

# Comparison of the Molecular Properties and Morphology of Polypropylenes Irradiated under Different Atmospheres and after Annealing

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**ABSTRACT:** Electron-beam irradiation, a well-known way of generating long-chain branching, was used to modify polypropylene. Samples were investigated with differential scanning calorimetry, polarized light microscopy, and size exclusion chromatography. Independently of the atmosphere, postannealing led to the deactivation of residual radicals and to the reduction of the nucleus density. In comparison with the initial polypropylene, the crystallization temperatures increased for nonannealed samples but decreased for annealed samples. Stable products were

obtained only by irradiation in nitrogen followed by annealing. A reaction including free radicals with oxygen in the ambient atmosphere led to increasing molar mass degradation and the formation of long-chain branching after storage. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 634–639, 2006

**Key words:** branched; differential scanning calorimetry (DSC); electron beam irradiation; poly(propylene) (PP); spherulites

## INTRODUCTION

Since the investigations of Charlesby,<sup>1</sup> it has been 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 the chemical structure and morphology of the polymer as well as the irradiation conditions, including the posttreatment.<sup>2,3</sup>

One way of creating long-chain branching in linear polypropylene (PP) without the use of additives is modification by electron-beam irradiation, as described by DeNicola and a coworker.<sup>4–6</sup> The influence of the irradiation dose on the formation of long-chain branching in PP was investigated by Auhl et al.<sup>7</sup> Long-chain-branched PP possesses advantageous properties that are important in many industrial applications, such as good thermoforming behavior, high melt strength, and uniform fine cell structure of extruded foams.<sup>8,9</sup>

The formation of oxidation products caused by irradiation in the presence of air has been described by

different authors.<sup>10–16</sup> First, the formation of hydroperoxide in the macromolecules is observed. Second, these meta products react into final products containing oxygen, such as ketones or esters. These reactions lead to oxidative degradation with respect to the molar mass.

Different patents by Scheve et al.<sup>17</sup> and DeNicola and a coworker<sup>4–6</sup> state that the material should be annealed after 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 the deactivation of substantially all residual free radicals.

The irradiation influences the supermolecular structure (SMS), too. Aggregates of chain-folded fibrillar or lamellar primary crystallites with definite geometrical arrangements are designated SMS. The types and structural features of the formed SMS are markedly influenced by, for example, the thermal conditions of crystallization or the presence of crystal nuclei. SMS of isotactic polypropylene (iPP) may be readily visualized by polarized light microscopy (PLM). A 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 between. A spherulite can be considered an optically uniaxial crystal. Therefore, the PLM of a spherulite shows a dark, central cross (Maltese cross) with wings coin-

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cident with the respective planes of the polarizer and analyzer.<sup>18</sup>

It is well known that polymer molecules are fractionated by size exclusion chromatography (SEC) according to their hydrodynamic volume. The size of the molecules depends on their molar mass and density in a dissolved state. Long-chain-branched molecules have a denser structure than linear molecules, and their density depends on the number and type of branches. By the coupling of SEC to a multi-angle laser light scattering (MALLS) detector, the molar mass 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 of the molecules. Conclusions with respect to trifunctional random branching can be drawn with theoretical considerations.<sup>19,20</sup> The method was described in detail by Krause et al.<sup>21</sup>

## EXPERIMENTAL

### Materials

The iPP homopolymer used in this study was Novolen PPH2150 (Basell Polyolefins Co. N.V., Hoofddorp, The Netherlands). The weight-average molar mass was calculated with 670,000 g/mol. According to the 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 pellets were irradiated with 1.5 MeV with the ELV-2 electron-beam accelerator (Budker Institute of Nuclear Physics, Novosibirsk, Russia), as described in detail by Dorschner et al.<sup>22</sup>

The irradiation was carried out at atmospheric pressure in a special vessel.<sup>23</sup> 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.

### Characterization

#### SEC

The instrument was a PL-GPC220 (Polymer Laboratories, Ltd., Church Stretton, United Kingdom) at 150°C equipped with a refractive-index detector and coupled to a MALLS detector (Dawn Eos, Wyatt Technology Corp., Santa Barbara, CA). The column set consisted of two PL mixed-B-LS columns (Polymer Laboratories). The flow rate was 1 mL/min. The eluent was 1,2,4-trichlorobenzene (Merck KGaA, Darmstadt, Germany).

#### Differential scanning calorimetry (DSC)

The DSC measurements were performed on a Q1000 (TA Instruments, New Castle, DE) coupled with an autosampler in the temperature range of -60 to 210°C at a scanning rate of  $\pm 10$  K/min. Samples of about 5 mg were investigated under a nitrogen atmosphere in a run cycle of first heating, cooling, and second heating. The glass-transition temperatures ( $T_g$ 's) were calculated from the second heating run with the half-step method, and a crystallinity value of 207 J/g for 100% crystalline PP was used.<sup>24</sup>

#### PLM

The samples were heated up to 200°C and cooled *in vacuo*. These samples were cut with a Mikrotom Leica 2055 (Leica Mikrosysteme Vertrieb GmbH, Bensheim, Germany) to a thickness of 10  $\mu$ m and were fixed with Entellan (Merck) on glass plates. The optical observations of the spherulites in the samples were performed with a polarizing transmitted light microscope (Zeiss Axioplan 2, Carl Zeiss AG, Oberkochen, Germany). The images were captured with a microscope camera (AVT-BC12, AVT-Horn, Aalen, Germany, and Optimas 6.5, Optimas Corp., Washington, DC).

## RESULTS

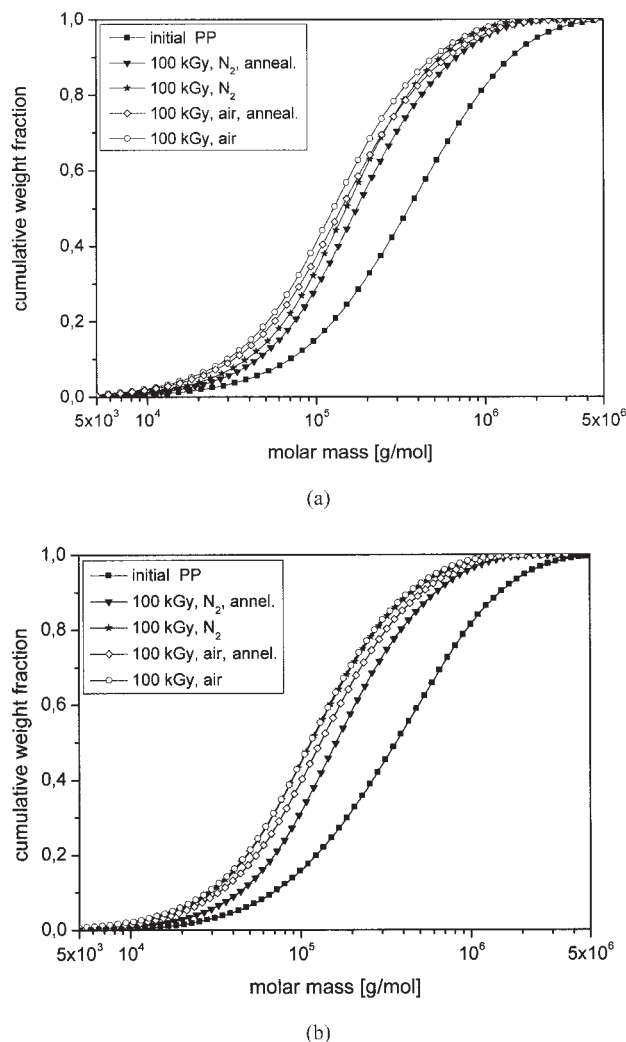
In this work, the influence of different irradiation conditions (irradiation atmosphere and annealing after the irradiation process) on the molecular parameters was investigated.

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 PP led to molar mass degradation<sup>7</sup> and was observed for all four variants. However, the degrees of degradation were different. Figure 1(a) shows the cumulative molar mass distributions of the initial iPP and the modified PP directly after the irradiation. The molar masses were as follows: sample I > sample III > sample II > sample IV. The molar mass of the annealed samples was higher than that of the nonannealed analogues. The sample irradiated in nitrogen showed higher molar masses than the same type of sample modified in air.

Additionally, the determinations were performed after storage of more than 1 year by SEC. The modified products were stored in a refrigerator at 5°C. Figure 1(b) shows the cumulative molar mass distribution of the initial iPP and the modified PP after 19 months of storage. The molar masses were as follows: sample I



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

> sample III > samples II and IV. No significant differences in the molar masses were obtained for samples without annealing (II and IV).

Figure 2 shows the trend of the weight-average molar mass for all the samples. Only sample I, which was irradiated under a nitrogen atmosphere and then annealed, became stable during storage. No changes in the molecular properties within more than 1 year could be observed by SEC. In contrast, all other products had 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 and was followed by degradation of about 4–6%.

Long-chain branching could be detected by a reduction of the mean square radius of gyration at the same molar mass. As expect, all samples showed a decrease in the radius of gyration<sup>7</sup> (see Fig. 3). Directly after the

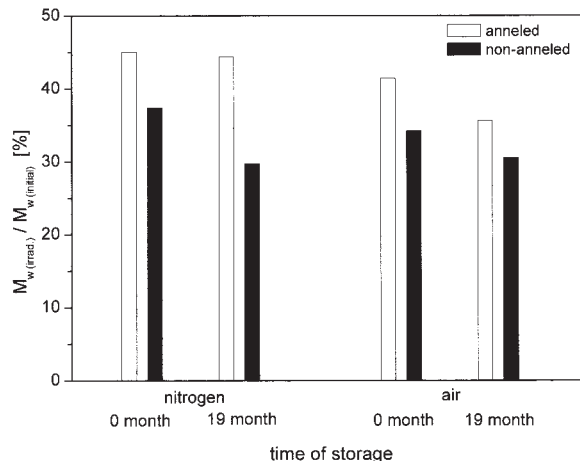
irradiation, the degree of long-chain branching was nearly the same [see Fig. 3(a)]. In contrast, the degree of long-chain branching was changed during storage. Sample I showed the highest mean square radius of gyration at the same molar mass [see Fig. 3(b)]. In comparison, the three other samples possessed a lower mean square radius of gyration at the same molar mass. That means that during the storage, additional formation of long-chain branching took place.

The characteristic temperatures of melting and crystallization were determined with the peak temperatures [melting peak temperature ( $T_m$ ) and crystallization peak temperature ( $T_{c,m}$ )] and the extrapolated onset temperature of the crystallization ( $T_{c,o}$ ).

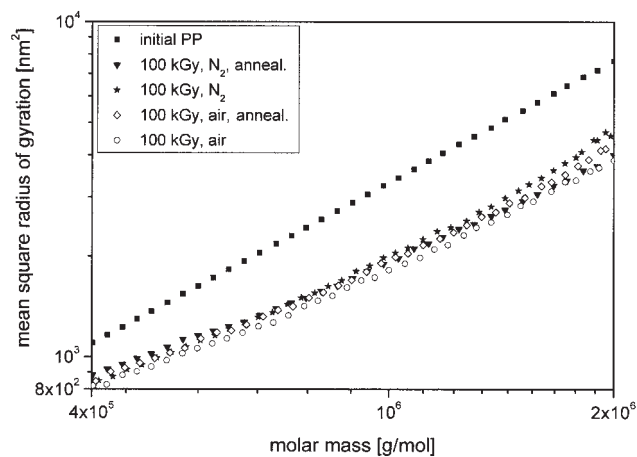
The irradiation at 100 kGy resulted in molar mass degradation and long-chain branching with respect to the irradiation conditions. The thermal behavior of long-chain branching in PP was expected to be comparable to that of the linear main chain because of the ability to crystallize. The overall crystallinity ( $\alpha$ ) of the irradiated samples without annealing (49%) was somewhat higher than that of the samples with annealing (ca. 46%; see Table I).

$T_m$  decreased after irradiation at 100 kGy in comparison with that of the initial material and was correlated with the molar mass degradation.  $T_m$  of the irradiated samples was independent of the irradiation conditions (see Table I).  $T_g$  was nearly unchanged (see Table I).

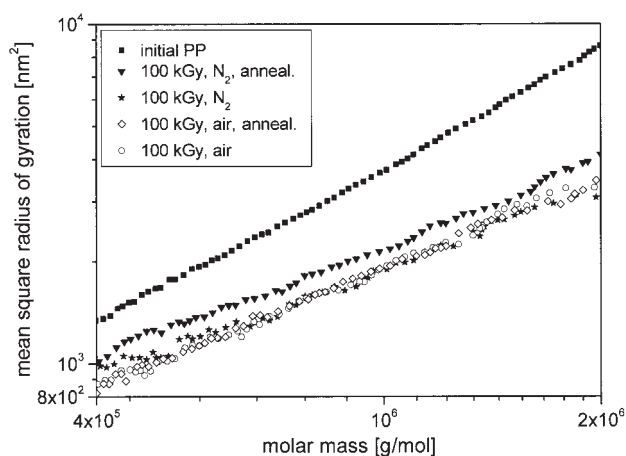
$T_{c,m}$  and  $T_{c,o}$  changed with different irradiation conditions (see Table I and Fig. 4). Both crystallization temperatures in comparison with those of the initial iPP decreased up to 2 K for the samples with annealing (samples I and III) and increased up to 4 K for the samples without annealing (samples II and IV). The difference of both crystallization temperatures for the variation of annealing was 6 K. The irradiation atmo-



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



(a)

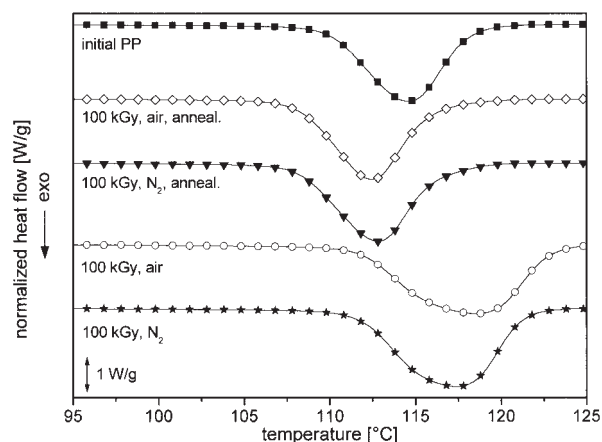


(b)

**Figure 3** Mean square radius of gyration with respect to the molar mass of the linear initial PP and samples irradiated at 100 kGy: (a) directly after the irradiation and annealing process and (b) after storage.

sphere was irrelevant to the crystallization temperatures. The temperature difference between  $T_{c,o}$  and  $T_{c,m}$  as a measure of the crystallization rate was unchanged.

Figure 5 shows PLM images of all the samples. The spherulites in the initial iPP had an average diameter



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

of about 60  $\mu\text{m}$ . The samples without annealing (samples II and IV) contained minimum spherulites and showed a fine-grained structure. In contrast, the samples with annealing (samples I and III) showed spherulites up to 120–150  $\mu\text{m}$  in diameter.

## DISCUSSION

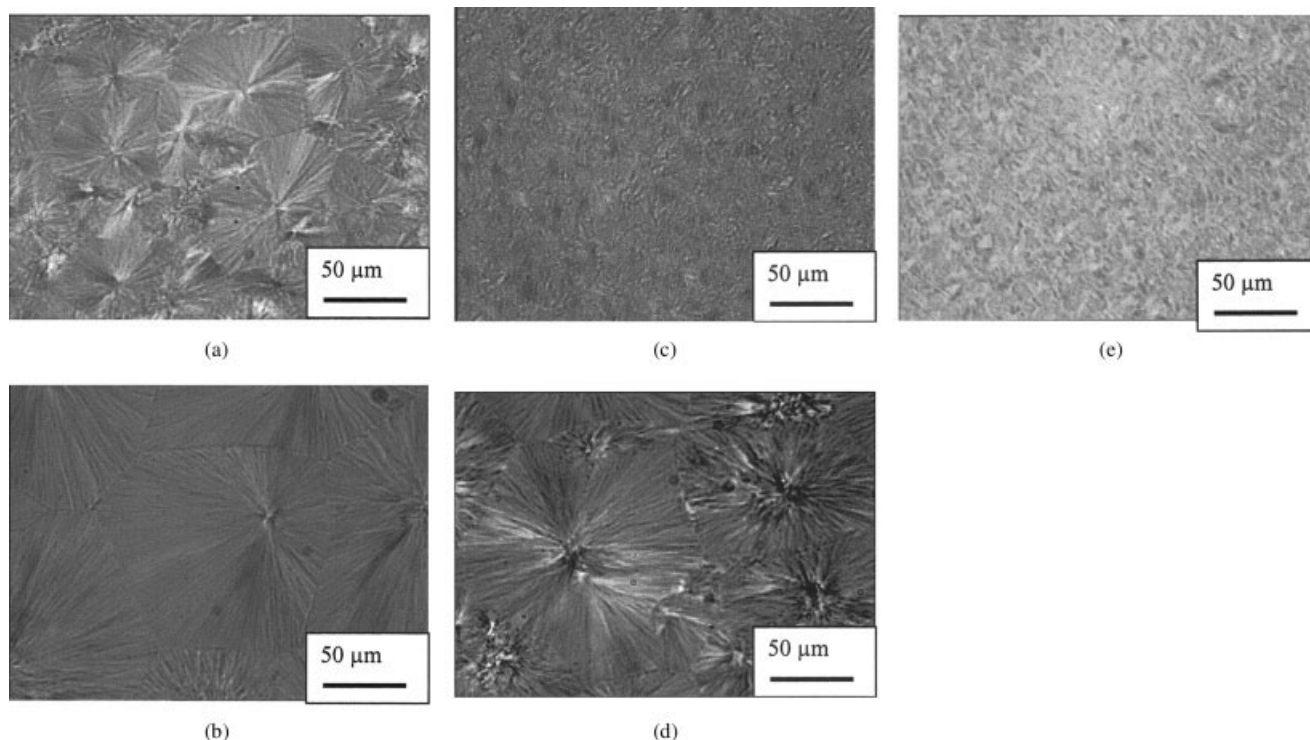
After irradiation, the modified samples showed different molar masses. This can be explained by the different irradiation conditions.

On the one hand, the irradiation atmosphere played an important role in the irradiation results. When air was present during irradiation, the radicals of the macromolecules, induced by the electron beam, reacted with oxygen-forming products containing oxygen. On the other hand, annealing led to the deactivation of substantially all residual free radicals. It seems possible that after irradiation during storage, these residual radicals reacted with the oxygen in air. The oxidative degradation of the polymer took place until all residual free radicals were trapped. It was assumed that the formation of products containing oxygen took place via the irradiation in air or during the storage of irradiated products without annealing. Both methods

**TABLE I**  
DSC Data of Cooling and Second Heating Runs of PP with Respect to the Irradiation Conditions at 100 kGy after Storage

Sample	Atmosphere	Annealing	$T_g$ (°C)	Melting Enthalpy (J/g)	$\alpha$ (%)	$T_m$ (°C)	$T_{c,m}$ (°C)	$T_{c,o}$ (°C)
iPP	—	—	−8	98.6	48	160.4	114.5	118.2
I	N <sub>2</sub>	Yes	−8	96.1	46	154.6	112.8	116.4
II	N <sub>2</sub>	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





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

of preparation led to modified PPs including oxidation products.

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

Samples II and IV without annealing showed the lowest molar masses. During storage, molar mass degradation took place. The final molar masses were nearly independent of the irradiation atmosphere.

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

Another aspect that has to be highlighted is the influence of the irradiation conditions on the forma-

tion of long-chain branching. The macromolecules of all samples (samples II, III, and IV) that underwent reactions with oxygen showed a denser structure after storage. Independently of the detailed irradiation conditions, the radii of gyration decreased for these samples [cf. Fig. 3(a,b)]. It was assumed that the macromolecules containing oxygen formed additionally branched molecules. The total number of the long-chain branching was increased.

The investigation of the crystallization behavior (Fig. 4) showed the strong influence of the irradiation conditions. Crystallization temperatures  $T_{c,m}$  and  $T_{c,o}$  of the samples with annealing (samples I and III) were 6 K, lower than those of the samples without annealing (samples II and IV). That means that the annealing step had a very important influence on the crystallization behavior of the samples. The samples without annealing (samples II and IV) crystallized earlier, and this is advantageous for faster processing.

The great influence of the annealing step was also observed in PLM images. The samples without annealing (samples II and IV) showed a fine-grained structure. Obviously, the formation of many stable crystal nuclei took place at high temperatures. This led to the crystallization temperature increasing up to 4 K. From the literature,<sup>25-27</sup> it is known that the addition of a nucleating agent to iPP leads to a higher nucleus density. The resulting spherulites are smaller, and a nucleated sample shows a higher crystallization tem-

perature. The crystallization of nucleated PP turns into heterogeneous nucleation. Additional stable crystal nuclei of PP are formed on the nucleating agent surfaces. This leads to the crystallization temperature increasing from 111 to 129°C.<sup>26</sup> Kim et al.<sup>27</sup> found with the addition of nucleating agents a maximal increase of the crystallization peak temperature up to 17 K.

In contrast, the samples with annealing showed great spherulites with low nucleus density. Therefore, the crystallization was more homogeneous, and the crystallization temperatures were lower. That means that the annealing step reduced the crystal nucleus density.

### CONCLUSIONS

Investigations of the irradiation of PP without additives under different atmospheres and with annealing have shown that different products are formed. The irradiation conditions strongly influence the final molecular properties.

The irradiation of PP in nitrogen with annealing led to a product with less molar mass degradation after irradiation. Only this sample was stable during more than 1 year of storage. A storage-stable product was generated with a lower degree of long-chain branching and lower crystallization temperatures.

In all other cases, the reaction with oxygen led to higher molar mass degradation after irradiation and additional degradation during storage. These three samples included products containing oxygen. Modification without annealing generated samples including free radicals. These residual radicals reacted during storage. Therefore, these samples were instable during storage. Furthermore, long-chain-branched PP was obtained with a higher degree of long-chain branching after storage. It can be concluded that the reactions of free radicals with oxygen lead not only to molar mass degradation but also to the formation of long-chain branching. Therefore, the products containing oxygen contributed to increasing the coil density of the macromolecules.

Furthermore, the annealing step after irradiation at 100 kGy strongly influenced the crystallization behavior of the irradiated samples. The samples with annealing showed great spherulites, and the crystallization temperatures were lower. In contrast, the samples without annealing crystallized at higher temperatures in comparison with the initial iPP and samples with

annealing. This behavior is favored for faster industrial processing. The PLM images of these samples showed a fine-grained structure. This leads to the conclusion that the annealing step is advantageous not only for the formation of long-chain branching by the reaction and deactivation of residual free radicals but also for the reduction of the number of crystal nuclei.

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