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# Polypropylene nanogel: "Myth or reality"

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ABSTRACT

The objective of this work is the investigation of the nanogel and microgel formation in modified PP. The modified PP in pellets was synthesized by gamma irradiation of pristine PP under a crosslinking atmosphere of acetylene in dose of 5, 12.5 and 20 kGy, followed by thermal treatment for radical recombination and annihilation of the remaining radicals. The thin film gel of the polypropylenes was obtained by extraction in boiling xylene for period of 12 h at 138 °C, followed by decantation in beaker at room temperature of 25 °C with the total volatilization of the xylene and deposition of dried material film on glass substrate under agitation by Settling process. The thin film gel formed of pristine PP and modified PP (i.e., irradiated) was characterized using scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and differential scanning calorimetry (DSC). The PP morphology indicated the nanogels and microgel formation with increase of spherulitic concentration and crystallinity at dose of 12.5 kGy.



## 1. Introduction

Ionizing radiation such as gamma radiation and electron beam has been used widely in industry for crosslinking of polymer. This technology can be well extended to the crosslinking of nanopolymeric materials or nanocomposites (Haji-Saeid et al., 2007). Potential applications of ionizing radiation involve irradiation of polyolefins as for example polypropylene and this process is one of the important tools in application of nanotechnology (Chmielewski et al., 2007).

When polyolefins are subject to ionizing radiation two main effects occur: crosslink and scission of macromolecules (Chapiro, 1962). The dominant effect between these competitive processes depends on the structural peculiarities and conditions of irradiation. Depending on the atmosphere of irradiation oxidation and branching are mechanisms to take in consideration. Milicevic and Suljovrujic (2010) studied the evolution of dielectric relaxations with gamma irradiation in PP and showed that degradation is the major reaction in the initial step of irradiation independent of the atmosphere. The iPP irradiated in acetylene presented the lowest value of $G(s)/G(x)$, dielectric losses and Dg while in air those values were the highest due to oxidative degradation with formation of carbonyl, and other polar groups. Lugao et al. (2000) comparing reducing ($H_2$) and crosslink(acetylene) atmospheres also verified that degradation occurs at early stages of irradiation ($<3$ kGy) changing with increase of dose probably owing to double bond formation and grafting, of acetylene, on PP macrochains changing them from linear to branched ones. This justifies the formation of microgels as highly branched molecules (Rosiak et al., 2005).

Questionable is the dimension scale in which the gel starts to form. What is the minimum extension of the gel observed when the polymer is modified by gamma in typical conditions of polymer irradiation? Are the nanogels the early stage of gel formation in irradiated PP? This topic was not largely investigated before representing a challenge for the scientists in the nanoscience area.

Khoury (1966) investigated the nature of some crystallization habits exhibited by isotactic polypropylene when the polymer is crystallized from moderately concentrated solutions in some solvents (xylene, mineral oil and amyl acetate). This study provides some detailed insight into the nature of the early stages of evolution of monoclinic polypropylene spherulites from solution as well as from the melt, and considers that a final analysis will have to account for the preferred molecular orientation with respect to the radial direction in the fully grown spherulites. Crystal phase in polyethylene gels prepared from solutions was studied by Pakhomov et al. (2002) with different concentrations in decalin and *p*-xylene, starting with very low concentrations ($C \geq 0.03\%$). The different boiling points of *p*-xylene (138 °C), decalin (186 °C), and mineral oil (about 300 °C) or, more precisely, to the remoteness of the boiling point from the crystallization temperature (90–110 °C) at which the gel network was formed are responsible by the straightening of chain segments. The appreciable convection

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in *p*-xylene stimulates the origin of crystallites but prevents their growth. In the study of the sol–gel transition of isotactic polypropylene (iPP) in organic solvents, the structure of gels was characterized by Matsuda et al. (1987) They obtained a somewhat different network structure where in composed by many spherulites in contact with each other, being bound with crystalline ties. This indicates that these spherulites and crystalline ties form a three-dimensional network structure (Matsuda et al., 1987) as microgel form. The gelation for crystalline polymer generally accompanies the formation of crystalline entity at a cross-linking point. Therefore the gelation process is regarded as a kind of crystallization from polymer solutions (Nakaoki et al., 1998; Domszy et al., 1986).

Characterization of heterogeneities produced by radiation induced cross-linking of diacrylates are reported by Krzeminski et al. (2010a). They observed a dual relaxation phenomenon assigned to structure consisting of clusters with high cross-link density formed in continuous domain of monomers with lower cross-link density. These clusters are considerate microgels in the early stage of polymerization.

Results of iPP exposed to gamma rays irradiation from 5 to 100 kGy under inert atmosphere was commented by Otaguro et al. (2010). The results showed that gamma irradiation of iPP produce chain scission, branching and crosslinking. In many cases, crosslinking and scission proceed, simultaneously; however, dependent on the molecular structure, one or another usually predominates (Clegg and Collyer, 1991; Cleland et al., 2003). In presence of acetylene occurs long chain branches formation with increase of molecular weight dispersion and average molecular weight after irradiation modification (Yoshiga et al., 2009).

The objective of this work is the investigation of the formation of nanogel and microgel in pristine and modified PP.

## 2. Experimental

### 2.1. Materials and methods

The isotactic Polypropylene (iPP) with melt flow index, MFI=1.5 dg min$^{-1}$ (ASTM D 1238-4) and *Mw*=338,000 g mol$^{-1}$ from Braskem – Brazil, was supplied in pellets. iPP pellets were conditioned in nylon bags in which acetylene 99.8%, supplied by White Martins was added. The irradiation process of the pellets placed in bags was performed in a $^{60}$Co gamma source at dose rate of 5 kGy h$^{-1}$. The radiation doses were 5, 12.5 and 20 kGy monitored by a Harwell Red Perspex 4034 dosimeter. After irradiation the pellets were submitted to thermal treatment at 90 °C for 1 h to promote the recombination and annihilation of residual radicals (Oliani et al., 2010a, 2010b).

#### 2.1.1. Melt flow index

The MFI was obtained using a Ceast apparatus in which the samples were flowed through an orifice of 2.00 mm diameter during 10 min under a loading of 2.16 kg at 230 °C.

#### 2.1.2. Gel fraction/sol fraction

The gel content was determined by extraction of sample of PP, packed in a stainless-steel sieve of 500 mesh, in boiling xylene containing antioxidant Irganox 1010 for a period of 12 h at 138 °C (ASTM D 2765-01). The gel fraction is determined by the relation between the mass of the dried gel and the initial mass of the sample multiplied by 100. The sol fraction, soluble part of the sample, was gotten for decantation in beaker at room temperature of 25 °C. Under agitation at 40 rpm in Quimis shake-table equipment gradual deposition occurred of material film on fine glass substrates by Settling process. With total volatilization of the xylene, dried film was formed. The initial concentration of the PP for the measure of gel fraction was approximately 0.1 g/100 cm$^3$.

#### 2.1.3. Scanning electron microscopy

SEM was done using an EDAX PHILIPS XL 30. In this work, thin coat of gold was sputter-coated onto the samples.

#### 2.1.4. Field emission scanning electron microscopy

The films obtained from the sol fraction of polypropylene (gels) were fixed in the specimen holder and coated with a thin layer of carbon. The samples were analyzed by scanning electron microscopy with field emission, JEOL FESEM, JSM-6701F, Japan, using the accelerating voltage of 5.0 kVA which allows the observation with more resolution than conventional SEM.

#### 2.1.5. Differential scanning calorimeter

Thermal analysis of the samples was carried out with a DSC instrument 822e, Mettler Toledo (Switzerland) in nitrogen atmosphere. For thermal crystallization the samples ($\pm$10 mg) were heated to 280 °C, held for 5 min then cooled to 25 °C; finally they were reheated to 280 °C. The heating and cooling rates were 10 °C min$^{-1}$. The degree of crystallization was determined by the following equation:

$$X_C(\%) = \frac{\Delta H_f \times 100}{\Delta H_0}$$

where $\Delta H_f$ is the melting enthalpy of the sample, $\Delta H_0$=melting enthalpy of the 100% crystalline PP which is assumed to be 209 kJ kg$^{-1}$ (Stojanovic et al., 2005; Brandrup et al., 1999).

## 3. Results and discussion

### 3.1. Gel fraction

The gel fraction inform about crosslink effect of the radiation in the material. It was observed the gradual increase of the gel percentage according to increase of the irradiation dose of the samples, Table 1. The melt flow index of pristine PP was 1.5 dg min$^{-1}$. In the samples of PP 5 kGy and PP 12.5 kGy was observed decrease in the melt flow index to 0.9 dg min$^{-1}$, indicative of crosslink of the material. In the PP 20 kGy sample occurred a decrease of the melt flow index to 0.5 dg min$^{-1}$, indicating the pronounced occurrence of crosslink.

### 3.2. Scanning electron microscopy

In interesting work of Du et al. (2010) it was investigated the interfacial interaction of the PP with organoclay and morphologies of the residue after extracted with boiling xylene. As shown in that work, boiling xylene extracts only free PP chains, as evidenced by scanning electron microscopy images of microspherical structure of the aggregates, similar to the micrographs seen in our work (Fig. 1).

**Table 1**
Gel fraction and MFI of the pristine PP and modified PP samples.

| Samples | Gel fraction (%) | Melt flow index (dg min$^{-1}$) |
|---|---|---|
| iPP | 1.14 | 1.5 |
| PP 5 kGy | 1.01 | 0.9 |
| PP 12.5 kGy | 2.27 | 0.9 |
| PP 20 kGy | 16.00 | 0.5 |

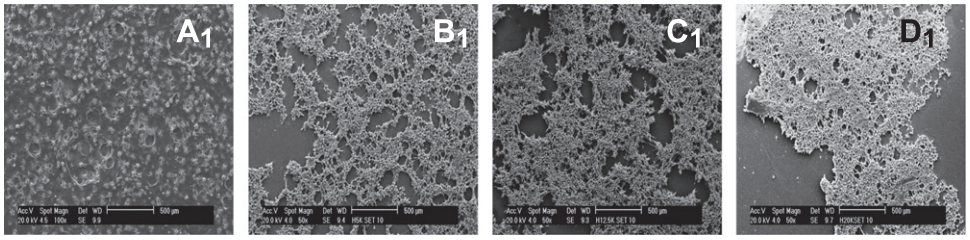


**Fig. 1.** SEM of the gel from solution crystallized in glass substrate, $F_s$=soluble fraction: ($A_1$) Pristine, ($B_1$) PP 5 kGy, ($C_1$) PP 12.5 kGy and ($D_1$) PP 20 kGy, scale bar=500 μm.

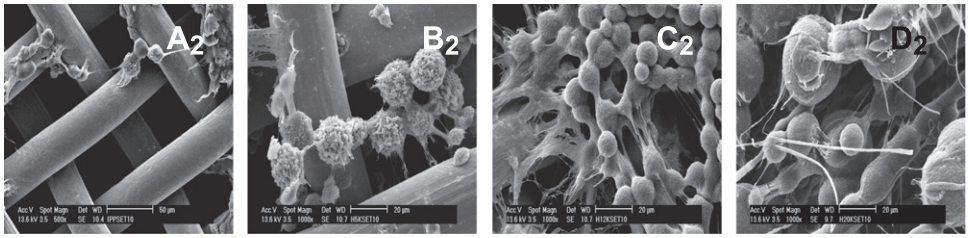


**Fig. 2.** Gel fraction content in of samples retained in stainless-steel sieve: ($A_2$) Pristine, scale=50 μm, ($B_2$) PP 5 kGy, scale=20 μm, ($C_2$) PP 12.5 kGy, scale=20 μm and ($D_2$) PP 20 kGy, scale bar=20 μm.

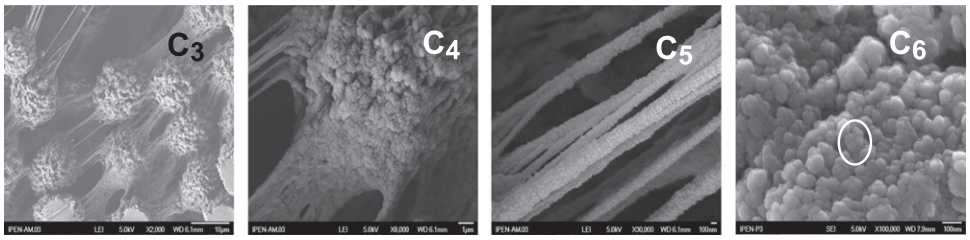


**Fig. 3.** FESEM images of nanogels formation in polypropylene thin films, $F_s$=soluble fraction of PP 12.5 kGy. ($C_3$) Microgels PP, scale bar=10 μm; ($C_4$) Microgel PP, scale bar=1 μm; ($C_5$) Nanofibers PP, scale bar=100 nm; ($C_6$) Nanogels PP, scale bar=100 nm.

The gel fraction was used by many researchers (Lugao et al., 2007; Yoshiga et al., 2009; Suljovrujic, 2009; Bonderer et al., 2010; Spadaro and Valenza, 2000). It is a gravimetric determination of the insoluble gel portion. Fig. 2 structures cross-linked named microgels that increase in the doses of 12.5 and 20 kGy.

The morphology of the insoluble material which is retained in the 500 mesh stainless-steel sieve after extraction in boiling xylene is presented in Fig. 2. The samples deposited on sieve show spherulites with average diameters of 17 μm for pristine; 20 μm for 5 kGy; 10 μm for 12.5 kGy and 13–31 μm for 20 kGy. The insoluble part consisting of microgels of PP, Fig. 2$A_2$, presented an irregular form while in $B_2$, $C_2$ and $D_2$, the spherical form predominates. These structures are evident in samples irradiated with higher doses (12.5 and 20 kGy).

### 3.3. Field emission scanning electron microscopy

The gel/microstructure has been observed at higher magnification through modern methods of scanning electron microscopy, such as FESEM. The structures presented in this Fig. 3 are composed of typical spherulites agglomerated or linked by nanofibrils. The fibrils as the spherulites are built by a crystalline phase (lamella) and an amorphous phase. Fig. 3$C_3$ shows spherulites with 10 μm diameter linked by nanofibrils with approximately 200 nm of diameter. The Figs. 3$C_4$, $C_5$ and $C_6$ present details of the Fig. 3$C_3$. The Fig. 3$C_5$ shows the morphology of nanofibers of polypropylene and in Fig. 3$C_6$ is observed an agglomeration of nanogels of polypropylene with an average diameter of 50 nm.

In the case of pristine PP the crystals grow in solution of the polymer, whereas, in modified PP, the crystal grows in the gel owing to the nucleation originating from the crosslink nucleus. This is responsible by the difference between the samples reported in Fig. 2. Analogous to Krzeminski et al. (2010a, b) work in which monomers rigid clusters having typical dimension of 15 nm were evidenced from the early steps of the curing process, it can be considered that evolution of nanogels, formed by radiation in PP, in size creates interstitial domains with lower crosslink density and large number of defects. These nanogels are considered nucleation points.

**Table 2**
DSC characteristics of PP gel of different irradiation dose during the second run of melting.

| | Melting peak temperature, $T_{m2}$ (°C) | Crystallization peak temperature, $T_c$ (°C) | Degree of crystallinity, $\chi_{C2}$ (%) |
|---|---|---|---|
| iPP | 156.3 | 111.8 | 43.0 |
| 5 kGy | 158.5 | 115.4 | 44.7 |
| 12.5 kGy | 158.2 | 116.5 | 45.6 |
| 20 kGy | 158.8 | 117.3 | 42.1 |

### 3.4. Differential scanning calorimeter

The DSC concerning the $T_{m2}$, $T_C$ and $\chi_{C2}$ results are presented in Table 2. It can be observed that melting temperature, crystallization temperature and crystallinity % increase with the dose, with exception of the sample irradiated with 20 kGy which presented the lower crystallinity, and Fig. 4.

The irradiation is responsible for crystallite nucleus formation with subsequent evolution to the spherulites network. On the

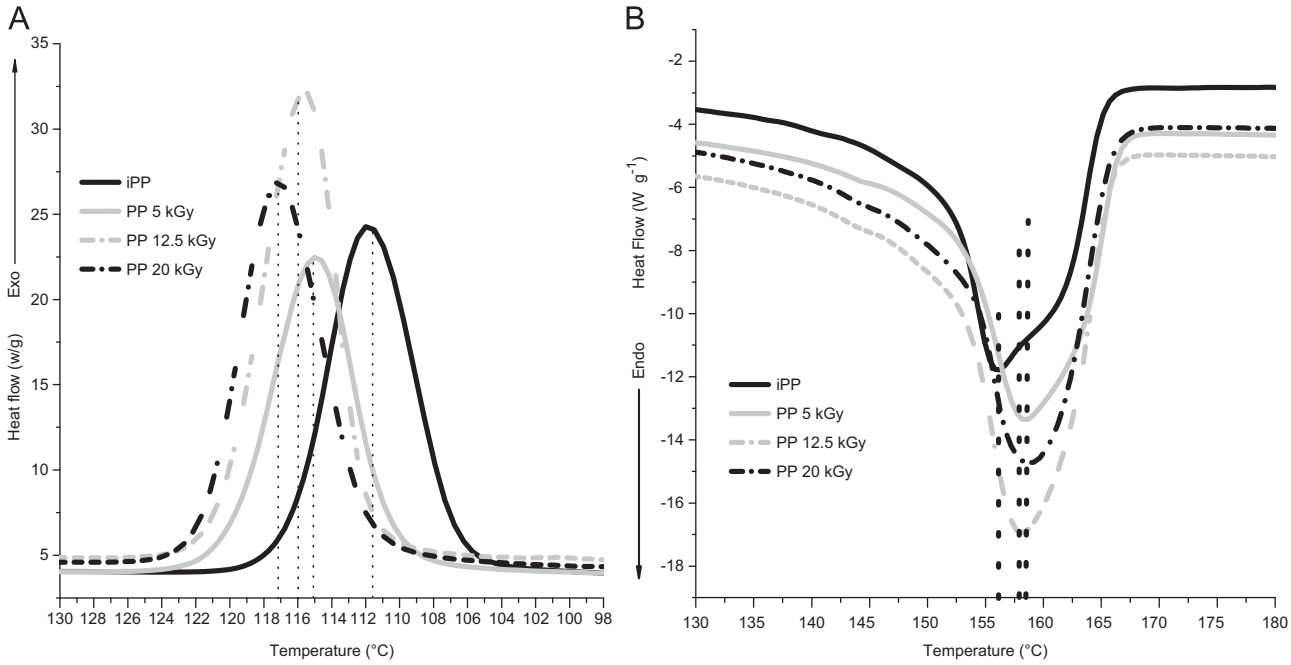


**Fig. 4.** DSC curves of: (A) crystallization of Gel PP during exothermic cooling segment; (B) melting of Gel PP of different irradiation dose in the second heating run.

other hand, in pristine iPP there are few nucleus due to the entanglement and practically no spherulites. Another reason for the absence of spherulites in this sample is the low crystallization temperature that difficults the arrangement between large and small crystallites. This difference in crystallite sizes can be seen in the melting curve that presents a peak and a shoulder at higher temperature. In the irradiated samples the crystallites rearrange to form spherulites. Concerning the crystallinity of the samples it is known that chain scission favors this property but not exclude the contribution of long chain branching originated from the acetylene reaction, according to Otaguro et al. (2010). This effect is observed in Table 2, for low doses ($<20$). The crystallinity decreases for the sample of 20 kGy due to the increase of crosslinking, this sample has the highest value of gel fraction (16%).

Finally the lower melting temperature of the pristine sample denotes the existence of small and imperfect crystallites, but also crystallites more perfect and larger, corresponding to the shoulder in Fig. 4. The higher melting temperatures for the irradiated samples denote larger and more perfect crystals than those corresponding to the lower pristine peak, originating from scissions in the chains.

## 4. Conclusion

The main difference between the pristine PP and modified PP (i.e. irradiated) is the fact that in the former the crystals grow in solution. The formation of nanogels comes from irradiated sites prior to crosslink bonds and minor from small segments originating from scissions. Evolution of nanogels in size creates interstitial domains with lower crosslink density and large number of defects. These nanogels are considered nucleation points.

The irradiation is responsible by the crystallite nucleus formation with subsequent evolution to the spherulite network. On the other hand, in pristine iPP there is few nucleus due to the entanglement and practically no spherulites. Formation of nanogels was observed in films from solution of the irradiated PP, these nanogels are composed by crystalline and amorphous fraction and therefore the crosslink nucleus are responsible for their formation. From this work the main conclusion is that nanogel is present in the irradiated PP and has crystallinity.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.radphyschem.2011.12.011.

## References

Bonderer, L.J., Feldman, K., Gauckler, L.J., 2010. Platelet-reinforced polymer matrix composites by combined gel-casting and hot-pressing. Part I: polypropylene matrix composites. Compos. Sci. Technol. 70, 1958–1965.
Brandrup, J., Immergut, E.H., Grulke, E.A. (Eds.), 1999. Wiley Interscience.
Chmielewski, A.G., Chmielewska, D.K., Michalik, J., Sampa, M.H., 2007. Prospects and challenges in application of gamma, electron and ions beams in processing of nanomaterials. Nucl. Instrum. Methods B 265, 339–346.
Chapiro, A., 1962. Radiation chemistry of polymeric systems. IX – Radiation effects in polymers of the cross-linking type. Interscience, London, 385–493.
Cleland, M.R., Parks, L.A., Cheng, S., 2003. Applications for radiation processing of materials. Nucl. Instrum. Methods. B 208, 66–73.
Clegg, D.W., Collyer, A.A., 1991. Irradiation effects on polymers. In: Clough, R.L., Gillen, K.T., Dole, M. (Eds.), Chapter 3 – Radiation Resistance of Polymers and Composites. , Elsevier Applied Science, pp. 79–156.
Domszy, R.C., Alamo, R., Edwards, C.O., Mandelkern, L., 1986. Thermoreversible gelation and crystallization of homopolymers and copolymers. Macromolecules 19 (2), 310–325.
Du, X., Zhang, Z., Yu, H., Wan, D., Xing, H., Tang, T., 2010. Synthesis and characterization of a novel covalently functionalized organoclay and its polypropylene nanocomposite. J. Appl. Polym. Sci. 115, 1105–1112.
Haji-Saeid, M., Sampa, M.H., Ramamoorthy, N., Guven, O., Chmielewski, A.G., 2007. The role of IAEA in coordinating research and transferring technology in radiation chemistry and processing of polymers. Nucl. Instrum. Methods-B 265, 51–57.
Khoury, F., 1966. The spherulitic crystallization of isotactic polypropylene from solution: on the evolution of monoclinic spherulites from dendritic chain-

folded crystal precursors. J. Res. Nat. Bur. Stand. – A. Phys. Chem. 70 A (1), 29–61.

Krzeminski, M., Molinari, M., Troyon, M., Coqueret, X., 2010a. Characterization by atomic force microscopy of the nanoheterogeneities produced by radiation-induced cross-link polymerization of aromatic diacrylates. Macromolecules 43, 8121–8127.

Krzeminski, M., Molinari, M., Troyon, M., Coqueret, X., 2010b. Calorimetric characterization of the heterogeneities produced by the radiation-induced cross-linking polymerization of aromatic diacrylates. Macromolecules 43, 3757–3763.

Lugao, A.B., Artel, B.W., Ojeda, T., Tokumoto, S., Siemens, R., Makuuchi, K., Villavicencio, A.L.C.H., 2000. Reaction mechanism and rheological properties of polypropylene irradiated under various atmospheres. Radiat. Phys. Chem. 57, 389–392.

Lugao, A.B., Artel, B.W., Yoshiga, A., Lima, L.F.C.P., Parra, D.F., Bueno, J.R., Liberman, S., Farrah, M., Terçariol, W.R., Otaguro, H., 2007. Production of high melt strength polypropylene by gamma irradiation. Radiat. Phys. Chem. 76, 1691–1695.

Matsuda, H., Inoue, T., Okabe, M., Ukaji, T., 1987. Study of polyolefin gel in organic solvents I. Structure of isotactic polypropylene gel in organic solvents. Polym. J. 19 (3), 323–329.

Nakaoki, T., Shuto, H., Hayashi, H., Kitamaru, R., 1998. High resolution solid-state $^{13}C$ NMR study of isotactic polypropylene gel. Polymer 39 (17), 3905–3908.

Oliani, W.L., Lima, L.F.C.P., Parra, D.F., Dias, D.B., Lugao, A.B., 2010a. UV stability of HMS-PP (high melt strength polypropylene) obtained by radiation. Radiat. Phys. Chem. 79, 325–328.

Oliani, W.L., Parra, D.F., Lugao, A.B., 2010b. Study of the morphology, thermal and mechanical properties of irradiated isotactic polypropylene films. Radiat. Phys. Chem. 79, 383–387.

Otaguro, H., Lima, L.F.C.P., Parra, D.F., Lugao, A.B., Chinelatto, M.A., Canevarolo, S.V., 2010. High-energy radiation forming chain scission and branching in polypropylene. Radiat. Phys. Chem. 79, 318–324.

Pakhomov, P.M., Chmel, A.E., Khizhnyak, S.D., Galitsin, V.P., 2002. Crystal phase in polyethylene gels. Dokl. Phys. Chem. 386 (1–3), 222–224.

Rosiak, J.M., Ulanski, P., Kadlubowski, E., 2005. Conventional and radiation synthesis of polymeric nano and microgels and their possible applications. In: Proceedings of a Consultants Meeting. International Atomic Energy Agency. Bologna, pp. 99–120.

Spadaro, G., Valenza, A., 2000. Influence of the irradiation parameters on the molecular modifications of an isotactic polypropylene gamma-irradiated under vacuum. Polym. Degrad. Stab. 67, 449–454.

Stojanovic, Z., Kacarevic-Popovic, Z., Galovic, S., Milicevic, D., Suljovrujic, E., 2005. Crystallinity changes and melting behavior of the uniaxially oriented iPP exposed to high doses of gamma radiation. Polym. Degrad. Stab. 87, 279–286.

Suljovrujic, E., 2009. The influence of molecular orientation on the crosslinking/oxidative behaviour of iPP exposed to gamma radiation. Eur. Polym. J. 45, 2068–2078.

Milicevic, D.S., Suljovrujic, E., 2010. Properties of isotactic polypropylene irradiated in various atmospheres. Chem. Ind. 64, 201–208.

Yoshiga, A., Otaguro, H., Parra, D.F., Lima, L.F.C.P., Lugao, A.B., 2009. Controlled degradation and crosslinking of polypropylene induced by gamma radiation and acetylene. Polym. Bull. 63, 397–409.