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Anomalous nonlinearities in steady shear of polyethylene melts

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Abstract

High-density polyethylene (HDPE) melts have been previously identified as having an unusually high degree of molecular order, but the rheological implications of this have heretofore not been explored. This has been a serious oversight, inasmuch as HDPE melt processing is one of the major tasks of the world's polymer industry. Here, we investigate several industrial samples of HDPE, covering a range of molecular weight ($8.5 \times 10^4 < M_w < 13.7 \times 10^4$) and temperature ($190^\circ \leq T \leq 250^\circ\text{C}$) using a Rheometrics Mechanical Spectrometer 800. Remarkable manifestations of liquid-state order are found that agree with theoretical predictions for a liquid-crystal polymer (LCP). These include indications of an approach to a sign change in $N_1(\dot{\gamma})$ at low values of the steady-shear rate, $\dot{\gamma}$, and a kink in the Non-Newtonian viscosity $\eta(\dot{\gamma})$. Some evidence on transient normal stress and on dynamic properties $G'(\omega)$ and $\eta'(\omega)$ is also presented. The collective data appear to confirm that the HDPE melt may be considered to be a LCP, and also that the LCP rheological theories can be applied. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: High-density polyethylene; Negative normal stress; Anomalous viscosity; Liquid crystal polymer

1. Introduction

Fluid mechanics problems associated with the polymer melt processing industry always involve non-linear rheological behavior of the melts. In most cases, it is sufficient to model the melt as being isotropic, amorphous, and unstructured at rest, with molecular orientation arising only due to the flow field. For semicrystalline polymers, the definition of melt is usually understood to mean that when the temperature (T) exceeds the solid-state crystalline melting range (characterized by T_m), the above-cited qualities prevail just as for fully amorphous polymers such as polystyrene. A major exception is the liquid-crystal polymer (LCP) whose molecules normally contain rigid structural units, and whose melts contain regions of strong local order and can experience phase transitions at high temperatures.

Despite the frequent success of this general concept of disorder in polymer melts, it can now be challenged by data that have emerged in recent years about polyethylene, the most common of all

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polymers and normally regarded as having the simplest and most flexible molecular structure (polymethylene chains, $-\text{CH}_2-$). In our laboratory [1] we have seen evidence of a yield stress in melts of high-density polyethylene (HDPE) persisting to over 240°C (whereas $T_m \cong 137^\circ\text{C}$). This seems consistent with NMR studies [2,3] that indicate ordered structures in HDPE melts persist to at least 150°C , the ordered regions occupying the same volume fraction as the crystalline fraction in solid HDPE. Theoretical modeling by molecular dynamics simulation has demonstrated [4] that the natural rest state of an isolated HDPE molecule is not the amorphous random coil but, rather, the folded-chain conformation known to compose also the solid HDPE crystal for $T < T_m$. These experimental and theoretical indications of liquid-state order in HDPE melts suggest that we might regard them as a special class of LCP. This was previously advanced as an explanation for an anomaly observed in extrusion, when an abrupt drop in pressure took place (with the screw speed constant) at 151°C , this temperature being identified as a LCP structural transition [5]. Additional transitions were recently reported [6] at 208°C and 227°C by using the torque in a melt blender as a method of detection; the fact that this temperature range is commonly used in industrial melt processing makes this discovery particularly important.

One other rheological study has also produced evidence that HDPE melts have a LCP nature [7]. There, melt index (MI) measurements on well-characterized HDPE melts at 190°C showed that the MI varied with the weight-average molecular weight M_w in such a way as to suggest that the viscosity varied as $\eta \propto M_w^{5.4}$, a behavior seen previously only with LCP melts [8].

Basic rheological studies of liquid-state LCP systems have sometimes yielded surprising results. Lyotropic systems received most of the early attention, and for these it was reported [9–11] that the normal stress function $N_1(\dot{\gamma})$ measured in a cone-and-plate geometry as a function of steady-shear rate $\dot{\gamma}$ changed sign as $\dot{\gamma}$ changed.

For the melt state, researchers have so far produced little correspondingly peculiar thermotropic LCP normal stress behavior to parallel that of the lyotropic systems; there has been no observation of a sign change in $N_1(\dot{\gamma})$.

Recently, major progress was made with LCP theory, and various rheological anomalies in LCP liquid systems have been predicted that parallel the behavior of lyotropic LCP fluids. It appears likely that these theories should apply also to the LCP melt state. Of particular note is the work of Marrucci and Maffettone [12–14], used to characterize normal and shear stress for rodlike polymers assembled in a nematic phase to establish a polydomain structure. In their model, $N_1(\dot{\gamma})$ is predicted to change sign twice as $\dot{\gamma}$ increases and $\eta(\dot{\gamma})$ is predicted to have a ‘kink’ in the $\dot{\gamma}$ -range just above the first sign change in N_1 ; see Fig. 1. The viscosity kink has been found in lyotropic LCP systems [9,10,15,16], but this and the N_1 sign change have not yet been observed in bulk LCP melts. The theory predicts no yield stress, but a Newtonian viscosity plateau at low $\dot{\gamma}$ that develops into shear-thinning behavior at a $\dot{\gamma}$ corresponding to the low- $\dot{\gamma}$ maximum in $N_1(\dot{\gamma})$. Similar predictions have also been made by Larson [17] with a comparable but more refined theory.

In the present work, we have taken a different experimental approach in seeking these predicted LCP melt phenomena. We reason that polyethylene melts, particularly those of HDPE, possess sufficient molecular order to be likely candidates of exhibiting thermotropic LCP-type rheology. Moreover, HDPE is not affected by ambient humidity (as are some polyester LC-P products) and is chemically inert at the primary temperature of testing used here (190°C); thermal degradation occurs only above 345°C [18] and oxidative degradation is prevented by a blanket of nitrogen gas and the presence of antioxidants in the melt.

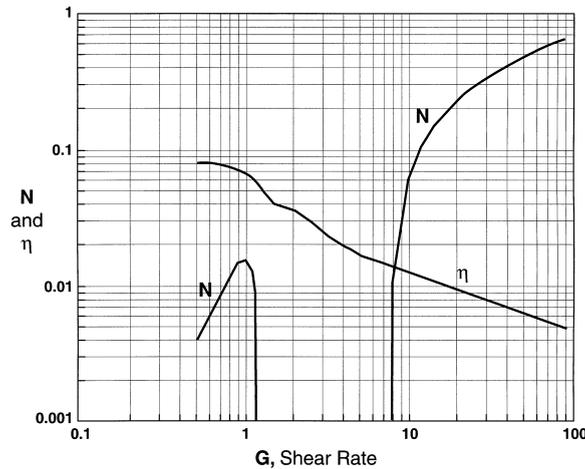


Fig. 1. Predictions of the theory of Marrucci and Maffettone [12], redrawn from Fig. 1 (1990). Here, all the variables are in dimensionless form: N is the first normal stress function, η is viscosity, and G is shear rate. Special parameters in this model, used for making these predictions, can be found in the source work [12]. Those parameters would also be needed for converting the variables to dimensional form.

2. Experimental

2.1. Materials

Eight commercial samples of HDPE (polymerized by Ziegler-Natta catalysis) were obtained, from seven different resin producers. Characterization data for the four samples used in this report are given in Table 1. The samples were not purified and, therefore, retained all additives introduced by the manufacturers, most importantly the anti-oxidants which surely varied among the samples, but none of these additives were revealed to us or analyzed in this study. These same samples were used in the two previous studies reported by our laboratory, on the correlation of melt index with M [7] and the rheological evidence for high-temperature phase transitions [6].

2.2. Apparatus

A Rheometrics Mechanical Spectrometer 800 (RMS) was employed for steady-shear and dynamic (low strain oscillatory) tests. The oven surrounding the samples during testing was continually purged

Table 1
Characterization of linear HDPEs from different producers

Sample	M_w	M_n	M_w/M_n	Density at 25°C, g/cm ³
A	85 149	17 347	4.93	0.960
B	78 292	13 340	5.87	0.961
C	82 960	17 449	4.76	0.960
D	137 000	28 000	4.89	0.957

with nitrogen gas, to suppress sample oxidation, and nitrogen also filled a plastic ‘shroud’ that enclosed the entire RMS. Samples were tested with two platen geometries, a cone-and-plate set and a parallel-plate set; the cone angle was 0.1 rad, and all platen diameters were 25 mm.

2.3. Procedure

In all the cases, the pelletized HDPE samples obtained from suppliers were given a controlled thermo/mechanical history (molding) before introduction into the RMS for shear testing. The molding operation, in a Carver press, produced flat discs (25 mm diameter, 2 mm thick) for insertion between the RMS platens. Molding was conducted at 170°C after pre-heating for 5 min. The loaded sample was then placed under 3 tons of force for 5 min, followed by an increase to 7 tons for 5 min. After the mold was water-cooled for 10 min, the plastic disk was removed at room temperature and inserted between the RMS platens that had been pre-heated in mounted position within the RMS oven. With the sample in position, the oven was closed and the polymer heated for 3 min, when the upper platen force transducer assembly was lowered to the proper working position. The loading procedure was terminated when the parallel plates were separated by 1.5 mm or when the cone flattened tip position was separated from the opposing platen by 53 μm . These platen-positioning steps encountered considerable resistance by the HDPE melt, which has a rubbery and not free-flowing consistency even at high temperatures. Melt extruded beyond the platen rim by this procedure was removed by a razor blade. With the system at operating temperature and the nitrogen blanket/purge in place, a holding period of 2 min was allowed before beginning measurements. When dynamic testing was the objective, a shear strain amplitude $\dot{\gamma}$ of 10% was used, after a strain sweep showed that this ($\dot{\gamma}$) was sufficiently small to produce dynamic properties in the linear viscoelastic regime. The range of angular frequency (ω) was usually extended to 10² rad/s. Some experiments were then continued in a descending- ω order (from 10² to 10⁻² rad/s) to examine whether molecular degradation had occurred during the increasing- ω sequence. Excellent reproducibility of data in the descending- ω and ascending- ω sequence always prevailed, indicating that neither the mechanical experience nor the residence time at high temperature caused degradation of any sort.

Steady-shear testing was always conducted with a fresh sample. Tests began at the lowest shear rate (usually $\dot{\gamma} \cong 0.005 \text{ s}^{-1}$) and continued up to the major hydrodynamic stability limit, when secondary flow caused radial ejection of the sample. In cone-and-plate tests we compute the $\dot{\gamma}$ as $\dot{\gamma} = \Omega R/\psi$, with Ω the steady angular platen speed, R the platen radius, and ψ the cone angle [19,20], and simultaneous data on $\eta(\dot{\gamma})$ and $N_1(\dot{\gamma})$ are obtained. With the parallel plates, for which $\dot{\gamma}(r)$ is non-uniform, we follow the conventional practice of characterizing the flow by the ‘Newtonian equivalent’ value of shear rate at the platen rim, $\dot{\gamma}_R = \Omega R/h$ (with h the inter-platen spacing) and report the corresponding viscosity and normal stress function (N_1-N_2) as functions of $\dot{\gamma}_R$.

Steady-shear measurements were made with unidirectional platen rotation. The normal practice of taking a stress value for clockwise (CW) platen rotation, followed immediately by one taken for counterclockwise (CCW) rotation, and then reporting an average of the two, was abandoned when early tests showed that stress transients upon start-up from rest, and after changing shear direction, were usually too long to make the dual-direction procedure practical. Moreover, the flow reversal caused anomalous transients that made the averaging process meaningless. (Such behavior has apparently not been reported for HDPE heretofore). However, separate runs with fresh samples sheared in CW and CCW directions showed that there was no geometrical bias of the sort associated with platen misalignment, and independent calibrations confirmed this.

Despite the advantages of unidirectional shear, the steady-stress state could not be achieved quickly with HDPE melts at any temperature. The transients of torque and normal force were extended and peculiar, sometimes with oscillations, leading to anomalous behavior in the properties $\eta^+(t)$ and $N^+(t)$, where N^+ refers to either of the two normal stress functions involved here [N_1 or $(N_1 - N_2)$]. These transients often resembled the behavior observed with lyotropic LCP systems (in the case of η^+) and predicted by the recent theories for nematic LCP systems [12–14,17] for $N^+(t)$ as well.

It was found by experience that these transients passed within about 5 min in most cases, so the RMS was programmed to perform a $\dot{\gamma}$ -sweep in the following fashion: begin at $\dot{\gamma} = 0.005 \text{ s}^{-1}$ and wait for 5 min, then collect torque and normal stress data for 30 s and average it (to be reported as the steady state result), then step to the next $\dot{\gamma}$ and repeat the procedure at intervals that were selected by the operator to achieve an equal number of data points per decade of $\dot{\gamma}$.

3. Results and discussion

3.1. Steady flow

Our primary focus here is on steady-state shear flow behavior, so the dynamic results will be mentioned later only for specific comparison purposes. Remarks on the transients will be brief, but descriptions of these phenomena are available elsewhere [21] and will be reported separately in greater depth.

Fig. 2 displays results for Sample A at 190°C , obtained with parallel plates. The anomalous drop in $N_1 - N_2$, with a minimum at about $\dot{\gamma}_R = 0.05 \text{ s}^{-1}$, is interpreted here as the same phenomenon as

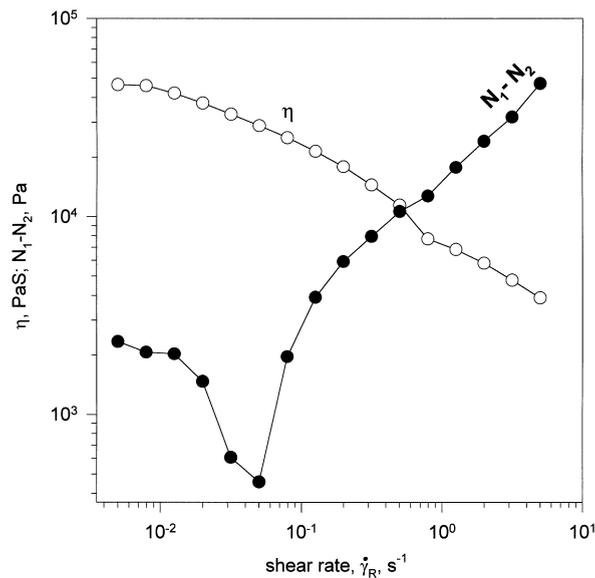


Fig. 2. Steady shear viscosity (η) and normal stress function ($N_1 - N_2$) obtained with parallel-plate shearing of HDPE Sample A at 190°C . Here, $\dot{\gamma}_R$ is the nominal shear rate at the platen rim.

predicted in Fig. 1 near a dimensionless shear rate $G = 1.2$, namely the trend of N_1 changing sign. A plot resembling Fig. 2 was presented earlier in connection with a lyotropic system [11]. Further support for this interpretation is the obvious kink in $\eta(\dot{\gamma})$ at $\dot{\gamma}_R = 0.8 \text{ s}^{-1}$, which strongly resembles the kink in Fig. 1 near $G = 2$. The fact that the normal stress function does not actually change sign in Fig. 2 could be attributed to the contribution of N_2 , which is normally expected to have a sign opposite to N_1 ; thus, as N_1 approaches zero at the $\dot{\gamma}_R$ of its sign change, the non-zero values of N_2 would begin to dominate the function $N_1 - N_2$ and sign change of N_1 would not be measurable. Of course, the logarithmic stress scale cannot show negative values, but a plunge of the data towards zero would take the values below the RMS sensitivity in the region $0.04 < \dot{\gamma} < 0.05 \text{ s}^{-1}$ anyway. In this steady-shear mode of operation, no negative normal stresses could be detected in this $\dot{\gamma}$ -regime.

There are several resemblances between Figs. 1 and 2, in addition to the viscosity kink and descent of N from both directions toward an apparent sign change. One such similarity is the fact that the low- $\dot{\gamma}_R$ maximum in normal stress in Fig. 2 occurs at a value of $\dot{\gamma}_R$ close to that at which $\eta(\dot{\gamma}_R)$ departs from its Newtonian plateau, just as shown in Fig. 1 for $N_{\max}(G)$ relative to $\eta(G)$. Another is the quantitative similarity of the spacing along the shear rate axis between the two branches of the normal stress functions descending toward the sign change (i.e. toward zero). In Fig. 2 the peak at low $\dot{\gamma}_R$ has a shoulder at $\dot{\gamma}_R = 0.013 \text{ s}^{-1}$. Moving across to higher $\dot{\gamma}_R$, one encounters the high- $\dot{\gamma}_R$ normal stress branch at $\dot{\gamma}_R = 0.08\text{--}0.09 \text{ s}^{-1}$, a factor of seven further along the $\dot{\gamma}_R$ axis. Similarly, in Fig. 1 the low- G peak has a right-hand ‘corner’ at about $G = 1.2$, and a line extended horizontally to the right from that point intersects the descending right-hand N branch at about $G = 8.4$, also higher by a factor of seven.

The question about the role of N_2 in parallel-plate (PP) testing has no counterpart in cone-and-plate (CP) testing, where N_2 is not involved in the interpretation of the vertical thrust. Thus, most of the subsequent tests employed the CP platens.

The nature of the unexpected minimum in $N_1 - N_2$ discovered in the PP tests required more complete definition, so the following CP test was designed to utilize more data points per decade of $\dot{\gamma}$ (increasing from 5 points/decade in Fig. 2 to 10 points/decade). Results, for the same HDPE Sample A, are given in Fig. 3. Again the normal stress minimum is seen, even more dramatically than in Fig. 2, at the same value of shear rate (i.e. 0.05 s^{-1}) despite the different meanings of $\dot{\gamma}$ and $\dot{\gamma}_R$ in the two geometries. The maximum in N_1 at low $\dot{\gamma}$ in Fig. 3 is better resolved than the one in Fig. 2, showing a sharp right-hand corner/shoulder that clearly resembles a similar feature in Fig. 1. As measured from this corner, the $N_1(\dot{\gamma})$ branch descending toward zero from the right is located at a $\dot{\gamma}$ -value higher by a factor of 7, just as in Fig. 2. Values of the normal stress maxima in Figs. 2 and 3 agree, at about 2000–3000 Pa. Collectively, these extensive similarities between the PP and CP tests reinforce the reliability of the basic observations.

However, the $\eta(\dot{\gamma})$ kink in Fig. 3 has a somewhat different character than in Fig. 2, possibly because the range of shear rate is less and, therefore, the nature of $\eta(\dot{\gamma})$ is less easy to determine. To investigate the source of this difference, we repeated the CP testing but returned to the use of only five data points per decade of $\dot{\gamma}$. The result, in Fig. 4, demonstrates that the normal stress sign change (descent of N_1 toward zero) has almost been lost, along with the low- $\dot{\gamma}$ maximum which has now only a few points to define it. Because the data in Fig. 4 extend to higher $\dot{\gamma}$ than in Fig. 3, it is possible to see that the viscosity kink is still present in the CP data, looking much as it did with PP testing.

Similar tests at 190°C were performed on most of the other HDPE samples [21], and results were similar to those displayed here in Figs. 2–4.

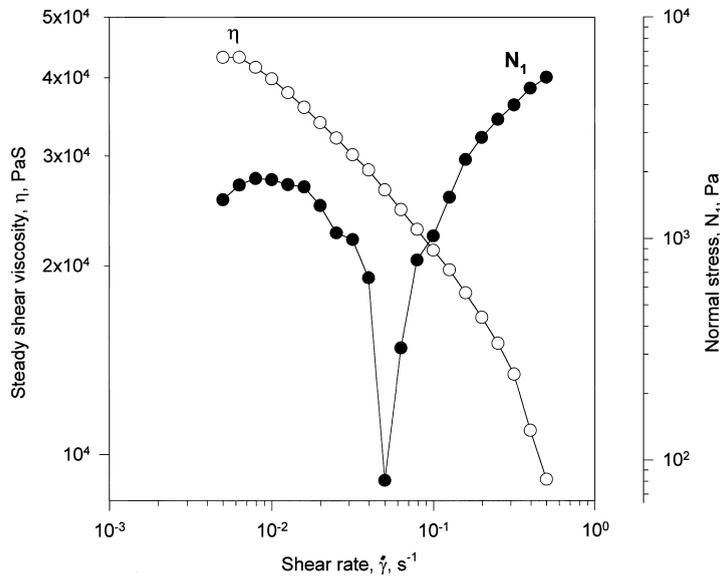


Fig. 3. Data for HDPE Sample A, N_1 and η at the uniform shear rate obtained with cone-and-plate shearing at 190°C. Cone angle was 0.1 radian. Ten points per decade of $\dot{\gamma}$.

Our earlier work [6] with HDPE phase transitions at high temperatures (208°C, 227°C) also showed that the rheological behaviour at even higher temperatures was anomalous, suggesting that microstructural order of some sort could still be present. For example, the torque in a Haake Rheocord 90 melt blender did not decay with temperature as $\exp(E/RT)$ as is seen with typical amorphous polymers and small-molecule liquids where viscosity behaves this way at temperatures far above T_g . An

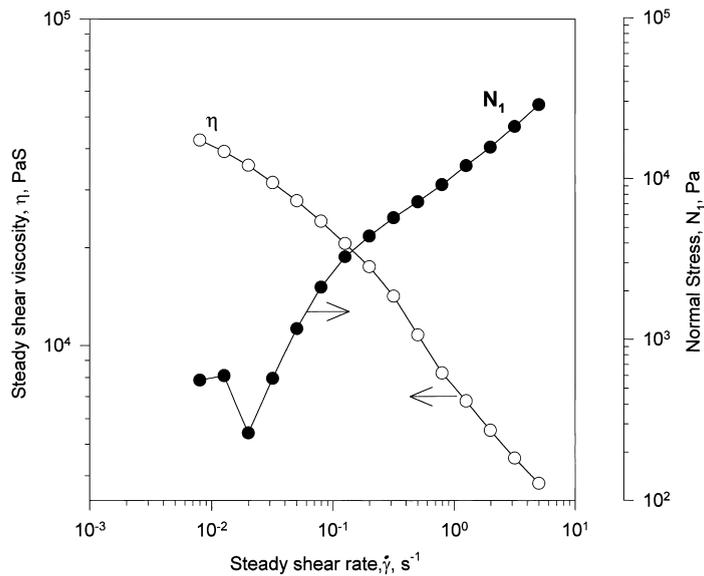


Fig. 4. Data of HDPE Sample A at 190°C, obtained with cone-and-plate shearing but only five points per decade of $\dot{\gamma}$.

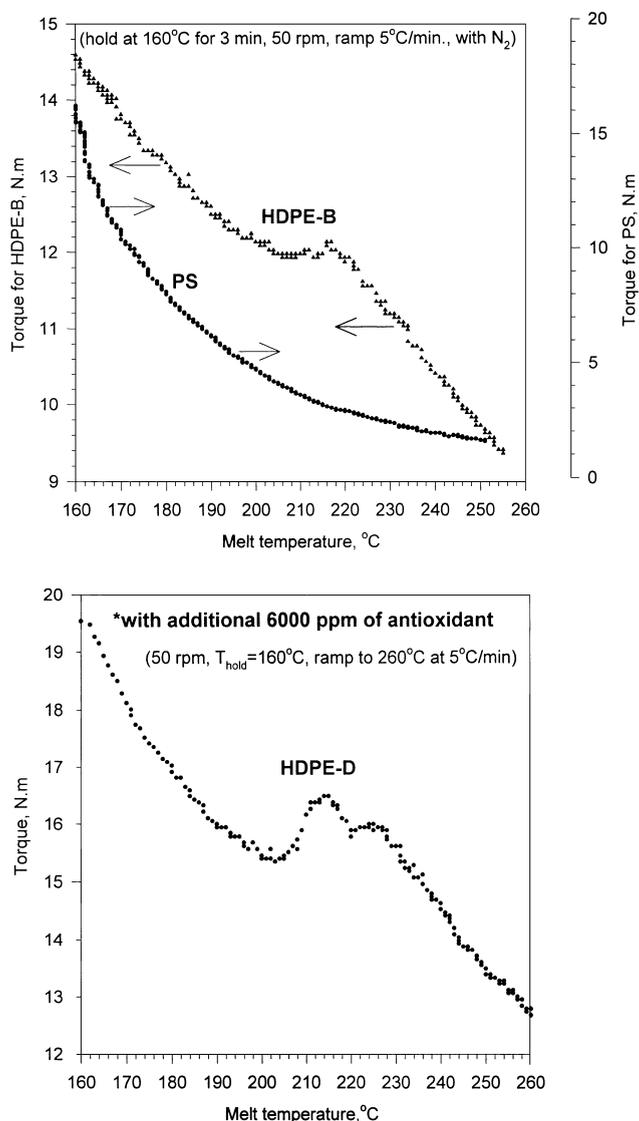


Fig. 5. Evidence for phase transitions in (a) HDPE melt, Sample B (upper plot) and (b) HDPE Sample D (lower plot). The transitions are believed to occur at the base of the left-hand decreasing branch of the curves (208°C) and at the beginning of the right-hand branch (220°C–227°C). Data on other HDPE sample are available elsewhere [6,21]. The lower curve in (a) represents a melt of atactic polystyrene. In (b) an additional 6000 ppm of antioxidant, provided by the resin manufacturer, has been added to supplement the normal content of antioxidant (approximately 1000 ppm).

example of this torque behavior is given in Fig. 5(a), with HDPE Sample B. Whereas the polystyrene sample shown for reference behaves in classical Arrhenius fashion, Sample B at $T > 220^\circ\text{C}$ displays a virtually linear decline with temperature in that regime. To demonstrate that these phenomena do not represent chemical changes due to oxidation, we display in Fig. 5(b) the same behaviour, with a large excess of antioxidant added to Sample D. (The double peak is probably due to molecular structure features of this sample, which has a small degree of branching not shared by our other samples.)

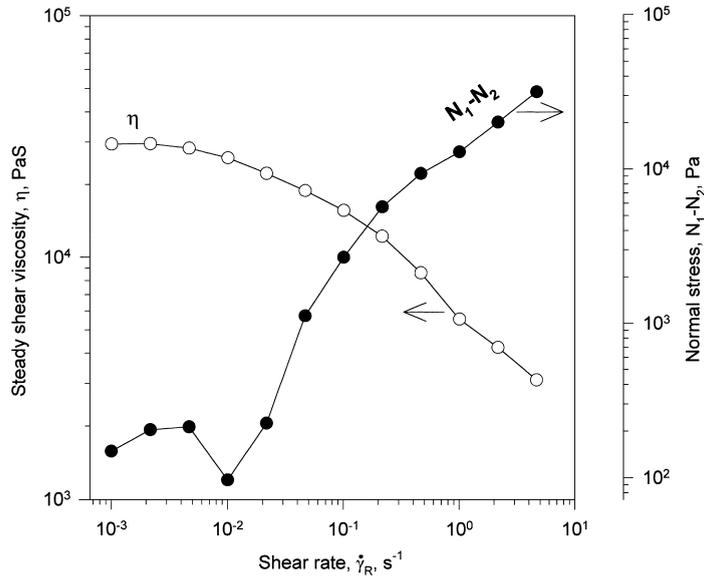


Fig. 6. Normal stress and viscosity functions for HDPE Sample B, at 230°C, as measured in parallel-plate shear.

Based on the supposition that HDPE could still be in a LCP molecular conformation at those high temperatures, we used the RMS to test Sample B at 230°C, corresponding to the peak in its blender torque curve, (Fig. 5(a)), at which the principal phase transition is believed to occur. Results, given in Fig. 6, showed both the viscosity kink and a clearly defined normal stress anomaly. This result led to testing well above the transition. Sample A was tested at 240°C, with steady-shear PP data displayed in Fig. 7a. Once more, the viscosity kink and the normal stress anomaly appeared, which encouraged testing at still higher temperatures. Sample C was therefore examined in the CP at 250°C (Fig. 8). Here, $N_1(\dot{\gamma})$ was measured, and the anomaly is just as well defined as for $N_1 - N_2$ with Sample A in Fig. 7(a). It seems clear that LCP order prevails for a wide range of temperatures above the 230°C transition, implying that the latter is not a transition to the isotropic state (a conclusion implied also by the linearity (non-Arrhenius nature) of the torque/temperature curves in Fig. 5 at high temperatures).

It is important to recognize that the normal stress minima displayed in all these figures are well-defined and reproducible. The minimum points correspond to transducer normal force values well above the noise level; transducer sensitivity is about 2 gm weight, whereas all the normal stress minima and the approaches to them are represented by points in the range 2–20 gm weight.

These observations are also not a consequence of wall slip, which sometimes accompanies the shear flow of PE melts. Slip is reported to begin at a wall shear stress of about 0.1 MPa for HDPE melts [22], far above the maximum stresses achieved here (on the order of 0.02 MPa) and enormously beyond the normal stress and viscosity kink anomalies. Furthermore, the results being observed here are not changed by variation of the parallel-plate spacing; h -dependence is often taken as evidence of slip [23].

The possible effect of certain commercial additives in these sample was also explored by testing specimens that were prepared with and without those additives (e.g. processing aids that may consist of immiscible fluorinated polymers of low M_w). No differences whatever could be found, so it was clear that processing aids were playing no role in the anomalous phenomena reported here.

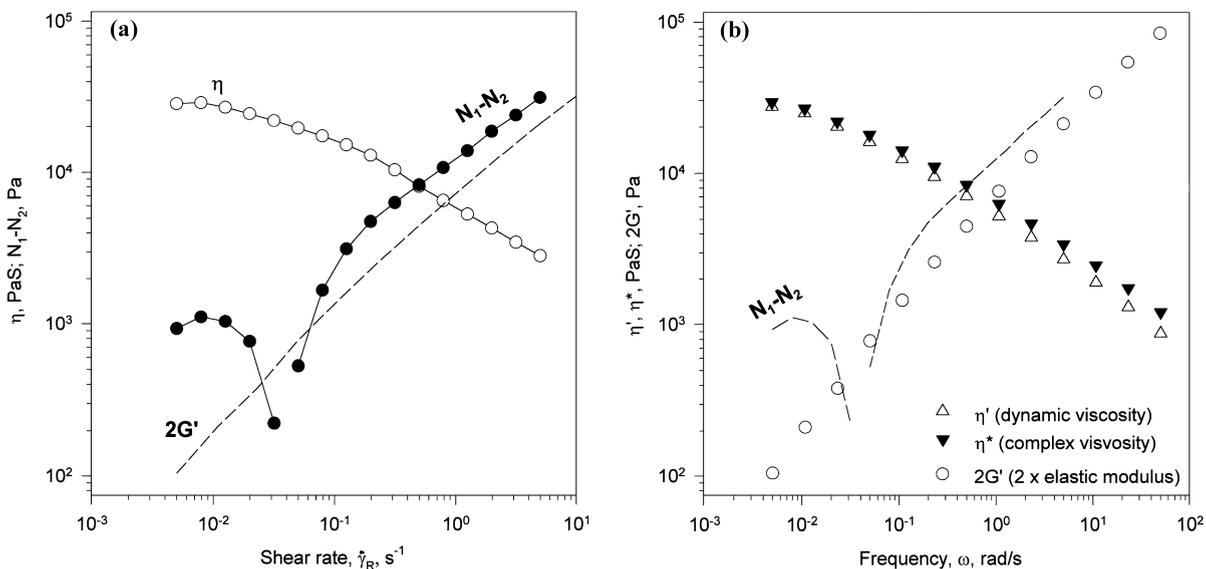


Fig. 7. (a) Normal stress and viscosity functions for HDPE Sample A at 240°C with parallel-plate shear. The dashed line represents the dynamic property $2G'(\omega)$ from Fig. 7 (b) for comparison with N_1-N_2 . (b) dynamic properties for HDPE, Sample A. The dashed line represents the steady- $\dot{\gamma}$ normal stress function from Fig. 7 (a), for comparison with $2G'(\omega)$.

The fact that CP and PP results were virtually identical is strong support for the contention that the results are true rheological phenomena and not dominated by secondary flows and other hydrodynamic stability problems that tend to be specific for one kind of platen geometry.

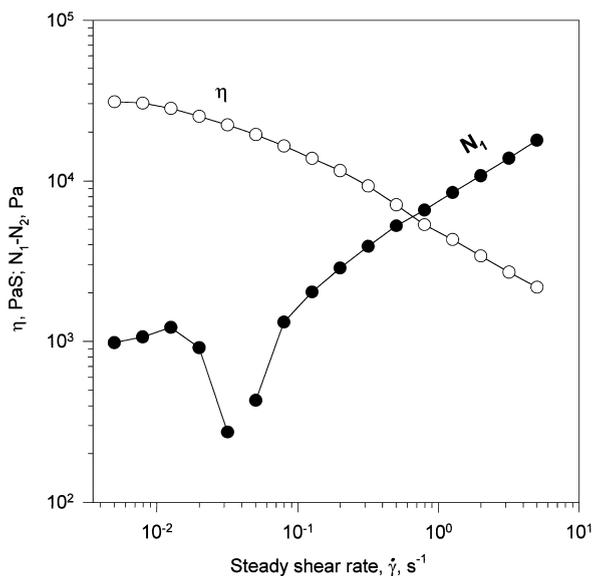


Fig. 8. Normal stress and viscosity function for HDPE Sample C at 250°C, using cone-and plate shear.

There is also ample evidence that the RMS 800 was performing well. There have been frequent calibrations by a Rheometrics service engineer and, more importantly, the instrument detected no anomalies when used to test familiar amorphous melts. Tests [21] on polystyrene at 190°C showed no spurious normal stress minimum or viscosity kink in steady-shear, and dynamic data conformed to the Cox–Merz rule and showed a good match of $2G'(\omega)$ by $N(\dot{\gamma})$. Such results verify both that the polystyrene melt was behaving as a classical unstructured viscoelastic fluid, rheologically simple, and also that the RMS 800 was functioning properly.

3.2. Dynamic tests with HDPE

Steady-shear tests of the HDPE melts were normally accompanied by oscillatory-shear dynamic tests (on fresh samples) as well. A representative set of such data is given in Fig. 7(b), for Sample A, where η' , $G' = \eta''\omega$ and $\eta^* = [(\eta')^2 + (\eta'')^2]^{1/2}$ are displayed together; $2G'(\omega)$ rather than $\eta''(\omega)$ is given to facilitate comparison with the $\dot{\gamma}$ -dependent function $N_1 - N_2$ in Fig. 7(a). The functions $\eta'(\omega)$ and $\eta^*(\omega)$ have no kink at any ω , and low ω they appear to superimpose with $\eta(\dot{\gamma})$ in Fig. 7(a) at low $\dot{\gamma}$. The function $2G'(\omega)$, however, does not come close to superposition with $N_1 - N_2$ in Fig. 7(a). This is emphasized in Fig. 7(a) by the dashed line representing $2G'(\omega)$, and in Fig. 7(b) by the dashed line showing $N_1 - N_2$. Only at high $\dot{\gamma}$ (high ω) is their behavior similar, with the two functions running parallel. For low ω , $2G'(\omega)$ fails totally to mimic the normal stress function, so for HDPE $2G'(\omega)$ should never be used as a means of predicting normal stress functions vs. $\dot{\gamma}$. Similar results emerged from a previous study of other LCP melts [24]. The absence of a kink in the dynamic viscosity functions and the absence of a sharp minimum in $G'(\omega)$ are reasonable and expected. In steady-shear, the kink in $\eta(\dot{\gamma})$ and the $N_1(\dot{\gamma})$ sign change arise because, at those $\dot{\gamma}$, the liquid-crystal domains change their motion (e.g. from one of steady oriented shear to tumbling), according to the theoretical models [12,13,17], and there is no mechanism in small-amplitude oscillatory strain for such a transition to occur.

3.3. Stress transients in steady-shear

It remains to demonstrate that the sequence of data acquisition used here produced steady-state stress information. First, we address the low- $\dot{\gamma}$ range, which was most relevant to the major goals of this work. Our general observation was that when $\dot{\gamma} < 0.1 \text{ s}^{-1}$ the normal stress transient was a well behaved function of time, either monotonically increasing or demonstrating a gradual overshoot, and achieved its steady state within 5 min. Examples are given in Fig. 9, for Sample A at 190°C. When $\dot{\gamma} \geq 1 \text{ s}^{-1}$, there was generally a sharp initial overshoot with a non-smooth decay to steady state. Examples of such behavior for both shear and normal stress starting from rest to $\dot{\gamma} = 1 \text{ s}^{-1}$ are available elsewhere [21] and will be incorporated in a separate publication. In these cases the shear stress reached its plateau value after 5 min. (although long-term oscillations about this level were seen), but the normal stress required 20–25 min. and the 5 min point was essentially a stress decay half-life. Recording the normal stress at 5 min. in this higher- $\dot{\gamma}$ case would essentially over-represent its steady state magnitude by 25%. Errors of this sort (premature recording of data, for convenience only) are diminished when the higher $\dot{\gamma}$ are achieved by a sequential-step sweep program, such as used in this work. Here, $\dot{\gamma}$ begins from rest with a step into the low- $\dot{\gamma}$ regime ($\dot{\gamma} = 0.1 \text{ s}^{-1}$) which leads monotonically to its steady state after 5 min. Then, when $\dot{\gamma}$ is stepped up into the high- $\dot{\gamma}$ regime ($\dot{\gamma} = 1 \text{ s}^{-1}$), a sharp peak results but it is

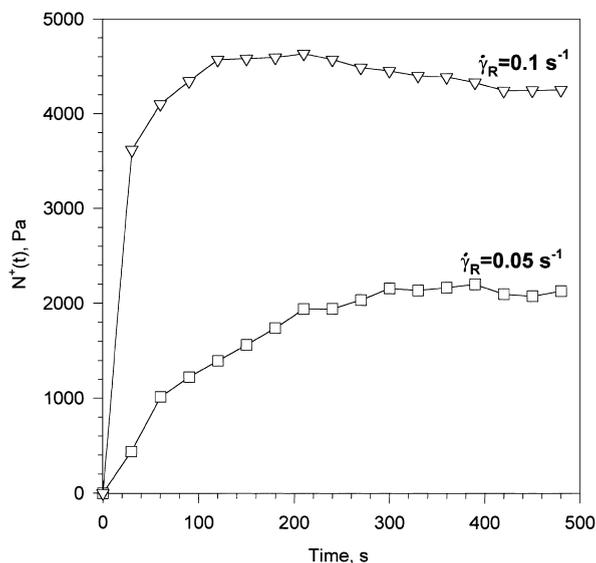


Fig. 9. N_1-N_2 function for abrupt onset of steady shear from rest position for HDPE Sample A at 190°C, using parallel plate shearing in the low- $\dot{\gamma}_R$ regime.

less high than it would be if starting from rest with a jump to $\dot{\gamma} = 0.1 \text{ s}^{-1}$. The result is that steady state is achieved in less than another 5 min. longer. This type of behavior justifies the method used here to achieve steady state data over the whole range of $\dot{\gamma}$. Stress transients of this character have been reported for LCP melts [24,25].

3.4. Alternatives

In seeking alternative explanations for the rheological anomalies presented here, one is drawn to the possibility that fluid mechanical instabilities and secondary flows of well-known kinds may be responsible for either the normal stress or viscosity-kink anomaly, or both. We believe this is not the case.

Part of our belief is based on the fact that our results reflect so closely the acknowledged behavior of LCP fluids, both data and theory. Moreover, these HDPE results are totally unlike the behavior of other melts (e.g. polystyrene) and solutions tested in our laboratory over a 30-year period of rheological investigation.

We have also examined the literature on flow instabilities in these shearing geometries [23,26] and found no evidence for instabilities that could give the results reported here. We recognize that secondary flows can exist with viscoelastic liquids at shear rates well below that at which sample ejection occurs. One such instability, for example, is known as an ‘edge effect’ and manifested externally at the platen rim by the fluid appearing to cut in at the mid-plane and flow out along each of the platen surfaces [23,26]. When it occurs, this phenomenon can be seen visually within 15 sec after shearing is initiated (when $\dot{\gamma}$ is in the range 5–10 s^{-1}). The consequences on measured torque and normal thrust are the onset of a slow drift downward, so that the transient appears not to be approaching a steady state limit. In our tests, however, none of these indicators appeared. Moreover, the $\dot{\gamma}$ -range in

which the normal stress anomaly occurred (around 0.05 s^{-1}) is two orders of magnitude lower than that at which the edge effect is commonly reported [23].

Another intriguing question about these anomalies is, Why have they not been reported before? One might expect that such a common polymer as HDPE would have received abundant rheological attention over the years. Indeed, the literature contains many examples [27,28] of such work, including superposition of $\eta(\dot{\gamma})$ data from many instruments to cover wide ranges of $\dot{\gamma}$. We suspect that the viscosity kink may have been overlooked because it is a rather subtle effect, and also because the procedures we followed (similar to those of LCP investigators) have not been common. For example, in rotational viscometry, it has been standard procedure to average consecutive CW and CCW torque measurements. However, for a structured fluid like HDPE melts, this sequence of shearing alters the structure in a major way (perhaps destroying it), as our early tests showed. The stress transients are surprisingly long, so most workers would not let either a CW or subsequent CCW test run long enough to achieve steady state. In our case, unidirectional shearing for at least 5 min for each sample was used. We cannot project how the kink phenomenon would affect measurements in capillary viscometry, but possibly structural damage near the wall would obscure the effect, and residence times within the capillary might not be long enough to achieve steady state.

We note that the more dramatic anomaly is in the normal stress, at very low $\dot{\gamma}$, but most HDPE melt work in the past has not included N_1 measurements, being focussed instead on $\eta(\dot{\gamma})$. There has also been little incentive to examine the very low- $\dot{\gamma}$ regime. Moreover, the academic community has preferred to bypass polyethylene for studies of fundamental fluid rheology; the favorite materials were solutions and melts of polymers that had molecular weight distributions which could be easily measured and were, ideally, monodisperse. Neither of these attributes describes HDPE. Thus, academic laboratories have used HDPE (and other polyethylenes) primarily for melt processing studies, and their industrial counterparts had relatively little interest in N_1 (or in very low $\dot{\gamma}$).

In our laboratory, abundant evidence of many types supports the LCP nature of HDPE. For example, the blender torque curves of Fig. 5 imply that RMS temperature sweeps on viscosity should yield $\eta(T)$ data that would reveal basic information about the LCP states of HDPE. Data on $\eta(T)$ are available [21] and will be published elsewhere.

4. Conclusions

1. The rheology of HDPE proves to be more complex than previously believed, especially at low shear rates where the first normal stress function appears capable of changing sign twice as $\dot{\gamma}$ increases, and the viscosity function exhibits a kink.
2. Inasmuch as these rheological features had been predicted (and, in some cases, found) only for liquid-crystal polymers, we conclude that HDPE should be considered to be a special kind of LCP from a rheological and melt processing viewpoint. This may ultimately explain some of the HDPE special properties, such as unusual orientability in the melt and consequent high melt strength and subsequent superior properties in the solid state.
3. HDPE appears to fulfill the predictions of LCP rheological theories as well as (or better than) polymers of acknowledged LCP molecular structure. Since those theories had received little experimental support from other sources, they must now be regarded as validated for the first time.

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