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FERMILAB-Pub-93/084

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March 1993

Submitted to *Polymer Preprints*

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Electron Spin Resonance Study of Irradiated Polystyrene Fibers

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March 26, 1993

Abstract

An electron spin resonance (ESR) study was performed on samples of irradiated polystyrene fiber. The ⁶⁰Co irradiations were carried out at both room temperature and 77 K for 1 h, using a dose rate of approximately 1 Mrad/h. After irradiation, the samples were stored in liquid nitrogen until they were analyzed. The ESR spectra were recorded at different temperatures between 70–300 K. The polystyrene fibers irradiated at room temperature show an ESR spectrum different from those irradiated at 77 K at all temperatures of measurement. The former present an ESR signal whose main contribution is from the benzyl radical. The spectra from the latter indicate the formation of the cyclohexadienyl radical.

Introduction

Particle detectors based on inorganic and organic scintillating materials have been used in nuclear and high energy physics experiments for many years [1]. Plastic scintillators, which consist of a polymer matrix doped with fluorescent compounds, are noteworthy for their fast response and the ease in which they can be manufactured. New applications for this type of detector have resulted from the development of scintillating plastic optical fibers [2]. Several detectors have already been built and many others are being designed using various arrangements of polystyrene-based scintillating fibers. Currently, their use still presents a major drawback. The scintillating fibers in some applications are exposed to a significant radiation dose over the detector lifetime, and although polystyrene is considered quite resistant to radiation-induced degradation, its optical characteristics do change. Radiation damage in polystyrene-based plastic scintillators shows as an increase in absorption which is responsible for a decrease in the light yield of the detector during the exposure [3, 4].

Transmittance measurements of undoped polystyrene samples irradiated at high dose rate show a large absorption increase immediately after irradiation. A fraction of this absorption is transient in nature and will disappear with time. This annealing process can be enhanced by treating the samples with oxygen or heating them under vacuum. A permanent absorption remains as an indication of the radiation-induced damage that occurred in the polystyrene matrix (Figure 1). This increase in absorption results from products formed by reactions of radical species created during irradiation. In an earlier electron spin resonance (ESR) study performed by Harrah [5], the major radical species in polystyrene, at doses up to 10 Mrad, was assigned to the benzyl radical formed by α -hydrogen abstraction in the polymer back-bone. The formation of other radical species, such as the cyclohexadienyl radical, was observed in samples exposed to doses between 10–50 Mrad. In a recent ESR study, Busfield *et al* [6] report the observation of benzyl and cyclohexadienyl radicals in polystyrene irradiated at 77 K and at room temperature. In addition, they mention the dependence of the results upon the nature of the sample. Commercial polystyrene, due to the presence of plasticizers and stabilizers, may yield different radical ratios after irradiation.

In order to provide reliable information on the degradation mechanism of our polystyrene-based fibers, an ESR study was performed using samples

prepared by the same processes as those actually utilized for the production of the fibers. Here we present the results of the ESR study performed on polystyrene fibers irradiated to 1 Mrad at 77 K and at room temperature.

Experimental Section

Styrene was purified using a *tert*-butylcatechol removal column supplied by Aldrich Chemical Co. and was then vacuum distilled. It was placed in a coated aluminum mold, degassed by repeated freeze-pump-thaw cycles, and then thermally polymerized in a poly(alkyleneglycol) bath without the use of an initiator. The temperature profile was 24 h at 110 °C, 48 h at 125 °C, 12 h at 140 °C, and then a ramp down over 16 h to 90 °C. The polystyrene sample, thus prepared, was drawn into a 2 mm diameter fiber by Bicorn [7].

For this study, a few segments about 5 cm in length were cut and then degassed for a week prior to irradiation. The irradiations were performed at Argonne National Laboratory using a ^{60}Co source. In all exposures, the dose rate was approximately 1 Mrad/h and the total dose was 1 Mrad. The samples were irradiated in sealed suprasil quartz ESR tubes. The fiber sections irradiated at 77 K were placed in a liquid nitrogen dewar; those irradiated at room temperature were taped around the exterior of the dewar. Between irradiation and ESR analysis, the samples were kept in liquid nitrogen. The ESR measurements were carried out at Argonne National Laboratory, Chemistry Division, with a Varian E109 ESR spectrometer operating at a microwave frequency of 9.28 GHz. The temperature was controlled by a LTR-3 liquid-transfer Heli-Tran refrigerator. The sample tubes were annealed in order to eliminate the ESR signal they would otherwise produce after irradiation.

Results and Discussion

Polystyrene samples irradiated at room temperature were studied at temperatures between 70–300 K. Figure 2 shows two representative spectra recorded at 80 K (top) and at 290 K (bottom). Both measurements show the three-line spectrum assigned to the disubstituted benzyl radical. The predominant radical species under these conditions is the tertiary benzyl radical formed by the loss of a hydrogen atom. The cyclohexadienyl radical, resulting from

hydrogen atom addition to the phenyl ring, cannot be clearly identified in these spectra. Furthermore, its presence in room temperature irradiations has only been detected after very large doses.

Polystyrene samples irradiated at 77 K were also studied from 70–300 K. Figure 3 shows two representative spectra recorded at 70 K (top) and at 235 K (bottom). The signal intensity decreases as the observation temperature increases, since the radical species react at higher temperature. These spectra are different from those shown in Figure 2. The triplet spectrum recorded at 70 K indicates the formation of the cyclohexadienyl radical as an important radiation product during low temperature irradiations. An asterisk marks the side lines of the cyclohexadienyl radical spectrum in Figure 3. The benzyl radical peaks are masked by the presence of other species. The contribution from a phenyl radical anion cannot be ruled out since the center line seems to decrease in intensity at a faster rate than the side lines. Even as the observation temperature increases, the sample irradiated in liquid nitrogen still shows the presence of the cyclohexadienyl radical.

The results from the room temperature irradiations may indicate that cyclohexadienyl radical disappears by further reaction at room temperature, while its demise is slower at lower temperatures. This implies that the benzyl radical is less reactive than the cyclohexadienyl radical in the polymer matrix.

Conclusions

The radical species observed in irradiated polystyrene fibers depends upon the irradiation temperature. The spectra recorded after room temperature irradiation are explained by the presence of the disubstituted benzyl radical as the major product. No substantial change is observed in the spectra during the measurements from 70–300 K. The results from the low temperature irradiations indicate the formation and trapping of several radical species. The cyclohexadienyl radical is identified by its absorption at the wings of the signal. Characterization of the other species contributing to the signal cannot be achieved with the current procedure. In order to identify species, either short-lived or in small concentration, a system with higher resolution and one where the sample could be irradiated *in situ* is required.

Acknowledgements

This work was supported by the US-DOE, at FNAL under contract No. DE-AC02-76CHO3000 and at ANL under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, under contract No. W-31-109-ENG-38.

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Figure Captions

Figure 1. Transmittance spectra of a polystyrene sample (1 cm thick).

Figure 2. ESR spectra recorded at 80 K (top) and at 290 K (bottom) of a polystyrene fiber after 1 Mrad irradiation at room temperature.

Figure 3. ESR spectra recorded at 70 K (top) and at 235 K (bottom) of a polystyrene fiber after 1 Mrad irradiation at 77 K.

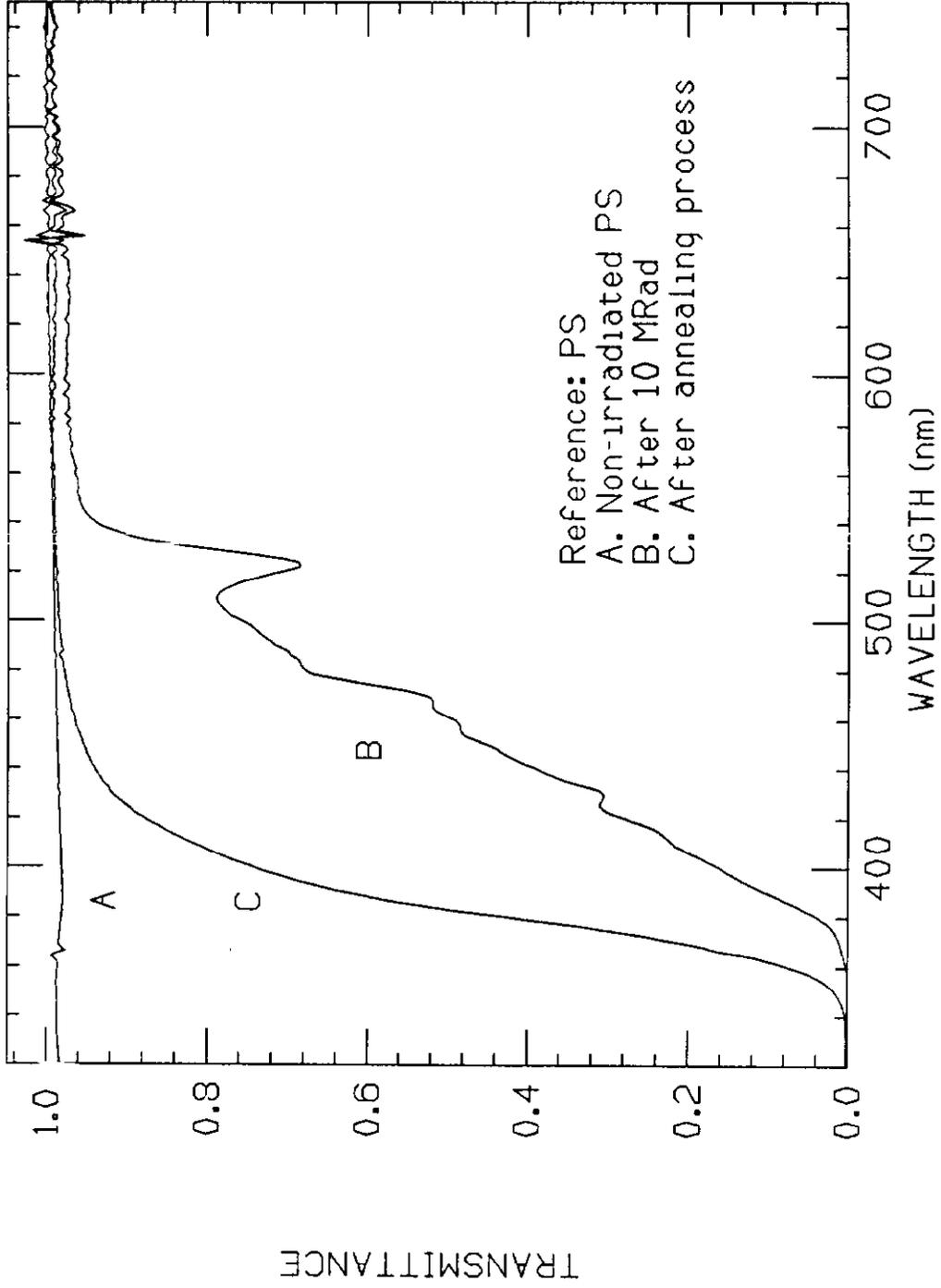


FIGURE 1

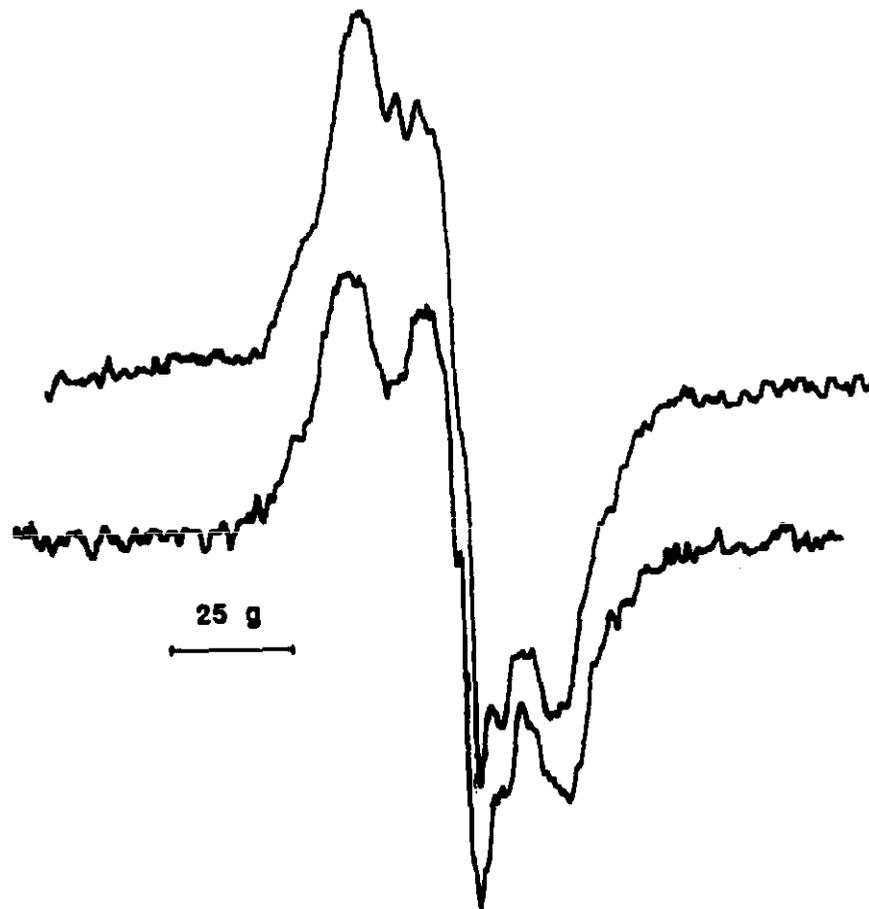


FIGURE 2

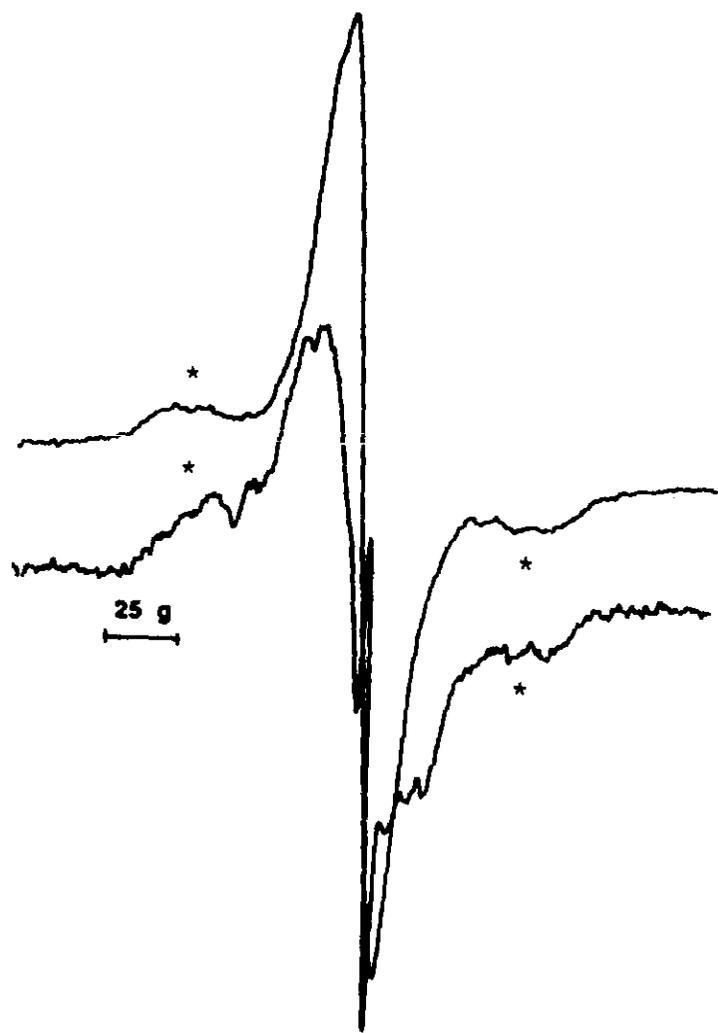


FIGURE 3