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Characterization study of gamma-irradiated, high melt-strength polypropylene

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Abstract

Polypropylene undergoes simultaneous crosslinking and degradation when irradiated. However, there is some speculation regarding the occurrence of branching under special conditions. It is also well known that the melt-strength property of a polymer increases with molar mass and with long chain branching. The aim of this study was to examine the amount of branching, as well as the formation and molar mass of branched molecules. The hypothesis that PP fragments are grafted with high molar mass PP molecules to form the branched molecules was also investigated.

Temperature rising elution fractionation (TREF) was performed to fractionate the sample and allow the study of molecular configuration and molar mass. To verify crystal parameters, TREF fractions were analyzed with DSC. Molar mass distribution was determined by SEC. The results showed that the primary reaction in the initial step of irradiation was degradation. The highly modified molecules were present in both the high and the low molecular weight fraction, but the high molecular weight fraction appeared to have higher concentrations. The results also confirm the presence of branching.

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1. Introduction

PP irradiation has been used to produce commercial grades of controlled rheology PP, based on the fragile behavior of PP molecules towards radiation. Nevertheless, the irradiation of PP under N₂ (in order to produce controlled rheology PP,

improving elongational viscosity by promoting long-chain branching) was only recently reported in the patent literature [1–3].

PP suffers from low melt strength (MS) i.e. the melted PP does not exhibit an increase in resistance to stretching during elongation. It is well known that the MS properties of a polymer are directly proportional to its molecular weight. It has also been shown that long chain branching increases the entanglement level (high melt strength PP – HMSPP), thereby increasing MS as

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well. In spite of being the fastest-growing polymeric commodity, these new grades of PP and their development have been barely studied and, with a few notable exceptions [4,5], their general chemical characterizations have been given even less attention.

HMSPP polymers, as proposed by Montell patents, are produced by low-temperature, low-dose irradiation of high molecular weight isotactic PP in N_2 atmosphere. The most commonly known reactions would be degradation and crosslinking. However, as has been shown, degradation should be the first and more intense reaction during the initial stages. According to Montell patents, another reaction is likely to occur: branching, or T links, competing with crosslinkings, or H links. Radicals are likely to decay rapidly in the amorphous phase, but, under annealing, the radicals entrapped in the crystal phase are likely to move to the boundary and react. Professor Silverman et al. [6] have formed a hypothesis concerning T link formation and have also studied the radical decay of PP. It is easy to understand the difficulties in differentiating H links from T links. When only present in small quantities, it may even be difficult to distinguish these links from the bulk or from virgin polymer, since the chemical groups and links are (chemically speaking) essentially the same. Fractionation of HMSPP followed by infrared study of each fraction has previously been performed by LUGAO's group [7], which concluded that branching was likely to occur and would be concentrated in the high molecular weight fraction.

This work seeks to contribute to the development of a sound analytical procedure for solving this PP puzzle.

2. Experimental

Materials – H603-grade PP samples were kindly supplied by OPP Petroquímica. Samples had the following characteristics: melt flow index (IF) = 1.5, melt strength (MS) = 16.34, M_n = 46,425; M_w = 477,700; M_z = 2,058,000. Crosslinking agents were analytical grade and had not undergone any further purification.

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

Characterization – TREF was conducted as follows by OPP staff in its laboratories. Sample (2 g) was dissolved in 180 ml of ortho-dichlorobenzene (ODCB) over 1 h at 140 °C. Sample was passed through a fractionating column heated to 140 °C, then began the cooling phase at 12 °C/h to 25 °C, when the first fraction was recovered. Heating commenced at 15 °C/h and fractions were taken at 40, 80, 100 and 140 °C. Fractions were precipitated with acetone and methanol and filtered for gravimetric analysis.

3. Results

Table 1 shows the rheological features of PP samples after irradiation. 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, and, therefore, improved performance. Table 1 shows the results of our irradiation synthesis. If we compare these results with those of standard resins possessing the same level of IF, the HMS resin had MS factors 4–9 times higher. Therefore, one could easily assume that major structural changes would likely occur.

Surprisingly, the TREF results of the virgin sample were very similar to those of the other rheologically modified resins (Fig. 1). Fraction 1 is the product at 25 °C; fraction 2 is at 40 °C and so on. The increase in elution mass of fractions 5 (120 °C) and 6 (140 °C) for both irradiated resins is one

Table 1
Rheological characteristics of the irradiated samples

Sample no.	Sample	Flow index [g/10 min]	Melt strength [cN]	Extensibility [cm/s]
1	Virgin PP	1.5	16.3	7.9
2	HMS 1	3.3	96.2	10.9
3	HMS 2	2.2	48.9	10.1

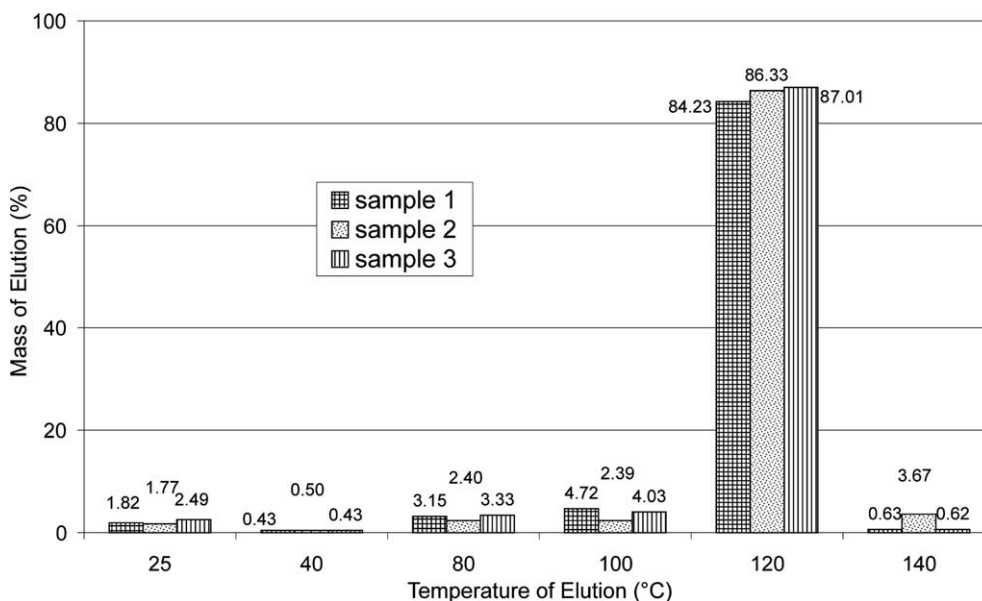


Fig. 1. TREF results for resins 1, 2 and 3.

possible explanation. These observations can be attributed to the increase in molar mass, but this increase can only occur by H or T links. So, at first glance, this fraction is a combination of molecules from former virgin fractions 5 and 6, with fragments of lower temperature fractions.

DSC results were quite striking as shown in Table 2. As expected, the entire first fractions were

composed of material of low molecular weight. However, no crystals were observed. This can be explained by the fact that this fraction was composed almost entirely of non-isotactic molecules. Another important observation from the DSC results is the clear decrease in the melting temperature (second melting) of each equivalent fraction as compared with non-irradiated ones.

Table 2
DSC and SEC results of each fraction of TREF

Samples	T_c (°C)	T_{m2} (°C)	M_w	M_n	M_z	M_w/M_n
PP fraction 1	There were no crystalline fusion		183,300	31,630	942,100	5.8
PP fraction 2	Not enough material		Not enough material			
PP fraction 3	96	116	148,200	23,640	600,100	6.3
PP fraction 4	104	137	132,200	25,210	484,600	5.2
PP fraction 5	119	164	409,300	71,940	1,573,000	5.7
hms1 fraction 1	There were no crystalline fusion		93,080	30,190	221,200	3.1
hms1 fraction 2	Not enough material		Not enough material			
hms1 fraction 3	96	126	90,290	24,680	228,500	3.6
hms1 fraction 4	109	140	90,770	23,800	255,900	3.8
hms1 fraction 5	120	149/163	376,100	69,130	1,380,000	5.4
hms1 fraction 6	121	149/163	352,200	65,650	1,334,000	5.4
hms2 fraction 1	There were no crystalline fusion		Not enough material			
hms2 fraction 3	102	131	55,030	19,760	134,800	2.8
hms2 fraction 4	114	145	Not enough material			
hms2 fraction 5	120	147/161	258,500	63,590	1,032,000	4.1

SEC results also showed equivalent molecular weights. This is an indication that the fractions of the irradiated samples had more defects than simple degradation products.

SEC results were quite interesting also, as all the fractions eluted at the same temperature had much lower M_n , M_w and M_z . As more mobile molecules can be eluted first, one can conclude that the branched molecules are composed of fragments of highly degraded PP molecules. Another interesting feature is the molecular weight distribution, which is quite constant in virgin PP (5 to 6) but changes its profile in the irradiated fraction. The M_w/M_n is negligible in the lower temperature elution fractions, but increases considerably in higher fractions. This leads us to surmise that highly modified molecules tend to concentrate in the high molecular weight fractions (Table 2).

4. Conclusions

TREF analyses showed very similar elution profiles, even where huge differences in MS exist. SEC results showed that the irradiated molecules were quite degraded. DSC results showed that equivalent elution fractions had significant minor melt temperatures. Synthesizing these results, we conclude that the modified molecules were present throughout all fractions, but the greater distribution of molecular weight for higher elution temperature lead us to

propose that those fractions have a higher concentration of modified molecules. High MS properties can be achieved only by increasing molecular weight or by the addition of long chain branching. Therefore, such modified molecules are likely to be partially crosslinked and partially branched.

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