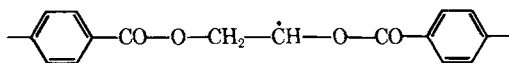
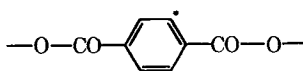


**Concentration of Radicals in γ -Irradiated
Poly(ethylene Terephthalate)**

Several earlier ESR studies of γ -irradiated poly(ethylene terephthalate) (PET) have been reported,¹⁻⁸ and at least two radical species have been identified.^{7,8} Two major products of radiation damage are radicals I and II.



Radical I



Radical II

Radical II can be separated from radical I by heat treatment at 150°C, where radical I decays. The relative concentrations of these radicals were of interest as part of a study concerned with the relative stability of polymers to ionizing radiation.

Previously it was reported^{4,8} that radical I constitutes 95% of the radical concentration in the crystalline regions of biaxially oriented PET film. Radical II and an unidentified

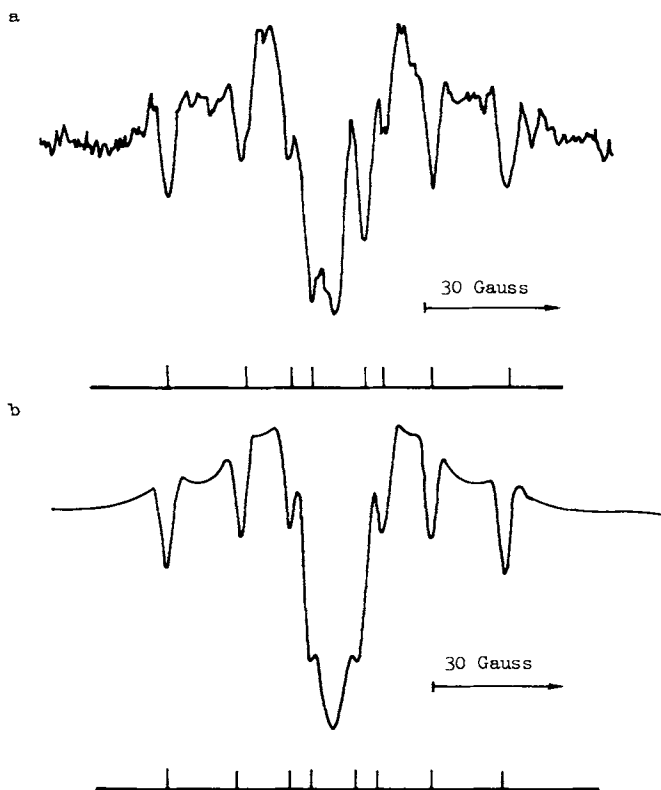


Fig. 1. Second-derivative ESR spectrum of γ -irradiated PET with surface of film perpendicular to H_0 : (a) observed; (b) computer-generated.

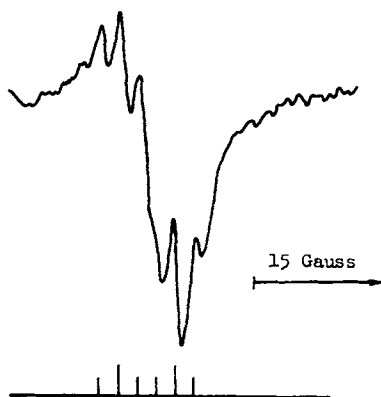


Fig. 2. ESR spectrum of PET after heating sample at 150°C. Surface of film perpendicular to H_0 .

radical (radical III) accounted for the remaining 5%. Measurements at this laboratory indicate that radical I accounts for only 1–2% of all radicals in the gross polymer. For a polymer approximately 50% crystalline these results imply vastly different trapping efficiencies (G values) for the amorphous and crystalline regions.

All the samples were prepared from biaxially oriented film (duPont Mylar; crystallinity 40–50%) of 1 mil thickness (2.54×10^{-3} cm) which was cut into strips and placed in quartz tubes and then evacuated at 10^{-6} torr for 12 hr. The samples were then sealed in the tubes under vacuum and exposed to γ -radiation from a ^{60}Co source at a dose rate of 1.6 Mrads/hr at 35°C. Total doses ranged from 5 to 100 Mrads. ESR spectra of the irradiated samples were obtained with a Varian V4502 ESR spectrometer.

A second-derivative absorption spectrum of γ -irradiated film (dose = 30 Mrads) is shown in Figure 1a. The spectrum was obtained with the surface of the film perpendicular to the external magnetic field H_0 . The spectrum consists of eight lines due to radical I and a single broad component superimposed on the eight lines. The splittings for the eight lines are 17, 29, and 34 gauss as previously reported.⁸ Figure 1b is the computed spectrum, which was calculated by superimposing the idealized spectrum of radical I with its eight lines of equal intensity and a spectrum consisting of one broad line due to radical II with unresolved hyperfine structure. The slight discrepancy between the observed and computer-generated spectrum is probably due to a trace of unidentified radicals, possibly radical III.

Since computer simulation indicated that the spectrum is largely a superposition of eight lines from radical I and a broad central peak from radical II, the relative concentrations of the two radicals were obtained by double integration of the first-derivative spectrum. The total concentration was obtained from the integrated intensity of the entire spectrum and the concentration of radical I was measured from the integrated intensity of one of the outer lines of the octet. The octet signal from radical I accounted for 1–2% of the total integrated intensity.

The double integration was performed numerically by a method which approximates the first moment of the first-derivative spectrum and involves an error of less than 5%.⁹ Since only relative concentration measurements were made, none of the experimental difficulties associated with absolute concentration measurements were encountered; and care was taken to avoid saturation of one radical species at the expense of another.

When the sample of Figure 1 was heated at 150°C for 1 hr, the spectrum in Figure 2 was observed with the film surface perpendicular to H_0 . At other orientations, no hyperfine structure was observed and only a singlet with halfwidth of about 20 gauss was observed. This spectrum is probably due to radical II trapped in the oriented crystalline

regions of the polymer (the radicals in the amorphous regions presumably decaying at 150°C) and consists of six lines with splittings of 5 and 15 gauss.

Radical II has also been observed in samples exposed to low doses of γ -radiation (6-10 Mrad). Figure 3 shows a spectrum of PET film exhibiting no trace of radical I



Fig. 3. ESR spectrum of PET after a dose of 6 Mrads. Surface of film perpendicular to H_0 .

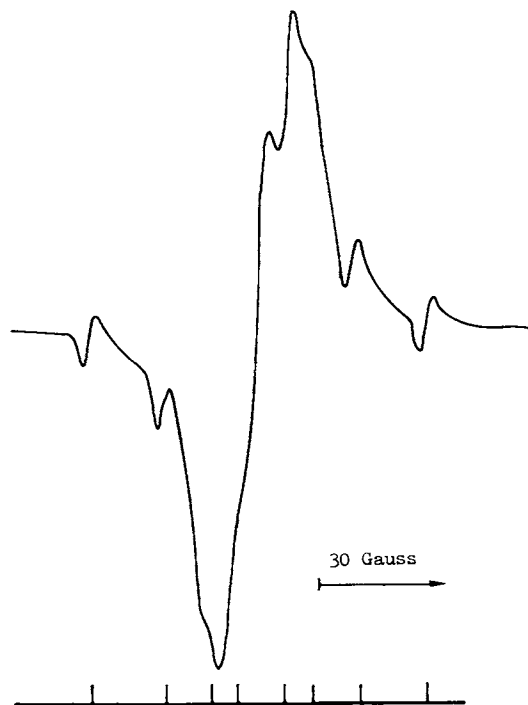


Fig. 4. Observed spectrum of PET after a total dose of 50 Mrads. Surface of film perpendicular to H_0 .

after a dose of 6 MRad. This first-derivative spectrum was obtained with the surface of the film perpendicular to H_0 . In this sample, as opposed to the heat-treated sample of Figure 2, there is a large concentration of radical II in the amorphous regions of the polymer where the radicals are randomly oriented. Thus the hyperfine structure was not resolved even in the perpendicular orientation. The fact that no signal was detected from radical I at this low dose implies different trapping efficiencies for amorphous and crystalline regions, an observation which has been previously reported.¹⁰

Upon further exposure to γ -radiation (dose > 50 Mrads) the spectrum of Figure 4 was obtained. Here the eight-line spectrum of radical I is present but its concentration does not exceed 2%.

If radical I accounts for 90% of the radicals in the crystalline regions and radical II accounts for 98% of the radicals in the gross polymer, then the logical consequence of these results is that radical I is contained almost exclusively in crystalline regions and radical II almost exclusively in amorphous regions. Previous results have indicated that radical II is the most abundant species in amorphous regions.⁴ However, another implication is that the G values for the amorphous regions are at least an order of magnitude larger than for the crystalline regions. Slight differences of G values at low doses have been reported; however such large differences have not been observed.¹⁰

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