

Comonomer-controlled synthesis of long-chain branched (LCB)-polyethylene

O. Santoro, L. Piola, K. Mc Cabe, O. Lhost, K. den Dauw, A. Fernandez, A. Welle, L. Maron, J.-F. Carpentier, E. Kirillov

▶ **To cite this version:**

O. Santoro, L. Piola, K. Mc Cabe, O. Lhost, K. den Dauw, et al.. Comonomer-controlled synthesis of long-chain branched (LCB)-polyethylene. European Polymer Journal, 2022, 177, pp.111477. 10.1016/j.eurpolymj.2022.111477 . hal-03780247

HAL Id: hal-03780247
https://hal.science/hal-03780247

Submitted on 3 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

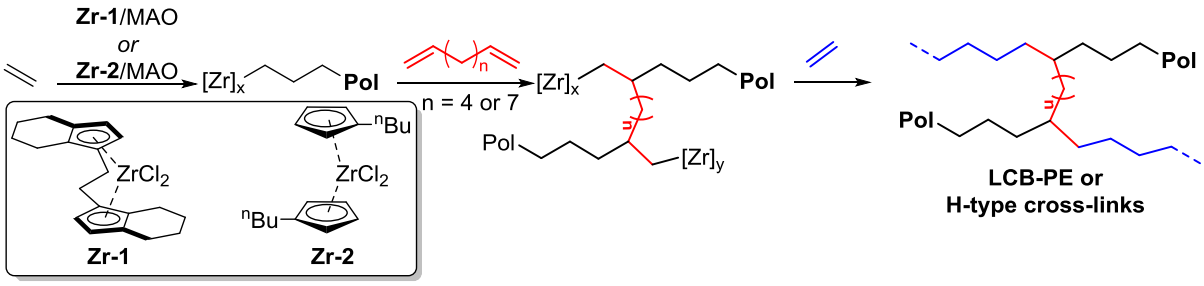
Comonomer-Controlled Synthesis of Long-Chain Branched (LCB)-Polyethylene

Orlando Santoro,[a,†] Lorenzo Piola,[a,†] Karl Mc Cabe,[c] Olivier Lhost,[b] Katty Den Dauw,[b] Alvaro Fernandez,[b] Alexandre Welle,[b] Laurent Maron,[c,*] Jean-François Carpentier[a,*] and Evgueni Kirillov[a,*]

[a] Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes (ISCR), UMR 6226, F-35042 Rennes, France

[b] TotalEnergies One Tech Belgium, Zone Industrielle Feluy C, B-7181 Seneffe, Belgium

[c] Université de Toulouse, CNRS, INSA, UPS, LPCNO, UMR 5215, 135 avenue de Rangueil, F-31077 Toulouse Cedex 4, France



Abstract

In this contribution, we disclose the ability of α,ω-diene comonomers, namely 1,7-octadiene and 1-10-undecadiene, as long-chain branching (LCB)/cross-linking promoters in the ethylene polymerization catalyzed by bis(indenyl) and bis(cyclopentadienyl) catalyst systems, namely *rac*-{EBTHI}$ZrCl_2$ (**Zr**-1) and (nBuCp)$_2ZrCl_2$ (**Zr-2**). Both under

† Those two authors equally contributed to this work.

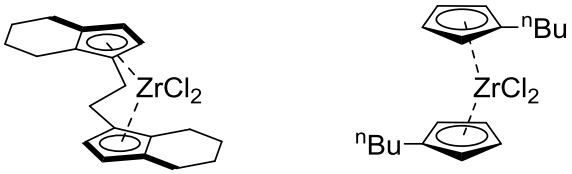
* Correspondence to Laurent Maron (laurent.maron@irsamc.ups-tlse.fr), Jean-François Carpentier (jean-francois.carpentier@univ-rennes1.fr) and Evgueni Kirillov (evgueni.kirillov@univ-rennes1.fr).

homogeneous and heterogeneous (slurry) conditions, **Zr-1**-based systems efficiently produced LCB/cross-linked polymers even with very small amounts of diene, as demonstrated by melt rheology measurements. On the other hand, higher co-monomer concentrations were required for the homogeneous **Zr-2**/MAO system, while only linear PEs were isolated in the presence of its silica-supported version ***supp*-Zr-2** operated under heterogeneous conditions, regardless of the amount of diene employed. Rheological and NMR spectroscopy studies proved that consumption of the diene and formation of LCB/cross-linked structures take place during the early stages of the polymerization. The experimental observations were rationalized by DFT computations.

Introduction

During the last three decades, metallocene-catalyzed ethylene/diene copolymerization has emerged as an efficient method towards post-functionalized- [1,2,3,4,5,6] and long-chain branched (LCB) polyethylene (PE) [7,8,9,10,11,12,13,14,15,16,17]. The latter aspect proved particularly interesting, since LCB-PEs most often exhibit significantly better processability than their linear counterparts, albeit retaining the excellent mechanical properties (i.e. impact resistance) typically found in metallocene-PE [18,19,20,21]. In this scenario, we have recently identified Al-, Zn- and B-alkenyl species as suitable LCB promoters in the ethylene polymerization catalyzed by *rac*-{EBTHI}$ZrCl_2$- and (nBuCp)$_2ZrCl_2$-based systems (**Zr-1** and **Zr-2**, respectively, Chart 1), proposing the incorporation of its alkenyl moiety into the growing PE chain as a crucial step for LCB formation [22,23,24]. Herein, we disclose the ethylene copolymerization with two α,ω-dienes, namely 1,7-octadiene and 1-10-undecadiene, catalyzed by the previously investigated **Zr-1** and **Zr-2**-based catalyst systems, both under homogeneous and heterogeneous (slurry) conditions. The rheological properties of the produced PEs as well as the difference between Al-alkenyl co-reactants and α,ω-dienes

comonomer in the formation of LCB-PE are discussed. As for our prior studies, these zirconocene catalysts were chosen because of their opposite tendency to *naturally* form LCB as well as for their different ability to incorporate comonomers. Indeed, **Zr-1** was shown to afford LCB-PEs by macromonomer incorporation along with displaying high comonomer incorporation ability. On the other hand, **Zr-2** proved less prone to comonomer insertion and capable of producing, in the absence of a suitable LCB-promoted, essentially linear PEs [25]. With respect to the nature of the α,ω-diene, the *in house*-prepared 1,10-undecadiene was employed for the tests under homogeneous conditions to favor the formation of branches over that of cycles embedded into the growing chain [26], thus avoiding complications in the characterization of the resulting materials and in the subsequent analysis of the results. Given that supported catalysts are largely employed in industrial PE production, it was decided to use the commercially available 1,7-octadiene to implement a more easily scalable (and economically viable) process.



Zr-1 **Zr-2**

Chart 1. Structure of the metallocenes used in this study: *rac*-{EBTHI}$ZrCl_2$ (**Zr-1**) and (nBuCp)$_2ZrCl_2$ (**Zr-2**).

Results and Discussion

Ethylene polymerization in the presence of 1,10-undecadiene: homogeneous conditions

Complexes **Zr-1** and **Zr-2**, activated by methylalumoxane (MAO), were tested in the ethylene polymerization under homogeneous conditions in the presence of 1,10-undecadiene (Table 1). For both catalyst systems, the presence of the diene had a positive effect on the

productivity of the process [27]. However, while for **Zr-2** the productivity progressively increased with $[diene]_0$, a detrimental effect was observed with **Zr-1** at comonomer concentrations higher than 0.5 mM. This was attributed to the formation of insoluble (allegedly cross-linked) PE hampering the diffusion of the monomer in the reaction medium (fouling). For **Zr-1** a progressive drop of T_m of the resulting polymer was observed upon increasing the amount of diene, while such values for the samples synthesized with **Zr-2** (**PE5**–**PE8**) were found in a very narrow range (133–134 °C), regardless of the diene concentration.

None of the PEs isolated with **Zr-1**/MAO/diene systems, as well as **PE7** (Table 1) could be analyzed by GPC due to their insolubility in dichlorobenzene at 135 °C. Such poor solubility was thought to be due to the formation of "H-type" cross-linked polymers (Chart 2) at this initial diene concentration, $[Diene]_0$ (*vide infra*) [28].

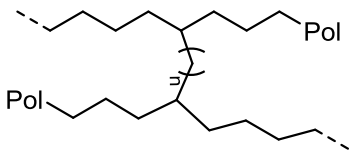


Chart 2. "H-type" cross-linked polyethylene.

In order to gain more information on the kinetics aspects of the LCB/cross-links formation, a polymerization test at shorter reaction time (3 instead of 15 min) was performed with the **Zr-2**/MAO system in the presence of 5 mM of diene (Table 1, entry 8). No vinyl moieties were detected in the ^{1}H NMR spectrum of the corresponding polymer (**PE8**, see the Supporting information, Figure S2), suggesting that all of the diene incorporated was involved in the formation of "H-type" branched structures/cross-links (Chart 2) [7, 29]. The amount of unreacted diene was determined by ^{1}H NMR in the presence of an internal standard (2-methoxynaphtalene) in the concentrated quenching solution of the polymerization

(see the Supporting information, Figure S3). Since <2% of unreacted diene was detected, it was assumed that nearly quantitative comonomer consumption occurred and that, given the short reaction time, the formation of LCB/cross-linking takes place in the early stages of the polymerization.

Table 1. Ethylene polymerization in the presence of 1,10-undecadiene catalyzed by **Zr-1**- and **Zr-2**/MAO systems (homogeneous conditions).

Entry	Sample ID	Catalyst	$[Diene]_0$ (mM)	Productivity ($kg_{PE}/g_{Zr}\cdot h$)	T_m[a] (°C)	M_n[b] (kDa)	M_w[b] (kDa)	M_w/M_n[b]	Crystallinity[c] (%)
1	**PE1**	**Zr-1**	0	35	136	43	140	3.3	48
2	**PE2**		0.5	60	134	insoluble sample			51
3	**PE3**		1.5	46	133	insoluble sample			51
4	**PE4**		5.0	31	130	insoluble sample			47
5	**PE5**	**Zr-2**	0	42	134	30	109	3.6	47
6	**PE6**		0.5	50	133	36	145	4.0	57
7	**PE7**		5.0	55	133	insoluble sample			53
8[d, e]	**PE8**		5.0	100	134	n.d.			44

Reaction conditions: [Zr] = 10 mM, Al_{MAO}/Zr= 5000, T = 60 °C, 15 min, toluene = 150 mL, P_{Et} = 4 barg. [a] Determined by DSC from second run. [b] Determined by HT-GPC. [c] Calculated from $[(\Delta H_m/\Delta H^0_m) \times 100]$, where ΔH_m is the heat of fusion of the sample (in J/g) determined by DSC and ΔH^0_m is the theoretical heat of fusion for 100% crystalline PE (293 J/g) [30]. [d] The reaction was stopped after 3 min. Diene left in the quenching solution < 2%. [e] No vinyl moieties detected in the ^1H NMR spectrum of the polymer.

The effect of $[Diene]_0$ on the rheological behavior of the samples was investigated. Samples **PE1**–**PE3** exhibited similar values of viscosity at low frequency and the enhancement of shear thinning upon increasing the comonomer concentration (Figure 1, top). On the other hand, **PE4** (prepared at $[Diene]_0$ = 5 mM) showed values of viscosity at low frequency ca. one order of magnitude higher than those of **PE1**–**PE3** and more pronounced shear thinning. These observations indicate that the extent of LCB/cross-linking is proportional to the amount of diene introduced; this is consistent with previous reports [31, 32, 33]. Further evidence supporting this statement could be achieved by analyzing the van Gurp-Palmen plots [34, 35] for **PE1–PE3** (Figure 1, bottom). In fact, all curves tend to phase

angle values lower than 90 ° (90 ° is indicative of purely linear polymers, *vide infra*) [35]; moreover, the inflection points observed for **PE2** and **PE3** are diagnostic for highly branched structures [33,36,37,38].

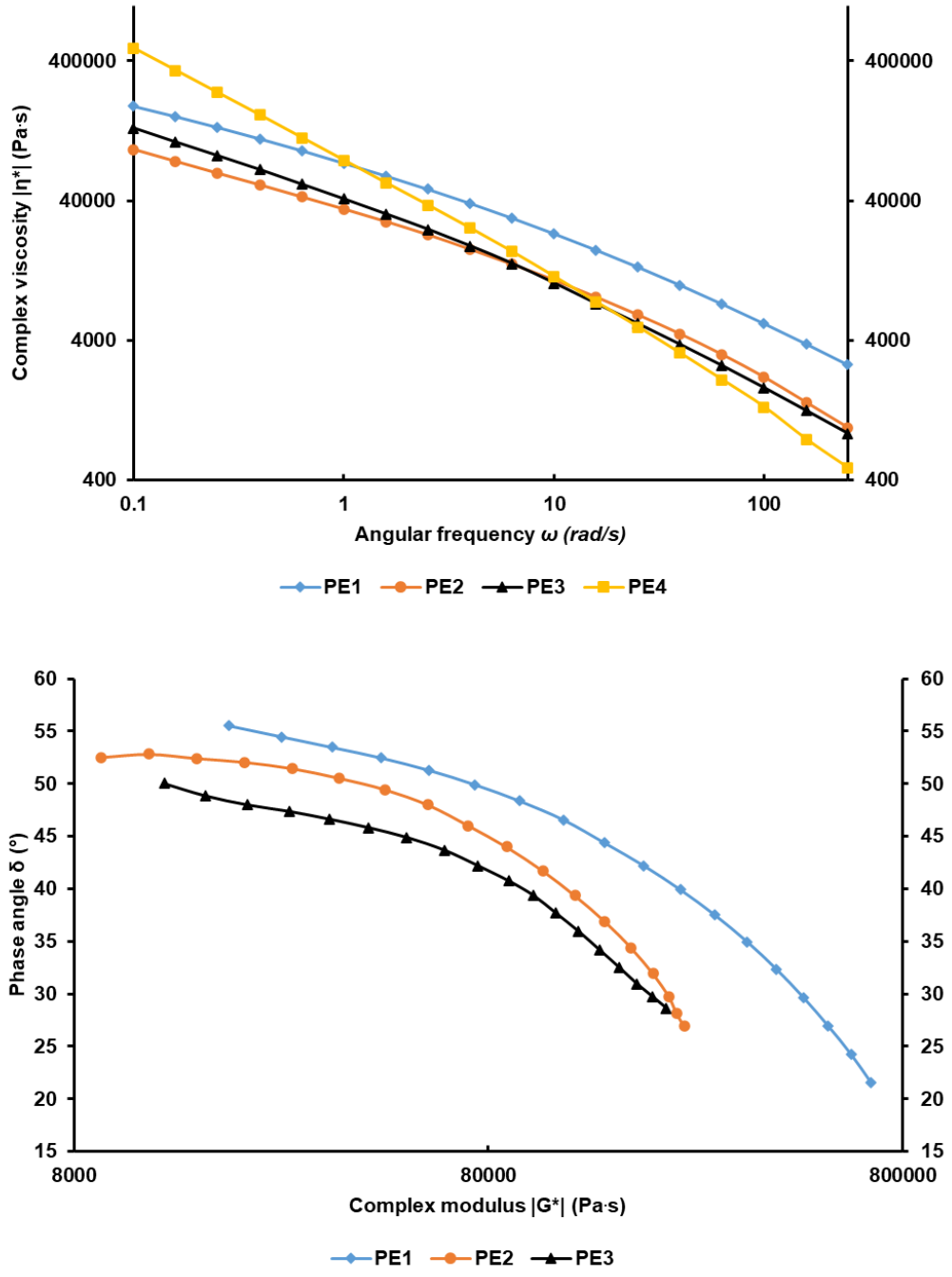
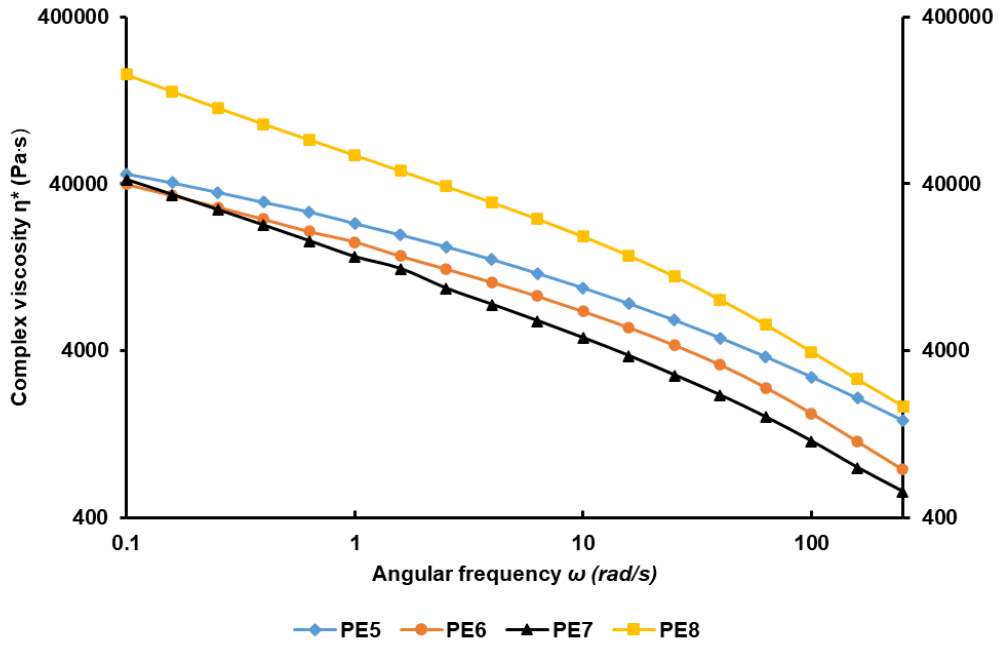


Figure 1. Rheological properties of **PE1**–**PE4**: |η*| = f(ω) (top), van Gurp-Palmen plot (bottom, no **PE4** shown [39]). Shear strain (γ) 10%, angular frequencies (ω) from 0.1 to 250 rad·s^{-1}, T = 190 °C, N_2 atmosphere.

Similar considerations could be drawn by observing the rheological behavior of the samples prepared with **Zr-2**/MAO/diene systems (**PE5**–**PE8**, Figure 2). Both the strengthening of the shear thinning and the decrease of phase angle at low |G*| values observed on the van Gurp-Palmen plots are in line with the amount of diene employed. Interestingly, **PE7** and **PE8**, synthesized with the same $[Diene]_0$ (5.0 mM) but at different reaction times (15 and 3 min, respectively), exhibited a different rheological response. Indeed, the curves for **PE8** are indicative of a greater LCB-density compared to that of **PE7**, supporting the hypothesis that LCB/cross-linking occurs during the early stages of the polymerization; longer reaction times generates linear chains reducing the impact of said crosslinks on the PE rheological properties the (*vide infra*) [40].



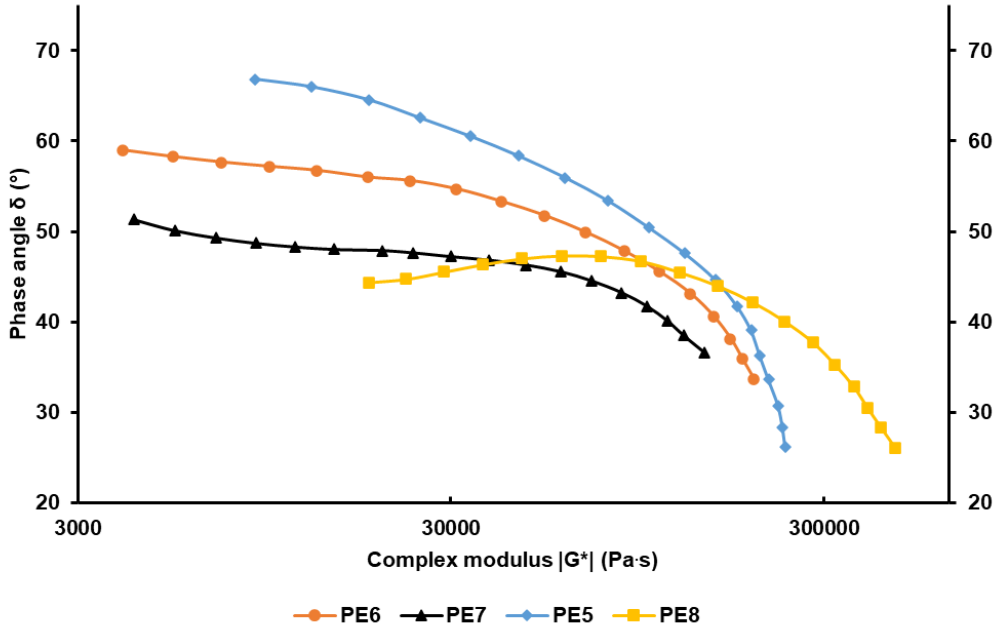


Figure 2. Rheological properties of **P5**–**PE8**: |η*| = f(ω) (top), van Gurp-Palmen plot (bottom). Shear strain (γ) 10%, angular frequencies (ω) from 0.1 to 250 rad·s^{-1}, T = 190 °C, N_2 atmosphere.

It has to be noted that with **Zr-1**, a remarkable variation of the corresponding PE rheological properties was observed even for concentrations of diene as low as 0.5 mM, while a similar response was attained with the **Zr-2**-based system only at higher diene feed (5 mM). This could be accounted to the different co-monomer incorporation ability of the two metallocenes, which is in the order **Zr-1** >> **Zr-2** [41].

Ethylene polymerization in the presence of 1,7-octadiene: heterogeneous conditions

In order to assess the industrial viability of the process, polymerization tests catalyzed by heterogeneous ***supp*-Zr-1** and ***supp*-Zr-2**, synthesized from **Zr-1** and **Zr-2** according to reported procedures [42,43], were conducted in the presence of 1,7-octadiene [44] as the LCB/cross-linking-promoter and by using triisobutylaluminum (TIBAL) as the scavenger

(Table 2) [45]. The productivity of the ***supp*-Zr-1**-based system proved only slightly dependent on the diene concentration. On the other hand, while the polymers' T_m, M_n and dispersity values were also found in a very narrow range for [1,7-octadiene]$_0$ up to 300 ppm (Table 2, entries 1–5), a PE insoluble in dichlorobenzene at 135 °C was obtained upon increasing the diene concentration to 500 ppm (**PE14**, Table 2, entry 6) [46]. A significant and progressive drop of the melt flow index (MI2) [47], indicative of the increase of polymer viscosity, was also observed.

The van Gurp-Palmen plots for such samples (**PE9**–**PE14**, Figure 3) showed a drop of the phase angle at low |G*| consistent with the amount of 1,7-octadiene employed in the polymerization; they also featured clear inflection points. This clearly indicates the presence of LCB/cross-linking and, remarkably, that its extent can be tuned by selecting an appropriate concentration of diene.

Table 2. Ethylene polymerization in the presence of 1,7-octadiene and 1-hexene [45] catalyzed by ***supp*-Zr-1**- and ***supp*-Zr-2**/TIBAL systems (heterogeneous conditions).

Entry	PE ID	Catalyst	[Diene]$_0$ (ppm)[mM]	Productivity (kg_{PE}/g_{cat}·h)	T_m [a] (°C)	M_n [b] (kDa)	M_w [b] (kDa)	M_w/M_n [b]	*MI2* (g/10 min)
1	**PE9**	***supp*-Zr-1**	0	5.1	120	28	79	2.8	1.06
2	**PE10**		50 [0.5]	5.3	119	28	82	2.9	0.77
3	**PE11**		100 [1.0]	4.9	119	27	84	3.1	0.53
4	**PE12**		200 [2.0]	5.3	120	28	88	3.1	0.38
5	**PE13**		300 [3.0]	5.3	120	28	94	3.4	0.18
6	**PE14**		500 [5.0]	5.4	120	insoluble sample			n.d.
7	**PE15**	***supp*-Zr-2**	0	7.8	122	24	53	2.2	10.8
8	**PE16**		500 [5.0]	6.2	123	19	46	2.3	15.1
9[c]	**PE17**		500 [5.0]	4.0	132	23	60	2.6	6.60
10	**PE18**		1500 [15]	5.9	124	19	44	1.7	16.2
11[c]	**PE19**		1500 [15]	3.3	131	21	54	2.5	10.4
12	**PE20**		3000 [30]	5.3	123	18	43	1.9	18.8
13[c]	**PE21**		3000 [30]	3.2	131	20	54	2.5	14.5

Reaction conditions: supported catalysts = 2 mg, T = 85 °C, 60 min, *iso*-butane = 75 mL, P_{Et} = 25 barg, H_2 = 800 ppm, 1-hexene = 2.44 wt%. [a] Determined by DSC from second run. [b] Determined by HT-GPC. [c] No 1-hexene.

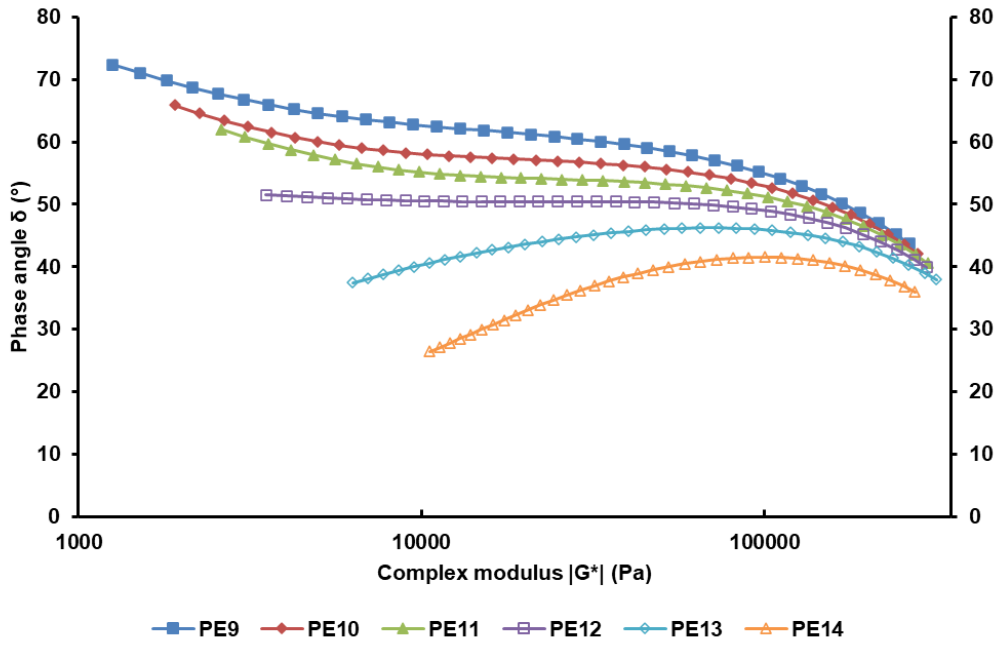


Figure 3. Rheological properties of **P9-PE14:** van Gurp-Palmen plot. Shear strain (γ) 10%, angular frequencies (ω) from 0.1 to 250 rad·s^{-1}, T = 190 °C, N_2 atmosphere.

As regards the tests performed with ***supp*-Zr-2** (Table 2, entries 7–13), the presence of the diene exerted a detrimental effect on the catalyst productivity; as expected, the latter drop was more pronounced in the runs performed without 1-hexene (Table 2, entries 9, 11 and 13) [27]. Both thermal- and molecular features of the PEs proved independent of the diene concentration and only affected by the presence/absence of 1-hexene. In fact, the drop of T_m obtained in the presence of 1-hexene is due to the formation of short-chain branching (SCB) derived from insertion of the comonomer into the growing chain. Moreover, a slight broadening of the molecular weight distributions was observed, tentatively accounted to chain-transfer events occurring more often after the comonomer insertions [48]. This is in agreement with the larger distributions obtained with **supp-Zr-1**, which exhibits higher comonomer incorporation ability. The increase of MI2 values could be accounted for to the presence of larger content of SCB arising from the incorporation of 1,7-octadiene not evolving into LCB/cross-link formation (*vide infra*).

In contrast to the homogeneous **Zr-2**, the van Gurp-Palmen data for the samples synthesized with ***supp*-Zr-2** (Figure 4) were compatible with that of *purely* linear PEs, regardless of diene concentration. This indicated that the insertion of 1,7-octadiene did not evolve into the formation of branched/cross-linked structures (as suggested by the increase of the Melt Flow Index). Interestingly, the same outcome was observed both in the presence and in the absence of 1-hexene; this indicates that the insertion of such comonomer, detrimental to LCB formation, is not in competition with that of 1,7-octadiene. The opposite tendency towards branching formation displayed by homogeneous- and supported **Zr-2** (i.e., LCB vs. SCB, respectively) was also observed with the Al-alkenyl LCB-promoter [23]. Again, this could be possibly rationalized in terms of steric effects exerted by the silica support [48], which reduces accessibility to the metal center, eventually hampering the insertion of the larger comonomer 1,7-octadiene.

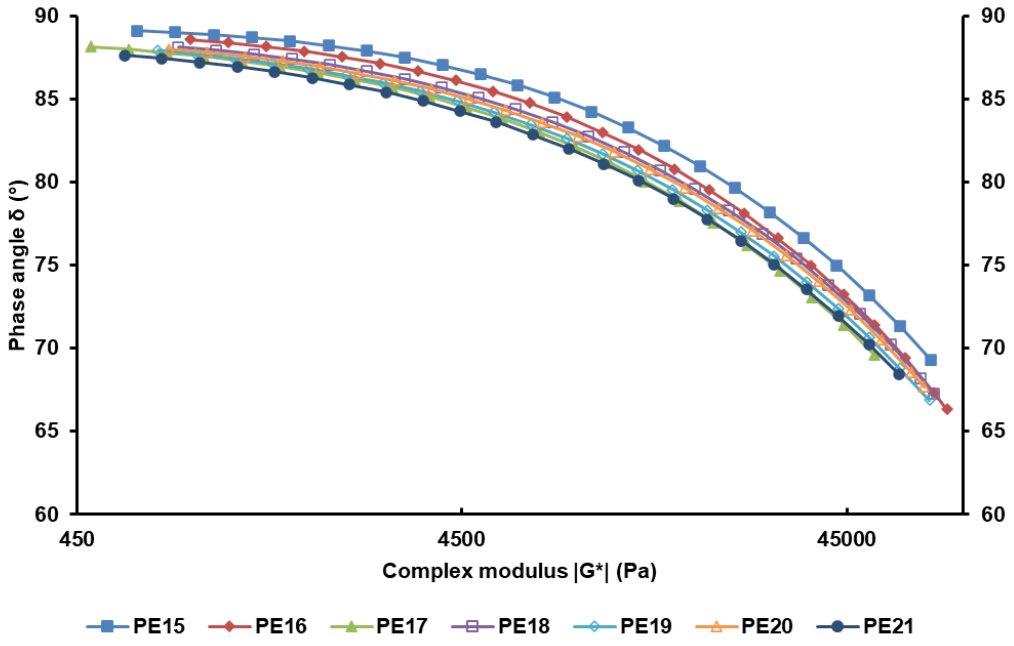
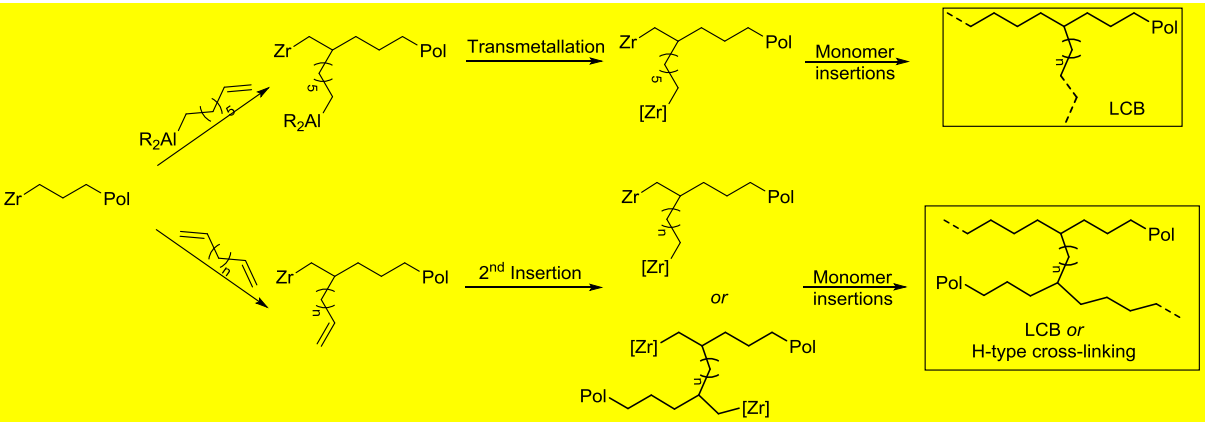


Figure 4. Rheological properties of **P15-PE21**:van Gurp-Palmen plot. Shear strain (γ) 10%, angular frequencies (ω) from 0.1 to 250 rad·s^{-1}, T = 190 °C, N_2 atmosphere.

On the difference between Al-alkenyl species and α,ω-diene as LCB promoters

The comparison between the results reported herein and those reported in our previous contributions [22,23,24] indicates that α,ω-dienes are more efficient LCB/cross-linking promoters than *i*BuAl(oct-7-en-1-yl)$_2$ (**Al-1**). In fact, PEs exhibiting rheological properties compatible with LCB were obtained in the presence of rather low amounts of diene (ca. 50 equiv. with respect to the catalyst), while the amount of **Al-1** required to achieve similar outcomes was found to be at least one order of magnitude higher. It is assumed that such different efficiency depends on the pathways towards LCB formation and the nature of LCB/cross-linking generated with the two types of co-reactants (Scheme 1).



Scheme 1. Putative pathways for the formation of LCB/cross-linking in the presence of Al-alkenyl species or α,ω-diene co-monomers.

In both cases, the first step of the mechanism is assumed to imply the insertion of a vinyl group into the Zr–C(alkyl) bond of a growing polymer chain. The second part of the mechanism involves a transmetallation to zirconium in the case of **Al-1** and the insertion of the second vinyl group in another Zr–C(alkyl) bond in the case of *α,ω*-dienes. In both cases, further insertion of monomers/propagation leads to the formation of LCB./cross-linking. We

assume that the rate of insertion of the pendant double bond of the α,ω-diene co-monomer is much higher than the rate of transmetallation form Al to Zr. Hence, the higher efficiency of dienes would be justified mostly by this kinetic aspect. Similarly, the rapid formation of crosslinks leading to more intricate macromolecular structures also likely occurs.

In order to evaluate this hypothesis, the effect of the reaction time on the LCB density was investigated. The results of the polymerization of ethylene catalyzed by ***supp*-Zr-1** in the presence of both **Al-1** and 1,7-octadiene are summarized in Table 3. In the benchmark reactions with 1000 ppm of TIBAL only, the productivity of the catalyst in the 20-min reaction was found nearly twice of that in the test performed over 60 min (Table 3, entries 1 and 2, respectively). The same outcome was obtained when a 1:1 TIBAL/1,7-octadiene mixture was employed (Table 3, entries 3 and 4). These results suggest that, both in the presence and in the absence of the diene, the catalyst undergoes rather fast deactivation (inversely to a "comonomer effect" [22,23,24]) and that most of the LCB/cross-linked polymer is produced during the early stages of the polymerization. Remarkably, when the reaction was performed in the presence of **Al-1** as the only co-reactant, the productivity of the catalyst was found to be constant, regardless of the reaction time (60, 20 or 10 min, Table 3, entries 5, 6 and 7, respectively). These results can be rationalized considering the formation of stable Zr/Al heterobimetallic species which stabilize the catalyst, preventing its early deactivation.

Table 3. Polymerization of ethylene with ***supp*-Zr-1**/TIBAL/**Al-1** or 1,7-octadiene - effect of the reaction time.

Entry	PE ID	TIBAL (ppm)	Co-reactant (ppm)	$Time_{pol}$ (min)	Productivity (kg_{pol}/kg_{cat}·min)	T_m (°C)	T_{cryst} (°C)
1	**PE22**	1000	none	60	2.25	134	119
2	**PE23**	1000	none	20	5.25	134	118
3	**PE24**	1000	1,7-octadiene (1000)	60	3.15	131	117

4	**PE25**	1000	1,7-octadiene (1000)	20	6.40	128	114
5	**PE26**	0	**Al-1** (1000)	60	2.85	133	118
6	**PE27**	0	**Al-1** (1000)	20	2.15	133	118
7	**PE28**	0	**Al-1** (1000)	10	2.44	133	119

Reaction conditions: ***supp*-Zr-1** = 35–40 mg, H_2 800 ppm, T = 80 °C, toluene = 150 mL, P = 4 barg.

The melting and crystallization temperatures of the polymers synthesized in the presence of Al-based co-reactants were found in a narrow range (133–134 °C and 117–118 °C, respectively) and proved to be independent from the reaction time. Slightly lower T_m and T_c values were detected for the polymers produced in the presence of 1,7-octadiene.

No significant effect of the reaction time on the rheological behavior of the polymers prepared in the presence of TIBAL (**PE22** and **PE23**) was observed. In fact, the van Gurp-Palmen curve of both curves tends to a phase angle at low |G*| of ca. 80° (Figure 5).

On the other hand, the rheological properties of **PE24** and **PE25**, obtained by using 1,7-octadiene, showed that higher LCB/cross-linking densities could be achieved at shorter reaction times. Indeed, the van Gurp-Palmen plot curve for **PE25** (20-min reaction) showed a lower phase angle at low |G*| than that of **PE24** (60-min test). These results, further suggest that consumption of the diene occurs during the early stages of the polymerization, affording PEs with high LCB/cross-linking density. At longer reaction times, since no more α,ω-diene is present in the reaction medium, formation of essentially linear polymer chains occurs, contributing to a *dilution* of the LCB/cross-linking density within the whole polymer.

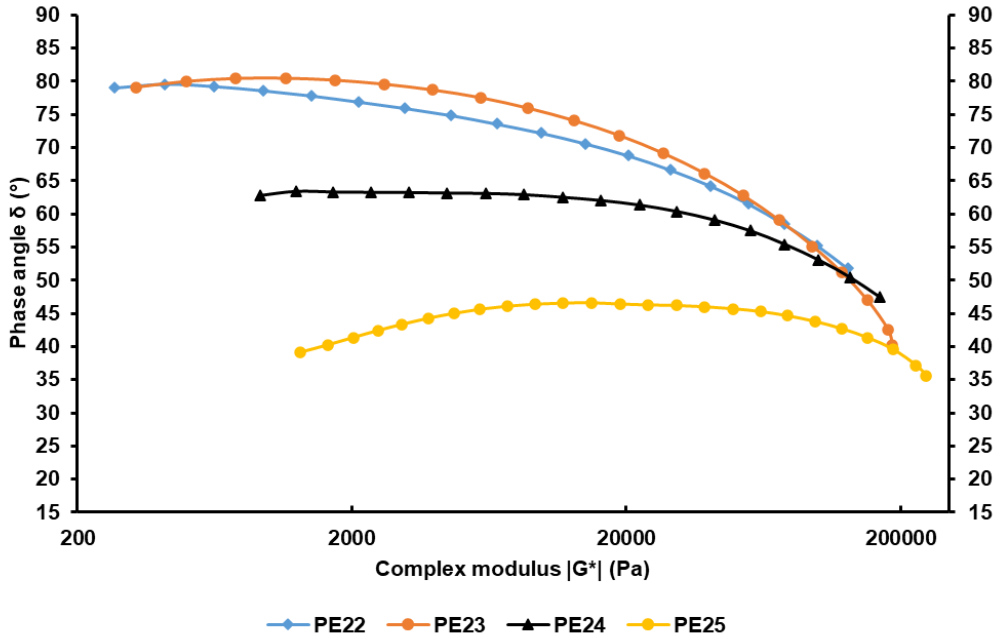


Figure 5. van Gurp-Palmen plot for the PEs obtained with ***supp*-Zr-1**/TIBAL/1,7-octadiene mixtures – Effect of the reaction time. Shear strain (γ) 10%, angular frequencies (ω) from 0.1 to 250 rad·s^{-1}, T = 190 °C, N_2 atmosphere.

All samples obtained in the presence of **Al-1** exhibited a rheological behavior compatible with presence of LCB (Figure 6). In fact, lower phase angles at low |G*| values with respect to the reference polymer (**PE22**) were observed on the van Gurp-Palmen plot. Remarkably, all curves were found in a rather narrow range, regardless of the reaction time. These results suggest that, contrary to the case of *α,ω*-dienes, the LCB density remains constant throughout the polymerization process. As aforementioned, we assume that this could be accounted for by the formation of stabilizing Zr/Al bimetallic species.

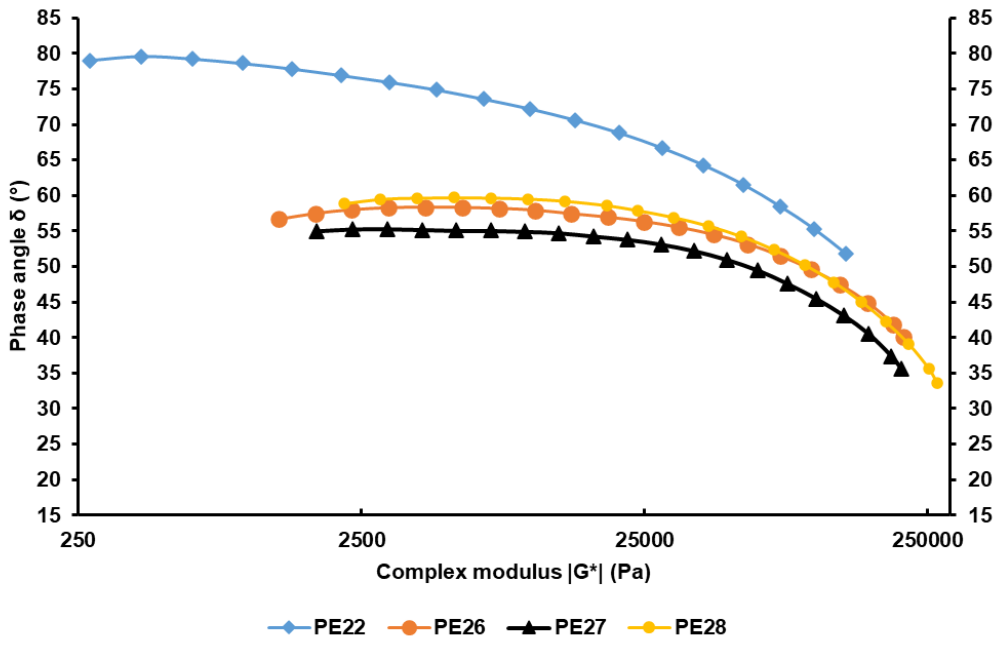
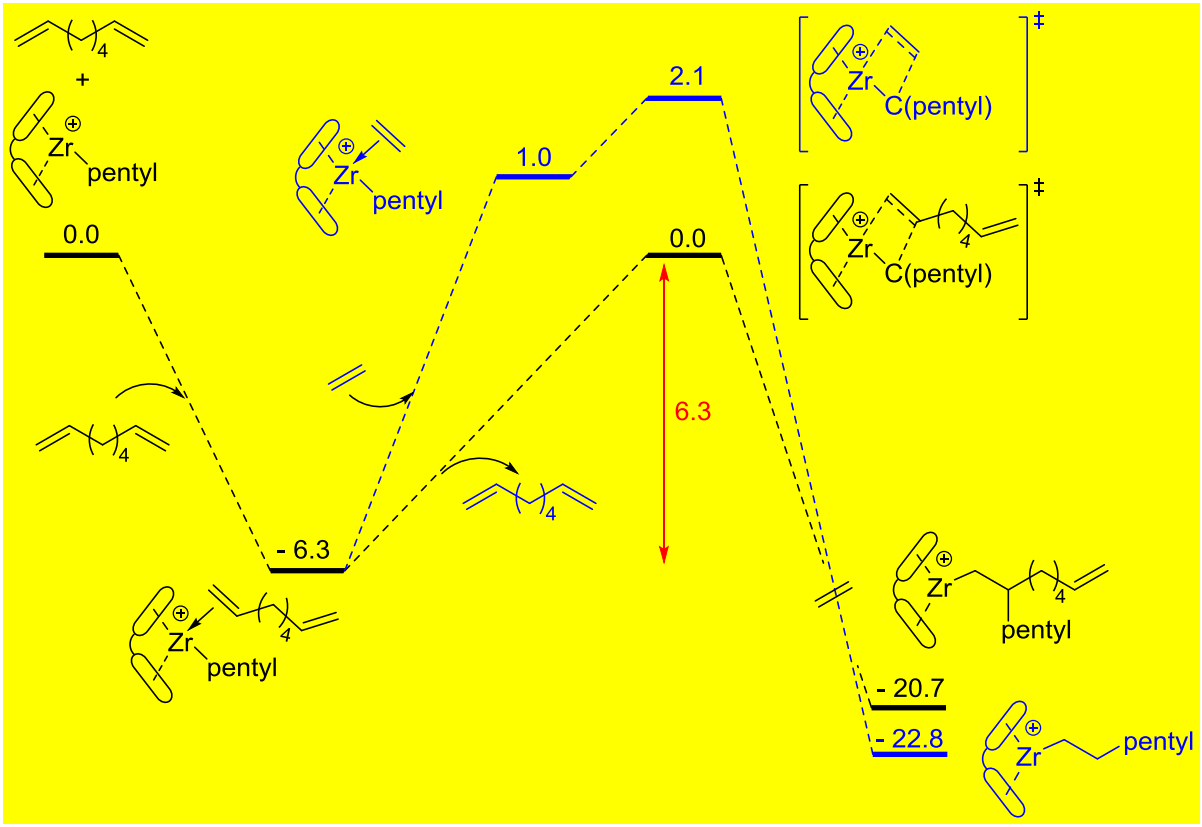


Figure 6. van Gurp-Palmen plot for the PEs obtained with ***supp*-Zr-1**/TIBAL/**Al-1** systems – Effect of the reaction time. Shear strain (γ) 10%, angular frequencies (ω) from 0.1 to 250 rad·s^{-1}, T = 190 °C, N_2 atmosphere.

DFT studies on the LCB formation with Zr-1 and Zr-2 systems in the presence of 1,7-octadiene. In this study, we aimed at rationalizing the mechanism of formation of LCB structures during polymerization of ethylene with **Zr-1** and **Zr-2** systems, in the presence of 1,7-octadiene, by theoretical computations of the first, second and third insertion steps. The purpose of this study is to analyze the various coordinated co-catalyst catalyst species and examine the change in structure as subsequent insertions of ethylene continue. 1,7-octadiene is examined here on the basis that such a compound is present, in excess, during the synthesis of the referenced **Al-1** co-catalyst agent.

Following the computational protocol that has been outlined in our previous studies [22,23,24], the coordination energies of 1,7-octadiene was investigated with either **Zr-1** or **Zr-2** systems. The first coordination and insertion of the diene moiety to [**Zr-1–methyl**]$^+$

catalyst indicates an initial stabilizing interaction of –6.3 kcal·mol^{-1} (See the Supporting information, Scheme S2). Kinetically, either first insertion is inconclusive with a $\Delta H_{Transition_state}$ of 0.2 kcal·mol^{-1}, highlighting the competitive environment of [**Zr-1–methyl**]$^{+}$ catalyst is subjected to when the diene moiety is present in the reaction mixture. Of great interest regarding the product formations observed thus far, is the fact that the 1,7-octadiene insertion product is initially thermodynamically competitive with respect to the insertion of ethylene monomer, although at the cusp of the methodology (2 kcal·mol^{-1}), $\Delta H_{Product}$ = 1.8 kcal·mol^{-1}. Further studies were conducted in order to explore if the same trends are reproduced at longer polymeryl chain lengths: C3 and C5, with the respective [**Zr-1–propyl**]$^{+}$ (Scheme S3) and [**Zr-1–pentyl**]$^{+}$ catalysts (Scheme 2).

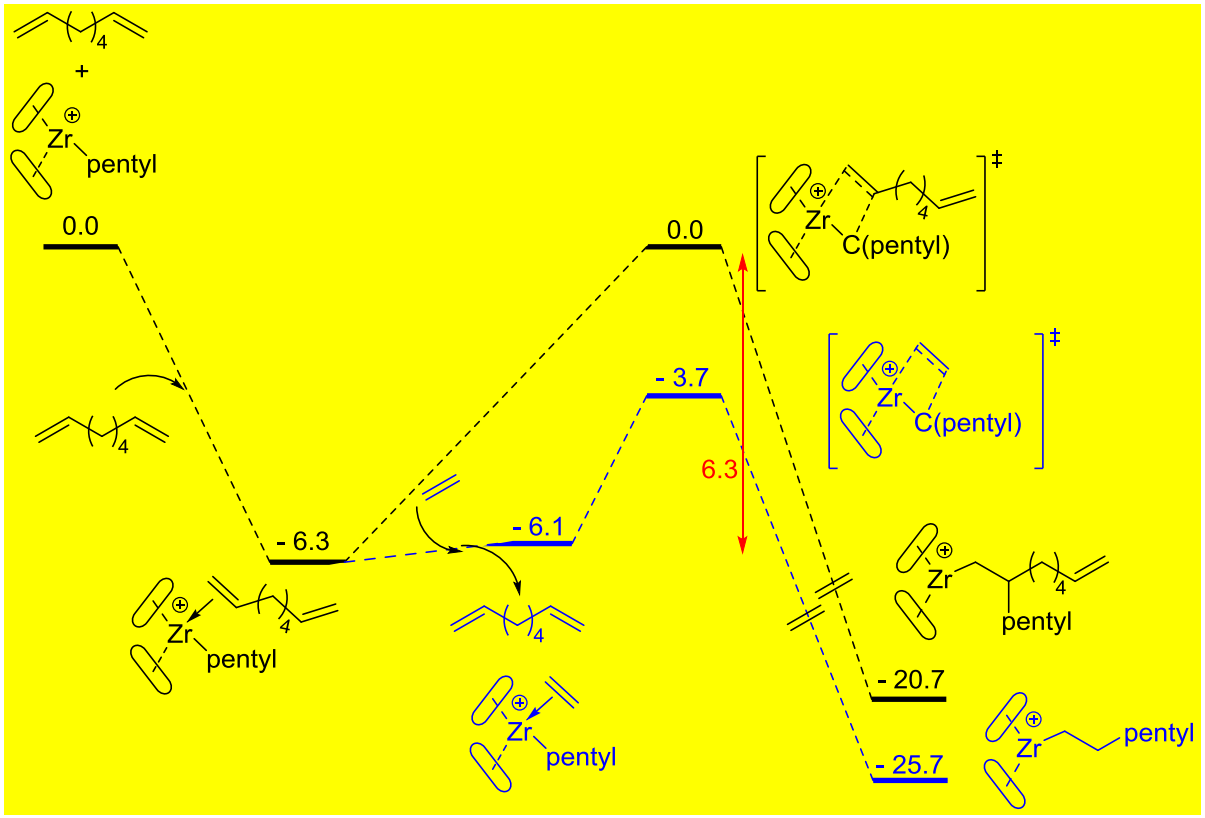


Scheme 2. A comparison between the third insertion of ethylene monomer vs. 1,7-octadiene vinyl group coordination/insertion to [**Zr-1–pentyl**]$^{+}$ following a dissociation of the diene.

The second insertion (Scheme S3) demonstrates a similar reactivity to the first coordination. A $\Delta H_{Transition_State}$ of 2.4 kcal·mol^{-1} could insight some doubt regarding the kinetic propensity of linear product formations whilst postulating the ability of a more stable 1,7-octadiene insertion product to form. As the chain propagates affording [**Zr-1–pentyl**]$^{+}$ (Scheme 3), the products that are produced favor a linear polymer. This is similar to the observed **Zr-Al-1** environment studied previously [22,23]. The 1,7-octadiene insertion events are plausible but rare in comparison. This is beneficial for increased propagation and consequently may influence branching at shorter chain lengths; having an impact on the formation of LCB and/or cross-links during growth. The fact that the branched products could arguably be in some state of competition thermodynamically in the first and second insertions, suggests a plausible environment for more products with pendant olefinic functions. The latter could warrant sufficient conditions to rapidly incorporate into other growing chains, enabling cross-linked structures. Unfortunately, difficulties in unequivocal characterizing LCB vs cross-links concentrations by melt rheology enforces the general conclusion that the presence of a diene (1,7-octadiene) is agreeably beneficial for formations of cross-links recalling samples **PE2–PE4**.

The same computational analysis was conducted using the [**Zr-2–R**]$^{+}$ system. Interestingly, the experimental observations indicate a diene moiety had no influence on LCB PE formation favoring a more linear PE product regardless of 1,7-octadiene concentrations. Computationally, one would expect the data to result in a kinetic preference for monomer insertions relative to diene coordination mechanisms. In fact, the first and second insertions (Schemes S4 and S5) indicate that the coordination of the diene molecule provides a slightly more stabilizing interaction to the [**Zr-2–R**]$^{+}$ catalyst (<1.4 kcal·mol^{-1} for R = Me). Observing the two transition states located, the insertion of the diene is preferred. The reactivity presented would indicate the 1,7-octadiene insertion event is theoretically possible

and kinetically driven. As the chain propagates to longer lengths, e.g. [**Zr-2–pentyl**]$^+$ (Scheme 3), a growing propensity for linear product formations occurs, which is in agreement with a more linear rheology fingerprint presented (Figure 2).



Scheme 3. A comparison between the third insertions of ethylene monomer vs. 1,7-octadiene vinyl group coordination/insertion in [**Zr-2–pentyl**]$^+$.

The energy profile demonstrates the growing preference for ethylene monomer coordination and insertion as the chain propagates. The coordination of the diene molecule remains slightly stronger relative to monomer coordination but highlights the competition that is present about the [**Zr-2–pentyl**]$^+$ system. In contrast to initial insertion steps, the ethylene insertion seems to be becoming increasingly favorable at longer polymeryl chain lengths. Furthermore, the products formed indicate a preference and thermodynamic control for a linear PE material.

Though the initial competition to the [**Zr-2–R**]$^+$ system may give rise to preferred insertions of 1,7-octadiene, at longer polymeryl chains on the catalyst, an ethylene coordination/insertion is both more kinetically and thermodynamically favored giving rise to a linear product.

Conclusions

In conclusion, we have investigated the ability of *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (**Zr-1**)- and bis(butylcyclopentadienyl)zirconium dichloride (**Zr-2**)-based catalyst systems to produce "LCB-PE" upon using an α,ω-diene comonomer as LCB/cross-linking promoter. Under homogeneous conditions, 1,10-undecadiene proved to be such an effective promoter in combination with the **Zr-1,2**/MAO catalyst systems. In fact, the rheological properties of the corresponding PEs proved to be sensibly affected, even by the use of quite small amounts of *α,ω*-diene. On the other hand, a similar response was attained with the Cp-based catalyst **Zr-2** only at higher $[Diene]_0$ concentration (5 mM). This was accounted to the different co-monomer incorporation ability of the two metallocenes (**Zr-1** >> **Zr-2**). [41] Under heterogeneous (slurry) conditions, ***supp*-Zr-1** exhibited a behavior similar to that of its homogeneous version, while in the presence of ***supp*-Zr-2**, only linear PEs were isolated regardless of the amount of diene introduced.

Rheological and NMR spectroscopy studies proved that the consumption of the α,ω-diene and the formation of LCB/cross-linked structures take place during the early stages of the polymerization, inducing concentration of branches and cross-links in a limited fraction of macromolecules. Hence, in order to achieve even distribution of LCB, the α,ω-diene should be progressively introduced in the reaction medium. Differently, the formation of branches promoted by Al-alkenyl species constantly occurs during the whole polymerization process allowing for the regular distribution of LCB, even if all of the co-reactant is

introduced in the initial feed. These experimental observations were in line with DFT computational results.

Acknowledgements: LM is a senior member of the Institut Universitaire de France. CalMip is acknowledged for a generous grant of computing time.

Funding sources: This work was gratefully supported by TotalEnergies One Tech Belgium (postdoctoral and PhD fellowships to OS, LP and KMC).

Appendix A: Supplementary data

Supporting information to this article (NMR spectroscopy and rheological analyses of polymers, computational details, Cartesian coordinates) can be found online at DOI:

References

[1] S. Marathe, S. Sivaram, Regioselective Copolymerization of 5-Vinyl-2-norbornene with Ethylene Using Zirconocene-Methylaluminoxane Catalysts: A Facile Route to Functional Polyolefins, Macromolecules 27 (1994) 1083–1086. https://doi.org/10.1021/ma00083a003.

[2] T.C. Chung, H.L. Lu, C.L. Li, Synthesis and Functionalization of Unsaturated Polyethylene: Poly(ethylene-co-1,4-hexadiene), Macromolecules 27 (1994) 7533–7537. https://doi.org/10.1021/ma00104a005.

[3] D.-H. Lee, K.-B. Yoon, J.-R. Park, B.-H. Lee, Copolymerizations of olefins and dienes with homogeneous and heterogeneous catalysts, Eur. Polym. J. 33 (1997) 447–451. https://doi.org/10.1016/S0014-3057(96)00184-X.

[4] W. Hou, D. Zhang, M.A. Camacho-Fernandez, Y. Zhang, G. Liu, Y. Tang, Z. Guan, Z. Huang, Double-Linear Insertion Mode of α,ω-Dienes Enabled by Thio-iminoquinoline Iron Catalyst ACS Catal. 10 (2020) 15092−15103. https://doi.org/10.1021/acscatal.0c04567.

[5] J. Li, L. Wang, Y. Qin, Q. You, T. Li, L. Sun, X. Li, G. Xie, Binuclear titanium complexes coordinated by rigid p-phenylene linked bis-β-carbonylenamine: Synthesis, structure, ethylene polymerization and copolymerization with 1,5-hexadiene, Appl. Organomet. Chem. (2020) e5772. https://doi.org/10.1002/aoc.5772.

[6] M. Kateb, M. Karimi, G.-R. Nejabat, S.M.M. Mortazavi, S. Ahmadjo, Synthesis of 1-hexene/1,7-octadiene copolymers using coordination polymerization and postfunctionalization with triethoxysilane, J. Appl. Polym. Sci. 137 (2020) 48934–48942. https://doi.org/10.1002/APP.48934.

[7] A. K. Mehta, C.S. Speed,J.A.M. Canich, N. Baron, B.J.Folie, M. Sugawara, A. Watanabe, H.C. Welborn Jr., Long-Chain Branched polymers and their production, US Patent 6,300,451 B1, 2001 (to Exxon Chemical Patents Inc.).

[8] E. Kokko, P. Pietikäinem, J. Koivunen, J.V. Seppälä, Long-chain-branched polyethene by the copolymerization of ethene and non-conjugated α, ω-dienes, J. Polym. Sci. 39 (2001) 3805–3817, https://doi.org/10.1002/pola.10033.

[9] P. Pietikäinem, R. Väänänen, J.V. Seppälä, Copolymerization of ethylene and nonconjugated dienes with Cp_2ZrCl_2/MAO catalyst system, Eur. Polym. J. 35 (1999) 1047–1055, https://doi.org/10.1016/S0014-3057(98)00192-X.

[10] P. Pietikäinem, J.V. Seppälä, L. Ahjopalo, L.-O. Pietilä, Copolymerization of ethylene and non-conjugated dienes with Cp_2ZrCl_2/MAO catalyst system: effect of polymerization temperature on the copolymer structure, Eur. Polym. J. 36 (2000) 183–192. https://doi.org/10.1016/S0014-3057(99)00053-1.

[11] S. Paavola, T. Saarinen, B. Löfgrena P. Pitkänen, Propylene copolymerization with non-conjugated dienes and α-olefins using supported metallocene catalyst, Polymer 45 (2004) 2099–2110. https://doi.org/10.1016/j.polymer.2004.01.053

[12] N. Naga, Y. Imanishi, Copolymerization of ethylene and 1,7-octadiene, 1,9-decadiene with zirconocene catalysts, Macromol. Chem. Phys. 203 (2002) 2155–2162, https://doi.org/10.1002/1521-3935(200211)203:15<2155::AIDMACP2155>3.0.CO;2-7.

[13] A. Williamson, G. Fink, Alternating copolymers of ethylene and diolefins containing pendent functional groups, Macromol. Chem. Phys. 204 (2003) 1178–1190, https://doi.org/10.1002/macp.200390091.

[14] D.M. Sarzotti, A. Narayan, P.M. Whitney, L.C. Simon, J.B.P. Soares, Microstructural Characterization of Molecular Weight Fractions of Ethylene/1,7-Octadiene Copolymers Made with a Constrained Geometry Catalyst, Macromol. Mater. Eng. 290 (205) 584–591, https://doi.org/10.1002/mame.200500064.

[15] S. Mehdiabadi, J.B.P. Soares, Production of Ethylene/α-Olefin/1,9-Decadiene Copolymers with Complex Microstructures Using a Two-Stage Polymerization Process, Macromolecules 44 (2011) 7926–7939. https://doi.org /10.1021/ma201368c.

[16] V. Karimkhani, F. Afshar-Taromi, S. Pourmahdian, F.J. Stadler, Revisiting the long-chain branch formation mechanism in metallocene catalyzed polyethylenes, Polym. Chem. 4 (2013) 3774–3790. https://doi.org/10.1039/c3py00319a.

[17] Y. Liu, Y. Qin, J.-Y. Dong, Assessing 1,9-Decadiene/Ethylene Copolymerization with Ziegler−Natta Catalyst to Access Long Chain-Branched Polyethylene, ACS Omega 6 (2021) 675−679. https://dx.doi.org/10.1021/acsomega.0c05211.

[18] P. Liu, W. Liu , W.-J. Wang ,B.-G. Li, S. Zhu, A Comprehensive Review on Controlled Synthesis of Long-Chain Branched Polyolefins: Part 1, Single Catalyst Systems, Macromol. React. Eng. 10 (2016) 156−179. https://doi.org/10.1002/mren.201500053.

[19] S.-Y. Lai, J.R. Wilson, G.W. Knight, J.C. Stevens, P.-W. Chum, Elastic substantially linear olefin polymers, U.S. Pat. 5,272,236, 1993 (to Dow Chemical co.).

[20] P. Brant, J.A.M. Canich, A.J. Dias, R.L. Bamberger, G.G. Licciardi, P.M. Henrichs, Long chain branched polymers and a process to make long chain branched polymers, WO Pat. 94/07930, 1994 (to ExxonMobil Chemical co.).

[21] Y.S. Kim, C.I. Chung, S.Y. Lai, K.S. Hyum, Melt rheological and thermodynamic properties of polyethylene homopolymers and poly(ethylene/α-olefin) copolymers with respect to molecular

composition and structure, J. Appl. Polym. Sci. 59 (1996) 125–137, https://doi.org/10.1002/(SICI)1097-4628(19960103)59:1<125::AIDAPP18>3.0.CO;2-Z.

[22] O. Santoro, L. Piola, K. Mc Cabe, O. Lhost, K. Den Dauw, A. Vantomme, A. Welle, L. Maron, J.-F. Carpentier, E. Kirillov, Long-Chain Branched Polyethylene via Coordinative Tandem Insertion and Chain-Transfer Polymerization Using *rac*-{EBTHI}$ZrCl_2$/MAO/Al–alkenyl Combinations: An Experimental and Theoretical Study, Macromolecules 53 (2020) 8847–8857, https://doi.org/10.1021/acs.macromol.0c01671.

[23] O. Santoro, L. Piola, K. Mc Cabe, O. Lhost, K. Den Dauw, A. Vantomme, A. Welle, L. Maron, J.-F. Carpentier, E. Kirillov, Al-alkenyl-induced formation of long-chain branched polyethylene via coordinative tandem insertion and chain-transfer polymerization using $(nBuCp)_2ZrCl_2$/MAO systems: An experimental and theoretical study, Eur. Polym. J. 54 (2021) 54, 110567–110578. https://doi.org/10.1016/j.eurpolymj.2021.110567.

[24] O. Santoro, L. Piola, K. Mc Cabe, O. Lhost, K. Den Dauw, A. Fernandez, A. Welle, L. Maron, J.-F. Carpentier, E. Kirillov. Group 12 and 13 metal-alkenyl promoted generation of long-chain branching in metallocene-based polyethylene, Eur. Polym. J. 54 (2022) 173, 111257–111266. https://doi.org/10.1016/j.eurpolymj.2022.111257.

[25] E. Kokko, A. Malmberg, P. Lehmus, B. Löfgren, J. V. Seppälä, Influence of the catalyst and polymerization conditions on the long−chain branching of metallocene–catalyzed polyethenes *J. Polym. Chem. Sci. A Polym. Chem.* **2000**, *38*, 376–388.

[26] In the copolymerization of ethylene with α,ω-dienes, the formation of cycles within the polymer chain can occur as a result of consecutive insertions of the two vinyl moieties of the diene. This is generally observed for 1,5-hexadiene and, to a much lower extent, with 1,7-octadiene [see ref. 10], while it can be virtually ruled-out for higher α,ω-dienes that would generate less stable larger cycles.

[27] The addition of a comonomer often results in a catalyst productivity boost ("*comonomer effect*"), see for example: Q. Wu, A. García-Peñas, R. Barranco-García, M.L. Cerrada, R. Benavente, E. Perez, J. M.A. Gómez-Elvira, New Insight into the Comonomer Effect through

NMR Analysis in Metallocene Catalysed Propene–co–1-Nonene Copolymers, Polymers 11 (2019) 1266–1287. https://doi.org/10.3390/polym11081266.

[28] Gelation of the reaction medium and related mass-transfer issues occurred for $[Diene]_0 \geq 1.5$ mM.

[29] The involvement of the second vinyl group in the formation of cycles was excluded due to the size of the diene employed (see ref. 26).

[30] S. Wang, C. Wu, M.Q. Ren, R.M.V. Horn, M.J. Graham, C.C. Han, E. Chen, S.Z.D. Chen Liquid-liquid phase separation in a polyethylene blend monitored by crystallization kinetics and crystal-decorated phase morphologies, Polymer, 50 (2009), pp. 1025-1033. https://doi.org/10.1016/j.polymer.2008.12.028.

[31] F.L. Stadler, Detecting very low levels of long-chain branching in metallocene-catalyzed polyethylenes, Rheol. Acta 51 (2012) 821−840. https://doi.org/10.1007/s00397-012-0642-x.

[32] A. Takeh, J. Worch, S. Shanbhag, Analytical rheology of metallocene-catalyzed polyethylenes, Macromolecules 44 (2011) 3656−3665. https://doi.org/10.1021/ma2004772.

[33] F.J. Stadler, V. Karimkhani, Correlations between the Characteristic Rheological Quantities and Molecular Structure of Long-Chain Branched Metallocene Catalyzed Polyethylenes, Macromolecules 44 (2011) 5401−5413. https://doi.org/10.1021/ma200550c

[34] S. Trinkle, C. Friedrich, Van Gurp-Palmen-plot: a way to characterize polydispersity of linear polymers, Rheol. Acta 40 (2001) 322–328. https://doi.org/10.1007/s003970000137.

[35] S. Trinkle, P. Walter, C. Friedrich, Van Gurp-Palmen Plot II – classification of long chain branched polymers by their topology, Rheol. Acta 41 (2002) 103–113. https://doi.org/10.1007/s003970200010.

[36] F.J. Stadler, H. Munstedt, Correlation between the shape of viscosity functions and the molecular structure of long-chain branched polyethylenes, Macromol. Mater. Eng. 294 (2009) 25–34, https://doi.org/10.1002/mame.200800251.

[37] F.J. Stadler, S. Chen, S. Chen, On “modulus shift” and thermorheological complexity in polyolefins, Rheol. Acta 54 (2015) 695–704, https://doi.org/10.1007/s00397-015-0864-9.

[38] Z.-C. Yan, F.J. Stadler, Classification of thermorheolegical complexity for linear and branched polyolefins, Rheol. Acta 57 (2018) 377–388. https://doi.org/10.1007/s00397-018-1088-6.

[39] The van Gurp-Palmen plot for **PE4** was not shown due to its unusual shape. Moreover, an unusual trend is also observed on the dlog|η*|/dlog ω vs δ plot for this sample (see the supporting information, Figure S4). Such deviation may stem from some machine errors at low torque, albeit the raw data were manually checked, and no anomalies were detected. Another possible explanation could be that the true Newtonian viscosity value, which we could obtain from the proposed approach, is apparently underestimated; see: F.J. Stadler, H. Munstedt, Numerical description of shear viscosity functions of long-chain branched metallocene-catalyzed polyethylenes, J. Non-Newtonian Fluid Mech. 151 (2008) 129−135. https://doi.org/10.1016/j.jnnfm.2008.01.010.

[40] It has to be noted that the higher viscosity values observed for **PE8** vs **PE7**, along with LCB/crosslinking, could also be due to M_w variation effects.

[41] C. Lehtinen, B.A. Löfgren, A comparison of (n-butCp)$_2$ZrCl$_2$ and other simple metallocenes with bridged Et(Ind)$_2$ZrCl$_2$ and Me$_2$Si(Ind)$_2$ZrCl$_2$ catalysts in ethene/propene copolymerization, Eur. Polym. J. 33 (1997) 115–120, https://doi.org/10.1016/S0014-3057(96)00103-6.

[42] V. Cirriez, A. Welle, A. Vantomme, Dual Catalyst Composition. WO Patent 2019/025528, 2018 (to Total Research and Technology Feluy).

[43] K. A. Giffin, V. Cirriez, O. Santoro, A. Welle, E. Kirillov, J.-F. Carpentier, Meso- and rac-[bis(3-phenyl-6-tert-butylinden-1-yl)dimethylsilyl]zirconium dichloride: Precatalysts for the production of differentiated polyethylene products with enhanced properties, Polymers 14 (2022) 2217. https://doi.org/10.3390/polym14112217

[44] For the industrially relevant and potentially scalable tests, the commercially available 1,7-octadiene was preferred to *in-house* synthesized 1,10-undecadiene employed in the homogenous polymerizations.

[45] 1-Hexene is added to the reaction mixture in order to increase the catalyst activity (see reference 27), while H_2 is used to both control the polymer M_w and for catalyst reactivation.

[46] Fouling and mass-transfer issues occurred for $[1,7\text{-octadiene}]_0 > 500$ ppm, hence such runs were not considered.

[47] The Melt Flow Index (MI2) is defined as the number of grams of polymer extruded in ten minutes as measured by ASTM Method D 1238.

[48] G.B. Galland, M. Seferin, R.S. Mauler, J.H.Z. Dos Santos, Linear low-density polyethylene synthesis promoted by homogeneous and supported catalysts, Polym. Int. 48 (1999) 660–664, https://doi.org/10.1002/(SICI)1097-0126(199908)48:8%3C660::AID-PI212%3E3.0.CO;2-L.