Characterization of branched ultrahigh molar mass polymers by asymmetrical flow field-flow fractionation and size exclusion chromatography

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ABSTRACT

The molar mass distribution (MMD) of synthetic polymers is frequently analyzed by size exclusion chromatography (SEC) coupled to multi angle light scattering (MALS) detection. For ultrahigh molar mass (UHM) or branched polymers this method is not sufficient, because shear degradation and abnormal elution effects falsify the calculated molar mass distribution and information on branching. High temperatures above 130 °C have to be applied for dissolution and separation of semi-crystalline materials like polyolefins which requires special hardware setups. Asymmetrical flow field-flow fractionation (AF4) offers the possibility to overcome some of the main problems of SEC due to the absence of an obstructing porous stationary phase. The SEC-separation mainly depends on the pore size distribution of the used column set. The analyte molecules can enter the pores of the stationary phase in dependence on their hydrodynamic volume. The archived separation is a result of the retention time of the analyte species inside SEC-column which depends on the accessibility of the pores, the residence time inside the pores and the diffusion ability of the analyte molecules. The elution order in SEC is typically from low to high hydrodynamic volume. On the contrary AF4 separates according to the diffusion coefficient of the analyte molecules as long as the chosen conditions support the normal FFF-separation mechanism. The separation takes place in an empty channel and is caused by a cross-flow field perpendicular to the solvent flow. The analyte molecules will arrange in different channel heights depending on the diffusion coefficients. The parabolic-shaped flow profile inside the channel leads to different elution velocities. The species with low hydrodynamic volume will elute first while the species with high hydrodynamic volume elute later. The AF4 can be performed at ambient or high temperature (AT-/HT-AF4). We have analyzed one low molar mass polyethylene sample and a number of narrow distributed polystyrene standards as reference materials with known structure by AT/HT-SEC and AT/HT-AF4. Low density polyethylenes as well as polypropylene and polybutadiene, containing high degrees of branching and high molar masses, have been analyzed with both methods. As in SEC the relationship between the radius of gyration (R_g) or the molar mass and the elution volume is curved up towards high elution volumes, a correct calculation of the MMD and the molar mass average or branching ratio is not possible using the data from the SEC measurements. In contrast to SEC, AF4 allows the precise determination of the MMD, the molar mass averages as well as the degree of branching because the molar mass vs. elution volume curve and the conformation plot is not falsified in this technique. In addition, higher molar masses can be detected using HT-AF4 due to the absence of significant shear degradation in the channel. As a result the average molar masses obtained from AF4 are higher compared to SEC. The analysis time in AF4 is comparable to that of SEC but the adjustable cross-flow program allows the user to influence the separation efficiency which is not possible in SEC without a costly change of the whole column combination.

1. Introduction

Ultrahigh molar mass (UHM) polymers have typically a weight average molar mass $\langle M_w \rangle$ of above 500 kg/mol. Especially ultrahigh molar mass polyethylene (UHMPE) is superior to traditional

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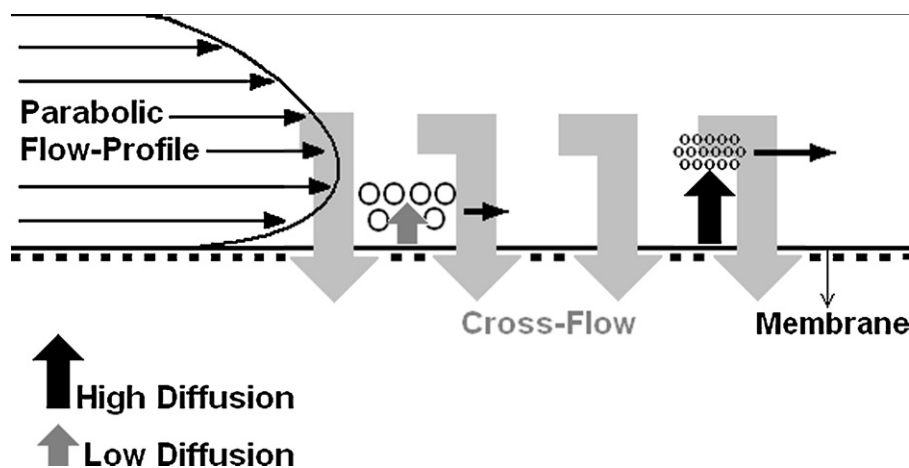E-mail address: hpasch@sun.ac.za (H. Pasch).

Fig. 1. Cross-section of the AF4 channel, scheme of size separation.

materials with regard to mechanical stability and specific weight and, therefore, used for special applications such as ultra-strong fibers, implants or toothed wheels. For the development of new products made from UHMPE, knowledge of the molar mass distribution and the chain structure is extremely important. These parameters influence the mechanical properties of the final product, the morphology as well as the rheological behavior of the melt [1].

The most common method for the molar mass determination of semi-crystalline polyolefins is high temperature size exclusion chromatography (HT-SEC) [2–6]. Amorphous materials like polybutadiene can be analyzed with SEC at ambient temperature [7–9]. In SEC the separation of the polymers takes place in a porous stationary phase. Unfortunately, the polymers, particularly those with very high molar masses, may undergo shear degradation during the chromatographic separation process [2,10–17]. Furthermore, branched chains often co-elute with smaller linear ones which then prevents a correct analysis of the chain structure [18–26]. Field-flow fractionation (FFF), which was discussed by Giddings et al. [27–29] for the first time in the 1960s, has the potential to overcome the above mentioned drawbacks of SEC for the analysis of very large molecules. The separation in asymmetrical flow field-flow fractionation (AF4) is provided by a cross-flow perpendicular to the solvent flow as it is shown in Fig. 1.

The solvent flow passes the empty channel and forms a parabolic velocity profile which is deformed towards the accumulation membrane like it is visible in Fig. 1. The cross-flow leaves through a semi-permeable membrane. The inlet streams are always higher than the cross-flow and will automatically be adjusted if the cross-flow changes, e.g., if a gradient is applied, to provide a constant outlet stream through the detectors. As a consequence of the cross-flow a field force perpendicular to the carrier-flow is formed which depends on the cross-flow velocity. As a result of this field force the analyte molecules or particles will move towards the accumulation membrane. The material of the membrane is mostly cellulose for ambient temperature and ceramic for high temperature use. The arrangement of the analyte at the membrane causes a concentration gradient over the channel cross-section which leads to an increased diffusion of the analyte molecules. The equilibrium between movement induced by the field-force and the diffusion leads to an arrangement of the analyte molecules or particles in different channel heights. The position of the molecules is influenced by the cross-flow velocity, the carrier flow velocity and the diffusion coefficients of the analyte structures. As the ability to diffuse depends on hydrodynamic size, i.e., small molecules diffuse faster than larger ones of similar structure, the large molecules will be situated closer to the membrane where the flow velocity is lower due to the parabolic-shaped flow velocity profile in the channel (Fig. 1). As a result the polymer molecules will elute according to their size beginning with the smallest and fastest moving molecules if all species have the same chain structure and constant chemical composition [27–33]. Only a narrow zone above to the accumulation membrane contains analyte molecules, while the remaining layers contain pure solvent.

AF4 has been applied for characterization of large biological molecules like proteins [34] or vesicles [35], as well as synthetic polymers like polystyrene [36], styrene–butadiene-rubber [37] and polyacrylamide [38]. The dissolution of semi-crystalline polyolefins requires temperatures above 130 °C and chlorinated solvents and, therefore, the AF4 has to be carried out at these harsh conditions. The first high temperature FFF separation of PS was done by Giddings et al. [39]. The authors mentioned the possibility to separate PE by HT-FlowFFF but did not report any results. Several years later, Mes et al. [40] described a successful separation of polyolefins with HT-AF4. The first commercial instrument for HT-AF4 was developed in cooperation with Postnova Analytics (Landsberg/Lech, Germany) and Polymer Laboratories (Church Stretton, England).

In this paper the applicability of AF4 for the characterization of polyolefins and polybutadienes with partially high degrees of branching and high molar masses is shown. The complete differential molar mass distributions from AF4-MALS are presented for the samples, which were never published for PE material before. The AF4-measurements are compared with SEC-separations using standard conditions and standard columns like they are used in many laboratories all over the world with the aim to show the huge error which can occur easily in molar mass and branching determination with SEC–MALS. A huge variety of theoretical papers dealing with FFF is present in the literature, but until now only a few papers exist which demonstrate the successful use of AF4 for the analysis of polymers with complex chain structures and the additional information which is accessible by AF4-MALS. The new results from AF4-MALS presented in this work, e.g., the correct information on branching and the visualization of ultrahigh molar mass material in LDPE and branched PB, offer the possibility to figure out new structure–property-relationships for those important samples.

2. Experimental

2.1. Instrumentation

The AF4 experiments were carried out on two AF2000 instruments from Postnova Analytics (Landsberg/Lech, Germany). One system was especially configured to be used at high temperature
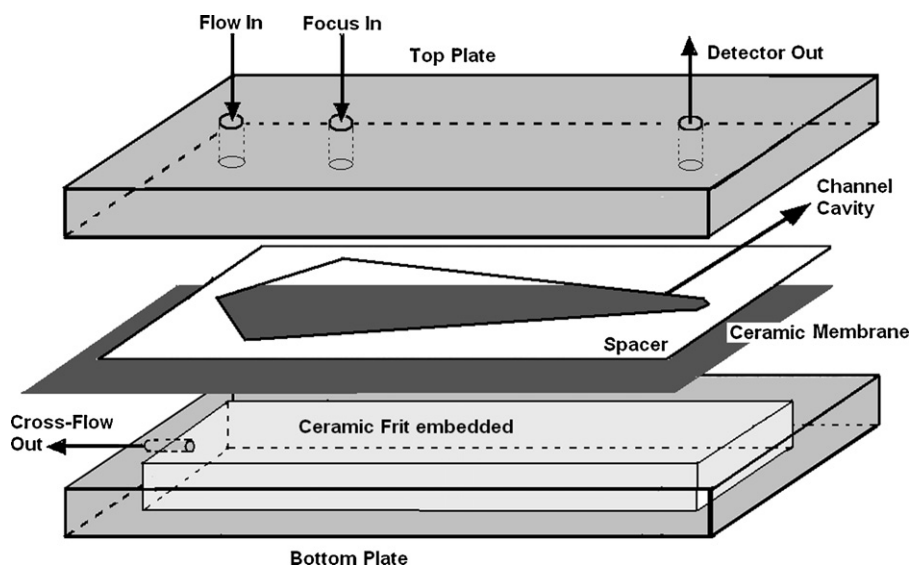
Fig. 2. Scheme of a HT-AF4 channel.

above 130 °C. For this aim the AF4 pump system was connected to a PL GPC-220 chromatograph (Polymer Laboratories, Church Stretton, England). The HT-AF4-channel was situated inside this column oven. All AF4 channels were connected to three pumps from Postnova Analytics and to an additional pump management system which ensures a constant flow rate out to the detectors during the whole separation. The HT-AF4-channel setup is shown in Fig. 2.

A spacer of 350 μm thickness was used for the separation of the UHM material. It was clamped between two plates made from stainless steel. The thickness of the spacer was measured before and after its use in the channel. The results proved that there was no change of the thickness during the use in the FFF-channel. For high temperature a ceramic membrane with a cut-off of approx. 150 kg/mol PE in 1,2,4-trichlorobenzene (TCB) was applied for separation. The AT measurements were performed using a cellulose membrane with a cut-off of 10 kg/mol PS in THF. The design of the AT-AF4-channel was similar to the HT-AF4 but the ceramic frit was exchanged for a stainless steel frit as support for the cellulose membrane.

Note that the use of flexible membranes, e.g., cellulose, can influence the real channel thickness e.g., by swelling processes. This has to be taken into account if theoretical calculation of the particle size from the elution volume is used for data evaluation. For the MALS detection this procedure is not necessary because the molar mass and radius of gyration are directly calculated from the scattering intensity and the angular dependence of the scattered light independently from the retention time.

The HT-SEC measurements were realized using two PLgel mixed B columns with a particle size of 10 μm (Polymer Laboratories, Church Stretton, England) which were installed inside the PL GPC-220 chromatograph next to the AF4 channel. These columns represent the standard of many laboratories which are doing polyolefin analysis. For this reason the mentioned particle size was used. However, columns with higher particle size e.g., PL mixed A (20 μm) would avoid more of the shear degradation but the lower filtration would also lead to more noisy light scattering signals. The injection and the switch between the two separation systems were controlled by three six port HT-valves (Valco Instruments, Waterbury, USA). The outlet of the channel and the columns was connected to an infrared detector (IR4, PolymerChar, Valencia, Spain) and a HT-MALS detector (Heleos 2, Wyatt Technology). The MALS operates at a wavelength of 658 nm and offers 18 different scattering angles between 2° and 158° to calculate the correct molar mass and radius

of gyration also in case of large polymer coils. The lowest angle was not usable. Thus, 17 scattering angles were included for calculation of molar mass and radius of gyration. The separation was performed at a temperature of 145 °C in 1,2,4-trichlorobenzene (TCB).

The ambient temperature AF4 instrument was equipped with a manual injection valve from Rheodyne (Rohnert Park, USA). The system was connected to a 18-angle MALS (Dawn DSP, Wyatt Technology) operating at a wavelength of 633 nm and a RI detector (PN 3140, Postnova Analytics). The MALS enables to detect the scattered light at 18 different angles between 2° and 158°. The signal from the lowest angle was saturated. For this reason this angle was excluded from the calculations. The SEC measurements at ambient temperature were realized by replacement of the AF4-channel by two PL columns (mixed B and C).

2.2. Materials and methods

2.2.1. High temperature experiments

The low density polyethylene samples CSTR-LDPE 1 and 2 were synthesized by free radical polymerization in a continuous stirred tank reactor (CSTR) under high pressure of approx. 2000 bar and temperatures up to 245 °C. The details of synthesis and rheological data have been reported in [21]. The samples differ in the amount of chain transfer agent propionic aldehyde (PA) added during the synthesis. For CSTR LDPE 1 1.6×10^{-3} kg/h and for CSTR LDPE 2 2.8×10^{-3} kg/h PA was used.

The technical polyethylene sample PE 1 was a broad distributed high density polyethylene (HDPE) and PE 2 was a broad distributed low density polyethylene (LDPE). The two technical polypropylene samples PP 1 and 2 had broad molar mass distributions and different degrees of branching. Both were synthesized by Ziegler–Natta catalysis. All polyolefins were produced by LyondellBasell (Frankfurt, Germany).

The polyolefins have been dissolved in TCB which was distilled before use. The dissolution time was 4 h under gentle rotation at 160 °C. The concentration of the polymer solution was 2 mg/mL. 1 mg/mL butyl hydroxytoluene (BHT) was added to the solvent, to minimize thermo-oxidative degradation of the polymers during the dissolution process. In addition, the solvent was flushed with Argon gas to repress the remaining oxygen. The specific refractive index increment used in TCB at 145 °C was −0.091 for PE [4] and −0.097 for PP [41].

2.2.2. Ambient temperature experiments

The narrow distributed PS standards were produced by PSS (Mainz, Germany). The weight average molar masses given by PSS are 62, 250 and 1000 kg/mol with polydispersities between 1.02 and 1.04.

The technical polybutadiene samples PB 1–3 were synthesized by Ziegler–Natta catalysis. The samples are broadly distributed and exhibit different degrees of long chain branching.

The PS and PB samples have been dissolved in HPLC grade THF with a concentration of 3 mg/mL. BHT was added in the same amount as for the polyolefin samples to avoid oxidative degradation during the dissolution process. The dissolution time was 16 h at ambient temperature and additional 4 h at 50 °C for the PB samples. The separation was performed at 25 °C. The specific refractive index increment used in THF at 25 °C was 0.184 for PS [42] and 0.132 for PB [43].

2.2.3. Calibration

The correctness of the used refractive index increments was checked with low molar mass samples of known M_w (standards from PSS, Mainz, Germany). A second order Berry extrapolation method was used for evaluation of the MALS data. The RI-detector operates with a white light source. For this reason, the detector constant had to be adapted to the used refractive index increments by calibration with low molar mass samples of known M_w and known concentration. The calibration was performed in SEC-mode to ensure proper separation of impurities e.g., stabilizer from the main peak.

2.2.4. Separation conditions

The inlet and detector flow rates of all SEC and AF4 separations were 0.5 mL/min and the injection volume was 200 μL for all experiments.

At the beginning of the AF4-separation a focusing step of 5 min was used. During the focus period the injection flow rate and outlet flow rate were 0.5 mL/min. The focus flow was automatically adjusted by the system depending on the applied cross-flow in a way which provides the constant detector flow of 0.5 mL/min. The cross-flow during focusing is constant and corresponds to the first value given in the diagrams (Figs. 4 and 10). The focus step covered the first 5 min of the cross-flow program which is displayed in the figures. After the focus period the focus flow is stopped. Now cross-flow and injection flow are still active and the programmed cross-flow decay is started as it is visible in Fig. 4 for the polyolefins and in Fig. 10 for the polystyrene and rubber. During the gradient decay the injection flow is increased in the same manner like the cross-flow decrease to hold the detector flow constant.

3. Results and discussion

3.1. Analysis of thermoplastic polymers

In previous work it has already been demonstrated that HT-AF4-MALS is able to separate a linear HDPE into narrow disperse fractions [40,44]. It was shown that the conformation plots from HT-AF4 and HT-SEC are similar and that the expected slope for a linear polymer coil was found after separation with both methods. In this study the correct separation and detection of the system was investigated by injection of a linear HDPE into HT-AF4 and HT-SEC. The HDPE was of low molar mass to avoid shear degradation effects in HT-SEC for better comparison. In Fig. 3 the conformation plots from both methods are overlaid.

Both graphs are completely congruent and the slope of the R_g–M-relationship of 0.6 is very close to the theoretical value of 0.588 for a linear polymer in a good solvent [45]. These results indicate that all system parameters are correctly adjusted and the separation is comparable for both methods.

As has been pointed out before, the velocity of the cross-flow determines the vertical position of the polymer molecules in the channel, and therefore it is essential to know its precise influence in order to optimize a separation. For this reason, the sample PE 2 was analyzed using different cross-flow gradients. The obtained calibration curves are shown in Fig. 4.

Both, the slope of the cross-flow decay and the shape of the gradient function (e.g., linear, exponential or stepwise) determine the quality of the separation. A flat gradient leads to an increased separation which in Fig. 4 is manifested as a decreased steepness of the molar mass vs. elution volume plot. The increase of the elution interval of the polymer for longer gradients is caused by peak broadening and improved separation. In another paper the separation of narrow PS standards at different cross-flows was addressed and it was shown that the increased separation strongly over compensates the band broadening [44].

In Fig. 4 the advantage of using complex gradient functions with e.g., an exponential-like decay becomes obvious. This special type of gradient yields a significantly better separation than a comparable linear one of the same duration. The shape of the gradient allows the selective retention of the high molar mass molecules which leads to its better separation from the low molar mass material. In addition, the low average cross-flow value of the exponential gradient leads to a decreased loss of small molecules through the pores of the membrane and saves a large amount of the solvent compared to a linear gradient which would deliver a comparable separation.

The results demonstrate the enormous flexibility of AF4 as compared to SEC. The adjustment of the cross-flow function enables to create flexible calibration curves. An expensive and time consuming change of the SEC columns is not necessary. Finally the exponential-like gradient (see gradient 4 in Fig. 4) was chosen for the further measurements because of the good separation and the lower material loss for low molar mass samples.

Two highly branched ultrahigh molar mass LDPE samples were injected in HT-SEC and HT-AF4 to test the maximum performance of the HT-AF4 system. The sample material with molar masses above 1000 kg/mol is known to be very sensitive to shear degradation in SEC separation [2]. A second drawback of SEC–MALS especially in case of highly branched material is the abnormal interaction of branched molecules with the stationary phase of the column. As a result, the molar mass and the radius of gyration show an abnormal increase at high elution volumes. This effect seems to be caused by the late co-elution of high molar mass molecules together with small structures which are eluting according to the regular SEC mechanism [25].

In Fig. 5(a and b) the fractograms from HT-AF4 and elugrams from HT-SEC of two different LDPE samples are shown.

Fig. 5 shows that the radius of gyration or the molar mass which was detected by HT-AF4 is clearly higher than the one detected in the corresponding HT-SEC run. This indicates increased shear degradation in either the packing or the frits of the SEC columns [2,10–17]. Radii up to 1000 nm and molar mass values above 10^8 g/mol can be recognized in the fractogram of the HT-AF4 separation for both LDPE samples. The number of these extremely large molecules can be very low which leads to an increased noise in these upper radius or molar mass regions. HT-SEC is not able to show molar masses above 10^8 g/mol and radii above 200 nm.

For both LDPE samples a strong curvature of the radius and the molar mass at high elution volumes is visible in the HT-SEC results. The radius (Fig. 5b) seems to be more sensitive to the abnormal late elution phenomenon. It re-increases earlier than the corresponding molar mass at high elution volumes. For this reason the co-elution of large and small molecules could be a good explanation for the
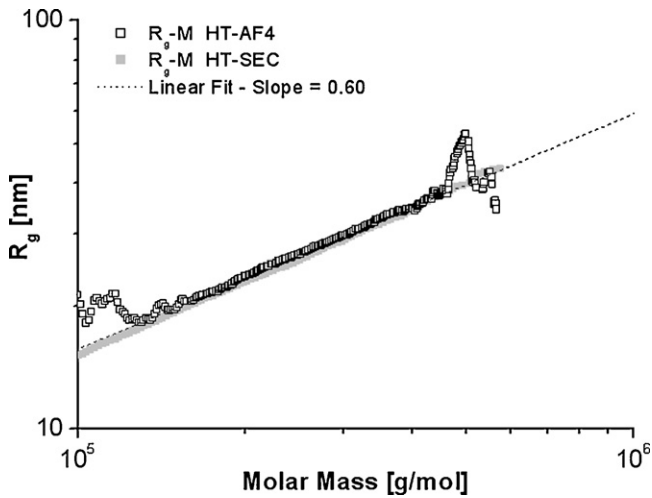
Fig. 3. Conformation plot from HT-SEC and HT-AF4 separation of linear PE 1, data obtained by IR-MALS.

phenomenon. The z-averaged radius of polydisperse fractions will be more sensitive to a small amount of co-eluting large molecules compared with the weight-averaged molar mass value. For a correct SEC separation every slice of the eluting material is assumed to be nearly monodisperse. In the case of co-elution of large and small molecules in the late elution part of the sample the resulting fractions will be more and more polydisperse and the detected masses and radii are averaged values. The radius is a z-average while the mass is a weight average [25]. This means that the radius will be more sensitive to large structures compared to the molar mass value, which explains the higher sensitivity of the radius and the start of the re-increase at lower elution volumes in Fig. 5(b). The SEC separation turns into an apparent SEC separation if interaction or abnormal high retention of the passing components with the column packing occurs.

The HT-AF4 shows no co-elution of species with different hydrodynamic size in the conducted experiments, because no stationary phase is used which could interact with the sample and lead to abnormal high retention of large material. The molar mass as well as the radius increases steadily with the elution volume which is an
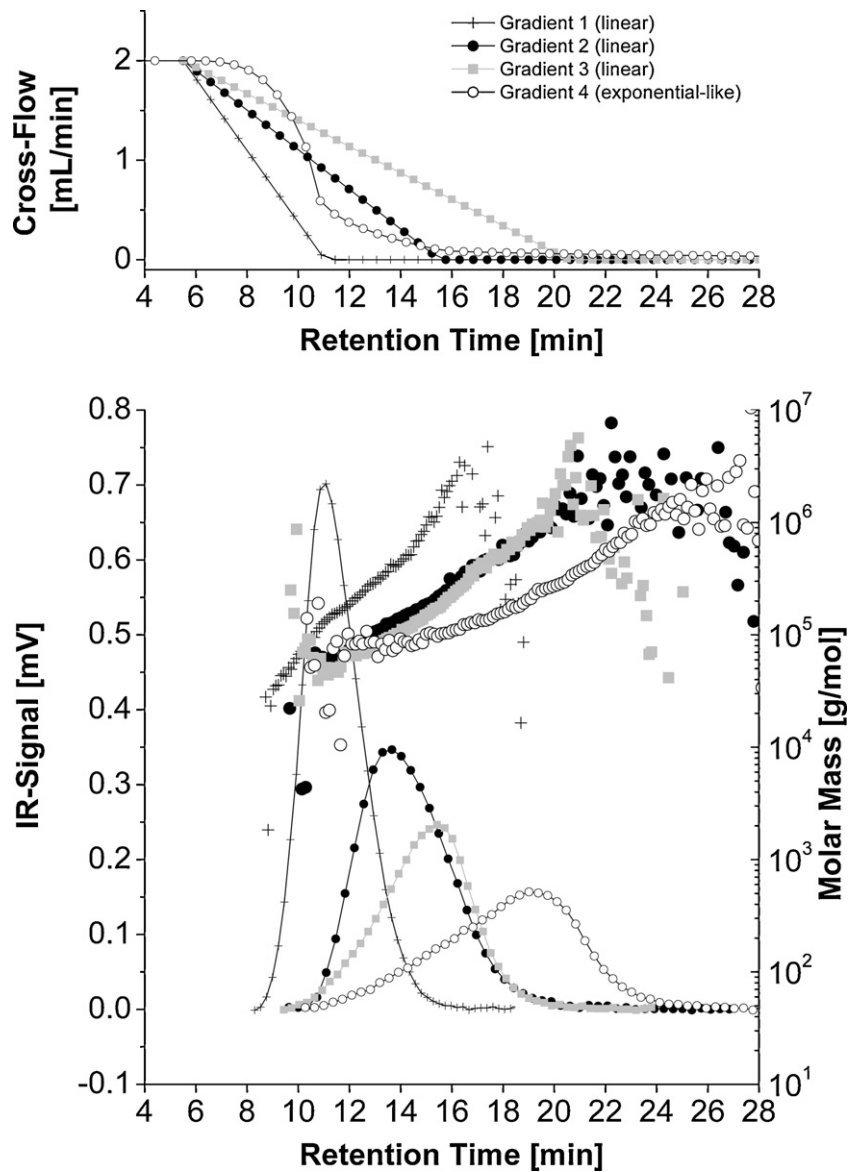

Fig. 4. Fractograms and detected calibration curves of PE 2 separated with different cross-flow gradients in HT-AF4-IR-MALS; the gradients start with the same cross-flow value of 2 mL/min, gradients 1–3 are linear with different duration, gradient 4 represents an exponential decay.
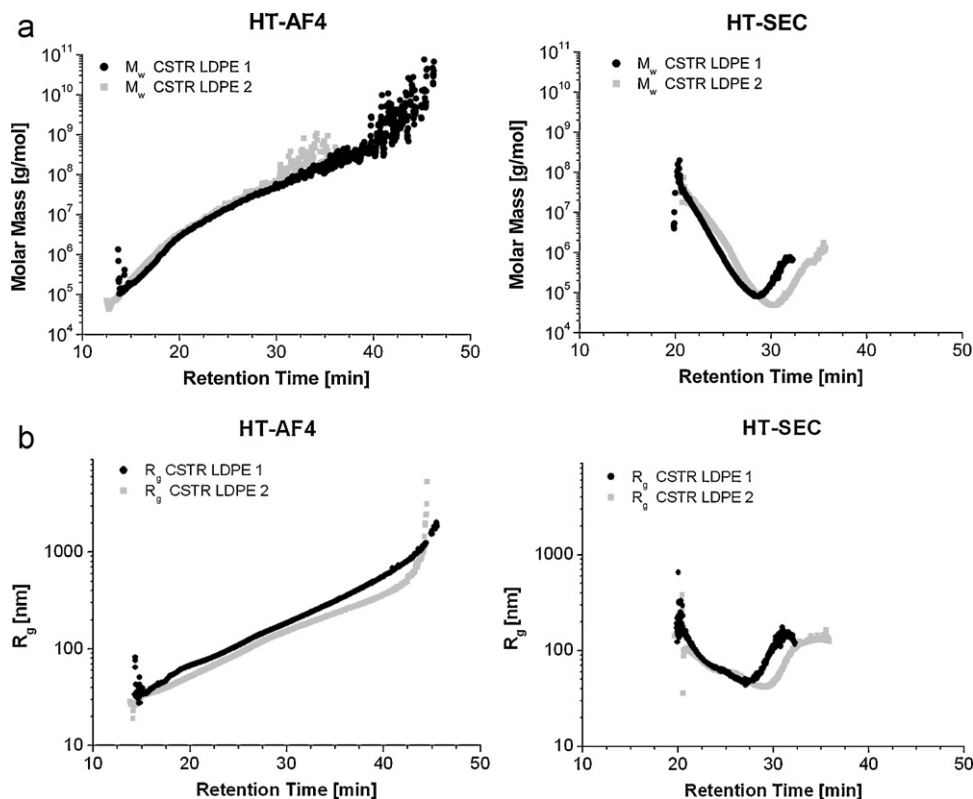
Fig. 5. Overlay of fractograms obtained with HT-AF4 and elugrams from HT-SEC, (a) CSTR-LDPE 1 and 2, molar mass obtained by light scattering detection, (b) CSTR-LDPE 1 and 2, R_g obtained by light scattering detection.

indication for narrow dispersed size fractions. As a result also the lower radius values are visible in HT-AF4 which are not accessible by HT-SEC. The curvature of the molar mass vs. elution volume curve prevents the correct calculation of the differential molar mass distribution because of the missing separation. Even when comparing the MMD from HT-AF4 and HT-SEC, a linear extrapolation of the molar mass vs. elution volume curve is necessary, which does not consider the high masses of the co-eluting material. In Fig. 6 the linear extrapolation is shown.

Contrary to HT-SEC, the data from HT-AF4 show a linear dependence between R_g and the elution volume in Fig. 5(b). This indicates a proper separation of the polymer molecules according to their

Fig. 6. Overlay of the elugrams from HT-SEC for sample CSTR LDPE 1 and 2, fit procedures for the determination of the MMD the late co-eluting part being not considered.

hydrodynamic size for the whole sample. Fig. 7 shows the differential molar mass distributions and the conformation plots of both CSTR-LDPE samples 1 and 2 obtained by HT-SEC-IR-MALS as well as HT-AF4-IR-MALS.

The negative effects in HT-SEC, which were already mentioned above, manifest themselves for the LDPE samples in an even more pronounced way: the R_g-curve in the conformation plot is strongly bent in the low molar mass range. The reason for this behavior is the enlarged sensitivity of the R_g-value for high molar mass molecules in case of co-elution. The curvature of the conformation plot from HT-SEC prevents a correct determination of the branching in the LDPE samples. A possible solution for this problem would be the branching calculation using the Mark–Houwink plot from intrinsic viscosity measurement. The intrinsic viscosity is less sensitive to the co-elution of large material. As a result the curvature of the Mark–Houwink plot from SEC will be decreased [40].

The lower hydrodynamic volume of branched molecules normally leads to a reduced slope of the R_g–M-relationship which is significantly lower than the value of 0.588 for a linear polymer [45]. Since HT-AF4 shows no co-elution effects, the conformation plot provides correct information about the chain branching. The R_g–M_w dependence is linear and the reduced slopes of 0.32 and 0.36 (Fig. 7) indicate very compact molecules as a result of the very high degree of branching in the LDPE samples.

The comparison of the MMDs from HT-AF4 and HT-SEC shows the immense error of the HT-SEC results. The HT-SEC of both materials gives nearly similar results except a small difference in the molar mass average values (Table 1). Both MMDs show a very small high molar mass shoulder and a broad main peak in the lower molar mass area. In contrary, the MMD from HT-AF4 shows a strong bimodality for CSTR LDPE 1 with a comparable low and high molar mass part. For CSTR LDPE 2 the high molar mass part of the MMD is shifted towards lower values, which leads to an overlay of both peaks. The lower mass value of CSTR LDPE 2 is expected because
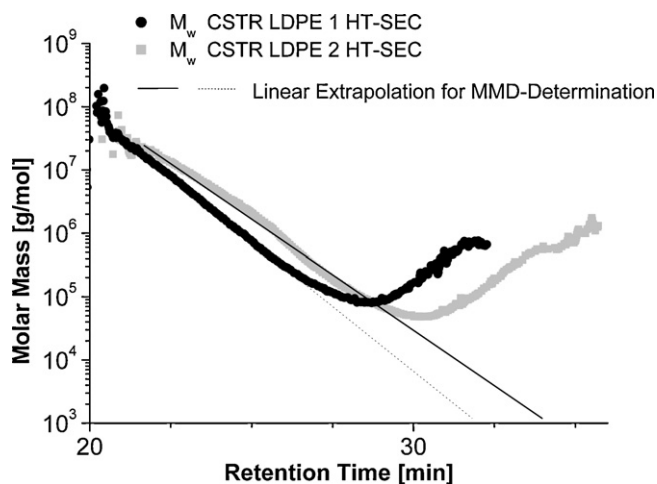
Table 1
Average values for the molar mass and the radius of gyration for UHM LDPE samples, obtained from light scattering detection.

Sample	Separation method	$\langle M_w \rangle$ (kg/mol)	$\langle R_g \rangle$ (nm)	PD
PE CSTR LDPE 1	HT-AF4	12,830	236	31.66
		18,090[b]	236[b]	11.49[b]
	HT-SEC	1769	82	6.49
		1579[a]	82[a]	9.77[a]
		4664[b]	82[b]	4.67[b]
PE CSTR LDPE 2	HT-AF4	6246	117	12.78
		7956[b]	126[b]	5.58[b]
	HT-SEC	663	64	15.77
		603[a]	64[a]	6.51[a]
		3092[b]	64[b]	4.13[b]

[a] Values for linear extrapolation of the detected molar mass-calibration curve (Fig. 6).
[b] Values calculated for fraction with $M_w > 300$ kg/mol (no material loss in this fraction).

of the higher amount of chain transfer agent used during the synthesis. The bimodality of CSTR LDPE 2 is reduced and now visible as a low molar mass shoulder. The average values from HT-AF4 in Table 1 confirm the significant differences between the two LDPE materials.

Consequently, it can be confirmed that also highly branched LDPE molecules with molar masses above 1000 kg/mol are degraded during the HT-SEC measurement while this is not the case in HT-AF4 separation. For the LDPE material it is known that the ultrahigh molar mass fraction is overrepresented in samples

Fig. 7. MMD from HT-AF4- and (apparent) HT-SEC separation overlaid with corresponding conformation plots obtained from IR-MALS, (a) CSTR-LDPE 1, (b) CSTR-LDPE 2.

from laboratory scale reactors compared to technical samples [21]. The present HT-AF4 results strongly indicate that this fraction was underestimated in previous SEC results because these are falsified by shear degradation.

The low molar mass part of the MMDs in HT-AF4 is falsified by the loss of small polymer molecules. Due to the cut-off of the ceramic membrane, molecules below 100 kg/mol diffuse through the HT-AF4-membrane. As a result the part of the MMD below 100 kg/mol is missing in HT-AF4. The MMD from HT-SEC shows also the low molar mass part as a result of the linear extrapolation. After finishing the experiments a new HT-AF4-membrane with a much smaller pore size (cut off of approx. 20 kg/mol PE in TCB) was developed by Postnova Analytics. It now allows a full characterization even of broad distributed polyolefin samples.

However, the missing low molar mass part in the results from the older HT-AF4-membrane can also lead to increased molar mass average values. With the aim to provide a better comparison of the average values from AF4 and SEC, the high molar mass average was also calculated for the high molar mass part of the MMDs over 300 kg/mol for both separation methods (Table 1). This procedure avoids the falsification which is due to the material loss through the membrane and allows a good comparison between the MMD from HT-SEC and HT-AF4. The average values of the high molar mass part from HT-AF4 are still much higher compared to the HT-SEC results. This means that the high HT-AF4 values are the result of the low shear stress in the channel and not caused by the loss of small molecules through the HT-membrane. Another reason for the low molar mass values from SEC can be found in the abnormal high retention of the branched material. The mass average values of the non-extrapolated SEC results in Table 1 are higher than the values without extrapolation. This means that there is additional high molar mass material incorporated in the late eluting part of the sample.

All results clearly indicate that HT-SEC does not provide the correct information about the LDPE samples due to the falsified MMD as a result of the late co-elution of large, branched material. The extent of shear forces and the late co-elution effect depends on various parameters. The most important influence may be the kind and shape of the column packing particles and differences in the sample preparation as well as the chosen flow rate. These problems are reflected by differences in the molar mass average values obtained from (apparent) SEC separation in different laboratories for the analyzed LDPE samples [21]. For this reason the impact of different SEC parameters on the late elution phenomenon and the shear degradation will be analyzed much more in detail in a separate study.

In addition to the LDPE, branched PP samples were analyzed by HT-SEC and HT-AF4 to prove the universal applicability of the HT-AF4 system. In Fig. 8 the elugram from HT-SEC and the fractogram from HT-AF4 are displayed for two branched PP samples.
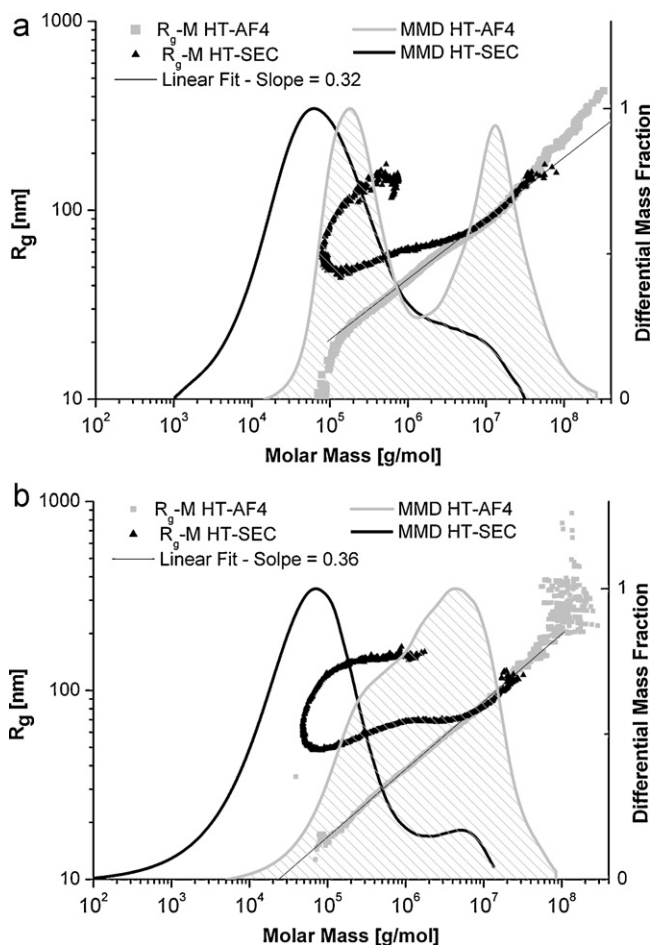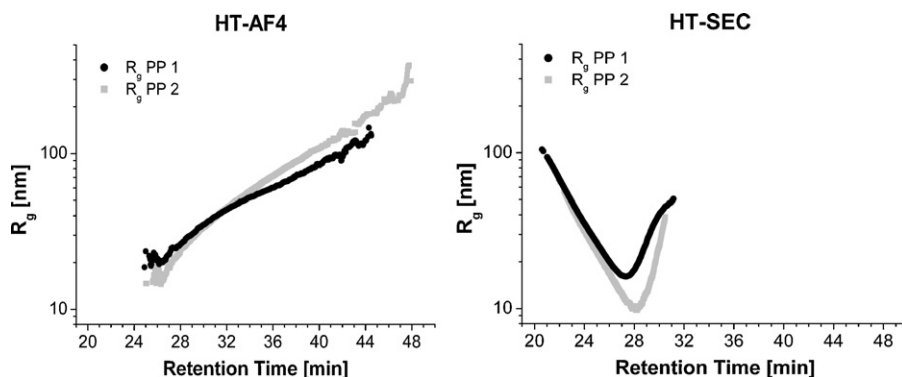
Fig. 8. Overlay of fractograms obtained with HT-AF4 and elugrams from (apparent) HT-SEC for branched PP samples PP 1 and 2, R_g obtained by light-scattering detection.

The PP samples show the same problems of late co-elution in SEC as the LDPE samples. The radius in Fig. 8 is very sensitive to large structures. As a result it is a good indicator for shear degradation and late co-elution effects. For both PP samples the radius re-increases at high elution volumes in HT-SEC. HT-AF4 does not show this behavior. In this method no stationary phase is used which could interact with the large, branched molecules. In addition, the radii from AF4 are significantly higher than those from SEC for both PP samples. The results show that AF4 is not restricted to the analysis of PE. Also other polyolefins can be separated by HT-AF4 and additional information will be accessible.

3.2. Analysis of elastomers

Another important group of synthetic polymers is rubber. Different types of rubber are used in various large volume applications including the production of car tires. Rubber materials (polybutadiene, polyisoprene) often exhibit high degrees of branching and extreme molar mass values which lead to problems in SEC characterization [18–26]. Synthetic polybutadiene from Ziegler catalysis was analyzed using SEC- and AF4-RI-MALS. The AF4-SEC-setup was the same as the HT-system but without the column-oven and with manual injection instead of the autosampler. For ambient temperature application the AF4 channel was equipped with a cellulose membrane instead of ceramic membrane and THF was used as a mobile phase. The concentration detection was performed with an RI detector because of the high refractive index increment of PS or PB in THF (0.184 and 0.132 mL/g) [42,43]. A mixture of three narrow PS standards was analyzed with both methods to check if the calibration, normalization and alignment of the detectors are correct and to ensure comparable separation quality in SEC and AF4. The results are shown in Fig. 9(b).

The results shown in Fig. 9 prove that AF4 allows a comparable separation like it will be provided by SEC with two columns but in a shorter analysis time. All masses measured with light scattering show values that are in agreement with data from the producer of the standards. This means that the MALS-detector was correctly calibrated and normalized. The plateau area of the molar mass is a good indication for a correct inter-detector delay [19]. Due to the comparable separation with both methods in the tested mass-range, the same cross-flow program was used for all AF4 runs. The shape of the cross-flow gradient is given in Fig. 10.

A polydisperse polybutadiene sample (PB 1), which was known to be only very lightly branched, was separated with both methods – AF4 and SEC. The results of the separation are displayed in Fig. 11.

It is shown in the figure, that the falsification of the molar mass from SEC–MALS is low for a lightly branched PB with no gel content and low amounts of high molar mass molecules. As a result the slope of the R_g–M-relationship and the molar mass distribution from SEC is correct for most of the sample. The comparison of the data from SEC and AF4 shows, that it is possible to get the same separation in AF4 and SEC even for smaller molecules. Both molar
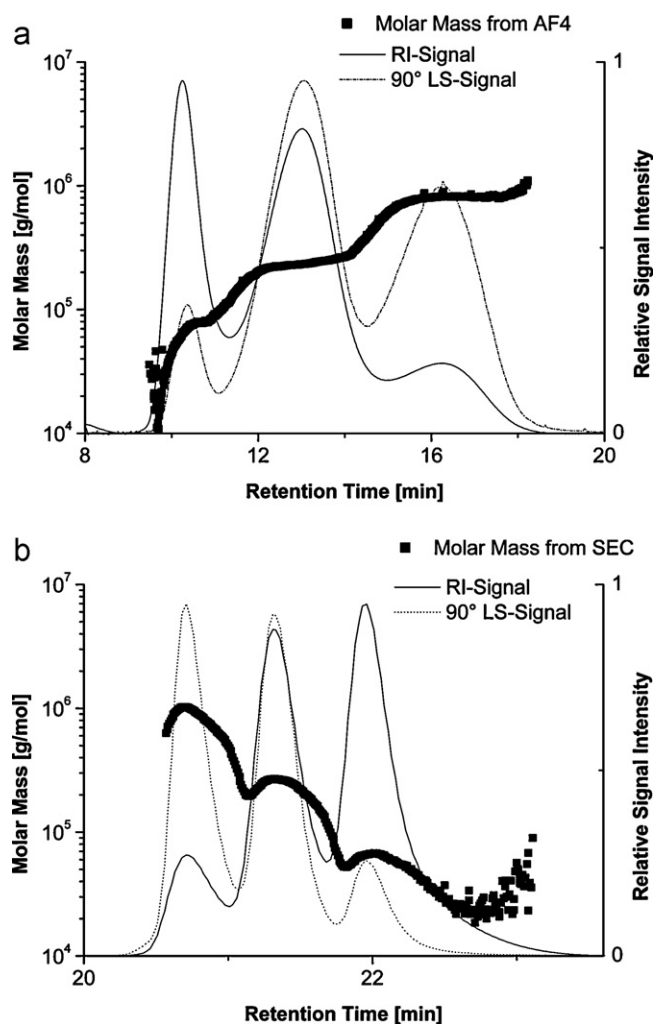

Fig. 9. Separation of a mixture of three PS standards with molar masses of 62, 250 and 1000 kg/mol, molar mass obtained by RI-MALS, flow-rate = 0.5 mL/min, (a) fractogram from AF4, and (b) elugram from SEC.
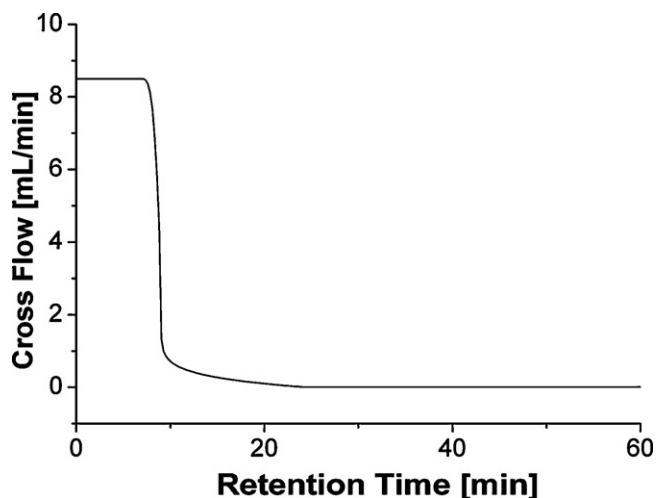
Fig. 10. Cross-flow gradient used for separation of PS and PB at ambient temperature, detector flow rate = 0.5 mL/min, focus time = 5 min, injection flow = 0.2 mL/min.

mass distributions are very similar. The conformation plot from both methods is congruent. This means that SEC is still sufficient to separate this special PB with only low late co-elution effects. AF4 is able to reproduce these correct results because only a very small amount of material is lost through the membrane.

The sample PB 2, which was also synthesized by Ziegler catalysis, contains a higher amount of long chain branching and a broader molar mass distribution. A significantly higher portion of material with molar masses above 500 kg/mol is present in this sample.

The comparison of the molar mass distribution from SEC and AF4 in Fig. 12 shows, that the sample contains molecules with higher molar mass than PB 1. The increased high molar mass part gets only visible in the results from AF4 due to the shear degradation of the larger molecules in the SEC columns. On the other hand, the molar mass distribution of PB 2 is broader. There are more small molecules present in sample PB 2 which have sizes in the range of the cut-off of the used cellulose membrane (approx. 10 kg/mol). As a result, the low molar mass region of the MMD from SEC is more pronounced. Another explanation for the difference in the low molar mass part could be the occurrence of shear degradation of high molar mass molecules during the passage of the SEC columns and frits. Degradation of larger species could lead to formation of low molar mass fragments which may be visible as increased low molar mass tail in the MMD obtained from SEC.
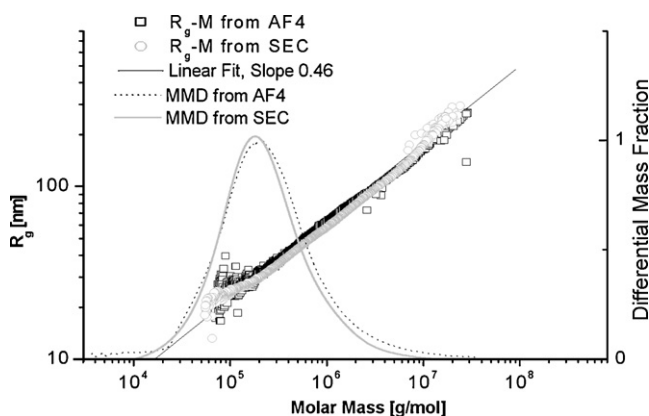

Fig. 11. Differential molar mass distribution and conformation plot from SEC- and AF4-RI-MALS for PB 1.
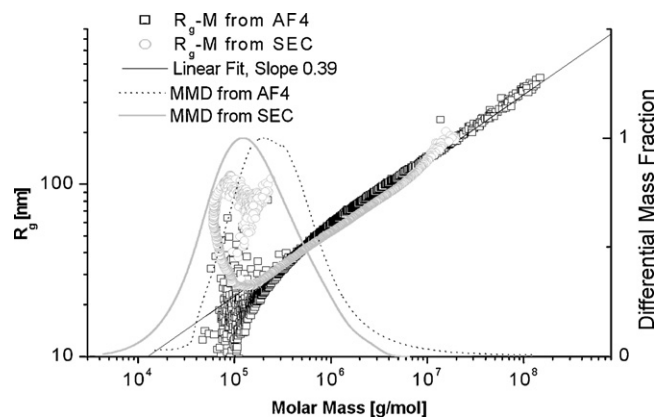

Fig. 12. Differential molar mass distribution and conformation plot from SEC- and AF4-RI-MALS for PB 2.

When comparing the conformation plots from SEC and FFF it becomes clear that the larger amount of branched molecules in sample PB 2 leads to an increased late co-elution in SEC. The radius increases up to a value of above 100 nm for low molar mass values. The separation in AF4 is not prone to such co-elution problems. As a result the conformation plot shows no curvature, as it was already shown for the polyolefins. The average slope of 0.39 from AF4 confirms the larger amount of highly branched material in sample PB 2. The slope of the R_g–M-relationship from SEC is falsified by the late co-elution effect and cannot be used for branching determination. An additional advantage of the AF4 technique is the absence of shear degradation which enables to prove the R_g–M-relationship also for the ultrahigh molar mass fraction. In Fig. 12 the conformation plot from AF4 provides information about molecules up to 2×10^8 g/mol while SEC only shows maximum masses up to 10^7 g/mol.

Additional information on synthetic rubbers provided by AF4 is the presence of very high molar mass molecules, which are visible by the light scattering but due to the small concentration there is no signal visible in the RI-detector. In Fig. 13(a and b) the RI and the LS signal from AF4 and SEC with and without filtration is displayed for sample PB 3, which shows the described phenomenon.

In Fig. 13(a) a multimodal light scattering signal is visible in AF4 due to a small amount of ultrahigh molar mass material. After filtration the high molar mass portion is removed and the LS signal gets unimodal similar to the signal from SEC which was the same with and without filtration. The RI signals from AF4 in Fig. 13(b) show a slight bimodality before filtration. After filtration or after SEC separation the RI signal gets unimodal in SEC the elution range of the RI signal is visible and is fully covered by the light scattering signal. In AF4 no corresponding RI signal is visible for most of the LS signal before filtration. This means there may be a small portion of very large molecules which is only visible in AF4. After filtration the large material is filtered out and the high molar mass tail of the LS signal in AF4 disappears. The syringe filter had an average pore size of approx. 450 nm. As a result, nearly all molecules above this diameter have been removed. The (apparent) SEC separation shows similar results as the AF4 run of the filtered sample because the columns and frits will also act like filtration devices. The disappearance of the high molar mass tail of the 90° LS signal by filtration strongly indicates that the minimum size of these particles is approx. 450 nm. The results clearly demonstrate that AF4 is able to show even very low concentrations of ultrahigh molar mass material in such heterogeneous samples, which normally are filtered out by the SEC columns. Even low amounts of very high molar mass material or large gel particles can strongly influence the application properties of a polymer material. The additional
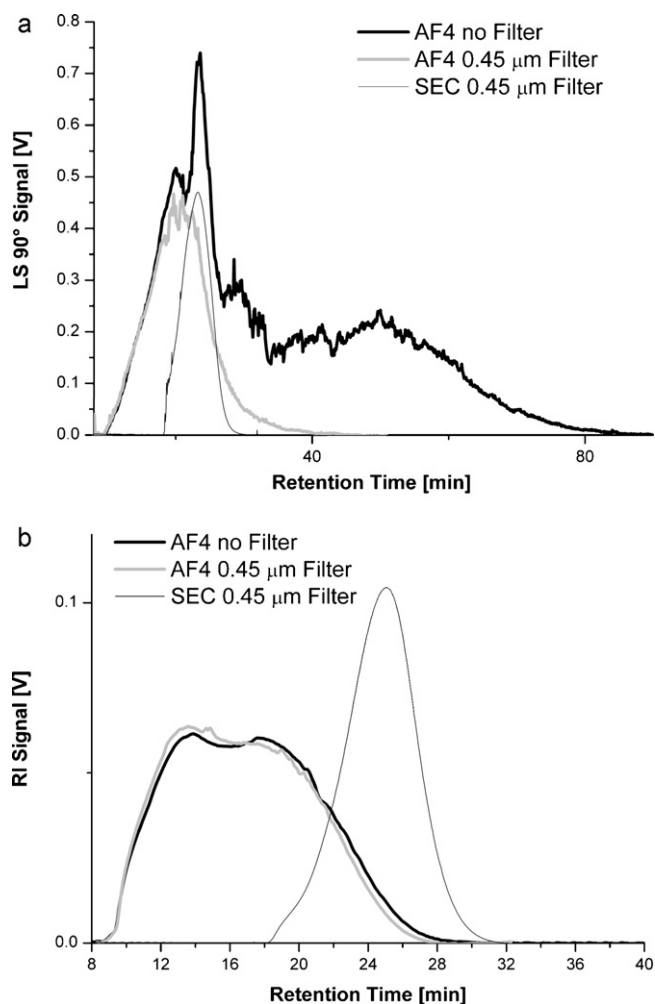
Fig. 13. Separation of sample PB 3 from AF4- and SEC-RI-MALS, with and without filtration, flow rate = 0.5 mL/min, (a) elugram from SEC and fractogram from AF4-LS 90° signals, (b) elugram from SEC and fractogram from AF4-RI signals.

information from AF4 may be very important for the further development of such problematic samples and for a better understanding of the polymerization process or possible side reactions.

4. Conclusions

We have demonstrated that HT-AF4 enables to separate ultrahigh molar mass samples up to a radius of gyration of above 1000 nm without the disturbing effects typical for SEC, namely the shear degradation of high molar mass structures and the anomalous late co-elution effects. The problems of erroneous branching calculation and molar mass determination as a result of a curvature in the conformation plot do not exist in AF4 and as a result the molar mass averages calculated from HT-AF4 are significantly higher than those obtained from HT-SEC.

Molecules with a molar mass below 100 kg/mol are, however, not fully recovered in HT-AF4 using the older ceramic membranes, thus leading to an overestimation of the calculated average molar masses for samples which contain such small molecules. However, this error can be minimized by exclusion of the low molar mass fraction from the average calculation. The examination of the data below the cut-off mass range has shown that the error of the missing low M_w-part is very low compared to the positive effect of missing shear degradation. On the other hand, polymers (UHM HDPE or LDPE) with molar masses below 100 kg/mol are often not correctly measured with HT-SEC due to the abnormal late and co-elution of large or branched material which leads to a falsification of the calculated MMD. It can be concluded that for polyolefin samples with molar masses above 100 kg/mol, HT-AF4 is a very powerful tool which allows a precise characterization of the molar mass distribution and branching. After finishing the experiments a better ceramic membrane became available which shows a much lower cut off compared with the older membranes. As a result HT-AF4 now can also be used for characterization of samples containing molecules with low molar masses. The increased flexibility and efficiency of the separation combined with the additional information may make HT-AF4 an excellent complementary technique to HT-SEC in the near future.

The commercially available membranes for AF4 separation at ambient and mid temperatures exhibit a very low cut-off below 10 kg/mol. This means that it is possible to analyze e.g., rubber samples nearly completely with this method. It was shown that AF4 is able to separate samples with the same or even higher resolution than SEC in the overlapping size separation range of both methods and with a better resolution for the ultrahigh molar mass molecules. AF4 enables to obtain new structural information on rubber samples or other polymer samples that are not correctly measured in SEC. The drawbacks of ambient temperature SEC which are similar to the problems at high temperature can be overcome by using AF4. In addition, it was shown that AF4 is extremely sensitive regarding to small amounts of very high molar mass material in rubber samples which are completely filtered out during a common SEC analysis.

In addition to the new information about the polymer samples, (HT)-AF4 offers features which are not known from traditional methods: the focus technology allows the injection of very high volumes without increasing band broadening. The variable cross-flow adjustment can be used to influence the separation efficiency in a very flexible way. To summarize, the application of AF4 for the characterization of synthetic polymers allows an extended view on molecular properties which apparently are more complex as has been found by traditional separation methods in the past.

References

[1] S. Trinkle, C. Friedrich, Rheol. Acta 40 (2001) 322.
[2] A.W. de Groot, W.J. Hamre, J. Chromatogr. 648 (1993) 33.
[3] S. Pang, A. Rudin, Polymer 33 (1992) 1949.
[4] S. Pang, A. Rudin, J. Appl. Polym. Sci. 46 (1992) 763.
[5] T. Sun, P. Brant, R.R. Chance, W.W. Graessley, Macromolecules 34 (2001) 6812.
[6] S. Wu, D. Lilge, J. Appl. Polym. Sci. 50 (1993) 1753.
[7] C. Jackson, Y.-J. Chen, J.W. Mays, J. Appl. Polym. Sci. 61 (1996) 865.
[8] L. Friebe, O. Nuyken, H. Windisch, W. Obrecht, Macromol. Chem. Phys. 203 (2002) 1055.
[9] R. Kaulbach, U. Gebauer, K. Gehrke, M.D. Lechner, K. Hummel, Angew. Makromol. Chem. 226 (1995) 101.
[10] E.L. Slagowski, L.J. Fetters, D. Mcintyre, Macromolecules 7 (1974) 394.
[11] H.G. Barth, F.J. Carlin Jr., J. Liq. Chromatogr. 7 (1984) 1717.
[12] M. Parth, N. Aust, K. Lederer, Int. J. Polym. Anal. Charact. 8 (2003) 175.
[13] N. Aust, J. Biochem. Biophys. Methods 56 (2003) 323.
[14] P.J. Wang, B.S. Glasbrenner, J. Liq. Chromatogr. 10 (1987) 3047.
[15] M.D. Zammit, Polymer 39 (1998) 5789.
[16] N. Aust, M. Parth, K. Lederer, Int. J. Polym. Anal. Charact. 6 (2001) 245.
[17] M. Zigon, N.K. The, C. Shuayo, Z. Grubisic-Gallot, J. Liq. Chromatogr. 20 (1997) 2155.
[18] P.J. Wyatt, Anal. Chim. Acta 272 (1993) 1.
[19] S. Podzimek, T. Vlcek, C. Johann, J. Appl. Polym. Sci. 81 (2001) 1588.
[20] S. Podzimek, T. Vlcek, J. Appl. Polym. Sci. 82 (2001) 454.

[21] F.J. Stadler, J. Kaschta, H. Münstedt, F. Becker, M. Buback, Rheol. Acta 48 (2009) 479.
[22] M. Wintermantel, M. Antonietti, M. Schmidt, J. Appl. Polym. Sci.: Appl. Polym. Symp. 52 (1993) 91.
[23] C. Johann, P. Kilz, J. Appl. Polym. Sci.: Appl. Polym. Symp. 48 (1991) 111.
[24] D.J. Frater, J.W. Mays, C.J. Jackson, Polym. Sci. Part B: Polym. Phys. 35 (1997) 141.
[25] M. Gerle, K. Fischer, S. Roos, A.H.E. Müller, M. Schmidt, S.S. Sheiko, S.A. Prokhorova, M. Möller, Macromolecules 32 (1999) 2629.
[26] V. Percec, C.-H. Ahn, W.-D. Cho, A.M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S.A. Prokhorova, S.S. Sheiko, S.Z.D. Cheng, A. Zhang, G. Ungar, D.J.P. Yeardley, J. Am. Chem. Soc. 120 (1998) 8619.
[27] J.C. Giddings, Sep. Sci. 1 (1966) 123.
[28] K.D. Caldwell, L.F. Kesner, M.N. Myers, J.C. Giddings, Science 176 (1972) 296.
[29] G. Liu, J.C. Giddings, Chromatographia 34 (1992) 483.
[30] K.-G. Wahlund, J.C. Giddings, Anal. Chem. 59 (1987) 1332.
[31] J.J. Kirkland, W.W. Yau, F.C. Szoka, Science 215 (1982) 296.
[32] J.C. Giddings, N.M. Myers, K.D. Caldwell, J. Sep. Sci. Technol. 16 (1981) 549.
[33] S.K. Ratanathanawongs-Williams, in: M.E. Schimpf, K.D. Caldwell, J.C. Giddings (Eds.), Field-Flow Fractionation Handbook, vol. 720, Wiley & Sons, New York, 2000, pp. 257–278.
[34] S.K. Ratanathanawongs-Williams, D. Lee, J. Sep. Sci. 29 (2006) 1720.
[35] S. Oh, D. Kang, S.M. Ahn, R.J. Simpson, B.H. Lee, M.H. Moon, J. Sep. Sci. 30 (2007) 1082.
[36] K.-G. Wahlund, A. Zattoni, Anal. Chem. 74 (2002) 5621.
[37] D.Y. Bang, D.Y. Shin, S. Lee, M.H. Moon, J. Chromatogr. A 1147 (2007) 200.
[38] G. Yohannes, J. Shan, M. Jussila, M. Nupponen, H. Tenhu, M.L. Riekkola, J. Sep. Sci. 28 (2005) 435.
[39] M.E. Miller, J.C. Giddings, J. Microcolumn. Sep. 10 (1998) 75.
[40] E.P.C. Mes, H. de Jonge, T. Klein, R. Welz, D.T. Gillespie, J. Chromatogr. A 1154 (2007) 319.
[41] B. Coto, J.M. Escola, I. Suarez, M.J. Caballero, Polym. Test. 26 (2007) 568.
[42] S. Mori, M. Ishikawa, J. Liq. Chromatogr. Rel. Technol. 21 (1998) 1107.
[43] R.J. Angelo, R.M. Ikeda, M.L. Wallach, Polymer 6 (1965) 141.
[44] T. Otte, R. Brüll, T. Macko, H. Pasch, J. Chromatogr. A 1217 (2010) 722.
[45] J.C. Le Guillou, J. Zinn-Justin, Phys. Rev. Lett. 39 (1977) 95.