APPENDIX II.3

A SENSITIVE METHOD TO DETECT VERY LOW LEVELS OF LONG CHAIN BRANCHING IN HIGH DENSITY POLYETHYLENE FROM MOLAR MASS DISTRIBUTION AND LINEAR VISCOELASTIC RESPONSE

E. van Ruymbeke , V. Stéphenne, D. Daoust, P. Godard,
C. Bailly, R. Keunings

3.1 INTRODUCTION

The characterization of long chain branching (LCB) in polymers is crucial for the understanding of their viscoelastic behaviour in the melt and, as a consequence, for the prediction of their processing behaviour. To have a large impact on melt flow behaviour, branches must be longer than about twice the entanglement length (M_e) in the melt. In polyethylene (PE), branches have to be at least of the order of 180 carbon atoms in length to be considered as long [Jordan *et al*. (1989)]. Low density polyethylene (LDPE) obtained by radical chemistry is known to include many types of LCB at concentrations ranging from 0.6 to 4.1 branches per 1000 carbon atoms [Axelson *et al*. (1979); Bovey *et al.* (1976)]. On the other hand, high-density polyethylene (HDPE) obtained with transition metal catalysts is predominantly linear but may also contain low levels of LCB (up to about 0.1-0.2 per 1000 carbon atoms; exceptionally up to 0.66 per

1000 carbon atoms) [Malmberg *et al*. (1998); Swogger *et al*. (1993); Wang *et al*. (1998)]. Long branches are introduced in HDPE by incorporation of vinyl-terminated macro-monomers into the growing backbone. There are three major types of transition metal catalysts for HDPE: Ziegler, Phillips and metallocene, the first one being dominant in industry. Presence of LCB has been demonstrated for Phillips and metallocene-catalyzed HDPE [Hogan *et al*. (1981); Lai *et al*.; Malmberg *et al.* (1999); Vega *et al*. (1999)]. In most cases, LCB was detected among the longest molecules [Agarwal *et al*. (1983); Gabriel *et al*. (2002); Tung *et al.* (1959); Doerpinghaus et al. (2003)]. According to Soares *et al.* [1998], long chain branched metallocene HDPE can be viewed as a mixture of linear, three-armed stars, and H-shaped molecules with very small amounts of more highly branched chains. By nature of the catalyst, Ziegler HDPE contains a very low amount of vinyl unsaturations during polymerization. Hence, inclusion of LCB by incorporation of macro-monomers is highly unlikely. For decades, reports on the presence of LCB in Ziegler catalyzed HDPE have been very scarce. Agarwal *et al.* (1983) showed evidence of small levels of LCB in the high molar mass portion of a Ziegler HDPE. In a recent paper, Reinking *et al*. (2000) have reported a new Ziegler Vanadium-based catalyst able to produce LCB by a new metathesis mechanism.

LCB concentration in transition metal catalyzed HDPE may be so low (less than 0.1 per 1000 carbon atoms) that it cannot be easily detected (and thus quantified) by solution-based chromatographic or spectroscopic methods such as multi-detector Size Exclusion Chromatography (SEC) and Nuclear Magnetic Resonance (NMR) [Janzen *et al.* (1999); Shroff *et al*. (1999)]. By contrast, rheological measurements are very sensitive to traces of LCB, even at concentrations where solution-based techniques become unresponsive [Janzen *et al.* (1999); Shroff *et al*. (1999); Vega *et al*. (1998, 2002); Gabriel *et al.* (2002)]. In consequence, many authors have tried to exploit rheology to characterize low levels of LCB. At low concentration, increased LCB leads to higher zero-shear viscosity (η_0)

as well as more pronounced shear thinning and melt elasticity [Gabriel *et al*. (2002); Lohse *et al.* (2002); Vega *et al*. (1998); Wood-Adams *et al*. (2000, 2001); Kolodka *et al.* (2004), Doerpinghaus *et al.* (2004)]. The main problems, however, are to get an accurate value of the zero-shear viscosity, which is not easily accessible because of very long relaxation times of branched molecules [He *et al.* (2004)], and to separate the effects of molar mass (MM), molar mass distribution (MMD), and LCB. In shear experiments, broadening the MMD and increasing the level of LCB can have similar effects [Doerpinghaus *et al*. (2003) ; Vega *et al*. (2002) ; Robertson *et al.* (2004)]. Rheology alone can be ambiguous. For instance, the LCB Dow Rheology Index (DRI), solely based on shear rheology, is specifically designed for polymers with similar, narrow MMD and is not applicable otherwise [Lai *et al*. (1994)]. Another example of LCB characterization by rheology is the flow activation energy (E_a) method. E_a is deduced from the temperature sensitivity of viscosity curves and is often used in the literature to detect LCB in thermorheologically simple polymers as, for example, polystyrene or polyisobutene. However, branched PE is known to be thermorheologically complex [Kolodka *et al.* (2004); Wagner *et al.* (2004)]. Therefore, an apparent activation energy, ($\hat{E}_a$), calculated from the temperature dependence of viscosity, must be used [Wood Adams *et al.* (2001)]. LCB in HDPE can in principle be observed from an $\hat{E}_a$-enhancement [Bersted *et al*. (1985); Hughes (1983); Wood-Adams *et al*. (2001), Vega *et al.* (2002), Starck *et al.* (2002)]. Unfortunately, the situation is confusing. Several authors have shown that the absence of an $\hat{E}_a$-enhancement does not systematically preclude the presence of low LCB levels [Shroff *et al*. (1999); Wasserman *et al.* (1996)].

Recently, approaches combining information coming from both chromatographic techniques in solution and shear rheology in the melt have emerged. Shroff *et al.* (1999), Janzen *et al.* (1999) and Wang *et al.* (2004) have coupled melt rheology and solution SEC-viscometry approaches to detect LCB. An LCB level has been inferred from

comparison of experimental melt viscosity curves with the MMD (Tuminello's inversion method) [Wood-Adams et al. (2000)]. Thimm *et al.* (2000) have also applied their own inversion scheme for LCB detection purposes. Crosby *et al.* (2002) have proposed the dilution-rheology method, able to give qualitative indications of the LCB level without resorting to solution techniques. Making the method quantitative requires determination of the MMD by SEC. Use of the dilution-rheology approach is however restricted to long chain branched polymers with a well-defined architecture, like metallocene HDPE. Recently, Michel (2002) has introduced a new rheological index to quantify LCB in polypropylene. This index, which could also be useful for HDPE, is obtained from the ratio of weight-average MM values inferred from the linear viscoelasticity data.

The objective of the present work is to report on the development of a qualitative method based on the viscoelastic response of the polymer to detect low levels of LCB in various types of HDPE. This method is based on double reptation modelling and combines chromatographic and linear viscoelasticity data. Experimental storage (G') and loss (G'') moduli are compared with moduli computed from the experimental MMD, by use of a modified Time-Dependent Diffusion (TDD) reptation model combined with the double reptation mixing rule [van Ruymbeke *et al.* (2002)]. We test Ziegler, Phillips and metallocene-catalysed HDPE's with high polydispersity and different low concentrations of LCB. We also study two relatively narrow-disperse fractions of the Ziegler sample, obtained by Successive Solution Fractionation (SSF) [Stéphenne (2002)]. The results are compared with those obtained by classical solution (^{13}C-NMR) and rheological approaches (zero-shear viscosity and flow activation energy) to highlight the high sensitivity of the new method.

3.2 THEORETICAL BACKGROUND

3.2.1 Flow activation energy

A common method to investigate the presence of LCB is the determination of flow activation energy E_a or apparent activation energy $\hat{E}_a$. For thermorheologically simple polymers, the temperature dependence of the viscoelastic behavior can be described by a single horizontal time shift factor a_T:

$$\eta(T) = a_T(T)\eta(T_0)b_T \cong a_T(T)\eta(T_0), \quad (1)$$

where $\eta(T)$ and $\eta(T_0)$ are the viscosity at temperatures T and T_0, respectively. The modulus shift factor, b_T, does not depend strongly on temperature and is often neglected [Ferry (1980); Wood-Adams *et al.* (2001)]. Far from the glass transition temperature, the horizontal shift factor follows an Arrhenius relationship:

$$a_T = \frac{\eta_0(T)}{\eta_0(T_0)} = \exp\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right). \quad (2)$$

For thermorheologically complex polymers –including long chain branched PE- the effect of temperature cannot be described by a single time shift factor [Carella et al. (1986)]. These polymers present a spectrum of activation energies. Therefore, in order to compare their behaviour, an apparent zero shear rate activation energy, $\hat{E}_a$, calculated from viscosities, must be used [Wood-Adams *et al.* (2001)]:

$$\eta_0(T) = \eta_0(T_0)\exp\left(\frac{\hat{E}_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right). \quad (3)$$

As opposed to the corresponding branched polymers, linear samples show thermorheologically simple behaviour, if they are analyzed far enough from their glassy region.

Whereas linear molecules relax by reptation, long chain branched chains require an additional relaxation process (arm retraction) whose temperature dependence (and thus E_a or $\hat{E}_a$) can in principle be different from that of reptation. In ethylene polymers, the presence of LCB is often associated with an increase of E_a [Bersted *et al*. (1985); Hughes (1983); Wood-Adams *et al*. (2001); Starck et al. (2002) ; Vega *et al.* (2002)]. For sparsely long chain branched HDPE (which is in fact a blend of linear and branched chains), an increase of E_a above the value reported for linear HDPE can be related to the volume fraction of branched polymer. E_a values reported for linear HDPE usually range between 25 and 28 kJ/mole [Carella *et al*. (1996); Starck *et al*. (2002); Vega *et al*. (1999)]. E_a does not depend on MM [Wasserman *et al.* (1996)]. While a higher value for E_a can be attributed to the presence of LCB, the absence of LCB cannot be concluded from absence of an E_a-enhancement. Moreover, the experimental ranges of temperatures and frequencies influence E_a [Shroff *et al*. (1999); Wood-Adams *et al*. (2001)].

Some materials, notably LDPE, require an additional vertical shift [Shroff *et al.* (1992); Wood-Adams *et al*. (2001)]. A vertical activation energy (E_v) can be obtained from the vertical shift factor in the same way as E_a is calculated from the horizontal one. According to the Rouse model, this shift factor is defined from the polymer density ρ and ρ_0 at temperature T and T_0 [Rouse (1953)]:

$$b_T = \frac{\rho T}{\rho_0 T_0}. \qquad (4)$$

Nevertheless, the vertical shift factor does not allow correct superposition of data for some polymers [Carella *et al.* (1984)]. In addition, it has been shown that E_v does not necessarily correlate with the level of LCB [Shroff *et al.* (1992)].

3.2.2 Zero-shear viscosity

Raju *et al.* (1979a) have studied the linear viscoelastic behavior of linear HDPE fractions with polydispersity below 1.2. They also considered a series of nearly monodisperse polyethylenes obtained by hydrogenation of anionic polybutadienes and found a similar outcome [Raju *et al*. (1979b)]. Their result has become the standard zero-shear viscosity molar mass relation for HDPE (at 190 °C):

$$\eta_0 = 3.4 \times 10^{-15} (M_w)^{3.6}, \qquad (5)$$

with η_0 in Pa.s and M_w in g/mol. Since at low LCB level, the zero-shear viscosity of long chain branched HDPE is expected to be higher than predicted from Eq. (5), η_0 can in principle be used to detect the presence of LCB [Gabriel *et al*. (2002); Lohse *et al.* (2002); Vega *et al*. (1998); Wood-Adams *et al*. (2000, 2001); Kolodka *et al.* (2004) ; Doerpinghaus *et al.* (2004)]. However, this method suffers from two difficulties. First, the validity of Eq. (5) is not guaranteed for truly linear HDPE with broad MMD. Second, the zero-shear viscosity can be very difficult to measure for samples with long terminal relaxation times [He *et al.* (2004)] This requires time-consuming creep or steady shear measurements that are more difficult to perform and prone to error from polymer degradation than oscillatory measurements. Moreover, some level of extrapolation is often required to obtain η_0. In other words, significant errors on the experimental determination and the predicted value of η_0 are possible, which could lead to wrong conclusions about the presence of LCB.

3.2.3 Proposed method

In a previous paper [van Ruymbeke *et al.* (2002)], we have investigated the ability of various reptation models to quantitatively predict the linear viscoelastic response of polydisperse entangled linear polymers from knowledge of their MMD. By comparing theoretical predictions for dynamic moduli to experimental results for

three different polymers (including HDPE) and various MMD shapes, we came to the conclusion that the time-dependent diffusion model proposed by des Cloizeaux, suitably modified to treat short chains and to include the Rouse relaxation, provides accurate quantitative predictions.

The double reptation theory proposed by Tsenoglou (1987) and des Cloizeaux (1988) relates the relaxation modulus *G(t)* of an entangled linear polymer to its molecular weight distribution *w(M)* trough the mixing rule:

$$G(t) = G_N^0 \left(\int_{\log M_e}^{\infty} [F_{mono}(t,M)]^{1/\beta} w(M) dLogM \right)^{\beta}, \qquad (6)$$

Here G_N^0 is the plateau modulus, M_e the molar mass between entanglements, and $w(M) = dW(M)/dlog(M)$ with $W(M)$ being the weight fraction of chains with molar mass below M. The original double reptation theory sets the mixing exponent to a value of 2, but slightly higher values (β=2.25) are consistently found to yield more accurate predictions. $F_{mono}(t,M)$ is the relaxation function of the monodisperse polymer of molar mass M. Inclusion of constraint release effects through double reptation yields

$$F_{mono}(t,M) = F_{sr}(t,M)^{\beta}, \qquad (7)$$

where $F_{sr}(t,M)$ is the relaxation function of a test chain in a *fixed* network of entanglements. Following conclusions of van Ruymbeke *et al*. (2002), adopt the time-dependent diffusion relaxation function proposed by des Cloizeaux (1990):

$$F_{TDD}(t,M) = \frac{8}{\pi^2} \sum_{podd} \frac{1}{p^2} \exp(-p^2 U(t)), \qquad (8)$$

where $U(t,M)$ is given by:

$$U(t) = \frac{t}{\tau_{rept}} + \frac{M^*}{M} g\left(\frac{Mt}{M^* \tau_{rept}}\right), \tag{9}$$

and g is conveniently approximated by

$$g(x) = -x + x^{0.5}\left[x + (\pi x)^{0.5} + \pi\right]^{0.5}. \tag{10}$$

In Eq. (9), the reptation time τ_{rept} is linked to the molar mass through

$$\tau_{rept} = KM^3. \tag{11}$$

When combined, Eqs. (6) to (11) represent the time-dependent diffusion with double reptation model (TDD-DR). In addition to G_N^0 and M_e (which are directly related), the TDD-DR model has basically two material parameters: M^* , which is a measure of the fluctuations importance for the polymers analyzed, and K. An empirical modification of the model is proposed by van Ruymbeke *et al*. (2002) and used here to include the influence of short chains. For MM below $4M_e$, we take $F_{mono}=F_{sr}$ and rescale τ_{rept} to ensure continuity along the MM scale. Inclusion of Rouse relaxation as described by van Ruymbeke *et al*. (2002) was found unnecessary for HDPE.

In the proposed method, we will compare the experimental dynamic moduli at 190°C with the predictions obtained from the experimentally determined MMD, with the help of the reptation model described above. Experimental master curves will be used only with thermorheologically simple samples (zPE and F1). Discrepancies will appear in the reptation-dominated frequency region in the presence of LCB. The sensitivity of the method is expected to be high because the arms-fluctuation and backbone reptation dynamics of branched chains are dramatically different from the reptation of linear chains [McLeish *et al*.(1999)].

The material parameters of the model have to be obtained beforehand by fitting at least one calibration sample, the linearity of which is guaranteed and the MMD of which is known accurately. In this paper, we will use the material parameters obtained by van Ruymbeke *et al.* (2002) for a temperature of 190 °C:

$$G_N^0 = 2.6x10^6\ (Pa),\ K = 1.4x10^{-17}\ (g/mol)^3,\ M^* = 70000\ (g/mol). \quad (12)$$

The linearity of the calibration samples was ensured by the synthesis conditions and checked by ^{13}C-NMR. The self-consistency and quality of the predictions for other samples tested by van Ruymbeke *et al.* (2002) and in this paper is a further guarantee of the validity of these parameters.

3.3. MATERIALS AND METHODS

3.3.1 Samples

HDPE samples synthesized by Ziegler (zPE), Phillips (pPE), and metallocene (mPE) catalysts are used. zPE has been fractionated by Successive Solution Fractionation (SSF) into two narrower fractions of low (F1) and high (F2) MM as described below. The main characteristics of these samples are described in Table 1.

3.3.2 Successive Solution Fractionation

Fractionation of zPE according to MM is accomplished by way of Successive Solution Fractionation (SSF). The method and experimental setup have been described in detail elsewhere [Stéphenne (2002)]. The SSF procedure consists of three consecutive steps: dissolution, precipitation and extraction. A 0.7 wt % solution is prepared by dissolving 12 g of zPE sample in 2200 ml of diphenyl ether, at 160 °C and under mechanical stirring. In order to inhibit

degradation of the sample, the solvent is stabilized with Irganox 1010 antioxidant (2 g/l) and nitrogen is purged through the solution. The system is kept isothermally at that temperature during 120 minutes. During the precipitation step, the solution is cooled to room temperature at 0.75 °C/min. The column is next heated to the first extraction temperature (147 °C) at a rate of 1 °C/min. After 120 minutes at 147 °C, the solution is pumped through a metallic filter introduced in the SSF vessel and precipitated in a large excess of non-solvent methanol. The same procedure is repeated at the final dissolution temperature (160 °C). The precipitate is then filtered, stabilized with Irganox 1010 (2000 ppm) and dried in vacuum at 50 °C.

In order to check that the molecular distribution of the samples is not altered during the fractionation procedure, the following test has been performed. zPE is kept in solution (diphenyl ether) at 160 C for 48 h under nitrogen atmosphere. After the test, SEC reveals no modification of the MMD.

3.3.3 Characterization techniques

A. Differential Scanning Calorimetry (DSC)

Thermal analysis is carried out with the help of a differential scanning calorimeter Mettler Toledo 821e. A weighed (≅ 10 mg) sample is sealed in a standard Aluminum pan (40 µl) and subjected to a heating–cooling–heating cycle. Previous thermal effects are erased by preheating the sample at 220 °C. Subsequently, the sample is cooled from 220 to –20 °C at 10 °C/min, annealed at –20 °C for 2 minutes, and heated to 220 °C at 10 °C/min.

B. Nuclear Magnetic Resonance (NMR)

The concentration of long chain branches is determined by ^{13}C-NMR spectroscopy. The spectra are obtained at 135 °C, without broad band decoupling, using a Bruker Advance 500 pulsed NMR spectrometer at

125 MHz. Polymer solutions are prepared by dissolving 150 mg polymer in 3.5 ml of deuterated 1, 1, 2, 2-tetrachloroethane (TCE-d_2). Detailed parameters of the experiment are listed hereafter: pulse angle, 90°; relaxation time, 15 s; acquisition time, 1.5 s and number of scans, 10000.
The chemical shifts assigned to different hydrocarbon groups follow the literature [Liu et al. (1999); Randall (1977)]. Long chain branching density (LCBD) is calculated using the following equation [Randall (1977)] :

$$LCBD = \frac{I_{A\alpha}}{3I_{Atot}}, \quad (13)$$

where $I_{A\alpha}$ and I_{Atot} are the integral areas of α-CH_2 resonance and total intensity of carbons, respectively.

C. Size Exclusion Chromatography (SEC)

Molar mass distributions are measured on a Waters Alliance GPC/V 2000 instrument with Differential Refractive Index detection (SEC-DRI). Filtered samples are injected in the system at an injection volume of 323 µl. Two Stryragel HT6E and one Styragel HT2 columns are used at a flow rate of 1 ml/min. Narrow PS standards covering the entire MM range of the samples are used for calibration purposes. SEC is carried out at 135 °C in 1,2,4-trichlorobenzene, stabilized with BHT (2 g/l). Polymer concentration is 2 g/l. The following Mark-Houwink relationships (valid only for linear species) are used for universal calibration [Otocka *et al*. (1971); Scheinert (1977)]:

$$[\eta]_{PS} = 1.21\ 10^{-4} * M^{0.71}\ (dl/g), \quad [\eta]_{PE} = 5.10\ 10^{-4} * M^{0.706}\ (dl/g). \quad (14)$$

D. Rheological measurements

Dynamic moduli

Dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, are determined with a strain-controlled rheometer (ARES from Rheometrics) in dynamic mode with a parallel-plate configuration at temperatures ranging from 140 °C to 220 °C. Linearity of the viscoelastic regime is always checked beforehand with the help of a strain sweep test. Relaxation of the sample is also checked before each test by measuring normal force decay. We use 25 mm diameter plates. The angular frequency sweep interval is 10^{-2} - 10^{2} rad/s, with a strain amplitude of 5 %. Such a test lasts about 1 h. All measurements are performed under a dry nitrogen atmosphere. We stabilize the samples (in fluff form) by adding 3000 ppm of Irganox B215 antioxidant (slurry procedure). For thermorheologically simple samples (zPE and F1), master curves established at a reference temperature T_0 of 190 °C have been calculated by applying the time-temperature superposition principle [Ferry (1980); Macosko (1996)] with the help of the instrument software. For thermorheologically complex samples, vertical shift factors have been determined according to the method proposed by Wood-Adams *et al.* (2001) for PE, from the crossover moduli, G_X, at temperature T_0=190°C and T:

$$b_X(T) = \frac{G_X(T)}{G_X(T_0)}. \qquad (15)$$

As expected for thermorheologically complex polymers, no single horizontal shift factor can be found. Fig. 1 shows this effect for sample pPE: while the experimental data superimpose very well at high frequencies, discrepancies appear at lower frequencies.

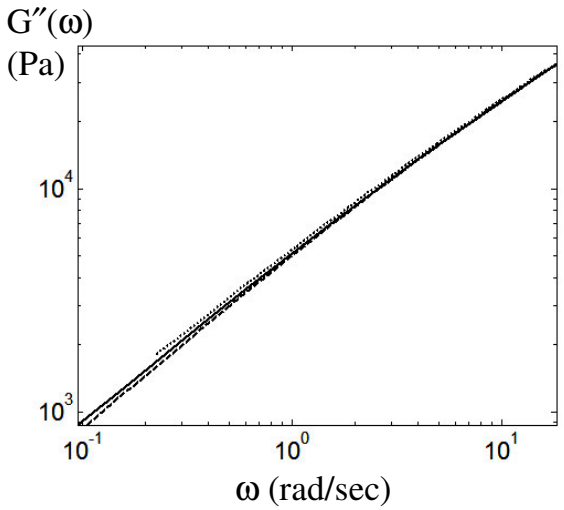

FIG. 1: Effect of thermoreological complexity on loss modulus G" vs. $a_T(\omega)$ for pPE. master curve has been build from experimental data at 150°C (····), 190)°C (—) and 220°C (---).

A better way to detect the effect of the thermorheological complexity of a polymer is to use the van Gurp – Palmen plot [Trinkle, 2002], which expresses the phase angle, δ, between stimulus and material response versus the absolute value of the complex modulus, $/G^*/$, from experimental data. This curve is temperature invariant and thus, provides a good method to check for the time temperature superposition principle [van Gurp and Palmen, 1998]. Results obtained for samples zPE and pPE (see Table 1), after a vertical shift as described in Eq. 15, are shown in Fig. 2.

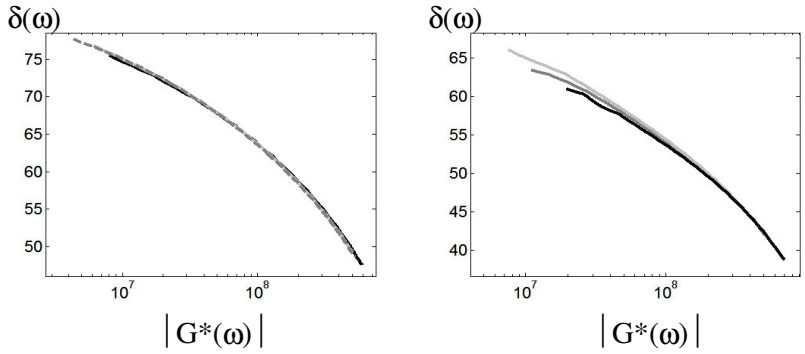

FIG. 2: Effect of thermoreological complexity on phase angle δ vs. $|G^*|$, for a) zPE, b) pPE. Experimental data at 150°C (black curve), 190°C (grey curve) and 220°C (light grey curve).

As it is shown on this figure, data for sample zPE superimpose well, contrary to sample pPE, for which the effect of the thermorheological complexity is clearer than in Fig. 1.

Zero-shear viscosity (start-up test)

In order to determine the zero-shear viscosity (η_0), the transient viscosity in the linear limit ($\eta^+(t)$) is measured with a strain-controlled rheometer (RMS 800 from Rheometrics) in steady mode with a parallel plate configuration at 150 °C. 40 mm diameter removable plates are used. Relaxation of the sample is always checked before test by measuring normal force decay. Applied shear rate is 0.001 s^{-1} and the test lasts 1000 s. All measurements are performed under a dry nitrogen atmosphere. We stabilize the samples (all in fluff form) by adding 3000 ppm of Irganox B215 antioxidant. The zero-shear viscosity is deduced from the steady-state value obtained after the longest experimental time. No clear plateau has been observed after 1000 s for pPE, mPE and F2.

It has been checked that the molecular structure of the polymer is not modified during the oscillatory and start-up tests. The storage modulus *G'* at 0.1 rad/s (very sensitive to molecular structure changes) does not change after 2 h at 240 °C.

3.4 RESULTS AND DISCUSSION

3.4.1 Molar Mass Distribution (MMD)

MMD's of zPE, pPE, and mPE, as determined by SEC-DRI, are shown in Fig. 3.

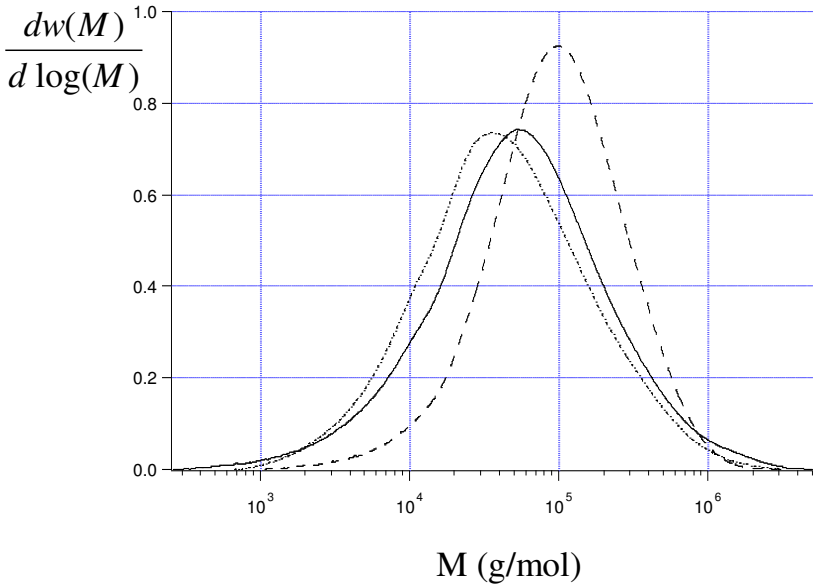

FIG. 3: Molar mass distributions of zPE (—), pPE (- • -) and mPE (--) determined by SEC-DRI.

Corresponding average MM values are listed in Table 1.

TABLE 1: *Main characteristics of all investigated samples.*

	MI[a]	ρ[b]	M_w[c]	M_n[c]	M_z[c]
zPE	0.65	0.958	147700	21700	658700
pPE	0.70	0.963	113600	21800	475600
mPE	-	0.950	176400	56700	405700
F1	-[g]	-	73500	21100	181000
F2	-[g]	-	350800	85600	935400

	H[d]	LCBD[e]	$T°_m$[f]	$T°_{cc}$[f]
zPE	6.8	-h	137.5	115.5
pPE	5.2	1.6	135.5	117.5
mPE	3.2	5.1	134.5	122.5
F1	3.5	-[h]	133.0	120.5
F2	4.1	-[h]	135.5	117.5

a : Melt flow index measured at 190 °C and under 2.16 kg (in g/10 min).
b : Density measured with pycnometer at 23 °C (in g/cm3).
c : Weight, number and z average molar masses (M_w, M_n, M_z) in g/mol.
d : Polydispersity index (M_w/M_n).
e : LCB density measured by ^{13}C-NMR (in /10^4 C).
f : Pure melting and crystallization ($T°_m$ and $T°_{cc}$) temperatures in °C, estimated by DSC at 10°C/min.
g : Not enough matter available for correct characterization.
h : Below ^{13}C-NMR detection limit of 1/10^4 C.

Although the samples have similar weight average molar masses (M_w), they are characterized by distinct MMD's. As expected from the catalyst systems used, zPE and pPE present a broader MMD than metallocene mPE. All samples include very long chains, above 10^6

g/mol. It must be remembered, however, that MM's have been determined by SEC-DRI. In solution, long chain branched polymers assume a more compact configuration than linear chains, and thus the MM of long chain branched polymers can be underestimated by SEC-DRI. However, the error on MMD may considered to be negligible at LCB levels below $1/10^4$ carbon atoms [Crosby *et al*. (2002)].

MMD's of F1 and F2 fractions are shown in Fig. 4.

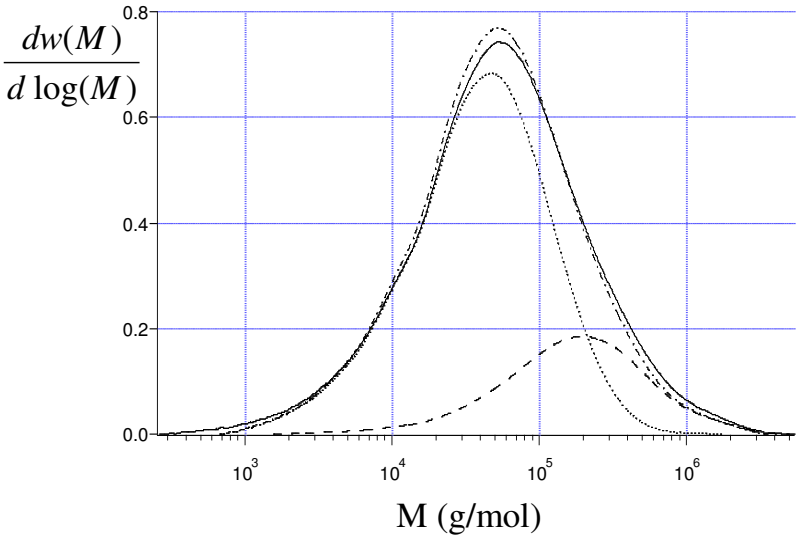

FIG. 4: Molar mass distributions of zPE and fractions . Original sample (—), fraction F1 (●●●), fraction F2, (- -) MMD rebuilt from fractions (- ● -). F1 and F2 fractions respectively represent 78 and 22 wt % of the total collected matter.

Average MM values are given in Table 1. F1 is characterized by a relatively low M_w (about 74000g/mol) and does not contain a significant fraction of chains longer than 10^6g/mol. Very long molecules of zPE are all included in fraction F2 which has therefore

very high M_w (about 350000 g/mol). For zPE, original and rebuilt MMD's, obtained by summing weighted distributions of fractions F1 (78 wt %) and F2 (22 wt %)), are compared in Fig. 4. This confirms that neither significant degradation nor loss of material has happened during the fractionation process. Consequently, F1 and F2 samples are well representative of the original zPE sample.

3.4.2 Short Chain Branching (SCB)

All characterized samples are very crystalline. In Table 1, density is above 0.950, melting temperatures around 135 °C or more, and crystallization temperatures between 115 and 122 °C. From the literature, it can therefore be concluded that SCB content in these samples is low, about a few wt % [Alamo (1994); Peacock (2000)].As a consequence, SCB has no effect on the rheology of our HDPE samples and will be neglected in this study [Wood Adams *et al.* (2000)].

3.4.3 Long Chain Branching (LCB)

A. NMR method

A long chain branching density (LCBD) has been evaluated by ^{13}C-NMR. It must be kept in mind that the NMR approach cannot distinguish between branch lengths for branches equal to or longer than six carbon atoms, while the rheologically relevant branch lengths are those long enough to entangle, that is at least 180 carbon atoms for PE. With the exception of very sophisticated methods and instruments, ^{13}C-NMR is unable to quantify branching levels below about $1/10^4$ carbon atoms [Crosby *et al*. (2002); Janzen *et al*. (1999); Shroff *et al*. (1999), Wood Adams *et al.* (2000)].

Results are presented in Table 1 for all investigated samples. No LCB has been detected for Ziegler-catalyzed zPE nor its F1 and F2 fractions. If LCB is present, it is at LCBD below detection limits of

^{13}C-NMR. Phillips and metallocene catalyzed HDPE's contain small amounts of LCB. mPE is more branched. As a consequence, MMD's obtained by SEC-DRI may be considered as correct for F1, F2, zPE and pPE samples. On the other hand, the apparent MMD is probably slightly underestimated for mPE. This underestimation is not critical for the interpretation of the results by the proposed method.
Particularly at such low LCB levels, LCB characterization by NMR encounters several experimental difficulties and limitations already discussed in the literature [Crosby *et al*. (2002); Janzen *et al*. (1999); Shroff *et al*. (1999)]. In our opinion, LCBD's reported here must be seen as relative rather than absolute values.

B. Rheological methods

For all samples investigated, *G'* and *G''* moduli at 190 °C are plotted as a function of angular frequency in Fig. 5 and Fig. 6, respectively.

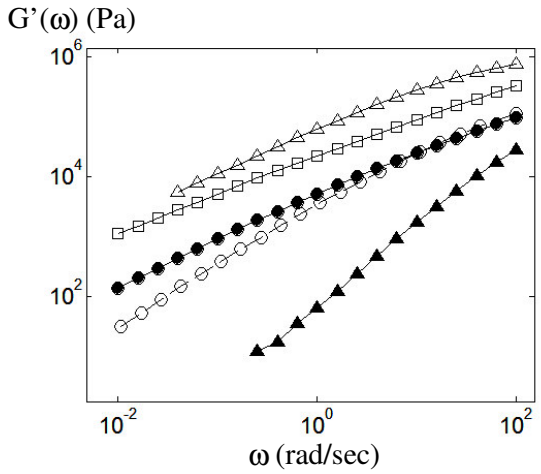

FIG. 5: Storage modulus G'(ω) of zPE (OO), pPE (●●), mPE (□), F1 (▲▲) and F2 (Δ), at 190°C.

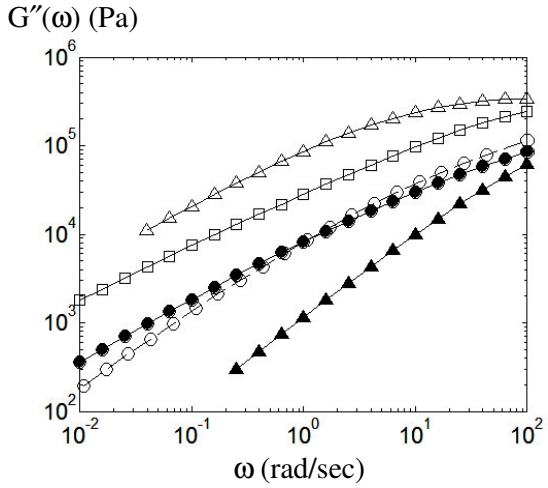

FIG. 6: Loss modulus G" (ω) of zPE (OO), pPE (●●), mPE (□), F1 (▲▲) and F2 (Δ), at 190°C.

Inspection of the low frequency moduli, reflecting the longest relaxation times, and MMD data, particularly the z-average molar mass M_z which is relevant to the longest molecules, suggests the presence of LCB in samples pPE and mPE. On the single basis of M_z values measured for all samples and the assumption of linearity, moduli should indeed be ordered in the terminal zone according to the following classification: F2 > zPE > pPE > mPE > F1. But the experimental ranking is rather: F2 > mPE > pPE > zPE > F1. For zPE and its fractions, no conclusions can be drawn. Such a naive approach is too simple.

Flow Activation energy method

According to the procedure proposed by Wood Adams *et al.* (2001), the activation energy spectrum, $E_{a,i}$, is calculated from the storage moduli of all investigated samples. Results are shown in Fig. 7 and reported in Table 2.

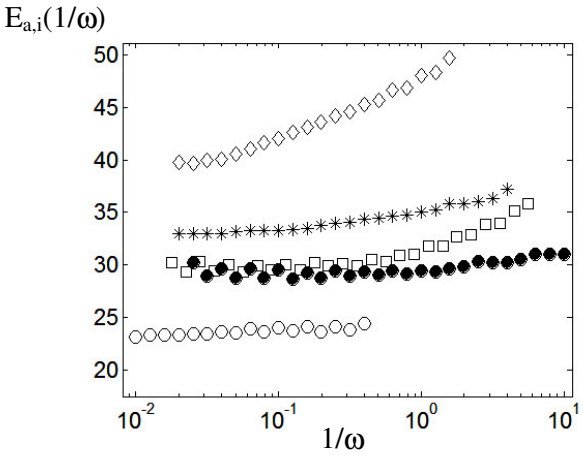

FIG. 7: Activation energies spectrum ($E_{a,i}$ vs. 1/ω) of zPE (●●), pPE (∗∗), mPE (◊◊), F1 (○○) and F2 (□□).

TABLE 2: Horizontal (E_{ai}) and vertical (E_v) flow activation energies for all investigated samples.

	$E_{a,i}$ (kJ/mole)	**E_v (kJ/mole)**
zPE	30	0
pPE	33→37	3.3
mPE	40→50	8.6
F1	23	0
F2	30→36	8

Because of the difficulty to obtain accurate values for viscosity [He *et al.* (2004)], we do not calculate the apparent activation energy, which is a weighted average of $E_{a,i}$ [Wood Adams *et al.* (2001)]. A vertical shift factor is needed for samples pPE, mPE and F2. Corresponding vertical activation energies E_v are listed in Table 2. Samples pPE and mPE present the highest $E_{a,i}$ values, respectively from 33 to 37

kJ/mole and from 40 to 50 kJ/mole, well above $E_{a,i}$ values reported for linear HDPE (between 25 and 28 kJ/mole), and F1 the lowest, about 23 kJ/mole. The thermorheologically simple behavior of this last sample is demonstrated by the constant value of its activation energies. $E_{a,i}$. The values calculated for unfractionated zPE, around 30 kJ/mol, also seem constant. In contrast, the zPE highest fraction , F2, shows a time-dependent activation energy, starting from 30 kJ/mole, up to36 kJ/mol.

Thus, for samples F1, pPE and mPE, LCBD measured by NMR is well correlated with E_a. F1 is linear while both pPE and mPE include long chain branches, but at different concentrations. By contrast, the situation is not clear at all for zPE and F2. ^{13}C-NMR gives no indication of LCB but both samples present E_a values slightly above those reported for linear chains (30 instead of 25-28 kJ/mole) and F2 presents a thermorheologically complex behaviour. Thus, on the basis of $E_{a,i}$ data alone, we conclude that unfractionated zPE behaves as a linear sample, in spite of its high activation energy value, while fraction F2 is visibly branched.

*Zero-shear viscosity (*or $\eta^+(t)$*) method*

The well-established dependence of η_0 on weight average molar mass M_w (Eq. (3)) is expected to hold for all linear HDPE's [Raju *et al*. (1979a 1979b)]. In Fig. 8, η_0 is displayed as a function of M_w at 150 °C for all the characterized samples. Eq. (3) shifted to 150 °C (assuming an activation energy of 25 kJ/mole) is also drawn for comparison purposes.

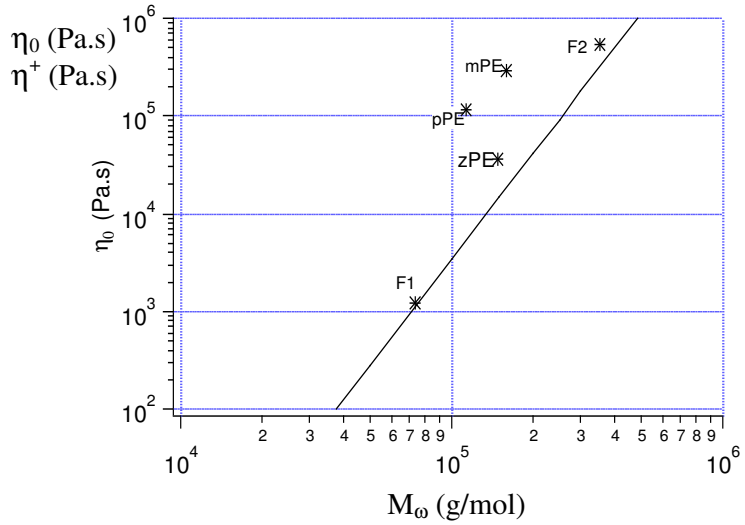

FIG. 8: Zero-shear viscosity $\eta 0$ (for zPE and F1) or η^+ (for pPE, mPE and F2) versus weight-average molar mass Mw. The stars are the experimental data and the line represents Eq. (3) shifted to 150 °C.

Determination of η_0 was impossible after 1000 s of the start up test, for samples pPE, mPE and F2. After such time, $\eta^+(t)$ is still increasing with time. For these samples, Fig. 8 shows the value of $\eta^+(1000\ s)$ measured at the end of the test, instead of their zero-shear viscosity. Fig. 8 shows that Eq. (3), only valid for linear species, holds for F1 – and perhaps for unfractionated zPE- but not for the other HDPE samples. The latter are characterized by higher η_0 values than those predicted from Eq. (3). It can thus be concluded that all samples, except F1 and zPE, contain LCB.

Proposed method

In Fig. 9, the experimental dynamic moduli are compared with theoretical moduli predicted by the reptation model from the

experimental MMD's. Taking into account their constant horizontal shift factor, master curves could been used for F1 and zPE.

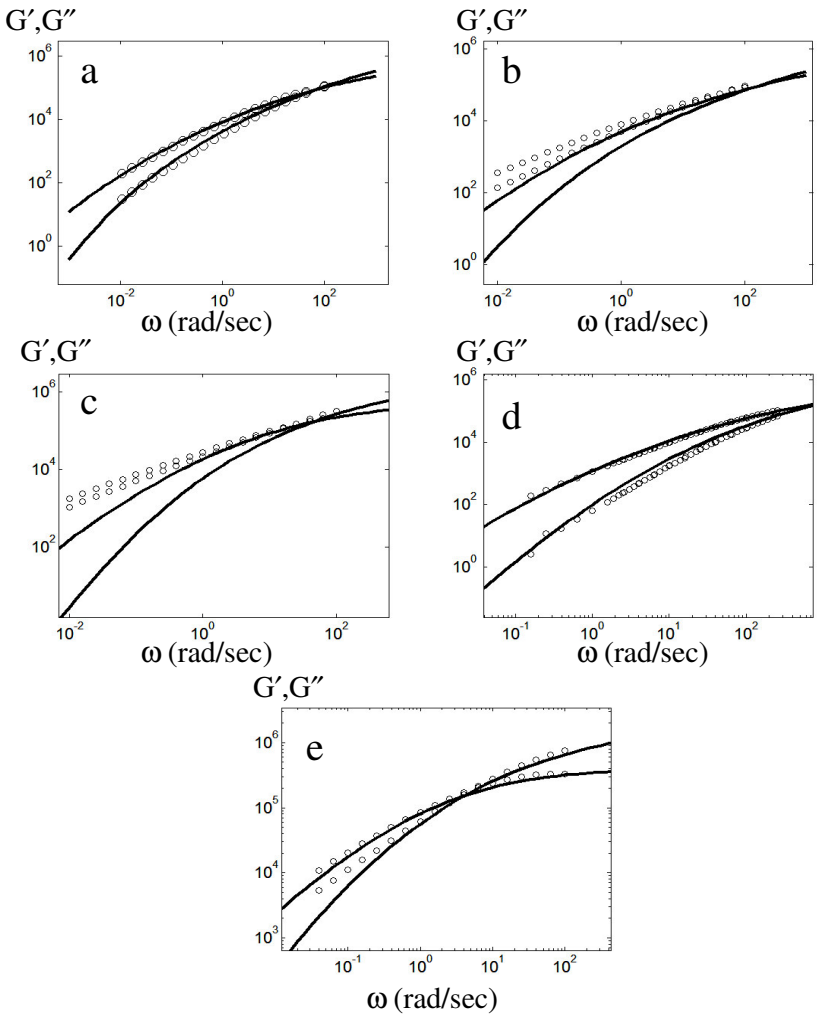

FIG. 9: Experimental (●●●) and predicted (—) dynamic moduli using the proposed method for (a) zPE, (b) pPE, (c) mPE, (d) F1, (e) F2, at 190°C. Master curves have been used for zPE and F1.

It can be observed that a very good agreement is obtained for these two samples. On the contrary, differences between experimental and predicted curves are evident for all the other samples. Experimental curves show large departures from the predicted ones based on the assumption of a linear architecture. This implies that these three samples are not purely linear but include some long chain branched molecules, leading to a completely different spectrum of relaxation times.

Linearity of F1, already deduced from both NMR, η_0, and E_a measurements, is confirmed by our method. The latter also demonstrates the presence of LCB in pPE and mPE, already deduced from NMR, η_0 and $E_{a,i}$ data. In accordance with η_0 and $E_{a,i}$ results, tour method clearly shows that F2 includes some LCB, which confirms the thermorheological complexity observed in the $E_{a,i}$ spectrum of that sample . F2 being a high MM fraction of zPE, zPE thus incorporates some LCB on its longest molecules. The LCB concentration is however so low that it does not significantly influence the activation energy spectrum of unfractionated zPE in the accessible frequency range Thus, zPE appears to be thermorheologically simple.

In the terminal zone, where only the longest relaxation times contribute to the viscoelastic behaviour, G' and G'' must follow the well-known frequency dependence:

$$G' \propto \omega^2 \, , \, G'' \propto \omega . \qquad (16)$$

From Fig. 5 and Fig. 6, it can be seen, for all samples except F1, that much lower experimental frequencies are required to achieve transition to the terminal regime. This implies that differences between predicted and experimental moduli for zPE would probably be observed at lower frequencies, outside the accessible range. The steady shear experiment reported above confirms this. Concentration of long chain branched molecules from zPE into a high MM fraction F2 has enabled the identification of LCB in zPE with our method, in good

agreement with the results obtained by analyzing the activation energies spectrum [Wood Adams *et al.* (2001)], while the NMR method has proved insensitive. The fractionation step has in essence brought the effect of LCB on dynamic moduli back into the experimental window.

3.5. CONCLUSIONS

A sensitive method based on the linear viscoelastic response has been successfully applied to the detection of LCB in sparsely branched HDPE. The method requires only the experimental determination of the MMD and linear viscoelastic data in the melt, provided that reptation model parameters are known. This method is more straightforward than an inverse one as proposed by Tuminello (1994) and therefore less prone to modeling errors. Contrary to the DRI and other LCB indices especially developed for metallocene PE's, the proposed method can be successfully applied to transition metal catalyzed HDPE with broad MMD and different molecular architectures. Its sensitivity is comparable to the one based on the activation energy spectrum analysis and more sensitive than ^{13}C-NMR method. Contrary to the zero-shear viscosity approach, our method is easily applicable to HDPE characterized by very long relaxation times. The zero-shear viscosity method is also more prone to experimental uncertainties (extrapolation, polymer degradation, possible deviations from Eq. (3) for broad HDPE samples). Moreover, it is a “one point” determination as opposed to the proposed method that reveals a complete frequency-dependent pattern. On the other hand, our method is not applicable to polymers with LCB level so low that rheological behavior is not significantly affected in the experimental frequency window. In such cases, the interest of MM fractionation has been emphasized. Presence of LCB on the longest molecules has been revealed in this manner for the Ziegler catalyzed HDPE sample.
As such, our method does not allow quantification of the LCB content. This is only possible at the moment by ^{13}C-NMR spectroscopy. Unfortunately, NMR cannot distinguish branch lengths for branches

equal to or longer than six carbon atoms, while the rheologically relevant branch lengths are those long enough to entangle, that is at least 180 carbons for PE. The ^{13}C-NMR technique is also less sensitive than our method. A highly sensitive quantitative rheology-based method is therefore still very much needed.

REFERENCES

Agarwal, R., J. Horsk, J. Stejskal, O. Quadrat and P. Kratochvil, "Distribution of molecular weights and branching of high-density polyethylene," J. Appl. Polym. Sci., 28, 3453-3466 (1983).

Alamo, R. G. and L. Mandelkern, "The crystallization behavior of random copolymers of ethylene," Thermochemica Acta, **238**, 155-201 (1994).

Axelson, D. E., F. C. Levy and L. Mandelkern, "A quantitative analysis of low-density (branched) polyethylene by 13C transform nuclear magnetic resonance at 67.9 MHZ," Macromolecules, **12**, 41-52 (1979).

Bersted, B. H., "On the effects of very low levels of long chain branching on rheological behavior in polyethylene," J. Appl. Polym. Sci., **30**, 3751-3765 (1985).

Bovey, F. A., F. C. Schilling, F. L. McCrackin and L. H. Wagner, "Short-chain and long-chain branching in low-density polyethylene," Macromolecules, **9**, 76-86 (1976).

Carella, J.M., J.T. Grotto and W.W. Graessley, Macromolecules, **19**, 659 (1986).

Carella, J.M., W.W. Graessley and L.J. Fetters, "Effects of chain microstructure on the viscoelastic properties of linear polymer melts:

Polybutadienes and hydrogenated polybutadienes", Macromolecules, **17**, 2775-2786 (1984).

Carella, J. M., "Comments on the paper: Comparison of rheological properties of metallocene-catalyzed and conventional high-density polyethylene," Macromolecules, **29**, 8280 (1996).

Crosby,B. J., M. Mangnus, W. de Groot, R. Daniels and T. C. B. McLeish, "Characterization of long chain branching: dilution rheology of industrial polyethylenes", J. Rheol., **46(2)**, 401-426 (2002).

des Cloizeaux, J."Double reptation vs Simple reptation in polymer melts. ", J. Europhys. Lett., **5**, 437-442 (1998).

des Cloizeaux, J. "Relaxation and Viscosity Anomaly of Melts Made of Long Entangled Polymers. Time-Dependent Reptation.", Macromolecules, **23**, 4678-4687 (1990).

Doerpinghaus, P.J., D.G.Baird, "Separating the effects of sparce long-chain-branching on rheology from those due to molecular weight in polyethylenes", J. Rheol., **47 (3)**, 717-736 (2003).

Ferry, J. D., "*Viscoelastic properties of polymers"*, Wiley, New-York (1980).

Gabriel, C. and H. Münstedt, "Influence of long-chain branches in polyethylenes on linear viscoelastic flow properties in shear," Rheol. Acta., **41**, 232-244 (2002).

Gabriel, C., E. Kokko, B. Lofgren, J. Seppala and H. Munstedt, "Analytical and rheological characterization of long-chain-branched metallocene-catalyzed ethylene homopolymers", Polymer, **43 (24)**, 6383-6390 (2002).

He, C.X., P. Wood-Adams and J.M. Dealy, "Broad frequency range characterization of molten polymers", J. Rheol., **48 (4)**, 711-724 (2004).

Hogan, J.P., D. D. Norwood and C. A. Ayres, "Phillips petroleum company reactor polyethylene technology," J. Appl. Polym. Sci., **36**, 49-60 (1981).

Hughes, J. K., "Analysis of long chain branching in high density polyethylene," SPE Antec Technol. Papers, **29**, 306-309 (1983).

Janzen, J and R. H. Colby, "Diagnosing long-chain branching in polyethylene," J. of Molecular Structure, **485-486**, 569-584 (1999).

Jordan, E. A., A. M. Donald and L. J. Fetters, "Transition from linear to star-branched diffusion in entangled polymer melts," ACS Polym. Prepr., **30**, 63-64 (1989).

Kolodka, E., W.J. Wang, S. Zhu and A. Hamielec, "Rheological and thermomechanical properties of long-chain-branched polyethylene prepared by slurry polymerisation with metallocene catalysts", J. Applied Pol. Sci., **92** (1), 307-316 (2004).

Lai, S. Y., J. R. Wilson, G. W. Knight and J. C. Stevens, *Elastic substantially linear olefin polymers*, US Patent 5, 272, 236.

Lai, S., T. A. Plumley, T. I. Butler, G. W. Knight and C. I. Kao, "Dow rheology index (DRI) for insite technology polyolefins (ITP): Unique structure-processing relationships," SPE Antec Technol. Papers, **40**, 1814-1815 (1994).

Liu, W., D. G. Ray III and P. L. Rinaldi, "Resolution of signals from long-chain branching in polyethylene by 13C-NMR at 188-6 MHZ," Macromolecules, **32**, 3817-3819 (1999).

Lohse, D. J., S. T. Milner, L. J. Fetters, M. Xenidou, N. Hadjichristidis, R. A. Mendelson, C. A. Garcia-Franco and M. K. Lyon, "Well-defined, model long chain branched polyethylene. 2. Melt rheological behavior", Macromolecules, **35**, 3066-3075 (2002).

Macosko, C., *Rheology : Principles, measurements and applications* (Wiley-VCH, New-York, 1994).

Malmberg, A., E. Kokko, P. Lehmus, B. Löfgren and J. V. Seppälä, "Long chain branched polyethylene polymerised by metallocene catalysts $Et(Ind)_2ZrCl_2$/MAO and $Et(IndH_4)_2ZrCl_2$/MAO,"Macromolecules, **31**, 8448-8454 (1998).

Malmberg, A., J. Liimatta, A. Lehtinen and B. Löfgren, "Charasteristics of long chain branching in ethene polymerization with single site catalysts," Macromolecules, **32**, 6687-6696 (1999).

Mavridis, H. and R. N. Shroff, "Temperature dependence of polyolefin melt rheology," Polym. Eng. Sci., **32**, 1778-1791 (1992).

McLeish, T. B. C. and S. T. Milner, "Entangled dynamics and melt flow of branched polymers ", Adv. Polym. Sci., **143**, 195-256 (1999).

Michel, J. C., "Introduction of a new rheological long chain branching index for isotactic polypropylene melt," SPE Antec Technol. Papers, 359-363 (2002).

Otocka, E. P., R. J. Roe, N. Y. Helman and P. M. Muglia, "Distribution of long and short branches in low-density polyethylenes," Macromolecules, **4(4)**, 507-512 (1971).

Peacock, A. J., *Handbook of polyethylene*, *(*Marcel Dekker, New-York, 2000).

Raju, V. R., G.G. Smith, G. Marin, J. R. Knox and W. W. Graessley, "Properties of amorphous and crystallisable hydrocarbon polymers I.

Melt rheology of fractions of linear polyethylene," J. Polym. Sci. Phys. Ed., **17**, 1183-1195 (1979a).

Raju, V. R., H. Rachapudy and W. W. Graessley, "Properties of amorphous and crystalizable hydrocarbon polymers IV. Melt rheology of linear and star-branched hydrogenated polybutadiene," J. Polym. Phys. Ed., **17**, 1223-1235 (1979b).

Randall, J. C., *Polymer sequence determination-carbon-13 NMR method*, (Academic Press, New-York, 1977).

Reinking, M. K., G. Orf and D. McFaddin, "Mechanistic studies on the formation of long-chair branching in polyethylene," Int. Confer. On polyolefins, Houston, 259-267 (2000).

Rouse, P.E., Jr. "The theory of the linear viscoelastic properties of dilute solutions ofcoiling polymers », J. Chem. Phys., **21**, 1272, (1953).

Robertson, C.G., C.A. Garcia-Franco, and S. Srinivas, "Extent of branching from linear viscoelasticity of long-chain-branched polymers" , J. Polym. Sci. part B-Polym. Phys., **42 (9)**, 1671-1684 (2004).

Scheinert, W., "Characterization of long chain branching of polyethylene as a function of the molecular weight by coupling of gel permeation chromatography and automatic viscometry at high temperature," Angew. Makromol. Chem., **63**, 117-138 (1977).

Shaw, M. T. and W. H. Tuminello, "A closer look at the MWD-viscosity transform," Polym. Eng. Sci., **34**, 159-165 (1994).

Shroff, R. N. and H. Mavridis, "Long chain branching index for essentially linear polyethylenes," Macromolecules, **32**, 8454-8464 (1999).

Soares, J and A. Hamielec, *Metallocene-catalysed polymers : Materials, properties, processing and markets* (Plastics Design Library, New York, 1998).

Starck, P., A. Malmberg and B. Löfgren, "Thermal and rheological studies on the molecular composition and structure of metallocene- and Ziegler-Natta catalysed ethylene-α-olefin copolymers," J. Appl. Polym. Sci., **83**, 1140-1156 (2002).

Stephenne, V., PhD Thesis (Université catholique de Louvain Belgium), références !!.

Swogger, K. W. and C.I. Kao, "Process Technology for unique polymer design using Dow constrained geometry catalyst," Polyolefins VIII SPE Retes 13-20, Houston (1993).

Thimm, W., C. Friedrich, T. Roths, S. Trinkle and J. Honerkamp, "Characterization of long chain branching effects in linear rheology," Condensed matter, 1-24 (2000).

Trinkle, S., P. Walter, C. Friedrich, "van Gurp-Palmen Plot II – Classification of long chain branched polymers by their topology", Rheol. Acta, **41**, 103-113 (2002).

Tsenoglou,C., "Viscoelasticity of binary polymer blends", ACS Polym. Preprints, **28**, 185-186 (1987).

Tung, L. H., "A light- scattering study of low pressure polyethylene fraction," J. Polym. Sci., 36, 287-294 (1959).

Van Gurp, M., J. Palmen, "Time-temperature superposition for polymeric blends", Rheol. Bull., **67**, 5-8 (1998).

van Ruymbeke, E., R. Keunings, V. Stephenne, A. Hagenaars and C. Bailly, "Evaluation of reptation models for predicting the linear

viscoelastic properties of entangled linear polymers" Macromolecules, **35**, 2689-2699 (2002).

Vega, J. , M. Aguilar, J. Peon, D. Pastor and J. Martinez-Salazar, "Effect of long chain branching on linear viscoelastic melt properties of polyolefins", E-Polymers Art., **46** (2002).

Vega, J. F., M. Fernandez, A. Santamaria, A. Munoz-Escalona and P. Lafuente, Rheological criteria to characterize metallocene catalysed polyethylenes," Macromol. Chem. Phys., **200**, 2257-2268 (1999).

Vega, J. F., M. Fernandez, A. Santamaria, A. Munoz-Escalona and P. Lafuente, "Small-amplitude oscillatory shear flow measurements as a tool to detect very low amounts of long chain branching in polyethylene," Macromolecules, **31**, 3639-3647 (1998).

Wagner, M.H., S. Kheirandish and M. Yamaguchi, "Quantitative analysis of melt elongational behavior of LLDPE/LDPE blends", Rheol. Acta**, 44 (2)**, 198-218 (2004).

Wang, W.-J., D. Yan, P. A. Charpentier, S. Zhu, A. E. Hamielec and B. G. Sayer, "Long chain branching in ethylene polymerization using constrained geometry metallocene catalyst," Macromol. Chem. Phys., **199**, 2409-2416 (1998).

Wang, W.J., S. Kharchenko, K. Migler, and S.P. Zhu, "Triple-detector GPC characterization and processing behavior of long-chain-branched polyethylene prepared by solution polymerisation with constraint geometry catalyst", Polymer, **45** (19), 6495-6505(2004).

Wasserman S.H., W.W. Graessley, " Prediction of linear viscoelastic response for entangled polyolefin melts from molecular weight distribution", Polym. Engineering and Sci.,36 (6), 852-861(1996).

Wood-Adams, P. M. and J. M. Deaby, "Using rheological data to determine the branching level in metallocene polyethylenes," Macromolecules, **33**, 7481-7488 (2000).

Wood-Adams, P. M. and S. Costeux, "Thermorheological behavior of polyethylene: Effects of microstructure and long chain branching" macromolecules, **34**, 6281- (2001).

Wood-Adams, P. M., "The effect of long chain branches on the shear flow behaviour of polyethylene," J. Rheol., **45(1)**, 203-210 (2001).

Wood-Adams, P. M., J. M. Deaby, A. W. de Groot and O. D. Redwine, "Effect of molecular structure on the linear viscoelastic behavior of polyethylene," Macromolecules, **33**, 7489-7499 (2000).