
34. Theurkauff G, Bader M, Marquet N, Bondon A, Roisnel T, Guegan JP, Amar A, Boucekkine A, Carpentier JF, Kirillov E (2016) Discrete ionic complexes of highly isoselective zirconocenes. Solution dynamics, trimethylaluminum adducts, and implications in propylene polymerization. Organometallics 35: 258-276
35. Babushkin DE, Brintzinger HH (2007) Modification of methylaluminoxane-activated ansa-zirconocene catalysts with triisobutylaluminum-transformations of reactive cations studied by NMR spectroscopy. Chem Eur J 13: 5294-5299
36. Zuccaccia C, Macchioni A, Busico V, Cipullo R, Talarico G, Alfano F, Boone HW, Frazier KA, Hustad PD, Stevens JC, Vosejpka PC, Abboud KA (2008) Intra- and intermolecular NMR studies on the activation of arylcyclometallated hafnium pyridyl-amido olefin polymerization precatalysts. J Am Chem Soc 130: 10354−10368
37. Gao Y, Mouat AR, Motta A, Macchioni A, Zuccaccia C, Delferro M, Marks TJ (2015) Pyridylamido Bi-hafnium olefin polymerization catalysis: Conformationally supported Hf...Hf enchainment cooperativity. ACS Catal 5: 5272-5282
38. Rocchigiani L, Busico V, Pastore A, Macchioni A (2016) Comparative NMR study on the reactions of Hf(IV) organometallic complexes with Al/Zn Alkyls. Organometallics 35: 1241-1250
39. Froese RDJ, Hustad PD, Kuhlman RL, Wenzel TT (2007) Mechanism of activation of a hafnium pyridyl-amide olefin polymerization catalyst: Ligand modification by monomer. J Am Chem Soc 129: 7831-7840