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# Thermorheology as a method to analyze long-chain branched polyethylenes

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ABSTRACT

This paper presents correlations between polyethylenes of different compositions and branching architectures and their viscoelastic behavior in dependence on the temperature and demonstrates how effectively rheological experiments can be used for analytical purposes. Long-chain branched polyethylenes are known to be thermorheologically complex. But the thermorheological complexity of long-chain branched linear low-density metallocene polyethylenes (LCB-mLLDPE) differs from that of low-density polyethylenes (LDPE) in the way that the activation energy of LDPE becomes constant by a temperature-dependent modification of the moduli whereas a constant activation energy cannot be obtained for LCB-mLLDPE. These findings are explained by the assumption that the LCB-mLLDPE investigated consist of at least two species with distinctly different activation energies. This interpretation is supported by the thermorheological analysis of a blend of known parts of an LDPE and a linear low-density polyethylene (LLDPE). A thermorheological complexity was found similar to that of the LCB-mLLDPE which reflects the different activation energies of the two components. Results of that kind make it possible to get information on the composition of LCB-mLLDPE not available from common analytical methods.

## 1. Motivation

The time–temperature superposition principle plays an important role in the field of rheology. On the one side it is of practical importance as the time dependence of rheological functions of thermorheologically simple materials can be calculated for each temperature chosen if the material-specific activation energy or the WLF constants are known. In that way the measuring time can be reduced and the frequency or time window extended. At measuring temperatures distinctly higher than the glass transition temperature, the relaxation times follow an Arrhenius-type dependence. Then the shift factor $a_T$ can be expressed by:

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{1}$$

$E_a$ is the activation energy, $R$ the universal gas constant, $T$ the measurement and $T_0$ the reference temperature.

On the other side, the activation energy is in the focus of analytical interest. In the literature the activation energy is rather often discussed as a tool to analyze molecular structures and branching topographies. Polyethylene is the most frequently investigated material, as it is commercially available in a great variety of modifications and possesses the "simplest" molecular structure. The studies of Vega et al. and Stadler et al. demonstrate that the activation energies of linear low-density polyethylenes discriminate significantly between materials containing more or less side groups [1,2]. The activation energy of linear polyethylenes ranges from 27 kJ/mol to around 40 kJ/mol depending on the amount and kind of comonomers. Furthermore, the literature frequently shows the effect of long-chain branches (LCB) on the thermorheological behavior of polymer melts [1,3–11]. Long-chain branching may result in thermorheological complexity and elevated activation energies in comparison to the linear counterparts. For example, commercial low-density polyethylene (LDPE) is thermorheologically complex resulting in stress-dependent or modulus-dependent activation energies [5,12–15]. The thermorheological complexity of LDPE originates from a vertical modulus shift $b_T = G(T_0)/G(T)$, which is higher than the density change with temperature [16], associated in the literature with the modulus shift according to the Rouse theory [17,18].

The thermorheological complexity is not restricted to LDPE. Other long-chain branched polymers are known to be thermorheologically complex, too. Amongst these are e.g. branched tetrafluoroethylene-hexafluoropropylene-vinylidenefluorides (THV), branched isotactic polypropylenes, as well as several branched polyethylene copolymers like ethylene–vinylalcohol copolymers or ethylene–vinylacetate copolymers and various miscible and immiscible blends [5,19–23].

Furthermore, a couple of studies deal with long-chain branched metallocene polyethylenes (LCB-mPE) [20,24,25]. A distinct thermorheological complexity is reported, which is different from that

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**Table 1**
Molecular characteristics.

| | $T_m$ [°C] | $M_w$ [kg/mol] | $M_w/M_n$[–] |
|---|---|---|---|
| LLDPE L6-3 | 123.5 | 113 | 3.2 |
| LDPE 2 | 110.0 | 230 | 13.7 |
| LCB-mLLDPE LB-6 | 95.1 | 84 | 3.0 |
| LCB-mLLDPE LB-7 | 105.9 | 70 | 2.5 |

of LDPE. Overlapping processes with different temperature dependences, which involve a temperature-dependent change in the shape of the spectrum are an explanation of the thermorheological complexity [26]. Such it is impossible to construct a master curve. It was postulated that LCB-mPE consists of two species, i.e. linear and long-chain branched molecules, with different activation energies [e.g. [24]]. Consequently, the construction of master curves in case of LCB-mPE may not be possible. These qualitative findings raise the questions in which way the various features of the thermorheological complexity can be used to get an insight into the molecular architecture.

Therefore, the aim of this paper is to compare the thermorheological behavior of different long-chain branched polyethylenes and to determine activation energies even in the case of thermorheological complexity. The focus lies on a deeper insight into the special thermorheological features of LCB-mPE. The systematic characterization of various polyethylenes supports the main aim to relate the thermorheological behavior and the activation energy to definite molecular architectures. In addition to the established methods for molecular analyses like e.g. size exclusion chromatography (SEC) coupled with multi-angle laser-light scattering (MALLS) or nuclear magnetic resonance (NMR), another very sensitive "tool" based on rheological measurements could be established, then.

## 2. Rheology

The rheological measurements were performed under nitrogen atmosphere with a Bohlin Gemini C-VOR rheometer using a 25 mm plate–plate geometry. The polymers were stabilized with 0.5 wt.% Irganox 1010 and 0.5 wt.% Irgafos 168 from Ciba. Thermal stability as well as reproducibility were ensured. For each temperature a new sample was used in order to minimize gap errors. Further experimental details can be found in a preceding paper [16].

## 3. Materials

A high-temperature size exclusion chromatograph (PL 220, Varian Inc.) equipped with Shodex columns [UT 807 (1×) and UT 806 M (3×)] and coupled with a multi-angle laser-light scattering (MALLS) apparatus (Wyatt Dawn EOS, Wyatt Corp.) was used to characterize the molecular structure of the polyethylenes. Measurements at 140 °C were carried out with 1,2,4-trichlorobenzene (TCB) as the solvent.

The molecular characteristics of the samples are given in Table 1. The LLDPE L6-3 is a commercial linear low-density metallocene grade with 1.2 mol% hexene as comonomer (from NMR measurements) serving as a linear reference material [16]. LDPE 2 is one of the two commercial tubular grades previously investigated by Keβner et al. [16]. The long-chain branched metallocene-catalyzed linear low-density polyethylene LCB-mLLDPE LB-6 is also commercially available, while the LCB-mLLDPE LB-7 is an experimental grade. LB-6 contains 23 wt.% octene as comonomer according to the manufacturer. From infrared spectroscopy an octene content of 18 wt.% was estimated for the LB-7.

The radii of gyration $\langle r_g^2 \rangle^{0.5}$ as a function of molar mass $M_{LS}$ are depicted in Fig. 1. The lower detection limit of our SEC coupled with MALLS is about 20 nm. The LLDPE L6-3 follows the relationship valid for linear polyethylenes [27,28]. In contrast, LDPE 2 deviates from the linear relationship as long-chain branches lead to a contraction of the molecules. The LCB-mLLDPE materials, on the other hand, distinctly differ from the LDPE. The radii of gyration are very close to those of the linear PE, hence, long-chain branches cannot be detected by this method. Obviously, the effectivity of the long-chain branches of the LCB-mLLDPE materials and LDPE 2 with respect to the coil dimension is considerably different. This conclusion is supported by the double-logarithmic plot of the zero-shear viscosity $\eta_0$ as a function of the weight-average molar mass $M_w$ (cf. Fig. 2). The

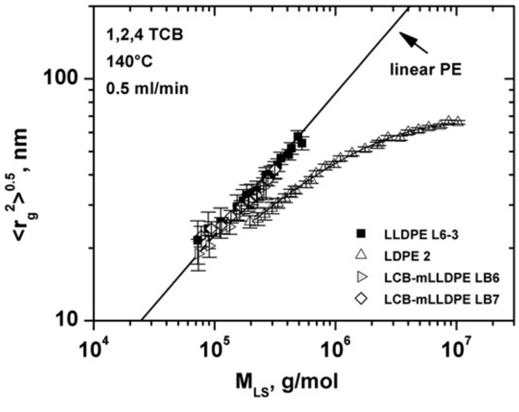

**Fig. 1.** Radii of gyration as a function of molar mass determined by light scattering.

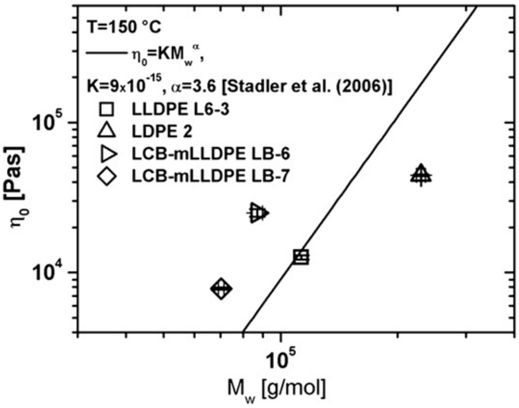

**Fig. 2.** $\eta_0(M_w)$-plot of the polyethylenes investigated.

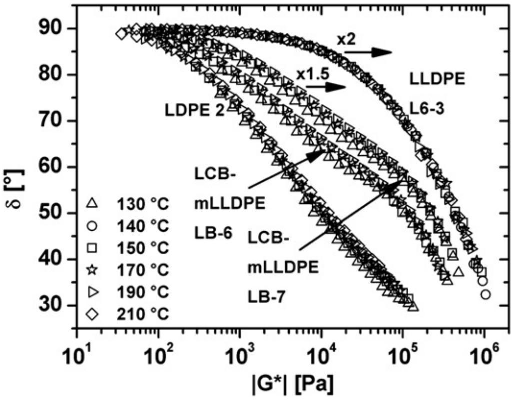

**Fig. 3.** $\delta(|G^*|)$-plot of the polyethylenes investigated. LCB-mLLDPE LB-7 is shifted by the factor of 1.5 along the modulus axis for the matter of a better distinction, LLDPE L6-3 by a factor of 2.

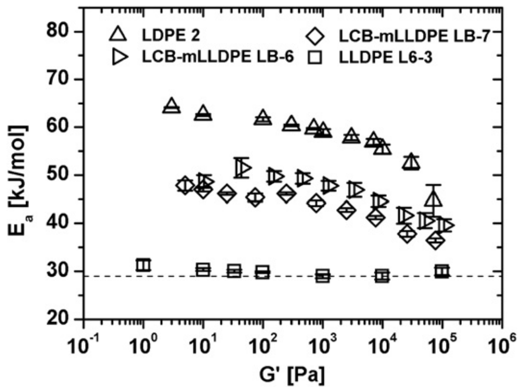

**Fig. 4.** Activation energies as a function of the storage modulus.

zero-shear viscosity of LLDPE L6-3 comes to lie on the line valid for linear polyethylenes. That of LDPE 2 is located below the reference line of linear materials, which is attributed to statistically branched tree-like molecules in the literature [29]. The zero-shear viscosities of the LCB-mLLDPE materials lie above the reference line of linear materials. An exponential dependence of the zero shear-rate viscosity on molar mass is known from the literature for star-like branched polymers, which exceeds the power law valid for linear polymers at high molar masses [29–32]. In conclusion, the results of the $\langle r_g^2\rangle^{0.5}(M_{\mathrm{LS}})$-plot and the $\eta_0(M_{\mathrm{w}})$-plot indicate that the two LCB-mLLDPE materials may contain linear molecules, as well as star-like branched molecules. The amount of the latter is small, however, as they do not show any effect on the radius of gyration. These conclusions are further elucidated by the following results on the thermorheological behavior of the materials.

## 4. Results and discussion

### 4.1. Materials of various branching architectures

The thermorheological behavior of the polyethylenes investigated can qualitatively be classified by the plot of the phase angle $\delta$ versus the magnitude of the complex modulus $|G^*|$ (cf. Fig. 3) for various temperatures, i.e. the so-called van Gurp-Palmen plot. This method is rather sensitive. It was previously shown that LLDPE L6-3 is thermorheologically simple, thus measurements at different temperatures superimpose in this plot [16]. The modulus shift of $b_{T,\mathrm{Rouse}} = \rho_0 T_0/\rho T$ predicted by the Rouse theory [17,18] is negligibly small as a split of the curves of LLDPE L6-3 cannot be observed. In contrast, LDPE 2 is thermorheologically complex. A temperature-dependent modulus shift $b_T$ exists resulting in a systematic split between the data measured at different temperatures, but the shape of the curves remains similar. It is obvious that $b_T$ exceeds $b_{T,\mathrm{Rouse}}$ predicted from theory (cf. [16]). The long-chain branched metallocene polyethylenes LB-6 and LB-7 are thermorheologically complex, too, but in a different way: Besides the split, the shapes of the curves change with temperature and they show pronounced inflection points. A systematic split with temperature does not exist. At low phase angles the curves almost superimpose, while at higher $\delta$ the curves separate. Therefore, a definite modulus shift factor does not exist.

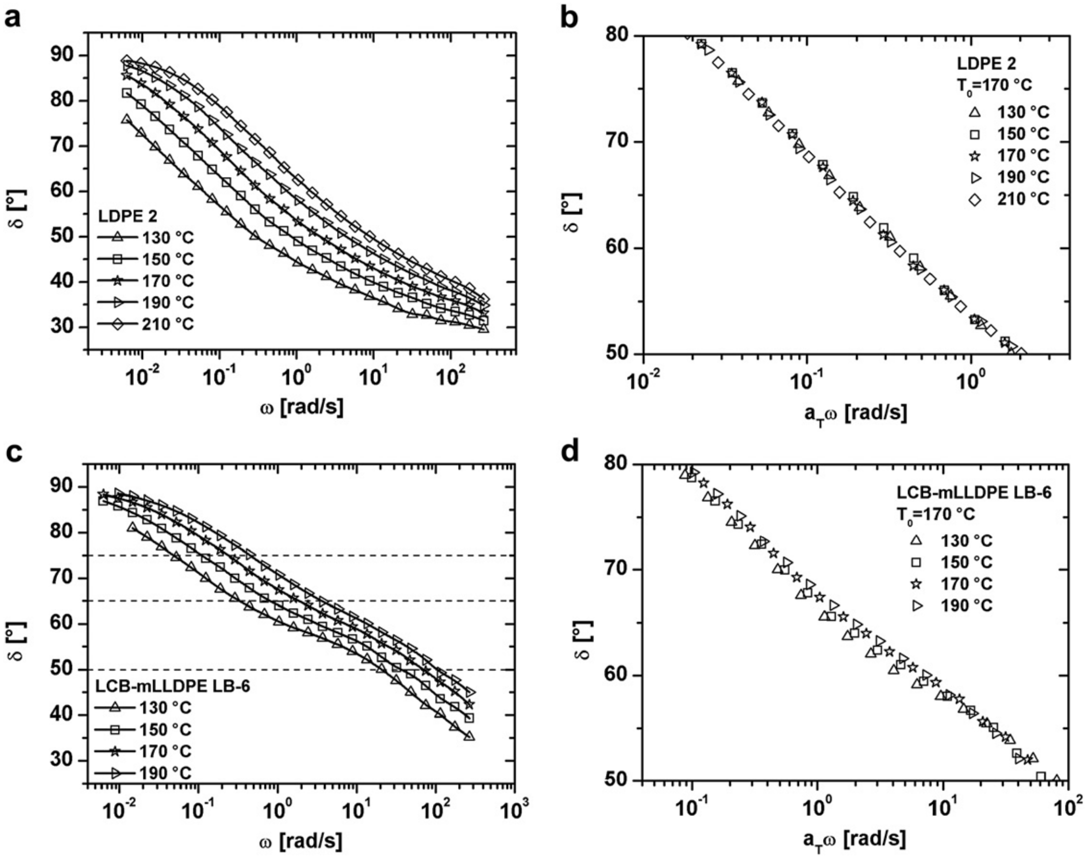

**Fig. 5.** (a) Characteristics of $\delta$ as a function of $\omega$ at different temperatures for LDPE 2 (b) Section of the master curve $\delta(a_T\,\omega)$ of LDPE 2. (c) Characteristics of $\delta$ as a function of $\omega$ at different temperatures for LCB-mLLDPE LB-6. (The broken lines indicate the phase angles for which the activation energies were determined (cf. Fig. 6)). (d) Section of the shifted curves for LCB-LLDPE LB-6.

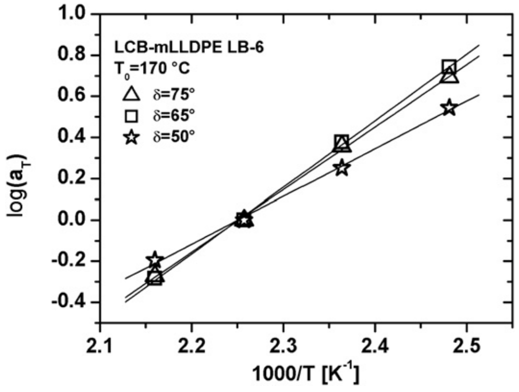

**Fig. 6.** Arrhenius-plots of the shift factors for various phase angles.

In order to analyze the thermorheological behavior in more detail, the activation energies are determined. If the moduli as a function of the angular frequency $\omega$ are considered the thermorheological complexity results in modulus-dependent activation energies. Fig. 4 shows the activation energies of the polyethylenes investigated as a function of the storage modulus $G'$. They were determined from the temperature dependence of the shift factors taken at various constant $G'$ according to Wood-Adams and Costeux [8]. As expected an activation energy independent of the storage modulus is found for the linear, thermorheologically simple LLDPE L6-3. Its value of 29 kJ/mol is in agreement with the literature [2]. The activation energies of the thermorheologically complex long-chain branched polyethylenes exhibit a decrease with increasing storage modulus.

From such an evaluation it is difficult to decide, however, whether the non-constant activation energies are due to a vertical modulus shift or to some other properties of a material.

From a straightforward consideration according to Verser and Maxwell the shift factor $b_T$ of LDPE can be related to a temperature-dependent change of the linear steady-state compliance [12,16]. On the other side, the $\delta(|G^*|)$-plot (cf. Fig. 3) of the LCB-mLLDPE which possess a branching architecture different from that of the LDPE (cf. Figs. 1 and 2) reveals that no constant $b_T$ exists for these materials as the shapes of the curves are different.

Some insight into the complex behavior can experimentally be obtained by determining the activation energy with respect to $\delta(\omega,T)$ or $\tan\delta(\omega,T)$ which do not depend on $b_T$ as:

$$\tan\delta(\omega,T_0) = \frac{G''(\omega,T_0)}{G'(\omega,T_0)} = \frac{b_T\cdot G''(a_T\omega,T)}{b_T\cdot G'(a_T\omega,T)} = \tan\delta(a_T\omega,T) \qquad (2)$$

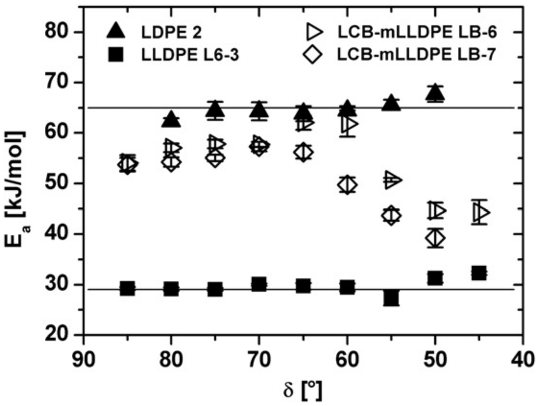

**Fig. 7.** Activation energies as a function of the phase angle.

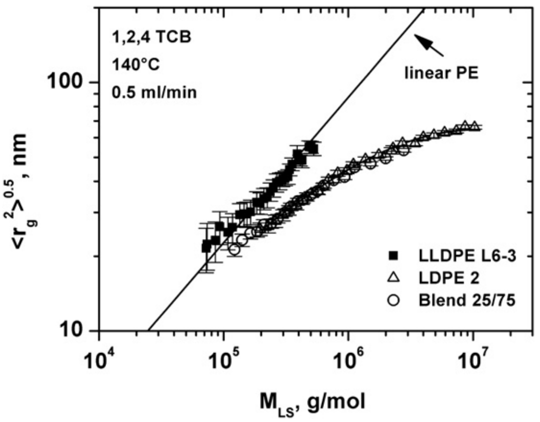

**Fig. 8.** Comparison of the radii of gyration as a function of molar mass of the blend LLDPE/LDPE 25/75 and its components.

Fig. 5 a to d show the $\delta(\omega)$-curves of LDPE 2 and LCB-mLLDPE LB-6, as well as parts of the time–temperature shifts.

According to the $\delta(|G^*|)$-plot in Fig. 3, the shapes of the $\delta(\omega)$-functions of the LDPE 2 are temperature invariant (cf. Fig. 5a), i. e. in good approximation the curves measured at different temperatures are similar to each other and can be shifted along the $\omega$-axis to form a master curve (cf. Fig. 5b). This does not hold for the LCB-mLLDPE LB-6 as shown in Fig. 5c. The shape of $\delta(\omega)$ changes with temperature. Therefore, shift factors $a_T$ leading to a master curve cannot be determined and a master curve does not exist (cf. Fig. 5d). The same behavior was found for the LCB-mLLDPE LB-7. Nevertheless, activation energies can be determined if the logarithms of the shift factors at a constant $\delta$ are plotted versus the reciprocal absolute temperature 1/T (cf. Fig. 6). As can clearly be seen the activation energy becomes a function of the phase angle $\delta$, now.

The activation energies for the four samples are shown in Fig. 7 as a function of $\delta$. LLDPE L6-3 and LDPE 2 exhibit constant activation energies in this plot. However, the LCB-mLLDPE LB-6 and LB-7 differ considerably from these results: their activation energies are a function of the phase angle. At high values of $\delta$ the activation energies range at around 55 kJ/mol, then an intermediate zone with non-constant activation energies follows before the activation energies reach substantially lower values of $E_a$ at small $\delta$. The first consequence from these findings is that the different branching architectures of the two LCB-mLLDPE and the LDPE result in different activation energies. A further consequence is the conclusion that at least two species with different activation energies present in the LCB-mLLDPE are the reason for the thermorheological complexity found.

## 5. Blend of LDPE and LLDPE

In order to check the assumption that from $E_a(\delta)$ conclusions with respect to the composition of a PE can be drawn a blend of linear molecules with short relaxation times and a lower activation energy and long-chain branched molecules with longer relaxation times and a higher activation energy was investigated as a model system. 25 vol.% LLDPE L6-3 and 75 vol.% LDPE 2 were mixed together in a kneader at 60 rpm and 160 °C for 10 min.

The radii of gyration as a function of the molar mass are plotted for the blend and its components in Fig. 8. The radii of gyration of the blend deviate from the reference line of linear polyethylenes; i. e. the blend exhibits a contraction of the molecules. The effectiveness of the long-chain branches in the blend are comparable to the pure LDPE, i. e. their effectiveness is distinctly different from the

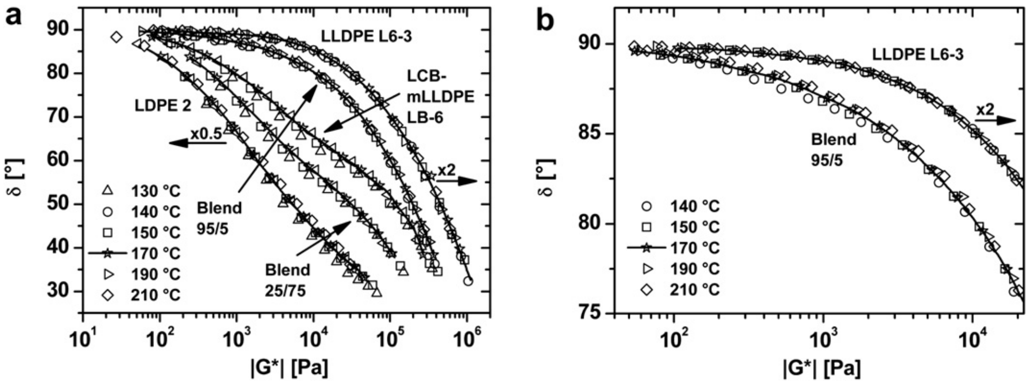

**Fig. 9.** (a) δ(|G*|)-plot at different temperatures of blends consisting of LLDPE L6-3 and LDPE 2 comparison to its components and the LCB-mLLDPE LB-6. (b) δ(|G*|)-plot at different temperatures of the blend consisting of 95 vol.% LLDPE L6-3 and 5 vol.% LDPE 2 in comparison to the linear L6-3.

long-chain branches of the LCB-mLLDPE, which cannot be distinguished from a linear polyethylene with respect to the dependence of the radii of gyration on the molar mass (cf. Fig. 1). Moreover, the blend shows a behavior very similar to the LDPE 2 in the $\eta_0(M_w)$-plot. Thus the blend of LDPE 2 and LLDPE L6-3 cannot be distinguished from the LDPE 2 by these two methods.

Fig. 9 a shows the δ(|G*|)-plot of the blend in comparison with its components and the LCB-mLLDPE LB-6 which allows a qualitative assessment of the thermorheological complexity. It can clearly be seen that the blend behaves similarly to the LCB-mLLDPE supporting the assumption of a nonuniform architecture of these polyethylenes. Additionally, the results of a blend consisting of 5 vol.% LDPE 2 and 95 vol.% LLDPE L6-3 are shown in order to check the "resolution limit" of the thermorheology. Fig. 9b compares the δ(|G*|)-curves of the blend 95/5 with the LLDPE L6-3 in a higher resolution. A systematical split with the temperature is observable for the blend, while the curves of the LLDPE L6-3 show quite good agreement. Such, the influence of 5 vol.% of a long-chain branched PE is detectable with thermorheology, though the effect is quite small. Therefore, the interplay of two differently thermally activated components is discussed by means of the 25/75 blend in the following.

The activation energy as a function of δ of the blend 25/75 is compared with those of its components and with that of the LCB-mLLDPE LB-6 in Fig. 10. The activation energies of LLDPE L6-3 and LDPE 2 can be regarded as constant. The blend, however, exhibits a step in the activation energy comparable with that of the LCB-mLLDPE. From these findings it is evident that the thermorheological complexity of the LCB-mLLDPE can be reproduced by blending linear and long-chain branched polyethylene molecules, which show a thermorheological simplicity in the $E_a(\delta)$-plots.

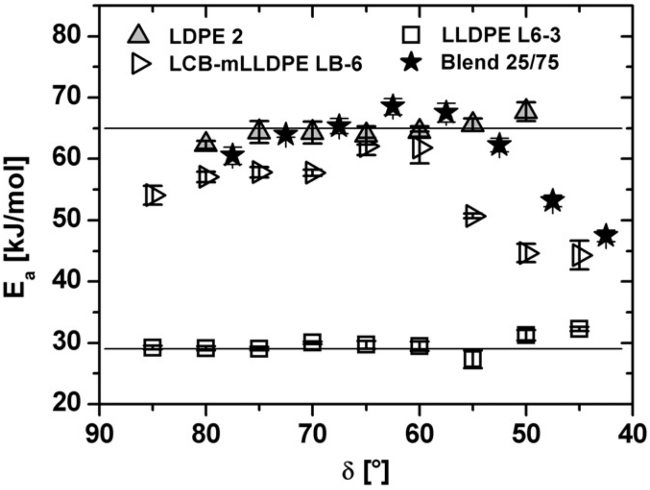

**Fig. 10.** Activation energies as a function of the phase angle of the blend consisting of 25 vol.% LLDPE L6-3 and 75 vol.% LDPE 2 in comparison to its components and LCB-mLLDPE LB-6, respectively.

## 6. Conclusions

The experimental results presented do show that there exist three different kinds of the thermorheological behavior for polyethylene. As well known linear polyethylenes are thermorheologically simple, long-chain branches effect thermorheological complexity. Of the thermorheologically complex species two types have to be distinguished. LDPE exhibits a method-independent activation energy if a vertical shift of the moduli is applied, long-chain branched LLDPE synthesized by metallocene catalysts show a step in the activation energy pointing towards the presence of differently activated species. This behavior cannot be corrected by a vertical shift.

The findings on the blend of a linear LLDPE and a branched LDPE support the assumption that the two LCB-mLLDPE investigated consist of at least two species different with respect to their branching architecture. It is not unreasonable to assume that these two species are linear and branched molecules, resulting from a nonuniform insertion of long-chain branches. Molecules of such structures show distinctly different activation energies. The experimental result that the LDPE becomes thermorheologically simple by shifting the moduli with the factor $b_T$ can be interpreted in the way that all the molecules of the LDPE show a similar time–temperature behavior which may lead to the conclusion of not too different molecular architectures which is in accordance with the literature [33,34]. The physical background of the vertical shift factor is not known, however, up to now.

Very interesting is the fact, that from the thermorheological investigations performed, hints to the unknown structure of LCB-mLLDPE could be obtained which were not available from the commonly used analysis of the radius of gyration as a function of molar mass as it does not reveal any significant difference from the linear polyethylene (cf. Fig. 1). By a more detailed evaluation of the thermorheological behavior it can be concluded that the higher activation energies at larger phase angles belong to molecules with longer relaxation times, the lower ones to those with shorter times. Such a behavior is evident for the blend of an LDPE and an LLDPE due to the increasing effectiveness of branches with growing molar mass (cf. Fig. 8) and the distinctly higher activation energy of the LDPE. For the two LCB-mLLDPE which show

$E_a(\delta)$-functions similar to the blend it can be concluded that the branched species have long relaxation times. As the branches do not show up in the radius of gyration as a function of molar mass (cf. Fig. 1) the results of the thermorheological measurements in Fig. 10 can be interpreted in a way that the LCB-mLLDPE contains relatively few molecules with very long branches. The fact that the activation energy of linear homopolymers of around 27 kJ/mol is not reached gives rise to the assumption that short-chain branched molecules may exist.

The results obtained so far give a hint how powerful rheological methods could be to get an insight into the branching architecture of polymers in cases where the common method of light scattering does not differentiate (cf. Fig. 1). $\eta_0(M_w)$ of the two LCB-mLLDPE investigated exhibit differences (cf. Fig. 2) which clearly point to the existence of long-chain branches with a star-like structure. The analysis of the thermorheological behavior and the determination of activation energies allow additional qualitative conclusions with respect to the uniformity of the molecular structure.

This conclusion is supported by the findings on the blend. The analysis of the radii of gyration as presented in Fig. 8 does not give any hint to the linear component due to several experimental reasons. First of all, the lower detection limit of our SEC coupled with MALLS is 20 nm. Furthermore, the radii of gyration of the LDPE 2 have been truncated at molar masses below 200 000 g/mol as indications for non-ideal separation in the GPC became visible as stated in our previous paper [16]. The results of the neat LLDPE L6-3, however, range only up to 500 000 g/mol, i. e. above this value only the molecules of the LDPE 2 appear. The $<r_g^2>^{0.5}(M_{LS})$-curve of the blend agrees with that of the neat LDPE 2 in the $M_{LS}$ range between 200 000 g/mol and 500 000 g/mol. This behavior becomes obvious as the molar-mass distributions – which are not shown at this point – of the blend and the LDPE 2 agree in good approximation in-between this molar-mass range, because the amount of the neat LLDPE L6-3 is very small.

The thermorheological complexity and the activation energy as a function of the phase angle $\delta$ in Fig. 10 make it obvious that the blend 25/75 contains components with activation energies smaller than that of the LDPE used. The fact that at higher $\delta$, i. e. at longer relaxation times the activation energy of the LDPE 2 is found in good approximation is not surprising, due to its larger viscosity and elasticity in the linear range in comparison to the LLDPE blend component which gives rise to a distinctly longer terminal relaxation time. These results demonstrate the analytical potential of the rheological methods applied.

Another fact has to be mentioned with respect to the usability of the methods discussed. Besides the limited sensitivity of the size exclusion chromatography coupled with multi-angle laser-light scattering, investigations of this kind on polyolefins have to be performed at temperatures above 100 °C in the dissolved state which need a lot of sophisticated experimental measurements. The same experimental condition holds for any conclusions drawn from $\eta_0(M_w)$ as the absolute value of $M_w$ has to be regarded which is preferably determined by light scattering.

The analysis presented in this paper which makes use of the activation energy as a function of the phase angle only needs well established dynamic-mechanical experiments at different temperatures in the molten state. It is relatively easy to apply and offers a great potential for getting a deeper insight into the branching architecture of polyolefins.

## 7. Summary

The differences of the thermorheological behavior and the activation energies of four polyethylenes could be related to their chain topographies. Thermorheological simplicity was found for the linear polyethylene as expected. Thermorheological complexity could be connected with the presence of long-chain branches. A more detailed analysis of the thermorheological complexity even differentiated between LDPE and LCB-mLLDPE. The moduli of LDPE are shifted by the factor $b_T$ reflecting the temperature dependence of the linear steady-state compliance. However, master curves can be obtained and a constant activation energy can be determined if $\delta(\omega,T)$ is evaluated. The two LCB-mLLDPE investigated exhibit a thermorheological complexity quite different from that of LDPE, however. A constant activation energy is not found even if the influence of $b_T$ is excluded in terms of the evaluation of $\delta(\omega,T)$. Compared to the constant activation energies of the LLDPE and LDPE a step in the activation energy as a function of the phase angle was observed. This behavior was found to be similar to that of a blend from LDPE and LLDPE. Thus, a thermorheological complexity comparable to that of the LCB-mLLDPE could be generated by blending two polyethylene species with different activation energies. These results strengthen the assumption that the LCB-mLLDPE investigated are blends of differently branched molecules. They throw some light on the power of rheological measurements with respect to an analysis of the branching architecture of polymers.

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