

# Influence of morphology and chemical structure on the inverse response of polypropylene to gamma radiation under vacuum

A. Valenza\*, S. Piccarolo, G. Spadaro

*Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, University of Palermo, 90128 Palermo, Italy*

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## Abstract

In this work the influence of the chemical structure and of the morphology on the gamma-radiation effects on polypropylene based polymers is studied on the basis of a previously discussed kinetic model [1]. For this aim an isotactic polypropylene and a random ethylene–propylene copolymer were irradiated under vacuum at one dose rate and several absorbed doses after well defined solidification conditions. We show that the model is reliable varying both the chemical structure and the morphology of the polypropylene based polymer. An inversion of the response of the material to gamma radiation under vacuum is always observed, and the inversion conditions depend on the irradiation parameters. In particular at a fixed dose rate we check an absorbed dose, depending on the ethylene and mesomorphic phase content in the polymer, in correspondence of which a significant change in the molecular response to gamma irradiation occurs. © 1998 Elsevier Science Ltd. All rights reserved.

*Keywords:* Polypropylene; Ethylene–propylene copolymer; Morphology

## 1. Introduction

The molecular structure of polymers can be significantly modified by ionising radiations. It is well known that the interaction of gamma rays with polymeric materials gives rise to free radicals which can stabilize in several ways. The main molecular effects are chain scission, chain branching and crosslinking. Usually all these effects coexist, the extension of which depending on several factors, such as the chemical structure and the morphology of the irradiated polymer and the environmental irradiation conditions.

The chemical structure affects the evolution of free radicals towards stable species [2–5]. For example the presence of hindering groups attached to the main chains favours chain scission with respect to chain branching and crosslinking, while aromatic groups increase the radiation resistance stabilizing the excited species formed by irradiation.

The morphology is also important in determining the final molecular structure of irradiated polymers where amorphous or more disordered structures undergo chain branching and crosslinking reactions more easily. In fact it is generally accepted that in a semicrystalline polymer the amorphous interfacial structure is a major contribution to gel formation. The mechanical entanglement of the

amorphous interfacial regions between different crystallites may enhance the possibility of intermolecular crosslinking [2,6,7].

In a previous work [1] the response of polypropylene to gamma-radiation under vacuum was studied on the basis of a simple kinetic model. We analysed the influence of 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. In the case of the examined polypropylene, degradation occurs with chain branching, the latter prevailing at high doses, giving rise to an inversion response, which was determined in terms of a macroscopic probe sensitive to molecular weight variations (e.g. viscosity). It was also shown that it is possible to obtain the equation of an ‘inversion curve’ as a function of dose rate and total absorbed dose.

In this work we want to apply the same approach to the study of molecular modifications induced by gamma irradiation in polypropylene based polymers having different morphologies. We have analysed the effect of irradiation on isotactic polypropylene and ethylene–propylene copolymers where different morphologies were induced by a previously adopted quenching technique [8]. The aim of this investigation is to test the reliability of our model varying the molecular structure and morphology and to show that it is possible to determine well defined

\* Corresponding author.

irradiation conditions which can stop changes due to physical ageing of thermodynamically unstable morphologies through crosslinking.

## 2. Experimental

The materials used in this work were an isotactic polypropylene (iPP), with  $M_w = 481\,000$  and polydispersity 6.4, kindly supplied by Montell and a random ethylene-propylene copolymer (EPC) with ca. 3.1% of ethylene content,  $M_w = 210\,000$  and polydispersity 6, kindly supplied by Borealis.

The melted polymeric samples, kept at 250°C for 30 min, have been subsequently quenched at three different cooling rates of ca. 0.04°C/s, 10°C/s and 600°C/s, giving rise to platelets about 150  $\mu\text{m}$  thick, the procedure, also involving the recording of the thermal history the polymer undergoes during solidification, is described in Ref. [8]. The structure and morphology of the samples depend on the cooling rate which was chosen to induce marked differences as discussed in the Section 3.

These samples have been subsequently irradiated to evaluate the dependence of their behaviour on initial morphology.

Irradiation was performed under vacuum, at room temperature (about 25°C) by the IGS-3, a panoramic 3000 Ci  $^{60}\text{Co}$  irradiator [9]. The dose rate, measured by a PTW Universal Dosimeter, was 6.7 KGy/h and the total absorbed doses were in the range of 25–900 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. There was some time lapsed between the time at the end of irradiation and the start of the tests in liquid nitrogen for each condition.

Rheological tests were performed with a Rheometrics Dynamic Analyzer (RDA2) used in the dynamic mode with the plate and plate geometry ( $R = 12.5\text{ mm}$ ). The

frequency sweep tests were carried out at 180°C and 20% strain in the range  $10^{-1}$  to  $5 \times 10^2$  rad/s.

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

## 3. Results and discussion

Let us firstly point out briefly the main features of the mathematical model previously discussed [1]. We assumed that the dominant reactions involving the evolution of free radicals, produced during irradiation under vacuum of polypropylene, are:

1.  $\beta$ -scission, with molecular weight decrease and formation of double bonds;
2. addition of free radicals to double bonds, with chain branching and molecular weight increase;
3. termination which can occur by addition reactions, with molecular weight increase, or by disproportionation reactions, with formation of double bonds.

The final molecular structure of the irradiated polypropylene depends on the free radicals and double bonds concentration, which in turn depends on the irradiation parameters dose rate,  $I$ , and total dose,  $D$ , and affects the kinetics of the main reactions involved. In fact for each  $I$ , at low  $D$  the main molecular effect is chain scission with a molecular weight decrease. Increasing  $D$ , the concentration of double bonds, formed through  $\beta$ -scission and termination reactions, increases, thus increasing the rate of the reaction of free radical addition to double bonds. So we forecast the existence of a  $D$  value, in correspondence of which the rate of chain scission reaction is balanced by the rate of chain addition reactions. Over this value the main molecular effect is the increase of molecular weight with chain branching, up to crosslinking. In this way we obtained the dependence of free radicals and double bonds concentration on  $I$  and  $D$  and we

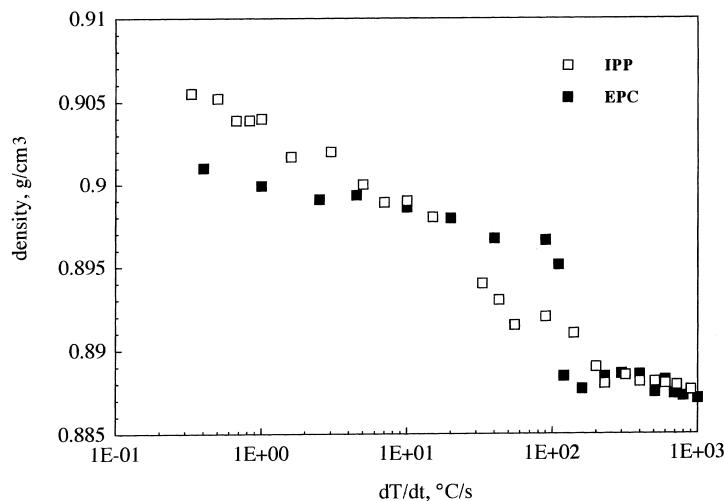


Fig. 1. Density versus cooling rate for iPP and EPC samples.

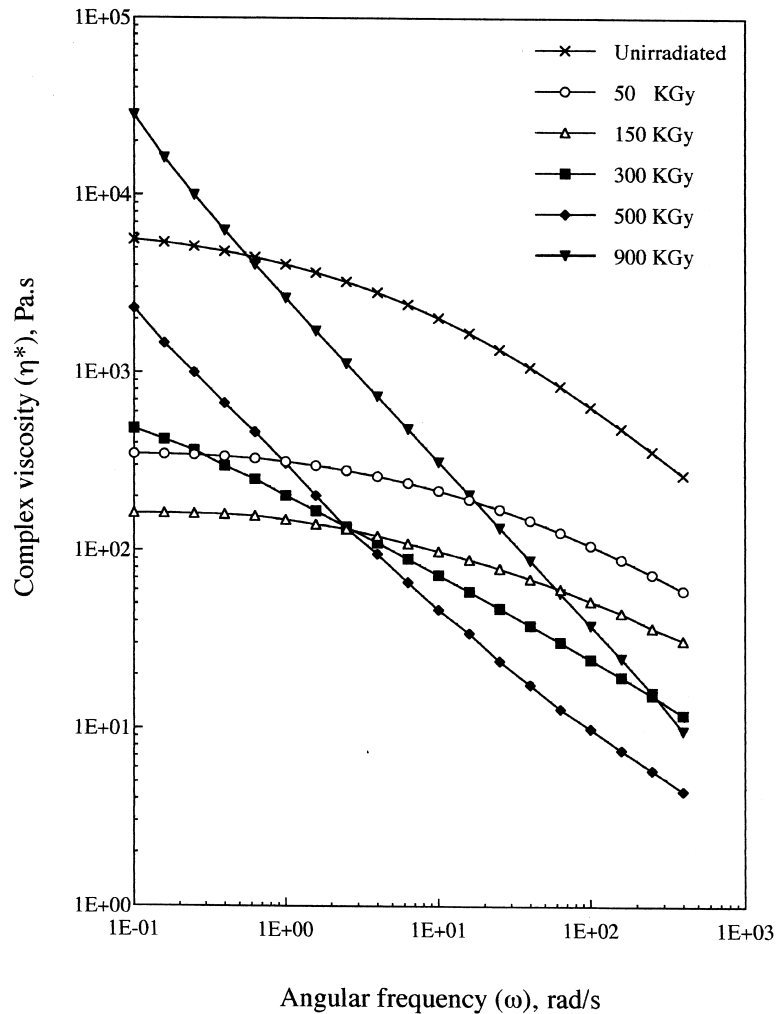


Fig. 2. Flow curves of iPP samples solidified at a cooling rate of 10°C/s.

showed [1] the existence of ‘scission-branching balance’ conditions, in correspondence of which an inversion of the molecular response of polypropylene to gamma radiation under vacuum can be observed.

The aim of this work is to see if our assumptions are verified varying both the chemical structure and the morphology of the polypropylene based polymers; in particular we devote our attention to the influence of these structural parameters on the values of the inversion absorbed dose at a fixed dose rate.

In Fig. 1 the dependence of density on cooling rate for the two polymers studied in this work is reported. This quantity has been used here and in previous works [8,10] to identify the structure formed from quenched tests since the samples it refers to are homogeneous. It has already been shown that in the low cooling rates range samples of iPP are spherulitic with a structure mostly  $\alpha$ -monoclinic. In the high cooling rates region (above 200°C/s) the structure obtained is mesomorphic and therefore non-spherulitic characterized by a low range order [11]. The two regions are connected by a transition region which is strongly affected by the chemical structure of the material (molecular weight,

tacticity, ethylene content etc.). Furthermore at low cooling rates the slope of the curve of density versus cooling rate is also a characteristic feature of the crystallization kinetics of the polypropylene used.

Although in this work we do not want to point our attention to such features, it is sufficient to refer to Fig. 1 to justify the rationale for the choice of the starting structures we have used to test their sensitivity to the behaviour under gamma-radiation. For both polymers we have used samples quenched at 0.04°C/s, 10°C/s and 600°C/s. At 600°C/s both the homopolymer, iPP, and the random copolymer, EPC, are completely mesomorphic. At 0.04°C/s both samples are crystalline with a higher density of iPP with respect to EPC due to the larger crystallinity attained related to the higher structural order of this polymer with respect to the copolymer. Finally the samples at 10°C/s show the same density due to a faster crystallization kinetics of EPC with respect to iPP associated with the lower molecular weight of the former polymer and also with the larger mobility the EPC is characterized of due to the ethylene sequences. In this region of cooling rates crystallization kinetics is mostly diffusion controlled [10].

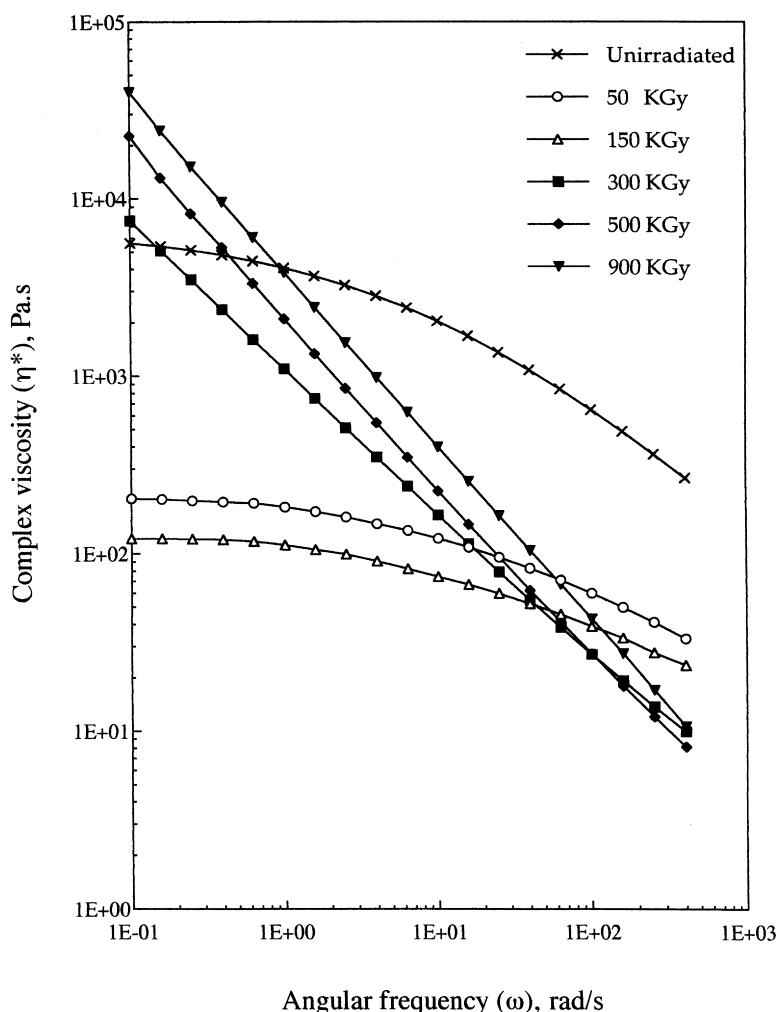


Fig. 3. Flow curves of iPP samples solidified at a cooling rate of 600°C/s.

In conclusion the samples quenched at 0.04°C/s and 10°C/s are both crystalline although the former must be considered as a sample with a very high degree of crystallinity with respect to the second one as also the WAXD patterns could further point out.

Samples of both iPP and EPC, subjected to the different cooling rates, were gamma irradiated under vacuum and their molecular response tested. The molecular modifications induced by irradiation were studied using dynamic mechanical tests in the melt state, which give rise to a complete set of information about the complex molecular events usually occurring during radiation processing of polymers. In fact the decrease of molecular weight is easily detected through the decrease of Newtonian (zero-shear) viscosity, chain branching and crosslinking, which are more difficult to be analysed, which can be related to the different viscoelastic parameters, i.e. shear thinning behaviour and relaxation times.

In Figs 2 and 3 the flow curves of iPP samples cooled at 600°C/s and 10°C/s and irradiated at various total absorbed doses are reported.

A general feature of both figures is that the flow curves

relative to samples irradiated at low total doses exhibit a melt viscosity lower than the unirradiated reference sample in the whole frequency range considered, according to the prevalence of chain scission phenomena. Increasing the dose, the melt viscosity of the irradiated sample increases and the slope of the flow curves becomes steeper, thus indicating that the main effects in these experimental conditions are chain branching and/or crosslinking. These results are in agreement with previous observations.

Looking at the differences between the samples solidified at the two cooling rates, we can observe a more pronounced tendency giving rise to chain branching reactions of the samples solidified at a higher cooling rate. This trend is shown well by a comparison of the flow curves of the samples irradiated at 300 KGy where a more marked shear thinning behaviour in the case of the material cooled at 600°C/s with respect to the corresponding one cooled at 10°C/s is observed. These results confirm in a first qualitative instance the tendency that the mesomorphic morphology is more sensitive to gamma radiation to give rise to chain branching.

A similar investigation for EPC is reported in Figs 4 and

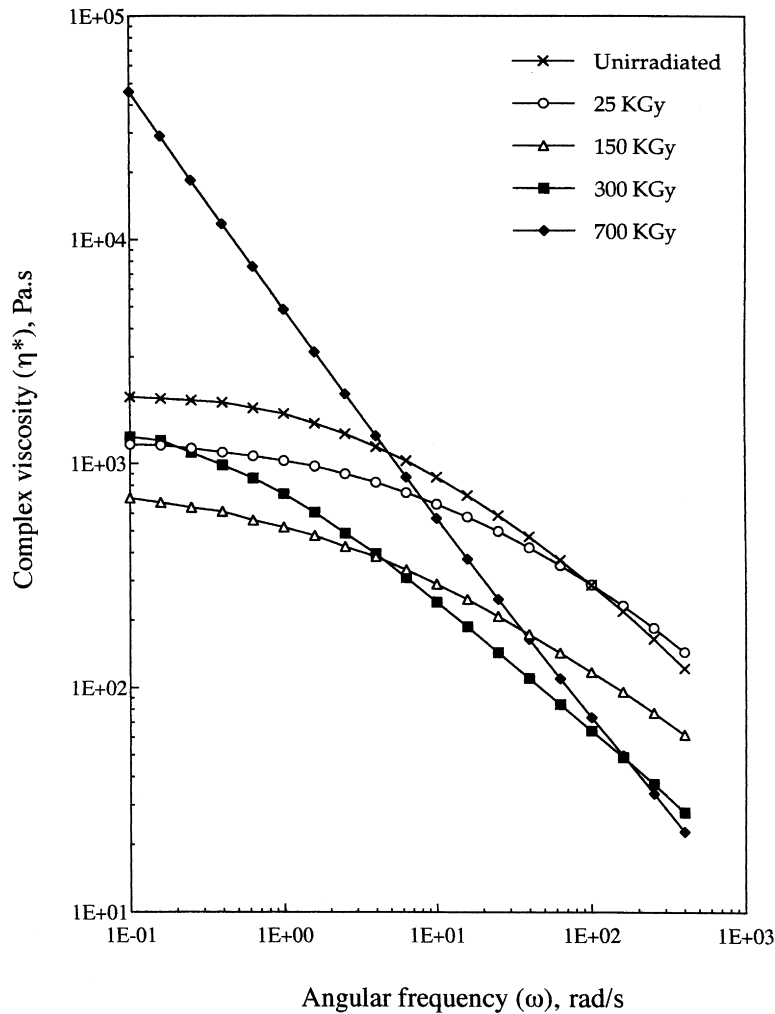


Fig. 4. Flow curves of EPC samples solidified at a cooling rate of 10°C/s.

5, where the flow curves for EPC samples cooled at 10°C/s and 600°C/s respectively and irradiated at various total doses are shown. The experimental results indicate the reliability of our model also for polypropylene copolymers, which similarly show an inversion response with the dose where a more marked tendency of the less crystalline material to give rise to chain branching is also observed.

With respect to the difference between the pure iPP and the EPC, we can observe that the inversion response is obtained at lower absorbed doses in the case of the copolymer, and this effect is more significant for samples solidified at a high cooling rate. The decrease of the inversion dose can be attributed to the presence of polyethylene segments in the polymer backbones which favours chain branching and crosslinking. The more marked influence of the amorphous content in the copolymer, EPC, is in agreement with the well known results reported in the literature, which indicate a more significant tendency to molecular weight increase up to crosslinking for irradiated polyethylene having a more disordered structure [2,5].

In order to provide a quantitative determination of the inversion conditions, it is useful to consider a rheological

parameter related to the molecular structure of the polymer. Following Ostwald and de Waele [12,13] we chose as parameter the 'power law' exponent,  $n$ , for the flow curves in the pseudoplastic region in the frequency range 10–100 rad/s.

$$\eta = K\dot{\gamma}^{n-1}$$

This parameter is the index of the pseudoplastic behaviour of the polymer, it ranges from 1, where the polymer behaves as a Newtonian fluid to 0 in the case of a behaviour similar to that of a plastic fluid. At intermediate values, a decrease of the index  $n$  is related to an increase of chain branching.

The dependence of  $n$  on the irradiation dose is reported in Fig. 6 for all of the samples examined. In all cases an initial increase of  $n$  is observed up to a maximum followed by a pronounced reduction on increasing the dose. This behaviour is clearly related to the afore mentioned molecular modifications due to gamma radiation, firstly the material undergoes molecular chain scission and, on increasing the dose, chain branching and/or crosslinking start to overcome chain degradation. With reference to our model we assume

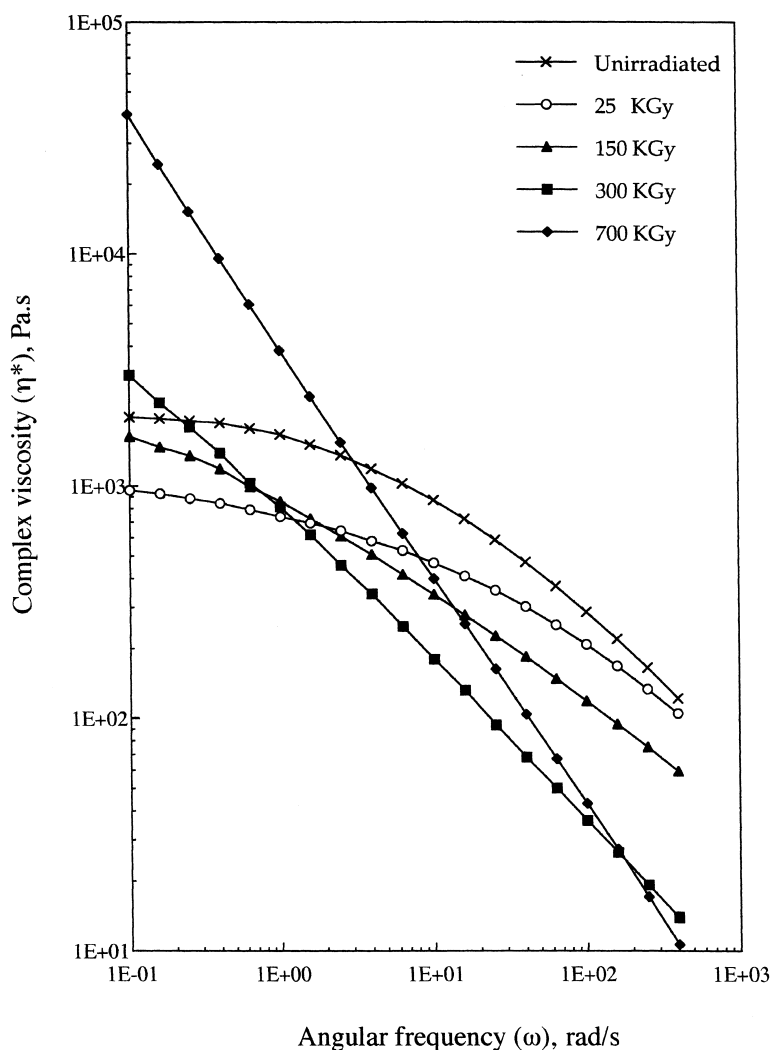


Fig. 5. Flow curves of EPC samples solidified at a cooling rate of 600°C/s.

as 'inversion point' the irradiation dose corresponding to the maximum of each curve.

We can observe significant differences among the curves related to iPP and EPC, the maxima occurring for iPP samples takes place at higher absorbed doses with respect to the curves representative of the EPC ones. Regarding the effect of the morphology, a slight difference is clearly observed for EPC samples, while this effect is not so evident for the polypropylene.

The above discussed effects are confirmed by solubility data reported in Tables 1 and 2, which give a more accurate evidence of the presence of chain branching and crosslinking phenomena. As a general consideration, at low absorbed doses, i.e. in the experimental conditions which favour chain scission, the polymers are completely soluble, while insoluble fractions, increasing with the dose, arise at high dose values. Looking at the influence of the chemical structure and of the morphology, the presence of polyethylene fragments in the polymer backbone and the increase of the amorphous content lower the dose values giving rise to increasing gel fractions.

Table 1  
Gel fractions for isotactic polypropylene

Irradiation dose (kGy)	Cooling rate 10°C/s (%)	Cooling rate 600°C/s (%)
50	0	0
150	0	0
300	0	38
500	47	55
900	81	93

Table 2  
Gel fractions for EP copolymer

Irradiation dose (kGy)	Cooling rate 10°C/s (%)	Cooling rate 600°C/s (%)
25	0	0
150	0	8.5
300	29	58
700	79	89

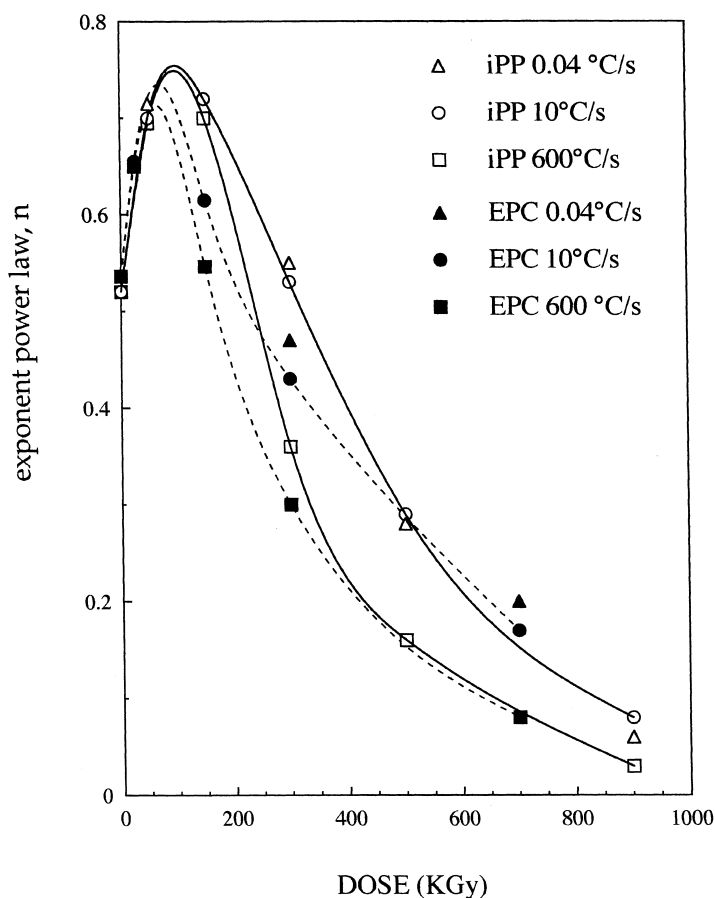


Fig. 6. Power law exponent,  $n$ , for the flow curves in the frequency range 10–100 rad/s as a function of dose.

#### 4. Concluding remarks

In this work the response to gamma irradiation under vacuum of polypropylene based polymers having different morphologies is presented. In particular an isotactic polypropylene and an ethylene–propylene copolymer, solidified at well defined cooling rates, are irradiated under vacuum at a fixed dose rate and various total absorbed doses. The molecular response is analysed through dynamic mechanical analysis in the melt state and solubility tests and the results are discussed on the basis of a simple kinetic model. According to the theoretical forecasts of the model, always an inversion in the response of polypropylene based polymers is observed.

As a general consideration, at low absorbed doses degradation phenomena are the main effect, while at high dose values chain branching and crosslinking prevail. Looking at the influence of the chemical nature and the morphology, the presence of polyethylene fragments and of the mesomorphic phase favours chain branching and crosslinking, thus allowing to obtain the inversion response of the material at lower total absorbed doses.

#### References

- [1] Sarcinelli L, Valenza A, Spadaro G. *Polymer* 1997;38:2307.
- [2] Dole M. *The radiation chemistry of macromolecules*. New York: Academic Press, 1972.
- [3] Charlesby A. *Radiation effects in polymers*. In: Jenkins A, editor. *Polymer science*, vol.2. Amsterdam: North-Holland, 1972.
- [4] Spinks JWT, Woods RJ. *Introduction to radiation chemistry*. New York: Wiley, 1990.
- [5] Clegg DW, Collyer AA. *Irradiation effects on polymers*. Oxford: Elsevier, 1991.
- [6] Dole M. *Polym Plast Technol Engng* 1979;13:41.
- [7] Jenkins H, Keller A. *J Macromol Sci-Phys* 1975;B11:301.
- [8] Saiu M, Piccarolo S, Titomanlio G, Brucato V. *J Appl Polym Sci* 1992;46:625.
- [9] Calderaro E, Oliveri E, Tallarita P. *Quaderni dell'istituto di applicazioni ed impianti nucleari*, vol. 3. Palermo: University of Palermo, 1980.
- [10] Piccarolo S. *J Macromol Sci-Phys* 1992;B31:501.
- [11] Corradini P, Petraccone V, DeRosa C, Guerra G. *Macromolecules* 1986;19:2699.
- [12] Ostwald W. *Kolloid-Z* 1925;36:99.
- [13] de Waele A. *Oil Color Chem Assoc J* 1923;6:33.