Fermi National Accelerator Laboratory

FERMILAB-Pub-91/74

Radiation Effects in Plastic Scintillators and Fibers *

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March 29, 1991

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* Included in Proceedings of the International Conference on Calorimetry in High Energy Physics, Fermi National Accelerator Laboratory, October 1990.

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We have studied radiation induced degradation of plastic scintillator, paying particular attention to polymer effects. Undoped polystyrene samples and three multi-component systems, each containing two organic fluorescent compounds in a polystyrene matrix, were analyzed. In the scintillator systems, p-terphenyl was used as the primary dopant with either dimethyl-POPOP, 3HF, or BBQ as the secondary dopant. Absorbance, fluorescence, and beta excitation measurements were carried out on each sample before, immediately after, and two weeks after irradiation. Radiation-induced absorption in the polymer was detected in the 300-400 nm spectral region. However, no substantial damage was noted in the dopants for scintillator samples receiving a total dose of 10 Mrad. Effects on fiber using p-terphenyl + 3HF scintillator as the core material are also described.

Talk presented at the International Conference on Calorimetry in High Energy Physics, Fermi National Accelerator Laboratory, October, 1990.

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We have studied radiation induced degradation of plastic scintillator, paying particular attention to polymer effects. Undoped polystyrene samples and three multi-component systems, each containing two organic fluorescent compounds in a polystyrene matrix, were analyzed. In the scintillator systems, p-terphenyl was used as the primary dopant with either dimethyl-POPOP, 3HF, or BBQ as the secondary dopant. Absorbance, fluorescence, and beta excitation measurements were carried out on each sample before, immediately after, and two weeks after irradiation. Radiation-induced absorption in the polymer was detected in the 300–400 nm spectral region. However, no substantial damage was noted in the dopants for scintillator samples receiving a total dose of 10 Mrad. Effects on fiber using p-terphenyl + 3HF scintillator as the core material are also described.

1 Introduction

Recently, there has been a renewed interest in plastic scintillators for detector applications in High Energy Particle Physics. Much of this has been driven by the development of high-quality plastic scintillating optical fiber which, in turn, has given birth to a whole new generation of scintillation detectors. The detector challenges of doing physics in the high-rate environment of the LHC or SSC has, however, emphasized one of plastic scintillator's most important properties, its short fluorescence decay time. The main drawback to the use of plastic scintillator has been its susceptibility to radiation damage.$^{1)}$

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*Presented by Alan Bross

There are three primary issues involved with the radiation stability of plastic scintillators and plastic scintillating fiber (PSF). They are: 1. Polymer hardness/optical stability, 2. Dopant stability, and 3. Stability of the fiber waveguide structure. Before we explore these areas in detail, it would be appropriate to briefly review some of the radiation damage issues that would be present at the SSC.[2)] The highest dose for any scintillation detector envisioned to be used at the SSC would occur at shower maximum in the EM calorimeter. If we assume that the SSC operates at a luminosity of $10^{34} cm^{-2} s^{-1}$, and take a typical configuration of a general 4π detector (Figure 1), over a ten year (10^8 sec) detector lifetime the integrated dose at $\eta = 3$ for shower maximum in the EM calorimeter would be roughly 40 Mrad. However, as can be seen from Figure 1, only a very small part of the detector is affected at this level. The vast majority of the EM calorimeter and virtually all of the hadronic calorimeter see much less than 5 Mrad total dose. Even within the EM calorimeter, the absorbed dose is concentrated in a region around shower maximum. For the minimum bias events that produce most of this dose, the region of severe damage is limited to a volume approximately 10 radiation lengths deep. For fiber tracking systems appropriate for the SSC, the dose from the charged particle flux ($L = 10^{34} cm^{-2} s^{-1}$, 10^8 sec) is:

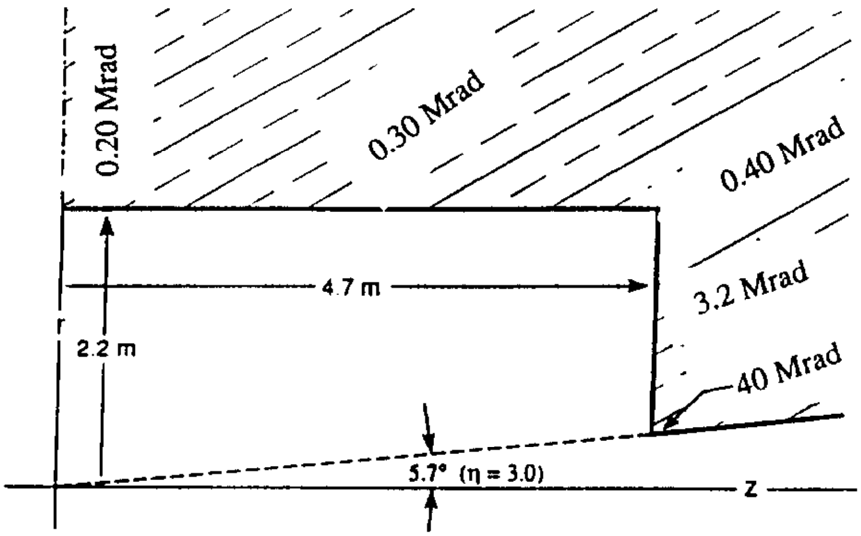

Figure 1: Radiation doses at shower maximum in the EM calorimeter for a conventional 4π detector operating at the SSC with $L = 10^{34} cm^{-2} s^{-1}$ for 10^8 sec.

$$\frac{dN_{charged}}{da} = \frac{4 \times 10^{9} Rad}{r_{\perp}(cm)^{2}}$$

At r = 40 cm, this corresponds to a dose of 2.6 Mrad. So we see, that for the above operating conditions, the survivability limit for most of the scintillation detectors that might be incorporated into a general purpose SSC detector is on the order of 5 Mrad.

2 Radiation Effects in Polymer Systems

For the majority of existing plastic scintillator detectors, the base plastic has been either polyvinyltoluene (PVT) or polystyrene (PS). For PSF detectors, almost all the fiber has used PS as the base material for the scintillator core. This section will focus on the radiation-induced damage to the polystyrene base of some common plastic scintillators and investigate how these changes affect the scintillation light output. These results will show how damage to the polymer plays a major role in the scintillation light losses for the systems studied. Damage to the dopants does not appear to be the major contributing effect in these systems.

2.1 Sample Preparation

We prepared three multi-component scintillator samples for the polymer effects study. Each sample consisted of a purified styrene solution doped with p-terphenyl as the "primary" dye (1.25% by weight) and with a wavelength shifter or "secondary" dye (0.01% by weight). The wavelength shifters used were dimethyl-POPOP (DM-POPOP), 3-hydroxyflavone (3HF), and BBQ. Samples containing a single dopant in a styrene solution were also made. The concentration of each dopant was the same as in the multi-component samples just mentioned, i.e., 1.25% for p-terphenyl, and 0.01% for each of the secondaries. In addition, solutions of undoped styrene were also prepared. The solutions were placed in Pyrex test tubes, degassed by repeated freeze-pump-thaw cycles, and then polymerized in a silicone oil bath. The polymerized samples were machined into 1 cm thick disks and then polished.

Before the irradiation, the samples were placed in stainless steel cans and were then evacuated for a period of one week in order to remove all moisture and most dissolved gases from the samples. Finally, the cans were back-filled with dry nitrogen and sealed. The samples were irradiated at the Nuclear Reactor Laboratory of the University of Michigan using a ^{60}Co source. The doped samples were irradiated to an integrated dose of 10 Mrad and the pure polystyrene samples to doses of 1, 5, 10, 50, and 100 Mrad. In all exposures, the dose rate was approximately 1 Mrad/h.

Absorbance, fluorescence, and beta excitation measurements were performed before, immediately after, and two weeks after irradiation. This last measurement was recorded after the samples were annealed in an oxygen atmosphere. Absorption/transmittance and fluorescence spectra were recorded using a Hewlett-Packard 8451A spectrophotometer. For all absorption/transmittance measurements, unirradiated pure polystyrene was used as the reference. The light yield measurements used a ^{207}Bi beta source (1 MeV electrons) for excitation. The scintillation light was viewed by a Hamamatsu R669 photomultiplier tube which was coupled directly to a Lecroy Model 3001 qVt multi-channel analyzer.

2.2 Irradiation of pure polystyrene

Pure polystyrene samples were irradiated at five dose levels. Immediately after irradiation the transmittance spectra (Figure 2) show a significant increase in absorption in the 350–600 nm range. All spectra indicate the formation of an absorption band at 525 nm whose strength increases with increasing radiation levels. After these measurements, the samples were annealed in oxygen for two weeks. The transmittance spectra recorded after the annealing process (Figure 3) prove that the samples undergo a substantial recovery, particularly for those irradiated at higher doses. However, considerable permanent absorption does remain in the polymer as a result of the radiation.

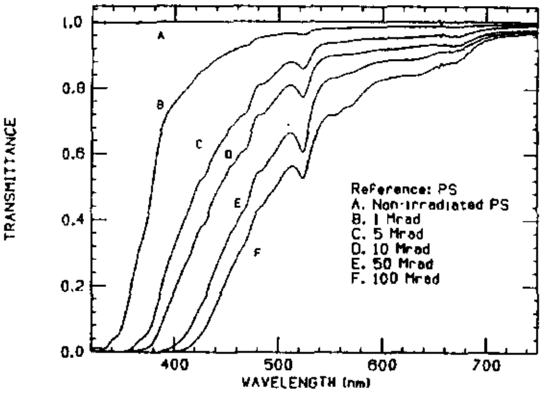

Figure 2: Transmittance data for pure polystyrene immediately after irradiation

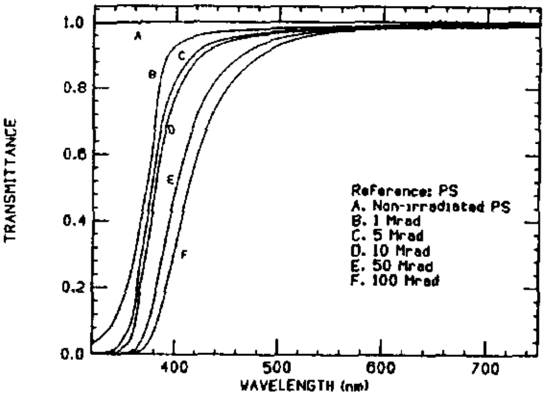

Figure 3: Transmittance data for irradiated pure polystyrene after the annealing process.

Another prominent feature is observed in the samples immediately after irradiation. When excited using 313 nm light, the samples show fluorescence in two regions, one centered around 380 nm and another in the wavelength region between 520 and 600 nm (Figure 4). Pure unirradiated polystyrene only shows a small amount of fluorescence in the wavelength region between 340 and approximately 400 nm when excited with 313 nm light. The new fluorescence band at 380 nm is permanent, but the band between 520 and 600 nm is transient in nature. This fluorescence decreases as the absorption band at 525nm disappears. Exciting this species with 500 nm light yields a fluorescence spectrum (Figure 5) that agrees with the 550 nm band seen in Figure 4. Irradiation causes the formation of several excited species. Among these new species, one is clearly detected. It absorbs at 525 nm, fluoresces in the wavelength region between 525 and 600 nm, and is long-lived. This excited species is observed for many weeks if the sample is kept in a nitrogen atmosphere. If the sample is placed in an oxygen atmosphere, however, the diffusion of oxygen into the sample appears to quench this fluorescent species. This phenomenon starts at the surface of the sample and propagates inward with an initial velocity of 10^{-5} mm/sec. The permanent 380 nm fluorescence band is likely due to polymer segments with increased conjugation and is related to the permanent radiation-induced absorption. The increase in the intensity of this 380 nm band after the anneal can be due to either the increased transmittance of the sample after the anneal or to an actual change in the molecular configuration of some of the radiation-induced states in the polymer.

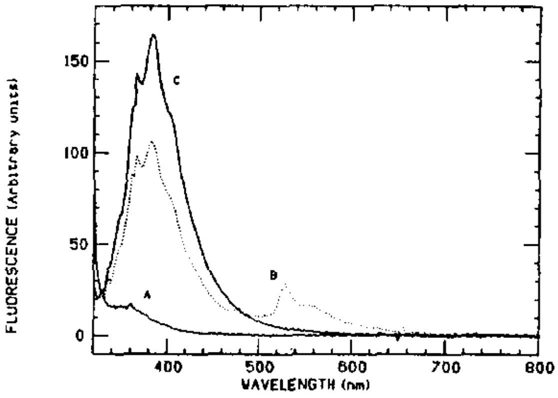

Figure 4: Fluorescence spectra of pure polystyrene: before (A), immediately after(B), and two weeks after 10 Mrad irradiation (C). Excitation wavelength 313 nm.

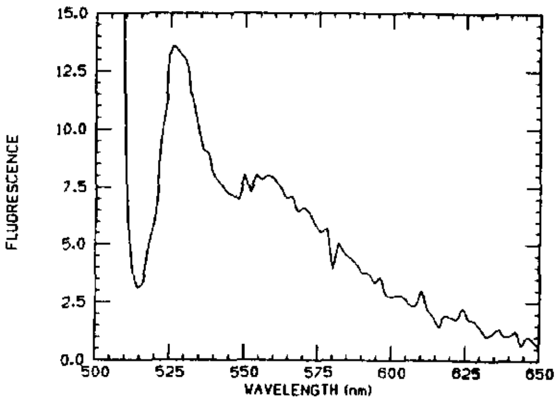

Figure 5: Fluorescence spectrum of irradiated pure polystyrene. Excitation wavelength 500 nm.

Pulse radiolysis measurements on polystyrene films and in cyclohexane solution [3, 4] have assigned an absorption similar to the one we see at 525 nm to singlet excimers of polystyrene. However, this species is short-lived. Other absorptions detected in this region have been assigned to charge transfer complexes with longer decay times.

2.3 Irradiation of Scintillators

The three scintillator samples were irradiated to a dose of 10 Mrad. Figures 6-8 give transmittance data for these samples before irradiation, immediately after irradiation, and after a two week oxygen anneal. For reference, the fluorescence distribution for the sample is also included with its transmittance data. As in the case of the pure polymer, we also see significant annealing in these samples. In addition, the induced absorption seen at 525 nm in the undoped polymer is also present in the doped samples.

Light yield measurements were performed on these samples using beta excitation as described in Section 2.1. The reduction in light output after annealing was 19±1.5% for the DMPOPOP sample, 22±1.5% for the 3HF sample, and 19±1.5% for the BBQ sample. However, looking at the transmittance data in Figures 6-8, we see that transmittance losses cannot account for all of the light loss in any of the three samples. Transmittance loss can only account for a 3±2% loss in the DMPOPOP sample, 1±2% loss in the 3HF sample, and a 6±2% loss in the BBQ sample.

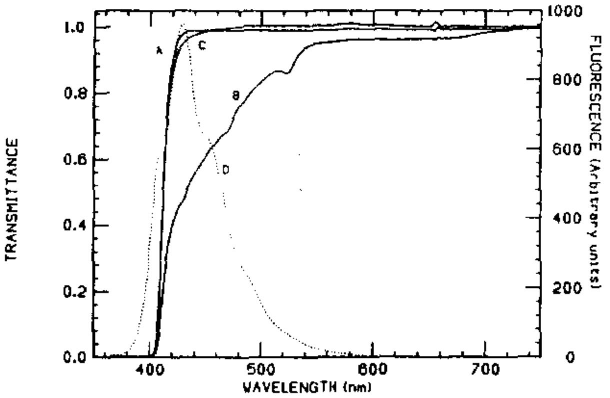

Figure 6: Transmittance data for the p-terphenyl plus DMPOPOP sample: before (A), immediately after (B), and two weeks after 10 Mrad irradiation (C). Dotted line indicates DMPOPOP fluorescence.

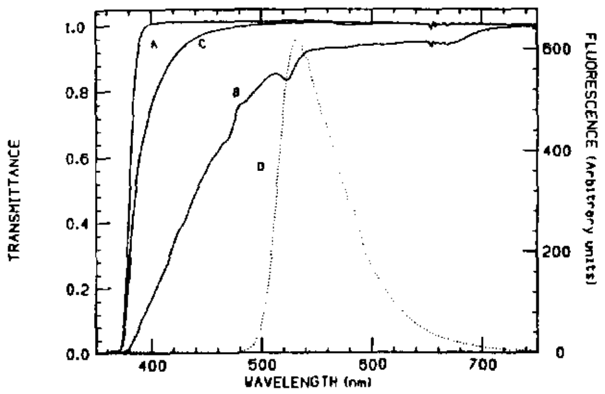

Figure 7: Transmittance data for the p-terphenyl plus 3HF sample: before (A), immediately after (B), and two weeks after 10 Mrad irradiation (C). Dotted line indicates 3HF fluorescence.

One possible explanation for the observed light loss is that the dopants are affected by the radiation. In order to study this, we used front-surface UV excitation to directly stimulate fluorescence of the various dopants. Samples of polystyrene doped only with a single compound were prepared so that we could study the primary and the various secondaries independently. Figure 9 shows the fluorescence from p-terphenyl in a sample with 1.25% p-terphenyl in polystyrene. Its fluorescence distribution is centered at approximately 350 nm. The excitation wavelength was 313 nm. The data show the fluorescence distributions before irradiation and after irradiation (10 Mrad) and annealing of the sample. As can be seen, there is little change in the fluorescence. The integrated intensity changes by 2±2%. The p-terphenyl fluorescence area is integrated between 320–380 nm since after irradiation the polymer fluorescence is detected at 380 nm. The intensity of the excitation source was monitored by using a fluorescence standard and the curves in Figure 9 have been corrected for changes in the excitation source intensity. Figures 10-12

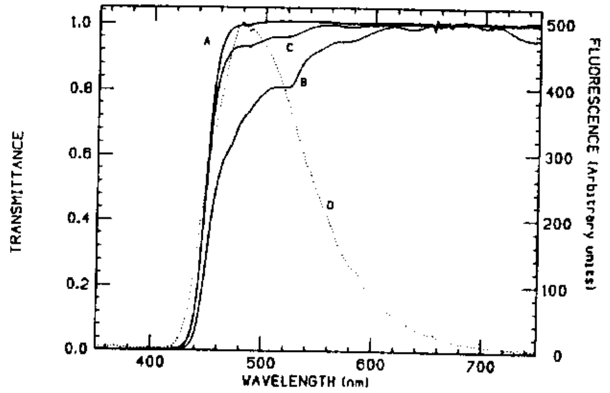

Figure 8: Transmittance data for the p-terphenyl plus BBQ sample: before (A), immediately after (B), and two weeks after 10 Mrad irradiation (C). Dotted line indicates BBQ fluorescence.

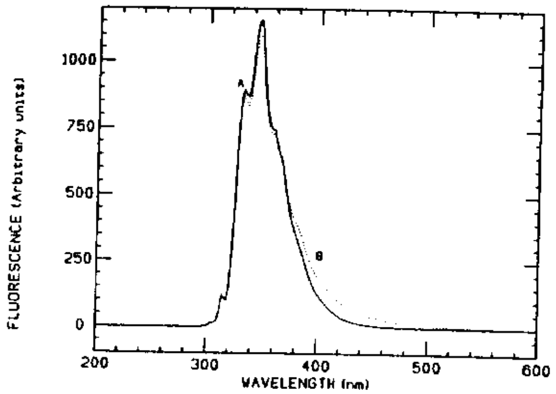

Figure 9: p-Terphenyl fluorescence in polystyrene: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

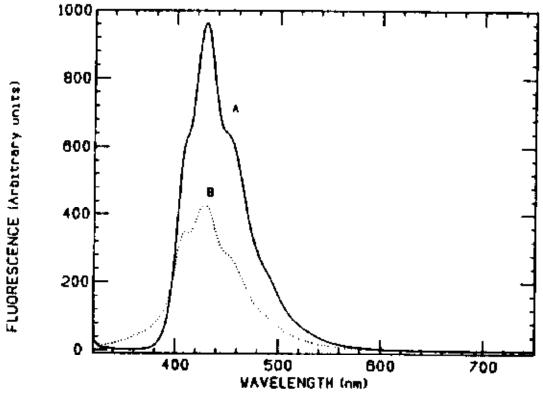

Figure 10: DMPOPOP fluorescence in polystyrene: 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

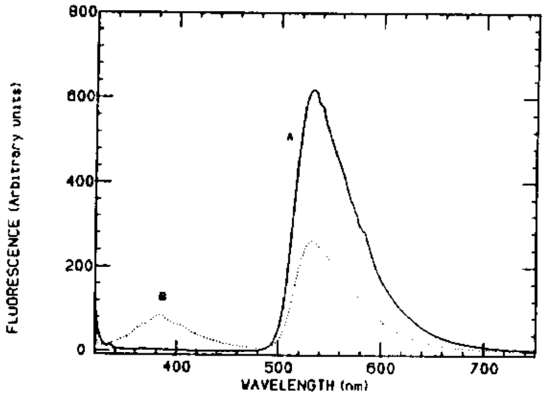

Figure 11: 3HF fluorescence in polystyrene: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

show the same data for samples prepared with 0.01% of the three secondaries, DMPOPOP, 3HF, and BBQ, in polystyrene. In all three figures we see a pronounced change in fluorescence intensity after the 10 Mrad irradiation and anneal. The drop in integrated fluorescence yield for DMPOPOP, 3HF, and BBQ is 42±2%, 51±2%, and 43±2% respectively. However, we also see evidence for polystyrene fluorescence.

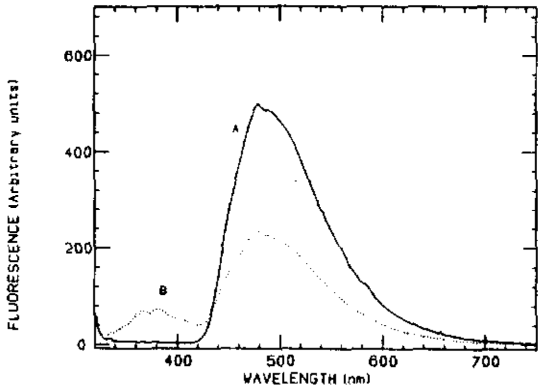

Figure 12: BBQ fluorescence in polystyrene: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 313 nm.

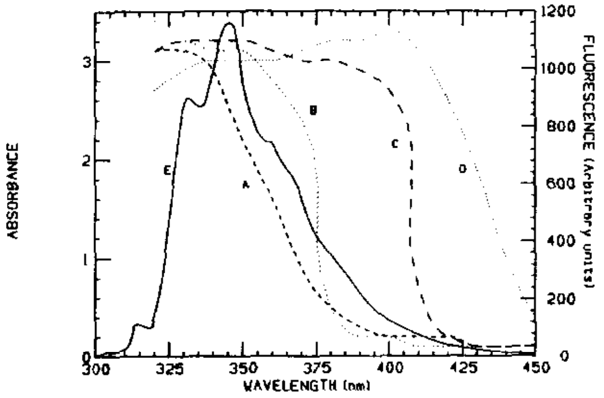

Figure 13: Absorption spectra of irradiated polystyrene (A) and non-irradiated samples of polystyrene (B), 3HF (C), DMPOPOP (D), and BBQ (E) in the region of p-terphenyl fluorescence (F).

In the data for 3HF and BBQ, the 380 nm fluorescence seen in the irradiated pure polystyrene samples (Figure 4) is also clearly evident. In the DMPOPOP sample, the polystyrene fluorescence and the fluorescence from DMPOPOP overlap, so no clear second peak is seen. However, we do see increased fluorescence after irradiation in the band between 320 and 395 nm. Again, this would indicate a contribution from polystyrene fluorescence. The radiation induced absorption in polystyrene at 313 nm is competing with absorption by the secondary. Figure 13 shows absorption data for samples of unirradiated pure polystyrene (reference: air), irradiated polystyrene, and unirradiated polystyrene doped (0.01%) with DMPOPOP, 3HF, and BBQ. As can be seen from these data, polystyrene absorption in the region between 320 and 380 nm has increased significantly after irradiation and does compete favorably with absorption by the secondaries. This effect does not eliminate the possibility, however, that some of the drop in light yield for the three secondaries could still be due to radiation induced degradation of the dopant.

In order to explore this in more detail, additional fluorescence measurements were performed using excitation light of longer wavelength. In these cases, the wavelength of the excitation light is less strongly attenuated by the radiation induced absorption in the polystyrene. Figure 14 gives the fluorescence data for BBQ doped polystyrene using $\lambda_{ex} = 450$ nm. The difference in integrated intensity is now only 4% (versus 43% from above). The corresponding losses in integrated intensity for the DMPOPOP sample with $\lambda_{ex} = 380$ nm are 10% and for the 3HF sample with $\lambda_{ex} = 360$ nm, 22%. For the 3HF case and to a lesser extent for the DMPOPOP case, polymer absorption is still significant (Figure 13). The 10% and 22% drops in intensity can, therefore, only be interpreted as upper bounds on the light loss due to dopant degradation. The actual losses are likely to be much smaller since we see such dramatic changes in the loss ratios when 313 nm excitation light is used versus 360 nm or 380 nm light. Polymer absorption in the wavelength region of p-terphenyl fluorescence competes with the transfer between the primary (p-terphenyl) and the secondary. One can estimate the size of this effect by comparing the fluorescence distributions (using $\lambda_{ex} = 350$ nm) before and after irradiation for a given secondary dopant. Using this technique, we determined that the losses in the integrated fluorescence intensities for the secondaries are 20±2%, 26±2%, and 22±2% for DMPOPOP, 3HF, and BBQ respectively. Using this analysis, it is seen that this "hidden" absorption can account for all the light loss (^{207}Bi measurements) we see in our scintillator samples.

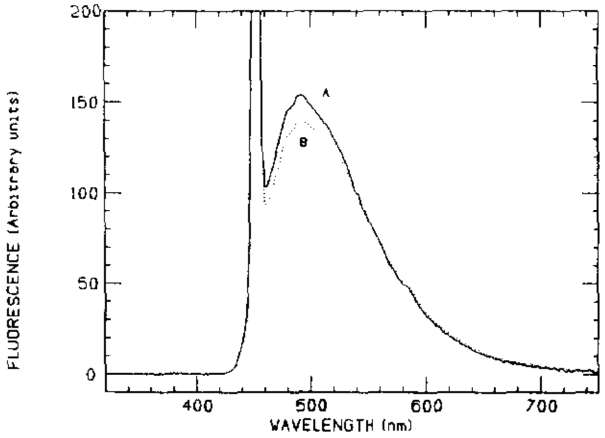

Figure 14: BBQ fluorescence in polystyrene: before 10 Mrad irradiation (A) and after the annealing process (B). Excitation wavelength 450 nm.

3 Radiation Effects in Fibers

Before describing results on irradiations of scintillating fiber, it will be useful to briefly discuss some aspects of light propagation in optical fiber. There are two distinct classes of light that can be transmitted in an optical fiber.[5) 6)] The first class, core light, consists of those rays that are total internally reflected at the core-cladding interface. Since the core-cladding interface is well controlled, this reflection coefficient can be very close to unity, yielding a long attenuation length for this light. The second class, cladding light, consists of rays which are beyond the angle for total internal reflection at the core-cladding interface but can be trapped at the cladding-air interface. Since this external interface cannot be well controlled, dust, scratches, fingerprints, etc. can significantly degrade the reflection coefficient for this light. The attenuation properties of these two classes are thus vastly different (Figure 15) and must be taken into consideration when discussing the properties of any optical fiber. For all relevant measurements, the cladding light should be eliminated. This is easily accomplished by painting black a short section (2 cm) of the fiber near the detector end of the fiber.

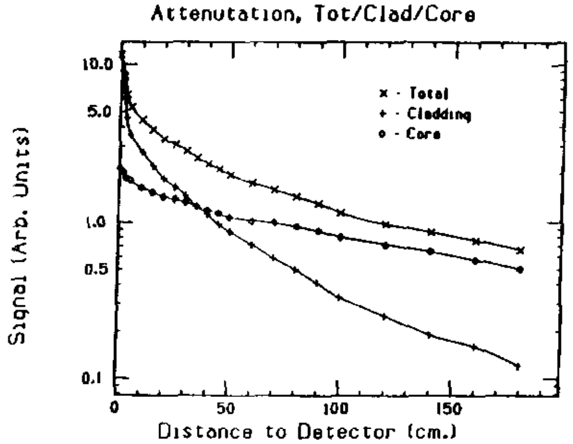

Figure 15: Attenuation data, signal versus distance, for core and cladding light in a 1 mm polystyrene scintillator core, acrylic clad fiber.

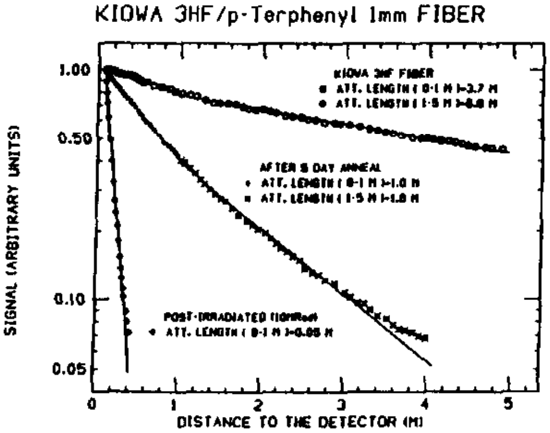

Figure 16: Attenuation data for p-terphenyl + 3HF fiber before, after a 10 Mrad dose, and after annealing.

Damage effects in scintillating optical fiber include degradation to the scintillator core, the polymer cladding, and possible core/cladding interface effects. Obviously, the effects described in Section 2 will also be present in the fiber. We should see both a drop in the intrinsic yield of the scintillator and a reduction in the attenuation length of fiber. Figure 16 shows data for a fiber that uses p-terphenyl and 3HF as the dopants in the polystyrene core. In this example, only changes in the attenuation length were measured. The sample was irradiated to a total dose of 10 Mrad in a Nitrogen atmosphere. The drop in attenuation length from 3.7 m to 1.0 m is not inconsistent with the spectroscopic measurements of Figure 8, where we were studying a bulk scintillator sample that was very similar to the material used for the core of this fiber. A 1 m attenuation length would correspond to approximately a 0.7%/cm transmittance loss. It appears that for this particular fiber the waveguide structure was not severely affected by the irradiation.

4 Conclusions

The light loss that was measured in the three test scintillators using beta excitation can be explained by polymer absorption in the wavelength region of p-terphenyl fluorescence (330–380 nm). This radiation-induced absorption then can effectively compete with the transfer between the p-terphenyl (the primary) and the secondary. The polymer absorption, as represented by the losses measured for the fluorescence intensity of the three secondaries under 350 nm excitation, can completely account for the light loss observed in the three test scintillators. Degradation of the dopants does not appear to be a major effect in this study. Attenuation length reductions seen for an irradiated p-terphenyl plus 3HF fiber seem to be consistent with the transmittance losses measured for bulk scintillator samples that are of similar composition to the fiber core material.

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