Determination of low amounts of long-chain branches in polypropylene using a combination of chromatographic and rheological methods

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Abstract

The focus of our investigations lies on the detection of low amounts of long-chain branching (LCB) in isotactic polypropylene (iPP) created by electron beam irradiation. The modified samples were investigated by rheological experiments in shear and elongational flow and by size-exclusion chromatography. The comparison of the results demonstrates the efficiency and the detection limits of these methods, particularly at very low degrees of long-chain branching. The combination of chromatographic and rheological methods enables a sensitive and comprehensive way for the characterisation of the long-chain branching phenomena.
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1. Introduction

Long-chain branched polypropylens possess advantageous properties, which are important in many industrial applications, e.g. good thermoforming behaviour, high melt strength, and uniform fine cell structure of extruded foams [1,2]. The optimization of the processing of this material depends on the rheological properties of the melt, which are strongly affected by molar mass, molar mass distribution and the presence of long-chain branching (LCB). One way to create long-chain branching in the linear polymer without using additives is the modification by electron beam irradiation. The latter has a distinct influence on the rheological properties as for example elongational and shear viscosity, flow activation energy and melt elasticity [3,4]. LCB affects on the other side strongly the molecular structure and the light scattering properties of the molecules respectively.

1.1. Influence of long-chain branching on scattering properties of the molecules

It is well known, that polymer molecules are fractionated by size-exclusion chromatography (SEC) according to their hydrodynamic volume. The size of the molecules depends on their molar mass and density in a dissolved state. Long-chain branched molecules have more dense structure than linear molecules and their density depends on the number and the type of the branches. By coupling SEC with multi-angle laser light scattering (MALLS) the molar mass M of every slice of the chromatogram can be determined absolutely without any calibration with a linear polymer standard. Additionally, light scattering data give information about the mean square radius of gyration $\langle s^2 \rangle$ of the molecules from which conclusions with

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respect to branching can be drawn using theoretical considerations [5]. The ratio of the mean square radius of gyration of a branched polymer $\langle s^2 \rangle_{\text{branch}}$ to that of a linear polymer $\langle s^2 \rangle_{\text{linear}}$ with comparable chemical structure is represented by g known as Zimm–Stockmayer's branching parameter [5].

$$g = \frac{\langle s^2 \rangle_{\text{branch}}}{\langle s^2 \rangle_{\text{linear}}} \tag{1}$$

The coil dimensions of a branched structure compared to a linear one are smaller at the same molar mass, thus the factor g will be lower than 1 for a branched polymer. The branching parameter g gets smaller with increasing degree of branching.

For the modified iPP a trifunctional randomly branched architecture can be assumed [6]. For this trifunctional, randomly branched polymer, g is expressed in terms of the degree of branching as:

$$g = \left[\left(1 + \frac{m}{7} \right)^{0.5} + \frac{4m}{9\pi} \right]^{-0.5} \tag{2}$$

with m as number of branching points along the molecule.

The number of long-chain branching per 1000 monomer units N_{LCB} is defined as:

$$N_{\text{LCB}} = 1000 \times M_{\text{M}} \times \frac{m}{M} \tag{3}$$

where M_{M} is the molar mass of the monomer unit and M is the molar mass of the branched polymer.

1.2. Influence of long-chain branching on the rheological properties of polymers

Although a great effort was made in the past to investigate the influence of LCB on the rheological properties of well-known polymers as polyethylene and polystyrene, up to now their effect is not fully understood. This is especially due to the great variety in long-chain branching. For example, the position, number and length of the branches can lead to many different topologies. The lack of analytical methods, which are able to detect low levels of LCB and to distinguish between different topographies, has led to the application of rheological methods to get insight into LCB. Model polymers and their blends were used in order to investigate the influence of different molecular structures [7,8]. Further contributions have been made from the theoretical side of view by several authors who found the exponential dependence of the zero shear-rate viscosity η_0 for model star polymers on the ratio of $M_{\text{a}}/M_{\text{e}}$, i.e. the molar mass of an arm M_{a} divided by the entanglement molar mass M_{e}, according to the following equation [9,10]:

$$\eta_0 \propto \left(\frac{M_{\text{a}}}{M_{\text{e}}} \right)^{\alpha} \times \exp \left(\upsilon \frac{M_{\text{a}}}{M_{\text{e}}} \right) \tag{4}$$

The value of M_{e} is a characteristic parameter for every polymer and α and υ are constants in the order of 1 and 0.5, respectively. Other theoretical contributions help us to describe the elongational viscosity in the non-linear region of deformation in which a strain-hardening behaviour is found for polymers with LCB [11,12]. Strain hardening means that at a constant Hencky strain-rate the elongational viscosity rises above the linear visco-elastic start-up curve given by three times the time dependent shear viscosity [13].

The rheological experiments in the melt and the light scattering experiments in solution are principally different ways for investigation of the amount of LCB in polypropylene. The aim of this work is to determine the detection limits of these two methods.

2. Experimental

2.1. Materials

The isotactic polypropylene (iPP) homopolymer used in this study was the Novolen PPH2150 (Basell Polyolefins, Hoofddorp, The Netherlands). The melt flow index was 0.3 g/10 min (230 °C; 2.16 kg) and the density at room temperature was 0.90 g/cm³. The peak melting temperature of the polypropylene was found to be 163 °C.

2.2. Electron beam irradiation

The iPP pellets were irradiated with 1.5 MeV using the electron beam accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia) as described in detail by Dorschner et al. [14].

The irradiation was carried out under a nitrogen atmosphere at atmospheric pressure in a special vessel [15]. The sample was irradiated with different total doses d up to 10 kGy. After the irradiation process, the polypropylene was annealed for 30 min at 80 °C and for 60 min at 130 °C in the vessel under nitrogen atmosphere, too.

2.3. Characterization

The molecular characterization of the polypropylene was carried out by high temperature size-exclusion chromatography (HT-SEC) coupled with a multi-angle laser light scattering detector and a refractive index (RI) detector.

The instrument used was a PL-GPC220 (Polymer, Shropshire, UK) at 150 °C coupled with a MALLS detector (DAWN EOS, Wyatt Technology, Santa Barbara, USA). The column set consisted of two columns PL Mixed-B-LS, 300 mm × 7.5 mm, 10 μm pore diameter (Polymer). The flow rate was 1 ml/min. The eluent was 1,2,4-trichlorobenzene (Merck, Darmstadt, Germany) stabilized with diphenylamine (Merck). The calculations of the molecular parameters (M_{w}, M_{n}, molar mass distribution) were carried out from the SEC data using commercial software ASTRA 4.73 (Wyatt Technology Corporation, Santa Barbara, USA). For the calculation of the number of LCB CORONA V1.40 for Windows was used (Wyatt Technology).

Shear creep measurements were conducted with a constant stress rheometer Bohlin CS-melt (Bohlin Instruments, Pforzheim, Germany) in order to determine the zero shear-rate viscosity η_0. Creep tests are very suitable for the determination of η_0 as the steady state of deformation is reached much faster than in oscillatory or stressing experiments. The measurements were performed at a temperature of 180 °C under nitrogen atmosphere using a plate–plate geometry of 25 mm in diameter and a gap of 1.5 mm. Cylindrical samples of 2 mm thickness and 25 mm diameter were prepared in a hot press at a temperature of 180 °C.

The elongational flow experiments presented in this study were performed by means of an oil bath extensional rheometer. This device was self-constructed at the Institute of Polymer Materials and has been described in detail by Münstedt et al. [16]. The principles of this rheometer go back to a design published by Münstedt [17]. For measuring the elongational viscosity a cylindrical sample is stretched vertically in a silicone oil bath. Constant strain-rate experiments at a constant temperature of 180 °C were run with different elongational rates between 0.01 and 1.0 s^{-1}. The tensile stress growth coefficient or elongational viscosity $\eta_E^+(t, \dot{\varepsilon}_0) = \sigma(t, \dot{\varepsilon}_0)/\dot{\varepsilon}_0$ is obtained from the measured tensile stress divided by the applied constant strain-rate.

3. Results and discussion

3.1. Size-exclusion chromatography

The molecular characterization of polypropylene was carried out using HT-SEC-MALLS at 150 °C. The cumulative molar mass distributions of the initial and the irradiated samples with doses varied from 1 to 10 kGy are plotted in Fig. 1. It was confirmed, that increasing the irradiation dose d a significant molar mass degradation takes place, reducing from $M_w = 669$ kg/mol to 444 kg/mol (Table 1).
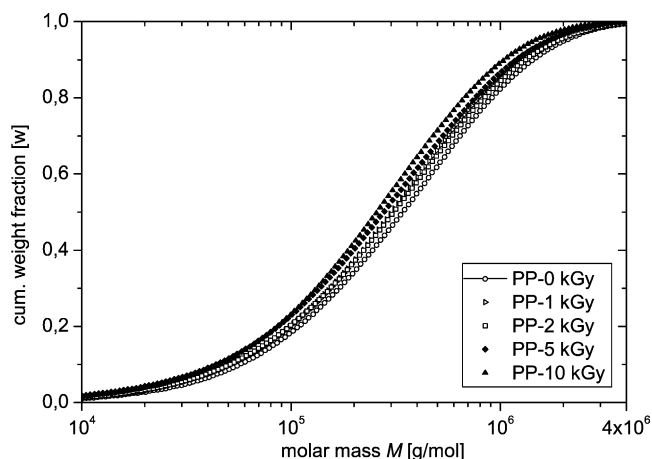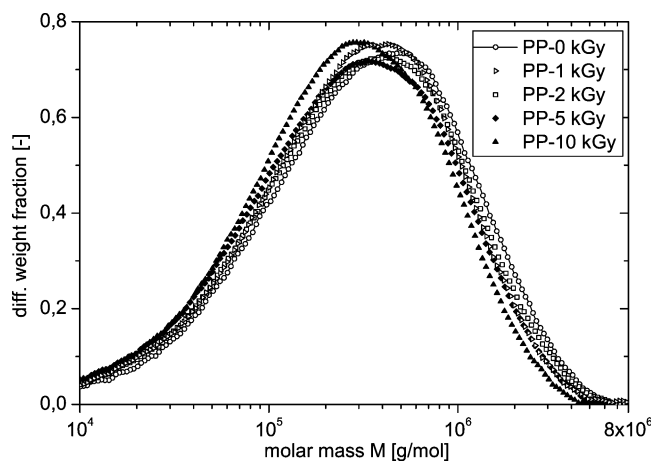

Fig. 2. Differential molar mass distribution of the initial iPP and the irradiated samples.

The molar mass distributions of the modified polypropylenes M_w/M_n listed in Table 1 become slightly narrower with the increase of the irradiation dose. Moreover, we can observe a reduced amount of high molar mass species in the modified polypropylene samples comparing the curves of the differential molar mass distributions in Fig. 2. This fact leads to the conclusion that the degradation process becomes apparent predominantly in the high molar mass area of the polymer.

The dependence of the mean square radius of gyration $\langle s^2 \rangle$ on the molar mass M for the initial isotactic polypropylene and samples irradiated with different doses is shown in Fig. 3. The decrease of the mean square radius of gyration at the same molar mass is an indication of an increasing coil density with increasing irradiation dose, which can be ascribe to the formation of long-chain branches. A significant deviation of the radius of gyration for molecules at the same molar mass can be observed only for the sample PP-10kGy. For a quantitative determination of the number of long-chain branches N_{LCB} of this sample we used Eq. (3).

Fig. 1. Cumulative molar mass distribution of the initial iPP and the irradiated samples.
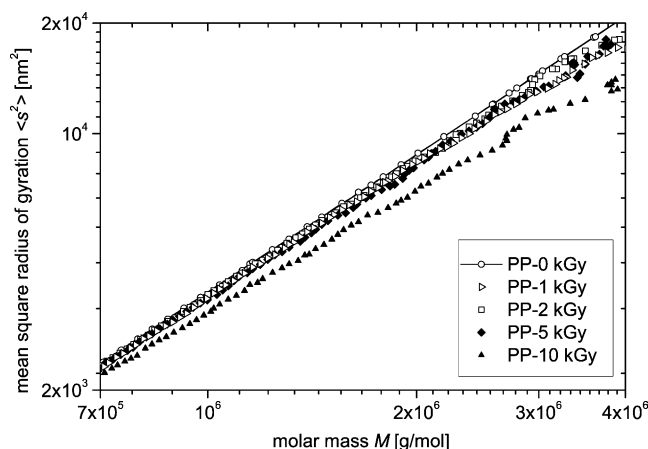

Fig. 3. Mean square radius of gyration $\langle s^2 \rangle$ vs. molar mass M of the initial iPP and the irradiated samples.

Table 1
Molecular and rheological characteristics of the investigated polypropylenes

Sample	d (kGy)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n	N_{LCB} (per 1000 monomers)[a]	η_0 (kPa s) (180 °C)
PP-0kGy	0	160000	669000	1654000	4.2	–	188
PP-1kGy	1	148000	563000	1445000	3.8	n.d.	195
PP-2kGy	2	157000	565000	1369000	3.6	n.d.	240
PP-5kGy	5	126000	473000	1135000	3.8	n.d.	260
PP-10kGy	10	122000	444000	1145000	3.7	0.08	203

n.d.: not detectable by SEC-MALLS.
  [a] Calculated by SEC-MALLS using Eq. (3).

Fig. 4 shows the distribution of N_{LCB} over the whole region of the molar masses for the sample irradiated with 10 kGy. N_{LCB} was found to be nearly constant in the range between 5×10^5 g/mol and 3×10^6 g/mol for this sample (see Fig. 4). The same linear dependence was already observed for samples irradiated in the dose range of 20–150 kGy [18]. This leads to the conclusion that the number of branching points along the molecule m correlates to the molar mass directly. The deviations of N_{LCB} from this constant value at lower and higher molar masses can be explained on the one hand with the limitations of the calculation method used in the applied commercial software. On the other hand the concentrations of the polymer solution in the beginning and at the end of the chromatographic separation process are presumably not sufficiently high for a correct interpretation of their light scattering properties and the calculation of their mean square radius of gyration, respectively. Hence, the constant central region of this curve was found to give us the appropriate value of the number of long-chain branches in this polymer amounting to 0.08 long-chain branches per 1000 monomer units for PP-10kGy. For the samples PP-2kGy and PP-5kGy a slight decrease of $\langle s^2 \rangle$ was found only in the high molar mass area. These values are situated near the detection limit and according to our previous explanation they could not be interpreted correctly.
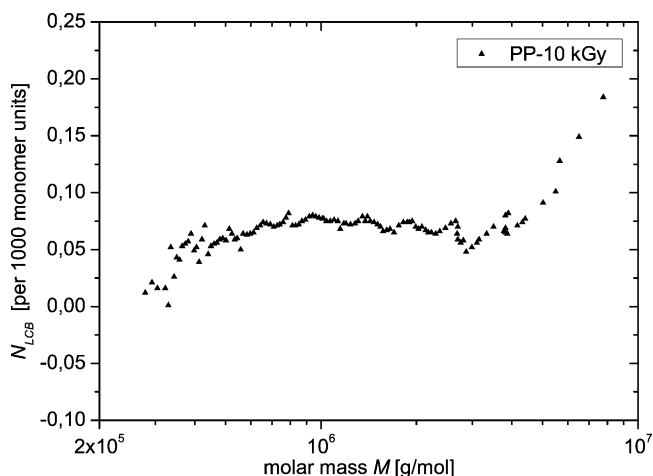
Concluding from these results, the detection limit of SEC-MALLS for these samples was found to be 0.08 long-chain branches per 1000 monomer units for the iPP modified at total irradiation dose d of 10 kGy.

3.2. Rheology

Shear rheology is a very sensitive tool to detect even low amounts of long-chain branching as can be concluded from Fig. 5. This is particularly true for the zero shear-rate viscosity η_0 if regarded as a function of weight-average molar mass M_w [19,20]. In Fig. 5 the straight full line represents the power law dependence for a series of commercial linear isotactic polypropylenes. This was also found to be valid for the linear iPP, which was used for irradiation.

For the samples irradiated with doses of 1–5 kGy, significantly increased zero shear-rate viscosities η_0 were observed. But η_0 decreased for the samples modified at 10 kGy (see Table 1, Fig. 5). For all irradiated PP, the molar mass dependence of η_0 deviates from the linear relationship corresponding to the linear commercial polypropylenes. Fig. 5 shows that all modified samples are located above the line of linear iPP. The comparison of branched and linear PP was illustrated by the ratio of $\eta_{0(branch)}/\eta_{0(linear)}$ at the same weight-

Fig. 4. Number of long-chain branches N_{LCB} vs. molar mass M for the sample irradiated with 10 kGy.
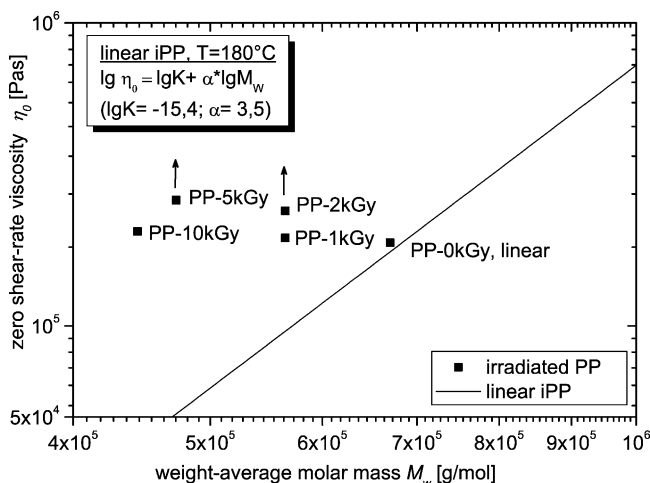

Fig. 5. Zero shear-rate viscosity η_0 vs. weight-average molar mass M_w for the initial iPP and the irradiated samples. (The arrows indicate that the actual zero shear-rate viscosity is higher than the plotted value, because a steady-state could not be obtained in these measurements.).
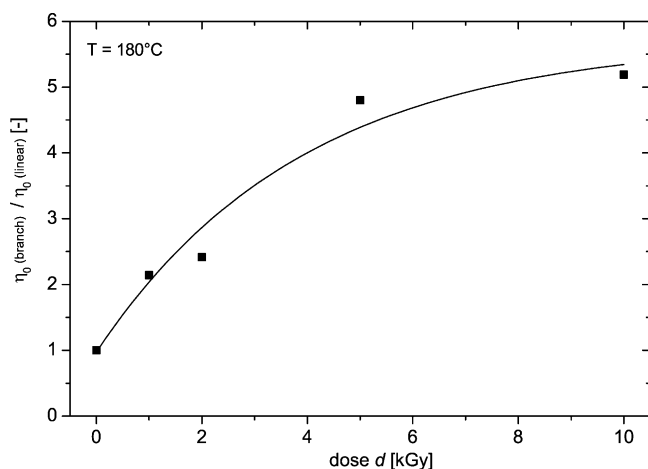
Fig. 6. Ratio of the zero shear-rate viscosities η_0 of branched and linear PP vs. the irradiation dose d for the initial iPP and the irradiated samples.

average molar mass M_w. A significant increase of this ratio was observed (Fig. 6). Similar behaviour was found for many model branched polymers, e.g. for star-shaped polystyrenes [21–23]. This increase were explained by low amounts of long-chain branches with relatively long arms and hence, a high ratio of M_a/M_e, which has an exponential influence on η_0 (see Eq. (4)). The zero shear-rate viscosity η_0 provides qualitative information about the existence of small amounts of branching (lower than 0.08 LCB per 1000 monomer units), which are formed after the application of an irradiation dose of only 1 kGy.

Elongational flow experiments are a sensitive tool for the investigation of long-chain branching, too. The occurrence of strain hardening is closely related to long-chain branching, if other reasons as high molar mass components or a very broad molar mass distribution can be excluded. Strain hardening means that at a constant Hencky strain-rate the elongational viscosity rises above the linear visco-elastic start-up curve given by three times the time-dependent shear viscosity.
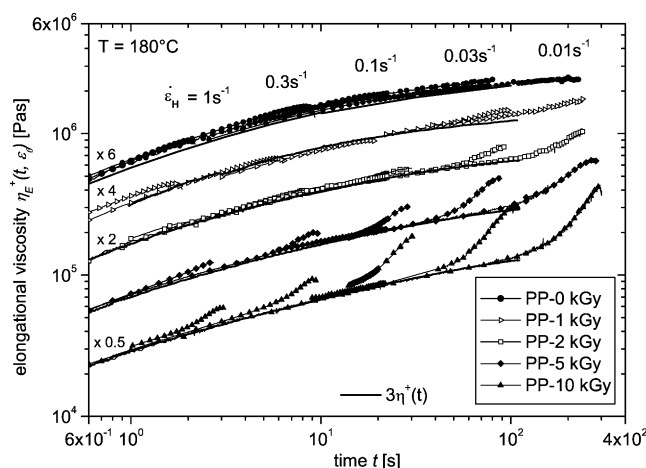

Fig. 7. Elongational viscosity η_E vs. time t for the initial iPP and the irradiated samples.

For linear polypropylenes no strain hardening was reported in the literature and this was observed for the untreated iPP, too (Fig. 7). A behaviour similar to the untreated iPP was found for the polypropylene irradiated with 1 kGy. The samples irradiated with 2–10 kGy show a strain hardening, which becomes more pronounced at higher irradiation doses and increases with lower strain-rates. The strain-rate dependence of randomly branched polyolefins was found to be characteristic for different branching topologies [24]. A strain-hardening behaviour, which is decreasing with increasing strain-rates, is typical of PE with a small amount of long-chain branching [24,25].

The rheological methods in shear and elongational flow give us a qualitative information about the existence of very small amounts of LCB in the polypropylene samples. Quantitative determination of the number of the LCB is only possible via calculations including the radius of gyration of the polymers or the molar mass from the chromatographic experiments.

4. Conclusions

The comparison of the results from SEC and rheological characterisation in shear and elongation flow clearly shows different limits of detection. On the one hand in the SEC-MALLS experiments a lower sensitivity to long-chain branching than in the rheological results was observed. On the other hand the chromatographic method gives a quantitative information about the molar mass distribution and about the distribution of branching depending on the molar mass as well.

These investigations clearly show that rheological experiments in shear and elongation flow are much more sensitive to the presence of low amounts of LCB than the quantities obtained by light scattering detection of the sample separated by SEC. This can be explained in the way that the entanglement network is much more sensitive towards long-chain branching than the hydrodynamic volume of the dissolved macromolecule. But additional information about the molecular parameters is necessary for a detailed characterisation via rheological experiments. These are the weight-average molar mass M_w in case of the molar mass dependence of the zero shear-rate viscosity η_0 and the molar mass distribution or high molar mass components in case of the strain hardening. For a comprehensive investigation of long-chain branched polymers a combination of molecular and rheological methods provides a powerful and sensitive tool.

Acknowledgements

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