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ORIGINAL CONTRIBUTION

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# Influence of molecular structure on rheological properties of polyethylenes

## Part II. Elongational behavior

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**Abstract** A conventional long-chain branched polyethylene (LDPE) and an octene copolymer (LLDPE) have been characterized in elongation using an apparatus which allows creep and stressing experiments with high accuracy. Whereas the LDPE shows a strain-hardening behavior known from literature, the elongational properties of the LLDPE are surprising. In the stressing experiments the strain-hardening is much more pronounced at lower strain rates than at higher ones. Two distinct plateaus of the strain rate are found in creep experiments at smaller stresses, indicating that two different processes have to be taken into consideration. The elongational viscosity calculated from the constant strain rate at short times is in good agreement with $3\eta_0$ obtained from shear experiments. The viscosity determined according to the second plateau in strain rate increases with declining stress. The recoverable compliance is smaller for the LLDPE than for the LDPE at higher stresses. This result reflects the differences in the molecular mass distribution of the two polyethylenes. At lower stresses the recoverable compliance of the LLDPE becomes higher than that of the LDPE. A hint to an explanation of the unusual elongational behavior of the LLDPE is obtained from an analysis of the molecular structure which shows the existence of a linear component of a relatively high molecular mass within the short-chain branched material. The results are discussed assuming a separate phase of the linear molecules within the matrix of the short-chain branched polyethylene of lower molecular mass.

**Key words** Elongational flow – strain-hardening – recoverable strain – polyethylenes – branching structure

## Introduction

For a thorough rheological characterization of polymers shear experiments are not sufficient. This is particularly true for all the processing operations where the elongation of a polymer melt has to be considered. Therefore, the long-chain and the short-chain branched polyethylenes described in Part I of this paper (Gabriel et al., 1997) were investigated in elongation.

In addition, elongational flow is more strongly influenced by long-chain branches than shear deformation, as has convincingly been shown by Münstedt and Laun (1981) on polyethylenes and recently by Hingmann and Marczinke (1994) on polypropylenes, for example. The investigations underlying this paper were undertaken for two reasons. Firstly, we try to make a contribution to understanding the different film blowing behavior often found for linear low density polyethylene (LLDPE) in comparison to classical long-chain branched polyethylene (LDPE) by a rheological characterization with respect to elongational flow. Secondly, the question should be answered whether the results on the depen-

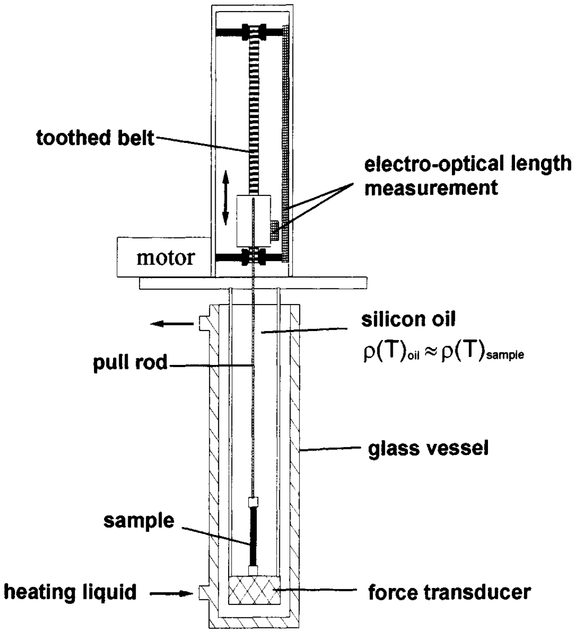

**Fig. 1** Extensional rheometer

dence of the elongational behavior on molecular parameters and particularly on the kind of branching known from low density polyethylene (LDPE) and high density polyethylen (HDPE) melts can be applied to the findings on a short-chain branched material, too. This paper deals with the second question. Molecular data and shear properties of the LDPE and the LLDPE are given in Part I (Gabriel et al., 1997).

## Experimental

The elongational experiments were carried out by an apparatus presented in Fig. 1. Its principles go back to a design published by Münstedt (1979). The modifications comprising a modern and fast driving unit, an optical displacement measuring device of high resolution and stability, and a computer control and data acquisition system make it a versatile instrument which allows experiments at various deformation modes and histories. The sample is suspended in a silicon oil bath of a density which is chosen to compensate the gravity of the specimen by buoyancy. Besides that, it serves as heating liquid effecting a very constant temperature distribution along the sample of a maximum length of 500 mm. The advantages of this apparatus lie in its ability to easily measure the recoverable portion of the elongation with high accuracy and to freeze in the sample at different states of deformation.

Another big advantage of this improved apparatus is its ability to perform experiments at constant stresses besides those at constant strain rates with high accuracy. Creep experiments are of importance because the steady-state of deformation is reached after smaller elongations than for stressing experiments. Therefore, in many cases the steady-state of elongation can be reached although the total length of the elongated sample is limited to 500 mm.

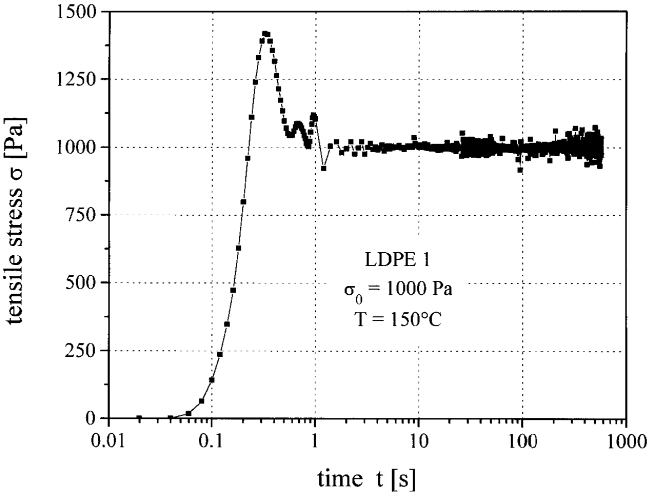

**Fig. 2** Time dependence of the stress in a creep experiment (LDPE 1)

The quality of a creep experiment is strongly dependent on the setting time for a constant stress value. Figure 2 demonstrates for a relatively low tensile stress of $10^3$ Pa that a constant level is reached after about 1 s. These favorable response times can be achieved by using a fast servomotor and a sophisticated electronic control unit which has to be able to keep the product of the two changing quantities force and sample length constant.

The cylindrical samples of 25 or 10 mm in length were prepared by extrusion through a capillary followed by retardation in silicon oil. After etching the surfaces of the sample ends the samples were glued to metal clamps. The total exposition time to temperature was distinctly lower than the stability limit determined by mechanical-dynamic measurements (cf. Fig. 4 of Part I).

## Elongational behavior

### Viscosity

A common way of characterizing polymer melts in elongational flow is stressing experiments at constant strain rates. Their results on the two polyethylenes are given in Figs. 3 and 4. LDPE 1 shows the expected behavior known from literature (Fig. 3). At higher strain

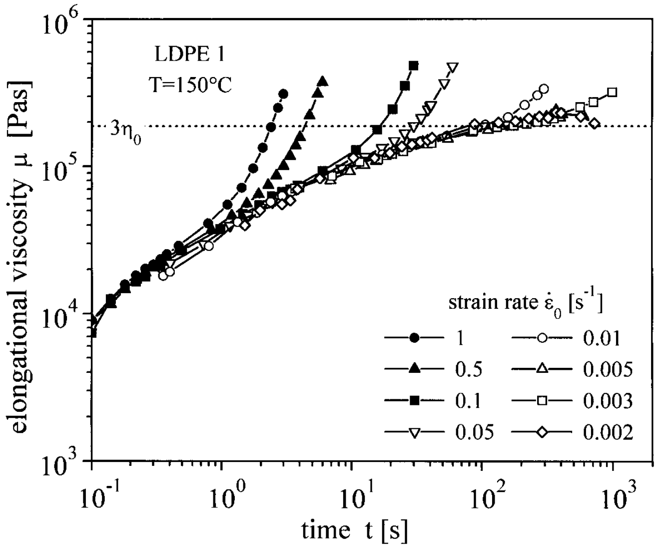

**Fig. 3** Time-dependent elogational viscosity of LDPE 1 measured at different strain rates

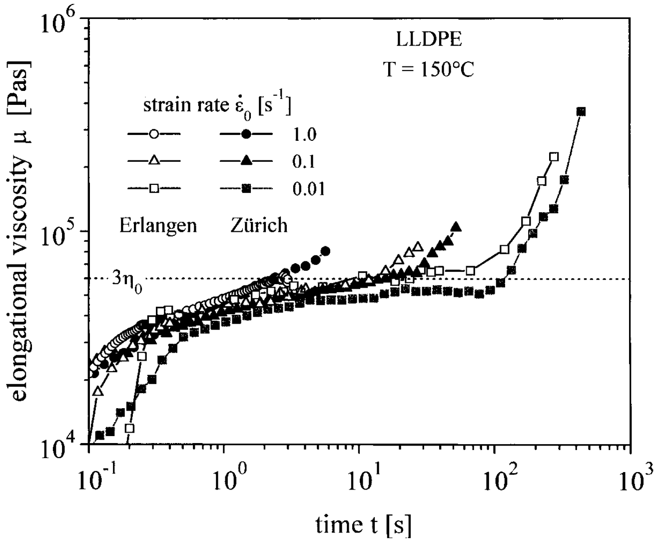

**Fig. 4** Time-dependent elongational viscosity of the LLDPE measured at different strain rates

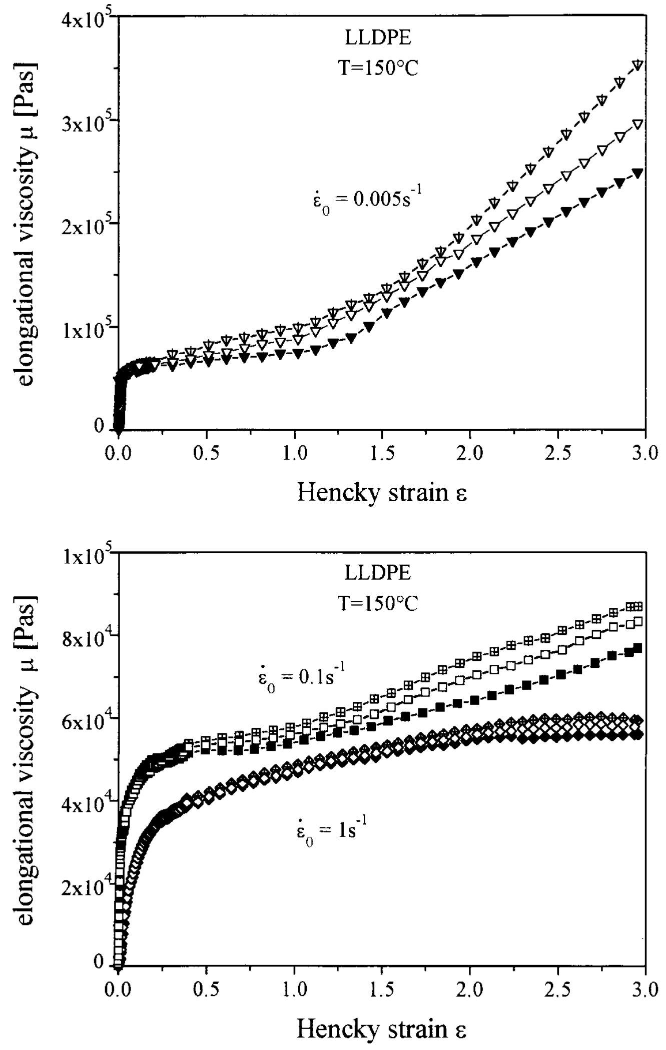

**Fig. 5** Reproducibility of $\mu(\varepsilon)$ for the LLDPE at three different strain rates. Three samples at each strain rate were measured

rates a pronounced increase of the elongational viscosity[1] with time, the so-called strain-hardening, is found which becomes weaker at lower strain rates and disappears at the smallest experimentally available value of $\dot{\varepsilon}_0 = 0.002\,\mathrm{s}^{-1}$. In all cases the samples have been elongated up to a Hencky strain of $\varepsilon = 3$ which corresponds to a stretching ratio of about 20. The curve at the lowest strain rate which sectionwise falls together with $\mu(t)$ at higher strain rates but shorter times is three times the shear viscosity $\eta(t)$ at small shear rates, as should be expected from the theory of linear viscoelasticity. The elongational viscosity of the LLDPE shows a time dependence significantly different from that of LDPE 1 as is demonstrated by Fig. 4. At higher strain rates a significant strain-hardening does not occur up to the measured Hencky strains of 3. At lower strain rates the viscosity increase becomes more and more pronounced. This surprising experimental result is supported by measurements at the Technical Universtiy of Zürich (Meißner, 1996) on the same product, but with the elongational rheometer published by Meißner and Hostettler (1994) which is based on a totally different measuring system and uses samples of a plate-like geometry. Taking that into account, the agreement between the results of the two measuring devices is good. Therefore, the probability is very high that the strain-

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[1] The term elongational viscosity is used for the time-dependent stress related to the applied elongation rate.

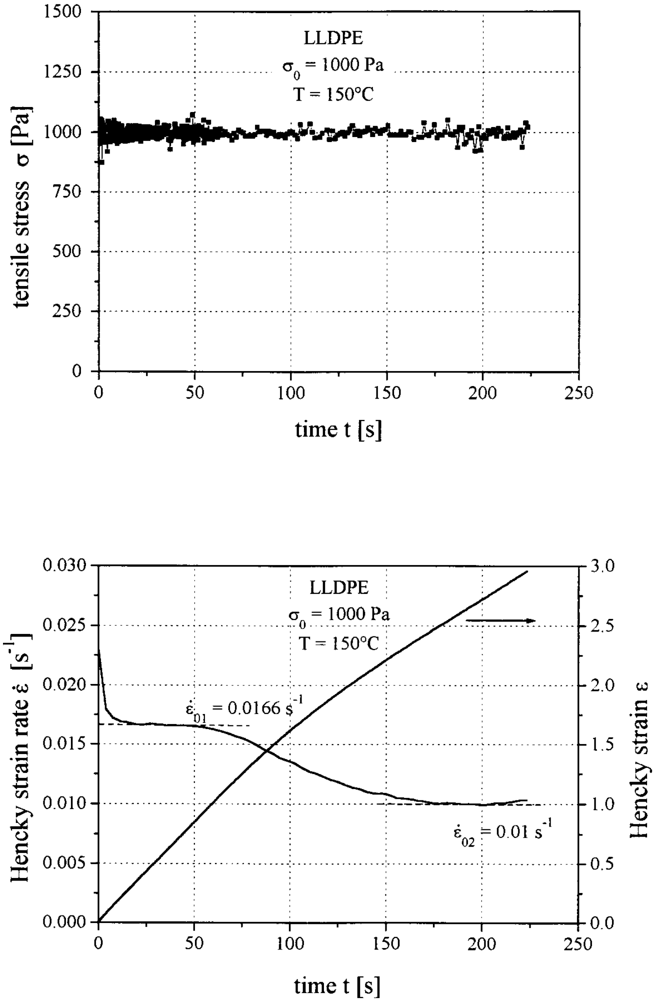

**Fig. 6** Creep experiment of LLDPE

hardening of the LLDPE at low strain rates is a real effect and not caused by an artefact.

The reproducibility of the strain-hardening effect of the LLDPE at small strain rates is demonstrated in Fig. 5 where the time-dependent elongational viscosity is linearily plotted as a function of Hencky strain at three different strain rates. It is obvious that the scatter between the three samples measured at each strain rate becomes higher the lower the strain rate, but this comparison on a linear scale demonstrates how pronounced the strain-hardening at small strain rates is.

The reproducibility of the time-dependent elongational viscosity of LDPE 1 is found to be better than that of the LLDPE. It increases from 0.3% at the highest applied strain rate of 1 $s^{-1}$ to 2.6% at a strain rate of 0.01 $s^{-1}$. These numbers are valid for the maximum elongation of $\varepsilon = 3$; they become lower for smaller elongations. The inferior homogeneity of the LLDPE samples has its origin in the lower viscosity and the smaller strain-hardening.

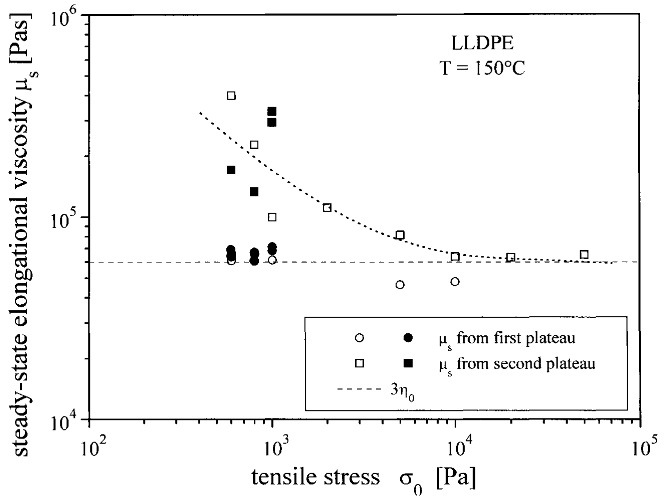

**Fig. 7** Elongational viscosities of the LLDPE calculated from the two strain rate plateaus of creep experiments (○□ initial sample length 25 mm, ●■ initial sample length 10 mm)

Comparing the time dependence of the viscosities of LDPE 1 and the LLDPE in the linear range it becomes obvious from Figs. 3 and 4 that the LLDPE reaches the steady-state faster than LDPE 1. At first glance, this finding is easily explained by taking into account the lower molecular mass and the more narrow molecular mass distribution of the LLDPE which should result in a smaller terminal relaxation time (cf. Table 1 of part I of this paper). Not easy to understand from the molecular structure commonly described by $M_W$ and $M_W/M_n$ is the strain-hardening of the LLDPE, however. It will be discussed in another section of this paper.

The unusual strain-hardening behavior of the LLDPE is confirmed by the creep experiment presented in Fig. 6. The strain rate as a function of creep time as obtained by a numerical differentiation of the creep curve $\varepsilon(t)$ shows two plateau values, one at short creep times and the other at longer ones. From the first plateau of the strain rate a viscosity of $6 \cdot 10^4$ Pas can be calculated which is in excellent agreement with $3\eta_0$ (cf. Table 1). The viscosity obtained from the second plateau of the elongational rate is distinctly higher. In Fig. 7 the viscosities calculated from the two plateaus of the strain rate are plotted as a function of stress for two different initial sample lengths. It is obvious that the two plateaus can be related to two processes. At shorter creep times one observes a linear response of the material documented by the constant viscosities in Fig. 7 obtained from the first plateaus of the strain rate curves. The viscosity values deduced from the second plateaus significantly increase with decreasing stresses. These results lead to the hypothesis that two different molecular processes within the

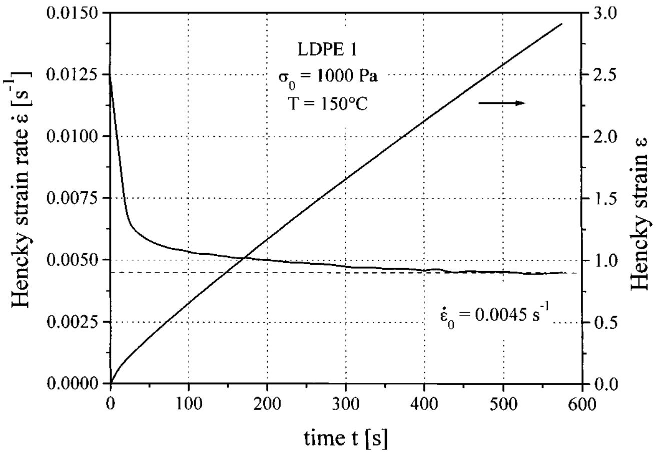

**Fig. 8** Creep experiment on LDPE 1

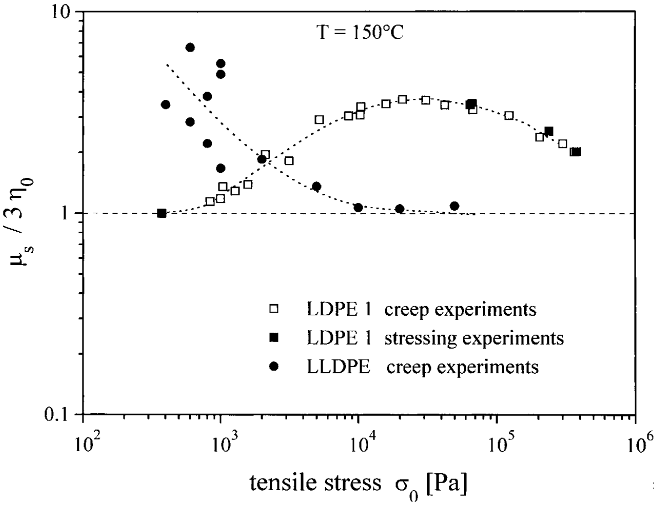

**Fig. 9** Steady-state elongational viscosity $\mu_s$ related to $3\eta_0$ as a function of stress for the two polyethylenes

**Table 1** Newtonian viscosities of the two polyethylenes at 150 °C (MBR: magnetic bearing rheometer, CSM: constant stress rheometer, ERM: elongational rheometer)

| | $\eta_0$ [$10^4$ Pas] | | $\mu_0$ [$10^4$ Pas] |
|---|---|---|---|
| | MBR | CSM | ERM |
| LDPE 1 | 6.0 | 6.3 | 18.8 |
| LLDPE | 2.0 | 2.0 | 6.0 |

LLDPE have to be considered. It should be mentioned that the scatter of the measured values is quite high at low stresses. This is mainly due to sample inhomogeneities occurring statistically during deformation. With regard to Fig. 7 another remark has to be made. The viscosity values taken from the first plateau of the strain rate are generally higher for the short samples than for the longer ones. This result reflects the influence of the naturally inhomogeneous deformation at the sample ends which becomes stronger the shorter the samples are. As the first plateau occurs up to Hencky strains of about 1, i.e. elongations of 2, this inhomogeneity has a stronger influence on the measurements in the case of the samples of 10 mm in initial length.

It has to be stressed that the creep experiment supports the experimental finding of a strain-hardening of the LLDPE at low stresses or strain rates. The differences in the elongational behavior of the two polyethylenes are obvious in creep, too, as a comparison of Figs. 6 and 8 demonstrates. The creep experiment on LDPE 1 in Fig. 8 does not show any indication of two plateaus of the strain rate as in the case of the LLDPE[2]. The strain rate steadily decreases from high values at the beginning of the experiment and approaches a steady-state. The corresponding elongational viscosity fits in very well with the curve of the steady-state viscosities in Fig. 9.

Another interesting result is obtained if one regards the time behavior of the LLDPE in the creep and stressing experiments. Whereas in creep at a stress of $10^3$ Pa the strain-hardening, indicated by a decrease of strain rate from the first plateau, starts at about 50 s, the corresponding time in the stressing experiment at $\dot{\varepsilon}_0 = 0.01$ s$^{-1}$ lies at around 100 s. From this consideration the advantages of creep experiments with respect to the attainment of a steady-state are obvious the reliability of which is decisively dependent, however, on the accuracy of the stress control.

The accuracy of the elongational measurements on the two polyethylenes gets some support from a comparison of shear and elongational viscosities in the linear range of deformation. As Table 1 shows, the Trouton ratio $\mu_0/\eta_0 = 3$ is excellently fulfilled. The shear experiments were performed by two different instruments. MBR denotes the creep apparatus used by Gabriel et al. in Part I of this paper, CSM stands for a controlled shear stress rheometer available on the market. The results from the two shear apparatuses show a convincing agreement.

In Fig. 9 the steady-state elongational viscosities as determined from creep and stressing experiments are plotted for the two polyethylenes as a function of stress. The values are normalized by $3\eta_0$ in order to facilitate their comparability. LDPE 1 shows the behavior known from literature (Münstedt and Laun, 1981). Starting from $\mu_s/\eta_0 = 1$, the viscosity ratio increases and runs through a maximum of a height of 4. The elongational viscosity of the LLDPE calculated from the second plateau value of $\dot{\varepsilon}(t)$ still increases at the lowest attainable stresses.

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[2] The applied stress is shown in Fig. 2 and demonstrates the accuracy of its time behavior.

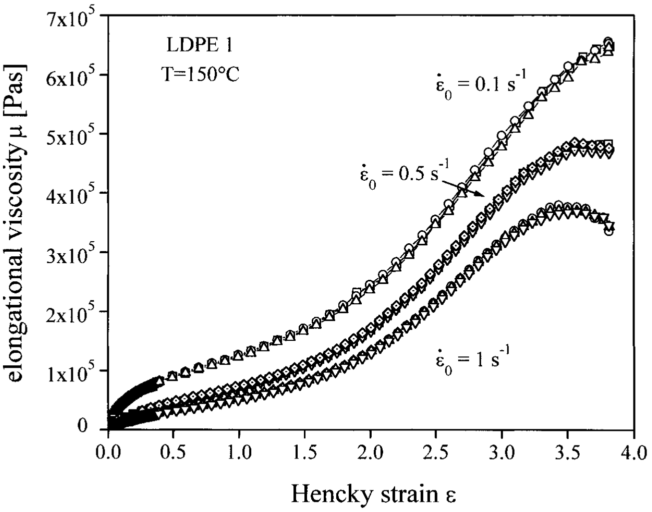

**Fig. 10** Extensional viscosity as a function of strain for LDPE 1 at three different strain rates. Initial sample lenght $l_0 = 10$ mm. Three samples at each strain rate were measured

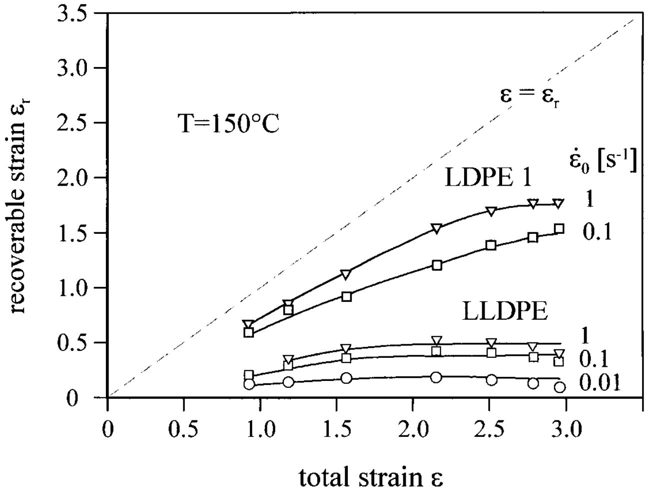

**Fig. 11** Recoverable strain as a function of total strain for the two polyethylenes at different strain rates $\dot{\varepsilon}_0$

The filled symbols in the case of LDPE 1 are taken from experiments at constant strain rates in which the initial sample length was reduced from 25 to 10 mm giving rise to higher total strains up to $\varepsilon = 3.8$. From the results represented in Fig. 10 a steady-state can be assumed at least at the two highest strain rates. The reproducibility of the measurements is good. The "steady-state" values of Fig. 10 fit perfectly in with the curve from the creep experiments in Fig. 9 indicating that the assumption of having reached steady states in the measurements of Fig. 10 is justified. The stress decrease at $\dot{\varepsilon}_0 = 1$ s$^{-1}$ is due to necking of the sample at high elongation.

## Elasticity

In addition to the viscous behavior in elongation the elasticity of the two polyethylenes was investigated. The elasticity in elongation is determined by a recoil experiment. At any state of deformation the stress on the sample can be set to zero. From the length $l_r$ after total recovery the recoverable strain $\varepsilon_r = ln\ l/l_r$ is calculated. $l$ describes the sample length just before the recovery starts. In Fig. 11 the recoverable strain $\varepsilon_r$ is plotted as a function of the total strain $\varepsilon$ for the two products at different strain rates. Obvious is the fact that under the applied conditions the recoverable strain for the LLDPE is distinctly smaller than for LDPE 1, a result which corresponds at first glance with the more narrow molecular mass distribution of the LLDPE. The dependence of $\varepsilon_r$ on $\varepsilon$ and the strain rate $\dot{\varepsilon}_0$ is well known from other investigations, e.g. Münstedt and Laun (1981). The recoverable part in relation to the total deformation is higher at shorter times than at longer, reflecting the nature of the viscoelasticity of polymer melts. $\varepsilon_r$ increases with $\varepsilon$ up to a plateau value which increases with strain rate.

A quantity more suitable for a theoretical description or a comparison with the results of other experiments is the compliance generally defined as $D = \varepsilon/\sigma_0$. $D_r = \varepsilon_r/\sigma_0$ is the recoverable compliance. $\sigma_0$ stands for the tensile stress on the sample. If only the elastic portion $\varepsilon_r$ of a deformation is regarded, $D_r$ can conveniently be determined from a creep recovery experiment. If the recoverable strain is measured after having reached the steady-state of deformation one obtains the steady-state recoverable compliance $D_e$.

This quantity is plotted as a function of $\sigma_0$ for the two polyethylenes in Fig. 12. At higher stresses, $D_e$ is larger for LDPE 1 than for the LLDPE as could be expected from Fig. 11. At lower stresses, however, $D_e$ of LDPE 1 approaches a plateau value whereas $D_e$ of LLDPE increases further and becomes higher than that of LDPE 1. The constant steady-state recoverable compliance of LDPE 1 is in good agreement with 1/3 $J_e^0$ as it should be in the range of linear viscoelasticity. $J_e^0$ is the recoverable steady-state shear compliance in the linear range found for LDPE 2. This quantity has been determined by shear creep recovery experiments (see Part I of this paper). LDPE 2 is a material polymerized in the same way as LDPE 1. Their densities are not distinguishable. LDPE 2, however, has been particularly stabilized as it has been used in the creep recovery experiments which last for a long period of time. The linear range of the LLDPE has not been reached at the lowest stresses applicable in elongational creep. But 1/3 $J_e^0$ found for the LLDPE in shear creep recovery (see

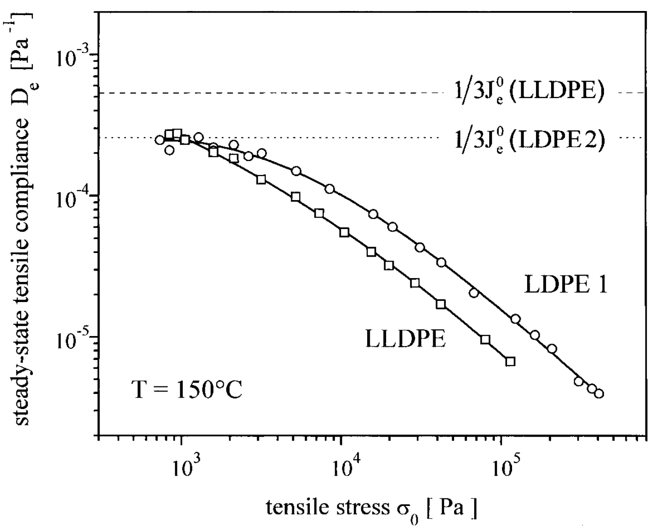

**Fig. 12** Recoverable steady-state tensile compliance as a function of tensile stress for the two polyethylenes

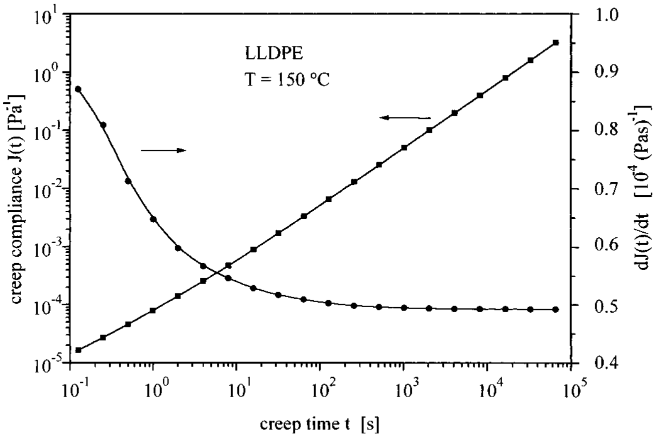

**Fig. 13** Shear creep compliance of the LLDPE measured in the linear range

Part I) indicates the expected level in the linear range of elongation.

## Discussion

The LDPE investigated shows a pronounced strain-hardening at high strain rates which becomes smaller at lower ones. This elongational behavior is well known for long-chain branched polyethylenes.

Surprising is the result on the LLDPE that there exists a significant strain-hardening at small strain rates but not at higher ones. This behavior has been found in stressing and creep experiments as well (cf. Figs. 4 and 6). It can only be found in elongational flow as a comparison with a creep curve of the LLDPE in shear demonstrates (Fig. 13). The measurement has been performed in the linear range of deformation using the creep apparatus of Part I of this paper. The creep compliance and its time derivative do not indicate the existence of two processes as in the case of creep experiments in elongation. It should be mentioned, however, that two molecular processes are distinguishable in the shear creep recovery experiments on the LLDPE (cf. Figs. 7 and 8 of Part I of this paper).

In the paper by Gabriel et al. it is reported that the LLDPE contains a distinct linear component of a higher molecular mass compared with the short-chain branched molecules. This high molecular mass component can explain the large steady-state recoverable compliances found in shear and elongation for the LLDPE at low stresses. But it does not give an explanation of the findings in shear that for the LLDPE the time dependences in creep and creep recovery do not follow the theory of linear viscoelasticity and that the time-temperature superposition principle is not fulfilled for the time-dependent compliances in shear (cf. Part I).

The strain-hardening of the LLDPE at low strain rates gives another hint to a peculiar rheological behavior of the LLDPE investigated. From a miscible high molecular mass component a strain-hardening effect at higher strain rates should be expected as found by Münstedt (1980) on anionic polystyrenes with a distinct tail of higher molecular mass.

For a rough explanation of the shear behavior of the LLDPE the immiscibility of the linear molecules with those of the short-chain branched has been postulated, giving rise to a separate phase of the linear component of high molecular mass within the matrix of short chain branched molecules (cf. Part I). At short times the elongational behavior is dominated by properties of the matrix of comparable low molecular mass leading to short relaxation and retardation times. At longer times the deformation of the separated phase comes into play resulting in a viscosity increase according to its higher molecular mass. This is reflected by the growing stress in the constant strain rate experiments and the declining strain rate in the creep test. The question of liquid-liquid phase separation in the LLDPE melt has already been discussed extensively in Part I of this paper. There are several hints given by Wignall et al. (1996) and Alamo et al. (1994, 1997) that liquid-liquid phase separation in LLDPE only occurs in the case of very high branching degrees. On the other hand, reports exist from other authors which support our hypothesis of the existence of a separated phase of a high molecular linear fraction in the LLDPE melt (Hill et al., 1993, 1997; van Rutien and Boode, 1992).

At stresses small enough the linear range of deformation should be reached for the separated phase, too, resulting in a constant elongational viscosity and a constant recoverable compliance. Figure 12 demonstrates how far away the lowest applied stress of 600 Pa is from the linear range if the level given by the steady-state recoverable shear compliance is regarded. It should be mentioned that the shear experiments were performed at stresses lower than 20 Pa.

The difference in the influence of a miscible and not miscible high molecular mass component is reflected by the elongational behavior. In the case of polystyrene the long molecules are compatible with the shorter ones forming an entanglement network which can only be deformed by cooperative movements of all molecules. This picture can explain the stress increase if the melt is deformed at high strain rates. If the imposed strain rate becomes lower the disentanglement becomes easier, resulting in a smaller stress build-up. In the case of the LLDPE where the high molecular mass component is assumed to form a separate phase most of its molecules do not interact with the matrix molecules, allowing widely independent motions.

A comparison of the findings of this work with literature is not very promising because only a few results on elongational properties of LLDPE are available. Schlund and Utracki (1987) investigated 11 different LLDPE products. For two products only, a strain-hardening could be observed, the quantitative feature of which was not worked out in detail because of apparent difficulties with the homogeneity of sample deformation. Like in the case of the LLDPE of this paper it has been proven, however, that the viscosity increase was not caused by a chemcial change of the material. Minoshima and White (1986) published results on a HDPE which exhibited a pronounced strain-hardening. Molecular data of the material and stability tests are not given, however.

As the relation of the differences in elongational flow to the processing behavior of the two polyethylene melts is addressed first film blowing experiments demonstrate that a better bubble stability and a higher homogeneity of the thickness of the produced films can be correlated with a strain-hardening behavior found in extensional flow (Kurzbeck et al., 1997). For the LDPE which possesses a pronounced strain-hardening in the range of elongational strain rates typical of the used film blowing equipment a better homogeneity of film thickness has been found in comparison to the LLDPE which shows a distinctly smaller strain-hardening at corresponding elongational strain rates. In addition, the strain dependence of the stress measured on the film blowing equipment mirrors the stress-strain behavior determined in the laboratory experiment.

The investigations regarding the film blowing performance of the two polyethylenes are still in progress. Their results will be published elsewhere.

## Conclusions

Our results demonstrate that, as LLDPE cannot generally be regarded as a homogeneous material, its rheological properties are dependent on its composition. Particularly, the elongational flow of the melts reacts very sensitively on structural differences within the materials. This fact may be a clue to understanding the somewhat confusing findings in literature if the strain-hardening of polyethylenes is discussed.

It has been shown that rheological measurements and molecular characterizations using gel permeation chromatography and the method of temperature rising elution fractionation have to be combined to get a deeper insight into the relationship between the molecular structure and properties of polyolefins.

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