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FERMILAB-Pub-91/308

Radiation Damage of Plastic Scintillators

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November 1991

* Submitted to *Transactions on Nuclear Science.*

Operated by Universities Research Association Inc. under Contract No. DE-AC02-76CHO3000 with the United States Department of Energy

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Abstract

Radiation damage studies were performed on polystyrene-based plastic scintillators which contained p-terphenyl plus either BBQ, 3HF, or dimethyl-POPOP as dopants. Several identical sample sets were prepared to observe, in different experiments, the effects of dose rate (1 Mrad/h vs. 30 Krad/h) and environment (N_2 vs. Ar vs. H_2). Transmittance and light yield measurements performed before irradiation, after irradiation, and after an oxygen annealing period showed no significant differences in the radiation susceptibility of the scintillators under the different experimental conditions. Two additional multi-component sample sets were also prepared; one set was made using pure dopants and the other made utilizing pure dopants which had previously been exposed to large doses of γ-radiation. No difference in either transmittance or light yield was observed between the two sample sets. Simultaneously, radiation damage studies were carried out on pure polystyrene samples. Special emphasis was put on irradiations in oxygen and on the oxygen annealing process. These experiments indicated that: (a) Irradiations in which oxygen is continuously available throughout the bulk of the the polystyrene sample are the most damaging; (b) During the oxygen annealing process, the annealing rate is proportional to the oxygen diffusion rate; and (c) Oxygen reacts with free radicals in the sample, contributing to an increase in permanent radiation-induced absorption.

1 Introduction

Plastic scintillation detectors are currently among the most widely used particle detection devices in nuclear and high energy particle physics. Their fast response time makes them particularly attractive for instrumentation for experiments in high luminosity hadron colliders. In addition, their relatively low cost and ease of manufacture facilitates their use in numerous detector geometries. In fact, their utilization in future experiments may only be limited by their resistance to radiation damage. The results reported here are part of an ongoing project within the Fermilab Particle Detector Group and within the Solenoidal Detector Collaboration that focuses on the investigation and development of radiation resistant plastic scintillators.

Various studies have shown that the light yield in plastic scintillators decreases as their integrated exposure to ionizing radiation increases [1, 2, 3, 4]. This effect could be caused by either polymer or dopant degradation. Further research has indicated that most of the commonly used dopants do not degrade under irradiation, but that the polymer does [5, 6, 7]. Moreover, the radiation-induced damage in the polymer is more significant in the blue/violet spectral region where most standard plastic scintillators emit. In other words, the light emitted by the dopants is partially being reabsorbed by the polymer. One approach to reduce such light output losses is to use fluorescent compounds which emit in the green/yellow region of the visible spectrum where changes in polymer transmittance after irradiation are small [8, 9, 10]. Other possibilities for reduction of these losses include improvement of the polymer radiation resistance using additives to stabilise the material, or the utilisation of new polymers other than polystyrene and polyvinyltoluene [11].

This study aims to understand the degradation and annealing mechanisms in polystyrene in order to account for the losses in transmittance and light yield observed in polystyrene-based plastic scintillators.

2 Preparation of Scintillators

The fluorescent organic compounds utilised in this study used p-terphenyl (pT) as the primary dopant and either 7H-benzimidazo[2,1-a]benz[de]isoquinoline-7-one (BBQ), 3-hydroxyflavone (3HF), or 1,4-bis(4-methyl-5-phenyloxazol-2-yl)benzene (DMPOPOP) as the secondary dopant or wavelength shifter. The concentration of the dopants was of 1.25% by weight for pT, and 0.01% by weight for the wavelength shifters. pT was purchased from Bicron Corp. and used without further purification. The secondary dopants were available from Aldrich Chem. Co. 3HF and DMPOPOP were purified by recrystallisation from methylene chloride and hexane, while BBQ was purified by column chromatography through neutral alumina. After purification, some of each dopant was placed

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*Work supported by the U.S. Department of Energy under contract No. DE-AC02-76CHO3000.

in glass vials. Two sets were thus prepared. One set was irradiated to a total dose of 10 Mrad and the other to 100 Mrad, both at a rate of 1 Mrad/h. Plastic scintillator samples were made in the manner described below using both irradiated and non-irradiated dopants.

Styrene was first deinhibited through a column and then purified by vacuum distillation. The glass polymerization tubes were cleaned with nitric and sulfuric acids, rinsed with distilled water, and treated for about 4 h with a 30% solution of dimethyldichlorosilane in chloroform. Finally, they were rinsed in turn with chloroform, methanol, and distilled water. This treatment builds a hydrophobic Langmuir layer on the walls of the tube which enables the removal of the plastic after polymerization. Styrene and the dopants were then placed in the test tubes and degassed with repeated freeze-pump-thaw cycles. The solutions were polymerized in a silicone oil bath at 110°C–24h, 125°C–48h, 140°C–12h and then ramped down to 90°C at a rate of 10°C/h. After removal from the oil bath, the test tubes were quenched in liquid nitrogen for a fast release of the plastic rods. The rods were then cut and polished into discs of 2.2 cm diameter and 1 cm thick.

The samples for radiation damage studies were placed in stainless steel cans and then evacuated for a week to remove all moisture from the samples. The cans were then back-filled with either nitrogen, hydrogen, oxygen, or argon. All samples were irradiated using a ^{60}Co source at the Nuclear Reactor Laboratory of the University of Michigan, at a rate of either 1 Mrad/h (high dose rate) or 30 Krad/h (low dose rate) to a total dose of 10 Mrad. During the irradiation, the sample temperature did not change by more than 5 °C. After irradiation, the samples were annealed for two weeks at either room temperature in an oxygen atmosphere or 92 °C in a nitrogen atmosphere. The annealing process refers to the slow disappearance of the radiation-induced color in the samples.

Transmittance and fluorescence spectra were recorded with a Hewlett-Packard model 8451A diode array spectrophotometer. For all absorbance/transmittance measurements, pure polystyrene was used as the reference. The fluorescence spectra were measured using as the excitation source the 254-nm or 313-nm line from a mercury lamp. Light output measurements were taken using a ^{207}Bi beta source and a Hamamatsu R669 photomultiplier tube (PMT) as the photodetector. The scintillator discs were placed directly on the PMT using immersion oil for optical contact. The pulse height spectra were recorded with a LeCroy qVt multi-channel analyzer. The samples were measured before irradiation, immediately after irradiation, and after the above mentioned annealing period.

3 Results and Discussion

Plastic scintillator samples made from irradiated and non-irradiated dopants were exposed, in nitrogen, to a total dose of 10 Mrad using a dose rate of 1 Mrad/h. The light yield measurements are shown in Figure 1. Here we show the relative light yield of a sample made with irradiated dopants to an identical sample made with non-irradiated dopants. The zero dose to dopants data is, by definition, always equal to one. These data indicate that the scintillator samples fabricated using dopants that had been previously irradiated make scintillators of the same quality as those made with non-irradiated dopants. Among these scintillators, no significant difference in light output can be observed either before or after irradiation of the plastic scintillator sample. None of the dopants used in this study shows significant changes after even 100 Mrad doses; which is in agreement with previous results.

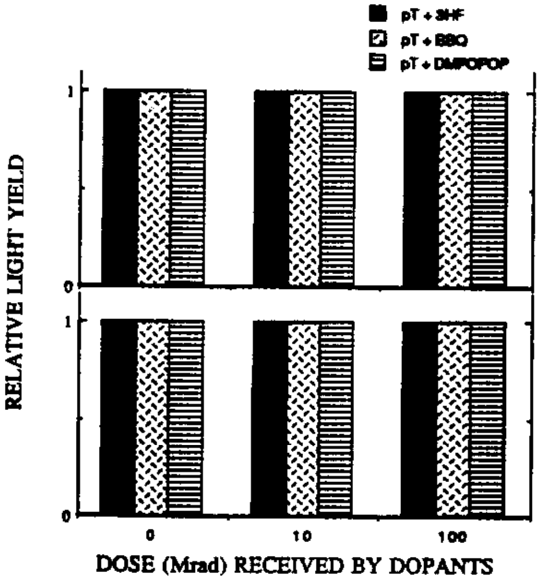

Figure 1. Relative light yield values for scintillator samples made of non-irradiated (0), irradiated to 10 Mrad (10), and irradiated to 100 Mrad (100) dopants. Bottom: before irradiation. Top: after annealing process.

After irradiation in nitrogen, polystyrene-based plastic scintillators exhibit a large amount of absorption at long wavelengths. However, much of this absorption is transient in nature and will disappear with time. The remaining absorption has been assigned to radiation-induced damage in the polystyrene matrix [5]. This damage results from reactions by free radicals in the polymer that were formed during irradiation. For polystyrene, the free radical most abundant at doses up to 10 Mrad is that formed by α-hydrogen abstraction in the polymer back-bone [12]. Irradiations of pure and doped polystyrene samples were carried out in hydrogen to observe if an excess of hydrogen atoms would favor the recombination of the α-radical with hydrogen, thus eliminating its side reactions to yield double bonds and crosslinks. As Figure 2 shows, there is no improvement in the radiation resistance of pure polystyrene samples when irradiated in hydrogen and, in fact, at short wavelengths the hydrogen atmosphere makes the induced absorption worse.

Figures 3–7 are representative of a radiation damage

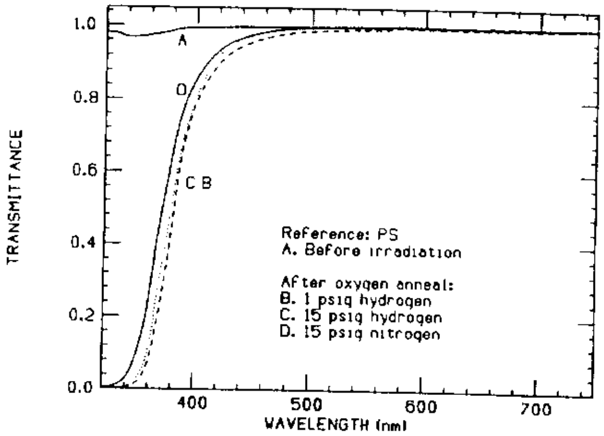

Figure 2. Transmittance spectra after the annealing process for pure polystyrene irradiated (10 Mrad) in different gases.

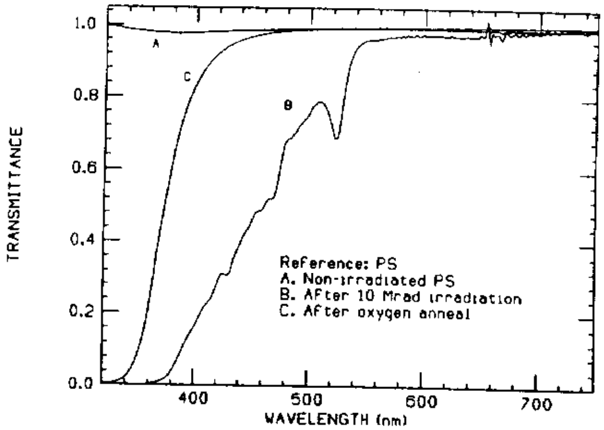

Figure 3. Transmittance spectra for pure polystyrene irradiated in nitrogen to a total dose of 10 Mrad at a 1 Mrad/h dose rate.

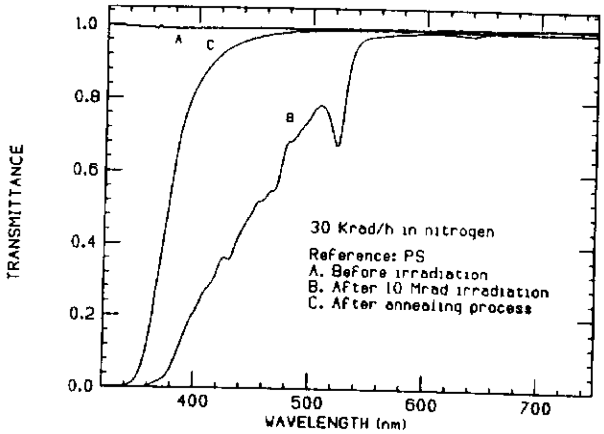

Figure 4. Transmittance spectra for pure polystyrene irradiated in nitrogen to a total dose of 10 Mrad at a 30 Krad/h dose rate.

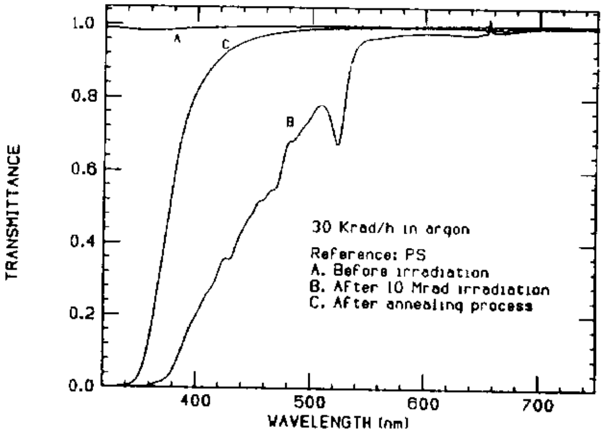

Figure 5. Transmittance spectra for pure polystyrene irradiated in argon to a total dose of 10 Mrad at a 30 Krad/h dose rate.

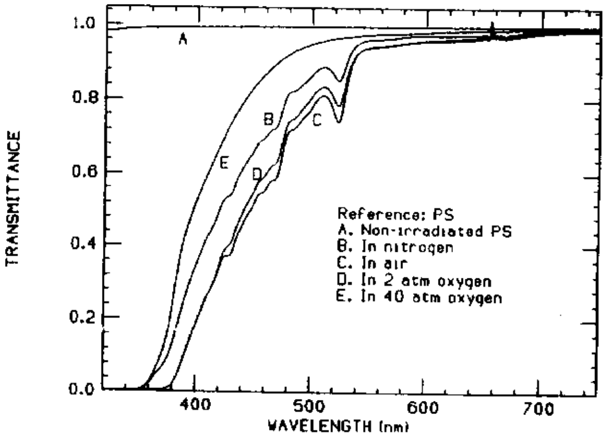

Figure 6. Transmittance spectra for pure polystyrene immediately after 10 Mrad irradiation.

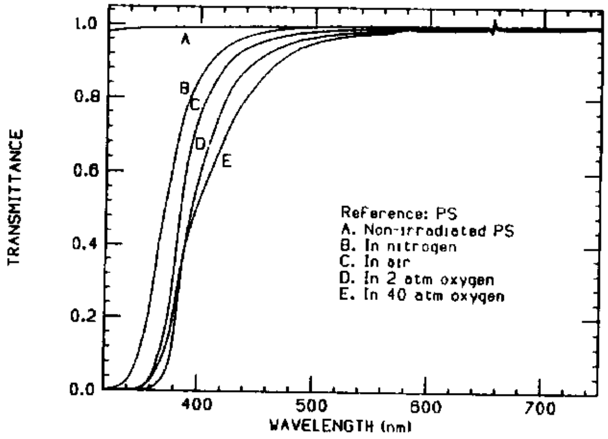

Figure 7. Transmittance spectra for pure polystyrene after the annealing period in oxygen.

study carried out to observe dose rate effects. Pure and doped polystyrene samples were irradiated to a total dose of 10 Mrad at either 1 Mrad/h or 30 Krad/h. These irradiations were performed both in nitrogen and in argon. As Figures 3–5 indicate, in inert atmosphere, there are no significant changes between high and low dose rates. These results confirm that the radiation-induced damage in plastic scintillators is proportional to the amount of oxygen available in the sample during irradiation, since oxygen can react with some of the species formed under irradiation. Therefore irradiations in air will show dose rate effects which are not present in irradiations in nitrogen or argon. Pure polystyrene samples were irradiated at 1 Mrad/h to a total dose of 10 Mrad in air (STP), in oxygen at 2 atm. absolute, and in oxygen at 40 atm. absolute. High dose rate irradiations in air or in nitrogen only differ in the oxidation products formed in air at the sample surfaces, since oxygen is consumed faster than it can diffuse into the sample. However, if oxygen is present throughout the sample during the irradiation, more oxidation products will be produced and these will decrease the sample transmittance. Figure 6 presents the transmittance data immediately after irradiation. At first glance, the irradiation under 40 atm. of oxygen shows less damage than the rest. However, the other samples have not yet annealed. Once the samples have been annealed in oxygen and only the permanent damage remains, we see that as the gas pressure of oxygen is increased (thereby increasing the oxygen concentration in the sample during irradiation), the larger are its transmittance losses (Figure 7).

The annealing effect refers to the process after irradiation by which most of the radiation-induced coloration in the scintillator sample disappears. This annealing process can be accelerated by either oxygen or heat. We have studied the oxygen annealing process in dry air and under pure oxygen (3 atm. and 22 atm.) by monitoring the disappearance of a radiation-induced fluorescent species in polystyrene. We have observed, in all irradiations of pure polystyrene, the formation of an absorption band at 525 nm, Figure 3. Exciting this species with 500 nm light yields a fluorescence band between 520 and 600 nm [3]. When the sample is placed in an oxygen atmosphere, however, diffusion of oxygen into the sample quenches this fluorescent species. Both the induced absorption band at 525 nm and this new green fluorescence band disappear. This phenomenon starts at the surface of the sample and propagates inward with an initial velocity of 10^{-5} mm/sec in air. We can then excite the sample under study with 500 nm light (313 nm light also excites this species quite strongly) and then measure the distance from the sample edge to the receding fluorescence volume as a function of time for the various annealing atmospheres, Figure 8. In all cases, the annealed distance is proportional to the square root of time (Figures 9–11). In other words, the annealing is proportional to the oxygen diffusion rate. These results disagree with those presented previously by Harmon *et al.* [13]. As Figures 9–11 indicate, the annealing process can

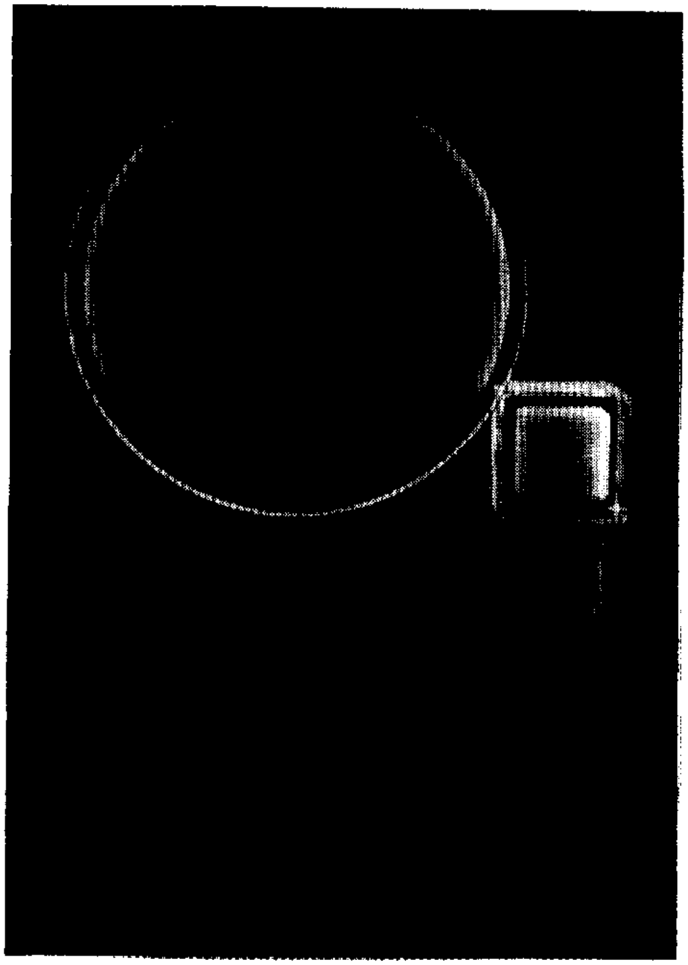

Figure 8. Fluorescence from partially annealed pure polystyrene samples excited with 313 nm light.

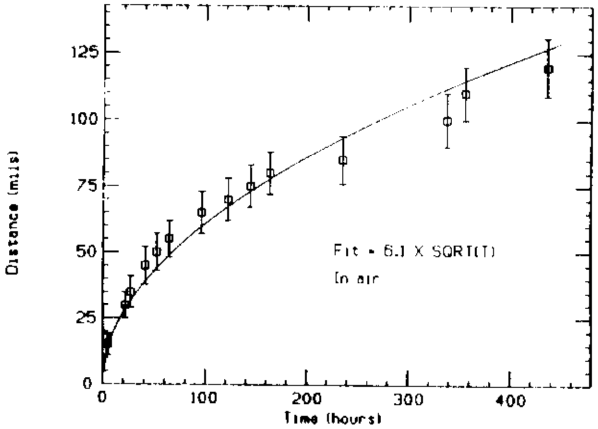

Figure 9. Annealing rate in air of a pure polystyrene sample after a 10 Mrad irradiation.

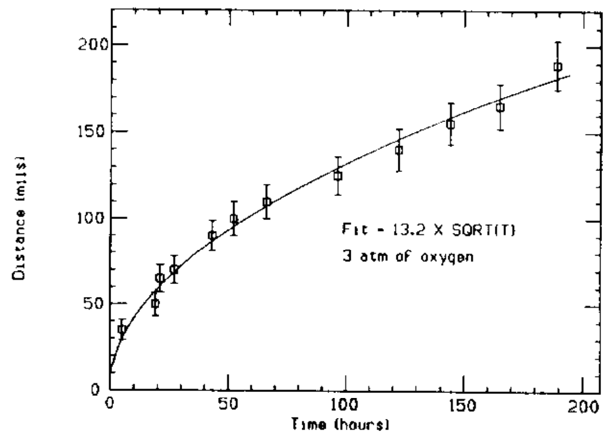

Figure 10. Annealing rate in 3 atm. of oxygen of a pure polystyrene sample after a 10 Mrad irradiation.

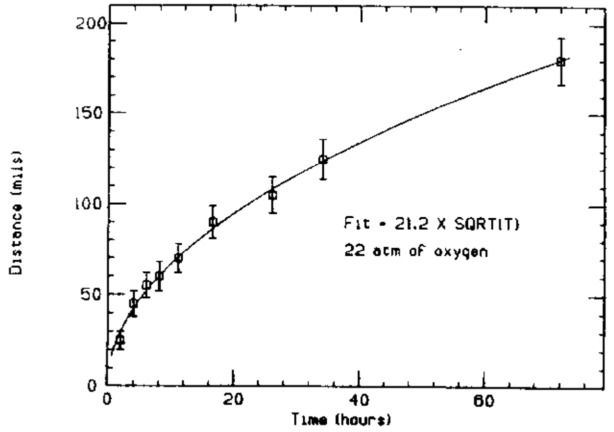

Figure 11. Annealing rate in 22 atm. of oxygen of a pure polystyrene sample after a 10 Mrad irradiation.

be accelerated by placing the samples under oxygen pressure. However, the annealing rate is not directly proportional to the oxygen pressure. This apparent discrepancy is likely caused by an oxygen solubility saturation effect in the sample.

Since the oxygen and thermal annealing processes should undergo different mechanisms, the final product should exhibit different characteristics. In the oxygen annealing process, oxygen will react with free radicals yielding oxidation products which should not be present in a thermally annealed sample. Two pure polystyrene samples have been irradiated in nitrogen to 10 Mrad and annealed, one by oxygen and the other by heat. This cycle has been performed four consecutive times to a total dose of 40 Mrad. After the first irradiation, there were no significant changes in transmittance between the two samples. The changes became more acute with the subsequent irradiations. After four cycles, the sample repeatedly annealed in oxygen absorbs more than that repeatedly annealed by heat (Figure 12).

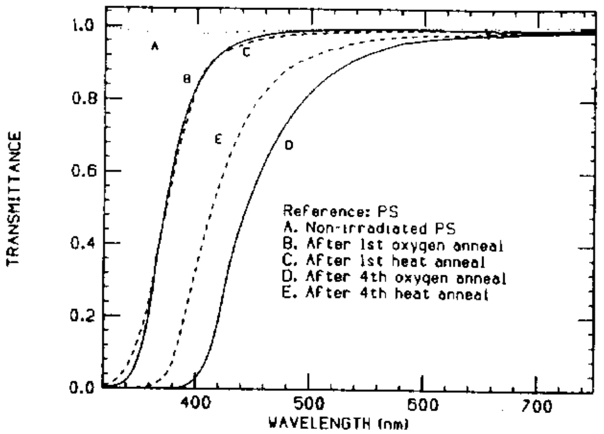

Figure 12. Transmittance spectra for pure polystyrene after several annealing processes by either oxygen or heat.

In order to study the lifetime of the radiation-induced transient absorption species in polystyrene, a sample was irradiated in nitrogen to 10 Mrad at high dose rate (1 Mrad/h). After irradiation, the sample was kept under nitrogen. Seven months later, a transmittance measurement of this sample indicated no change from the spectrum recorded immediately after irradiation. This transmittance spectrum (Figure 13) exhibits the same characteristics as those spectra recorded for other samples irradiated under similar conditions: a large absorption up to 400–450 nm and a small band at 525 nm. The sample was then placed under argon. The transmittance of this sample was measured again six weeks later. As shown in Figure 14, the transmittance spectrum has not changed. The annealing process at room temperature for 1 cm thick samples kept in either nitrogen or argon is extremely slow. In order to anneal a sample of this size in atmospherically inert conditions, the use of heat is required to both add mobility to the polymer chains and to overcome the en-

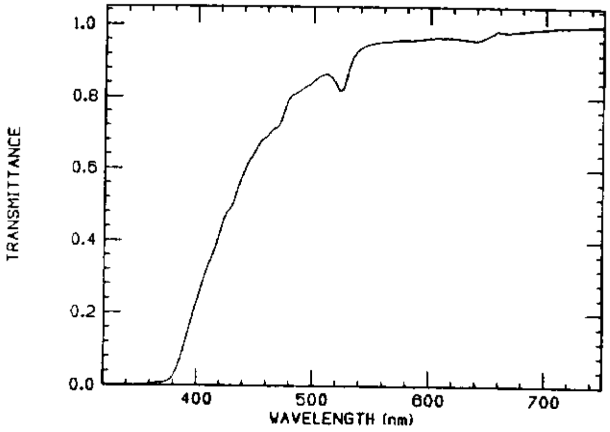

Figure 13. Transmittance spectrum for pure polystyrene kept in nitrogen for 7 months after its irradiation.

ergy barrier for the relaxation processes involved. Even at 90 °C, 1 cm thick samples require up to two weeks to anneal.

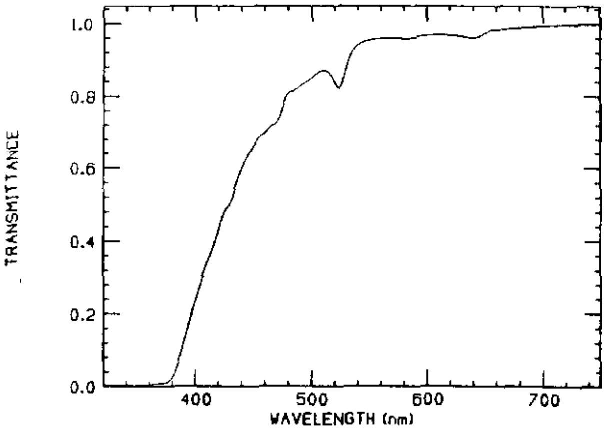

Figure 14. Transmittance spectrum for pure polystyrene kept in nitrogen for 7 months and then in argon for 6 weeks after its irradiation.

4 Conclusions

In the systems studied (pT+BBQ, pT+3HF, and pT+DMPOPOP), the light yield losses observed in irradiated samples are not due to dopant degradation, but to radiation-induced damage in the polystyrene matrix. The scintillator samples fabricated from irradiated dopants have the same light output as those from non-irradiated dopants. While no significant dose rate effects are observed in samples irradiated in inert atmosphere, pure polystyrene samples irradiated in air or oxygen at low dose rate will present larger transmittance losses than those irradiated at high dose rate. The oxygen annealing studies indicate that the annealing rate is proportional to the square root of time. Therefore this annealing process is dependent upon oxygen diffusion as expressed by the diffusion equation. The oxygen and thermal annealing studies show that oxygen reacts with radical species formed under irradiation as it diffuses into the sample. These oxidation products contain carbonyl and hydroxyl groups which absorb at longer wavelengths, thus decreasing the sample transmittance. A sample thermally annealed in nitrogen does not have oxidation products. After several irradiations, the thermally-annealed sample transmits more light than the oxygen-annealed one.

Acknowledgements

We thank C. W. Spangler of Northern Illinois University for many helpful discussions during these studies. We also wish to thank R. Blackburn of the Nuclear Reactor Laboratory of the University of Michigan for performing all sample irradiations. We extend our appreciation to N. Giokaris (Rockefeller University) and K. Johnson (Florida State University) for providing us with the dosimetry films for the low dose rate irradiations.

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