A sensitive method to detect very low levels of long chain branching from the molar mass distribution and linear viscoelastic response

E. van Ruymbeke[a]

Centre for Systems Engineering and Applied Mechanics (CESAME), Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

V. Stéphenne,[b] D. Daoust, and P. Godard

Unité de Physique et de Chimie des Hauts Polymères, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

R. Keunings

Centre for Systems Engineering and Applied Mechanics (CESAME), Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

C. Bailly[c]

Unité de Physique et de Chimie des Hauts Polymères, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

Synopsis

We have developed a sensitive method to detect very low levels of long chain branching in sparsely branched polymers and applied it to high-density polyethylene samples with broad molar mass distribution obtained by Ziegler–Natta, Phillips, and metallocene catalysis. We compare experimental dynamic moduli with predicted values. The predicted moduli, which are only valid for truly linear chains, are computed from a known molar mass distribution by the application of a modified time-dependent diffusion reptation model described in [van Ruymbeke *et al.*, Macromolecules **35**, 2689 (2002)]. Discrepancies between experimental and predicted moduli are observed at branching levels below the usual detection limit of ^{13}C nuclear magnetic resonance (about 1 branch per 10000 carbon atoms). Our method is easier to implement and the results more clearcut than those obtained by the zero-shear viscosity method. The sensitivity is comparable with the activation energy spectrum method described in [Wood-Adams *et al.*, Macromolecules **33**, 7489 (2000)]. The use of our method is however not restricted to thermorheologically complex polymers. The interest of polymer fractionation is also demonstrated for the detection of extremely low levels of long chain branching. *© 2005 The Society of Rheology.*
[DOI: 10.1122/1.2048743]

---

[a]Present address: FORTH, Department of Materials Science and Technology, Heraklion, Crete, Greece.
[b]Present address: Total Petrochemicals, Feluy, Belgium.
[c]Author to whom correspondence should be addressed; electronic mail: bailly@poly.ucl.ac.be

I. INTRODUCTION

The characterization of long chain branching (LCB) is crucial to understand the viscoelastic behavior of branched polymers in the melt and, as a consequence, for the prediction of their processing behavior. To have a large impact on melt flow behavior, branches must be longer than about twice the entanglement length in the melt. For polyethylene (PE), this length is of the order of 180 carbon atoms [Jordan *et al.* (1989)]. Low-density PE (LDPE) obtained by radical chemistry is known to include many types of branches, with concentrations ranging from 0.6 to 4.1 per 1000 carbon atoms [Axelson *et al.* (1979); Bovey *et al.* (1976)]. On the other hand, high-density PE (HDPE) obtained with the help of 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) [Swogger and Kao (1993); Malmberg *et al.* (1998); Wang *et al.* (1998)]. Long branches are introduced in HDPE by incorporation of vinyl-terminated macromonomers into the growing backbone. There are three major types of transition metal catalysts for HDPE: Ziegler–Natta, 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.* (1994); Malmberg *et al.* (1999); Vega *et al.* (1999)]. In most cases, LCB was detected among the longest molecules [Tung (1959); Agarwal *et al.* (1983); Gabriel *et al.* (2002); Doerpinghaus and Baird (2003)]. According to Soares and Hamielec [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.

Ziegler–Natta HDPE is a particularly tough test for any sparse LCB detection method. By nature of the catalyst, Ziegler–Natta HDPE only contains very low levels of vinyl unsaturations. Hence, inclusion of LCB by incorporation of macromonomers is highly unlikely. For decades, reports on the presence of LCB in Ziegler–Natta catalyzed HDPE have been very scarce. Agarwal *et al.* (1983) have shown evidence of minute levels of LCB in the high molar mass portion of a Ziegler-Natta HDPE. In a recent paper, Reinking *et al.* (2000) reported a new Ziegler vanadium-based catalyst able to produce LCB by a new metathesis mechanism. Very low LCB concentrations in transition metal-catalyzed HDPE (less than 0.1 per 1000 carbon atoms) are not easily detected by solution-based chromatographic or spectroscopic methods such as multidetector size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) [Janzen and Colby (1999); Shroff and Mavridis (1999)] although sophisticated methods can significantly reduce the detection threshold [Wood-Adams *et al.* (2000b)]. By contrast, rheological measurements are very sensitive to traces of LCB [Janzen and Colby (1999); Shroff and Mavridis (1999); Vega *et al.* (1998, 2002); Gabriel *et al.* (2002)]. Many authors have tried to exploit rheology to characterize sparsely long chain branched polymers. At low concentration, increased LCB leads to enhanced zero-shear viscosity (η_0) as well as more pronounced shear thinning and melt elasticity [Vega *et al.* (1998); Wood-Adams *et al.* (2000a, 2000b, 2001); Gabriel *et al.* (2002); Lohse *et al.* (2002); Doerpinghaus and Baird (2003); Wood-Adams and Costeux (2001); Kolodka *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), MM distribution (MMD), and LCB. In shear experiments, broadening the MMD and increasing the level of LCB can have similar effects [Vega *et al.* (2002); Doerpinghaus and Baird (2003); Robertson *et al.* (2004)]. Rheology alone is often ambiguous. For instance, the LCB Dow Rheology Index (DRI), solely based on shear rheology, is specifically designed for polymers with similar

and narrow MMD's and is not applicable otherwise [Lai *et al.* (1994)]. Another example of LCB characterization by rheology alone is the flow activation energy (E_a) method. E_a is deduced from the temperature sensitivity of dynamic viscosity and is often used in the literature to detect LCB in thermorheologically simple polymers. However, branched PE is often thermorheologically complex [Wood-Adams and Costeux (2001) and references therein; Kolodka *et al.* (2004); Wagner *et al.* (2004)]. Therefore, an apparent activation energy, ($\hat{E}_a$), calculated from the temperature dependence of the zero-shear viscosity, must in fact be used [Wood-Adams and Costeux (2001)]. LCB in HDPE can, in principle, be observed from an $\hat{E}_a$ enhancement [Bersted (1985); Hughes (1983); Wood-Adams and Costeux (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 levels of LCB [Wasserman and Graessley (1996); Shroff and Mavridis (1999)].

Recently, approaches combining information coming from both solution separation techniques and shear rheology in the melt have emerged. Shroff and Mavridis (1999), Janzen and Colby (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 the experimental MMD and a predicted MMD based on the viscosity data (Tuminello's inversion method) [Shaw and Tuminello (1994); Wood-Adams and Dealy (2000a)]. Thimm *et al.* (2000) also applied their own inversion scheme for LCB detection purposes. Crosby *et al.* (2002) proposed the dilution-rheology method, which is able to give qualitative indications about the LCB level without resorting to solution techniques. Making the method quantitative requires the 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, such as metallocene HDPE. Recently, Michel (2002) 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 to detect extremely low levels of LCB and to compare the results with those of established rheology-based approaches for HDPE samples with broad MMDs and obtained with different catalytic systems. The new method is based on double reptation modeling 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–Natta, Phillips, and metallocene-catalyzed HDPEs with high polydispersity and different concentrations of LCB. We also study two relatively narrow-disperse fractions of the Ziegler–Natta sample, obtained by Successive Solution Fractionation (SSF) [Stéphenne (2003)].

II. THEORETICAL BACKGROUND

A. Flow activation energy

A common method to investigate the presence of LCB in PE is the determination of the 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 time-independent horizontal time shift factor $a_T(T)$ with a usually small vertical modulus shift correction $b_T(T)$:

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

where $\eta(T)$ and $\eta(T_0)$ are the viscosity at temperatures T and T_0, respectively. The vertical modulus shift factor, b_T, does not depend strongly on temperature in the relatively narrow range accessible for semicrystalline polymers and is often neglected [Ferry (1980); Wood-Adams and Costeux (2001)]. Far from the glass transition temperature, the horizontal shift factor follows an Arrhenius relationship:

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

Linear HDPE shows thermorheological simplicity. By contrast, long chain branched PE is thermorheologically complex, which implies that the effect of temperature on the linear viscoelastic properties cannot be described by a single activation energy but requires a time-dependent spectrum of activation energies [Carella *et al.* (1986)]. In order to compare the behavior at different temperatures, an apparent zero-shear rate activation energy $\hat{E}_a$, calculated from viscosity, can be used [Wood-Adams and Costeux (2001)]:

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

Whereas linear molecules mainly relax by reptation, the relaxation of long chain branched chains is often dominated by arms length fluctuations, the temperature dependence of which can, in principle, be different from that of reptation. In ethylene polymers, the presence of LCB is often associated with an increase of the (apparent) activation energy [Hughes (1983); Bersted (1985); Wood-Adams and Costeux (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 $\hat{E}_a$ above the value reported for linear HDPE can be related to the volume fraction of a branched polymer. E_a values reported for linear HDPE usually range between 25 and 28 kJ/mol [Carella *et al.* (1996); Vega *et al.* (1999); Starck *et al.* (2002)] and do not depend on MM [Wasserman and Graessley (1996)]. While a higher (apparent) activation energy can be attributed to the presence of LCB, the absence of LCB cannot be inferred from a constant activation energy.

   Some materials, notably LDPE, require a significant vertical shift for correct time temperature superposition [Mavridis and Shroff (1992); Wood-Adams and Costeux (2001)]. The vertical shift factor reflects the temperature dependence of the entanglement plateau modulus:

$$b_T = \frac{G_N^0(T)}{G_N^0(T_0)} = \frac{\rho T M_e(T_0)}{\rho_0 T_0 M_e(T)}.\qquad(4)$$

B. 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 relationship for HDPE (at 190 °C):

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

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 [Vega *et al.* (1998); Wood-Adams *et al.* (2000a, 2000b); Wood-Adams and Costeux (2001); Gabriel *et al.* (2002); Lohse *et al.* (2002); Doerpinghaus and Baird (2003); Kolodka *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.

C. Proposed method

In a recent paper, van Ruymbeke *et al.* (2002) 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's, the authors came to the conclusion that the combination of: (i) The TDD model proposed by des Cloizeaux (1990), suitably modified to treat short chains and (ii) generalized double reptation [Tsenoglou (1987); des Cloizeaux (1998)] provides satisfying quantitative predictions.

The main equations of the model are summarized below. The relaxation modulus $G(t)$ of an entangled polydisperse linear polymer is linked to its molecular weight distribution trough the generalized double reptation mixing rule:

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

In Eq. (6), $w(M) = dW(M)/d \, Log(M)$ and $W(M)$ is the weight fraction of chains with molar mass below M, $F_{\mathrm{mono}}(t,M)$ is the relaxation function of the monodisperse polymer of molar mass M, and β is the mixing exponent. Values slightly above 2.0 for the mixing exponent ($\beta = 2.25$ has been used in this work) consistently yield more accurate predictions. Including constraint release effects through double reptation yields:

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

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), we adopt the TDD relaxation function proposed by des Cloizeaux (1990), which combines reptation and contour length fluctuations in a single kernel:

$$F_{sr\mathrm{TDD}}(t,M) = \frac{8}{\pi^2} \sum_{p \, \mathrm{odd}} \frac{1}{p^2} \exp(-p^2 U(t)), \tag{8}$$

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

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

and g is conveniently approximated by

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

In Eq. (9), the reptation time τ_{rept} is linked to the MM through a pure reptation scaling:

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

When combined, Eqs. (6)–(11) represent the TDD with double reptation model (TDD-DR). In addition to G_N^0, the TDD-DR model has basically two material parameters: A polymer-dependent molecular weight M^* in Eq. (9), which is a measure of the fluctuations intensity, and K in Eq. (11). An empirical modification of the model is proposed by van Ruymbeke *et al.* (2002) to include the influence of chains shorter than four times the molecular weight between entanglements (M_e). This modification is not used here. Indeed, it does not change the results for HDPE, presumably because of the low M_e value for this polymer. Inclusion of the Rouse relaxation as described by van Ruymbeke *et al.* (2002) was also found unnecessary for HDPE.

In the proposed method, we 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 for thermorheologically simple systems. Discrepancies will appear in the terminal region in the presence of LCB. The sensitivity of the method should be high because the arm length fluctuations and backbone reptation dynamics of branched chains are dramatically different from the corresponding relaxations of linear chains [McLeish and Milner (1999)]. Since it is based on a direct prediction of rheological properties from knowledge of the molecular distribution, our method is not affected by the narrow dynamic range accessible for PE (as opposed to inverse methods which "back-predict" the distribution from knowledge of rheology).

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 known accurately. In this article, we will use the material parameters obtained by van Ruymbeke *et al.* (2002) for a temperature of 190 °C:

$$G_N^0 = 2.6 \times 10^6 \text{ (Pa)}, \quad K = 1.4 \times 10^{-17} \text{ (g/mol)}^3, \quad M^* = 70\,000 \text{ (g/mol)}. \tag{12}$$

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 article is a further guarantee of the validity of these parameters. While we have made no attempt in this article to expand our detection method toward quantification of LCB, this should be possible, at least on an empirical basis, provided that calibration samples with known LCB in the same range are available.

III. MATERIALS AND METHODS

A. Samples

HDPE samples synthesized by Ziegler–Natta (zPE), Phillips (pPE), and metallocene (mPE) catalysts are used. Sample zPE has been fractionated by 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 I.

TABLE I. Main characteristics of all investigated samples.

	MI[a]	ρ[b]	M_w[c]	M_n[c]	M_z[c]	H[d]	LCBD[e]	T_m^o [f]	T_{cc}^o [f]
ZPE	0.065	0.958	14 7700	21 700	658 700	6.8	_[h]	137.5	115.5
pPE	0.70	0.963	113 600	21 800	475 600	5.2	1.6	135.5	117.5
mPE	$\cdots$	0.950	176 400	56 700	405 700	3.2	5.1	134.5	122.5
F1	$\cdots$[g]	$\cdots$	73 500	21 100	181 000	3.5	$\cdots$[h]	133.0	120.5
F2	$\cdots$[g]	$\cdots$	350 800	85 600	935 400	4.1	$\cdots$[h]	135.5	117.5

[a]Melt flow index measured at 190 °C under 2.16 kg (in g/10 min).
[b]Density measured with pycnometer at 23 °C (in g/cm^3).
[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]LCBD measured by ^{13}C-NMR (in /10^4 C).
[f]Pure melting and crystallization (T_m^o and T_{cc}^o) temperatures in °C, estimated by differential scanning calorimetry at 10 °C/min.
[g]Not enough matter available for correct characterization.
[h]Below ^{13}C-NMR detection limit of 1/10^4 C.

B. Successive solution fractionation

Fractionation of zPE according to MM is accomplished by way of SSF. The method and experimental setup have been described in detail elsewhere [Stéphenne (2003)]. The SSF procedure consists of three consecutive steps: Dissolution, precipitation, and extraction. A 0.7 wt % solution is prepared by dissolving 12 g of sample zPE in 2200 ml 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 for 120 min. During the precipitation step, the solution is cooled down 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 holding for 120 min at that temperature, the solution is pumped through a metallic filter introduced in the SSF vessel and precipitated in a large excess of methanol nonsolvent. The same procedure is repeated at the second dissolution temperature of 160 °C. The precipitate is then filtered, stabilized with Irganox 1010 (2000 ppm), and dried in vacuum at 50 °C.

The stability of the MMD during the fractionation procedure has been checked for zPE by keeping the sample in solution (diphenyl ether) at 160 °C for 48 h under nitrogen atmosphere. After the test, SEC reveals no modification of the MMD.

C. Characterization techniques

1. Differential scanning calorimetry

Thermal analysis is carried out with the help of a differential scanning calorimeter Mettler Toledo 821e. A weighed ($\cong$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 min, and heated to 220 °C at 10 °C/min.

2. Nuclear magnetic resonance

The concentration of long chain branches is determined by ^{13}C-NMR spectroscopy. The spectra are obtained at 135 °C, without broadband decoupling, using a Bruker Ad-

vance 500 pulsed NMR spectrometer at 125 MHz. Polymer solutions are prepared by dissolving 150 mg polymer in 3.5 ml deuterated 1,1,2,2-tetrachloroethane. Detailed parameters of the experiment are listed hereafter: pulse angle, 90°; relaxation time, 15 s; acquisition time, 1.5 s, and number of scans, 10 000.

The chemical shifts assigned to different hydrocarbon groups follow literature [Liu *et al.* (1999); Randall (1977)]. LCB density (LCBD) is calculated using the following equation:

$$\text{LCBD} = \frac{I_{A\alpha}}{3I_{A\,\text{tot}}},\tag{13}$$

where $I_{A\alpha}$ and $I_{A\,\text{tot}}$ are the integral areas of α-CH_2 resonance and total intensity of carbons, respectively [Randall (1977)].

3. Size exclusion chromatography

MMDs are measured on a Waters Alliance GPC/V 2000 instrument with Differential Refractive Index detection (SEC-DRI). Filtered samples are injected at a 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). The 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)]:

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

4. Rheological measurements

Dynamic moduli. Dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, are determined with a strain-controlled rheometer (ARES from TA Instruments) 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 and Costeux (2001) for PE, from the crossover moduli, G_X, at temperature $T_0=190$ °C and T:

$$b_T(T) = \frac{G_X(T)}{G_X(T_0)}.\tag{15}$$

As expected for thermorheologically complex polymers, no single horizontal shift factor can be found. Figure 1 shows this effect for sample pPE: While the experimental data superimpose very well at high frequencies, discrepancies appear at lower frequencies.
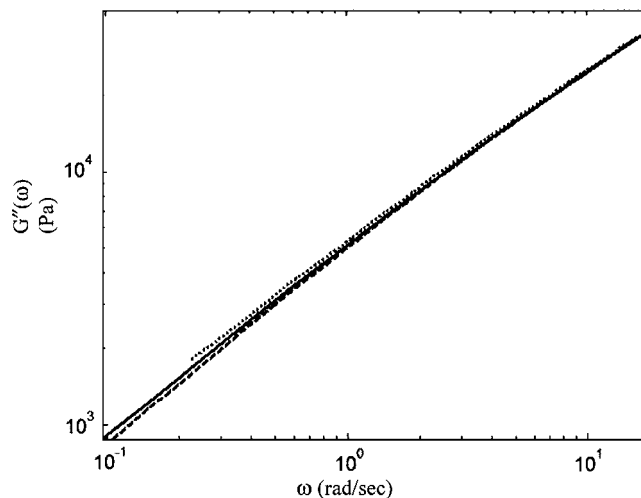
FIG. 1. Effect of thermoreological complexity on the loss modulus G'' vs $a_T(\omega)$ for pPE. Master curve built from experimental data at 150 °C (····), 190 °C (—), and 220 °C (---).

Stress growth tests. The stress growth curves $[\eta^+(t)]$ are measured on a strain-controlled rheometer (RMS 800 from Rheometrics) in steady shear mode with a parallel-plate configuration at 150 °C. We use 40 mm diameter removable plates. Relaxation of the sample is always checked before test by measuring normal force decay. The applied shear rate is 0.001 s^{-1} and the test lasts for 1000 s. All measurements are performed under a dry nitrogen atmosphere. Samples are stabilized as described above. When accessible, 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.

We have 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.

IV. RESULTS AND DISCUSSION

A. Molar mass distribution

MMDs of zPE, pPE, and mPE, as determined by SEC-DRI, are shown in Fig. 2. Corresponding average MM values are listed in Table I. Although the samples have similar weight average molar masses (M_w), they are characterized by distinct MMDs. 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. 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 be considered to be negligible at LCB levels below $1/10^4$ carbon atoms [Crosby *et al.* (2002)].

MMDs of F1 and F2 fractions are shown in Fig. 3. Corresponding average MM values are given in Table I. F1 is characterized by a relatively low M_w (about 74 000 g/mol) and does not contain a significant fraction of chains longer than 10^6 g/mol. Very long molecules are all included in fraction F2 which has therefore very high M_w (about 350 000 g/mol). For zPE, original, and rebuilt MMDs, obtained by summing weighted
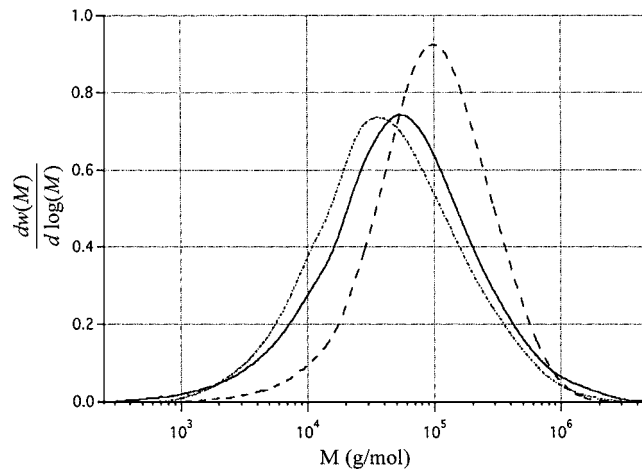
FIG. 2. MMDs of zPE (—), pPE (-•-), and mPE (--).

distributions of fractions F1 (78 wt %) and F2 (22 wt %), are compared in Fig. 3. 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 sample.

B. Short chain branching

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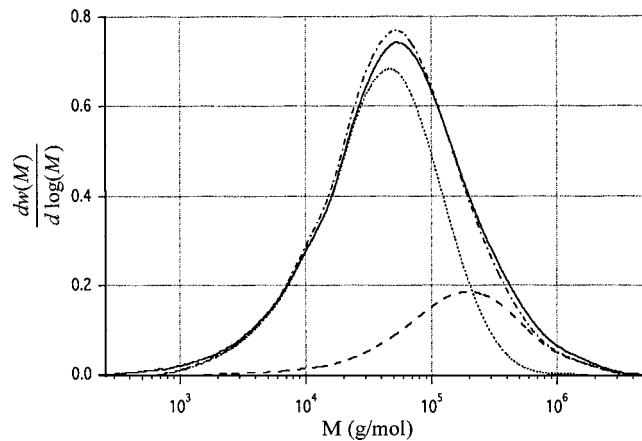

FIG. 3. MMDs of zPE and fractions. Original sample (—), fraction F1 (•••), fraction F2 (---), MMD rebuilt from fractions (-•-). F1 and F2 fractions, respectively, represent 78 and 22 wt % of the total collected matter.
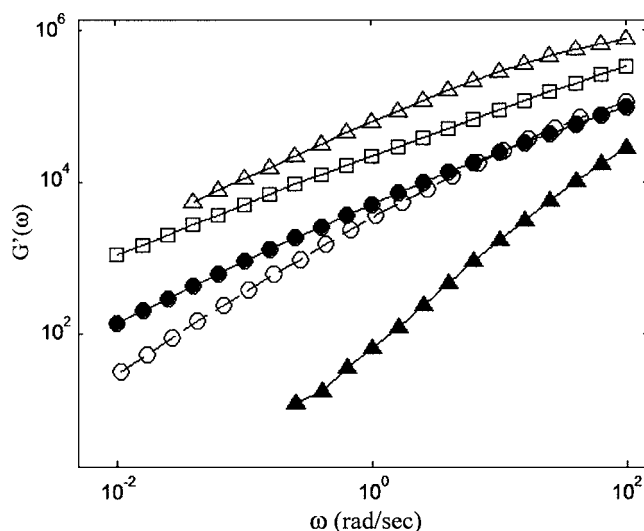
FIG. 4. Storage moduli $G'(\omega)$ of zPE ($\bigcirc\bigcirc$), pPE ($\bullet\bullet$), mPE ($\square\square$), F1 ($\blacktriangle\blacktriangle$), and F2 ($\triangle\triangle$), at 190 °C.

C. Long chain branching

1. Nuclear magnetic resonance method

LCBD has been evaluated by ^{13}C-NMR. It must be kept in mind that NMR cannot distinguish branches with lengths higher than six carbon atoms, while the rheologically relevant branches are those long enough to entangle, that is at least 180 carbon atoms for PE. Although the use of sophisticated methods and instruments can reduce the detection threshold significantly, quantification of LCB by ^{13}C-NMR is usually limited to levels above about $1/10^4$ carbon atoms [Janzen and Colby (1999); Shroff and Mavridis (1999); Wood-Adams *et al.* (2000b); Crosby *et al.* (2002)].

Results are presented in Table I for all investigated samples. No LCB has been detected for Ziegler–Natta catalyzed zPE or its F1 and F2 fractions. If LCB is present, it is at LCBD below the detection limit of our ^{13}C-NMR method. Phillips and metallocene catalyzed HDPEs contain small amounts of LCB. Sample mPE is more branched. At such low levels, the LCB values reported in Table I are relative rather than absolute. MMDs obtained by SEC-DRI may be considered as correct for F1, F2, zPE, and pPE. 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.

2. Rheological methods

For all samples investigated, G' and G'' moduli at 190 °C are plotted as a function of angular frequency in Figs. 4 and Fig. 5, respectively.

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 for the longest molecules, suggests the presence of LCB in samples pPE and mPE. On the single basis of M_z values 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.
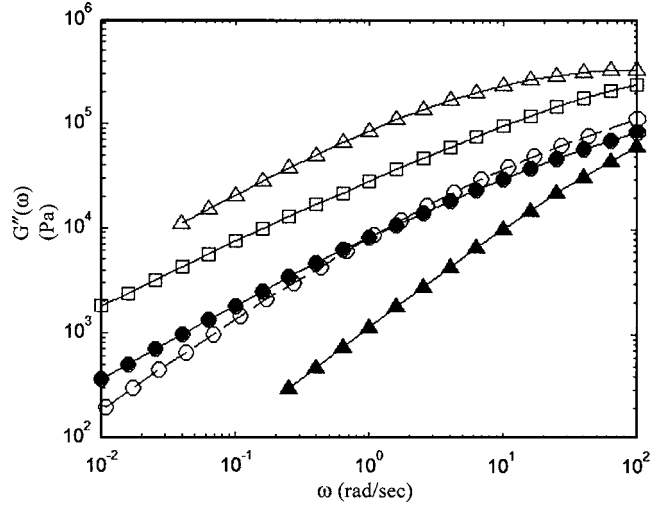
FIG. 5. Loss moduli $G''(\omega)$ of zPE (○○), pPE (●●), mPE (□□), F1 (▲▲), and F2 (△△), at 190 °C.

Flow activation energy method. According to the procedure proposed by Wood-Adams and Costeux (2001), the activation energy spectrum, $E_{a,i}$, is calculated from the storage moduli of all investigated samples. Results are shown in Fig. 6 and reported in Table II. Because it is difficult 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 and Costeux (2001)]. Samples pPE and mPE clearly show thermorheological complexity and present the highest $E_{a,i}$ values, respectively from 33 to 37 kJ/mol and from 40 to 50 kJ/mol, well above $E_{a,i}$ values reported for linear HDPE (between 25 and 28 kJ/mol). The thermorheologically simple behavior of F1 is demonstrated by the low and constant value of its activation energy (about 23 kJ/mol). The values calculated for unfractionated zPE, around 30 kJ/mol, also seem constant. By contrast, F2 shows a
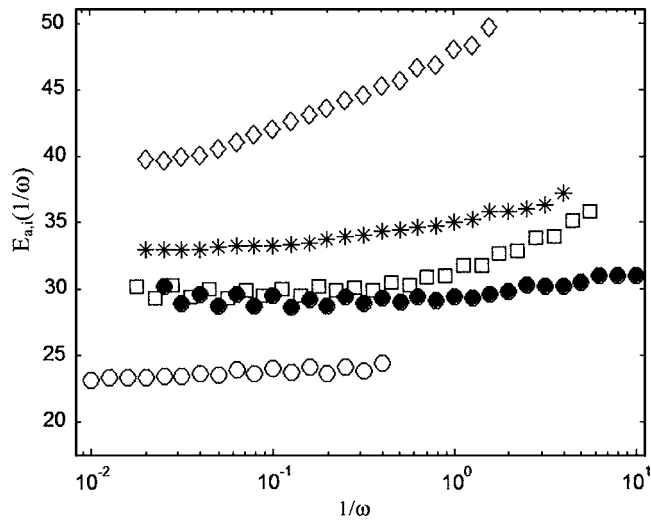

FIG. 6. Activation energies spectra ($E_{a,i}$ vs $1/\omega$) of zPE (●●), pPE (∗∗), mPE (◇ ◇), F1 (○○), and F2 (□□).

TABLE II. Horizontal (E_{ai}) flow activation energies for all investigated samples.

	$E_{a,i}$ (kJ/mole)
zPE	31
pPE	33–37
mPE	40–50
F1	23
F2	30–36

time-dependent activation energy, starting from 30 kJ/mol, up to 36 kJ/mol. A vertical shift factor is needed for samples pPE, mPE, and F2. For samples F1, pPE, and mPE, the LCBD measured by NMR correlates well with E_{ai}. Sample 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/mol) and F2 presents a thermorheologically complex behavior. 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 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. 7, we plot η_0, when accessible, or otherwise $\eta^+(1000 \text{ s})$ as a function of M_w at 150 °C for all of the samples. Equation (3) shifted to 150 °C (assuming an activation energy of 25 kJ/mol) is also drawn for comparison purposes. We could measure a steady viscosity level after 1000 s for the zPE and F1 samples; which we assume to represent the zero shear viscosity, considering the very low shear rate used (10^{-3} s^{-1}). On the other hand, no steady viscosity level was reached after 1000 s for samples pPE, mPE, and F2. Instead, we report the value $\eta^+(1000 \text{ s})$ measured at the end of the test. The zero-shear viscosity for those samples has to be higher than the measured figure. Figure
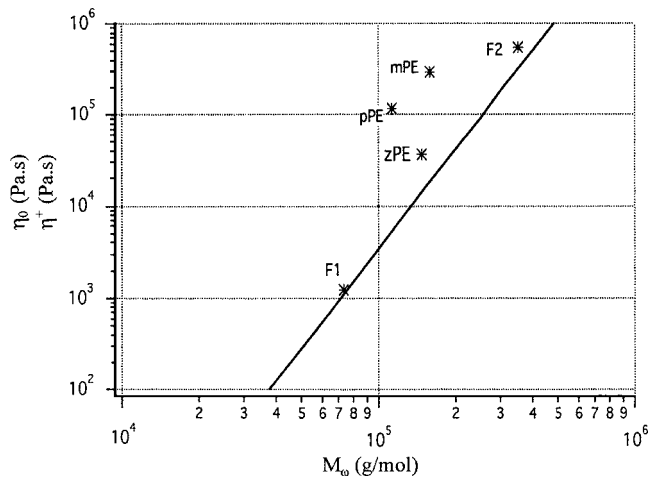

FIG. 7. Zero-shear viscosity η_0 (for zPE and F1) or η^+ (for pPE, mPE, and F2) vs weight-average MM *Mw*. The stars are the experimental data and the line represents Eq. (3) shifted to 150 °C.
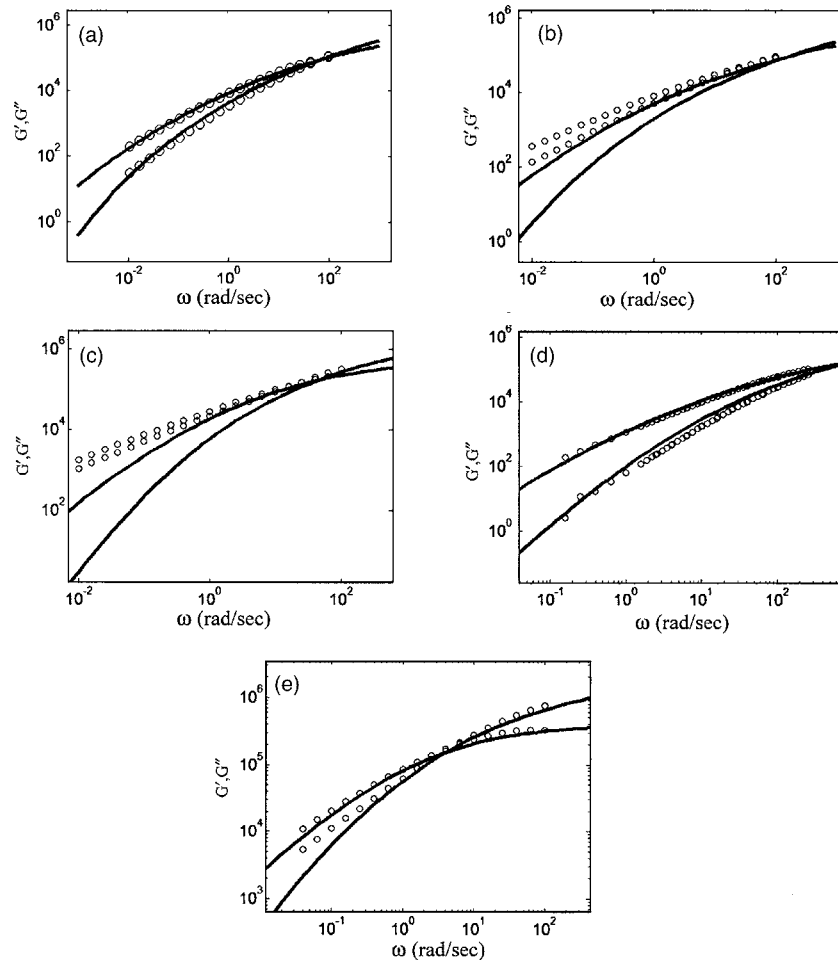
FIG. 8. Experimental (○○○) and predicted (—) dynamic moduli using the proposed method for (a) zPE, (b) pPE, (c) mPE, (d) F1, and (e) F2, at 190 °C. Master curves have been used for zPE and F1.

7 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). Therefore, F1 is certainly linear while the other samples are probably long chain branched (zPE being uncertain).

Proposed method. In Fig. 8, the experimental dynamic moduli are compared with theoretical moduli predicted by the reptation model from the experimental MMDs. Taking into account their constant horizontal shift factor, master curves could be used for F1 and zPE. 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 others. This implies that F2, mPE, and pPE 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 agreement with η_0 and $E_{a,i}$ results, our method clearly shows that F2 includes some LCB, which confirms the thermorheological

complexity observed from the $E_{a,i}$ spectrum. F2 being a high MM fraction of zPE, zPE thus incorporates some LCB in its high molar mass fraction. The LCB concentration is however so low that it does not significantly influence the activation energy spectrum of the unfractionated polymer 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 behavior, G' and G'' must follow the well-known frequency dependence:

$$G' \propto \omega^2, \quad G'' \propto \omega. \tag{16}$$

From Figs. 4 and 5, 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 startup 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 and Costeux (2001)], while our NMR method has proved insensitive. The fractionation step has in essence brought the effect of LCB on dynamic moduli back into the experimental window.

V. 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 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 approach based on the activation energy spectrum analysis but more general since it is not restricted to thermorheologically complex polymers. 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 a LCB level so low that the rheological behavior is not significantly affected in the experimental frequency window. In such cases, the interest of MM fractionation becomes evident. The presence of LCB on the longest molecules has been revealed in this manner for the Ziegler–Natta-catalyzed HDPE sample.

As it stands, our method does not allow quantification of the LCB content, although an empirical modification in this direction seems possible, provided that calibration samples with known LCB levels are available in the same range. Moreover, the method is general and can be applied for the detection of sparse LCB in other polymers than polyethylene. ^{13}C-NMR spectroscopy is the only absolute quantification method available at the moment. Unfortunately, NMR cannot distinguish branch lengths higher than six carbon atoms, while the rheologically relevant branches are much longer. An absolute quantitative rheology-based method is therefore still very much needed.

ACKNOWLEDGMENTS

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

Carella, J. M., J. T. Gotro, and W. W. Graessley, "Thermorheological effects of long-chain branching in entangled polymer melts," Macromolecules **19**, 659–667 (1986).

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., "Relaxation and viscosity anomaly of melts made of long entangled polymers: Time-dependent reptation," Macromolecules **23**, 4678–4687 (1990).

des Cloizeaux, J., "Double reptation vs simple reptation in polymer melts," Europhys. Lett. **5**, 437–442 (1988).

Doerpinghaus, P. J., and 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., 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," Annu. Tech. Conf.-Soc. Plast. Eng. **29**, 306–309 (1983).

Janzen, J., and R. H. Colby, "Diagnosing long-chain branching in polyethylene," J. Mol. Struct. **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," Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **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. Appl. Polym. Sci. **92**(1), 307–316 (2004).

Lai, S. Y., J. R. Wilson, G. W. Knight, and J. C. Stevens, US Patent No. 5,278,272 (1994).

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," Annu. Tech. Conf.-Soc. Plast.

Eng. **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 polymerized 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, "Characteristics 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," *Proceedings of the 60th Annual SPE Technical Conference*, Vol. 1, pp. 983–987 (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., Polym. 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. Sci., Polym. Phys. Ed. **17**, 1223–1235 (1979b).

Randall, J. C., *Polymer Sequence Determination-Carbon-13 NMR Method* (Academic, New York, 1977).

Reinking, M. K., G. Orf, and D. McFaddin, "Mechanistic studies on the formation of long-chair branching in polyethylene," *Proceedings of 'Polyolefins 2000' International Conference on Polyolefins (SPE)*, Houston (2000), pp. 259–267.

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-Catalyzed 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).

Stéphenne, V., PhD thesis, Université Catholique de Louvain, Louvain la Neuve, 2003. Electronic file accessible at ⟨http://edoc.bib.ucl.ac.be:81/ETD-db/collection/available/BelnUcetd-09032003-145631/⟩

Swogger, K. W., G. M. Lancaster, S. Y. Lai, and T. I. Butler, "Improving polymer processability constrained geometry single site catalyst technology," J. Plast. Film Sheeting **11**, 102–112 (1995).

Thimm, W., C. Friedrich, T. Roths, S. Trinkle, and J. Honerkamp, "Characterization of long chain branching effects in linear rheology," Los Alamos National Laboratory, e-print cond-mat/0009169.

Tsenoglou, C., "Viscoelasticity of binary polymer blends," Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) **28**, 185–186 (1987).

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

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 (on-line computer file), paper No. 46 (2002).

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).

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).

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 polymerization with constraint geometry catalyst," Polymer **45**(19), 6495–6505 (2004).

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

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

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

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

Wood-Adams, P. M., and S. Costeux, "Thermorheological behavior of polyethylene: Effects of microstructure and long chain branching," Macromolecules **34**, 6281–6290 (2001).