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# COMPOSITION AND CRYSTALLINITY EFFECTS IN THE DEGRADATION OF ETHYLENE-PROPYLENE COPOLYMERS BY $\gamma$ -RADIATION

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## ABSTRACT

The degradation by  $\gamma$ -radiation of amorphous ethylene-propylene (EP) copolymers containing 23 and 36% propylene has been studied by measuring the yields of radical intermediates (at 77 K), volatile products ( $H_2$  and  $CH_4$  at 300 K), and main-chain scission and crosslinking. The  $G$  values for these changes in the homopolymers polyethylene (PE) and polypropylene (PP) all increase with decreasing crystallinity. The values for the amorphous EP copolymers are much lower than would be predicted by linear extrapolation of the values for PE and PP of low crystallinity. We conclude that all of these radiation-induced chemical changes in polyolefins occur preferentially at crystalline surfaces and defects; consequently the  $G$  values will be lower for both highly crystalline and amorphous polymers than for polymers of low crystallinity.

## INTRODUCTION

Crosslinking is an important reaction on irradiation of polyethylene (PE) and causes marked changes in physical properties, such as solubility, strength, and heat resistance. Crosslinking and scission both occur in polypropylene (PP) with crosslinking predominating (formation of insoluble gel), i.e.,  $G(X) > G(S)/4$ , for irradi-

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ation in vacuum or an inert atmosphere. Although the radiation chemistry of these two polymers has been studied extensively, some important aspects are still unresolved, including the effect of crystallinity.

PE and PP contain three morphologically distinct regions: 1) crystallites, 2) amorphous regions, and 3) surface boundaries between the crystalline and amorphous regions. The radiation sensitivity of these polymers is related to the morphology of any particular sample and depends on the proportions of the three components. Keller and Ungar [1] deduced that crosslinking in PE does not occur in crystalline regions. They suggested that crosslinking was favored at the crystal surfaces, but were uncertain whether this indicated (1) a greater number of crosslinks than in the amorphous regions or (2) an increased tendency toward intramolecular rather than intermolecular crosslinks, although they favored (2).

We have previously reported the determination of crosslinking and scission yields in the  $\gamma$ -irradiation of amorphous ethylene-propylene copolymers (EP) using 1) soluble fraction measurements and 2) solid-state NMR [2]. Good agreement between  $G(S)$  and  $G(X)$  values derived by both methods indicated a random spatial distribution of these reactions in the copolymers. In the present study the effect of composition and crystallinity was investigated in comparison with the homopolymers PP and PE by using measurements of scission, crosslinking, radical formation, and gas evolution.

## EXPERIMENTAL

The ethylene-propylene copolymers were obtained from Japan Synthetic Rubber (EP07P and EP11). The compositions were determined by  $^{13}\text{C}$  NMR in solution in  $\text{CDCl}_3$  and found to contain 23% (EP23) and 36% (EP36) propylene, respectively, and no termonomer. Molecular weights were measured by GPC in  $\text{CHCl}_3$ . The polymer samples were used without further purification after it had been shown that the radical yields were unaffected by the presence of the small concentration of stabilizer. The polymers were evacuated at less than  $10^{-2}$  Pa for 24 h in glass or high purity quartz ampules and sealed. They were irradiated at 77 or 300 K by  $^{60}\text{Co}$   $\gamma$ -rays in an AECL Gammacell or in the pond facility of the Australian Nuclear Science and Technology Organization at dose rates of 1–10 kGy/h, as determined by Fricke dosimetry. The irradiated polymers were annealed above the glass transition temperature,  $T_g$ , to remove trapped radicals before opening the ampules.

ESR measurements were made with a Bruker ER200D X-band spectrometer at low microwave power (20  $\mu\text{W}$ ) to avoid power saturation. Spectra were recorded and doubly integrated by computer and concentrations obtained by comparison with pitch/KCl and DPPH standards.

Volatile products were determined by gas chromatography by using a technique developed previously in which small, thin-walled glass ampules containing the polymer samples are crushed in the injection system of the chromatograph [3].

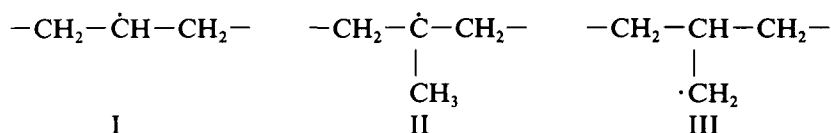
## RESULTS

### 1. Radical Intermediates

Radiation degradation of polyolefins involves radical intermediates which can be observed by ESR spectroscopy. The yield of radicals,  $G(R)$ , at 77 K provides a

measure of the extent of radical reactions involved in irradiations at higher temperatures and can be compared with  $G$  values observed for chemical changes.

The ESR spectrum of the EP copolymers after irradiation at 77 K is shown in Fig. 1. It comprises three radicals, I, II, and III, which have been observed previously in irradiated PE and PP [4, 5].



The concentration of trapped radicals increased linearly with radiation dose at 77 K up to 8 kGy and was greater for the higher propylene content as shown in Fig. 2. The  $G(R)$  values of 2.2 and 2.3 were obtained from the slopes in Fig. 2 and are higher than  $G(R) = 0.9$  reported previously by Kozlov et al. [6, 7].

Warming of the irradiated samples above 77 K caused the radical concentration to decrease progressively to below the detection limit of the ESR spectrometer ( $10^{15}$  spins/g) at 250 K ( $30^\circ$  above  $T_g$  of the unirradiated copolymers) as shown in Fig. 3, without any change in the spectral shape. This behavior is similar to that observed in amorphous *cis*-polybutadiene, but in marked contrast to partially crys-

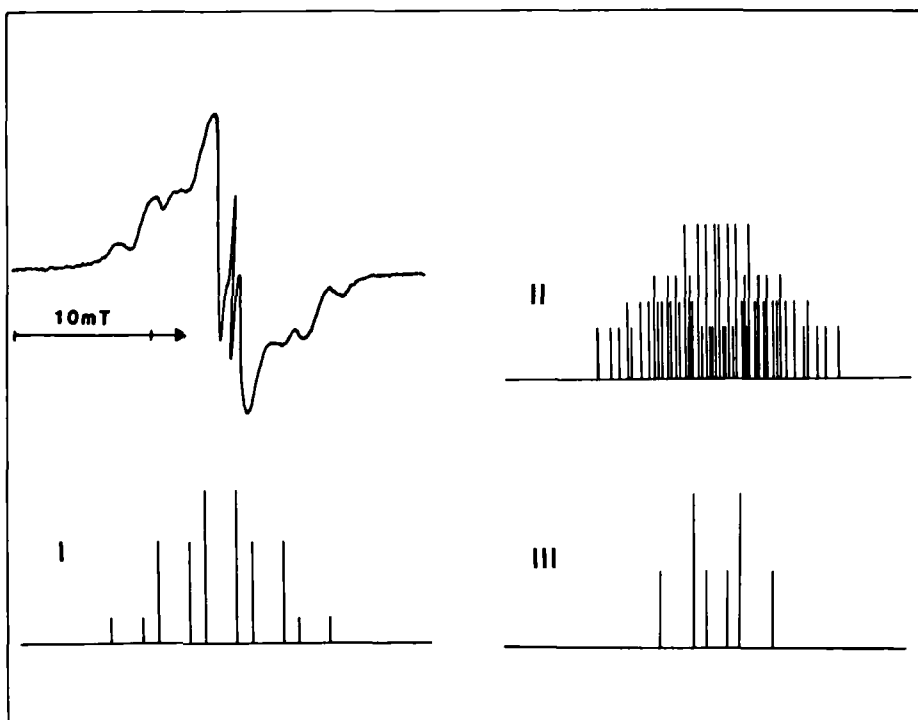


FIG. 1. ESR spectrum of EP23 after  $\gamma$ -irradiation in vacuum at 77 K, and the stick spectra for the component radicals I, II, and III (structures shown in the text) assigned in the literature.

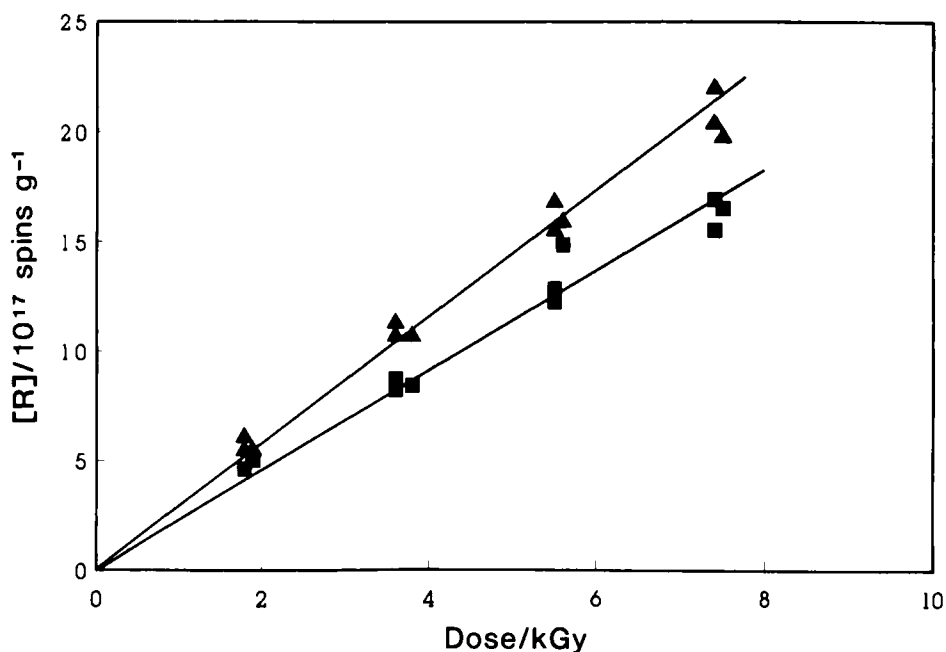


FIG. 2. Dose dependence of radical concentration for  $\gamma$ -irradiation in vacuum at 77 K: ( $\blacktriangle$ ) EP23, ( $\blacksquare$ ) EP36.

talline PP. This difference suggests that in PP the radicals cannot be associated entirely with the amorphous regions.

## 2. Volatile Products

The major gaseous product from irradiation of polyolefins is  $H_2$ , which results from C—H scission followed by H abstraction and recombination. Low molecular weight alkanes and alkenes are also observed, with yields depending on the extent and nature of the alkyl substituents [8].

The main volatile products from the irradiation of EP copolymers at 300 K were  $H_2$  and  $CH_4$  and the  $G$  values are given in Table 1.

## 3. Crosslinking and Chain-Scission

$G(X)$  and  $G(S)$  can be derived from the soluble fractions after irradiation to a series of doses above the gel dose,  $D_g$ , using the Charlesby-Pinner equation [9], or a similar relationship for different initial molecular weight distributions. Charlesby and Pinner suggested that at high radiation doses, i.e., for  $D > 6D_g \cdot G(X)/G(S)$ , a linear plot of  $s + s^{1/2}$  vs  $1/D$  should be obtained, whatever the initial distribution. Values of  $G(S)$  and  $G(X)$  obtained from soluble fractions of EP36 ( $M_w/M_n = 2$ ) and EP23 ( $M_w/M_n = 3$ ) after doses up to 20 times  $D_g$  are given in Table 1.

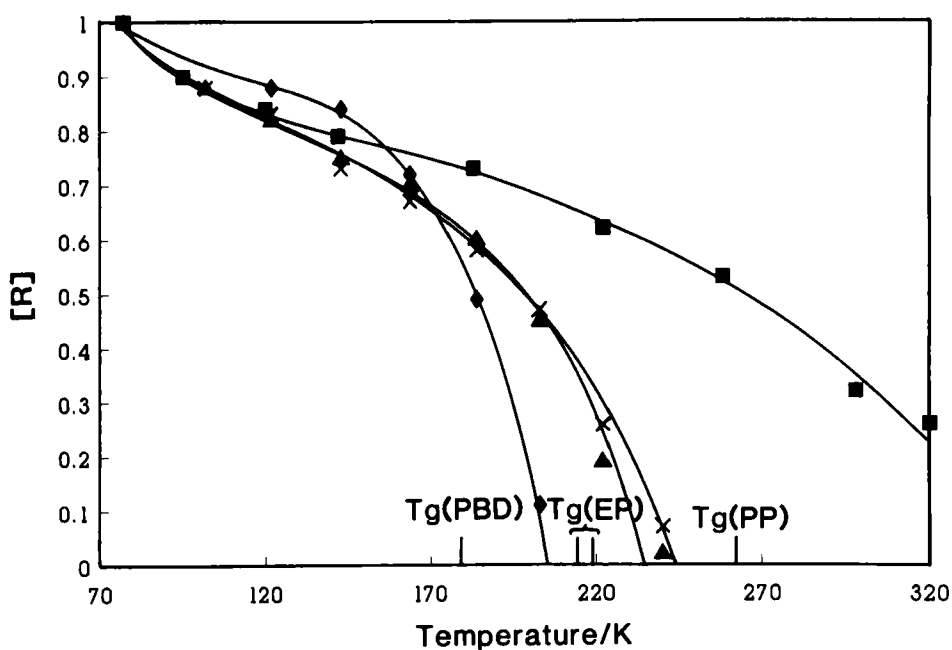


FIG. 3. Effect of warming from 77 K on the radical concentrations in  $\gamma$ -irradiated polymers: (■) semicrystalline polypropylene (PP), (◆) amorphous *cis*-polybutadiene (PBD); amorphous ethylene-propylene copolymers (EP): (×) EP23, (▲) EP 36. Radical concentrations ( $[R]$ ) in arbitrary units.

## DISCUSSION

The main aim of this work was to compare the  $G$  values for radiation-induced changes in amorphous EP copolymers with  $G$  values for the same changes in the semicrystalline homopolymers PE and PP. There should be effects due to composition and crystallinity.

TABLE 1. Radiation Chemical Yields ( $G$  values) for the Two Poly(Ethylene-*co*-Propylene) Samples

$G$ value	EP23	EP36
$G(R)$	2.33	2.24
$G(H_2)$	2.59	1.84
$G(CH_4)$	0.077	0.11
$G(X)$	0.45	0.82
$G(S)$	0.13	0.38
$G(S)/G(X)$	0.30	0.46

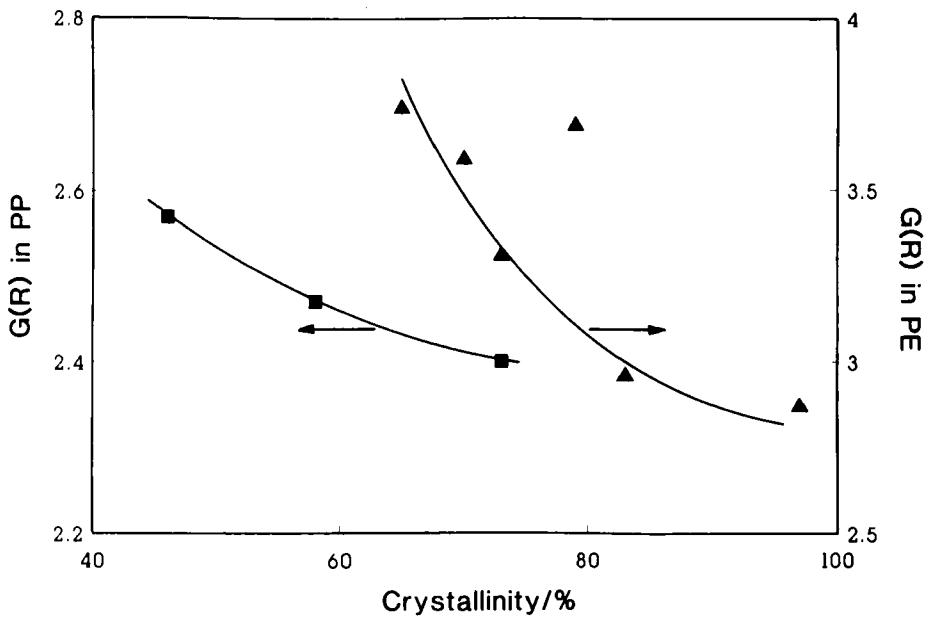


FIG. 4. Dependence of  $G(R)$  for  $\gamma$ -irradiation in vacuum at 77 K on the % crystallinity: (■) polypropylene (this work), (▲) polyethylene [10-12].

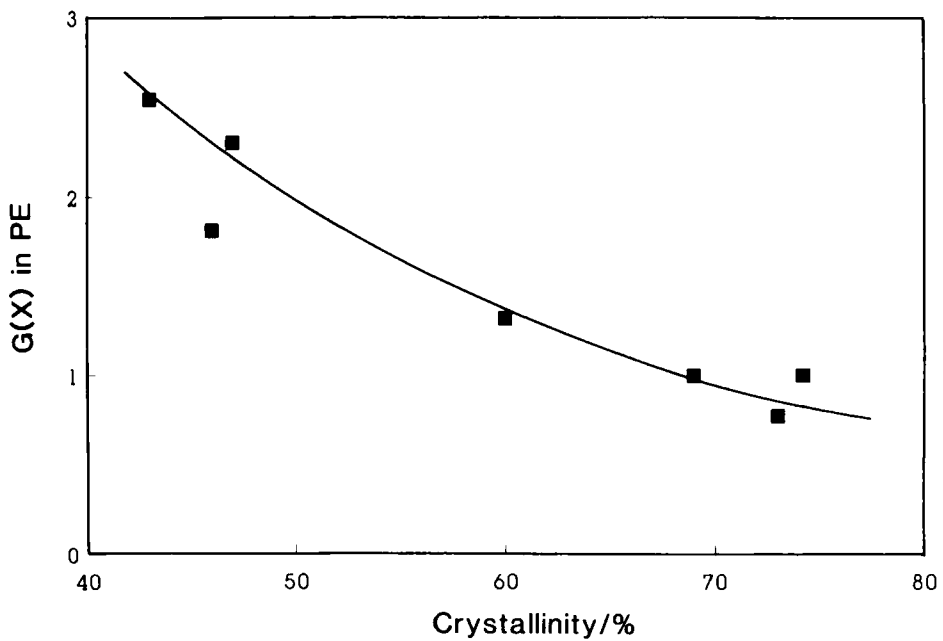


FIG. 5. Variation of  $G(X)$  in polyethylene with % crystallinity (literature values).

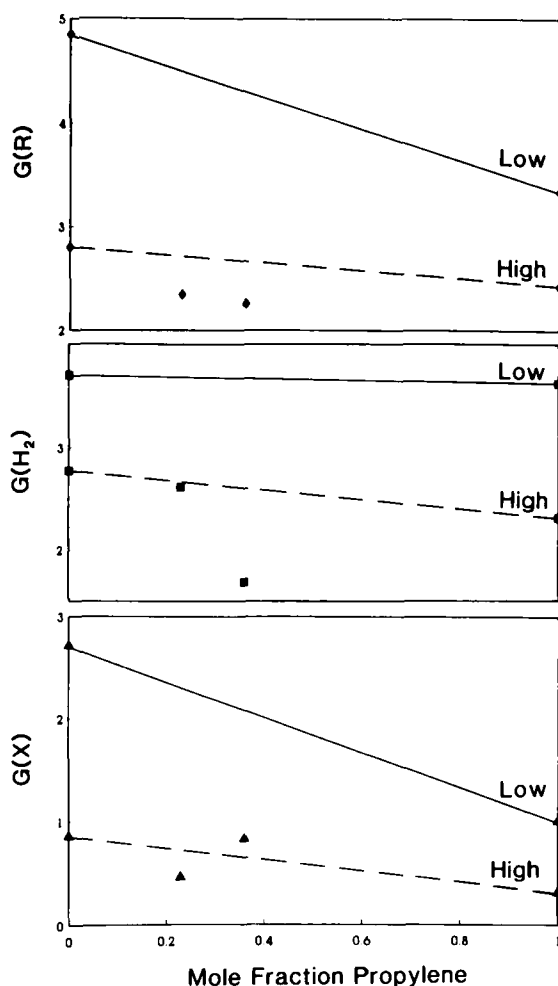


FIG. 6. Variation in  $G(R)$ ,  $G(H_2)$  and  $G(X)$  with composition in the homopolymers and copolymers of ethylene and propylene, showing the effect of crystallinity. Linear interpolations between values for the homopolymers: (—) low crystallinity, (---) high crystallinity.

The effects of crystallinity on  $G(R)$  for PE and PP are shown in Fig. 4. The  $G$  values for PP were obtained in this work, and the values for PE were reported by Dole et al. [10–12]. The  $G(R)$  values for both polymers decreased with increasing crystallinity. It appears, therefore, that radical formation is less likely in the crystalline regions than in the amorphous and boundary regions.  $G(X)$  for PE also decreases with increasing crystallinity according to values reported in the literature [12–17], as shown in Fig. 5.

Dole has concluded from gel-fraction and radical decay measurements that crosslinks are formed preferentially in the amorphous regions of PE [18]. Keller and Ungar showed that crosslinking did not occur in the crystalline regions of single



crystals and melt-crystallized PE and deduced that crosslinks formed preferentially at the surfaces of the crystallites [1].

The values of  $G(R)$ ,  $G(X)$ , and  $G(H_2)$  obtained for EP23 and EP36 in the present work are compared with the values for the homopolymers PE and PP in Fig. 6. Two lines are drawn in each diagram and correspond to linear relationships with composition for polymers of high and low crystallinity. For all three radiation-induced chemical changes, the  $G$  values for the copolymers are substantially lower than the predicted values for polymers of low crystallinity.

The low  $G$  values can be considered to be consistent with the almost total absence of crystalline regions if the radiation-induced chemical reactions occur preferentially at surfaces and defects of crystalline regions. Polymer samples with high crystallinity have larger and more perfect crystalline regions, and consequently less crystalline/amorphous surface and fewer crystalline defects than samples of low crystallinity [19, 20]. The proposal of Keller and Ungar for crosslinking in PE [1], and the similar proposal of Busfield et al. [5] for trapping of free radicals in PP, appear to be generally applicable to the polyolefin homopolymers, and also apply to the copolymers. Moreover,  $H_2$  formation shows the same behavior.

The concentrations of allyl radicals in amorphous EP copolymers and polybutadiene all decrease to zero at about  $30^\circ$  above  $T_g$ , whereas the concentration remains high in partially crystalline PP well above  $T_g$ . The stability of the allyl radicals above  $T_g$  is apparently due to the crystallinity of the PP and not an inherent property of the allyl radical. Busfield et al. [5] found that, during warming, the alkyl radicals in PP migrate to the surface of the crystallites and react to form allyl radicals and crosslinks.

The other major volatile product of the radiolysis of EP copolymers is  $CH_4$ , which is also obtained from PP and from PE-containing chain branches.  $G(CH_4)$  values for EP copolymers, normalized for the content of methyl substituents, are compared with PP in Table 2. There is a much higher radiation sensitivity of methyl branches in the copolymers than in PP, which can be attributed to the differences in morphology, i.e., the higher amorphous content. Similarly, higher  $G(CH_4)$  values have been reported in amorphous, atactic PP than in semicrystalline, isotactic samples [20]. Differences in morphology undoubtedly contribute to the variations in  $G(CH_4)$  for PP and in  $G(\text{alkane})$  and  $G(\text{alkene})$  for PE, which have been reported in the literature.

TABLE 2. Radiation Chemical Yields for Methane from EP Copolymers Compared with Polypropylene Normalized for the Content of Methyl Groups

Polymer	$G(CH_4)$
PP	4.3
EP36	6.1
EP23	6.7

## CONCLUSIONS

Radical trapping, main-chain scission and crosslinking, and hydrogen and methane formation during  $\gamma$ -irradiation of PE, PP, and EP copolymers occur preferentially at the crystalline/amorphous boundaries and in defects in the crystalline regions. Polymers with higher crystallinity have less crystalline/amorphous boundary surface and fewer defects and hence lower  $G$  values than samples of lower crystallinity. Completely amorphous samples can have significantly lower  $G$  values than partially-crystalline samples. Migration of radicals to the crystalline/amorphous surfaces can explain the enhanced degradation in the boundary region.

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