Rheological Characterization of Long-chain Branched Polyethylenes and Comparison with Classical Analytical Methods

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Summary: Long-chain branched polyethylenes are still of great interest today. In some cases their characterization is not an easy task with classical analytic methods (GPC-MALLS and NMR) because of the limited sensitivity at low concentrations of long-chain branches. Rheological methods make a valuable contribution to the characterization due to their high sensitivity with respect to long-chain branches. Using rheology it was possible to get an insight into the influence of different comonomers and comonomer concentrations on the long-chain branch incorporation in LLDPE. A variation of polymerization parameters such as polymerization pressure was found to influence the rheological behavior. From these findings some conclusions with respect to the molecular structure could be drawn.

Keywords: GPC-MALLS; long-chain branch; polyethylene; shear rheology; zero shear-rate viscosity

Introduction

Rheological methods are used to span the bridge between the molecular structure (molar mass M_w, molar mass distribution, long-chain branching) and processing properties of polyethylenes. Particularly the influence of long-chain branching is a topic of actuality.

Branches are considered to be long-chain branches if their length exceeds the entanglement molar mass M_e which is approximately 1300 g/mol for polyethylene (PE).[1–3] Branches below M_e (short-chain branches) are found not to influence most rheological properties. Their relevance lies in the modification of the crystallization behavior and following from that mechanical properties.[4–9]

This paper primarily focuses on the question which additional information with respect to branching rheological measurements can provide in comparison to classical analytical measurements. Although there are various rheological quantities which react on long-chain branching only the zero shear-rate viscosity η_0 and the viscosity function $|\eta^*(\omega)|$ are regarded in this article.

Experimental

Usual Method

One of the most common methods of detecting long-chain branches is the **g**el-**p**ermeation **c**hromatography with coupled **m**ulti-**a**ngle **l**aser-**l**ight **s**cattering (GPC-MALLS). Long-chain branches cause a coil contraction in comparison to a linear molecule of the same molar mass.

Fig. 1 shows as an example the radii of gyration of two low density polyethylenes

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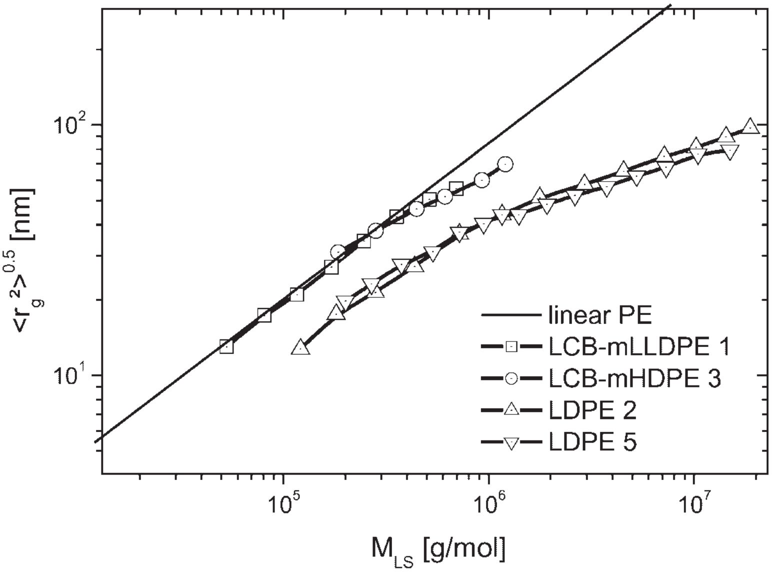

Figure 1.

Radius of gyration as a function of molar mass for two LDPEs and two long-chain branched metallocene catalyzed PEs.[10–12]

(LDPE), which significantly deviate from the linear standard at all molar masses. The typical number of long-chain branches for an LDPE is around 10 LCB/10,000 monomer.[12,13] The two long-chain branched metallocene catalyzed PEs exhibit a much smaller coil contraction which typically corresponds to around 1 LCB/10,000 monomer (Fig. 1).[14] The coil contraction for the two metallocene PE (LCB-mLLDPE 1 and LCB-mHDPE 3) is only observable for large molar masses (approximately M>300,000 g/mol). This finding is typical of lightly branched PE.[12,15,16]

Because of the reaction mechanism it is believed that LDPE has a highly branched treelike structure while LCB-mPE consists of a mixture of linear and lightly branched (star and comb) chains.[17]

Measured Rheological Quantities

The zero shear-rate viscosity η_0 follows from dynamic-mechanical experiments as

$$\eta_0 = \lim_{\omega \to 0} |\eta^*(\omega)| \qquad (1)$$

and from creep measurements as

$$\eta_0 = \lim_{t \to \infty} \frac{t}{J} \qquad (2)$$

where J is the shear compliance.

For many linear polymers the well-known correlation

$$\eta_0 = K_1 \cdot M_w^{\alpha} \qquad (3)$$

is found.[2] K_1 is a material and temperature dependent constant and α is an exponent usually found between 3.4 and 3.6 for $M_w > M_c$. M_c is the critical molar mass usually given by $2 \times M_e$. The η_0-M_w-correlation has been established for many commercially available polymers.

For metallocene catalyzed linear high density PEs (HDPEs) measured at 150 °C an exponent $\alpha = 3.6$ was established for molar masses between 3,000 and 923,000 g/mol.[18] This relationship is the base for the characterization of long-chain branches using $\eta_0(M_w)$, as for long-chain branched polymers the η_0-M_w-correlation for linear polymers is often not fulfilled. As can be seen from Fig. 2 the two LDPEs with a high amount of LCB come to lie below the η_0-M_w-line, while a low degree of long-chain

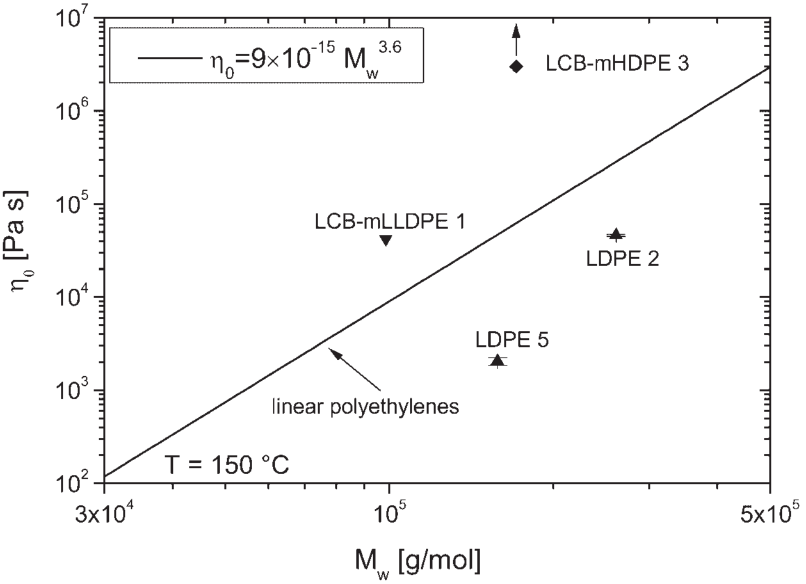

Figure 2.
Deviation of the long-chain branched PEs shown in Fig. 1 from the η_0-M_w-correlation for linear polyethylenes.[10–12]

branching, as found in the metallocene products, increases η_0 with respect to linear samples[a].

This means that the failure of the η_0-M_w-correlation for an unknown sample is a strong indication of the presence of long-chain branches. This method is used for the long-chain branch characterization in this paper.

These findings can be explained when comparing the results of the samples shown here with model star polymers which were anionically synthesized and thus are almost monodisperse in their molar mass distribution. Such sample series were published for polybutadiene[19–21], hydrated polybutadiene[22,23], polystyrene[24,25], and polyisoprene[26].

It was found for these long-chain branched polymers that a 4-arms star at low molar masses η_0 is below the η_0-M_w-correlation for linear samples. It crosses the η_0-M_w-line for linear samples at about $50 \times M_e$[b] and exceeds the zero shear-rate viscosity η_0 of the linear standard above that molar mass. This means that a short arm expected at low molar mass decreases the zero shear-rate viscosity η_0, while a long arm has the opposite effect.[10]

GPC-MALLS

Molecular characterization was carried out by means of a high temperature size exclusion chromatograph (Waters, 150 C) equipped with refractive index (RI) and additional infra-red (IR) (PolyChar, IR4) detectors. All measurements were performed at 140 °C using 1,2,4-trichlorobenzene (TCB) as solvent. The high temperature GPC was coupled with a multi-angle laser light scattering (MALLS) apparatus (Wyatt, DAWN EOS). Details of the experimental GPC-MALLS set-up and conditions of use have previously been published.[18]

Melt-State NMR

Melt-state nuclear magnetic resonance (NMR) spectroscopy was carried out on a

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[a] The zero shear-rate viscosity η_0 of LCB-mHDPE 3 could not be determined due to the long maximum relaxation time. The given value represents the highest measured viscosity η_{max}.

[b] M_e is the entanglement molar mass.

Bruker Advance 500 solid-state NMR spectrometer operating at a proton and carbon Larmor frequency of 500.13 and 125.75 MHz, respectively. The measurements were performed by K. Klimke and M. Parkinson of the Max-Planck Institute of Polymer Research in Mainz, Germany. All measurements were undertaken using a commercial Bruker, ^{13}C-^{1}H optimized, high temperature, 7 mm magic-angle spinning (MAS) probehead using zirconia rotors and rotor caps. Details of the experimental melt-state NMR set-up and conditions of use have previously been published.[27]

Shear Rheology

The rheological characterization in shear was carried out with a Bohlin CVOR "Gemini" operated at 150 °C and purged with nitrogen. Frequency sweeps in the linear-viscoelastic regime were carried out at angular frequencies between 1000 and 0.01 s^{-1}. Creep tests were used for the determination of the zero shear-rate viscosity. The description of the sample preparation, experimental set-up and methods is given elsewhere.[18]

Results

Influence of Comonomer Length and Content on Long-Chain Branching Incorporation of Long-Chain Branches into LLDPE

Sample Preparation

A set of one ethene homopolymer and 13 ethene-/α-olefin copolymers was synthesized using the catalyst system $[Ph_2C(2,7\text{-di-}^{tert}BuFlu)(Cp)]ZrCl_2$ as catalyst precursor and methylalumoxane (MAO) as cocatalyst. The chemical structure of this catalyst is given by Piel et al.[28]. Octene, Decene, Dodecene, Octadecene, and Hexacosene were used as comonomers – the latter being a waxy mixture of predominantly α-$C_{26}H_{54}$ but also small amounts of higher and lower molecular components are found in the comonomer. To our knowledge this is the longest α-olefin comonomer ever used in polyethylenes. Experimental details are published by Kaminsky et al.[29] The polymerization conditions and results of the analytic characterization are given in Table 1.

Table 1.
Properties of the polymers of the LCB-LLDPEs

sample	number n of comonomer	comonomer feed	n_c[a]	w_c[a]	M_w[d]	M_n	M_w/M_n [-]	η_o[b]
	[C_nH_{2n}]	[mol%]	[mol%]	[wt.%]	[kg/mol]	[kg/mol]		[kPa s]
F0	-	0	0.012 (<C2)/ 0.016 (>C2)[c]		173	85	2.0	445
F8A	8	10	1.1	4.3	240	112	2.1	1224
F8B	8	15	1.8	6.8	190	92	2.0	440
F8C	8	20	2.7	10.0	152	76	2.0	51
F10A	10	10	1.1	5.3	160	80	2.0	158
F10B	10	15	1.7	8.0	170	85	2.0	145
F12A	12	10	1	5.7	160	80	2.0	252
F12B	12	15	1.7	9.4	172	81	2.1	100
F18A	18	5	0.4	3.5	183	80	2.3	498
F18B	18	15	1.5	12.1	167	84	1.9	164
F18C	18	20	2.2	16.8	159	79	1.9	55
F26A	26	5	0.5	6.1	185	89	2.1	450
F26B	26	15	1.6	17.4	194	82	2.1	284
F26C	26	20	2.3	23.4	175	78	2.1	87

[a] As determined by melt-state NMR.

[b] at 150 °C.

[c] Branches >C_2 are taken to be the upper limit of the long-chain branch content (0.37 LCB/molecule, i.e. only a fraction of the chains is branched).

[d] absolute values detected by GPC-MALLS.

Analytical Characterization

The samples were characterized by melt-state NMR and GPC-MALLS.

In the case of the homopolymer F0 it was possible to determine a very small amount of branches longer than two carbons by melt-state NMR. Measuring this very small degree of long-chain branching (1.2 hexyl or longer branches per 10,000 monomers) took 2 days or 78,000 scans for a signal-to-noise ratio of 5, which illustrates the enormous experimental effort necessary for this measurement. Because no comonomer was used for this sample the branches are considered to be long-chain branches in the majority. Thus it can be concluded that a maximum of 0.37 LCB/molecule ($M_n = 85$ kg/mol) are present, i.e. approximately only every third molecule is long-chain branched. For the other samples this method of long-chain branch detection by NMR is not possible because the presence of short-chain branches masks the long-chain branch signal (See Stadler et al.[27] for an NMR-spectrum of F18C and F0).

The characterization by GPC-MALLS showed the typical polydispersity index M_w/M_n of approximately 2 for the samples (cf. Table 1). Weight-average molar masses M_w between 150 and 240 kg/mol were found.

Fig. 3 shows the radii of gyration $\langle r_g^2 \rangle^{0.5}$ (M_{LS}) of the octene series and F10B. For molar masses $M_{LS} > 300{,}000$ g/mol a significant contraction is found for this sample corresponding to a degree of branching of approximately 1 LCB/10,000 monomer, determined according to the Zimm-Stockmayer-theory[14] for trifunctional statistically distributed branching points. This value is in good agreement with the 1.2 hexyl or longer branches/10,000 monomer detected by melt-state NMR (especially when considering that it is the upper limit of the degree of long-chain branching).

By introducing comonomers the decrease of the radius of gyration becomes less pronounced. For the sample F8A the degree of branching is distinctly reduced in comparison to F0 although this sample only contains 1.1 mol% comonomer (Fig. 3). For the sample F8B the contraction is even smaller but still detectable while F8C comes to lie on the linear reference which indicates that the sample is predominantly linear.

When comparing the influence of the comonomer length on the degree of long-chain branching one will only notice very small differences between the various samples. In Fig. 3 the coil contraction is shown for F8B and F10B both having a comonomer content around 1.7 mol%. The contraction of the radius of gyration $\langle r_g^2 \rangle^{0.5}$ (M_{LS}) is similarly small for both samples although the contraction of F8B is slightly larger. The differences between the samples F8B and F10B are above the measurement uncertainty as well as the (very small) coil contraction of both samples.

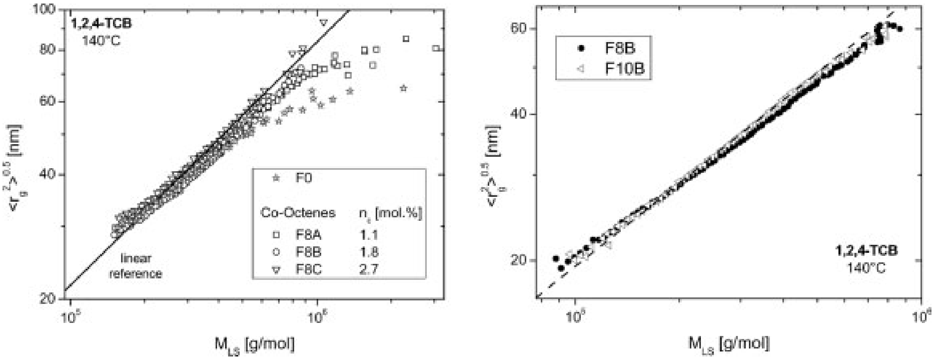

Figure 3.

Radius of gyration $\langle r_g^2 \rangle^{0.5}$ (M_{LS}) for F0 and the octene series (left) and radius of gyration $\langle r_g^2 \rangle^{0.5}$ (M_{LS}) for F8B and F10B (right).

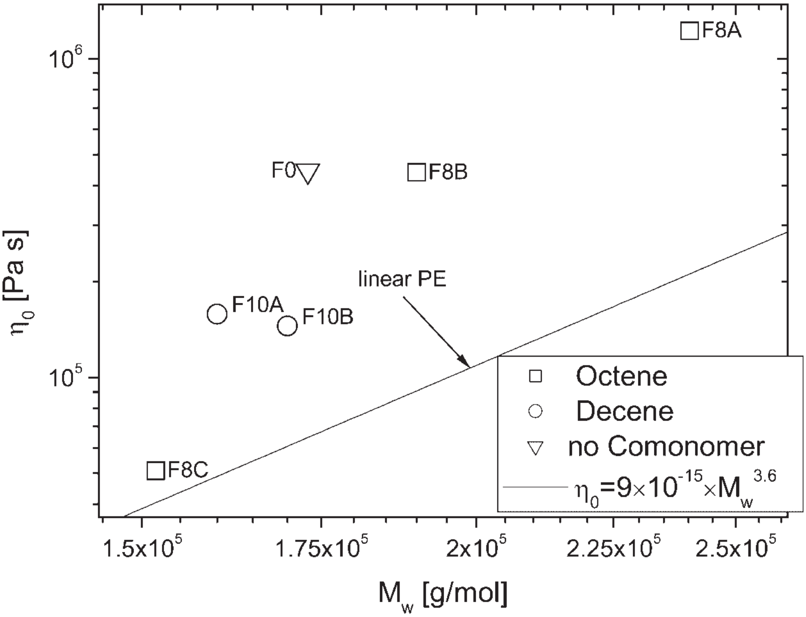

Figure 4.
Zero shear-rate viscosity and molar mass M_w for F0, F10A, F10B, F8A, F8B, and F8C.

Rheological Characterization

The zero shear-rate viscosities for the samples shown in Fig. 3 (F0, F8A, F8B, and F8C) are plotted in Fig. 4 as a function of molar mass M_w. The samples F0, F8A, and F8B show a very distinct deviation from the η_0-M_w-correlation established for linear PE[18]. The sample F8C is only slightly above the correlation. Thus it can be concluded that F0, F8A, and F8B contain a sizable amount of long-chain branches while F8C is predominantly linear.

However, as can be seen from this figure the molar masses M_w of the samples are quite different thus a direct comparison is difficult. Therefore, the zero shear-rate viscosity of a linear polymer of equal weight-average molar mass η_0^{lin} is defined which is calculated from M_w[c]. The ratio of η_0/η_0^{lin}, called zero shear-rate viscosity increase, is used for a further analysis.

The zero shear-rate viscosity increase η_0/η_0^{lin} is plotted in Fig. 5 as a function of the comonomer content. The homopolymer F0 has the highest zero shear-rate viscosity increase η_0/η_0^{lin} while the values of the co-octenes decrease as a function of comonomer content n_c. For the sample F8C with the highest comonomer content no distinct deviation from the η_0-M_w-correlation was found thus the value of η_0/η_0^{lin} is close to 1. The introduction of longer comonomer leads to a decrease of η_0/η_0^{lin} at even lower comonomer contents but surprisingly no dependence of the length of the comonomer was found for the comonomers decene, dodecene, octadecene, and hexacosene although the length of the corresponding short-chain branches varies between 8 and 24 C. For these longer comonomers it was found that approximately 2.5 mol% comonomer are sufficient to completely suppress the formation of long-chain branches under the chosen synthesis conditions. This finding is in accordance to the GPC-MALLS-measurement.

The sensitivity of rheological measurements is best demonstrated for the samples F8B and F10B (marked by arrows). The radii of gyration of F8B are smaller than the corresponding ones of F10B by less than

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[c] Because of the error in determining M_w ($\pm$5%) and the high exponent α (3.6) the error of η_0^{lin} is $\pm$20%.

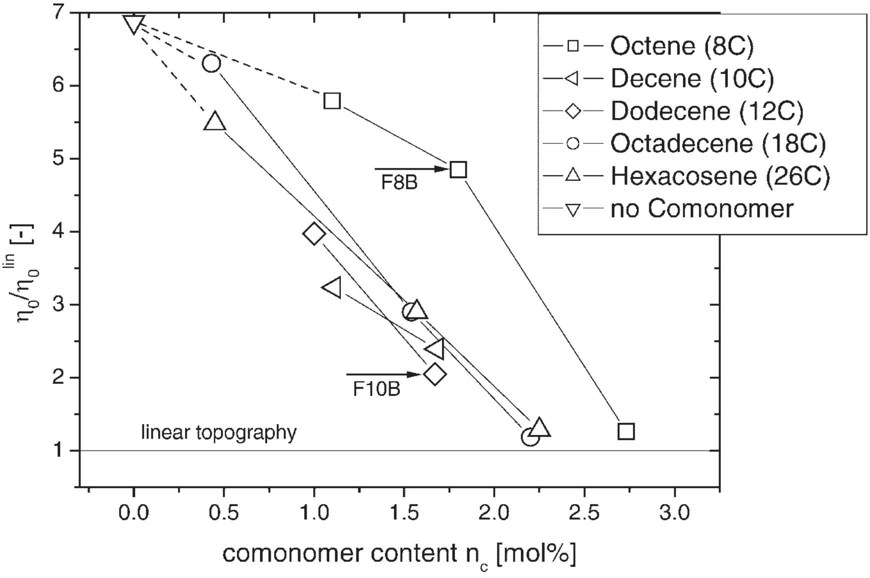

Figure 5.
Ratio of zero shear-rate viscosity η_0/η_0^{lin} as a function of comonomer feed and content, respectively. The approximate experimental error of η_0/η_0^{lin} is about ±20% (shown for octene series) assuming ±5% error in M_w.[27]

5% (cf. Fig. 3). The difference in η_0/η_0^{lin} between these samples attains a factor of almost 2.5.

Discussion

The differences found for samples with different comonomer lengths and contents are attributed to the sterical hindrance of the comonomer incorporated into the chain close to the vinyl chain end.[30] It is well established that the probability of chain termination is much higher than for ethene when incorporating a longer comonomer. This means that the probability of terminal vinyl sterically hindered by a short-chain branch is much higher than expected from the comonomer content.[31] As the macromers incorporated as long-chain branches are vinyl terminated chains the sterical obstruction of a certain fraction of the macromers by terminal short-chain branches leads to a decrease of the long-chain branch content.[30,31] These findings are explained in more detail elsewhere.[27]

Influence of Polymerization Pressure

Sample Preparation

A set of three ethene homopolymers was synthesized at various pressures using the catalyst system *rac*-$[Et(Ind)_2]ZrCl_2$ as precursor and methylalumoxane (MAO) as cocatalyst. The chemical structure of this catalyst is given by Piel et al.[28] The samples were synthesized at a temperature of 75 °C without hydrogen for molar mass control. The monomer pressure was 1, 3, and 5 bar, corresponding to 0.07, 0.22, and 0.37 mol/l ethene. Further experimental details are given by Piel et al.[28]

Analytical Characterization

The molar mass distribution of the samples synthesized under a pressure of 3 (B7) and 5 bar (B8) is found to have the typical shape for a metallocene catalyzed sample ($M_w/M_n \approx 2$) while the sample synthesized with 1 bar ethene (B6) shows a distinct high molecular tailing resulting in a higher M_w/M_n of 2.5. The weight average molar mass M_w increases from 69 kg/mol for the sample synthesized with 5 bar (B8) to

Table 2.
Molecular and rheological data of the samples polymerized at different pressures.

	monomer pressure	M_w	M_w/M_n [-]	LCB/10,000 Monomers	η_0 at 150 °C	η_0/η_0^{lin} [-]
	[bar]	[kg/mol]			[Pa s]	
B6	1 bar	106	2.5	5	$\gg$1,000,000	$\gg$200
B7	3 bar	76	1.8	n. d.	40,500	12
B8	5 bar	69	2.0	n. d.	11,600	4.9

n.d. - not detectable.

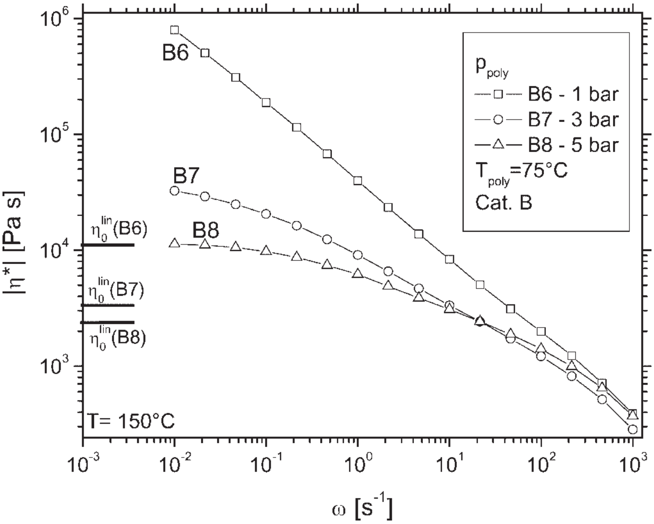

Figure 6.
Viscosity functions of the samples B6, B7, and B8.

106 kg/mol for the sample synthesized with 1 bar monomer pressure (cf. Table 2).

From the contraction of the radii of gyration approximately 5 LCB/10,000 monomers were found for B6 (1 bar) applying the Zimm-Stockmayer-theory.[14] For the other samples it was not possible to determine a degree of branching due to the low molar mass of these samples[d]. The GPC-MALLS data of these samples were published by Piel et al.[28]

Rheological Characterization

The viscosity functions of the three samples which are of completely different shape are given in Fig. 6. The zero shear-rate viscosity of a linear sample of equal molar mass η_0^{lin} is marked for all samples. It is obvious that for all samples the viscosity at $\omega = 0.01\ s^{-1}$ is much higher than η_0^{lin} indicating the presence of long-chain branches. While for B8 (5 bar) the zero shear-rate viscosity η_0 of 11,600 Pas is almost reached by the oscillatory test, for B7 (3 bar) the use of a creep test is necessary for the determination of $\eta_0 = 40{,}500$ Pas. For the sample B6 (1 bar) no indication of the terminal regime is evident not even at the lowest frequencies indicating that much lower frequencies would have to be applied for reaching η_0. However, it can be stated from Fig. 6 that η_0 of B6 must be much higher than 10^6 Pas which lies distinctly above the zero shear-rate viscosity η_0 of B7 ($\eta_0 = 40{,}500$ Pas).

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[d] The MALLS is operated at a wavelength of the laser of 623 nm, thus measuring radii of gyration below 20 nm is not possible, which corresponds to about 100 kg/mol for PE.

This means that the decrease of the polymerization pressure from 5 to 1 bar increases η_0 by a factor of more than 100 although only a factor of 4 would be expected from the change in M_w. From this result the conclusions can be drawn that the sample polymerized at 1 bar contains long-chain branches which are very effective with respect to η_0.

This underlines the very high sensitivity of rheological measurements on the detection branching.

Discussion

The increase in zero shear-rate viscosity η_0 with decreasing pressure can be understood by the following considerations: A smaller monomer pressure means a lower monomer concentration. Thus the ratio of the monomer to the macromer concentration becomes the smaller the lower the pressure and, therefore, the more probable is the macromer insertion resulting a higher molar M_w. Besides that a high molecular weight tail containing a lot of branches is formed.[28] Kokko et al.[32] also found high molecular tails or even bimodal MMDs for PE-samples copolymerized with α,ω-dienes which cause a much higher degree of branching in comparison to homopolymerizations.

These long chains have very long relaxation times thus the zero shear-rate viscosity becomes very high (see also Gabriel et al.[11]).

Conclusions

In comparison to classical analytical methods the rheological measurements can detect very minute differences in the material behavior. It is obvious, however, that the elucidation of the molecular structure requires both classical analytical and rheological measurements as they complement each other. Besides concentration the effect of long-chain branches with respect to rheological measurements increases with their length[28], while the signals of NMR-measurements are not dependent on the length of a long-chain branch for lengths above a certain threshold.[14] The detection of very low amounts of long-chain branches by GPC-MALLS is limited by the resolution of the apparatus. Rheological measurements, however, are able to detect even very small LCB-concentrations because of their distinct effect on different rheological quantities (η_0 and strain hardening). This is caused by the fundamental differences between the molecular mobilities of linear and long-chain branched chains.

Rheological measurements alone have the setback that the influence of different molecular parameters like molar mass distribution or long-chain branching can have the same effect on rheological properties. For example, long molecules in a narrow molar mass distribution can create the same rheological behavior in elongation as long-chain branches. To rule out these ambiguities the knowledge of the molar mass distribution is required.

The combination of GPC-MALLS (absolute value of M_w) and shear rheological measurements (zero shear-rate viscosity η_0) can be considered to be the most sensitive way of detecting even very small amounts of long-chain branches. The GPC-MALLS has the advantage to give some information on the radius of gyration as a function of the molar masses of the various molecules of a sample and following from that an insight into the branching architecture by using adequate methods.[14,33]

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