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A technique to infer structural information for low level long chain branched polyethylenes

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Abstract

A technique is proposed to relate the weight average molecular weight of linear chains, M_{wBL}, in low level long chain branched polyethylenes to their linear viscoelastic data. The new method is based on a previously reported empirical technique [Macromolecules 33 (2000) 7481] and was developed through the use of basic molecular theories. The new technique was applied to model systems whose linear viscoelastic properties were simulated using the molecular model of Milner et al. [Macromolecules 31 (1998) 9345] and to long chain branched metallocene polyethylenes. It is applicable to branched polyethylenes with low levels of long chain branching. In the case of a branched metallocene polyethylene, the structural parameter, M_{wBL}, inferred from the rheological data together with the GPC data such as M_{w} or M_{n} of the sample describes all aspects of the structure of the polymer. In the case of highly branched polymers, a possible modification of the technique is also proposed.

Keywords: Molecular structure; Metallocene polyethylene; Rheology

1. Introduction

With metallocene catalysts, polyethylene can be polymerized in such a way that long chain branches are incorporated into the polymer backbones thus improving the processability [3]. It is desirable to be able to evaluate the long chain branching level in industrial polymers in order to produce a polymer with expected flow properties. For branched metallocene polyethylenes, the average numbers of branch points per 1000 carbons (λ) can be directly measured with ^{13}C nuclear magnetic resonance or calculated from triple-detector gel permeation chromatography results [4] using the Zimm–Stockmayer equations [5]. These methods are costly and time consuming and alternate approaches are needed. Because of the strong effect of long chain branches on linear viscoelastic properties, techniques for inferring levels of long chain branching from linear viscoelastic properties are attractive. However, care must be taken when formulating and using such techniques as they are not primary measurements and one must be sure to have a full understanding of the assumptions and limitations. The object of this work is therefore to develop a technique to relate structural information to linear viscoelastic data based on the empirical method proposed by Wood–Adams and Dealy [1]. The assumptions in developing the new technique and the limitations of its application are clarified. In the case of highly branched polymers, a modification of the technique is also proposed. The development of the technique involved taking into account our current understanding of the structure of metallocene polyethylenes [6] and applying a molecular theory for predicting the linear viscoelasticity (LVE) of model branched systems.

2. Molecular structure of long chain branched metallocene polyethylene

Recent developments in the understanding of the details of the molecular structure of long chain branched metallocene polyethylenes [6,7] have provided a clear vision for correlating structural information with rheological data. In

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Nomenclature

Structural parameters

β	Average number of branch points per molecule
f_{s}	Weight fraction of stars in model system
$F_{\mathrm{N}}(n)$	Number fraction of chains with n branch points
M	Molecular weight
M_{w}, M_{n}	Weight and number average molecular weight
m	Reduced molecular weight (M/M_{w})
$M_{\mathrm{w,s}}$, $M_{\mathrm{n,s}}$	Weight and number average segment molecular weight
M_{wBL}	Weight average segment molecular weight
m_{gpc}	Peak (reduced) molecular weight in GPC MWD
m_{vis}	Peak (reduced) molecular weight in viscosity MWD
M_{a}	Molecular weight of the star arms in the model system
M_{e0}	Entanglement molecular weight
m_{B}	Peak (reduced) molecular weight in the viscosity MWD of the branched polymer (exactly equal to m_{vis})
m_{L}	Peak (reduced) molecular weight in the viscosity MWD of the linear equivalent (exactly equal to m_{gpc})
P_{b}	Flory branching probability

Rheological parameters

α	Exponent in the power law relationship between η_0 and M_{W} of linear polymers
η^*	Absolute value of the complex viscosity, Pa s
ω	Frequency, rad/s
ω_{c}	Critical frequency
ω_{L}	Frequency corresponding to m_{L}
ω_{B}	Frequency corresponding to m_{B}
G'	Storage modulus
G''	Loss modulus
$\phi(s)$	Unrelaxed fraction of entanglements
s	Fractional distance along the star arm from the free end
$\tau_{\mathrm{rep,L}}$	Reptation time of the weight average linear chain in a branched polymer
v	Negative of the slope in the power law region of the complex viscosity curve

this section we summarize some of the important facets of the molecular structure of long chain branched metallocene polyethylenes (LCB mPE) and later demonstrate how these can be related to rheological data. Note that the statistical models for the structure of LCB mPE [6,7] are based upon two assumptions: that (1) the polymerization follows the mechanism proposed by Soares and Hamielec [8] and that (2) the polymerization takes place in a continuous stirred tank reactor at steady state. Both of these assumptions are appropriate for the materials considered here.

For a branched chain, regardless of its architecture, it can always be considered to be made up of two types of segments: free arms (one end free and the other attached to a branch point) and inner backbones (both ends attached to branch points). Additionally linear chains in a branched polymer are considered to be a third type of segment. In LCB mPE made with one single-site catalyst, all three types of segments have identical Flory molecular weight distributions [9] with a polydispersity index $M_{\mathrm{w,s}}/M_{\mathrm{n,s}}$ of approximately 2, in which $M_{\mathrm{w,s}}$ and $M_{\mathrm{n,s}}$ are the weight and number average molecular weights of segments [6,7]. The average number of branch points per molecule, β, is the single parameter necessary to describe the topology of single-site catalyst LCB mPE. The only other parameter necessary to complete the description of the molecular structure of the whole system is a molecular weight, typically the number or weight average molecular weight of the molecular segments. With these two parameters, or two related measurable parameters, one can then describe analytically any aspect of the molecular structure of metallocene polyethylenes using the results of Refs. [6,7].

For example, M_{w} and $M_{\mathrm{w,s}}$ are related as:

$$M_{\mathrm{w}} = (\beta + 1)(2\beta + 1)M_{\mathrm{w,s}} \tag{1}$$

where M_{w} can be measured using GPC with a light scattering detector. Then if $M_{\mathrm{w,s}}$ is known, β can be calculated from Eq. (1). With the knowledge of any two parameters in Eq. (1), one can describe any aspect of the molecular structure of metallocene polyethylenes.

According to Costeux et al. [6], $F_{\mathrm{N}}(n)$, the number fraction of chains with n branch points, can be expressed as:

$$F_N(n) = C(n)P_b^n(1 - P_b)^{n+1} \tag{2}$$

where

$$C(n) = \frac{(2n)!}{n!(n+1)!}$$

and

$$P_b = \frac{\beta}{2\beta + 1}$$

P_b is the branching probability, and is usually small (~ 0.15) in typical long chain branched metallocene polyethylenes. From Eq. (2) we can calculate the fraction of linear chains, which is $F_N(0) = 1 - P_b$. When P_b is small, $F_N(0)$ is close to 1, which indicates that in such a system most of the chains are linear. The fraction of chains with one branch point (star-like) is $F_N(1) = P_b(1 - P_b)^2$, which is much smaller than that of linear chains. With increasing n, the fraction $F_N(n)$ decreases. Therefore, in metallocene polyethylenes with low level of long chain branching, there are mainly linear chains, some star-like molecules and fewer molecules with more than one branch point.

The understanding of the structure of metallocene polyethylene allows the development of 'model systems' which have much simpler molecular structures than metallocene polyethylenes but still exhibit certain appropriate statistical characteristics. The model system that we consider in this work is the simplest possible model analogue of mPE: a bi-disperse mixture of linear molecules and 3-arm stars where the linear chains and the star arms are of the same molecular weight. This system resembles metallocene polyethylenes with low levels of long chain branching, except that in the model system both the linear chains and the star molecules are monodisperse. A detailed description of model systems and the prediction of their linear viscoelastic properties are presented in Section 4. The purpose of considering the model system is that it will allow us to use the tube model to study the effect of level of long chain branching on certain aspects of LVE. Since our model system has specific statistical characteristics in common with real LCB mPE the observations that are made in our simulations are applicable to LCB mPE. This point will be further explained and validated later in this article.

3. Rheological determination of long chain branching level

Wood–Adams and Dealy [1] (WA&D) proposed an empirical method to infer the long chain branching level, λ, for single-site catalyst metallocene polyethylenes from linear viscoelastic data. Detailed information is given in Ref. [1] and the following is a brief summary of the technique. The technique was based on a comparison of the molecular weight distribution (MWD) from GPC and a MWD derived from the complex viscosity. The 'viscosity MWD' is derived from the measured complex viscosity by making use of a technique developed by Shaw and Tuminello [10] that is only applicable for strictly linear polymers. The transform equation relating the absolute value of the complex viscosity to the MWD function is:

$$w(\log m) = \left[\frac{-\ln(10)}{m\upsilon^2}\right] \times \left[\frac{\eta^*}{\eta_0}\right]^{1/\alpha}\left[\alpha\frac{d^2\ln\eta^*}{d\ln\omega^2} + \upsilon\frac{d\ln\eta^*}{d\ln\omega} + \left(\frac{d\ln\eta^*}{d\ln\omega}\right)^2\right] \tag{3}$$

The slope in the power law region of viscosity curve ($\sigma = k\dot{\gamma}^{-\upsilon}$) is $-\upsilon$, and α is the exponent in the relationship between viscosity and molecular weight (3.6 in this work). The zero-shear viscosity is given by η_0. The reduced molecular weight, m, is the true molecular weight divided by the weight average molecular weight:

$$m = M/M_w \tag{4}$$

According to Shaw and Tuminello [10], m is related to the frequency by

$$\omega = \frac{\omega_c}{m^{\alpha/\upsilon}} \tag{5}$$

The critical frequency (ω_c) is equal to the frequency at which the low frequency plateau ($\eta = \eta_o$) intersects the line fitted to the power law portion of the log–log viscosity curve, shown in Fig. 1.

For linear polymers, Shaw and Tuminello's technique gives a viscosity MWD very close to that determined by GPC. However, when this transform is applied to the LVE properties of a LCB polymer the resulting MWD is different from the GPC MWD as shown in Fig. 2. The viscosity MWD of a branched sample is bimodal and the low molecular weight peak (highest or primary peak) is shifted to the left of the peak of GPC MWD. The shift of the peak location is the basis of WA&D technique.

Transformation of complex viscosity to MWD was performed on several low level long chain branched metallocene polyethylenes. The molecular characteristics of the samples are listed in Table 1, where HDL1 is a linear sample, which was synthesized under the reaction conditions that minimize the likehood of LCB formation [4]. HDB1-4 are branched samples with increasing level of branching.

An empirical relation was then formed by directly

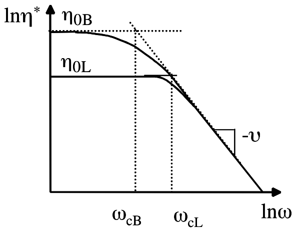

Fig. 1. Sketch of complex viscosity curves of linear and branched polymers.

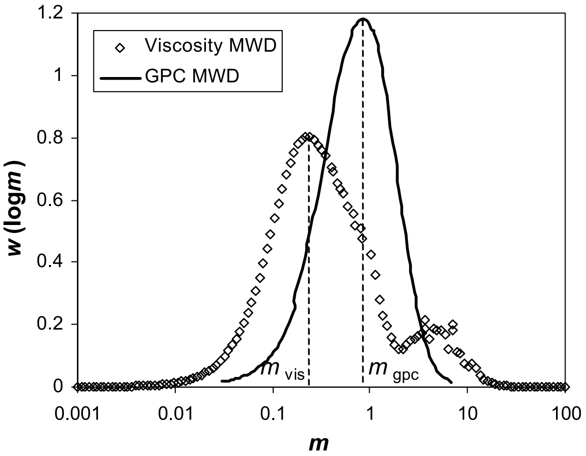

Fig. 2. Comparison of relative position of GPC and viscosity MWD peaks for a branched mPE. The dash lines indicate the peak locations.

relating λ, the branch points per 1000 carbons, to the shift of the peak location in two MWDs for these metallocene polyethylenes. The parameter λ was measured by ^{13}C nuclear magnetic resonance as indicated in Table 1. By fitting the results in Table 1, they found the following correlation:

$$\lambda = 0.1125 \times \log\left(\frac{m_{gpc}}{m_{vis}}\right) \tag{6}$$

where m_{gpc} and m_{vis} are the primary peak locations in GPC and viscosity MWD, respectively as shown in Fig. 2. We call m_{gpc}/m_{vis} the peak ratio.

To understand the physical meaning of the peaks in viscosity MWD, we choose the simple model system described previously. An appropriate molecular model [2] was then applied to the model systems of various compositions to predict their linear viscoelastic properties. For each model system, the viscosity MWD was calculated from the predicted complex viscosity, and the highest peak in the viscosity MWD is then identified and attributed to a relaxation mechanism based on molecular theory and certain assumptions. To calculate the linear viscoelastic properties of the model systems we use a slightly modified version of the theory of Milner et al. [2]. The main features of this theory and the details of our modification are presented in a following section.

Table 1
Molecular characteristics of metallocene polyethylenes

Resin	M_w[a]	M_w/M_n	m_{gpc}/m_{vis}	λ (LCB/10^3C[a])
HDL1	93,000	2.08	1	0
HDB1	77,000	1.98	1.73	0.026
HDB3	86,000	1.99	2.51	0.042
HDB4	96,000	2.14	4.69	0.08

[a] Molecular weight was measured by low angle laser light scattering detector gel permeation chromatography; LCB was measured by nuclear magnetic resonance.

4. Prediction of LVE for bi-disperse blends of stars and linear molecules

Here we summarize the main features of the Milner et al. model and the details are given in Ref. [2]. As mentioned previously, the model system we use is a bi-disperse mixture of linear molecules and 3-arm stars. The prediction of the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ requires taking into account all of the stress relaxation processes of the two components in the blend. We begin by considering that all molecules are confined in a tube defined by entanglements with other molecules. Linear chains free themselves from the entanglement stress by end fluctuations and reptation, whereas, for 3-arm stars the branch point prevents reptation.

The chronology of the relaxation processes is:

4.1. Dynamic dilution

At short times, both linear chains and 3-arm stars relax by end fluctuations. This is the fastest process to eliminate stress. At this timescale, linear chains are considered as 2-arm stars and the relaxation of all molecules is described in the same way. As this process continues, the fraction of unrelaxed material decreases, reducing the number of entanglements for each molecule. This ‘dilution’ of entanglements reduces the stress on the molecules, slowing down the process itself and the relaxation time grows exponentially with the distance on the arm from the free end.

4.2. Reptation of linear chains

Conventionally, the relaxation time needed for a linear chain with N monomers to reptate out of its entanglement tube is proportional to N^3. However, in this model, only the part of the linear chain that did not relax during dynamic dilution needs to reptate. All linear chains in the system we are considering have the same length and therefore will reptate simultaneously. Because the system consists of mostly linear chains, the reptation process frees most of the entanglements.

4.3. Constraint release

Just after reptation of the linear chains the stars are far less entangled, but cannot instantaneously adjust themselves to the new environment, in other words, the tube diameter for stars cannot increase as fast as reptation. Instead it gradually explores the ‘supertube’ of larger diameter determined by the remaining entanglements. This exploration is a Rouse type motion of the star tube, and is accompanied by a swelling of the tube as the unrelaxed fraction decreases. This process ends when the star tube is as large as the supertube defined by the entanglements of unrelaxed star arms.

4.4. Recovery of dynamic dilution

The star molecules then restart the fluctuation (retraction) relaxation process. The very long relaxation time typical of branched systems is due to this process.

In this work we used a slightly modified version of the model described above. In regimes 3 and 4, in addition to the relaxation described above, we dynamically compare the remaining unrelaxed chain length with the diluted tube diameter, and we consider that the whole relaxation process finishes when the following criterion is met:

$$(1-s)M_{\mathrm{a}} < \frac{M_{\mathrm{e}0}}{\phi(s)} \tag{7}$$

In this equation s is the fraction of the length of the arms that has fluctuated and freed itself from entanglements ($s=0$ at the end of the arm and $s=1$ at the branch point), M_{a} is the arm molecular weight, $M_{\mathrm{e}0}$ is the entanglement molecular weight and $\phi(s)$ is the unrelaxed fraction of entanglements. The left hand side of Eq. (7) is the unrelaxed arm length and the right hand side is the enlarged entanglement length. Therefore we assume that relaxation is complete when the unrelaxed arm length is smaller than the enlarged entanglement length. Actually when the criterion in Eq. (7) is met, the stars are not entangled any more and the remaining stress should be relaxed by Rouse motion. This Rouse motion in the diluted entanglement environment is so fast that we approximate that the relaxation is finished when Eq. (7) is met. This modification is manifested in the relationship between η_0 and f_{s} (weight fraction of star in the mixture) at low f_{s} as shown in Fig. 3. From Fig. 3 we can see that at low star fraction, the original model predicted that the zero shear viscosity of blends is lower than that of a purely linear system. This is due to the inclusion of regimes 3 and 4, which should not occur at such low star fractions. At these low levels, after the reptation of linear chains, the unrelaxed arm length is smaller than the enlarged entanglement length and therefore the stars must relax in a Rouse motion rather than via dynamic dilution.

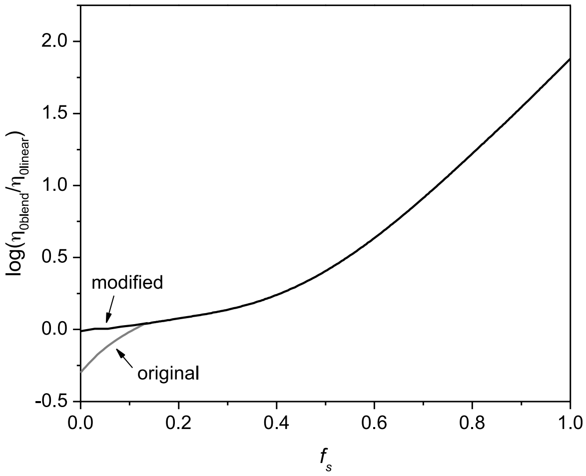

Fig. 3. Prediction of zero shear viscosity for bi-disperse model systems with various weight fractions of stars, f_{s}, using original and modified molecular model.

The modified molecular model was then used to predict the linear viscoelastic properties of model systems, which have various star arm length M_{a} and various weight fractions of star molecules f_{s}. As mentioned previously, in order that our simulated systems retain appropriate aspects of the molecular structure of long chain branched metallocene polyethylenes we set the molecular weight of the linear molecules, M_{L} equal to M_{a}. The arm length M_{a} and weight fraction of star molecules f_{s} of each model system are listed in Table 2.

The parameters in the molecular model are the usual monomer chemistry dependent parameters: the plateau modulus, G_0, the entanglement molecular weight, M_{e} and the Rouse time of an entanglement length, τ_{e}. For these three parameters we chose values typical for polyethylene: $G_0 = 4.9\times10^4$ Pa, $M_{\mathrm{e}} = 1250$ g/mol and $\tau_{\mathrm{e}} = 2\times10^{-7}$ s.

Fig. 4 shows an example of a complex viscosity curve for a monodisperse linear polymer and one of the simulated blends. Because the two systems have the same segment molecular weight, the early time relaxation mechanisms, arm fluctuation and reptation of linear chains are the same; therefore, they have the same behavior in the high frequency zone. Differences are shown in the low frequency region in that the branched system has a higher zero shear viscosity and a broadened transition from the Newtonian plateau to the power law zone.

The simulated complex viscosities of model systems were then transformed into viscosity MWDs by using Shaw and Tuminello's technique [10] (Eq. (3)). Fig. 5 shows the viscosity MWD of the binary system shown in Fig. 4. This transformation from complex viscosity to MWD was performed for all the model systems listed in Table 2 and the results were subjected to the analysis described in the following two sections.

Table 2
Arm length M_{a} and weight fraction of star molecules f_{s} of each model system

Systems	M_{a}	f_{s}
M1-1	100,000	0.05
M1-2	100,000	0.1
M1-3	100,000	0.2
M2-1	60,000	0.05
M2-2	60,000	0.1
M2-3	60,000	0.2
M3-1	40,000	0.05
M3-2	40,000	0.1
M3-3	40,000	0.2
M4-1	30,000	10^{-6}
M4-2	30,000	0.2
M4-3	30,000	0.4

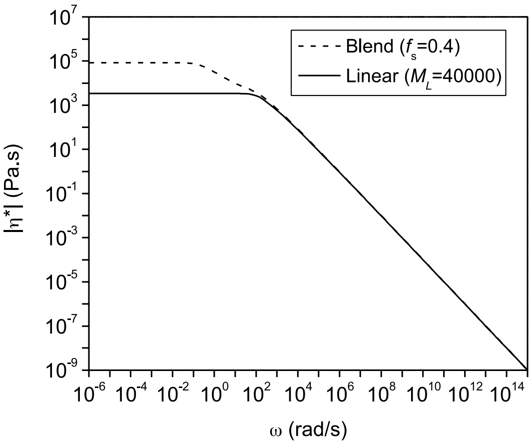

Fig. 4. Predicted complex viscosity of a monodisperse linear system (solid line) and a binary system (dashed line) with linear molecules of the same molecular weight.

5. Inferring a structural parameter from LVE data

Because the linear viscoelastic properties of polymers are the result of complex relaxation behavior of different chain architectures in a polydisperse environment, the viscosity MWD obtained from the linear viscoelastic properties has multiple peaks and their physical meanings are difficult to specify. Therefore, we start with the simpler model systems to identify each peak in the viscosity MWD.

Scanning from low to high molecular weight in Fig. 5 we can see one shoulder and two distinct peaks. Because the MWD in Fig. 5 was obtained from linear viscoelastic properties, these peaks are directly related to different relaxation mechanisms. The shoulder in the low molecular weight region corresponds to the early time 'dynamic dilution'. The tall (primary) peak results from the reptation of linear chains and the short peak at the high molecular weight is related to the long time recovered dynamic dilution of star molecules.

Now we explain why the viscosity MWD is compared to the GPC MWD. In fact, we assume there is a hypothetical linear polymer having exactly the same MWD as that of the corresponding branched polymer. We call such a hypothetical linear polymer a 'linear equivalent' of the branched polymer. Theoretically the viscosity MWD of the linear equivalent should be the same as the GPC MWD. Therefore, in the comparison between the viscosity MWD of a branched polymer and its GPC MWD, the GPC MWD is actually the viscosity MWD of the linear equivalent. The differences from the comparison should be due to the molecular chain structure (linear or branched) because the two parties have exactly the same MWD. For simplicity we still call the viscosity MWD of the linear equivalent GPC MWD, and its primary peak location, m_{gpc}, corresponds to the reptation of chains with an average molecular weight equal to that of the branched polymer, which is simply called m_{L} in the following equations. We now try to relate the peak ratio to topology information. The peak ratio is $m_{\mathrm{gpc}}/m_{\mathrm{vis}}$, where m_{vis} is the primary peak location in the viscosity MWD of the branched sample, which is expressed as m_{B} is the following equations.

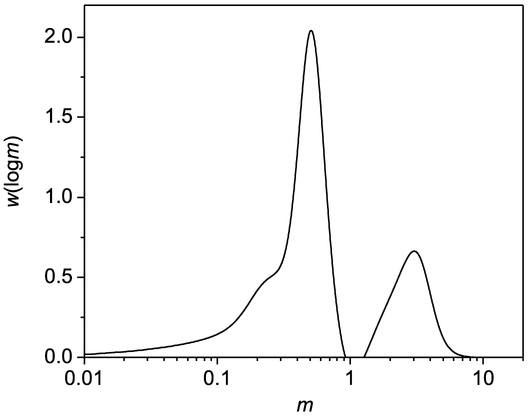

Fig. 5. Viscosity MWD calculated from complex viscosity using Eq. (3) for the blend with $f_s = 0.4$ and $M_L = 40,000$.

$$\log(PR) = \log\left(\frac{m_{\mathrm{gpc}}}{m_{\mathrm{vis}}}\right) = \log\left(\frac{m_{\mathrm{L}}}{m_{\mathrm{B}}}\right) \tag{9}$$

from Eq. (5) we obtain the following relation,

$$m = \left(\frac{\omega_{\mathrm{c}}}{\omega}\right)^{\upsilon/\alpha} \tag{10}$$

By substitute Eq. (10) into Eq. (9) we have

$$\begin{aligned}\log(PR) &= \log\left[\left(\frac{\omega_{\mathrm{cL}}\omega_{\mathrm{B}}}{\omega_{\mathrm{L}}\omega_{\mathrm{cB}}}\right)^{\upsilon/\alpha}\right] \\ &= \log\left[\left(\frac{\omega_{\mathrm{cL}}}{\omega_{\mathrm{cB}}}\right)^{\upsilon/\alpha}\right] + \left[\log\left(\frac{\omega_{\mathrm{B}}}{\omega_{\mathrm{L}}}\right)^{\upsilon/\alpha}\right] \end{aligned} \tag{11}$$

where ω_{B} and ω_{L} are the frequencies in the LVE data corresponding to primary peak locations in the viscosity MWD. From Fig. 1 we derive Eq. (12)

$$\frac{\eta_{0\mathrm{B}}}{\eta_{0\mathrm{L}}} = \left(\frac{\omega_{\mathrm{cL}}}{\omega_{\mathrm{cB}}}\right)^{\upsilon} \tag{12}$$

and then substitute Eq. (12) into Eq. (11):

$$\log(PR) = \frac{1}{\alpha}\log\left(\frac{\eta_{0\mathrm{B}}}{\eta_{0\mathrm{L}}}\right) + \frac{\nu}{\alpha}\log\left(\frac{\omega_{\mathrm{B}}}{\omega_{\mathrm{L}}}\right) \tag{13}$$

where $\eta_{0\mathrm{B}}$ and $\eta_{0\mathrm{L}}$ are the zero shear viscosities of branched sample and its linear equivalent, respectively.

For the GPC MWD (or equivalently for the viscosity MWD of the linear equivalent), the peak location corresponds to the reptation of chains with weight average molecular weight:

$$\omega_{\mathrm{L}} \sim \frac{1}{\tau_{\mathrm{repL}}} \propto M_{\mathrm{wL}}^{-\alpha} \tag{14}$$

where M_{wL} is the weight average molecular weight of the polymer.

For the viscosity MWD of the branched polymer with low level of long chain branching we assume that the primary peak corresponds to the reptation of the linear chains in the polymer:

$$\omega_B \sim \frac{1}{\tau_{repB}} \propto M_{wBL}^{-\alpha} \tag{15}$$

where M_{wBL} is the weight average molecular weight of the linear chains in the branched polymer. For metallocene polyethylene, long chain branching and molecular size have competing effects on processability and solid-state properties. Too much branching will lead to a significantly reduced molecular size and thus reduced solid-state properties [11]. Therefore for many commercial polymers, the branching level is kept at relatively low levels such that it will not significantly reduce the molecular size, and most of chains are linear. This means that the assumption that the primary peak location in the viscosity MWD is related to the reptation of linear chains in the sample is valid for typical commercial metallocene polymers. Eq. (15) also requires that the relaxation peak associated with the linear molecules is distinct from that of the branched molecules. This is valid for metallocene polyethylenes given that the average arm molecular weight of the branched molecules is equal to that of the linear molecules and the relaxation time of such an arm increases exponentially with the arm molecular weight M_a. We neglect the effect of early time dynamic dilution of arms in the branched system on the reptation of linear molecules in the system; therefore, Eqs. (14) and (15) have the same coefficient of proportionality.

By substituting Eqs. (14) and (15) into Eq. (13) and assuming $\upsilon = 1$, we have:

$$\log(PR) = \frac{1}{\alpha}\log\left(\frac{\eta_{0B}}{\eta_{0L}}\right) + \log\left(\frac{M_{wL}}{M_{wBL}}\right) \tag{16}$$

for linear polymers the zero shear viscosity and weight average molecular weight are related as following:

$$\eta_{0L} = kM_{wL}^{\alpha} \tag{17}$$

Combining Eqs. (17) and (16) gives:

$$\log\left(\frac{m_{gpc}}{m_{vis}}\right) = \frac{1}{\alpha}\log\left(\frac{\eta_{0B}}{k}\right) - \log(M_{wBL}) \tag{18}$$

The peak ratio m_{gpc}/m_{vis} and the zero shear viscosity η_{0B} can be obtained from rheological measurements and GPC data. Thus Eq. (18) offers a possibility to obtain the structural information M_{wBL} from rheological measurements. In the case of single-site catalyst metallocene polyethylene, M_{wBL} in Eq. (18) corresponds to the weight average molecular weight of segments $M_{w,s}$. If we know $M_{w,s}$ from Eq. (18) and the M_w of branched sample determined by GPC, the topological parameter β that describes the topology of the whole branched metallocene polyethylene system [6,7] can be obtained from Eq. (1).

In the case of a blend of several single-site catalyst branched metallocene polyethylenes, M_{wBL} obtained from Eq. (18) is the weight average molecular weight of the linear species in the blend, which depends on the weight fraction and the weight average molecular weight of linear chains of each metallocene polyethylene in the blend. For such a blend, the knowledge of M_w and M_{wBL} is insufficient to specify the composition of the blend and therefore to describe the topology of its constituents [6].

According to the assumptions in deriving Eq. (18), the equation is applicable to the branched polymers with a low level of long chain branching, i.e. those materials for whom the primary peak of viscosity MWD is at the left of that of GPC MWD. We note that the position of the primary peak depends not only on the branching level, but also on the molecular weight of the segments; therefore, the maximum value of the level of branching within which Eq. (18) is applicable cannot be provided. For highly branched polymers the peak due to the reptation of linear chains may not be visible in the viscosity MWD then the primary peak of viscosity MWD is at the right of that of GPC MWD, and a modification to the derivation of Eq. (18) is necessary. In this case we consider that the primary peak in viscosity MWD is related to the relaxation of arms, thus, Eq. (15) is written as:

$$\omega_B \sim \frac{1}{\tau_a} \propto \frac{1}{\exp(U(M_a))} \tag{19}$$

where τ_a is the relaxation time of arm and U, the barrier potential for arm retraction [12], is a function of the arm length proportional to M_a/M_{e0}

In this case, Eq. (18) can be written as:

$$\log\left(\frac{m_{gpc}}{m_{vis}}\right) = \frac{1}{\alpha}\log\left(\frac{\eta_{0B}}{k}\right) - k_1 M_a \tag{20}$$

where k_1 is a constant including all the effects of the temperature, the chemistry of the polymer and α. For metallocene polyethylenes, the knowledge of M_a, equal to the weight average molecular weight of segments $M_{w,s}$, together with the value of M_w, is sufficient to determine the branching density β from Eq. (1), which to describes any aspect of branching structure of the polymer. However, the level of branching of all commercial metallocene polyethylenes currently available is low enough so that Eq. (18) can be used. Eq. (20) may be applicable to hyperbranched polymers and might be used to obtain the weight average molecular weight of arms in these polymers.

6. Application of the technique

The zero shear viscosities, peak ratios and M_{wBL} for model systems and metallocene polyethylenes are listed in Table 3. We note that the peak ratios of HDB1-4 in Table 3 are different from those in Table 1 because they were calculated using improved procedures [13] than those in Ref. [1]. We plot the zero shear viscosity vs. the product of peak ratio and M_{wLB} on double logarithmic axes for both model systems and metallocene polyethylenes [1] in Fig. 6.

Table 3
The peak ratios, M_{wBL}, and zero shear viscosities for model systems and metallocene polyethylenes

Systems	Peak ratio	M_{wBL}	η_0 (Pa s) (150 °C)
M1-1	1.19	100,000	15,735
M1-2	1.38	100,000	26,648
M1-3	3.19	100,000	538,580
M2-1	1.07	60,000	1897
M2-2	1.15	60,000	2430
M2-3	1.47	60,000	5873
M3-1	0.96	40,000	319
M3-2	1.05	40,000	440
M3-3	1.17	40,000	628
M4-1	0.78	30,000	58
M4-2	1.08	30,000	174
M4-3	1.41	30,000	458
HDL1	1	93,000	6000
HDB1	1.90	63,636	11,022
HDB3	3.03	62,608	58,128
HDB4	3.98	54,156	191,158

For the model systems, the peak in the GPC MWD, m_{gpc}, is considered to be 1, and M_{wBL} equals to M_a. For metallocene polyethylenes, M_{wBL} was calculated from the M_w and λ in Table 1 by using following equation and Eq. (1).

$$\lambda = \frac{14,000 \times 2\beta(\beta+1)}{M_w} \tag{21}$$

From Fig. 6 we see that all the symbols scatter around a straight line, which is given by Eq. (18). By fitting the data in Fig. 6 we found $k = 1.38 \times 10^{-14}$, and $\alpha = 3.57$ (150 °C), which are very close to values observed for metallocene polyethylenes [4]. Therefore, we conclude that from rheological data of metallocene polyethylenes, and Eq. (18) we can obtain an additional structural parameter, $M_{w,s}$, which is able to describe the topology of the polymer.

We must now emphasize an important point; in this section we have demonstrated that our technique is applicable to both LCB mPE and our model systems comprised of stars and linear chains. The model system is bi-disperse, i.e. it contains chains of only two molecular weights while LCB mPE is polydisperse. This indicates that the technique is independent of polydispersity as long as the criteria outlined in Section 5 are met.

7. Conclusions

A technique to obtain a structural parameter, the weight average molecular weight of linear chains M_{wBL} in a branched sample, is proposed. The technique was applied to model systems and to branched metallocene polyethylenes, and found to be valid for both systems. The technique (Eq. (18)) is applicable for branched polyethylenes with low levels of long chain branching, for which the primary peak in the viscosity MWD is located at the left of that of GPC MWD. In the case of high-level branched systems, the modification of the technique (Eq. (20)) is proposed. For metallocene polyethylene, the structural parameter, M_{wBL}, obtained from rheological measurements together with the knowledge of the overall weight average molecular weight are able to fully describe all aspects of molecular structure. For blends of metallocene polyethylenes (or in the more complicated case, of any branched polymers) M_{wBL} and M_w are not sufficient to specify the composition and structure of constituents. However, the additional structural parameter, M_{wBL}, is not available by any analytical means and could be useful in the development of further understanding of the structure and behavior of highly branched polymers.

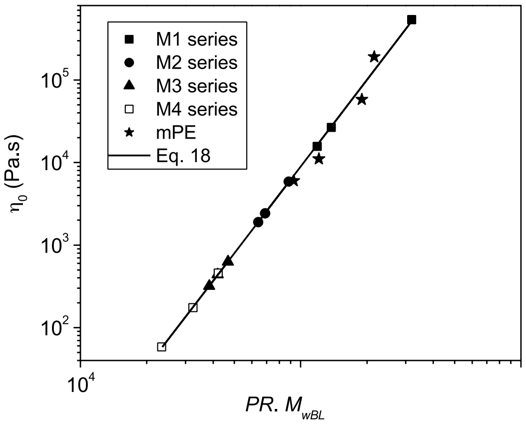

Fig. 6. The zero shear viscosity vs. product of peak ratio and M_{wBL} for model systems and mPEs.

References

[1] Wood-Adams PM, Dealy JM. Macromolecules 2000;33:7481–8.
[2] Milner ST, McLeish TCB, Young RN, Hakiki A, Johnson JM. Macromolecules 1998;31:9345–53.
[3] Lai SY, Wilson JR, Knight GW, Stevens JC. US Patent 5,272,236; 1993.
[4] Wood-Adams PM, Dealy JM, deGroot AW, Redwine OD. Macromolecules 2000;33:7489.
[5] Zimm BH, Stockmayer WH. J Chem Phys 1949;17:1301–14.
[6] Costeux S, Wood-Adams P, Beigzadeh D. Macromolecules 2002;35:2514–28.
[7] Read DJ, McLeish TCB. Macromolecules 2001;34:1928–45.
[8] Soares JPB, Hamielec AE. Macromol Theory Simul 1996;5:547.
[9] This would not be true for combined single-site catalysts systems as described by Costeux in Macromolecules 2003; 36:4168–4187, or for multiple-site catalysts.
[10] Shaw MT, Tuminello WH. Polym Engng Sci 1994;34:159.
[11] Bersted BH, Encyclopedia of fluid mechanics, vol. 7. Houston: Gulf Publishing Company; 1988. Chapter 22.
[12] Milner ST, McLeish TCB. Macromolecules 1998;31:7479–82.
[13] Wood-Adams PM, He C. Analysis of LCB quantification technique for polyethylene. Dow Chemical Company; 2000.