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Thermorheological Behavior of Various Short- and Long-Chain Branched Polyethylenes and Their Correlations with the Molecular Structure

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ABSTRACT: This paper deals with the characterization of a broad range of linear polyethylenes (PE) by means of thermorheology. It is demonstrated, in which way the thermorheological behavior can be related to the comonomer type and content of copolymers. In the first part of this paper, well-established analytical and rheological methods are applied to distinguish linear and branched samples. The resolution limit of these methods is demonstrated by the investigation of a blend from a linear-low density PE (LLDPE) and a branched low density PE (LDPE). Special attention is paid to nuclear-magnetic resonance (NMR) spectroscopy in order to reliably determine the comonomer type and content of the samples chosen. The main focus of this paper lies on thermorheological investigations and correlations with the molecular structure. The comparatively high sensitivity of such investigations is highlighted: even small amounts of long-chain branches (LCB) are revealed. The activation energy (E_a) of linear samples increases with growing comonomer length and content, respectively. As such, thermorheology is demonstrated to be an interesting rheological "tool" to get an insight into branching structures. Moreover, the experimental effort is relatively small as solely usual dynamic-mechanical experiments at different temperatures are required.

Introduction

Commercial linear low-density polyethylenes (LLDPE) are polymerized by Ziegler–Natta (ZN) or metallocene (m) catalysts using ethylene and an α-olefin, which is typically butene, hexene, or octene, respectively. Single-site catalysts (SSC) even allow the insertion of very few long-chain branches (LCB) into linear polyethylenes (PE) improving the processing properties. As such, the molecular structure and consequently the physical properties of these copolymers vary distinctly. Several studies in the literature aim to characterize the molecular structure of commercial as well as experimental LLDPE grades with analytical and rheological means in order to develop new grades and to improve the efficiency of catalysts.[1–4]

The aim of this paper is to present a rheological "tool" to probe the molecular structure of PE, which is simple to handle compared to the common analytical characterization methods. For this purpose, the thermorheological behavior and the determination of activation energies (E_a) are suitable methods, as they reliably discriminate between thermorheologically simple LLDPE and thermorheologically complex long-chain branched low-density polyethylenes (LDPE) or long-chain branched metallocene linear low-density polyethylenes (LCB-mLLDPE), respectively.[5] Some studies in the literature already deal with the relationship between the thermorheological behavior and the molecular structure of linear polyethylenes. These are summarized in the next section in order to derive the motivation and goals of this paper.

Literature Survey

Influence of the Length of Side Groups. *Homopolymers.* High-density polyethylenes (HDPE) possess activation energies E_a around 26–28 kJ/mol independent of the molar mass (M) and the polydispersity (PDI).[3,6–8]

The homopolymerization of higher α-olefins leads to an increase of E_a with increasing monomer mass as the rotational potential of the backbone units rises.[7] For example, for isotactic polypropylene (iPP), which differs from HDPE by replacing hydrogen atoms by methyl groups, activation energies between 36 and 44 kJ/mol are reported.[7–13] Higher values up to 58.5 kJ/mol were determined by Eckstein et al.,[10] while Rojo et al. found an E_a around 50 kJ/mol,[14] in case of syndiotactic polypropylenes. However, the influence of tacticity is not completely understood. Homopolymers of higher α-olefins like polyisobutylene even reach activation energies around 45 kJ/mol,[15] while 49–66 kJ/mol is found for poly-1-butene.[7,16,17]

Copolymers. Kolodka et al.[18] copolymerized iPP with a poly(ethylene-*co*-propylene) macromer with a number-average molar mass (M_n) of 2500 g/mol, which is below the critical entanglement length. E_a of around 40 kJ/mol was obtained independently of the branching frequency.

Furthermore, activation energies of around 30–33 kJ/mol are found in the literature for PE differing in the comonomer type and content.[9,19–21] The E_a values reported could not be correlated with the molecular structure. However, Hussein et al.[22] concluded from their results that E_a of poly(ethylene–octene) is higher than poly(ethylene–butene) at the same branching content.

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Influence of the Comonomer Content. Some authors[4,23,24] identified a relationship between E_a and the number of side chains or comonomer content, respectively. An increase from around 23 kJ/mol at 0 wt % up to 40 kJ/mol at 30 wt % hexene was determined in the range studied. Stadler et al.[3] found such a dependence to be valid regardless of the comonomer type inserted. Wood-Adams and Costeux[25] published E_a values of poly(ethylene−butene) copolymers. E_a increased from 26 kJ/mol at 0 wt %, characteristic of HDPE, to around 33 kJ/mol at 7 wt % comonomer content. At still higher butene contents, E_a was found to be constant. These results are consistent with other studies.[26−28] An increase of E_a with comonomer content was also found by Hussein et al.[22] for poly(ethylene−butene) and poly(ethylene−octene). However, it cannot be concluded from this study whether E_a becomes constant or still increases at higher comonomer content.

Some papers report even higher E_a for LLDPE but state that LCB may be an issue.[2]

Influence of the Comonomer Distribution. The catalyst chosen affects the homogeneity of the comonomer incorporation. From the literature, it is known that ZN catalysts, in general, lead to heterogeneous comonomer distributions. By comparison, the structure of polymers catalyzed with single-site catalysts (SSC) is more homogeneous. Additionally, heterogeneities of the comonomer distribution may appear with both catalyst types.[29−31] Nevertheless, no differences in the thermorheological behavior between m- and ZN-catalyzed LLDPE are reported in the literature.

Influence of Very Few Long-Chain Branches. Investigations of the correlations between the thermorheological behavior and the molecular structure of linear PE are often complicated by the presence of a small amount of LCB, which may be not detectable with analytical methods. Vega et al.[24] and Wood-Adams and Costeux[25] describe a synergistic effect of short-chain and long-chain branching on E_a. Furthermore, E_a of long-chain branched HDPE and LLDPE increased with the number of LCB. By contrast, Wasserman and Graessley[8] did not observe an elevated E_a for samples suspected to contain few LCB. Thus, the question remains whether few LCB noticeably affect the thermorheological behavior. Nevertheless, it is known from the literature that a significant amount of LCB, for example in LDPE and LCB−mLLDPE, results in thermorheological complexity and lead to a higher E_a compared to LLDPE.

Motivation

It is well-established in the literature that linear PE is thermorheologically simple. Furthermore, it is known that the molar mass and the polydispersity have no influence on the thermorheological behavior. LCB, however, affect the temperature dependence drastically, such that reliable correlations with the linear structure of PE (i.e., the comonomer length and content) are not possible, if a few LCB are present. A complete and comprehensive molecular characterization of the samples investigated is missing in many studies cited above. Moreover, the analytical and rheological characterization methods used were not sensitive enough to reveal small amounts of LCB and/or are time and cost consuming.[32,33]

Therefore, contradictory results on "apparently" linear PE are found in the literature. Furthermore, inconsistencies are obvious, as different methods for the evaluation of E_a were applied in these studies. Resuming the various findings, the prerequisites to establish relationships between the thermorheological behavior, especially E_a, and the comonomer length and content of LLDPE should exclude the presence of any LCB and apply a method for the determination of E_a which is independent of the experimental quantity used. An approach to a defined method was previously published,[34] and it is applied in this paper.

A broad range of linear polyethylenes is investigated with common analytical and rheological methods as well as with thermorheology. A detailed molecular characterization of the samples is carried out to detect small amounts of LCB and to get a comprehensive insight into the molecular structure. The temperature-dependent viscoelastic behavior is related to the molecular structure taking into account the detection limits and restrictions of the methods used.

Characterization Methods

Molecular Analysis. *Size Exclusion Chromatography (SEC) Coupled with Multiangle Laser-Light Scattering (MALLS).* The determination of the molar masses (M_n, number-average; M_w, weight-average), their distribution as well as the radii of gyration was carried out using a high-temperature size exclusion chromatograph ((SEC), PL 220, Varian Inc.) equipped with Shodex columns [UT 807 (1×) and UT 806 M (3×)] and coupled with a multiangle laser-light scattering (MALLS) apparatus (Wyatt Dawn EOS, Wyatt Corp.). The temperature was 140 °C and the solvent 1,2,4-trichlorobenzene (TCB). Supporting Information on the reliability of the determination of the radii of gyration is available.

^{13}C Nuclear Magnetic Resonance (^{13}C NMR) Spectroscopy. ^{13}C nuclear-magnetic resonance (^{13}C NMR) spectroscopy was applied in order to determine the comonomer type and content. These NMR measurements were performed in different laboratories and by different operators. A good agreement between the results of different setups was obtained. The reproducibility of such measurements was checked on a poly(ethylene−hexene) sample (L6−4). The measurement uncertainty is estimated to be ±10% at the maximum.

The main part of the NMR results originates from the Université catholique de Louvain (Département de Chimie) and was conducted and evaluated by C. S. Le Duff and X. Drooghaag. Details of these measurements are briefly given below. Further information on the measurement and evaluation of NMR data as well as on the quantitative determination of the comonomer content can be found in the literature.[35−39]

Preparation of Samples for the NMR Analysis. About 100 mg of each polymer were dissolved under argon in 2.5 mL of deuterated tetrachloroethane (TCE-d_2), preheated at 135 °C. To obtain a complete dissolution, the samples were rotated at 40 rpm in the NMR spectrometer at 135 °C for up to 1 h.

Acquisition of 1D ^{13}C NMR spectra. NMR spectra were acquired on a Bruker Avance DRX500 spectrometer operating at 500.13 MHz for ^{1}H (125.77 MHz for ^{13}C) and equipped with a 10 mm Bruker Selective Observe ^{13}C probe for temperatures up to 400 °C.

The probe temperature was set at 135 °C for the duration of the experiments. Spectra were referenced to the TCE-d2 peaks at 6.00 ppm for ^{1}H and 73.70 ppm for ^{13}C. One-dimensional ^{1}H spectra were recorded prior to ^{13}C experiments to ensure that the best field homogeneity was attained for each sample. One-dimensional ^{13}C were recorded using 32768 points and an acquisition time of 0.59 s. Between 3000 and 4000 scans were acquired per sample with a sweepwidth of 27.6 kHz and a delay of 15 s between scans, using inverse-gated Waltz16 ^{1}H decoupling.

The signal was Fourier transformed using an exponential multiplication function with a line broadening of 2 Hz and

Table 1. Molecular Characteristics of the "Reference Materials" and the Blend LL/L 95/5

sample	M_w [kg/mol]	M_w/M_n
mHDPE 1	205	2.6
mHDPE 2	45	2.7
LDPE 2	230	13.7
mLLDPE L6−1	113	3.2
blend from mLLDPE L6−1 and LDPE 2: LL/L 95/5	112	3.0

Table 2. Molecular Characteristics of the Poly(ethylene−butene) Copolymers

sample	catalyst	comonomer	n_c [mol %]	M_w [kg/mol]	M_w/M_n
L4−1	ZN	butene	0.7	85	3.7
L4−2	ZN	butene	2.7	148	4.2
L4−3	ZN	butene	2.8	88	3.6
L4−4	ZN	butene	3.7	128	4.2
L4−5	m	butene	5.4	108	2.0
L4−6	m	butene	5.7	112	2.5
L4−7	ZN	butene	7.6	85	3.7

zero-filled to a final spectral resolution of 0.42 Hz per point. Sample spinning was not found to significantly improve the resonances line shape, so all spectra were measured without it. A *J*-modulated spin−echo experiment was also measured to determine the number of ^{1}H coupled to ^{13}C in order to support the assignments of peaks.

Rheological Experiments. The resins were stabilized with 0.5 wt % Irganox 1010 and 0.5 wt % Irgafos 168 from the Ciba company. Disks of 25 mm diameter and 2 mm height were pressed. The rheological experiments were conducted under nitrogen atmosphere with a Bohlin Gemini C-VOR rheometer. Dynamic-mechanical data were recorded for at least four different temperatures in the range from 130 to 210 °C at angular frequencies ω between 0.01 and 300 s^{-1}. Whenever the terminal regime at 150 °C was not reached, creep experiments were carried out to determine the zero-shear viscosity. Details about creep experiments can be found in the literature.[40] A new sample was inserted in the rheometer whenever the temperature was changed in order to minimize gap errors. Thermal stability as well as reproducibility were ensured.

Materials

A broad range of different commercial and experimental PE grades was chosen which allow the systematical characterization of the relationship between comonomer content, type and distribution. As these samples result, on the one hand, from commercial manufacturers and, on the other hand, from a project subjected to a nondisclosure agreement (samples mLLDPE L4−5 and L6−3), no information about the polymerization conditions can be given. Nevertheless, at least the catalyst is known.

Particular attention was paid toward the possible presence of a small amount of long-chain branches. Thus, a blend of 95 vol % mLLDPE L6−1 and 5 vol % LDPE 2 (LL/L 95/5) was investigated to get an insight into the effect of a small amount of long-chain branched material (cf. Table 1) (Preparation: Kneader, 60 rpm, 160 °C, 10 min).

Tables 1−4 summarize the results of the molecular characterization. The comonomer content n_c is an average of the different NMR measurements carried out.

Table 1 contains the samples the properties of which are known. Therefore, they are used as "reference materials". For example, mHDPE 1 and mHDPE 2 were intensively investigated in terms of an IUPAC round robin test and are known as linear homopolymers. (mHDPE 1 was not investigated rheologically in this work; its zero-shear viscosity at 150 °C shown in the following was taken from Stadler et al.[41]). mLLDPE L6−1 and LDPE 2 were extensively studied before and results on the blend L/LL 95/5 were already partly discussed.[5,34]

Table 3. Molecular Characteristics of the Poly(ethylene−hexene) Copolymers

sample	catalyst	comonomer	n_c [mol %]	M_w [kg/mol]	M_w/M_n
L6−1	m	hexene	1.2	113	3.2
L6−2	m	hexene	2.6	124	2.9
L6−3	m	hexene	2.6	83	2.5
L6−4	m	hexene	3.0	116	2.5

Table 4. Molecular characteristics of the poly(ethylene−octene) copolymers

sample	catalyst	comonomer	n_c [mol %]	M_w [kg/mol]	M_w/M_n
L8−1	ZN	octene	1.1	129	4.5
L8−2	ZN	octene	1.6	135	4.6
L8−3	ZN	octene	3.8	96	4.9

In Table 2, the samples with butene as the comonomer are listed. Its content ranges from 0.7 mol % to 7.6 mol %. Hexene and octene comonomers cover a smaller range but the factor of about three in their concentrations will be large enough for differentiation (cf. Table 3 and Table 4). The nomenclature of the samples is chosen in the way that "L" stands for the linear structure anticipated, the first number for the carbon atoms of the comonomer and the second one denominates the sample within one category.

Results

Analytical Characterization. The branching architecture of the samples was analytically investigated by means of the well-established relationships between the radius of gyration $\langle r_g^2\rangle^{0.5}$ and the molar mass M_{LS}.[41,42] It should be mentioned that the lower resolution limit of the experimental setup used lies at a radius of gyration of around 20 nm.

First, the question whether the samples contain small amounts of LCB is addressed by means of SEC coupled with MALLS. Parts a and b of Figure 1compare $\langle r_g^2\rangle^{0.5}$ and the differential molar-mass distribution dW/d(log M), respectively, as a function of M_{LS} for mHDPE 1, mHDPE 2, mLLDPE L6−1, LDPE 2 and the blend LL/L 95/5. The power-law relationship between $\langle r_g^2\rangle^{0.5}$ and M_{LS} of linear PE is valid for mHDPE 1 and mHDPE 2. The linear fit of the double−logarithmically plotted $\langle r_g^2\rangle^{0.5}(M_{LS})$ values of mHDPE 1 serves as a reference for linear molecules in the following. While mLLDPE L6−1 fulfils this relationship, too, LDPE 2 deviates from the straight line. This is due to the LCB causing a coil contraction of the molecules.[34] The long-chain branched fraction of the blend LL/L 95/5 is not reflected by this plot as $\langle r_g^2\rangle^{0.5}$ follows the $\langle r_g^2\rangle^{0.5}(M_{LS})$ relationship of the linear PE within the measurement uncertainty.

The dW/d(log M) curves of the linear samples are typical of the narrow molar mass distribution characteristics for metallocene-catalyzed PE. In comparison, a broad distribution is observed in case of the LDPE polymerized by a free-radical process. The molar mass distributions dW/d(log M) of the neat LLDPE and the blend LL/L 95/5 are quite similar. Therefore, the molecular analysis with SEC and MALLS has to be regarded as not being capable to reveal low amounts of long-chain branched molecules within a linear matrix, if they are of the order given by the blend.

$\langle r_g^2\rangle^{0.5}$ as well as dW/d(log M) as a function of M_{LS} of the copolymers following the relationship for the linear PE are only partly presented. No hints to the presence of

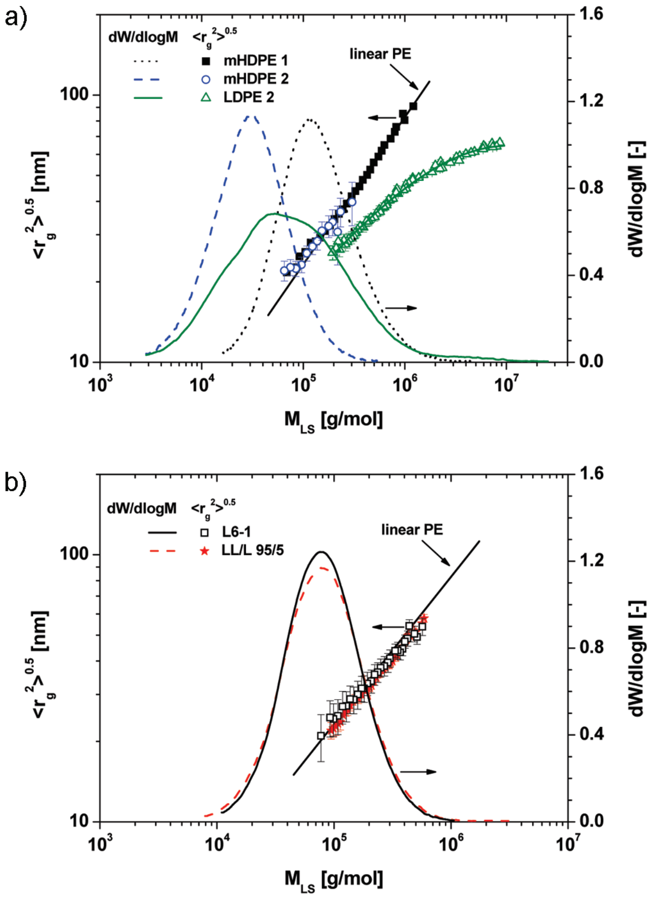

Figure 1. $\langle r_g^2\rangle^{0.5}(M_{LS})$ and $dW/d(\log M)$ as a function of M_{LS} of (a) the homopolymers and (b) mLLDPE L6−1 and the blend LL/L 95/5.

LCB are obtained for most of the samples of Table 2 to Table 4. There are some few exceptions, however, which will be discussed in the following.

Figure 2a shows somewhat surprising results of the ZN-LLDPE L4−2 and L4−4 in comparison to the linear reference (i.e., mHDPE 1). The two ZN-LLDPE samples deviate at high M_{LS} from the $\langle r_g^2\rangle^{0.5}(M_{LS})$-relationship of linear PE.

$dW/d(\log M)$ as a function of M_{LS} of these samples exhibits a broad molar mass distribution with high molar mass components. (The results were affirmed by comparative measurements at two other laboratories.)

From these results, it could be assumed that the ZN-LLDPE L4−2 and L4−4 are linear PE with a small portion of LCB molecules at high M_{LS}, but for ZN-catalysts an incorporation of LCB is not known. On the other hand, a contraction of molecules resulting in lower $\langle r_g^2\rangle^{0.5}$ than that of linear counterparts is known from the literature for linear samples with a high comonomer content.[43] Sun et al.[43] investigated the influence of short-chain branches on $\langle r_g^2\rangle^{0.5}$-($M_{LS}$) of structurally uniform α-olefin copolymers of ethylene with propene, butene, hexene and octene. Their results of $\langle r_g^2\rangle^{0.5}(M_{LS})$ could be described by a power-law analogous to that of the linear PE homopolymers. However, the proportionality constant decreased systematically with increasing comonomer length and content which can be interpreted as a contraction of $\langle r_g^2\rangle^{0.5}$ over the whole range of M_{LS}. Such a trend was found beginning with 5 wt % comonomer in the copolymers, however, a significant deviation from the homopolymer serving as a reference was observed above a comonomer content of around 20−30 wt %. According to these findings, a very inhomogeneous comonomer distribution of the ZN-catalyzed products L4−2 and L4−4 with a low comonomer content at low M and a high comonomer content at high M could be the reason for the contraction of $\langle r_g^2\rangle^{0.5}$ at high M_{LS}. However, ZN catalysts are known to preferentially insert comonomers in the regime of lower M, while molecules in the regime of higher molar masses are less side-chain branched. Furthermore, the average comonomer content of the samples investigated in the terms of this thesis is comparatively low and, thus, a pronounced deviation from the linear reference due to short-chain branches is implausible.

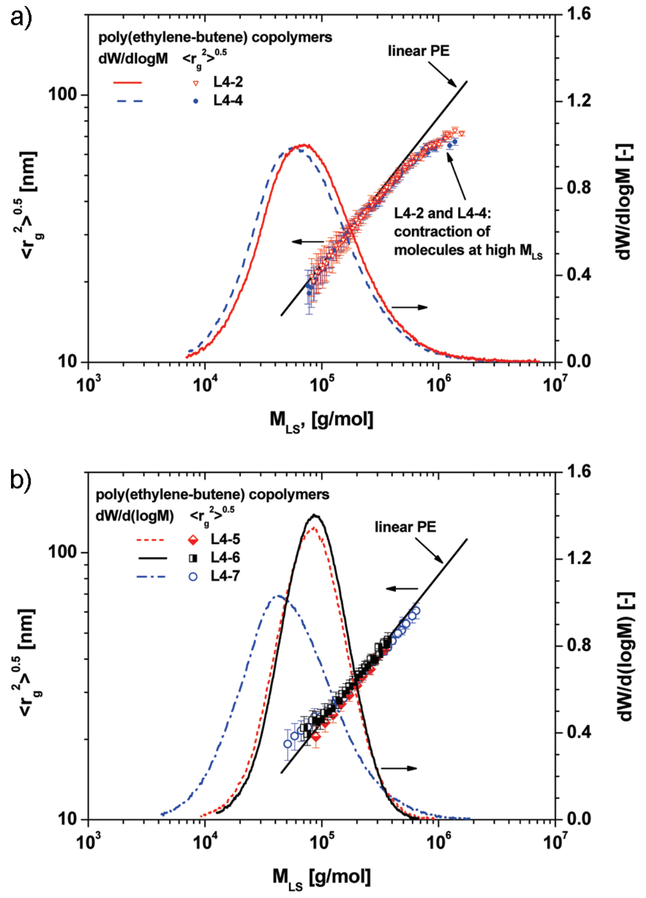

Figure 2. (a) $\langle r_g^2\rangle^{0.5}(M_{LS})$ and $dW/d(\log M)$ as a function of M_{LS} of poly(ethylene−butene) copolymers showing deviations from the linear structure (b) $\langle r_g^2\rangle^{0.5}$ and $dW/d(\log M)$ as a function of M_{LS} of several poly(ethylene−butene) copolymers.

In addition, Figure 2b and Figure 3 show exemplarily several butene and hexene copolymers, which were found to be linear according to the results of SEC-MALLS. The linear samples shown here coincide with the linear reference, i.e. mHDPE 1, indicating the absence of LCB. The molar mass distributions of the ZN-catalyzed samples are in general broader than those of the m-catalyzed samples.

$\langle r_g^2\rangle^{0.5}(M_{LS})$ of the ZN-catalyzed poly(ethylene−octene) samples is shown in Figure 4. These samples coincide with the reference line of linear PE in good approximation. However, $\langle r_g^2\rangle^{0.5}(M_{LS})$ of ZN-LLDPE L8−3 with the highest but still relatively low comonomer content of the octene samples shows a faint contraction of the molecules resulting in lower $\langle r_g^2\rangle^{0.5}$ values over the whole M_{LS} range in comparison to the $\langle r_g^2\rangle^{0.5}$ of mHDPE 1 or the copolymers with lower comonomer contents, respectively. The slope of a linear fit through its values is similar to that of the reference line of linear PE. Though, this small contraction is still in the order of the measurement uncertainty, this trend is in agreement with the

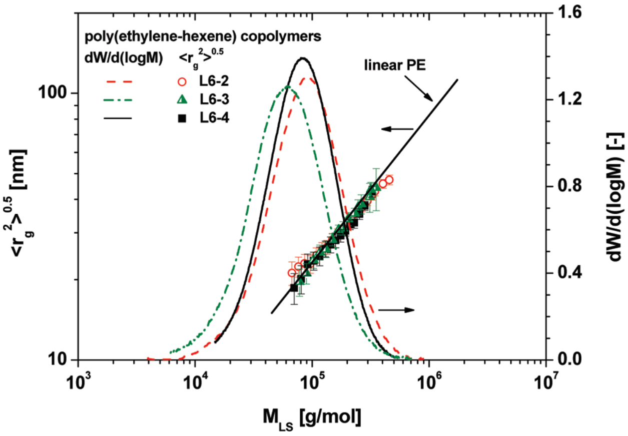

Figure 3. $\langle r_g^2\rangle^{0.5}(M_{LS})$ and $dW/d(\log M)$ as a function of M_{LS} of the poly(ethylene−hexene) copolymers.

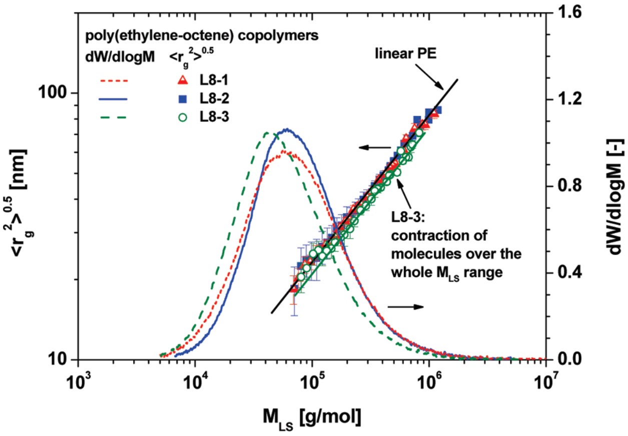

Figure 4. $\langle r_g^2\rangle^{0.5}(M_{LS})$ and $dW/d(\log M)$ as a function of M_{LS} of the poly(ethylene−octene) copolymers.

results of Sun et al.[43] on the influence of SCB on $\langle r_g^2\rangle^{0.5}$-($M_{LS}$). These authors demonstrated a similar contraction of the molecules of several PE copolymers which increases with increasing side-chain frequency.

The fact that the samples L4−6 and L4−7, which possess a comonomer content even higher than that of L8−3, coincide with the reference line of linear PE can also be understood by the results of Sun et al.[43] as the coil dimensions correlate with the comonomer type. The influence of an incorporated butene comonomer on the coil size is weaker than that of an octene comonomer.

Rheological Characterization. The double−logarithmic plot of the zero-shear viscosity η_0 as a function of the absolute weight-average molar mass M_w allows a qualitative discrimination of the branching architecture. $\eta_0(M_w)$ of the samples investigated is depicted in Figure 5. The zero-shear viscosities are averages from several reproducible measurements. η_0 was determined from dynamic-mechanical experiments, whenever the terminal regime was reached. Otherwise, the values given result from creep experiments which are appropriate to cover longer times.

The zero-shear viscosities of HDPE were found to be proportional to $M_w^{3.6}$.[41] This relationship is valid for mHDPE 1 and mHDPE 2, too. LDPE 2 significantly deviates from the reference line of linear materials indicating statistically (or treelike) branched molecules.[34,44] (Values higher than those of the reference line are attributed toward star-like branched molecules in the literature[44]). The $\eta_0(M_w)$ relationship holds for PE copolymers in good approximation, too, as frequently shown in the literature.[28,44]

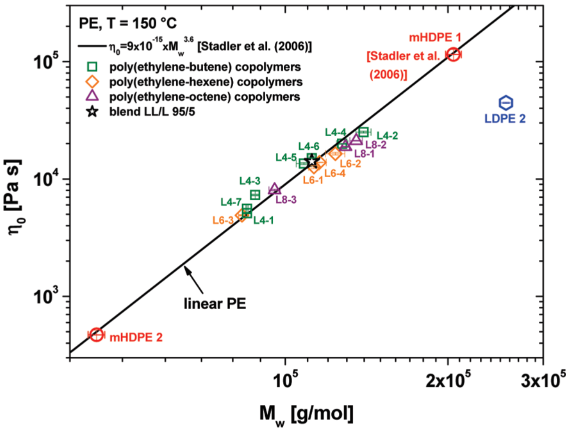

Figure 5. $\eta_0(M_w)$ of the polyethylenes investigated.

All the linear samples investigated in this paper fulfill the well-established power-law dependence within the accuracy of the analytical and rheological measurements. In order to probe the influence of few LCB on the $\eta_0(M_w)$-relationship the results of the blend LL/L 95/5 are depicted, too. The viscosities of the blend LL/L 95/5 and the matrix mLLDPE L6−1 differ only by about 10%. Within the experimental accuracy, the $\eta_0(M_w)$-relationship cannot reveal a small amount of LCB in LLDPE. As a consequence, $\eta_0(M_w)$ is not accurate enough to answer the question whether ZN-LLDPE L4−2 and L4−4 contain any LCB as indicated by $\langle r_g^2\rangle^{0.5}(M_{LS})$ (cf. Figure 2a).

Thermorheological Behavior. The detection of LCB by means of the analytical and rheological characterization is limited due to the low sensitivity toward LCB of the methods applied. However, it is known from the literature that thermorheology is very sensitive with respect to LCB. Therefore, it can be expected that further information on the samples may be gained from the thermorheological behavior.

In case of thermorheologically simple polymers, all relaxation times τ involved exhibit the same temperature dependence:

$$\tau(T) = a_T(T, T_0)\cdot\tau(T_0) \tag{1}$$

with T being the actual and T_0 the reference temperature.

The shift factor a_T is a function of the temperature allowing the construction of master curves from rheological properties.

For temperatures significantly higher than T_g an Arrhenius-equation of the type

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{2}$$

is valid (R is the universal gas constant, T the absolute temperature of the measurement, T_0 the reference temperature, and E_a the activation energy). In general, the shift factors of PE are known to follow such an Arrhenius dependence.

Equation 1 does not hold for thermorheologically complex materials as in such a case not all the relaxation times do shift with the same temperature-dependent factor. For many materials such a behavior can be described by a stress-dependent activation energy, for example. This quantity can be used for a qualitative discussion of the thermorheological complexity.

Qualitative Classification: $\delta(|G^*|)$ Plots. For a coarse classification of the materials with respect to their thermorheological behavior, the phase angle δ as a function of the

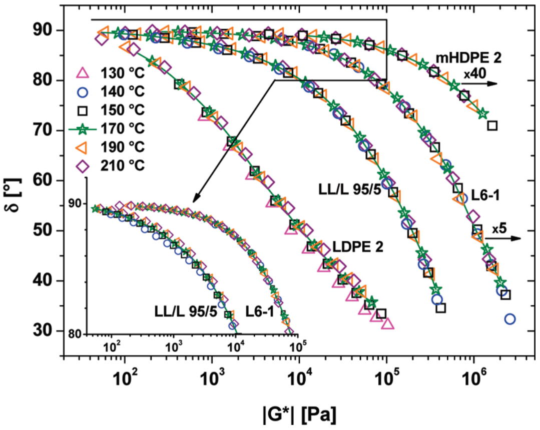

Figure 6. $\delta(|G^*|,T)$ of the homopolymer mHDPE 2, the blend LL/L 95/5 and its components.

magnitude of the complex modulus $|G^*|$ at different temperatures is used.[45]

Such a plot is exemplarily shown in Figure 6 for the "reference materials" mHDPE 2, LDPE 2, and mLLDPE L6−1 and the blend LL/L 95/5. In some cases, the curves were shifted along the |G*|-axis by the factors indicated, for the matter of a better distinction. The curves of mHDPE 2 and mLLDPE L6−1, measured at different temperatures, superimpose indicating thermorheological simplicity. In contrast to them, LDPE 2 splits systematically with temperature typical of a pronounced thermorheological complexity. This kind of thermorheological complexity was extensively discussed in a previous paper.[34]

The influence of very few long-chain branched molecules on the thermorheological behavior of a linear PE can be seen from the blend LL/L 95/5. The curves of the blend coincide with each other at lower δ or shorter relaxation times, respectively, while a slight but systematic split with temperature can be observed at high δ (cf. inset of Figure 6). This feature can be attributed to longer relaxation times at which the molecules carrying LCB come into play. Such a kind of thermorheological complexity—though more pronounced—was observed in the case of an LCB-mLLDPE before.[5] From this result one can conclude that δ(|G*|,T) reflects the low amount of LCB, which could neither be detected by SEC coupled with MALLS nor by $\eta_0(M_w)$.

In order to judge the significance of $\delta(|G^*|,T)$ toward the evaluation of a slight thermorheological complexity like that of the blend LL/L 95/5, however, the uncertainty of the dynamic-mechanical measurements performed has to be known. Figure 7 shows a section of $\delta(|G^*|,T)$ for mLLDPE L6−1 and the blend LL/L 95/5 at high phase angles. For the blend LL/L 95/5, the curves at three different temperatures are exemplarily plotted with the reproduction measurements performed on a second sample as indicated by the full symbols which come to lie within the open ones (cf. Figure 7). The measurement uncertainty was found to be typically around ±1%. Consequently, the thermorheological complexity of the blend LL/L 95/5 at high δ is reproducible and significant, though the split-up is quite small. Furthermore, the curves of the mLLDPE L6−1 at high δ superimpose in good agreement such that the comparison between the two materials plotted clearly indicates thermorheological simplicity for the mLLDPE L6−1 and thermorheological complexity for the blend LL/L 95/5.

$\delta(|G^*|,T)$ of almost all the samples superimpose as well as the curves of the mLLDPE L6−1. Therefore, they are not plotted here.

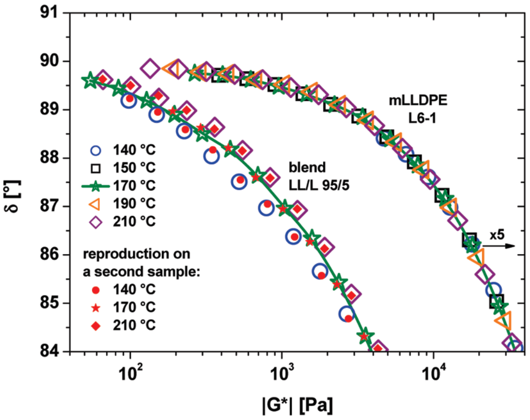

Figure 7. Demonstration of the reproducibility of dynamic−mechanical data to judge the significance of a slight thermorheological complexity by means of $\delta(|G^*|,T)$.

Thermorheological simplicity can be stated with exception of mLLDPE L4−6 and mLLDPE L6−4. Even the ZN-LLDPE samples L4−2 and L4−4 appear thermorheologically simple, although, the SEC-MALLS results indicated the presence of LCB at high molar masses (cf. Figure 2a).

Two explanations could be given for this finding. As the branching is mainly restricted to comparatively high molar mass components (cf. Figure 2a), the lowest applied angular frequency of about 0.01 s^{-1} may still be too high to probe the internal long relaxation times connected with the long-chain branched molecules. The dynamic-mechanical experiments, especially, for these two samples demonstrate that the terminal regime is not completely reached. The second explanation is related to the assumption that the decrease of the radius of gyration may originate from an extremely inhomogeneous distribution of short-chain branches. As E_a of linear PE molecules with different amounts of SCB are not much different, however, the resulting thermorheological complexity will be so small (see Literature Survey) that the time−temperature superposition principle will be found valid in good approximation.

The poly(ethylene−butene) mLLDPE L4−6 as well as the poly(ethylene−hexene) copolymer mLLDPE L6−4 turned out to show a small but reproducible thermorheological complexity: a systematic split at high δ occurred (cf. Figure 8 and Figure 9). For comparison the results of L4−5 containing almost the same butene content as L4−6 and L6−3 are shown in detail, too. These materials exhibit thermorheological simplicity, however. From these results, it can be assumed that L4−6 and L6−4 contain a small amount of LCB analogous to the blend investigated (cf. Figure 6). As shown for the blend, this small fraction cannot be detected with the common molecular analyses (cf. Figure 1b). Thermorheology seems to be sensitive enough to reveal such fine details of the molecular structure. It should be mentioned that L4−6 and L6−4 are commercial grades originating even from the same polymerization process. These conclusions are supported by the results of Resch,[46] who found a decrease of the linear steady-state compliance with increasing temperature in case of these two samples pointing toward a thermorheological complexity, too.

In summary, it could be shown that linear PE is thermorheologically simple even if an inhomogeneous comonomer distribution due to the insertion by ZN-catalysts is probable. Moreover, a comonomer content up to 7.6 mol % does not result in thermorheological complexity.

Quantitative Evaluation: E_a in Dependence on the Molecular Structure. In order to determine reliable and comparable activation energies the evaluation method chosen is crucial. Besides a shift along the time or frequency axis a weak modulus shift $b_{T,\mathrm{Rouse}} = \rho_0 T_0/\rho T$ considering the change of the density ρ and temperature according to the Rouse theory comes into play.[47,48]

In general, the modulus shift b_T is given as:

$$G(\omega, T_0) = b_T G(a_T \omega, T) \tag{3}$$

From $\delta(|G^*|,T)$, it is evident that the curves of purely linear PE measured at different temperatures superimpose within the accuracy of the experiments. This finding does not exclude the existence of the well-known density correction, however, as it is too small to be seen in this type of plot and, therefore, can be neglected. Furthermore, the moduli of LDPE vertically shift distinctly more strongly than LLDPE as demonstrated in a previous paper.[34] As a consequence, E_a of LDPE becomes a function of the quantity chosen for its determination, if the vertical shift factor is neglected.

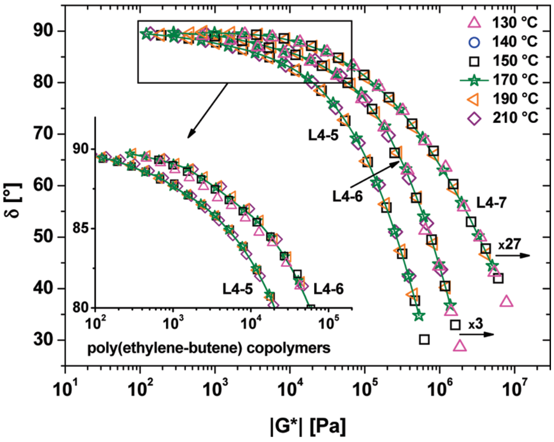

Figure 8. $\delta(|G^*|,T)$ of several poly(ethylene−butene) copolymers.

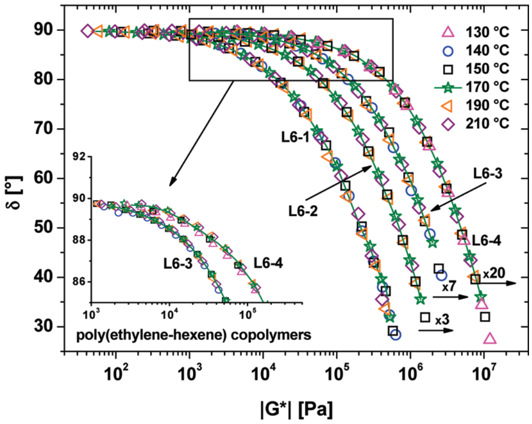

Figure 9. $\delta(|G^*|,T)$ of the poly(ethylene−hexene) copolymers.

To overcome these difficulties, b_T can generally be excluded by evaluating the temperature dependence using tan $\delta(\omega,T)$ or $\delta(\omega,T)$, respectively:

$$\tan\delta(\omega, T_0) = \frac{G''(\omega, T_0)}{G'(\omega, T_0)} = \frac{b_T \cdot G''(a_T\omega, T)}{b_T \cdot G'(a_T\omega, T)} = \tan\delta(a_T\omega, T) \tag{4}$$

G' is the storage modulus and G'' the loss modulus.

E_a can be determined from the phase angle δ measured as a function of ω at different temperatures (cf. Figure 10a) if ω at distinct δ are plotted semilogarithmically versus the reciprocal absolute temperature $1/T$ and straight lines are obtained as indicated in Figure 10b. Then, E_a can be calculated from the slopes of linear fits according to:

$$\omega(T) = \omega(T_0)\exp\left(-\frac{E_a}{RT}\right) \tag{5}$$

Figure 11 shows $E_a(\delta)$ of several samples. Within the accuracy of the measurements constant E_a values are found for mHDPE 2, mLLDPE L6−1 and LDPE 2, respectively. On the other side, E_a of the thermorheologically complex blend LL/L 95/5 deviates from that of the neat mLLDPE L6−1. Especially at high δ values, which correspond to long relaxation times, an increase of E_a appears, which can be attributed to the presence of LCB. This increase is found in a δ range, which agrees with that of the split of the $\delta(|G^*|,T)$-curves shown in Figure 6. Similar results were found for mLLDPE L4−6. The thermorheological complexity of this sample found from $\delta(|G^*|,T)$ (cf. Figure 8) is reflected by the increase of E_a at high δ. Taking the results on mLLDPE L4-6 into account, it can be concluded that this material contains a small amount of LCB in addition to the linear molecules. The rheological functions of such a “blend” exhibit a temperature-dependent change of their shape as previously discussed and seen from LL/L 95/5.[5] Therewith, this kind of thermorheological complexity differs from that found for statistically branched LDPE, as the latter possesses an average E_a,

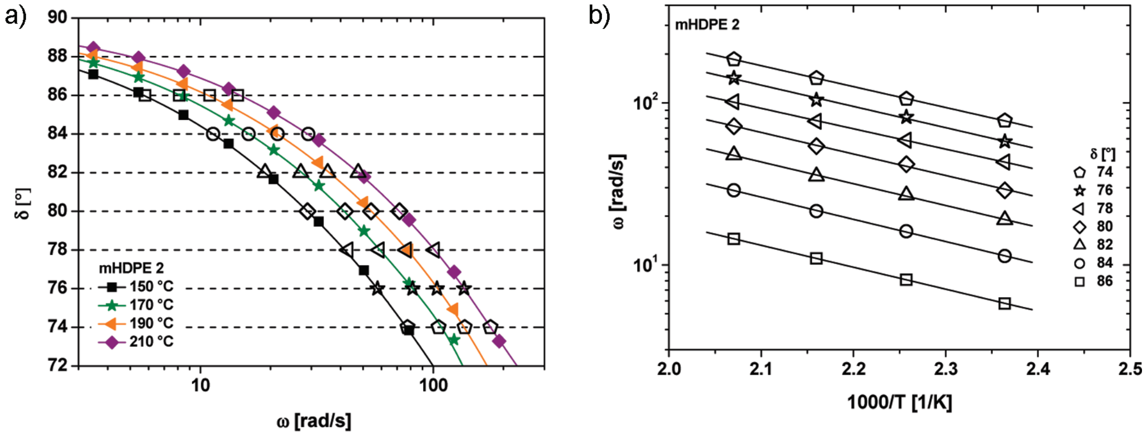

Figure 10. (a) $\delta(\omega,T)$ of mHDPE 2. (b) Arrhenius diagrams of mHPDE 2 at different constant δ.

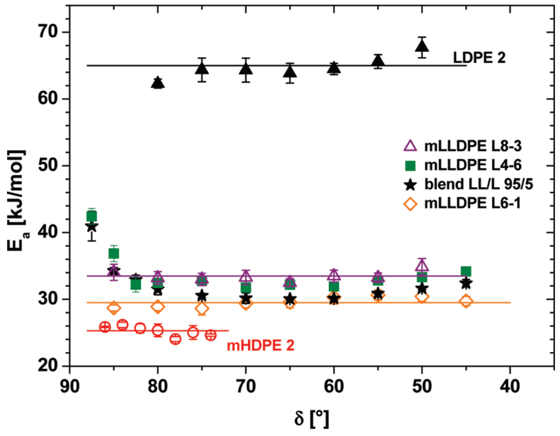

Figure 11. Activation energy as a function of the phase angle.

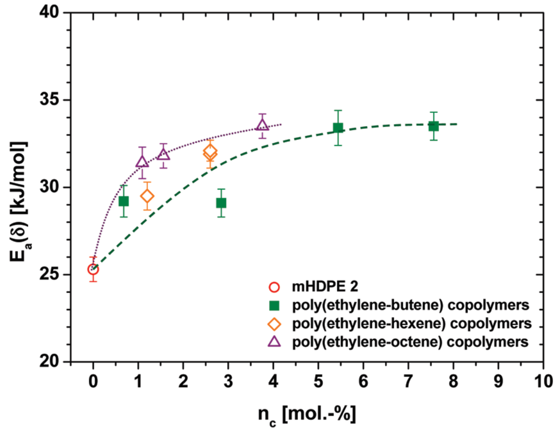

Figure 12. Activation energy of different linear PE as a function of the comonomer content (lines are drawn to guide the eye).

which is valid for all of its molecules and such for all of its relaxation times if evaluated from $\delta(\omega,T)$.

$\delta(|G^*|,T)$ of mLLDPE L6−4, shown in Figure 9, shows a small split-up at δ close to 90°. But for this material, an E_a dependent on δ could not be found. This very slight thermorheological complexity at angles close to 90° is not reflected in $E_a(\delta)$. It is quite likely, however, that mLLDPE L6−4 also contains a few LCB, as it originates from the same manufacturer and production route as mLLDPE L4−6. Therefore, the following discussion on the influence of the type and content of comonomers on the activation energies does not comprise results from these two grades as any LCB would disturb the analysis.

In order to find correlations between E_a and the molecular structure of the copolymers, the $E_a(\delta)$ values of the thermorheologically simple PE are plotted as a function of the comonomer content in Figure 12. The homopolymer mHDPE 2 exhibits the lowest E_a of around 25 kJ/mol. (For comparison, Stadler et al.[3] found 27 kJ/mol for mHDPE 1 and mHDPE 2 evaluated from $G'(\omega,T)$). The insertion of butene comonomers up to 4 mol % results in an increase of E_a up to 29 kJ/mol. Increasing the butene content even more leads to E_a-values up to 33.5 kJ/mol (for L4−5 and L4−7). From the results it seems to be probable that E_a reaches a plateau at high comonomer contents as reported by Wood-Adams and Costeux.[25]

Additionally, E_a of the poly(ethylene−hexene) and poly(ethylene−octene) copolymers are presented. Again, an increase of E_a with increasing comonomer content is observable. However, E_a of the samples with hexene as comonomer is higher than E_a of the poly(ethylene−butene) copolymers at the same comonomer content. A similar tendency is found with the poly(ethylene−octene) copolymers. E_a of these products exceeds that of the poly(ethylene−butene) and poly(ethylene−hexene) copolymers at the same comonomer content, hence, E_a increases with the length of the side branches.

Discussion

Comparison of the Characterization Methods Applied. The common analytical characterization by means of the relationships between $\langle r_g^2\rangle$ and M_{LS} and the rheological one using η_0 and M_w, respectively, are not sensitive enough to detect some few long-chain branched molecules in linear PE as demonstrated by the blend LL/L 95/5.

The significance of $\langle r_g^2\rangle(M_{LS})$ for the blend LL/L 95/5 is limited according to several points of view. First of all, the lower detection limit of the SEC-MALLS setup used is 20 nm. Furthermore, the radii of gyration of the LDPE 2 have been truncated at molar masses below 200 kg/mol as indications of a disturbance of the separation of the SEC became visible (cf. Figure 1, parts a and b).[34] The highest molar masses of the neat mLLDPE L6−1, however, range up to around 600 kg/mol, those of the LDPE 2 reach values up to 10 000 kg/mol. Therefore, in the blend above 600 kg/mol the molecules of the LDPE 2 should appear. However, $\langle r_g^2\rangle(M_{LS})$ of the blend agrees with that of the neat mLLDPE L6−1 over the whole M_{LS} range and, moreover, $dW/d(\log M)$ as a function of M_{LS} of the mLLDPE L6−1 remains unchanged by the addition of 5 vol % LDPE 2. That means, the amount of the LCB molecules is too low to be reflected by the SEC-MALLS setup.

However, a contraction of $\langle r_g^2\rangle$ at high M_{LS} pointing toward LCB was detected for the ZN-LLDPE samples L4−2 and L4−4. From this result it has to be concluded that these samples surprisingly possess long-chain branched molecules of a high molar mass.

The relationship between η_0 and M_w, however, does not reflect any LCB in the LLDPE samples investigated. Even the blend LL/L 95/5 and the ZN-LLDPE, which contain LCB according to $\langle r_g^2\rangle(M_{LS})$, appear as purely linear. This result demonstrates that $\eta_0(M_w)$ is not sensitive enough to reveal the small amounts of LCB in the samples.

The high sensitivity of the thermorheological behavior toward a few LCB in linear PE, however, could be demonstrated. $\delta(|G^*|,T)$ of the blend LL/L 95/5 indicates a thermorheological complexity, as the curves at angles close to 90° systematically split. Furthermore, thermorheological complexity was also observed for the mLLDPE samples L4−6 and L6−4 which were classified as purely linear according to $\langle r_g^2\rangle(M_{LS})$ and $\eta_0(M_w)$. $E_a(\delta)$ of thermorheologically complex samples is not constant, but increases at angles close to 90°, which correspond to long relaxation times related to long-chain branches. Moreover, a thermorheological complexity of these two samples is also observed by means of the temperature dependence of the linear steady-state compliance determined by creep-recovery experiments.[46] In conclusion, the relaxation times of the long-chain branched molecules in the samples mLLDPE L4−6 and L6−4 are covered by dynamic-mechanical as well as creep-recovery experiments, respectively.

However, in contrast to the results of the analytical investigations, no hints toward the LCB in the ZN-LLDPE samples L4−2 and L4−4 detected by SEC-MALLS could be gained from $\delta(|G^*|,T)$. An explanation for this finding is the limited frequency or time range covered by dynamic-mechanical experiments typically performed down to $\omega = 10^{-2}\ s^{-1}$.

At this frequency, the terminal regime is reached for purely linear samples of moderate M, while it may be far away for ZN-LLDPE L4−2 and L4−4, as it is well-known that long-chain branched molecules of high molar masses possess long relaxation times. Therefore, the relaxation times corresponding to the long-chain branched high molar mass tails of these two ZN-LLDPE are not fully covered by the dynamic-mechanical experiments performed.

In order to check this assumption, creep and creep-recovery experiments were carried out with the ZN-LLDPE sample L4−2 at 150 and 190 °C. The linear steady-state compliance J_e^0 was determined at long recovery times around 4000 s for 150 °C and 1500 s at 190 °C. These recovery times correspond to angular frequencies of $2.5 \times 10^{-4}\ \mathrm{s}^{-1}$ and $6.7 \times 10^{-4}\ \mathrm{s}^{-1}$, respectively. Details about such experiments can be found in prior publications.[5,34] A distinct temperature dependence of J_e^0 was found, which is comparable to that of the thermorheologically complex mLLDPE samples L4−6 and L6−4.[43] J_e^0 of the ZN-LLDPE L4−2 decreases from $(12.2 \pm 0.4) \times 10^{-4}\ \mathrm{Pa}^{-1}$ at 150 °C to $(8.6 \pm 0.3) \times 10^{-4}\ \mathrm{Pa}^{-1}$ at 190 °C. This finding demonstrates that the ZN-LLDPE L4−2 is thermorheologically complex, too, and confirms the finding of long-chain branched molecules of high molar mass by SEC-MALLS (cf. Figure 2a).

Relationship between E_a and the Comonomer Length and Content. The main finding of this paper, namely the relationship between the activation energy and the type and content of the comonomers investigated, will be discussed in the following.

It can be assumed that the probability P of a local displacement of a molecular segment is given as the product of the probabilities P_ν and P_a.

$$P = P_\nu \cdot P_a \qquad (6)$$

Thereby, P_ν describes the probability that a sufficient free volume is available for the molecular segment and P_a the probability to overcome the potential barrier for the segmental motion.

At temperatures near the glass transition temperature T_g, the influence of P_ν dominates, i.e., the free volume available determines the probability of the displacement of molecular segments. In that case, the so-called WLF equation holds. The free volume increases with increasing temperature and, thus, the relevance of P_ν decreases. At higher temperatures, enough free volume for molecular displacements is available and the limiting factor is P_a which is determined by the thermal activation of segmental motion. Thus, the Arrhenius equation, (2), holds.

The latter situation is valid for the PE samples investigated as all measurements were carried out far above T_g and the shift factors follow eq 2. Consequently, the thermal activation dominates the segmental motions. E_a is a measure of the potential barrier, which has to be overcome. It is obvious now that E_a increases, if the segments become bulkier. The comonomer type inserted and following from that the length of the side chain is decisive for the resistance of the segment with respect to its displacement. This model easily explains the enhancement of the activation energy from butene to octene as comonomer. Furthermore, it is not difficult to imagine that the hindrance of the segmental motion becomes the more pronounced the higher the concentration of the side groups is.

Conclusions

The results obtained demonstrate that thermorheological measurements are very sensitive and powerful to probe details of the molecular structure of PE.

Comparing the established characterization methods $\langle r_g^2 \rangle(M_{LS})$ and $\eta_0(M_w)$ the following can be stated:

- The $\langle r_g^2 \rangle(M_{LS})$-relationship valid for linear PE is not sensitive enough to reveal small amounts of LCB in linear PE as demonstrated by means of the blend of 5 vol % LDPE added to a hexene copolymer (LL/L 95/5).
- The $\eta_0(M_w)$-relationship which has been shown to differentiate between linear and long-chain branched molecules does not detect small amounts of LCB as demonstrated by means of the blend LL/L 95/5. All the samples investigated appear linear, if solely classified according to $\eta_0(M_w)$, though a contraction of $\langle r_g^2 \rangle$ and thermorheological complexity were observed for several of them.

The qualitative classifications of the thermorheological behavior by $\delta(|G^*|,T)$ leads to the following conclusions:

- Thermorheologically simple and complex polymers can sensitively be discriminated by $\delta(|G^*|,T)$.
- The small amount of LCB in the blend LL/L 95/5 could successfully be revealed. Furthermore, the high sensitivity of $\delta(|G^*|,T)$ allowed to find a thermorheological complexity pointing toward the presence of LCB for two samples (L4−6 and L6−4) which seemed to be linear according to $\langle r_g^2 \rangle(M_{LS})$ and $\eta_0(M_w)$.
- The sensitivity of $\delta(|G^*|,T)$ with respect to thermorheological complexity can only be exploited, if the frequency range applied matches the internal time scale of the molecules responsible for a thermorheological complex behavior. This fact explains the result that a thermorheologically simple behavior was found for two samples (L4−2 and L4−4), which contain long-chain branched molecules of high molar mass according to SEC−MALLS.

The following conclusions can be drawn from the quantitative evaluation of the thermorheological behavior using the activation energy E_a in dependence on the phase angle δ:

- Differences in the thermorheological behavior between m-catalyzed (more homogeneous comonomer distribution) and ZN-catalyzed (less homogeneous comonomer distribution) copolymers were not observed.
- $E_a(\delta)$ determined from $\delta(\omega,T)$ was found to be constant for most of the linear PE investigated and the LDPE. $E_a(\delta)$ of linear samples containing a few long-chain branched molecules increases at high phase angle, if the longest relaxation times are covered within the frequency range measured.
- $E_a(\delta)$ of linear PE increases with growing comonomer length and content. A maximal E_a of 33.5 kJ/mol is reached at the highest comonomer content investigated, i.e., 7.6 mol % butene.
- $E_a(\delta)$ representing the potential barrier for the flow of a polymer melt can be correlated with the mobility of the molecular segment, which has to be displaced. It is obvious that the mobility depends on the bulkiness of the molecular segment, and, thus E_a increases with growing comonomer length and content. The results demonstrate that E_a can be used as a direct probe of the molecular structure of short-chain branched polymers.

Summary

The molecular structure of a broad range of likely linear PE samples, a blend of LLDPE and LDPE as well as a LDPE are investigated by means of well-established analytical and rheological relationships. The results from these methods are compared with the conclusions drawn from investigations of the thermorheological behavior.

Thermorheology is found to be a very sensitive probe of the molecular structure. It is shown that the evaluation of $\delta(|G^*|,T)$ as well as $E_a(\delta)$ detects even few LCB in a linear PE if the frequency range of the dynamic-mechanical experiment matches the molecular time scale. Furthermore, $E_a(\delta)$ correlates with the comonomer type and content of linear PE. It becomes the larger the longer the comonomer and the higher its concentration. As such, thermorheology offers an interesting method to get an insight into molecular structures, particularly, those connected with the branching architecture. Investigations of this kind are comparatively simple and fast as only well established dynamic-mechanical experiments at different temperatures are needed. The results of this paper convincingly demonstrate, however, that the application of different methods and the careful assessment of their findings are necessary to obtain a reliable characterization of the molecular structure of branched polyethylenes.

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Supporting Information Available: The calibration curve used resulting from monodisperse anionic polystyrene standards is shown. In addition, a few representative Zimm diagrams are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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