

Long Chain Branching of Polypropylene by Electron Beam Irradiation in the Molten State

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SYNOPSIS

Electron beam irradiation of polymers generated modification effects in macromolecular structure and material properties. Thereby irradiation processing is mostly realized in polymer solid state. In this way the modification of linear polypropylene may result in long chain branching of polypropylene macromolecules. Objective of this paper is to investigate the effect of polymer in molten state during electron beam irradiation on macromolecular structure and material properties of polypropylene. For this procedure a special irradiation vessel (BG3) has been developed on which a rapid transfer of polymer films from solid to molten state and a defined temperature during electron beam irradiation is realizable. The irradiated samples were analyzed by high temperature size exclusion chromatography (HT-SEC) coupled with a multi angle laser light scattering (MALLS) detector and differential scanning calorimetry (DSC) measurements. With increasing irradiation dose, a high reduction of molar mass and an increasing number of long chain branching is found. Compared to the irradiation in solid state, the modification in molten state leads to a higher degree of branching. The rheological experiments in elongation flow clearly exhibit existence of long chain branching. Furthermore, DSC

measurements show that glass transition temperature and peak temperatures of melting and crystallization decrease.

KEYWORDS

Poly(propylene) (PP), branched, electron beam irradiation, gel permeation chromatography (GPC), differential scanning calorimetry (DSC)

INTRODUCTION

Long chain branched polypropylenes 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 (LCB) in the linear polymer without using additives is the modification by electron beam irradiation. The irradiation at room temperature is described for example in [3-9]. The latter has a distinct influence on the rheological properties as for example elongational and shear viscosity, flow activation energy and melt elasticity [10,11]. LCB affects on the other hand strongly the molecular structure and the light scattering properties of the molecules respectively.

Influence of long chain branching on light scattering properties of the molecules

It is well known, that polymer molecules are fractionated by SEC according to their hydrodynamic volume. The size of a molecule depends on its molar mass and density in the dissolved state. Long chain branched molecules have more dense

structure than linear molecules at the same molar mass and the density depends on the number and the type of the branches. By coupling SEC with MALLS the molar mass M of every slice of the chromatogram can be determined absolutely without any calibration. Additionally, light scattering data give information about the mean square radius of gyration $\langle s^2 \rangle$ of the molecules concluding with respect to branching using theoretical considerations [12]. The ratio of the mean square radius of gyration of a branched polymer $\langle s^2 \rangle_{branch}$ to that of a linear polymer $\langle s^2 \rangle_{linear}$ is represented by g known as Zimm-Stockmayer's branching parameter [12].

$$g = \frac{\langle s^2 \rangle_{branch}}{\langle s^2 \rangle_{linear}} \quad (1)$$

The coil of a branched chain is more compact than a linear one of the same molar mass, thus this 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 [13]. For such a trifunctional randomly branched polymer, g is expressed in terms of the degree of branching as

$$g = \left[\left(1 + \frac{m}{7} \right)^{0,5} + \frac{4m}{9\pi} \right]^{-0,5} \quad (2)$$

with m as the number of branching points along the molecule.

Irradiation in molten state

It is known, that the formation of chain branching or cross linking is located mainly in the amorphous regions. The material in the molten state contains no crystalline regions. This leads to the conclusion that all chains are available for branching reactions [14]. Therefore the chance of chain branching during irradiation in the

molten state of the material is much higher than in the solid state. In solid state the branching reactions is limited by diffusion of chain fragments. Moreover, the thermal degradation of molecular weight at high temperature is enhanced [15].

The temperature dependence of irradiation induced reactions of polyethylene is described by Wu et. al. [15], Qu et. al. [16] and Dijkstra et. al. [17]. Already the irradiation of polyethylene at room temperature can leads to the formation of insoluble parts by cross-linking. The irradiation of PE in molten state more cross-linked substances are obtained. It was observed that an amount of gel up to 90% for low density polyethylene is possible [15].

EXPERIMENTAL

Materials

The isotactic polypropylene (iPP) homopolymer used in this study was the 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/cm³. The iPP films (thickness 0.5 mm) were lab scale manufactured by a conventional cast film extrusion processing.

Electron beam irradiation

The iPP film were irradiated with 1.0 MeV using the electron beam accelerator ELV-2 (Budker Institute of Nuclear Physics, Novosibirsk, Russia) as described in detail by Dorschner et al. [18]. For electron beam irradiation in molten state a special irradiation vessel (BG3) has been developed on which a rapid transfer of polymer film samples from solid to liquid/ melt state according industrial pellet melting processes and keeping a defined melt temperature during electron beam irradiation

is realizable [19]. The BG3 (Figure 1) includes a metal heating foil as polymer film sample support and a temperature sensor for temperature control. The heating procedure will be controlled by a special X-ray resistant infrared sensor (Raytech Corporation, Shelton, USA) and a self-designed temperature controlling equipment. The samples were located on the supporting heating metal foil between two 50 μm thick infusible and high radiation resistant polyimide films from KaptonTM type (DuPont, Bad Homburg, Germany) to ensure a close contact to the heating foil to facilitated the polymer melting process and otherwise to prevent unacceptable adherence. The time needed for transferring the polymer samples from the solid into the molten state is about 3-4 minutes. The electron beam irradiation was carried out at 25 °C and a melt temperature of 200 °C up to an irradiation dose of 100 kGy under air environment.

Characterization

Size exclusion chromatography

The molecular characterization of the polypropylene was carried out by high temperature size exclusion chromatography (HT-SEC). The instrument used was a PL-GPC220 (Polymer Laboratories Ltd., Shropshire, 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 μm pore diameter (Polymer Laboratories Ltd., Shropshire, 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 polypropylene. The calculations of the

molecular parameters (M_w , M_n , molar mass distribution, radius of gyration) were carried out from the SEC data using commercial software ASTRA 4.73 (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 1st heating – cooling - 2nd heating. The calibration of temperature and transition heat was done with 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 [20].

Wide angle X-ray scattering (WAXS)

The WAXS measurements were obtained by a 4-circle diffractometer P4 with an area detection system HiStar / GADDS (Bruker AXS GmbH, Karlsruhe, Germany) using $\text{CuK}\alpha$ radiation.

Rheological measurements

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 of University Erlangen-Nürnberg and has been described in detail by Münstedt et al. [21,22]. 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 s⁻¹ and 0.3 s⁻¹.

The tensile stress growth coefficient or elongational viscosity is obtained from the measured tensile stress divided by the applied constant strain rate:

$$\eta_E^+(t, \dot{\epsilon}_0) = \sigma(t, \dot{\epsilon}_0) / \dot{\epsilon}_0 \quad (3)$$

RESULTS AND DISCUSSION

Size exclusion chromatography

The molecular characterization of polypropylene included the investigation of molar masses and radii of gyration. The weight average molar mass as function of irradiation dose is plotted in Figure 2. As expected, a molar mass degradation takes place subject to the irradiation dose. This is also illustrated by differential molar mass distribution of samples irradiated at 200 °C in Figure 3. A high molar mass degradation takes place, especially in the high molar mass amounts. The irradiation at 200 °C leads to higher molar mass degradation compared to the irradiation at 25 °C. This is observed especially at higher irradiation dose. It is assumed that the thermal degradation plays an important role by the irradiation in molten state.

Another question is the forming of chain branching. Therefore, the dependence of the mean square radius of gyration $\langle s^2 \rangle$ on the molar mass for the initial isotactic polypropylene (iPP) and different irradiated samples is shown in Figure 4. It is found, that the mean square radius of gyration for macromolecules at the same molar mass significant decreased for these samples. This deviation of the mean square radius of gyration is an indication of increasing coil density with increasing irradiation dose, which can be related to the formation of long chain branching.

Additional, the comparison of degree of branching for the irradiation at 25 °C and 200 °C is illustrated in Figure 4. In the case of 20 kGy, the irradiation at 200 °C leads to a higher decrease of radius of gyration compared with the irradiation at 25 °C. Furthermore, the radius of gyration for the sample irradiated at 60 kGy (25 °C) is higher than the radius of the sample irradiated at 20 kGy (200 °C). It is observed that the irradiation in molten state generated generally a lower radius of gyration or a higher degree of branching, respectively, compared to irradiation in solid state at the same irradiation dose. That means, the irradiation in molten state is more effective with respect to formation of long chain branching.

For the samples irradiated at 200 °C with higher dose than 40 kGy this interpretation in regard to long chain branching is not possible. An overlay of mean square radii of gyration and differential molar mass distributions in dependence on molar mass is shown in Figure 5. With increasing irradiation dose up to 100 kGy a significant molar mass degradation is observed. The amount of high molar mass molecules is decreased followed by a very strong scattering of calculated radii. The deviation of mean square radius of gyration and molar mass in high molar mass areas 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 of the chromatographic separation the concentrations of the polymer solution is presumably not sufficiently high for a correct interpretation of their light scattering properties and the calculation of their molar mass and mean square radius of gyration, respectively. Therefore, a quantitative statement of long chain branching is not made for samples irradiated higher than 40 kGy. But compared to irradiation at room temperature [7], an increasing of long chain branching is assumed. The knowledge of interplay of both competitive processes, formation of long chain

branching and molar mass degradation, is the key to a successful modification in regard to LCB. With increasing the irradiation dose in molten state the chain branching becomes more and more important. It is observed that the degree of branching is higher than irradiation in solid state. No changes of molar mass and radius of gyration is found if the polypropylene is heated up to the molten state without irradiation [23].

Differential scanning calorimetry

The characteristic temperatures of melting and crystallization were determined using the peak temperatures (melting T_m , crystallisation $T_{c,m}$), and the extrapolated onset temperature of the crystallization ($T_{c,o}$) (see Figure 6). The glass transition temperatures (T_g) were calculated from the 2nd heating run.

The irradiation results in long chain branching and molar mass degradation. The thermal behaviour of long chain branching in PP is expected to be comparable to that of the linear main chain because of the ability to crystallize. The overall crystallinity in the irradiated PP films was about 50% independent of the dose (see Table 1). The second process of degradation causes a change in the transition temperatures. Peak temperatures (T_m , $T_{c,m}$) as well as the extrapolated onset temperature $T_{c,o}$ decrease with increasing dose (see Figure 6). The temperature difference between $T_{c,o}$ and $T_{c,m}$ as a measure of crystallization rate is unchanged. Although the glass transition temperature T_g only varied by 4 K, the tendency is clear, the higher the dose the lower T_g .

Another aspect is the shape of the melting peak. With increasing dose multiple melting peaks are observed in the DSC curves. From WAXS experiments the formation of a β -modification could be excluded (see Figure 7). The origin of this

behaviour should be a result of melting and reorganization during heating. This phenomenon is already discussed for a long time. The difficulty is the high recrystallization rate of the material. That means high heating rates are necessary to prevent the reorganization during heating. Minakov et al. [24] investigated this process in PET using the combination of the results on a common DSC, Hyper DSC™ and a chip calorimeter to reach high heating rates. In Figure 8 the 2nd heating runs of PP irradiated with 100 kGy as example are plotted. For comparison the normalized heat flow is related to the heating rate. The lower melting peak temperature shifts how expected to higher values with increasing heating rate. The higher melting peak temperature as result of the reorganization shifts to lower values and is diminished at 80 K/min.

Rheology

Elongational flow experiments are a sensitive tool for the investigation of long chain branching, too. The occurrence of strain hardening is related to long chain branching, if other reasons as high molar mass components or a very broad molar mass distribution can be excluded. For linear polypropylenes no strain hardening was reported in literature and this was observed for the untreated iPP, too (Figure 9). The samples irradiated with 10 kGy at 200 °C show strain hardening, which increases at lower strain rates (see Figure 9). The strain rate dependence of randomly branched polyolefins was found to be characteristic for different molecular structures [25]. This behaviour was typically found for PE [25-27] and PP [8] with a small amount of long chain branching.

CONCLUSIONS

The electron beam irradiation of polypropylene in molten state is an additional way to create long chain branching without additives. In results of chromatographic measurements it could be detected a deviation of mean square radius of gyration between initial and irradiated samples. The rheological measurements in elongation flow confirmed the presence of long chain branching. With increasing the irradiation dose different effects are observed. As expected, a high molar mass degradation takes place. The samples irradiated at 200 °C are lower molecular than the samples irradiated at 25 °C. It is found, that the degree of long chain branching is increased. The comparison between the modification in the molten state and in the solid state leads to the conclusion that irradiation at 200 °C generated higher branched samples. Additionally, the DSC measurements have shown that a decreasing of melting peak temperature T_m , maximum crystallisation temperatures $T_{c,m}$, extrapolated onset crystallisation temperatures $T_{c,o}$ and glass transition temperature T_g occurs.

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FIGURE CAPTIONS

Figure 1: Irradiation vessel BG3 for electron beam irradiation of polymer films in molten state

Figure 2: Weight average molar mass M_w in dependence on irradiation dose d for the initial iPP and the irradiated samples at 200 °C and 25 °C.

Figure 3: Differential molar mass distribution for the initial iPP and the irradiated samples at 200 °C.

Figure 4: Mean square radius of gyration $\langle s^2 \rangle$ in dependence on molar mass M for the initial iPP and the irradiated samples up to 40 kGy at 200 °C and 25 °C.

Figure 5: Overlay of mean square radius of gyration $\langle s^2 \rangle$ and differential molar mass distribution in dependence on molar mass M for different irradiated samples with 40 kGy and 100 kGy at 200 °C.

Figure 6: Peak temperatures (melting T_m , crystallisation $T_{c,m}$) and the extrapolated onset temperature of PP crystallization ($T_{c,o}$) in dependence on irradiation dose for the initial iPP and the irradiated samples at 200 °C.

Figure 7: WAXS curves of sample irradiated with 100 kGy at 200 °C.

Figure 8: Melting (2nd heating) in dependence on heating rate for the samples irradiated with 100 kGy at 200 °C.

Figure 9: Elongational viscosity $\eta_E^+(t)$ in dependence on time t and different Hencky strain rates $\dot{\epsilon}_0$ at 180 °C for the initial iPP and the sample irradiated with 10 kGy at 200 °C.

TABLES

Table 1: DSC data of cooling and the 2nd heating run of PP films in dependence on irradiation dose

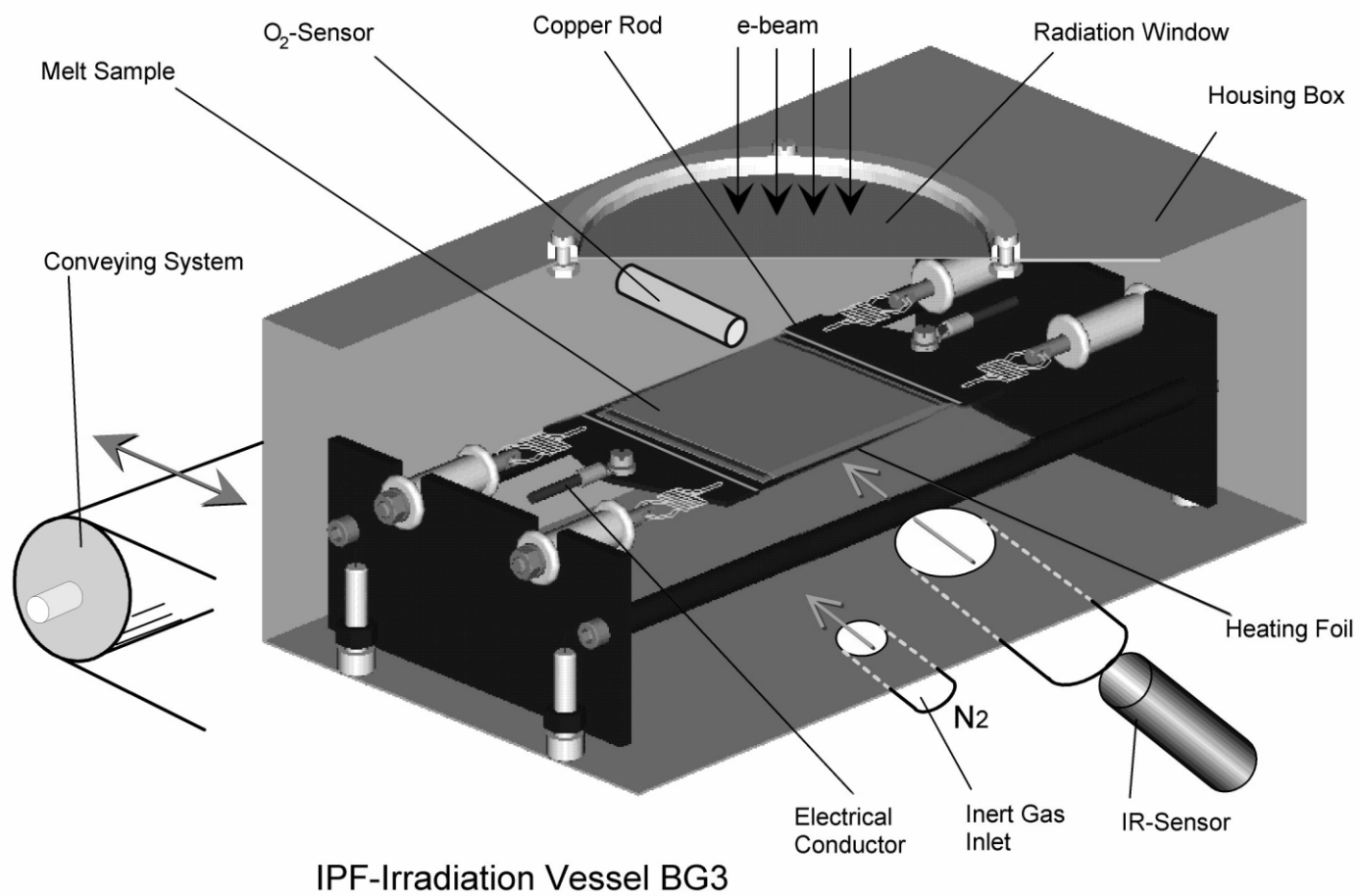


Figure 1

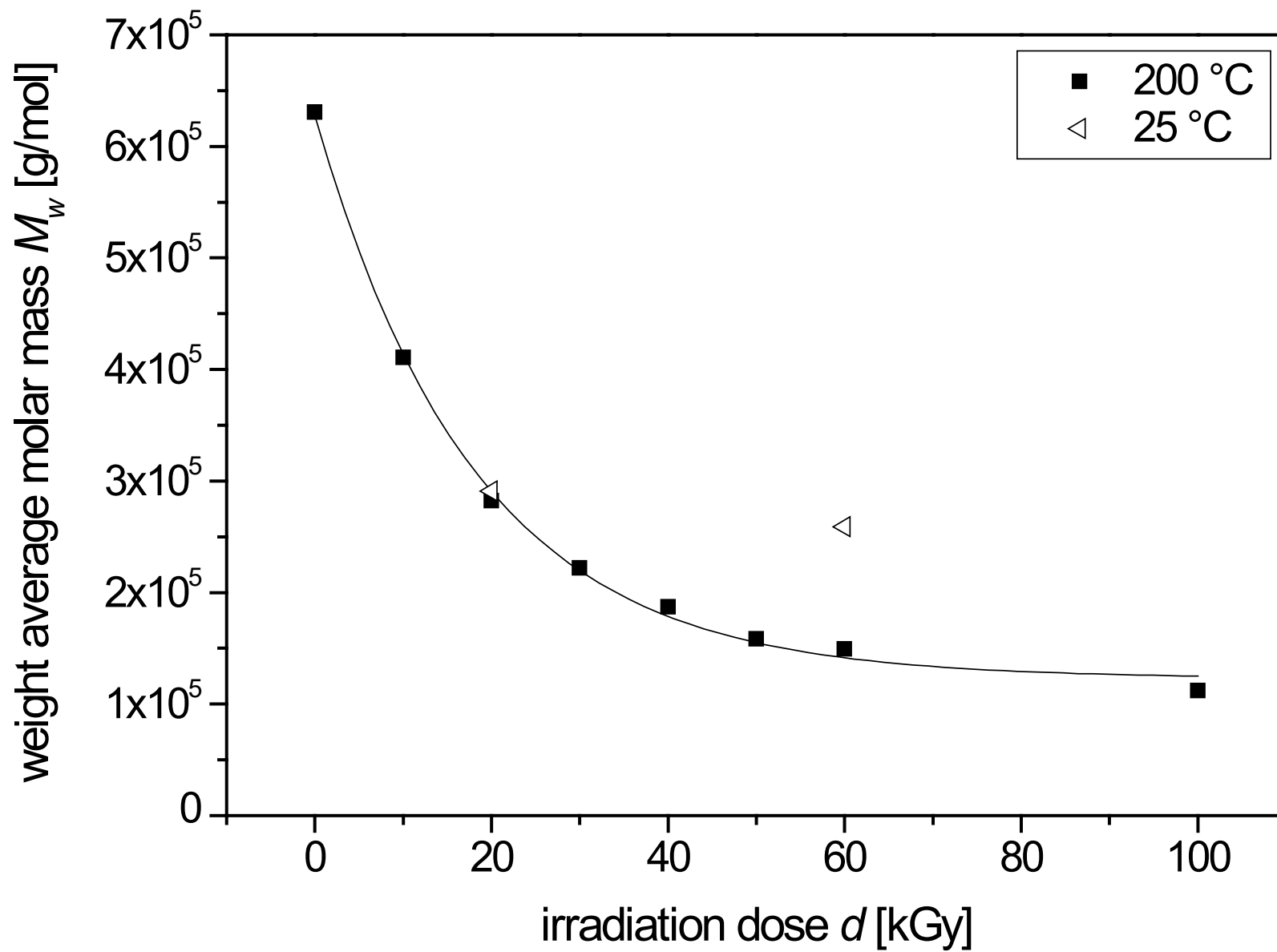


Fig 2

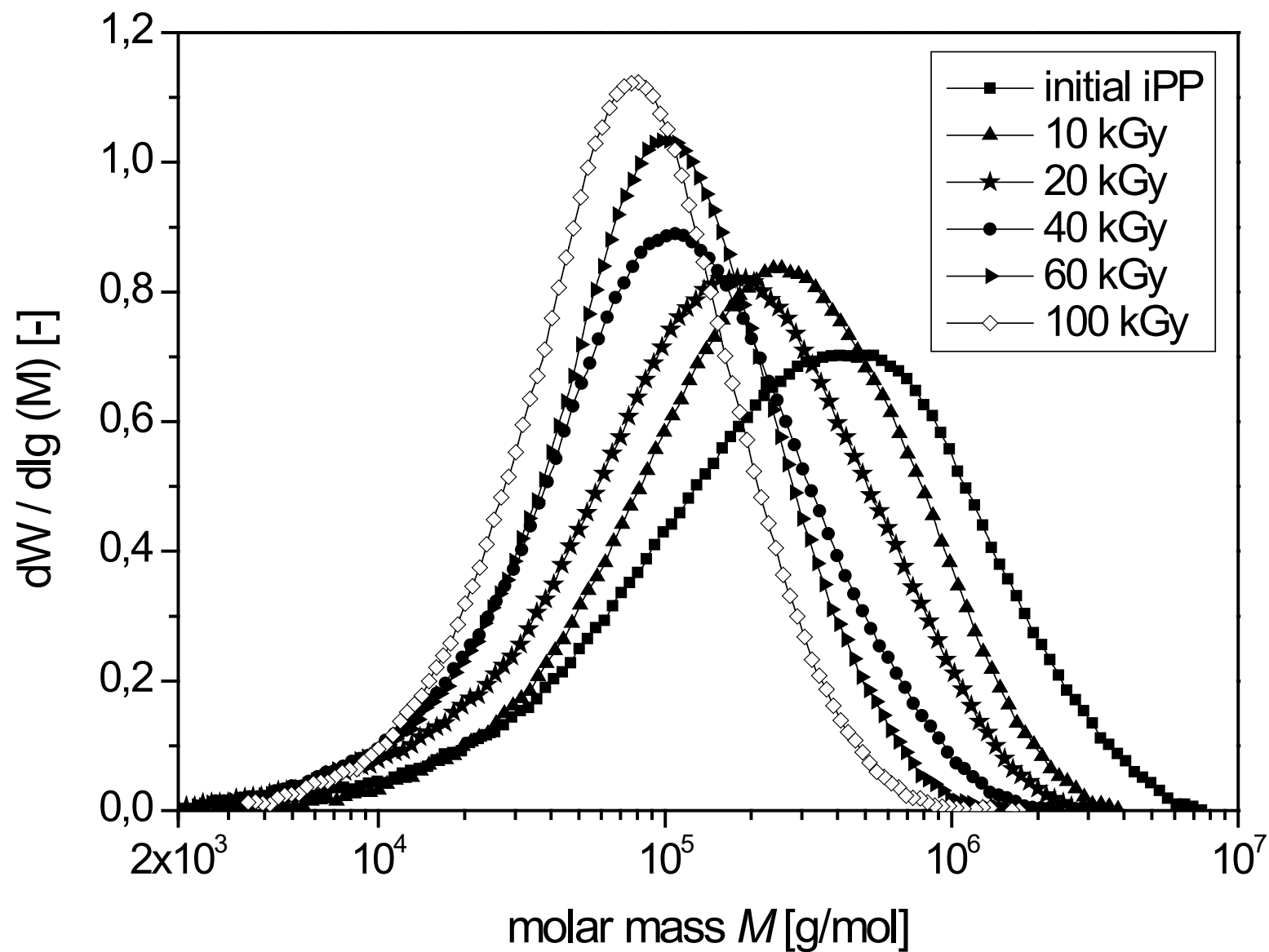


Fig 3

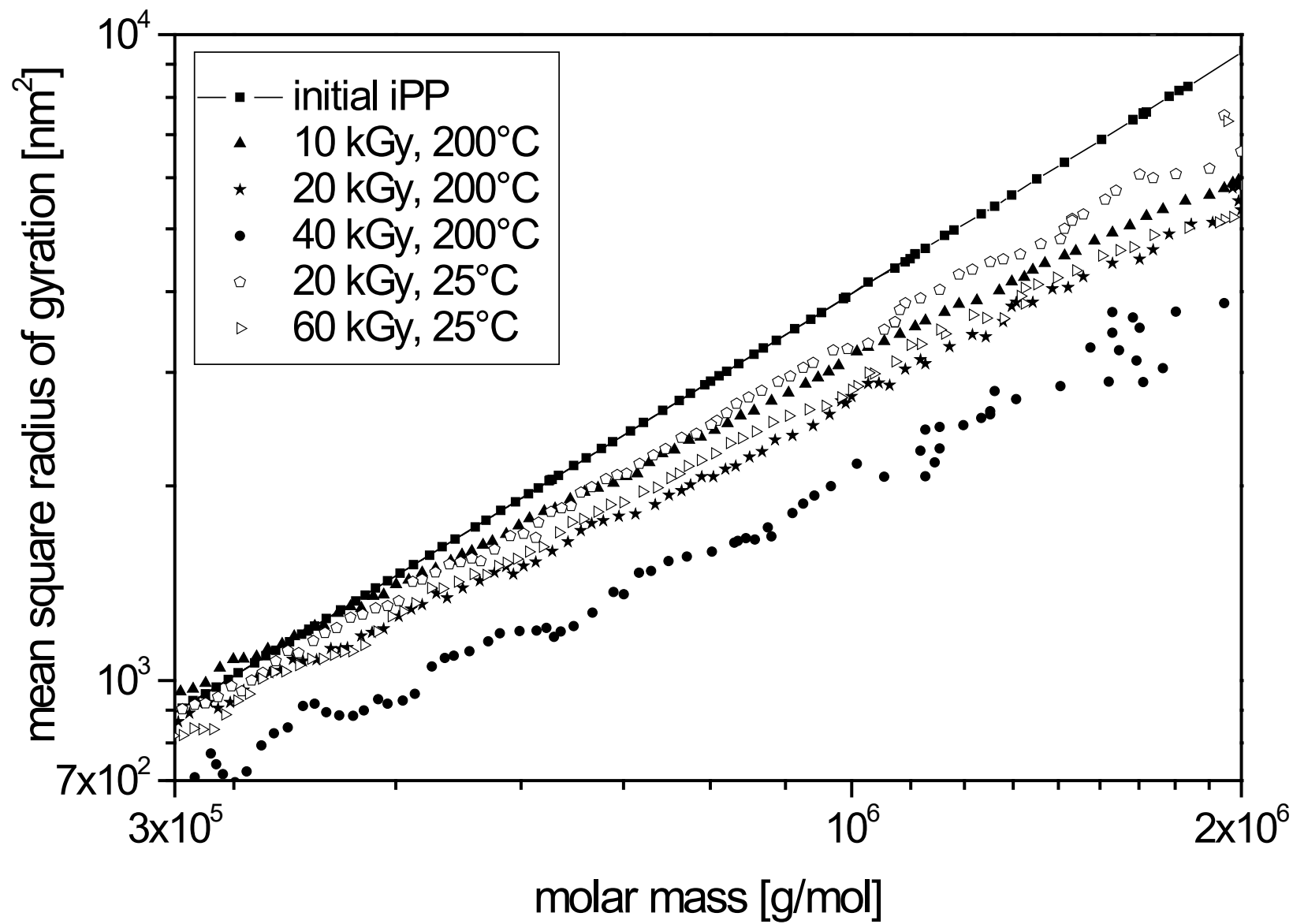


Fig 4

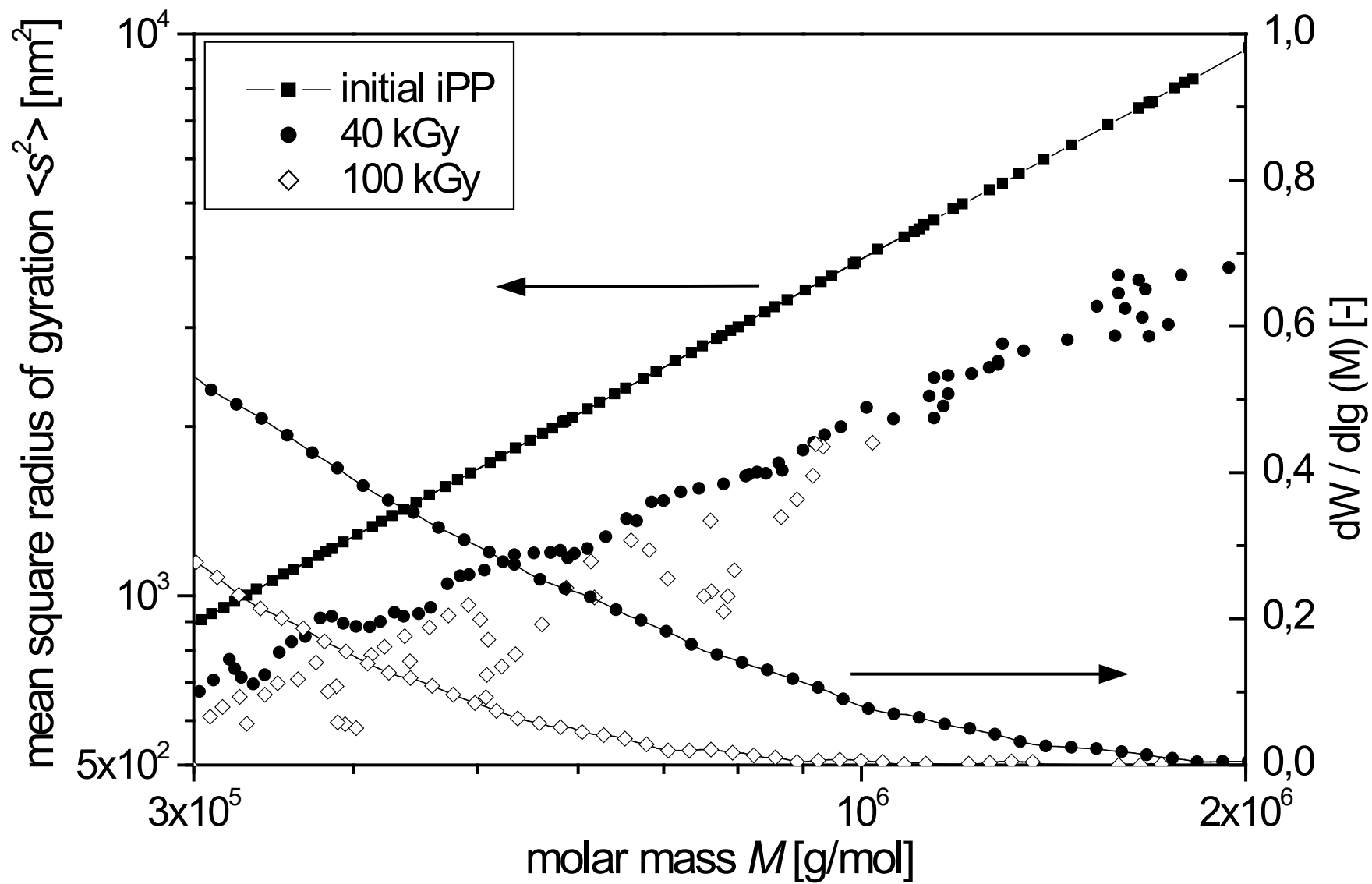


Fig 5

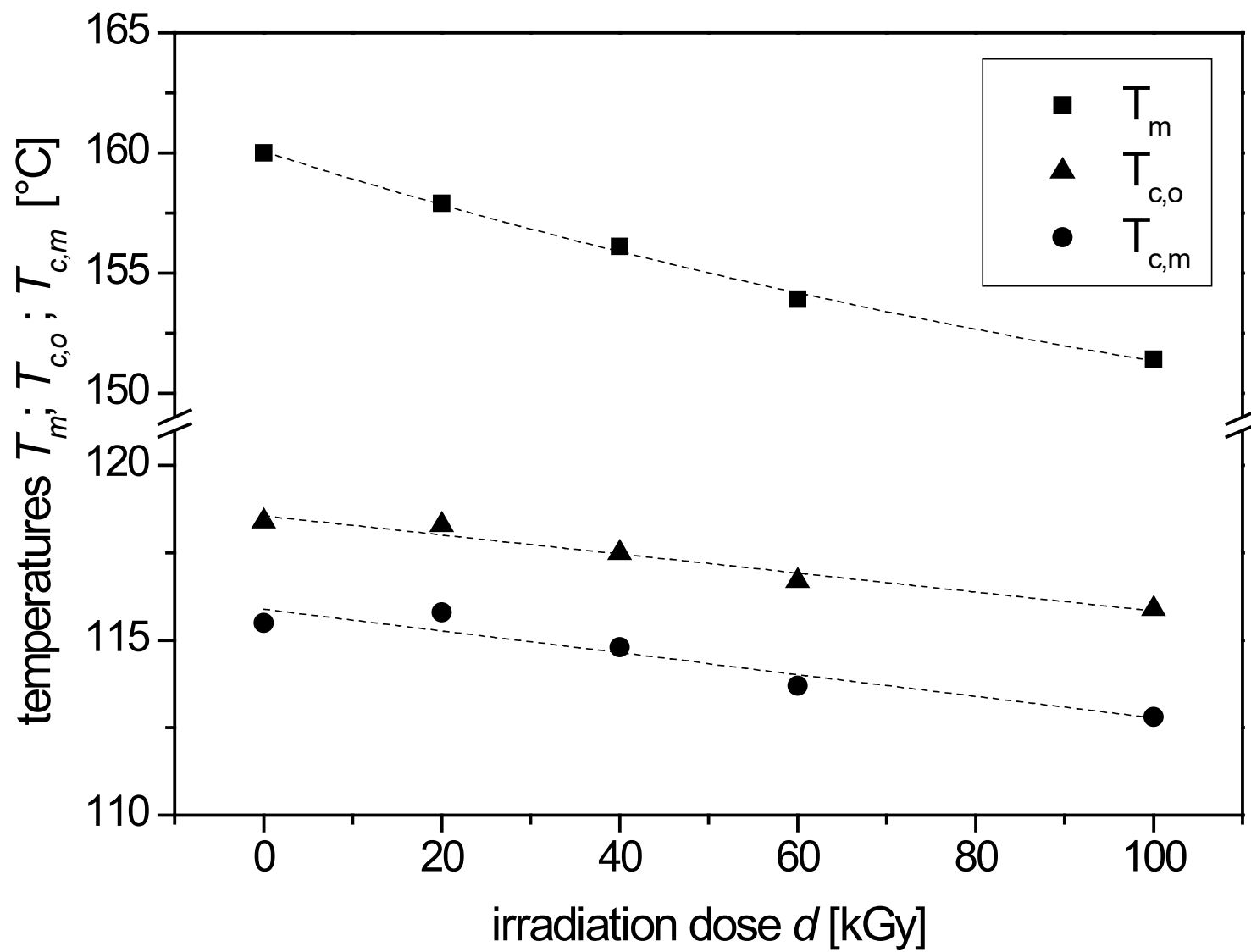


Fig 6

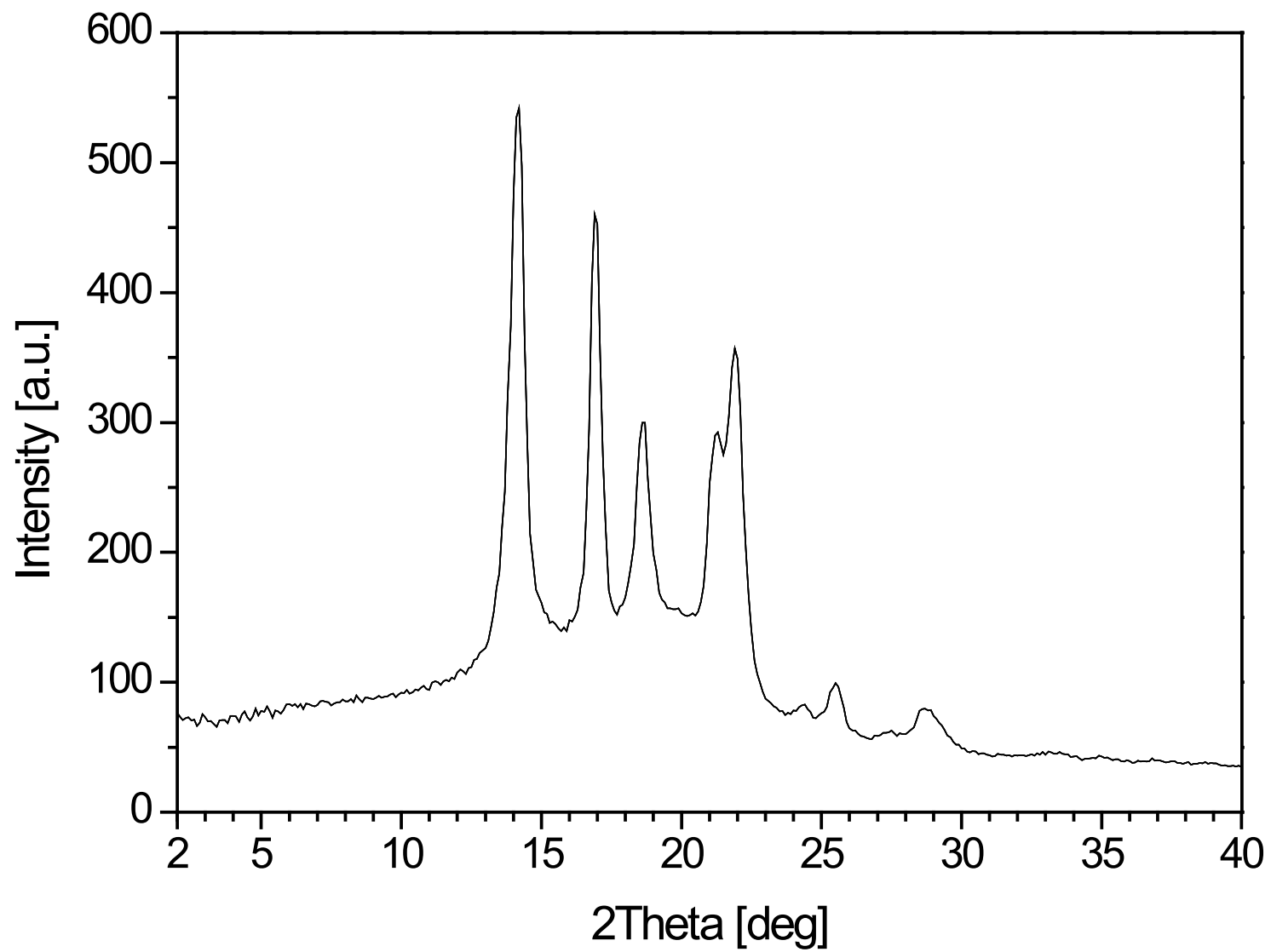


Fig 7

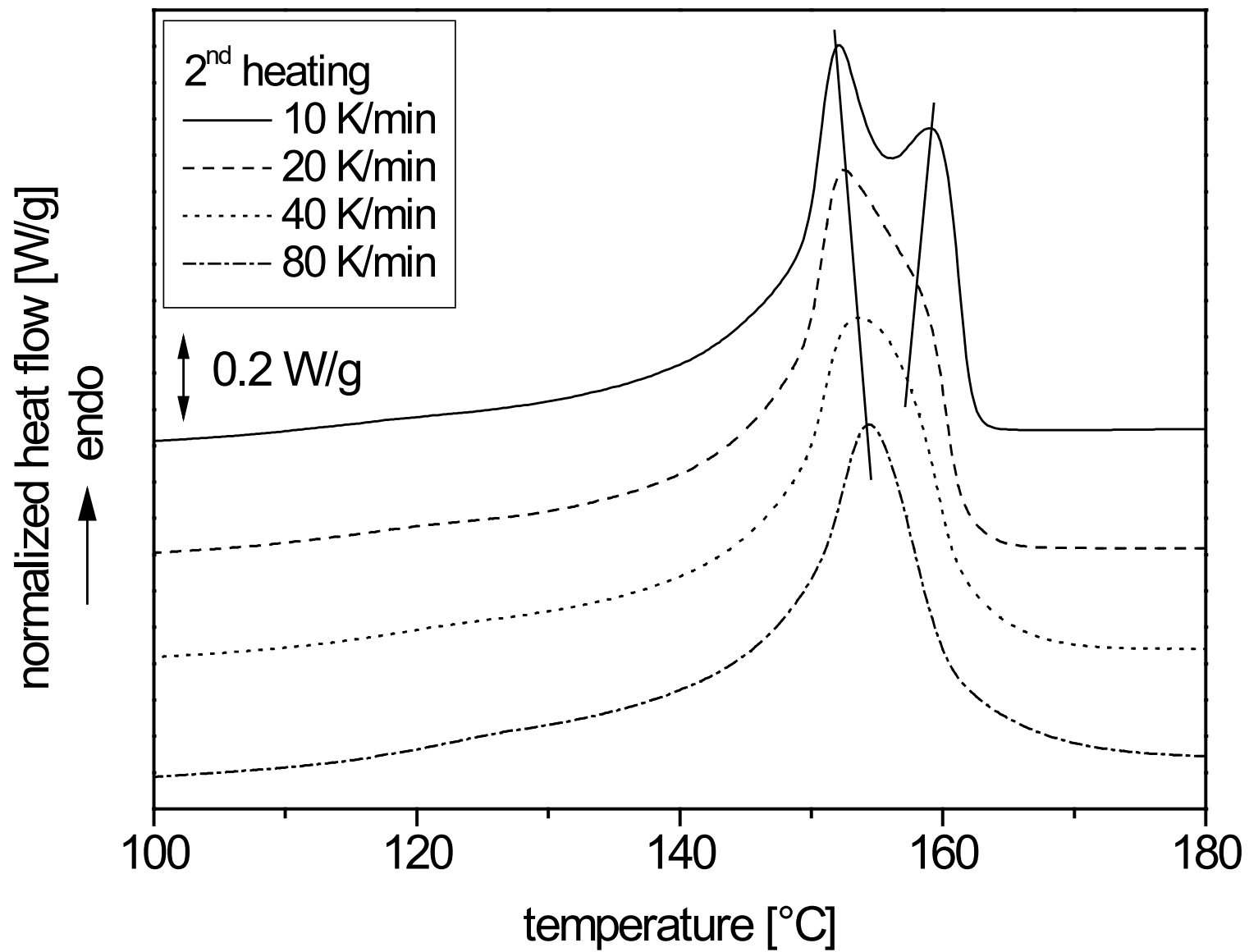


Fig 8

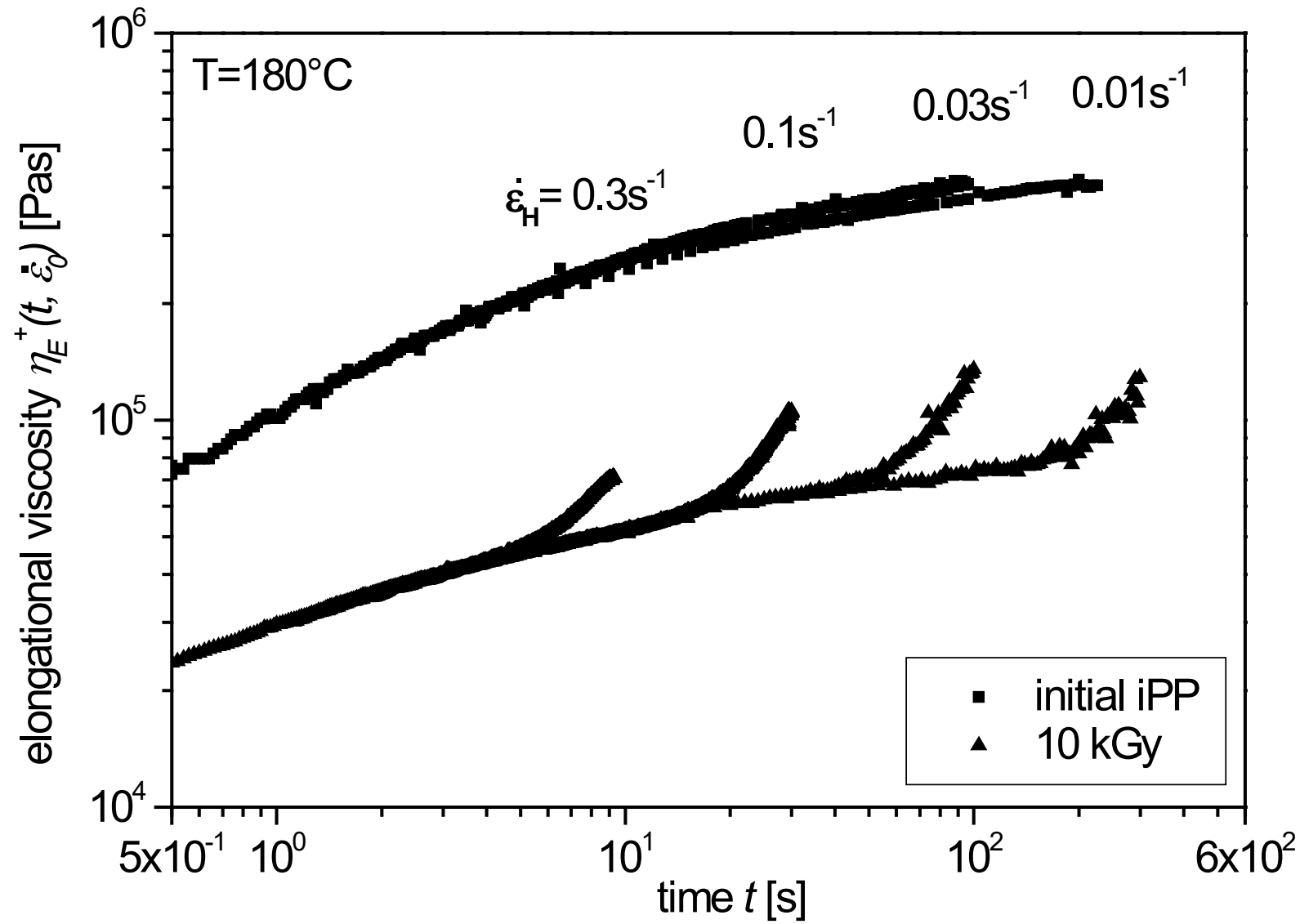


Fig 9

TABLES

Table 1

Irradiation dose d [kGy]	Glass transition temperature T_g [°C]	Melting enthalpie ΔH_m [J/g]	Crystal- linity α [%]	Melting peak temperature T_m [°C]	Maximum crystallisation temperature $T_{c,m}$ [°C]	Extrapolated onset crystallisation temperature $T_{c,o}$ [°C]
0	-7,7	100,9	49	160,0	115,5	118,4
20	-7,6	103,8	50	157,9	115,8	118,3
40	-8,5	104,3	50	156,1	114,8	117,5
60	-9,1	103,7	50	153,9	113,7	116,7
100	-11,0	101,6	49	151,4	112,8	115,9