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Using Rheological Data To Determine the Branching Level in Metallocene Polyethylenes

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ABSTRACT: A technique for using rheological information to determine the level of long chain branching in polyethylenes produced using a constrained geometry catalyst and having low levels of branching is described. The complex viscosity as a function of frequency is used, along with a molecular weight distribution (MWD) determined by gel permeation chromatography (GPC). A procedure previously proposed to infer the MWD of linear polymers from complex viscosity data is used to determine a “viscosity MWD” for the branched materials, and this is compared with the GPC MWD. The difference in the location of the peaks in the two curves is then correlated with the level of branching. Advice is provided regarding the range and density of experimental viscosity data needed for a reliable determination of long chain branching.

1. Introduction

An important application of rheology in polymer science is as a tool for the determination of molecular structure. For example, there has been considerable progress recently in the use of viscosity or complex viscosity data to infer the molecular weight distribution of linear polymers, although this is an ill-posed problem from a mathematical point of view. One method, which requires only viscosity data and is easy to use, is the one developed by Shaw and Tuminello[1] and refined by others.[2,3]

However, it is less straightforward to use rheological data to obtain information about long chain branching. First, to fully characterize long chain branching, it is necessary to specify both the distribution of the length of the branches and their partition among the molecules. Second, if the material is polydisperse, it is necessary to disentangle the effect of molecular weight distribution from that of long chain branching. This is difficult because both structural features have similar effects. For example, both broadening the MWD and increasing the level of long chain branching have similar effects on the viscosity curve.

We have addressed one aspect of this problem, namely the use of rheology to detect low levels of long chain branching in polyethylene. In particular, we studied a series of branched polymers polymerized in a continuous, stirred reactor using a constrained geometry catalyst. Additional details concerning the process and the nature of the branched polymers produced are provided in a companion paper.[4] While the procedure proposed here was developed using data for polyethylenes having a relatively narrow and simply described molecular weight distribution, it is believed that it may also be applicable to materials with somewhat broader distributions.

The overall objective was to develop a quantitative technique to infer the level of long chain branching (LCB), expressed, for example, as the number of branch points per 10^4 carbon atoms, from rheological data obtainable using standard instruments and procedures. It was recognized that such a technique should be able to distinguish between the effects of molecular weight, polydispersity, and LCB.

Table 1. Characteristics of Polymers Used

resin	M_W	M_W/M_N	wt % comonomer	LCB/10^4C (NMR)
HDL1	92 700	2.1	1.4 (butene)	−[a]
HDL2	38 500	1.9	0	−
HDL3	112 300	2.0	0	−
LDL1	108 800	2.3	11.4 (butene)	−
LDL2	97 000	2.3	14.8 (butene)	−
LDL3	119 800	2.3	21.2 (butene)	−
LLDPE1	145 200	4.5	− (octene)	−
LLDPE2	133 700	3.5	− (octene)	−
HDB1	77 100	2.0	0	0.26
HDB2	82 600	1.9	0	0.37
HDB3	85 700	2.0	0	0.42
HDB4	96 300	2.1	0	0.80
LDB1	109 300	2.2	octene	−
LDB2	90 300	2.2	octene	−
LDB3	89 400	2.3	octene	−

[a] Dashes indicate that measurement was not performed.

Although we initially tried to correlate a nonlinear viscoelastic property, the tensile stress growth function, with long chain branching, as described in the following section, we ultimately concluded that linear data provide the richest source of information regarding molecular structure.

The characteristics of the polymers used to develop the correlation reported here are summarized in Table 1. Detailed information about these materials can be found in a companion paper.[4] Malmberg et al.[5] have discussed the reaction conditions that lead to the introduction of long chain branches into polyethylene polymerized by metallocene catalysts.

Vega et al.[6] carried out an extensive study of the rheological properties of 23 metallocene-catalyzed polyethylenes and reported a number of interesting general trends regarding the general effects of low levels of long chain branching. However, they did not propose a quantitative method for the determination of the branching level.

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2. Using Extensional Flow Behavior To Infer the Level of LCB

Previous results for highly branched polyethylenes (LDPE) have suggested that a material's behavior in extension is strongly affected by the presence of long chain branching.[7] In particular, LDPEs exhibit strain hardening behavior in extensional flow. Hingmann and Marczinke[8] observed a similar trend in their study of several polypropylenes with lower levels of long chain branching.

Strain hardening behavior is characterized by a rise in the tensile stress growth coefficient above the LVE response. The tensile stress growth coefficient is defined in eq 1.

$$\eta_E^+(t,\dot{\epsilon}) \equiv \frac{\sigma_E(t,\dot{\epsilon})}{\dot{\epsilon}} \tag{1}$$

where σ_E is the principal normal stress difference and $\dot{\epsilon}$ is the Hencky strain rate. In the limit of very low Hencky strain rate, linear viscoelastic behavior is observed, and the tensile stress growth coefficient is just 3 times the value of the linear viscoelastic shear stress growth coefficient at the same value of t, as shown by eq 2.

$$\lim_{\dot{\epsilon}\to 0} \eta_E^+(t,\dot{\epsilon}) = 3\eta^+(t) \tag{2}$$

It has been widely believed that linear polymers do not exhibit strain hardening, which implies that strain hardening is due exclusively to long chain branching. On the basis of these observations, we initially attempted to use extensional flow data in an effort to quantify LCB in mPEs. The experiments were carried out using a Rheometric Scientific RME extensional rheometer. The design of this rheometer is based on that of an instrument developed by Meissner and Hostettler.[9] A small sample in the form of a strip is melted and supported on a cushion of nitrogen gas while a controlled rate of strain is applied and the tensile stress is measured.

To establish the amount of nonlinear viscoelastic information contained in the tensile stress growth coefficient, i.e., the degree to which strain hardening differentiated between the materials of interest, the data were replotted in terms of the reduced function, defined in eq 3.

$$\eta_{ER}^+(t,\dot{\epsilon}) \equiv \frac{\eta_E^+(t,\dot{\epsilon})}{3\eta^+(t)} \tag{3}$$

As indicated by eq 2, this function would be equal to one at all times if there were no strain hardening. The linear shear stress growth coefficient was calculated using a discrete spectrum.[4] Figure 1 shows the reduced tensile stress growth functions for one linear and three branched mPEs at a strain rate of 0.5 s^{-1}. The $\eta_{ER}^+(t,\dot{\epsilon})$ curves for the branched mPEs are different from those for the linear mPE, but the curves for the several branched materials are indistinguishable from each other. Furthermore, at the lower rates the curves for the linear materials are indistinguishable from those of the branched materials. We concluded that for the materials in this study extensional flow data do not contain more useful information concerning long chain branching than is contained in the LVE data. A similar conclusion was reached by Kasehagen and Macosko[10] as a result of their study of randomly branched polybutadiene.

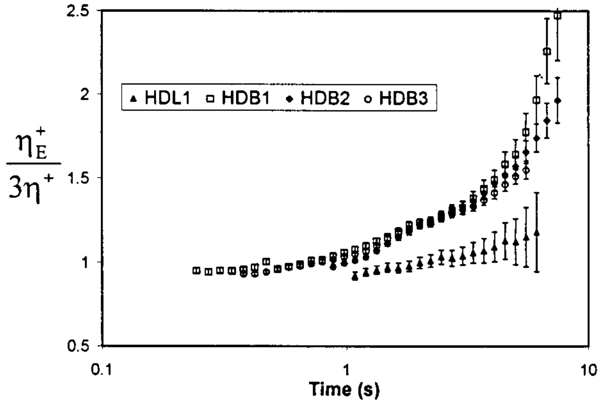

Figure 1. Effect of LCB on reduced tensile stress growth coefficient for high-density mPEs at 0.5 s^{-1}. Error bars were estimated using manufacturer's specifications for measurement resolution.

In any case, it has been observed[11,12] that very small amounts of high molecular weight material in a linear polymer can result in strain hardening in extension, and this throws into question the unique relationship between long chain branching and strain hardening.

3. Using Viscosity Data To Infer the Level of Long Chain Branching

The Dow rheology index[13] (DRI) is a parameter developed to correlate the level of LCB with viscosity data for mPEs. For these materials, the polydispersity is constant, and the problem of distinguishing between the effects of LCB and molecular weight distribution does not arise. This parameter is a measure of the extent to which the viscosity curve of branched mPEs deviates from that of linear mPEs. The quantity actually measured may be the viscosity or the complex viscosity, but assuming the Cox Merz rule to be valid for these materials, these are equivalent. (It has been demonstrated[4] that the Cox Merz rule is indeed valid for mPEs with low levels of LCB.)

Lai et al.[13] found that for strictly linear polyethylenes prepared using single-site catalysts the Cross equation (eq 4) gives a reasonably good fit to viscosity data.

$$\eta(\dot{\gamma}) = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^n} \tag{4}$$

They further showed that the characteristic time, λ, is proportional to the zero shear viscosity:

$$\eta_0\,(\mathrm{Pa\cdot s}) = 3.65 \times 10^5 \lambda(s) \tag{5}$$

They noted that the Cross model could also be fitted to the viscosity data for similar polymers into which a small level of long chain branching had been introduced but that the presence of the branches caused a departure from the above relationship. They proposed the use of this departure as an indicator of the level of long chain branching in such materials. To this end, they defined the Dow rheology index, DRI, as follows:

$$\mathrm{DRI} \equiv \frac{3.65 \times 10^5(\lambda/\eta_0) - 1}{10} \tag{6}$$

For a linear material obeying eq 6, the value of the DRI will be zero, and Lai et al.[13] found that the introduction of long chain branching results in positive values of the DRI, with the value increasing with the level of LCB. The DRI values for LDB1, LDB2, and LDB3 are 1.1, 3.9, and 14, respectively. However, the DRI parameter is only valid for materials having a polydispersity (M_w/M_n) of about two and thus is not able to distinguish between the effects of LCB and polydispersity.

Shroff and Mavridis[14] recently described several other techniques that have been proposed to relate the level of LCB to various rheological properties. In addition, they defined their own "long chain branching index" (LCBI) for ranking materials with very low levels of branching according to the level of branching. They assume that the mean-square radius of gyration for an "essentially linear" polymer is equal to that for a linear polymer of the same molecular weight and that the intrinsic viscosity of the branched material is also equal to that for the branched polymer. They also assume that the zero-shear viscosity is independent of polydispersity. Their index is defined as shown in eq 7, where it can be seen that this method requires only the zero-shear viscosity and the intrinsic viscosity of a sample.

$$\mathrm{LCBI} = \frac{\eta_0^{(1/a_3)}}{[\eta]} \frac{1}{k_3^{(1/a_3)}} - 1 \qquad (7)$$

where η_0 is the zero-shear viscosity of the branched material, and the two constants are fitted to the following relation for linear polymer:

$$\eta_0 = k_3 [\eta]_L^{a_3} \qquad (8)$$

Shroff and Mavridis do not provide a quantitative correlation of LCBI with level of branching. However, we calculated values of their index for our materials, and these are discussed below.

4. Using Viscosity Data Together with GPC Data To Determine LCB

The presence of long chain branching, even at quite low levels, has a very important effect on the shape of the viscosity curve. Since this effect is similar to that of broadening the molecular weight distribution, it is not possible to determine the molecular structure of a polymer from rheological data alone, without any other information about molecular structure.

Janzen and Colby[15] have discussed this problem in some detail and have proposed a method for using the zero-shear viscosity, together with GPC data to detect very low levels of long chain branching in polyethylene. This method requires values for several empirical constants that depend on the polymer system and the temperature.

We have previously proposed a technique for the use of the viscosity curve to determine the molecular weight distribution of linear polymers. While short chain branching was found not to interfere with this technique, when long chain branching is present, the MWD obtained by this technique is obviously incorrect. However, we have found that the degree of deviation of the predicted MWD from the GPC molecular weight is related to the degree of LCB in the materials we studied. A quantitative correlation based on this observation is described in this section.

4.1. Inferring MWD from Complex Viscosity for Linear Polyethylenes.

The method we have used to infer MWD from complex viscosity data is a modified version of the technique developed by Shaw and Tuminello.[1] This method has been described in detail elsewhere,[3] and only a summary is provided here. The equation used to calculate the logarithmic differential molecular weight distribution[16] is as follows.

$$w(\log m) = \left[\frac{-\ln(10)}{m\nu^2}\right]\left[\frac{\eta^*}{\eta_0}\right]^{1/\alpha}\left[\alpha \frac{\mathrm{d}^2 \ln \eta^*}{\mathrm{d} \ln \omega^2} + \nu \frac{\mathrm{d} \ln \eta^*}{\mathrm{d} \ln \omega} + \left(\frac{\mathrm{d} \ln \eta^*}{\mathrm{d} \ln \omega}\right)^2\right] \qquad (9)$$

The slope in the power law region ($\sigma = k\gamma^{-\nu}$) is $-\nu$, and α is the exponent in the relationship between viscosity and molecular weight (3.6 in this work). The critical frequency (ω_c) is equal to the shear rate at which the low shear rate plateau ($\eta = \eta_0$) intersects the line fitted to the power law portion of the log−log viscosity curve. The reduced molecular weight, m, is given by

$$m \equiv M/M_w \qquad (10)$$

which is assumed to be related to the frequency as follows:

$$\omega = \frac{\omega_c}{m^{\alpha/\nu}} \qquad (11)$$

The use of eq 9 to calculate the MWD implies the availability of experimental complex viscosity data that include the Newtonian plateau and the power law region. However, for most polydisperse polymeric systems it is not possible to measure the complex viscosity over the entire range of interest, and the data must therefore be extrapolated at both ends using well-behaved viscosity models. The extrapolation at the low-frequency end of the curve was accomplished by use of eq 12 to calculate the complex viscosity using a discrete relaxation spectrum, i.e., the set of parameters, $[G_i,\lambda_i]$, inferred from the measured storage and loss moduli.

$$\eta^*(\omega) = \left[\left(\sum_{i=1}^{N} \frac{\omega G_i \lambda_i^2}{1 + (\omega\lambda_i)^2}\right)^2 + \left(\sum_{i=1}^{N} \frac{G_i \lambda_i}{1 + (\omega\lambda_i)^2}\right)^2\right]^{1/2} \qquad (12)$$

This is an arbitrary procedure, as no new information is introduced, but it results in a smooth continuation of the experimental data, and it has been shown[4] that the details of this extrapolation have little effect on the MWD estimated using this method. The Vinogradov fluidity model, eq 13, was used to extrapolate at high rates.

$$\frac{\eta_0}{\eta^*} = \sum_{i=0}^{N} A_i \omega^{i\nu/N} \qquad (13)$$

In this equation, the negative of the power law slope, ν, is determined by fitting experimental data. It was found that for the polymers included in this study the optimum value for ν was always 1.

Once the complex viscosity curve has been extrapolated to a zero second derivative at each end, the logarithmic differential MWD is calculated from the

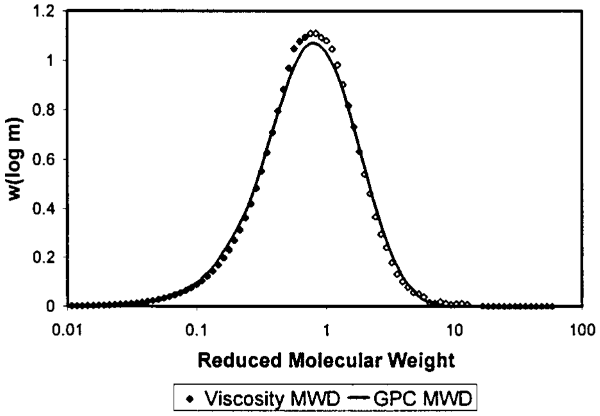

Figure 2. Comparison of viscosity MWD and GPC MWD for HDL1 (M_W = 100 900 and PI = 2.08). Open symbols are experimental data, and closed symbols are extrapolated data.

complex viscosity data using eq 9. We refer to this calculated MWD as the "viscosity MWD".

A direct measurement of the MWD can be carried out using gel permeation chromatography (GPC). GPC data are often reported in terms of weight fractions (wt_i) corresponding to molecular weights (M_i). These data must be converted to a discrete logarithmic MWD, as explained, for example, in ref 3. For linear polymers the viscosity MWD and the discrete logarithmic MWD function calculated from GPC data should be the same. The accuracy of the viscosity MWD is illustrated for HDL1 in Figure 2 where we see excellent agreement between the viscosity MWD and the GPC MWD.

Because the reliability of the procedure for determining MWD from the viscosity is central to the technique proposed here for the determination of LCB, we made a thorough study of the effects of molecular structure, measurement temperature, and data density on the accuracy of the distribution estimated using this procedure.

4.2. Effect of Molecular Structure on Accuracy of the Viscosity MWD for Linear Polyethylenes. To examine the effects of various molecular characteristics on the viscosity MWD, seven additional linear polyethylenes were chosen to permit the systematic variation of M_w, polydispersity index (PI), and comonomer content. The quality of the viscosity MWDs for these materials was then compared to that for HDL1. Two measures of the quality of the viscosity MWD were used: the peak ratio defined by eq 14 and the breadth ratio defined by eq 15:

$$\text{peak ratio} = \frac{\text{GPC MWD peak } m}{\text{viscosity MWD peak } m} \tag{14}$$

$$\text{breadth ratio} = \frac{\text{GPC MWD breadth at } w(\log m) = 0.5}{\text{viscosity MWD breadth at } w(\log m) = 0.5} \tag{15}$$

Unless otherwise indicated, the LVE data that were used to calculate the viscosity MWDs were measured at 150 °C, with a data point density of 7 points per decade of frequency.

The effect of M_W on the quality of the viscosity MWD is summarized in Table 2. These results can be understood by considering the effect of M_W on the complex viscosity curve. In addition to decreasing the zero shear viscosity, lowering the M_W causes an extension of the Newtonian plateau to higher shear rates. Therefore, the portion of the curve that contains useful information about the MWD is shifted to higher frequencies. Since the maximum frequency is governed by instrument limitations, and frequency is inversely related to molecular weight (eq 11), lowering M_W results in a movement of the experimental window toward the higher molecular weight end of the distribution.

Table 2. Effect of MW on Viscosity MWD Quality

resin	M_W	peak ratio	breadth ratio
HDL2	38 500	1.06	1.18
HDL1	92 700	0.96	1.04
HDL3	112 300	0.97	1.09

Table 3. Effect of Short Chain Branching on Viscosity MWD Quality

resin	wt % butene	peak ratio	breadth ratio
HDL1	1.44	0.96	1.04
LDL1	11.4	0.97	1.06
LDL2	14.83	0.92	1.04
LDL3	21.1	0.90	1.05

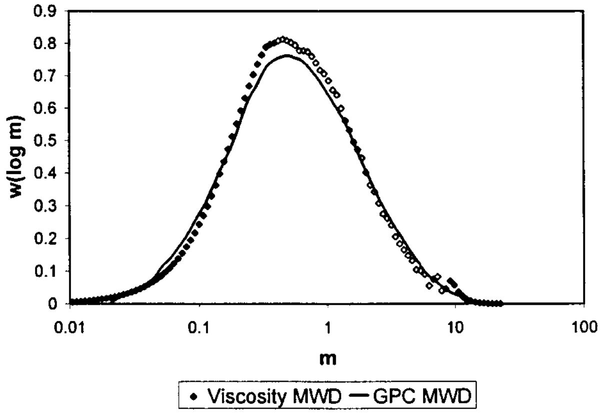

Figure 3. Comparison between viscosity MWD and GPC MWD for LLDPE2. Symbols as in Figure 2.

Table 4. Effect of Polydispersity on Viscosity MWD Quality

resin	M_W	M_W/M_N	peak ratio	breadth ratio
HDL1	92 700	2.1	0.96	1.04
LLDPE2	145 200	3.5	1.11	0.99
LLDPE1	133 700	4.54	1.07	0.96

In the case of HDL2, this reduces the amount of information available for the MWD prediction and results in a poorer prediction of the breadth of the viscosity MWD, but it is important to note that the location of the peak is affected much less. The quality of the viscosity MWDs predicted for the two higher molecular weight materials is excellent.

The effect of short chain branching on the viscosity MWD was studied using samples LDL1, LDL2, and LDL3, and the results are shown in Table 3. We conclude that short chain branching resulting from copolymerization with up to 21.2 wt % butene has no effect on the viscosity MWD.

The effect of polydispersity on the viscosity MWD was studied using two linear low-density polyethylenes, LLDPE1 and LLDPE2. Figure 3 shows the result for LLDPE2, while the results for both materials are summarized in Table 4. While the viscosity MWDs of LLDPE1 and LLDPE2 are not in as good agreement with the GPC data as is the case for HDL1, which has a narrower MWD, the agreement is still considered satisfactory. We note that there is no correlation be-

Table 5. Effect of LVE Data Measurement Temperature on Viscosity MWD Quality for LDL1

measurement temp (°C)	peak ratio	breadth ratio
130	0.97	1.06
150	0.97	1.09
170	0.96	1.09

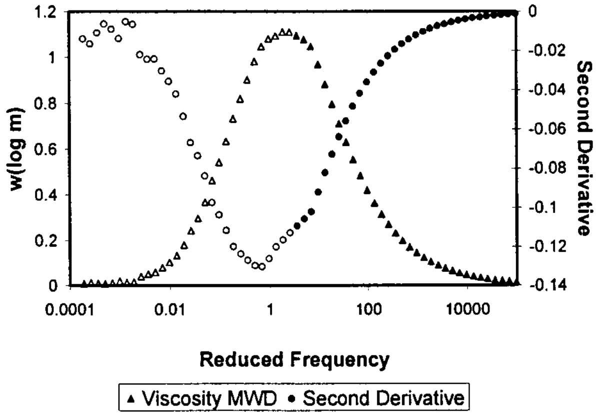

Figure 4. Second derivative of viscosity (as in eq 5) and viscosity MWD for HDL1. Symbols as in Figure 2.

tween polydispersity and the quality of the peak molecular weight prediction.

4.3. Effect of Measurement Temperature. The effect of the measurement temperature on the quality of the viscosity MWD was evaluated using a low-density, linear mPE, LDL1. Measurements were performed at 130, 150, and 170 °C, and the viscosity MWD was calculated from the data at each temperature. The results of this study are summarized in Table 5. The increase in measurement temperature moves the experimental window to higher molecular weights. This results in a slightly poorer prediction of the details of the MWD, particularly in the region just before the peak. Increasing the temperature in this range affects primarily the breadth of the viscosity MWD and has very little effect on the peak location.

4.4. Effect of LVE Data Density and Range. The effects of data range and density on the viscosity MWD have been previously investigated.[2,3] Increasing the range and the density of the LVE data results in a better MWD prediction. In terms of range, the ideal LVE data set would include the Newtonian plateau and the power law region, but this is usually beyond the capabilities of standard melt rheometers. In practice, however, the most important LVE information is in the region around the minimum in the second derivative ($d^2 \ln \eta^*/d \ln \omega^2$) of the logarithm of the complex viscosity.[2] The likelihood of predicting an accurate MWD with a given set of LVE data can be evaluated by plotting the second-derivative curve against the reduced frequency (ω/ω_c) as shown in Figure 4. We see here that the experimental window for HDL1 at 150 °C includes the minimum in the second derivative, which leads to the excellent quality of the viscosity MWD prediction for HDL1.

Any shift of the experimental window is likely to affect the quality of the viscosity MWD. A decrease in the molecular weight or an increase in measurement temperature will shift the experimental window to a lower reduced frequency. If the experimental window then no longer covers the minimum in the second derivative, the quality of the MWD will be compromised. This was the cause of the poor quality of the viscosity MWD in the case of HDL2, as this polymer has a very low molecular weight, and the experimental window does not include the minimum in the second derivative.

Table 6. Data Truncation Study: HDL1

data set	exptl freq range (rad/s)	max ω/ω_c in exptl data	rel location of exptl window	peak ratio	breadth ratio
original	0.036–500	2.58	3.73	0.96	1.04
truncation 1	0.036–96.54	0.50	0.72	0.96	1.12
truncation 2	0.036–25.90	0.13	0.19	0.95	1.20
truncation 3	0.036–6.95	0.04	0.05	0.90	1.17

To reveal the sensitivity of the accuracy of the viscosity MWD to the breadth of the experimental window, a high-frequency truncation study was performed using the data for HDL1. The data were truncated at three frequencies, and the viscosity MWD was recalculated using the truncated data set. In Table 6 we see that the quality of the viscosity MWD deteriorates as the experimental window is narrowed. The viscosity MWD becomes narrower, and the peak moves to higher molecular weights as more high-frequency data are lost. The breadth of the viscosity MWD is already affected by the first truncation, but the peak molecular weight is significantly changed from its original value only by truncation 3. We conclude that for a material with $M_w/M_n \cong 2$ complex viscosity data up to a reduced frequency of 0.13 are sufficient to determine the location of the peak molecular weight reliably. In the case of multiple peaks in the viscosity MWD, we can refer to the proximity of the experimental window to the second derivative minimum that corresponds to the MWD peak in question to evaluate the quality of the data. A measure of this proximity is the relative location, R, defined by eq 16. According to the results of the truncation study, as long as R is at least 0.19, one can still predict the location of the peak molecular weight.

$$R \equiv \frac{\text{maximum experimental } \omega}{\omega \text{ at second derivative minimum}} \qquad (16)$$

The quality of the viscosity MWD is much less sensitive to the low-frequency end of the complex viscosity data. We have shown previously[3] that a great deal of low-frequency data can be truncated, resulting in quite different low-frequency extrapolations without adversely affecting the viscosity MWD. There is a limit to the amount of information that can be missing from the low-frequency end, but since for most polyethylenes it is not difficult to extend the experimental window to low enough frequencies, we do not consider this limitation here.

Liu et al.[2] showed how data density affects the resolution of the viscosity MWD. If the data are too sparse, important details of the MWD, such as bimodality, will be lost. In the present work, data densities of 5, 7, and 9 points per decade were used for the various polymers studied. According to the criterion of Liu et al.,[2] these densities will resolve features that are 0.38, 0.27, and 0.21 decades of molecular weight apart, respectively.

On the basis of the accuracy of the peak molecular weight predictions reported here, it appears that the modified viscosity MWD technique has a better resolution than is indicated by the criterion of Liu et al. For example, for all of the linear materials studied in this work, the errors in the peak molecular weight predic-

Table 7. Peak Ratios for Branched mPEs

high-density mPEs				low-density mPEs			
resin	actual LCB/10^4C	peak ratio	predicted LCB/10^4C	resin	DRI	peak ratio	predicted LCB/10^4C
HDB1	0.26	1.73	0.27	LDB1	1.1	1.27	0.12
HDB2	0.37	2.31	0.41	LDB2	3.9	2.33	0.41
HDB3	0.42	2.51	0.46	LDB3	14	2.96	0.53
HDB4	0.80	4.69	0.76				

tions were less then 0.044 decades of molecular weight when the data density was 7 points per decade of frequency.

The results presented above show that the technique used for the calculation of the viscosity MWD of linear polyethylenes is robust, particularly in terms of the peak molecular weight prediction. As long as relative peak location, *R*, is greater than 0.19, the LVE data density governs the resolution in the peak molecular weight. For 7 points per decade of frequency the resolution in the peak molecular weight is 0.088 decades of molecular weight. This corresponds to an uncertainty in the peak molecular weight ratio of 11%, which is larger than the variations arising from differences in molecular structure, measurement temperature, and data truncation.

4.5. The Viscosity MWD of Polymers with Long Chain Branching. The viscosity MWD technique presented above is valid only for linear materials. Since the complex viscosity curve is affected by MWD and long chain branching (LCB), a viscosity MWD calculated for a branched material does not represent the GPC MWD. For a branched material, the viscosity MWD can be interpreted as the MWD of a linear polymer that would have the same complex viscosity curve as that of the branched material. The viscosity MWD was calculated for all the branched materials, and the results for HDB1−4 are compared to the GPC MWDs in Figures 5−8. We recall that samples HDB1−4 have increasing levels of LCB as do samples LDB1−3. The presence of LCB has several effects on the viscosity MWD. The viscosity MWD of a branched material in comparison to the GPC is broadened, the primary peak is shifted to a lower reduced molecular weight, and a secondary peak is added at high molecular weights. The degree of distortion in the viscosity MWD as compared to the GPC MWD increases as the degree of LCB increases. It was found that the shifting of the peak provided a simple and reliable measure of the difference between the viscosity and the GPC MWD, and as shown in the next section, this shift can be correlated with the degree of LCB. The LVE data used to determine the viscosity MWDs presented in this section were measured at 150 °C unless otherwise indicated.

4.6. Correlating the Viscosity MWD with the Degree of LCB. It was found that the feature of the viscosity MWD that was most sensitive to the degree of LCB was the shift in the primary peak as compared to the GPC MWD. To quantify the shift of the primary peak, we propose the use of the peak ratio, defined by eq 14. The peak ratio values for the branched materials are given in Table 7. The peak ratios for all of the linear materials (Tables 2−5) are in the range 1.0 ± 0.11, implying that there is a significant difference between the linear materials and the (long chain) branched mPEs.

Using the data for the high-density mPEs, for which we had ^{13}C NMR measurements of degree of LCB, a correlation was developed between peak ratio and degree of LCB, and this is given by eq 17.

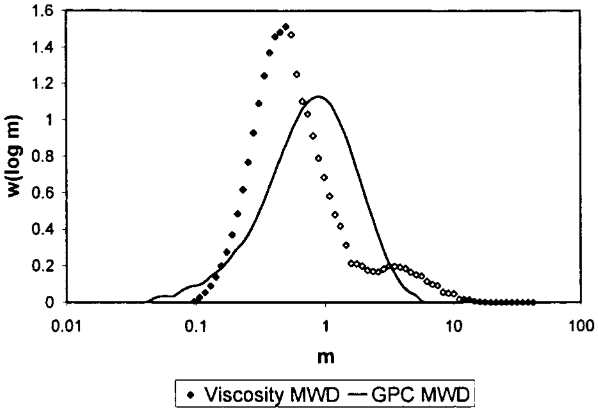

Figure 5. Comparison between viscosity MWD and GPC MWD for HDB1. Symbols as in Figure 2.

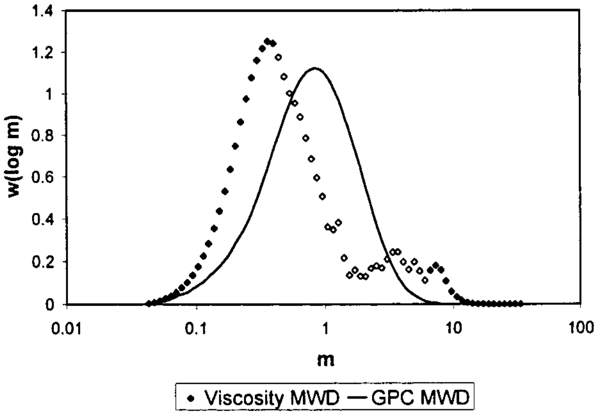

Figure 6. Comparison between viscosity MWD and GPC MWD for HDB2. Symbols as in Figure 2.

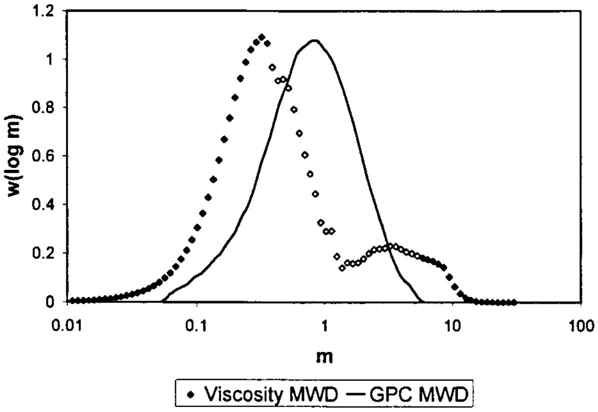

Figure 7. Comparison between viscosity MWD and GPC MWD for HDB3. Symbols as in Figure 2.

$$\frac{\mathrm{LCB}}{10^4C} = \frac{\text{GPC peak}}{\text{viscosity peak}} < 1, \quad 0$$

$$= \frac{\text{GPC peak}}{\text{viscosity peak}} \geq 1, \quad 1.125 \log\left(\frac{\text{GPC peak}}{\text{viscosity peak}}\right) \tag{17}$$

The coefficient of correlation for this relationship was 0.985. This correlation indicates that peak ratios less than 1 correspond to a linear material. For peak ratios greater than or equal to 1 a linear function of the logarithm of the peak ratio was found to give the degree of LCB. This function has only one fitted parameter, and it was found that functions with more parameters did not improve the fit of the data. Predictions of eq 17 are

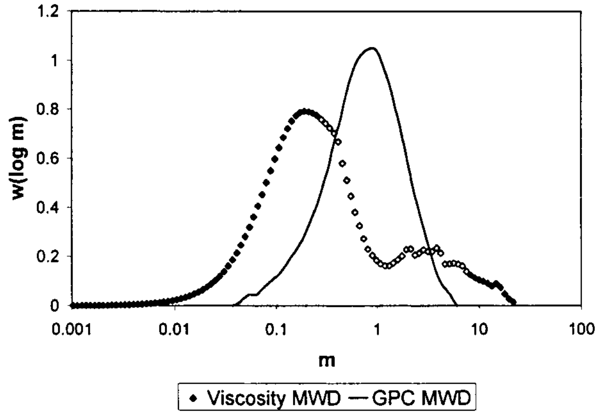

Figure 8. Comparison between viscosity MWD and GPC MWD for HDB4. Symbols as in Figure 2.

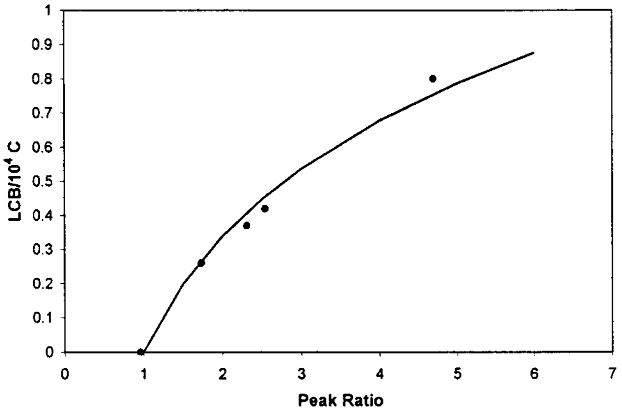

Figure 9. Relationship between degree of LCB and peak molecular weight ratio. Symbols are experimental data for HD series of materials, and line is eq 13.

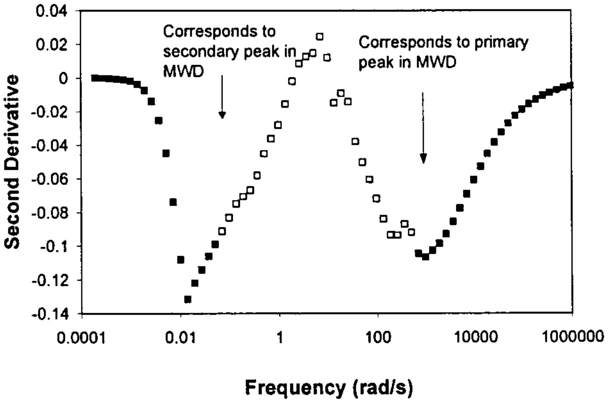

Figure 10. Second derivative of viscosity (as in eq 5) for HDB3. Symbols as in Figure 2.

compared with NMR data for the high-density mPEs in Figure 9.

Because of the importance of the calculated peak in the viscosity MWD, we need to ensure that no information is lost in determining this quantity. We note that for the branched materials, with the exception of LDB1, the experimental window does not cover the primary peak. However, as was demonstrated previously, the criterion for evaluating the quality of the prediction of the location of a peak MWD involves the location of the experimental window relative to the corresponding minimum in the second-derivative curve. Figure 10 shows the second derivative for HDB3. By inspection, we see that the experimental window is close enough to the relevant minimum in the second derivative to give a good prediction of the location of the peak. A more objective measure is the relative location parameter, *R*, as defined by eq 16. The *R* values corresponding to the primary peaks for all the branched materials are shown in Table 8. The lowest *R* value for the branched materials, 0.52, is significantly higher than the *R* value of 0.19 that was seen with the second truncation of the HDL1. Even with an *R* of 0.19 the peak molecular weight prediction was very good. Assuming that the *R* parameter is valid for the branched materials, we can thus have confidence in the predicted locations of the primary peaks in the viscosity MWDs of the branched materials.

Table 8. Relative Locations with Respect to Primary Peaks in MWD for Branched mPEs

high-density mPEs			low-density mPEs		
resin	LCB/10^4C	*R*	resin	DRI	*R*
HDB1	0.26	0.72	LDB1	1.1	19.3
HDB2	0.37	0.72	LDB2	3.9	3.73
HDB3	0.42	0.52	LDB3	14	0.52
HDB4	0.80	2.68			

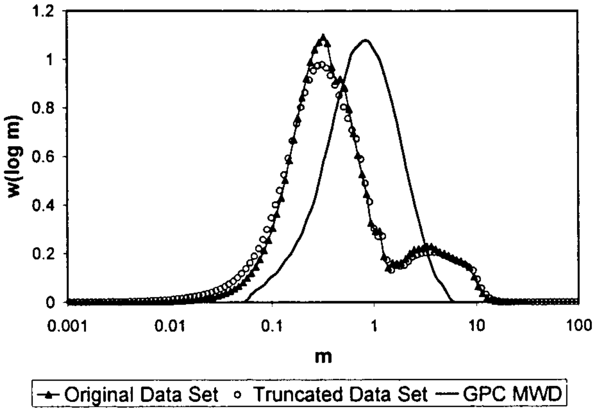

Figure 11. Results of HDB3 truncation study

A high-frequency truncation study of the data for HDB3 was performed to evaluate the applicability of *R* to branched materials. As for HDL1, high-frequency data were truncated, and the viscosity MWD was recalculated until the shortest data set that allowed for the same peak molecular weight was found. The results of this study are shown in Figure 11. The truncated data set included data up to a frequency of 258.28 rad/s and had an *R* of 0.19. This limiting value of *R* is in agreement with the results for HDL1. From this we conclude that *R* is a valid criterion for evaluating the quality of the viscosity peak molecular weight for branched materials and that as long as *R* is ≥ 0.19 the peak molecular weight prediction is reliable.

To test the possibility of falsely predicting LCB in a linear material, this correlation was used with all of the linear materials discussed above, and the highest degree of LCB that was predicted was 0.03LCB/10^4C. The uncertainty in the viscosity peak molecular weight due to data density for LVE data with 7 points/decade is 0.044 decades. This corresponds to an uncertainty in predicted degree of LCB of 0.05LCB/10^4C. Therefore, only when the predicted level of LCB is greater than 0.05 could it indicate the presence of LCB. It should be noted that the uncertainty in the degree of LCB predicted by this analysis arises primarily from uncertainty due to the data density of the LVE data. Issues such as uncertainty in the correlation parameters due

Table 9. Predicted Degree of LCB for Low-Density Branched MPEs

resin	LCB/10^4C
LDB1	0.12 ± 0.05
LDB2	0.41 ± 0.05
LDB3	0.53 ± 0.05

Table 10. Comparison of LCBI14 and Other Measures of LCB

resin	$\eta_0 \times 10^{-4}$ (Pa.s)	$[\eta]$ (dL/g)	LCBI[14]	LCB/10^4C NMR or GPC	LCB/10^4C rheol est
HDB1	6.38	1.40	0.23	0.26[a]	0.27
HDB2	1.74	1.45	0.47	0.37[a]	0.41
HDB3	37.0	1.47	0.71	0.42[a]	0.46
HDB4	76.5	1.56	0.87	0.80[a]	0.76
LDB1	15.1	1.49	0.39	0.1[b]	0.12
LDB2	16.7	1.28	0.66	0.4[b]	0.41
LDB3	22.9	1.22	0.85	0.6[b]	0.53

[a] Determined by NMR. [b] Determined by triple-detector GPC.

to limited data points have not been included in this analysis. The predicted degrees of LCB for LDB1−3 and the uncertainties in these predictions due to LVE data density are given in Table 9.

We also calculated values of the LCBI defined by Shroff and Mavridis[14] for our materials. The values of the parameters in eqs 7 and 8 for our linear materials were $a_3 = 4.7$ and $k_3 = 4.9 \times 10^3 P$. The results are shown in Table 10 and compared with branching levels obtained in the present study. We see that the LCBI fails to rank our materials in order of the level of LCB. We do not find this surprising, as this index is based on very little information about the branched material.

5. Conclusions

The degree of LCB in polyethylenes with low levels of branching can be inferred from rheological data together with a GPC molecular weight distribution. Whereas extensional flow data are not useful for quantifying LCB in such materials, or even ranking resins in terms of LCB, LVE data are sensitive to the degree of LCB. The effects of MWD and LCB on the LVE behavior can be distinguished by comparing the viscosity MWD calculated using the complex viscosity curve with the GPC MWD. The difference between the viscosity and the GPC MWDs for branched materials is related to the degree of LCB. This relation is described by a simple correlation (eq 17) that can be used to estimate the degree of LCB for a material that has unknown branching characteristics.

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