Thermorheological Behavior of Various Long-Chain Branched Polyethylenes

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Received October 24, 2007; Revised Manuscript Received December 4, 2007

ABSTRACT: To analyze the thermorheological behavior of various polyethylenes, the relaxation spectra were shifted. Not only linear and short-chain branched PE but also the classical high-pressure LDPE were found to be thermorheologically simple, i.e., the activation energy E_a is independent of the relaxation strength or the relaxation time, respectively. However, for the long-chain branched metallocene catalyzed polyethylenes investigated a significant dependence of the activation energy E_a on the relaxation time is detected. At shorter relaxation times E_a is very close to that of linear PE, but it increases with longer times. The lower E_a values are assumed to be due to linear molecules and the higher ones to different species of long-chain branched molecules. These findings offer the possibility to use the analysis of the thermorheological complexity to get an insight into the branching structure of polyethylenes. For the LCB−mPE investigated, it can be concluded that they are a mixture of linear and long-chain branched chains.

Introduction

The thermorheological behavior of melts has been an important issue since the use of polymers as engineering material. Besides its obvious practical relevance for processing, the thermorheological complexity offers the potential of a tool to gain an insight into the molecular structure of polymers.

For linear and short-chain branched PE a thermorheological simplicity was found, which means that rheological data determined at different temperatures can be shifted onto each other with respect to time to form a master curve. In such a case the temperature dependence of the shift factors $a_T(T, T_0)$ for PE follows an Arrhenius-type dependence:

$$a_\mathrm{T}\,(T, T_0) = \exp\left(\frac{E_a}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \qquad (1)$$

where E_a is the activation energy, R is the universal gas constant, $a_T(T, T_0)$ is the shift factor, T is the temperature of the measurement, and T_0 is the reference temperature. The activation energy of linear PE is found to be between 27 and 28 kJ/mol, while slightly higher values of typically 32−34 kJ/mol are reported for linear mLLDPE.[1−7] An increase of the activation energy E_a was found with increasing short-chain branch (SCB) content.[7−9] Still higher activation energies (35−50 kJ/mol) for *long-chain branched* mPE are reported in literature.[1,4,6,8,10−14]

The insertion of *long-chain branches* into metallocene-catalyzed polyethylene (mPE) often leads to a failure of the thermorheological simplicity indicated by a shift factor, which is not independent of time or frequency. Thus, *master curves* cannot be constructed.

Van Gurp and Palmen[15] proposed the plot of the phase angle as a function of the complex modulus $\delta(|G^*|)$ as a first qualitative check for the thermorheological behavior. In the case of a thermorheologically simple fluid no temperature dependence of the function of $\delta(|G^*|)$ should occur, while a thermorheological complexity should lead to a temperature dependence of the shape of $\delta(|G^*|)$.[1,15,16]

As an alternative method for the detection of a thermorheological complexity Dealy and Larson[17] proposed, e.g., a linear plot of the “apparent master curve” of the storage modulus $G'(a_T \times \omega)$. The thermorheological complexity shows up in this plot as a systematic disagreement between the shift factors at different temperatures and different frequencies (cf. Figure 2b).

Gabriel[1] characterized the thermorheological complexity by measurements of the shift factor a_T at different values of the storage modulus G'. Wood-Adams and Costeux[7] published a similar method but measured a_T at different values of the loss modulus G'' and additionally determined the shift factor from a deconvolution of the relaxation spectrum.

The theory of rubber elasticity motivates a vertical modulus shift $b_T = \rho_0 T_0/\rho T$ with ρ and ρ_0 being the densities at the measuring temperature T and the reference temperature T_0 on the absolute temperature scale, respectively, but this shift is so small that it can hardly be measured, as pointed out in the literature.[18] Therefore, no vertical shift will be applied.

A higher activation energy E_a in comparison to linear counterparts was found for *long-chain branched* polypropylene[19] and thermoplastic fluoropolymers.[16]

The questions arising from the different thermorheological behavior are how the thermorheological complexity depends on molecular parameters and in which way such correlations could be used to get an insight into the molecular structure of polyethylenes. Therefore, polyethylenes polymerized in various ways were investigated.

Experimental Section

Characterization Methods. SEC−MALLS. Molar mass measurements were carried out by means of a high-temperature size exclusion chromatograph (Waters, 150C) equipped with refractive index (RI) and infrared (IR) (PolyChar, IR4) detectors. All measurements were performed using 1,2,4-trichlorobenzene (TCB) as the solvent at 140 °C. The high-temperature SEC was coupled with a multiangle laser light scattering (MALLS) apparatus (Wyatt,

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10.1021/ma702367a CCC: $40.75

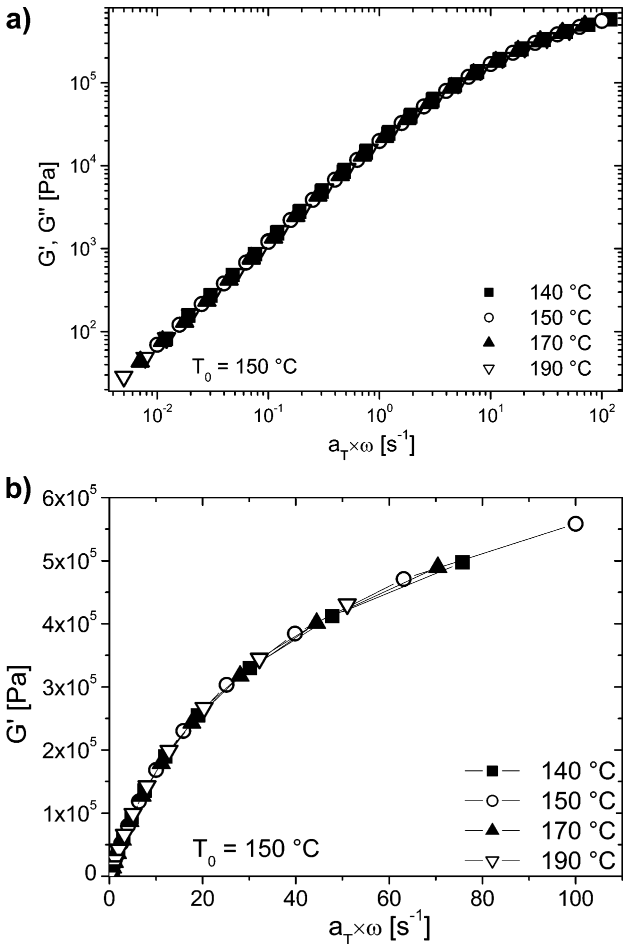

Figure 1. Master curve of the storage modulus G' as a function of the shifted frequency ($a_T \times \omega$) for the mHDPE C4 in (a) double logarithmic scaling and (b) linear scaling.

DAWN EOS). Details of the experimental SEC-MALLS setup and the measuring conditions were previously published elsewhere.[20]

Rheology. The samples were compression molded into circular disks of 25 mm in diameter and around 1 mm in height. Antioxidative stabilizers (0.5 wt % Irganox 1010 and 0.5 wt % Irgafos 38 (Ciba SC)) were added to the laboratory scale samples. More experimental details are given elsewhere.[20]

Shear rheological tests were carried out at constant temperatures in nitrogen atmosphere. Most tests were performed with a Bohlin/Malvern Gemini and a Rheometric Scientific/TA Instruments ARES. Dynamic-mechanical tests (frequency sweeps) were carried out in the linear viscoelastic regime with frequencies ω between 1000 and 0.01 s^{-1}. Oscillatory stresses $\hat{\tau}$ between 10 and 100 Pa or oscillatory strains $\hat{\gamma}$ between 2 and 10% were applied, depending on the viscosity of the sample. The thermal stability was ensured for all samples. Creep tests were performed in the linear and stationary regime. Detailed descriptions of the experimental techniques used are given elsewhere.[21−25]

Materials. Different metallocene-catalyzed linear and long-chain branched homopolymers (LCB-mHDPE) and also low-density polyethylenes (LDPE) were characterized. The synthesis of many of the samples was previously published by Piel et al.[26]

For the linear reference the mHDPE C4 was used, whose molecular and rheological data are given in Table 1. This sample has a high molecular shoulder in the molar mass distribution.

The data of the long-chain branched samples are given in Table 1, too. LDPE 1 and LDPE 2 are grades from Basell.[27−32] The content of long-chain branches (listed in column "LCB") is estimated by two different methods, described in detail elsewhere.[26] On one hand the concentration of the LCBs was estimated from the coil contraction detected by SEC−MALLS. On the other hand different rheological indicators, namely the characteristic phase angle δ_c, the zero shear-rate viscosity increase factor η_0/η_0^{lin}, and the steady-state elastic recovery compliance J_e^0 were adopted for the estimation of these quantities.[21,26,33]

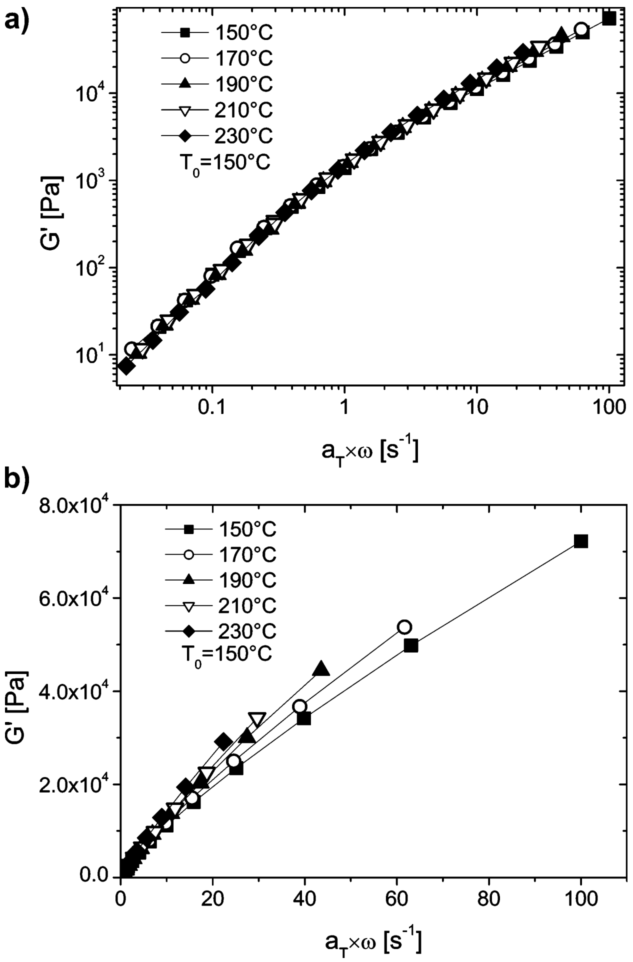

Figure 2. "Master curve" of the storage modulus G' as a function of the shifted frequency ($a_T \times \omega$) for the LCB−mHDPE B9 in (a) double logarithmic scaling and (b) linear scaling.

Results and Discussion

Time−Temperature Superposition. A qualitative distinction between various polymers can be obtained from the finding whether a polymer melt is thermorheologically simple or complex. A widely used proof for thermorheological simplicity is the attainment of a master curve by shifting $G'(\omega)$ according to Figure 1 either in a double logarithmic (Figure 1a) or a linear plot (Figure 1b). As Figure 1 clearly demonstrates the time−temperature superposition principle is valid for the linear mHDPE C4.

It was possible to find *master curves* similar to that in Figure 1 for all the linear and short-chain branched samples investigated in this article and for the two LDPEs. Master curves were also obtained for some short-chain branched samples characterized elsewhere.[9]

From Figure 2a, and particularly from the linear plot in Figure 2b, it becomes obvious that a *master curve* cannot be constructed with sufficient accuracy for the LCB−mHDPE B9. This sample, therefore, is classified as thermorheologically complex.

All the LCB−mHDPEs of Table 1 appeared to be thermorheologically complex − except for D4, whose degree of long-chain branching is very low. These findings may lead to the conclusion that long-chain branching introduced by metal-

Table 1. Rheological and Molecular Characteristics of the LCB−mHDPEs and LDPEs

type	name	M_w [kg/mol]	M_w/M_n	η_0 [Pa s] ($T = 150$ °C)	$\eta_0/\eta_0^{\mathrm{lin}}$ ($T = 150$ °C)	LCB
mHDPE	C4	224	3.0	1.1×10^5	1.0	none
LCB-mHDPE	B7	76	2.0	4.0×10^4	12.1	high
LCB-mHDPE	B8	69	2.0	1.2×10^4	4.9	medium
LCB-mHDPE	B9	66	1.8	6.3×10^3	3.1	low
LCB-mHDPE	B10	66	2.1	3.2×10^3	1.6	very low
LCB-mHDPE	B11	65	2.1	1.8×10^4	9.8	medium
LCB-mHDPE	B12	101	2.5	$\approx 2.0 \times 10^5$	≈ 17	very high
LCB-mHDPE	D4	74	2.0	4.5×10^3	1.5	very low
LDPE	LDPE 1	345	11	8.7×10^5	1.1	very high
LDPE	LDPE 2	258	7.5	5.4×10^4	0.2	very high

locene catalysts into HDPE implies a thermorheological complexity. To investigate such a supposition in more detail a representation of dynamic-mechanical data was used, which very sensitively indicates a thermorheological complexity, namely the plot of the phase angle δ as a function of the magnitude of the complex modulus $|G^*|$.

The sensitivity of this plot with respect to the temperature dependence is demonstrated in Figure 3a for the linear sample mHDPE C4 and the branched material B9. Whereas the measured points of the linear product come to lie on one curve with good accuracy, those of the long-chain branched LCB−mHDPE B9 are distinctly split up. In Figure 3b, $\delta(|G^*|)$ is represented for the statistically long-chain branched LDPE 2 in comparison to the reference curve for linear HDPE. In good approximation the curves for the different temperatures between 130 and 210 °C fall together; i.e., the LDPEs can be regarded to be thermorheologically simple.

The findings in parts a and b of Figure 3 lead to the conclusion that the occurrence of thermorheological complexity of long-chain branched polyethylenes depends on the branching architecture. This result, on the other hand, raises the question, whether it is possible to analyze the thermorheological complexity in more detail with the aim to get a deeper insight into the branching structure.

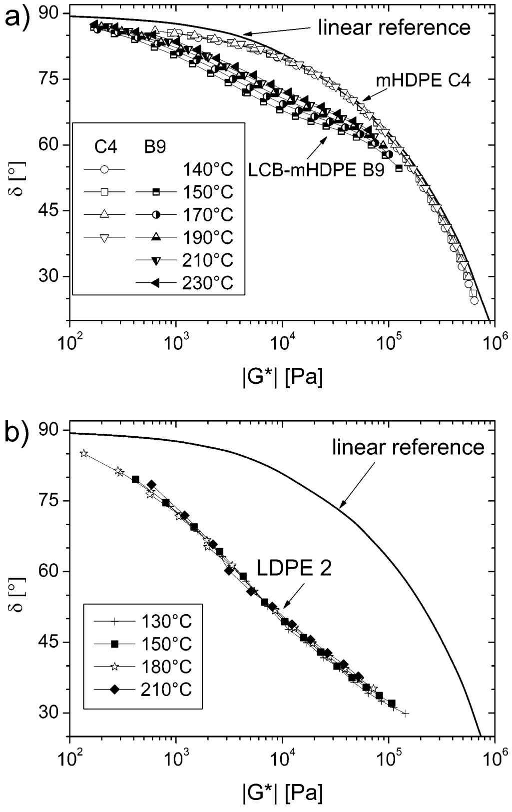

Figure 3. δ−$|G^*|$ plots of (a) mHDPE C4 and LCB−mHDPE B9 and (b) LDPE 2 at different temperatures. The linear reference was established elsewhere for linear mHDPEs.[34,35]

Table 2. Activation Energies of Some Thermorheologically Simple Polyethylenes

type	name	E_a [kJ/mol]	degree of LCB
HDPE	C1	27	none
HDPE	C2	27	none
HDPE	C4	27	none
LCB-mHDPE	D4	28	very low
LDPE	LDPE 1	65	high
LDPE	LDPE 2	57	high

One might argue that the thermorheological complexity can be eliminated by performing a modulus shift for B9 (Figure 3a). However, this cannot be done, as the shape of $\delta(|G^*|)$ changes with temperature.

Activation Energies for Various Thermorheologically Simple Polyethylenes. The plot $\delta(|G^*|)$, although very sensitive with respect to a classification of the thermorheological behavior, cannot be used, however, for a determination of the activation energy E_a according to eq 1, as this plot does not contain any time or frequency dependence.

For this purpose usually the shift of $G'(\omega)$ and $G''(\omega)$ is applied and E_a is calculated from a logarithmic plot of the shift factor a_T vs the reciprocal absolute temperature $1/T$. Results for E_a of some thermorheologically simple polyethylenes investigated are given in Table 2.

The activation energies of 27 kJ/mol found for the three linear homopolymers are in good agreement with the literature.[7−9]

The lightly branched sample LCB−mHDPE D4 basically shows the same thermorheological behavior as a linear HDPE. These results can easily be understood, as the degree of long-chain branching is so low that it does not affect the thermorheological behavior significantly enough to cause a thermorheological complexity.

The two commercial LDPE are highly branched. Their measured activation energies of around 60 kJ/mol are in good agreement with the literature, too.[1,8,25,29,32,37]

Description of Thermorheologically Complex Products. Thermorheological complexity means the failure of the time−temperature superposition principle. The physical reason behind this appearance is that not all the relaxation times are changed by the same factor anymore if the temperature is altered. For an assessment of the thermorheological complexity, it is, therefore, reasonable to analyze the temperature dependence of the spectra.

For this purpose the relaxation time spectra $g(\tau)$ of various samples were determined according to the procedure presented in detail elsewhere.[38] This method provides equidistant and smooth spectra with a rather large mode density. Figure 4 shows the spectra for two samples with two modes per decade and the corresponding splines. The splines connecting the modes

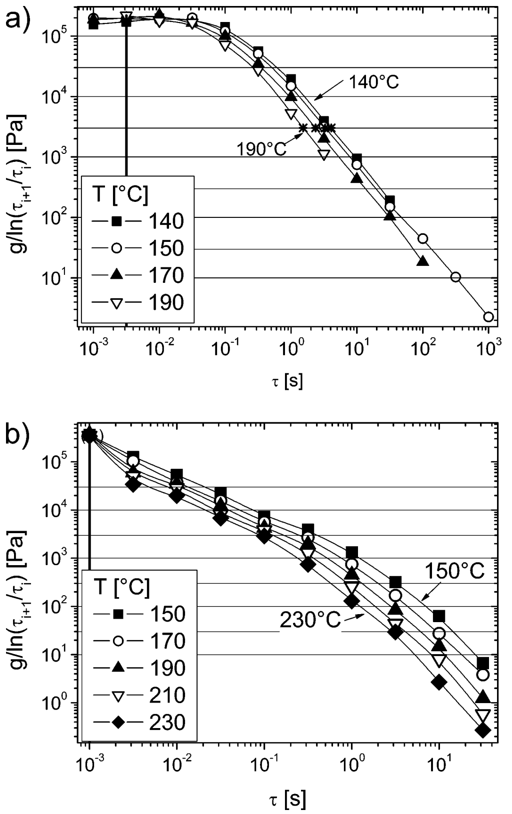

Figure 4. Plot of the relaxation spectrum $g(\tau)$ of (a) mHDPE C4 and (b) LCB−mHDPE B9 at different temperatures.

are cubic B-splines calculated by Microcal Origin. They are defined in the whole range, for which the spectrum is determined, but not for any extrapolations. The spectra shown are the averages of several data sets.

From such plots the shift factors a_T can be evaluated with respect to a constant relaxation strength g as indicated in Figure 4 by the faint lines. This is, in principle, the same method as used by Wood-Adams and Costeux[7] and Gabriel.[1] Both applied this method for $G'(\omega)$. Wood-Adams and Costeux[7] used a different method for the calculation of relaxation spectra but did not determine E_a from them.

It is obvious at a first glance that the relaxation spectra of the linear mHDPE C4 (Figure 4a) look very similar in shape, which is an indicator of thermorheological simplicity, while the spectra of the LCB−mHDPE B9 clearly diverge with increasing relaxation time τ, which means that a master curve cannot be obtained by shifting τ; i.e., this sample is thermorheologically complex.

These results become even more obvious when comparing the Arrhenius-plots of C4 and B9 (Figure 5), which can be described by

$$\tau = \tau_0(g) \exp \frac{E_a}{RT} \tag{2}$$

The relaxation times of C4 determined at different relaxation strengths show the same slope (Figure 5a) within the accuracy of the measurements. In the case of the LCB−mHDPE B9 (Figure 5b) the slopes, i.e., the activation energies, are not constant. The activation energies calculated according to eq 2 are given in Figure 6. While the slope of the mHDPE C4 (Figure 5a) varies statistically around $E_a = 27.4$ kJ/mol, the values for the LCB−mHDPE B9 increase with decreasing relaxation strength or increasing relaxation time, respectively.

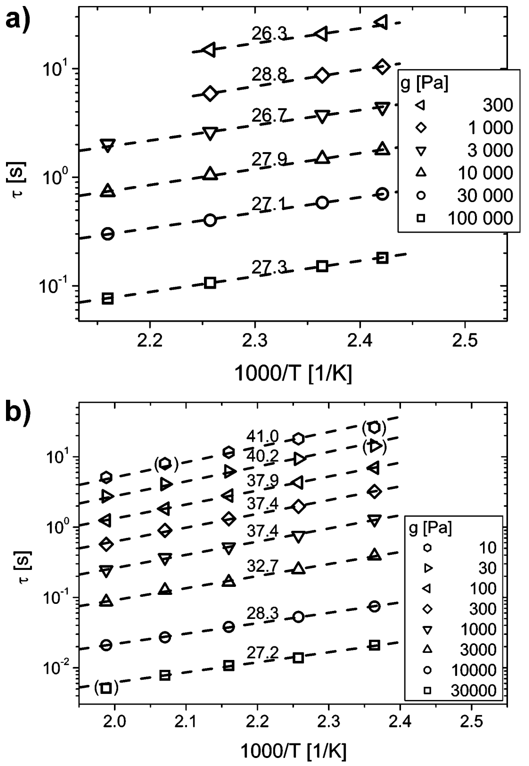

Figure 5. Arrhenius plots of mHDPE C4 (a) and LCB−mHDPE B9 (b) at different values of $g(\tau)$. The numbers give the activation energies in kJ/mol.

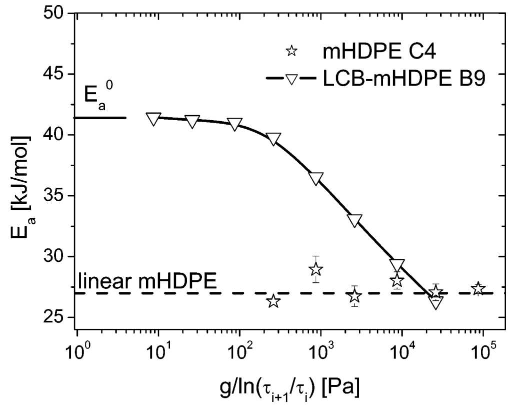

Figure 6. Activation energy E_a as a function of the relaxation strength g for the linear and the long-chain branched samples C4 and B9.

For mHDPE C4, $E_a = 27.4 \pm 0.8$ kJ/mol is found, which is in excellent agreement with the data obtained from the shift of other rheological functions for linear polyethylene homopolymers.[7−9] In the case of the branched LCB−mHDPE B9, E_a is strongly dependent on the relaxation strength g.

E_a attains a constant value at small relaxation strengths. This value is distinctly higher than that of the linear sample. E_a then decreases with growing g. The lowest E_a measured is very close to the value of the linear sample.

These results are interesting from two points of view. First, they demonstrate that determining the activation energy from the shift of relaxation spectra obtained at different temperatures is a reliable experimental method, as the activation energy found for the linear polyethylene is constant and in excellent agreement with data from literature. Second, there is a clear dependence of the activation energy on the relaxation strength for the long-chain branched PE synthesized by metallocene catalysts. This finding can be interpreted by assuming that the sample B9

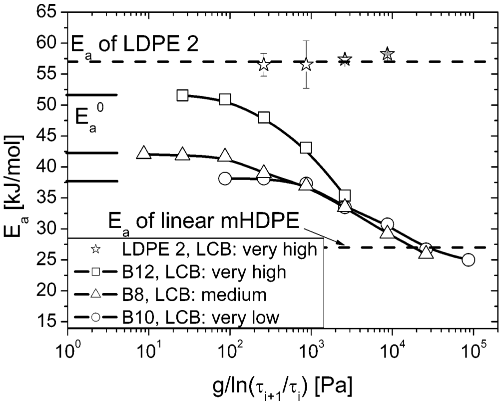

Figure 7. Activation energy E_a as a function of the relaxation strengths for LCB−mHDPEs and LDPE 2 with different degrees of long-chain branching.

Table 3. Terminal Activation Energies of All the Thermorheologically Complex Products Investigated

	M_w [kg/mol]	E_a^0 [kJ/mol]	$\eta_0/\eta_0^{lin\ a}$	long-chain branching
B10	66	38	1.6	very low
B9	66	41	3.1	low
B8	69	42	4.9	medium
B11	65	48	9.8	medium
B7	76	49	12.1	high
B12	101	52	≈17	very high

[a] Measured at 150 °C.

consists of a blend of various species, ranging from linear molecules with an activation energy of 27 kJ/mol to a type of long-chain branched molecules characterized by a constant activation energy E_a^0 distinctly different from that of HDPE.

Comparison of the Activation Energies of Various Long-Chain Branched Polyethylenes. Using the method discussed before, several other long-chain branched polyethylenes made by metallocene catalysts were investigated.

The findings are documented in Table 3 and Figure 7. The classical LDPEs with a treelike branching structure behave thermorheologically simple, but their activation energies are distinctly higher than that of the linear homopolyethylenes (cf. Table 2 and Figure 7). The metallocene-catalyzed PE investigated are thermorheologically complex. This complexity can further be characterized by determining the activation energies as a function of the relaxation strength. In Figure 7, it is demonstrated that such an analysis discriminates between different LCB−mHDPEs. All the three samples show a behavior similar to that of the LCB−mHDPE B9 in Figure 6. At small relaxation strengths, a plateau value E_a^0 of the activation energy is reached, which is denoted as "terminal activation energy" E_a^0. These values are different for the four samples represented in Figure 6 and Figure 7, however, and lie between the relaxation strength-independent activation energies of the linear HDPE and the treelike branched LDPE 2. With higher relaxation strengths, E_a decreases and approaches the value of the linear HDPE. This qualitatively similar feature of $E_a(g)$ for the four samples in Figure 6 and Figure 7 gives rise to the supposition that all of them are blends of linear and long-chain branched molecules.

In Table 3 the constant activation energies E_a^0 of all the LCB−mHDPE investigated are listed and compared to the effect of branching qualitatively deduced from the ratio η_0/η_0^{lin} [39,40] with η_0 being the zero shear-rate viscosity of the branched product and η_0^{lin} the value of the corresponding linear sample with the same molar mass M_w. In particular, in ref 26, it was shown that for the metallocene catalyzed polyethylenes η_0/η_0^{lin} becomes the higher the more pronounced the effectiveness of long-chain branches is.

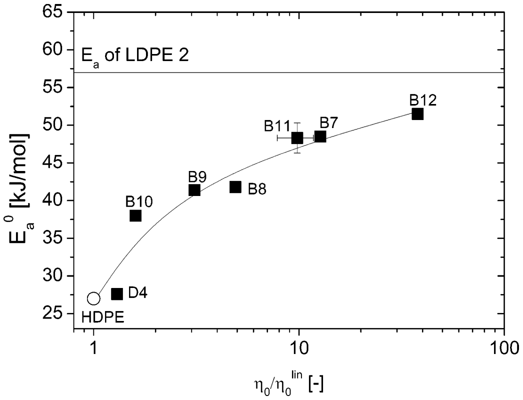

Figure 8. Terminal activation energy E_a^0 as a function of the zero shear-rate viscosity increase factor η_0/η_0^{lin}. The line is added to guide the eye. The error bars shown only for the LCB−mHDPE B11 for the sake of clarity refer to an error of ±20% with respect to η_0/η_0^{lin} and of ±2 kJ/mol with respect to E_a^0.

If E_a^0 is plotted as a function of η_0/η_0^{lin} (Figure 8), an empirical relationship between these two quantities is found. This result should not be overestimated but distinctly demonstrates that E_a^0 is higher for samples with a stronger effectiveness of long-chain branches. It seems that the correlation approaches E_a of LDPE 2 for very high degrees of long-chain branching.

Summary and Conclusions

For linear polyethylenes and long-chain branched species from the high-pressure process (LDPE) a constant activation energy E_a was found independently of the relaxation strength. In another paper[9] it was shown that short-chain branched polyethylenes behave thermorheologically simple, too, but the activation energy increases with the weight percentage of comonomers.

In comparison to the activation energy of 27 kJ/mol for HDPE LDPEs have higher activation energies around 60 kJ/mol. These values are too high to eventually be attributed to short-chain branches within the LDPE. Therefore, the large activation energies have to be correlated with the LCB architecture.

A comparison between LDPE and long-chain branched hydrogenated polybutadienes (hPBd), which can be regarded as model substances for polyethylenes shows that the activation energies of LDPE are slightly below the values typically found for these systems with pronounced long-chain branches.[2,3] Very short arms (e.g., $M_a = 2 \times M_e$)[41] lead to activation energies below 40 kJ/mol, while for very long arms an activation energy up to 78 kJ/mol was found. However, it is not clear from the literature, whether branched systems based on hPBd can be regarded as thermorheologically complex[43] or simple.[2,3]

The activation energies of the symmetric stars, the asymmetric 3-arm stars, H-type and the pom−pom samples published by Bonchev et al.[3] and Lohse et al.[2] increase with growing length of the shortest arm. The activation energy of a material with a pom−pom structure increases with the arm length.[2] However, it is also obvious from literature that the differences of the activation energies between the various branching structures are rather small (E_a = 65−75 kJ/mol) as long as the branches possess a sufficient length.

Thus, the lower E_a of LDPE in comparison to the model branched hPBds can be regarded as a consequence of the relatively short long-chain branches. Typically, segmental molar masses M_s[42] of around 15 000 g/mol are found for LDPE,[44] which are significantly below the branch lengths of 50 000 to 100 000 g/mol of the model branched systems with the high activations of $E_a = 70-75$ kJ/mol.[2,3]

The absence of a thermorheological complexity for LDPE can be explained by the assumption that every molecule in typical LDPE is *long-chain branched* and that the branching structure is not much different.

For the LCB−mPEs showing a thermorheological complexity a distribution of molecules with a different branching architecture has to be regarded. Activation energies around 27 kJ/mol lead to the assumption that some linear molecules are still present in the metallocene catalyzed samples, but that their relaxation times are smaller than those of the long-chain branched molecules. This conclusion is consistent with the rather narrow molar mass distribution given by $M_w/M_n \approx 2$. It is evident that long-chain branched molecules of a molar mass similar to that of linear molecules possess the higher relaxation times.

The finding of a constant activation energy at smaller relaxation strengths supports the assumption that there are molecules of a similar branching structure. Comparing B10, B7, and B12, for example, (cf. Table 3) the conclusion may be evident that E_a^0 increases with the weight-average molar mass M_w. Such an interpretation would be in agreement with the findings on well-defined hPBd from the literature that the activation energy increases with the arm length. However, the samples B9 and B11 do not fit in with this assumption as their terminal activation energies are somewhat higher than expected from their molar masses. This finding shows that the branching architecture has probably to be regarded in a more detailed way.

Worthwhile mentioning is the same trend for E_a^0 and η_0/η_0^{lin}, which gives a hint that both quantities should further be investigated with respect to their potential to get an insight into the branching architecture of polymers.

All in all, it can be concluded that a quantitative evaluation of the thermorheological complexity of branched polymers is a promising method to support their structural analysis. A deeper knowledge and more detailed results, which allow a comprehensive assessment of the possibilities of the method discussed are expected from investigations on blends of well-defined polyethylenes.

Acknowledgment. The authors would like to thank the German Research Foundation (DFG) for the financial support of this work. Additionally, the contributions of Mrs. I. Herzer (University Erlangen-Nürnberg) regarding the SEC−MALLS measurements and those of Prof. Dr. W. Kaminsky and Dr. C. Piel (University Hamburg) concerning the synthesis of many of the samples in this paper are gratefully recognized. Discussions with Dipl.-Ing. Ute Kessner (University Erlangen-Nürnberg) are gratefully acknowledged.

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MA702367A