

Shear and Elongational Rheology of Polyethylenes with Different Molecular Characteristics. II. Elongational Rheology

X. Wei,¹ J. R. Collier,² S. Petrovan³

¹Unilever, 40 Merritt Boulevard, Trumbull, Connecticut 06611

²Chemical and Biomedical Engineering, Florida Agricultural and Mechanical University/Florida State University, Tallahassee, Florida 32320

³Chemical Engineering Department, University of Tennessee, Knoxville, Tennessee 37996-2200

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ABSTRACT: The elongational viscosities of polyethylenes with different molecular characteristics were measured at different Hencky strains and temperatures with a capillary rheometer by the replacement of the capillary cylindrical die with a hyperbolic converging die. The hyperbolic shape of the die established a purely elongational flow field at a constant elongational strain rate throughout the die. The effects of molecular characteristics such as the molecular weight, molecular weight distribution, and long-chain branching and processing conditions such as the temperature and Hencky strain on the elongational rheology of the polyethyl-

ene samples were studied. Good master curves were generated for temperature and Hencky strain shifting and simultaneous shifting with respect to both the temperature and Hencky strain. Both the molecular weight distribution and long-chain branching seemed to promote strain rate thinning and reduce the elongational viscosity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1184–1194, 2007

Key words: molecular weight distribution/molar mass distribution; polyethylene (PE); elongational; processing; rheology; long-chain branching (LCB); viscosity

INTRODUCTION

Extensional deformation plays a significant role in many processing operations that involve a rapid change of shape,¹ such as fiber spinning, film blowing, blow molding, and melt or solution blowing for nonwoven manufacturing. To select and tailor materials for these operations and develop real-time, online processes and quality control analysis in these operations, knowledge of the effects of molecular characteristics, such as the molecular weight, molecular weight distribution (MWD), and long-chain branching (LCB), on the elongational rheology is important. Of all molecular characteristics, LCB shows the most interesting effects on the elongational rheology of polyethylenes (PEs) and other polymer melts.

LCB-PEs show rheological properties that differ significantly from those of linear polymers or polymers with side branches that are too short to entangle with surrounding polymeric chains.^{2–11} The most important difference lies in strain hardening, which has also been demonstrated for polypropylene (PP)^{8,12–16} and polystyrene.^{17,18} Low-density polyethyl-

ene (LDPE), which has multiple, irregularly spaced, long side branches, shows a strain-hardening phenomenon in uniaxial extensional flow and strain softening in shear flow. The terms *strain hardening* and *strain softening* refer to the behavior of the transient viscosities after the startup of the flow, according to McLeish and Larson.³ Their simulations, using a molecular constitutive equation for the dominant backbone stresses for an ideal multibranching polymer or pom-pom, covered a strain rate range of 0.0003–0.04 s⁻¹. They were able to show that nonlinear rheological properties of a pom-pom are qualitatively like those of LCB commercial melts, such as LDPE. Lohse et al.⁵ examined the melt rheology of well-defined model polymers (star and comb polymers), the LCB of which was precisely known from the synthesis. A branch is considered long if the molecular weight is at least greater than the entanglement molecular weight (M_e), which is around 1 kg/mol for PE.⁶ They found that when only 3% comb polymer ($M_e = 117$ kg/mol) was added to a linear polymer, a dramatic rise in the extensional viscosity was seen, indicating extensional thickening or strain hardening.

Gabriel and Mundstedt⁸ reported that for PEs of various branching structures, four different types of

Correspondence to: J. R. Collier (john.collier@eng.fsu.edu).

strain hardening can be observed. In type I, the strain hardening is approximately independent of the elongational rate. In type II, the strain hardening decreases with an increasing elongational rate. In type III, the strain hardening increases with an increasing elongational rate. In addition to that, materials have been found that do not show strain hardening within the experimental window (type IV). Stange et al.¹² studied the rheological behavior of blends of linear PP and different amounts of an LCB-PP. They found out that the dependence of the strain hardening on the strain rate changed with the amount of branched PP. The blends containing up to 50 wt % LCB-PP showed a decrease in the strain hardening with an increasing elongational strain rate, whereas for LCB-PP, an increase in the strain hardening with increasing strain was noticed. It was also found that low amounts of LCB-PP had a greater effect on the elongational viscosity. The elongational viscosity of LDPEs manufactured with tubular and autoclave reactors was analyzed by Wagner et al.⁹ with the molecular stress function model. A new strain energy function was presented that allowed the quantitative description of the strain-hardening behavior of the studied PE melts with two nonlinear material parameters. LDPE produced in autoclave reactors had a more treelike structure in comparison with the comblike structure of the tubular-reactor polymer.

The activation energy for flow is larger for branched polymers than for linear ones,⁵ and it seems that this is proportional to the branch length.¹⁹ This behavior can be attributed to the different relaxation mechanisms for branched and linear chains in an entangled environment.

Most of the experimental data on the extensional or elongational viscosity, obtained with a Meissner-type apparatus, cover a range of strain rates to a maximum of about 1 s^{-1} . The fiber-spinning method can be used to measure the elongational viscosity at higher elongational strain rates.²⁰

Previous research by Collier and his research group^{1,21-23} has shown that an essentially pure elongational flow of polymer melts or solutions can be generated with hyperbolic convergent dies in a capillary rheometer under the proper processing conditions. An experimental technique—the hyperbolically converging flow technique—has been developed that can measure the elongational viscosity of polymer melts and solutions at processing strain rates (up to hundreds of reciprocal seconds) and temperatures.^{1,22,24}

In this article, results are presented for the elongational viscosity measured with the hyperbolically converging flow technique. PEs of different molecular characteristics, such as the molecular weight, MWD, and LCB, were analyzed at Hencky strains of

4–7, temperatures of 135–180°C, and elongational strain rates in the range of industrial processes, such as melt spinning and melt blowing.

THEORETICAL

Measurement of the elongational viscosity by the hyperbolically converging flow technique

The theoretical foundation for the hyperbolic die technique used to characterize the elongational rheology of polymer melts and solutions was established previously by this group.^{1,21-23} A few fundamental aspects and the basic equations for the calculation of the elongational viscosity are given in the following.

Hyperbolic convergent dies were designed for the melt or solution to generate a constant elongational strain rate along the channel. This was accomplished by the description of the flow channel surface area with the equation $r^2 = A/(z + B)$, where z is the axial flow direction, r is the radius of the flow channel as a function of z , and A and B are geometry-defined constants. The four hyperbolic dies used in this research had a Hencky strain of 4, 5, 6, or 7. The Hencky strain is defined as the natural logarithm of the ratio of the die entrance area to the exit area for a constant-volume process. The elongational viscosity is calculated with the following equation:

$$\eta_e = \frac{\Delta P}{\dot{\epsilon} \varepsilon_H} \quad (1)$$

where η_e is the elongational viscosity, ε_H is the Hencky strain, ΔP is the pressure difference between the entrance and exit cross sections, and $\dot{\epsilon}$ is the elongational strain rate. $\dot{\epsilon}$ is given by eq. (2):

$$\dot{\epsilon} = \frac{v_0}{L} (\exp \varepsilon_H - 1) \quad (2)$$

where L is the centerline length of the die and v_0 is the entrance velocity.

Temperature shifting of the elongational viscosity

In the previous article of this two-part series,²⁵ the shear viscosity and temperature shifting based on the reduced-variable method²⁶ were presented. Both Cross and Carreau models²⁷ were used to estimate the zero-shear-rate viscosities at different temperatures. The same temperature shift factors can be used to shift both shear and elongational viscosities.²⁸ This can also be supported by the findings of Münstedt,²⁹ who calculated the activation energies for both shear and elongational flow from the zero-shear-rate viscosity and the elongational viscosity at

very low strain rates, respectively. He found that the values were identical.

Hencky strain shifting of the elongational viscosity

The dependence of the elongational viscosity on the Hencky strain is a result of orientation developing in the polymeric fluid as it is being attenuated. Two methods have been developed to calculate the Hencky strain shift factors and thus the reduced elongational viscosity and reduced elongational strain rate.³⁰ Method 1 is based on an orientation ratio being equal to the relaxation times. The shift factor, reduced elongational viscosity, and reduced elongational strain rate are defined by

$$(a_H)_1 = \frac{[\text{TR} - 3]\varepsilon_{H_0}}{[\text{TR} - 3]_0\varepsilon_H} \quad (3)$$

$$[\eta_e(\dot{\varepsilon}, \varepsilon_H)]_{r1} = \frac{\eta_e(\dot{\varepsilon}, \varepsilon_H)}{[(a_H)_1]^2} \quad (4)$$

$$(\dot{\varepsilon}_r)_1 = (a_H)_1\dot{\varepsilon} \quad (5)$$

where $(a_H)_1$ is the Hencky strain shift factor defined by method 1; η_e and η_s are the elongational viscosity and shear viscosity, respectively; η_e/η_s is the Trouton ratio (TR); and subscript r indicates reduced variables. Subscript 0 indicates the values of the variables ([shear strain rate, $\dot{\varepsilon}$, ε_H , and $[\text{TR} - 3]$) at the reference state. Method 2 is based on an orientational viscosity ratio. The shift factor, reduced elongational viscosity, and reduced elongational strain rate are defined by

$$(a_H)_2 = \frac{\eta_e(\dot{\varepsilon}_0, \varepsilon_H) - 3\eta_{s0}}{\eta_e(\dot{\varepsilon}_0, \varepsilon_{H_0}) - 3\eta_{s0}} \quad (6)$$

$$[\eta_e(\dot{\varepsilon}, \varepsilon_H)]_{r2} = \eta_e(\dot{\varepsilon}, \varepsilon_H) \left[\frac{\varepsilon_{H_0}}{(a_H)_2\varepsilon_H} \right] \quad (7)$$

$$(\dot{\varepsilon}_r)_2 = (a_H)_2\dot{\varepsilon} \quad (8)$$

where $(a_H)_2$ is the Hencky strain shift factor defined by method 2 and η_{s0} is the zero-shear-rate viscosity.

Simultaneous temperature and Hencky strain shifting of the elongational viscosity

According to the temperature shifting and Hencky strain shifting shown previously, the elongational viscosity curves taken at different temperatures can be generated into a single master curve. The elongational viscosity curves taken at different Hencky strains can be generated into a single master curve as well. Therefore, by combining these two shifting operations, that is, shifting with respect to temperature and shifting with respect to the Hencky strain, and by using the appropriate shift factors, we could obtain a generalized

master curve and extend the elongational strain rate range of the experimental geometry. This would facilitate matching the material to the processing conditions. Also, one of the long-term objectives of this research group is to design an online elongational rheology sensor for polymer processing processes involving elongational flow. A generalized master curve and the associated shift factors would be very useful tool in developing such a sensor.

The reduced variables are defined by

$$[(\eta_e)_{rTH}]_1 = \frac{\eta_e T_0}{(a_T)_1 T [(a_H)_1]^2} \quad (9)$$

and

$$(\dot{\varepsilon}_{rTH})_1 = (a_T)_1 (a_H)_1 \dot{\varepsilon} \quad (10)$$

for method 1 and by

$$[(\eta_e)_{rTH}]_2 = \frac{\eta_e T_0}{(a_T)_1 T} \frac{\varepsilon_{H_0}}{(a_H)_2 \varepsilon_H} \quad (11)$$

and

$$(\dot{\varepsilon}_{rTH})_2 = (a_T)_1 (a_H)_2 \dot{\varepsilon} \quad (12)$$

for method 2.

In the above equation, T is the temperature, T_0 is the reference temperature, a_T the temperature shifting factor, and subscript TH indicates a reduced variable obtained by using simultaneous temperature and Hencky strain shifting factors.

EXPERIMENTAL

Materials

Four metallocene PEs, one conventional LDPE, and one conventional linear low-density polyethylene (LLDPE) are studied. The sample source, melt index (MI), density, weight-average molecular weight (M_w), polydispersity index (PI), and LCB values of the PE samples are given in Table I. PE samples PE-1, PE-2, PE-3, and PE-4 were metallocene-catalyzed resins and had narrow MWDs (PI \approx 2). PE-5 was a conventional LDPE resin (i.e., it was manufactured by a free-radical, high-pressure polymerization process and hence had 20–30 short-chain branches per 1000 carbon atoms and ca. 3 long-chain branches per 1000 carbon atoms that had a range of lengths with an upper limit approaching the length of the main polymer chain³¹), whereas PE-6 was a conventional LLDPE. PE-1, PE-2, PE-3, PE-4, and PE-6 had similar melt flow indices. PE-1, PE-2, and PE-4 were branched copolymers of ethylene and octene-1 with controlled and sparse LCB. PE-3 and PE-6 were

TABLE I
Molecular Characteristics of the PE Samples

Sample	Sample source	MI (g/10 min)	Density (g/cm ³)	M_w	PI	M_z^a	LCB (1/10 ⁴ C)
PE-1	Dow Affinity PL 1840	1.0	0.909	87,400	2.43	160,200	0.57
PE-2	Exxon Exact 0201	1.1	0.902	88,700	2.14	158,900	0.79
PE-3	Exxon Exact 3132	1.2	0.900	111,000	2.04	180,400	— ^b
PE-4	Dow Affinity PL 1880	1.0	0.902	115,800	2.12	183,700	0.18
PE-5	Equistar NA 952	2.0	0.919	116,000	9.1	— ^c	— ^c
PE-6	Mobil NTX 101	0.9	0.917	122,700	3.44	319,700	— ^b

^a z-average molecular weight.

^b Not applicable (PE-3 and PE-6 were linear PE resins with no LCB).

^c Not available.

copolymers of ethylene and hexene with no LCB. All six PE samples were blown-film-grade and were the same materials used in the first article of this series.²⁵ The polymer samples and the molecular data in Table I were provided by Dr. Donald Baird of Virginia Polytechnic Institute and State University.

Instruments and techniques

Elongational viscosity measurements were performed with a Rheometrics Advanced Capillary Extrusion Rheometer 2000 (ACER). The capillary cylindrical die was replaced with a hyperbolic converging axisymmetric die.²² In this research, four hyperbolic convergent dies with Hencky strains of 4, 5, 6, and 7 were used. The PE samples were tested at temperatures of 135, 150, 165, and 180°C. The experimental procedure was as follows. The hyperbolic die was inserted into the ACER cavity for capillary dies. The pellets of the polymer sample were loaded into the preheated barrel and allowed to melt and attain the desired steady-state temperature. When the barrel temperature reached the set testing temperature and remained stable within $\pm 1^\circ\text{C}$, the pressure transducer, positioned right above the die entrance, was calibrated. The measurement was then performed by the ram being pushed, at a constant speed corresponding to a constant chosen elongational strain rate, through the barrel that was filled with the sample being tested. From the barrel, the sample was further forced through a die of a known Hencky strain. From the knowledge of the elongational strain rate, Hencky strain, and measured steady-state pressure, the elongational viscosity was then calculated. By sweeping the chosen elongational strain rates until a steady state of pressure (or stress) for each strain rate was accomplished, we recorded a flow curve of the elongational viscosity versus the elongational strain rate.

Measurements of the shear rheology were taken with an Advanced Rheometric Expansion System rheometer (TA Instruments), as reported in the first article in this series.²⁵ Circular disks of PE specimens were prepared by compression molding at 200°C. The parallel-plate geometry was used with plates with a

25-mm diameter and a 1-mm gap. The experimental temperatures were the same as those for the elongational viscosity measurements for all PE samples.

RESULTS AND DISCUSSION

Effects of the molecular characteristics on the elongational rheology of polymer melts

The effects of M_w , MWD, and LCB on the elongational viscosity of PE samples measured at a Hencky strain of 4 and 135°C is shown in Figure 1. The elongational viscosities of different samples at the same Hencky strain converged at a high strain rate, except for PE-5, the conventional broader MWD LDPE. The elongational viscosities of different samples flattened out differently at low strain rates. The onset of strain rate thinning was in the order of PE-5 < PE-4 < PE-2 < PE-1 < PE-6 < PE-3. The strain rate thinning might have been caused by the MWD and/or LCB. A comparison of PE-3 and PE-6, having no LCB, showed that a broader MWD promoted strain rate thinning because the onset of strain rate thinning

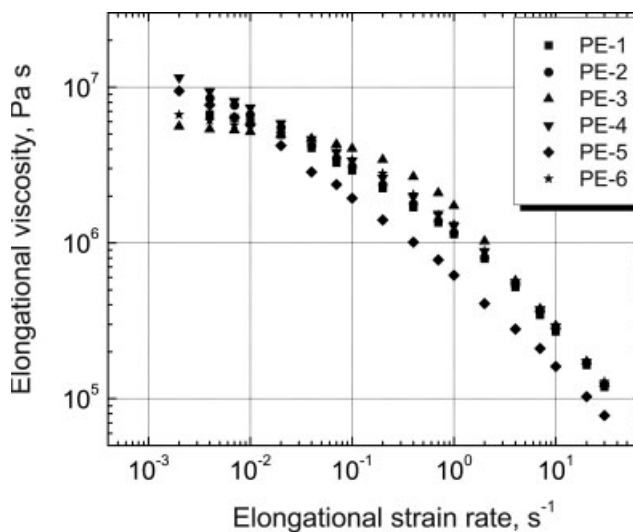


Figure 1 Elongational viscosity of different PE samples at a Hencky strain of 4 and 135°C.

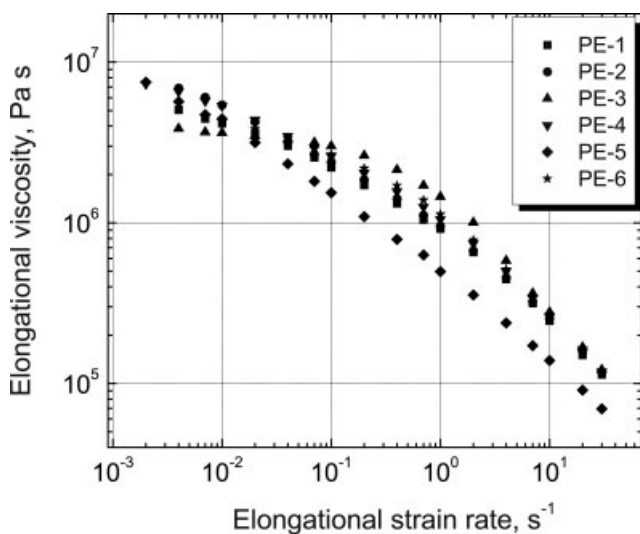


Figure 2 Elongational viscosity of different PE samples at a Hencky strain of 4 and 150°C.

was at a lower elongational strain rate for PE-6, which had a higher PI. Keeping this in mind, we found that comparisons of PE-1 and PE-2 (having comparable molecular weights but different LCB contents), PE-2 and PE-6, and PE-1 and PE-6 showed that LCB also promoted the onset of strain rate thinning.

This explains why the onset of strain rate thinning was at a lower strain rate for PE-5, which was a conventional LDPE with a higher PI and LCB. Hence, PE-5 showed a different shape for the elongational viscosity curve and lower elongational viscosity when the elongational strain rate was higher than 0.02 s⁻¹. A comparison of PE-3 and PE-6 at a strain rate higher than about 0.07 s⁻¹ showed that broaden-

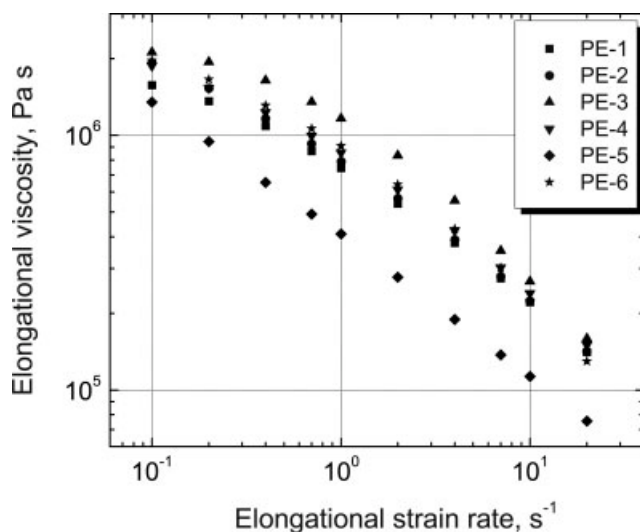


Figure 3 Elongational viscosity of different PE samples at a Hencky strain of 4 and 165°C.

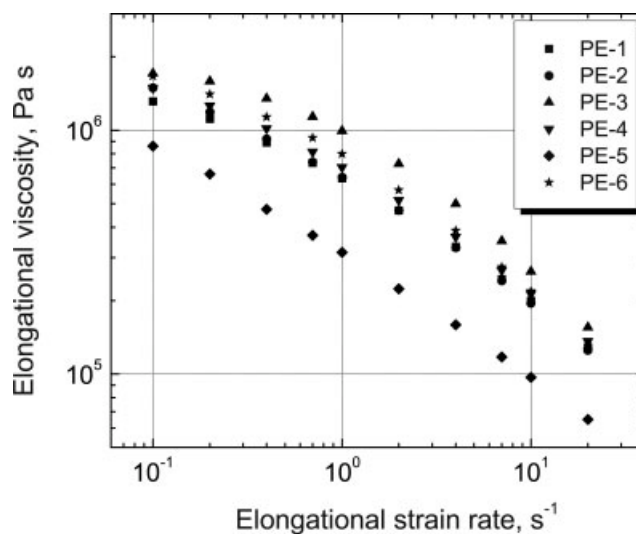


Figure 4 Elongational viscosity of different PE samples at a Hencky strain of 4 and 180°C.

ing the MWD seemed to reduce the elongational viscosity because even though PE-3 had a lower molecular weight, its viscosity was higher than that of PE-6 at the same strain rate. PE-2 had a higher molecular weight and LCB but lower PI than PE-1. PE-1 and PE-2 had almost the same elongational viscosity at a strain rate higher than 0.04 s⁻¹. Hence, the effect of LCB was to reduce the elongational viscosity. Figures 2–4 show similar observations at the same Hencky strain but at different temperatures. The same pattern of the elongational viscosity curves, but shifted to higher values, was recorded for Hencky strains of 5, 6, and 7.

The effects of LCB on the elongational rheology at low and high strains are elegantly shown in Figure 5,

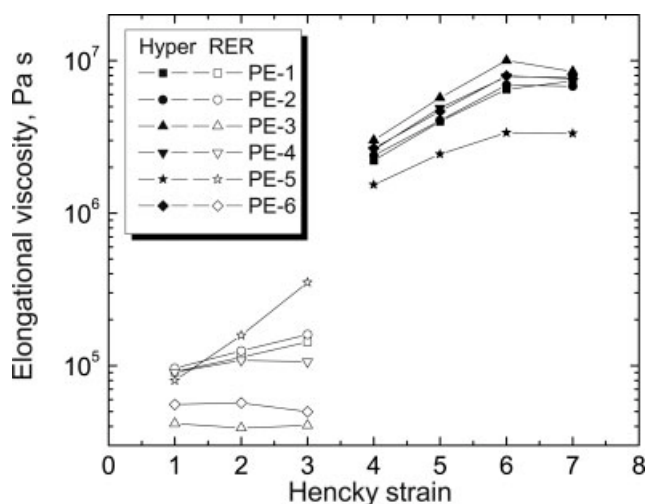


Figure 5 Strain hardening at a strain rate of 0.1 s⁻¹ and 150°C.

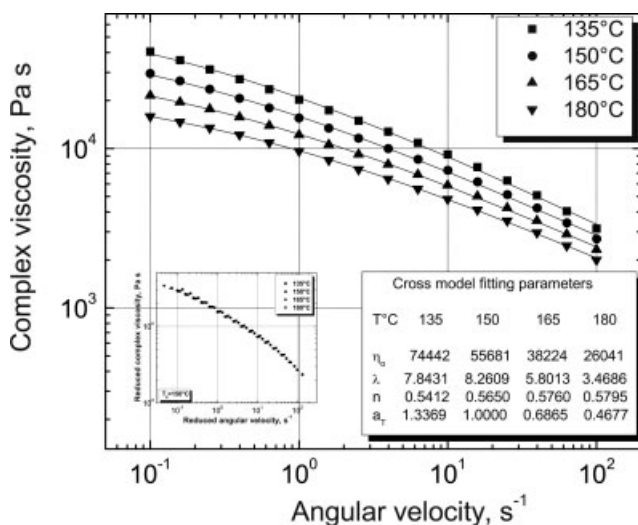


Figure 6 Complex viscosity data and Cross model fitting results for PE-4.

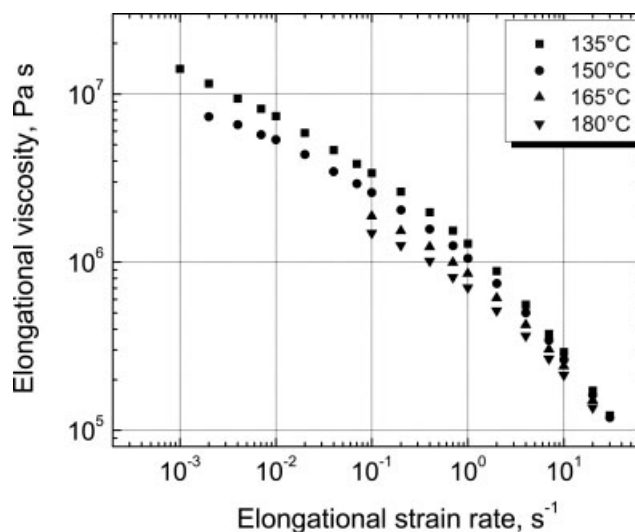


Figure 8 Elongational viscosity of PE-4 at a Hencky strain of 4.

in which all PE data, obtained with a Meissner-type device and the hyperbolically converging flow technique, are presented for an elongational strain rate of 0.1 s^{-1} and a temperature of 150°C . Data at Hencky strains of 1–3 were obtained with a Rheometrics Extensional Rheometer 9000 (RER) device,³² and those at Hencky strains of 4–7 were obtained from hyperbolic convergent dies. A few interesting results are revealed by the analysis of the data from Figure 5. First, all PEs, having LCB, showed strain hardening in the entire spectrum of tested Hencky strains. Second, linear PEs (PE-3 and PE-6) showed strain hardening only at high strains. In other words, all LDPEs showed strain hardening at strains higher than 3, but only LCB polymers showed this behavior

at lower strains. Third, one should keep in mind that the strain hardening reported in the literature generally refers to the transient phenomenon observed in Meissner-type devices, which might be considered the startup of an extensional flow experiment. That is why some authors present their data on elongational viscosity as the transient elongational viscosity^{3,7,12,13} or tensile stress growth coefficient.¹⁷ The strain hardening in hyperbolically converging flow technique experiments results from the steady-state behavior of polymer molecules in a converging elongational flow. For hyperbolic dies, the residence time of the fluid elements in the region of a constant elongational strain rate is equal to the Hencky strain divided by the elongational strain

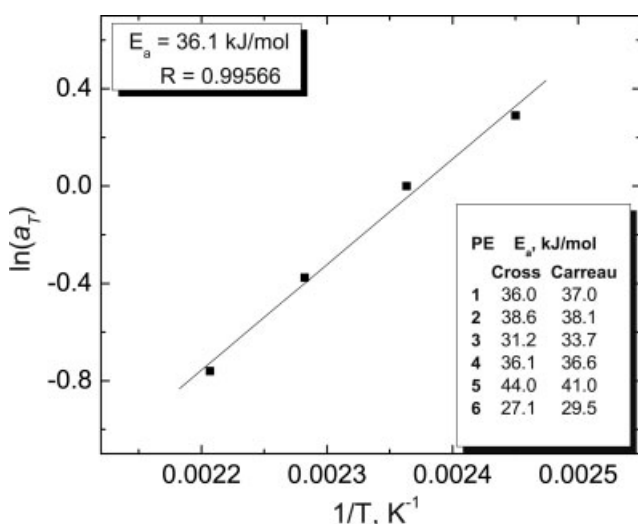


Figure 7 Arrhenius plot for the shift factors of PE-4 (Cross model). E_a is the activation energy.

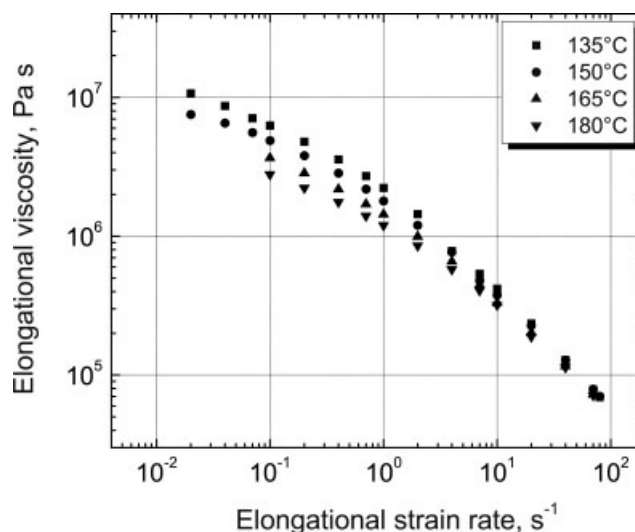


Figure 9 Elongational viscosity of PE-4 at a Hencky strain of 5.

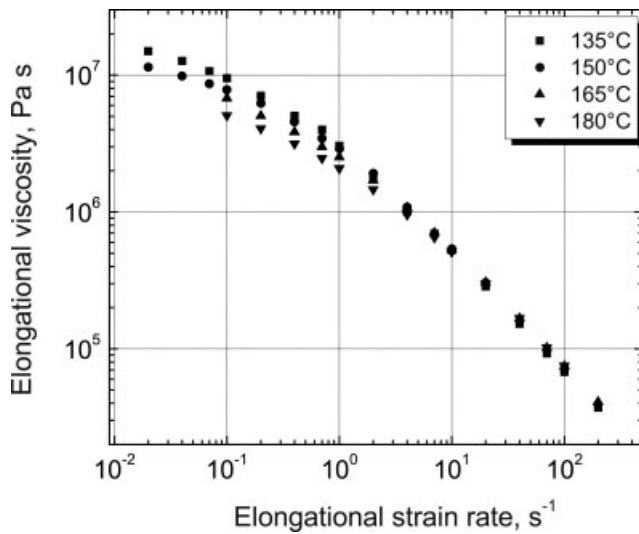


Figure 10 Elongational viscosity of PE-4 at a Hencky strain of 6.

rate, whereas the comparable time for the Meissner-type devices is the time from the startup of the experiment.

Effect of the processing conditions on the elongational rheology of polymer melts

Besides the molecular parameters discussed previously, the rheological properties can be affected by the processing conditions as well. The most important processing parameters that affect the elongational viscosity of a polymer include the temperature, strain, and strain rate. The elongational viscosity of polymer melts increases with decreasing temperature and increasing Hencky strain. In the

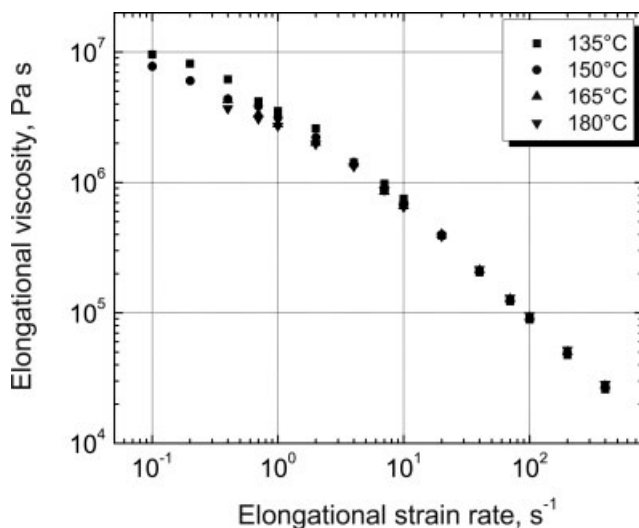


Figure 11 Elongational viscosity of PE-4 at a Hencky strain of 7.

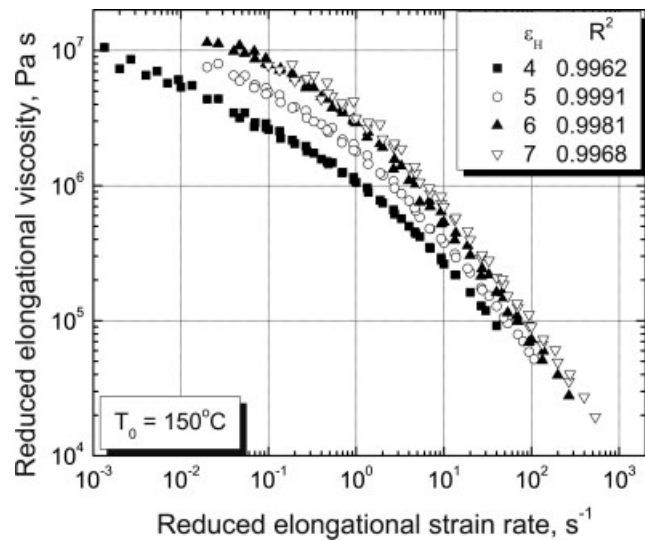


Figure 12 Temperature master curves of the elongational viscosity of PE-4 with Cross model shift factors.

next subsections, the shifting of the elongational viscosity curves with respect to the temperature, Hencky strain, and both the temperature and Hencky strain is presented.

Temperature shifting of the elongational viscosity

The same technique described in the previous article²⁵ for shifting complex viscosity curves with respect to temperature can be used to perform the shifting of the elongational viscosity curves, with the same shear viscosity shift factors.²⁸ Shifting with respect to the temperature of the complex viscosity curves for PE-4 is illustrated in the following. A sim-

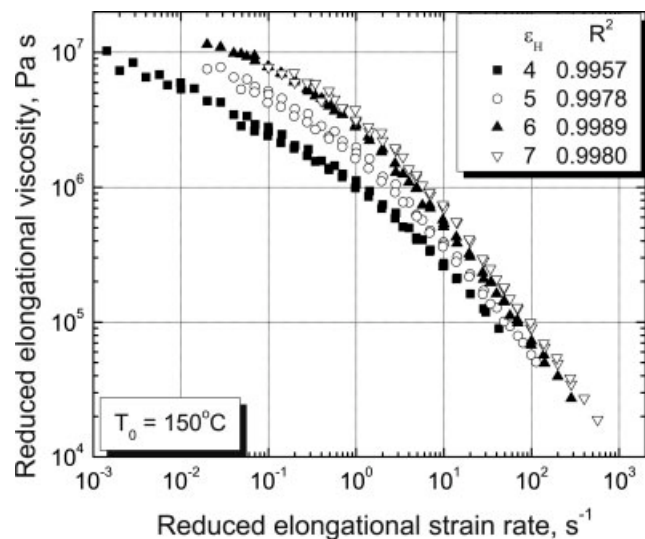


Figure 13 Temperature master curves of the elongational viscosity of PE-4 with Carreau model shift factors.

TABLE II
 R^2 Values for the Polynomial Fit of the Temperature Shifting Master Curves of the PE Samples

Sample	R^2							
	Hencky strain 4		Hencky strain 5		Hencky strain 6		Hencky strain 7	
	Cross	Carreau	Cross	Carreau	Cross	Carreau	Cross	Carreau
PE-1	0.9980	0.9976	0.9976	0.9983	0.9965	0.9983	0.9971	0.9983
PE-2	0.9986	0.9981	0.9992	0.9995	0.9972	0.9988	0.9967	0.9977
PE-3	0.9958	0.9951	0.9959	0.9957	0.9947	0.9954	0.9940	0.9944
PE-4	0.9962	0.9957	0.9991	0.9978	0.9981	0.9989	0.9968	0.9980
PE-5	0.9989	0.9968	0.9990	0.9987	0.9989	0.9995	0.9968	0.9989
PE-6	0.9968	0.9948	0.9964	0.9949	0.9955	0.9949	0.9928	0.9910

ilar illustration is provided in the first article²⁵ in this series for PE-1.

The complex viscosity of PE-4 at four different temperatures is shown in Figure 6. Data from this figure show that changing the temperature does not significantly affect the functional dependence of the complex viscosity on the angular velocity; it merely alters the zero-shear-rate viscosity and the angular velocity at which the transition from a constant complex viscosity to power-law behavior occurs. This similarity provides the basis for the method of reduced variables.

The three-parameter Cross model was used to fit the complex viscosity curves of PE-4 at each temperature. The fitted complex viscosity data are given as solid lines in Figure 6. The parameters in the Cross model were also obtained and are shown in the legend of Figure 6, together with the shift factors calculated by the use of 150°C as the reference temperature. The generated master curve is shown in the inset of Figure 6. Similarly, the master curves of dynamic moduli were also created with the same shift factors. The Arrhenius plot of $\ln a_T$ versus the

reciprocal of the temperature ($1/T$) is shown in Figure 7, from which the activation energy was calculated; it is shown in the inset. The three-parameter Carreau model was also used to fit the complex viscosity curves of PE-4 at each temperature, and shift factors were calculated in a similar way. The activation energy, presented for all PEs in the legend of Figure 7, increased with an increase in LCB, and the linear polymers (PE-3 and PE-6) showed values close to those found by other researchers.^{5,19}

Figures 8–11 show the effect of the temperature on the elongational viscosity of PE-4 measured at different Hencky strains. The temperature master curves generated with the shift factors derived from the Cross and Carreau models are shown in Figures 12 and 13 for PE-4. The elongational viscosity decreases with increasing temperature. This is because increasing the temperature increases the mobility of macromolecular chains. With an increasing strain rate, the viscosity differences at different temperatures appear to diminish because the curves almost converge at higher strain rates.

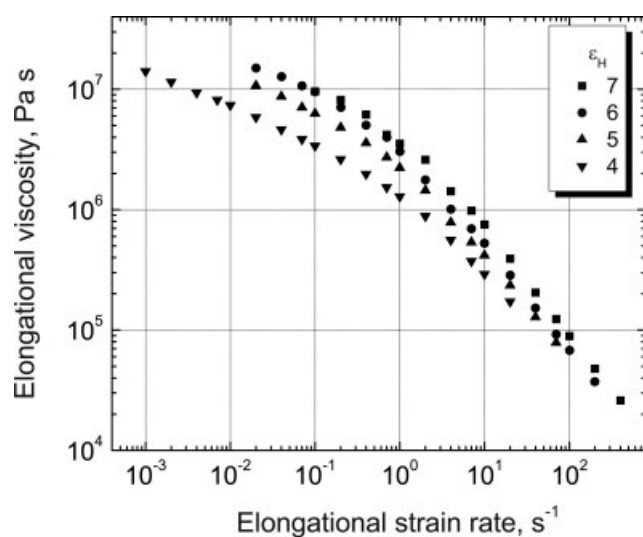


Figure 14 Elongational viscosity of PE-4 at 135°C.

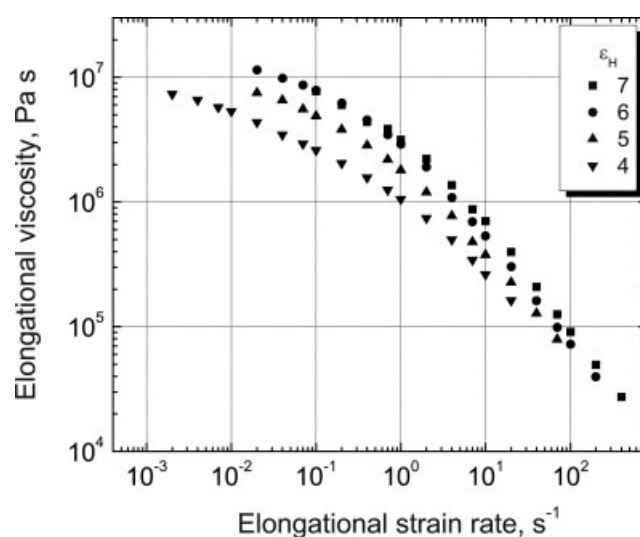


Figure 15 Elongational viscosity of PE-4 at 150°C.

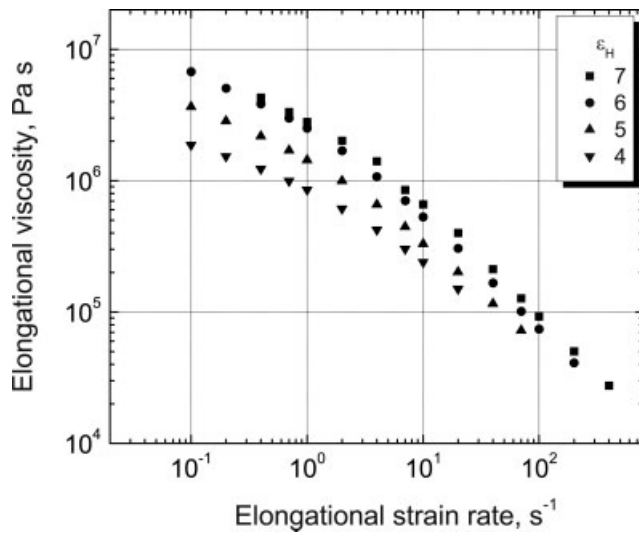


Figure 16 Elongational viscosity of PE-4 at 165°C.

Both the Cross and Carreau models yield good master curves for the elongational viscosity. This can also be shown by the high coefficient of determination (R^2) values (>0.99) for the polynomial fit of all temperature master curves for all samples, which is given in Table II. The elongational viscosity data measured at very low strain rates fell nicely on the master curves, and this indicated that these data were probably accurate, although the resulting pressure drop values in the measurements were somewhat low.

Hencky strain shifting of the elongational viscosity

The elongational viscosity of the PE samples was measured at four different temperatures (135, 150,

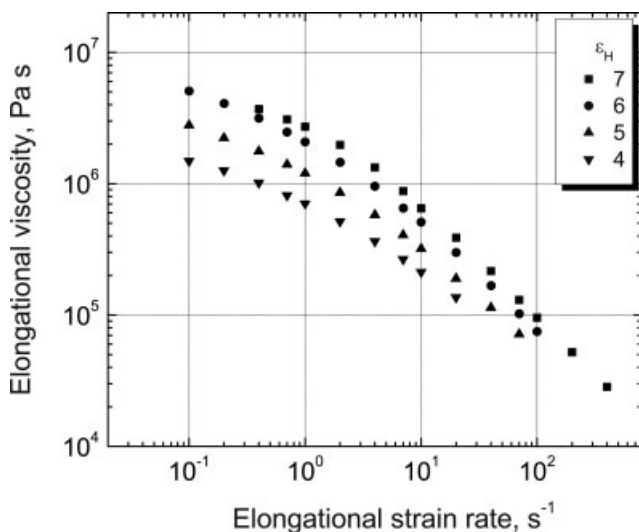


Figure 17 Elongational viscosity of PE-4 at 180°C.

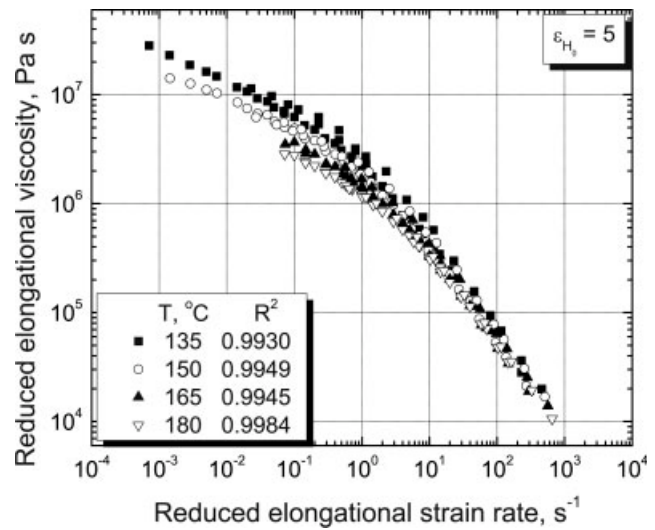


Figure 18 Hencky strain master curves of the elongational viscosity of PE-4, generated with method 1.

165, and 180°C) and at four Hencky strains (4, 5, 6, and 7) for each temperature. The effect of the Hencky strain on the elongational viscosity of PE-4 measured at four different temperatures is shown in Figures 14–17. As the Hencky strain increases, a higher degree of orientation is imparted to the molecular chains, and this results in a higher elongational stress leading to a higher elongational viscosity. The elongational viscosity curves have similar shapes at the different Hencky strains. This similarity provides the basis for the method of reduced variables for combining data taken at different Hencky strains into one master curve for the sample.

To calculate the shift factors for Hencky strain shifting, the reference Hencky strain was taken to be

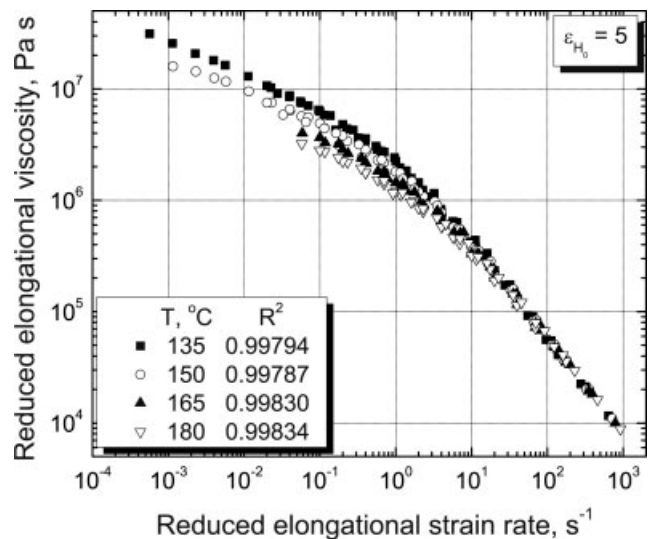


Figure 19 Hencky strain master curves of the elongational viscosity of PE-4, generated with method 2.

TABLE III
 R^2 Values for the Polynomial Fit of the Hencky Strain Shifting Master Curves of the PE Samples

Sample	R^2							
	135°C		150°C		165°C		180°C	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
PE-1	0.9935	0.9975	0.9940	0.9973	0.9973	0.9988	0.9979	0.9983
PE-2	0.9979	0.9976	0.9965	0.9968	0.9989	0.9980	0.9988	0.9982
PE-3	0.9812	0.9915	0.9924	0.9922	0.9950	0.9956	0.9928	0.9963
PE-4	0.9930	0.9979	0.9949	0.9979	0.9945	0.9983	0.9984	0.9983
PE-5	0.9919	0.9984	0.9918	0.9987	0.9917	0.9989	0.9959	0.9990
PE-6	0.9927	0.9944	0.9949	0.9949	0.9955	0.9963	0.9964	0.9971

5. The Cox–Merz rule was assumed to apply to the PE samples so that the shear viscosity at the shear rate of 1 s^{-1} was equal to the complex viscosity at the angular velocity of 1 rad/s . The reference shear rate (angular velocity) and elongational strain rate were taken to be 1 s^{-1} . At each temperature, the elongational viscosity curves of PE-4 were shifted to a master curve. These master curves are shown in Figures 18 and 19 for methods 1 and 2 of Hencky strain shifting, respectively. Both methods seem to fit the data very well for all PE samples, with slightly less correlation for PE-3 at 135°C with method 1 and for PE-5 with method 1. This is also shown by the R^2 values for the second-order polynomial fit of the Hencky strain master curves, which is given in Table III. Except for PE-3, for which method 1 gave a poorer R^2 value of 0.9812 at 135°C , R^2 values for all PE samples were higher than 0.99 for both methods, indicating that good master curves could be created with these methods for PE samples. The R^2 values showed that method 2 gave slightly better results than method 1. This was also found in previous

studies of nylon samples accomplished by this research group.³³

Simultaneous temperature and Hencky strain shifting of the elongational viscosity

Shifting of the elongational viscosity curves with respect to both the temperature and Hencky strain was performed with the temperature shift factors based on the Cross model that gave the highest values for R^2 for the complex viscosity master curve data fit.

The resulting general master curves for sample PE-4 with both methods are presented in Figures 20 and 21. The reference temperature was 150°C , and the reference Hencky strain was 5. The R^2 values are shown in Table IV for all samples. Except for PE-3 and PE-5, for which method 1 gave poorer values of 0.9882 and 0.9897, respectively, R^2 values for all PE samples were higher than 0.99 for both methods, indicating that good master curves could be

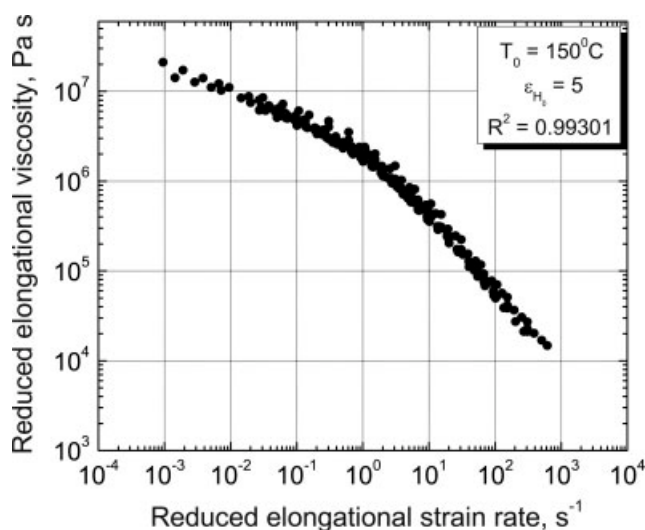


Figure 20 General master curves of the elongational viscosity of PE-4, created by simultaneous temperature and Hencky strain shifting (method 1).

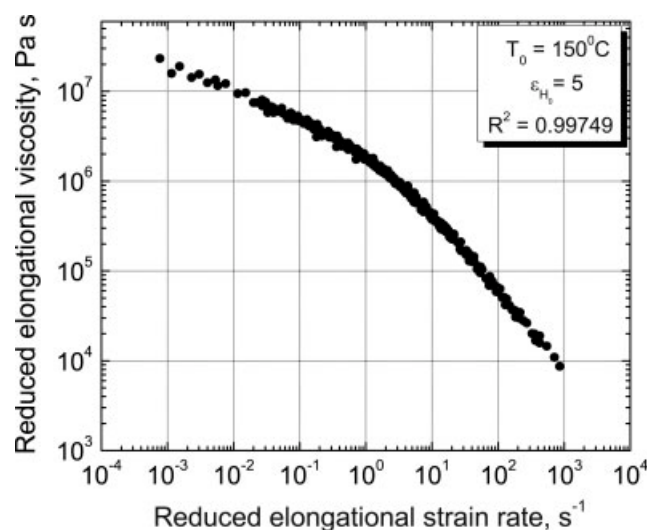


Figure 21 General master curves of the elongational viscosity of PE-4, created by simultaneous temperature and Hencky strain shifting (method 2).

TABLE IV
 R^2 Values for the Polynomial Fits of the Simultaneous Temperature and Hencky Strain Shifting Master Curves

Sample	Method 1	Method 2
PE-1	0.9939	0.9963
PE-2	0.9972	0.9966
PE-3	0.9882	0.9929
PE-4	0.9928	0.9971
PE-5	0.9897	0.9982
PE-6	0.9930	0.9945

generated with these methods. Again, both a visual inspection and the R^2 values showed that method 2 gave slightly better results than method 1. In both Figure 20 and 21, there are 16 elongational viscosity curves (at four temperatures and four Hencky strains) shifted to generate the corresponding general master curves.

CONCLUSIONS

The elongational viscosity of the PE melts was considerably affected by their molecular characteristics. The elongational viscosities of different samples flattened out differently at low elongational strain rates. Both the MWD and LCB content enhanced strain rate thinning. The onset of strain rate thinning occurred at a lower strain rate for the conventional LDPE, so the conventional LDPE showed a different shape for the viscosity curve and lower elongational viscosity. Moreover, both the PI and LCB seemed to reduce the elongational viscosity.

Besides the molecular characteristics discussed previously, the rheological properties were considerably affected by processing conditions such as the temperature, Hencky strain, and elongational strain rate. All samples showed strain rate thinning and Hencky strain hardening for the elongational viscosity. The elongational viscosity of the polymer melts increased with decreasing temperature and increasing Hencky strain. Both the Cross and Carreau models yielded good master curves for the temperature shifting of the elongational viscosity. Good master curves for the Hencky strain shifting of the elongational viscosity were generated with two methods to calculate the Hencky strain shift factors. Method 2 gave slightly better results than method 1: method 1 was based on the orientation ratio being equal to the relaxation times the ratio, whereas method 2 was based on the orientational viscosity ratio. By combining the shift factors from the temperature and Hencky strain shifting, we also generated good general master curves for the simultaneous temperature and Hencky strain shifting.

All studied LDPEs showed strain hardening at strains higher than 3 in measurements performed

with the hyperbolically converging flow technique, but only LCB polymers showed this behavior at lower strains.

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