Physical Properties

Melt elongation and structure of linear polyethylene (HDPE)

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SUMMARY

Different linear polyethylenes (HDPE) were elongated in the molten state at constant strain rates up to very large total strains (maximum stretch ratio $\lambda = 270$). The structure of these polyethylenes was investigated by GPC, C-13-NMR, and IR. From the structural parameters it follows that the strain hardening of the HDPE melts investigated here is not due to the short chain branches of the mainly linear molecules but influenced by a small amount of very long molecules of the molecular weight distribution. For the influence of the temperature on the strain hardening phenomenon an unexpected result was found additionally.

INTRODUCTION

During the very recent past the investigation of the elongational behaviour of polymer melts has been a subject of increasing activity. For melts of linear polyethylene (HDPE), however, this investigation was limited to relatively small total strains because of the following reasons [1-4]: (a) The preparation of the samples for the elongational tests was not well enough worked out resulting into inhomogeneities of each sample at the onset of the tensile test, (b) during elongation additional inhomogeneities started to develop, especially at large strains. In this paper we report about four different linear polyethylenes, which were elongated in the melt up to very large strains. It is the first time that with HDPE maximum elongations up to a Hencky strain of $\varepsilon = 5.6$ (corresponding to a stretch ratio of $\lambda = 270$) could be achieved with a tolerable homogeneity of the deformation. The resulting elongational viscosities reflect variations of structural parameters, therefore we also include results from GPC, C-13-NMR, and IR measurements.

TEST MATERIAL AND MOLECULAR CHARACTERIZATION

The linear polyethylenes under investigation were made by radical polymerization. Three of the four specimens are commercial products, two of them are copolymers with butene-1. We use the following notation and give the molecular parameters M_w, M_n, and M_w/M_n (from gel-permeation-chromatography), the densities, and the CH_3-concentrations (from infrared) in <u>Table 1</u>:

HDPE-1: Hostalen GF 7740 F2[1])   HDPE-3: Experimental product[1])
HDPE-2: Hostalen GF 7750 M[1])   HDPE-4: Lupolen 6031 HX[2])

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Table 1: Molecular parameters, density, and $CH_3/1000$ C					
Material	M_w [g/mol]	M_n [g/mol]	M_w/M_n	ρ (23°C) [g/cm^3]	$CH_3/1000$ C
HDPE-1	225'000	24'000	9.4	0.943	8
HDPE-2	253'000	18'000	14.1	0.950	5
HDPE-3	263'000	17'000	15.5	0.960	3
HDPE-4	150'000	20'000	7.5	0.964	2

In Figure 1 the molecular weight distributions are shown as histograms. As the GPC measurements were always performed under identical conditions, the resulting molecular weight distributions allow one to perform a relative comparison. The weight percentage of the molecules with molecular weights M exceeding the x-fold of M_w is given in Table 2.
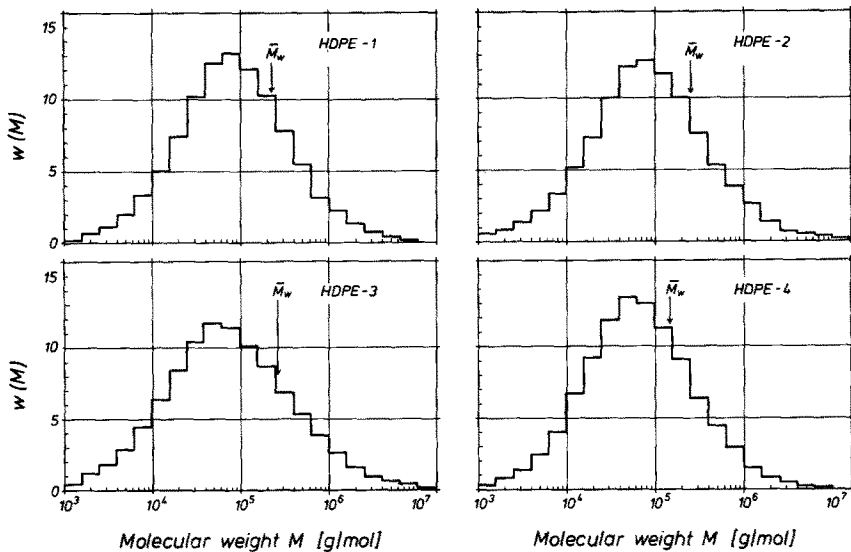

Figure 1: Histograms of the molecular weight distributions of HDPE 1-4

It follows from Figure 1 and Tables 1 and 2 (x=1) that the molecular weight distributions of HDPE-1 and -4 are more narrow than those of HDPE-2 and -3. But for x > 2 Table 2 shows, however, that HDPE-3 and -4 have a larger amount of long molecules than HDPE-1 and -2.

Table 2:	Weight percentage of molecules with M > x M_W					
Material	x = 1	2	3	5	10	15
HDPE-1	20.5	10	6.25	3.25	1.225	0.65
HDPE-2	18.5	9.5	6.25	3.25	1.375	0.775
HDPE-3	18	10	6.75	3.75	1.5	0.85
HDPE-4	23.5	12	7.25	3.75	1.4	0.7

Figure 2 gives the C-13-NMR spectra of HDPE-1, -3, and -4. For comparison the spectrum of a branched polyethylene specimen[3] is also included. The peaks were identified by means of the data published by Axelson, Levy and Mandelkern [5].
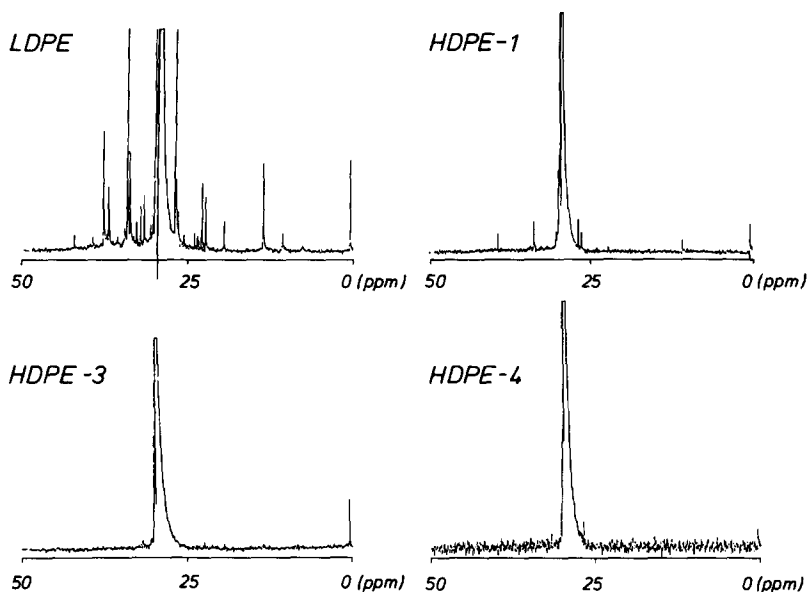

Figure 2: C-13-NMR spectra of HDPE-1, HDPE-3, and HDPE-4; comparison with a branched polyethylene LDPE

It follows from the diagrams of Figure 2 that in contrast to the LDPE sample with many branches, the HDPE samples have only a small amount of side chains. HDPE-1 is one of the copolymers. Therefore most of its short chain branches are ethyl chains. In addition, a very small amount of long chain branches is detectable. HDPE-3 is the homopolymer corresponding to HDPE-1 and is almost completely linear. The spectrum shows a few butyl and amyl short chain branches. The number of methyl short chain branches

3) LDPE: Lupolen 1810 H from BASF Aktiengesellschaft, Ludwigshafen am Rhein, Germany

is nearly negligible. No spectrum was taken for the second copolymer HDPE-2. Compared with HDPE-1 the concentration of butene-1 during polymerization was less for HDPE-2. Therefore, the branching structure of HDPE-2 is between that of HDPE-1 and -3. HDPE-4 has a small amount of methyl, ethyl, butyl, and amyl short chain branches. No long chain branches are detectable for HDPE-4 as well as for HDPE-3. As far as the concentrations of methyl groups are concerned the IR data of Table 1 support the qualitative conclusions from the C-13-NMR spectra: HDPE-1 and -2 contain more short chain branches than HDPE-3 and -4.

EXPERIMENTAL

In order to achieve very large elongations with melts of HDPE the rotary clamp technique described in [6] had to be modified. In addition a special extrusion and cooling procedure was installed in order to prepare the samples. Experimental details are given elsewhere [7].

The elongational tests were performed with constant strain rates $\dot{\varepsilon}_0$. $\dot{\varepsilon}_0$ is the $\dot{\varepsilon}_{11}$ component of the strain rate tensor

$$\underline{\underline{\dot{\varepsilon}}} = \frac{1}{2} \{\nabla \underline{v} + (\nabla \underline{v})^T\} \tag{1}$$

$\underline{v}$ represents the velocity field. $\nabla \underline{v}$ is the velocity gradient and $(\nabla \underline{v})^T$ its transpose. The cross sectional area $q(t)$ of the sample is reduced during such a test according to

$$q(t) = q_0 \exp (-\dot{\varepsilon}_0 t). \tag{2}$$

q_0 is the initial cross sectional area. From the recorded force $F(t)$ acting on the sample, we obtain the transient elongational viscosity

$$\mu(t) = \frac{\sigma(t)}{\dot{\varepsilon}_0} = \frac{F(t)}{\dot{\varepsilon}_0 q(t)}, \tag{3},$$

where $\sigma = F/q$ is the tensile stress.

In order to control the test performance (homogeneity of the deformation and error of the true strain rate), quality parameters for each individual test were determined [6].

RESULTS

In Figure 3 the elongational viscosities $\mu(t)$ of HDPE-1 and HDPE-4 are plotted in double logarithmic scales for several constant strain rates $\dot{\varepsilon}_0$. The test temperature was 170°C for HDPE-1 and 150°C for HDPE-4. For comparison, in this figure the three-fold of the linear viscoelastic shear viscosities $\eta(t)$ is also included. The $3\eta(t)$-curves correspond to the linear viscoelastic elongational viscosities $\mu(t)$. $\eta(t)$ was measured in a sandwich-type shear rheometer at constant shear rates $\dot{\gamma}_0 = 0.001$ or 0.0015 s^{-1}.
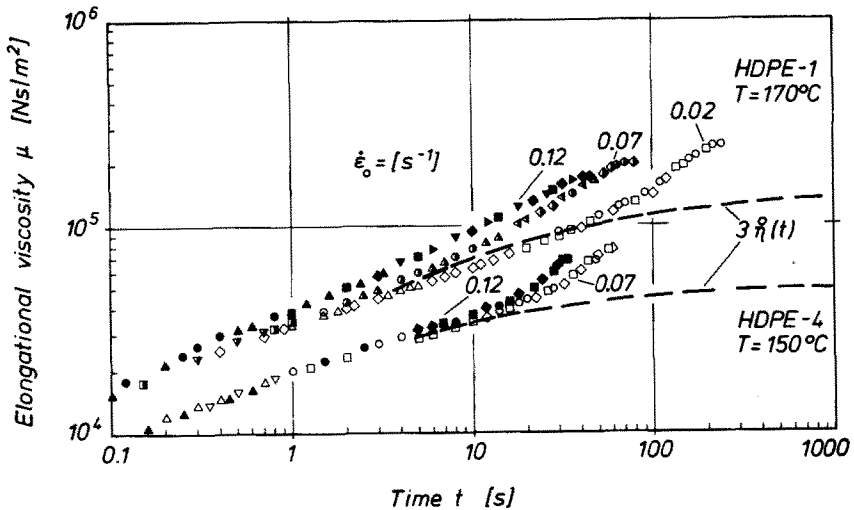
Figure 3: Elongational viscosity $\mu(t)$ of HDPE-1 at $170°C$ for different strain rates ($\dot{\varepsilon}_O$ = 0.02, 0.07, and 0.12 s^{-1}) and of HDPE-4 at $150°C$ ($\dot{\varepsilon}_O$ = 0.07 and 0.12 s^{-1}); comparison with tne linear viscoelastic response $3\eta(t)$

For HDPE-4 and small elongations, i.e. short times, all the measured elongational viscosities fall together with $3\overset{O}{\eta}(t)$, i.e. in this range of deformation the material behaves linear viscoelastic. At larger elongations ($\varepsilon > 1$) HDPE-4 shows an increase of $\mu(t)$ above $3\overset{O}{\eta}(t)$. This strain hardening phenomenon is well known for branched polyethylene, and it
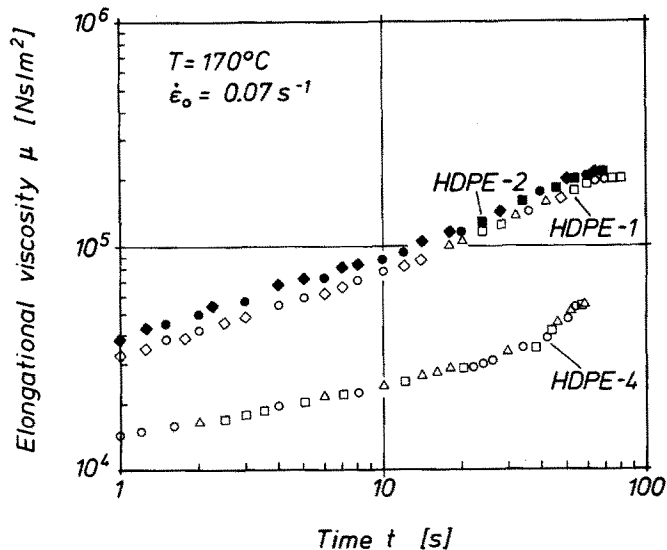
Figure 4: Elongational viscosity $\mu(t)$ of HDPE-1, HDPE-2, and HDPE-4 at $170°C$ for $\dot{\varepsilon}_O$ = 0.07 s^{-1}

appears in a less pronounced manner for all the linear polyethylene melts we investigated so far. For HDPE-1 the agreement of $\mu(t)$ and $3\overset{o}{\eta}(t)$ exists only in a much shorter range of elongations, but the curves have a smaller slope at higher deformations.

The different strain hardening of the HDPE-melts is better illustrated in Figures 4 and 5. In both diagrams the strain rate is $\dot{\varepsilon}_0 = 0.07$ s⁻¹. The steepest slope of these curves after the linear viscoelastic growth occurs at a strain $\varepsilon = 3$. Therefore, we define as a strain hardening parameter the derivative $d\log\mu/d\log\varepsilon$ at $\varepsilon = 3$. The resulting data are given in Table 3.
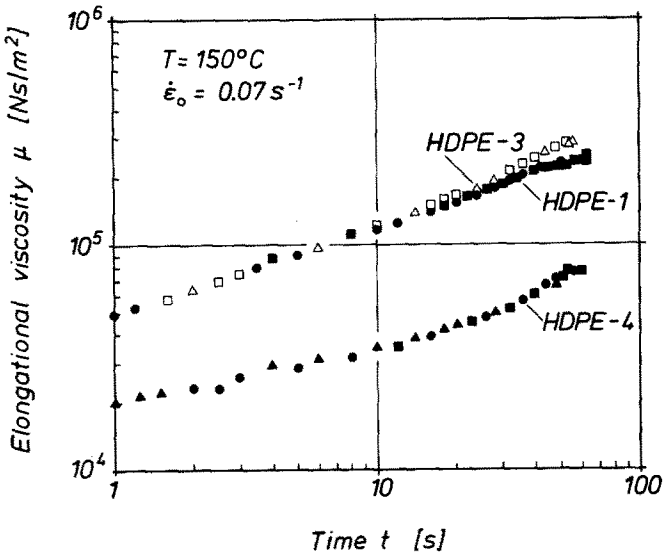

Figure 5: Elongational viscosity $\mu(t)$ of HDPE-1, HDPE-3, and HDPE-4 at 150°C for $\dot{\varepsilon}_0 = 0.07$ s⁻¹

Short chain branches do not seem to enhance the strain hardening of HDPE. The homopolymer samples show a steeper rise above $3\overset{o}{\eta}(t)$ than the copolymer samples: The curves for HDPE-1 and -3 coincide under the same conditions up to $\varepsilon \approx 0.85$, after which the homopolymer HDPE-3 increases more than the copolymer HDPE-1 (Figure 5). The differences in strain hardening may be connected with the differences in the molecular weight

Table 3: Strain hardening parameter $d\log\mu/d\log\varepsilon$ ($\varepsilon = 3$)		
Material	T = 150°C	T = 170°C
HDPE-1	0.16	0.41
HDPE-2		0.49
HDPE-3	0.52	
HDPE-4	0.62	1.11

distributions: The steepest increase is shown by HDPE-3 and -4, which have more long molecules than HDPE-1 and -2. The fact that a few long linear molecules have a pronounced effect on the elongational behaviour of polymer melts has already been assumed for polystyrene [8,9]. The results presented in this paper with samples of a known branching structure support this conclusion, because HDPE-3 and -4 certainly have no long chain branches.

For HDPE-1 and HDPE-4 there is more strain hardening at 170°C than at 150°C (Figure 6, Table 3). This fact refutes the possible hypothesis that a crystallization is induced by the extension of a molten polymeric material that is semi-crystalline in the solid state. A conclusive explanation for this unexpected behaviour cannot be given presently.
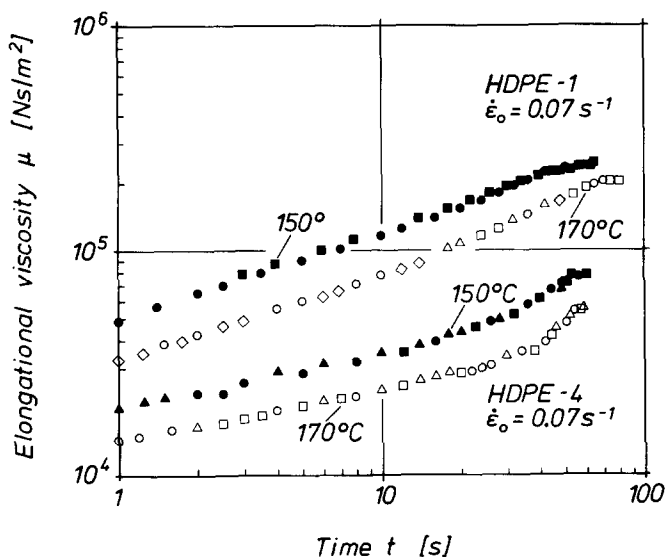

Figure 6: Elongational behaviour of HDPE-1 and HDPE-4 at 150 and 170°C for $\dot{\varepsilon}_o$ = 0.07 s^{-1}

At the maximum strains investigated, the elongational viscosities reach constant equilibrium values. Whether they correspond to a true steady state or to a maximum in the elongational viscosities, as demonstrated for LDPE [10], cannot be decided because of the still limited range of total elongations. Larger elongations could not be achieved, because the samples became inhomogeneous above the maximum elongations shown.

CONCLUSIONS

1) The difficult preparation of homogeneous and isotropic samples and the occurence of inhomogeneities during deformation are responsible for the few data in the literature concerning the melt elongational behaviour of linear polyethylene. By means of experimental improvements we could achieve, for the first time, homogeneous elongations up to ε = 5.6 (λ = 270) for melts of linear polyethylene.

2) The investigated HDPE melts exhibit strain hardening outside the linear viscoelastic region: The measured elongational viscosities exceed the linear curves, which had been obtained in shear at sufficiently small shear rates. The strain hardening of HDPE is, however, less pronounced than the strain hardening found for LDPE by other authors.

3) From previous investigations with LDPE, it was concluded that long chain branches lead to strain hardening. The present results given for HDPE indicate that also a small amount of very long, linear molecules in the molecular weight distribution of polymers with no or almost no long chain branches leads to the same phenomenon.

4) Short chain branches have no enhancing influence on the strain hardening of HDPE melts.

5) The strain hardening of linear polyethylene is more evident at 170°C than at 150°C. This fact is in contradiction to the assumption that the melt starts to crystallize due to extension.

6) At large deformations, up to the strains investigated, the HDPE melts reach constant viscosity values.

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