

# Inverse response of polypropylene to gamma radiation under vacuum

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The effect of gamma radiation under vacuum on polypropylene is analysed on the basis of a simple kinetic model. The influence of the irradiation parameters, total absorbed dose and dose rate, on the rates of the main reactions occurring during irradiation, i.e.  $\beta$ -scission, addition to double bonds and termination, is studied. Using kinetic equations, and free radical and double bond balance relationships, we show that it is possible to rationalize the response of polypropylene to gamma radiation. In particular, on the basis of the mathematical solutions of these equations, we obtain the equation of an 'inversion curve', implicit function of the irradiation parameters, which gives the dose values enhancing chain branching and molecular weight increase at fixed dose rate and vice versa. These 'inversion conditions' are also found experimentally analysing the rheological behaviour of a commercial polypropylene irradiated under vacuum. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Radiation processing is a useful tool to modify the molecular structure of polymers. It is well known that the interactions of gamma photons with organic molecules cause the formation of excited species, which, for polymeric materials, essentially evolve towards free radicals<sup>1</sup>. The latter are very reactive and stabilize in several ways, depending on many factors, such as the molecular structure and the morphology of the polymer and the irradiation conditions. On account of the complexity of the response of a polymer to gamma radiation, many attempts to describe this processing have been undertaken<sup>2,3</sup>.

This work falls in this research field. In particular we studied the response of a polypropylene (PP) to gamma radiation under vacuum. Polypropylene is extensively used for medical tools, which are often sterilized by means of gamma-rays, so much effort has been devoted to increase its radiation resistance. The main effect of gamma-radiation on PP, as already reported<sup>2,7</sup>, is molecular degradation with worsening of the properties. This result is attributed to the presence of tertiary carbon atoms, which favours chain scission. Though the main effect is molecular degradation, also chain branching and crosslinking can occur in gamma-irradiated PP. In fact in correspondence to some experimental conditions, gamma-irradiated PP presents insoluble fractions<sup>2,8</sup>.

The aim of this work is to predict the main molecular effect of gamma radiation under vacuum on PP for each irradiation condition. We study the influence of dose rate,  $I$ , and the total absorbed dose,  $D$ , on the main

reactions occurring during irradiation, i.e.  $\beta$ -scission, free radical addition to double bonds, and free radical termination reactions. In particular we present a mathematical approach to modelling the effects of gamma radiation under vacuum on a PP and the experimental verification of our assertions through the study of molecular modifications.

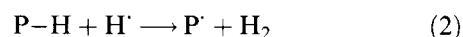
## DISCUSSION

Considering the high complexity of the response of a polymer to gamma radiation, we made the following simplifying hypotheses:

- (i) The rate of radicals generation is proportional to  $I$ .
- (ii) The free radicals stem from C–H bond cleavage. In fact the macromolecular radicals formed through main-chain scission essentially undergo recombination, because of their very low mobility. On the other hand, when the scission involves side groups, the resulting radicals can have the possibility to diffuse far enough to their radical partners and give rise to the chemical reactions which cause the molecular modifications of the polymer.
- (iii) No distinction between internal and terminal macroradicals and internal and terminal double bonds is made.

On these bases the reactions considered possibly dominant are:

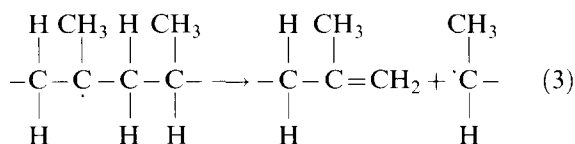
### Initiation



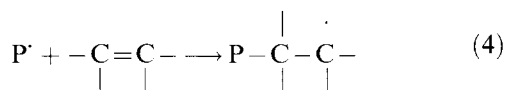
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**Propagation**

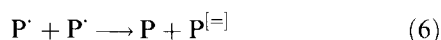
*β-scission*



*addition of free radicals to double bonds*



**Termination**



It is worth noting that the reactions of the hypothesized mechanism considered earlier are the most commonly used to describe gamma-radiation effects on polypropylene<sup>2,3</sup>.

We have formation and consumption of free radicals and double bonds. Termination reactions are the ‘natural death’ of free radicals, while scission and addition are chain-reactions and do not consume free radicals, but only modify the molecular structure of the polymer. In particular, reaction (3) causes chain length reduction, thus lowering  $M_w$ . Reactions (4) and (5) cause chain branching and crosslinking respectively, which could allow an increase in  $M_w$  in some irradiation conditions.

The corresponding kinetic equations are:

$$\text{Scission} \quad \frac{dSc}{dt} = K_S [\text{P}^\cdot] \quad (7)$$

$$\text{Addition} \quad \frac{dAd}{dt} = K_A [\text{P}^\cdot] [\text{DB}] \quad (8)$$

$$\text{Termination} \quad \frac{dTer}{dt} = K'_T [\text{P}^\cdot]^2 \quad (9)$$

$$\frac{d(Ter - \text{DB})}{dt} = K''_T [\text{P}^\cdot]^2 \quad (10)$$

The rates of the termination reactions (equations (9) and (10)) are bimolecular with respect to the free radical concentration, whereas  $\beta$ -scission (equation (7)) and free radical addition to double bonds (equation (8)) are monomolecular.

On the basis of these equations and our simplifying hypotheses, it is possible to write the following balance equations:

Free radical balance:

$$\frac{d[\text{P}^\cdot]}{dt} = \phi I - K'_T [\text{P}^\cdot]^2 - K''_T [\text{P}^\cdot]^2 = \phi I - K_T [\text{P}^\cdot]^2 \quad (11)$$

with

$$K_T = K'_T + K''_T$$

$\phi$  is the ‘quantic yield’, which we define as a proportionality factor between the dose rate and the radical concentration increase.

Double bond balance:

$$\begin{aligned}
 \frac{d[\text{DB}]}{dt} &= \frac{dSc}{dt} + \frac{d(Ter - \text{DB})}{dt} - \frac{dAd}{dt} \\
 &= K_S [\text{P}^\cdot] + K''_T [\text{P}^\cdot]^2 - K_A [\text{P}^\cdot] [\text{DB}] \quad (12)
 \end{aligned}$$

The dependence of free radical and double bond concentration on  $I$  and the irradiation time, which is related to  $D$ , can be obtained solving equations (11) and (12) (see Appendix).

The steady state values for free radical and double bond concentration are:

$$[\text{P}^\cdot]_{ss} = \sqrt{\frac{\phi I}{K_T}} \quad (13)$$

and

$$[\text{DB}]_{ss} = \frac{K_S}{K_A} + \frac{K''_T}{K_A} \sqrt{\frac{\phi I}{K_T}} \quad (14)$$

Following this mathematical approach, we can study the influence of the irradiation parameters,  $D$  and  $I$ , on the final molecular structure of the irradiated polypropylene.

We will begin discussing these effects considering as constant parameter the total absorbed dose.

Below a limiting value of  $D$ , the concentration of double bonds is very low, and thus the rate of addition reaction is negligible; the molecular structure of the irradiated PP depends on the competition of the rates of scission and termination reactions, so the main effect is  $\beta$ -scission, which causes  $M_w$  decrease.

Increasing  $D$ , the concentration of double bonds formed through  $\beta$ -scission and termination reaction (equation (6)) increases, thus enhancing the rate of addition reaction of radicals to double bonds. This reaction minimizes degradation together with termination (equation (5)), but its influence is more marked with respect to termination. In fact addition is a ‘chain reaction’, while termination is the ‘natural death’ of the free radicals. Remembering that addition (equation (8)) is monomolecular, and termination (equation (9)) is bimolecular with respect to free radical concentration, and  $[\text{P}^\cdot]$  is related to  $I$  according to the solution of equation (11), we can say that  $I$  plays an important role in the irradiation effects on the molecular modification of polypropylene.

The decrease of  $I$  lowers the degradation, so we can suppose the existence of a dose rate in correspondence of which the main effect is  $M_w$  increase. More generally we can find an ‘inversion curve’ implicit function of  $I$  and  $D$ , the mathematical expression of which can be obtained comparing the rates of the previous reactions.

As a first approximation these conditions can be obtained comparing the rates of addition (equation (8)) and scission (equation (7)):

$$\frac{dAd}{dt} = \frac{K_A}{K_S} [\text{DB}] \quad (15)$$

The rates of these reactions are the same when

$$[\text{DB}] = \frac{K_S}{K_A} \quad (16)$$

Note that this expression takes into account chain branching and chain scission phenomena due only to addition and scission reactions.

The steady state value of double bond concentration (equation (14)) shows that it is possible to reach a double bond concentration higher than the value obtained through equation (16):

$$[\text{DB}]_{\text{SS}} = \frac{K_S}{K_A} + \frac{K_T''}{K_A} \sqrt{\frac{\phi I}{K_T}} > \frac{K_S}{K_A}$$

Here is evidence the contribution to  $[\text{DB}]_{\text{SS}}$  of the two sources of double bonds:  $\beta$ -scission (reaction (3)) and termination (reaction (6)).

The exact determination of the 'inversion conditions', a function both of  $I$  and  $D$ , can be derived from the assumption

$$\frac{d\text{Ter}}{dt} + \frac{d\text{Ad}}{dt} = \frac{d\text{Sc}}{dt} \quad (17)$$

and considering equations (7), (8) and (9), we obtain

$$[\text{DB}] = \frac{K_S}{K_A} - \frac{K_T'}{K_A} [\text{P}'] \quad (18)$$

This last equation represents the 'inversion curve', an implicit function of both dose rate and total absorbed dose, which gives the  $D$  values enhancing chain branching and molecular weight increase, at a fixed  $I$ , and vice versa.

## EXPERIMENTAL

We used an isotactic polypropylene MOPLEN T30G (Himont-Italy), with molecular characteristics given by the supplier:  $M_w = 481\,000$ ;  $M_w/M_n = 4.2$ .

Circular samples (25 mm diameter) were cut from an extruded ribbon, 1 mm thick, obtained from pellets using a Brabender single screw extruder model PLE 651. The thermal profile was 120, 140, 160 and 180°C and the rotational speed was 20 rpm.

Before the irradiation the samples were kept for about 60 min in glass tubes under vacuum at  $1.3 \times 10^2$  Pa. During this period they were also washed three times with pure nitrogen.

Irradiation was performed under vacuum in this glass tube, at room temperature (about 25°C) by the IGS-3, a panoramic 3000 Ci  $^{60}\text{Co}$  irradiator<sup>9</sup>. The dose rates were in the range of 0.004–8 kGy h<sup>-1</sup> and the integrated doses in the range of 10–550 kGy; a variance of 5% in the radiation absorption was accepted. As a rule, for each condition the analysis was carried out on samples immediately after irradiation. All samples were taken in liquid nitrogen during the time between the end of irradiation and the start of the tests.

Rheological tests were performed with a Rheometrics dynamic analyser (RDA2) used in the dynamic mode with the plate and plate geometry ( $R = 12.5$  mm). The frequency sweep tests were carried out at 180°C and 20% strain in the range from  $10^{-1}$  to  $5 \times 10^2$  rad s<sup>-1</sup>. Stress relaxations were performed at 180°C with a step shear strain of 5%.

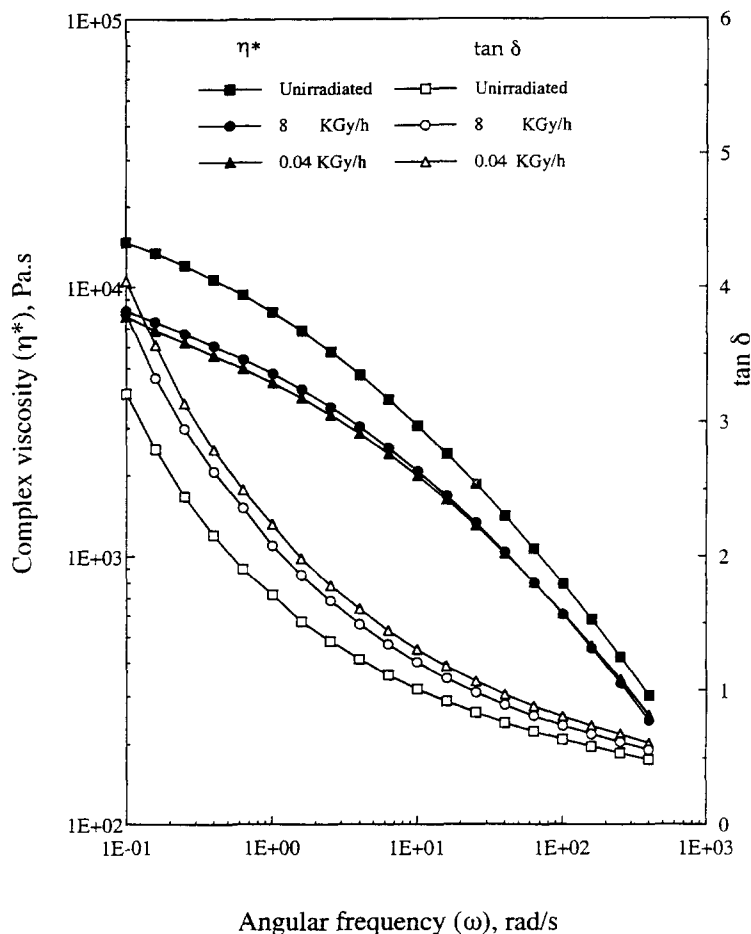


Figure 1 Complex viscosity,  $\eta^*$ , and loss factor,  $\tan \delta$ , for samples irradiated at 10 kGy

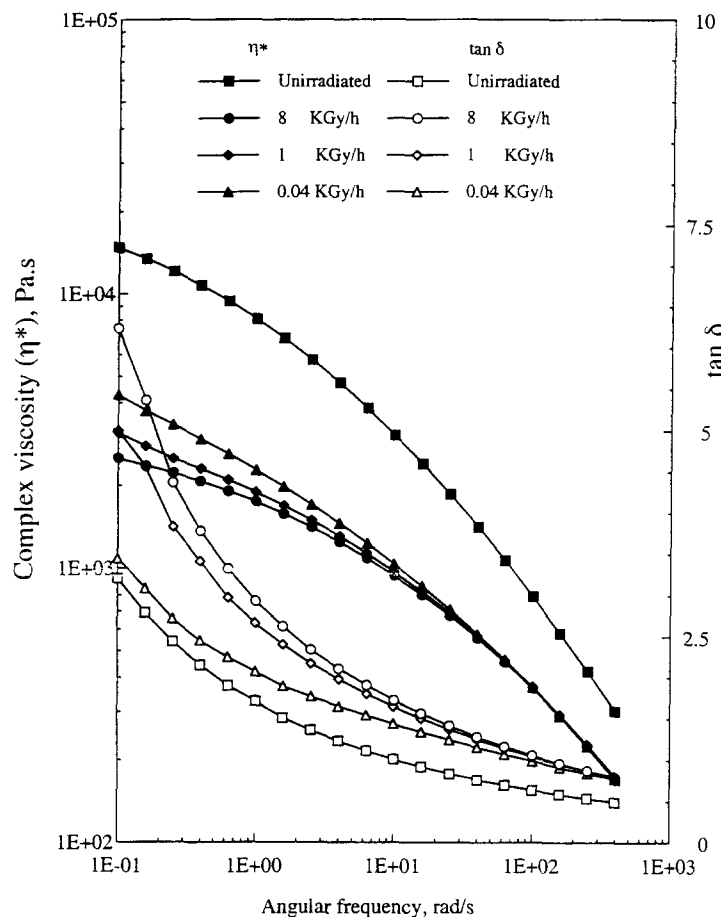


Figure 2 Complex viscosity,  $\eta^*$ , and loss factor,  $\tan \delta$ , for samples irradiated at 50 kGy

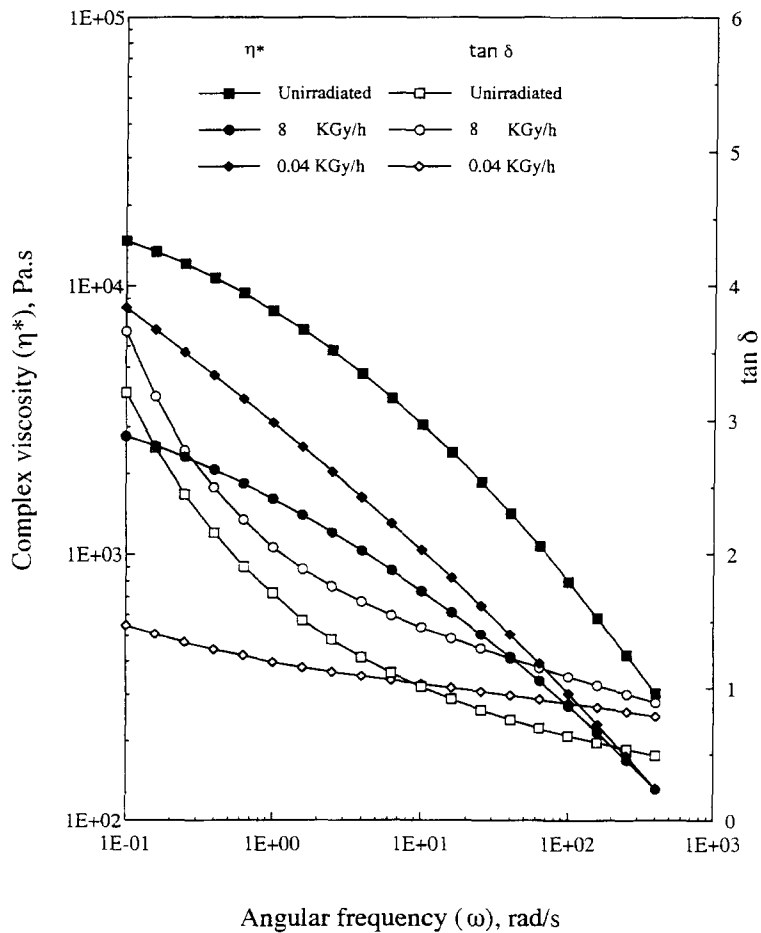


Figure 3 Complex viscosity,  $\eta^*$ , and loss factor,  $\tan \delta$ , for samples irradiated at 100 kGy

Solubility tests were conducted by means of a Soxhelt extractor, using xylene as solvent. Samples were exposed to refluxing xylene close to its boiling point for at least 72 h.

## RESULTS

Among all the molecular characterizations, we chose melt viscosity analysis to detect the modifications induced in PP by gamma rays. Dynamic mechanical methods in the melt state give rise to a complete set of information about the complex molecular events occurring during gamma radiation. In fact the decrease of molecular weight is easily detected through the decrease of Newtonian viscosity. Chain branching and cross-linking, which are more difficult to analyse, can be related to the different viscoelastic parameters, i.e. complex viscosity,  $\eta^*$ , and loss factor,  $\tan \delta$ . This approach is widely reported for the determination of gel point during curing of thermosets<sup>10</sup> and recently this kind of analysis was also used to study gamma radiation induced gelation in polyethylene<sup>11</sup>.

We can start considering the effects of irradiation at low total absorbed dose. In *Figure 1*  $\eta^*$  and  $\tan \delta$  for samples irradiated at 10 kGy are reported. As pointed out in the first part of the paper, in these conditions the concentration of double bonds is low and the main effect is chain scission with molecular degradation, as shown by the values of melt viscosity which, for irradiated samples, is lower with respect to the values of the

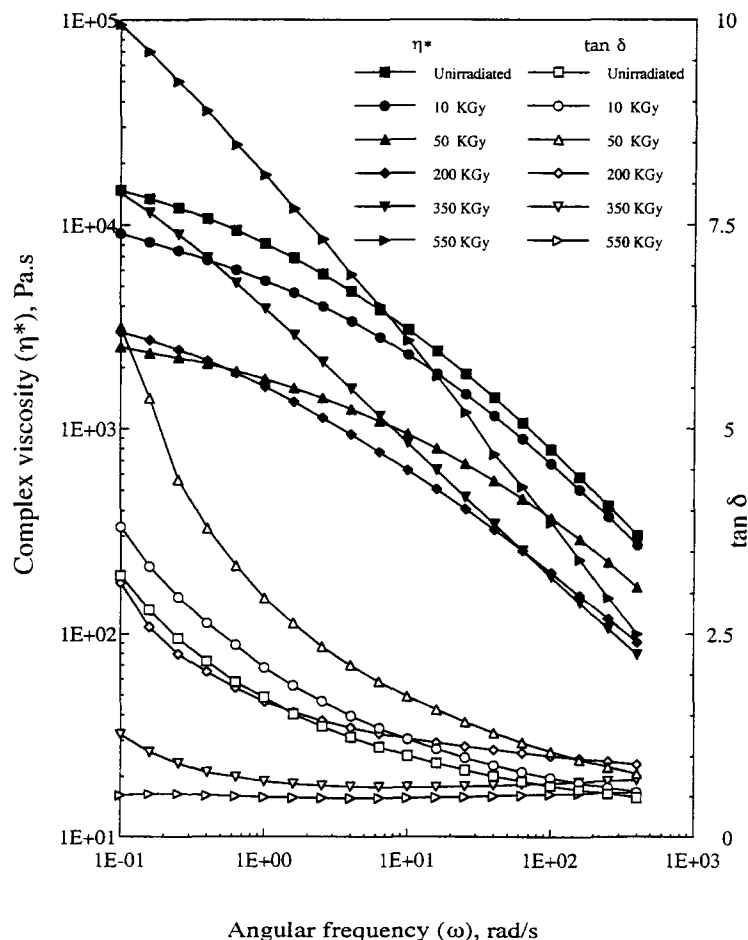
unirradiated reference one, in the whole frequency range considered. At the same time the loss factor is increased by irradiation.

In *Figure 2* values of the same parameters are reported for samples irradiated at 50 kGy. The increase of  $D$  causes an increase of double bond concentration, and the rate of addition becomes significant. This last reaction, the kinetics of which are monomolecular with respect to free radical concentration, is favoured by the decrease of  $I$ : the lower the dose rate the lower the degradation.

At 100 kGy, *Figure 3*, the total dose is large enough to make very significant the effect of double bond concentration at the different dose rates, and we clearly observe the 'inverse response' of PP. In fact the melt viscosity and the loss factor of the polymer irradiated at high dose rate still indicate degradation phenomena, whereas the flow curve relative to the sample irradiated at 0.04 kGy h<sup>-1</sup> is markedly steeper than the curve relative to the reference material, and the loss factor is very low. It is well known that this is the typical behaviour of branched polymer close to its gel point<sup>11</sup>. For these last irradiation conditions we cannot exclude the presence of microgels in the bulk of the polymer, even though the polymer is completely soluble in boiling xylene.

These experimental results confirm the existence of 'inversion conditions', depending on  $D$ , in correspondence of which the molecular weight starts to increase.

The overall effect of  $D$  is shown in *Figure 4*, where the flow curves and the loss factor for samples irradiated at



**Figure 4** Complex viscosity,  $\eta^*$ , and loss factor,  $\tan \delta$ , for samples irradiated at 8 kGy h<sup>-1</sup>

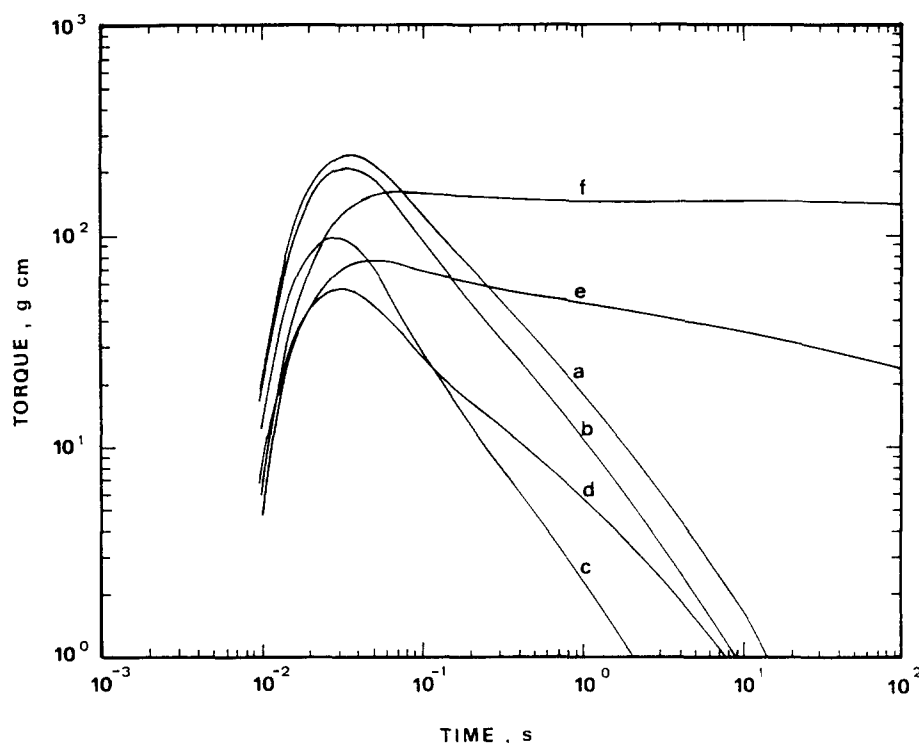


Figure 5 Relaxation curves for samples irradiated at  $8 \text{ kGy h}^{-1}$

Table 1 Solubility data for polypropylene samples irradiated at  $8 \text{ kGy h}^{-1}$

Irradiation dose (kGy)	Gel (%)
10	0
50	0
200	0
350	60
550	75

$8 \text{ kGy h}^{-1}$  are reported. At this value of  $I$ , for  $D$  up to  $50 \text{ kGy}$ , the main effect is degradation with the decrease of melt viscosity. At  $200 \text{ kGy}$  the melt viscosity of the irradiated sample increases, the slope of the flow curve becomes steeper and the loss factor decreases. At  $550 \text{ kGy}$   $\eta^*$  and  $\tan \delta$  curves show the typical behaviour of a crosslinked polymer. These molecular effects are further confirmed by stress relaxation curves, reported in Figure 5. Samples irradiated up to  $200 \text{ kGy}$  have stress relaxation behaviour typical of an uncrosslinked polymer, even though the slower stress recovery rate for the polymer irradiated at  $200 \text{ kGy}$  indicates the presence of chain branching, previously observed in the flow curve. On the other hand the relaxation curves of samples irradiated at higher doses tend towards a steady state value, thus revealing the presence of crosslinking. Furthermore solubility data, reported in Table 1, show significant amounts of gel fractions for samples irradiated at  $350$  and  $550 \text{ kGy}$ .

#### CONCLUDING REMARKS

In this work the inversion response of PP to gamma-radiation under vacuum is presented.

We show that it is possible to forecast the complete effects of irradiation, on the basis of the hypothesis that the main reactions involving the evolution of free

radicals, generated by the interactions of gamma rays with the polymer, are:  $\beta$ -scission, addition of free radicals to double bonds and termination.

By means of the kinetic equations and balance relationships we obtain the dependence of free radicals and double bonds concentration on the irradiation parameters.

The radicals and double bonds concentration affects the final molecular structure of the irradiated polypropylene.

Comparing the rates of reactions occurring during irradiation we achieve a mathematical equation of an 'inversion curve', implicit function of the irradiation parameters  $I$  and  $D$ , which gives the total absorbed dose values enhancing chain branching and molecular weight increase at fixed dose rate and vice versa.

Rheological measurements, performed on PP irradiated under vacuum, give evidence of the molecular modifications, proving the inversion phenomena.

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## APPENDIX

Solution of equation (11):

$$\frac{[P^{\cdot}]}{[P^{\cdot}]_{SS}} = \frac{\exp(2K_T[P^{\cdot}]_{SS}t) - 1}{\exp(2K_T[P^{\cdot}]_{SS}t) + 1}$$

Plotting the free radicals concentration  $[P^{\cdot}]$ , as a function of the irradiation time we have different curves varying the dose rates. The slope at the origin of each curve is  $\phi I$  and the increase of the dose rate increases the rate of attainment of the steady state.

Solution of equation (12):

$$[DB] = \frac{1}{\exp\left(-\int_0^t K_D[P^{\cdot}] dt\right)} \times \int_0^t \left\{ K_S[P^{\cdot}] + K_T''[P^{\cdot}]^2 \exp\left(-\int_0^t K_D[P^{\cdot}] dt\right) \right\} dt$$

## NOMENCLATURE

$I$	Dose rate
$D$	Total absorbed dose
$P-H$	Polymer chain
$P^{\cdot}$	Macromolecular radical
$P^{[=]}$	Double bond formed during irradiation
$[P^{\cdot}]$	Macromolecular radical concentration
$[P^{\cdot}]_{SS}$	Macromolecular radical concentration in steady state
$[DB]$	Double bond concentration
$[DB]_{SS}$	Double bond concentration in steady state
$\frac{dSc}{dt}$	Rate of $\beta$ -scission reaction
$\frac{dAd}{dt}$	Rate of addition reaction
$\frac{dT_{er}}{dt}$	Rate of termination reaction without formation of double bonds
$\frac{d(T_{er}-DB)}{dt}$	Rate of termination reaction with formation of double bonds
$K_A$	Kinetic constant for addition reaction
$K_S$	Kinetic constant for $\beta$ -scission reaction
$K_T'$	Kinetic constant for termination reaction without formation of double bonds
$K_T''$	Kinetic constant for termination reaction with formation of double bonds
$\phi$	Quantic yield