

Shear and Elongational Flow of Some Branched Polyethylenes

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SYNOPSIS

The elongational properties of some branched polyethylenes are studied. Experimental results of their flow behavior are presented. The Cogswell technique of calculating the elongational viscosity together with another approach based on the work of Huang and Shroff are utilized. The results show close agreement between these two methods. Certain parameters related to material elasticity are employed. Results suggest that the elastic parameters achieve relatively high levels only if the molecular weights are sufficiently high.

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INTRODUCTION

The rheological properties of molten polymers are dependent on the molecular weight, molecular weight distribution, and degree of long-chain branching (LCB). It is now well recognized that a good understanding of the relationship between molecular structure and the rheological properties would be of benefit to processing as well as to enhancing scientific understanding.

In the past, the viscous behavior of polymer melt flows has been emphasized more than their elongational and elastic behavior. However, over the last 20 years or so, this situation has been shifting somewhat. The extensional flow of polymer melts has been the subject of moderate to extensive study by some authors (see, e.g., Ref. 1). This has been partly in response to the increasing recognition that such flows do occur quite commonly in processing and also that the tensile properties are difficult to correlate with the shear behavior. The purpose of the present contribution is to present some data of the shear and elongational behavior of some branched polyethylenes (i.e., LDPEs) and the behavior of some parameters related to their elastic response.

THE FLOW OF POLYETHYLENE MELTS

Polyethylenes are, of course, some of the most commonly used polymers. Interestingly, their elongational behavior is unusual (see Ref. 1). The properties are found to be strongly dependent on the molecular structure and, in particular, LCB has been found to have significant effects on their rheological behavior.^{2,3} Rheological behavior of branched polymers of relatively high molecular weight can lead to complex shear behavior. The melt viscosity can be either higher or lower than that of a comparable linear material.^{4,5} Further, branching can result in "thermorheologically complex behavior"—the normal shift of rheological measurements with temperature through time-temperature superposition does not apply (e.g., Ref. 1).

One of the studies of interest here is by Romanini et al.⁶ This work was concerned with branching effects on the flow behavior. In particular, it was found that the Newtonian viscosity undergoes a considerable decrease and the elastic deformation that may be recovered after extrusion is lower as the LCB is increased. These effects are presumably due to the more reduced size of the branched macromolecule. This study also found that the molecular weight distribution (MWD) has a lower effect on the rheology than does the molecular weight (M_w) and LCB.

La Mantia et al.⁷ looked at the influence of LCB on the elongational behavior of polyethylenes. They

found that the strain-hardening effect increases with the number of branch points; the elongational viscosity tends to increase with LCB level.

EXTENSIONAL FLOW

Discussions on the importance of extensional flows have appeared in some publications (e.g., Ref. 1). Several techniques have been utilized to obtain measures of the elongational viscosity of melts. A relatively simple and quick method of determining the elongational viscosity was developed by Cogswell,⁸ which involves converging flows. Briefly, it is assumed here that a material adopts a conical flow pattern when flowing through the converging section into a capillary and that the velocity at the outer boundary of this flow pattern is zero. It is also assumed that the total entrance pressure drop in the converging section is the sum of that due to the shear flow and that due to the extensional flow such that the flow pattern achieved is the one corresponding to the minimum pressure drop. It has been argued that the elongational viscosity calculated is an apparent one, as it is not clear if a steady state has been attained in the converging section.⁹ It has been found that such a convergent flow analysis gives quick and reliable information on the elongational flow of melts in a wide range of strain rates and temperatures.⁹ Cogswell's method of calculating elongational viscosities has been fairly widely used and also has been incorporated in the software of at least one capillary rheometer (Rosand).

Huang and Shroff¹⁰ carried out a further converging flow analysis. This gives the following relations:

$$\sigma_{22} = 2P_E(d \ln P_E / d \ln \gamma_{12}) \quad (1)$$

$$P_E = P_0 - F(\beta) \sigma_{12} \quad (2)$$

where σ_{22} is the stress normal to the die wall at the exit and σ_{12} and γ_{12} are the wall shear stress and shear rate at the die exit. P_E and P_0 are the extensional pressure loss and the experimentally measured entrance pressure loss, respectively. $F(\beta)$ is a shape factor dependent on the converging die angle β . An apparent elongational viscosity, using Huang and Shroff's analysis, can be calculated using

$$\eta_{el} = \sigma_{22} / \gamma_{22} \quad (3)$$

and taking the average extensional rate to be

$$\gamma_{22} = (1/8) \sin(\beta/2) [1 + \cos(\beta/2)] \quad (4)$$

It should be pointed out that Huang and Shroff did not attempt to calculate the elongational viscosity using this approach, but we do so in this article using our data below. Huang and Shroff also utilized a "Weissenberg" number defined as

$$Wnc = \sigma_{22} / 2\sigma_{12} \quad (5)$$

They found that a linear polyethylene (PE) or a branched PE with a low level of LCB shows a monotonic increasing value of Wnc vs. the stretch rate; highly branched materials were found to exhibit a maximum.

ELASTIC PARAMETERS

Most long-chain materials, including polymer melts, are, of course, viscoelastic. A linear theory of viscoelasticity exists.¹ This is strictly valid only for small deformations and rates of deformations. Perhaps the most popular apparatus for studying these properties is the dynamic mechanical spectrometer. Unfortunately, most practical processing involves large deformations and large strain rates. The most commonly observed nonlinear phenomena is the dependence of the shear viscosity on the shear rate and the appearance of the nonzero first normal stress difference. No universal theory exists for the nonlinear viscoelasticity. However, some useful concepts have been advanced in the last few decades. Some idealized fluid behavior patterns have been postulated and limited theoretical developments achieved. One such theory is the rubberlike liquid model.¹ For steady simple shear flow, the rubberlike fluid theory finds that the recoverable shear is

$$\gamma_r = N_1 / 2\sigma_{12} \quad (6)$$

i.e., it is the ratio of the first normal stress difference over twice the shear stress at the exit wall. This is not exactly equal to the actual recoverable shear except at low shear rates.¹ The rubberlike theory also gives for the steady-state compliance

$$J_S^0 = N_1 / 2\sigma_{12}^2 \quad (7)$$

The steady-state compliance is known to be essentially independent of temperature and molecular weight but strongly dependent on the MWD. It is

known that the ultimate recoil after steady shear, γ_r , approaches a steady value at large flow rates, unlike a rubberlike fluid.¹

It is widely accepted that the first normal stress difference is dependent on the entrance pressure for converging flows. In fact, White and Kondo¹¹ found that

$$N_1 = 0.5P_0 \quad (8)$$

so that for the recoverable shear one can put

$$\gamma_r = 0.5(P_0/2\sigma_{12}) \quad (9)$$

This equation is used to calculate the recoverable shear and is referred to as RS below.

The ratio of the entrance pressure drop over twice the shear stress (at the exit) appears in connection with the following (and therefore appears to be an important parameter):

- (a) The Bagley end correction—

$$\delta P_{\text{Total}} = 2\sigma_{12}(L/R + a) \quad (10)$$

or

$$a = P_0/2\sigma_{12} \quad (11)$$

where δP_{Total} is the total pressure loss for flow through a capillary (of length L and radius R) and its entry section (i.e., the converging section represented by the end correction “ a ”).

- (b) The converging flow analysis of Cogswell⁸ assumes that, for a flat entry flow, there exists a conicylindrical flow with a natural half-angle of

$$\tan \theta = [(3/4)(n + 1)P_0/2\sigma_{12}] \quad (12)$$

- (c) For the rubberlike fluid, as pointed out above,

$$\gamma_r = N_1/2\sigma_{12} = 0.5(P_0/2\sigma_{12}) \quad (13)$$

and

$$J_S^0 = P_0/4\sigma_{12}^2 \quad (14)$$

It is not known what exactly is implied by the recoverable shear and the compliance as calculated using these equations. However, it is clear that both are related quite closely to the elastic behavior of the material con-

cerned. Calculations for several branched materials are presented below.

EXPERIMENTAL

An off-line twin-bore capillary rheometer (Rosand Precision Ltd. RH7) was used. The bore : die contraction ratio was 15 : 1. One die was of 1 mm diameter and 16 mm long; the other had the same diameter but had an effectively zero length (i.e., an orifice die) giving an entrance pressure drop directly. The dies had a flat entry, i.e., a full convergence angle of 180°. The operating temperature was 190°C throughout.

The materials were six LDPEs with some information about their molecular characteristics. Table I lists the data available. The first four materials, LDPE1 to LDPE4, are from one supplier and are known to be in decreasing order of LCB level, i.e., LDPE1 is the most branched material of the first four and LDPE4 is the least branched of this set. The relative order of branching levels was determined by the material supplier using a GPC equipped with a viscosity detector.¹² These LCB data are classified. This set of four materials also has a decreasing order of MWD and, therefore, just from these data, it is not possible to separate the effects of branching and MWD. Except for the melt flow index, no other data about the last two (LDPE5 and LDPE6) were available. The results are included because they are pertinent to the present contribution.

RESULTS

Figure 1 shows the shear viscosities of the six materials. It is seen that LDPE2 is the most viscous and LDPE1 is the least viscous among the first four polymers. This might be expected as LDPE1 is the most branched and therefore probably has the

Table I

	M_w	M_n	MFI	MWD
LDPE1	304,900	16,700	3.2	18.26
LDPE2	267,800	17,000	0.3	15.75
LDPE3	178,700	17,000	1.8	10.51
LDPE4	142,700	14,700	0.9	9.71
LDPE5	—	—	15	—
LDPE6	—	—	4	—

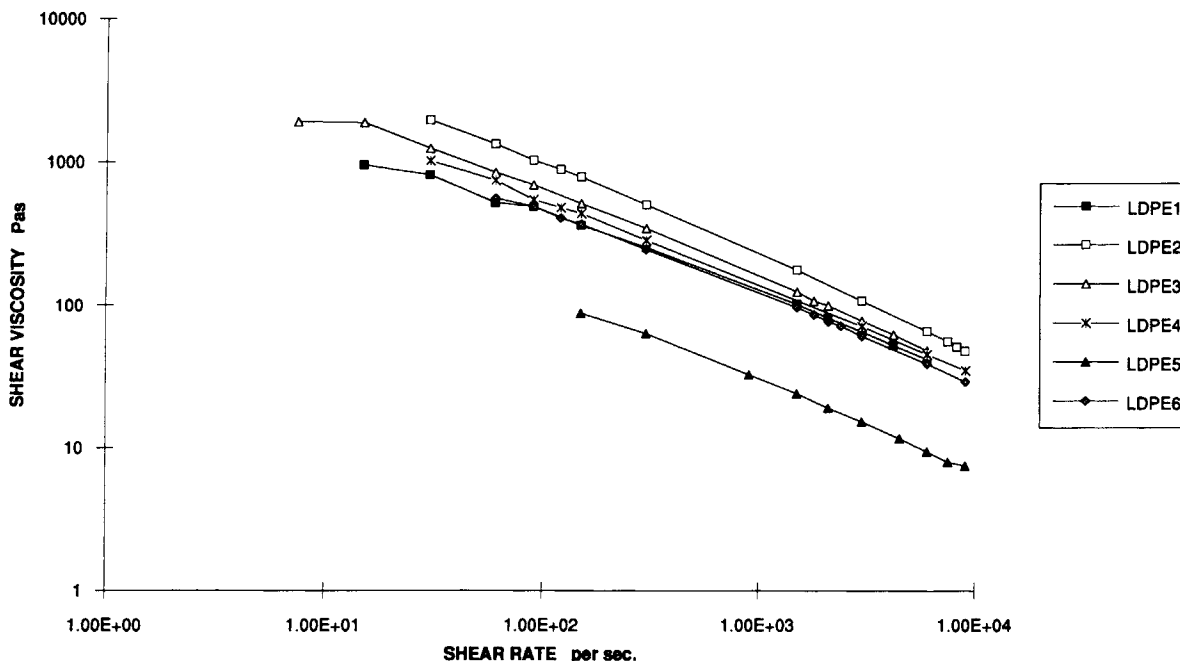


Figure 1 Shear viscosities for the LDPE melts at 190°C.

smallest molecular size; the materials do not have the same molecular weights and it can be seen that LDPE2 is more viscous than is LDPE3 even though it is more branched. Note that LDPE5 is the least viscous material. LDPE1 has a higher M_w than that of LDPE2, but, presumably, because it is more branched, it has a lower shear viscosity. This argument cannot be carried over to the case for LDPE3 and LDPE4. LDPE1 and LDPE6 have similar shear resistances as suggested by their quite close MFIs. These results do not entirely agree with those of Han and Kwack¹³ who used three LDPEs of M_w 201,000, 143,000, and 110,000 and having a decreasing degree of branching and MWD. Their results at 200°C give the shear viscosities to be decreasing with lower M_w at low shear rates, but this status changes at higher shear rates (i.e., shear viscosity curves cross over as expected for differing MWD materials). If the temperature was decreased, then these curves perhaps may not cross as found by Thomas and Hagan¹⁴ for two polystyrenes.

Figure 2 shows the Cogswell elongational viscosities of the materials. Again, LDPE2 has the highest viscosity but the most branched material, LDPE1, has a higher tensile resistance than that of the rest of the materials. Extensional thinning behavior is seen mostly, but LDPE3, LDPE5 and LDPE6 show some stretch thickening. LDPE4 data are similar to those of LDPE3.

Munstedt and Laun¹⁵ presented some elongational data for various branched materials. Their LDPEs (samples 4–8 in their article) seem to show that decreasing M_w gave decreasing tensile viscosities. All these polymers except one (sample 8) had molecular weights greater than those used in the present article. Our results here do not entirely agree with this. Note that though the shear viscosities of LDPE1 and LDPE6 are similar, their elongational viscosities are quite different. Figure 3 shows the entry pressures for the polymers. These are largely in the order of their elongational viscosities. It can be seen that all the entry pressures are tending to converge at high flow rates. The entry pressures for LDPE1, LDPE3, and LDPE4 are quite similar even though their molecular characteristics are quite different. This may be because the molecular size has a greater effect on the reduction of flow resistance at relatively higher molecular weights than at intermediate or lower molecular weights.

The Cogswell elongational viscosities and their corresponding stretch rates were calculated for the materials. The Huang and Shroff approach was also used to calculate the elongational viscosities. Figures 4–6 show typical comparative results. It is seen that for LDPE2 and LDPE4 both approaches give quite similar tensile results, and for LDPE3, there is not a significant difference, especially if one accounts for the fact that there has been wide discrepancies

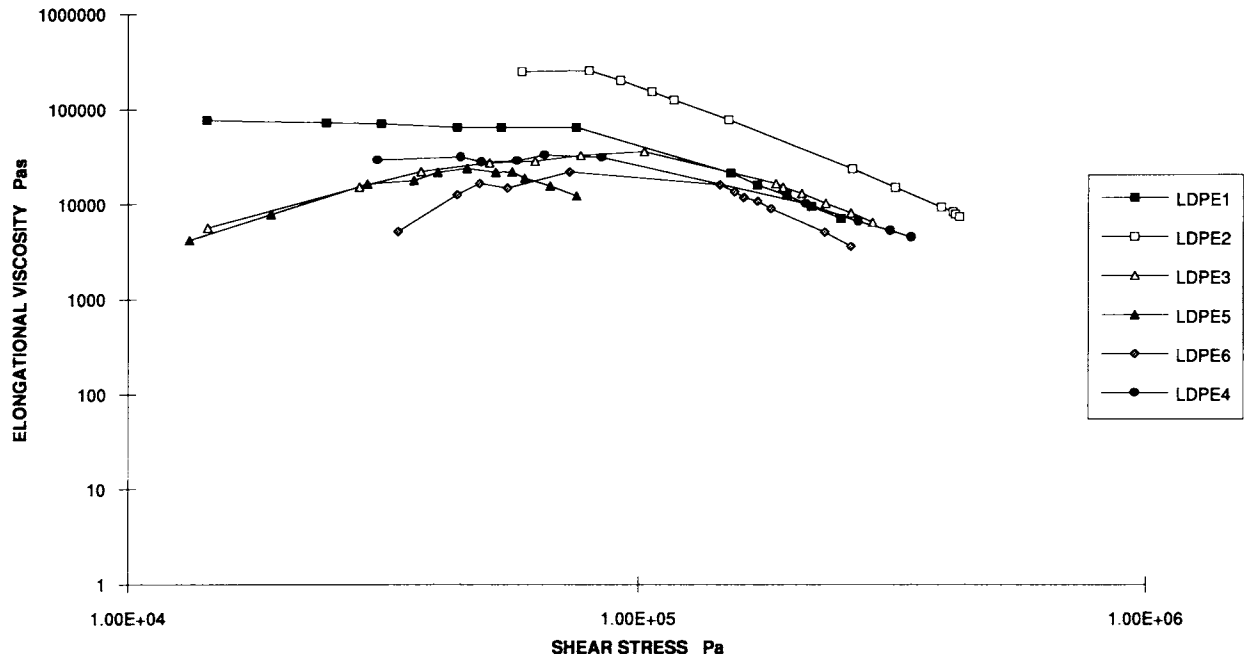


Figure 2 Elongational viscosities for the LDPE melts at 190°C.

of some past results involving different equipment.¹⁶ The other materials generally showed excellent agreement, as for Figure 4.

Figure 7 shows the recoverable shear results. In a limited flow range, the RS values for LDPE1

through LDPE4 lie according to their order in the degree of LCB but not outside this. It is seen that all the materials show an approach to a finite RS value at large shear stress unlike a ideal rubberlike fluid. LDPE1 has a higher RS than that of LDPE2

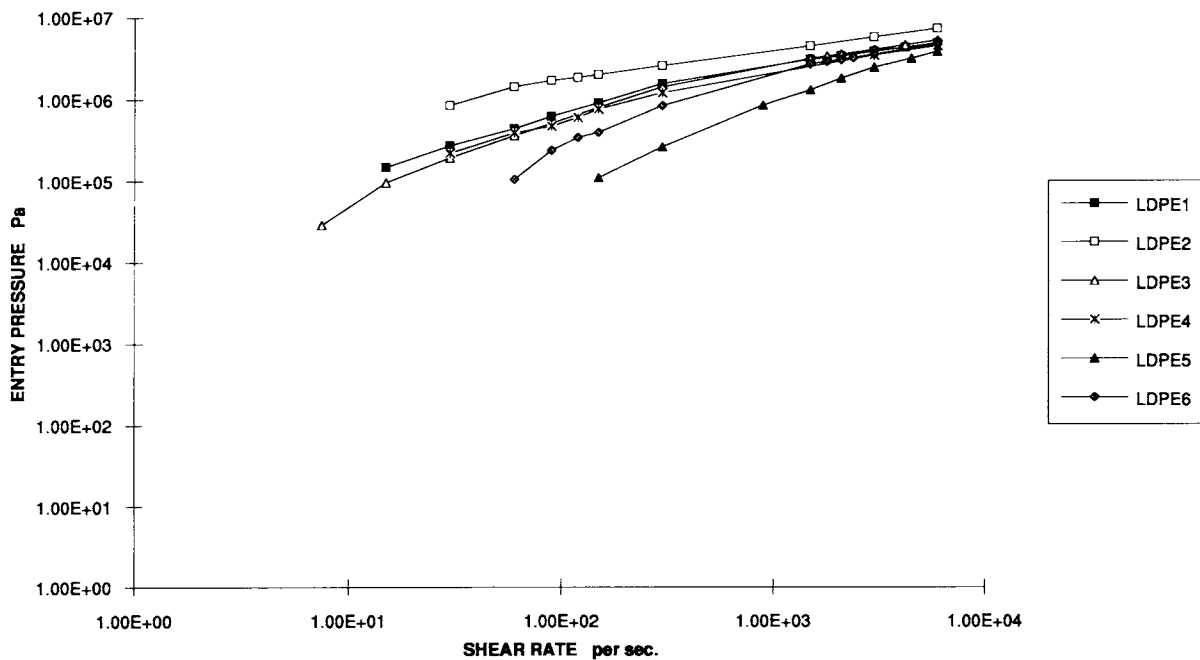


Figure 3 Entry pressures for LDPE melts at 190°C.

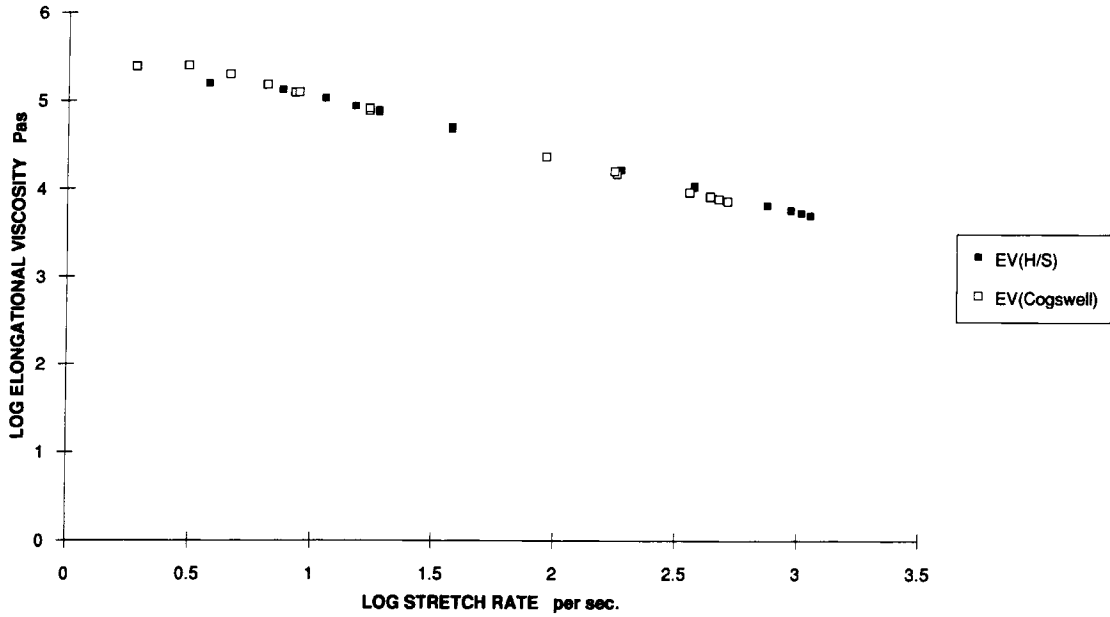


Figure 4 Elongational viscosities for LDPE2 at 190°C.

throughout; LDPE3 has an initially lower RS than that of LDPE4, but the converse is the result at high stresses.

Figure 8 shows the calculated compliances of the materials. The values are widely different at low flow rates but converge to a relatively low value. LDPE1 always has a higher compliance than that of LDPE2; both are higher than those of LDPE3 and LDPE4.

The last two show a similar comparative behavior as in the RS values.

Figure 9 shows the calculated Weissenberg numbers according to the Huang and Shroff expression. The stretch rate range is similar to that presented by Huang and Shroff for their materials. LDPE3 and LDPE4, both of relatively low levels of LCB, show a monotonic increasing value of Wnc ; LDPE2

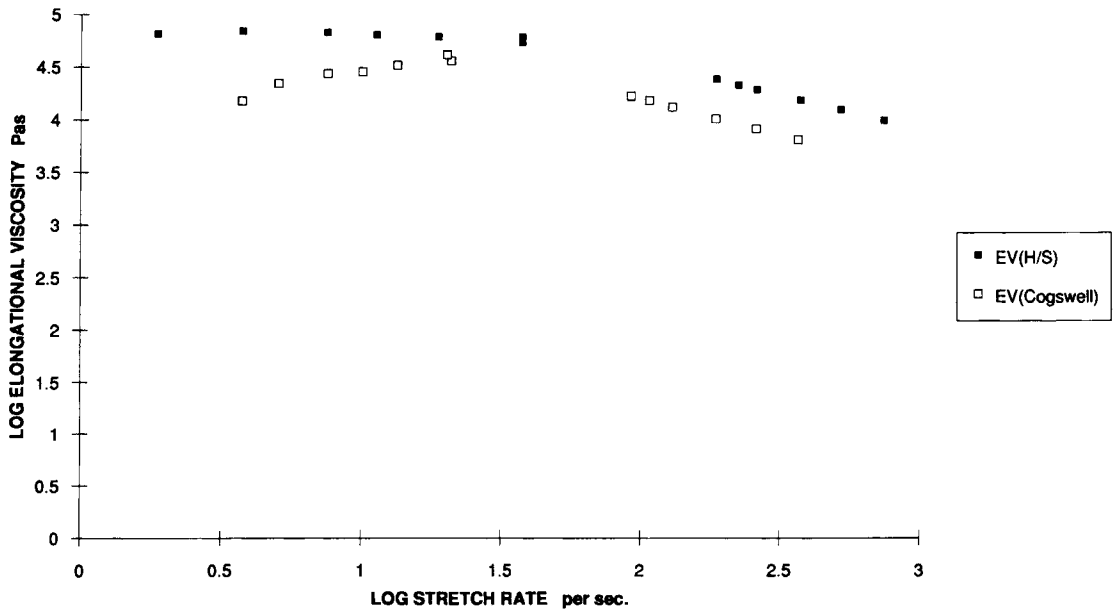


Figure 5 Elongational viscosities for LDPE3 at 190°C.

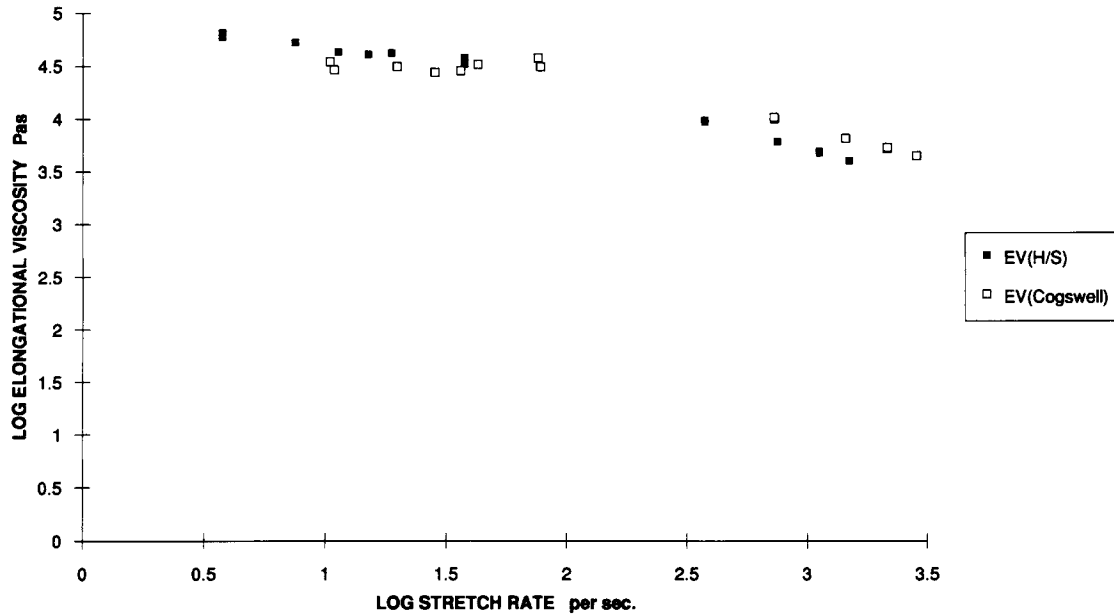


Figure 6 Elongational viscosities for LDPE4 at 190°C.

shows a maximum, but the highest molecular weight polymer (which also is the most branched), LDPE1, shows an inflection and not a maximum.

CONCLUSIONS

The above results partly agree with some of the published results. These suggest the following con-

clusions: The calculated Weissenberg number, the recoverable shear, and compliance are higher only if the material is of sufficiently high molecular weight, i.e., only if the molecular weight is relatively high does the elasticity increase with the level of branching. At intermediate M_w , there is a somewhat complex behavior. Elasticity is generally attributed to some sort of entanglements or temporary cross-

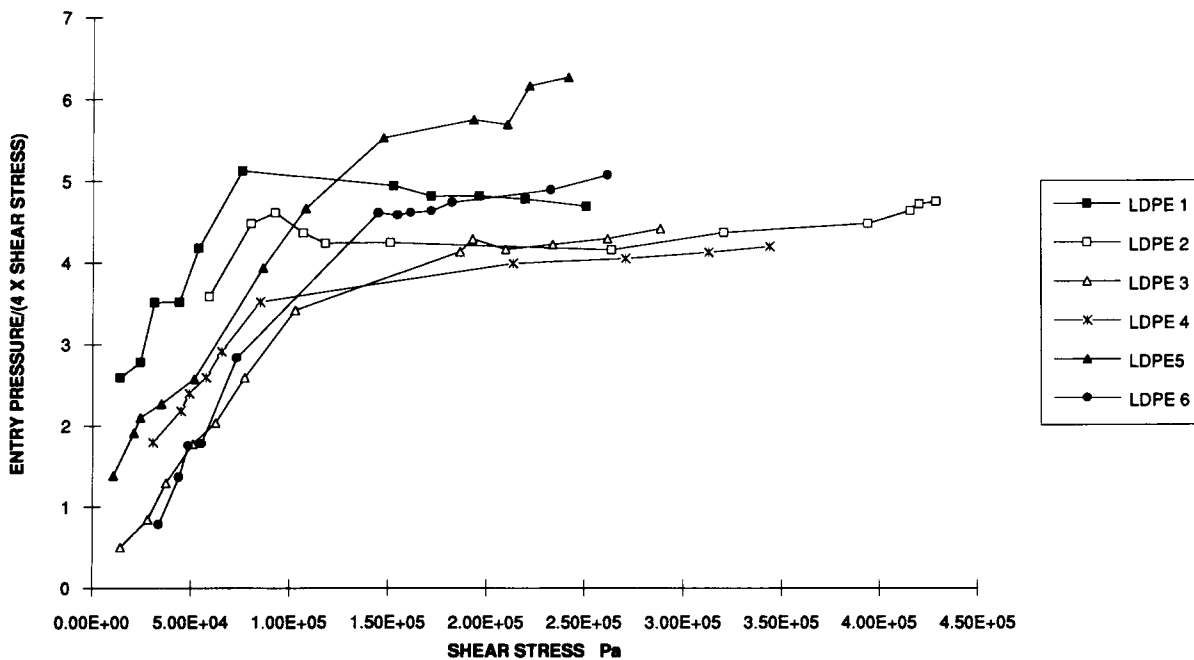


Figure 7 "Recoverable shear" for LDPE melts at 190°C.

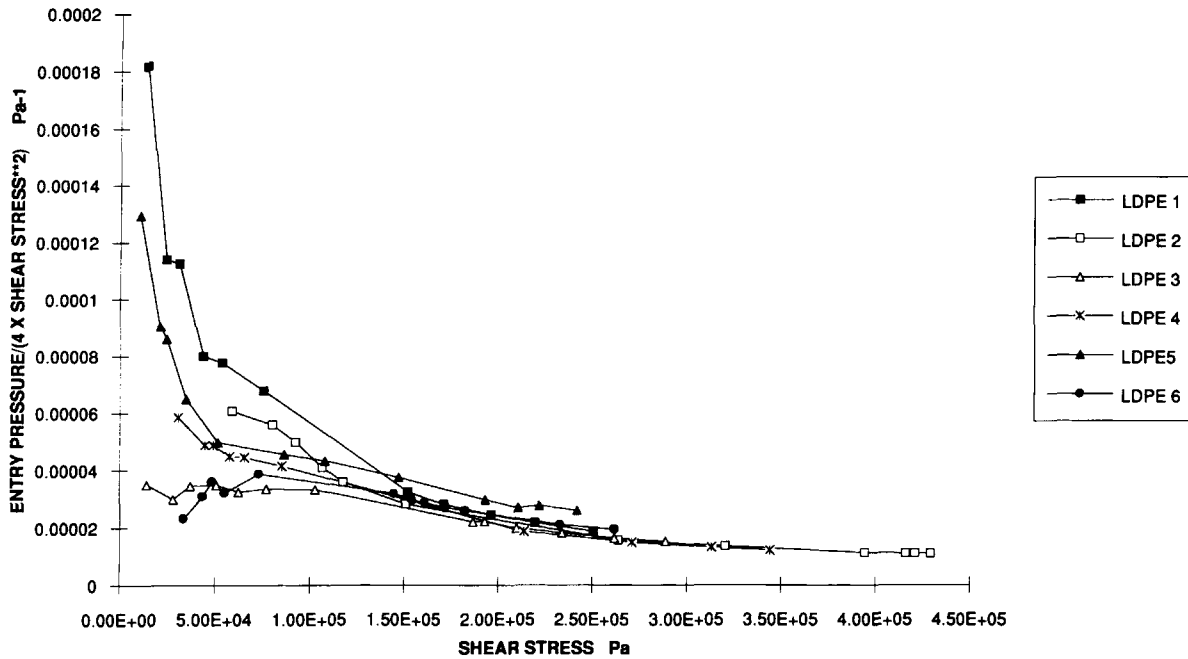


Figure 8 "Compliance" for the LDPE melts at 190°C.

links. For higher molecular weight materials, the above results show that the more branched material has a lower flow resistance but higher elasticity. It appears that for such a material there may be some cooperative motion between the molecules that tends to reduce the flow resistance (besides the contribution of the molecular size) but maintain some

of the entanglements to store the elastic energy. It appears that the detailed molecular configuration does play a significant role in both the shear and elongational flow. For example, as shown in the above results, it is not always the case that a more branched material has a lower shear viscosity than that of a less branched material. The present work

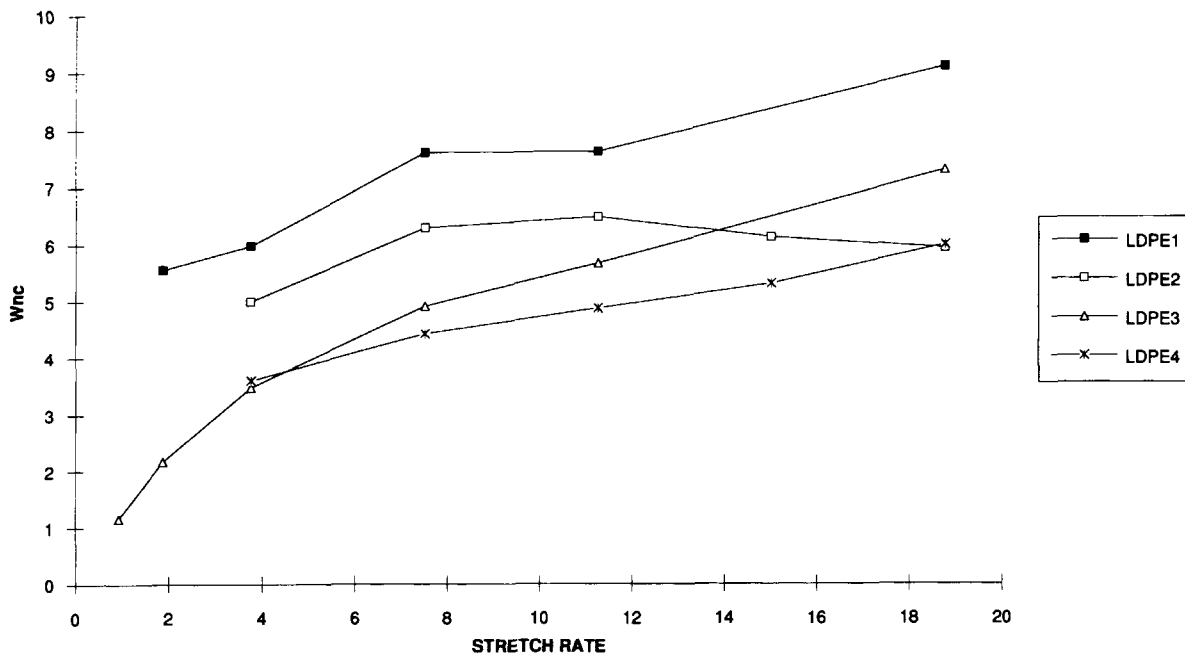


Figure 9 "Weissenberg number"-stretch rate relationship at low stretch rates.

also suggests that the Cogswell and Huang–Shroff approaches to calculating the elongational viscosities give similar results. The absolute value of the molecular weight partly determines the behavior pattern rheologically besides other parameters such as temperature and kind of deformation.

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Received November 21, 1993

Accepted April 22, 1994