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Analytical and rheological characterization of long-chain branched metallocene-catalyzed ethylene homopolymers

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Abstract

The aim of this paper is to compare the results of analytical and rheological characterization techniques with respect to the analysis of long-chain branches (LCB) in polyethylenes. The materials investigated are metallocene-catalyzed ethylene homopolymers into which LCB were introduced by the selection of appropriate polymerization conditions. The samples were characterized analytically by ^{13}C NMR, IR-spectroscopy, and size exclusion chromatography coupled with a multi-angle laser light scattering detector. The rheological characterization was performed using dynamic–mechanical measurements and creep and creep recovery experiments in shear.

It was found that the analytical methods were in good qualitative agreement for the most highly branched sample whose LCB content was 0.12 LCB/1000 C as determined by ^{13}C NMR spectroscopy. However, even a 10-times lower LCB content, which is almost beyond the detection limit of ^{13}C NMR measurements, had a significant impact on the rheological behavior. Rheological experiments clearly indicated the presence of LCB by changes in the frequency dependence of dynamic–mechanical material functions and the molecular mass dependence of the zero shear-rate viscosity in comparison to linear polyethylenes. © 2002 Published by Elsevier Science Ltd.

Keywords: Long-chain branched polyethylene; Analytical characterization; Rheological characterization

1. Introduction

Highly active metallocene-catalysts are used in olefin polymerization to achieve linear polymers of narrow molecular mass distributions with superior mechanical properties [1,2,12]. Due to their narrow molecular mass distribution these polyolefins in general suffer from a poor processability compared to conventional polyolefins of higher polydispersity. Long-chain branches (LCB) in polyethylenes in general give rise to a significantly improved behavior in industrial production processes. Such an influence of LCB led to the development of new polyethylenes of narrow molecular mass distributions and sparse amounts of LCB using single-site catalyst systems [10]. Interestingly enough these sparse levels of LCB are sufficient to improve the processing behavior of polyethylene melts in the desired manner.

The mechanism of LCB formation is generally viewed as the incorporation of vinyl-terminated chains into the growing backbone [10]. In a series of publications Malmberg et al. [21] and Kokko et al. [15,16] have demonstrated in which way polymerization conditions in metallocene catalysts may change the branching structure.

The level of LCB in these new polyethylenes is sometimes so low that it cannot easily be detected analytically. This paper therefore intends to compare the results from different analytical methods with those from rheological investigations. The analytical methods were ^{13}C NMR, IR-spectroscopy, and size exclusion chromatography coupled with a state-of-the-art multi-angle laser light scattering (MALLS) detector. These methods give direct information about the molecular structure of polymers. The results from these analytical methods were compared with rheological measurements in the transition zone from the rubbery behavior to the flow regime and the terminal zone itself. For use of rheological measurements as a probe into the molecular structure correlations have to be established. These correlations are well established for the influence of molecular mass and molecular mass distribution, but much less is known about the influence of LCB on the rheological

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Table 1
Polymerization conditions

Run	Catalyst	p (C_2H_4) (bar)	Cat. (μmol/l)	V (toluene) (dm^3)	t (min)	Yield (g)
270	$Et[Ind]_2ZrCl_2$	2.5	0.30	0.65	60	45
271	$Et[Ind]_2ZrCl_2$	1.0	0.75	0.65	60	43
272	$Me_2Si[Ind]_2ZrCl_2$	2.0	0.45	0.65	45	44
273	$Me_2Si[Ind]_2ZrCl_2$	5.0	0.15	0.65	60	38
275	$Et[H_4Ind]_2ZrCl_2$	0.5	1.54	1.3	35	46
276	$Et[H_4Ind]_2ZrCl_2$	0.3	1.54	1.3	45	43
277	$Et[H_4Ind]_2ZrCl_2$	3.0	0.27	1.3	20	48

Polymerization temperature 80 °C; cocatalyst (MAO) concentration 3.0 mmol/dm^3. A small amount of hydrogen was used in run 277.

behavior in shear. Thus, the present paper also intends to contribute to the understanding of the flow behavior of long-chain branched polyethylenes by the comparison of rheological with analytical data. The study includes six experimental metallocene-catalyzed homopolyethylene samples of different degrees of long-chain branching and one linear homopolyethylene sample from the IUPAC working party IV 2.2, project subgroup 5.

2. Experimental

2.1. Materials

The catalysts *rac*-ethylenebis(indenyl)zirconium dichloride, $Et[Ind]_2ZrCl_2$; *rac*-dimethylsilylbis(indenyl)zirconium dichloride, $Me_2Si[Ind]_2ZrCl_2$; and *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride, $Et[H_4Ind]_2ZrCl_2$, and the cocatalyst methylaluminoxane (MAO) were obtained from Witco GmbH (Bergkamen, Germany). Ethylene (grade 3.5), hydrogen (grade 5.0), and nitrogen (grade 5.0) were supplied by Oy AGA Ab (Espoo, Finland) and toluene (pro-analysis) by Merck (Darmstadt, Germany). Ethylene and toluene were purified by passing them through columns containing molecular sieves consisting of Al_2O_3, and CuO. The metallocene catalysts, MAO, and nitrogen were used without further purification.

2.2. Polymerization procedure

Based on the earlier work [15,16] on the effect of catalyst, monomer concentration and hydrogen on the polymer structure, polymerization conditions were chosen to produce samples with different molecular mass and LCB content. For example, samples produced with the same catalyst but lower monomer concentration, are expected to contain more LCB. Table 1 shows the detailed polymerization conditions.

Polymerization reactions were carried out in a 1.0 or 2.0 dm^3 stainless steel Büchi autoclave. After the reactor was carefully evacuated, toluene, MAO, and hydrogen (used in run 277) were introduced under vacuum and the reactor was filled with nitrogen to the ambient pressure. Ethylene was then fed and the pressure in the gas phase was adjusted. Finally, after the ethylene concentration in the reactor had reached equilibrium, the catalyst was introduced into the reactor. The ethylene pressure was kept constant in the gas phase by a continuous monomer feed. The polymerizations were stopped by degassing the reactor, and the reaction mixture was treated with a dilute solution of hydrochloric acid in ethanol. After overnight stirring the polymer was filtered, washed with ethanol, filtered again, and dried.

2.3. Polymer characterization

The molecular masses (M_w, M_n) of the polymers were determined at Helsinki University of Technology (HUT) with a Waters Corp. (Milford, MA) GPC, model 150C ALC, equipped with a refractometer detector and three Waters styragel HMW columns covering the molecular mass range from 10^2 to 10^8 g/mol. 1,2,4-Trichlorobenzene was used as solvent and the chromatograms were collected at 140 °C. The molecular masses were calculated with the universal calibration, which was based on 11 narrow polystyrene standards. For the determination of absolute molecular masses and the analysis of LCB a coupled size exclusion chromatography and multi-angle laser light scattering apparatus (SEC–MALLS) was used at the Institute of Polymer Materials (LSP). The SEC used is a Waters 150C with four Shodex columns, the light scattering detector a DAWN EOS from Wyatt Technology with 18 scattering angles. 1,2,4-Trichlorobenzene was used as solvent and the chromatograms were collected at 135 °C. For comparison, molecular masses were also calculated at LSP using the universal calibration method with the Mark-Houwink constants recommended by the IUPAC working party IV 2.2, project subgroup 5, for the characterization of polyolefins [7]). The 13 narrow polystyrene standards from Polymer Laboratories covered a molecular mass range from 580 to 11.6×10^6 g/mol.

The vinyl bond content of the polymers was analyzed from melt-pressed films with a FTIR-spectrometer model Magna 750 (Nicolet Instrument Corp., Madison, WI) at ambient temperature. The samples were melt-pressed into 200 μm thick disks at 170 °C using a Fontijne TP400 table press. In the FTIR measurements, 32 scans were collected using 2 cm^{-1} resolution. The vinyl bond content was calculated from the 908 cm^{-1} absorbance peak by the method described by Haslam et al. [11].

The polyethylene microstructure—branching and end-groups—was measured by ^{13}C NMR spectroscopy. The measurements were carried out using a Gemini 2000XL NMR spectrometer (10 mm broadband probe, 75 MHz) (Varian Inc., Palo Alto, CA) operating at 125 °C under nitrogen atmosphere. In a typical run, 300–500 mg of polymer was dissolved in a mixture of deuterated benzene

Table 2
Molecular structures of the polyethylene samples characterized by gel permeation chromatography, FTIR-spectroscopy, and ^{13}C NMR spectroscopy

Run	GPC		FTIR	^{13}C NMR					M_n (kg/mol)
	M_w (kg/mol)	M_n (kg/mol)	C=C/1000 C	Branching/1000 C			Chain ends/1000 C		
				Hexyl +	Ethyl	Methyl	Saturated	Unsaturated	
270	96	42	0.35	0.06	0.00	0.00	0.30	0.33	44
271	167	52	0.26	0.12	0.00	0.00	0.37	0.24	46
272	164	66	0.23	0.04	0.13	0.00	0.27	0.25	54
273	133	55	0.22	Traces	0.19	0.00	0.29	0.25	52
275	144	65	0.05	Traces	0.00	0.22	0.30	0.10	70
276	114	54	0.03	0.03	0.00	0.25	0.41	0.07	59
277	95	33	0.01	0.00	0.00	0.06	0.78	0.00	36

(10 wt%) and 1,2,4-trichlorobenzene (90 wt%). The acquisition time was 2.5 s, delay 6.0 s, pulse angle 45°, and at least 8000 transients were collected. The assignment of chemical shifts in ^{13}C NMR spectra was based on literature values [3,26]. The ^{13}C NMR based vinyl bond content was calculated from the area of the allyl peak and M_n from the area of saturated and unsaturated (allyl peak) end-groups.

The determination of the frequency dependent storage and loss modulus was carried out using a strain controlled shear rheometer with plate and plate geometry (ARES, Rheometric Scientific). Creep experiments with a magnetic bearing creep apparatus [20] were performed on selected samples for the determination of the zero shear-rate viscosity. For a more detailed description of the methodology of creep recovery experiments the reader is referred to Refs. [7,8]. The rheological experiments were performed at a temperature of 150 °C, which is well above the melting temperature of 138 °C of the linear and the high-density polyethylenes with a low degree of LCB. Time-sweep experiments at low frequencies and creep experiments showed that the thermal stability of the samples was excellent. In addition, it was taken care of that the experiments were performed in the linear range of deformation in dynamic–mechanical analysis (maximum strain 0.05) and in the linear stress regime in the creep experiments (shear stresses around 10 Pa).

3. Results and discussion

3.1. Molecular characterization

Table 2 shows the results of the characterization obtained with GPC, FTIR, and ^{13}C NMR. The catalyst choice and polymerization conditions had a significant effect on the polymer structure. The comparison of the results obtained with the different analysis methods shows a good agreement; the number-average molecular mass (M_n) determined with GPC and ^{13}C NMR and the vinyl bond content obtained with FTIR and ^{13}C NMR are similar. The accuracy of ^{13}C NMR measurements, however, suffers from a poor signal-to-noise ratio at low vinyl and branch contents. Amounts less than 0.01/1000 C are beyond the detection limit.

3.2. Characterization with ^{13}C NMR spectroscopy

The ^{13}C NMR analysis revealed, in addition to the saturated and unsaturated chain ends, small amounts of methyl, ethyl, and hexyl + (more than six carbon atoms) branches (Fig. 1). Methyl branches were found in the samples prepared with $Et[H_4Ind]_2ZrCl_2$ and ethyl branches in the samples produced with $Me_2Si[Ind]_2ZrCl_2$. Low amounts of methyl branches have been found in polyethylenes produced with various metallocene catalysts [27] or ethyl [13,17]. $Et[Ind]_2ZrCl_2$-catalyzed polyethylenes have the highest hexyl + branch content. Though the length of hexyl + branches cannot be determined, the melt rheological properties of homopolyethylenes produced with metallocene catalysts [21,29] indicate that polymers contain branches long enough to form entanglements (> 250 atoms). Considering the most likely mechanistic route for the hexyl + branch formation in metallocene-catalyzed polyethenes [10], the hexyl + branches should be treated as LCB.

The average LCB (hexyl +) content is well below one branch per polymer chain. In the most highly branched sample (271), the fraction of LCB molecules is less than 40% (branch concentration vs. chain end concentration corrected for LCB).

The ratio between the saturated and unsaturated chain ends was roughly about one in the $Et[Ind]_2ZrCl_2$- and $Me_2Si[Ind]_2ZrCl_2$-catalyzed polyethylenes (Table 2). The polymers produced with $Et[H_4Ind]_2ZrCl_2$ had substantially less unsaturated chain ends than saturated ones. The excess amount of saturated chain ends compared to unsaturated ones suggests that chain transfer to the aluminium is a major chain transfer mechanism under these polymerization conditions. Other important chain transfer reactions, which formed the unsaturated chain ends, are β-H elimination and chain transfer to the monomer [15,16].

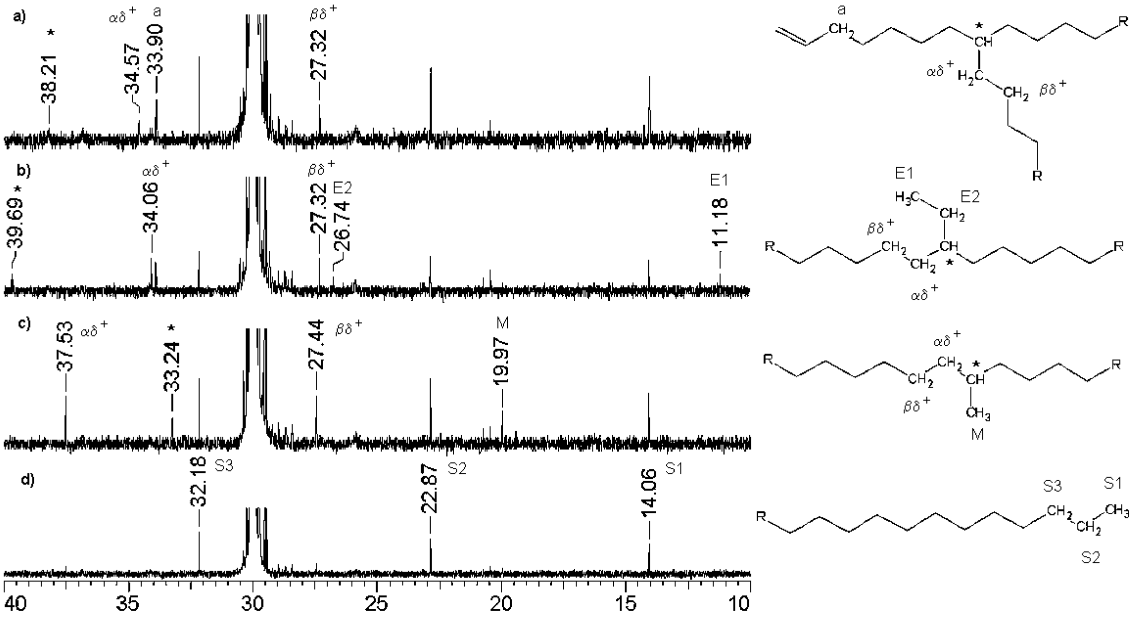

Fig. 1. Assignment of the peaks identified in the samples by ^{13}C NMR. (a) Allyl peak of unsaturated chain end (33.90 ppm) and a branch longer than six carbon atoms (38.21, 34.57, and 27.32 ppm); (b) ethyl branch (39.69, 34.06, 27.32, 26.74, 11.18 ppm); (c) methyl branch (37.53, 33.24, 27.44, and 19.97 ppm); (d) saturated chain end (32.18, 22.87, and 14.06 ppm).

3.3. Characterization with SEC–MALLS

The investigation of molecular mass by coupled SEC–MALLS in general reveals a small influence of LCB on the radius of gyration of the investigated polyethylenes. Fig. 2 shows selected samples. Sample 271 shows the most pronounced reduction of the radius of gyration in comparison to samples 277 and IUPAC 5A. The molecular mass dependence of the root mean square radius of the two samples is in good experimental agreement. The slope found is close to 0.5, a value, which is expected for linear polyethylenes. For the other samples, the reduction of the radius of gyration is smaller compared to sample 271 (not shown in Fig. 2). This finding is reasonable as sample 271 exhibits the highest amount of LCB (or hexyl + side groups; cf. Table 2). From the contraction factor $g(M)$, which relates the radius of gyration of a long-chain branched sample to that of a linear sample, it becomes obvious that polymers contain some LCB and sample 270 is less long-chain branched than sample 271 (Fig. 3). For the other materials the contraction factors fall in between the values of linear polyethylene ($g = 1$) and the long-chain branched sample 270.

Table 3 shows a comparison of the weight-average

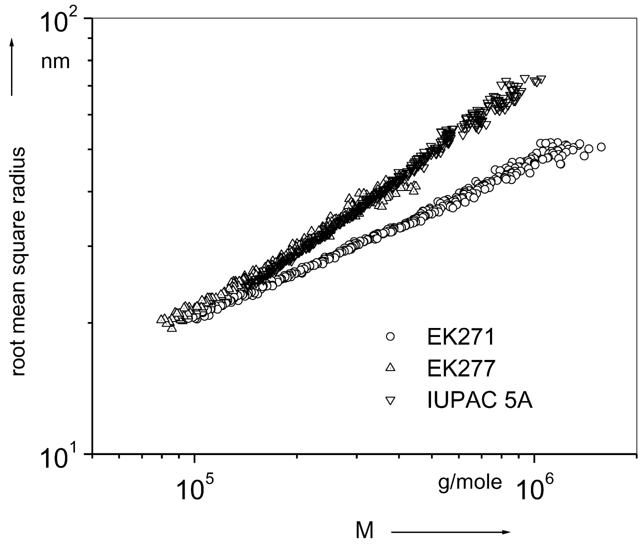

Fig. 2. Molecular mass dependence of the root mean square radius of gyration of two linear (EK277 and IUPAC 5A) and a long-chain branched polyethylene 271 as determined from SEC–MALLS.

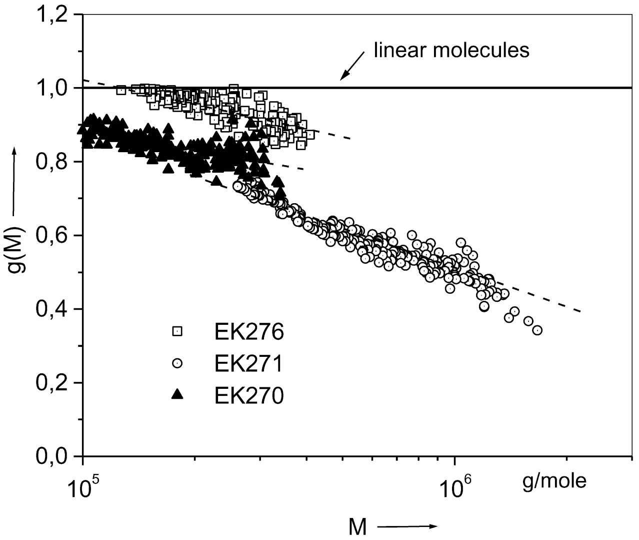

Fig. 3. Molecular mass dependence of the contraction factor of three long-chain branched polyethylenes.

Table 3
Comparison of weight-average molecular masses as determined in different laboratories by different methods

Run/sample	HUT with UC M_w (kg/mol)	LSP with UC M_w (kg/mol)	LSP with MALLS M_w (kg/mol)
270	96	109	111
271	167	177	216
272	164	171	189
273	133	146	145
275	144	153	159
276	114	128	126
277	95	106	102
IUPAC 5A	–	216	218

HUT stands for Helsinki University of Technology, LSP for Institute of Polymer Materials, University Erlangen-Nürnberg, UC for universal calibration and MALLS for multi-angle laser light scattering. For the polyethylenes investigated the error for the determination of the weight-average molecular mass is around ±5%.

molecular masses M_w determined by the universal calibration method (UC) at Helsinki University of Technology (HUT) and at the Institute of Polymer Materials (LSP) with the data obtained from coupled SEC–MALLS at LSP. For the universal calibration data a small systematic deviation of about 10% of M_w is found between HUT and LSP. The linear samples 277 and IUPAC 5A show a very good agreement for M_w determined at LSP by UC and MALLS. The deviations between these two methods are the more pronounced the higher the degree of LCB is. For sample 271 the strongest deviation of M_w of more than 20% is found. This effect has to be attributed to the influence of LCB on the radius of gyration.

From the molecular mass dependence of the contraction factor several other quantities related to the degree of long-chain branching can be derived. The model underlying the calculation of number and degree of LCB is that of Zimm and Stockmayer [30], which is implemented in the Wyatt light scattering software of the SEC–MALLS apparatus. For the calculation trifunctional branch points and narrow molecular mass distributions of each SEC-slice are assumed. Table 4 shows a comparison of weight-average values of the contraction factor g_w,[2] the weight- and number-average number of LCB per molecule (B_w and B_n) and the weight-average number of LCB per 1000 carbon atoms (L_w). The weighted contraction factors are between 0.9 and 1 for most of the samples; only for the most highly branched ones (samples 272, 270, 271) a significant reduction down to values of 0.76 is found. For comparison, a classical LDPE with a high degree of long-chain branching (the sample that was described by Gabriel and Münstedt [7]) reaches values of $g_w = 0.4$. The corresponding numbers of LCB per molecule (B_w) are well below one for the slightly branched samples, for the highly branched samples values of 1.5 up to five are obtained. The classical LDPE on average contains about 34 branches per molecule. The estimated degree of long-chain branching from SEC–MALLS is in qualitative agreement with the results from ^{13}C NMR. Sample 271 achieves the highest values in both methods, sample 270 and sample 272, which display a very similar degree of branching, range second (compare Tables 2 and 4).

The conclusions from SEC–MALLS with respect to the degree of LCB are in qualitative accordance with the results from ^{13}C NMR measurements. Weight-average branching values obtained by SEC–MALLS appear to give somewhat higher values than number-average values obtained with ^{13}C NMR.

Both experimental methods indicate that 271 is the polyethylene sample with the highest degree of long-chain branching. For the other samples a clear separation is difficult, but sample 270 appears to contain more LCB per 1000 C than the others. The SEC–MALLS measurements demonstrate that branching is more pronounced at higher molecular masses indicating rather heterogeneous branching structure. The discrepancies between the results obtained with ^{13}C NMR and SEC–MALLS could be related to the heterogeneity in the branching. Furthermore, it has to be taken into account that in addition to regular three-arm stars (T-type polymers), a small amount of polymers with two or more branches (a comb or a branch-on-branch), or H-type polymers are present due to the polymerization method.

Table 4
Comparison of weight-average values of the contraction factor g_w, the number of LCB per molecule B_w (weight-average) and B_n (number-average), and the degree of long-chain branching per 1000 carbon atoms L_w as determined from SEC–MALLS

Run/sample	g_w	B_w	B_n	L_w (number of LCB/1000 C)
270	0.88	1.56	0.45	0.32
271	0.76	5.28	0.38	0.42
272	0.89	1.47	0.03	0.12
273	0.94	0.66	0.14	0.07
275	0.99	0.10	0.01	0.01
276	0.95	0.57	0.18	0.07
277	0.953	0.69	0.01	0.06

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[2] Similar to the definition of weight-average molecular mass of a molecular mass distribution a weight-average of the molecular mass dependence of the contraction factor $g(M)$ can be defined. This quantity is sensitive to values of the contraction factor in the high molecular mass regime.

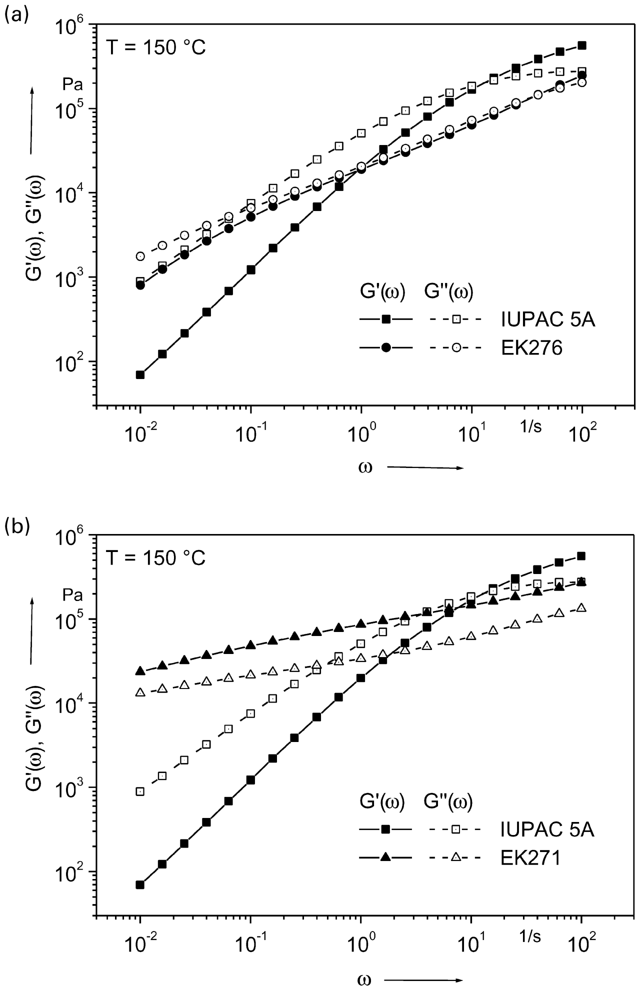

Fig. 4. Frequency dependence of the storage and loss modulus of a linear (IUPAC 5A) and a long-chain branched polyethylene (a) EK276 (b) EK271.

3.4. Rheological characterization

Dynamic–mechanical analysis. The frequency dependence of storage and loss moduli of the samples IUPAC 5A, 276 and 271 is shown in Fig. 4(a) and (b). The linear sample IUPAC 5A with a narrow molecular mass distribution ($M_w/M_n = 3.0$; this value is slightly higher than that of the long-chain branched samples) exhibits the typical behavior of a linear polyethylene melt with transitions of the dynamic moduli into the flow regime at small frequencies and into the plateau of rubber elasticity at high frequencies (Fig. 4(a)). In the case of sample 276 with a slight degree of LCB storage and loss modulus are more or less parallel in the high frequency regime (Fig. 4(a)). Only at low frequencies the storage modulus becomes smaller than the loss modulus indicating the transition to the flow regime. For sample 271 with a high degree of LCB (Fig. 4(b)) no indication of a viscous behavior is observable as the storage modulus is higher than the loss modulus in the accessible range of angular frequencies.

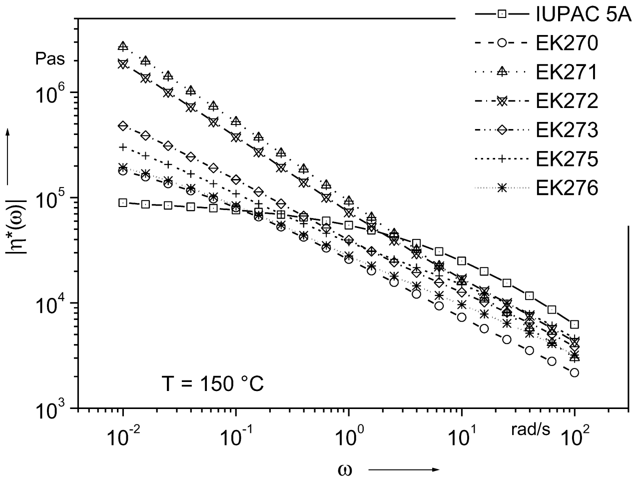

Fig. 5. Complex viscosity functions of a linear (IUPAC 5A) and the long-chain branched polyethylene samples EK270–276.

In order to give an overview of the dynamic rheological behavior of all the samples, the absolute value of the complex viscosity is plotted in Fig. 5 as a function of angular frequency. It is obvious that the samples containing LCB show enhanced viscosities at low frequencies in comparison to the linear, high molecular mass polyethylene IUPAC 5A. Another striking feature of the samples is their pronounced shear-thinning behavior in comparison to the linear IUPAC 5A although their polydispersities of the molecular mass distribution are similar or even smaller compared to IUPAC 5A ($M_w/M_n = 3.0$).

From Fig. 5 the following conclusions can be drawn. Sample 271, for which LCB could clearly be detected using ^{13}C NMR and SEC–MALLS, has the highest viscosity at low angular frequencies. The rheological behavior of sample 272 is quite similar to that of sample 271, although the molecular characterization points to only a small amount of LCB in sample 272. Different lengths of LCB in these samples (sample 272 containing less but longer branches) could be responsible for this discrepancy. The samples 270 and 276 exhibit comparable complex viscosity functions, especially in the low frequency regime. The samples 273 and 275, for which only traces of LCB could be found using ^{13}C NMR, fall in between the viscosity functions of the samples 271 and 272 on the one side and 270 and 276 on the other. The increased low shear-rate viscosity of the samples 273 and 275 could be explained by their weight-average molecular masses that are higher than for the samples 270 and 276 (Table 3).

The investigation of the dynamic material functions clearly shows that analytically barely detectable amounts of LCB as present in the particularly polymerized samples can lead to a drastic change in the rheological behavior of polyethylene melts. It can be concluded that small amounts of LCB in polyethylenes lead to a significant change in the frequency dependence of dynamic–mechanical material functions. LCB cause a broadening of the transition between the rubbery plateau and the terminal zone. A similar

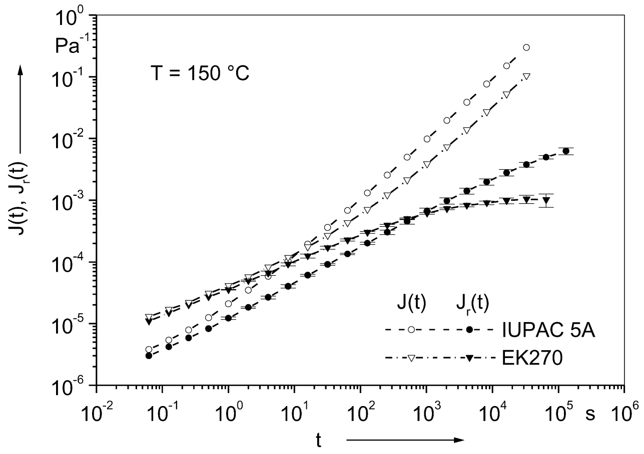

Fig. 6. Time-dependent creep and recoverable creep compliances of the linear IUPAC 5A and the long-chain branched sample EK270.

behavior has been observed (e.g. by Fetters et al. [4]) for four-arm stars of polyisoprene, by Graessley and Roovers [9] for star-branched polystyrenes and by McLeish et al. [23] for H-shaped polyisoprenes. For polyethylenes with a low degree of long-chain branching a similar behavior has been reported by Wood-Adams et al. [28].

Creep and creep recovery experiments. As the terminal zone is not accessible in dynamic–mechanical experiments creep and creep recovery experiments in shear were performed on selected samples (IUPAC 5A, 270 and 276). Fig. 6 shows the results on IUPAC 5A and 270. The creep and recoverable compliances of 276 did not differ significantly from those of 270 and are therefore not shown. In the long-time regime, in which $lgJ(t)$ as a function of lgt reaches a constant slope of one for both IUPAC 5A and sample 270, the creep compliance $J(t)$ of sample 270 is smaller than that of the linear IUPAC 5A. The zero shear-rate viscosity η_0 of the long-chain branched sample 270 is therefore significantly higher than that of the linear sample of distinctly higher M_w.

Fig. 6 also shows the recoverable compliances $J_r(t)$ of sample 270 and IUPAC 5A. Whereas for the linear sample a steady-state is not obtained in the recovery experiment for the sample 270 a steady-state recoverable compliance J_e^0 can be determined. Its value is close to 10^{-3} Pa^{-1}. The J_e^0 of IUPAC 5A is much higher than 10^{-2} Pa^{-1}, which gives strong evidence for the presence of high molecular mass components in this sample.[3] As the width of the molecular mass distribution strongly affects the elastic behavior of polymer melts no further discussion with respect to the influence of LCB on elasticity is attempted. For this matter the reader is referred to Gabriel [5] and Gabriel and Münstedt [8], where the influence of polydispersity and the degree of LCB on elasticity is discussed.

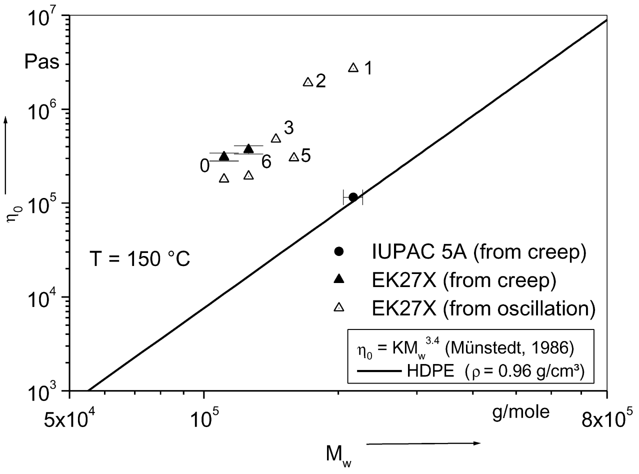

Fig. 7. Molecular mass dependence of the zero shear-rate viscosity of linear and long-chain branched polyethylenes. The filled symbols denote the zero shear-rate viscosities determined from creep experiments, the open symbols those from dynamic–mechanical analysis at an angular frequency of 0.01 s^{-1}. (The capital X in the sample notification stands for the numbers indicated at the symbols).

Molecular mass dependence of the zero shear-rate viscosity. Fig. 7 shows the zero-shear viscosity η_0 as a function of the weight-average molecular mass M_w. The solid line indicates the M_w dependence of η_0 of linear polyethylenes [18,19,24]. This relation is found to be fulfilled by the linear polyethylene IUPAC 5A and has also been proven to be valid for several linear polyethylenes of different M_w [5]. In contrast, η_0 of the long-chain branched samples 270 and 276 (filled symbols) as determined from creep experiments in the terminal zone are significantly higher than the relationship for linear polyethylene.[4] For sample 276 η_0 is twenty times higher compared with linear polyethylene of the same M_w. The open symbols in Fig. 7 indicate the low shear-rate viscosities as determined from the dynamic–mechanical analysis at an angular frequency of 0.01 s^{-1} (Fig. 5). These values are obviously smaller than the η_0 values determined in creep experiments. Nevertheless, they clearly indicate that small amounts of LCB lead to a significant increase in the zero shear-rate viscosity.

Comparing the results of ^{13}C NMR and SEC–MALLS with rheological measurements in the linear regime it becomes obvious that η_0 is a very sensitive quantity for probing the presence of small amounts of LCB in polyethylenes. The theoretical background for this conjecture is the exponential dependence of η_0 upon the number of entanglements per side chain of a long-chain branched polymer [4,24,25]. Due to the small entanglement molecular mass of polyethylene ($M_e = 1200$ g/mol) the

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[3] For IUPAC 5A a seeming inconsistency might be observed from comparing the time to achieve steady-state conditions in the creep and creep recovery data, which is much larger for the latter. The reason for this apparent discrepancy is that the viscous deformation dominates the creep compliance and therefore masks the small contribution of the elastic deformation at long experimental times. For times of 128, 1024 and 8192 s the creep compliance is larger than the recoverable compliance by factors 7, 15 and 40. A time dependence of $J_r(t)$ is therefore hidden behind the viscous contribution t/η_0 to the creep compliance $J(t)$.

[4] Details on the determination of the zero shear-rate viscosity from creep data can be found in Ref. [6].

number of entanglements per arm becomes quite large for polyethylenes with a slight amount of LCB having weight-average molecular masses higher than 100 kg/mol. As a consequence, the exponential dependence leads to increased values of the zero shear-rate viscosity in the molecular mass regime investigated in this study.

It should be noted, however, that certain combinations of M_w and degree and structure of LCB might lead to zero shear-rate viscosities of polyethylenes of a small amount of LCB that are indistinguishable from those of linear polyethylenes [8,14]. In such a case a second rheological method like, e.g. elongational rheometry or a measurement of shear-thinning behavior or frequency dependence of dynamic–mechanical material functions is needed to detect the presence of LCB.

4. Conclusions

From the experimental results the following conclusions can be drawn with respect to the characterization of long-chain branching in polyethylenes:

- ^{13}C NMR measurements indicate the presence of small amounts of methyl and ethyl branches as well as branches that are longer than six carbon atoms for the metallocene-catalyzed polyethylene samples 270–276.
- The number-average density of long-chain branching, as measured by ^{13}C NMR, indicates that the samples contain 0.1–0.4 branches per molecule.
- SEC–MALLS measurements show an average long-chain branch content that is qualitatively comparable with the results from ^{13}C NMR although the absolute values are different. From SEC–MALLS it becomes clear that the branching structure of the polyethylenes investigated is heterogeneous as the contraction factor is strongly dependent on the molecular mass.
- The zero shear-rate viscosity as a function of molecular mass is a very sensitive indicator for the presence of LCB in polyethylenes. Small amounts of LCB in metallocene-catalyzed polyethylenes can be related to an increase of zero shear-rate viscosity in comparison to linear polyethylenes of the same molecular mass.
- Small amounts of long-chain branching in metallocene-catalyzed polyethylenes are responsible for a change in the frequency dependence of storage and loss modulus in comparison to linear samples. LCB lead to a broadening of the transition from the rubbery to the terminal zone.
- Rheological measurements show differences for the polyethylenes investigated, which cannot be fully explained by the analytical results from ^{13}C NMR or SEC–MALLS. Rheological measurements turn out to be a very sensitive analytical tool for the detection of the presence of very small amounts of LCB in polyethylenes.

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