

**COMPARISON OF THE MOLECULAR PROPERTIES AND MORPHOLOGY FOR
POLYPROPYLENE IRRADIATED AT DIFFERENT ATMOSPHERE AND POST
ANNEALING**

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Comparison of the molecular properties and morphology for polypropylene irradiated at different atmosphere and post annealing

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SYNOPSIS

The electron beam irradiation as a well known way to generate long chain branching was used to modify polypropylene (PP). The samples were investigated by differential scanning calorimetry (DSC), polarized light microscopy (PLM) and size exclusion chromatography (SEC). It was found, independent of the atmosphere the post annealing lead to the deactivation of residual radicals and to the reduction of nuclei density. In comparison to the initial PP, the crystallisation temperatures of the non-annealed samples increase but decrease for the annealed samples. Stable products only were obtained by irradiation in nitrogen followed by annealing. The reaction of including free radicals with oxygen at the ambient atmosphere leads to increasing of molar mass degradation and formation of long chain branching after storage.

KEYWORDS

Poly(propylene) (PP), branched, electron beam irradiation, differential scanning calorimetry (DSC), spherulites

INTRODUCTION

Since the investigations of Charlesby [1] it is well known that the interaction of electrons with polymeric materials produces free radicals. The main molecular effects are chain scission followed by molar mass degradation, chain branching and crosslinking. Usually, all these reactions take place simultaneously and depend on different parameters, such as chemical structure and morphology of the polymer as well as the irradiation conditions including post treatment [2,3].

One way to create long chain branching (LCB) in the linear polypropylene without using additives is the modification by electron beam irradiation as described by DeNicola et al. [4-6]. The influence of irradiation dose on the formation of long chain branching in polypropylene is investigated by Auhl et al. [7]. Long chain branched polypropylene 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 [8,9].

The formation of oxidation products caused by irradiation in the presence of air is described by different authors [10-16]. Firstly, the formation of hydroperoxide in the macromolecules is observed. Secondly, these meta products reacted to final products containing oxygen, for example ketones or esters. These reactions lead to oxidative degradation with respect to molar mass.

In different patents by Scheve et al. [17] and DeNicola et al. [4-6] is described that the material should be annealed after the irradiation. The first annealing step at about 80 °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.

The irradiation influences the supermolecular structure, too. Aggregates of chain folded fibrillar or lamellar primary crystallites with definite geometrical arrangements are designated supermolecular structure (SMS). The types and structural features of formed SMS are markedly influenced e. g. by the thermal conditions of crystallisation or presence of crystal

nuclei. SMS of iPP may be readily visualized by polarized light microscopy (PLM). Spherulite is a spheriform cluster of primary crystallites with spherical symmetry. Crystallites start from a central nucleus and uniformly grow in all spatial directions, radially, with noncrystallographic small angle branching in between. A spherulite can be considered an optically uniaxial crystal. Therefore, the PLM of a spherulite show a dark central cross (maltese cross) with wings coincident with the respective plans of polarizer and analyser [18].

It is well known, that polymer molecules are fractionated by 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 a multi angle laser light scattering (MALLS) detector 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. Conclusions with respect to trifunctional randomly branching can be drawn using theoretical considerations [19,20]. The method detailed is described by Krause et al. [21].

EXPERIMENTAL

Materials. The isotactic polypropylene (iPP) homopolymer used in this study was Novolen PPH2150 (Basell Polyolefins Company N.V., Hoofddorp, The Netherlands). The weight average molar mass was calculated with 670000 g/mol. According 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.

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. [22].

The irradiation was carried out at atmospheric pressure in a special vessel [23]. The samples were irradiated with doses of 100 kGy. The annealing after the irradiation process was performed for 30 min at 80 °C and for 60 min at 130 °C in the vessel, too.

Characterization.

Size exclusion chromatography

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 MALLS detector (DAWN EOS, Wyatt Technology Corporation, Santa Barbara, USA). The column set consisted of 2 columns PL Mixed-B-LS (Polymer Laboratories Ltd., Church Stretton, UK). The flow rate was 1 ml/min. The eluent was 1,2,4-trichlorobenzene (Merck KGaA, Darmstadt, Germany).

Differential scanning calorimetry

The DSC measurements were performed on a Q1000 (TA-Instruments, New Castle, USA) coupled with an autosampler in the temperature range of –60 °C to 210 °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 glass transition temperatures were calculated from the 2nd heating run using the half step method, and the crystallinity using the value of 207 J/g for 100% crystalline PP [24].

Polarized light microscopy (PLM)

The samples were heated up to 200 °C and cooled in vacuum. These samples were cut with Mikrotom Leica 2055 (Leica Mikrosysteme Vertrieb GmbH, Bensheim, Germany) to a piece with a thickness of 10 μm and were fixed with Entellan® (Merck KGaA, Darmstadt,

Germany) on glass plates. The optical observations of the spherulite in the samples were performed with a polarizing transmitted light microscope ZEISS AXIOPLAN 2 (Carl Zeiss AG, Oberkochen, Germany). The image were captured using a microscope camera AVT-BC12 (AVT-Horn, Aalen, Germany) and OPTIMAS 6.5 (Optimas Corporation, Washington, USA).

RESULTS

In the present work, the influence of different irradiation conditions (irradiation atmosphere, annealing after the irradiation process) on the molecular parameters was investigated.

Four samples were modified at 100 kGy:

- I: irradiation in nitrogen with annealing
- II: irradiation in nitrogen without annealing
- III: irradiation in air with annealing
- IV: irradiation in air without annealing

As expected, the irradiation of polypropylene led to a molar mass degradation [7] and would be observed for all four variants. But the degrees of degradation were different. Figure 1a shows the cumulative molar mass distribution of initial iPP and the modified polypropylene directly after the irradiation. It was found that the molar mass of the sample I > sample III > sample II > sample IV. It can be seen the molar mass of the annealed samples was higher than the non annealed analogies. The sample irradiated in nitrogen showed higher molar masses than alike sample modified in air.

Additionally, the determinations were performed after storage of more than one year by SEC. The modified products were stored in the refrigerator at 5 °C. Figure 1b shows the cumulative molar mass distribution of initial iPP and the modified polypropylene after the storage of 19 month. It was found that the molar mass of the sample I > sample III >

samples II and IV. No significant differences in molar masses were obtained for samples without annealing (II, IV).

Figure 2 shows the trend of weight average molar mass for all samples. Only the sample I, which was irradiated in nitrogen atmosphere followed by annealing, become stable during storage. No changes in the molecular properties within more than one year could be observed by SEC. In contrast, all other products have a lower molecular stability. The samples irradiated in nitrogen (Sample II) showed a molar mass degradation during storage of 8%. The irradiation in air with (Sample III) or without (Sample IV) annealing led to products followed by degradation about 4-6 %.

Long chain branching could be detected by decreasing of the mean square radius of gyration at the same molar mass. As expect, all samples shows a decrease of radius of gyration [7] (see Figure 3). Directly after the irradiation, the degree of long chain branching was nearly the same (see Figure 3a). In contrast to that the degree of long chain branching was changed during storage. The sample I shows the highest mean square radius of gyration at the same molar mass (see Figure 3b). In comparison the three other samples possess a lower mean square radius of gyration at the same molar mass. That means that during the storage an additional formation of long chain branching took place.

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 ($T_{c,o}$).

The irradiation at 100 kGy results in molar mass degradation and long chain branching in dependence on irradiation conditions. The thermal behaviour of long chain branching in PP is excepted to be comparable to that of the linear main chain because of the ability to crystallize. The over all crystallinity α in the irradiated samples without annealing (49%) was somewhat higher than in the samples with annealing (about 46%) (see Table 1).

The melting peak temperature T_m decrease after irradiation at 100 kGy compared to the initial material which correlated with molar mass degradation. The melting peak temperature

T_m of irradiated samples is independent of irradiation conditions (see Table 1). The glass transition temperature T_g was nearly unchanged (see Table 1).

The maximum crystallisation temperatures $T_{c,m}$ as well as the extrapolated onset crystallisation temperature $T_{c,o}$ changed with different irradiation conditions (see table 1, Figure 4). It was found that both crystallisation temperatures in comparison to initial iPP decrease up to 2 K for the samples with annealing (Samples I, III) and increase up to 4 K for the samples without annealing (Samples II, IV). The difference of both crystallisation temperatures for variation of annealing was found to be 6 K. The irradiation atmosphere was irrelevant to the crystallisation temperatures. The temperature difference between $T_{c,o}$ and $T_{c,m}$ as a measure of the crystallization rate is unchanged.

Figure 5 shows the images of polarized light microscope of all samples. The spherulites in initial iPP had average diameter about 60 μm . The samples without annealing (Samples II, IV) contained minimum spherulites and show a fine grained structure. In contrast, the samples with annealing (Sample I, III) showed spherulites up to 120-150 μm diameter.

DISCUSSION

After irradiation, the modified samples showed different molar masses. This can be explained by the different irradiation conditions.

On the one hand, the irradiation atmosphere plays an important role for the irradiation result. If air was present during irradiation than the radical of macromolecules induced by electron beam react with oxygen forming products containing oxygen. On the other hand, the annealing leads to the deactivation of substantially all residual free radicals. It seems to be possible that after the irradiation during the storage these residual radicals would react with the oxygen in air. The oxidative degradation of polymer take place up to all residual free radicals are trapped. It was assumed the formation of products containing oxygen takes place by the irradiation in air or during storage of irradiated products without annealing. Both methods of preparation lead to modified polypropylenes including oxidation products.

It was observed that the sample irradiated in nitrogen with annealing (sample I) were subjected to a lower molar mass degradation. Additionally, no significant changes of molecular properties during storage were observed. For this sample an influence of oxygen was not pointed out. By irradiation in air followed by annealing (sample III) the reaction with oxygen takes place only during the irradiation step. In comparison to irradiation in nitrogen followed by annealing (sample I) the molar mass of samples III after the irradiation was lower caused by oxidative reactions during irradiation. Both samples were annealed after the irradiation process. Therefore, this deviation is reasonable by additional oxidative degradation during irradiation.

The samples (II, IV) without annealing showed the lowest molar masses. During the storage a molar mass degradation takes place. The finally molar masses were nearly independent of irradiation atmosphere.

The reaction of radicals with oxygen takes place during the irradiation (sample III, IV) and during storage (samples II, IV). This results point out the important role of irradiation in absence of air and the realisation of a thermal post treatment for molecular stability. The molar mass degradation during storage is a hint for the influence of oxygen.

Another aspect that has to be highlighted is the influence of irradiation conditions on the formation of long chain branching. The macromolecules of all samples (II, III and IV) which undergo reactions with oxygen showed a more dense structure after storage. Independent of the detailed irradiation conditions the radii of gyration were decreased for these samples (compare Figure 3a and 3b). It was assumed that the macromolecules containing oxygen form additionally branched molecules. The total number of long chain branching was increased.

The investigation of crystallisation behaviour (Figure 4) showed a strong influence of irradiation conditions. It was found that the crystallisation temperatures $T_{c,m}$ and $T_{c,o}$ of samples with annealing (sample I, III) were 6 K lower in comparison to the samples without

annealing (sample II, IV). That means the annealing step have a very important influence on crystallisation behaviour of samples. The sample without annealing (sample II, IV) earlier crystallised which is advantageous for faster processing.

The great influence of annealing step was also observed by images of polarized light microscope. The samples without annealing (sample II, IV) show a fine grained structure. Obvious the formation of many stable crystal nuclei take place at high temperatures. This led to an increasing of crystallisation temperature up to 4 K. From the literature is known [25-27] the addition of nucleating agent to initial iPP leads to higher nuclei density. The resulting spherulites have minor size and the nucleated sample shows a higher crystallization temperature. The crystallisation of nucleated polypropylene turned into heterogeneous nucleation. Additional stable crystal nuclei of PP are formed on the nucleating agent surfaces. This leads to an increasing of crystallization temperature from 111 °C up to 129 °C [26]. Kim et al. [27] found for the addition of nucleating agents a maximal increase of crystallisation peak temperature up to 17 K.

In contrast it was found, the samples with annealing showed great spherulites with low nuclei density. Therefore, the crystallisation was more homogeneous and the crystallisation temperatures were lower. That means the annealing step reduced the crystal nuclei density.

CONCLUSION

The investigations of irradiation of polypropylene without additives at different atmosphere and annealing step have shown different products were formed. It was observed that the irradiation conditions the final molecular properties strongly influenced.

The irradiation of PP in nitrogen with annealing leads to product with smaller degradation of molar mass after the irradiation. Only this sample was stable during storage more than one year. It is generated a storage stable product with lower degree of long chain branching and lower crystallisation temperatures.

In all other cases the reaction with oxygen led to higher molar mass degradation after the irradiation and an additional degradation during storage. These three samples include

products containing oxygen. The modification without annealing step generated samples including free radicals. These residual radicals were reacted during storage. Therefore, these samples were instable during storage. Furthermore, long chain branched polypropylene were obtained with a higher degree of long chain branching after storage. It can be concluded that the reactions of free radicals with oxygen not only leads to molar mass degradation but also to the formation of long chain branching. Therefore, the products containing oxygen contribute to increasing the coil density of macromolecules.

Furthermore, the annealing step after the irradiation at 100 kGy strongly influenced the crystallisation behaviour of the irradiated samples. The samples with annealing showed great spherulites and the crystallisation temperatures were lower. In contrast, the samples without annealing crystallized at higher temperatures in comparison to initial iPP and samples with annealing. This behaviour is favoured for faster industrial processing. The images of polarized light microscope of these samples showed a fine grained structure. This leads to the conclusion that the annealing step not only advantageous the formation of long chain branching by reaction and deactivation of residual free radicals but also the number of crystal nuclei is reduced.

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Figure chapter

Figure 1: Cumulative molar mass distribution of the initial PP and the samples irradiated at 100 kGy. a) Directly after irradiation and annealing process. b) After storage.

Figure 2: Weight average molar mass of irradiated PP $M_{w(irrad.)}$ divided by weight average molar mass of initial PP $M_{w(initial)}$, before and after storage.

Figure 3: Mean square radius of gyration $\langle s^2 \rangle$ in dependence on molar mass M of the linear initial PP and the samples irradiated at 100 kGy. a) Directly after irradiation and annealing process. b) After storage.

Figure 4: Crystallization behaviour of the initial iPP and the samples irradiated at 100 kGy after storage.

Figure 5: Polarized optical micrographs of PP after storage a) initial PP, b) sample I, c) sample II, d) sample III, e) sample IV. (Identical sample preparation)

Table chapter

Table 1: DSC data of cooling and the 2nd heating run of PP in dependence on irradiation condition at 100 kGy after storage.

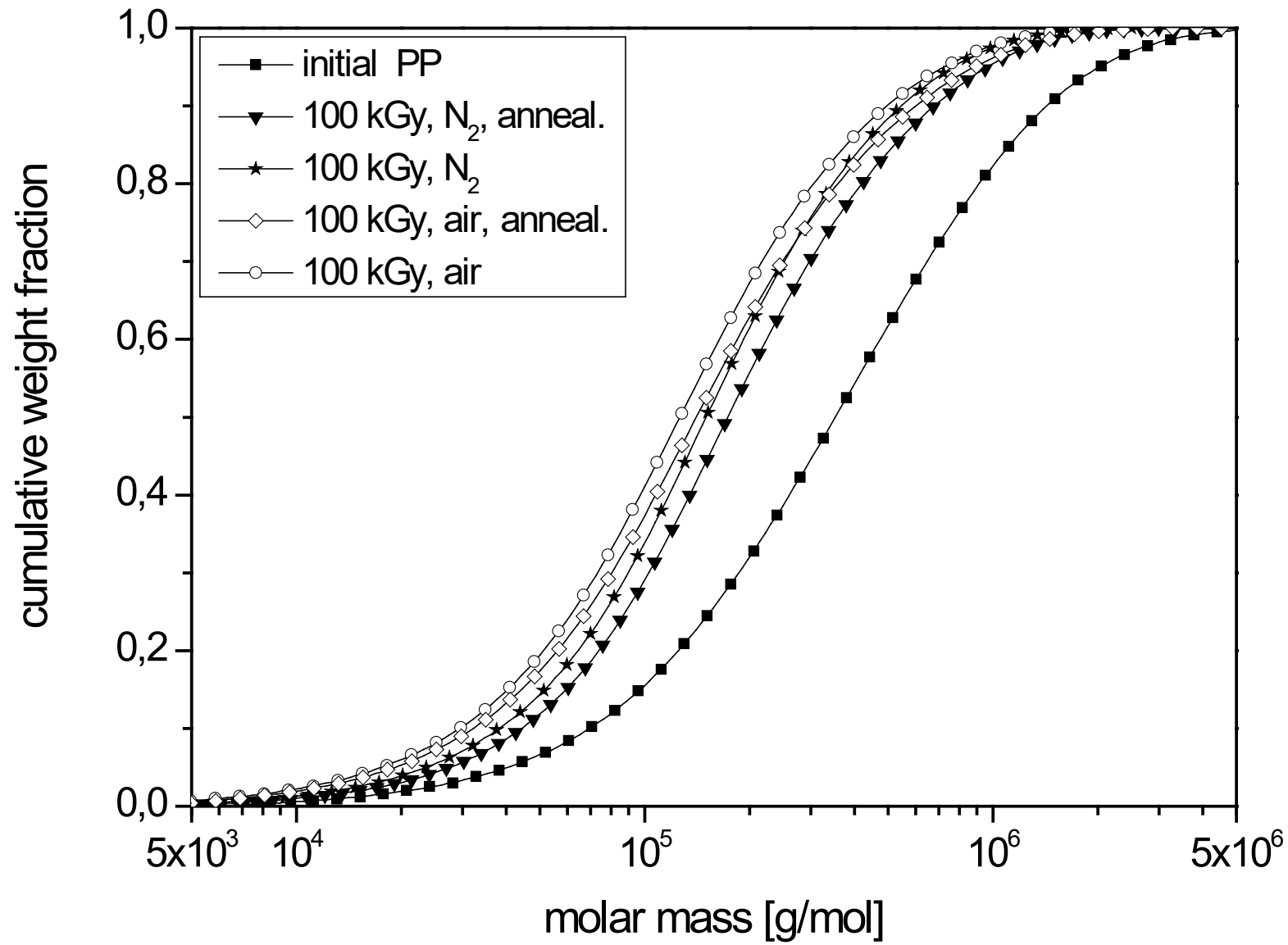


Figure 1a

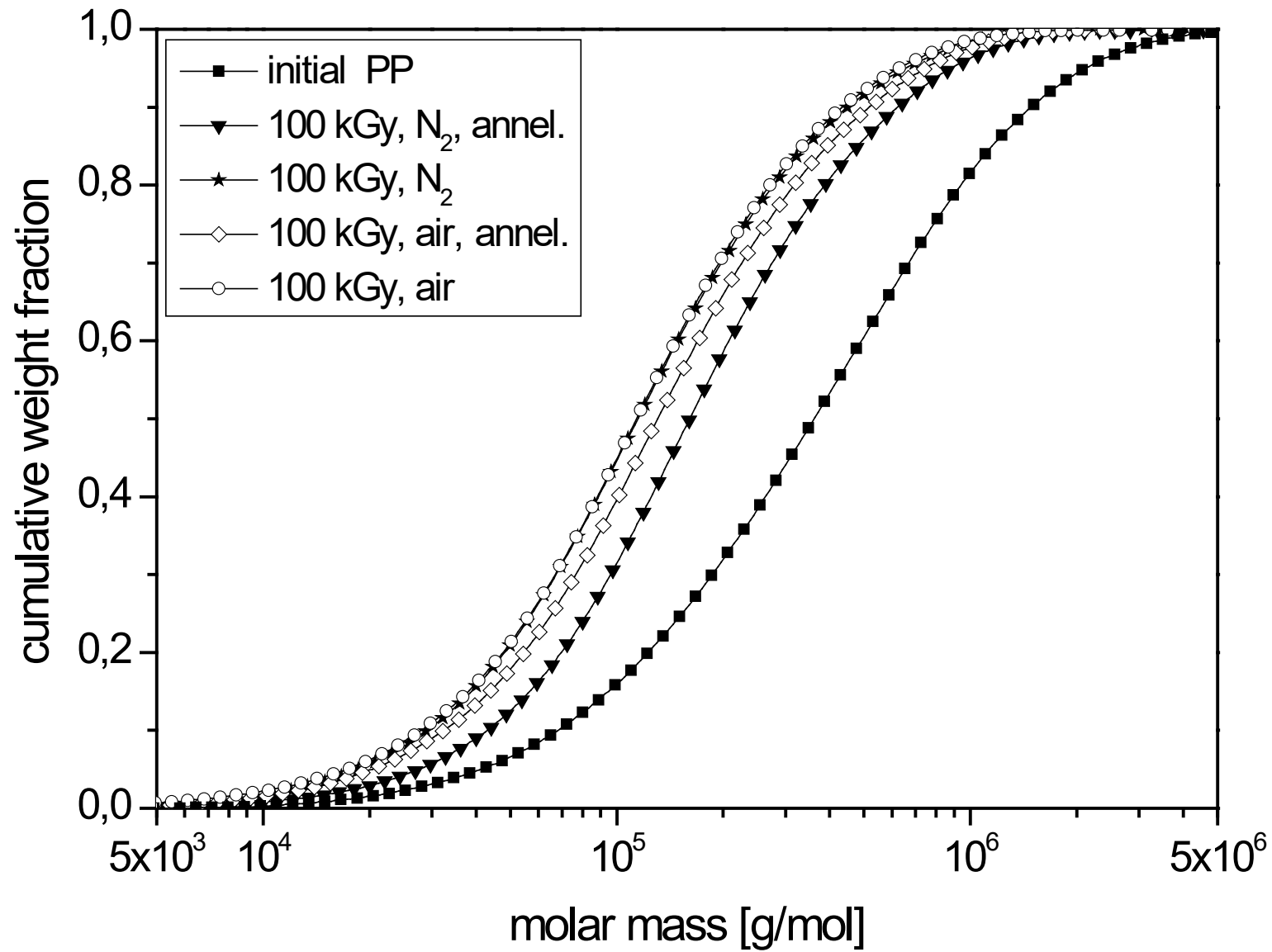


Figure 1b

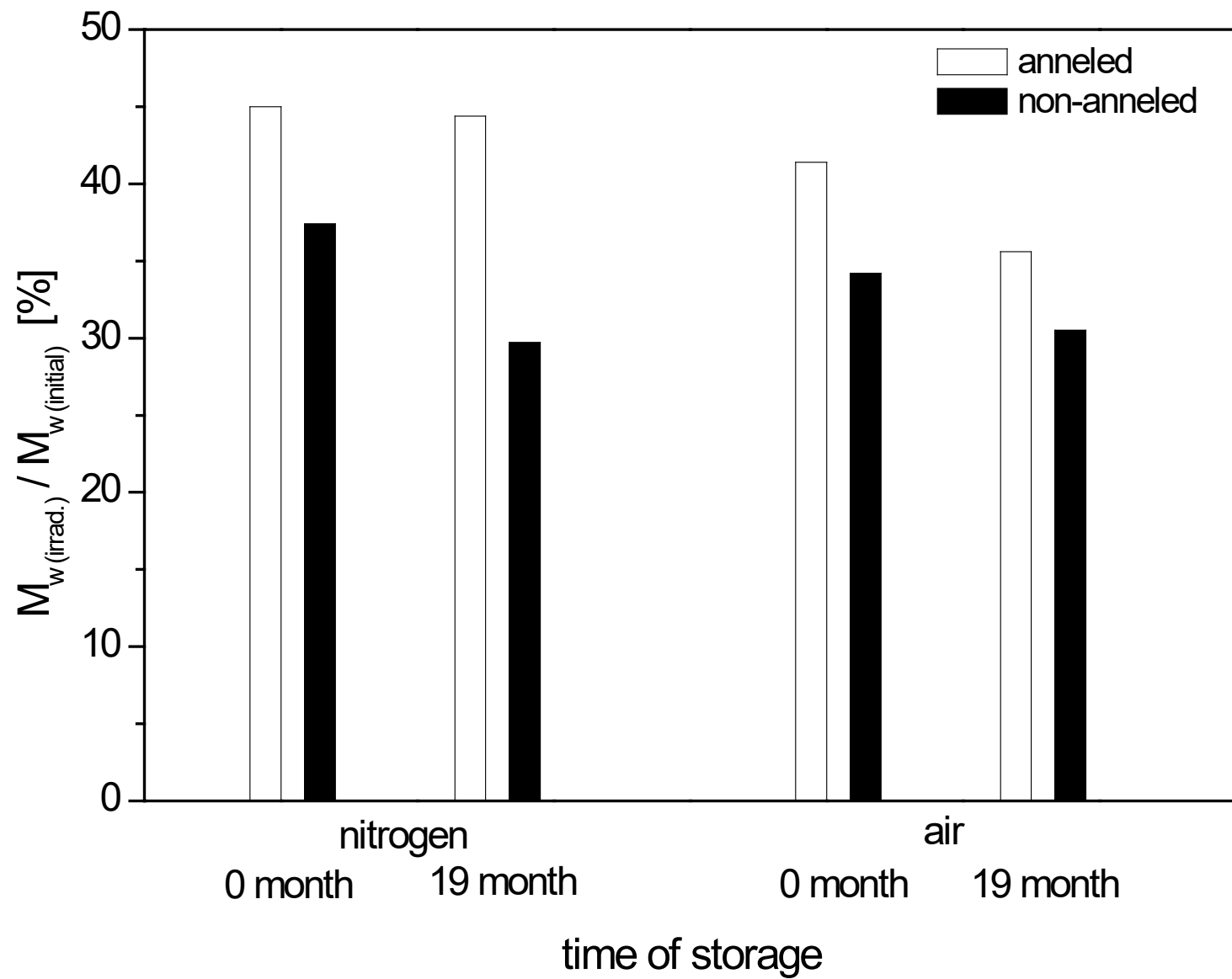


Figure 2

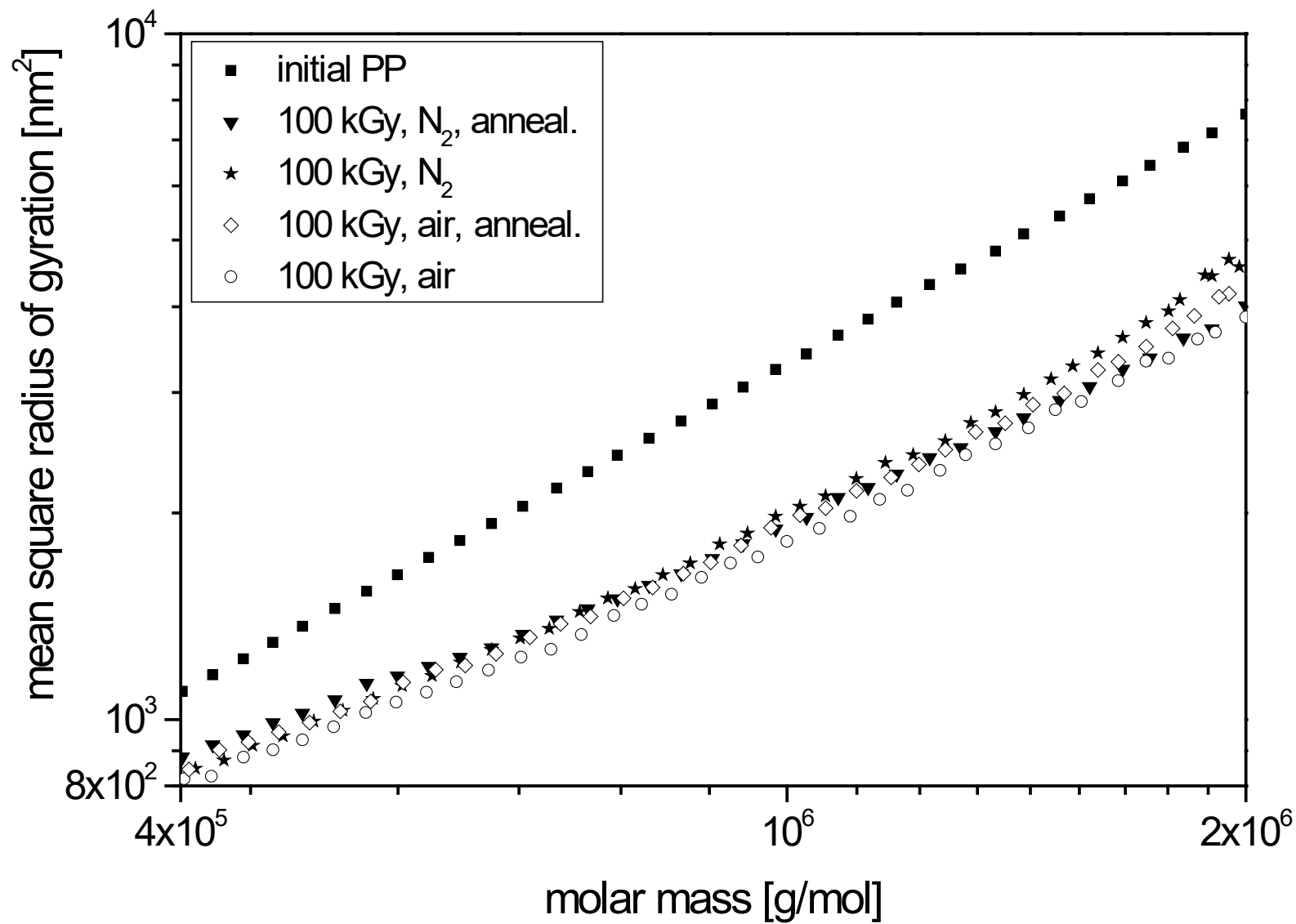


Figure 3a

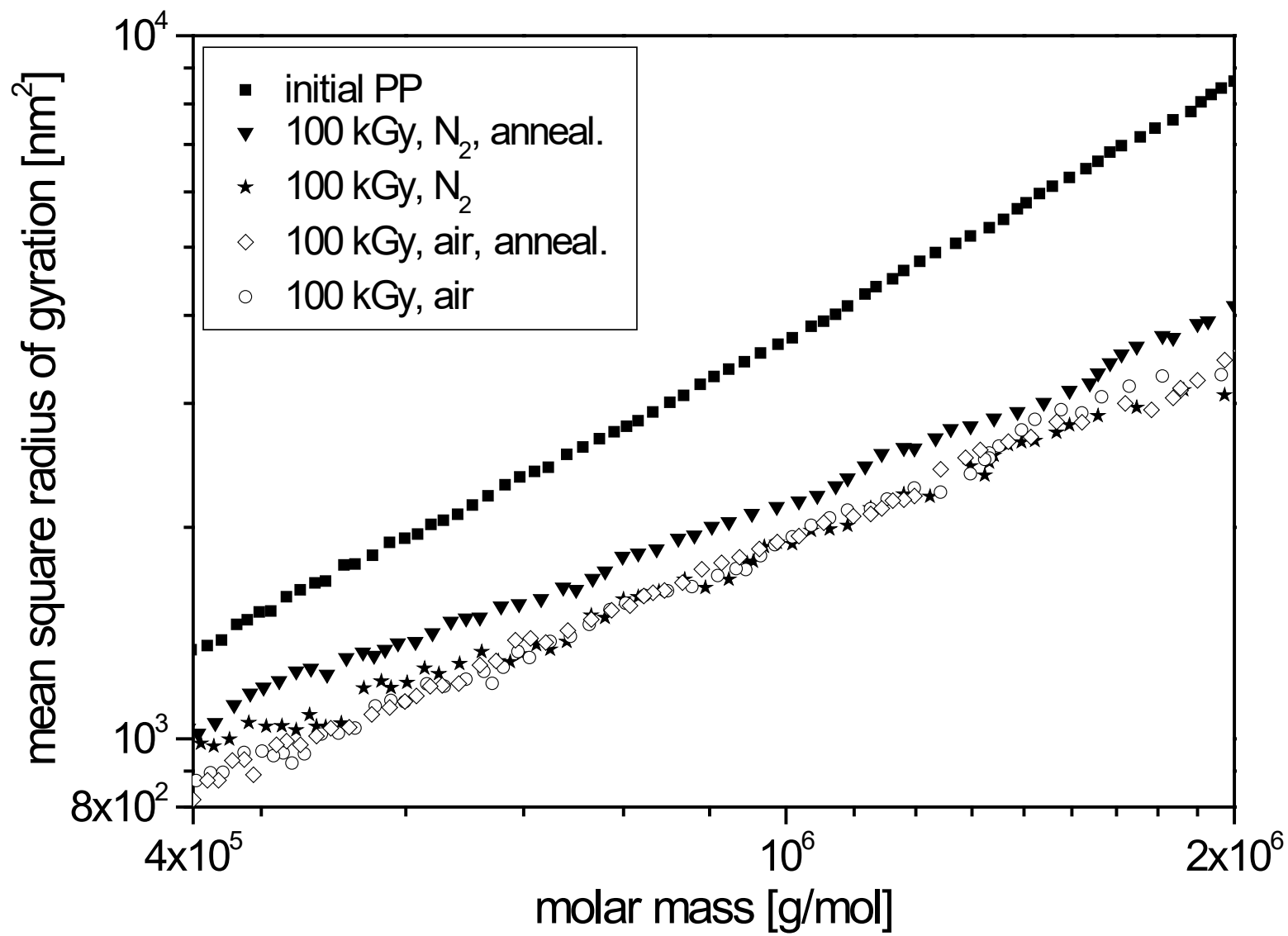


Figure 3b

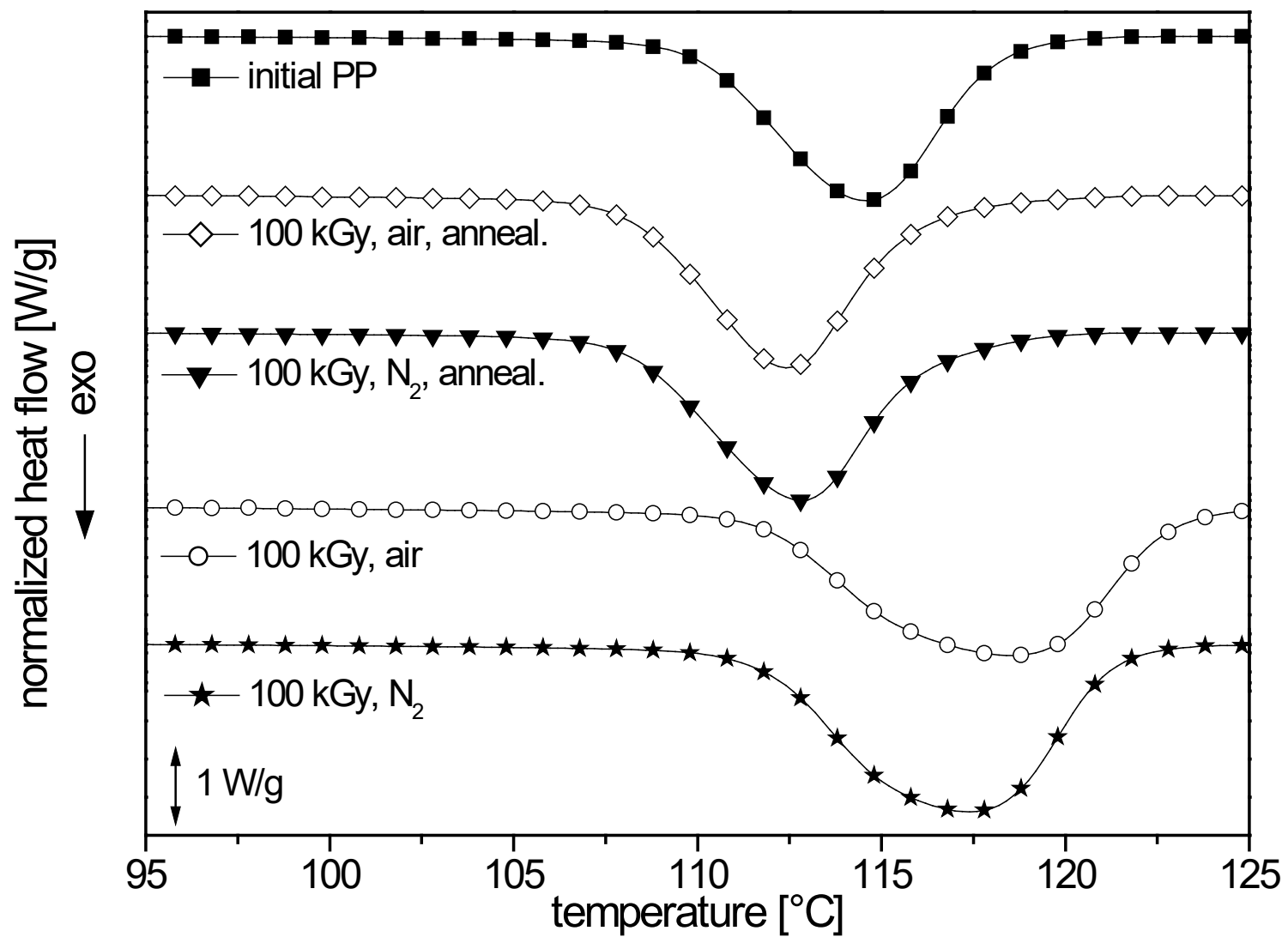


Figure 4

Figure 5

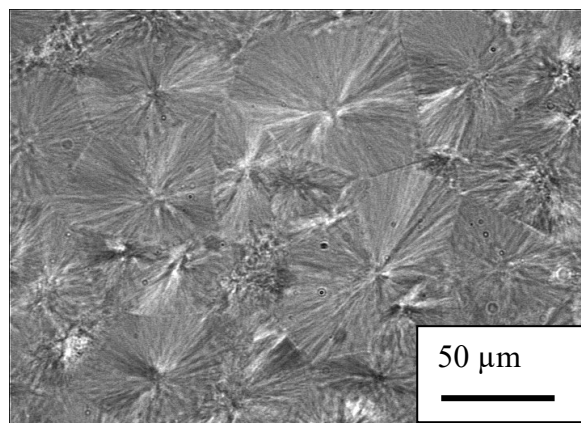


Figure 5 a

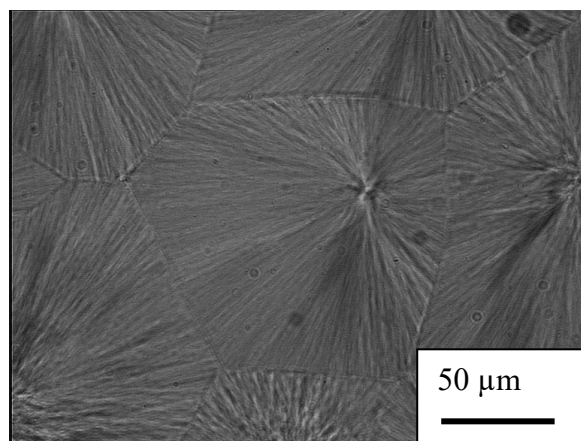


Figure 5 b

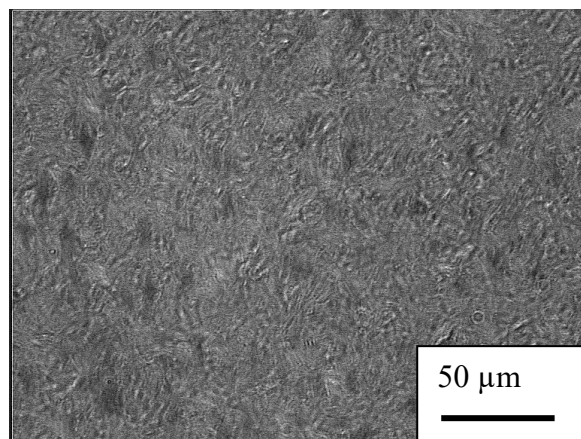


Figure 5c

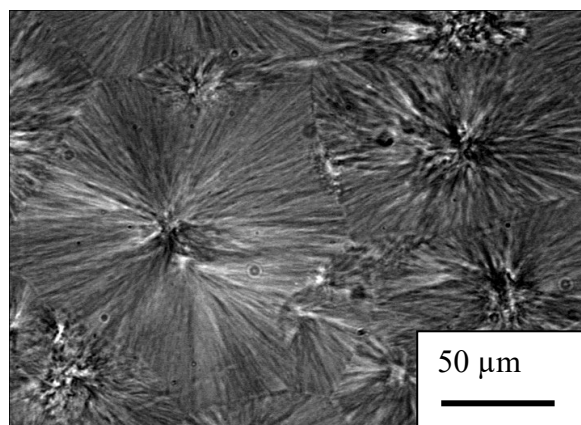


Figure 5d

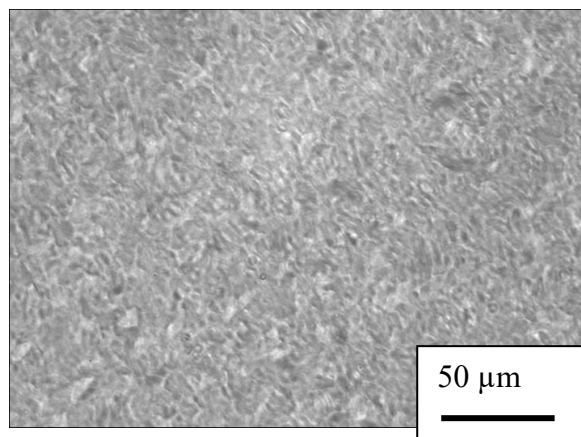


Figure 5e

Table 1

sample	atmos- phere	Annea- ling	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]	Onset crystallisation temperature $T_{c,o}$ [°C]
iPP	-	-	-8	98,6	48	160.4	114.5	118.2
I	N ₂	yes	-8	96,1	46	154.6	112.8	116.4
II	N ₂	no	-8	99,3	48	155.1	117.4	121.3
III	air	yes	-9	97,2	47	153,7	112,4	116,0
IV	air	no	-9	100,4	49	155,4	118,6	122,9