



# Temperature rising elution fractionation, infra red and rheology study on gamma irradiated HMSPP

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## Abstract

It is well known that polypropylene undergoes simultaneous crosslinking and degradation under irradiation. However, there are speculations regarding the formation of branching under special conditions. It is also well known that the melt-strength property of a polymer increases with molecular weight and with long-chain branching due to the increase in the entanglement level. This study was a contribution to the understanding of the following points: the role of molecular weight, the role of structural modifications on nucleation properties; the structural changes on polypropylene.

The results showed that degradation was the major reaction in the initial step of irradiation, however, the largely modified molecules concentrated in the high molecular weight fraction. The results also confirm that the branching formation is likely to occur. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The fathers of radiation chemistry of polymers (Chapiro, 1962; Charlesby, 1960; Dole, 1973) have studied Polypropylene irradiations in air or inert medium. It was shown that PP undergoes pronounced degradation in air and have similar trends to in crosslinking and degradation under inert medium. Other authors (Black and Lyons, 1957; Schnabel and Dole, 1963) have already showed the effect of low-dose irradiation in vacuum. It was showed that an expressive degradation occurs even in vacuum and low dose at the initial stages of irradiation. Controlled rheology PP or visbreaking PP was already introduced in the market and produced in some case by irradiation. For example, Williams et al. (1998) (US Pat. No. 5,820,981, 1998) disclose a process for reducing the molecular weight of a propylene polymer by activating the first portion of the

polymer by exposing to ionizing radiation, adding the irradiated polymer to the second portion of unirradiated polymer, adding a stabilizing amount of an antioxidant to the mixture, and visbreaking by shear mixing in an extruder.

PP has been extensively studied, as already shown, for several years, and even industrially used to produce PP grades of controlled rheology, nevertheless the use of irradiation of PP under N<sub>2</sub> to promote long-chain branching in order to improve the elongational viscosity was never reported before the clever patents of (Scheve et al., 1990; DeNicola et al., 1995) to Himont now Montell (US Patent 4,916,198; US patent 5,414,027).

PP suffers from low melt strength, i.e., the melted PP does not exhibit an increase in resistance to stretching during elongation. It is well known that the melt-strength properties of a polymer increase with molecular weight and with long-chain branching due to the increase in the entanglement level (high melt strength PP–HMSPP). In spite of being the most fast-growing polymeric commodity nowadays those new grades of PP and its development have been barely studied and its

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general chemical characterization have been even less studied with few exceptions (Yoshi 1986; Lugao et al., 2000).

HMSPP as proposed by the Montell patents are produced by low-temperature and low-dose irradiation of high molecular weight isotática PP in N<sub>2</sub> atmosphere. So the well-known reactions would be mostly degradation and crosslinking. Degradation, however, is supposed to be the first and more intense reaction at the initial steps as already shown. So, according to the Montell patents, another reaction is likely to occur, branching or T links competing with crosslinkings or H links. Radicals are likely to decay very fast in amorphous phase, but under annealing the radicals entrapped in the crystal phase is likely to move to the boundary and react. The group lead by professor Silverman (Wenxiu et al., 1985) has already hypothesized on T links formation and also studied the radical decay of PP. It is easy to understand the difficulties in differentiating Hs from T's links and even these links if in very small amount from the bulk or from virgin polymer, as the chemical groups and chemically speaking links are essentially the same.

This work is a contribution to the development of a sound analytical procedure for this PP puzzle.

## 2. Experimental

**Materials** PP samples were H603 grade kindly supplied by OPP Petroquímica with the following characteristics: Flow Index—FI=XX, Melt strength—MS=MMM,  $M_n=46,425$ ,  $M_w=477,700$ ,  $M_z=2,058,000$ . Acetylene was Atomic absorption grade without further purification.

**Irradiation** The samples were irradiated in a Co-60 source from EMBRARAD, with 12.5 kGy of total dose. Dosimetry was performed using the Harwell Red Perspex 4034.

**Characterization** The fourier transform infrared spectra were measured on a Nicolet FTIR at a resolution of 4 cm<sup>-1</sup>. Temperature Rising Elution Fractionation (TREF) was conducted on an apparatus assembled by OPP staff in its laboratories as follows: 2 g of sample was dissolved in 180 ml of ortho-dichlorobenzene (ODCB) for 1 h at 140°C; sample was passed through a

fractionating column heated to 140°C and started the cooling phase at 12°C/h to 25°C and recovers the first fraction; heating was done at 15°C/h and fractions were taken at 40°C, 80°C, 100°C and 140°C; fractions were precipitated with acetone and methanol and filtered for gravimetric analysis.

## 3. Results

Fig. 1 shows the relation between FI and MS of commercial OPP resins. It is possible to get acquainted with the direct relation between FI and MS, as both are related to molar mass and branching structure. Table 1 shows the rheological PP samples after irradiation had the following rheological features. It is possible to observe the tremendous enhancement in the processing characteristics of PP. Even increasing the flow index after irradiation, the resin showed much higher values of MS and also higher values of extensibility, showing improved performance. Table 1 shows the results of our irradiation synthesis. If we compare the results of MS with standard resins at the same level of FI the HMS resin had numbers of MS 4–9 times higher than the standard ones. So, one could easily suppose that major structural changes were likely to occur.

Surprisingly, the TREF results of the virgin sample were very similar to the other rheologically modified resins. Fraction 1 is the product at 25°C; Fraction 2 is at 40°C and so on. One possible explanation to that is the increase in the fraction 6 (140°C) for both irradiated resins. The increase in the fraction 6 can be attributed to

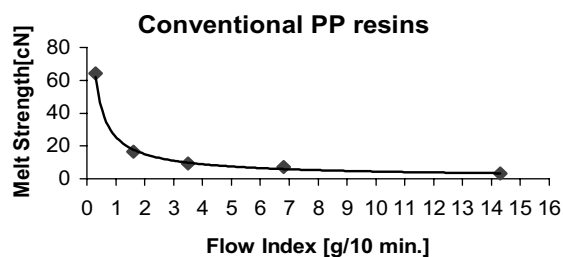


Fig. 1. Standard resins of OPP company and the relation between their Flow Index (FI) and Melt Strength (MS).

Table 1  
Rheological characteristics of the irradiated samples

| Sample no. | Sample                                                       | Flow index (g/10 min) | Melt strength (cN) | Extensibility (cm/s) |
|------------|--------------------------------------------------------------|-----------------------|--------------------|----------------------|
| 1          | Virgin H603 PP                                               | 1.50                  | 16.34              | 7.94                 |
| 2          | C <sub>2</sub> H <sub>2</sub> irradiated 20 kGy (sample 131) | 3.33                  | 96.2               | 10.90                |
| 3          | C <sub>2</sub> H <sub>2</sub> irradiated 2.5 kGy (sample 23) | 2.18                  | 48.87              | 10.12                |

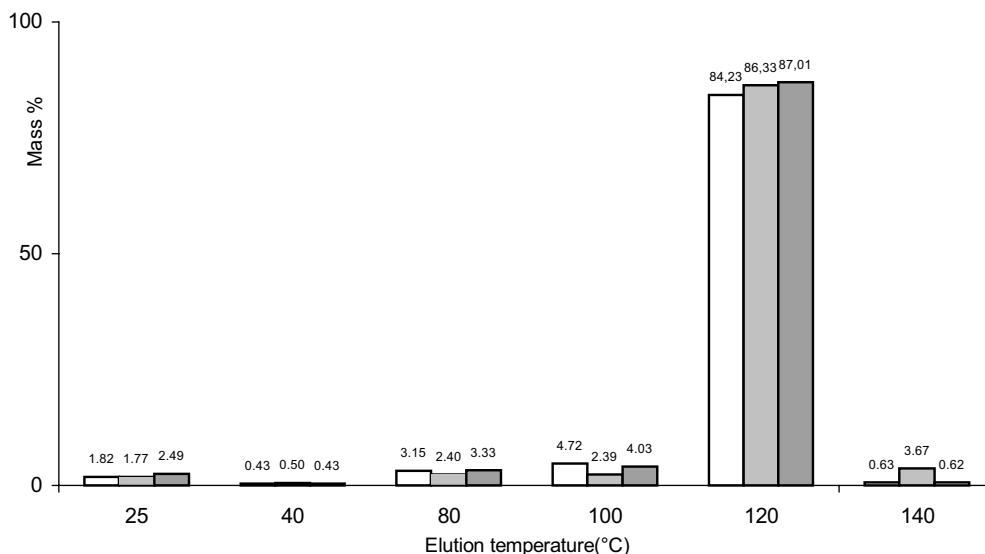


Fig. 2. TREF results for resins 1, 2 and 3.

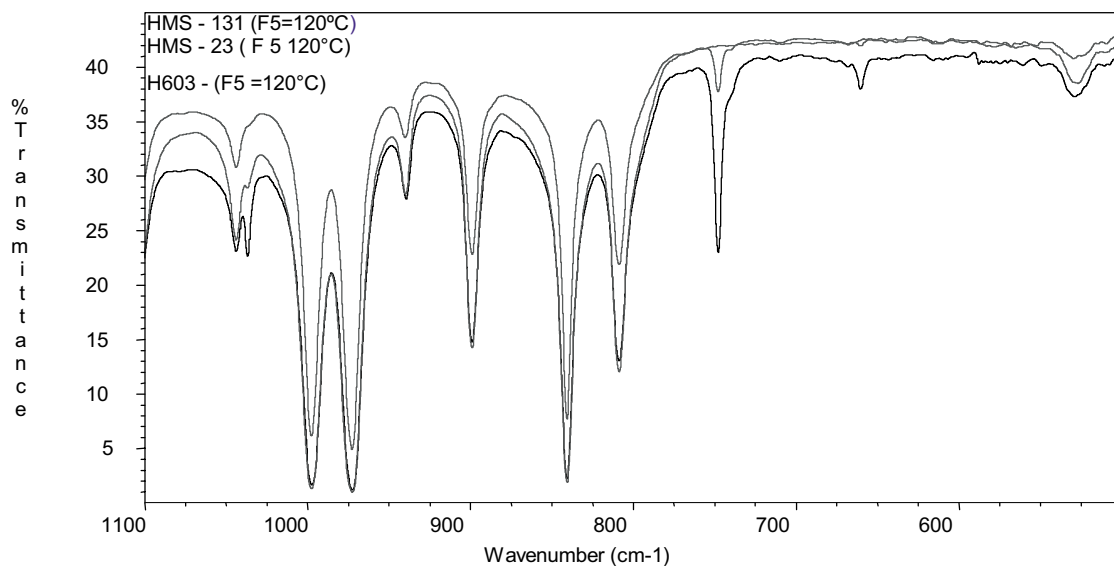


Fig. 3. IR of fraction 5.

the increase in molar mass, but this increase can occur only by Hs or Ts links. So, at the first glance, this fraction is a combination of molecules from former virgin fractions 5 and 6, with lower temperature fractions. Fig. 2.

The infrared spectra of fractions of polypropylene irradiated samples present slight differences from the non-irradiated sample. It can be noted that in fraction 5 (separated at 120°C) the relative intensity of the bands at ca. 840 and 800  $\text{cm}^{-1}$  is greater in the irradiated sample

than in the non-irradiated one. This fact is indicative of a higher crystallinity in the irradiated polymer, as described in the literature (Koenig, 1992). Fig. 3.

#### 4. Conclusions

The rheology results prove that the method of synthesis is very effective to improve the melt strength and extensibility of the resin, even at higher melt flow

index. Furthermore, this result directs us to the conclusion that pronounced changes were likely to occur in the molecule. But so far, the TREF showed changes only in the high molecular mass fraction. This confirms the hypothesis that a few giant molecules have a tremendous effect in changing the elongational viscosity of the polymer. IR showed no changes in the low-temperature fraction.

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