Communications to the Editor

Trapped Electrons in γ-Irradiated Polyethylene Identified by Electron Spin Resonance Spectroscopy[1]

Phenomena such as thermoluminescence and electrical conductivity in irradiated polymers have been attributed to ionic species, including trapped electrons, but direct evidence for the precise nature of these species has been lacking.[2] Since physically trapped electrons have been recently detected by optical[3a] and electron spin resonance[3b] (esr) spectroscopy in low molecular weight hydrocarbons after γ irradiation at −196°, we became interested in the possibility of their identification in γ-irradiated polyethylene, and here we report our findings.

Two types of polyethylene were used in this work. The first was an antioxidant-free low-density sample supplied by the E. I. du Pont de Nemours Co. in the form of small molding pellets. This material was designated as Alathon 1414, and the following physical properties were given: melt index = 1.2, density = 0.915 g cm^{-3}, and $\bar{M}_n = 3.1 \times 10^4$. The second material was a commercial sample of Marlex 50. An effort was made to remove the antioxidant from crushed material by extraction with boiling acetone for 4 days, followed by drying at 115° under a vacuum of 10^{-5} torr for 2 days. Samples for γ irradiation and esr studies were fabricated from the pellets or powder by compression under vacuum in a glass tube at a temperature of 120–140°. This technique gave uniform cylindrical rods 3 or 5 mm in diameter which fitted conveniently into the tail section of the esr dewar. The Alathon samples were encapsulated in glass tubes and evacuated to a pressure of less than 10^{-5} torr for several hours before sealing off. Some of the Marlex-50 samples were treated similarly but the omission of this latter step and storage of the samples instead under liquid nitrogen for up to 24 hr before irradiation made little difference to the outcome of the results. Those samples in glass capsules were removed at −196° before irradiation. All samples were kept in the dark at −196° during and after irradiation.

A full description of our experimental techniques for esr measurements on trapped electrons has been submitted for publication.[3b] For irradiated samples where the yield of trapped electrons is small in comparison to that of other paramagnetic species present, it is important to reduce the microwave power so as to achieve maximum discrimination between the trapped-electron signal and the broad background spectrum. In γ-irradiated 3-methylpentane and 3-methylhexane glasses, the maximum signal intensity for the trapped electron occurs at a microwave power of 0.025 mW corresponding to a value of the microwave magnetic field $H_1 \simeq 6.3 \times 10^{-3}$ G. At microwave powers which are about a factor of 10 lower, the signal intensities of both the trapped electron and the other paramagnetic species increase linearly with H_1, which is proportional to the square root of microwave power, and it is in this region that we have observed the clearest esr spectrum of the trapped electron in irradiated polyethylene.

The first-derivative esr spectrum A of irradiated Alathon in Figure 1 shows a well-defined narrow singlet ($g = 2.002 \pm 0.001$, $\Delta H_{ms} \simeq 4$ G) situated in the center of a poorly resolved underlying spectrum. Only the latter remains in the spectrum B taken after the sample had been exposed to filtered light ($\lambda > 1000$ nm) from an infrared lamp. The complete removal of the singlet by photobleaching with infrared light indicates that this light-sensitive contribution to the esr signal is due to trapped electrons, since the same behavior has been observed in esr studies on lower hydrocarbons.[3b] Moreover, this effect of photobleaching is analogous to the results of optical studies[3a] on the trapped electron in γ-irradiated 3-methylpentane.

Microwave power saturation studies verified that the singlet in Figure 1A became saturated at about the same power level (0.025 mW) as that observed for the saturation of the trapped-electron signal in 3-methylpentane and 3-methylhexane;[3b] at much higher powers ($\gg$0.1 mW), it became difficult to distinguish the singlet from the underlying signal in polyethylene. The spectroscopic characteristics (g and ΔH_{ms} values) for the trapped electron singlet in polyethylene are also similar to those determined in the lower hydrocarbon glasses,[3b] ΔH_{ms} for polyethylene is somewhat lower.[3b]

The corresponding esr spectra of γ-irradiated Marlex 50 are illustrated in Figure 2. Spectrum A shows the presence of a very pronounced singlet which is clearly resolved from the underlying spectrum. After photobleaching the sample with near-infrared light ($\lambda >$ 1000 nm), the singlet was eliminated (spectrum B) and only minor changes resulted from additional photobleaching with light of shorter wavelengths (spectrum C). As before, the singlet in Marlex 50 saturates readily with microwave power, and the spectroscopic characteristics coincide with those given for the Alathon specimen. The intensity of the singlet was lower in the esr spectrum of an irradiated sample of untreated Marlex 50, and there was evidence of some additional hyperfine structure in the underlying spectrum which was not removed on photobleaching with infrared light ($\lambda > 1000$ nm), but which largely disappeared on subsequent photobleaching at shorter wavelengths ($\lambda > 640$ nm).

Our preliminary results show that the radiation yield of trapped electrons in Marlex 50, $G(e^-) \approx 0.5$, is greater than in Alathon 1414. This result was unexpected because in the low molecular weight hydrocarbon glasses,[3b] the magnitude of $G(e^-)$ is always reduced by any tendency toward increased crystallinity

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(2) See, *e.g.*, M. Dole and D. M. Bodily, Advances in Chemistry Series, No. 66, American Chemical Society, Washington, D.C., 1967, p 31.

(3) (a) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 1279 (1966); (b) J. Lin, K. Tsuji, and F. Williams, *J. Amer. Chem. Soc.*, **90**, 2766 (1968).

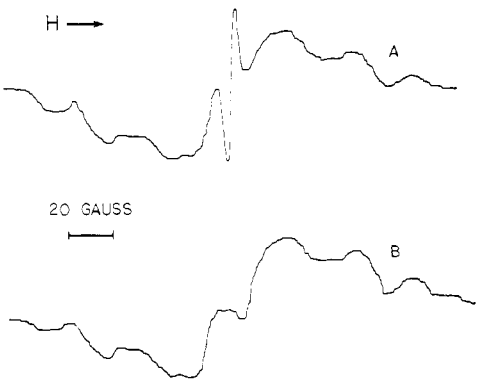

Figure 1. Electron spin resonance first-derivative spectra of γ-irradiated Alathon 1414 polyethylene at $-196°$: dose, 0.25 Mrad; sample diameter, 3.2 mm. Spectrum A was recorded before and spectrum B after bleaching with infrared light from a 250-W ir lamp. Corning filters No. 2030 and 4308 were used ($\lambda > 1000$ nm); microwave power, 0.002 mW. For comparison with Figure 2, the spectrometer gain setting was 1000 for both A and B.

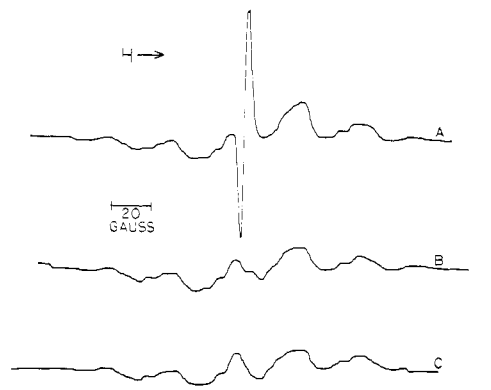

Figure 2. Electron spin resonance first-derivative spectra of γ-irradiated Marlex 50 polyethylene at $-196°$: dose, 0.12 Mrad; sample diameter, 4.8 mm. Spectrum A was recorded before and spectrum B after bleaching with infrared light ($\lambda > 1000$ nm) as in Figure 1. Spectrum C was recorded after additional photobleaching with red light ($\lambda > 640$ nm); microwave power, 0.002 mW. Spectrometer gain settings were 500, 400, and 500 for A, B, and C, respectively.

in the sample. At the present time, the physical nature of the electron trap in hydrocarbons is not established, and it is conceivable that in polyethylene, the electron is trapped at defects in the crystalline regions of the polymer rather than in the amorphous regions.

Both in the Alathon and Marlex specimens, a slow thermal decay of the esr singlet is detectable at $-196°$ after irradiation and amounts to as much as a 20% decrease in the amplitude of the signal measured over a period of 1 hr. At higher temperatures, the decay is more rapid, and work is now in progress to obtain additional data on the thermal stability of the trapped electron in polymers.

During the course of this work, we have come across some earlier esr studies of γ-irradiated polyethylene by Alfimov, Nikol'skii, and Buben.[4] From the changes which occurred on photobleaching, these authors also interpret the original esr spectrum after irradiation as consisting of a singlet superimposed on a radical spectrum. However, in their studies, the singlet appears to be much broader ($\Delta H_{ms} \approx 20$ G)[4b] as may be judged by the fact that the resolution of the two center lines in the underlying spectrum is totally obscured in the spectrum taken before photobleaching. A broad line in the center of the esr spectrum could well be due to unresolved hyperfine interaction from a paramagnetic species produced by electron capture. The Russian authors[4] report that a similar line was observed following the radiolysis of polyethylene containing benzene, but the identity of the trapping center (chemical or physical) in irradiated polyethylene was not specified.

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(4) (a) M. V. Alfimov, V. G. Nikol'skii, and N. Ya. Buben, *Kinet. Katal.*, **5**, 268 (1964); (b) V. G. Nikol'skii, M. V. Alfimov, and N. Ya. Buben, *Zh. Fiz. Khim.*, **37**, 2797 (1963).

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