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Solution and bulk rheological behavior of poly(ethylenes) based on VERSIPOL™ catalysts

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Abstract

Palladium catalysts $[(ArN{=}C(Me){-}C(Me){=}NAr)Pd(CH_2)_3(COOMe)]^+BAr'^-_4$ (VERSIPOL™) or $[(ArN{=}C(Me){-}C(Me){=}NAr)Pd(CH_2)_3(COOMe)]^+BF^-_4$ (Ar = 2,6-*i*-Pr_2–C_6H_3, 2,6-Me_2–C_6H_3 or C_6H_5 and Ar′ = 3,5-$(CF_3)_2$–C_6H_3) were synthesized and tested, in dichloromethane, for the polymerization of ethylene. The influence of the substituent present on the diimine ligand on the molar mass of the resulting polymers was examined first. Poly(ethylene)s obtained in the presence of catalysts containing the bulky 2,6-*i*-Pr_2 group, prepared at different ethylene pressures, exhibited almost identical weight average molar mass values, but were characterized by great differences in hydrodynamic volume, radius of gyration and intrinsic viscosity values. These differences were attributed to the evolution of the topology going from hyperbranched to almost linear. Similar observations were made earlier. The major part of the work dealt with new results on the behavior of these PE samples examined in terms of particle scattering function $q^{5/3}\,I(q)$ (Kratky–Porod) plot based on small angle neutron scattering experiments and on the semi-dilute solution behavior. Some results on the bulk rheological properties of these polymers were presented in the last section and corroborated the results obtained in dilute or semi-dilute solution. The data were compared also to PE obtained with other catalysts.

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Keywords: Poly(ethylene); Branched polymers; Palladium

1. Introduction

Low-density polyethylene (LDPE), constituted of identical ethylene monomeric units exhibits a very complex molecular structure. LDPE is characterized by a rather broad molar mass distribution. In most cases, short and long chain branching coexist. Branching is well known to decrease the density and the melting temperature, to impede the crystallization and to modify the solid-state properties as compared to the linear ones. Short branches rather affect the crystallization [1], whereas long chains influence more the rheological properties [2,3]. Control of branching in polyolefins has been a long-standing problem. In free radical polymerization of ethylene (at high pressure and temperature), branches are likely to be formed due to the occurrence of intra and intermolecular chain transfer reactions. In coordination polymerization of olefins branching results basically from copolymerization of ethylene with higher α-olefins (1-hexene,…). Brookhart et al. developed a new generation of palladium (II) complexes containing symmetrical 1,4-diazabutadiene ligands with bulky substituents very efficient for the polymerization of ethylene [4–6]. The unique feature of these catalysts is to provide access in the absence of any comonomer, to dendritic to hyperbranched to almost linear PEs just by changing the ethylene pressure [7–9]. PEs prepared at different ethylene pressures are characterized by great differences in hydrodynamic volume, radii of gyration intrinsic viscosity values and in polymer flow behavior [10,11]. The mechanism to

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explain these topology differences is based on palladium migration (chain walking mechanism). The extent of palladium migration determines the number and length of the branches and the extent of 'macromonomer' formation.

The purpose of the present work is to further examine the structural parameters i.e. the topologies of such polyethylenes in relation with the ethylene pressure.

The effect of varying ligand substitution and counter-ion on the molecular characteristics of PE will be discussed first. After a few remarks on the dilute solution behavior of PEs obtained in the presence of catalysts containing the bulky 2,6-*i*-Pr_2 group, prepared at different ethylene pressures, new results on their structural characteristics, based on small angle neutron scattering experiments, and on the semi-dilute solution behavior will be presented. The final section is devoted to the bulk rheological behavior. It is well known that branching significantly affects the rheological properties of molten polymers. The first part of that section deals with the actual state of art on the influence and the quantification of long chain branching in polyolefins. Then some results on the bulk rheological properties of PEs, obtained with the VERSIPOL™ catalyst, will be presented and compared to data obtained in dilute or semi-dilute solution.

2. Experimental section

2.1. Materials

CH_2Cl_2 was first dried over $MgCl_2$ and then distilled under dry Argon over P_2O_5. Ethylene was used as received. Toluene and THF were distilled over sodium/benzophenone.

2.2. Synthesis of the palladium catalyst

The diimine palladium catalysts $[(ArN{=}C(Me){-}C(Me){=}NAr)Pd(CH_2)_3(COOMe)]^+BAr'^-_4$ (VERSIPOL™); Ar = 2,6-Me_2–C_6H_3 (2) or 2,6-*i*Pr_2–C_6H_3 (3) and Ar′ = 3,5-$(CF_3)_2$–C_6H_3 have been synthesized according to procedures described in the literature [4,5,12–15]. For catalysts 1 and 4, the procedure is the following.

2.3. (COD)$PdCl_2$ (η^2,η^2-cycloocta-1,5-diene palladium(II) dichloride)

One gram (6.7 mmol) of $PdCl_2$ is dissolved in 5 mL of concentrated hydrochloric acid at elevated temperature. After cooling, the solution is diluted with 70 mL of ethanol and filtered. Under stirring, 1.5 mL of cyclooctadiene diluted with 5 mL of ethanol are added. A yellow precipitate is immediately formed. The suspension is filtered. The precipitate is washed with 5×10 mL of diethylether and dried under vacuum 24 h (Yield: 97%). ^{1}H NMR ($CDCl_3$) 6.32 (m, 4H, =CH–), 2.67 (m, 8H, –CH_2–). Anal. Calcd for $C_8H_{12}PdCl_2$: C, 33.65; H, 4.21%. Found: C, 33.69; H, 4.31%.

2.4. (COD)PdClMe (η^2,η^2-cycloocta-1,5-diene palladium(II)methyl choride)

Under inert atmosphere, 1 g (3.54 mmol) of (COD)$PdCl_2$ is dissolved in 35 mL of dichloromethane. Under stirring, 0.59 mL (4.26 mmol) of tetramethyltin are added and the reaction is let running up to discoloration of the solution (around 48 h). The reaction medium is filtered through Celite. The solvent is evaporated and the remaining white crystals are washed with diethylether (2×20 mL). (Yield: 85%) ^{1}H NMR ($CDCl_3$) 5.88 (m, 2H, =CH– *trans*), 5.13 (m, 2H, =CH– *cis*), 2.51 (m, 8H, –CH_2–), 1.15 (s, 3H, Pd*Me*Cl).

2.5. NaB[3,5-$(CF_3)_2C_6H_3]_4$

All manipulations are made under inert atmosphere. 5 g (0.017 mol) of 3,5-bis(trifluoromethyl)bromobenzene are dissolved in 50 mL of diethylether. This solution is added during 2 h, to 0.51 g (0.021 mol) of magnesium turnings in 15 mL of diethylether. The solution is refluxed during 30 min. A grayish solution is obtained. 0.34 g (0.003 mol) of $NaBF_4$ are then added and the reaction is run during 48 h, a brownish suspension is obtained. 100 mL of an aqueous solution of Na_2CO_3 (7.5% w/v) are added and the medium is stirred 20 min before filtration. The product is extracted from the aqueous phase with 4×20 mL of diethylether. The organic phase is dried over 10 g of sodium sulphate and after filtration the solvent is removed. Beige solid is recovered, washed with 5 mL of pentane, 5 mL of toluene and 3×10 mL of dichloromethane, and dried overnight under vacuum. (Yield: 60%) ^{1}H NMR ($CDCl_3$) 7.54 (s, 8H, H_o), 7.38 (s, 4H, H_p).

2.6. Diimine ligand Ph–N=(Me)C–C(Me)=N–Ph

In a round-bottom flask, 30 mmol of aniline, 15 mmol of butane-2,3-dione and five drops of formic acid are added to 50 mL of methanol. Rapidly, a yellow precipitate is formed. After 24 h, the medium is filtered and the yellow solid washed with 2×25 mL of cold methanol. After drying under vacuum, a yellow solid is recovered (Yield: 73%). ^{1}H NMR ($CDCl_3$): 7.34 (t, 4H, o-Ar), 7.08 (t, 4H, m-Ar), 6.75 (d, 2H, p-Ar), 2.12 (s, 6H, ArN=C*Me*–C*Me*=NAr). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85%. Found: C, 81.48; H, 6.66; N, 11.85%.

2.7. Complex Ph–N=(Me)C–C(Me)=N–PhPdClMe

Under inert atmosphere, 2 mmol of (COD)PdClMe and 2 mmol of Ph–N=(Me)C–C(Me)=N–Ph are dissolved in diethylether. The reaction is run during 24 h at 25 °C. The air-stable yellow-orange precipitate that is formed is recovered by filtration. Orange crystals are isolated by recrystallisation from CH_2Cl_2/hexane (Yield: 95%). ^{1}H NMR ($CDCl_3$): 7.50–6.70 (m, 10H, *Ar*), 1.44 (s, 6H, N=C*Me*–C*Me*=N), 0.35 (s, 3H, Pd–*Me*). Anal. Calcd for $C_{17}H_{19}N_2PdCl$: C, 51.93; H, 4.87; N, 7.12%. Found: C, 51.82; H, 4.80; N, 6.94%.

2.8. Complex (1)

Under inert atmosphere, 0.5 mmol of Ph–N=(Me)C–C(Me)=N–PhPdClMe and 0.5 mmol of NaB[3,5-$(CF_3)_2C_6H_3]_4$ are added to 50 mL of diethylether in a round-bottom flask. 0.55 mmol of CH_2=CHC(O)OMe (methyl acrylate) are added and the reaction is run during 48 h at 25 °C. After filtration, the solvent is evaporated and the solid is washed with hexane (2×20 mL) and recrystallized from dichloromethane/hexane (50/50). Orange crystals are obtained (Yield: 68%). ^{1}H NMR ($CDCl_3$): 7.50–7.00 (m, 10H, *Ar*), 3.02 (s, 3H, O*Me*), 2.31 (s, 3H, (N=CMe–C′*Me*=N)), 2.30 (t, 2H, CH_2C(O)), 2.25 (s, 3H, N=C*Me*–C′Me=N), 0.91 (t, 2H, Pd–CH_2), 0.60 (pentet, 2H, PdCH$_2$*CH$_2$*CH$_2$C(O)). Anal. Calcd for $C_{53}H_{38}N_2O_2BF_{24}Pd$: C, 48.67; H, 2.93; N, 2.14%. Found: C, 46.94; H, 2.58; N, 2.11%.

2.9. Complex (4)

Under inert atmosphere, 0.5 mmol of iPr_2Ph–N=(Me)C–C(Me)=N–(iPr_2Ph)PdClMe and 0.5 mmol of $NaBF_4$ are added to 50 mL of diethylther in a round-bottom flask. 0.55 mmol of CH_2=CHC(O)OMe (methyl acrylate) are added and the reaction is run during 48 h at 25 °C. After filtration, the solvent is evaporated and the solid is washed with hexane (2×20 mL) and recrystallized from dichloromethane/hexane (50/50). Orange crystals are obtained (Yield: 77%). ^{1}H NMR ($CDCl_3$): 7.20–7.40 (m, 6H, *Ar*), 3.12 (septuplet, 4H, C′*H*Me$_2$, C″*H*Me$_2$), 3.03 (s, 3H, O*Me*), 2.38 (s, 6H, N=C*Me*–C′*Me*=N), 2.37 (t, 2H, CH_2C(O)), 1.38 (d, 6H, CH*MeMe*′, C′H*MeMe*′), 1.35 (d, 6H, CH*MeMe*′, C′H*MeMe*′), 1.31 (d, 6H, CH*MeMe*′, C′H*MeMe*′), 1.28 (d, 6H, CH*MeMe*′, C′H*MeMe*′), 1.28 (t, 2H, Pd–CH_2), 0.69 (quintuplet, 2H, PdCH$_2$*CH$_2$*CH$_2$C(O)). Anal. Calcd for $C_{32}H_{49}N_2O_2BF_4Pd$: C, 55.99; H, 7.14; N, 4.08%. Found: C, 55.93; H, 7.12; N, 3.89%.

2.10. General procedures for polymerization reactions

The polymerization runs were carried out at 25 or 35 °C in a 250 mL or 1 L Buchi reactor equipped with magnetic or mechanical stirring, purged via argon and vacuum exchange. After addition of the solvent (dichloromethane or toluene) and the catalyst, the reactor was pressurized with ethylene. The resulting polymers were precipitated two times from their solution into methanol and dried in vacuum to constant weight.

2.11. Characterization of the polymers

The structural parameters of the polymers were investigated by ^{1}H NMR spectroscopy (Bruker WM-200 spectrometer at 200 MHz at 297 K).

The molar masses of the polymers were determined by size exclusion chromatography (SEC), light scattering (LS) in THF ($dn/dc_{\text{poly(ethylene)}} = 0.075$ cm^3/g at 632.8 nm). The viscosity measurements were made with a Sematech equipment using a 0.5 mm capillary tube.

QELS measurements were performed at 25 °C in the homodyne mode using a photon correlation spectrometer and an Ar laser operating at 488 nm. Optical clarification of the solutions for the scattering measurements was achieved by filtration using 0.45 μm DynaGard filters or by centrifugation. The correlation functions of the scattered intensities $g^2(q, \tau)$ were measured in the angular range $\theta =$ 20–150° by using the ALV 5000 autocorrelator. They were analyzed with the CONTIN software, that gives the distribution function $G(D)$ of the translational diffusion coefficient D of the scattering particles. The hydrodynamic radius (R_h) of the particles in solution is calculated through the Stokes–Einstein relationship [16].

Small angle neutron scattering (SANS) experiments were done with the PAXY diffractometer (Laboratoire Léon Brillouin (LLB), CEA-CNRS—Saclay). The temperatures were between 283.15 and 333.15 K. PE samples were dissolved in toluene-d_8. The concentrations were comprised between 0.25 and 4 wt%. Standard quartz cells with 0.2 cm path length were used. The samples were measured with the PAXY instrument in two different configurations. In the first configuration, a wavelength of 1.2 nm was selected and the effective distance between the sample and the planar square multi-detector 5 m. This allows a momentum transfer range of $q = 5.2\times10^{-3}$ to 3.4×10^{-2} Å^{-1}. The counting time per sample was approximately 2 h. In the other configuration, the S–D distance was 2 m with a detector offset and the wavelength of 0.8 nm leading to a momentum transfer of $q = 2.0\times10^{-2}$ to 0.23 Å^{-1}. The intensities were corrected for a small solute incoherent scattering contribution.

The rheological behavior was studied using a Rheometrics Scientific ARES rheometer with parallel plate geometry. The angular frequency ω varied from 10^{-3} to 10^2 rad/s, and the temperature ranged from 298 to 373 K.

3. Results and discussion

3.1. Influence of the ligand and the counter-ion of the palladium complex on the molecular characteristics of the PEs

Various palladium catalysts were synthesized following the reaction pathway indicated on Fig. 1. As already published [4,5] the ligand is synthesized by reacting the 2,3-butanedione with the corresponding aniline. It is then added

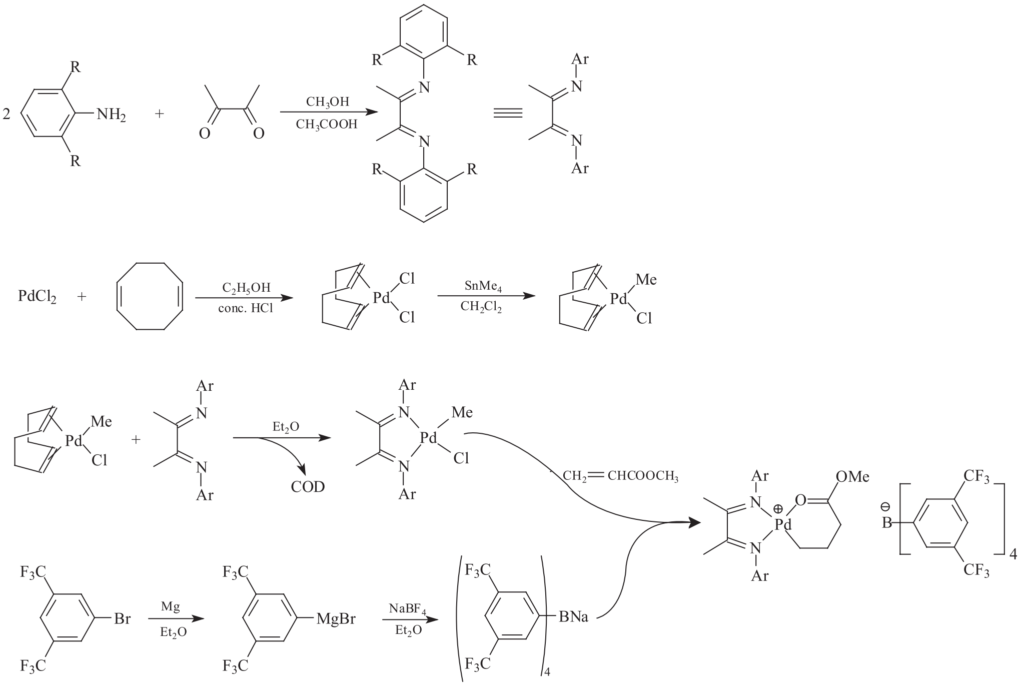


Fig. 1. Synthesis of palladium complexes.

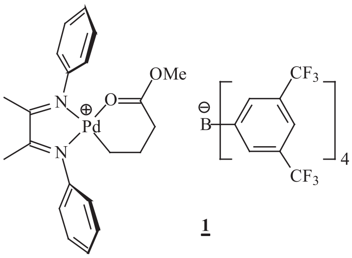
to CODPdMeCl to yield the neutral complex DiiminePd-MeCl. This latter is reacted with NaB[3,5–$(CF_3)_2C_6H_3]_4$ in the presence of methyl acrylate in order to lead to the desired cationic complex (Fig. 2) with pretty good yields (>75%). For complex 3, several isomers were observed (Fig. 3, 3: 87%, 3′: 11%, 3″: 2%).

The results concerning the polymerization of ethylene with these diimine catalysts are presented in Table 1. They call for following comments:

- The polymerization yield and the molar masses are the highest with the catalyst containing the 2,6-isopropyl substituent, i.e. the more bulky substituent.
- When the 2,6-isopropyl group is replaced by a methyl group, the molar mass of the PEs decreased.
- In the absence of any substituent on the phenyl group (complex 1), only oligomers are obtained.

This evolution is explained by the decrease of the steric hindrance around the axial sites of the palladium complex. Other authors made the same observations [17,18].

A already observed [9] with BF_4^- as the counter-ion



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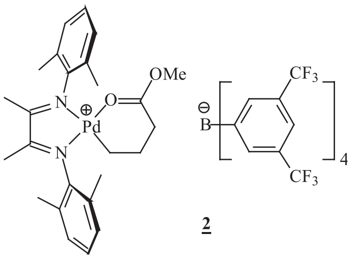

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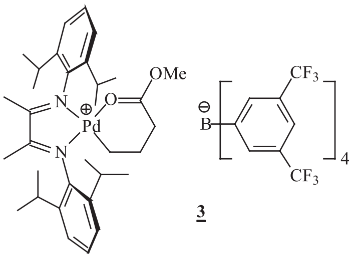

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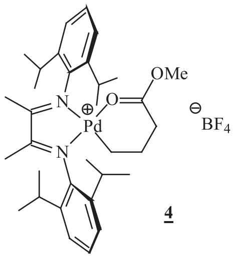

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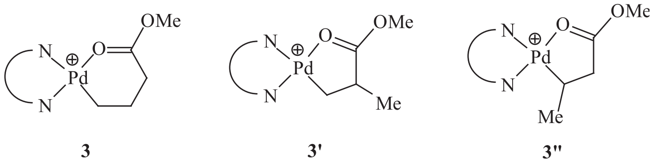
Fig. 2. Structure of the different 1,2-diimine cationic palladium complexes employed for the synthesis of PE.



3 3' 3''

Fig. 3. Isomers obtained for complex (c).

(catalyst 4) instead of BAr'^{-}_4, a decrease in activity and molar mass values is observed, which is probably due the stronger coordination of BF_4^-, an effect which has been extensively studied [19,20].

3.2. Molecular characteristics of PEs synthesized with complex 3 (VERSIPOL™)

On a second stage, polyethylenes were prepared in dichloromethane with catalyst 3 at different ethylene pressure and characterized by SEC with refractive index detection (using linear PS as standards) and online light scattering detection to access to real molar masses. Table 2 summarizes the different results. Light scattering weight average molar masses are almost identical whatever the polymerization pressure, whereas strong differences in molar mass values appeared when calibration with linear PS is used. PEs obtained at an ethylene pressure of 1 bar are characterized by lower hydrodynamic volumes, and are much more compact than samples obtained at 6 bar. These differences were not revealed by ^{1}H and ^{13}C NMR spectroscopy. Several groups have already made these observations [8,9,21]. These results have been discussed in terms of slower ethylene coordination to palladium at low ethylene pressure, with respect to palladium chain walking processes. However, it is also clear now, that faster insertion of polymeric α-olefin products into the palladium–carbon bond of the growing polymer chains, leading to more long chain branches, also contributes to these topological differences. Such a secondary process is expected to be favored at lower ethylene pressure, where competition with ethylene insertion is diminished. This is confirmed by the incorporation of long polymeric α-olefin (macromonomers) into PE chains, when copolymerized with ethylene [9,22] or when using an analogous Pd-α-diimine catalyst to oligomerize ethylene in the presence of 1-pentene [23].

3.3. Dilute solution behavior of PEs synthesized with complex 3 (VERSIPOL™)

In order to learn more about the evolution of the branching type or branching density within these PE samples synthesized under identical experimental conditions, except for polymerization pressure, their solution properties were also studied in dilute regime, by solution viscosimetry measurements, static light scattering and quasi-elastic light scattering (QELS). The results are summarized in Table 3.

- Strong differences in intrinsic viscosity values were noted between samples prepared at 6, 3 or 1 bar; the highest values corresponding to samples prepared at 6 bar. These measurements confirmed the lower hydrodynamic volume of the 1 bar samples, and their higher compactness, already observed by SEC [9]. Guan et al. determined the evolution of $[\eta]$ with the multiple detector SEC, and came to the same conclusions [21].
- The gyration radii (R_g) measured by LS and hydrodynamic radii (R_h) values of the PE samples are displayed on the same Table 3. PEs obtained at 6 bar are characterized systematically by higher R_g values. Besides, the R_g values are always

Table 1
Influence of the structure of the ligand frame on the polymerization of ethylene performed in dichloromethane

Run	Catalyst	Catalyst (μmol)	Yield (g)	Activity[a]	TOF[b]	M_w[c] (g/mol)	M_w[d] (g/mol)	M_w/M_n[e]	Number of CH_3/1000C[f]
1	1	10	5.2	4860	1040	Oligomers (C_4–C_8)			
2	2	50	14.2	2630	560	17,400	19,500	1.6	119
3	3	50	27.2	5000	1080	403,000	419,000	1.9	116
4	3	100	41.1	3800	815	351,000	425,000[g]	2.4	123
5	4	100	18.5	1710	370	187,000	234,000[g]	2.1	100

$T=35$ °C, 150 mL CH_2Cl_2, 18 h, stirring velocity = 200 rpm, $P_{Eth}=6$ bar.

[a] Activity: g_{PE}/h mol_{Pd} bar.

[b] Turn over frequency (($molC_2H_4$)(mol Pd)$^{-1}$ h^{-1}).

[c] Weight average molar mass determined by SEC-RI (linear PS calibration).

[d] Weight average molar mass determined by SEC-LS.

[e] Molar mass distribution estimated by SEC.

[f] Determined by ^{1}H NMR.

[g] Bimodal distribution.

Table 2
Experimental conditions and characteristics of PE obtained with catalyst 3: Polymerization solvent dichloromethane

Run	P_{Eth} (bar)	Loading (μmol)	Yield (g)	Activity[a]	TOF[b]	M_w[c] (g/mol)	M_w[d] (g/mol)	M_w/M_n[e]	M_{wLS}/M_{wRI}	Number of CH_3/1000C[f]
3	6	50	27.2	5000	1080	403,000	419,000	1.9	1.04	116
6	6	10	8.1	7500	1610	349,000	400,000	1.8	1.15	105
7	6	50	29.0	5370	1150	390,000	388,500	1.8	1.00	118
8	3	50	23.0	8520	910	312,000	396,000	1.9	1.27	118
9	1	50	18.7	20,800	740	218,100	393,600	1.5	1.80	119
10	1	10	2.7	15,000	540	209,000	393,000	1.8	1.88	115
11	1	100	44.1	24,500	875	227,000	429,000	2.0	1.89	107

$T=35$ °C, 150 mL CH_2Cl_2, 18 h.

[a] Activity: g_{PE}/h mol_{Pd} bar.

[b] Turn over frequency (($molC_2H_4$)(mol Pd)$^{-1}$ h^{-1}).

[c] Weight average molar mass determined by SEC-RI (linear PS calibration).

[d] Weight average molar mass determined by SEC-LS.

[e] Molar mass distribution estimated by SEC.

[f] Determined by ^{1}H NMR.

higher than the R_h ones. To quantify this evolution, ρ (defined by the expression (1)) has been calculated. This parameter is well known to be dependent on the structural characteristics of the polymers:

$$\rho = \frac{R_g}{R_h} \qquad (1)$$

This parameter has been calculated for PEs synthesized at different ethylene pressures. The resulting ρ values are comprised between 1.11 and 1.99, the highest value corresponding to the sample synthesized at 6 bar. These values were compared to those obtained for macromolecules going from hard spheres ($\rho=0.8$) to random coil ($\rho=1.7$) configurations [24]. With a ρ value of 1.99, the behavior of the PEs synthesized at 6 bar can be assimilated to that of a almost linear chain and the behavior of the PEs synthesized at 1 bar (ρ around 1) to that of a hard sphere. This is again a strong argument in favor of a higher compactness of samples obtained at 1 bar [25]. Similar observations were made by Guan et al. [8]. The second virial coefficient values, A_2 are lower for PEs synthesized at 1 bar, which is in agreement with observations made on other hyperbranched structures.

We have just demonstrated that, in dichloromethane, poly(ethylene) topologies, going from hyperbranched to almost linear PE, can be tailored via ethylene pressure, i.e. by monomer insertion versus catalyst isomerization, taking advantage of the 'chain-walking' VERSIPOL™ catalyst. Until now, all the ethylene polymerization attempts in the presence of this catalyst were conducted in halogenated solvents such as dichloromethane [10] or chlorobenzene [21]. In Table 4, we presented the experimental conditions and some characteristic data of PEs synthesized in toluene with the same catalyst under identical other experimental conditions. From the results depicted in Table 4, it can be seen that the ratio of the weight average molar mass based

Table 3
Influence of the polymerization pressure on the molecular characteristics of PEs (preparation solvent dichloromethane)

Run	P_{Eth} (bar)	M_w[a]	M_w[b]	A_2 ($\times 10^7$)[b]	$[\eta]_{Tol}$ (mL g^{-1})	$[\eta]_{THF}$ (mL g^{-1})	R_g[b] (Å)	R_h[c] (Å)	$\rho=R_g/R_h$
3	6	419,000	475,000[d]	3.00	99.5	102.0	286	172	1.66
6	6	400,000	–	3.86	97.8	88.8	312	157	1.99
7	6	388,500	445,000	2.83	101.5	–	275	140	1.96
7Af4	6	387,000	438,000	3.34	95.9	–	248	158	1.57
8	3	396,000	431,000	2.88	76.1	–	254	166	1.49
9	1	393,600	422,000	1.73	37.2	37.7	152	122	1.24
10	1	393,000	336,000	1.31	36.4	34.9	139	125	1.11
11	1	429,000	447,000	1.03	34.4	–	162	138	1.17
11Af5	1	424,000	415,000	1.10	33.2	–	161	139	1.16

$T=35$ °C, 150 mL CH_2Cl_2, 18 h, samples 7Af4 and 11Af5 correspond to samples 7 and 11 fractionated in supercritical propane (Ref. [26]), respectively, (f4 means fraction 4) Number of branches per 1000C is equal to 116 for sample 7Af4 and to 111 for sample 11Af5.

[a] Weight average molar mass determined by SEC-LS (g mol^{-1}).

[b] Determined by static LS, A_2 is expressed in mol L/g^2.

[c] Determined by QELS.

[d] Bimodal distribution.

Table 4
Experimental conditions and characteristics of PE obtained with catalyst: Polymerization solvent toluene

Run	P_{Eth} (bar)	Loading (μmol)	Yield (g)	Activity[a]	TOF[b]	M_w[c] (g/mol)	M_w[d] (g/mol)	M_w/M_n[e]	M_{wLS}/M_{wRI}	Number of CH_3/1000C[f]
12[g]	6	17	5.8	11,400	2440	220,000	226,000[h]	2.1[h]	1.03	110
13[g]	3	17	7.3	285,00	3060	224,000	250,000[h]	2.1[h]	1.12	112
14[g]	1	17	6.7	78,700	2810	216,500	298,000	1.6	1.38	114
15[g]	0.2	17	3.5	206,700	1480	233,700	305,000	1.8	1.31	110
16	6	16.6	7.7	4290	920	326,200	343,700	2.0	1.05	105
17	3	16.6	10.1	11,240	1200	266,300	319,600	1.9	1.20	106
18	1	16.6	10.5	34,900	1250	310,600	403,800	1.9	1.30	106

$T = 35$ °C, 18 h, 30 mL toluene.

[a] Activity: g_{PE}/h mol $_{Pd}$ bar.

[b] Turn over frequency ((mol C_2H_4)(mol Pd)$^{-1}$ h^{-1}).

[c] Weight average molar mass determined by SEC-RI (linear PS calibration).

[d] Weight average molar mass determined by SEC-LS.

[e] Molar mass distribution estimated by SEC.

[f] Determined by ^{1}H NMR.

[g] $T = 25$ °C, 5 h, 30 mL toluene.

[h] Bimodal distribution.

on SEC/online light scattering measurements ($M_{w,SEC,LS}$) to the weight average molar mass value based on calibration with linear PSs ($M_{W,RI}$) only slightly increases from 1.03 to 1.31 with decreasing ethylene pressure. The evolution is the same whether the samples were synthesized in 5 h or in 18 h. Similarly only slight differences were observed between intrinsic viscosity values for samples prepared in toluene at different ethylene pressures. This evolution is rather different from that of samples prepared in dichloromethane, where $M_{w,SEC,LSr}/M_{W,RI}$ ratios going from 1.04 to 1.89 were determined, corresponding to big differences in hydrodynamic volumes, and attesting the changes in topology with ethylene pressure. As discussed later in the text, a similar conclusion could be drawn from the studies of the PE bulk rheological behavior. From these results it can be concluded that PE topology is less affected by changes in ethylene pressure when the synthesis is performed in toluene. As proposed by Guan et al. for samples synthesized in chlorobenzene, these changes in branching topology with ethylene pressure originate from the competition between chain-walking and ethylene insertion. At high ethylene pressure, the trapping is fast, and, therefore, the average walking distance is short. Therefore, the polymers formed are relatively linear. At low ethylene pressure, ethylene trapping is slower, as a result the catalyst may walk many carbons before being trapped, branching increases. In the presence a highly polar solvent such as toluene, the kinetics of that exchange may be completely different. Additional side reactions made also occur with the cationic catalyst limiting, or affecting the growth of the chain. As the main aim of the present work was to develop catalysts allowing the control of branching via ethylene pressure, and as toluene seems not to be the appropriate solvent, we decided not to go further in the studies of samples prepared in toluene.

3.4. Determination of the overlap concentration of PEs synthesized with complex 3

It is well established that macromolecules require quite a large volume in space, and often at about already fairly low concentrations around 1%, the radii from different coils start to overlap. At higher concentrations the coils of linear chains have the possibility to interpenetrate, and eventually a transient network of entangled chains is obtained. For branched species, the concentration at which chains start to interpenetrate has been shown to be higher than for the linear equivalent. In addition its value depends on branching density. The overlap concentration c^*, which is an important parameter to be used in theories dealing with semi-dilute solutions, represents the mean concentration of segment in a freely swollen coil of individual macromolecules. To determine this concentration, different suggestions have been made taking either the radius of gyration R_g or the hydrodynamic radius R_h obtained from diffusion measurements.

$$c^*_{R_g} = \frac{M}{N_A \frac{4}{3}\pi R_g^3} \quad c^*_{R_h} = \frac{M}{N_A \frac{4}{3}\pi R_h^3}$$

One can also use the intrinsic viscosity, $c^*_\eta = 1/[\eta]$

We then examined the evolution of the intrinsic viscosity in large domain of concentrations in order to determine the c^*_{visco} values and the evolution of the segment density of the PE with increasing polymerization pressure. Results are presented on Table 5 and Fig. 4. The mean values of c^* are by 2.7, 1.3 and 0.8 wt% for samples prepared, respectively, at 1, 3 and 6 bar. These measurements confirmed the existence of topological differences between samples prepared at different polymerization pressures.

Table 5
c^* determination for PEs obtained at 1, 3 or 6 bar ethylene pressure

Run	P_{Eth} (bar)	M_{w}[a]	$[\eta]_{\mathrm{Tol}}$ (mL g^{-1})	c^*_{η} (%)	c^*_{visco}[b] (%)	$c^*_{R_g}$ (%)	$c^*_{R_h}$ (%)
3	6	419,000	99.5	1.0	0.7	0.7	3.3
6	6	400,000	97.8	1.0	–	0.7	4.1
7	6	388,000	101.5	1.0	0.8	0.8	5.6
8	3	396,000	76.1	1.3	1.6	1.0	3.4
9	1	393,600	37.2	2.7	2.7	4.4	8.6
10	1	393,000	36.4	2.7	–	4.9	8.0
11	1	429,000	34.4	2.9	2.7	4.0	6.5

[a] Weight average molar mass determined by SEC-LS.

[b] c^* determined from Fig. 4.

3.5. Small-angle neutron scattering studies on PEs synthesized with complex 3

Small-angle neutron scattering (SANS) techniques are well known to provide direct access to shape, size and interactions of the scattering particle over a wide range of length scales. Therefore, this method should also be very powerful to get additional informations on the evolution of the structural parameters of the PEs synthesized at different ethylene pressures. Neutron scattering experiments were conducted on two PE samples (raw and fractionated ones) obtained at 6 and 1 bar, respectively. The molecular characteristics of the raw samples are given in Tables 2 and 3. Their fractionation in supercritical propane, and the data on the resulting fractions are given elsewhere [26]. Fig. 5 depicts a representation derived from the so-called Kratky–Porod plot obtained from the neutron scattering data and its evolution with ethylene pressure. The measurements were made at a concentration of 4 wt%. We examined the raw samples in the asymptotic domain ($qR_g > 1$). In this domain structural information can be obtained even for identical molar masses and rather broad molar mass distributions [27]. For all the samples the evolution of $I(q)q^{5/3}$ as a function of q, is characterized by the presence, at intermediate angles, of a maximum which is more pronounced at lower ethylene pressure, i.e. with increasing branching density. At larger angles, the same limit is approached. This behavior at intermediate angles is typical for branched structures [28]. This confirms again the long branched structures and the different topologies revealed by other characterization methods, corresponding to topologies going from hyperbranched to only slightly branched. No differences were observed between the fractions, characterized by sharper molar mass distributions, and the raw product. This confirms our preliminary experiments [29]. These conclusions are in contradiction with data obtained by Guan [30] who performed also neutron scattering experiments on samples prepared at 1 bar (and 34 bar). Neither for the 1 bar; nor for the 34 bar samples they observed a peak in the Kratky–Porod representation. The dilute solution measurements made on these samples yet attested their branched topology, and the evolution of branching with ethylene pressure. The authors attributed these apparently contradictory conclusions to the polydispersity of the samples who may smear the subtle differences in topology between the samples.

This prompted us to perform additional measurements on PE fractions at different polymer concentrations, and temperatures in order to verify that the presence of the maximum is not due to the presence of aggregated species, or to chain overlapping phenomena. These measurements were made over a large domain of concentrations, below c^* for samples prepared at 1 bar and encompassing c^* for the 6 bar samples. Whatever the concentration, the evolution of

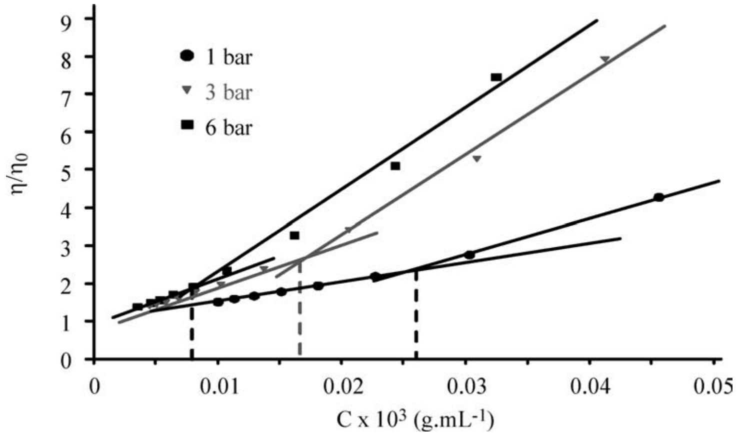


Fig. 4. Determination of c^* for PEs prepared at different ethylene pressures (Source Ref. [26]).

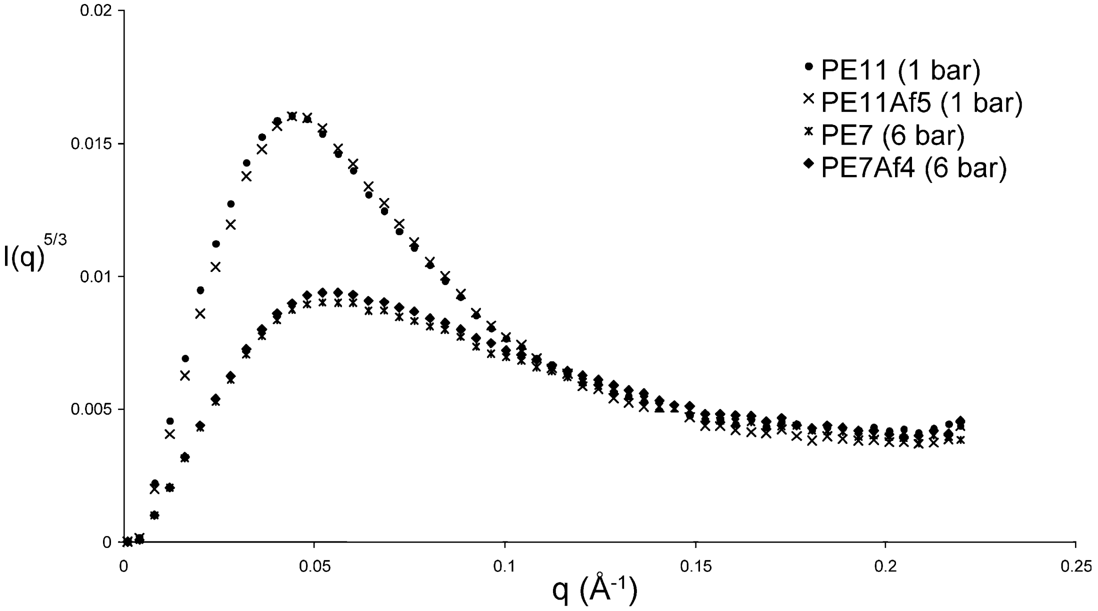


Fig. 5. $I(q)q^{5/3}$ as a function of q (Kratky–Porod representation) for PEs obtained at 1 and 6 bar (measured by SANS in toluene d_8 at 25 °C and 4 wt%) (unfractionated and fractionated samples).

$I(q)q^{5/3}$ as a function of q (Fig. 6(a) and (b)), is again characterized by the presence, at intermediate angles, of a maximum which is more pronounced at higher concentrations. As expected the position of the maximum shifted to high q values with increasing concentration. On the contrary no shift of the position of the peak is observed with temperature (Fig. 7). These results confirm that the peak can be attributed to structural effects and not the presence of aggregates. The careful physico-chemical studies described above attested the hyperbranched nature of samples obtained at a 1 bar pressure. It is rather difficult to interpret quantitatively the position of the maximum of the evolution of $I(q)q^{5/3}$ versus q in hyperbranched polymers. The situation is especially complex for PEs obtained in the presence of Pd diimine catalysts characterized by the presence of short branches, long branches and even branch on branch topologies, difficult to quantity. Burchard [31] proposed in 2004 a model, which, provided the branch length and number are known, evidences in a Kratky representation (Iq^2 versus qR_G), a peak around $2qR_G$. This is rather far from our experimental results. A few years ago Guan [32] proposed to assimilate hyperbranched PEs, obtained in the presence of VERSIPOL™ catalysts, to multibranched polydisperse star-shaped polymers. Neither Buchard'model, nor polydisperse star model fitted with our data. Therefore, we used our q values as an indication for the interparticular distances D_{app} [33,34].

$$D_{app} = 1.22\left(\frac{2\pi}{q_{MAX}}\right)$$

Strictly this relation is only valid for uniform spherical particles on a face-centered cubic lattice [35] that is not our case. The determination of D_{app} should allow us to compare our experimental data. Data in Fig. 5 show that, for almost the same concentration, $D_{app}/2$ goes from 85 to 70 Å, the highest value corresponding to samples prepared at 1 bar. We extrapolated also $D_{app}/2$ obtained from Fig. 6(a) and (b) to zero concentration and obtained $D_{app}/2_{c=0}$ values going from 114 Å at 1 bar to 95 Å at 6 bar. The value of 95 Å determined for the samples prepared at 6 bar is much lower than the value measured by light scattering. It is obvious that the $D_{app}/2_{c=0}$ determined for the sample prepared at 6 bar is

Table 6
Results of the rheological studies

Polym. solvent	Run	P_{Eth} (bar)	M_w[a] (g mol^{-1})	$\tau_{50\,°C}$ ($\times 10^3$) (s)	$\eta_{0 50\,°C}$ (Pa)	J_e ($\times 10^4$) (Pa^{-1})	E_A (kJ/mol)
CH_2Cl_2	11	1	419,000	–	50	–	48.8
	8	3	396,000	625	4800	1.3	58.4
	7	6	388,000	2150	19,700	1.1	58.0
Toluene[b]	14	1	298,000	90	970	0.9	55.6
	13	3	250,000	645	7800	0.8	58.8
	12	6	226,000	1470	17,700	0.8	59.3

T=35 °C, 150 mL CH_2Cl_2, 18 h.

[a] Weight average molar mass determined by SEC-LS.

[b] T=20 °C, 30 mL toluene, 5 h.

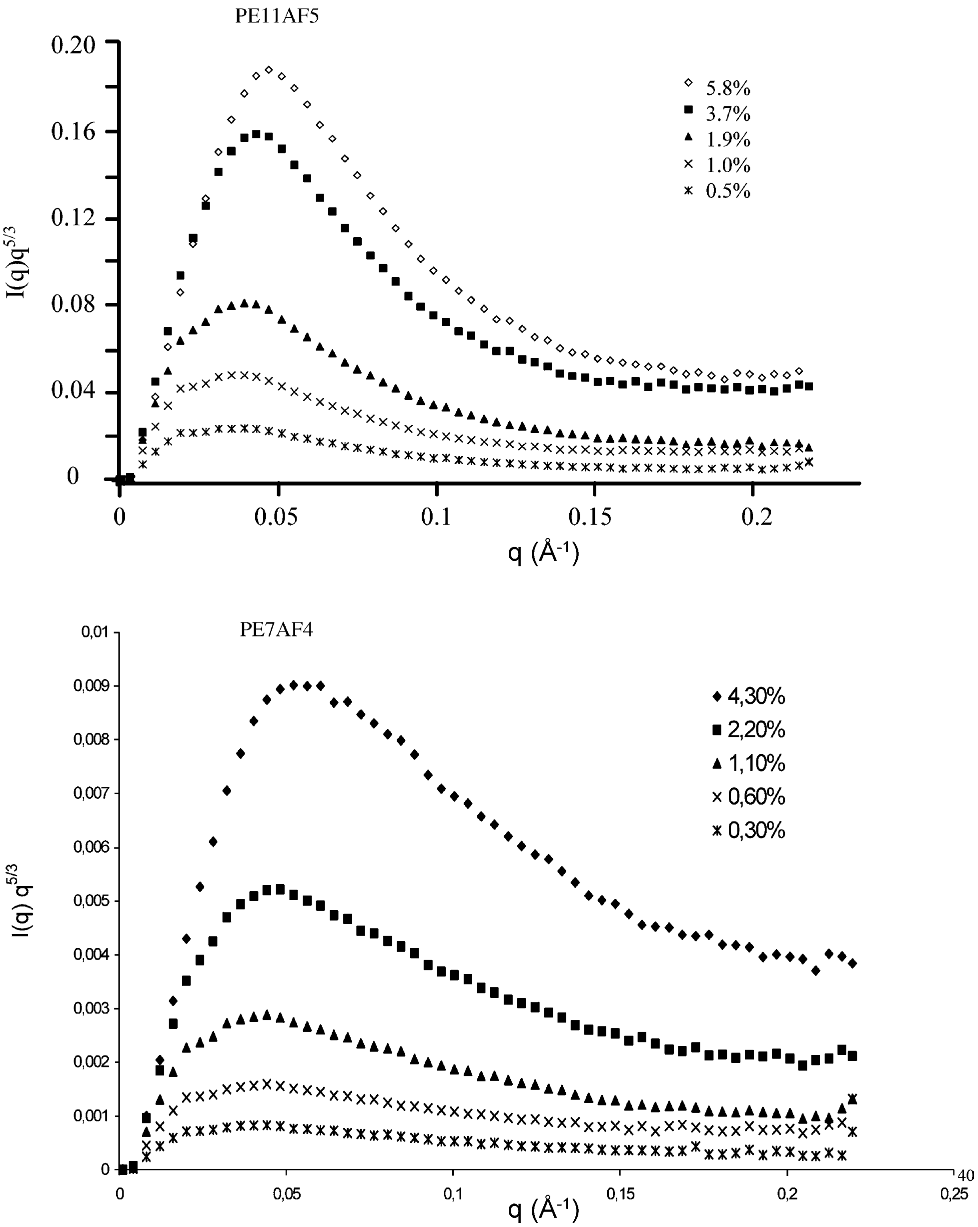


Fig. 6. $I(q)q^{5/3}$ as a function of q (Kratky–Porod representation) for PEs obtained at 1 and 6 bar (determined at 25 °C): Influence of the concentration on the shape and position of the peak.

largely underestimated. This is probably due to the fact that this sample is only slightly branched. It has to be pointed out that such a contradiction between R_g values measured by light scattering and neutron scattering techniques was also observed for some of their hyperbranched samples by Richtering et al. [36].

3.6. Osmotic modulus of PEs synthesized with complex 3

The reduced osmotic modulus, that is a function of $X = A_2M_wc$ parameter and of the architecture of the polymers, was determined in semi-dilute regime. In diluted regime, linear and branched polymer chains have the same osmotic pressure, which is independent on the macromolecular architecture. On the contrary, when the polymers are studied in the semi-diluted regime, differences are observed [37]. Indeed, highly branched molecules, which are more compact, will occupy more easily a reduced volume than less branched ones. The values of the reduced osmotic modulus of PEs obtained at 1 and 6 bar of ethylene pressure are presented in Fig. 8 together with the values of the theoretical models. The results for PEs are located between the values for hard spheres and flexible linear chains. The behavior of PE obtained at 1 bar is closer to the hard sphere model and is in good agreement with the dilute solution results.

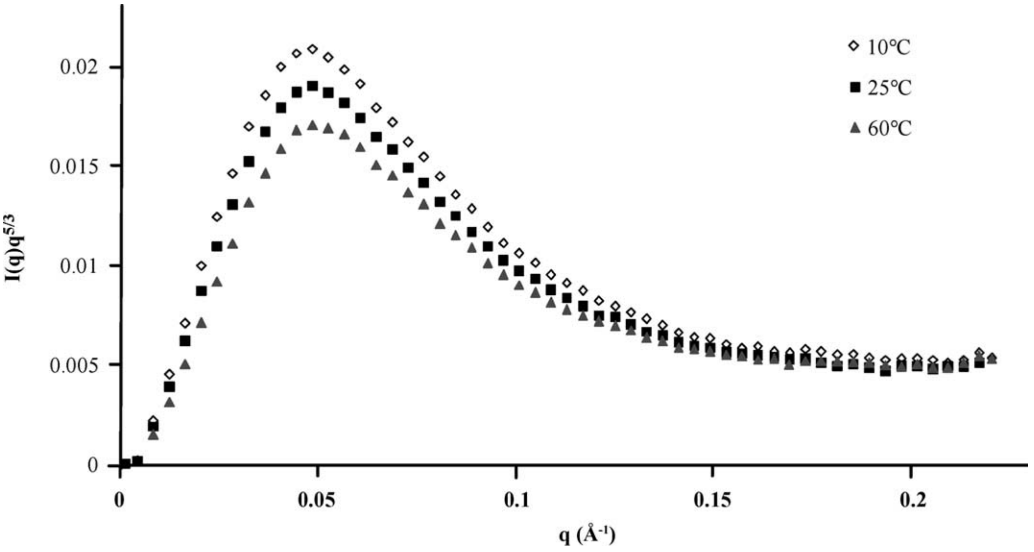


Fig. 7. $I(q)q^{5/3}$ as a function of q (Kratky–Porod representation) for PEs obtained at 1 bar: Influence of the measurement temperature on the shape and position of the peak.

3.7. Bulk rheological behavior of PEs synthesized with complex 3

It is well known that branching significantly affects the rheological properties of molten polymers. Long chain branching for instance increases the zero-shear viscosity, shifts the onset of shear thinning towards much lower shear rates and enhances strain-hardening in elongation. However, it is usually difficult to discriminate between the effects of molar mass distribution and number and length of branches.

Fujimoto et al. [38], Roovers [39] and more recently Daniels et al. [40] have experimentally studied the rheology of well defined comb polymers and shown the existence of long-time relaxation processes that are not present for linear polymers and are related to the backbone reptation. The more recent pompom model offers a new way to understand rheological phenomena of branched polymers [41–45]. Comparison with experimental data were carried out on well controlled H-shaped polymer melts and it was shown that increasing the length of the backbone shifts the second peak to lower frequencies.

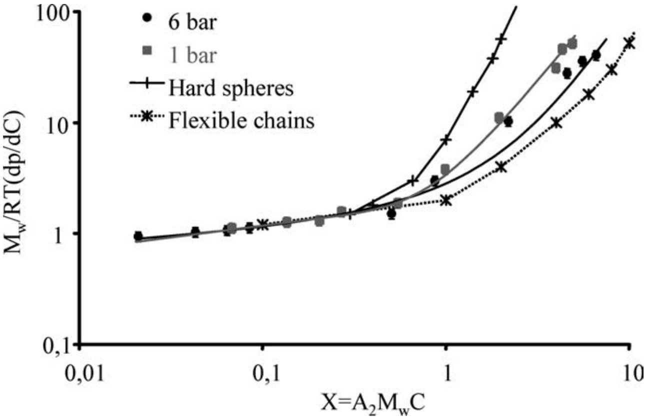


Fig. 8. Reduced osmotic modulus as a function of the parameter $X = A_2M_wc$: Experimental and theoretical curves (Source Ref. [29]).

Vega et al. [46] and Yan et al. [47] have studied the rheological properties of different branched polymers which were previously characterized by SEC and ^{13}C NMR, respectively. The authors have shown significant effects of LCB density on the shear thinning effect. For the same molecular weight, higher LCB density leads to higher viscosity at low shear rates and lower viscosity at high shear rates. However, by studying monodisperse polymers in a wide range of branching extent, Janzen and Colby [48] clearly showed that the relationship between zero-shear viscosity and LCB density is non-monotonic. As a matter of fact, the zero-shear viscosity increases with LCB density until to a critical value then decreases for the highest LCB values, which correspond to lower hydrodynamic volumes of the chains. Vega et al. [46] tested 13 metallocene catalyzed polyethylene samples. From the Cole–Cole diagram, the authors were able to determine the zero shear viscosity and a characteristic relaxation time. By plotting these parameters as a function of the weight average molecular weight, three groups of samples clearly appear: One group corresponds to linear samples, whereas the two others correspond to long chain branched polymers with different amounts of branches. Vega et al. [46] also measured the activation energy for the thermal shift factor versus the degree of hexyl branching per 1000 carbon atoms. The highest values of activation energy were found for the branched polymers. Another way to characterize LCB is non-linear dynamical oscillatory rheology (also called Fourier transform rheology FTR), which consists in analyzing the response in the Fourier space to a large

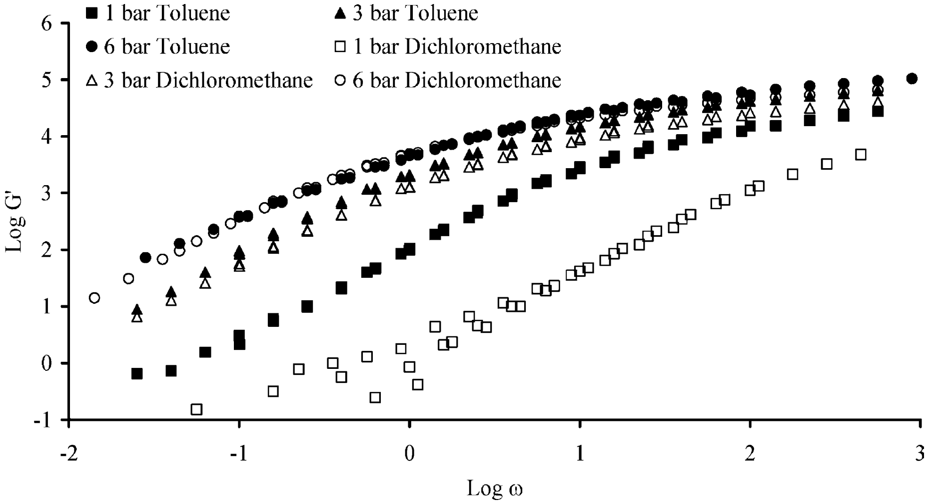


Fig. 9. G' master curves for PEs synthesized at different temperatures in different solvents versus angular frequency at the reference temperature $T_0 = 50$ °C.

amplitude sinusoidal strain. Wilhelm et al. [49–51] have studied the non linear dynamical response for different well defined linear polymers. They have in particular correlated the relative intensity of the third harmonic with the molar mass of the tested polymer. Fleury et al. [52–53] have compared different rheological methods including FTR in order to characterize the LCB.

As discussed above, chain walking mechanism in competition with chain propagation causes the formation of branches during the homopolymerization of ethylene in the presence of VERSIPOL™ catalysts. PEs differing significantly in branching density, and chain topology, going from hyperbranched to almost linear structures were obtained with such catalysts. This was clearly revealed by the dilute and semi-dilute solution behavior. It appeared also that the amorphous PE samples obtained at an ethylene pressure of 1 bar are viscous, oil-like, whereas samples obtained at 6 bar behave rather like rubbers. DSC measurements made on such samples, revealed, as expected, that their melting temperature T_m decreases and the glass transition temperature T_g increases compared to conventional linear or slightly branched PEs. This prompted us to investigate the bulk rheological properties by dynamic mechanical analysis in the linear viscoelastic domain. η_0 (zero-shear viscosity), τ (mean relaxation time) and J_e (elastic compliance) were determined for PE samples prepared in dichloromethane (at 1, 3 or 6 bar ethylene pressure) using the Cole–Cole representation. For purpose of comparison, some preliminary results on samples obtained in toluene were also added. (Table 6 and Fig. 9). They show unambiguously strong differences in viscoelastic behavior between PEs obtained at 1, 3 and 6 bar, respectively, whatever the preparation solvent. The difference is yet less pronounced for samples prepared in toluene. This confirms the observations made on the evolution of the topology of PEs prepared in toluene based on dilute solution measurements The different polymerization times (30 h for reactions conducted in dichoromethane and 5 h for those conducted in toluene) for a given pressure, have also to be considered. A clear answer on that point would requires further investigations. These measurements are can be related to different polymer topologies. Moreover these PEs exhibited higher activation energy than conventional HDPE or LLDPE. As mentioned in the introduction, similar results were reported recently by Zhu et al. [10,11].

4. Conclusions

The combination of various characterization methods has shown that the structural parameters of PEs prepared in the presence of palladium catalysts containing diimine ligands are different provided these PEs are prepared at different ethylene pressures, all other experimental conditions being identical. This result opens new perspectives in the control of branching in poly(olefin)s. As it could be anticipated, such differences affect more the bulk rheological properties in the melt. These branched PEs obtained in the presence of palladium diimine catalysts represent a new class of polyethylenes with almost unique branching structure and ethylene pressure tailorable chain topology. They behave very differently from conventional polyethylenes.

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