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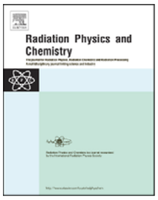

High-energy radiation forming chain scission and branching in polypropylene

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

$$M^{+} + e^{-} \longrightarrow M^{*} \qquad \text{(R2)}$$

$$M^{*} \longrightarrow R_1^{\bullet} + R_2^{\bullet} \qquad \text{(R3)}$$

$$R_1^{\bullet}\ (or\ R_2^{\bullet}) + M \longrightarrow R_1M^{\bullet} \qquad \text{(R4)}$$

Scheme 1

$$\begin{array}{ll}
\textit{Initiation} & PH \xrightarrow{\gamma} P^{\bullet} \\
\textit{Propagation} & P^{\bullet} + O_2 \longrightarrow PO_2^{\bullet} \\
 & PO_2^{\bullet} + PH \longrightarrow PO_2H + P^{\bullet} \\
\textit{Terationmin} & PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow \textit{Inative products} + O_2 \\
 & PO_2^{\bullet} + P^{\bullet} \longrightarrow POOP \\
 & P^{\bullet} + P^{\bullet} \longrightarrow PP
\end{array}$$

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