Shear and extensional rheology of sparsely branched metallocene-catalyzed polyethylenes

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Synopsis

The purpose of this study was to identify any rheological effects that are consistent with the presence of sparse levels of long chain branching (LCB) in three commercial metallocene-catalyzed polyethylenes (MCPE) all of the same melt flow index of 1.0. Two Dow INSITE MCPEs with apparently varying levels of LCB of approximately 0.17 and 0.57/10 000 carbon atoms and one Exxon EXXPOL MCPE with no LCB were studied. The breadth of distribution as determined by M_w/M_n of the three samples was 2.11 for the Exxon and one of the Dow samples, and 2.42 for the other Dow sample that had the highest degree of LCB. The MCPE with the highest branching seemed to have a slightly higher molecular weight tail in the distribution. Both the Dow samples had significantly higher flow activation energies than the Exxon sample, consistent with the presence of LCB, but this method could not distinguish between the two branched polymers. The differences in M_w could also not account for the appreciably higher zero-shear viscosities of the branched samples relative to the linear sample. Despite the differences in M_w and LCB content in the two Dow samples, they exhibited almost identical shear flow curves at temperatures between 120 and 170 °C. They also exhibited very similar shear stress growth behavior. Under constant extension rate deformation, the two samples with LCB showed a significant degree of strain hardening relative to the linear sample. Comparison between the two Dow samples revealed that the sample with the higher degree of LCB showed a greater degree of strain-hardening behavior. The extensional behavior is consistent with the LCB content determined by means of solution light scattering. © 2000 The Society of Rheology. [S0148-6055(00)00905-6]

I. INTRODUCTION

There are some aspects of the molecular architecture of commercial polyethylene (PEs) that make them unsuitable for the study of the effects of long-chain branching (LCB) on rheology. Conventional low-density polyethylene (LDPE), produced commercially by a free radical polymerization process under high temperature-pressure conditions, is characterized by short-chain branching and random LCB with a very high branching frequency ($> 0.5/1000$ carbon atoms) [Benedikt and Goodall (1998); Randall (1980)]. High-density polyethylenes (HDPE) and linear low-density polyethylenes (LLDPE), produced commercially by Ziegler–Natta or Phillips-type catalysts, are known to have a LCB content of about one to two orders of magnitude lower than the branching frequency in LDPE [Hogan *et al.* (1967); Randall (1980)]. Another characteristic of all the conventional PEs is that the breadth of molecular weight distribution (MWD) is large.

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The breadth of distribution, indicated by M_w/M_n, can be up to 20 for LDPE and usually between 5 and 15 for HDPE [Raff and Doak (1965)]. The mechanism of polymerization of conventional PEs is such that an increase in the number of long-chain branches is accompanied by an increase in the breadth of distribution. This is why it has been difficult to ascertain the effects of LCB alone on the rheology of these materials as the effects of LCB and MWD are intertwined and cannot be easily separated. Hence, researchers in the past have resorted to other laboratory techniques, such as peroxide reaction or irradiation, to produce PEs with fairly controlled molecular architecture.

The presence of LCB has been known to have some significant effects on the shear rheology of polyethylenes. Graessley and Raju (1984) found that the molecular weight dependence of the zero-shear viscosity, η_0, of linear polyethylenes was $\eta_0 = 3.40 \times 10^{-14} M_w^{3.6}$, which is in good agreement with the 3.4–3.6 power found for most flexible linear polymers [Vinogradov and Malkin (1980)] and reported by others for linear polyethylenes [Raju *et al.* (1979b); Mendelson *et al.* (1970)]. But the zero-shear viscosity of three-arm and four-arm star polyethylenes, produced by the hydrogenation of three-arm and four-arm polybutadienes, respectively, had a higher dependence on the molecular weight than 3.6 [Raju *et al.* (1979a)]. Lusignan and co-workers (1995, 1996, 1999) carried out a systematic study on the effects of branching on the zero-shear viscosity of polyesters. In particular, holding the average molecular weight between branch points, M_b, constant they systematically varied the molecular weight. They observed that the exponent in the relation between η_0 and M_w could be greater or less than 3.4 depending on the magnitude of M_b. Lusignan and co-workers (1995, 1996, 1999) proposed a general phenomenological description for describing the molecular weight dependence of the zero-shear viscosity in the presence of branching

$$\eta_0 = KM_b[1+(M_b/M_c)^{2.4}](M_w/M_b)^{\beta}, \tag{1}$$

where K is a coefficient having units of Pa s/(g/mol) specific to a given polymer at a given temperature, M_c is the critical molecular weight for entanglements, and β is an exponent given by

$$\beta = \max[1,3/2+B\ln(M_b/90M_{Kuhn})]. \tag{2}$$

Bersted (1985) introduced different levels of LCB in HDPEs by peroxide treatment and found that the activation energy increased from about 23 kJ/mol for a linear HDPE to about 31 kJ/mol for a polymer with a branching density of 0.52 LCB/10 000 carbon atoms. The degree of LCB was evaluated using ^{13}C nuclear magnetic resonance (NMR) in that study. Another rheological effect is that the introduction of LCB in a polymer can shift the onset of shear thinning to lower shear rates relative to that of a linear polymer [Dealy and Wissburn (1990)]. To summarize, it is now known that a polyethylene with LCB usually has a higher η_0, higher activation energy, and lower shear rate for the onset of shear thinning than a linear polymer having similar molecular weight.

The presence of LCB has been known to affect the extensional behavior of conventional PEs. Münstedt and Laun (1981) and Meissner (1984) have shown that a LDPE strain hardened while a HDPE with similar zero-shear viscosity did not. This pronounced strain hardening in LDPE was attributed to the large number of LCBs. Münstedt (1980) and Münstedt and Laun (1981) were able to show that HDPE could also strain harden, but not to the degree of LDPE, provided that it had a high molecular weight tail in its MWD. Münstedt *et al.* (1998) recently showed that while LDPE strain hardens significantly under constant rate elongational deformation at all extension rates, LLDPE would strain harden at very low extension rates of about 0.005 s^{-1} and not at higher rates. The

authors attributed this to the presence of a very high molecular weight linear component in the MWD. Hence, LCB and the presence of a high molecular weight tail can induce strain hardening in elongation but the degree of hardening is greater when it is caused by LCB.

In case of ready-made commercial samples, one does not have an idea of the molecular architecture *a priori*, and hence, LCB content has to be determined by analytical techniques. There are some inherent limitations, though, when it comes to analyzing LCB using these techniques. Size-exclusion chromatography (SEC) coupled with low-angle laser-light scattering (LALLS) uses the Zimm–Stockmayer [Zimm and Kilb (1959); Zimm and Stockmayer (1949)] relationships to determine the number of branches per molecule. The derivation of the Zimm–Stockmayer equation is based on the assumption that the SEC solution is in the theta state, whereas SEC is usually performed in good solvents [Barth and Mays (1984)]. Thus, the LCB content evaluated by this method may not be absolutely correct. If g' is the ratio of intrinsic velocities of branched and linear PE and g denotes the ratio of their respective mean-square radii of gyration, then the two are related by

$$g' = g^k. \tag{3}$$

Though the value of k has been postulated to be 0.5 by Zimm and Kilb (1959), it has been known to lie anywhere between 0.5 and 1.5 [Barth and Mays (1984)]. In the case of sparse levels of branching, such differences in k can significantly affect the accuracy of the calculated branching content.

Another technique used to determine the degree of LCB is ^{13}CNMR. This technique is unsuitable for copolymers of PE with 1-hexene or 1-octene comonomers because branches having 4-carbon atoms or more give rise to the same spectral pattern irrespective of chain length [Randall (1980)]. Hence, NMR cannot distinguish a butyl or hexyl group from a long branch. In addition, the sensitivity of NMR is such that it cannot accurately determine branching densities less than 1 LCB/10 000 carbons [Janzen and Colby (1999)]. It should be noted that for polyethylenes, a branch is usually considered ''long'' when its molecular weight exceeds the critical entanglement molecular weight, which corresponds to about 2100 g/mol, or about 175 carbon atoms [Dealy and Wissbrun (1990); Porter *et al.* (1968); Vinogradov and Malkin (1980)].

With the advent of metallocene-catalysis technology, it is now possible to obtain commercial polyethylenes that are linear and have a narrower molecular weight distribution than that of conventional PEs, with M_w/M_n for metallocene-catalyzed polyethylenes (MCPE) approaching 2 [Benedikt and Goodall (1998)]. Furthermore, LCB can be introduced in a controlled manner [Benedikt and Goodall (1998)]. For example, Dow's constrained-geometry catalysts (CGC) have been used to produce PEs with branching frequencies believed to be between 0.1 and 30 LCB per 10 000 carbons [Hamielec and Soares (1996); Soares and Hamielec (1998)]. Unlike conventional polyethylenes (CPEs), addition of LCB does not broaden the MWD by using CGC [Lai *et al.* (1993)]. Hence, it may be possible to deconvolute the effects of MWD and LCB using these MCPEs.

Researchers at Dow have shown that incorporation of LCB leads to a higher flow activation energy and enhanced shear thinning [Lai *et al.* (1993); Chum *et al.* (1995)]. Kim *et al.* (1995) reported that for two MCPEs with identical melt flow index (MI) = 1.04 and M_w/M_n = 2.0, but one linear and the other with sparse LCB, the activation energy of a linear polymer is 25.0 kJ/mol while that of a lightly branched polymer is 32.6 kJ/mol. The parameter they used to quantify LCB is known as the Dow Rheology Index

(DRI). The Cross model was used to determine the zero-shear viscosity and the characteristic relaxation time, τ_0. These were used to obtain DRI according to the following relation:

$$\text{DRI} = \frac{A\left(\dfrac{\tau_0}{\eta_0}\right) - 1}{10},\tag{4}$$

where $A = 3.65 \times 10^5$ Pa. For a linear polymer, DRI = 0. We would like to point out that DRI has no theoretical basis but utilizes the heuristic that a polymer melt with a greater number of LCB shear thins at lower shear rates. As such, the DRI is a relative indicator of LCB and does not directly relate to the actual number of LCBs in the polymer. There are cases in which this method does not have the sensitivity required to pick up subtle differences in molecular architecture.

Janzen and Colby (1999) extended the observations of Lusignan and co-workers to quantitatively predict the degree of branching in polyethylenes. In particular, they proposed that the behavior of branched polymers is captured in Eq. (1) through the dependence of the exponent β on M_b as given in Eq. (2). With K, B, M_c, and M_{Kuhn} provided as known constants, then given measured values of η_0 and M_w, they solved for M_b. Furthermore, they proposed that M_b was directly related to the long-chain branch content which is given in terms of the parameter α which is defined as the fraction of the total carbons that are long-branch vertexes

$$\alpha = \frac{M_0}{2}(M_b^{-1} - M_w^{-1}),\tag{5}$$

where M_0 is the molecular weight of the repeat unit (i.e., for PE $M_0 = 14.027$). They reported excellent agreement between values of α obtained using Eqs. (1), (2), and (5) and values obtained stoichiometrically by treatment of PE with known very small amounts of peroxides. They reported detecting values of α less than 10^{-4} (i.e., 1 branch/10^4 carbon atoms), which is well below that detectable by customary spectroscopic techniques.

In this study, we have used three commercially available MCPEs, all of which have a MI of 1.0 and similar MWD defined by M_w/M_n which is between 2.11 and 2.42. Our goal is to determine if there are rheological indications that are consistent with the SEC–LALLS branching information that suggests that the two Dow polyethylenes contain sparse LCB while the Exxon resin is devoid of LCB. Furthermore, we wish to establish if any nonlinear rheological method can be used to detect subtle differences in the branching content of the two Dow materials because small differences in molecular architecture have been known to have significant effects on processing conditions and stability limits [Meissner (1974)].

II. EXPERIMENT

A. Materials

Three metallocene-catalyzed LLDPE samples that exhibited a MI of 1.0 were selected. Two of these contained controlled degrees of sparse LCB and are commercially available: Dow Affinity PL 1840 and PL 1880, which are copolymers of ethylene and 1-octene. The third sample used was Exxon Exact 3022 which contains 1-butene as the comonomer and does not contain any LCB. All three samples had relatively narrow MWD (see Table I and Fig. 1), in the range of 2.11 and 2.42. Based on the SEC–LALLS

TABLE I. Molecular data of the materials studied.

Sample	Molecular weight data				LCB $n/10\,000\,C$
	M_n	M_w	M_z	M_w/M_n	
Dow Affinity PL 1840	36 300	87 900	160 000	2.42	0.5695
Dow Affinity PL 1880	55 100	116 400	183 000	2.11	0.1773
Exxon Exact 3022	45 300	95 800	165 000	2.11	None

technique for estimation of LCB, the degree of LCB for PL 1840 and PL 1880 was estimated by the Dow Chemical Company to be 0.5695 to 0.1773 LCB/10 000 carbons atoms, respectively. SEC–LALLS is based on the fact that a branched polymer has smaller hydrodynamic volume in solution than a linear polymer and a smaller radius of gyration [Barth and Mays (1984); Flory (1937)]. A form of the Zimm–Stockmayer relation was used to calculate the LCB density [Zimm and Kilb (1959); Zimm and Stockmayer (1949)]. The MWDs, provided by the Dow Chemical Company, of the three polymers were determined using SEC.

B. Testing methods

All shear rheological experiments were performed using a Rheometrics Mechanical Spectrometer, RMS 800. A set of 25 mm diameter parallel plates was used for dynamic testing while a 0.1 rad cone-and-plate (25 mm diameter) was used for the steady and
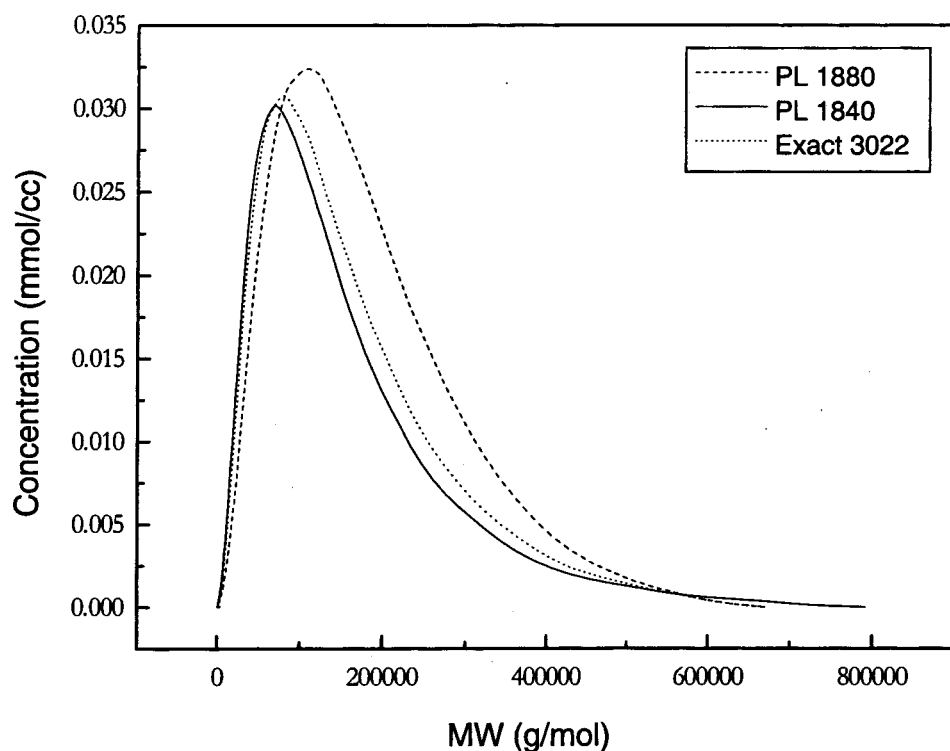
FIG. 1. Molecular weight distribution of MCPEs.

stress-growth experiments. The test sample was maintained in a nitrogen atmosphere during all tests. The test samples were prepared on the heated plates of the rheometer by placing polymer pellets on the lower plate and then bringing the upper plate down to press the molten polymer into a flat disk. All the results shown represent the average values of two to three runs on each sample. The stress-growth curves have an error of less than 2%.

Constant extension rate deformation experiments were performed using a Rheometrics Extensional Rheometer, model RER 9000. Cylindrical samples were immersed in a heated 10 centistoke methyl silicone fluid (Nye Lubricants, New Bedford, MA; specific gravity ≈ 0.85 at 135°). The oil was selected in order to provide a neutrally buoyant, uniformly distributed temperature environment for the immersed sample. The cylindrical samples were compression molded in a fixture capable of producing 15 specimens having diameters of 6 mm and lengths of 22 mm. The mold was heated to 180 °C and polymer pellets were dropped in. The chamber was kept under vacuum in order to avoid oxidative degradation. A plunger was used to pack the molten polymer in a hydraulic press at about 8000 lbs and then cooled slowly at room temperature. These samples were glued to aluminum clips using a two-part epoxy adhesive (EPOXY-PATCH, Dexter Adhesives and Structural Materials). The samples were inspected visually during and after the test for uniform deformation throughout the sample. For the samples that deformed uniformly, the test results were within an error of 5%.

III. RESULTS AND DISCUSSION

A. Experiments in shear

In order to determine if these samples showed any behavior consistent with the presence of LCB, the activation energies of the MCPEs were first investigated. Small amplitude frequency sweeps were performed at 120, 130, 140, 150, 160 and 170 °C and the G'' curves were shifted along the frequency axis to 170 °C using the time-temperature superposition principle. In the frequency range used, the zero-shear viscosity was not observed. That is why shifts in η_0 were not used to calculate the activation energy. Because the shear flow was dominated by G'', in that its values were higher than G', G'' was considered a better candidate for the shifting process. When well above T_g, the shift factors, a_T, are known to have an Arrhenius-type relationship with temperature as shown below [Baird and Collias (1998); Dealy and Wissbrun (1990)]

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{6}$$

where E_a is the activation energy, R is the universal gas constant, T_0 is the reference temperature and T is the test temperature. Figure 2 shows the plot of $\ln(a_T)$ vs $1/T$ for the three MCPE samples. The slopes of these curves gave the value of E_a/R, from which the activation energies were calculated to be 27.0 ± 2.5 kJ/mol for Exact 3022, 35.0 ± 2.0 for PL 1840, and 36.0 ± 2.0 for PL 1880. These values were in good agreement with those found in the literature for linear and sparsely branched polyethylenes [Bersted (1985)]. The activation energy of the samples containing LCB, namely PL 1840 and PL 1880, was seen to be significantly higher than that of the linear Exact 3022. Based on earlier findings, the higher activation energy of the samples with LCB suggested that they indeed contained LCB [Bersted (1985); Dealy and Wissbrun (1990); Kim *et al.* (1995)]. However, the similarity in E_a of PL 1840 and PL 1880, within the error of the measurements, suggested that this method was incapable of distinguishing between the two samples with
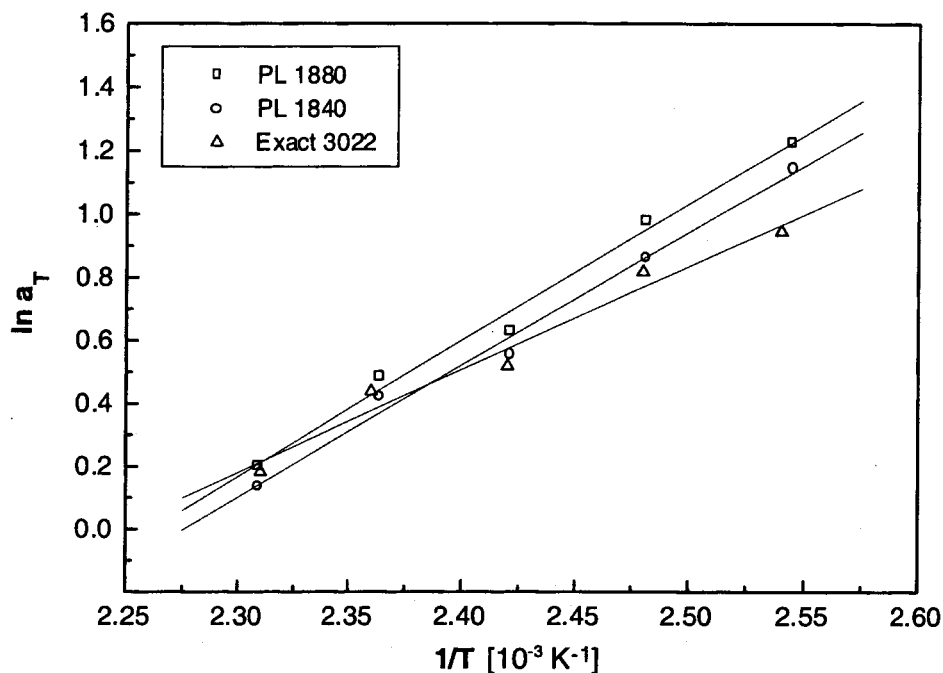
FIG. 2. Plot of $\ln a_T$ vs $1/T$ for MCPEs for evaluation of flow activation energy. The lines indicate the linear regression of the data.

subtle differences in LCB. It should be noted that this finding is contrary to those of Hughes (1983), who was able to show that there is a linear relationship between E_a and the concentration of dicumyl peroxide, which was used to create various degrees of LCB less than 1 in 10 000 carbon atoms.

The results from dynamic oscillatory experiments in the frequency range of 0.1 to 100 rad/s were combined with those of steady shear experiments to produce the flow curves shown in Fig. 3. It can be seen that the complex viscosity and steady-shear viscosity parts of the curve overlapped well. Therefore, we assumed that the dynamic oscillatory data is an accurate representation of steady-shear values. The zero-shear viscosity values of PL 1840 and PL 1880 at 150 °C, shown in Table II, were very similar, and much higher than those of Exact 3022. Despite the higher M_w of Exact 3022 relative to that of PL 1840, its value of η_0 was lower. It has been observed on several occasions that for the same molecular weight, a material with LCB has a higher zero-shear viscosity [Charlesby (1955); Graessley and Raju (1984); Janzen and Colby (1999); Wild *et al.* (1971); Wild *et al.* (1976); Yan *et al.* (1999)]. This could account for the higher value of η_0 of PL 1840 relative to that of Exact 3022 by almost one order of magnitude, even though its M_w is lower than that of Exact 3022. On the other hand, despite the 32% higher M_w of PL 1880 relative to that of PL 1840, its zero-shear viscosity was very close to that of PL 1840. Had PL 1840 and PL 1880 been linear, the 32% higher M_w of PL 1880 would have corresponded to almost a 2.6 times increase in the zero-shear viscosity of PL 1880 based on $\eta_0 = K M_w^{3.4}$. Hence, it seems that there may be a contribution to η_0 of PL 1840 from LCB.

Before continuing with the rheological investigations of these three PEs, we evaluate the approach of Janzen and Colby (1999) given in Eqs. (1), (2), and (5) to determine whether a difference can be detected in the two Dow samples. Values for the parameters
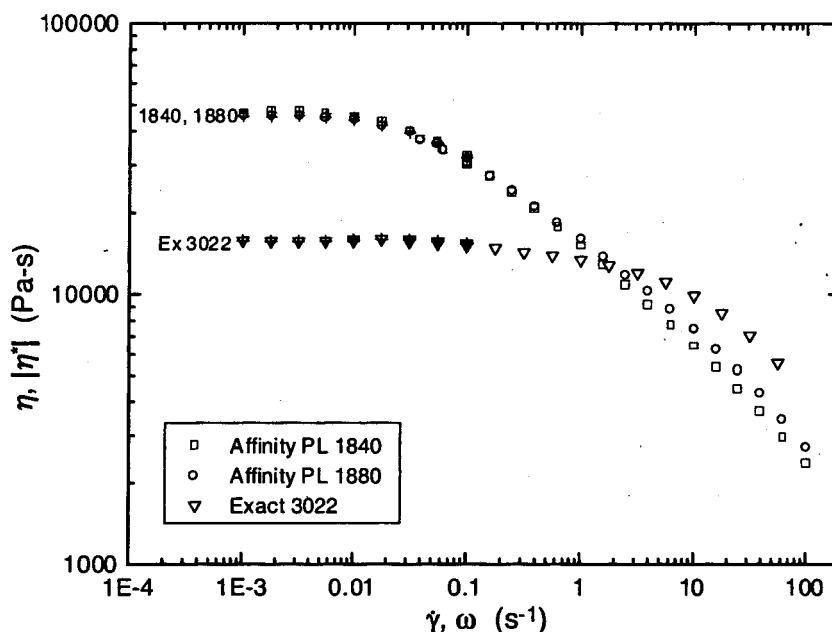
FIG. 3. Shear flow curves of MCPEs at 150 °C.

in these equations were taken from the Janzen and Colby paper [$K = 5.22 \times 10^{-6}$ Pa s/(g/mol), $B = 6.0$, $M_0 = 14.027$ g/mol, $M_c = 2100$ g/mol, $M_{Kuhn} = 145.9$ g/mol]. Using the International Mathematics and Statistics Libraries subroutine NEQNF (Absoft 6.0) Eqs. (1) and (2) were solved to find M_b for PL 1840 and PL 1880. These values were calculated to be 75 150 and 110 529, respectively, leading to values of α of 1.443×10^{-5} and 0.342×10^{-5}, respectively. These values are about a factor of three lower than those predicted by dilute solution methods, but, nonetheless, are in fair agreement.

The shear-thinning behavior of the linear and long-chain branched samples was found to be quite different. The shear rate for the onset of shear thinning was significantly lower, around 0.05 s^{-1}, for the samples with LCB, whereas the onset of shear thinning for the linear sample was around 2 s^{-1}. Furthermore, shear-thinning behavior seemed to be enhanced, i.e., there was more sensitivity to shear rate for the samples with LCB, consistent with previous work [Bersted *et al.* (1981); Lai *et al.* (1993)]. Interestingly, the

TABLE II. Melt Index and zero-shear viscosity of the materials studied.

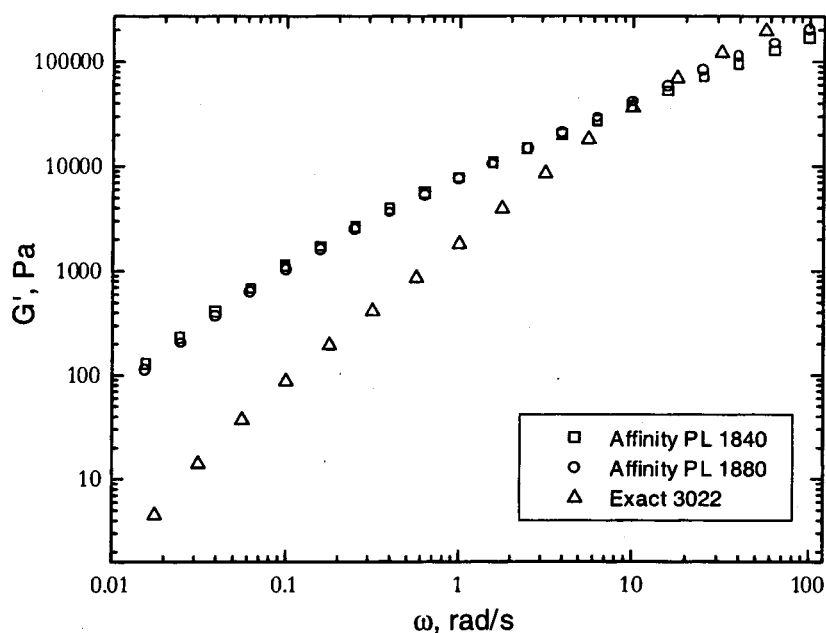| Sample	MI	$\eta_{0,150\,°C}$ (Pa s)	$\eta_{0,190\,°C}$ (Pa s)
Dow Affinity PL 1840	1	46 800±200	15 700
Dow Affinity PL 1880	1	45 370±153	17 200
Exxon Exact 3022	1	15 780±117	6500

FIG. 4. Frequency sweep depicting G' of MCPEs at 150 °C.

flow curves of PL 1840 and PL 1880 were almost identical in spite of the differences in their branching content and M_w. There were some differences in the flow curves at frequencies greater than 10 s^{-1}, which suggested that the relaxation spectra of PL 1840 and PL 1880 could be slightly different at short relaxation times. The linear viscoelastic functions G' and G'' for the three MCPEs are shown in Figs. 4 and 5, respectively. Again, the two branched samples are seen to be very similar while the linear Exact 3022 behaved quite differently. Particularly at low frequencies, G' of PL 1840 and PL 1880 was higher than that of Exact 3022.

Because the behavior of branched polyethylenes at the start of steady-shear flow was observed by Meissner (1974) to be sensitive to subtle differences, we investigated this behavior for the samples of interest here. In order to make a fair comparison of the stress growth of the three MCPEs, each was subjected to a steady shear rate such that the Deborah number, De, was unity. The Carreau–Yasuda model, shown in Eq. (7), was used to fit the shear flow data in Fig. 3 to determine zero-shear viscosities and the character-istic relaxation times, λ_c. The nonlinear least-squares fitting scheme provided in the MicroCal Origin software was utilized to obtain the Carreau–Yasuda parameters

$$\eta(\omega) = \eta_0[1+(\lambda_c\omega)^a]^{n-1/a}. \qquad (7)$$

The reciprocal of λ_c was used as an indicator of the shear rate for the onset of shear thinning. The model parameters are shown in Table III.

For PL 1840, PL 1880, and Exact 3022, the onset of shear thinning was estimated to be at shear rates of 0.045, 0.042, and 2.77 s^{-1}, respectively. Interestingly, the DRIs calculated using Eq. (4) for PL 1840 and PL 1880 are 1.98 and 2.17, respectively. While SEC–LALLS suggested that PL 1840 had three times the number of LCBs than PL 1880,
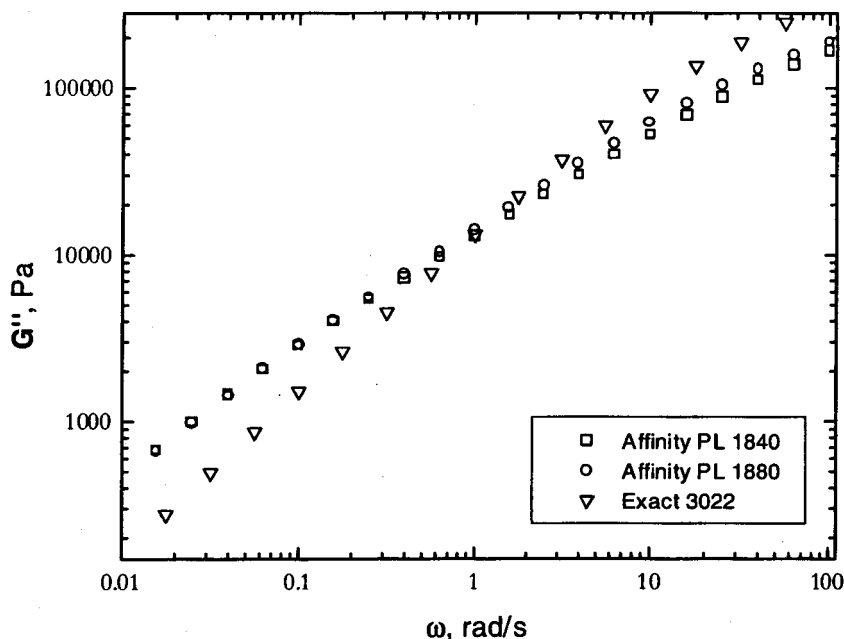
FIG. 5. Frequency sweep depicting G'' of MCPEs at 150 °C.

the DRI seemed to show that PL 1880 has a higher degree of LCB by about 8%. Similar shear rates for the onset of shear thinning were obtained for PL 1840 and PL 1880.

The transient viscosities at the startup of shear flow for the three materials at a De of 1.0 are shown in Fig. 6. The transient viscosities were normalized with the steady-state value that was attained at longer times (300 s) for PL 1840 and PL 1880. The Exact 3022 curve was normalized with the complex viscosity value at that shear rate as a steady-state value was not reached due to edge fracture. As seen in Fig. 6, there seemed to be no difference in the viscosity growth behavior of the two branched samples. There was a slight overshoot in the curves for both PL 1840 and PL 1880. On the other hand, the Exact 3022 started to fracture at De = 1. Hence, there was a significant difference in the flow stability between Exact 3022 PL 1840, and PL 1880 in shear flow. The viscosity growth of Exact 3022 at a shear rate of 0.3 s^{-1}, however, showed that it could also go through a maximum. Hence, at similar De, there was a noticeable difference between the branched and unbranched polymers, but the two PEs with LCB behaved very similarly.

The first normal stress differences at De = 1 and shear rates of 0.1, 0.3, and 0.5 s^{-1} for PL 1840 and PL 1880 are shown in Fig. 7. The growth behavior was fairly reproduc-

TABLE III. Carreau–Yasuda model parameters for MCPEs.

Sample	η_0 (Pa s)	λ_c (s)	a	n
PL 1840	47 250	22.6	1.20	0.63
PL 1880	45 710	23.9	1.23	0.66
3022	15 740	0.361	0.98	0.66
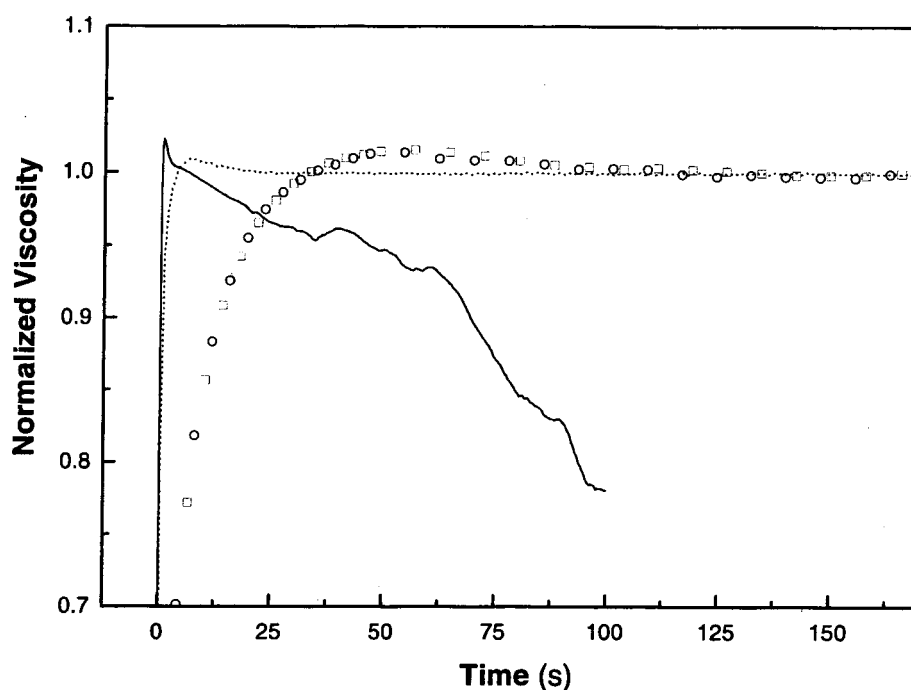
FIG. 6. Transient shear stress growth curves of MCPEs at De $= 1$ at 150 °C. $(-)$ Exact 3022, ($\square$) PL 1840, ($\bigcirc$) PL 1880, and (- -) Exact at $\dot{\gamma} = 0.3$.

ible, as can be seen from the multiple results shown in this plot. It was found that the N_1 of PL 1840 attained slightly higher steady-state values compared to that of PL 1880 at De $= 1$ and shear rates of 0.1 and 0.3 s^{-1}. The peak values of N_1 for PL 1840 and PL 1880 at a shear rate of 0.5 s^{-1} were 14897 ± 25 and 13835 ± 88 Pa, respectively. Hence, PL 1840, which had the higher degree of LCB, exhibited higher peak values in the growth of N_1. In an earlier study of LDPEs with slight differences in branching content, but otherwise similar in MI and MWD, Meissner (1974) had reported that the peak values in N_1 were different for three LDPEs. The results obtained in the case of PL 1840 and PL 1880 are in agreement with Meissner's previous study.

B. Extensional rheology

Constant extension rate tests were performed at 135 °C instead of 150 °C, because at higher temperatures the melt strength was too low for consistent homogeneous sample deformation for all three samples. The melt strength seemed especially low for the Exact 3022 sample because it was very prone to necking under extension at 150 °C, but necking was eliminated at 135 °C. From these experiments, a first comparison is made between the extensional rheology of the linear Exact 3022 and PL 1880, both of which do not have high molecular weight tails, unlike PL 1840. As can be seen in Fig. 8, there are distinct differences in the stress growth of PL 1880 and Exact 3022. As expected, the extensional stress of the linear sample rises and reaches a steady-state value for both extension rates. The stress in PL 1840, however, does not attain such a steady state value, but continues to rise. This would be expected for highly branched species like LDPE, but it is remarkable that a PE with sparse branching levels (about 1 branch-point every 4–5 chains) can exhibit strain hardening. It should be noted that PL 1840 seemed to have a
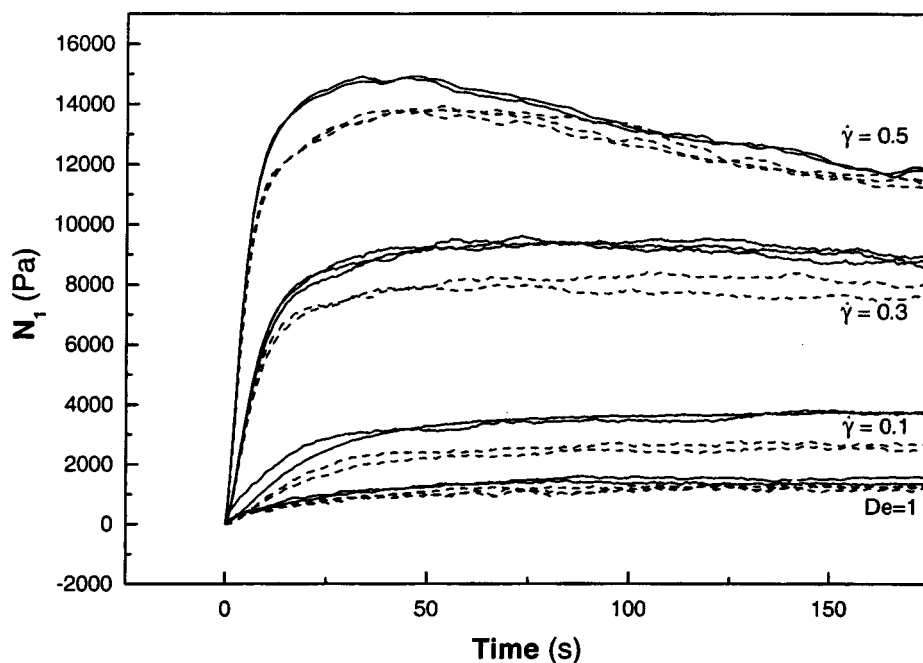
FIG. 7. Transient N_1 growth curve for PL 1840 and PL 1880 at 150 °C. Solid lines are for PL 1840 and dashed lines for PL 1880.

high molecular weight tail in the MWD, shown in Fig. 1, with chains up to 800 000 g/mol that were detectable. The average molecular weights of the three MCPEs, shown earlier in Table I, indicate that PL 1880 had the highest weight average molecular weight, M_w, followed by Exact 3022 and PL 1840.

In order to emphasize the strain hardening, transient shear and extensional viscosities are shown for PL 1840 in Fig. 9. The steady plateau value of the shear viscosity growth curve at a shear rate of 0.001 s^{-1} was assumed to represent η_0. The solid curve under the extensional growth curves was generated by multiplying the transient shear viscosity at $\dot{\gamma} = 0.001\,\mathrm{s}^{-1}$ by 3. The extensional viscosities seemed to be rising higher than 3η, which is commonly observed in the limit of low deformation rate. In Fig. 10, the extensional viscosity of Exact 3022 seemed to reach 3η_0. At the test temperature of 135 °C, the Exact material was susceptible to necking only at very high strains. This would explain the drop in the extensional viscosity towards the end of each extensional growth curve.

The most significant result was the comparison of extensional stress growth of the two branched MCPEs. From Fig. 11, one can see that the stress growth occurred differently in PL 1840 and PL 1880. Stress values for PL 1840 were higher than those of PL 1880 at all extension rates. (These results were repeatable within an error of ±3% so that the error bars would be smaller than the size of the symbols.) PL 1880 also strain hardened, but not to the extent that PL 1840 did. The higher strain hardening in PL 1840 may have been due to the apparent higher degree of LCB. Another possible reason behind the higher strain hardening may be the presence of a high molecular weight tail that was evident in the MWD of PL 1840 but not in that of PL 1880. It is unclear as to what
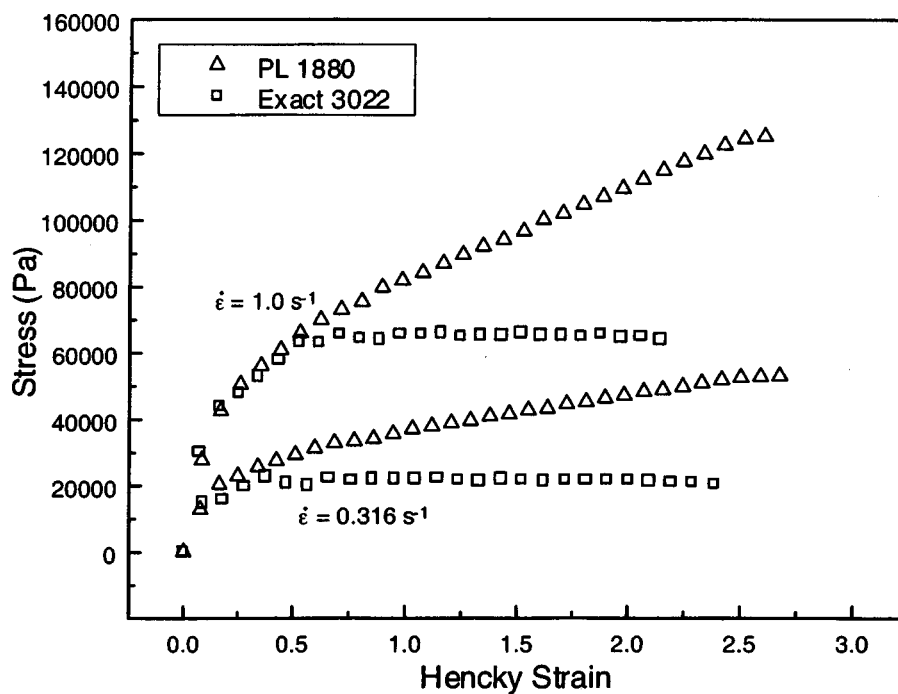
FIG. 8. Extensional stress growth of Exact 3022 and PL 1880 at 135 °C.
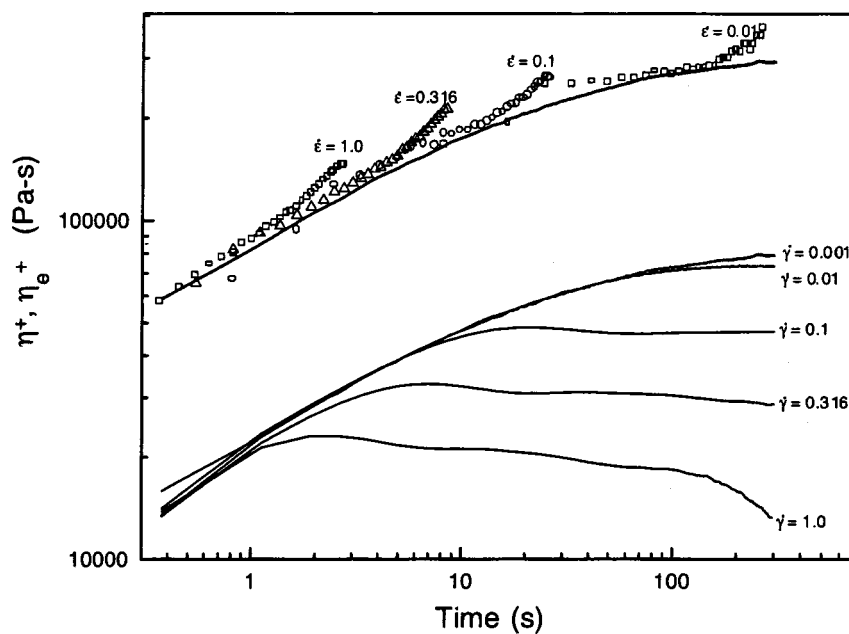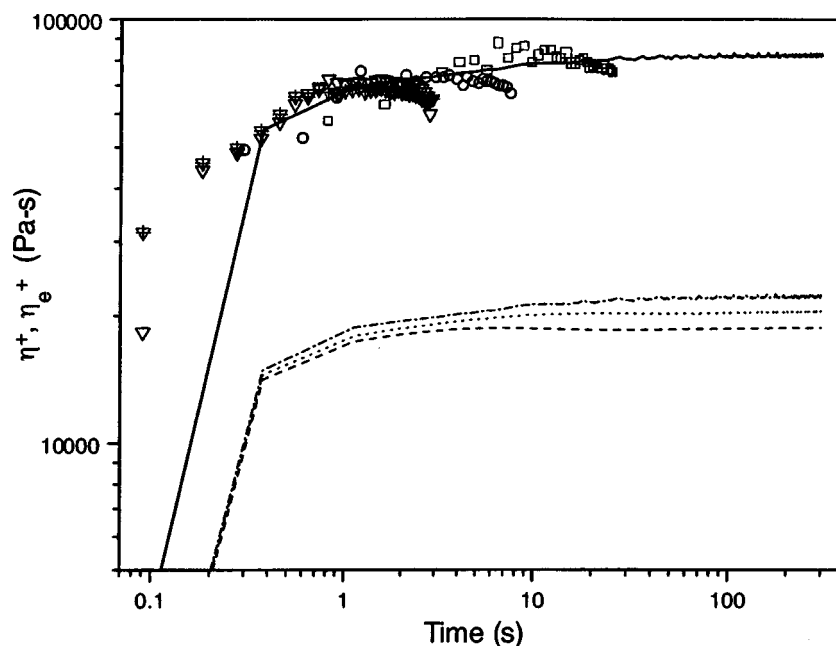

FIG. 9. Transient-shear and extensional viscosities of PL 1840 at 135 °C.

FIG. 10. Transient-shear and extensional viscosities of Exact 3022 at 135 °C. (∇) $\dot{\epsilon} = 1.0$, ($\bigcirc$) $\dot{\epsilon} = 0.316$, ($\square$) $\dot{\epsilon} = 0.1$, ($-$) $\dot{\gamma} = 0.1$, ($\cdot$) $\dot{\gamma} = 0.316$, and (- -) $\dot{\gamma} = 1.0$.

concentration of high molecular weight fractions has to be present in the distribution to affect strain hardening significantly. Based on the assumption that the SEC–LALLS analysis was accurate, this result provided the first clear indication that the presence of a higher degree of LCB in PL 1840 made it rheologically different.

IV. CONCLUSIONS

Based on the results presented, we are able to draw a few conclusions. First, there were rheological differences in the three MCPEs which most likely could be attributed to the varying LCB contents in their structure. The activation energy of the linear PE, Exact 3022, was lower than that of the Dow MCPEs which was at least consistent with the presence of LCB. This result was consistent with the SEC–LALLS information concerning the LCB content of these materials. However, the activation energy was not found to be sensitive enough to detect the small differences in the degree of LCB in PL 1840 and PL 1880. The zero-shear viscosity was very highly dependent on the presence or absence of LCB. The presence of LCB may account for the higher zero-shear viscosity of PL 1840 relative to that of Exact 3022, even though PL 1840 has a higher M_w than Exact 3022. The presence of very sparse levels of LCB in PL 1840 and PL 1880 shifted the onset of shear thinning to lower shear rates than that of the linear Exact 3022 and rendered greater shear-rate sensitivity to them than Exact 3022. The transient-shear viscosity upon startup of steady-shear deformation seemed to grow very similarly for PL 1840 and PL 1880. There was a noticeable difference in the steady-state values of N_1 as well as the peak value of N_1 at higher shear rates for PL 1840 and PL 1880. We feel that without prior knowledge of the apparent degree of LCB between PL 1840 and PL 1880,
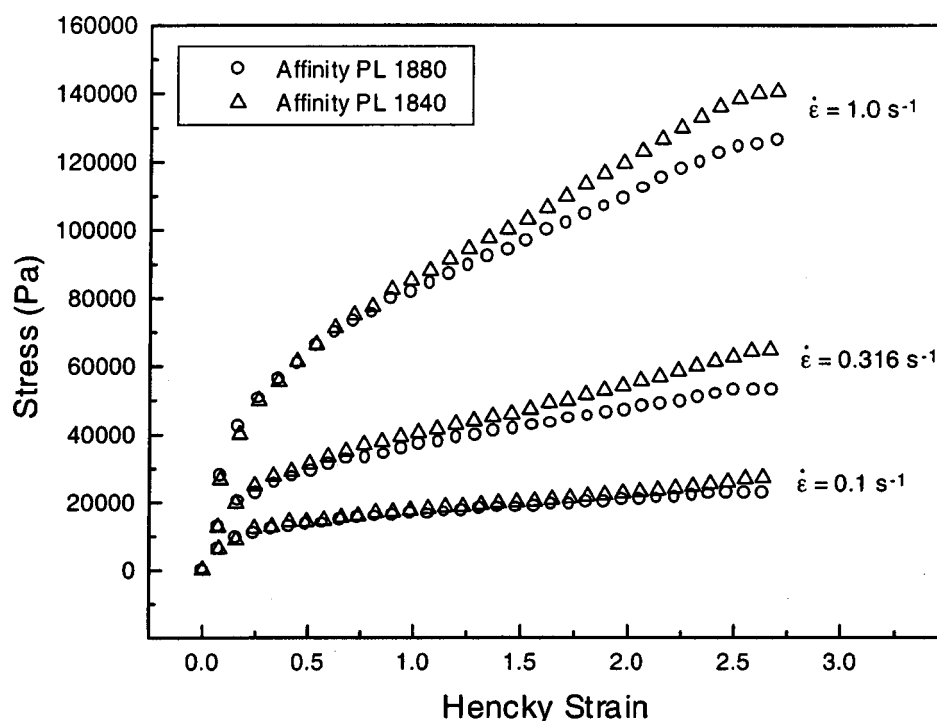
FIG. 11. Extensional stress growth of PL 1840 and PL 1880 at 135 °C.

shear rheology alone could not distinguish between the two materials, except for the differences in N_1. Extensional rheology suggests that the presence of very small amounts of LCB can induce strain hardening. Furthermore, enhanced strain hardening of PL 1840 suggests that it may have a higher degree of LCB than PL 1880. Hence, the extensional results are consistent with SEC–LALLS analysis and the method of Janzen and Colby concerning the degree of LCB in the three samples.

ACKNOWLEDGMENTS

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