High-energy radiation forming chain scission and branching in polypropylene

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ABSTRACT

The degradation of high molecular weight isotactic polypropylene (iPP) subjected to gamma rays irradiation up to 100 kGy in inert atmosphere was analyzed. The investigation relied upon complex viscosity, elastic modulus, gel fraction, morphology of the insoluble fraction and deconvoluted molecular weight distribution (MWD) curves. At low irradiation doses, already at 5 kGy, the MWD curve is strongly shifted to the low molecular weight side showing chain scission, which is confirmed using the calculated chain scission distribution function (CSDF). At high dose levels, the appearance of a shoulder in the high molecular weight side of the MWD curve indicates the formation of chain branching. The presence of a considerable insoluble fraction at these high dose levels indicates also the formation of cross-linking, which has different morphology then the insoluble fraction present in the original iPP. The rheological results show changes in the molecular structure of irradiated samples in agreement with the gel content data. The chromatographic and rheological data has shown that gamma irradiation of iPP produces chain scission, branching and cross-linking.

1. Introduction

High-energy radiation such as gamma and X-rays, e-beams and ion beams has been widely used in the plastic and rubber industries due to their unique characteristic and advantages, therefore there is already a number of well-established industrial applications of radiation processing. The most relevant industrial application are based on cross-linking technology, such as wire and cable industry, packing films, foams, and radiation curing used on a large scale in surface finishing coatings, lacquer and inks. The radiation degradation has its great application in the irradiation of PTFE, which reduces its molecular weight allowing easier processing, as well as in the visbreaking process of polyolefin. Finally radiation-induced grafting is another powerful method for modifying existing polymers, creating an almost unlimited range of new materials (Guven, 2003).
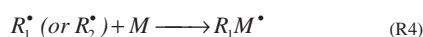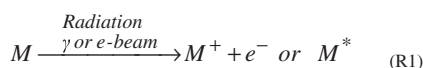
High-energy irradiation of a macromolecule (M) leads to the formation of very reactive species like ions and excited state. Free radicals are formed mostly by the decay of excited species to the ground state, as shown in reactions R1, R2 and R3 in the Scheme 1(Guven, 2003).
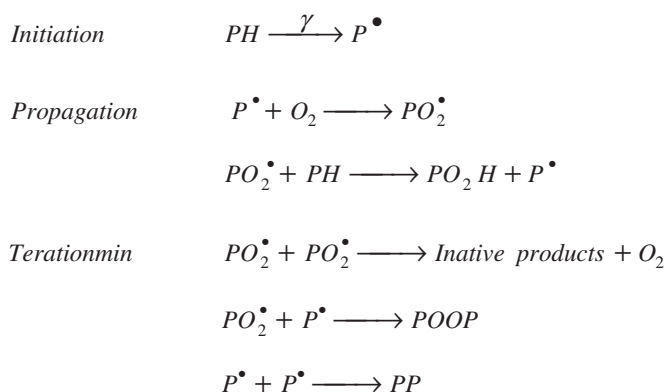
In the first reaction R1 the ionization of the polymer molecule due to the Compton's effect (for gamma radiation) produces one electron which induces many other secondary ionizations or can be trapped by ions formed in the reactions (M^+) converting into activated molecules (R2). The excited long molecular chain of a polymer (M^*) has an energy exceeding the strength of the C–C covalent bond which breaks by chain scission forming free macro radicals (R3), some of which can react with the macromolecule (M) producing chain branching (Guven, 2003); (Rätzsch et al., 2002). The protection of polymers against high doses (20–1000 kGy) requires efficient additives, which prevents and/or stop chain reactions.

Thermo-oxidation and thermo-mechanical processes, ultra-violet radiation, as well as radiation processes can degrade the polymer. The degradation phenomenon is a chain reaction, which in the presence of oxygen includes several steps of chain initiation, chain propagation, chain branching and chain termination. The scheme of the reactions in which the H atom of a polymer chain P is removed is well recognized in the literature (Guven, 2003); (Rätzsch et al., 2002); (Singh and Sharma, 2008). The main reactions, in a very simplified way, are shown in the Scheme 2.

The alkyl radicals ($P\bullet$) formed by the hydrogen abstraction of the main polymer chain is the primary species of the chain reaction which leads to extensive degradation. In the presence of

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$$M \xrightarrow[\gamma \ or \ e\text{-}beam]{Radiation} M^+ + e^- \ or \ M^* \quad (R1)$$

$$M^+ + e^- \longrightarrow M^* \quad (R2)$$

$$M^* \longrightarrow R_1^\bullet + R_2^\bullet \quad (R3)$$

$$R_1^\bullet \ (or \ R_2^\bullet) + M \longrightarrow R_1 M^\bullet \quad (R4)$$

Scheme 1

Initiation $\qquad PH \xrightarrow{\gamma} P^\bullet$

Propagation $\qquad P^\bullet + O_2 \longrightarrow PO_2^\bullet$

$\qquad\qquad\qquad PO_2^\bullet + PH \longrightarrow PO_2H + P^\bullet$

Terationmin $\qquad PO_2^\bullet + PO_2^\bullet \longrightarrow Inative \ products + O_2$

$\qquad\qquad\qquad PO_2^\bullet + P^\bullet \longrightarrow POOP$

$\qquad\qquad\qquad P^\bullet + P^\bullet \longrightarrow PP$

Scheme 2

oxygen it can react with the alkyl radicals forming peroxy radicals, which abstracts one hydrogen producing hydro-peroxide (propagation step). The termination mechanism is the formation of oxidized products, grafts (branching), cross-linking. In the case of irradiation process with electron beam or gamma rays, the preferential transformations depend on the polymer structure and the treatment conditions used before, during and after the irradiation process. Even those polymers that are called radiation-degrading types can be cross-linked by radiation in the presence of reactive additives. The oxidized products, produced during the irradiation process, can modify the molecular weight distribution (MWD) curve. Measurements of weight average molecular weight ($\overline{M_w}$) are sometimes used to monitor changes in the molecular characteristic obtained by the degradation process (Azizi et al., 2008). A simultaneous formation of chain scission and chain branching cause changes in the average molecular weights, which are considered difficult to be analyzed.

Many techniques have been used to identify and quantity the level of short- and long-chain branching in polypropylene. Weng et al. (Weng et al., 2002) reported the determination of the branching density (number of branchs per 1000 carbons) using ^{13}CNMR for an in-situ synthesized metallocene polypropylene having long-chain branching. However, ^{13}CNMR is not readily applicable to polypropylene when modified in a post-reactor process, because usually the branched or cross-linked structures are present in small quantities and are shielded by the surrounding carbons, reducing or even eliminating the NMR peaks. On the other hand, rheology is one suitable tool owning the advantage for the determination of molecular structure and to detect small amount of long-chain branching (LCB) although is an indirect way (Azizi et al., 2008); (Tian et al., 2006); (Ruymbeke et al., 2005);

(Lugão et al., 2007). The quantitative determination of the number of LCB in polypropylene can be done via calculations including the radius of gyration of the polymer or the molar mass from chromatographic experiments (Krause et al., 2004).

Size exclusion chromatography (SEC) measures the molecular weight distribution MWD curve of a polymer, giving important information related to its molecular structure, although it is somewhat insensitive to low concentrations of LCB. In addition, polymers with high molecular weight are sometimes insoluble into ordinary solvent used in the SEC experiments.

The main objective of this paper is to study the polypropylene degradation using gamma radiation. For this purpose, an isotactic polypropylene (iPP) with high molecular weight with no anti-oxidant was irradiated with dose levels ranging from 0 to 100 kGy at inert conditions. Changes in the properties of the irradiated iPP were measured as a function of the rheological characteristics (complex viscosity and elastic modulus) and gel fraction for the insoluble material. The soluble fraction was analyzed by chromatography experiments (SEC) in order to get information upon chain scission and chain branching calculating the Chain Scission Distribution Function (CSDF) curves (Canevarolo, 2000); (Caceres and Canevarolo, 2004); (Machado et al., 2004). Comparing the MWD curves of the polymer before and after the degradation process the CSDF function calculates the average number of chains that have been submitted to scission or branching, as a function of their initial molecular weights (Canevarolo, 2000); (Caceres and Canevarolo, 2004); (Machado et al., 2004); (Pinheiro et al., 2004); (Berzin et al., 2006); (Pinheiro et al., 2006); (Cáceres and Canevarolo, 2006). From these curves, it is possible to get quantitative information with respect to the scission rate occurring during each irradiation dose.

2. Experimental part

An isotactic polypropylene (iPP) with high molecular weight (MFI=0.5 g/10 min from Braskem, Brazil) was supplied in non-processed sphere form without any antioxidant. The iPP pellets were conditioned into nylon bags which were fluxed several times with nitrogen in order to reduce as much as possible the internal oxygen concentration. The bags were submitted to the irradiation process in a commercial ^{60}Co source with dose levels ranging from 5 up to 100 kGy. After irradiation, the samples were heat treated at 100 °C during 1 h to annihilate the remaining radicals present.

The concentration of the cross-linked material, forming the insoluble fraction, was measured using boiling xylene following the ASTM D2765 standard method. The morphology of the insoluble fractions retained in the filter was observed using a Phillips scanning electron microscope (MEV), operating at an accelerating voltage of 10 eV. Melt flow rate was measured at 230 °C using a Ceast Melt Flow Modular Line following the ASTM D1238 standard method. The irradiated pellets were compression-molded into discs with dimension of 25 mm diameter and 1.7 mm of thickness for the oscillatory test. This measurement was performed on a rheometer Physica MCR300, at a temperature of 200 °C and constant strain of 5% with nitrogen blanketing.

The molecular weight distribution MWD curves of the irradiated samples were measured by size exclusion chromatography (SEC) using a Waters 150C at 140 °C equipped with a refractive-index detector. The samples were solubilized into 1, 2, 4-trichlorobenzene, stabilized with 0.5% w/w Irganox 1010 to reduce thermo-oxidative degradation and measured at a flow rate of 1 mL.min^{-1}. The MWD curves, average molecular weights and polydispersity were calculated using the Millennium software. The MWD curves were exported as ASCII files from the

size-exclusion chromatograph. These curves were deconvoluted into three Gaussian curves using the Origin®7.5 software. The partial concentrations of the low and the high molecular weight fractions of the deconvoluted curves were estimated by integrating their peak areas. The chain scission distribution function (CSDF) curves were calculated using an Excel macro running software, called *CSDF4.1 Program,* available upon request, following the method already proposed in the literature (Canevarolo, 2000; Caceres and Canevarolo, 2004; Machado et al., 2004). The MWD curve of pristine, non-irradiated iPP was used as reference.

3. Results and discussion

Fig. 1 shows the gel fraction of the iPP samples, pristine and after varying levels of irradiation. The iPP used in this work is of a high molecular weight type in which was found up to 7% of insoluble polymer. The irradiation process under nitrogen atmosphere changes the gel content dramatically. Already at very low dose levels (5 kGy) the gel content is reduced to the limit of detection. As
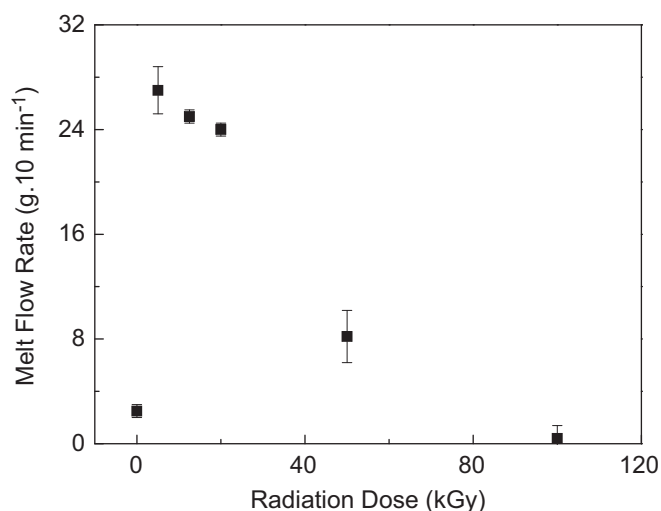

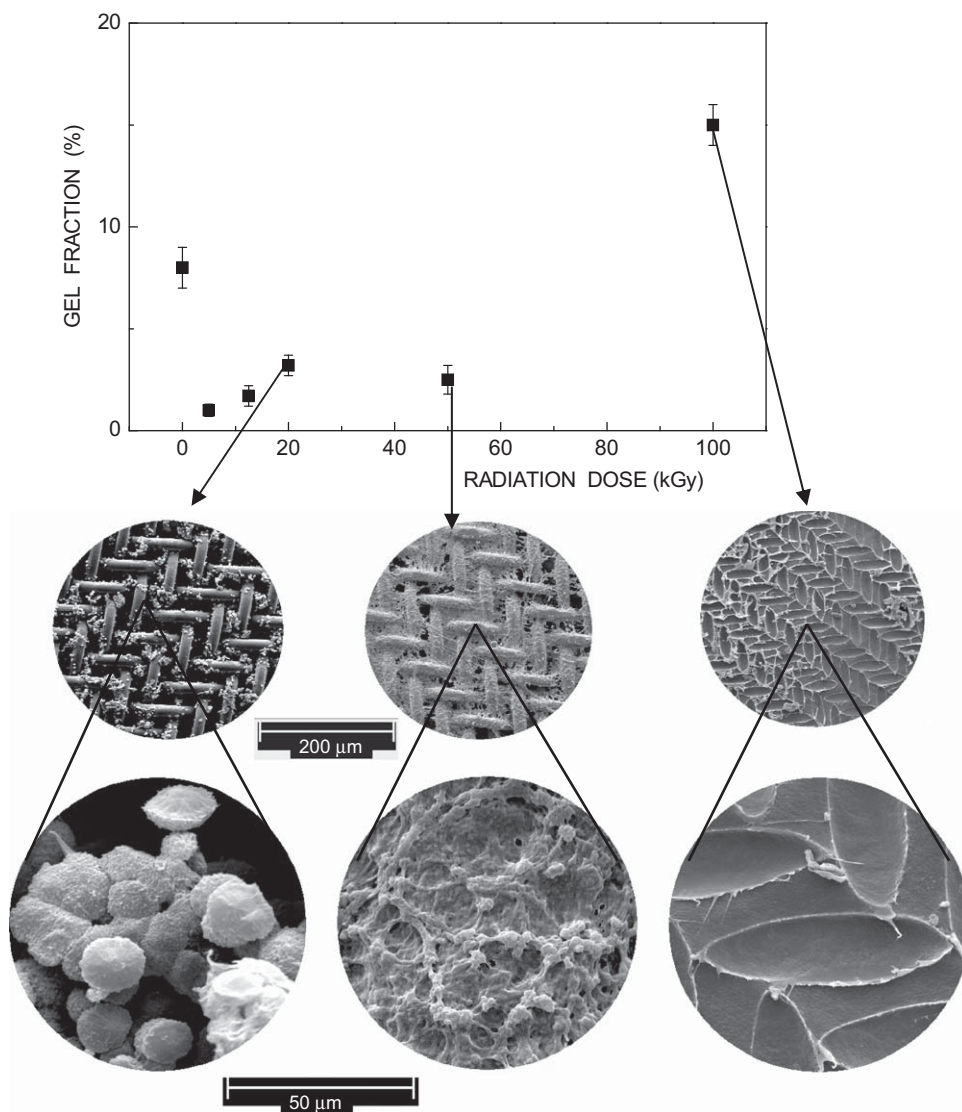**Fig. 2.** Melt flow rate of gamma-irradiated iPP as a function of irradiation dose.

Fig. 1. Gel fraction content of pristine and irradiated iPP. The insets are SEM micrographs of the insoluble fraction.

the dose level is increased up to 100 kGy the gel content also increases almost linearly reaching a value of 15%, twice as much that presented in the original sample. The sample at 50 kGy has shown an unexpected low gel content. The morphology of the insoluble material which is retained in the 500 mesh steel grid during Sohxlet extraction is also presented in Fig. 1, seen as insets with increasing magnification. The initial insoluble material and those irradiated with low dose levels (up to 20 kGy) show a morphology of irregular and agglomerated particles each one having an average diameter of 15 microns. At 50 kGy level, a continuous thin film has been formed on the surface of the steel grid. The film surface is rough showing domains that are surrounded by irregular material, better seen at a higher magnification. Samples irradiated at 100 kGy produces a gel that deposit over the steel grid as a continuous polymer film. The film was stripped off from the grid and its surface in contact with the grid, was observed in the MEV. Up to the highest magnification used, the morphology is a continuous non-porous film, showing the grid marks in low relief. The film morphology has been greatly affected by the changes in the molecular weight, produced by the degradation process during the gamma irradiation.

Fig. 2 shows the melt flow rate of the initial and irradiated polymer. The high molecular weight of the iPP used in this work, added to its large gel content, reflects the very low melt flow rate
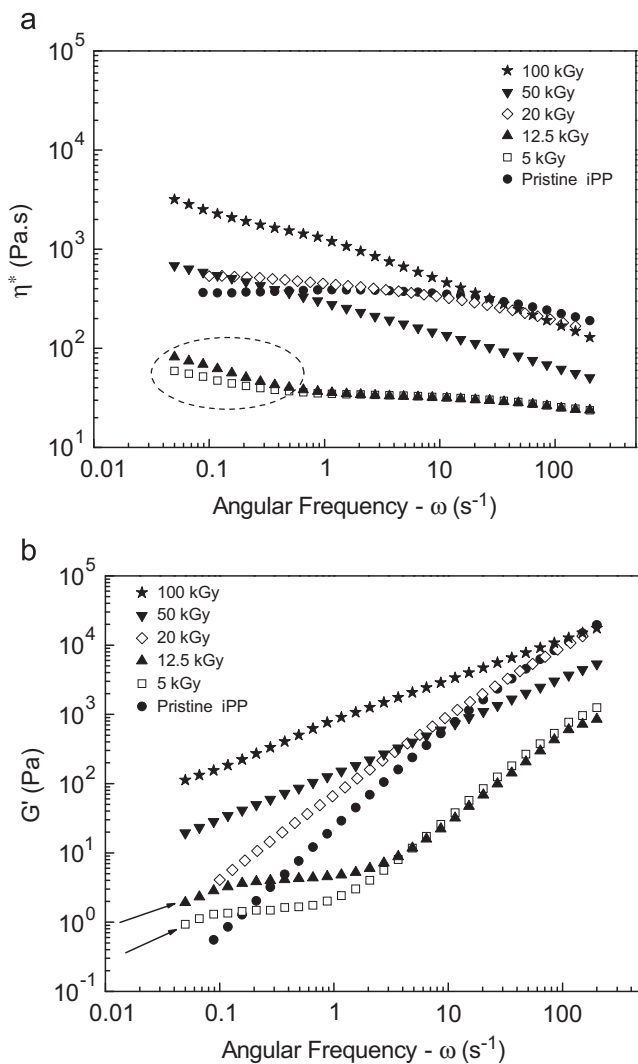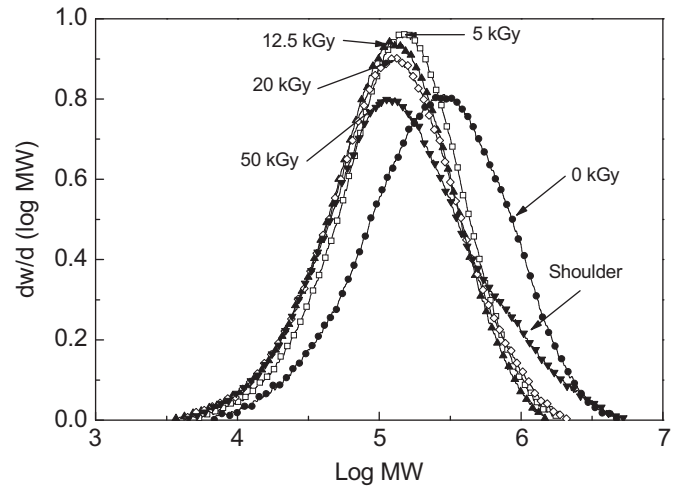

Fig. 4. Molecular weight distribution curves of pristine iPP and after irradiation with doses up to 50 kGy. The curves are shifted to lower molecular weights and at the highest dose, there is the formation of a shoulder (as highlighted).
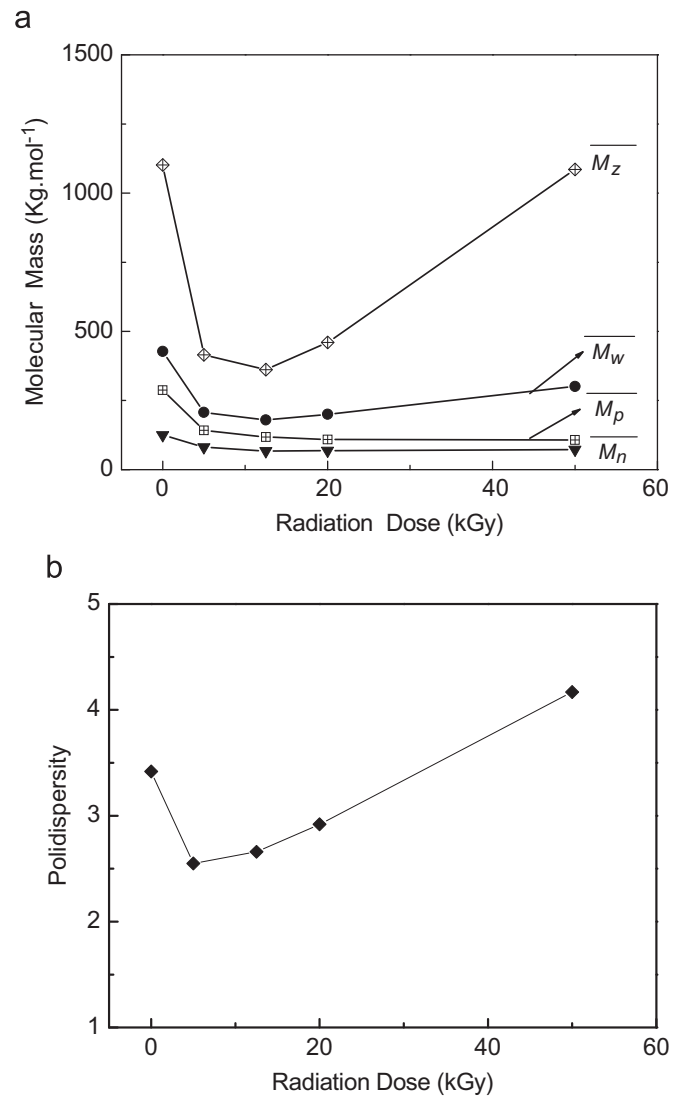

Fig. 3. (a) Complex viscosity and (b) shear storage modulus vs. angular frequency at 200 °C for pristine and irradiated iPP.

Fig. 5. Changes in (a) various average molecular weight and (b) polydispersity of pristine and irradiated iPP with doses up to 50 kGy.

(MFR) of the pristine polymer, which is in the range of 0.5 g/10 min. After irradiation, even at the lowest dose level used (5 kGy) the MFR increases dramatically reaching up to 27 g/10 min. As the dose level is increased further the MFR drops almost linearly to return to very low values (almost not showing flow) when irradiated at 100 kGy. These results are in straight agreement with the gel content data presented in Fig. 1.

It is well established that small amounts of branching, scission and cross-linking can change the rheological properties of a polymer. The complex viscosity curves of the initial and irradiated iPP measured at 200 °C are shown in Fig. 3(a). The pristine iPP shows a Newtonian behavior up to frequencies of $10 \, \mathrm{s}^{-1}$. Upon irradiation, already at low dose levels up to 12.5 kGy, the complex viscosity decreases severely for all frequencies measured indicating that at least a fraction of low molecular weight material is formed lubricating the flow. The viscosity at low frequencies, highlighted by the dashed area, is not Newtonian indicating the formation of a gel. Increasing the dose level, the

complex viscosity increases, maintaining the non-Newtonian behavior, thus revealing the presence of a gelated molten material. This effect is more preeminent in the $G\prime$ storage modulus curve, presented in Fig. 3(b). The terminal zone of the $G\prime$ curve is mainly affected by the longest relaxation times and so $G\prime$ of linear polymers follow the well-known frequency dependence, i.e., $G\prime \propto w^2$ (Azizi et al., 2008; Tian et al., 2006; Ruymbeke et al., 2005). $G\prime$ increases with the irradiation dose at low frequency and the terminal slope decreases from 1.42 for pristine iPP to 0.61 after 100 kGy. This result shows that there is a longer relaxation mechanism, which is due to the presence of a high molecular weight fraction (gel) formed during the irradiation process.

The molecular weight distribution curves of the initial and irradiated samples are shown in Fig. 4. The irradiation process creates a great shift downwards in the MWD curves, already affecting at the lowest measured dose level of 5 kGy. Increasing the dose level, the downward shift is still present but happens at a
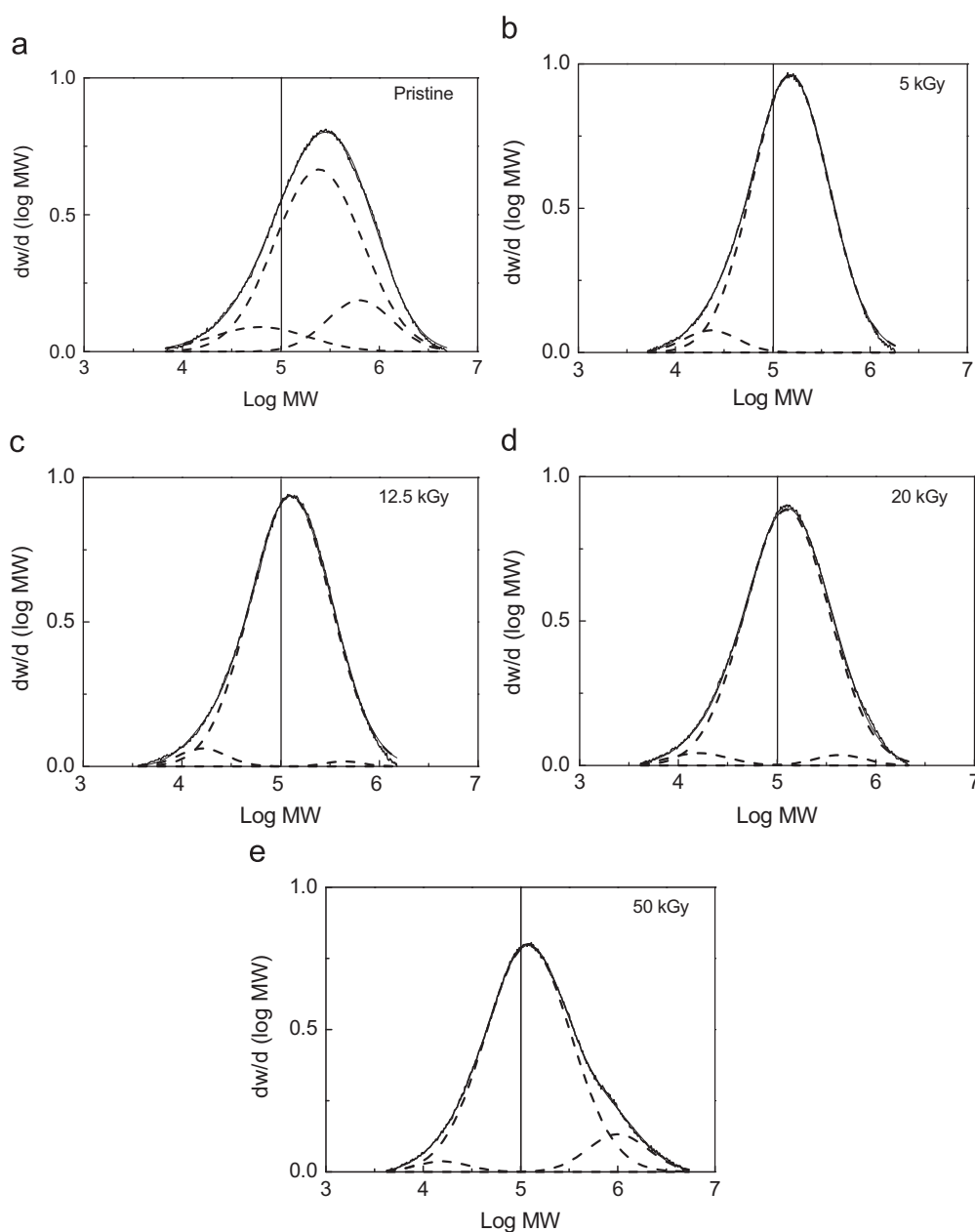

Fig. 6. Deconvolution in three Gaussian peaks of the molecular weight distribution curves presented in Fig. 4 for various irradiation dose levels up to 50 kGy.

lower rate. This shifting is due to the polymer chain scission that is taking place during the irradiation. It is interesting to notice that, even at the lowest dose level used, the level of chain scission is great enough to completely change the physico-chemical behavior of the irradiated polymer. Observing closely the 50 kGy MWD curve one can see a shoulder at the high molecular weight side (arrow in Fig. 4) showing the presence of a high molecular weight fraction, which is produced at the highest dose level. As the SEC technique measures only soluble polymer chains this fraction is made of newly formed branched chains.

Fig. 5(a) shows the average molecular weights $\overline{M_n}, \overline{M_w}, \overline{M_z}$ and the molecular weight in the maximum of the MWD curve $\overline{M_p}$, whereas Fig. 5(b) presents the polydispersity ($\overline{M_w}/\overline{M_n}$). The low order average molecular weights $\overline{M_n}$ and $\overline{M_p}$ show a small reduction after the initial dose levels and then levels off. On the other hand, the higher order averages molecular weights $\overline{M_w}$ and mainly $\overline{M_z}$ are much more sensitive to the irradiation process increasing continuously. It is well known that lower orders MW averages are very sensitive to low molecular weight fractions and the higher orders, specially $\overline{M_z}$, are sensitive to the presence of polymer fractions with high molecular weight. The irradiation process is causing a mixed degradation mechanism including chain scission, branching, and cross-linking with conversion rate depending on the dose level. At low dose level, below 12.5 kGy, the effect is mainly chain scission, happening preferably in the more constrained chain segments. Chains that are bonded together forming the cross-linked agglomerates presented in the pristine polymer are the ones more suitable to suffer scission. As the dose level increases above 12.5 kGy the radical chains formed during the chain scission are in sufficient number to recombine forming bigger branched chains and cross-linked agglomerates. The behavior of the polydispersity fits to this mechanism: drops immediately after irradiation starts, rising continuously with increasing dose levels showing the strong contribution of chain scission at low doses and the ever crescent formation of chain branching at higher dose levels.

In order to better characterize these two fractions, one of low molecular weight formed by chains that have being broken and the other of a high MW formed by branched chains, the MWD curves were deconvoluted into three Gaussian peaks. Fig. 6(a)–(e) shows the deconvoluted MWD curves obtained for varying dose levels. In general terms the MWD curve is three modal having a central major peak flanked by two minor peaks. The major peak, which is in the range of one to three hundred thousand Daltons (D), corresponds to the chains that will form the bulk of the final polymer. The other two are the low molecular weight fraction formed by broken chains (30,000 D) and the high molecular weight fraction formed by branched chains with MW up to one million Daltons. A line at 100,000 D was drawn in every plot as a guide to the eyes. The pristine iPP is of high molecular weight reflecting its low melt flow rate (0.5 g/10 min). Upon irradiation, even at low doses, the main peak is downshifted and a low molecular weight fraction is formed, seeing in the deconvoluted curve at 5 kGy. Increasing the dose the low molecular weight fraction peak tends to reduce and a high MW fraction starts to appear at 12.5 kGy increasing for higher irradiation doses. Dose up to 20 kGy is considered of a low level taking into reference the standard sterilization dose, which is of 25 kGy (either gamma or e-beam). From the data obtained in this work it is possible to advance that goods made by non-stabilized iPP, which will be sterilized by standard irradiation procedure, will suffer great molecular weight damage.

The content of both low and high molecular weight fractions was assessed measuring their deconvoluted peak areas. Fig. 7 shows their content (as partial weight fraction) as a function of the irradiation dose level. The low molecular weight fraction is mainly formed at low doses reducing its concentration with increasing irradiation levels. On the contrary, the high molecular weight fraction is null at low doses and increases continuously with increasing irradiation levels. SEC measurements could not be performed at the 100 kGy irradiated sample because it was almost insoluble due to the great level of chain branching and cross linking. From the analysis of the MWD data we can conclude that chain scission is always being produced but it is converted into highly branched and eventually cross-linked chains.

The changes in the MW during the gamma irradiation can be also analyzed applying the chain-scission distribution function (CSDF) mathematical tool. The curves are shown in Fig. 8. The CSDF curve quantifies the changes in the MW of the chain fraction in comparison to its original MW value. In general terms either positive or increasing CSDF values are understood as chain scission and negative or decreasing values indicate chain branching (cross-linking is not considered because only the soluble fractions of the sample are measured by SEC and so analyzed by CSDF). All CSDF curves are placed in the positive side indicating that the chains are going through a strong scission process, which increases with the irradiation dose. When only chain scission is taking place, the expected CSDF curve values are
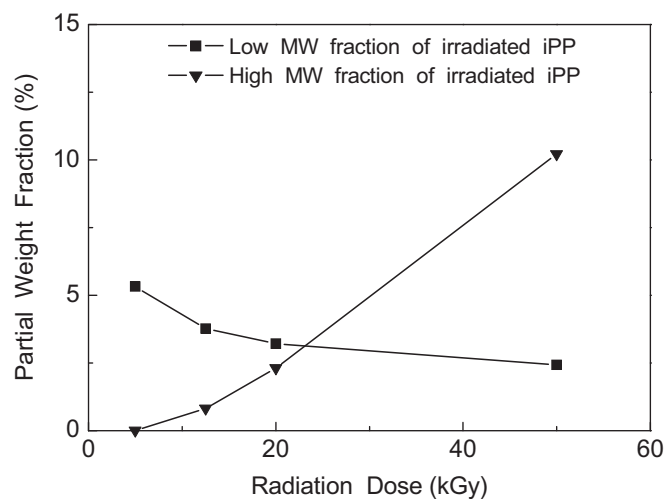

Fig. 7. Partial weight fraction (area under each curve) of low and high molecular weight fractions as a function of irradiation dose.
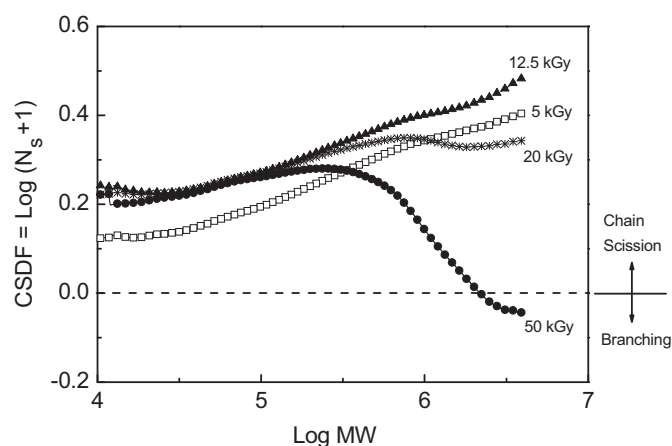

Fig. 8. Chain scission distribution function CSDF curves of iPP after the irradiation process showing chain scission and increased branching at high molecular weight with increasing irradiation dose.

positive and its shape is of an increasing exponential curve. The data show an exponential increase up to roughly one million Daltons, above that, the curve drops down. This drop indicates that an increase in molecular weight, i.e. chain branching, is taking place preferentially in the high molecular weight chains. The higher the dose the greater is the drop indicating the continuous increase in the chain-branching process. This result is in accordance with all measurements presented in this paper: melt flow rate, gel fraction and rheological properties.

4. Conclusions

The unstabilized iPP irradiated with gamma rays in inert atmosphere showed a degradation process, which includes a mixture of chain scission and chain branching. At low irradiation doses, below 12.5 kGy the chain scission is the preferential process producing free macro radicals that are neutralized, greatly reducing the molecular weight of the polymer. As the dose level is increased above 12.5 kGy, the concentration of newly formed free macro radicals is too great to be neutralized and so some macro radicals attack neighboring chains leading to chain branching and ultimately to cross-linking. The morphology of the insoluble fraction produced at high dose levels is different from the insoluble fraction present in the original material.

Acknowledgements

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