Separating the effects of sparse long-chain branching on rheology from those due to molecular weight in polyethylenes

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Synopsis

The effects of sparse (< 1 branch per chain) long-chain branching (LCB), molecular weight (MW), and molecular weight distribution on the shear rheological properties of commercial polyethylenes are often convoluted. In this paper a method for separating the effects of sparse LCB in metallocene-catalyzed polyethylenes (mPE) from those of molecular weight and its distribution based on time–molecular weight superposition is proposed. Four metallocene polyethylenes with degrees of long-chain branching [i.e., M of the arm (M_a) is greater than that for the onset of entanglements, M_c] as determined from dilute solution measurements ranging from zero (linear) to 0.79 LCB/10^4 CH$_2$, along with a conventional Ziegler–Natta polymerized linear low-density polyethylene (LDPE), and a tubular free-radical polymerized LDPE are investigated. In general, it is observed that sparse LCB (for levels < 1.0 LCB/10^4 CH$_2$) increases the zero shear viscosity, η_0 (e.g., by a factor of 7) and decreases, but even to a greater degree, the critical shear rate ($\dot{\gamma}_c$) for the onset of shear thinning (e.g., by a factor of 100). The breadth of the molecular weight distribution just affects $\dot{\gamma}_c$ but not η_0 for the range of data used in this study. Furthermore, the dynamic storage modulus G' shows similar enhancement at low frequencies as viscosity does, while the primary normal stress difference coefficient, $\Psi_{1,0}$, exhibits a greater dependence on long-chain branching than that predicted from the zero-shear viscosity enhancement. The results for the mPEs are consistent with recent molecular theories for randomly branched molecules in that it is the spacing between branch points and not the number of branches at a point that is important. Furthermore, the results are consistent with the idea that the branches are located on the longest chains, and hence, have the greatest effects on the longest relaxation modes. © *2003 The Society of Rheology.* [DOI: 10.1122/1.1567751]

I. INTRODUCTION

The combined effects of molecular weight (MW), molecular weight distribution (MWD), and long-chain branching (LCB) all contribute to the rheological properties of polyethylene resins and usually in a convoluted manner [Laun and Schuch (1989)]. The development of metallocene polyethylenes (mPE) may provide the ability to distinguish the individual contributions arising from molecular structure because of their narrow molecular weight distribution and controlled levels of sparse long-chain branching. Of most interest here is the effect that sparse (< 1 LCB/10^4 CH$_2$) long-chain branching has on the steady and dynamic oscillatory shear properties of mPE resins. Long-chain

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branching refers to branches having a molecular weight (M_a) greater than the critical molecular weight for entanglements, M_c. The influence of LCB has long been recognized for the case of low-density polyethylene (LDPE), which has a high degree of long-chain branching [Laun and Schuch (1989)]. Unfortunately, the free-radical polymerization process by which LDPE is manufactured also gives rise to a broad molecular weight distribution [Kiparissides *et al.* (1993)]. Therefore, this convolution with MWD has obscured the distinct effects of LCB. In particular, it is of interest in this paper to separate the effects of MW and MWD on viscosity, dynamic moduli, and normal stresses from those due to sparse LCB for commercial polyethylenes (PEs).

A. Metallocene and other sparsely branched polyethylenes

Metallocene polyethylenes should not suffer as much from the convolution of LCB and MWD. Branched mPE resins made using constrained geometry catalysts are believed to have controlled amounts of random, sparse long-chain branching while retaining a relatively narrow molecular weight distribution of approximately two [Lai *et al.* (1993)]. In this case, sparse branching in mPE resins generally refers to less than one branch per molecule. This differs significantly from the highly branched structure of LDPE resins which contain multiple random branches on a chain. As a result, mPE resins now potentially allow researchers to focus exclusively on the effects of long-chain branching independent of other molecular factors.

Recent work with random, sparsely branched metallocene PE resins indicates that long-chain branching does have a discernable effect on shear rheology. Wood-Adams *et al.* (2000) performed a comprehensive study on the rheological implications of molecular structure and observed that the zero-shear viscosity, breadth of the relaxation spectrum, and dynamic loss angle δ were most sensitive to the presence of sparse long-chain branching. Their work relied on knowledge of dilute solution measurements of the degree of sparse LCB which seem to be only qualitative at best [Janzen and Colby (1999)]. Similar results were observed by Kim *et al.* (1996). Kim *et al.* (1996), and Bin Wadud and Baird (2000) studied the temperature dependence of mPE resins and found the flow activation energy (E_a) to be sensitive to the presence of low levels of random long-chain branching. However, Bin Wadud and Baird were unable to distinguish the level of branching from E_a alone for systems with only subtle differences in the degree of LCB (e.g., there was no statistical difference in E_a for a PE with 0.56 vs 0.18 LCB/10^4 CH$_2$). Instead, Bin Wadud and Baird found that nonlinear viscoelastic measurements of the transient primary normal stress difference (N_1^+) and transient extensional viscosity (η_E^+) were more sensitive to the degree of branching found in the sparsely branched mPE systems they studied. Again, they relied on dilute solution measurements to assess the level of LCB, but their results were at least consistent with these measurements. These relatively few results represent a significant step in understanding the influence of random branching on the rheology of commercial polyethylene resins.

Bersted and co-workers (1981) studied sparsely branched PEs generated by blending various levels of a randomly branched LDPE with a linear high-density PE (HDPE). Although the breadth of the MWD was quite large, it was similar for all the polymers. They observed that η_0 increased at first with increasing levels of the branched PE and then decreased when the fraction of branched species approached unity. They attributed the increase to increasing amounts of the more viscous branched component and the decrease to the decrease in the radius of gyration with increasing branching level. They used a logarithmic rule of mixtures to predict the viscosity behavior at all shear rates as they considered the materials to be blends of a linear HDPE and a branched LDPE.

Janzen and Colby (1999) quantified the enhancement in viscosity at low branching levels and the decrease at levels greater than about 1 LCB/chain observed by Bersted and co-workers. Their technique employs a phenomenological description developed by Lusignan and co-workers (1996, 1999) based on the synthesis of randomly branched, flexible chain polyesters combined with the assumed branching structure of a Cayley tree. The phenomenological description appears in Eqs. (1) and (2):

$$\eta_0 = AM_b\left[1+\left(\frac{M_b}{M_c}\right)^{2.4}\right]\left(\frac{M_w}{M_b}\right)^{s/\gamma}, \quad M_c \leq M_b \leq M_w. \tag{1}$$

Here, A is a numerical prefactor having units of (Pa s mol)/g and is specific to molecular composition and temperature, M_b is the molecular weight between branch points, M_c is the critical molecular weight for entanglements, M_w is the weight-average molecular weight, and s/γ is an exponent that depends logarithmically on M_b as shown in Eq. (2),

$$s/\gamma = \max\left[1, \frac{3}{2} + \frac{9B}{8}\ln\left(\frac{M_b}{90M_{\text{Kuhn}}}\right)\right], \tag{2}$$

where B is a material specific constant, and M_{Kuhn} is the molecular weight of a statistical Kuhn segment. The value of M_b can be calculated using the following equation if the number of branch points, α, is known,

$$M_b = \left[\frac{2\alpha}{M_1} + M_w^{-1}\right]^{-1}, \tag{3}$$

where M_1 is the repeat unit molecular weight. Significant zero-shear viscosity enhancement is observed at large values of M_b (i.e., low degrees of LCB), and pronounced viscosity reduction at low values of M_b. The Janzen and Colby approach coincides with what Bersted and co-workers predicted should occur from their work on blends. However, Janzen and Colby attributed the increase and decrease in viscosity to the molecular weight between branch points while Bersted and coworkers attributed it to the amount of the sparsely branched material. The branching structure in the blends may be different than that in the metallocene systems.

Before leaving this section we must make note of an important study by Yan and co-workers (1999) who polymerized a series of metallocene catalyzed polyethylenes using Dow Chemical's constrained catalyst system of varying degrees of branching from 0.0 to 0.44 LCB/10^4 CH$_2$. Because they did not use any comonomers (e.g., hexene or octene), they could use nuclear magnetic resonance (NMR) to estimate the level of branching. Most of the samples were of nearly identical M_w ($\sim$ 110 000 g/g mol) but one was as high as 130 000 and another as low as 100 000 while the MWD was about 2.0. They observed viscosity enhancement at low shear rates whereas at high shear rates the viscosity values merged. They reported dynamic oscillatory results which followed the viscosity behavior. They claimed that the activation energy correlated to branching level, but on further evaluation of their data distinctions between samples with only slightly different levels of branching could not be made. For example, between levels of 0.35 and 0.45 LCB/10^4CH$_2$ E_a was indistinguishable which is what Bin Wadud and Baird (2000) reported. Because there was some variation in M_w, the effect of sparse LCB was somewhat convoluted with M_w and, hence, the full effect due to sparse LCB was partially disguised.

B. Model polymer systems

The difficulties in quantifying the degree of sparse branching in commercial systems are well documented [Janzen and Colby (1999)]. Conventional methods of characterization, such as dilute solution low-angle laser light scattering (LALLS) and C^{13} NMR measurements, are often limited when the degree of long-chain branching is small (< 0.3 LCB/1000 C) or short-chain branching (SCB) is also present [Schroff and Mavridis (1999)]. In essence, the dilute solution methods are at best estimates of the degree of branching. Furthermore, in the metallocene PEs there is believed to be a range of branching architectures (stars, combs, and random), but with the dominant one being random branching [Soares and Hamielec (1995, 1996)]. For this reason a knowledge of the rheological behavior of model polymer systems could be helpful in understanding the behavior of sparsely branched systems. We briefly summarize here the key findings on the work with model systems.

One of the first studies employing systematically branched polymers was performed by Kraus and Gruver (1965). They found that above a characteristic molecular weight three-and four-arm star-branched polybutadiene (PB) resins exhibited zero-shear viscosity enhancement over their linear PB equivalents. That is, the viscosity of the branched species was greater than that of the linear species for the same weight-average molecular weight. Kraus and Gruver hypothesized that enhanced entanglement coupling was occurring between neighboring molecules above the characteristic molecular weight. Similar studies by Graessley *et al.* (1976) and Raju *et al.* (1979a) on polyisoprene (PI) and hydrogenated polybutadiene (HPB) systems, respectively, have yielded similar results.

In addition to the number of branches, the length of branches was also investigated. Several researchers have found that the zero-shear viscosity of star-branched polymers depends exponentially upon the arm molecular weight M_a above a critical molecular weight [Raju *et al.* (1979a), Carrella *et al.* (1986), Fetters *et al.* (1993)]. Furthermore, in studies by Jordan *et al.* (1989) and Gell *et al.* (1997) it was found that the length of the shortest arm in asymmetric PB and poly(ethylene-alt-propylene) (PEP) three-arm stars must exceed the critical molecular weight for entanglement, M_c, in order to manifest zero-shear viscosity enhancement. This finding certainly reiterates the importance of entanglement coupling as the mode of enhancement.

Perhaps the most interesting studies on model branched systems were performed by Roovers and Graessley (1981) and Roovers (1984). These authors investigated the effects of topology on the zero-shear viscosity behavior of comb and H-shaped polystyrenes (PS). Roovers (1984) observed that H-shaped polystyrene molecules exhibit a substantially greater degree of viscosity enhancement than either three or four-arm stars of equivalent molecular weight. This observation is believed to be due to a long-time relaxation mechanism associated with the central segment between branch points. Therefore, one assumes that the number of branch points per molecule may have an additional influence on shear rheological properties.

More recently Lohse and co-workers (2002) reported melt rheological studies on model long-chain branched polyethylene where the branching level and type were known precisely from the synthesis. These polymers were generated by means of hydrogenation of polybutadiene and, hence, every chain was branched uniformly. Although they present a significant amount of data, the only definitive conclusion that they arrived at was that chains with LCB exhibited a greater degree of shear thinning than linear chains. They did not draw any conclusions about the effect of architecture (i.e., combs, three-arm stars, etc.) on the degree of shear thinning. Furthermore, they could draw no definitive conclu-

sions on the comb systems in terms of the effect of number of branches versus M_a (arm molecular weight).

The work carried out on the model systems was all done on systems which were typically uniformly and highly branched and of narrow MWD. In many cases MW was extremely high and high degrees of entanglement coupling were present. Hence, the direct application of what has been learned from the model systems to the randomly sparsely branched systems is somewhat unclear at this point. Certainly viscosity enhancement occurs in star polymers, but it is not related to the degree of branching (i.e., the number of branch points). The viscosity enhancement in the H and comb polymers may be the most pertinent to the sparsely branched PEs as it suggests that the number of branch points along a chain may provide additional enhancement of viscosity.

In the current study, a series of six commercially available PE resins are analyzed to better understand the effects of sparse long-chain branching on steady and dynamic oscillatory shear rheology and to separate the effects of MW and MWD from those to due to sparse LCB. Four of these resins are narrow molecular weight distribution metallocene-catalyzed polyethylenes, of which three are sparsely long-chain branched. The remaining two resins are conventional LLDPE and LDPE resins that will serve as comparative resins throughout the study. The complete significance of the behavior of the mPEs is better demonstrated with the inclusion of data for the two conventional PEs as LLDPE has a broader MWD than the linear mc-PE and LDPE is highly branched and of broad MWD. The molecular weight distributions and long-chain branching have been obtained from dilute solution characterization measurements (Provided by Dow Chemical Company). The goal of this study is to establish the effects that sparse long-chain branching has on the steady and dynamic shear rheological properties of polyethylenes. In order to focus exclusively on the effects of LCB, the role of M_w will be removed using the time-molecular weight superposition approach outlined earlier. This should allow for a more accurate depiction of the role of sparse long-chain branching relative to MWD on the rheology of commercial mPE resins.

II. EXPERIMENT

A. Materials

A series of six commercial polyethylene resins were chosen for this study. These resins typify the range in molecular structure found in commercial polyethylenes and afford a sufficient quantity of material to perform complete rheological analysis. Furthermore, each of the resins analyzed has a melt index close to one. The use of resins with similar melt indices provides an industrial measure with which to compare these resins, as well as expose the deficiencies of using the melt index as a measure of rheological response. The particular resins chosen for this study and their relevant indices are tabulated in Table I.

The first four resins listed in Table I are metallocene-catalyzed polyethylene resins. The mPE resins were specifically chosen to compare the effects of level of sparse long-chain branching on melt rheology. The Affinity PL1840 and PL1880 resins are manufactured by Dow Chemical using INSITE® catalyst technology. These two resins are solution polymerized ethylene-octene copolymers. The Exact 0201 and 3132 resins are manufactured by ExxonMobil Chemical using EXXPOL® catalyst technology. The Exact 0201 resin is an ethylene-octene copolymer while the Exact 3132 is an ethylene-hexene copolymer. The Affinity PL1840, Affinity PL1880, and Exact 0201 resins were identified as having sparse long-chain branching by their respective manufactures. The Exact 3132

TABLE I. Materials studied.

Resin	Density g/cm^3	MFI dg/min
Exact 0201	0.902	1.1
Exact 3132	0.900	1.2
Affinity PL1840	0.909	1.0
Affinity PL1880	0.902	1.0
NTX101	0.917	0.9
NA952	0.919	2.0

was specified as a strictly linear mPE copolymer. All four resins have melt indices between 1.0 and 1.2. The densities of these materials are also similar and imply equivalent comomoner content.

The remaining two resins listed in Table I are conventional linear low-density polyethylene (LLDPE) and low-density polyethylene. The NTX101 resin is an ethylene-hexene copolymer manufactured by ExxonMobil using a Zielger-Natta gas-phase polymerization process. The NA952 resin is an ethylene homopolymer manufactured by Equistar using a high-pressure, high-temperature tubular free-radical polymerization process. The NTX101 was chosen as a linear reference material, while the NA952 resin was chosen as a densely branched reference material.

B. Analytical methods

Molecular weight distribution information was obtained using combined high temperature gel permeation chromatography (GPC), intrinsic viscosity measurements, and low-angle laser light-scattering measurements. This triple-detector technique provides absolute molecular weight determination and can be used to determine branch content in the sparsely branched mPE resins. The degree of sparse branching is calculated using the Mark–Houwink and Zimm-Stockmayer relations [Flory (1953); Zimm and Stockmayer (1949)]. In the case of the highly branched NA952 resin, C^{13} NMR measurements were used to quantify the branch content. The major limitation to using this method with LDPE is that it cannot distinguish branches having lengths greater than six carbon atoms ($M_{branch} > 85$ g/mol) [Janzen and Colby (1999)]. Therefore, one may expect some short-chain branches (85 g/mol $< M_{branch} < M_c$) to be counted with the long-chain branches. Thus, the reported branching value is most likely larger than the true number of long-chain branches. All of the molecular characterization of these resins was performed by researchers at Dow Chemical (Freeport, TX) and the analysis of the branching level for the sparsely branched systems is discussed in detail elsewhere [Wood-Adams *et al.* (2000)]. However, it should be noted that the repeatability of the measurements is of the order of $\pm 10\%$.

All measurements of the shear viscoelastic properties were performed using a Rheometrics Mechanical Spectrometer Model 800 (RMS-800). A set of 25-mm-diam parallel-plate fixtures was used for the small-amplitude dynamic oscillatory measurements while a set of 25 mm cone and plate fixtures was used for all steady shear measurements. The cone angle used for all steady shear measurements was 0.1 rad. All testing was performed within an inert nitrogen atmosphere to prevent thermo-oxidative degradation. The test samples were prepared by compression molding preforms at 170 °C under nominal pressure and allowing them to cool slowly under no pressure. This method provides homogeneous samples with minimal residual stress. The shear rheometry results represent the

TABLE II. Molecular weight distribution and LCB.

Resin	M_w	M_w/M_n	M_z	LCB /10^4 C
Exact 0201	88 700	2.14	158 900	0.79
Exact 3132	111 000	2.04	180 400	⋯
Affinity PL1840	87 400	2.43	160 200	0.57
Affinity PL1880	115 800	2.12	183 700	0.18
NTX101	122 700	3.44	319 700	⋯
NA952	235 500	17.1	2 619 300	39[a]

[a]C^{13} NMR measurement.

average of at least three runs using different samples each run. All testing was performed at a melt temperature of 150 °C. The calculated errors for the dynamic oscillatory and the steady shear viscosity measurements were found to be less than ±5% and ±10%, respectively.

III. RESULTS AND DISCUSSION

A. Molecular characterization

The results of the molecular characterization are tabulated in Table II. It should be noted that the results for LCB and MW were provided by Dow Chemical Company (see the Acknowledgments). The weight average molecular weight (M_w), molecular weight distribution, z-average molecular weight (M_z), and long-chain branching content are reported for each resin. The weight average molecular weights vary between 87 400 g/mol for the Dow Affinity PL1840 resin to 235 500 g/mol for the Equistar NA952 resin. The molecular weight distributions of the metallocene resins are relatively narrow at approximately two, although we note that the Dow 1840 resin has a breadth of 2.41. The NTX101 has a broader MWD at 3.44, and the NA952 has the broadest molecular weight distribution at 17.1. The z-average molecular weights have been provided to further quantify the full distribution curves featured in Fig. 1. The most important parameter for this study is the estimate for the degree of long-chain branching. The mPE resins vary in long-chain branching content from zero for the linear Exact 3132 resin to 0.79 LCB/10^4 carbons for the Exact 0201 resins. The repeatability of these measurements is about ±10%, making the difference in branching levels between the Dow PL1840 and Exxon 0201 resins statistically significant (but certainly only mildly so). The Affinity PL1840 and PL1880 resins yield intermediate values. The NTX101 resin is also linear and contains no long-chain branches, while the densely branched NA952 contains 39 branches/10^4 carbons. Although short-chain branching may be included in the value for the NA952 resin, the high degree of branching is confirmed by the very broad molecular weight distribution.

B. Shear viscosity

The flow curves for each of the six resins are plotted in Fig. 2. Each flow curve consists of steady shear and dynamic oscillatory data where it is assumed that the magnitude of complex viscosity is representative of the shear viscosity at high frequencies or shear rates. The steady shear data cover the shear rate range of 0.001–0.1 s^{-1} and the dynamic oscillatory data cover the frequency range of 0.1–100 rad s^{-1}. The low-frequency intersection between steady and dynamic oscillatory data is in good agreement for all resins and implies that the Cox–Merz rule holds at low shear rates [Cox and Merz
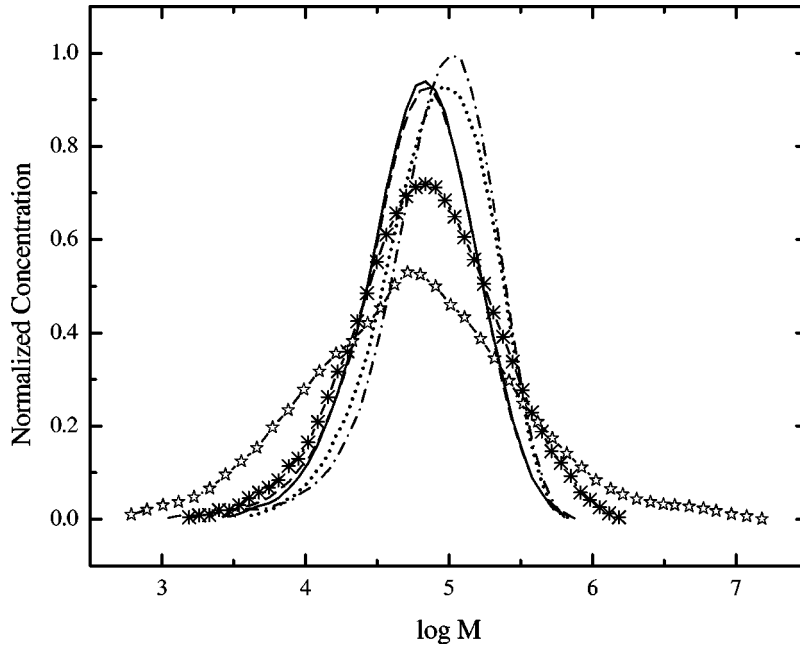
FIG. 1. Molecular weight distribution curves for Exact 0201 (——), Exact 3132 (···), Affinity PL1840 (− − −), Affinity PL1880 (—·—), NTX101 (—●—), and NA952 (—∗—).
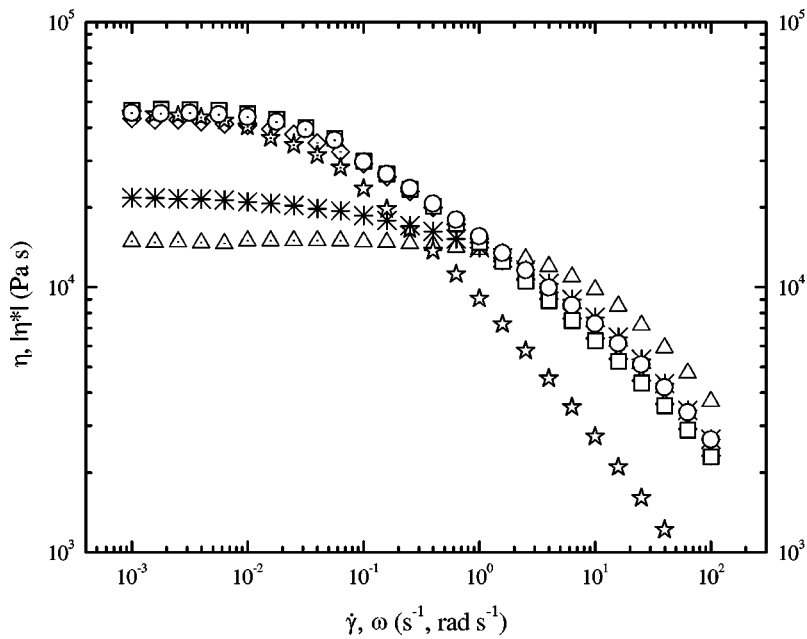
FIG. 2. Steady shear and complex viscosities at 150 °C. (◇) Exact 0201, (△) Exact 3132, (∗) NA952, (●) NTX101, (□) Affinity PL1840, and (○) Affinity PL1880. Dotted symbols represent steady shear measurements; open symbols represent dynamic oscillatory measurements.

(1958)]. Data collected at higher shear rates using a capillary rheometer (but not shown here for clarity) suggest that the Cox–Merz rule holds true for the branched resins but deviates slightly for the linear resins [Doerpinghaus (2002)].

Despite similarities in the shear viscosity curves of the sparsely branched mPE resins, the molecular structure of these materials is different based on the MW and branching data. One of the most prominent differences is M_w according to GPC–LALLS data tabulated in Table II. Therefore, an appropriate method for removing M_w dependence of the shear rheological properties is desirable. One such method is the time–molecular weight (TMW) superposition principle. This principle is obeyed by polymers having similar, narrow molecular weight distributions [Vinogradov and Malkin (1980)]. First, the observed shift in the zero-shear viscosity η_0 with M_w follows the classical relationship presented by Berry and Fox (1968) for linear, flexible chain molecules above their critical molecular weight for entanglement, M_c. This relationship appears as

$$\eta_0 = KM_w^{3.4}, \tag{4}$$

where K is a prefactor that is dependent upon molecular composition and temperature. Second, the longest relaxation time τ_1 is observed to be directly proportional to the product of the steady-state compliance J_s^0 and the zero-shear viscosity as given in Eq. (5) [Ferry (1980)],

$$\tau_1 \propto J_s^0 \eta_0. \tag{5}$$

Because the steady-state compliance is often found to be independent of M_w above $2M_c$ [Ferry (1980)], the resulting relationship for the longest relaxation time yields the same M_w dependence as the zero-shear viscosity. Therefore, combining these concepts leads to equivalent shifting along the time, or rate, axis, and the viscosity axis. The actual superposition is then applied using the shift factor a_M, given as

$$a_M = \frac{\eta_0(M)}{\eta_0(M_{\text{ref}})}, \tag{6}$$

where $\eta_0(M)$ refers to the zero-shear viscosity at a given M_w, and $\eta_0(M_{\text{ref}})$ refers to the zero-shear viscosity at the reference M_w. Applying this principle to linear materials with similar, narrow molecular weight distributions should shift rheological data obtained at different M_w to a single master curve.

Using the characteristic relationship between zero-shear viscosity and M_w for *linear* polyethylenes at $190\,^{\circ}\text{C}$ [i.e., $\eta_0 = 3.4 \times 10^{-15} M_w^{3.6}$, Raju *et al.* (1979b)], it is proposed to normalize all of the viscosity flow curves by their respective M_w and shift to a reference molecular weight. The most logical reference material is the Exact 3132 resin because it is linear and of narrow molecular weight distribution. Application of the shift factor a_M [$= \eta_0(M)/\eta_0(M_{\text{ref}})$] should provide a clear picture of the individual contributions of sparse long-chain branching to the steady shear viscosity. As a point of further clarification we calculate η_0 for the equivalent linear polymer having the same M_w as the branched polymer. Then use this value along with η_0 of the linear Exact 3132 resin to calculate a_M.

The shifted viscosity curves found in Fig. 3 exhibit significant features. The most obvious feature is the separation of the branched resins. η_0 of the Exact 0201 and PL1840 resins are greater than six times η_0 of the Exact 3132 resin, compared to a factor of three before shifting. Furthermore, PL1880 shifts to an intermediate value that is less than three times η_0 of Exact 3132. These differences in viscosity must be primarily
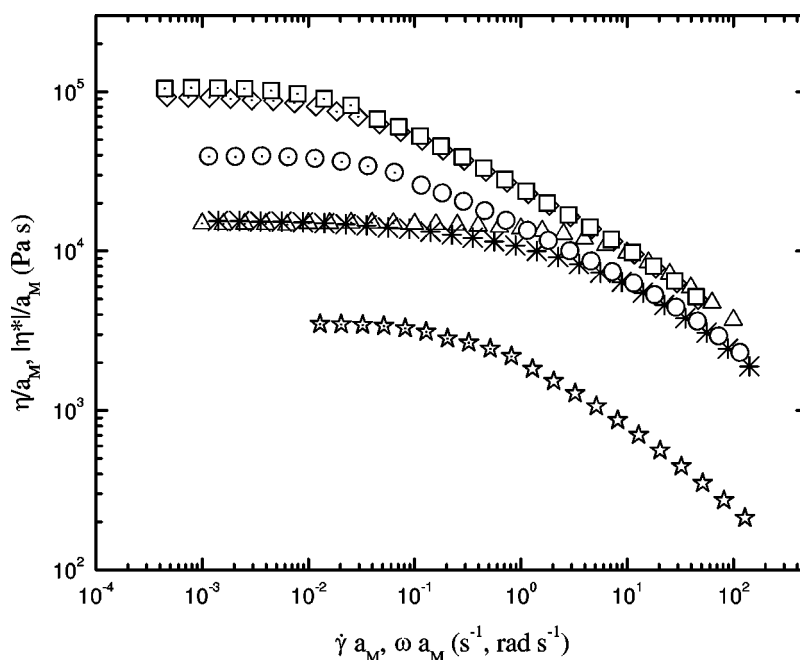
FIG. 3. Shifted steady shear and complex viscosities, $M_{\text{ref}} = 111\,000$ g/mol. ($\diamond$) Exact 0201, ($\triangle$) Exact 3132, (∗) NA952, (●) NTX101, (□) Affinity PL1840, and (○) Affinity PL1880. Dotted symbols represent steady shear measurements; open symbols represent dynamic oscillatory measurements.

attributed to the presence of long-chain branching rather than differences in breadth of MWD. This is further supported by the fact that η_0 of the conventional LLDPE falls directly on the linear mPE reference, in spite of the difference in breadth of MWD. This shows that for this range of difference in breadth of distribution, there is no contribution to η_0 from the broader MWD. Furthermore, even though the breadth of MWD for the Dow PL1840 sample is greater than that of the Exxon 0201 sample, the curves still superimpose on top of each other. This further strengthens the argument for enhancing η_0 by the presence of LCB by proving that MWD does not significantly affect η_0. Quite surprisingly, the shear viscosity curve for NA952 is reduced precipitously from its original unshifted value. This is in spite of the fact that M_w is relatively large compared to the other resins. Hence, the difference must be related to the high level of LCB.

The results obtained from the shifted flow curves in Fig. 3 appear to agree qualitatively with the phenomenological relation of Janzen and Colby (1999). The sparsely branched resins exhibit a noticeable degree of enhancement of η_0, while the densely branched LDPE shows a significant reduction in η_0. Figure 4 illustrates the predictions of Eqs. (4) and (5) for three different values of M_w. In all cases, the viscosity initially increases before reaching a maximum below one long-chain branch per molecule and then begins to decrease. The maximum degree of η_0 enhancement and the point of no enhancement are determined by the M_w of the system. Using the dilute solution measurements for long-chain branching content combined with Eqs. (1), (2), and (3), the degree of viscosity enhancement can be estimated for each of the branched resins. The experimentally observed enhancement [$\Gamma = \eta_0(\text{branched})/\eta_0(\text{linear})$] and the predicted enhancement are shown in Table III. We note here that η_0 (linear) is calculated from the relation in Eq. (4) using M_w of the branched polymer. In other words, we
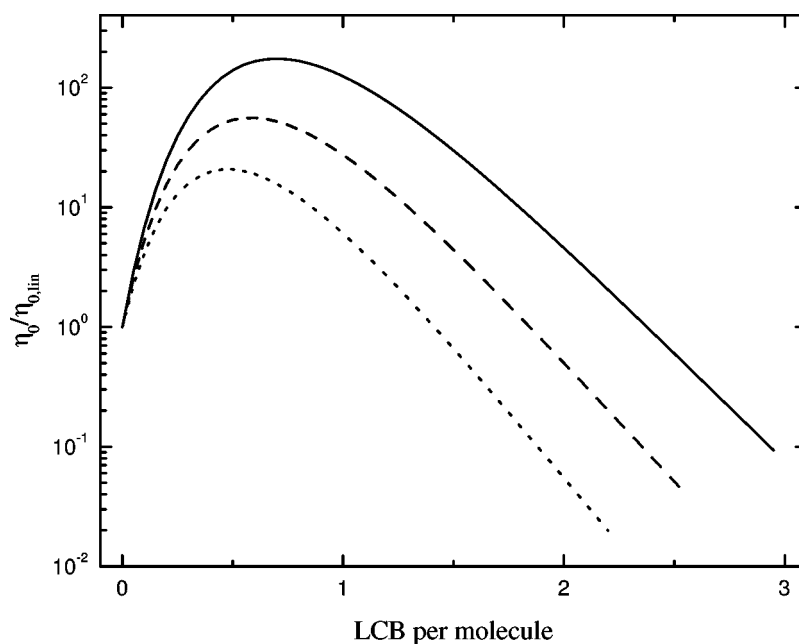
FIG. 4. Predicted zero-shear viscosity versus long chain branches per molecule using the Janzen and Colby (1999) viscosity relation. (——) M_w = 100 000 g/mol, (···) M_w = 88 000 g/mol, (− − −) M_w = 120 000 g/mol.

calculated η_0 of the equivalent linear polymer. From the measured long-chain branching values, the predicted degrees of enhancement are considerably higher for the sparsely branched resins, and lower for the densely branched LDPE, than the observed enhancement. This may be due to the unknown accuracy of the dilute solution measurements of the degree of long-chain branching which was discussed briefly in the introduction. Of course, the validity of the Janzen and Colby approach as applied to PE could be questioned as there is no easy way to validate it. On the other hand, the significant under prediction of η_0 of LDPE is most likely a consequence of the over estimation of the degree of long-chain branching provided by C^{13} NMR characterization (which counts all branches > 6 carbons). Nevertheless, the observed enhancement for the sparsely branched resins and reduction for the densely branched resin is in qualitative agreement with the phenomenological treatment of Janzen and Colby (1999) and with the predicted behavior proposed by Bersted and co-workers (1981).

TABLE III. Observed η_0 enhancement Γ_{obs} vs predicted η_0 enhancement Γ_{pred} from the Janzen and Colby viscosity relation.

Resin	Γ_{obs}	Γ_{pred}
Exact 0201	6.0	41
Exact 3132	1.0	1.0
Affinity PL1840	6.8	22
Affinity PL1880	2.5	8.0
NTX101	1.0	1.0
NA952	0.2	< 0.01

Although enhancement of η_0 is observed in the sparsely branched metallocene resins, no difference between the Dow PL1840 and the Exxon 0201 resins is observed in spite of the fact that the Exact 0201 resin is believed to be more highly branched (0.79 LCB/10^4 carbons) than the Dow PL140 resin(0.57 LCB/10^4 carbons). This lack of differentiation is believed to be due to one or more of three possible reasons. First, although the dilute solution measurements are believed to be statistically different, the difference in the branching level could be quite small. Thus, having similar M_w, MWD, and degree of LCB will lead to the same shear rheological behavior. Even though there is a difference in the MWD between the two resins, it apparently does not contribute to an increase in η_0 as evidenced by the results for the two linear polymers reported earlier. Second, based on the Janzen and Colby treatment, it is possible that two resins with the same η_0 can have different degrees of LCB especially in the range of branching level where enhancement of η_0 is a maximum. Finally, it is possible that the distribution of molecular structures within the polymers may be different as a result of different catalysts and reaction conditions used. Numerical studies by Soares and Hamielec (1995, 1996) predict that a distribution of molecules containing linear, star, and higher branched structures exist in sparsely long-chain branched metallocene polyethylenes. Because dilute solution measurements indicate an average number of branches, the exact concentration of linear and branched species within the whole polymer is unknown. From observations by Roovers (1984), polymer macromolecules containing two branch points exhibit much greater zero-shear viscosity dependence upon M_w than three-arm stars of comparable M_w. Therefore, one may infer that variations in the catalyst systems used by the respective manufactures may give rise to a different distribution of linear and branched species which is reflected in the zero-shear viscosity measurements. The possibility of different branching structure is actually confirmed by fitting of the multimode pom-pom model to transient extensional data for these two resins [Doerpinghaus and Baird (2003)]. In particular, they found that, first of all, they could distinguish between the two resins using extensional stress growth measurements and second, a higher number of effective branch points was associated with the longest relaxation modes for the Exxon 0201 versus the Dow 1840 resin.

In addition to the effect on η_0, the onset of shear thinning is also affected by shifting the viscosity flow curves. In an attempt to better visualize these effects, Figure 5 presents the flow curves reduced by η_0 versus shifted shear rate for each resin. The results clearly point out the dramatic effect that long-chain branching has on the onset of shear-thinning in sparsely, randomly branched systems. The onsets of shear-thinning behavior are shifted to $\dot{\gamma} = 0.02 \text{ s}^{-1}$ for PL1840 and Exact 0201, 0.06 s^{-1} for PL1880, 0.15 s^{-1} for NTX101, and 0.13 s^{-1} for NA952. Surprisingly, this represents a two-order of magnitude decrease in the onset of shear thinning between the linear mPE resin and the sparsely branched mPE resins. The observed decrease in the onset of shear thinning is considerably greater than the observed enhancement of η_0. If the onset of shear thinning behavior is related to the terminal relaxation time, then the relation described by Eq. (5) does not hold for sparsely branched resins and that an additional dependency arising from long-chain branching exists. In other words, the magnitude of the shift in the onset of shear thinning behavior to lower shear rates is more than an order of magnitude greater than the enhancement of η_0. Based on fits of the pom-pom model to shear and extensional data by Doerpinghaus and Baird (2003), it seems that the branches attach themselves to the longest chains and this may, thereby, account for the increase in the relaxation times in a non-linear manner. In addition, we note the onset of shear thinning for the linear NTX101 resin occurs at a shear rate about an order of magnitude lower than that for the Exact 3132 which is due to the broader MWD of the NTX101 resin. However, the
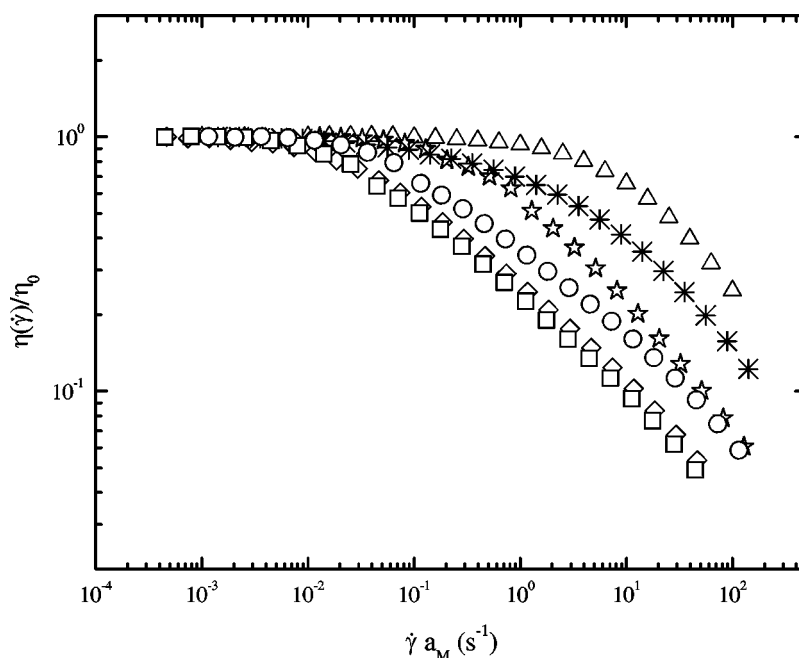
FIG. 5. Normalized shear viscosities. ($\diamond$) Exact 0201, ($\triangle$) Exact 3132, ($*$) NA952, ($\bullet$) NTX101, ($\square$) Affinity PL1840, ($\bigcirc$) Affinity PL1880.

reduction in shear rate for the onset of shear thinning is less than that caused by the presence of sparse LCB. We note also that the broader MWD leads to a reduction in shear rate for the onset of shear thinning but to no effect on the magnitude of η_0, while branching affects both the magnitude of η_0 and the onset of shear thinning.
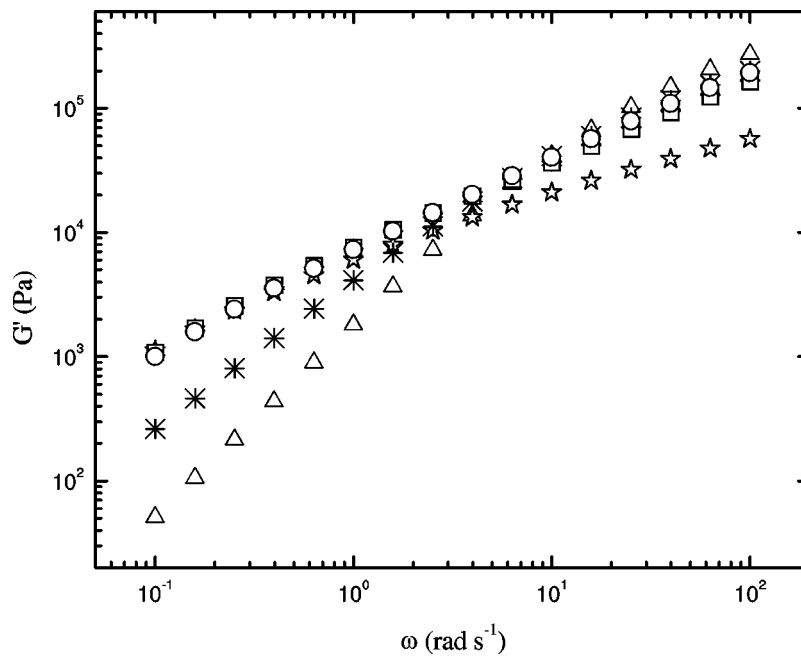
C. Dynamic moduli

We next turn our attention to the sensitivity of the dynamic moduli to the effects of sparse long-chain branching. The dynamic storage (G') and loss (G'') moduli for each resin over the frequency range of 0.1–100 rad/s are presented in Figs. 6 and 7. G'' is nearly identical over the whole frequency range for all the resins except the highly branched LDPE whose magnitude is significantly less than the others. At high frequencies G'' of the linear Exact 3132 resin is slightly higher. However, in general the effects of sparse branching, MW, and MWD are more convoluted for G'' than for the viscosity. Figure 7 presents the storage modulus as a function of frequency. Just as for the viscosity function G' for the three branched resins is basically the same over the whole frequency range. At high frequencies even G' of the linear resins overlap with the values for the sparsely branched resins. Only the values of G' for the highly branched resin are different from those of the other resins. Once again, the influence of molecular weight is convoluted with that of long-chain branching and molecular weight distribution.

In order to separate the effects of M_w we again apply time-molecular weight super-position to the storage moduli which leads to the results found in Fig. 8. As seen for the shear viscosity, once the effect of MW is removed by the shifting procedure the effect of sparse LCB can be more readily observed. In particular, at low frequencies G' is about an order of magnitude higher for the sparsely branched resins relative to the linear resins. G' values of the pair of Affinity PL 1840 and Exact 0201 are about a factor of two higher
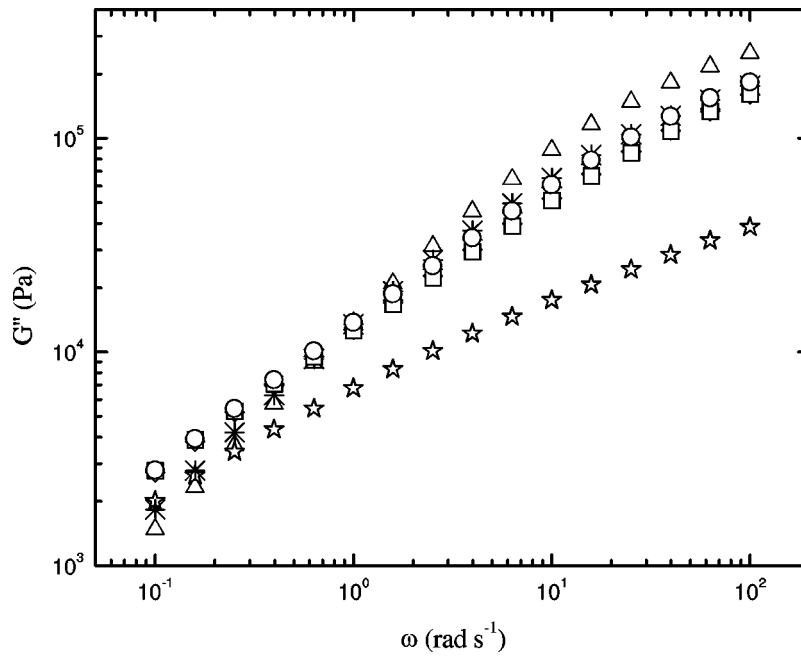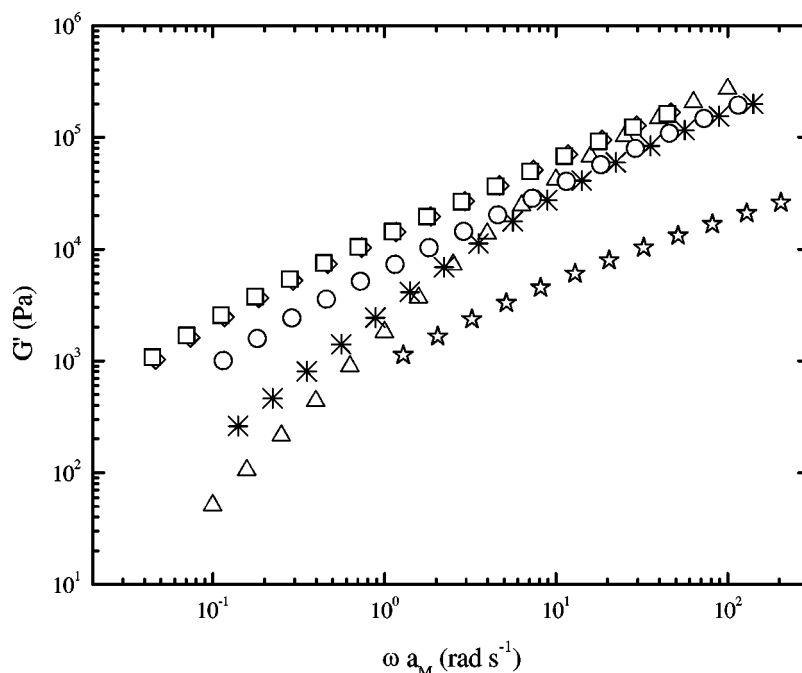
FIG. 6. Dynamic loss moduli at 150 °C. (◇) Exact 0201, (△) Exact 3132, (∗) NA952, (●) NTX101, (□) Affinity PL1840, and (○) Affinity PL1880.

FIG. 7. Dynamic storage moduli at 150 °C. (◇) Exact 0201, (△) Exact 3132, (∗) NA952, (●) NTX101, (□) Affinity PL1840, and (○) Affinity PL1880.

FIG. 8. Shifted dynamic storage moduli, M_{ref} = 111 000 g/mol. ($\Diamond$) Exact 0201, ($\triangle$) Exact 3132, ($*$) NA952, ($\bullet$) NTX101, ($\square$) Affinity PL1840, and ($\bigcirc$) Affinity PL1880.

than those of Affinity PL 1880 at low frequencies. However, again we are not able to distinguish between the Affinity PL 1840 and Exact 0201 resins. This dependence of G' upon the apparent degree of long-chain branching as based on dilute solution measurements appears consistent with previous studies for a somewhat different range of mPE resins. [Wood-Adams and Dealy (2000)]. We note that the NTX101 resin has noticeably greater values of G' relative to those of the Exact 3132 resin in the lower frequency range which is consistent with the broader MWD but which is different from the viscosity data in which at low shear rates there was superposition of the data. In other words, the broader MWD has no effect on η_0 but does increase G' at low frequencies. The values of G' for the two linear resins merge at high frequencies. This again is consistent with our work involving the fitting of the multimode pom-pom model to shear and extensional data in which it was observed that branching was most likely not present in the lower molecular weight chains [Doerpinghaus and Baird (2003)]. Hence, at high frequencies the sparsely branched mcPEs behave like linear polymers.
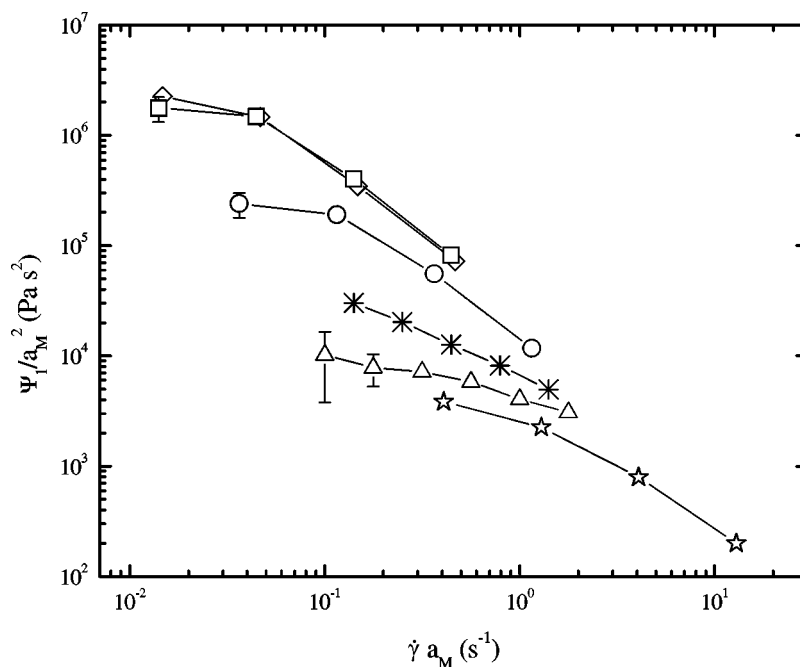
D. Primary normal stress difference

Along with the dynamic storage modulus, another strong indicator of elastic properties is the primary normal stress difference (N_1). N_1 typically exhibits greater dependence on M_w than η_0 [Vinogradov and Malkin (1980)], and as such may be more sensitive to the presence of long-chain branching. The measured values of N_1 are reported in Fig. 9. The results indicate that NA952 exhibits the greatest value of N_1 at all rates examined, closely followed by the sparsely branched mPE resins. The linear mPE resin exhibits the lowest values of N_1 over the range tested. Again there is no statistical difference between the values of N_1 for the three sparsely branched resins. These observations appear to be
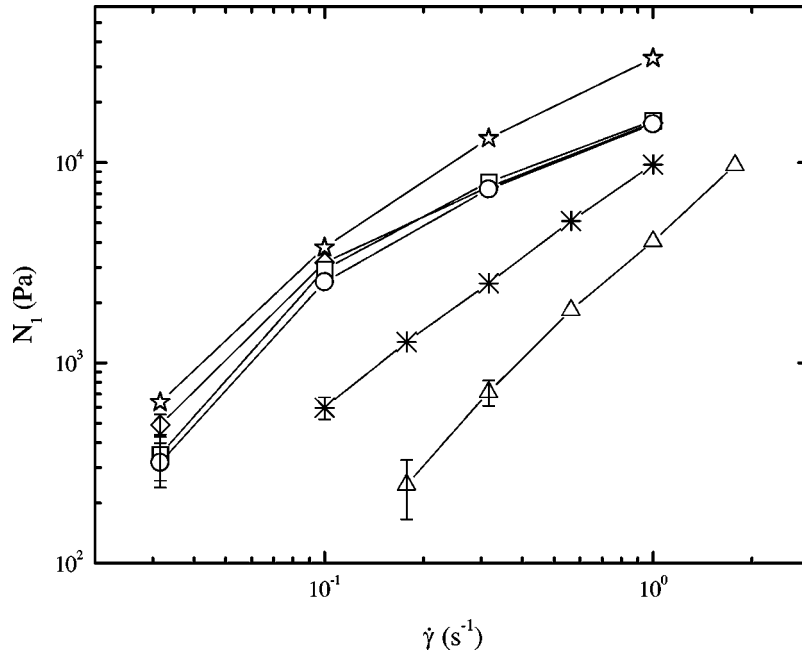
FIG. 9. Primary normal stress differences (N_1) at 150 °C. ($\diamond$) Exact 0201, ($\triangle$) Exact 3132, ($*$) NA952, ($\bullet$) NTX101, ($\square$) Affinity PL1840, and ($\bigcirc$) Affinity PL1880. Lines have been drawn to aid eye.
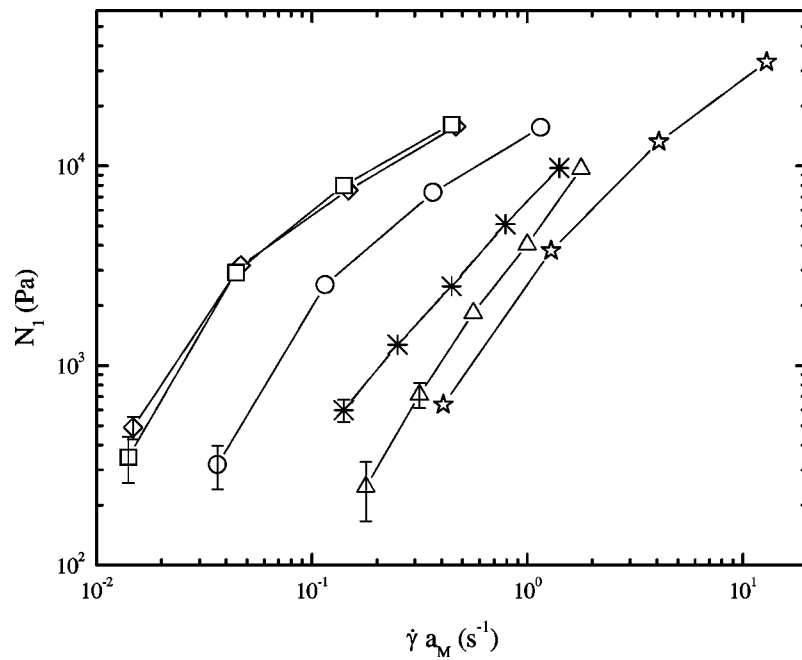
FIG. 10. Shifted primary normal stress difference, $M_{ref} = 111\,000$ g/mol. ($\diamond$) Exact 0201, ($\triangle$) Exact 3132, ($*$) NA952, ($\bullet$) NTX101, ($\square$) Affinity PL1840, and ($\bigcirc$) Affinity PL1880. Lines have been drawn to aid eye.

FIG. 11. Shifted primary normal stress difference coefficient (Ψ_1), M_{ref} = 111 000 g/mol. ($\diamond$) Exact 0201, ($\triangle$) Exact 3132, (*) NA952, ($\bullet$) NTX101, ($\square$) Affinity PL1840, and ($\circ$) Affinity PL1880. Lines have been drawn to aid eye.

consistent with shear viscosity results presented earlier. Again we apply the time–MW shift procedure to determine if the differences between these resins will become more evident. Figure 10 shows the shifted values of N_1. Once again, the sparsely branched mPE pair of Exact 0201 and PL1840 are differentiated from the less branched PL1880 resin. Next are the conventional LLDPE resin, the linear mPE resin, and finally the densely branched LDPE. As shown earlier for the G' data, the broader molecular weight distribution found for the NTX101 contributes to additional elasticity. Although the range of available data is limited, the results agree well with G' data over the same interval.

To better illustrate the impact that long-chain branching has on the elastic properties of PE melts the primary normal stress difference coefficient, Ψ_1, is investigated. In the limit of infinitesimal deformation rates $\Psi_{1,0}$ becomes directly proportional to the square of the zero-shear viscosity, η_0^2 [Ferry (1980)]. The molecular weight invariant (shifted) values of Ψ_1 are plotted in Fig. 11. Due to the limited amount data available for the Exact 3132 resin, an accurate determination of $\Psi_{1,0}$ is not possible. Nevertheless, the results exhibit some interesting trends. First, the degree of enhancement between the PL1880 and the remaining sparsely branched mPE resins has increased noticeably. In fact, the degree of enhancement using available data is a factor of about 100 for the two sparsely branched resins, PL1840 and Exact 0201, relative to the linear resin, Exact 3231. This enhancement is considerably greater than the zero-shear viscosity enhancement *squared* (about a factor of three at the lowest shear rates). This may represent an additional dependency of Ψ_1 on LCB or may include the effects of branching on the steady-state compliance, J_s^0. Second, all of the normal stress coefficient curves appear to con-

verge at higher rates. This phenomenon has also been observed by Wood-Adams (2001), and implies that the effects of branching are most prominent in the low shear rate regime, as expected.

IV. CONCLUSIONS

The application of the time-molecular weight superposition principle provides the ability to differentiate the effects of sparse LCB from those due to MW and MWD on the shear rheological properties of polyethylene resins. The effects of long-chain branching and molecular weight distribution can be effectively separated from those due to weight-average molecular weight. In this case, the true enhancing effect of long-chain branching on the zero-shear viscosity, dynamic storage modulus, and primary normal stress difference are only realized after the overlying effects of weight-average molecular weight have been removed.

The molecular weight invariant analysis of the sparsely branched metallocene polyethylenes used in this study show a significant degree of enhancement in steady and dynamic oscillatory shear rheological properties. The zero-shear viscosity of mPE resins was found to increase by a factor of 6 with as little as 0.6 LCB/10^4 carbons relative to the linear polymer of similar MW, yet η_0 for the densely branched LDPE was observed to decrease by a factor of four relative to the linear resin at much higher branching content. Furthermore, the onset of shear-thinning behavior is markedly shifted to lower shear rates because of sparse long-chain branching. Sparse LCB increases η_0 and decreases the critical shear rate for the onset of shear thinning, while MWD only influences the critical shear rate. The dynamic storage modulus shows that most of the elastic character resulting from sparse long-chain branching is evident at lower deformation rates, and that elasticity is only mildly sensitive to a broadening molecular weight distribution. The primary normal stress difference data agrees with the zero-shear viscosity and storage modulus results, but also suggests a much stronger dependence on long-chain branching than either η_0 or G'.

Comparing the dilute solution and C^{13} NMR branching measurements, in combination with the Janzen and Colby treatment, to the observed rheological enhancement answers several questions concerning the influence of long-chain branching, but also raises others. A threefold increase in long-chain branch content results in a zero-shear viscosity enhancement of 2.7 between the Affinity PL1840 and PL1880 resins. Conversely, an increase in LCB content from 0.57 to 0.79 LCB/10^4 carbons does not result in any additional effect on shear rheological properties. This may imply that dilute solution measurements of sparsely branched mPE resins are inaccurate, or the distribution of linear and branched macromolecular species in the polymers are statistically different as a result of the different catalysts used in the synthesis of the metallocene-catalyzed polyethylene manufactures.

The enhanced values of η_0, the onset of shear thrinning at lower shear rates and the increase in the elastic properties at low branching levels relative to the linear PE's are consistent with the concept that branching primarily occurs on the higher molecular weight chains (i.e. chains with the longest relaxations modes).

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