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The influence of various deformation histories on elongational properties of low density polyethylene^{*})

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Summary

The elongational viscosity of low density polyethylenes depends on the mechanical history as is demonstrated on the samples IUPAC A and IUPAC C and some other specimens. IUPAC C which stems from the same batch as IUPAC A but has undergone an additional extrusion shows a significantly lower elongational viscosity whereas the shear viscosity remains nearly unchanged. The elastic behaviour measured by the recoverable strain is not influenced by a mechanical pretreatment. The viscosity decrease is found to be canceled to its greatest extent after dissolving the sample in xylene and evaporating the solvent. Pure elongation seems to be more effective in creating the viscosity decrease than pure shear. A similar effect could not be found for linear polyethylene and polystyrene. This result leads to the assumption that the branched molecules give rise to a mechanically induced change of the entanglement structure which can be reverted by dissolving. The evidence of the elongational behaviour for film blowing is discussed.

Zusammenfassung

Die Dehnviskosität von Polyäthylenen niedriger Dichte hängt von der mechanischen Vorgeschichte ab, wie an den Proben IUPAC A und IUPAC C und einigen anderen Produkten gezeigt wird. IUPAC C, das aus der gleichen Charge wie IUPAC A stammt, aber einer zusätzlichen Extrusion unterworfen wurde, zeigt eine deutlich niedrigere Dehnviskosität, während die Scherviskosität nahezu unverändert bleibt. Das über die reversible Dehnung gemessene elastische Verhalten wird durch eine mechanische Vorbehandlung nicht beeinflusst. Die Viskositätsabnahme kann nahezu vollständig rückgängig gemacht werden durch Auflösen der Probe in Xylol. Dehnung scheint eine effektivere Viskositätsabnahme zu bewirken als Scherung. Ähnliche Effekte einer mechanischen Vorgeschichte konnten für lineares Polyethylen und Polystyrol nicht gefunden werden. Dieses Ergebnis legt die Annahme nahe, daß die Verzweigungen zu einer mechanisch induzierten Veränderung der Verhakungsstruktur führen können, die reversibel ist. Die Bedeutung des Dehnverhaltens für das Folienblasen wird diskutiert.

Key words

Low density polyethylene, elongational properties, deformation histories, film blowing.

I. Introduction

It has been published recently that a previous deformation applied by means of an extruder or a Brabender plastograph changes the extrudate swell of low density polyethylenes reversibly (1). In parallel, end-use properties like the transparency of blown films are improved (2). A similar effect on the extrudate swell has been observed on polyacetale (3) and on an amorphous ethylene-vinylacetate copolymer (4).

Because of the increasing number of publications on the influence of a deformation history on rheological and end-use properties of polymer melts it seems a valuable contribution to this topic to disclose that the two very similar low density polyethylenes IUPAC A and IUPAC C investigated by the IUPAC Working Party on Structure and Properties of Commercial Polymers (cf. (5)) are distinguished from each other by the fact that IUPAC C, stemming from the same batch as IUPAC A has undergone a particular mechanical treatment. Similar to the LDPE samples in (2), the mechanical pretreatment leads to an improved transparency of the blown films and, in addition, to a higher draw-down ratio and following from that a smaller film thickness (5). The comprehensive rheological characterization of the LDPE IUPAC A and IUPAC C points to two rheological quantities which showed up differences for the two samples identical from a molecular point of view. The first normal stress differences for IUPAC A were somewhat higher than those for IUPAC C and the stress-strain

^{*}) Dedicated to Professor Dr. Reif on the occasion of his 60th birthday.

behaviour in elongation showed some indication of a lower tensile stress for IUPAC C (5). These results from the literature give strong evidence that besides molecular quantities some other structural parameters may influence the flow behaviour of polymer melts.

The aim of this paper is to demonstrate that LDPE melts can be changed gradually by an increasing mechanical treatment, that this process is reversible to a great deal, and that elongational measurements are a very sensitive tool for investigating this effect.

II. Experimental

The experiments were carried out using the extensional rheometer described in (6) which offers the possibility to perform elongational measurements at constant tensile stresses σ_0 (creep tests) or constant strain rates $\dot{\epsilon}_0$ on a small amount of material. In the creep test the Hencky strain

$$\epsilon = \ln (l/l_0) \quad [1]$$

is recorded as a function of time (l_0 initial sample length, l actual sample length), in the constant strain-rate experiment the stress σ is measured. From the steady state of either experiment the steady-state elongational viscosity

$$\mu_s = \frac{\sigma_0}{\dot{\epsilon}_0} \quad [2]$$

is calculated.

At any state of elongation the recoverable strain

$$\epsilon_r = \ln (l/l_r) \quad [3]$$

can be determined by setting σ equal zero (l_r sample length after total recovery).

different from that of the samples of table 1, however. The different mechanical pretreatments are listed in table 1. The notation "viscometer" means that the samples were extruded at low shear rates using a nitrogen-driven capillary viscometer, "extruder" indicates the sample preparation by means of a laboratory extruder. The remark "pelletized" includes an extruding process necessary for obtaining the strands for pellets, "refined" describes a strong mechanical deformation applied to the melt before pelletizing.

The subscript "d" of some symbols indicates that the measurements were carried out on specimens previously dissolved in xylene and carefully extruded at low shear rates by means of a capillary viscometer after the evaporation of the solvent¹).

IV. Dependence of the steady-state elongational viscosity on deformation history

Figure 1 shows typical creep curves of LDPE 1, LDPE 2, and LDPE 4 at a tensile stress of $\sigma_0 = 3.1 \times 10^4$ Pa and a temperature of 125 °C. Taken from the same bath, they are distinguished by the different mechanical treatments listed in table 1. The three samples were elongated up to a total strain of $\epsilon = 3.6$ that means a stretching ratio of $\lambda = 36$. After a region with decreasing strain rate $\dot{\epsilon}$ a steady state of elongation is reached where $\dot{\epsilon}$ is constant.

Although the zero-shear-rate viscosity of LDPE 1 is only 10% higher than that of LDPE 4 their stretching behaviour shows remarkable differences. LDPE 4 which has undergone the strongest mechanical treatment (see table 1) elongates much more easily than LDPE 1. The extrusion of LDPE 1 through a laboratory

Table 1. Elongational viscosity μ_s and recoverable strain $\epsilon_{r,s}$ in the steady state for LDPE samples of different mechanical histories before and after dissolving (Tensile stress $\sigma_0 = 2 \times 10^4$ Pa, temperature $T = 125$ °C)

Sample	Mechanical pretreatment	$\epsilon_{r,s}$	μ_s [10^6 Pa s]	Dissolved in xylene		
				μ_{sd} [10^6 Pa s]	$\epsilon_{r,sd}$	μ_{sd}/μ_s
LDPE 1	pelletized, viscometer	1.41	3.1	3.5	1.41	1.13
LDPE 2	pelletized, extruder	1.37	2.2	3.3	1.41	1.50
LDPE 3	refined, pelletized, viscometer	1.42	2.3	3.1	1.47	1.35
LDPE 4	refined, pelletized, extruder	1.41	1.9	3.2	1.43	1.68
LDPE 5	refined, pelletized, viscometer	1.42	1.9	2.6	1.42	1.37
LDPE 6	pelletized, viscometer	1.24	1.0	1.1	1.29	1.10

III. Sample preparation

All the samples investigated have been prepared from low density polyethylenes of the density 0.918 g/cm³ at ambient temperature. The specimens LDPE 1 to LDPE 4 in table 1 have been taken from the same batch. LDPE 1 is identical with IUPAC A, LDPE 3 with IUPAC C. Similar, LDPE 7 to LDPE 10 in table 3 stem from the same batch which is

¹) The polyethylene samples were dissolved in xylene of 100°C. Most of the solvent evaporates during 16 hours at ambient temperature. The final drying is carried out at 100°C over 2.5 hours in a vacuum oven. The zero-shear-rate viscosity of the previously dissolved samples is within the accuracy of the measurements of $\pm 3\%$ the same as that of the original material. This result indicates a negligible solvent content remaining after drying.

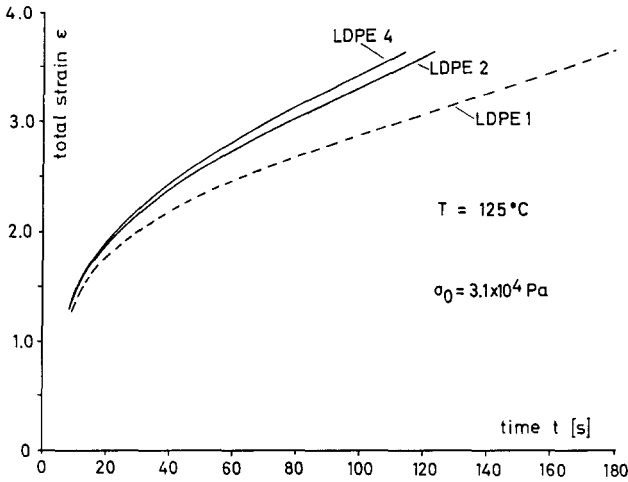


Fig. 1. Creep curves of LDPE samples with various mechanical histories

extruder instead of a capillary viscometer leads to an extensibility which reaches nearly the level of LDPE 4 (cf. the curves of LDPE 1 and LDPE 2)²⁾.

The steady-state elongational viscosities of LDPE 1, LDPE 2, and LDPE 4 according to

equation [2] are plotted versus the applied tensile stresses in figure 2. The shape of $\mu_s(\sigma_0)$ for the three samples is very much the same. From the Trouton viscosity $3 \eta_0$ at small tensile stresses the elongational viscosity increases and runs through a maximum which is about eight times higher than the stress-independent viscosity (cf. (7)). Whereas the Trouton viscosities of LDPE 1 and LDPE 4 differ only by 10%, the elongational viscosity of LDPE 1 is higher by a factor of 1.6 than that of LDPE 4 in the maximum region. These differences are much more pronounced than those found in stress-strain curves where the steady state of elongation has not been reached (5). In comparison, the viscosity functions of the two samples in shear show only small differences in the linear range but are indistinguishable in the nonlinear range of deformation (cf. fig. 2).

This result demonstrates that the steady-state elongational viscosity reacts very sensitively on a previous mechanical treatment of the LDPE sample which was the modest one in the case of LDPE 1 and the strongest in the case of LDPE 4 (cf. table 1).

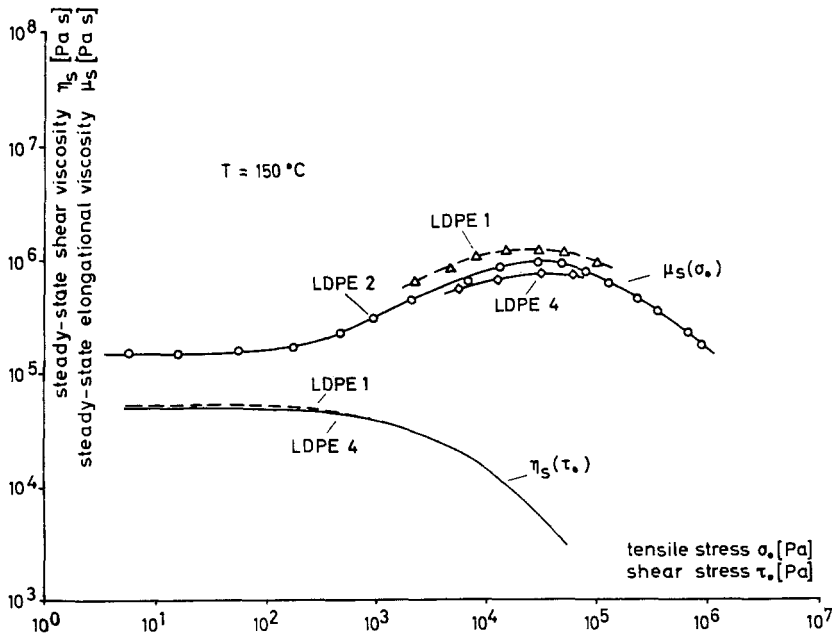


Fig. 2. Steady-state elongational viscosities of LDPE with various mechanical histories

²⁾ A thermal degradation as the source of the decreasing elongational viscosity can be excluded because of the only

faint change of the zero-shear-rate viscosity which reacts very sensitively on alterations of the weight average molecular weight.

Because of the good reproducibility of the results, in a more detailed investigation of the influence of a deformation history on the elongational properties of LDPE, measurements were carried out at one tensile stress of $\sigma_o = 2 \times 10^4$ Pa, only. The data in the fourth column of table 1 describe once more the findings represented in figure 1 and figure 2. In addition, it comes out that the sample preparation of the refined LDPE in the laboratory extruder i. e. a further mechanical treatment diminishes the elongational viscosity by another 15% (cf. LDPE 3 and LDPE 4).

The proof, that this viscosity decrease is not due to a chemical change of the product, becomes obvious from the reversibility of the effects by dissolving the mechanically pretreated samples in xylene according to the procedure described in section III. The steady-state elongational viscosities measured on the dissolved and carefully extruded specimens are listed in the fifth column of table 1. The samples LDPE 2, LDPE 3, and LDPE 4 show the same viscosities within the accuracy of the measurements after the dissolving procedure. For LDPE 4 does this mean a viscosity increase of 68%. In the case of LDPE 1 a viscosity increase of 13% is observed indicating that the mechanical treatment during the pelletizing process has already imposed a measurable mechanical history on the sample.

The somewhat lower μ_{sd} of the dissolved samples LDPE 2, LDPE 3, and LDPE 4 in comparison to the dissolved LDPE 1 may be due to a slight scission of the molecule chains during the additional extrusion processes the latter three samples had to undergo. Such an interpretation is supported by the values of the zero-shear-rate viscosity which is somewhat lower for LDPE 4 with the stronger mechanical pretreatment compared with LDPE 1 (cf. fig. 2).

A reversibility of the effect of a mechanical pretreatment on the elongational viscosity by dissolving is found, too, for the two other low density polyethylenes LDPE 5 and LDPE 6 listed in table 1. The specimen LDPE 5 was pretreated in a similar way as LDPE 3, LDPE 6 similar to LDPE 1.

Despite of the differing molecular parameters particularly in the case of LDPE 6, the ratios of the viscosity after dissolving to the viscosity before dissolving correspond to those of the

samples which had undergone the similar pretreatment (see last column of table 1).

V. Dependence of the steady-state recoverable strain on mechanical pretreatment

In the third column of table 1 the recoverable strain measured at a stress of $\sigma_o = 2 \times 10^4$ Pa and a temperature of $T = 125^\circ\text{C}$ is given for the polyethylene samples exposed to different mechanical histories. Within the accuracy of the measurements which can be assumed to lie around $\pm 3\%$ an influence of the various mechanical treatments is not obvious. Dissolving the samples does not change the elasticity (compare the third and sixth column of table 1).

A first hint that a previous mechanical treatment does not influence the recoverable strain can be deduced from (5) where no differences of this quantity were found for IUPAC A and C.

VI. Elongational viscosity and recoverable strain after pure elongation and pure shear

In order to find out experimentally whether the stretching or the shear component of the mechanical pretreatment causes the reversible change of the elongational properties, LDPE 1 has been subjected to pure stretching in the tensile rheometer (6) and to pure shear in a sandwich-type rheometer³⁾.

The samples were elongated at 125°C and a strain rate of $\dot{\epsilon} = 0.2 \text{ s}^{-1}$ to stretching ratios λ of 10 and 25. The frozen elongated samples were cut into pieces and extruded once more. The elongational viscosity μ_s and the recoverable strain $\epsilon_{r,s}$ in the steady state measured at a tensile stress of $\sigma_o = 2 \times 10^4$ Pa and a temperature of 125°C are given in table 2. μ_s decreases with increasing stretching ratio which becomes particularly obvious at the higher elongation⁴⁾.

In order to generate a pure shear deformation a compression molded sheet of 1 mm thickness

³⁾ This apparatus based on a design published in (8) is particularly equipped for performing experiments at high shear rates up to $\dot{\gamma} = 500 \text{ s}^{-1}$.

⁴⁾ In order to make sure that not a small amount of silicone oil remaining on the surface of the elongated sample causes the viscosity decrease, another specimen was stretched in air using a tensile testing machine. This procedure yielded the same effect on the elongational viscosity as the predeformation in the silicone oil bath.

Table 2. Elongational viscosity μ_s and recoverable strain $\epsilon_{r,s}$ in the steady state of a low density polyethylene exposed to pure shear and pure stretching

Mechanical pretreatment	$\sigma_0 = 2 \times 10^4$ Pa, $T = 125^\circ\text{C}$ μ_s [Pa s]	$\epsilon_{r,s}$
none	3.2×10^6	1.41
$\dot{\epsilon} = 0.2 \text{ s}^{-1}$, $\lambda = 10$	2.9×10^6	1.39
$\dot{\epsilon} = 0.2 \text{ s}^{-1}$, $\lambda = 25$	2.6×10^6	1.38
compression molded 100 bar, radial flow	3.1×10^6	1.39
additional shear $\gamma \approx 20$, $\dot{\gamma} \approx 500 \text{ s}^{-1}$	3.1×10^6	1.37
compression molded 100 bar, radial flow, dissolved in xylene	3.6×10^6	1.42
pressure molded 100 bar, small shear	3.2×10^6	1.41

was deformed between two metal plates up to a total shear of $\gamma \approx 20$ at a shear rate of around $\dot{\gamma} = 500 \text{ s}^{-1}$. As can be seen from table 2, the compression-molding procedure leaves the elongational viscosity unchanged within the accuracy of the measurement. The additional shearing does not show any influence on the elongational viscosity either. Dissolving the compression-molded sample in xylene results in a higher viscosity. The value of μ_s is in good agreement with that of the dissolved LDPE 1 in table 1.

For comparison, table 2 contains μ_s for a sample which has been prepared from a material kept under the same pressure of 100 bar as the sheared sample, but in the barrel of a capillary viscometer. This procedure yields the same elongational viscosity as the compression molding.

The differences of the recoverable strains in table 2 can be regarded to lie within the experimental error.

From these results the conclusion can be drawn that the elongational component of a mechanical deformation plays a dominant role in causing a reversible change of the elongational viscosity of a LDPE melt.

VII. Discussion

Three facts concerning the influence of a mechanical pretreatment on the elongational viscosity of polymer melts have to be stated:

1. The nearly total reversibility of the described effects by dissolving the polymer points to a structural rather than a molecular change of the sample⁵.
2. The described effects seem to be restricted to branched polymers. For linear polyethylenes and for polystyrenes an influence of a mechanical pretreatment on the elongational viscosity could not be found. On the other hand, an influence of a mechanical history on viscoelasticity has been reported for a branched acetal polymer (3) and an amorphous branched ethylene-vinylacetate copolymer (4).
3. Elongation seems to be more effective than shear in causing a reversible structural change to the sample.

A discussion of these results in the light of entanglements leads to the assumption that branched molecules possess another entanglement structure than linear molecules. The stretching deformation, in particular, seems to cause a reduction of the entanglements due to branching which are able to reform in the dissolved state. A model can only be rather speculative but one could imagine that owing to the degree of stretching the branched parts become more and more orientated in line with the backbone of the molecule giving rise to a smaller extension of the molecule and following from that to a lower probability of forming entanglements. These structural changes seem to be very stable since keeping the melt at moderate temperatures and extruding it carefully at low shear rates as done during sample preparation does not extinguish the influence of the previously imposed history. A high molecular mobility present in solution and at fairly elevated melt temperatures is necessary for a structural rearrangement of the molecules.

What does remain incomprehensible, however, is the fact that such a change of the entanglement structure is much stronger reflected in the elongational than in the shear viscosity. This point may have a chance to be clarified if an explanation can be given for the

⁵ In (1) it has been reported that a heat treatment effects a similar reversibility of mechanically induced changes in viscoelasticity as dissolving. This effect could not be verified, however, with the LDPE investigated because of the cross-linking caused by the exposure of the sample to the high temperatures necessary for achieving reversibility.

totally different shape of the viscosity functions of a LDPE in shear and elongation (see fig. 2).

The particular sensitivity of the elongational viscosity to molecular changes and therewith to variations of the entanglement structure is evident from investigations of the influence of a small high molecular weight component on the elongational behaviour of polystyrenes (9) and polyethylenes (10).

The independence of the recoverable strain of a previous mechanical treatment is difficult to understand in the light of the changes in extrudate swell of about 30% reported in (1), which reflect the changing elasticity of the melt.

From (5) it comes out, however, that not only the absolute but also the relative values of the extrudate swell of IUPAC A and IUPAC C are dependent on external parameters like length to radius ratio L/R of the capillary or shear stress and shear rate. For the extrudate swell at $L/R = 0$, corresponding to the recoverable strain imposed on the sample by stretching it in the entrance region of the capillary, and for a true shear stress of $\tau_o = 10^4$ Pa which is comparable with the applied tensile stress of $\sigma_o = 2 \times 10^4$ Pa applied in the elongational experiments, a 7% higher extrudate swell of IUPAC A is found (5). This difference can be regarded to lie within the accuracy of the methods demonstrating the qualitative agreement in the case of the IUPAC low density polyethylenes between the elasticity determined from elongational experiments and extrudate swell measurements⁶⁾.

VIII. Relevance of the results to film blowing

For a correlation of the results of the elongational experiments to a processing operation like

film blowing it is essential to know whether the differences measured on the melt are still existent in the blown film material. Unfortunately, films of the samples discussed in the foregoing sections are not available. Therefore, film blowing as well as rheological experiments were performed on a LDPE similar to LDPE 1 or IUPAC A, respectively. The material mechanically pretreated in an extruder gives thinner films with less haze than the normal pelletized resin.

The results of the elongational experiments carried out similarly to those in table 1 are given in table 3. Analogous to the samples investigated before, the steady-state elongational viscosity of the refined product is smaller than that of the basic resin. The differences are not as high as for LDPE 1 and LDPE 3 in table 1. This fact could be explained by a less effective mechanical treatment. The results on the blown film material show a further decrease of the elongational viscosity probably due to the additional deformation history imposed on the melt by the extruder of the film blowing equipment. This finding means that the decrease of the elongational viscosity by refining is not reverted but magnified during the film-blowing process. Therefore, the lower pulling forces of refined LDPE products and their extensibility into thinner films can qualitatively be related to the changes of the elongational viscosity.

The recoverable strains are the same within experimental error. They do not change after dissolving in xylene according to the procedure described in section III. Dissolving leads to a significant increase of the elongational viscosity which is the most pronounced in the case of LDPE 10 with the lowest initial value. The basic

Table 3. Elongational viscosity μ_s and recoverable strain $\epsilon_{r,s}$ in the steady state of a low density polyethylene after different mechanical pretreatments (Tensile stress $\sigma_o = 2 \times 10^4$ Pa, temperature $T = 150$ °C)

Sample	Mechanical pretreatment	$\epsilon_{r,s}$	μ_s [10^5 Pa s]	Dissolved in xylene	
				μ_{sd} [10^5 Pa s]	$\epsilon_{r,sd}$
LDPE 7	pelletized, viscometer	1.36	6.6	7.4	1.36
LDPE 8	refined, pelletized, viscometer	1.34	6.2	7.0	1.36
LDPE 9	film-blown, viscometer	1.36	6.1	6.8	1.36
LDPE 10	refined, film-blown, viscometer	1.34	5.5	6.9	1.36

⁶⁾ Unfortunately, for the measurements on LDPE samples reported in (1) only very few experimental data are given. It is not clear, for example, whether equilibrium values of the extrudate swell were taken and whether the

entrance pressure losses remained the same. Both experimental conditions have to be fulfilled if one wants to compare extrudate swell data obtained under the constant loads of the used melt indexer.

resin LDPE 7 exhibits a viscosity increase after dissolving which points to the mechanical history imposed on it by pelletizing. All these observations are in parallel with the findings on the samples in table 1.

In this context it may be worth mentioning that for some deliberately taken LDPE products in parallel to a decrease of the elongational viscosity by means of a mechanical pretreatment an increase of the rate of crystallization is found (11). A great deal of this effect can be reverted by dissolving the LDPE in xylene or annealing it at temperatures above 220 °C. Despite of the obvious similarities in the elongational and crystallization behaviour of LDPE it seems questionable to relate these phenomena to the same molecular origin. Whereas the crystallization behaviour is connected with the density of heterogeneous nuclei (e. g. impurities) and homogeneous nuclei (parallel sections of the polymer chains), the viscoelasticity of a melt reflects the interaction between an ensemble of molecules (e. g. entanglement network). Up to now there is no evidence for a relation between the homogeneous nuclei and the polymer network. On the other hand, no influence of the heterogeneous nuclei on the rheological properties is known because they are generally small in size and concentration.

Furthermore, the differences in the rate of crystallization are found to disappear for the films blown from polyethylenes which have undergone various mechanical pretreatments as is shown on films of LDPE 7 and LDPE 8 (11). Contrary to these findings, the differences in the elongational viscosity are still preserved in the blown films as it is obvious from table 3.

There is another effect which supports the assumption that the different optical properties of the blown films are not connected with the crystallization behaviour. By immersion in paraffin or silicone oil the haze of thin films of

IUPAC A can significantly be reduced (5). The same result was found for the films blown from the other batch (LDPE 7). These findings point to surface roughness as the source of the different optical properties.

A surface structure is expected to be more closely related to flow properties than to the crystallization behaviour. Open remains the question, however, in which way the differences in the rheological behaviour showing up most distinctly in the elongational viscosity can count for the surface roughness.

An obvious correlation is given, however, between the extensibility of the melt and its draw-down force and the elongational viscosity.

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