Microgel Spherulities Formation in Polypropylene Thin Films

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Abstract. The objective of this work is to study the formation of microgel in pristine PP and modified PP. The modified PP in pellets was synthesized by gamma irradiation of pristine PP under a crosslinking atmosphere of acetylene in different doses 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 becker at room temperature of 25°C with the total volatilization of the xylene and deposition of dried material film on fine glass blades under agitation by Settling process. The thin film gel formed of pristine PP and modified (i.e., irradiated) was characterized using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The PP morphology indicated the microgel formation with increase of spherulitic concentration and crystallinity when increase of dose irradiation, except at 20 kGy.

Introduction

Isotactic polypropylene in the monoclinic α phase crystallizes both from solution and from the melt with a unique microscopic texture that has long provided something of a morphological puzzle [1].
The kinetics of melting and the non-isothermal crystallization of PP gels obtained through irradiation in bulk, boiling in xylene and subsequent drying was investigated by means of DSC. When the irradiation dose increases the melting temperatures decrease, the enthalpies are low and do not depend on the dose applied [2].
Khoury [3], 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 of the mechanism of growth and hitherto little understood the origin of atypical fine structures of spherulites of the monoclinic crystalline modification of polypropylene.
Intermolecular crosslinking between pendant vinyl groups and radical centers located on different macromolecules produce crosslinks that are responsible for the aggregation of macromolecules, which leads to the formation of a macrogel. It must be remembered that both normal and multiple crosslinks may contribute to the rubber elasticity of a network, whereas small cycles are wasted links [4].
According to the literature [5] if recombination occurs only intermolecularly, i.e. between two radicals localizes on separate chains, these macromolecules are linked together, average molecular weight of the polymer increases and, when the absorbed dose is sufficiently high, a macroscopic gel is formed.
In general, suitable polymer network architectures consist of netpoints and molecular switches, which are sensitive to an external stimulus. The netpoints determining the permanent shape can be of chemical (covalent bonds) or physical (intermolecular interactions) nature. Suitable crosslinking chemistry enables covalent crosslinks, while physical crosslinks are obtained in a polymer, whose morphology consists of at least two segregated domains, e.g., a crystalline and an amorphous phase [6].
The common way to investigate the effects of irradiation by either electron beam or γ-rays is to determine the yield of an event. An event change may involves the measurement of the changes in,

for example, molecular weight, solution viscosity or gel content, or the measurement of the amounts of specific gaseous materials evolved during exposure. As stated above one of the main effects of exposure of polymeric materials to high energy radiation is that the material undergoes scission of the main chain and the creation of free radicals, unsaturation (double bonds), crosslinks, end-links. Changes in the molecular size distribution will be a consequence of main chain scission, crosslinking and end-linking [7,8].

Otaguro et al. [9], exposed iPP to gamma rays irradiation from 5 to 100 kGy under inert atmosphere. The results showed that gamma irradiation of iPP produce chain scission, branching and crosslinking.

Cross-linking and chain scission are the main irreversible chemical changes, which determine the properties of the irradiated polymer. Usually they occur simultaneously. Investigations have revealed that the likelihood of the occurrence of cross-linking and chain scission is the same at lower radiations doses [10].

The preparations of the gels by stirring solutions at elevated temperatures and then cooling to room temperature by polyolefin is generally used for researchers [11-22].

The gelation for crystalline polymer generally accompanies the formation of crystalline entity as a cross-linking point. Therefore the gelation process is regarded as a kind of crystallization from polymer solutions [23].

Crystallization is deemed to consist of two separate processes: the primary nucleation and crystal growth. The former typically takes place in homogeneous melts or solutions, where the elementary process is the molecular transformation from a random coil to a compact chain-folded state. The latter occurs at crystal-melt or crystal-solution interfaces, where polymers come close and partially attached to the crystal surface followed by chain-folding and reorganization. Polymer crystallization usually happens in far from equilibrium and gives typical nonequilibrium crystal morphology of very thin lamellar form [24].

Matsuda et al. [25] studied sol-gel transition of isotactic polypropylene (iPP) in organic solvents and investigate the structure of gels using an ordinary microscope, a polarizing microscope, and a scanning electron microscope. They obtained a somewhat different network structure wherein, existed many spherulites in contact with each other, being bounded with crystalline ties. This indicates that these spherulites and crystalline ties form a three-dimensional network structure.

The objective of this work is to study the formation of microgel in pristine PP and irradiation modified PP.

Experimental

Materials and Methods

The isotactic Polypropylene (iPP) with MFI = 1.5 dg min^{-1} (ASTM D 1238-4) from Braskem – Brazil, was supplied in pellets. The MFI was obtained using a Ceast apparatus operating at 230ºC with a charge of 2.16Kg. The irradiation process of the pellets was performed under acetylene atmosphere in a ^{60}Co gamma source and dose rate of 10kGy h^{-1}. The irradiation 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 [26,27]. The acetylene (99.8%) was supplied by White-Martins S/A, of Brazil.

Gel fraction/Sol fraction

The gel fraction constitutes the insoluble fraction to be determined after elimination of solvent for drying in the vacuum until constant weigh. The fraction gel is determined by the relation between the mass of the dried gel and the initial mass of the sample multiplied by 100. The gel content was determined by extraction in boiling xylene containing antioxidant Irganox 1010 for a period of 12 h at 138°C (ASTM D 2765-01). The extraction was done involving the sample of PP in a stainless-steel grid of 500 mesh. The sol fraction the soluble part of the sample, was gotten by the decantation in becker at the room temperature of 25°C, with the total volatilization of the xylene and gradual deposition of dried material film on fine glass blades under agitation for 40 rpm in Quimis shake-table equipment by Settling process of thin films confection. The initial concentration of the PP for the measure of gel fraction was of approximately 0.1 g/100 cm^3.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was done using an EDAX PHILIPS XL 30. The nonconducting materials, like most of polymers, need to be coated using a metal including silver, gold or gold-palladium, or carbon to their outer surfaces be conductive. In this work, very thick coating of gold is sputter-coated onto the samples.

Thermal Analysis

Thermal analysis of the samples was carried out with a differential scanning calorimeter (DSC) instrument 822e, Mettler Toledo (Switzerland) in a nitrogen atmosphere. For thermal crystallization the samples (± 10 mg) were heated to 280°C, held for 5 min then cooled to 25°C; finally they were heated to 280°C. The heating and cooling rates were 10°C min^{-1}.

Results and Discussion

Gel fraction and Melt flow rate

Table 1 – Gel fraction and Melt Flow Index of the samples of pristine PP and modified PP

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

It was observed the gradual increase of the gel percentage according to increasing of the irradiation dose of the samples, Tab.1. The used polypropylene was of the Braskem mark, whose average of the determined melt flow index was of 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 for 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 for 0.5 dg min^{-1}, indicating the pronounced occurrence of crosslink.

Scanning Electron Microscopy (SEM)

The SEM images on pristine and irradiated PP samples are shown in Fig. 1 and 2 for the material retained in the grid during the gel fraction evaluation, and that deposited on glass plate during xylene evaporation, respectively. It can be seen that the spherulites are present on the irradiated samples only and the sample irradiated with 12.5 kGy had the higher spherlulitic concentration in both cases.

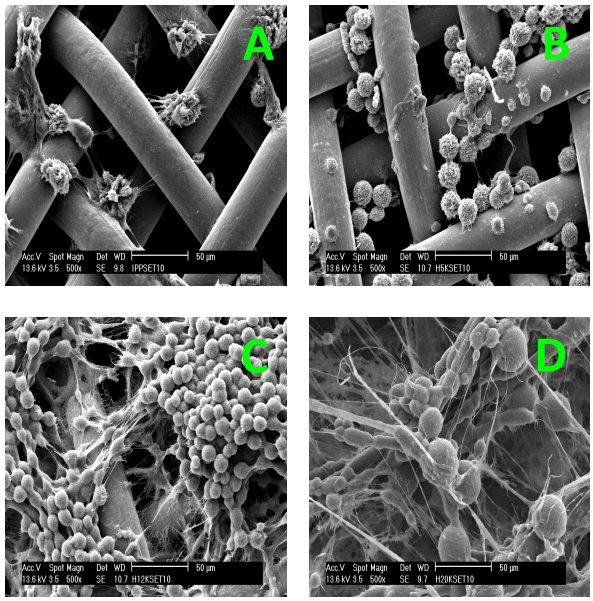

Fig. 1 – SEM of the Gel fraction content in stainless-steel grid of samples (A) PP; (B) PP 5 kGy; (C) PP 12.5 kGy; (D) PP 20 kGy, scale= 50 μm.

Elzubair et al. [17], estimated the degree of crosslinking in a gamma-irradiated UHMWPE via determination of the gel fraction using 100 mesh stainless-steel cage and swelling ratio. The gel fraction was used by many researchers [28, 29] which is a gravimetric determination in terms of the insoluble gel portion [30, 31].

The morphology of the insoluble material which is retained in the 500 mesh stainless-steel grid after Sohxlet extraction is also presented in this work, Fig.1.

In the samples deposited on stainless-steel grid, Fig.1, show spherulites with average diameters of 28 μm for pristine, 17 μm for 5 kGy, 11 μm for 12.5 kGy and 11-28 μm for 20 kGy, respectively.

The insoluble part consisting of microgels of PP, Fig 1A, is observed as some crystals of irregular form while in B, C and D the insoluble material presents spherical form increasing in concentration from B to D.

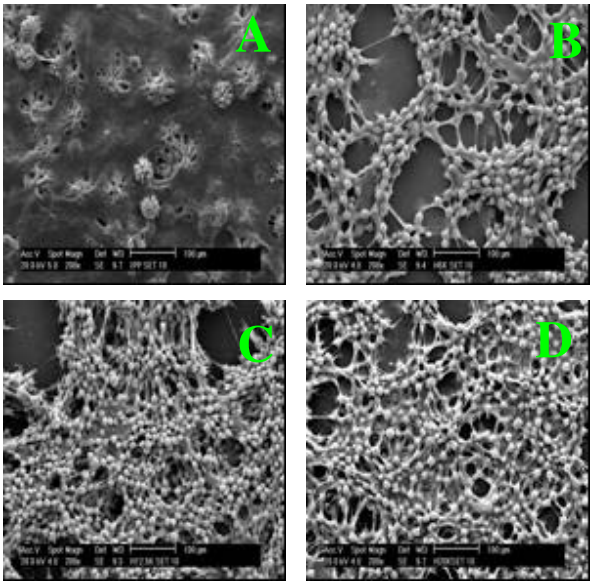

Fig.2 – SEM of the Sol fraction from solution crystallized in glass substrate, Fs= soluble fraction (A) PP; (B) PP 5 kGy; (C) 12.5 kGy and (D) 20 kGy, scale= 100 µm.

The samples deposited on glass blades, Fig.2, show spherulites with average diameters of 60 µm for pristine, 19 µm for 5 kGy and 12.5 kGy and 15 µm for 20 kGy, respectively. Already in the retained samples in the steel screen was showed an increase of the spherical structures amount with irradiation dose.
In Fig.2A, is observed the formation of thin film around an only spherulite, also in Fig.2B, at low dose the organization of spherulites was also deficient. When the samples are exposed to higher radiation doses, Fig.2C and 2D, more nucleation points are formed conducting to microgel creation as observed.

Thermal Analysis

Differential Scanning Calorimetry (DSC)

The DSC experiments were performed by a heating run followed by cooling and a second heating. The curves presented in Fig. 3 and 4 have been obtained on the cooling after the first heating and on the second heating for the samples deposited on the glass plates, respectively.

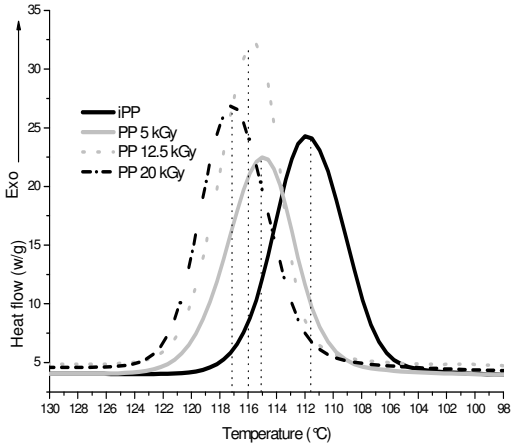

Fig.3 – DSC crystallization curves of PP, PP 5 kGy, PP 12.5 kGy and PP 20 kGy (cooling segment)

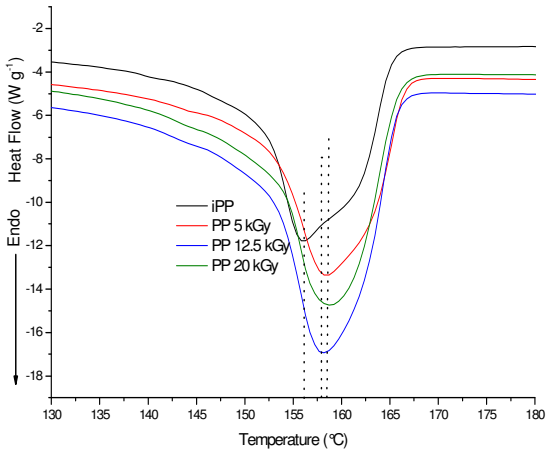

Fig.4 – DSC of Gel PP of different irradiation dose, during endothermic melting in the second heating run

The phenomena crosslinking and crystallization can take place simultaneously and will influence each other [32].

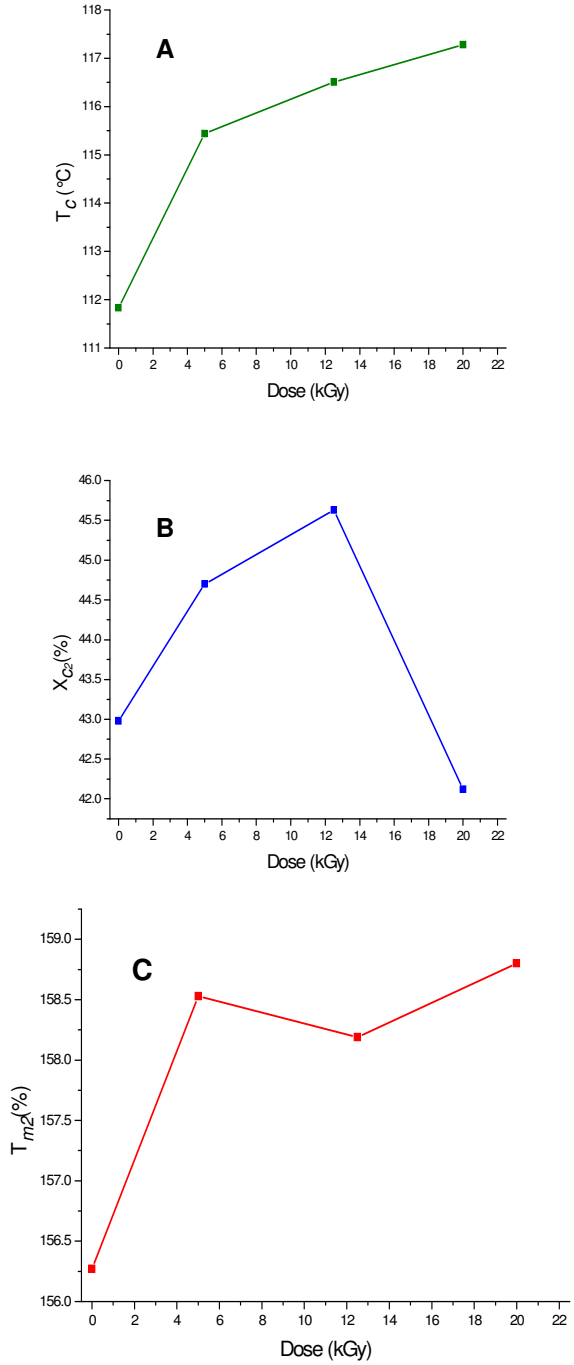

Fig. 5 – DSC characteristics of PP gel of different irradiation dose: (A) Crystallization peak temperature (T*c*); (B) Degree of crystallinity (χ_{C2}) and (C) Melting peak temperature (Tm_2)

The data extracted from the curves presented in Fig.3 and 4 have been plotted as a function of the dose in the Fig. 5A, 5B and 5C. We can observe that values of the variables presented in these figures for the pristine samples are lower than the corresponding for the irradiated samples with exception of the crystallinity of the PP irradiated with 20 kGy.

Discussion

The SEM micrographies showed a significant difference between the pristine and modified iPP samples. The irradiation is responsible for crystallite nucleus formation with subsequent evolution to the spherulite network. On the other hand, in pristine iPP there is a 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 of the great and little crystallites to form the spherulites. This difference in crystallite size 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 the chain scission favours this property. This effect can be observed in Fig.5B for low doses. On the other hand, the crystallinity decreases for the sample of 20 kGy due to the increasing of the crosslinking, confirmed by the value of 16% for the gel fraction, Tab.1.

Finally the lower melting temperature of the pristine sample denotes the existence of small and imperfect crystallites, but also 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, originated from scissioned chains.

Conclusions

The crystallinity decreased for the dose of 20 kGy due to the increase of the crosslinking, confirmed by the value of 16% for the gel fraction and showed in Fig.1D – SEM. The low melt flow index of 0.5 dg min^{-1} for PP 20 kGy sample is also an indicative of crosslinked material.

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. Therefore spherulites observed are microgels linked by tie molecules, effect of molecular nucleation from gamma irradiation.

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