

# An ESR Study of the Radiolysis of Semi-Crystalline Ethylene-Propylene Copolymers Containing DOP Mobilizer

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**ABSTRACT:** The radiolysis of a poly(ethylene-*co*-propylene), Elpro, marketed by Thai Polypropylene Co. Ltd for the manufacture of medical goods has been investigated at 77 K. Calcium stearate was blended with the Elpro as a processing aid; and dioctyl phthalate, DOP, was added in various amounts as a radiation stabilizer. The ESR spectra of Elpro and Elpro+Ca were very similar and characterized principally by the presence of PP  $\alpha$ -carbon radicals. The spectra of the samples containing DOP were similar to those for Elpro but with an additional narrow singlet arising from DOP radicals. On annealing the irradiated polymers to

higher temperatures, the singlet was lost between 250 and 270 K, and at room temperature the principal radicals remaining were allyl radicals. The G-values for radical formation at 77 K for Elpro and Elpro+Ca at 77 K were 3.0 and 3.2, respectively, but incorporation of DOP resulted in lower G-values, ranging from 1.6 to 1.4 for 0.5 and 2.5 phr DOP, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 638–643, 2006

**Key words:** ESR; G-value; gamma radiation; mobilizer; poly(ethylene-*co*-propylene); radical

## INTRODUCTION

Copolymers of ethylene and propylene have a wide range of commercial applications, one of which is in the manufacture of medical goods, such as syringes and catheters. Medical goods require sterilization before use, and this can be carried out by autoclaving or by processing under ethylene oxide gas, but these methods have inherent disadvantages in the case of polymeric materials. For example, autoclaving can lead to oxidation of a polymer, and ethylene oxide is a known carcinogen and can be retained in the polymer matrix. Therefore, radiation sterilization is becoming the preferred method for sterilization of many polymeric medical goods.

Radiolysis of polymers can result in yellowing and a loss of tensile properties. Therefore, radiation stabilizers are added to the polymers used in manufacturing medical goods to reduce these undesirable effects. One type of stabilizer used is low molecular weight aliphatic compounds. They are mobile in the polymer matrix, so they are believed to be capable of scaveng-

ing radicals by proton transfer before other chemical reactions occur in the polymer, such as double bond formation, chain scission, or crosslinking. These stabilizers are called mobilizers, and one common mobilizer that is used to stabilize polyolefins is dioctylphthalate, DOP.

There have been many previous ESR studies of the radiolysis of poly(propylene), PP. The studies have been reviewed by Ranby and Rabek<sup>1</sup> and later by Busfield et al.<sup>2</sup> The spectra observed at 77 K following irradiation of PP at 77 K appear to vary from sample to sample, probably because of variations in crystallinity, crystallite size, and quality. However, studies of the radiolysis of PP at 77 K reported by Iwasaki et al.<sup>3</sup> at 77 K and Busfield et al.<sup>2</sup> at 195 K found an 8 or 9 line spectrum. It is generally agreed that the principal radicals present at 77 K are: I, the tertiary  $\alpha$ -carbon radical; II, the main-chain radical formed by loss of the methyl group; and III, the methylene radical located on the side-chain. On annealing to room temperature, these radicals decay and a 17 line spectrum is observed, which has been assigned to allyl radicals.<sup>2</sup> Over time these radicals convert to polyene radicals.

The most recent study of radical formation on irradiation of poly(ethylene), poly(propylene), and poly(ethylene-*co*-propylene), PE/PP, is that of O'Donnell and Whittaker.<sup>4</sup> They also reported that on radiolysis of PE/PP under vacuum at 77 K, the major radicals formed are radicals I, II, and III above. O'Donnell and

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Whittaker measured the radical yields at 77 K for the two homopolymers poly(ethylene) and poly(propylene), and for two amorphous copolymers that contained 0.23 and 0.36 mol fractions of propylene. They found that the radical yields were unaffected by the presence of a small amount of stabilizer in the samples, but that the radical yields for the two homopolymers were dependent on the polymer crystallinity. For the two amorphous copolymers, they obtained G-values for radical formation of 2.2 and 2.3 for  $F_{PP} = 0.23$  and 0.36, respectively. O'Donnell and Whittaker also measured the yields for formation of hydrogen and methane and reported G-values of 2.6 and 0.08 and 1.8 and 0.11, respectively, for the two copolymers, indicating a much higher probability for scission of a carbon hydrogen bond than for scission of the methyl side chain in the propylene units.

In the present study, to better assess the role of the stabilizer, we have reexamined radical formation in a semicrystalline PE/PP copolymer. The study also included samples containing calcium stearate as a processing aid and various amounts of DOP mobilizer. The effect of the mobilizer on the nature of the radicals formed at 77 K, the yields of the radicals, the thermal stabilities of the radicals, and the percentage crystallinity of the polymers are reported herein.

## EXPERIMENTAL

### Materials

Poly(ethylene-*co*-propylene), Elpro grade P 750 J, was obtained from Thai Polypropylene Co. Ltd. It is produced especially for manufacture of medical products and has an MFI of 12. It was used without further purification. The copolymer was blended in a Brabender blender at 160°C with 0.08 phr of calcium stearate as a lubricant, and then various amounts of DOP mobilizer in the range 0.5–2.5 phr. The calcium stearate was obtained from Reidel-de-Haen, and the DOP was obtained from Aldrich. After blending, the copolymer samples were pressed into 150 × 120 × 1 mm sheets in a hot press at 160°C.

### Measurement of the glass transition and melting temperatures

The glass transition temperature,  $T_g$ , and the melting temperature,  $T_m$ , of the copolymer samples were measured using a TA Instruments modulated DSC 2920 with a heating rate of 10°C/min under nitrogen. The instrument was calibrated with high purity indium and zinc prior to the measurements on the polymer. For measurements  $\approx 5$  mg of sample was placed in an aluminum pan and the pan crimped. The second DSC scans were used to measure  $T_g$  and  $T_m$  so as to eliminate the effects of the thermal history of the samples.

### Preparation and irradiation of the samples

Polymer samples for ESR measurements were cut from the pressed sheets in the form of  $\approx 1 \times 1$  mm rods, which were placed in Spectrosil quartz ESR tubes with an internal diameter of  $\approx 3$  mm. The lengths of samples in the tube were in the range 2.5–3 cm and weighted  $\approx 18$ –25 mg cm<sup>-1</sup>. The tubes were evacuated ( $<10^{-2}$  Pa) for 12–24 h to remove all oxygen, then sealed under vacuum.

The samples were irradiated in a vacuum Dewar at 77 K using <sup>60</sup>Co gamma radiation (Nordion Gamma-cell-220) at a dose rate of 3.5 kGy h<sup>-1</sup> to doses within the range 0–10 kGy. After irradiation, one end of the sample tube was raised above the liquid nitrogen level and heated to remove any ESR signal arising from the quartz, while the other end containing the sample was retained under the liquid nitrogen at 77 K.

### ESR studies

A Bruker ER200D X-band ESR spectrometer interfaced to a PC computer was used for the acquisition of the spectra, which were obtained as the first derivative. The spectra were delineated using a sweep width of 30 mT, a modulation of 0.2 mT, and a microwave power of 200  $\mu$ W (30 dB) for measurements of the radical yields. Spectra were obtained at 77 K using a liquid nitrogen insert and over the temperature range of 120–300 K using a Varian variable temperature facility. The spectra were doubly integrated by means of computer software to give spectral peak areas. A Varian strong pitch (1% pitch in KCl) standard reference sample with a radical concentration of  $3 \times 10^{15}$  spins/cm was used to convert the peak areas into radical concentrations.

## RESULTS AND DISCUSSION

### DSC measurements

A typical DSC trace for Elpro is presented in Figure 1. These scans yield values of  $T_g = 259$  K and  $T_m = 421$  K measured at the peak of the melting transition. The values can be compared with the corresponding values for isotactic PP of  $T_g = 256$  K and  $T_m = 444$  K reported by Quirk.<sup>5</sup> The area under the melting transition for Elpro corresponds to 98.6 J g<sup>-1</sup>, which is less than that for isotactic PP of 209 J g<sup>-1</sup> reported by Quirk. The DSC traces for Elpro plus calcium stearate, Elpro-Ca, and Elpro-Ca with 0.5 and 2.5 phr of DOP were very similar to those for Elpro, but with heat of the melting transitions of 97.6, 90.8, and 89.4 J g<sup>-1</sup>, respectively. Thus, the addition of the calcium stearate has only a minor effect on the polymer crystallinity, but the further addition of the DOP results in a drop in the average crystallinity by 8–9%.

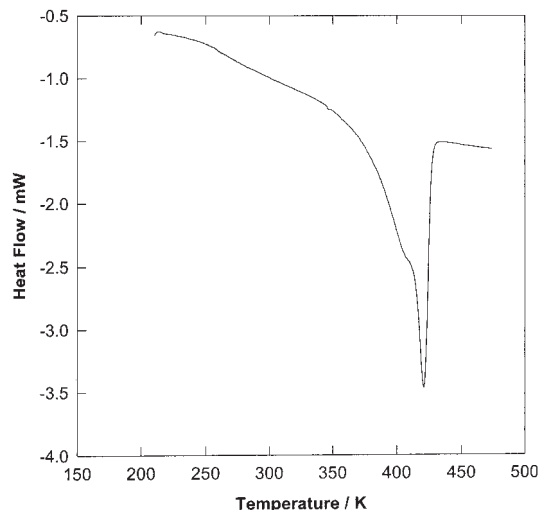


Figure 1 DSC scan for Elpro.

### ESR studies

The ESR spectrum at 77 K of Elpro following irradiation at 77 K under vacuum is shown in Figure 2. Delineation of spectra at different microwave powers and calculation of the areas of the peaks under absorption spectra led to the plot in Figure 3, which shows that the relationship is linear up to approximately 200  $\mu\text{W}$ . Thus, all further ESR spectra were obtained at this microwave power to avoid any effects of power saturation. The Elpro spectrum in Figure 2 is very similar to that reported by Iwasaki et al.<sup>3</sup> for isotactic PP and by Busfield et al.<sup>2</sup> at 195 K. Gvozdic et al.<sup>6</sup> suggest that this spectrum arises principally from radical I, characterized by an octet, and radical III characterized by a quartet, with radical III being the predominant radical.

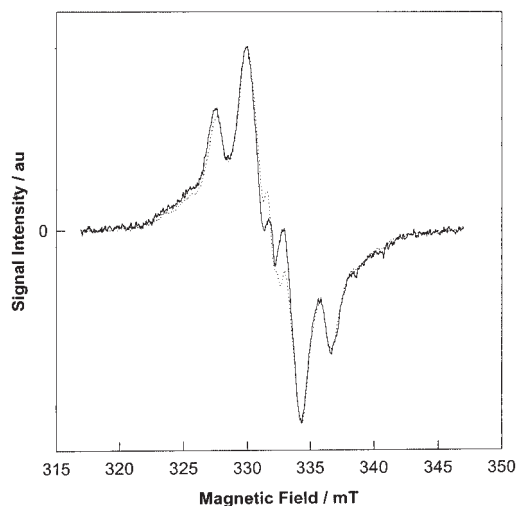


Figure 2 ESR spectrum of Elpro (—) and Elpro+Ca (····) obtained at 77 K after radiolysis under vacuum at 77 K to a dose of 8 kGy.

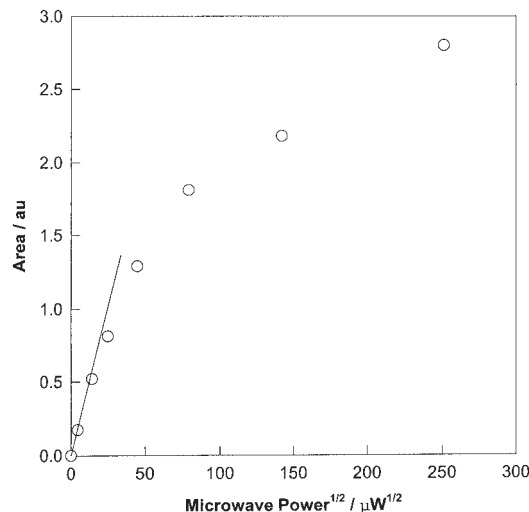


Figure 3 ESR spectrum area versus power<sup>1/2</sup> plot for Elpro following radiolysis at 77 K under vacuum.

The ESR spectrum at 77 K of Elpro-Ca following irradiation at 77 K under vacuum is also shown in Figure 2. The spectrum is similar to that found for Elpro alone, except in the center of the spectrum. Subtraction of the spectra for Elpro-Ca and Elpro shows that the difference is due to the presence of a central singlet with a  $\Delta H_{PP}$  of 5.8 mT in the Elpro+Ca spectrum. The origin of this broad singlet, which contributes only 1% of the total area of the Elpro+Ca spectrum, is uncertain, but it may arise from a radical associated with the carboxyl group in the calcium stearate.

The ESR spectra at 77 K of Elpro-Ca containing various additional amounts of DOP following irradiation at 77 K under vacuum all showed similar features. A typical spectrum is shown in Figure 4a for the polymer containing 2.5 phr DOP. All of the spectra for the polymers containing 0.5 to 2.5 phr DOP can be analyzed in terms of the spectrum for Elpro and var-

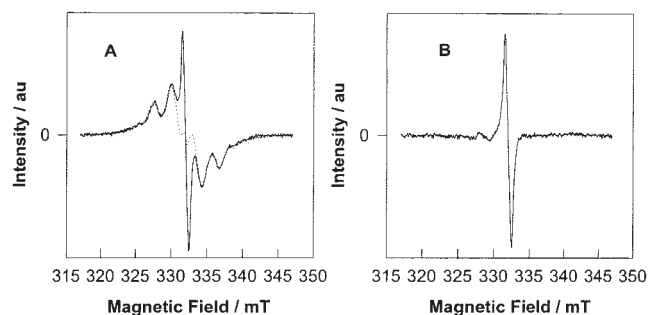
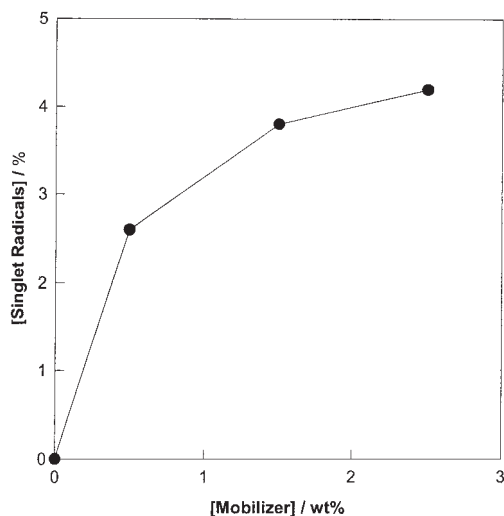


Figure 4 (a) ESR spectrum of Elpro+Ca+DOP 2.5 phr (—) and Elpro (····) obtained at 77 K after radiolysis under vacuum at 77 K to a dose of 8 kGy and (b) ESR spectrum of the singlet representing the difference between the two spectra in Figure 4(a).

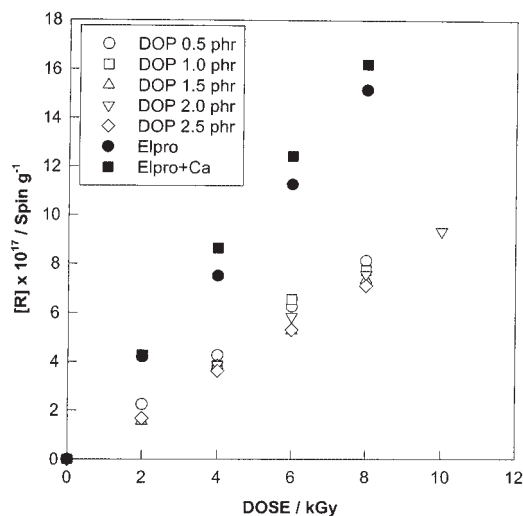


**Figure 5** Plot of the percentage contributions of the singlet to the ESR spectra of Elpro samples containing various DOP concentrations following radiolysis under vacuum at 77 K.

ious percentage contributions from a narrow singlet,  $\Delta H_{PP} = 1.0$  mT, as demonstrated in Figure 4(a). The narrow singlet, which constitutes the difference between the two spectra, is shown in Figure 4(b).

The singlet in Figure 4(b) is similar to the singlet that has been observed by Babanalbandi et al.<sup>7</sup> on radiolysis of poly(ethylene terephthalate), and it is believed to arise through formation of a carbonyl radical as a result of ester group scission in the DOP. The percentage contributions of the singlet to the spectra for the polymers containing different amounts of DOP are shown in Figure 5. The percentage contribution of the singlet is greater than the weight percentage of the DOP present in the sample, indicating a preference for radical formation at the DOP.

ESR spectra for all of the polymers were obtained at various irradiation doses over the range 0–1.0 kGy. The radical concentrations were calculated and are presented as a function of dose in Figure 6. The plots are linear over the range of doses studied, and the values of  $G(R)$  were calculated from the slopes of the plots. They are presented in Table I. The value of  $G(R)$  for Elpro of 3.0 is greater than the range of values 2.40–2.57 reported by O'Donnell and Whittaker<sup>4</sup> for PPs that varied in crystallinity between 73 and 46%. The value is also considerably larger than the values, 2.33 and 2.24, reported by these workers for amorphous PP/PE copolymers with  $F_{PP}$  of 0.23 and 0.36, respectively. The larger  $G$ -value for Elpro could reflect a lower crystallinity of Elpro compared to PP, since O'Donnell and Whittaker<sup>4</sup> found that for PP,  $G(R)$  increases as the crystallinity decreases. The value of  $G(R)$  for Elpro+Ca, 3.2, is slightly higher than that found for Elpro, again possibly reflecting the slightly lower crystallinity of this polymer sample compared to Elpro.



**Figure 6** Plots of radical yields versus dose for various Elpro samples for radiolysis under vacuum at 77 K.

The values of  $G(R)$  for the polymers containing the DOP mobilizer were all much smaller than those for Elpro+Ca, ranging between 1.6 and 1.4 as the concentration of the DOP ranged between 0.5 and 2.5 phr, respectively. Thus, there is a large decrease in the  $G$ -value even for addition of a small amount of DOP. The lower values of  $G(R)$  in the presence of the mobilizer are consistent with the DOP behaving as a radiation stabilizer, even though at 77 K it will not be mobile in the polymer matrix. This suggests that the mechanism of stabilization may be energy transfer to the DOP and loss to heat through the aromatic groups in the DOP molecules prior to bond scission reactions taking place. Additionally, the aromatic units in DOP may scavenge hydrogen atoms, thus reducing the extent of hydrogen abstraction reactions.

Following radiolysis at 77 K under vacuum, the polymers were annealed to higher temperatures. The variations in the radical concentration for the polymers as the temperature was raised from 120–350 K are shown in Figure 7. The concentrations for all of the polymers fall almost linearly between 120 and 310 K

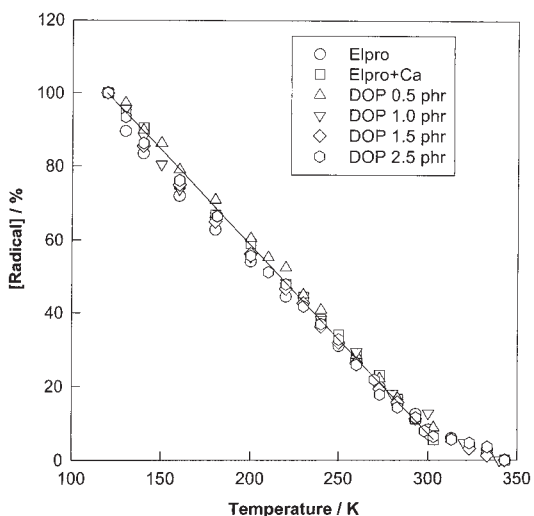
**TABLE I**  
 **$G(R)$  Values for Irradiation of the Polymers Under Vacuum at 77 K and Measured at 77 K**

Polymer	$G$ -value*
Elpro	$3.0 \pm 0.1$
Elpro+Ca	$3.2 \pm 0.1$
Elpro+Ca+ DOP 0.5 phr	$1.62 \pm 0.05$
Elpro+Ca+ DOP 1.0 phr	$1.6 \pm 0.2$
Elpro+Ca+ DOP 1.5 phr	$1.5 \pm 0.1$
Elpro+Ca+ DOP 2.0 phr	$1.50 \pm 0.05$
Elpro+Ca+ DOP 2.5 phr	$1.43 \pm 0.03$

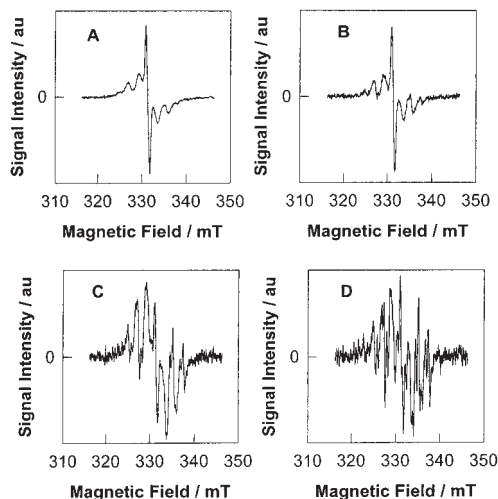
\* Errors are 95% error estimates.

and follow the same decay curve. Over this temperature range, approximately 95% of the radicals present at 120 K are lost. Importantly, no significant discontinuity was observed in the radical decay curve, either at the melting temperature for DOP of 223 K or at the  $T_g$  for Elpro, 259 K. Thus, as the mobility of the DOP increases between 220 and 260 K, there is no apparent change in the progression of the radical decay process. Above 310 K, the slope of the decay curve decreases slightly, and the radical concentration falls more slowly to zero at approximately 340 K. This behavior differs from that reported by O'Donnell and Whitaker<sup>4</sup> for the amorphous PP/PE copolymers with  $F_{PP} = 0.23$  and 0.36, for which the radical concentrations fall to zero at  $\approx 250$  K and the decay curves are not linear.

The evolution of the ESR spectra during thermal annealing of the samples containing DOP were similar. These spectra are represented in Figure 8 by the sample containing 2.5 phr DOP. Although there was some decrease in the radical concentrations as the samples were warmed from 77 K to 120 K, the ESR spectra were identical at the two temperatures, as a comparison between Figure 4 and Figure 8(a) reveals. As the samples were further heated to 250 K, the line-widths of the spectra of the Elpro radicals decreased, but the underlying 9-line spectrum of the Elpro radicals and the singlet remain; see Figure 8(b). Based upon a study by Gvozdic et al.,<sup>6</sup> the change in the line-widths over this temperature range may be partially associated with a loss of any type II and III radicals present. At 250 K, the samples are almost 30°K above the melting temperature of DOP, but the increasing mobility of the DOP has little effect on the nature of the ESR spectrum observed.



**Figure 7** Radical concentration versus annealing temperature plot for various Elpro samples following radiolysis at 77 K under vacuum.



**Figure 8** Spectra for Elpro+Ca+DOP 2.5 phr at various annealing temperatures following radiolysis at 77 K under vacuum: (a) 120 K, (b) 250 K, (c) 273 K, and (d) 303 K.

When the temperature of the sample is further increased from 250 to 270 K, the singlet of the DOP radicals is lost, as shown in Figure 8(c). Over this temperature range, the Elpro passes through its glass transition temperature, so polymer chain mobility within the amorphous regions increases. The DOP is located in the amorphous region, so the extra polymer mobility above  $T_g$  facilitates the decay of the DOP radicals; but since they represent only a small fraction of the total number of radicals present, their disappearance is not observable in Figure 7.

When the samples are further annealed to room temperature, the line-widths of the peaks in the spectrum decrease further, revealing the presence of multiple lines. The spectra were similar to that reported by Busfield et al.,<sup>2</sup> which was assigned to PP allyl radicals. The spectrum shown in Figure 8(d) for the sample containing 2.5 phr DOP at 303 K is not only similar to that observed for the other Elpro samples containing the mobilizer; it is also similar to that observed for Elpro and Elpro+Ca. Presumably, because these radicals are relatively stable, they must be located at the interfacial regions between the crystalline and amorphous phases, since they disappear completely at 350 K, well below the crystalline melting temperature, 421 K.

## CONCLUSIONS

DSC studies on Elpro indicated a  $T_g$  at 259 K and a  $T_m$  at 421 K and the heat of melting was  $98 \text{ J g}^{-1}$ . Addition of 0.08 phr of calcium stearate did not affect the percentage crystallinity of the polymer greatly, but the further addition of DOP caused an 8–9% decrease in the polymer crystallinity.

Radiolysis of Elpro under vacuum at 77 K resulted in a broad ESR spectrum at 77 K, which was charac-

terized by 9 principal lines. A similar spectrum was observed for Elpro+Ca after radiolysis under vacuum at 77 K, but with a small broad central singlet that contributed approximately 1% of the area of the spectrum. Addition of DOP mobilizer to Elpro+Ca produced a spectrum following 77 K vacuum radiolysis that was characterized by two components. One component arose from the radiolysis of the Elpro; and another component, characterized by a narrow singlet, arose from the DOP. The contribution of the second component to the overall spectrum at 77 K increased with DOP content, but it is not linear in the DOP concentration, falling with increases in the DOP content at the higher concentrations.

The radical yield for the semicrystalline Elpro,  $G(R) = 3.0$ , irradiated at 77 K under vacuum was found to be larger than that reported previously for isotactic PP and amorphous PE/PP copolymers, and may reflect the lower crystalline content of the Elpro relative to PP. Addition of 0.08 phr of calcium stearate to the Elpro increased the radical yield slightly, again perhaps because of a slight lowering of the crystalline content. Addition of 0.5 phr of DOP to the Elpro+Ca resulted in a drop of the radical yield at 77 K by a factor of approximately 2; but on further addition of DOP to 2.5 phr, the radical yield fell only by a further  $\approx 15\%$ . These results at 77 K suggest that the DOP provides radiation protection to the copolymer via an energy transfer process, since the DOP is not mobile in the polymer matrix at this temperature.

Annealing the irradiated copolymers to higher temperatures revealed that the radical concentrations fall

almost linearly between 120 K and 310 K, with no evidence of any discontinuity at either the melting point of DOP or the  $T_g$  for Elpro. The narrow singlet component of the spectra of the samples containing DOP was found to disappear at the  $T_g$  of Elpro during the annealing process. At room temperature the spectra of all of the annealed samples were assigned to allyl radicals.

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## References

1. Ranby, B.; Rabek, J. F. *ESR Spectroscopy in Polymer Research*; Springer-Verlag: Berlin, 1977.
2. Busfield, W. K.; Morley-Buchanan, T.; Pomery, P. J. *J Polym Sci* 1986, 24, 3089.
3. Iwasaki, M.; Ichikawa, T.; Toriyama, K. *J Polym Sci Part B* 1967, 5, 423.
4. O'Donnell, J. H.; Whittaker, A. K. *Pure Appl Chem* 1992, 29, 1.
5. Quirk, R. P.; Alsamarraie, M. A. A. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; pp V/27-33.
6. Gvozdic, N.; Basheer, R.; Mehta, M.; Dole, M. *J Phys Chem* 1981, 85, 1563.
7. Babanalbandi, A.; Hill, D. J. T.; Whittaker, A. K. *Polym Adv Technol* 1998, 9, 62.