remove byproducts, which can affect the physical properties, would destroy the unique morphology that the technique provides.[7]

Since the polymer literature states that Et_2AlCl should not be able to reduce Ti to the 2+ oxidation state, but the organometallic literature proposes 2+ as the active state for cyclotrimerizing butadiene, this study has defined an area for future investigation that could be very valuable to both fields. Cyclododecatrienes are very versatile starting materials in synthetic chemistry and Ziegler–Natta catalysis is the most commercially important means of synthesizing polymers.

By following the product distribution of this reaction with time, we provided strong evidence for the proposal that *cis*-PB and *trans*-PB are produced at different catalytic sites. These results, combined with the experiments adding *ttt*-CDT to the catalyst prior to polymerization, suggest an interaction between *ttt*-CDT and the site for cis polymerization. Specifically, *ttt*-CDT either poisons the cis sites or converts them to sites for cyclotrimerization. Finally, we have shown that the catalyst particles are active toward diene polymerization to the exclusion of cyclotrimerization. We feel that our findings have led to a better understanding of these systems and, perhaps, might result in improved stereoregular diene catalysts.

Registry No. PB, 9003-17-2; *ttt*-CDT, 676-22-2; *ctt*-CDT, 706-31-0; OD, 29965-97-7; Et_2AlCl, 96-10-6; $Ti(OBu)_4$, 5593-70-4; butadiene, 106-99-0; poly(1-butene), 9003-28-5; polystyrene, 9003-53-6.

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Shear Modification of Low-Density Polyethylene: Its Origin and Its Effect on the Basic Rheological Functions of the Melt

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ABSTRACT: A low-density polyethylene has been subjected to repeated extrusion on a twin-screw extruder to investigate the effect of a mechanical treatment, commonly called shear modification, on the basic rheological functions of the melt. The dynamic quantities and the steady-state shear viscosity are hardly modified by the mechanical treatment, whereas the buildup of the extensional viscosity under a constant Hencky strain rate is slower after every extrusion running. The steady-state extensional viscosity drops by at least a factor 3 after five extrusions. This explains the decrease in die swell and increase in melt index often observed after shear modification. Heat and solution treatments nullify the effect of shear modification, which indicates that its origin is of a physical and not of a chemical nature. Solutions of the as-received polymer with concentrations of 1.5, 5, and 25 wt % were prepared. The polymer was then recollected by rapid quenching and evaporation of the solvent at ambient conditions. After 10^2 s in the molten state at 120 °C no effect of this solution treatment on the mechanical properties could be detected, whereas the effect of the mechanical treatment diminishes gradually to disappear completely after 10^4 s when the melt temperature is 200 °C. This indicates that a reduced interpenetration of the molecules is not the origin on a molecular basis of the effect of shear modification. The fact that the longest relaxation times of the melt are also of the order of 10^4 s at 200 °C is a strong indication that the physical change brought about by the mechanical treatment is a change in the conformation of the molecules. The fact that the flow behavior of strongly sheared long-chain branched material is similar to that of linear chain polymer melts supports the idea that an alignment of side chains along the chain backbone is effected by the mechanical treatment. This idea is further substantiated by the fact that the strain measure of the strongly sheared material approaches the strain measure predicted by the Doi–Edwards theory developed for linear chain polymer melts.

Introduction

It has been known for a long time that a technique called "shear modification", "shear working", or "shear refining" causes a reversible modification of the rheological properties of melts of thermoplastics consisting of long-chain branched molecules.[1-15] There is also a number of reports on shear modification of linear polymers.[17-20] Whereas agreement exists on the susceptibility of long-chain branched materials to shear modification, the situation is less clear for linear molecules. The origin of the effect is

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Table I
Some Characteristics of the Material

polym	grade	$[\eta]^a$	density[b]	melt index[c]	$\bar{M}_n{}^d$	$\bar{M}_w{}^d$	$\bar{M}_z{}^d$
LDPE	Stamylan 2800	1.80	920	0.3	17	120	360

[a] In Decalin at 408 K in dL/g. [b] At 296 K in kg/m^3. [c] At 463 K in dg/min. [d] With gel permeation chromatography in kg/mol.

probably of a different nature for branched and linear macromolecules.

When long-chain branched polymers with a melt index lower than 3 are kneaded on an extruder, a Brabender, or another shearing device, decreases in recoverable shear, extrudate swell, and entrance pressure drop and an increase in melt flow index are observed, whereas the flow curve is generally hardly influenced by the mechanical treatment. Furthermore, extensibility of the material is increased,[12,16] and films blown from shear-modified material show less haze[2,4,7,12] and are more transparant[4,7,12] than films blown from the original material. Upon extrusion through a die, the onset of elastic turbulence is delayed to higher shear rates[1,5] after shear modification. All these effects have repeatedly been shown to be a result of a physical and not of a chemical process, because the modification does not involve a change of molecular mass or molecular mass distribution as shown by GPC measurements or measurements of the intrinsic viscosities.[3,5,6] Moreover shear modification can be reversed by heat treatment[1,5,6,7,9,14] and solution treatment.[1,3,4,6] The shear component of the flow during the mechanical treatment has not been proven to be essential to create the effect, and although an extensional component in the flow might be more effective, the mechanical treatment will further be denoted as "shear modification" for historical reasons.

The phenomenon of shear modification has been studied extensively. Yet, a clear picture of the effect of the treatment on the flow properties of the material is still lacking. It has been stated that mechanical treatment diminishes the elasticity of the melt, whereas the viscosity is hardly affected. Only few authors have described the effect in terms of basic rheological functions.[3,4,5,12,16] It is the aim of this work to add to this picture and to discuss the effect of shear modification in terms of a constitutive equation.

Also, the general picture of the origin of the changed rheological properties resulting from the mechanical treatment of long-chain branched polymers is very vague. A disrupture of the entanglement network is generally believed to be the consequence of a shear treatment. An idea advanced by Münstedt,[12] namely, that prolonged shearing causes an alignment of the side chains of branched molecules along the main chain, will be further elaborated by experiments and calculations based on the constitutive equation of Doi and Edwards[21] and the picture of the molecular motion of polymer chains advanced by de Gennes.[22,23]

Experimental Section

Materials. It has been reported that shear modification is most pronounced for polymers consisting of highly long-chain branched molecules with a high molecular mass.[5,10] Therefore, a commercial grade of DSM of low-density polyethylene (LDPE) was selected with a high molecular mass and a broad molecular mass distribution. Especially the high molecular mass tail is known to be long-chain branched. Some characteristics of the material are collected in Table I.

Mechanical Treatment. Shearing was executed on a twin-screw extruder. The residence time of the material in the extruder was approximately 2 min, and the maximum temperature was 250 °C. To prevent thermal degradation of the LDPE 0.5 wt % Irganox 1044 was added before the operation, and in addition 0.1 wt % 2,5-di-*tert*-butyl-4-methylphenol was mixed in prior to every extrusion running. After each extrusion a sample was collected for the measurements, and the polymer was reextruded. In this way material was produced that had passed through the extruder between one and five times. Table II gives the code for each material treatment mode.

Table II
Codes for the Material Treatment Modes

code	material treatment mode
B	as-received granulate of the LDPE Stamylan 2800
A1	B extruded once on a twin-screw extruder
A3	B extruded three times on a twin-screw extruder
A5	B extruded five times on a twin-screw extruder
S1.5	B dissolved in xylene to a concentration of 1.5 wt % and recovered from solution by quenching and solvent evaporation at ambient conditions
S5	B dissolved in xylene to a concentration of 5 wt % and recovered from solution by quenching and solvent evaporation at ambient conditions
S25	B dissolved in xylene to a concentration of 25 wt % and recovered from solution by quenching and solvent evaporation at ambient conditions
BS	B dissolved in xylene to a concentration of 25 wt % and recovered from solution by evaporation of the solvent at 130 °C
A5S	A5 dissolved in xylene to a concentration of 25 wt % and recovered from solution by evaporation of the solvent at 130 °C

Solution Treatment. The effect of dissolving the material was studied by preparing polymer solutions in xylene at 130 °C. Solutions of the as-received polymer with concentrations of 1.5, 5, and 25 wt % were prepared. The solutions were then poured in stainless steel trays and quenched to room temperature to form gels. After complete evaporation of solvent at ambient conditions, dry gel films were obtained.

In addition, 25 wt % concentration solutions were made of the as-received polymer and of the materials that had been kneaded four and five times on the twin-screw extruder. These solutions were kept at 130 °C until all solvent had evaporated. The code connected with every treatment mode can be found in Table II.

Dynamic Measurements. A Rheometrics mechanical spectrometer, type RMS 7200, was utilized with a parallel platen system for the oscillation measurements. The phase angle, δ_G, and the dynamic modulus, G_d, were measured at 120 °C and at temperatures ranging from 150 to 210 °C with intervals of 20 °C for angular frequencies, ω, ranging from 10^{-1} to 10^2 rad·s^{-1} with intervals of 0.2 in log ω. For material B the dynamic quantities were also measured in the frequency range $-2 \leq \log \omega \leq 2.5$ at 230 °C. Disk-shaped samples were compression moulded at 170 °C applying 8.3×10^4 Pa for 5 min and 8×3.10^5 for 5 min. The samples were then water cooled under a pressure of 3.1×10^6 Pa.

Flow Curve Measurements. Flow curves at 190 and 120 °C were measured on a Rheograph 2000. As a capillary with a length/diameter ratio of 30/1 was used, the Bagley correction was considered to be unnecessary. The Rabinowitsch correction on the shear rates has been applied.

Constant Simple Elongation Rate Experiments. All materials were subjected to a constant elongation rate of 0.1 s^{-1} at 120 °C on a Göttfert Rheostrain. Materials BS and A4 were also subjected to strain rates of 0.03 and 0.3 s^{-1}. A detailed description of the apparatus is given in ref 24–26.

An 8-mm-thick sheet was prepared by compression moulding under the following conditions: 7 min at 160 °C without pressure; 5 min at 160 °C under a pressure of 6×10^4 Pa; 5 min at 160 °C under a pressure of 3×10^5 Pa; 5 s at 160 °C under a pressure of 3×10^6 Pa. The sheet was then water-cooled under a pressure of 3×10^6 Pa. Cylindrical samples with a length of 20 mm and a diameter of 5 mm were cut from this sheet on a lathe.

In addition, 2.5-mm-thick plates were compression moulded from the gel films of materials S1.5, S5, and S25 at 80 °C to prevent morphological changes in the material during sample preparation as much as possible. Dumbbell-shaped samples were cut from the plates to execute uniaxial stretching experiments

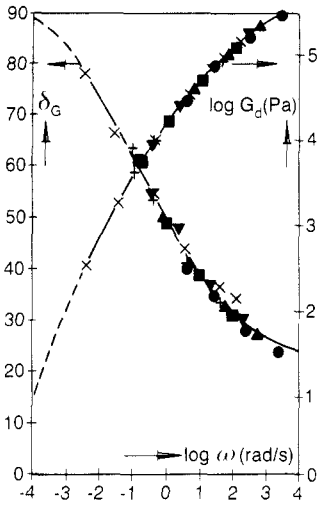

Figure 1. Master curve at 190 °C of the phase angle, δ_G, and the dynamic modulus, G_d, of material B.

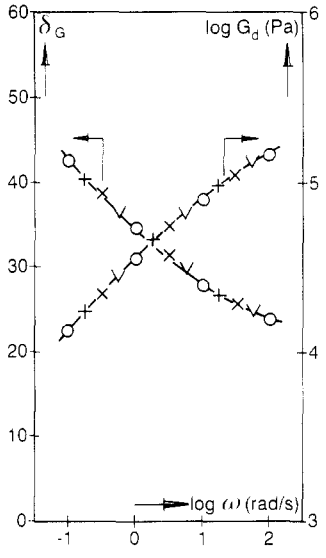

Figure 2. Phase angle, δ_G, and dynamic modulus, G_d, of materials B (○), S1.5 (+), S5 (×) and S25 (V) at 120 °C.

at 120 °C. The tensilte testing was started 10^2 s after introduction of the samples into the measuring chamber.

Density Measurements. Densities were measured in a density gradient column at 23 °C. Samples were sheets, prepared in a press under the same circumstances as the samples for the constant elongation rate experiments. No effect of the mechanical treatment on the density was detected.

Results

Dynamic Measurements. Figure 1 shows the master curve of the phase angle δ_G and the dynamic modulus G_d at 190 °C for material B. This curve was constructed by first shifting the phase angle curves along the horizontal axis, then shifting the modulus curves over the same distance along the frequency axis, and finally effecting superposition of the modulus curves via a small shift along the modulus axis.[27] Master curves of δ_G and G_d constructed in the same way of material A5 revealed a negligible effect of the mechanical treatment. The phase angle of material A5 is equal to that of material B over the whole frequency range, while the modulus is 5–10% lower.

Figure 2 shows the dynamic quantities δ_G and G_d at 120 °C of materials B, S1.5, S5, and S25. No effect of the solution treatment on these quantities can be detected.

Flow Curves. The effect of shearing on the steady-state shear viscosity can be seen in Figure 3, where the flow

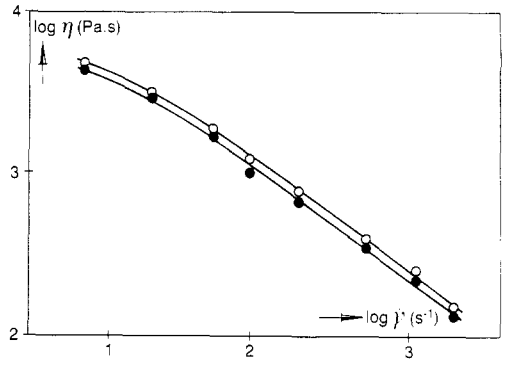

Figure 3. Shear viscosity as a function of shear rate at 190 °C of materials B (○) and A5 (●).

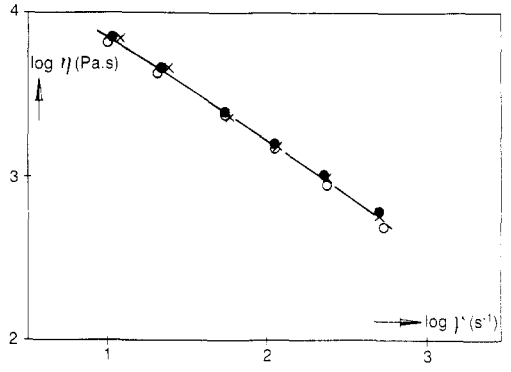

Figure 4. Shear viscosity as a function of shear rate at 120 °C of materials S1.5 (○), S5 (●) and S25 (×).

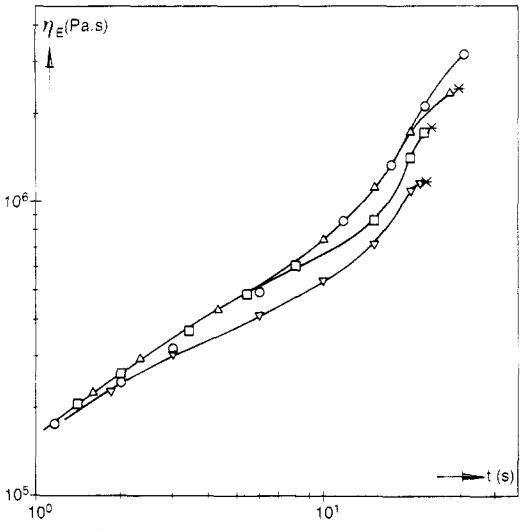

Figure 5. Buildup of the elongational viscosity at a Hencky strain rate of 0.1 s^{-1} at 120 °C for materials B (○), A1 (□), A3 (△) and A5 (▽).

curves of materials B and S5 at 190 °C are plotted. Over the whole range of shear rates the steady-state shear viscosity of S5 is approximately 5% lower than that of material B.

Solvent treatment produces no measurable change in steady-state shear viscosity as is demonstrated by Figure 4, showing the flow curves of materials S1.5, S5, and S25.

Elongational Viscosity. A completely different picture is obtained from the constant elongation rate experiments. Figure 5 is a double-logarithmic plot of the buildup of the elongational viscosity as a function of time at 120 °C. The stress buildup viscosity, η_E^+, is defined as

$$\eta_E^+(t) = \sigma_E^+(t)/\dot{\epsilon} \quad (1)$$

where σ_E^+ is the elongational stress and $\dot{\epsilon}$ is the constant

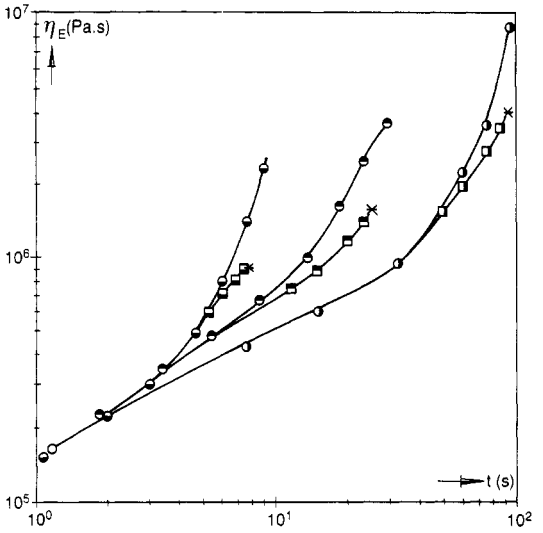

Figure 6. Buildup of the elongational visocisty at a Hencky strain rate of 0.03 s^{-1} (⊖, ⊟), 0.1 s^{-1} (◑, ◨), and 0.3 s^{-1} (⊖, ⊟) for materials BS (circles) and S5 (squares).

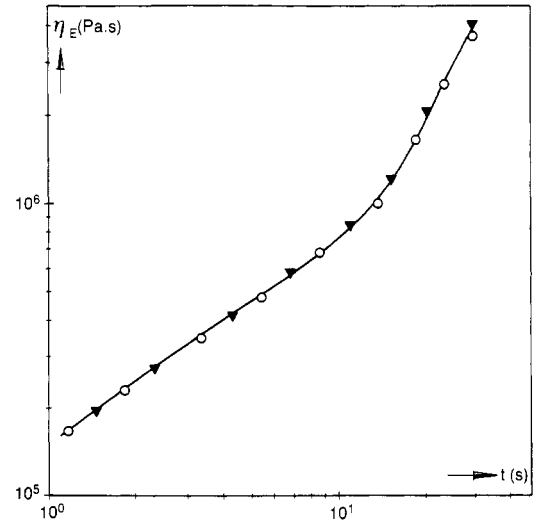

Figure 7. Buildup of the elongational viscosity at a Hencky strain rate of 0.1 s^{-1} at 120 °C for materials BS (○) and A5S (▼).

strain rate applied. Samples of materials B, A1, A3, and A5 have been subjected to a constant Hencky strain rate of 0.1 s^{-1}. A large reduction of the elongational viscosity at Hencky strains larger than 1 is achieved by shear modification. The extent of the reduction is clearly bound up with the amount of shear the material has undergone, because every extrusion causes a further decrease of the resistance of the material against uniaxial elongation. The gradual disappearance of the so-called strain-hardening effect[28-30] is accompanied by a reduction in achievable Hencky strain. The maximum value of the elongational viscosity reached in the constant elongation rate experiments is probably close to the steady-state value, which means that the steady-state elongational viscosity at a Hencky strain-rate of 0.1 s^{-1} is higher than 3×10^6 Pa·s for material B, whereas it is approximately 1.2×10^6 Pa·s for material S5. The difference in amount of strain hardening exists at all elongation rates as shown in Figure 6, where η_E^+ is plotted against time for several elongation rates. As shown in Figure 7 the amount of strain hardening for materials BS and A5S is even slightly higher than that for material B.

Upon dissolution of the material, followed by quenching and filtration, the original solution concentration has no influence on the elongational viscosity of the material, as

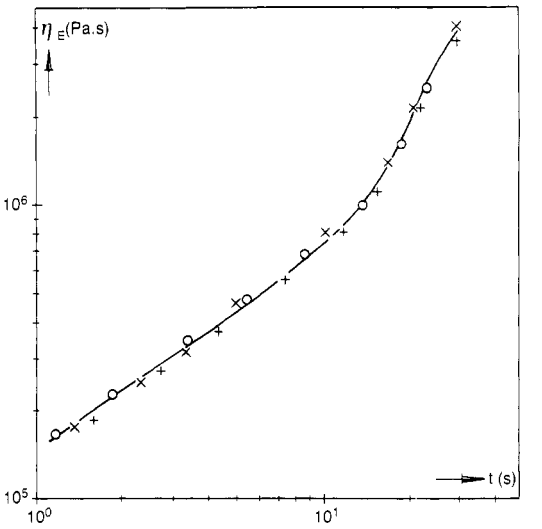

Figure 8. Buildup of the elongational viscosity at a Hencky strain rate of 0.1 s^{-1} at 120 °C for materials S1.5 (○), S5 (×), and S25 (+).

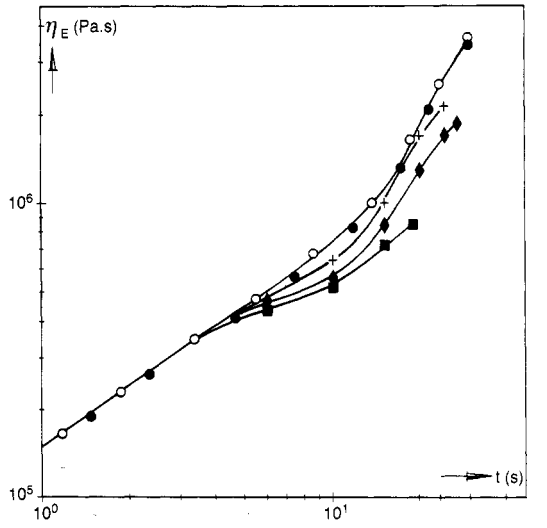

Figure 9. Buildup of the elongation viscosity at a Hencky strain rate of 0.1 s^{-1} at 120 °C material A5 after a heat treatment at 120 °C (■), 160 °C (◆), and 200 °C (+), during 2 h, for material A5 after a heat treatment at 200 °C during 3 h (●) and for material BS (○).

is demonstrated in Figure 8, which shows the buildup viscosity of materials S1.5, S5, and S25 at an elongation rate of 0.1 s^{-1} at 120 °C. These buildup curves of the elongational viscosity are also identical with those of BS and A5S.

As any effect of the solution treatment might have disappeared during preparation of the cylinders, the tensile testing was repeated for the dumbbell-shaped samples, which had only been in the molten state at 120 °C during 10^2 s. Although the scatter in the measuring results increased because the reduced sample cross section leads to lower stresses, again no influence of the original solution concentration could be detected within experimental error. Upon heat treatment the elongational viscosity of the shear-modified material increases again (Figure 9). The rate of increase is clearly temperature dependent. Even after 2 h at 200 °C the viscosity of the most strongly sheared material has not yet reached the level of the materials recovered from solution.

Theory and Discussion

Nature of Shear Modification. It has been reported many times that shear modification does not have its origin

in thermal degradation.[1,3-7,9,14] We find that repeated extrusion does not cause a significant change in the dynamic quantities of the LDPE melt and that the modification of the extensional viscosity by shearing is completely reversible by a solvent treatment, as is demonstrated in Figure 6, showing identical curves for materials BS and A5S and by a heat treatment as demonstrated in Figure 9.

In conclusion, the chemical changes going along with the mechanical treatment applied in this study are too small to cause a considerable change in flow properties. The origin of the modification must therefore be of a physical and not of a chemical nature.

Lifetime of Shear Modification. That the idea of entanglement reduction[3,4,14,18] is too vague as an explanation for shear modification is demonstrated by the results plotted in Figure 8 and by the additional experiments on the dumbbell-shaped samples of materials S1.5, S5, and S25. Even if it would not be possible to make true solutions of the polymer in xylene, which has been asserted by Ajji et al,[31] a strong reduction of intramolecular contacts is obtained by mixing small amounts of the LDPE in xylene. Upon quenching of the solution, the diminished interpenetration of the molecular coils is retained in the crystals. Even after 10^2 s at 120 °C any effect of a solution treatment is completely wiped out. In contrast, the effect of mechanical treatment is largely retained after even much longer times at high temperature. This indicates that the effect on a molecular level of shear modification and a decreased interpenetration of polymer coils are two different phenomena and, further, that the influence of the solution treatment on the rheological properties of the material is negligible or that it disappears very fast at high temperatures.

The results given in Figure 9 show that only prolonged heating at temperatures above the melting temperature gradually diminishes the effect of high shear. The time needed to completely nullify the effect of shear modification at 200 °C is of the order of 10^4 s.

The onset of elasticity in a polymer melt reflects most clearly the length of the longest relaxation times. For the investigated LDPE melt, the frequency at which the phase angle starts to deviate from 90° is of the order of 10^{-4} rad/s at 190 °C (Figure 1). This deviation happens when $\omega\tau_1 \simeq 1$, where τ_1 is the longest relaxation time of the system. In other words, the dynamic measurements clearly show that relaxation mechanisms with relaxation times of up to 10^4 s are present in the polymer melt at 190 °C.

The lifetime of orientation imposed in rheological experiments is of the same length as the lifetime of shear modification. This is a strong indication that the physical change brought about by the mechanical treatment is an orientation of molecules.

Shear Modification in Connection with the Doi–Edwards Theory and Chain Reptation. The theory of Doi and Edwards[21] was developed for linear chain polymers. It assumes that upon macroscopic deformation of a polymer melt a very fast retraction takes place of chains within their tubes representing the restraints imposed by the surrounding macromolecules on their mobility. A short time after the imposition of a macroscopic strain to the polymer melt, the chains have retracted to their equilibrium end-to-end distance, and the net microscopic strain is a pure rotation of chain segments.[32] The theory leads to a single-integral factorable constitutive equation, containing a memory function and a nonlinear strain tensor **Q** which is based on the nonaffine microscopic deformation.

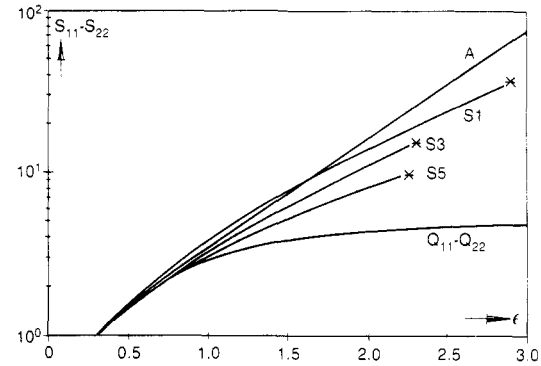

Figure 10. Strain measures, S_{11}–S_{22}, obtained from constant strain rate experiments for materials, A, S1, S3, and S5, together with the theoretical strain measure, Q_{11}–Q_{22}, predicted by the Doi–Edwards theory.

It is clear that complete chain retraction is impossible for long-chain branched molecules, because retraction of chain segments between two branch points is strongly hindered. As could be expected on this basis, the strain measures, S_{11}–S_{22}, for uniaxial extension of LDPE melts differ from the theoretical strain measure, Q_{11}–Q_{22} of the Doi–Edwards constitutive equation, although experimental data for long-chain branched polymer melts can usually be very well described by a factorable single-integral constitutive equation.

In Figure 10 the Doi–Edwards strain measure for simple extension, Q_{11}–Q_{22} is plotted together with the strain measures, S_{11}–S_{22}, calculated from the constant strain rate experiments[26,33] for materials A, S1, S3, and S5. It appears that the more strongly the material has been sheared, the closer its strain measure approaches the theoretical function predicted by the molecular kinetic theory of Doi and Edwards. This result in combination with the observation that melts of HDPE usually display very little or no strain hardening at all leads to the conclusion that melts of branched polymers are modified by high shear in such a way that their rheological behavior, especially in simple elongation, resembles that of melts of linear polymers.

This conclusion supports the image advanced by Münstedt according to which kneading aligns the side chains of branched molecules along the main chain. Also the fact that a solution treatment nullifies the shear modification, as has been observed by many researches[1,3,4,6] and in this study, is in accordance with the proposed image. Dissolving the modified material would increase the mobility of the branches to such an extent that the alignment is destroyed immediately and that after the solvent is removed, the material has returned to its original state.

On the basis of the Doi–Edwards theory the molecular explanation of shear modification is as follows: complete chain retraction is impossible for branched molecules, which gives rise to strain hardening in simple elongation; high shear aligns the branches along the backbone, thereby making chains retraction possible, which diminishes the extent of strain hardening.

According to the reptation idea the longest relaxation times present in a melt of long-chain branched molecules are those connected with the relaxation of the backbone.[34,35] In a stress relaxation experiment the stress will have relaxed completely only when the backbone has acquired random orientation by reptating out of its original tube. Now, the stress contribution from the arms must be completely removed before the branch point can take one diffusive step, thereby allowing reptation of the

backbone. This means that the alignment of the branches along the backbone disappears in a time much shorter than the disengagement time of the backbone which is the longest relaxation time of the molecule. This is in contradiction with the observation that the characteristic time of shear modification is of the same length as the longest relaxation time of the polymer melt.

The maximum in the curve of the steady-state elongational viscosity vs the Hencky strain rate has also been ascribed to drag of the arms into the tube backbone.[35] According to McLeish the tension due to stretching of the backbone can become sufficiently high to make an alignment of chain arms along the backbone entropically favorable beyond a critical strain rate. In this respect it would be interesting to investigate the effect of an "elongation modification" of long-chain branched molecules. It is to be expected that a similar degree of modification can be obtained in elongation with much less effort than in shear as chain backbones are stretched much more in elongational flow than in shear flow. This is probably also the reason why a mechanical treatment has a much more pronounced effect on the rheological properties in simple elongation than on the flow properties in simple shear.

Conclusions

Shear modification produces minor changes in the linear viscoelastic behavior of melts of branched polymers and in their steady-state shear viscosity. The elongational viscosity, on the other hand, is greatly reduced by a mechanical treatment. This is the origin of the reported increase in melt flow index and of the decrease in swell ratio. A lower viscosity corresponds to a smaller pressure drop over the entrance zone of the capillary during measurement of the melt index and therefore to a higher pressure drop over the capillary, which produces a higher flow rate. A lower elongational viscosity corresponds to a smaller degree of chain orientation due to the elongational component in the entrance flow and therefore to a smaller degree of recovery or extrudate swell after passage through the capillary.

The fact that shear modification is reversible through a solution or heat treatment shows that high shear produces a physical change in the material and no considerable thermal degradation.

The concept of network disentanglement is too general to serve as an explanation for the origin of the effect of mechanical treatment. The fact that a solution treatment has a much shorter lasting effect or no effect at all on the rheological properties of the material implies that reduced interpenetration of the molecules is not the cause of the lower elongational viscosity.

The idea of alignment of side chains along the backbone as the origin of shear modification is supported by measuring data and on theoretical grounds. The mechanical treatment causes a strong decrease of strain hardening in constant Hencky strain rate experiments. The flow behavior of fully sheared long-chain branched material is therefore similar to that of linear chain polymer melts. The strain measure for strongly sheared material, calculated from constant strain rate experiments, approaches the theoretical strain measure of the Doi–Edwards constitutive equation, an equation derived for linear chain materials. The time scale connected with the effect of shear modification is the same as the time scale connected with the disappearance of orientation in the melt during rheological measurements. This is in disagreement with the reptation idea applied to long-chain branched polymer melts if it is assumed that shear modification produces alignment of side chains along the backbone.

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