

# Study of the Effect of $\gamma$ -Dose Rate on the Oxidation of Polypropylene

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## SYNOPSIS

Polypropylene PP (high and low crystallinity) was  $\gamma$ -oxidized, in the presence of air, using different dose rates (from 2 to 100 rad/s). Oxidation outcomes were identified and quantified by FTIR spectroscopy coupled with derivatization reactions (NO and SF<sub>4</sub>). The difficulty to separate secondary and tertiary hydroperoxides from FTIR measurements after NO treatment was addressed. Polymer physical degradation was also monitored during the  $\gamma$ -irradiation process. GPC was used to follow molecular weight changes and tensile tests for elongation at break modifications. Comparison of the extent of oxidation product formation over  $\gamma$ -irradiation allowed us to investigate the importance of  $\gamma$ -dose rate on chemical and physical changes of PP. From this, different mechanisms of ketone and ester formation were examined; relationship between the molecular weight changes and the elongation at break modifications was also investigated. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Items molded from polypropylene (PP) for medical purposes can be sterilized by autoclaving, use of ethylene oxide, or exposure to  $\gamma$ -rays. The first method is effective but time consuming. The second is coming under close scrutiny because of concerns about human exposure to ethylene oxide. Thus, sterilization by  $\gamma$ -rays is becoming the method of choice.

Unfortunately PP experiences a complex degradation process under  $\gamma$ -exposure in the presence of air. This considerably limits its use because most of its valuable physical and chemical properties are lost during the degradation. The direct consequence is that the material crumbles into pieces. To postpone this undesirable degradation, additives are introduced in the polymer. For instance, phenol- and piperidine-based stabilizers proved to be effective at preserving PP against  $\gamma$ -oxidation.<sup>1</sup> The effect of  $\gamma$ -irradiation on PP has been investigated in bulk,<sup>2</sup> in solution,<sup>3</sup> and in IPP copolymers<sup>4</sup> using different

techniques. Martakis et al.<sup>5</sup> recently published an article on the effects of  $\gamma$ -sterilization on IPP grades of different distribution of molecular weights used for medical devices. Focusing on mechanical properties changes, they found that the polypropylene grade of broader distribution of molecular weight and lower  $M_n$  had a higher  $\gamma$ -irradiation and post-irradiation resistance. From their quantitative analysis of oxidation products of IPP obtained during  $\gamma$ -irradiation, Lacoste et al.<sup>6</sup> found that all  $\gamma$ -products accumulated progressively, *tert*-hydroperoxide being the dominant  $\gamma$ -products.

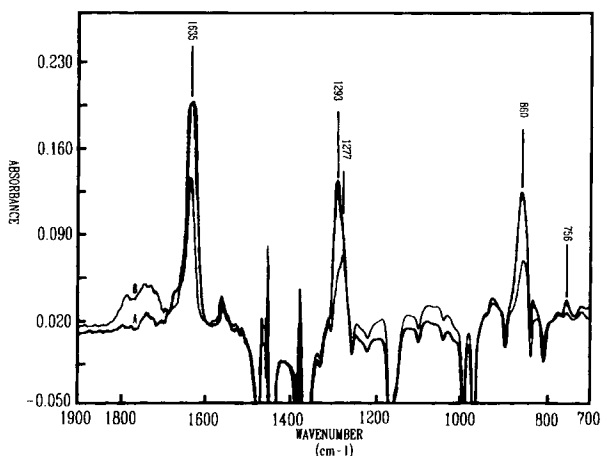
In this article a detailed investigation of the effect of  $\gamma$ -irradiation dose rate on physical and chemical changes of PP films is done. FTIR, coupled with chemical derivatization (NO, SF<sub>4</sub>) and measurements of elongation at break and molecular weight modifications, were employed to describe the  $\gamma$ -irradiation and the effects of dose rate on PP (high and low crystallinity).

## EXPERIMENTAL

### Polymers

Films of PP were obtained by melting polymer pellets under pressure at 200°C in a film mold 0.1 mm

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**Figure 1** FTIR modifications of  $\gamma$ -oxidized PP film spectrum just after NO treatment (A) and 3 days after a storage at room temperature (B).

thick and then quenching in a bath. For low crystallinity PP film ( $M_n = 30899$ ,  $M_w = 197895$ ), the quenching was rapid at  $0^\circ\text{C}$ . To get PP film with high crystallinity ( $M_n = 31738$ ,  $M_w = 192110$ ), a slow cooling to  $20^\circ\text{C}$  was performed.

Waters model 150-C GPC (AT-80 M/S Shodex, Showa Denko Japan) working at  $135^\circ\text{C}$  was used to calculate the molecular weight distributions of studied films. Samples were dissolved in 1,2,3-trichlorobenzene, and standard antioxidant [4,4-thiobis (2-*tert*-butyl-6-methyl phenol)] was added to prevent any further degradation. Polystyrene was used for calibration.

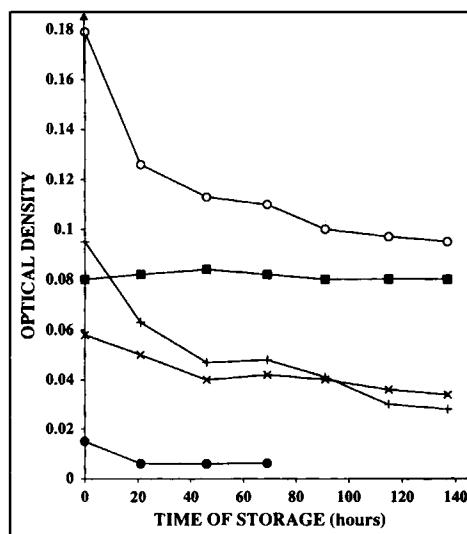
### Oxidation Conditions

$\gamma$ -Oxidation was performed in air at room temperature (RT), using a  $^{60}\text{Co}$   $\gamma$ -ray source (National Institute of Materials and Chemical Research, Tsukuba, Japan). Samples were irradiated with different  $\gamma$ -activity (2, 4, 10, 20, and 100 rad/s).

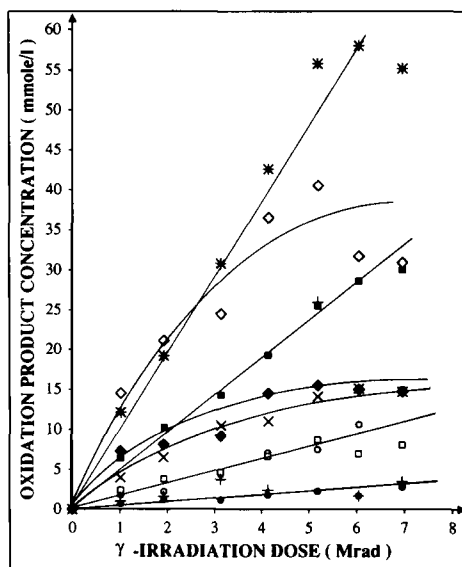
### Polymer Characterization

After exposure to  $\gamma$ -rays, oxidation products were identified and quantified by FTIR spectroscopy (Perkin-Elmer model 1750) coupled with derivatization reactions (NO,  $\text{SF}_4$ ). The  $\text{SF}_4$  treatment of degraded PP leads to the conversion of carboxylic acids into acid fluorides, which show a sharp absorption at  $1841\text{ cm}^{-1}$  on FTIR spectrum (for more details, see, e.g., refs. 6 and 7). The NO treatment is much more complex. Due to the instability of nitrates and nitrites produced from the NO reaction with hydroperoxides and alcohols, respectively, the

NO treatment of oxidized PP must be done at low temperature ( $\approx -20^\circ\text{C}$ ).<sup>6</sup> It is completed after 72 h (control from total loss of the  $-\text{OH}$  absorption at  $3400\text{ cm}^{-1}$ ). Overlapping of the IR bands of *sec*- and *tert*-nitrates (at  $1277$  and  $1293\text{ cm}^{-1}$ ) makes it difficult to quantify precisely secondary and tertiary hydroperoxides just after the NO treatment (Fig. 1, curve A). The IR spectrum of the PP treated and kept at RT in air shows that the intensity of the band at  $1635\text{ cm}^{-1}$  (nitrite + nitrate), at  $1293\text{ cm}^{-1}$  (tertiary nitrates), at  $1277\text{ cm}^{-1}$  (secondary nitrates), at  $756\text{ cm}^{-1}$  (tertiary nitrites) and at  $860\text{ cm}^{-1}$  (nitrates) are reduced while the band at  $3400\text{ cm}^{-1}$  is rebuilt a little bit. The IR spectrum recorded after 3 days of storage displays a drastic decrease at  $1635$ ,  $756$ , and  $860\text{ cm}^{-1}$ , while the band at  $1277\text{ cm}^{-1}$  stands clearly with a shoulder at  $1293\text{ cm}^{-1}$  (Fig. 1, curve B). These changes are the results to the disappearance of tertiary nitrates (at  $1293$ ,  $1635$ , and  $860\text{ cm}^{-1}$ ) from *tert*-hydroperoxides and of tertiary nitrites (at  $756\text{ cm}^{-1}$ ) from *tert*-alcohols. To confirm our interpretation, we repeated the experience with low linear density polyethylene (LLDPE) and PP at different storage temperatures (RT, 35, 40, and  $45^\circ\text{C}$ ). Remember that LLDPE oxidizes to only *sec*-hydroperoxides, leading to *sec*-nitrates after NO treatment.<sup>8</sup> The intensity changes of the nitrate and/or nitrite bands during the storage time are presented in Fig. 2. In the first 50 h of storage, one can notice a sharp decrease of the bands at  $1635$  and  $1293\text{ cm}^{-1}$  for



**Figure 2** The optical density changes of the nitrate and/or nitrite bands vs. the storage time. PP: (○)  $1635\text{ cm}^{-1}$ , (+)  $1293\text{ cm}^{-1}$ , (×)  $1277\text{ cm}^{-1}$ , (●)  $756\text{ cm}^{-1}$ ; LLDPE: (■)  $1277\text{ cm}^{-1}$ .



**Figure 3** Kinetic accumulation of PP (high crystallinity)  $\gamma$ -initiated oxidation products (at a dose rate of 4 rad/s): (○) acid, (\*) ketone, (■) ester, (◆) secondary hydroperoxide, (◇) tertiary hydroperoxide, (×) free hydroperoxide, (+) tertiary alcohol, (●)  $\gamma$ -lactone, (□) perester.

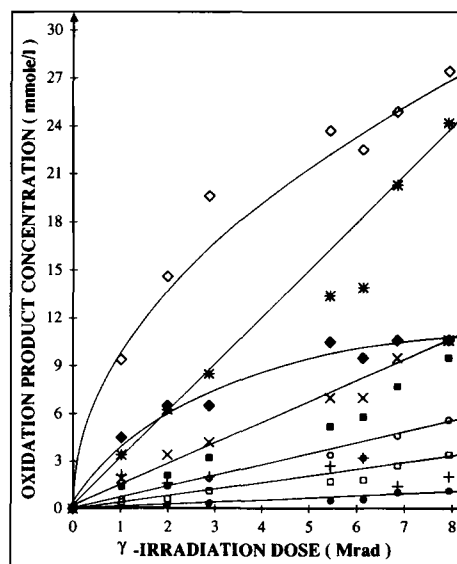
PP. Then they reach a plateau. The band at  $1277\text{ cm}^{-1}$  experiences a less important decrease. The absorbance at  $756\text{ cm}^{-1}$  is reduced very slightly. For PE, the band at  $1277\text{ cm}^{-1}$  remains constant during all the storage time. This is consistent with a good stability of *sec*-nitrates. This finding suggests that the decrease of the band at  $1277\text{ cm}^{-1}$  noticed is only apparent in the case of PP. It is due to the decrease of the strong band at  $1293\text{ cm}^{-1}$  that mingles with the one at  $1277\text{ cm}^{-1}$ . From this point, a good deconvolution of these IR bands is possible by recording the IR spectrum just after the NO treatment and 3 days later. Indeed, after 3 days no further significant reduction in the intensity of  $1293\text{ cm}^{-1}$  band is observed when the treated PP is stored at room temperature for an extended time. With this method, the quantification is estimated reliable from  $\pm 10\%$  to  $\pm 15\%$ .

The molecular weight distribution is monitored during all the  $\gamma$ -degradation through GPC analysis. The conditions set for it are given above. Elongation at break is also followed. For this, samples in the form of dumbbell specimens (70 mm long with a  $15 \times 3\text{ mm}$  neck) are tested using a Tensilon model UCT-1T (Orientec, Japan) after being  $\gamma$ -irradiated. Tensile tests are performed at a crosshead speed of 10 mm/min. The results reported are based on five tests.

## RESULTS

### Chemical Changes

Throughout the  $\gamma$ -oxidation, the formation of carbonyl, hydroperoxide, and hydroxyl was observed from FTIR measurements for both samples of PP (high and low crystallinity). Further characterization and quantification of  $\gamma$ -products were achieved through NO and  $\text{SF}_4$  derivatization. The exposure of oxidized PP to  $\text{SF}_4$  gas permits a clean quantification of the carboxylic acids at  $1841\text{ cm}^{-1}$ . The residual carbonyl peaks are attributable to ketones at  $1720\text{ cm}^{-1}$ , esters at  $1740\text{ cm}^{-1}$ , peresters at  $1760\text{ cm}^{-1}$  and  $\gamma$ -lactones at  $1780\text{ cm}^{-1}$  that do not react to gaseous  $\text{SF}_4$ . It is difficult to obtain a high level of precision in their quantification due to the overlapping of IR bands; the uncertainty was estimated at  $\pm 15\%$ . Hydroperoxide and alcohol buildup were determined through NO exposure (see above). FTIR values for quantification of PP oxidation products were given by Lacoste et al.<sup>6</sup> Note that we did not observe any formation of unsaturated groups contrary to the case of PE.<sup>9</sup> The results obtained at two different  $\gamma$ -activity (4 and 100 rad/s) are presented in Figures 3 and 4. Comparing the two figures, one can notice that the production of ketones and esters is very sensitive to the dose rate effect. At low dose rate, these products reach a higher concentration than at high dose rate. However, production of the



**Figure 4** Kinetic accumulation of PP (high crystallinity)  $\gamma$ -initiated oxidation products (at a dose rate of 100 rad/s): (○) acid, (\*) ketone, (■) ester, (◆) secondary hydroperoxide, (◇) tertiary hydroperoxide, (×) free hydroperoxide, (+) tertiary alcohol, (●)  $\gamma$ -lactone, (□) perester.

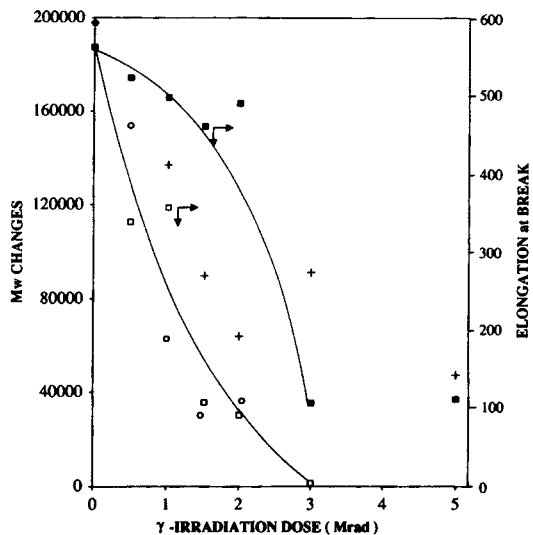


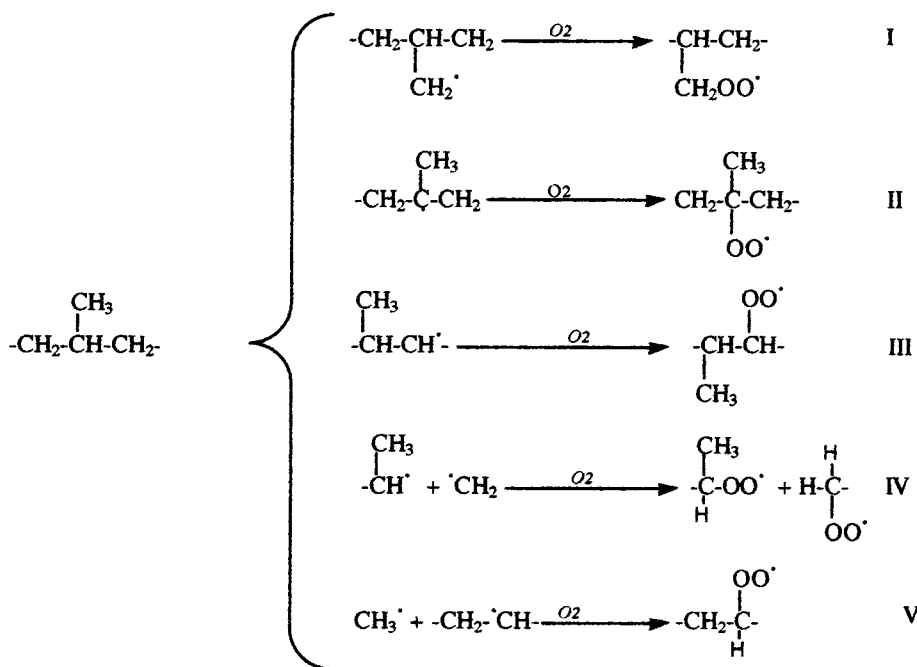
Figure 5 Elongation at break [(□) at 2 rad/s and (■) at 100 rad/s] and  $M_w$  [(○) at 2 rad/s and (+) at 100 rad/s] changes during  $\gamma$ -oxidation of PP low crystallinity.

other oxidation species does not seem to be affected by the  $\gamma$ -irradiation activity, even considering experimental errors. These differences are also accompanied by stoichiometry changes: at low  $\gamma$ -activity, ketone is the dominant product, followed by *tert*-hydroperoxide, which reaches a plateau in the

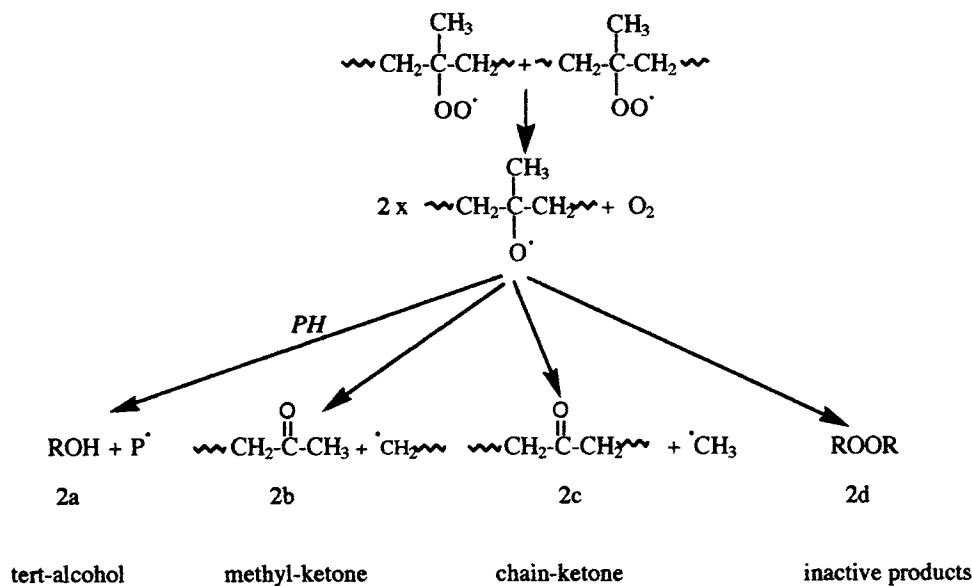
long run; to the contrary, at high  $\gamma$ -activity, the latter overnumbers the former. Note that all types of hydroperoxide tend to a stationary state that is more evident at 4 rad/s. This observation contradicts the linearity recorded in the kinetic formation of these species by other authors.<sup>6</sup> Peresters and acids in the one hand, and  $\gamma$ -lactones and *tert*-alcohols in the other hand, are yielded at the same extent at 4 rad/s. At 100 rad/s, acids, peresters, and *tert*-alcohols present the same accumulation kinetic followed by  $\gamma$ -lactones. It is worth noting the low concentration of  $\gamma$ -lactones recorded in both cases.

### Physical Changes

During the degradation process of polymers, there is generally a change in physical properties such as the average molecular weight, the molecular weight distribution, and the elongation at break. In the case of PP, the most significant deficiencies that result from these modifications are embrittlement to the point of catastrophic failure and change of color. The former deficiency is best indicated by loss of the elongation at break. The influence of radiation dose on elongation at break and average molecular weight is illustrated in Figure 5 for PP low crystallinity. It can be seen that  $M_w$  decreases with in-



Scheme 1



Scheme 2

creasing  $\gamma$ -irradiation dose whatever the dose rate. Oppositely, a difference in the behavior of the elongation at break is noticed. At 100 rad/s, the elongation at break of PP (low crystallinity) presents a slight decrease up to 2 Mrad dose; failure of mechanical properties occurs around 2.5 Mrad dose. On the contrary, at 2 rad/s, it decreases sharply from the beginning of the  $\gamma$ -degradation process, reaching a minimum at 1.5 Mrad. In the case of PP high crystallinity (not shown), whatever the dose rates of irradiation, with increasing the  $\gamma$ -dose,  $M_w$  and elongation at break decrease markedly and sample rupture is reached in a short irradiation time corresponding to less than 1 Mrad dose.

## DISCUSSION

The  $\gamma$ -degradation process involves initiation, propagation, and termination stages. The initiation reaction may take place on different sites of the PP chain when energy is absorbed from  $\gamma$ -ray, causing scission of a covalent backbone. Whatever the radiation dose rate, no preferred initiation routes exists because  $\gamma$ -ray attacks occur in a statistical way. Afterwards, propagation occurs by unzipping or by radical abstraction of neighboring H atom. The result of this is that radical is transferred to another chain or further down the same chain. After combination with oxygen and H abstraction, the first  $\gamma$ -product expected is hydroperoxide. It was observed that *tert*-hydroperoxide formation is favored comparatively to *sec*- and *free* ones. This is probably

due to a preferential attack of macro radicals on the labile *tert*-hydrogen of the polymer chain (II) (Scheme 1).

In contrast to LLDPE where *sec*-hydroperoxides accumulated continuously at high dose rate and plateaued at a low one,<sup>9</sup> the kinetic buildup of all types of hydroperoxides tends to a plateau in the case of PP; this is noticeable after 3 Mrad dose. Behavior is similar to that observed during the photo-oxidation of PP.<sup>6</sup> But the plateau is less visible for *tert*-hydroperoxides at 100 rad/s. Comparing our results with other articles<sup>6</sup> that showed a linearity in hydroperoxide formation during the  $\gamma$ -oxidation at 194 rad/s, one can conclude that the greater the  $\gamma$ -dose rate, the bigger will be the chance to obtain linear kinetic accumulation of  $\gamma$ -products. This issue, which could be a matter of investigation, is why hydroperoxide concentration reaches a stationary state in the range of  $\gamma$ -dose rate used in this report.

Also, hydroperoxide concentration level showed an insensitiveness to the  $\gamma$ -irradiation activity ranging from 2 to 100 rad/s beyond 7 Mrad dose. This is surprising, because we expected a higher concentration level with a lower dose rate as was observed in the case of LLDPE.<sup>9</sup> It seems that whatever the irradiation dose rate—ranging from 2 to 100 rad/s—hydroperoxide formation in PP presents an upper limit in their concentration over  $\gamma$ -degradation process.

Ketone appeared to be the dominant  $\gamma$ -product at a low dose rate of irradiation. This was no longer true at a high one. Its formation is mainly ascribed to the decomposition of *tert*-hydroperoxides to al-

Table I Concentration (mmole/l) of Oxidation Products Quantified in PP at 2.5 Mrad Dose (the Usual Sterilization Dose) and the Ratio Ketone/Ester During the  $\gamma$ -Degradation with Different Dose Rates

Dose Rate (rad/s)	<i>tert</i> -Hydroperoxide	Sec-Hydroperoxide	Free-Hydroperoxide	Acid	Ketone	<i>tert</i> -Alcohol	Ester	Lactone	Perester	Ketone/Ester
2	37.0 ± 1.5	15.4 ± 1.5	11.0 ± 1.5	6.3 ± 1.5	41.5 ± 1.5	2.1 ± 1.5	22.0 ± 1.5	2.0 ± 1.5	6.5 ± 1.5	1.9
	27.0 ± 0.7	11.4 ± 0.7	9.6 ± 0.7	5.3 ± 0.7	35.0 ± 0.7	3.0 ± 0.7	15.5 ± 0.7	1.1 ± 0.7	5.5 ± 0.7	1.3
4	27.6 ± 1.6	11.9 ± 1.6	8.9 ± 1.6	4.0 ± 1.6	27.6 ± 1.6	1.2 ± 1.6	12.6 ± 1.6	1.2 ± 1.6	4.1 ± 1.6	2.2
	25.7 ± 0.7	12 ± 0.7	9.1 ± 0.7	3.9 ± 0.7	24.8 ± 0.7	1.1 ± 0.7	11.4 ± 0.7	1.1 ± 0.7	3.9 ± 0.7	0.96
10	23.7 ± 1.5	8.7 ± 1.5	8.7 ± 1.5	3.5 ± 1.5	21.6 ± 1.5	0.9 ± 1.5	10.5 ± 1.5	0.8 ± 1.5	3.5 ± 1.5	2.1
	20.7 ± 0.7	9.1 ± 0.7	9.1 ± 0.7	3.7 ± 0.7	21.4 ± 0.7	1.3 ± 0.7	10.0 ± 0.7	1.3 ± 0.7	3.7 ± 0.7	1.03
20	21.8 ± 1.5	7.5 ± 1.5	7.5 ± 1.5	2.3 ± 1.5	19.0 ± 1.5	0.7 ± 1.5	9.6 ± 1.5	1.9 ± 1.5	4 ± 1.5	2
	20.7 ± 0.7	9.8 ± 0.7	7.8 ± 0.7	1.8 ± 0.7	19.1 ± 0.7	1.0 ± 0.7	7.8 ± 0.7	1.1 ± 0.7	2.3 ± 0.7	0.92
100	18.0 ± 0.4	8.9 ± 0.4	4.6 ± 0.4	2.0 ± 0.4	8.4 ± 0.4	2.0 ± 0.4	3.1 ± 0.4	0.4 ± 0.4	1.2 ± 0.4	2.7
	15.3 ± 0.3	7.0 ± 0.3	3.5 ± 0.3	1.7 ± 0.3	7.6 ± 0.3	1.6 ± 0.3	2.7 ± 0.3	0.4 ± 0.3	1.0 ± 0.3	0.5

koxy radicals that undergo a  $\beta$ -scission.<sup>6</sup> This means that ketone is produced at the expense of *tert*-hydroperoxides. Consequently, these species must display the same behavior in their kinetic accumulation that is in contradiction with our results. We believe that their formation from peroxy radicals is more probable following Scheme 2.

Indeed, the decomposition of the O—O bond can occur easier for peroxy radical than for hydroperoxides due to the difference in their dissociation energy (37 kcal/mol for peroxy radical against 42 kcal/mol for hydroperoxide). Using the NMR technique, Vaillant<sup>10</sup> showed that the formation of methyl-ketone is favored during the photo-oxidation of PP. This means that route 2b is predominant. A high concentration level of ketones has been recorded at a low dose rate. This can find an explanation in the mass production of peroxy radicals that may favor ketone production. On the other hand, the formation of alcohol from reaction 2a seems not to be affected by the  $\gamma$ -radiation activity. In other words, the hydrogen abstraction from the polymer chain leading to alcohol is not favored in a high radical concentration as stated by our experimental data. Regarding the formation of acid groups, satisfactory mechanisms have been proposed.<sup>6</sup> That mechanism involving *tert*-hydroperoxide received support from our work. Indeed, whatever the  $\gamma$ -ray activity, acid concentration reached, in the long run, a same level as was observed previously for *tert*-hydroperoxide. The absence of plateau in the case of acid kinetic accumulation may be simply explained by additional reactions of acid formation that is not predominant.

Among  $\gamma$ -products that mingle in the carbonyl region after SF<sub>4</sub> treatment, ester is the only specie that displayed a significant difference in its accumulation at a low and high dose rate. This product can be issued from alkoxy radical attack on ketone proposed by Geuskens and Kabamba.<sup>11</sup> These reactions fit our experimental results. Different mechanisms of peresters and  $\gamma$ -lactones productions have been proposed in the literature.<sup>6,11</sup> From our data, it is quite difficult to support those mechanisms or to propose alternative ones.

Significant molecular weight degradation has been caused by the  $\gamma$ -treatment. For both types of PP, the decrease of  $M_w$  occurred at the very beginning of the  $\gamma$ -degradation process whatever the irradiation dose rate was. These results indicate that chain scission events take place early in the  $\gamma$ -degradation process. This result is in good support of the proposed production of  $\gamma$ -products from scission reactions.

Remember that over oxidation process, cross-linking and scission reactions occur simultaneously. The competition between these two reactions can be also assessed through monitoring of the elongation at break. If changes of the elongation at break corroborate with the ones of  $M_w$  at a low dose rate, it is not the case at a high one for PP low crystallinity. In the latter conditions, measurements reveal that PP maintains its key physical properties though  $M_w$  decreases. This brings evidence that changes in elongation at break cannot be essentially controlled by changes in molecular weight. This is understandable if we suppose that chain scission reactions take place mainly in the amorphous phase without significantly affecting tie molecules responsible for the mechanical properties.<sup>12</sup> Then at a low dose rate, radicals produced in the amorphous part have enough time to migrate to the located part of tie molecules, destroying them. On the opposite side, at a high dose rate, due to the mass production of radicals, this migration is limited due to the predominance of crosslinking reactions. However, these explanations cannot be applied in the case of PP high crystallinity where  $M_w$  and elongation at break decreased in concert with increasing the  $\gamma$ -activity.

For practical utilization of  $\gamma$ -irradiation, many applications require sterilization dose at 2.5 Mrad. Table I presents the concentration of  $\gamma$ -products recorded at this dose using different dose rates. Note that PP low crystallinity generates more  $\gamma$ -products than PP high crystallinity. This result is a confirmation that oxidation takes place mainly in the amorphous part of the polymer. The table clearly shows that the lower the dose rate, the higher the concentration of  $\gamma$ -products at the sterilization dose, a feature that we have tentatively explained in our previous articles.<sup>8,9</sup> This difference in  $\gamma$ -products formation due to change of the dose rate may have an influence on the right choice of additive to protect PP medical devices supposed to be sterilized by  $\gamma$ -rays.

## CONCLUSION

In this report, change of the  $\gamma$ -dose rate of degradation allowed us to address some fundamental questions. On a molecular level, it has been found that: (1) ketones are probably issued from peroxy

radical instead of hydroperoxide groups, (2) esters are produced from ketone species, a point that was confirmed by calculating the ratio ketone/ester that does not meet significant variations from one dose rate to the other ( $2.18 \pm 0.29$  and  $0.94 \pm 0.26$  for PP low and high crystallinity, respectively, from Table I).

Still, some points such as the plateau, the upper concentration limit observed in the formation of all types of hydroperoxides, and whatever the dose rate, remain unclear.

According to the changes of elongation at break, high dose rate gives the lowest physical changes. This is due to the predominance of crosslinking reactions, an explanation supported by the low level of  $\gamma$ -products recorded at a high dose rate in both PP.

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