Deriving comprehensive structural information on long-chain branched polyethylenes from analysis of thermo-rheological complexity*

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* this paper is dedicated to Dr. Victor Hugo Rolon-Garrido, a friend and a rising star in rheology, who tragically perished in a traffic accident. Victor and I collaborated on the understanding of elongational properties of polyolefins. Besides the tragedy for science the loss is aggravated by the fact that his newborn daughter will never get to know her father well.

Abstract

An advanced analytic method, based mainly on thermorheological analysis of standard frequency sweeps at several temperatures, is introduced which can determine a host of rheological indicators for long-chain branched polyethylenes and other materials with an Arrhenius-type temperature dependence. The method can be used to classify and categorize unknown samples to material types (tubular and autoclave low density polyethylene, long-chain branched metallocene polyethylene). For long-chain branched metallocene polyethylenes, it is, furthermore, possible to determine molar mass and branching degree using established relations with rheological behavior. It is, therefore,

possible to gain a rather comprehensive picture of the molecular structure of long-chain branched polyethylenes using only a relatively simple set of rheological experiments. An automated analysis routine facilitates the evaluation.

Keywords

long-chain branched polyethylene, thermorheological analysis, activation energy spectrum.

Introduction

In recent years, the use of polyethylenes with controlled topography has significantly increased, especially since the introduction of metallocene or single-site catalysts, which are able to incorporate higher olefins and, consequently, vinyl terminated chains, which form long-chain branches (LCB) [1-4]. Furthermore, significant effort has been put into other methods of producing long-chain branched polymers in other ways, e.g. by electron beam or γ -irradiation of polypropylene (PP) [5-7] or polylactide (PLA) [8], by copolymerization with branching agents (PP, PE, fluoropolymers)[9-11], and by copolymerization with macromonomers [12-14]. Furthermore, classical low density polyethylenes (LDPE) with their supposed tree- or comb-like topography are increasing in commercial importance, but, despite all efforts in the last 80 years since the first synthesis [15], their structures are still not completely understood.

While, in general, it is recognized that long-chain branches are very beneficial for polymer processing [16], it is still not possible to draw quantitative conclusions from long-chain branching topography to polymer processing behavior. This is also the reason why so much effort has been put into answering the questions on how to create and characterize LCB-structures. Characterizing the rheological behavior has proven to be quite successful in linking these two fields, but to this day, many questions remain open [17].

The basic problem about the characterization of the long-chain branching topography is that for many products, the number of long-chain branches is relatively low, which makes them difficult to detect by e.g. nuclear magnetic resonance (NMR), and, furthermore, that it is not possible to determine the branch length for branches longer than 6-8C [1, 18-20]. By using gel permeation chromatography (GPC) or asymmetric flow field fractionation (A4F) coupled with a multi-angle laser-light scattering device (MALLS) it is possible to detect the molar mass distribution (MMD) and the corresponding coil size distribution [18, 21, 22]. However, besides some shortcomings of GPC-MALLS as well as A4F-MALLS, these techniques are paramount today. Long-chain branches reduce the coil radius, which can be analyzed according to the Zimm-Stockmayer theory [23] or theories derived

from this basic model stemming from 1949 (e.g. [24]). While the Zimm-Stockmayer theory suffers from being insensitive to branching topography – taking only one parameter, the number of branches per chain m , into account – the extensions of that theory have so many parameters that it is impossible to extract anything useful from them unless one wants to validate a certain structure (e.g. derived from reaction kinetics simulations).

Hence, even the most up-to-date analytical techniques are unable to determine the structure of statistically branched materials sufficiently accurately. A team of experts in polymer chemistry, analytics, and rheology have dissected a model H-polymer, which was assumed to be structurally perfect [25]. Only after removing several different side products, it was possible to obtain the rheological behavior described by theory. This example shows that even in the most ideal cases, accomplishing a full picture of the architecture of a polymer is very challenging and requires the full range of analytics in addition to rheology, which of course cannot be done as a routine analysis.

Rheology has proven to be a very successful tool to analyze the structure of various polymers. For polyethylene, the deviation from the relation between zero shear-rate viscosity η_0 and weight average molar mass M_w valid for linear materials has proven to be useful for the detection of LCBs, especially because this correlation is relatively insensitive to comonomer content within the technologically relevant range and because tacticity does not play a role for PE [26-37]. In the last years, the analysis of the complex modulus, viscosity, and compliance as a function of time or shear rate/frequency dependencies as well as the analysis of relaxation spectra have added knowledge to the behavior of LCB-PE [34, 37-49]. Other quantities used for the rheological analysis of LCB-PE include the recoverable compliance [43, 47, 50-54] and the strain-hardening in elongation induced by long-chain branches [16, 55-59]. However, except for the η_0 - M_w -relation, the abovementioned indicators are influenced additionally by the molar mass distribution in a non-trivial way and so far it has not been possible to clearly distinguish between effects of branching and molar mass distribution in rheology as both have rather similar behavior. It is especially difficult to distinguish between the effects of branching and molar mass distribution, if both change at the same time. Furthermore, recently some contradictory data was published which suggests that also the η_0 - M_w -relation could be influenced by the molar mass distribution [60], while other data advocate the opposite [26]. In the past, it was tried to convert the molar mass distribution into rheological data (or vice versa) and to interpret a mismatch between measured and calculated data as the footprint of long-chain branching [61-66].

However, while in the proximity of the glass transition temperature branches influence the thermorheological behavior only to a very slight degree (or not at all), because branching points have almost no effect on the free volume [67], for semicrystalline materials, such as PE, a significant

influence of branches on the thermorheological behavior becomes obvious at least 100K above the glass transition temperature [68-70]. The activation energy of linear *PE* is found to be around 27-28 *kJ/mol*, while higher values are reported for linear *mLLDPE*, which scale with comonomer content and length (=short chain branch length) [34, 71-79]. Stadler et al. [73] found that the influence of comonomer length on activation energy can be understood in terms of the weight fraction of side chains (the fraction of carbons and hydrogens, which are not part of the main chain). This correlation is not only valid for ethylene- α -olefin copolymers (LLDPEs) but also for other olefin-homopolymers (polypropylene and polybutene). While the thermorheologically simple behavior of PE is unaffected by short chain branches (SCB), long-chain branches lead to a failure of the time-temperature superposition (TTS)-principle. This behavior is called thermorheological complexity, i.e., the shape of the material functions depends on temperature and, hence, a master curve cannot be constructed any more for LCB-PE.

The origin of the thermorheological complexity is probably caused by the branches themselves, because Carella *et al.* [80] found 3-arm stars to be thermorheologically complex. Other groups [75, 76, 81] did not analyze this point with respect to thermorheological complexity.¹ Data of Lohse *et al.* [75] clearly show at least a small amount of thermorheological complexity for most of the long-chain branched topographies. Hence, unfortunately, it cannot be said with definite certainty whether structurally homogeneous materials (such as stars, combs, or H), following an Arrhenius-temperature dependence, are thermorheologically complex or simple. But the authors consider it to be very likely that such materials are thermorheologically complex. The consequence of thermorheologically complex behavior is that materials with a thermorheological complexity cannot be modeled exactly anymore, as the parameters used to calibrate a model depend on the temperature.

For LCB-PE, the thermorheological complexity has been analyzed with several different methods, all relying on slicing the material functions into several sections with respect to the time-temperature superposition, whose Arrhenius *apparent* activation energy is then determined individually [70-72, 82-87]. The resulting quantities are then plotted as the “activation energy spectrum” [70, 72, 82-87]. The alternative of plotting the *apparent* activation energy data as a function of frequency, at which this quantity was determined at the reference temperature, is deprecated, as it introduces ambiguities, such as that the result depends on the reference temperature and it complicates comparison of different samples significantly.

¹ Unfortunately, most of the data on model polymers is on materials following a WLF-temperature dependence, which is not branching topography sensitive. This is the main reason, why relatively little is known about the influence of long-chain branches on the thermorheological complexity in model polymers.

A first challenge in the field of thermorheological complexity is its detection. Van Gorp and Palmen [42] introduced the $\delta(|G^*|)$ -plot as the most sensitive way to check for thermorheological complexity known today.

This paper introduces an improved analysis method as well as an analysis as to which conclusions can be drawn from rather simple frequency sweeps at different temperatures with respect to molar mass distribution and degree of long-chain branching. This kind of analysis tool has the clear benefit that the analysis can be performed solely based on rheological measurements and, thus, allows for getting some additional insight into the branching structure, conveniently.

Experimental

Samples

Samples from several polyolefin manufacturers were used for this paper. They are grouped into 5 different groups:

1. LLDPE without any LCBs (Lx, where x is a number).
2. LCB-mLLDPE (mLBx) – $M_w/M_n=2.8\ldots4.2$
3. LCB-mLLDPE with a broader molar mass distribution (mLBbx) – $M_w/M_n=4.5\ldots5.1$
4. Tubular low density polyethylenes (tLDPEx)
5. Autoclave low density polyethylenes (aLDPEx)

The samples were numbered according to increasing molar masses and are listed in Table 1. The rheological parameters (last three columns) will be explained later.

Table 1: designation, molecular and rheological data of the materials

#	type	M_w [g/mo l]	M_w/M_n [-]	$E_a^0(G')$ [kJ/mo l]	$E_a^{\max}(\delta)$ [kJ/mo l]	$\delta_{\max}$ [°]
L1	ZN-LLDPE	263000	4.2	28.0	-	-
L2	mLLDPE	254500	2.6	28.0	-	-
mLB1	LCB-mLLDPE	81200	2.8	39.0	57.5	80.9
mLB2		126000	3.3	40.0	52.7	78.9
mLB3		134200	3.3	40.7	61.3	71.9
mLB4		154500	3.3	42	76.1	62.7
mLB5		179000	4.2	41.7	82.4	61.7
mLB6		186600	3.5	42.3	100.2	54.5

mLB7		188700	3.4	95.1	56.9	
41.5						
mLBb1	LCB-mLLDPE	152000	4.5	42.0	62.0	50.7
mLBb2	with a	168000	5.1	40.0	54.2	55.0
mLBb3	broader molar mass distribution	176400	4.9	39.7	73.7	45.5
#		M _w [g/mol]	M _w /M _n [-]	E _a ⁰ (G') [kJ/mol]	E _a ^{max} (δ) [kJ/mol]	δ _{max} [°]
tLDPE1	Tubular LDPE	153500	5.5	57.4	66.5	44.8
tLDPE2		155500	6.6	57.4	66.5	44.6
tLDPE3		166100	4.9	58.2	65.2	45.5
tLDPE4		167900	5.5	58.0	68.8	40.9
tLDPE5		168100	6.2	53.7	61.6	44.1
tLDPE6		182700	6.4	57.6	69.6	38.5
tLDPE7		198000	7.6	59.6	72.6	40.3
tLDPE8		199800	8.5	57.1	69.7	41.2
aLDPE 1	Autoclave LDPE	204300	10.1	57.5	67.2	50.7
aLDPE 2		218000	9.1	57.1	65.9	53.7
aLDPE 3		281300	9.7	58.1	66.1	52.4

GPC

The molecular weight distribution of the samples was determined using a PL GPC 220 machine running at 160°C (Polymer Laboratories, UK) using PLgel Olexis™, 300X7.5 mm columns. 4 mg of sample was dissolved in 4 ml 1,2,4-trichlorobenzene (TCB). The TCB solvent was stabilized with 125ppm BHT (2,6-bis(1,1-dimethylethyl)-4-methylphenol) and was degassed for 1 hour with dry nitrogen to remove oxygen and volatile compounds. Then, the prepared sample/TCB solution was sealed to prevent contacting oxygen and placed in a preheated oven (170°C) for 1 hour, then shaken for 1 hour to completely dissolve the polymer. Vials filled with 2ml sample were introduced to the GPC-machine by auto-sampler. The first vial of each auto-sampling load was filled with only TCB solvent, only, to evaluate the base line. The sample solution then passed the GPC machine and the molar mass distribution of the polymer molecules was analyzed with Mark-Houwink parameters calibrated by PS standards.

Rheology

Rheological measurements were carried out on an ARES rheometer (TA instruments) in oscillatory shear using a 25 mm parallel plate and a strain of 5-15%, which is in the linear viscoelastic regime (adjusted depending on viscosity and frequency of the sample). The auto-strain function was used to keep the materials within the linear viscoelastic regime and to adjust the strain to obtain stress signals of sufficient strength to deliver good data. Dynamic experiments were performed under continuous purge of dry nitrogen. The frequency was changed from 0.05 to 300 rad/s and temperature was varied from 150°C to 230°C with 20°C increments. The linear viscoelastic and thermal stability limit were determined before these measurements.

Evaluation Method

The evaluation is run automatically by a Matlab®-script, whose flow diagram is given in Figure 1. In the first step, $\log G'$, $\log G''$, and $\log \omega$ are determined and the $\log G'$ and $\log G''$ are vertically shifted if necessary (because a proper thermal expansion compensation of the geometries was performed in the experiments and the vertical shift due to density change was negligibly small, no vertical shift was applied for all measurements in this paper; using logarithmized values, of course, implies that no negative values must be present). Next, the input range is determined by finding the global minimum and maximum value of $\log G'$, $\log G''$, and δ and a vector with the values of $\log G'$, $\log G''$, and δ is created, at which later the corresponding $\log \omega$ will be determined. This vector by default is 100 points in linear spacing for $\log G'$ and $\log G''$, but 1000 points for δ , due to the larger curvature of $\delta(\log \omega)$.

In the second step, the data is parameterized by fitting it with a 4th order polynomial. Different polynomial orders were tested, but for all data tested a 4th order polynomial could be successfully fitted with sufficient accuracy (see Fig. SI1), while higher order polynomial orders could potentially lead to unreasonable oscillations. In the third step, the polynomials fitting $\log G'(\log \omega)$, $\log G''(\log \omega)$, and $\delta(\log \omega)$ are interpolated to search for the logarithmic frequency $\log \omega$, at which the fitted curves of e.g. $\log G'(\log \omega)$ attain the prescribed value (e.g. a certain $\log G'$).

These logged frequencies $\log \omega(\log G'=x)$, $\log \omega(\log G''=y)$, and $\log \omega(\delta=z)$ are plotted vs. $1000/T$ and a linear relation is fitted, whose slope m is used to determine the *apparent* activation energy (e.g. $E_a(\log G'=x)$) by

$$E_a = m \times 2.3 \times R \quad (1)$$

with R being the gas constant. This equation was derived from the Arrhenius equation

$$a_T(T) = a_T(T_0) \exp(E_a/RT) \quad (2)$$

The error in the determination of the *apparent* activation energy was estimated the following method:

1. Calculate the activation energy from e.g. $E_a(\log G'=x)$ for the 4 out of 5 temperatures (for temperatures T1, T2, T3, T4; T1, T2, T3, T5; T1, T2, T4, T5; T1, T3, T4, T5; T2, T3, T4, T5)
2. Determine the standard deviation of E_a from these 5 individual subsets and of the full dataset.

In the fifth step the E_a -data are analyzed with respect to their G' , G'' , or δ -dependencies. This is done by plotting the “activation energy spectra” with respect to the evaluated quantities (G' , G'' , or δ). The contents of the sixth step will be discussed later in this manuscript.

This procedure is very similar in principle to the method applied previously [70, 71, 82], however, with the decisive difference of doing the analysis by a PC-program and not by hand and, furthermore, for a significantly larger number of chosen G' , G'' , or δ . The digital (vs. manual) evaluation makes the result more accurate, because a parameterization leads to more exact results, as long as the function fits the data well enough – this is often not the case, if the input data are too error afflicted. The larger number of evaluable data can be used to find finer structures than with manual evaluation. Furthermore, the analysis time of the automated routine is within few seconds, while doing the same manually (with significantly less discrete slices to be analyzed) takes at least 30 min.

The reliability of the results can be estimated from the quality of the fitted polynomials and the size of the standard deviation of the activation energy spectrum (except for the “peak” in $E_a(\delta)$, which will be discussed later). Of course, it is necessary to crop measurement artefacts before performing this analysis.

Figure 1: scheme of the script used for the data evaluation

Results

Input data and Arrhenius plots

Figure 2a-d show $\log G'(\log \omega, T)$ and $\delta(\log \omega, T)$ of L1 and tLDPE5, respectively, which are fitted by 4th order polynomials with very high accuracy, thus, allowing for the necessary parameterization of the data in the following. In general, $\log G'(\log \omega)$ and $\log G''(\log \omega)$ are easier to fit than $\delta(\log \omega)$, due to their smaller curvature changes. The data of $\log G''(\log \omega)$ are shown in SI; they typically show the smallest degree of thermorheological complexity [84].

While, the shape of the material functions of L1 do not change significantly with temperature (Fig. 2a,b), it can be seen that the shape of the material functions of tLDPE5 (Fig. 2c,d) does not change significantly with temperature, which agrees to previously published results and which differs from LCB-mPE (cf. e.g. mLB6, Fig. 2e,f) [82, 84].

This becomes obvious from Figure 2e,f showing $\log G'(\log \omega, T)$ and $\delta(\log \omega, T)$ of mLB6, which demonstrates that especially the shape of $\delta(\log \omega)$ shows a significant temperature dependence for this class of materials. Hence, setting up a physically reasonable master curve of these data is not possible.

a)

b)

c)

d)

e)

Figure 2: storage modulus and phase angle functions at different temperatures. a) L1, $\log G'(\log \omega, T)$, b) L1, $\delta(\log \omega, T)$, c) tLDPE5, $\log G'(\log \omega, T)$, d) tLDPE5, $\delta(\log \omega, T)$, e) LCB-mLLDPE mLB6, $\log G'(\log \omega, T)$, f) LCB-mLLDPE mLB6, $\delta(\log \omega, T)$

For this reason, the temperature dependence has to be evaluated by determining the shift factors for each quantity (in this publication G' , G'' , δ) individually.

Previously, it was argued that using the relaxation spectrum is the physically most meaningful quantity for this piecewise shift, as a spectrum is a material function, while other quantities (G' , J'' , δ , ...) are only derived from it [70, 84]. However, as our intention with this article is to establish an easy-to-use thermorheological complexity analysis method and as determining proper spectra is not trivial [88], it was decided to analyze the thermorheological complexity from G' , G'' , and δ , only. Of course, every other viscoelastic quantity, including relaxation or retardation spectra, could be analyzed with the same approach as well – only minor changes of the code would be necessary.

The piecewise determined Arrhenius-plots are given in Figure 3. Each subfigure contains $\log \omega(\log G'=x)$ or $\log \omega(\delta=z)$ at several of the 100 x and z -values, at which these quantities were determined, respectively, i.e. 100 Arrhenius-plots – for sake of clearness only several of them are shown in Figure 3. Plots containing all Arrhenius plots determined for the materials are given in Fig. S13&4. To illustrate the thermorheological complexity, a thick black line was fitted to one of the Arrhenius-plots and then dashed duplicates were shifted up or down to illustrate the change of slope and, thus, activation energy.

The Arrhenius-plots of ZN-LLDPE L1, a purely short-chain branched material, determined from G' (Figure 3a), demonstrate a thermorheologically simple behavior, where the slope, corresponding to E_a , remains constant. For sake of clarity only several of the data are given in Figure 3 – the complete dataset is given in SI. For a truly thermorheologically simple material such as ZN-LLDPE L1 the slope and, thus, the activation energy E_a is independent of the quantity (G' , G'' , δ , ...) and the value of the

modulus/phase angle, which is investigated. For such a material the activation energy does not change when evaluating the material at different values for G' , G'' , δ , or any other viscoelastic quantity. This can be seen from the thick black line, whose shifted counterparts (broken thick lines) are in very good agreement with the slopes of the curves obtained from the ω -T shift at various values of G' . That means the activation energy is constant within the range of data measured and indicates a thermorheologically simple behavior.

When comparing these Arrhenius plots to the ones of LCB-mLLDPE mLB4 (Figure 3b), a sparsely long-chain branched material, it becomes obvious that the slope/*apparent* activation energy determined from $G'(\omega)$ increases with decreasing $G'(\omega)$, while for the same quantity determined from δ a more complex picture emerges (Figure 3c). This becomes obvious from the shifted broken lines clearly not agreeing to the data next to them. While the Arrhenius-plots for $\log\omega > 1$ and < 0 show an approximately constant slope, the Arrhenius-plots between these limits have a much higher slope, which additionally is not constant, leading to a “wave-like” appearance, when looking at all Arrhenius plots (see Fig. SI3&4, Fig. SI4b (calculated for mLB4 from δ has the “wave-like”, while the other plots do not). This feature, occurring at different $\log\omega$ -ranges for different materials, is caused by the temperature dependence of the shoulder of $\delta(\omega)$ (see Figure 2d, $0 < \log\omega < 1$).

Clearly, these “wave-like Arrhenius plots” always have a significantly higher error in *apparent* activation energy than regular Arrhenius plots. Typically, the uncertainty of E_a is around $\pm 0.1 \dots \pm 0.3$ kJ/mol, while for such “wave-like” Arrhenius plots standard deviations > 1 kJ/mol are found, typically between 1 and 6 kJ/mol (rarely > 3 kJ/mol). Usually, it is assumed that the uncertainty of the determination of E_a is $\pm 10\%$. Considering typical activation energies of LCB-PE between 30 and 70 kJ/mol [89], the uncertainty in the determination of *apparent* activation energy in regular Arrhenius plots is very low and shows the high numerical accuracy of the analysis method, while the uncertainty in the determination of “wave-like” Arrhenius plots is still acceptable.

One could argue that it is not possible to determine an activation energy from such “wave-like Arrhenius plots”, as the activation energy only correct, if a constant slope is found for all input data (i.e. here if $E_a(G')$, $E_a(\delta)$, ... are constant. Hence, already the question whether it is possible to evaluate a thermorheologically complex dataset requires some physical compromise. For this reason, we consider all activation energies determined from **thermorheologically complex materials** to be **apparent activation energies**.

However, for the purposes of analyzing the data it is possible to set physical meaningfulness aside partially. In the strict sense thermorheologically complex data cannot be analyzed in terms TTS-principle, as the slicewise evaluation method, discussed in this article, requires restricting the

relaxation time range analyzed to such a small area, that the TTS-principle is fulfilled locally. In other words, the slicewise evaluation of thermorheologically complex data makes these data thermorheologically simple by restricting the evaluated data to a tiny frequency or time range. Therefore, we calculate local activation energies, but keep in mind that these might also depend on the temperature range evaluated due to the temperature dependence of shape of the spectrum [84], which, of course, leads to significantly larger error bars than for thermorheologically simple cases.

For tLDPE5 a much higher slope and consequently a much higher *apparent* activation energy in comparison to mLB4 is obvious, determined from G' (Figure 3d), which further increases towards low $\log\omega$. This is in contrast to the same plot determined from δ (Figure 3e), which shows an almost constant slope except for the highest $\log\omega$, which is in agreement with Keßner et al. [82].

c)

d)

e)

Figure 3: piecewise Arrhenius-plots. a) ZN-LLDPE L1, determined from G' , b) LCB-mLLDPE mLb4, determined from G' , c) LCB-mLLDPE mLb4, determined from δ , d) tLDPE5, determined from G' , e) tLDPE5, determined from δ . The different symbols stand for different values of G' or δ at which $\log\omega$ was determined. The values next to the y-axis stand for the values of $\log G'$ or δ , at which the Arrhenius plot next to it was determined.

The resulting activation energy spectra (Figure 4) can be used to assess the branching structure. The activation energy spectra of G' and G'' have been introduced in detail previously [70-72, 82-84] and clearly show an increase of E_a with decreasing G' and G'' , i.e. with decreasing ω , (Figure 4a) for LCB-mLLDPE mLB6 and tLDPE5, while ZN-LLDPE L1 shows almost constant values of E_a , proving thermorheological simplicity.

As can be seen, the error bars in Figure 4, calculated from the standard deviation of different temperature subsets, are typically in the range of ± 0.1 -0.3 kJ/mol, which is very low and underlines the precision of the input data and of the high numerical accuracy of the method developed. Higher errors are only found when using the fitted polynomials to extrapolate by up to 1 decade for allowing for increasing the range in which 3 or more temperatures can be evaluated, which is logical considering that any extrapolation is much more error afflicted than an interpolation, especially when using a generic function for the fitting (e.g. a polynomial) and not a function derived from physical laws.

The range, in which results of $E_a(G')$ can be obtained is usually significantly larger than for $E_a(G'')$, which is due to the larger dynamic range of G' in comparison to G'' in the terminal regime. For thermorheologically simple materials, such as L1 (Figure 4), the activation energies determined from G' and G'' are very similar.

However, the activation energy spectra of δ were found to display additional interesting features (Figure 4b), which will be further explored in the remainder of the paper. The ZN-LLDPE L1 again shows a constant value of around 28 kJ/mol, which is in the range expected for this material with relatively low comonomer content [72-74]. In contrast to this, the activation energy spectrum of tLDPE5 shows an increase of E_a between $\delta=30$ and 40° , followed by a broad peak and a plateau for $\delta>55^\circ$. Although the height of the “peak” is only around 3.5 kJ/mol, it is a pattern that was consistently found for all LDPEs and, therefore, is concluded not to be an artefact. This finding is in contrast to Keßner et al. [82], who postulated that E_a is constant for LDPEs when evaluating it with respect to δ . However, when looking at the original graphs in [82] and [86], it becomes clear that the authors found the same shape but with significantly fewer points and, consequently, assumed that the broad peak and the increase at the beginning are measurement artefacts. In the section “Molecular reasons for the thermorheological behavior”, we will give physical reasons for this behavior.

The activation energy spectrum $E_a(\delta)$ of LCB-mLLDPE mLB6 (Figure 4b) also increases with increasing δ for low δ , then has a sharp peak with $E_a \approx 100$ kJ/mol, followed by a decrease, which seems to converge to about the same E_a (ca. 40 kJ/mol) as $E_a(G'(\omega \rightarrow 0)) \approx 43$ kJ/mol in the same frequency

range. The peak is related to the clear difference in shape, namely in the difference of the plateaus of $\delta(\omega)$, which, as discussed previously [84], decrease with increasing T .

Due to inherent experimental inaccuracies on one side and the significance on the other, the following criteria for analyzing the $E_a(\delta)$ -peak are proposed:

1. An amount of thermorheological complexity in the $\delta(|G^*|)$ -plot (see also [37]) of at least 1° in a systematic way needs to be present in a temperature interval of 60K, i.e. the value of δ at a chosen constant $|G^*|$ needs to increase systematically with increasing temperature by a total of at least 1° within 60K (e.g. 150°C - 210°C)
2. The standard deviation of E_a in the peak area needs to be significantly smaller than the height of the peak.
3. The height of the peak of $E_a(\delta)$, defined by the difference of the peak E_a and the E_a at $\delta+10^\circ$ and $\delta-10^\circ$ needs to be at least 2 kJ/mol. This criterion is an experience value from the samples discussed in this article.

Furthermore, the activation energies determined from different rheological quantities must be significantly different (see Figure 4 and [82] for examples), which is not directly related the $E_a(\delta)$ -peak but serves well as an additional check.

When all criteria are fulfilled, it should be ensured that the resulting peaks are the consequence of measured thermorheological complexity and not of experimental uncertainties. While these definitions seem to be arbitrary at first glance, they were chosen based on experience with these data and previously published data. Condition 1: The $\delta(|G^*|)$ -plot has been established to be the most sensitive check for thermorheological complexity [42]. Condition 2 is simply a quality check, whether the experimental accuracy is sufficient to conclude that such a peak is present and condition 3 checks for the significance of the peak. If the peak is significantly below 2 kJ/mol it is hard to consider the effect as thermorheological complexity. For the samples checked in the paper, either all conditions were fulfilled or all conditions failed at the same time.

a)

b)

Figure 4: Activation energy spectra of 3 materials with different topography, a) $E_a(G')$ and $E_a(G'')$, b) $E_a(\delta)$

The exact peak position is analyzed by the program by finding the maximum value in $E_a(\delta)^2$ and the characteristic values $\delta_{\max}$ and $E_a^{\max}$ are associated to it. Obviously, the former refers to the phase angle, at which the peak is located (marked in Figure 4b by the vertical lines).

While the numerical evidence for the presence of the peak is very strong, one might wonder what causes such a counterintuitive behavior (a maximum in $E_a(\delta)$). Figure 5 shows the phase angle as a function of angular frequency $\delta(\omega)$ for LB6 at 150°C (reference temperature) and at 230°C (the other temperatures are given in pale gray). When trying to shift the data measured at 230°C, one can see that the high frequencies can be shifted with $E_a=32$ kJ/mol relatively well, while in the plateau regime

² As mentioned before, the activation energy was determined at 1000 values of δ . Hence, the difference between 2 neighboring is below 0.1°. As the resolution of dynamic-mechanical experiments is usually around 0.2° with a modern rheometer, it is safe to simply pick the largest value found for $E_a(\delta)$ instead of trying to interpolate to find the maximum.

at 150°C ($0.1 \text{ s}^{-1} < \omega < 30 \text{ s}^{-1}$) a significantly higher shift factor ($E_a > 100 \text{ kJ/mol}$) is necessary to obtain a very local overlap only. The reason for this significant increase is also obvious from Figure 5. The plateau at 150°C is located between ca. $\delta = 50^\circ$ and 53° , while at 230°C, the plateau has turned into a shoulder between ca. $\delta = 54^\circ$ and 60° .

As the frequencies, at which the plateaus/shoulders begin and end are about a factor 10 apart, it is logical that a δ -shift of the height of the plateau, as is typically observed for LCB-mPE [84], will require a significant increase in shift factor a_T (and consequently in E_a) to get a local match.

It is also visible that the change of plateau level as a function of temperature will lead to changed shift factors and thus to a change in *apparent* activation energy. That is the reason for the “wave-like” appearance of the Arrhenius plots (Figure 3c and the corresponding figures in SI). For the same reason, the peaks in E_a also always have significantly higher error bars than the rest of the spectrum.

Figure 5: plot of $\delta(\omega)$ of LB6 with different attempts to shift the data of 230°C onto 150°C.

Influence of structure

After having established the usefulness of the characterization method, it shall be tested how different sample topography and molar mass distribution is reflected in the data. Figure 6 compares the $E_a(\delta)$ -plots for different LCB-mPEs. While the molar mass distributions of the LCB-mPE in Figure 6a are comparable ($M_w/M_n \approx 2.5\text{--}4.2$), the peaks of $E_a(\delta)$ become the higher the lower $\delta_{\max}$, i.e., the more significant the long-chain branches are for the behavior. This the equivalent of the finding for LCB-mPE that the higher the number of LCB/10000 monomer λ the more significant the deviation from the linear relation in the $\delta(|G^*|)$ -plot (see [90] for the definition of the linear reference of the

$\delta(|G^*|)$ -plot for PEs with narrow molar mass distribution, which is the average of several mPEs with distinctly different molar masses), the higher $\eta_0/\eta_0^{\text{lin}}$ and the more significantly several other rheological quantities deviate from the values found for linear samples [2, 47].

For low δ , the *apparent* activation energy E_a increases from about 20 kJ/mol to a level around 30-40 kJ/mol just before the onset of the peak.³ The peak itself is relatively sharp for the narrowly dispersed LCB-mPEs (LBx), while it is broader and with a lower *apparent* activation energy peak for the LCB-mPE with broader molar mass distribution (LBbx). After the peak a falloff in E_a is found. The activation energies found for the highest phase angles ($\omega \rightarrow 0$) are about the same as the activation energy E_a from G' for $\omega \rightarrow 0$ (see Keßner et al. [82] and Resch et al. [84] for a comparison for these data for LDPE and also Figure 4).

When comparing these results to the LCB-mPEs with a broader molar mass distribution ($M_w/M_n \approx 5$, Figure 6b), it is obvious that the height of the peak decreases significantly from about $E_a^{\text{max}} = 105$ kJ/mol for $\delta_{\text{max}} = 55^\circ$ (mLB6) to $E_a^{\text{max}} = 54$ kJ/mol (mLBb2), while the trend of the increase of E_a^{max} as δ_{max} decreases is retained. This finding suggests that the value E_a^{max} is influenced by the molar mass distribution and the LCB-structure of the sample. As both quantities are most likely varied in parallel (mLBx vs. mLBbx series), it is hard to say without making unscientific statements, to which degree molar mass and long-chain branching distribution contribute to these differences.

This MMD-dependence can be understood from the relaxation spectra, which tend to be smeared out when the MMD broadens [48]. As the features are more smeared out, it is clear that the directly measured rheological quantities (G' , G'' , δ , ...) are determined from a broader range of relaxation times [84]. Furthermore, one has to assume that architectural inhomogeneity and broad MMD⁴ lead

³ This activation energy E_a of about 20 kJ/mol is significantly below the values found for linear PE. But as pointed out in Figure 4, linear PE measured with the same setup (an identical automated test protocol was used for all materials) and with the same evaluation routine (using the same parameters) shows a very constant activation energy [72, 73]. Furthermore, in measurements for previous publications the authors encountered the same kind of “too low” E_a at the highest frequencies and considered them to be measurement errors [70, 84]. However, considering that a variety of lab-scale and commercial LCB-mPE measured on 4 different rheometers (2 different TA ARES, TA AR-G2, Malvern Bohlin Gemini) show this effect, it is concluded that it is not an artefact, e.g. stemming from insufficient gap correction or density correction [91].

It is, however, completely elusive, as to what causes these effects, as there is a general agreement that LCBs increase the activation energy, but no process is known to the authors, that certain molecular structures cause a decrease of temperature sensitivity. Only effects related to order-disorder transitions, which can also occur in mLLDPEs in rare cases, were reported to show significantly reduced E_a , although the mechanism in this case is also far from well-understood [92].

⁴ The statistical nature of the LCB-formation in LCB-mPE leads to few long long-chain branches, which are predominantly found for high molecular materials. E.g. when assuming that 1 branch point per 10000 regular carbons is found – a typical value of LCB-mPE – then a chain with 10000C $\rightarrow$

to more different molecular motions, occurring simultaneously, influencing each relaxation mode, which result the activation energy spectrum of the relaxation spectrum being smeared out additionally. This point is discussed in more detail elsewhere [37, 38, 47, 48, 84, 93]. Hence, the peak of the activation energy spectrum with respect to δ can be seen as an indicator of the molar mass distribution and architectural inhomogeneity, which will be further elaborated later.

While it is obvious from a comparison of Figure 6a and b that broadening of the MMD leads to a lower E_a -peak, it is also clear that the fact that higher $\delta_{\max}$ automatically mean lower $E_a^{\max}$ makes a simple correlation between $E_a^{\max}$ and M_w/M_n , for example, impossible. Instead less obvious correlations have to be employed, which allow for analyzing and classifying the samples properly.

$M=140000$ g/mol should have 1 branch point. Considering that the typical LCB-mPEs have M_n of 40000-100000 g/mol, it is clear that a significant fraction of the chains do not have branch points statistically and, thus, are linear. A broader molar mass distribution means that also the distribution of branch points among the chains are more inhomogeneous, i.e. the topography distribution is more complex, as a more pronounced high molecular fraction with highly branched molecules exists. It is unclear, however, what kind of effects on the thermorheological behavior this more inhomogeneous molar mass and long-chain branching topography distribution have.

Figure 6: activation energy spectra of a) regular LCB-mLLDPE (mLB1-7, $M_w/M_n \approx 3$) and b) broader distributed LCB-mLLDPE (mLBb1-3, $M_w/M_n \approx 5$)

To test whether these trends can also be obtained for another class of materials, the data of the LDPEs were assessed in the same way. Here, the variability of the results with respect to $\delta_{\max}$ is significantly smaller.

When comparing the data, acquired for the different LDPEs (Figure 7), it becomes immediately obvious that the peak is not very high for the LDPEs in comparison to the low pressure PEs. This is in agreement with the trend of the peak height becoming lower with increasing M_w/M_n , as all LDPE have a rather broad MMD. Furthermore, due to the much higher degree of long-chain branching (typically LDPE has 10 times as high long-chain branching frequency as LCB-mPE) [30, 70, 93], the fraction of linear chains, which is not so short that it can be considered to be a wax (and has thus Newtonian properties), is negligibly small. A comparison between the different groups of high pressure materials reveals that tubular LDPE (Figure 7a) have a slightly higher peak than autoclave LDPE (Figure 7b), which typically has an even broader molar mass distribution due to the less homogeneous reaction conditions in an autoclave reactor (cf. Table 1) [56]. The question is, however, whether this small difference is significant.

However, the similarity in shape for all of the materials is clear from Figure 7. Additionally, there seems to be a weak trend of decreasing peak height with increasing $\delta_{\max}$. tLDPE 1 and 2 are very similar in their behavior and, thus, overlap in their data points in the following figures.

Another question arising is what causes these differences in behavior between LDPE and LCB-mPE. To answer this, one has to understand both material classes on a molecular level. Hence, the discussion for this question was moved to the next section (Molecular reasons for the thermorheological behavior).

Figure 7: activation energy spectra of a) tLDPE and b) aLDPE

When reading the maximum values of $E_a(\delta)$ from Figure 6 and Figure 7, one can notice clear differences between the different material classes (Figure 8, the numbers next to the symbols are the consecutive numbers for each material as given in Table 1). In general, $E_a^{\max}$ decreases as $\delta_{\max}$ increases, but it is clear that LCB-mPE have significantly higher $E_a^{\max}$ than the other samples at comparable $\delta_{\max}$ but the general trend of $E_a^{\max}(\delta_{\max})$ is visible for all material classes except for the aLDPEs, which are too similar in their characteristics to make a reliable statement. The trend lines are very similar in slope and, hence, it is hypothesized that the y-scaling of the trend line to a large extent depends on the molar mass distribution and the topography distribution, which can be assumed to be similar within one group of materials. It is surprising though that the trend line for the tLDPEs seems to be similar in slope to the LCB-mPEs, although their manufacturing method and branching topography is clearly different. While for both groups of LCB-mPE, the trend lines are very clear, for LDPE, a significantly higher amount of scatter is observed. The obvious reason is that the peak is rather low but also the products are not as well defined.

It should be pointed out that while, at first glance, the activation energy spectra of the LDPEs (Figure 7) look relatively similar, so they can be clearly be separated. While it has been long known that tubular and autoclave LDPE have different processing and elongational properties their differences in shear rheology were considered to be relatively small [56, 94, 95]. This thermorheological complexity analysis method allows distinguishing the two types.

Figure 8: maximum value of activation energy spectra from the phase angle's frequency dependence E_a^{max} as a function of δ_{max} . Lines added to suggest trends. The numbers next to the datapoints refer to the material numbers according to Tab. 1.

Along with the activation energy spectrum of δ , also the activation energy spectra of G' and G'' were determined (Figure 4a), which themselves differ and show for all thermorheologically complex cases that $E_a(G')$ is higher than $E_a(G'')$. It was previously established that both functions approach a constant value $E_a^{0G'}$ and $E_a^{0G''}$, respectively [71]. In the following, we will only consider $E_a^{0G'}$, as $E_a^{0G''}$ is less sensitive to topography and, hence, not as suitable for the thermorheological analysis. The plot $E_a^{0G'}(\delta_{max})$ clearly shows that high and low pressure LCB-PE (LDPE vs. LCB-mPE) can be easily distinguished by having $E_a^{0G'}$ around 57 and 41 kJ/mol, respectively (Figure 9). However, while this difference seems to be significant alone, published results on lab scale products show that higher E_a^0 -values are possible for highly branched LCB-mPE and special LDPEs [56, 70-72], making this plot less meaningful than it seems at a first glance.

The most significant finding is, however, that both groups of LCB-mPE with significantly different molar mass distribution are not distinguishable by their $E_a^{0G'}$, which can be explained by the fact that $E_a^{0G'}$ is a quantity determined by the whole spectrum, including the corresponding activation energies. Like the zero shear-rate viscosity η_0 , it is, therefore, not dependent on the molar mass distribution very much [26].

Figure 9: terminal value of activation energy spectra $E_a^{0G'}$ as a function of δ_{max} . The numbers next to the datapoints refer to the material numbers according to Tab. 1.

The fact that $E_a^{0G'}$ is insensitive to molar mass distribution, while E_a^{max} clearly is, can be utilized for closer analyzing the molecular structure. This is done by subtracting these two indicators, which leads to the activation energy difference $E_a^{max} - E_a^{0G'}$, which nicely correlates with the molar mass distribution of the long-chain branched polymer, which in combination with different previously discussed quantities can be used for branching analysis (Figure 10).

While it would be nice to use the E_a -plateau of LDPEs as a base for peak-height normalization, this is not possible, as LCB-mPE do not converge to a clear plateau and, hence, it is not possible to compare LDPEs with other PEs. This is the deeper reason why $E_a^{0G'}$ was used, which also has rather similar values to $E_a^{0\delta}$ (apparent activation energy determined from δ in the terminal regime ($\omega \rightarrow 0$)) for the samples, where both quantities can be determined.

It is clear from Figure 10 that the broadening of the MMD (in combination with the unknown changes to long-chain branching topography distribution) of LCB-mPE decreases $E_a^{max} - E_a^{0G'}$ by about 40 kJ/mol (compared at $\delta_{max}=55^\circ$). Regrettably, it is not possible to distinguish between the effects of molar mass distribution, which can be easily determined by GPC and the effects of changes in long-chain branching topography distribution, as corresponding samples where either only molar mass distribution or LCB-distribution are varied independently, are not available. LDPEs are lower than broad LCB-mPE by another 5-20 kJ/mol – giving a more accurate number for the difference is not possible due to the different slopes observed.

Figure 10: activation energy difference $E_a^{\max} - E_a^{OG'}$ as a function of $\delta_{\max}$. Lines added to suggest trends. The numbers next to the datapoints refer to the material numbers according to Tab. 1.

Molecular reasons for the thermorheological behavior

It is well established that long-chain branched chains have higher activation energies than linear ones due to a larger number of conformation possibilities and processes [96], which need to occur for a place change in the material [34, 71-79]. Furthermore, in comparison to linear chains of comparable molar mass, LCB-chains with sufficiently long branches (segment length $> ca. 5M_e$ for 3-arm stars) at sufficiently low concentrations have significantly longer relaxation times than linears of comparable molar mass [34, 37-48]. Hence, the reason for thermorheological complexity comes from the fact that the branched chains have a higher E_a and dominate the spectrum at longer relaxation times [84], as the branched segments cannot reptate and, thus, have to relax by fluctuations [97-99]. While molecular models, regrettably, do not contain information on the thermorheological behavior, experiments on model branched polymers, mostly on hydrogenated 1,4 polybutadienes (hPBd), show that the introduction of branches leads to an increase of the *apparent activation energy* (when ignoring thermorheological complexities), which depends on the length of the branches and seems to reach a saturation level for $E_a \approx 75-80$ kJ/mol for materials with medium or long branches above several entanglement molar masses and with at least 1 branch point [75, 76, 81].

Hence, it can be concluded that fluctuation movements have a higher activation energy than reptation motions. In combination with the fact that reptation is faster than fluctuation for molecular segments of comparable length, it is clear that the terminal regime of LCB-materials with an Arrhenius temperature dependence has a higher activation energy than the rubbery regime.

The shape of the different rheological functions is determined by the shape of the spectrum and as different parts of the spectrum have different activation energies [70], the shape of spectrum and

viscoelastic functions change with temperature. It was previously established that the slope of $d\log|\eta^*|/d\log\omega(\omega)$ is connected to $\delta(\omega)$ via the Kramers-Kronig relations [46, 49, 100-102]. As a consequence of this, shifting one of the two main modes more along the time axis at a higher rate than the other one, which is exactly what happens for thermorheologically complex materials when changing temperature [84], varies the average slope between the two main relaxation modes. With increasing temperature, the two main relaxation modes merge increasingly, which leads to the above-discussed transition from a clear plateau to a small shoulder at higher T for $\delta(|G^*|)$ [48, 56]. For PE, this effect is not very obvious, though, as the temperature range, in which rheological data is measured, as well as the temperature dependence are relatively small, and, thus, only a restricted part of this effect can be observed, which nevertheless has proven its usefulness in thermorheological analysis. This shift of the main relaxation modes is the reason for the peak in the activation energy spectrum of the phase angle $E_a(\delta)$.

The molecular reason for the peak in the activation energy spectrum of the phase angle $E_a(\delta)$ is, therefore, the change of the shape of the spectrum. The flatter the plateau in $\delta(\omega)$, i.e. the clearer the processes are separated in $H(\tau)$, the higher is the peak in activation energy, theoretically going to infinitely high, when having a completely flat and infinitely long plateau. Unfortunately, no data on monodisperse model polymers with varied topography was available to the authors to test this hypothesis. Based on this explanation, it is clear that the shape of $\delta(\omega)$, the thermorheological complexity, and activation energy difference $E_a^{\max} - E_a^{0G'}$ are related to each other.

The shape of $\delta(\omega)$ itself is, furthermore, determined by the molar mass distribution, as obviously all viscoelastic functions are not only determined by the (molar mass dependent) branching structure but also by the molar mass distribution [65, 96, 103]. One of the recurring problems in rheology of branched polymer melts is to distinguish these effects properly. While methods exist relating molar mass distribution and viscoelastic functions of linear materials [65, 103], determining molar mass distribution of long-chain branched polymers only from rheological data has been an impossible task so far, as the rheological footprint of LCBs and high molecular tails resemble each other remarkably. Although it has been clear for a long time that thermorheological complexity analysis is one possible key technique to dissecting these two parameters, it was not clear so far how this can be achieved. Based on models relating MMD and rheological behavior, it is clear that every curve shape of polydisperse polymer melts, including branched materials, can be modeled to a certain molar mass distribution [96]. However, in order to truly distinguish between the effects of MMD and branching, one needs to use additional measurements. In this area of rheology, the number of well-defined materials is still too small to get a good base for drawing conclusions how e.g. a shape change χ of

the molar mass distribution $dW/d\log M$ of a polymer Y changes rheological behavior when the sample has a LCB-distribution $z(M)$ as well.

On the side of molecular characterization, this is primarily light scattering attached to the standard GPC-measurement (or alternatively of A4F-experiments) – a suitable, expensive but not very sensitive and difficult method. On the rheology side, nonlinear elongational and shear rheology, producing information on strain hardening and various coefficients related to startup flow and nonlinear oscillations have been proposed, but so far, it has proven difficult to establish unambiguous quantities distinguishing effects of MMD and LCB. While the thermorheological behavior, especially the activation energy difference $E_a^{\max} - E_a^{0G'}$, seems to be a good candidate to achieving this task at least qualitatively, significantly more data have to be collected before being able to conclude on its usefulness scientifically accurately.

The shape of the activation energy spectra $E_a(\delta)$, in particular, but also $E_a(G')$ and $E_a(G'')$ is determined by the contributions of different molecular topographies. LDPE in general is highly branched with typically about 1 long chain branch point every 1000 carbons (the more numerous short-chain branches, dominantly C4-branches, are not important for this discussion), which means that there is a main chain molar mass around 14000 g/mol between the branch points, which corresponds to 10-15 entanglement lengths [104]. Hence, there are only few and rather low molecular chains, which are not branched.

This is in contrast to the structure of LCB-mPE, which typically has about factor 10 less branch points, which according to molecular modeling results, means that the dominating topography for LCB-mPE being linear and star-like chains [93, 105]. Chains with more than 1 branch point are usually only present in rather small fractions (below 10%).

It is established that all molecular motions for linear materials – segmental relaxations, entanglement fluctuations, and reptation – have the same temperature dependence, as otherwise, it would be impossible to have a thermorheologically simple material [89]. Furthermore, it is known that LCBs increase the *apparent* activation energy in the terminal regime, as their fluctuations have a higher activation energy than linear chains' reptation movements.

Consequently, we find for LDPEs that the *apparent* activation energy starts increasing to LCB-typical levels ($E_a > 30$ kJ/mol) at very high frequencies (=low δ , high G' , high G''). Only the entanglement or sub-entanglement fluctuation controlled regime at the shortest relaxation times/highest frequencies have a low *apparent* activation energy, but that regime is almost inaccessible with normal dynamic-mechanical tests. Hence, only a sharp increase of the *apparent* activation energy at the highest frequencies is accessible for the measurement. Results by Laun [106] reach the same result by

capillary rheology experiments, which can reach higher shear rates than dynamic-mechanical tests can access angular frequencies. The long relaxation times (low ω , high δ , low G' , low G'') are dominated by terminal fluctuations of LCB-chains, which leads to a relatively constant activation energy, as the difference in activation energy of polymer chains with a significant number of branch points is approximately constant [107]. Furthermore, one has to keep in mind that LDPE is highly polydisperse both in molar mass distribution as well as in branching architecture. Hence, the resulting behavior is the average behavior of a whole host of different chains, which leads to an additional averaging out of the thermorheological complexity and, thus, to a relatively flat $E_a(\delta)$ -peak.

For LCB-mPE, the situation is different. Here, the terminal relaxation of the linear chains is typically at the high frequency end of the accessible frequency range (for grades in the industrially relevant molar mass range), while the terminal range is dominated by the LCB-chains. As the average molar mass of the branched species are significantly higher than, statistically, the linear ones and branching in general increases relaxation times, both regimes are relatively clearly distinguishably located in the accessible frequency range. As both regimes overlap to some degree, the transition between them is gradual, which leads to the gradual change of *apparent* activation energy in $E_a(G')$ and $E_a(G'')$. The peak in $E_a(\delta)$ is due to the distinctly different levels of the plateau or shoulder of δ in the regime between these two regimes, as explained earlier. I.e. the slope of the spectrum between the two main relaxation modes changes as a function of temperature.

Conclusions

These established correlations exemplify that the previously established correlations for LCB-mPE also apply for the regular and the broadly distributed LCB-mPE. Hence, the simple analysis routine described above can determine a couple of characteristic quantities, which can be used for classifying the behavior of an unknown material.

With the established correlations in this and previous articles, the following conclusions can be drawn for an unknown material:

1. Type of material – linear PE, short-chain branched PE, LCB-mPE, LDPE
2. For linear PE and short-chain branched PE, also the comonomer content can be assessed as long as the type of comonomer is known [72, 73].

Hence, a qualitative distinction between linear PE, LDPE, and LCB-mPE (with some qualitative hints to combined effects of branching and molar mass distribution – here significantly more work has to be done in future studies) can be done.

In summary, it is possible to determine a set of linear viscoelastic quantities, which can be further evaluated by an automated routine and is, therefore, quick and easy to do.

The scripts for running the analyses are available from the authors upon request as p-code, requiring a standard Matlab license to run it. Compatibility with GNU Octave has not been checked.

Outlook

The analysis method presented was tested for a range of polyethylenes, which are polydisperse in molar mass distribution and branching topography, although the LCB-mPEX-series can be considered to be as well defined as an industrially relevant product can be. The materials, however, do not cover the whole range of thermorheologically complex materials, known to exist. This would clearly exceed the scope of one paper and many such datasets were not available.

It would, therefore, be very interesting to test other materials for their thermorheological behavior, which would lead to new insights into their structure and how it is related to thermorheological behavior. Especially, testing the method for samples with a defined molecular structure, such as anionically synthesized hydrogenated polybutadienes with defined architecture would be very interesting. Regrettably only very few such polymers were produced and for even fewer their rheological data were made available.

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**Branching
topography
classification**