Gamma-Sterilization Effects and Influence of the Molecular Weight Distribution on the Postirradiation Resistance of Polypropylene for Medical Devices

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SYNOPSIS

In the present study, the dose-rate effects of γ-irradiation in air on two isotactic polypropylene grades of different molecular weight distribution, used for medical devices, were investigated. The thermal, mechanical, rheological, and photometric properties of these materials were examined using DSC, stress–strain measurements, MFI, and a yellow index. At low dose rates (0.12 Mrad/h), the oxygen diffusion parameter prevailed. At high dose rates (2.84 Mrad/h), the thermal degradation became dominant. However, at high dose rates, an increase in sample temperature was monitored. This temperature rise is thought to increase the oxygen diffusion rate, peroxide decomposition, and radical migration. As a result, intermediate dose rates (in the region of 0.72 Mrad/h) gave the lowest changes in physical properties in both samples. Furthermore, it was found that the polypropylene grade of broader molecular weight distribution and lower M_n had a higher γ-irradiation and postirradiation resistance. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, the industry that provides sterile disposable devices for hospital and medical use (plastic syringes, tubing, vials, etc.) has had a profound tendency in substituting the conventional sterilization techniques, such as autoclave or ethylene oxide treatment, by γ-irradiation. However, γ-irradiation has been known to cause damage to polymers after treating them with the minimal sterilization dose of 2.5 Mrad, the extent of which depends on the chemical structure of the material and, also, on such factors as irradiation dose, dose rate, and irradiation temperature.[1] For polymers with marginal radiation resistance, such as polypropylene,[2] the dose rate and irradiation atmosphere can cause a limited shelf life of the product and, therefore, they are important variables.

Polypropylene (PP) is a very important polymeric material used in a wide range of biomedical and medical applications. However, the material has a drawback in that after exposure to γ-irradiation it becomes brittle to the point of catastrophic failure and changes in color to a light or deep yellow. The former deficiency is unacceptable for product integrity. The latter does not necessarily indicate significant loss of desirable physical properties, but is usually unacceptable from an aesthetic point of view. Syringes for single use made out of PP must have a small degree of yellowing ($\Delta Y_1 < 10$) at an absorbed irradiation dose of 2.5 Mrad, which is the minimum required dose for sterilization. Various factors have been reported to cause yellowing in syringes, among them, the wrong choice of the rubber piston antioxidant, which can cause bleaching at the surface of the piston and diffusion into the polypropylene barrel, creating a local discoloration,[3] and the wrong stabilization of the PP itself or excessive supplied doses. This yellowing degrades the appearance of

the syringe, giving an unpleasant and insecure feeling to the user.
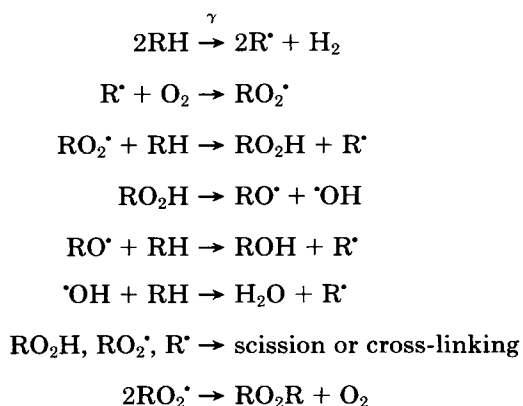
In the present study, the effect of M_n and molecular weight (MW) distribution in the postirradiation resistance of PP was examined. Another object of the present study is the dose rate effect on PP. Finally, the PP grade that is less likely to be yellowed when subjected to the minimum sterilization treatment of 2.5 Mrad as well as the optimum dose rate are also determined.

The effect of γ-irradiation on PP (both isotactic [iPP] and atactic) has been studied in the bulk,[4] in solution,[5] with added stabilizers,[6] and in iPP copolymers.[7]

The two main effects of γ-irradiation on iPP, i.e., changes in the chemical and physical properties, depend on the efficiency of the cross-linking and/or chain-scission reactions. A measure of main-chain scission is $G(S)$ = number of breaks for 100 eV of radiant energy absorbed, whereas a measure of the cross-linking reactions is $G(X)$ = number of cross-links (consisting of two cross-linked polymer units) formed for 100 eV of energy absorbed.

The minimum and maximum estimates of cross-link $G(X)$ and chain-scission $G(S)$ radiochemical yields for iPP irradiated at room temperature under vacuum or inert atmosphere (nitrogen) are $G(X)$ = 0.068–0.14 and $G(S)$ = 0.10–0.27.[8] With the help of the Charlesby–Pinner equation, the $G(S)/G(X)$ ratio for iPP was found to be 1–1.5, depending on the degree of crystallinity.[8,9] This result means that upon irradiation and under vacuum conditions the chain-scission reactions are slightly higher. This perhaps can be realized since PP has a structure between polyethylene, which primarily cross-links, and polyisobutylene (quaternary carbon atom), which degrades largely by chain scission upon irradiation.[10] Radiation doses that cause only minor degradation to polyethylene may render PP useless.[2]

Irradiation of iPP in air results in an autooxidative reaction as follows:

$$2RH \xrightarrow{\gamma} 2R^{\bullet} + H_2$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$

$$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}$$

$$RO_2H \rightarrow RO^{\bullet} + {}^{\bullet}OH$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

$${}^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet}$$

$$RO_2H, RO_2^{\bullet}, R^{\bullet} \rightarrow \text{scission or cross-linking}$$

$$2RO_2^{\bullet} \rightarrow RO_2R + O_2$$

where R represents the PP chain and R$^{\bullet}$ is the "cleaved" chain that occurs during irradiation.[8] Carbonyl compounds are also formed. These and the unstable peroxides (half-life of 25 h in the presence of oxygen) formed in the irradiated polymer eventually breakdown, and as a result, a change in the properties occurs.[11]

Irradiation in the presence of air accentuates an oxidative degradation, which increases with a decreasing dose rate. Three mechanisms are operative: diffusion of oxygen into the polymer, breakdown of peroxides, and radical migration. Therefore, the sample thickness can be important. With thin films, all reactive species are transformed to peroxides during irradiation at low dose rates. After irradiation with higher dose rates, diffusing oxygen can react with residual free radicals, which in some polymers decay slowly. Therefore, a PP sample that looks nice and still has good properties after sterilization can become very brittle after a time due to radicals created by the irradiation.

In the present study, differential scanning calorimetry (DSC) was employed to describe the γ-irradiation and dose-rate effects on two PP grades (injection molding) of different M_n and molecular weight distribution (MWD). The thermal evaluations were supplemented by mechanical and rheological testing. Two fully characterized γ-sterilizable PP grades have been used for this purpose. The effect of M_n and MWD of a PP, subject to γ-irradiation at different dose rates, giving the lowest changes in physical properties, is determined.

Several studies have been appeared in the literature demonstrating the utility of DSC (or DTA) in the study of polymer oxidation.[3,12–15] There are two methods for studying the thermal oxidation by DSC: the isothermal and the continuous scanning method. In the former, the sample is maintained at a constant, specified temperature throughout the experiment, and the period of time before the onset of rapid thermal oxidation is monitored. This time interval is called the oxidative induction time (OIT). The end of the induction period is signaled by an abrupt increase in a sample's temperature, evolved heat, or weight gained. In the continuous method, the material is degraded at a programmed heating rate. The isothermal method was applied in the present work to study the oxidation behavior of the materials. A pure oxygen atmosphere was used to lower the OIT temperature. Although the use of oxygen has been questioned,[16,17] the purpose of the present study was not to predict lifetimes but to compare the two PP grades. The continuous method instead was used to quantitatively investigate the

effect of irradiation and dose rate on T_m and ΔH_m, which are directly related to the micromorphology and degree of crystallinity of PP, respectively.

The traditional melt flow index test was used to determine the molecular weight before and after irradiation. Suffice it to say that the higher the melt flow index the lower the molecular weight.

MATERIALS

The PP grades used were provided by Neste Chemicals International, Belgium. The samples of PP had the characteristics shown in Table I (see also Fig. 1). Both materials were equally stabilized. Because the materials are produced using different processes (slurry, spheripol), there is great variability in the fine structure, in the M_n, in the MWD, and in the crystallinity. The PP grades investigated in this work were suitable for the production of syringe barrels.

EXPERIMENTAL

The samples in the form of dumbbell specimens were γ-irradiated ($\cong 2.5$ Mrad) at three different dose rates of 0.12, 0.714, and 2.84 Mrad h^{-1}, designated hereafter as t = 22 h, t = 3.5 h, and t = 55 min, respectively. They were irradiated in air using a ^{60}Co γ-ray source. Samples were also aged in an air-circulating oven at 120°C for 24 h.

To obtain the thermodynamic melting point (T_m) and the oxidation induction time (OIT) of the samples, a DuPont 9000 Thermal Analyzer was used, fitted with a DSC module. The T_m thermographs were obtained using hermetic pans, at a heating rate of 20°C/min, and the OIT test was performed in an oxygen atmosphere (oxygen flow was kept at 150 mL/min) using perforated pans, at 155°C. The sample size was accurately weighted: 11.5 mg. The

Table I Characteristics of PP Samples

Property	PP Grades	
	VC10	VC12
MFI (230°C/2.16 kg)	9.0	15.4
MFI (190°C/2.16 kg)	3.7	6.1
M_w	254.800	257.500
M_n	79.900	59.500
D	3.2	4.3

cell was calibrated for quantitative measurements using indium and tin standards. Reproducible results were obtained by keeping the mass and geometry of the samples under examination constant.

Virgin, irradiated, and aged samples were subjected to tensile properties characterization by being clamped in an Instron 1010 Model. The resistance of PP to γ-irradiation, dose-rate insensitivity, and aging was measured by the percent change in various physical properties, i.e., tensile yield strength and elongation at break. The measurements were carried out at room temperature and at a cross-head speed of 200 mm/min.

The rheological properties of the samples were examined by measuring their melt flow index (MFI), using a Ceast melt-flow index machine Model 6542. All measurements were carried out according to ASTM D 1238-88, at 190°C/2.16 kg. A lower test temperature was used merely for convenience, since at 230°C, the flow rate was too high to obtain reliable results, especially for the irradiated samples.

Evaluation of the yellow index was performed on the irradiated/aged samples (at all experimental dose rates) by Neste Chemicals International, Belgium.

RESULTS

Figure 1(a)–(c) and Table II show the effects of dose rate on the two PP grades in terms of OIT as measured by DSC at 155°C in an O_2 atmosphere. A log scale is used for the OIT. The length of OIT decreases with decreasing dose rate in both samples, as expected. Oven aging at 120°C for 24 h after irradiation increases the OIT. It is further observed that aged samples that have been previously irradiated for t = 3.5 h exhibit a higher OIT value compared to the other two irradiation conditions. The thermally only aged samples exhibit larger OIT values compared to those of the γ-irradiated ones. As can be seen, the VC12 sample exhibited larger OIT values. Furthermore, VC12 exhibited, in general, higher OIT values in every condition.

Figure 2 and Table III show the rheological results, where it can be seen that the MFI of the irradiated samples was drastically increased upon irradiation. Moreover, the MFI of the VC12 sample is always higher than that of VC10. It is also noted that samples irradiated at t = 3.5 h maintained a "lower" MFI compared to the other two irradiation conditions of t = 55 min and t = 24 h.

In Table IV and Figures 3(a), 3(b), 4, 5(a), and 5(b) are given the stress–strain results in terms of
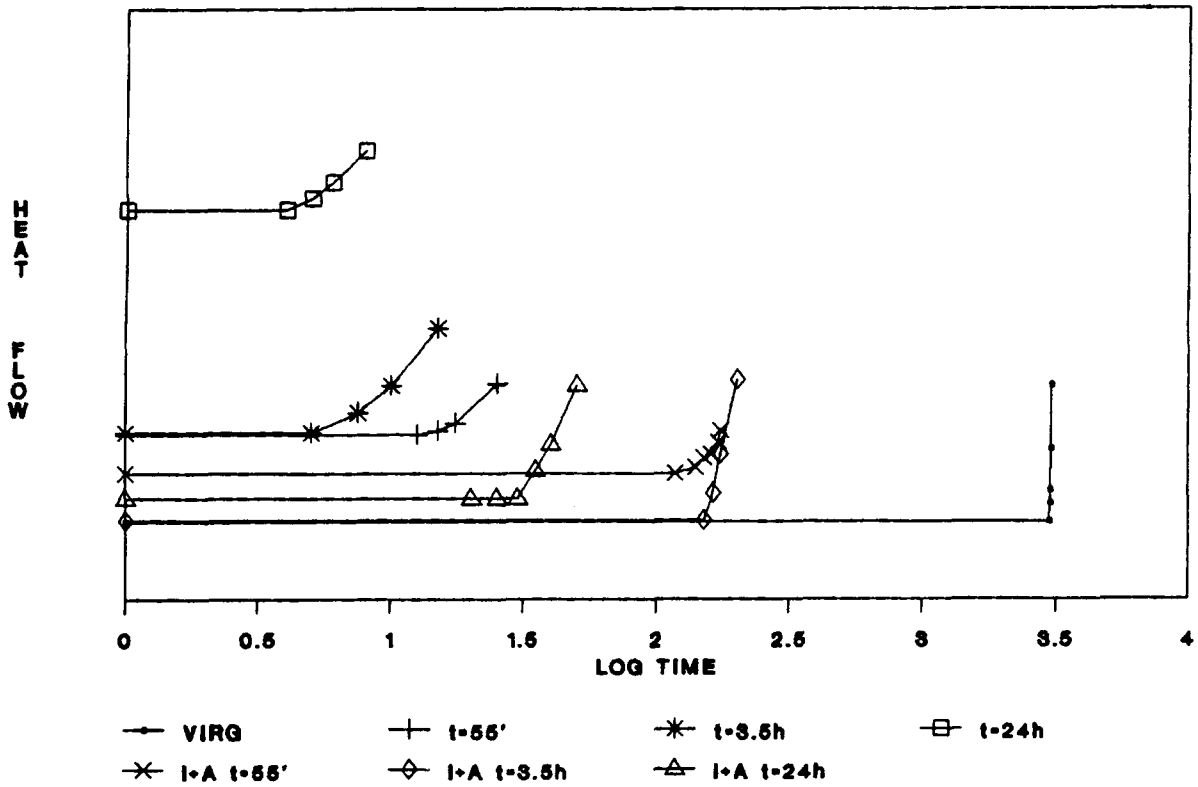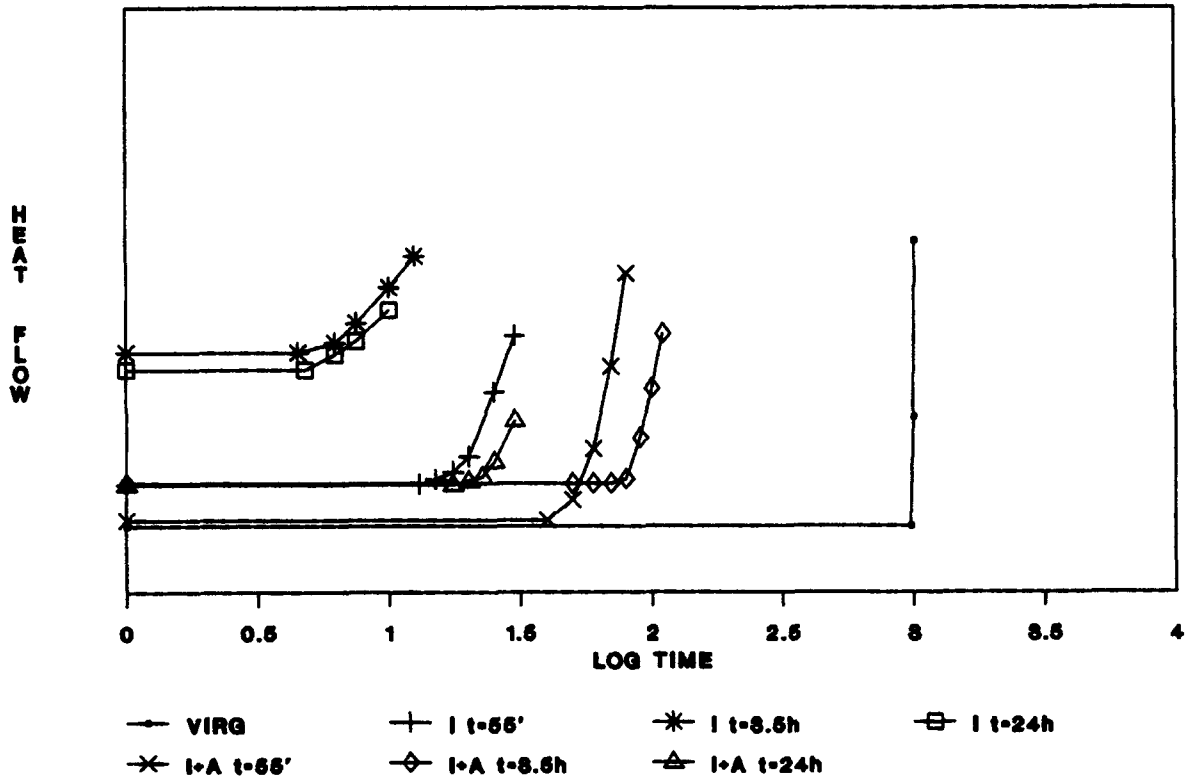
Figure 1 (a) Oxidation induction time (OIT) obtained from DSC, exhibiting the dose-rate effect on VC10 PP grade; (b) OIT obtained from DSC, exhibiting the dose-rate effect on VC12 PP grade; (c) OIT: the effect of dose rate on the oxidation stability of two sterilizable PP grades.
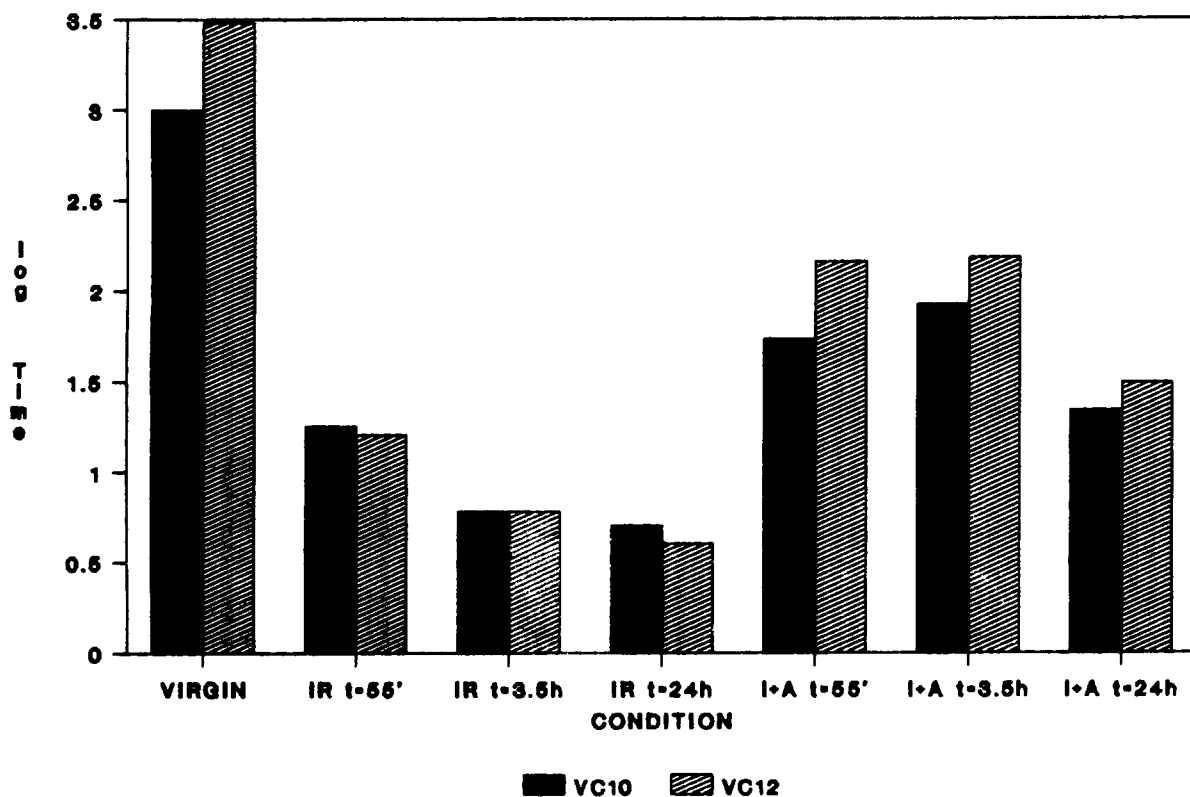
Figure 1   (*Continued from the previous page*)

tensile yield and elongation at break. Embrittlement is best indicated by loss of ultimate elongation [Fig. 3(b)]. Tensile strength at yield changes slightly after irradiation and increases after aging. Elongation at break decreases with irradiation and diminishes with further aging. The percentage elongation of both materials decreases to a greater extent in the case of t = 55 min compared to t = 3.5 h.

From Table V and Figure 6 it can be seen that

the VC10 sample has a lower degree of crystallinity compared to VC12, as measured by DSC. The thermally only aged samples, in general, show higher degrees of crystallinity. Irradiation and aging of the PP samples lower somehow their melting point (T_m) but increase their degree of crystallinity (ΔH_m).

In Table VI are given the yellow index values of the irradiated/aged samples. "Virgin" PP samples have a yellow index value less than 10 units. The

Table II   Oxidation Induction Time (Min)

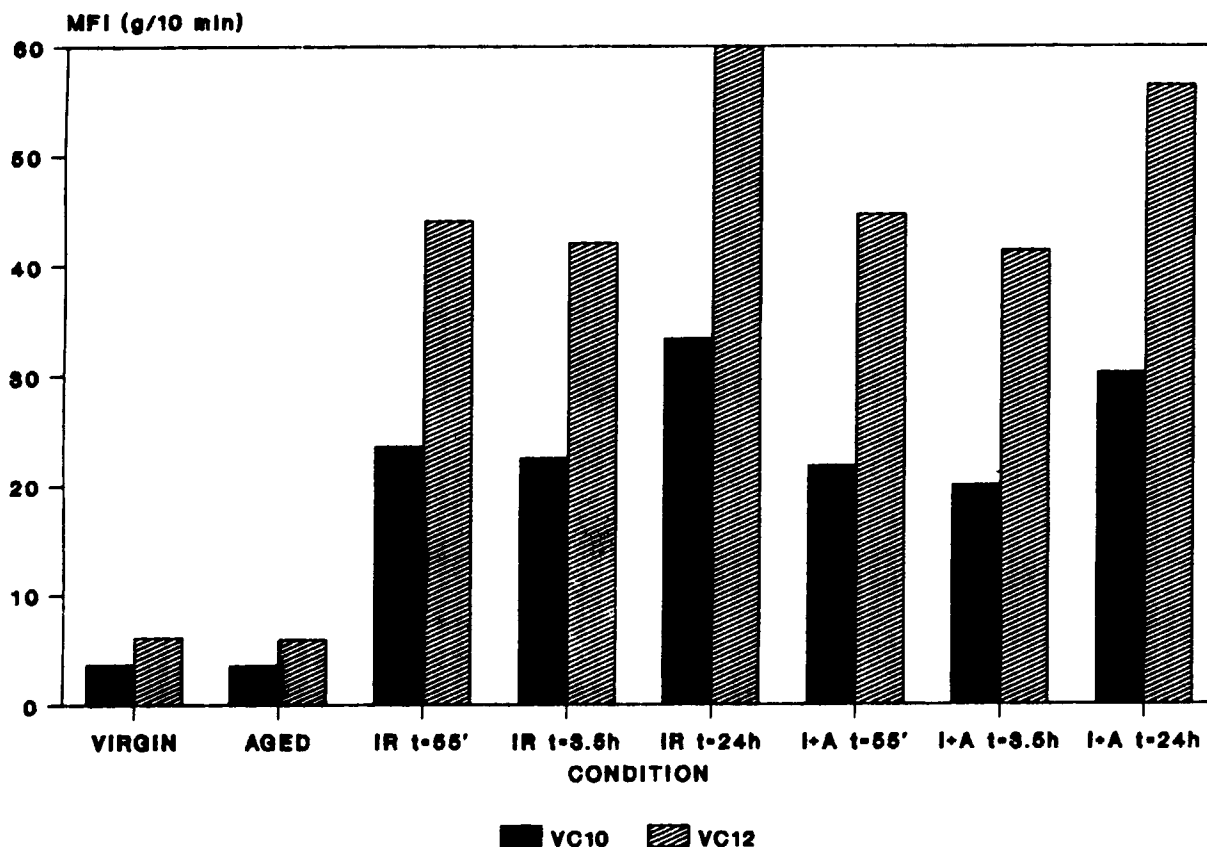| Condition	VC10		VC12	
	Time (min)	Log Time	Time (min)	Log Time
Virgin	993	2.997	3022	3.480
Irradiated t = 55 min	18	1.255	16	1.204
Irradiated t = 3.5 h	6	0.778	6	0.778
Irradiated t = 24 h	5	0.699	4	0.602
Irradiated/aged t = 55 min	54	1.732	145	2.161
Irradiated/aged t = 3.5 h	84	1.924	154	2.187
Irradiated/aged t = 24 h	22	1.342	31	1.491

**Figure 2**   Effect of dose rate on MFI of VC10 and VC12.

yellow index increases as the dose rate decreases. The yellow index of VC12 is much lower than that of VC10.

DISCUSSION

Nature of the Chemical Changes

The mechanism responsible for the degradative initiation of PP upon irradiation is most probably
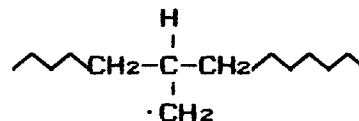
Table III   Melt Flow Index (MFI) (190°C/2.16 kg)

Condition	VC10 (g/10 min)	VC12 (g/10 min)
Virgin	3.7	6.1
Irradiated t = 55 min	23.5	44.0
Irradiated t = 3.5 h	22.5	42.7
Irradiated t = 24 h	33.4	60.2
Irradiated/aged t = 55 min	21.0	44.6
Irradiated/aged t = 3.5 h	20.2	41.3
Irradiated/aged t = 24 h	30.3	56.4
Aged	3.6	5.9

caused by the loss of the labile H being present at the tertiary carbon atom,[18] i.e.,
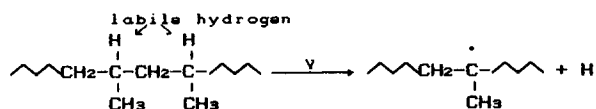
However, irradiation at room temperature results in the formation of the resonance stabilized radical[19]:

γ-Irradiation of PP may also give

as the primary radical product.[20,21]

Once a C—H bond is broken and a backbone radical is formed, scission of C—C links in the backbone adjacent to the radical site becomes much

Table IV   Stress–Strain Measurements

	VC10			VC12		
	TS[a] (yield) (N/mm^2)	Elongation		TS (yield) (N/mm^2)	Elongation	
Condition		%	% Loss		%	% Loss
Virgin	25.4	925	—	29.8	89	—
Irradiated t = 55 min	26.0	754	18.5	29.8	34	61.8
Irradiated t = 3.5 h	25.1	818	11.6	30.1	44	49.4
Irradiated t = 24 h	27.0	673	27.2	30.6	35	60.7
Irradiated + aged t = 55 min	27.4	25	97.3	28.4	14	84.3
Irradiated + aged t = 3.5 h	27.5	27	97.1	29.1	17	81.0
Irradiated + aged t = 24 h	27.4	20	97.8	28.8	14	84.3
Aged	26.0	121	86.9	29.5	73	18.0

[a] TS = tensile strength.

more favorable because of the 63–170 kJ/mol (15–40 kcal/mol) drop in the C — C bond energy in the radical as compared with the saturated backbone.

Owing to the limited rate of diffusion of oxygen in PP, high dose rates and sample thicknesses ($\geq$ 3 mm) will both have the effect of starving the deeper polymer layers of oxygen, so that the typical vacuum reaction will occur there, except very close to the surface of the polymer. In the absence of oxygen, γ-irradiation of PP leads to the formation of tertiary alkyl and allyl radicals. After the "labile" hydrogen loss, there are two possible routes to H abstraction: intramolecular and intermolecular.
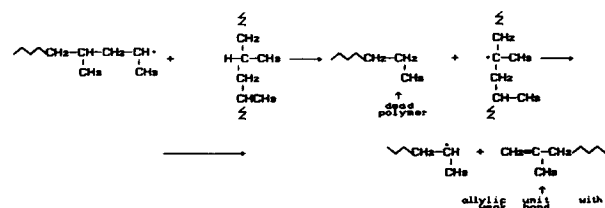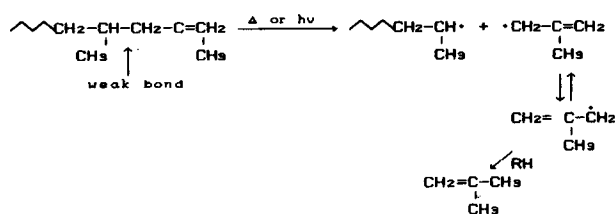
Intramolecular
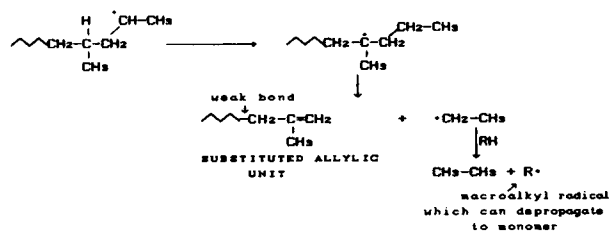
There are also other systems giving higher MW degradation products such as
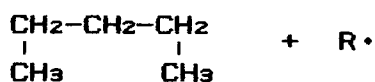

Intermolecular



If we consider the allylic unit,

Dulog et al.[22,23] because of the favorable configuration of the iPP, showed that the intramolecular reaction between two adjacent radicals is facilitated in comparison with the intermolecular one. In addition to the above reactions, another reaction can occur without volatile loss:
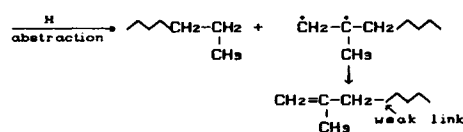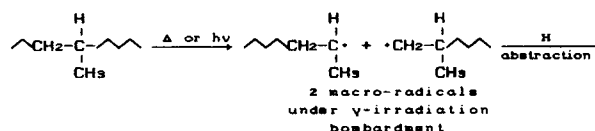
By recombination of two radicals, a cross-link can be formed:
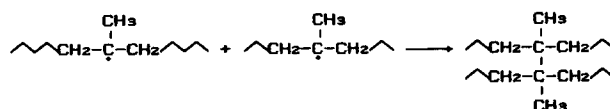
Let us now consider the results obtained at a low dose rate, i.e., t = 24 h. Under these irradiation con-
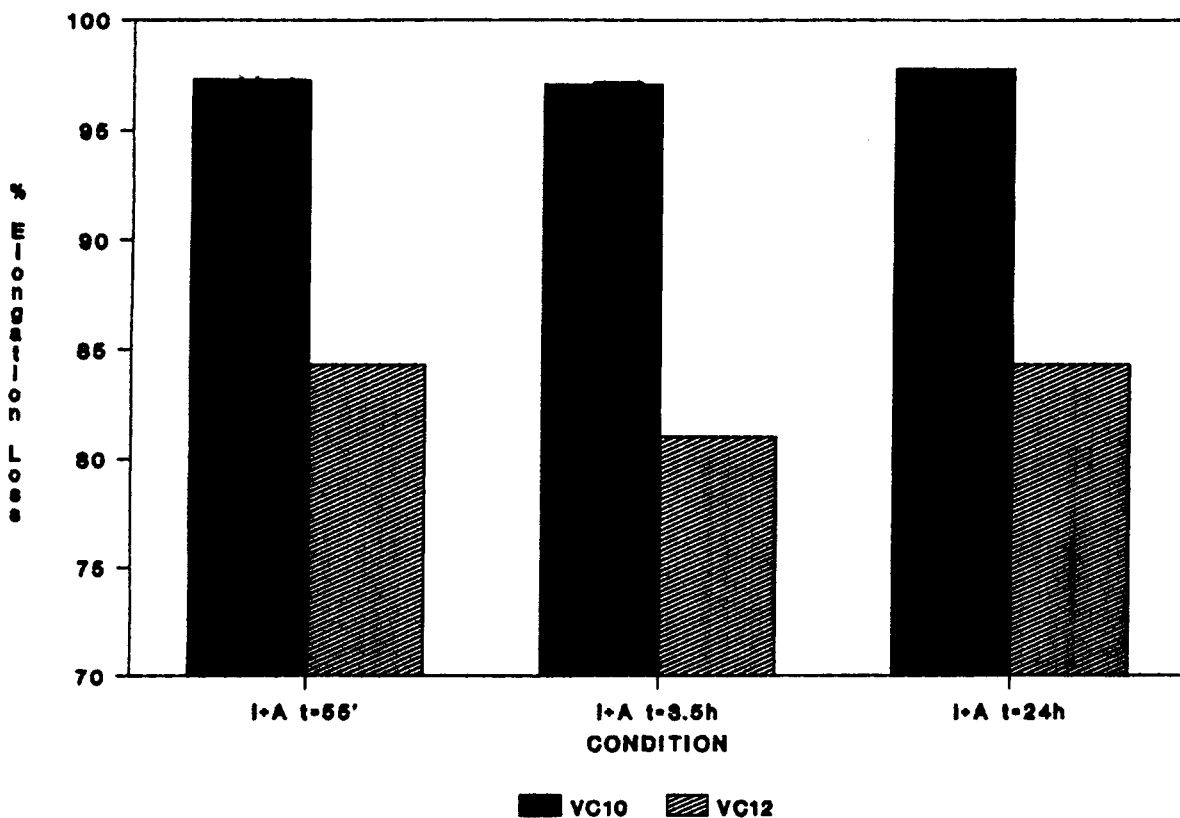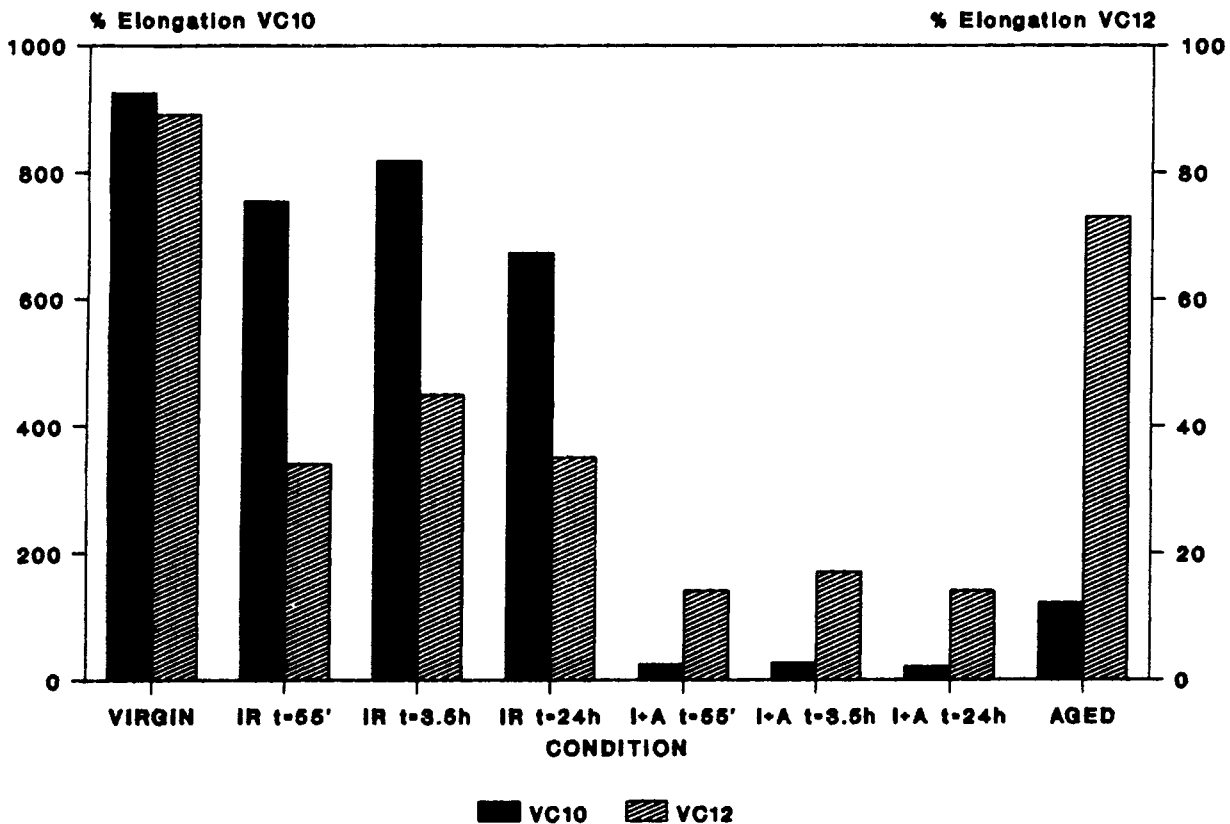
Figure 3   (a) Dose-rate effect on % elongation of VC10 and VC12 (measurements obtained at a crosshead speed of 200 mm/min); (b) dose-rate effect on % elongation loss of VC10 and VC12.
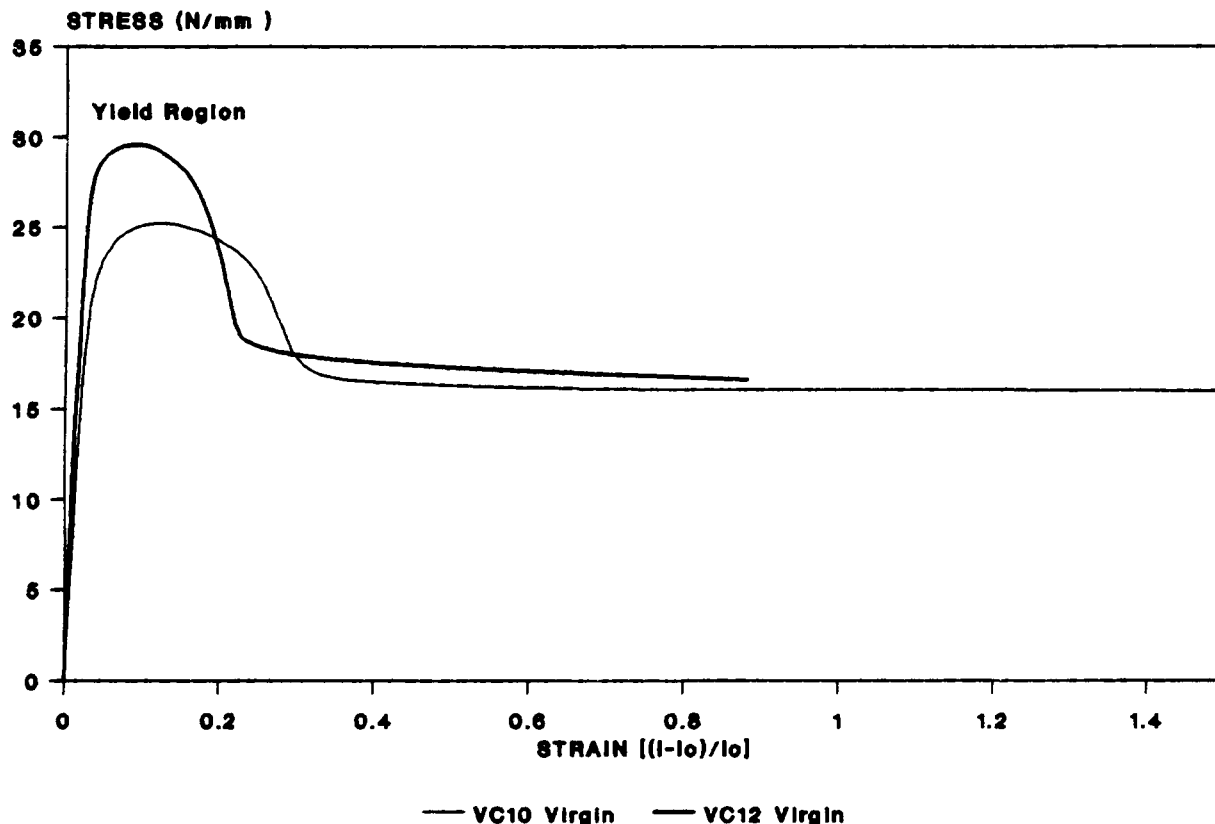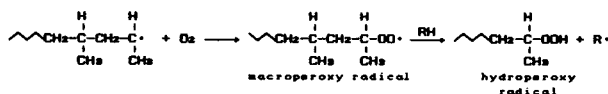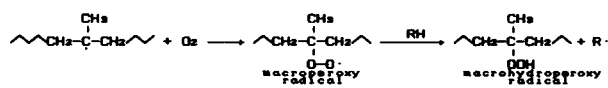
Figure 4 Stress–strain curves of VC10 and VC12 in the "virgin" state. Comparison of the yield breadth (at low strains).

ditions, the effect of O_2 is more pronounced to the whole degradation process. Hence,
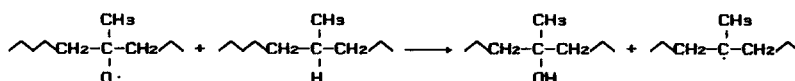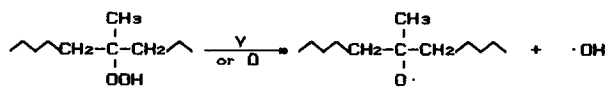

Also,

The specificity of the *tert*-peroxy attack on tertiary C — H in PP has been shown by the spin-trapping of the macroalkyl radical so generated.[24]
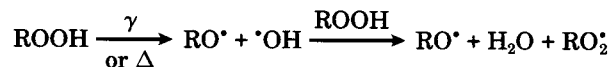
The macrohydroperoxide—the first molecular product of the chain oxidation of most polymers—is susceptible to both γ-irradiation and thermal cleavage because of its extremely weak O — O link (ca. 190 kJ/mol or 45 kcal/mol):

The decomposition is often suggested to involve hydrogen-bonded hydroperoxide dimers[25]:
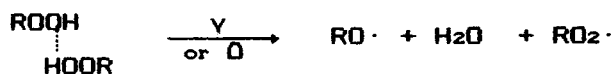
A radical-induced decomposition of the macrohydroperoxides is more probable:

$$ROOH \xrightarrow[\text{or } \Delta]{\gamma} RO^{\bullet} + {}^{\bullet}OH \xrightarrow{ROOH} RO^{\bullet} + H_2O + RO_2^{\bullet}$$

Thermal or γ-initiated decomposition of PP hydroperoxides is complex, either because of simultaneous unimolecular and pseudobimolecular processes or because of neighboring group-assisted reactions.[24-26]

The macroalkoxy and hydroxyl radicals may both abstract hydrogen from the surrounding polymer matrix to generate an alcohol, water, and new macroalkyl radicals that can then take part in many cycles of the chain-oxidation:
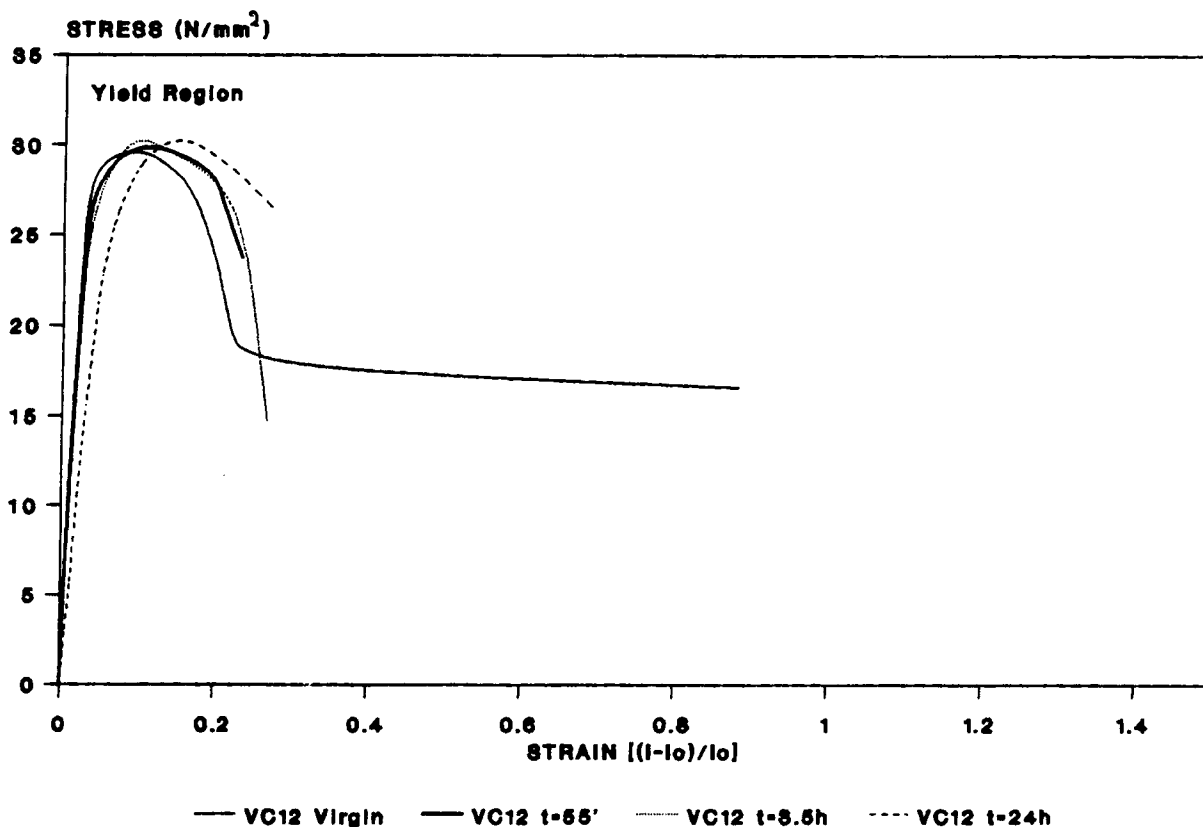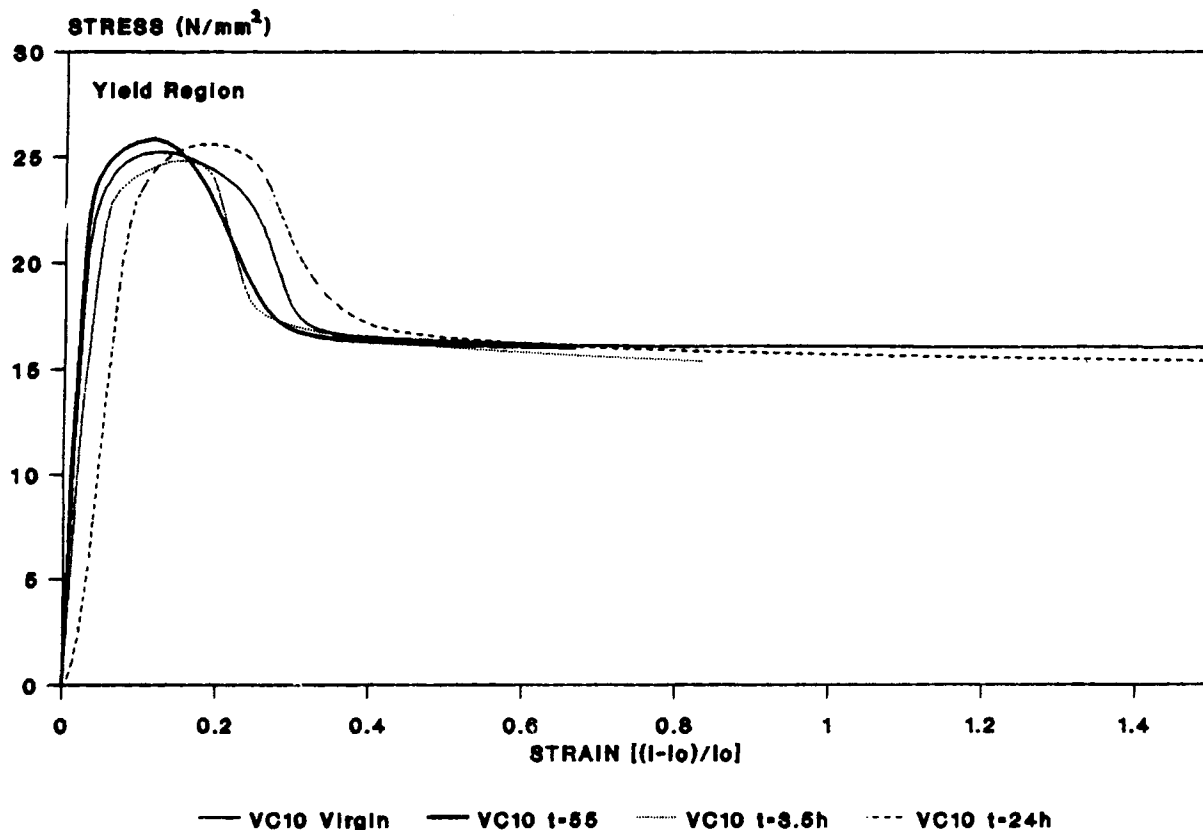
Figure 5 (a) Stress–strain curves of VC10 subjected to irradiation–dose-rate effect on the yield breadth; (b) stress–strain curves of VC12 subjected to irradiation–dose-rate effect on the yield breadth.

Table V   DSC Major Transitions at High Temperatures

	VC10		VC12	
Condition	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
Virgin	170.2	75.1	172.1	87.7
Irradiated t = 55 min	167.3	77.7	167.8	77.4
Irradiated t = 3.5 h	167.4	85.3	170.2	79.1
Irradiated t = 24 h	169.2	74.9	168.1	85.6
Irradiated + aged t = 55 min	165.4	83.1	167.8	88.7
Irradiated + aged t = 3.5 h	167.0	88.6	169.2	89.9
Irradiated + aged t = 24 h	167.3	84.2	168.3	87.4
Aged	167.3	85.6	171.1	89.8

An additional important facet of the macroalkoxy radical is its ability to undergo a β-scission that may cleave the backbone:
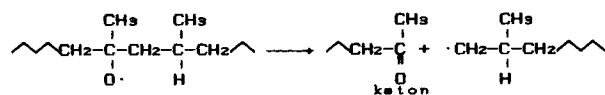
In PP, this scission occurs in the amorphous domains. This scission process generates two chain ends that are free to restructure and can often lead to increased crystallinity as oxidation degradation proceeds. This restructuring leads to the formation of surface cracks that act as stress concentrators during elongation.[25]
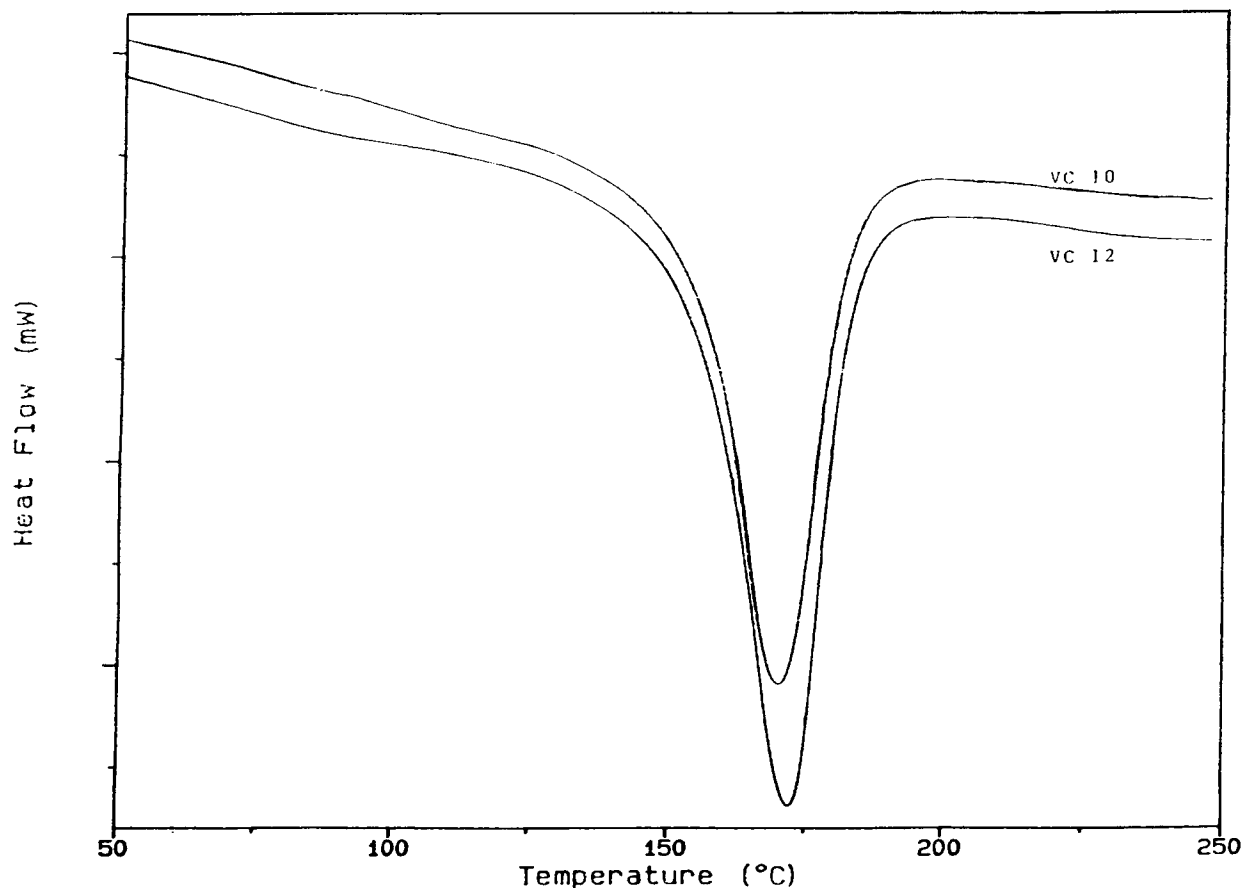
**Figure 6**   DSC thermograms of VC10 and VC12 in the virgin state.

Table VI Yellow Index of PP After Irradiation and Aging (120°C/24 h)

	PP Grade	
Condition	VC10	VC12
Irradiated t = 55 min	17.2	13.1
Irradiated t = 3.5 h	23.8	21.36
Irradiated t = 24 h	43.6	22.2

The macroalkyl radical can react with O_2 or abstract H or depropagate to monomer:

[chemical reaction scheme]
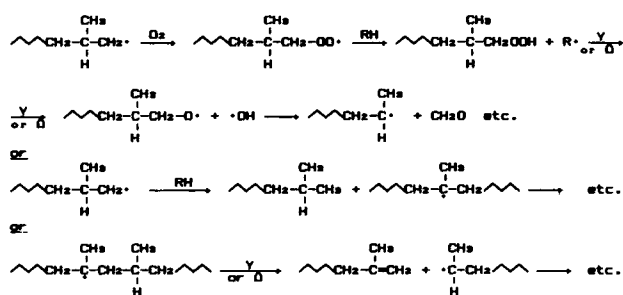
However, PP gives negligible yields of monomers during degradation.[25] Peroxy radicals eventually terminate by reaction with other radicals to give dialkyl peroxides, carbonyl species, or alcohols:

[chemical reaction scheme]
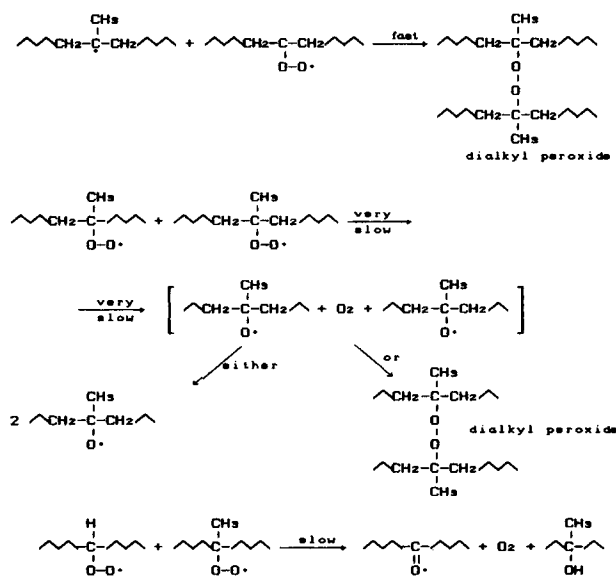
PP cross-links only under special conditions such as high peroxide levels; otherwise, backbone scission dominates whether as a result of oxidative processes or in the oxygen-free melt from radical rearrange-

ments such as in the depropagation reactions mentioned above.

The dose-rate effect is a time-dependent phenomenon that occurs in radiation oxidation. It arises whenever one or more steps in the oxidation chemistry becomes rate-limiting within the time scale of the experimental time. Such steps include oxygen diffusion, peroxide breakdown, and radical migration.[27]

In the case where the dose-rate effect is strictly caused by oxygen diffusion, the effect appears only over the dose rate range of which significant changes in the extent of oxidative penetration occurs. At dose rates above that of which oxidation is limited to essentially a surface effect, little or no effect may be observed. Similarly, at dose rates ranging below that at which homogeneous oxidation occurs, no further dose-rate effect occurs. However, as the dose rate decreases, the peroxide breakdown becomes gradually more important while the dose rate effect caused by oxygen diffusion tends to disappear. At extremely lower dose rates, the radical migration starts to contribute to the degradation.

The dose-rate effect may be due to one or more of possible mechanisms that have been observed to occur over a wide range of dose rates. It is to be understood that the above remarks apply for irradiation in air and at constant temperature.

Effect on Physical Properties

Considering the MFI results (see Table III and Fig. 2), it can be clearly seen that generally upon irradiation both grades exhibited a drastic increase in MFI values, the extent of which is directly dependent on the dose rate, i.e., the higher the dose rate, the lower the degradation of the materials. However, it can be noticed that at dose rate t = 3.5 h, the MFI values tend to be lower compared to the corresponding ones of t = 55 min, indicating this way that the materials have undergone, relatively, a lower degradation. These results seem to deviate from the view that "the higher the dose rate, the lower the polymer's damage." It is, thus, believed that at very high dose rates a contribution of some other parameter, beside the γ-irradiation-induced degradation, is added to the whole system. This contributing parameter responsible for the degradation enhancement apparently is due to a critical temperature rise, developed locally as a result of increased vibrational movements of the chains, above which chain-scission mechanisms have more favorable conditions to occur.

The above interpretation is supported by the mechanical measurements obtained. Therefore, looking at the stress–strain measurements [Table IV and Fig. 3(a)], the percentage elongation of both materials decrease to a greater extent in the case of t = 55 min compared to t = 3.5 h. A similar trend can also be found in reported results in the literature.[28] As far as OIT values of the irradiated samples are concerned, no reliable conclusions can be drawn due to an alleged latent state involving trapped radicals in the bulk of the materials. This "latent" state is explained in more detail later.

At low dose rates, i.e., t = 24 h in our case, PP gains a greater amount of chromophores, giving rise to increased yellowing. Indeed, qualitatively and quantitatively (Table VI), it was found that samples irradiated at lower dose rates exhibited a higher yellowing discoloration compared to those treated at higher rates. This is in accordance with the above-described mechanism. Besides this imposed physical change, it can also be seen from the results that at t = 24 h both materials have undergone the worst damage, i.e., MFI values reached a maximum, whereas OIT (irradiated/aged) and % elongation reached only a minimum. Therefore, the O_2 involvement during the irradiation, the concentration of which (in the bulk) is rate-dependent, created a more severe damage to the polymers. Two main chromophores are thought to be responsible for the yellowing of PP samples: the $\diagdown C = O$ and POOH. Due to harsh employed aging conditions, the COOH number must have been reduced.[29]

Irradiation causes a drastic decrease in OIT values. However, irradiated samples subjected to oven aging (120°C, 24 h) showed increased OIT values irrespectively from the dose rate. This is attributed to the fact that during the accelerated aging process the free radicals formed upon irradiation, which are trapped within the bulk of the polymer, decayed through oxygen diffusion, giving rise to all oxidizing degradation reactions and products, but also through recombination–cross-linking reactions, such as

$$R^{\cdot} + R^{\cdot} \rightarrow R - R \tag{1}$$

$$RO_2^{\cdot} + R^{\cdot} \rightarrow ROOR \tag{2}$$
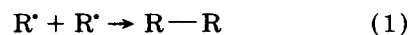
Of course, reaction products of (1) are more likely to survive under such severe aging conditions, due to the stronger $C - C$ bonds that are formed compared to reaction products of (2), which, due to the

weak $O - O$ bond, undergo further bond cleavage there, i.e.:

$$ROOR \xrightarrow{\Delta(\text{heat})} 2RO^{\cdot} \tag{3}$$

following all the oxidizing degradation reactions already described. Therefore, as a result of the predominance of the recombination–cross-linking reactions during aging, we get this increase of OIT. In the case of the irradiated samples, they exhibit lower OIT, because the trapped free radicals formed after irradiation are activated and become more energetic to the applied test conditions. As a result, the oxidative degradation reactions commenced at an earlier stage. This is further supported by the rheological results, where MFI values of the irradiated/aged samples are lower compared to the irradiated ones, indicating an increase in molecular weight (Table III). Therefore, it can be alleged that the samples in the irradiated state are in a "latent" condition.

These trapped radicals were previously attributed to possibly alkyl radicals, located in crystalline domains slowly reinitiating oxidation chains.[18] However, more recent evidence implicates initiation by the unstable hydroperoxide groups identical to those from all chain-oxidation processes, e.g., photooxidation or peroxidic species from the O_3 that always accompanies γ-irradiation in air.[25] In addition, deterioration may result from exposure to two or more combined processes. For example, photo or gamma deterioration is nearly always a composite of light or γ-radiation attack and thermal oxidation.

In polyolefins, when irradiated, the predominant structural change occurs in the amorphous region or on the surface of the crystals.[30] In our case, there are distinct differences in physical properties between VC10 and VC12 due to different M_n (number-average molecular weight). This gives rise to differences in the degree of crystallization, which mainly effects the properties of the materials. VC10 has a lower degree of crystallinity compared with VC12, as measured by DSC (Fig. 6). This is verified by the enthalpy of fusion (ΔH_m values in the virgin state) as well as from the melting point (T_m values) (Table V). This is due to the characteristic structural feature of PP in that high MW polymer (greater number of longer chains in this case—Fig. 7) does not crystallize as easily as does lower MW material.[31] The tensile at yield (TS_y) and the yield region (breadth) are referred to the quantity and the quality of the crystallites, respectively. A similar correlation exists between ΔH_m and the breadth of
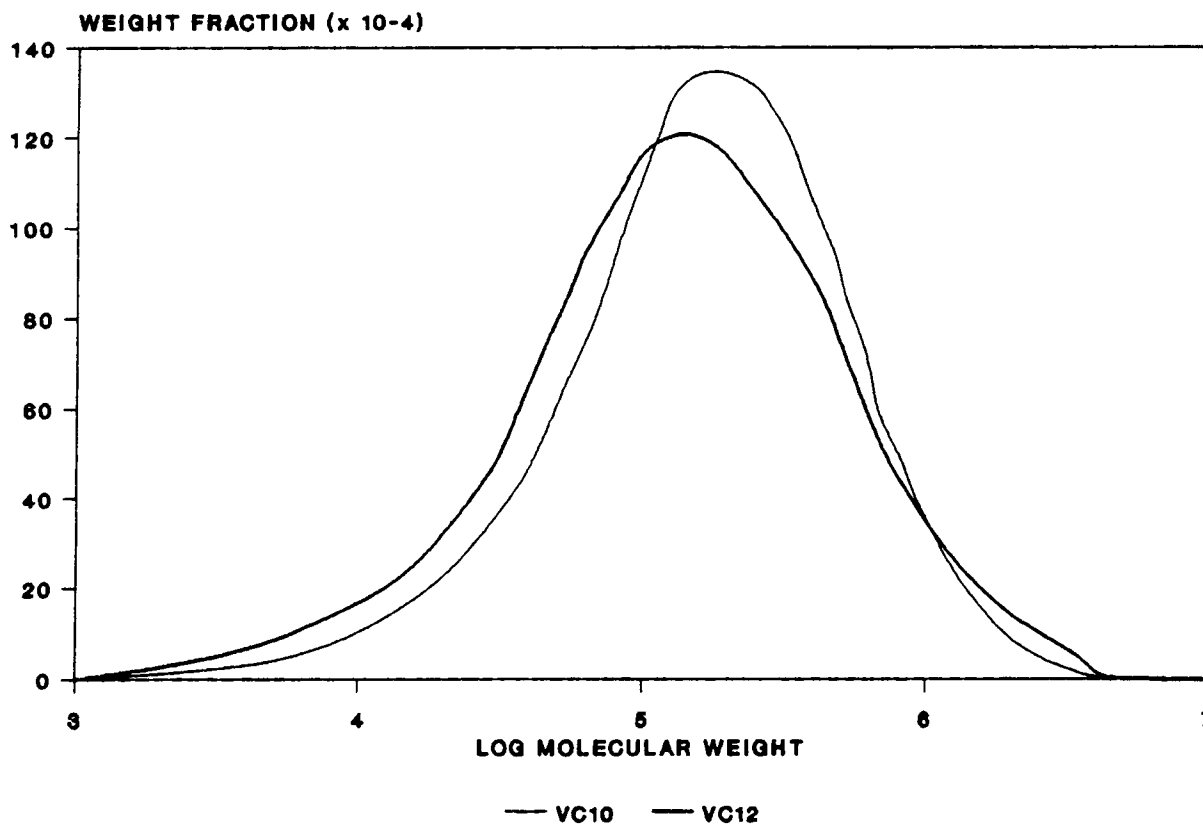
WEIGHT FRACTION (x 10-4)

LOG MOLECULAR WEIGHT

—— VC10   —— VC12

Figure 7   Differential weight fraction plot of the two PP grades (obtained by Neste Chemicals, Belgium).

the corresponding melting curve. In Figures 4 and 6 are given representative curves of VC10 and VC12 in the "virgin" state.

After irradiation (see Table V), it can be noticed that between VC10 and VC12 two different effects are encountered as far as enthalpy of fusion (degree of crystallization) is concerned, i.e., ΔH_m values of VC10 are increased, whereas the corresponding ones of VC12 are reduced. This can be explained as follows: As has already been described, the lower the molecular weight (the shorter the polymer chain), the higher the degree of crystallization. After the chain scission (in the amorphous region) induced by irradiation, the polymer chains become shorter and, hence, as entanglement is reduced, they can obtain a better packing order, giving rise, this way, to an increased crystallization. Since VC10 has a greater M_n than does VC12, it is believed that after the γ-irradiation-induced chain scission its chains still are long enough and have the margin to perform recrystallization; hence, a ΔH_m increase is obtained. On the other hand, for VC12, due to its lower M_n,

the greater number of shorter chains it inherently has (see Fig. 7) give the polymer the opportunity to attain a higher degree of mesomorphous and crystalline regions. After irradiation, it is believed that this augmented, susceptible to γ-irradiation, mesomorphous region, is being damaged, thus giving rise to a decrease in ΔH_m values. In parallel to these results, from Figure 5(a) and (b), it can also be seen that the breadth of the yield region in the case of VC10 is sharpened, while becoming broader in the case of VC12. Hence, γ-irradiation affects both the amorphous and mesomorphous regions of the polymer. It has been reported[32] that the structure of crystallites is weakly affected by γ-irradiation and only at doses well above the required ones for sterilization (i.e., ~ 2 MGy). Therefore, it can be suggested that in the case of VC10 the main damage is inflicted upon the amorphous part of the polymer, whereas in VC12, it is upon the amorphous and the augmented mesomorphous regions.

Considering now the results obtained from OIT and stress–strain measurements [Tables II and IV

and Figs. 1 and 3(b)], it can be seen that VC10 has undergone a greater postirradiation degradation (irradiated + aged samples) as far as OIT values and % loss in elongation is concerned. This arises from the fact that % elongation loss reaches a maximum ($\sim$ 97% loss), and OIT, a minimum. This suggests that the damage inflicted in the "surplus" amorphous area of VC10 created a substantial amount of radicals that led to enhanced degradative phenomena, compared to VC12. This is also the reason why VC10 exhibited intense yellowing discoloration compared to VC12, which produced a faint one, even though both materials are equally stabilized. This is illustrated in Table VI, where it can be seen that the lowest yellow index is exhibited by VC12 at all dose rates. A distinct difference can be appreciated at low dose rates ($t = 24$ h), where the yellow index of VC12 is more or less half of the corresponding one of VC10.

CONCLUSION

High dose rates undoubtedly give the lowest physical changes, mainly due to the low oxygen diffusion under these conditions, but from the results obtained, it can be drawn that an optimum dose rate region exists ($t = 3.5$ h) corresponding to an irradiator with a ^{60}Co activity of approximately 1.5–2 million Curries, above which results inversely can be encountered. Furthermore, it was found that the PP grade of broader molecular weight and lower M_n, i.e., VC12, had a higher γ-irradiation and postirradiation resistance.

Also, it can be concluded that polymers like PP, which is considered to be a marginal radiation-resistant material, can obtain an enhanced radiation resistance by inherently having an increased degree of crystallization arising from a specific MWD. This, in effect, can compensate in minimizing the side effects (namely, undesirable discoloration, reduced postirradiation service life of the product, etc.) that a low activity/low dose rate γ-irradiator, for instance, can impose on this material, due to its dose and dose-rate sensitivity. Hence, the versatility of γ-irradiation polypropylene is promoted by this way, so that it can be sterilized (2.5 Mrad) at low dose rates, giving, comparatively, degradative phenomena to a lesser extent, as in the case of VC12.

Finally, medical polymers designed to have higher γ-irradiation stability not only serve for the mutual benefit of the industry as a whole, but also mainly protect and serve the public health.

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