

**CHARACTERIZATION OF ELECTRON BEAM IRRADIATED POLYPROPYLENE:  
INFLUENCE OF IRRADIATION TEMPERATURE ON MOLECULAR AND  
RHEOLOGICAL PROPERTIES**

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## **Characterization of electron beam irradiated polypropylene: Influence of irradiation temperature on molecular and rheological properties**

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### **SYNOPSIS**

The aim of the investigations was to analyze the influence of the temperature during the irradiation process of polypropylene on the molar mass, the formation of long chain branching (LCB) and the final branching topology. A linear isotactic polypropylene homopolymer was modified by electron beam irradiation at different temperatures with two irradiation doses in order to insert long chain branching. The samples were analyzed by size exclusion chromatography (SEC) coupled with a multi angle laser light scattering detector (MALLS), by differential scanning calorimetry (DSC), and by shear and elongational rheology. The shear and elongational flow behaviour is discussed in terms of the influence of molecular parameters and used to analyse the topology of the irradiated samples. With increasing temperature, a slight reduction of the molar mass, an increasing of long chain branching and an increase of crystallization temperature were found.

**KEYWORDS:** poly(propylene) (PP), electron beam irradiation, branched, differential scanning calorimetry (DSC), rheology.

## **INTRODUCTION**

Commercial linear isotactic polypropylene (iPP) has many desirable and beneficial physical properties such as high stiffness, good resistance to corrosive chemicals and low specific gravity. Long chain branched polypropylene has further advantageous properties, which are important in many industrial applications, e.g. high melt strength, good thermoforming behaviour and uniform fine cell structure by foam extrusion [1,2].

### *Electron beam induced reactions in polypropylene and preparation of long chain branching.*

The molecular structure of linear polypropylene can be significantly modified by electron beam irradiation. The main reactions during the irradiation process are chain scission, chain branching and cross-linking. Usually all these reactions coexist. The effect, which predominates, is depending on several factors, such as chemical structure and morphology of the polymer as well as the irradiation conditions and post treatment [3-6].

In polypropylene, the dominant reactions after formation of free radicals are first  $\beta$ -scission, with molar mass decrease and formation of double bonds. Furthermore, the addition of free radicals to the double bonds takes place with forming chain branching followed by increasing of molar mass. Additionally, disproportionation or recombination reactions of two polymer radicals occur followed by changed molar masses [4-8]. Therefore, the electron beam irradiation has two effects on the molecular structure: reduction of the molar mass and formation of chain branching [9,10].

In different patents [11-14] the irradiation by electron beam under oxygen free or reduced active oxygen atmosphere to form branched PP is described. This is achieved by using vacuum or by replacing the air by inert gas, i.e. nitrogen. Furthermore, the temperature of the polymer material should be kept at less than 40°C because an additional increase of the temperature in the material takes place during the irradiation. The dose of electron beam irradiation should be about 10-90 kGy. After the irradiation, the material should be annealed in two steps. The first annealing step at 40-120 °C is necessary for a sufficient migration of

chain fragments to free radicals to form chain branches. The second annealing step at a temperature of at least 120°C is sufficient to allow deactivation of substantially all residual free radicals [9,15]. The radical reactions, which are necessary for forming branches, take place in the bulk and are presumably diffusion limited. It can be expected that higher temperatures are a requirement for a sufficient migration of chain fragments to free radicals to form chain branches [12].

The irradiation of polypropylene can also be carried out at increased temperatures [16,17]. A continuous method for producing polypropylene powder mixtures of increased stress crack resistance and melt strength using low energy radiation is described in patent [16]. The samples are irradiated between 20°C and 150°C under inert conditions. Another patent [17] shows a process to cross-link polypropylene-polyethylene-blends using low energy radiation. It was found that a temperature range from 110°C up to 120°C during irradiation is favourable to cross-linking. At temperature higher than 125°C the degradation is predominant in comparison to the cross-linking.

#### *Irradiation at elevated temperatures*

An increase of the temperature induce different processes in the polymer bulk [18]: Faster decrease of the concentration of radicals induced by irradiation, decrease of addition reaction, increase of the frequency of  $\beta$ -scission reaction, increase of the chain diffusion to the amorphous phase, and partial melting of pellets. On this way the molecular chain architecture will be modified depending on the temperature during the irradiation.

Additionally, the melting and crystallisation behaviour of polypropylene should be considered. The melting of certain parts of the polymer crystals starts with increasing temperature. Therefore, the crystallinity of the modified samples decrease. This leads to the conclusion that the amount of the amorphous phase rises and therefore more chains are available for branching reactions [18].

In comparison to polypropylene the temperature dependence of irradiation induced reactions of polyethylene is described by Wu et.al. [19], Qu et.al. [20] and Dijkstra et.al. [21]. The

irradiation of polyethylene at room temperature already can lead to the formation of insoluble parts. With increasing irradiation temperature up to the molten state more cross-linking takes place. It is observed that an amount of gel up to 90% for low density polyethylene is possible [19].

*Influence of long chain branching on the SEC separation process.*

Molecular data of polyolefins can be extracted from measurements of the high temperature size exclusion chromatography (SEC). It is well known, that polymer molecules in SEC are separated by their hydrodynamic volume. The size of a molecule depends on its molar mass and on its density in the dissolved state. Long chain branched molecules have more dense structures than linear molecules at the same molar mass. The density depends on the number of the branches. Therefore, the conventional SEC using linear polymer standards for the calibration is not suitable for investigations of the molar mass of branched polymer structures, due to the fact that the calculated molar mass averages would be lower than the true values. By coupling the SEC with multi angle laser light scattering (MALLS) detector the molar mass of every slice of the chromatogram can be determined directly. Additionally, light scattering data give information about the radius of gyration of the molecules and their branching structure, respectively. The calculation of the parameter  $g$  known as ZIMM-STOCKMAYER's branching parameter [22] and the number of branching points along the trifunctional randomly branched molecule  $m$  [9,22] is described by Krause et al. [23].

*Influence of long chain branching on the rheological properties of polymers.*

Correlations between rheological properties and the molecular structure can be used to investigate the long chain branching topology. From measurements on rather well defined long chain branched polymers [24-28] some results were obtained, which allow insight into relationships between rheology and the topography of long chain branching. These correlations have been explained theoretically, e.g. the exponential dependence of the zero

shear viscosity  $\eta_0$  for star polymers on the ratio of  $M_a/M_e$ , i.e. the molar mass of an arm  $M_a$  divided by the entanglement molar mass  $M_e$ , according to the following equation [29,30]:

$$\eta_0 \propto \left(\frac{M_a}{M_e}\right)^\alpha \exp\left(\nu \frac{M_a}{M_e}\right) \quad (1)$$

The value of  $M_e$  is a characteristic quantity of a polymer and  $\alpha$  and  $\nu$  are constants in the order of 1 and 0.5, respectively. Gabriel et al. [24] concluded from investigations on a number of different commercial polyethylenes that slightly long chain branched PE with a star-like molecular structure come to lie above the values of linear PE whereas a position beneath indicates a highly branched tree-like topology. This was explained by the exponential dependence of  $\eta_0$  on the ratio of  $M_a/M_e$ .

In elongational flow the occurrence of an increase of the elongational viscosity, which is called strain hardening, is closely related to molecular parameters and particularly, to long chain branching [10,33,37]. If determined from stressing experiments this means that at a constant Hencky strain rate the elongational viscosity rises above the linear viscoelastic start-up curve given by three times the time dependent shear viscosity. The strain hardening behaviour of randomly branched polyolefins is found to be characteristic for different branching topologies [10,33]. Therefore, the rheological methods can be used to get a further insight into the evolving molecular structures.

Light scattering in solution and rheological experiments in the molten state are different ways to investigate long chain branching. The branching character, e.g. a star, comb or a tree-like, cannot be detected directly by SEC-MALLS. For the characterization of the chain branching topology rheological experiments in elongation and shear flow can provide a hint. The aim of this work is to combine the results of these two methods in order to investigate the branching structure of the samples more thoroughly.

## **MATERIALS AND METHODS**

### *Materials*

The isotactic polypropylene (iPP) homopolymer used in this study was Novolen PPH2150 (Basell Polyolefins Company N.V., Hoofddorp, The Netherlands). According to data sheet 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/cm<sup>3</sup>.

#### *Electron beam irradiation.*

The iPP granulate was irradiated with 1,5 MeV using an electron beam accelerator (ELV-2, Budker Institute of Nuclear Physics, Novosibirsk, Russia) described in detail by Dorschner et al. [34]. The irradiation was carried out in a special vessel [35]. The sample was placed onto a support in this vessel, which includes heating elements and temperature sensors for temperature control. The irradiation was carried out under nitrogen at atmospheric pressure. Before the vessel was filled with nitrogen it was evacuated to 10<sup>-2</sup> Pa in order to minimize the concentration of oxygen.

Prior to the irradiation, the samples were heated up to a definite temperature, which has been retained unchanged during irradiation. The sample was irradiated with total doses of 20 kGy and 100 kGy. Total doses were accomplished on a step-by-step basis with a dose of 10 kGy per pass in order to minimize the temperature increase, which results from the irradiation. It is to be beard in mind that during the irradiation process a certain heating-up of the samples takes place. At a dose rate of 10 kGy an increase of the temperature of approximately 5 K has to be expected. For this reason the experimental temperature implies a slightly higher value. Afterwards, the irradiated PP was annealed for 60 min at 130°C or 150°C, respectively, to realize a deactivation of the residual radicals. The annealing step was carried out in the vessel under nitrogen atmosphere, too.

#### *Size exclusion chromatography*

The molecular characterization of the polypropylene samples was carried out by high temperature size exclusion chromatography (HT-SEC). The instrument used was a PL-GPC220 (Polymer Laboratories Ltd., Church Stretton, UK) at 150°C equipped with a

refractive index (RI) detector and coupled with a multi angle laser light scattering (MALLS) detector (DAWN EOS, Wyatt Technology Corporation, Santa Barbara, USA). The column set consisted of 2 columns PL Mixed-B-LS, 300 mm x 7,5 mm, 10  $\mu\text{m}$  particle size (Polymer Laboratories Ltd., Church Stretton, UK). The flow rate was 1 ml/min. The eluent was 1,2,4-trichlorobenzene (Merck KGaA, Darmstadt, Germany) stabilized with diphenylamine (Merck KGaA, Darmstadt, Germany) against the thermo-oxidative degradation of the polymer. The calculations of the molecular parameters (e.g.  $M_w$ ,  $M_n$ , molar mass distribution, radius of gyration) were carried out from the SEC data using commercial software ASTRA 4.73 and CORONA V1.40 for Windows (Wyatt Technology Corporation, Santa Barbara, USA).

#### *Differential scanning calorimetry (DSC)*

The DSC measurements were performed on a Q1000 (TA-Instruments, New Castle, USA) coupled with an autosampler in the temperature range of  $-60\text{ }^\circ\text{C}$  to  $210\text{ }^\circ\text{C}$  at a scan rate of  $\pm 10\text{ K min}^{-1}$ . Samples of about 5 mg were investigated under nitrogen atmosphere in a run cycle of 1<sup>st</sup> heating – cooling - 2<sup>nd</sup> heating. The calibration of temperature and transition heat was done with an In standard. The glass transition temperatures were calculated using the half step method, and the crystallinity using the value of 207 J/g for 100% crystalline PP [36].

#### *Rheology*

The rheological measurements in shear were performed at a temperature of  $180\text{ }^\circ\text{C}$  under nitrogen atmosphere using a rotational rheometer with plate-plate geometry of 25 mm in diameter and a gap of about 1.5 mm. The zero shear viscosity  $\eta_0$  was determined from creep measurements at low shear stresses of around 10 Pa, i.e. in the linear range of deformation, using a constant stress rheometer (Malvern Instruments Ltd., Malvern, UK). Creep tests are very suitable for the determination of  $\eta_0$  as the steady state of deformation is reached faster than in oscillatory or stressing experiments [37].

The elongational flow experiments 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. [37,38]. 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 conducted with different Hencky strain rates  $\dot{\epsilon}_H$  between 0.01 s<sup>-1</sup> and 1.0 s<sup>-1</sup>. The tensile stress growth coefficient or elongational viscosity is obtained from the measured tensile stress divided by the applied constant strain rate:

$$\eta_E^+(t, \dot{\epsilon}_0) = \sigma(t, \dot{\epsilon}_0) / \dot{\epsilon}_0 \quad (2)$$

The strain hardening factor  $X_E$  is defined as the deviation from Trouton's law. It is determined according to the following equation:

$$X_E(t) = \frac{\eta_E^+(t, \dot{\epsilon}_0)}{3\eta^+(t)} \quad (3)$$

## **RESULTS AND DISCUSSION**

### *Molecular Characterization*

It was found, that for the irradiation at elevated temperatures a slightly decrease of molar mass take place (see Table 1). If the samples were irradiated with 20 kGy at 25-190 °C then the molar masses were nearly unchanged. And the irradiation of polypropylene with 100 kGy at 25-150 °C led to a slightly decrease of molar mass (see Figure1). Only in case of 210 °C a very high molar mass degradation takes place caused by thermal degradation (see Table 1). The molecular degradation was a hint of increased rate of  $\beta$ -scission reactions. It was found, that in experiments with annealing of linear iPP at 210 °C without irradiation do not lead to a molar mass degradation. This is shown in the comparison to cumulative molar mass distribution of the initial iPP and an annealed iPP under nitrogen atmosphere in Figure 1. The perceptible deviation of results lie within the limits of the experimental error of SEC-

MALLS. One can conclude, that such behaviour can only be a result of the increase of the temperature during irradiation.

Figure 2 shows the dependence of the mean square radius of gyration on the molar mass for differently treated samples. After irradiation at 20 kGy and 100 kGy, all samples show lower radii of gyration than the initial sample caused by the branching process, which has taken place. Moreover, the decrease of the radius of gyration was clearly dependent on the irradiation dose and on the irradiation temperature. The samples irradiated at 25-80 °C have the same radius of gyration and branching density, respectively. At temperatures above 110 °C the radii of gyration were decreasing with irradiation temperature and this indicated a more pronounced branching and higher degree of long chain branching. That means that the temperature influenced the forming of long chain branching. A possible explanation for these effects is the different diffusion possibility of the chain fragments and the increasing of amorphous phase depending on the temperature. Higher temperatures enable the better diffusion of the chain fragments followed by formation of long chain branching with differently large chain fragments.

The influence of temperature on the branching structure with differently large chain fragments can be investigate with a calculation of the molar mass of arms or so-called length of long chain branching, respectively. Gabriel et al. [24] used the following equation to estimate the molar mass of long chain branching  $M_a$  for a low branched star-like structure:

$$M_a = \frac{M}{m + 2} \quad (4)$$

The value 2 was added to the number of long chain branches per molecules  $m$  to obtain correct values for the molar mass of long chain branches  $M_a$ . This equation describes a trifunctional three-arm star [24]. This calculation is only feasible for slightly branched polymers with a star-like molecular structure. If a higher number of long chain branches per molecule  $m$  is found than the structure is similar to a comb- or tree-like architecture. For a highly branched polyolefin (e.g. LDPE) the molar mass of long chain branches  $M_a$  is estimated to high if a star-like structure is assumed. In this case it is necessary to consider

the chain segments between the different branching points along the molecules. The number of the inner segments between the branching points  $m$  can be described with the term  $(m-1)$ . The term  $(m+2)$  describes the number of chains between branching points and chain ends per molecules. Therefore, the following equation is applied to calculate the molar mass of segments  $M_s$ :

$$M_s = \frac{M}{(m+2)+(m-1)} \quad (5)$$

Figure 3 shows a schematic illustration of a long chain branched molecule with three branching points. In this case one can observe two segments ( $s$ ) between the different branching points and five segments ( $end$ ) between branching point and chain end.

The resulting quantity  $M_s$  describes the average molar mass of segments per molecules. If the segments between branching points and chain ends are observed then this described the molar mass  $M_a$  or length of long chain branching. It cannot mirror the true structure. This estimation considers the assumed architecture of molecules and it is unessential to differ between comb- or tree-like (see Figure 3).

The calculation of the molar mass of segments  $M_s$  (using equation 5) for irradiated samples supports the assumption of an influence of temperature on branching structure. Figure 4 shows the distribution of  $M_s$  over the whole region of the molar masses for selected samples.  $M_s$  was found to be nearly constant in the range between  $5 \cdot 10^5$  g/mol and  $3 \cdot 10^6$  g/mol for all samples (see Figure 4). This leads to the conclusion that the number of branching points along the molecule  $m$  correlates directly to the molar mass. The deviations of  $M_s$  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 at the beginning and at the end of the chromatographic separation process the concentrations of the polymer 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 molar mass of segments  $M_s$  in this polymer.

The values calculated for  $M_S$  are given in Table 1 and Figure 5 for the irradiated samples. The main decrease of the molar mass of segments  $M_S$  is observed with increasing the temperature about 110 °C. For the samples irradiated with 100 kGy,  $M_S$  is about 31,000 g/mol in the temperature range of 25-80 °C. By increasing the temperature up to 110 °C  $M_S$  decreases to a value of 25,500 g/mol at the same molar mass of the polymer. At temperatures of 130 °C and 150 °C, it is determined a values of  $M_S$  about 22,000 g/mol and 19,000 g/mol, respectively. The same effect of temperature is observed for the sample irradiated at 20 kGy, too. In this case the molar mass of segments  $M_S$  decreases from 189,000 g/mol at 25-80 °C up to 145,000 g/mol at 110 °C and 95,000 g/mol at 170 °C or 190 °C, respectively. If the value of  $M_S$  at 25 °C is compared to the one in the molten state then  $M_S$  decrease to 50%.

These results are in good agreement with the assumption, that the temperature during the irradiation process plays an important role in the induction for the rate of  $\beta$ -scission reactions in the polymer. At room temperature large chain fragments will predominantly arise, which react to form branched molecules with large arms. Therefore, this form is similar to low branched stars or combs. By increasing the temperature short chain fragments are expected to be formed predominantly. These fragments then can react with the main chain or already formed chain branches to create various branching structures. These structures can be described as higher branched. Consequently, the increasing of temperature gives a higher amount of shorter fragments followed by increasing the number of shorter branching arms.

### *Thermal Analysis*

In the present work, the irradiation temperature will be varied. Therefore, DSC measurements show the influence of heating the samples during irradiation on molecular properties. Furthermore, The influence of long chain branching on the melting and crystallisation behaviour and crystallinity of polypropylene was investigated. For the samples irradiated with 20 kGy the characteristic temperatures are not changed significantly with

irradiation temperature. Therefore, in this paper the melting and crystallisation behaviour is discussed only for the samples irradiated with a dose of 100 kGy.

The melting behaviour of the initial polypropylene is shown in Figure 6. The onset of the melting is at approximately 100 °C. It follows that the samples irradiated at about 100 °C are partially molten. The molecular changes observed occur by irradiation about 110 °C. This finding is associated with the increasing of amorphous part and the improved diffusion of chains.

The glass transition temperature  $T_g$  of the samples irradiated at various temperatures was unchanged up to an irradiation temperature of 110 °C. At higher irradiation temperatures  $T_g$  shift to lower values. This is only a small tendency (see Table 2). The crystallinity  $\alpha$  was not influenced by the irradiation (see Table 2). The melting peak temperatures  $T_m$  of all irradiated samples are lower than  $T_m$  of the virgin material (see Table 2, Figure 6, 7) and were not influenced by the irradiation temperature (see Figure 7). Therefore, the decrease of melting temperature after the irradiation should be caused by molar mass degradation and a reduced lamellae thickness due to the higher nucleation density.

At irradiation temperatures of 25 °C and 50 °C the maximum crystallisation temperature  $T_{c,m}$  decreased after the irradiation. With increasing the irradiation temperature the crystallisation temperature  $T_{c,m}$  increased as well as the onset temperature  $T_{c,o}$  (see Table 2, Figure 6, 7).

Gahleitner et al. [39] described that long chain branching leads to a significant increase of the nucleation density and, consequently, to a higher crystallisation temperature of the samples. Therefore, it is assumed that the reason for the observed earlier crystallisation is the existence of more long chain branching. It is improbable that the crystallisation behaviour is influenced by the molar mass of samples because the molar mass is nearly unchanged in dependent on irradiation temperature. A higher crystallisation temperature is particularly valuable in industrial applications for which an earlier solidification is desired because this leads to faster processing.

### Rheological characterization in shear flow

Shear rheology is a very sensitive tool to detect even slight changes of the molecular structure and low amounts of long chain branching [23,24,40]. This is particularly true for the zero shear viscosity if regarded as a function of weight average molar mass  $M_w$  [24,40]. In Figure 8 the straight full line represents its power law dependence for a series of commercial linear isotactic polypropylenes (iPP) [10]. This relationship is also valid for the linear iPP, which was used for irradiation (star symbol). The zero shear viscosities  $\eta_0$  of the samples irradiated with 20 kGy and 100 kGy at different temperatures were found to deviate from this relationship (see Figure 8). If compared with linear polypropylenes of the same molar masses very interesting results are obtained. The samples irradiated with 20 kGy are located above the line of linear iPP whereas those irradiated with 100 kGy are mainly beneath this line. For both series significantly decreasing zero shear viscosities  $\eta_0$  with increasing irradiation temperature were observed (cf. Table 1 and Figure 8). The significant reduction of the molar mass and zero shear viscosity of sample irradiated at 20 kGy and 210 °C can be attributed to a pronounced thermal degradation.

A more quantitative comparison of the zero shear viscosities  $\eta_0$  of branched and linear PP  $\eta_{0(br)} / \eta_{0(lin)}$  at the same weight average molar masses  $M_w$  is given in Figure 9. From the exponential dependence of  $\eta_0$  on the ratio of  $M_a/M_e$  it follows that the values greater than 1 for the samples irradiated at 20 kGy (25 °C) point to molecular structures with relatively high molar masses of the long chain branches. For the samples irradiated with 100 kGy at 25 °C the ratio  $\eta_{0(br)} / \eta_{0(lin)}$  becomes nearly 1. It can be concluded that molecular structures are generated, which contain a higher number of branches with relatively small molar mass. From the statistical branching process it has to be assumed that these branches are randomly distributed along the backbone or side chains, respectively. Therefore, a tree-like topology is highly probable for samples irradiated at 100 kGy.

A significant reduction of the ratio  $\eta_{0(br)} / \eta_{0(lin)}$  was observed for the samples irradiated at 20 kGy and 100 kGy with increasing irradiation temperature. The decrease of  $\eta_{0(br)} / \eta_{0(lin)}$  taken at the same  $M_w$  can formally be related to a reduction of the molar mass of arms  $M_a$  of the

chain branching [25,41,42]. But  $M_a$  cannot be measured or calculated directly from chromatographic measurements. However, for slightly branched molecules the length of the outer segments with free ends corresponds to long chain branches attached to the backbone (cf. Figure 3). For this reason, a relation of  $M_a$  to the segment molar mass  $M_S$  as calculated by eq. 5 can be assumed for the interpretation of the results. From Table 1 it can be seen that the segment molar mass  $M_S$  and hence the length of the chain branches becomes shorter with higher irradiation temperature. Using these model assumptions the decrease of  $\eta_{0 (br)}/\eta_{0 (lin)}$  can be explained by the decrease of the molar mass of long chain branching.

The same conclusion on the change of the molar mass of the branches can be drawn using a model proposed only recently by Inkson et al. [40] for comb-shaped polyethylene. Hereby, the shift of the zero shear viscosity  $\eta_0$  is described as a function of the number and length of the branching arms. It was found that both the decrease of the length of chain branching as well as the increase of the number of chain branching leads to a lower zero shear viscosity  $\eta_0$  at the same weight average molar mass. Comparing the influence of both parameters on the zero shear viscosity the length of chain branching has the highest effect. Our observed results on the zero shear viscosity  $\eta_0$  correlate well with the model predictions that  $\eta_0$  decreases with increasing number of long chain branching and a decreasing molar mass of long chain branching.

#### *Rheological characterization in elongational flow*

The strain hardening behaviour of branched polyolefins is found to be characteristic for different branching topographies [10,33]. Therefore, this rheological method can be used to get a further insight into the molecular structures of the samples. The strain rate dependence of the elongational viscosity can be used to draw further conclusions with respect to the topography of the various polypropylene molecules, as the molar mass distributions are very similar. The cumulative molar mass distributions of different irradiated samples is shown in

Figure 1. It was found that the molar mass distributions of irradiated samples were very similar (see Table 1).

In elongational experiments, no strain hardening was found for the untreated linear iPP, which is consistent with results reported in literature for linear polypropylenes of a similar molar mass distribution (Figure 10a). The samples irradiated with 100 kGy at 25-110 °C show strain hardening, which increases with increasing strain rate (Figure 10a). This behaviour is typically found for LDPE having a high number of long chain branches and a tree-like molecular structure [33,44]. Therefore, this dependence indicates a high degree of branching with small arm molar masses  $M_a$  and it can be concluded that a highly branched topography is probable. The strain rate dependence did not change pointing to a similar molecular structure for the samples irradiated at various temperatures (see Figure 11). This conclusion is supported by the only slight changes about 5,000 g/mol calculated for the segment molar mass  $M_s$  (see Table 1).

The samples irradiated with 20 kGy show a different strain hardening behaviour, the strain rate dependence of which changes with rising irradiation temperatures (see Figure 10b). At low irradiation temperatures between 25 °C and 80 °C the strain hardening factor  $X_E$  decreases with higher strain rates (Figure 11). This dependence was found for metallocene catalysed polyethylenes and points to a small degree of branching with high molar masses  $M_a$  of the branches [10,33]. However, for temperatures of 110-190 °C the strain hardening factor  $X_E$  runs through a maximum, which increases in height. A similar behaviour was found for LDPE followed by increasing strain hardening with an increasing number of long chain branching determined as the number of CH<sub>3</sub> per 1000 C-atoms [31]. From the strain hardening factor  $X_E$  of the samples irradiated with 20 kGy it can be concluded that the number of branches increases while the length of branches decreases with irradiation temperature. The chromatographic measurements support this finding as the degree of long chain branching increases and the molar mass of segments  $M_s$  decreases from 189,000 g/mol at 25 °C to 95,000 g/mol at 190 °C.

Compared to the other samples irradiated with 20 kGy, for the highest applied temperature of 210°C the values at small elongation rates are very low between 1.5 and 2 and the strain hardening factor  $X_E$  increases with higher strain rates. This corresponds to the significantly lower molar mass and lower zero shear viscosity of the sample, which is originated from a pronounced degradation during irradiation. The behaviour can be explained by low molar masses of the branches.

The error bars indicate the reproducibility of the experiments and from that it can be found that toward low strain rates the scattering increases. This can be attributed to the low tensile forces at large stretch ratios of the specimens since the force can be measured less accurate at smaller strain rates and lower viscosities.

## **CONCLUSIONS**

It is known, that the modification of linear polypropylene by means of electron beam irradiation is an efficient way to generate a long chain branched macromolecules. In this paper the influence of temperature during irradiation on molecular structure is described. Different effects by increasing the temperature of irradiation were found. This originates from reactions depending on temperature, such as  $\beta$ -scission or chain diffusion, and a partial melting of the pellets, which causes a change of crystallinity.

The observed results show a slightly reduction of weight average molar mass  $M_w$  and an increase of the degree of long chain branching with increasing the irradiation temperature. At temperatures higher than 100 °C the polypropylene is partially molten followed by an increasing of amorphous part. With it occurs that the chain branching reactions becomes more pronounced. If the samples are irradiated over 100 °C then a decrease of molar mass of segments  $M_S$  takes place. The molar mass of segments  $M_S$  is related to the length of long chain branching. That means that with increasing temperature the formed branched molecules have more and shorter long chain branching. The irradiation at 210 °C leads to a

significant molar mass degradation. Therefore, this irradiation temperature is too high for advantageous application.

Additionally, a shift of the crystallisation maximum and of the onset temperatures toward higher temperatures is observed. This is attributed to the insertion of long chain branching. The irradiation of polypropylene in the molten state regarding the molar mass, melting and crystallisation behaviour is described with more details by Krause et al. [45].

The investigation of rheological properties in shear and elongation clearly shows that molecular structure is changed by irradiation at different temperatures.

The results on the molar mass dependence of the zero shear viscosity indicate that the number of long chain branching is increasing and the molar mass of long chain branching is decreasing with irradiation temperature. From elongational rheology it can be concluded that the strain hardening characteristics of the samples prepared by electron beam irradiation with 20 kGy and 100 kGy are determined by the long chain branching topography. A change of molecular architecture from a slightly branched star-like type to a higher branched tree-like type is found for samples irradiated at 20 kGy. For the samples irradiated with 100 kGy it can be assumed that the type of topography did not change with increasing irradiation temperature since the strain rate behaviour is very similar. The results from uniaxial elongation experiments support the conclusions from shear flow experiments that the irradiation at elevated temperatures results in a higher number of long chain branching with smaller values of  $M_a$  and are consistent with results from size exclusion chromatography.

The irradiation of polypropylene at different temperatures is one way to generate long chain branched samples with different branching structure. Another way is using different irradiation doses in the range of 10-150 kGy at room temperature, resulting in a significant decrease of the ratio  $\eta_{0(br)} / \eta_{0(lin)}$  and a changing strain rate dependence of the strain hardening. From that, it is concluded that the branching topology is changed from star-like to tree-like. Comparing the results from shear and elongational rheology it can be concluded that both the increase of irradiation dose at room temperature or the increase of temperature during irradiation at the same dose leads to an increasing degree of long chain branching.

Therefore, it is possible to influence the branching structure not only by different irradiation doses but also by irradiation temperature. In both cases the branching topology can be varied. The combination of both irradiation parameters can be used to tailor the desired properties of a polypropylene with respect to molar mass, long chain branching and rheological behaviour.

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## REFERENCES

- [1] Phillips, E. M.; McHugh, K. E.; Ogale, K.; Bradley, M. B. *Kunststoffe* 1992, 82, 671.
- [2] Park, C. B.; Cheung, L. K. *Polym. Eng. Sci.* 1997, 37, 1.
- [3] Krause, B.; Häußler, L.; Voigt, D., Comparison of the molecular properties and morphology for polypropylene irradiated at different atmosphere and post annealing, *Journal of Applied Polymer Science*, accept.
- [4] Valenza, A.; Piccarolo, S.; Spadaro, G. *Polymer* 1999, 40, 835.
- [5] Sarcinelli, L.; Valenza, A.; Spadaro, G. *Polymer* 1997, 38, 2307.
- [6] Tobita, H.; Kawai, H. *e-Polymers* 2002, 48.
- [7] Rätzsch, M.; Bucka, H.; Hesse, A.; Reichelt, N.; Borsig, E. *Macromol. Symp.* 1998, 129, 53.
- [8] Lazar, M.; Hrcakova, L.; Borsig, E.; Marcincin, A.; Reichelt, N.; Rätzsch, M. *J. Appl. Polym. Sci.* 2000, 78, 886.
- [9] Sugimoto, M.; Tanaka, T.; Masubuchi, Y.; Takimoto, J.; Koyama, K. *J. Appl. Polym. Sci.* 1999, 73, 1493.
- [10] Auhl, D.; Stange, J.; Münstedt, H.; Krause, B.; Voigt, D.; Lederer, A.; Lappan, U.; Lunkwitz, K., *Macromol.* 2004, 37, 9465.
- [11] Scheve, B. J.; Mayfield, J. W.; DeNicola, A. J., Jr. (Himont Inc.). U.S. Patent 4,916,198, April 10, 1990.
- [12] DeNicola, A. J., Jr. (Himont Inc.). *Europ. Patent* 0,351,866, July 21, 1989.
- [13] DeNicola, A. J., Jr. (Himont Inc.). *Europ. Patent* 0,384,431, February 21, 1990.
- [14] DeNicola, A. J., Jr. (Himont Inc.). U.S. Patent 5,047,485, September 10, 1991.
- [15] Yoshii, F.; Makuuchi, K.; Kikukawa, S.; Tanaka, T.; Saitoh, J.; Koyama, K. *J. Appl. Polym. Sci.* 1996, 60, 617.
- [16] Rätzsch, M.; Hesse, A.; Bucka, H.; Reichelt, N.; Panzer, U.; Mehnert, R. (Danubia Petrochem Polymere). *Europ. Patent* 0,792,905, September 03, 1997.
- [17] Lawton, E. J. (General Electric Company). *German Patent* 1,247,638, August 17, 1967.

- [18] Rätzsch, M.; Arnold, M.; Borsig, E.; Bucka, H.; Reichelt, N. *Progr. Polym. Sci.* 2002, 27, 1195.
- [19] Wu, G.; Katsumura, Y.; Kudoh, H.; Morita, Y.; Seguchi, T. *J. Polym. Sci. Part A: Polym. Chem.* 1999, 37, 1541.
- [20] Qu, B.J.; Ranby, B. *Polym. Eng. Sci.* 1995, 35, 1161.
- [21] Dijkstra, D.J.; Hoogsteen, W.; Pennings, A.J. *Polymer* 1989, 30, 866.
- [22] Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* 1949, 17, 1301.
- [23] Krause, B.; Voigt, D.; Lederer, A.; Auhl, D.; Münstedt, H. *J. Chrom. A* 2004, 1056, 217.
- [24] Gabriel, C.; Münstedt, H. *Rheol. Acta* 2002, 41, 232.
- [25] Graessley, W. W.; Roovers, J. *Macromol.* 1979, 12, 959.
- [26] Fetters, L. J.; Kiss, A. D.; Pearson, D. S.; Quack, G. F.; Vitus, F. *J. Macromol.* 1993, 26, 647.
- [27] Wood-Adams, P.; Dealy, J. M.; deGroot, A. W.; Redwine, O. D. *Macromol.* 2000, 33, 7489.
- [28] Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou M.; Hadjichristidis, N.; Mendelson, R. A.; Garcia-Franco, C. A.; Lyon, M. K. *Macromol.* 2002, 35, 3066.
- [29] Pearson, D. S.; Helfand, E. *Macromol.* 1984, 17, 888.
- [30] Ball, R. C.; McLeish, T. C. B. *Macromol.* 1989, 22, 1911.
- [31] Münstedt, H.; Laun, H. M. *Rheol. Acta* 1981, 20, 211.
- [32] Hingmann, R.; Marczinke, B. *J. Rheol.* 1994, 38, 573.
- [33] Gabriel, C.; Münstedt, H. *J. Rheol.* 2003, 47, 619.
- [34] Dorschner, H.; Jenschke, W.; Lunkwitz, K. *Nucl. Instr. Methods Phys. Res. B* 2000, 161-163, 1154.
- [35] Körber, H.; Lappan, U.; Geißler, U.; Lunkwitz, K.; Hanke, R. (Institute of Polymer Research Dresden). German Patent 19,930,742, July 19, 2001.
- [36] Gaur, U.; Wunderlich, B. *J. Phys. Chem. Ref. Data* 1981, 10, 1051.
- [37] Münstedt, H.; Kurzbeck, S.; Egersdörfer, L. *Rheol. Acta* 1998, 37, 21.
- [38] Münstedt, H. *J. Rheol.* 1979, 23, 421.

[39] Gahleitner, M. *Prog. Polym. Sci.* 2001, 26, 895.

[40] Janzen, J.; Colby, R. H. *J. Mol. Struct.* 1999, 485-486, 569.

[41] Lagendijk, R.; Hogt, A. H.; Buijtenhuijs, A.; Gotsis, A. D. *Polymer* 2001, 42, 10035.

[42] Münstedt, H. *J. Rheol.* 1980, 24, 847.

[43] Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B. Analytical model for the catalysis of dual reactor metallocene polyethylenes and a prediction of their rheology, *Proc. XIVth Int. Congr. on Rheology*, August 22-27, 2004, Seoul, Korea.

[44] Malmberg, A.; Gabriel, C.; Steffl, T.; Münstedt, H.; Löfgren, B. *Macromol.* 2002, 35, 1038.

[45] Krause, B.; Stephan, M.; Volkland, S.; Voigt, D.; Häußler, L.; Dorschner, H. *J. Appl. Polym. Sci.* 2006, 99, 260.

## FIGURE CAPTIONS

Figure 1: Cumulative molar mass distribution for initial iPP, annealed PP at 210°C, and for selected samples irradiated with 20 kGy and 100 kGy.

Figure 2: Mean square radius of gyration  $\langle s^2 \rangle$  in dependence on molar mass  $M$  for the samples irradiated with 20 kGy and 100 kGy.

Figure 3: Schematic structure of long chain branched macromolecules

Figure 4: Molar mass of segments  $M_S$  in dependence on molar mass  $M$  for the selected samples irradiated with 20 kGy and 100 kGy.

Figure 5: Molar mass of segments  $M_S$  in dependence on irradiation temperature  $T$  for the samples irradiated with 20 kGy and 100 kGy.

Figure 6: Normalized heat flow of 2<sup>nd</sup> heating and cooling for the initial iPP and the samples irradiated with 100 kGy at 25 °C and 150 °C.

Figure 7: Melting peak temperature  $T_m$  of PP (2<sup>nd</sup> heating run), extrapolated onset and maximum crystallization temperature of PP  $T_{c,o}$ ,  $T_{c,m}$  in dependence on irradiation temperature  $T$  for the samples irradiated with 100 kGy.

Figure 8: Zero shear viscosity  $\eta_0$  in dependence on weight average molar mass  $M_w$  for the initial iPP and for the samples irradiated with 20 kGy and 100 kGy.

Figure 9: Ratio of the zero shear viscosities  $\eta_0$  of branched and linear PP in dependence on the irradiation temperature  $T$  for the samples irradiated with 20 kGy and 100 kGy.

Figure 10: Elongational viscosity  $\eta_E$  in dependence on time  $t$ . a) for the initial iPP and the samples irradiated with 100 kGy; b) for the samples irradiated with 20 kGy.

Figure 11: Strain hardening factor  $X_E$  in dependence on strain rate  $d\varepsilon_0/dt$  for the samples irradiated with 20 kGy and 100 kGy.

## TABLES

Table 1: Molecular and rheological data of the polypropylenes investigated

Table 2: DSC data of cooling and the 2<sup>nd</sup> heating run of PP pellets irradiated with 100 kGy

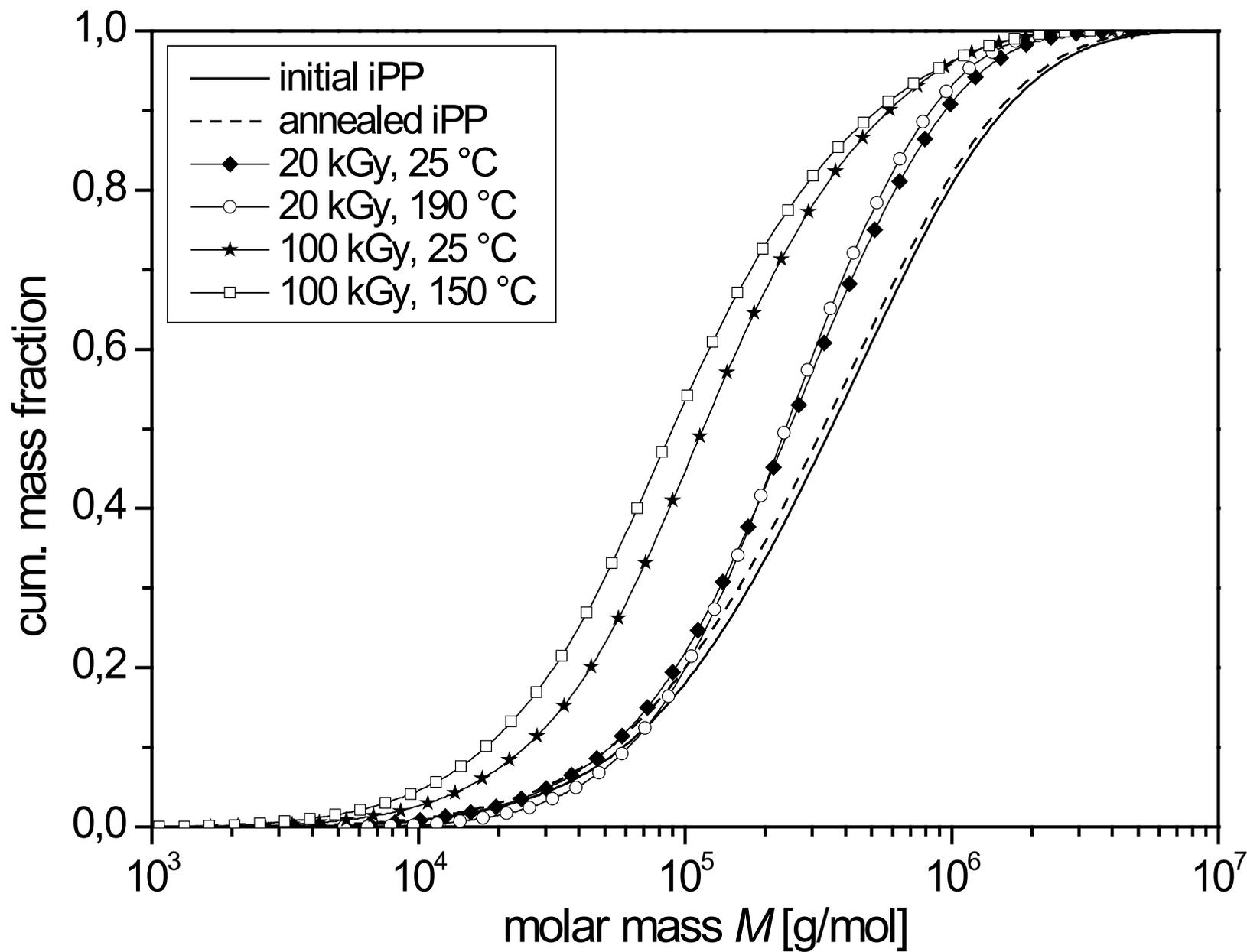


Figure 1

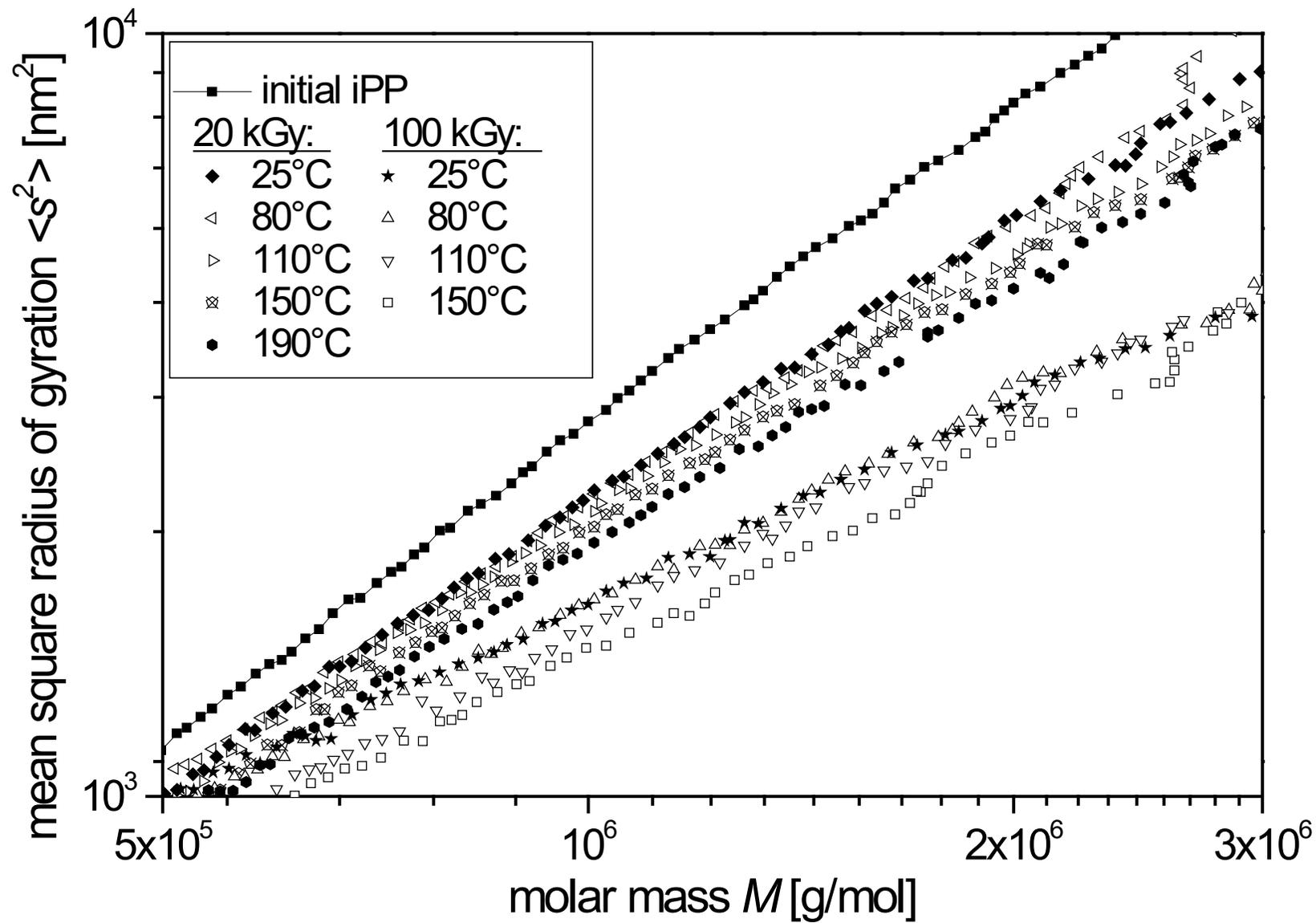


Figure 2

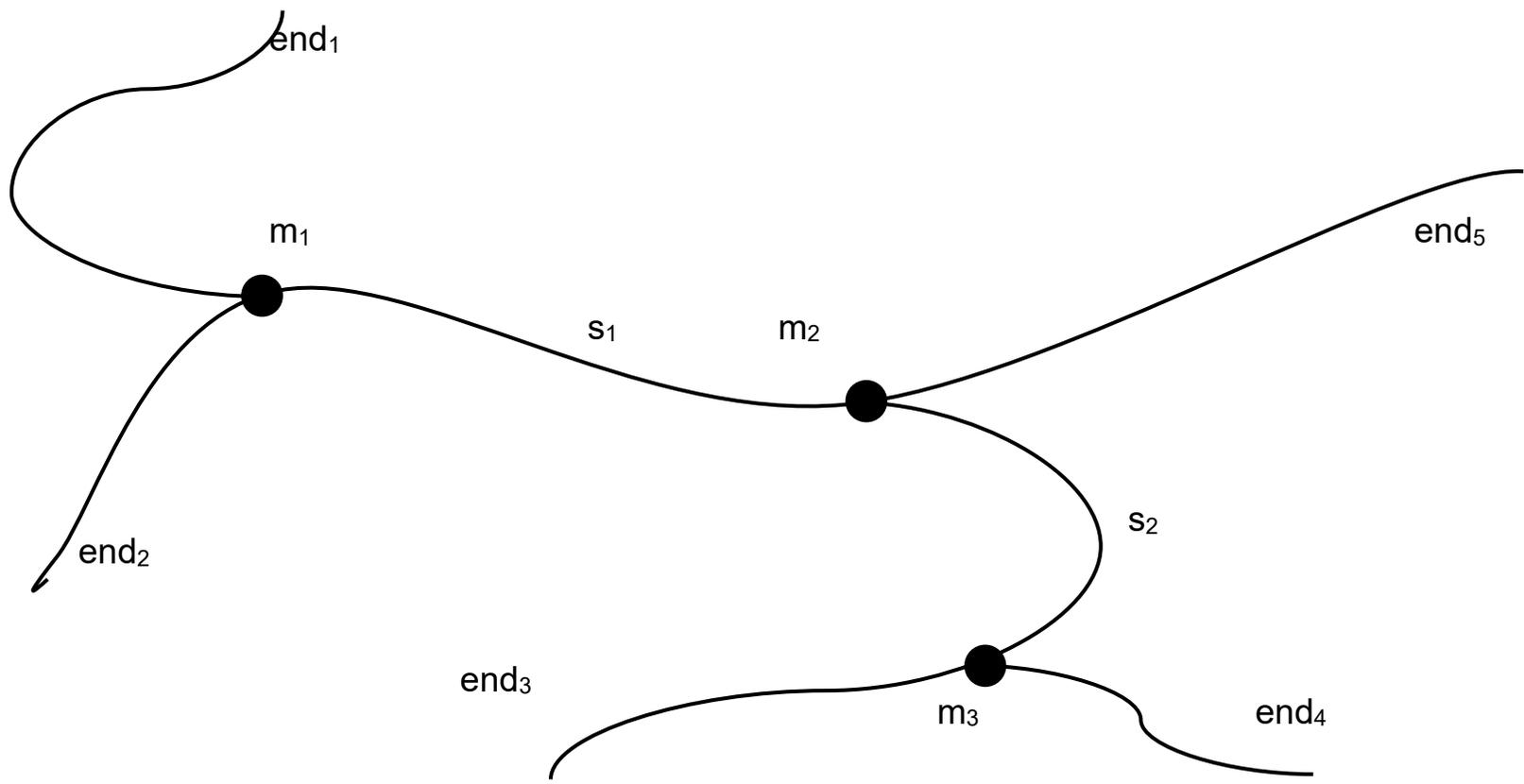


Figure 3

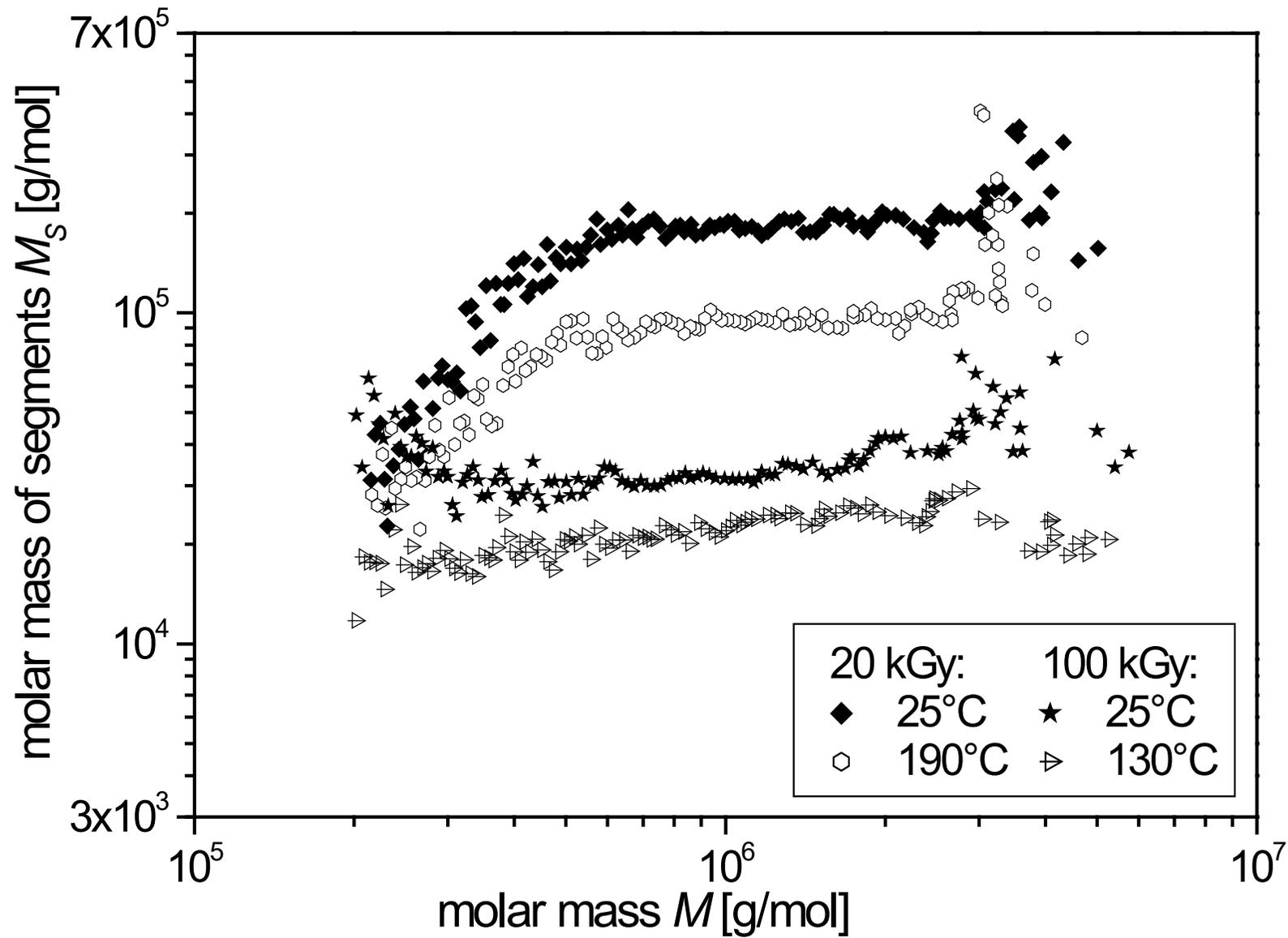


Figure 4

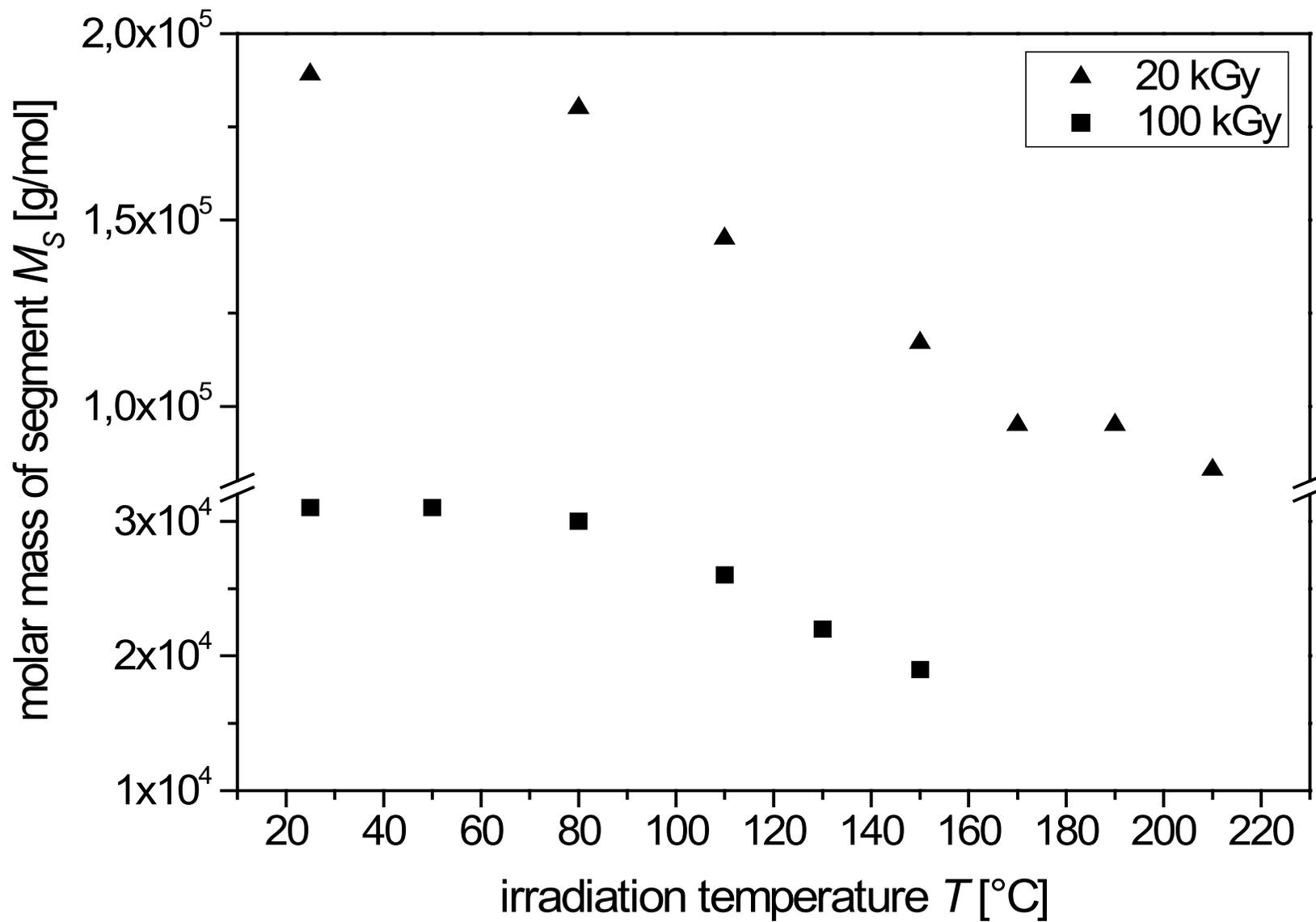


Figure 5

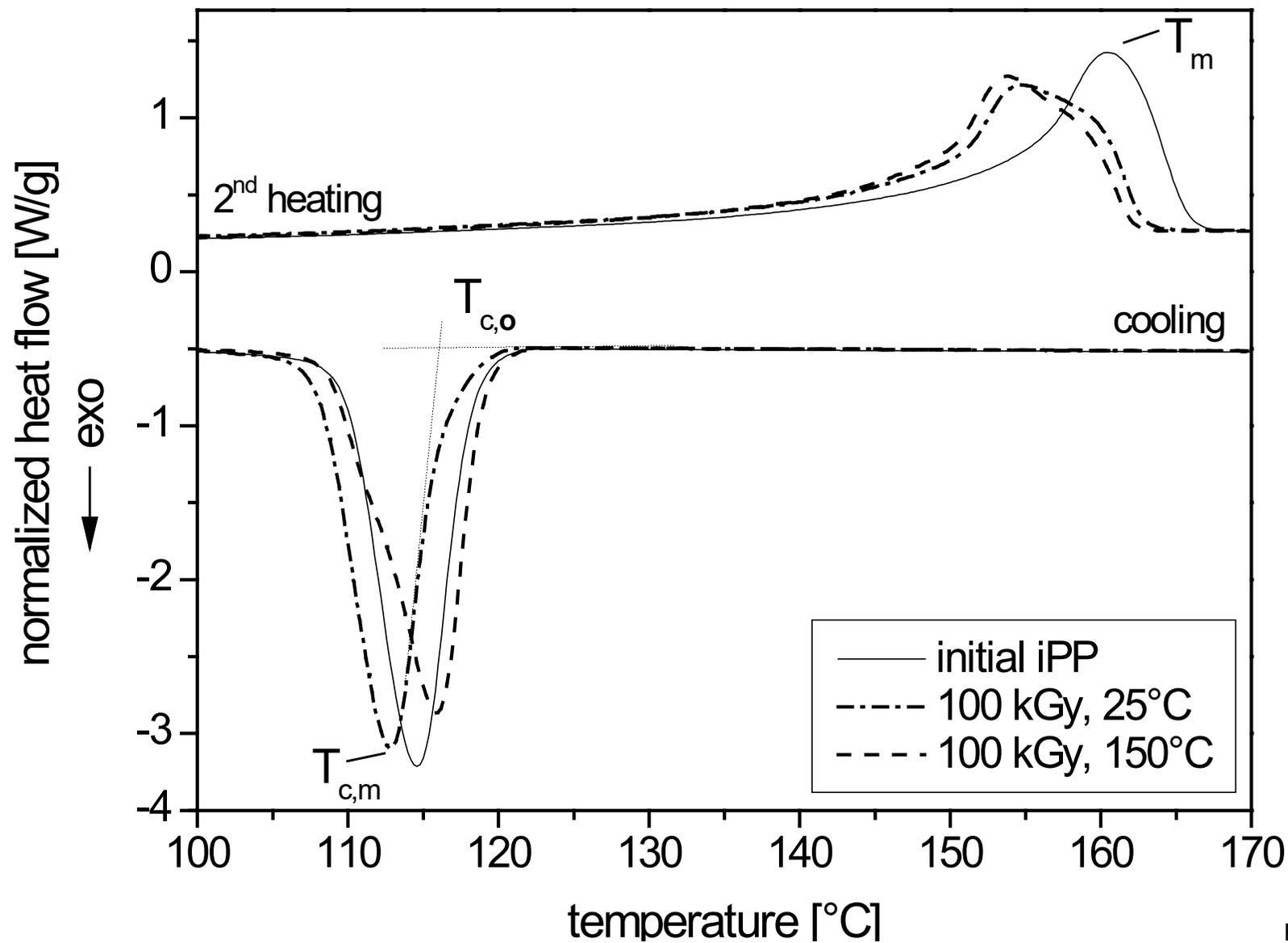


Figure 6

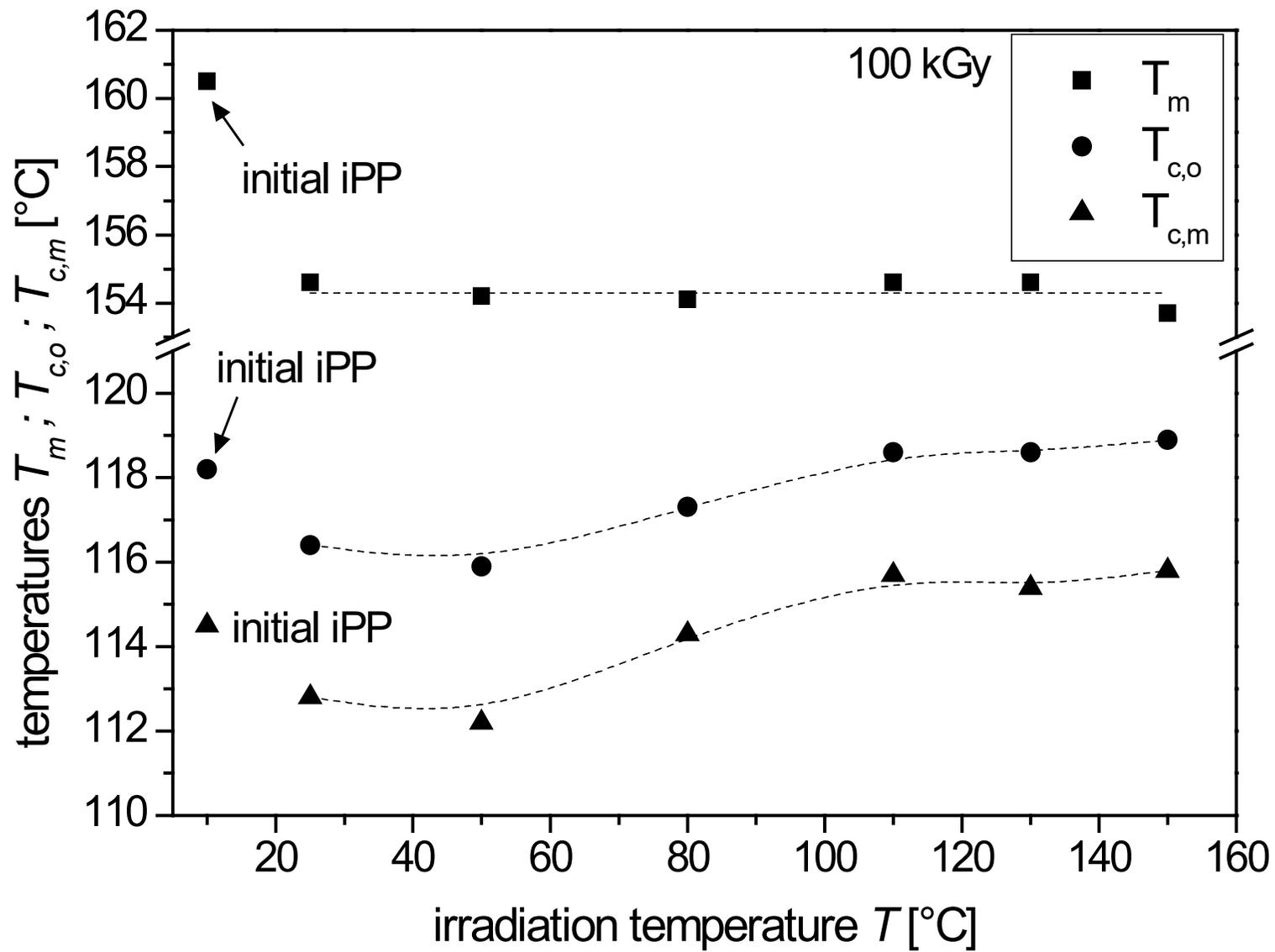


Figure 7

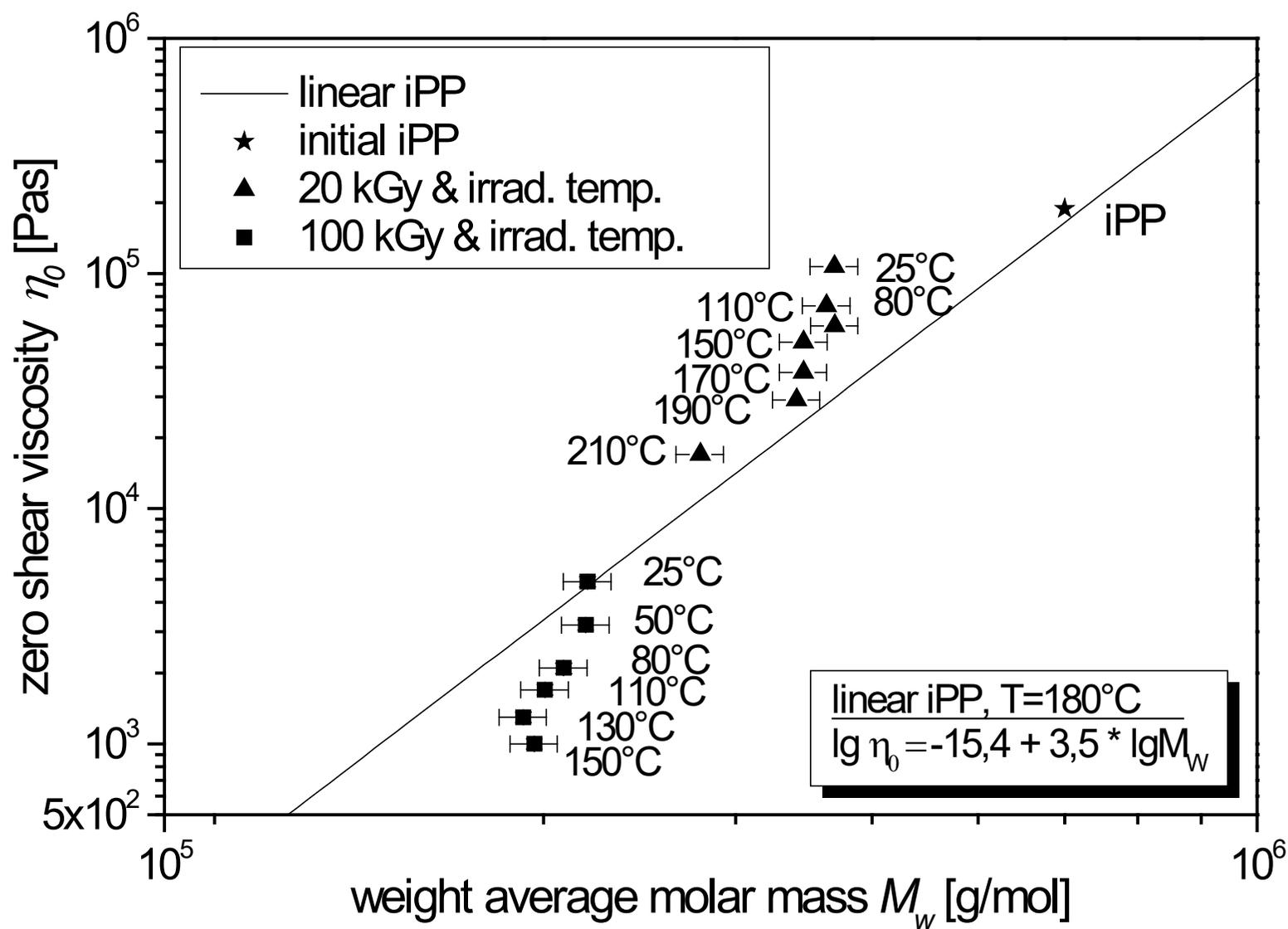


Figure 8

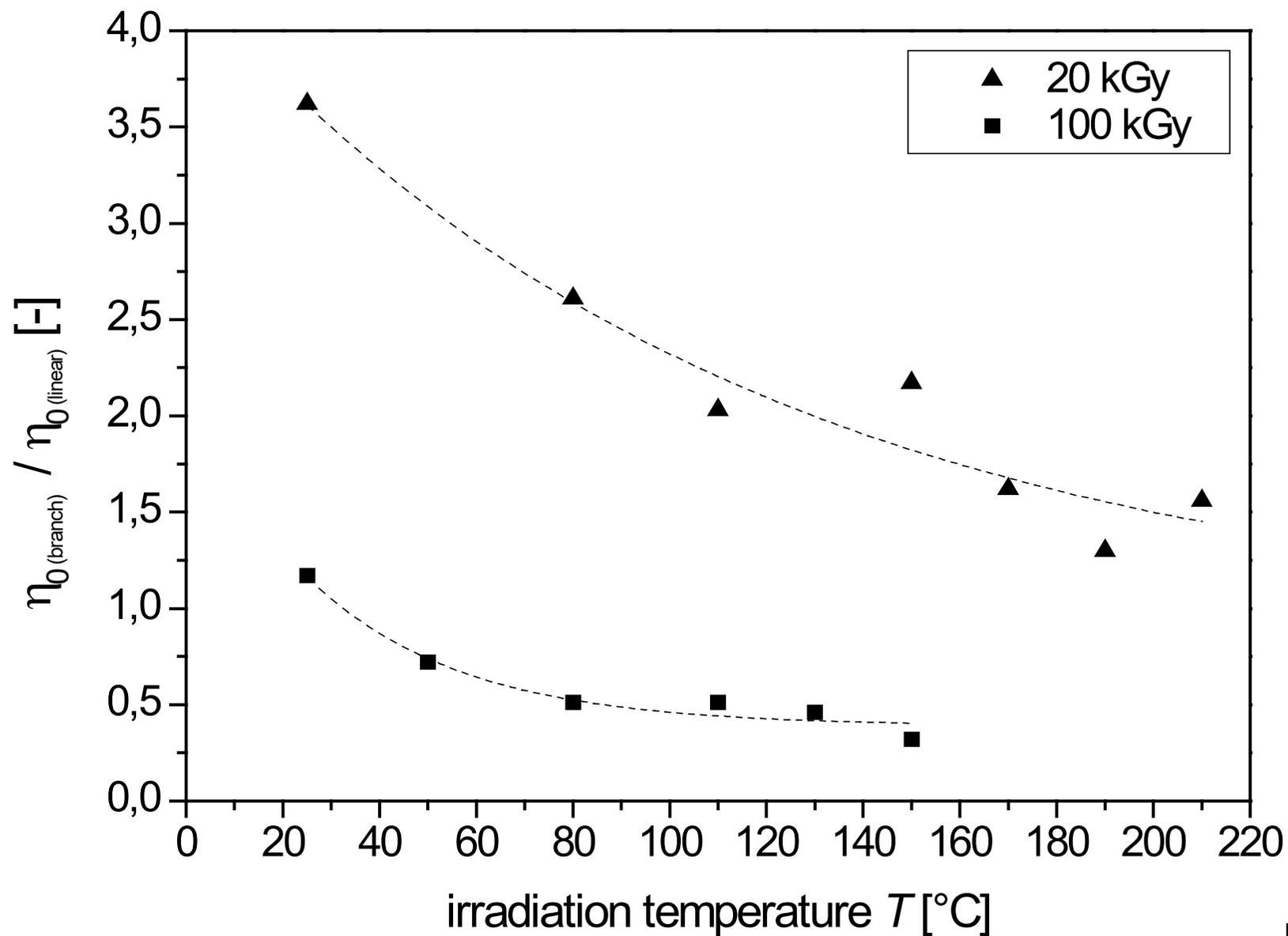


Figure 9

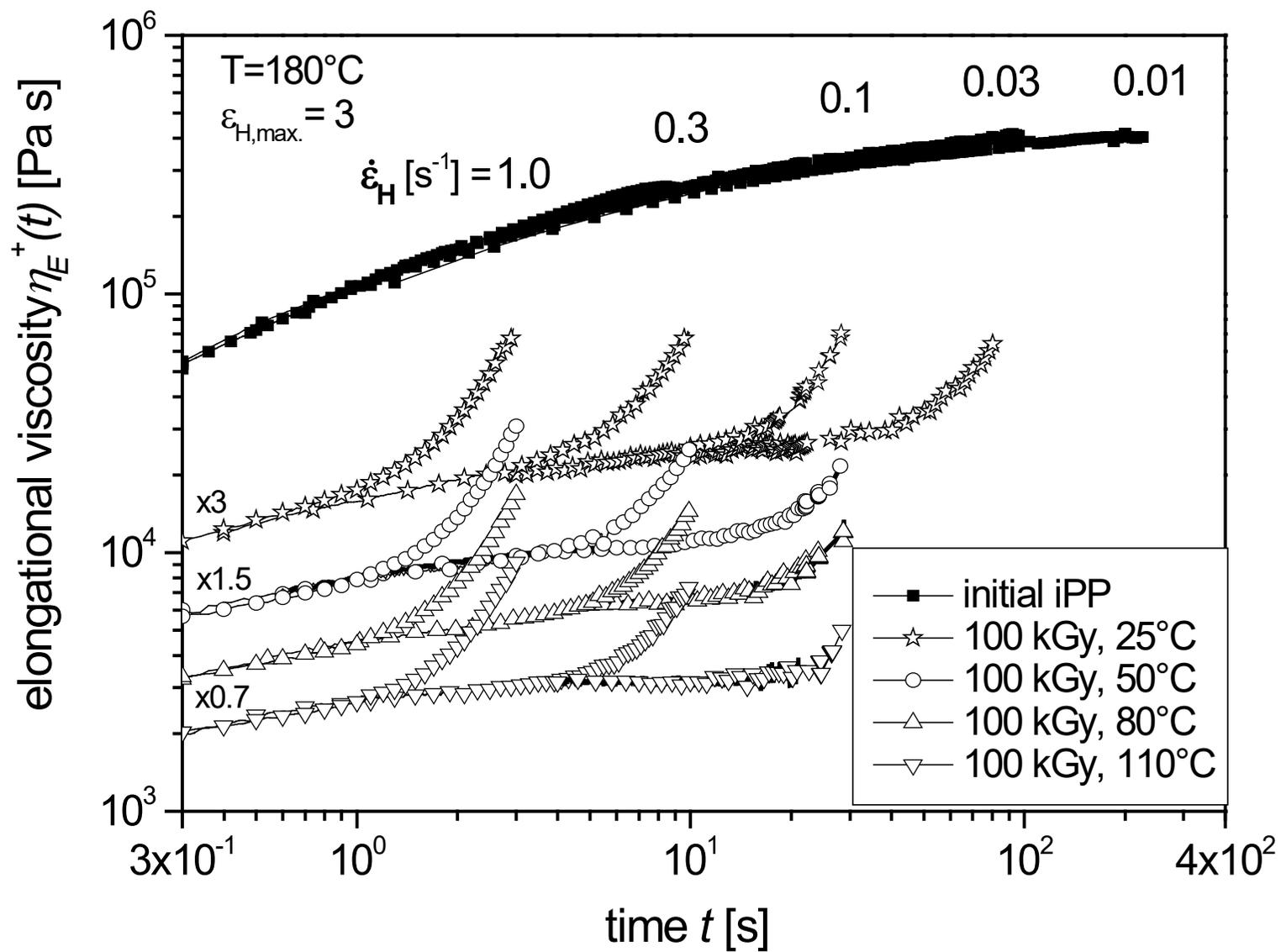


Figure 10a

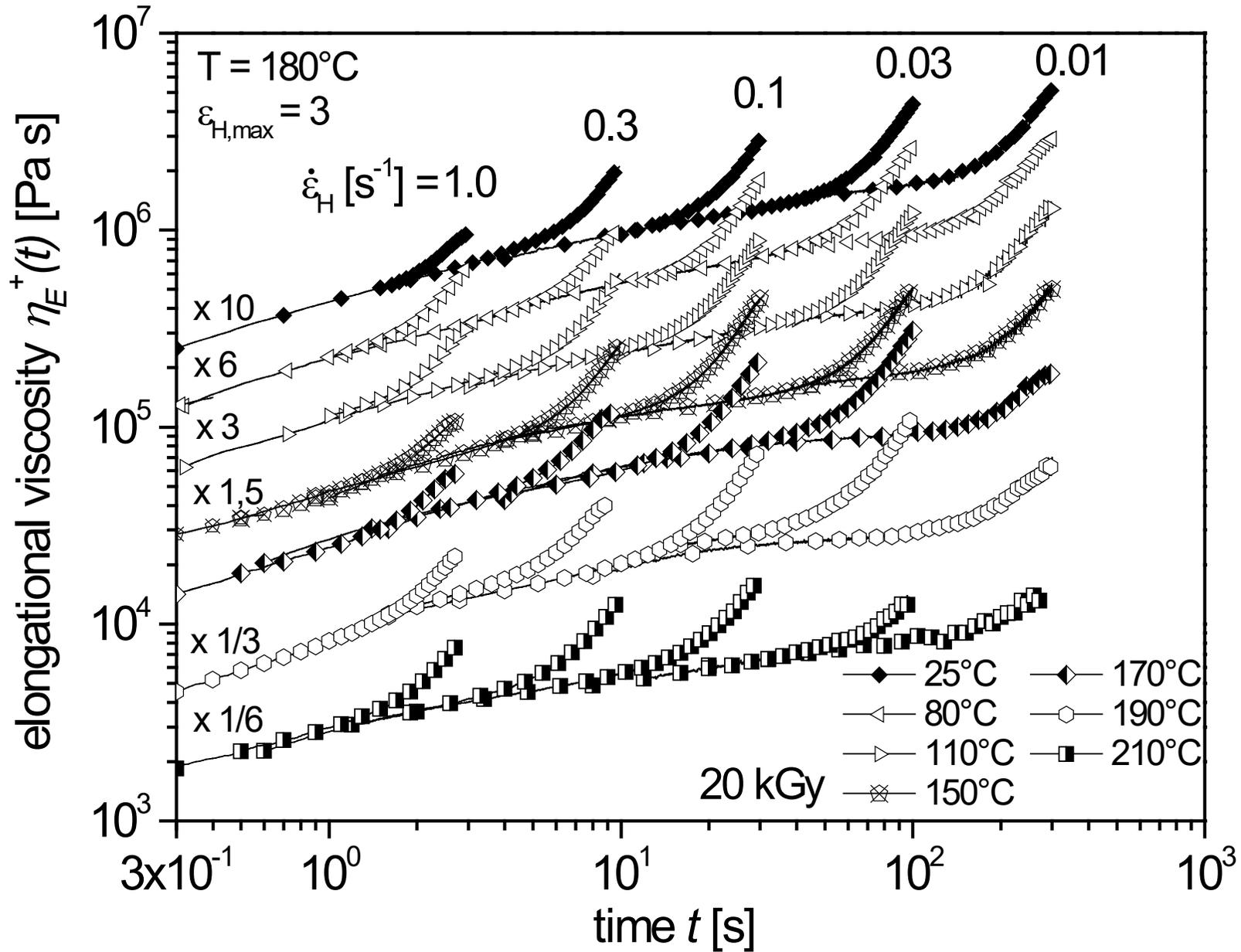


Figure 10b 34 / 37

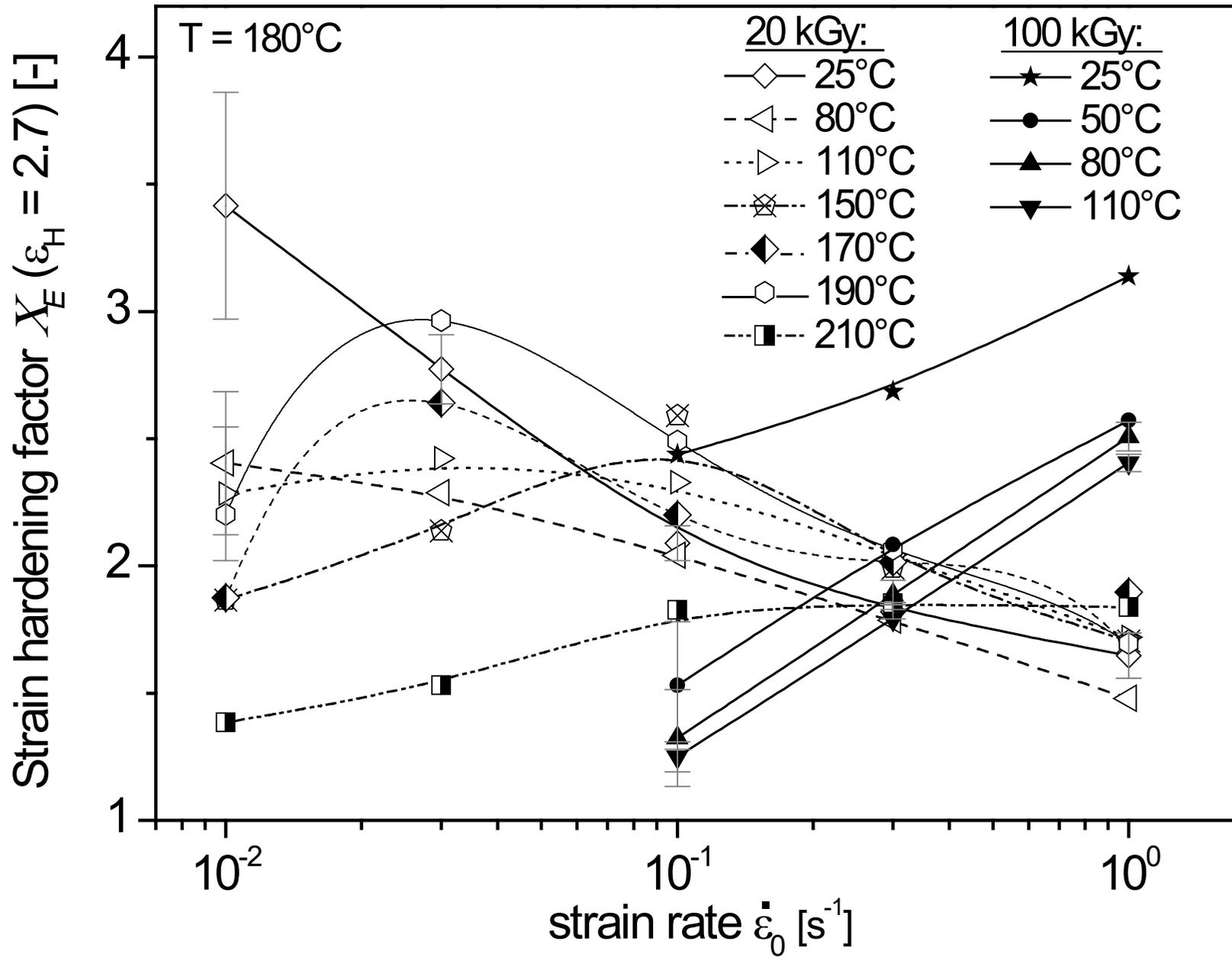


Figure 11  
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Table 1

Irradiation dose d [kGy]	Irradiation temperature T [°C]	Weight average molar mass $M_w$ [kg/mol]	Polydispersity $M_w/M_n$ [-]	Molar mass of segments $M_S^*$ [kg/mol]	Zero shear viscosity $\eta_0$ (180°C) [kPa s]
0	initial	669	4,2	-	188
20	25	411	3,0	189	107
20	80	404	2,7	180	73
20	110	411	2,6	145	60
20	150	385	2,8	117	51
20	170	385	2,9	95	38
20	190	379	2,6	95	29
20	210	309	2,6	83	17
100	25	244	3,3	31	5.5
100	50	240	3,3	31	3.2
100	80	235	3,3	30	2.1
100	110	222	3,7	26	1.7
100	130	212	3,5	22	1.3
100	150	218	3,8	19	1
100	210	101	3,8		

\* calculated by SEC-MALLS using eq. 5

Table 2

Irradiation temperature T [°C]	Glass transition temperature $T_g$ [°C]	Melting enthalpy $\Delta H_m$ [J/g]	Crystallinity $\alpha$ [%]	Melting peak temperature $T_m$ [°C]	Maximum crystallisation temperature $T_{c,m}$ [°C]	Extrapolated onset crystallisation temperature $T_{c,o}$ [°C]
initial	-6,8	97,6	47	160,5	114,5	118,2
25	-7,7	98,8	48	154,6	112,8	116,4
50	-7,9	96,9	47	154,2	112,2	115,9
80	-7,7	99,0	48	154,1	114,3	117,3
110	-7,9	99,8	48	154,6	115,7	118,6
130	-8,0	99,4	48	154,6	115,4	118,6
150	-8,4	97,7	47	153,7	115,8	118,9