Fermi National Accelerator Laboratory

FERMILAB-Pub-92/184

Radiation Damage to 2-(2'-Hydroxyphenyl) Benzothiazoles

A.D. Bross and A. Pla-Dalmau

Fermi National Accelerator Laboratory
P.O. Box 500, Batavia, Illinois 60510

C.W. Spangler

Department of Chemistry
Northern Illinois University

July 1992

Submitted to *Radiation Physics and Chemistry*

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

Disclaimer

RADIATION DAMAGE TO 2-(2′-HYDROXYPHENYL)BENZOTHIAZOLES

A. D. Bross and A. Pla-Dalmau
Particle Detector Group
Fermi National Accelerator Laboratory
P. O. Box 500, Batavia, IL 60510, USA

C. W. Spangler
Department of Chemistry
Northern Illinois University, DeKalb, IL 60115, USA

ABSTRACT

The fluorescent organic compound 2-(2′-hydroxyphenyl)benzothiazole (HBT) has been modified by substitution at various positions of the phenyl ring in order to increase its quantum yield. Each derivative has been tested as a dopant in a polystyrene matrix for plastic scintillator applications. The transmittance, fluorescence, scintillation light yield, and radiation damage characteristics of these compounds in polystyrene have been determined. In addition, a comparative study of the HBT derivatives and 3-hydroxyflavone (3HF) has been performed. Only samples doped with the 4CNHBT derivative exhibit light yield and radiation resistance similar to those doped with 3HF.

KEYWORDS

Plastic Scintillators; Polystyrene; Phenylbenzothiazoles; Radiation Damage.

INTRODUCTION

Plastic scintillators have been used as particle detection devices in nuclear and high energy particle physics for many years. However, only recently was attention focused on preparing highly-efficient plastic scintillators with short decay times and excellent resistance to radiation damage. The results reported here are part of an ongoing project that focuses on the investigation and development of radiation resistant plastic scintillators.

Standard plastic scintillators consist of a polymer matrix such as polystyrene doped with one or two fluorescent organic compounds referred to as the primary dopant and the secondary dopant or wavelength shifter. Ionizing particles passing through the scintillator excite polymer molecules which, in turn, can transfer energy to the primary dopant through the Förster mechanism. The energy is then transferred to the secondary dopant through the emission and reabsorption of a photon (Birks, 1964). Such plastic scintillators commonly emit in the blue violet region of the light spectrum. This spectral region is affected by radiation-induced damage in the polystyrene matrix which is manifested by an absorption increase or coloring in the polymer. This absorption will cause a decrease in the light yield of the scintillator after its exposure to ionizing radiation (Zorn, 1992). Intrinsic plastic scintillators consist of a polystyrene matrix that is doped with a single fluorescent organic compound. This fluorescent compound functions as both primary and secondary dopant. In order to be used as a dopant, this compound should exhibit a large spectral shift between absorption and emission spectra (Bross, 1990). These plastic scintillators emit in the green/yellow region of the visible spectrum, therefore, they are less susceptible to light yield losses due to new radiation-induced absorptions in the polymer.

Fluorescent organic compounds such as 3-hydroxyflavone (3HF) and 2-(2'-hydroxyphenyl)-benzothiazole (HBT), when excited by UV or ionizing radiation undergo an excited-state intramolecular proton transfer (ESIPT). This process yields a large separation between absorption and emission spectra. Since these two compounds have absorption and emission peaks at approximately 350 nm and 530 nm respectively, they were among the first materials tested as dopants for intrinsic plastic scintillators. The main drawback is that the light output of these two compounds is lower than that of the blue-emitting compounds.

Several 3HF and HBT derivatives were prepared in the search for an intrinsic scintillator with both high light yield and emission at long wavelength. In order to achieve these goals, the 3HF and HBT structures were modified by addition of different substituents to the phenyl ring (Pla-Dalmau, 1990; Bross *et al*, 1992). The spectroscopic characteristics and radiation damage properties of a series of HBT derivatives are reported herein. Figure 1 and Table 1 present the list of HBT derivatives studied and their corresponding substitution pattern. These compounds have mostly been investigated as intrinsic plastic scintillators. Nevertheless, data on studies as wavelength shifters in standard scintillator systems are also included. In addition, the new HBT scintillators are compared to 3HF-doped scintillators which are widely used green-emitting scintillators.

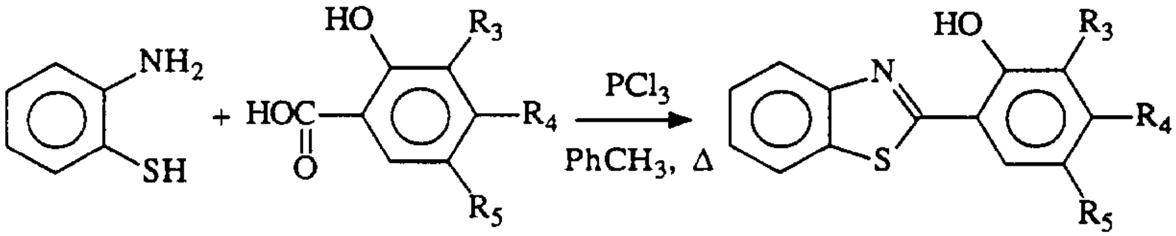

Figure 1. Substitution pattern in HBT.

Table 1. List of HBT derivatives studied.

R_3	R_4	R_5	Name	Description
H	H	H	HBT[a]	2-(2′-hydroxyphenyl)benzothiazole
Cl	H	H	3CHBT	2-(2′-hydroxy-3′-chlorophenyl)benzothiazole
F	H	H	3FHBT	2-(2′-hydroxy-3′-fluorophenyl)benzothiazole
Ph	H	H	3PHBT	2-(2′-hydroxy-3′-biphenyl)benzothiazole
H	CN	H	4CNHBT[b]	2-(2′-hydroxy-4′-cyanophenyl)benzothiazole
H	Me	H	4MHBT[c]	2-(2′-hydroxy-4′-methylphenyl)benzothiazole
H	H	Cl	5CHBT	2-(2′-hydroxy-5′-chlorophenyl)benzothiazole
H	H	Me	5MHBT[c]	2-(2′-hydroxy-5′-methylphenyl)benzothiazole
H	H	Ph	5PHBT	2-(4′-hydroxy-3′-biphenyl)benzothiazole

[a] Available from Polysciences. [b] Synthesized by C. J. Kelley and R. Pai. [c] Available from Frinton.

EXPERIMENTAL SECTION

Sample Preparation

Styrene was first deinhibited by passage through a chromatography column available from Aldrich Chemical Co. and then purified by vacuum distillation. Glass polymerization tubes were cleaned with nitric and sulfuric acids, rinsed with distilled water, and then treated for about 4 hours with a 30% solution of dichlorodimethylsilane 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. Appropriate dopants were then added to the polymerization tubes filled with purified styrene and the various solutions degassed with repeated freeze-pump-thaw cycles. The solutions were polymerized in a silicone oil bath at 110 °C for 24 hours, at 125 °C for 48 hours, and finally at 140 °C for 12 hours. The bath temperature was then ramped down to 90 °C at a rate of 10 °C/h. After removal from the oil bath, the 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.

Fluorescent Compounds

The parent compound, 2-(2′-hydroxyphenyl)benzothiazole (HBT), and two derivatives, 2-(2′-hydroxy-4′-methylphenyl)benzothiazole (4MHBT) and 2-(2′-hydroxy-5′-methylphenyl)benzothiazole (5MHBT) were purchased from Frinton and further purified by sublimation. 2-(2′-Hydroxy-4′-cyanophenyl)benzothiazole (4CNHBT) was prepared at Massachusetts College of Pharmacy and Allied Health Sciences (Pai, in preparation). The remaining derivatives were prepared in our laboratory using a modification of the procedure described by Williams and Heller (1970) and Anthony *et al.* (1984). Equimolar amounts of 2-aminothiophenol and the corresponding salicylic acid derivative were dissolved in dry toluene in a flask provided with mechanical stirring. The solution was warmed to 40 °C and an equimolar amount of phosphorous trichloride was added dropwise to the reaction mixture. The solution was heated to 100 °C for 6–8 hours, and then cooled to room temperature. The reaction mixture was extracted several times with a 20% by weight sodium carbonate solution, washed with distilled water, and then dried over magnesium sulfate. Evaporation of the solvent produced a solid residue which was purified by flash chromatography through silica gel. The color of each derivative ranged from white to slightly yellow depending upon the nature and position of the substituent in the phenyl ring. The purity of each derivative was verified using spectroscopic techniques (nuclear magnetic resonance: ^{1}H NMR and ^{13}C NMR) and melting point determinations. The absorbance and fluorescence properties of the derivatives were characterized. Elemental analyses (C, H) were performed for 3FHBT, 3PHBT, and 5PHBT since they had not been previously reported in the literature. The HBT derivatives were used as dopants for intrinsic plastic scintillators in a 1% by weight concentration to ensure optimum coupling with polystyrene and as wavelength shifters for standard scintillator systems at a 0.01% by weight concentration. In the latter case, p-terphenyl was used as the primary dopant at a 1.25% by weight concentration. In order to determine the absorptivity coefficients, dilute solutions (10^{-4} M, M $\equiv$ $mol/Liter$) of HBT and each derivative in polystyrene were prepared. Table 2 depicts the photophysical characteristics of HBT and its derivatives.

Table 2. Photophysical characteristics of HBT and its derivatives in a polystyrene matrix.

Compound[a]	λ^b_{max} (nm)	λ^c_{em} (nm)	ε^d (L mol^{-1} cm^{-1})	Relative[e] Quantum Yield
HBT	340	530	14000	1.0
3CHBT	344	540	6000	1.64
3FHBT	340	540	23000	0.93
3PHBT	350	560	10000	1.17
4CNHBT	350	530	20000[f]	2.45
4MHBT	340	530	11000	1.03
5CHBT	350	545	16000	1.64
5MHBT	346	550	15000	0.92
5PHBT	355	560	10000	1.52

[a]The concentration of the derivatives in polystyrene is 1% by weight for these samples. [b]Maximum absorption wavelength. [c]Maximum emission wavelength. [d]Absorptivity coefficient (from low concentration samples). [e]Quantum yield values relative to HBT. [f]In styrene solution.

Irradiations

The samples for radiation damage studies were placed in stainless steel cans and then evacuated for two weeks to remove all moisture and most dissolved gas from the samples. The cans were then back-filled with dry nitrogen. All samples were irradiated with a ^{60}Co source at the Nuclear Reactor Laboratory of the University of Michigan at a rate of approximately 1 Mrad/h to a total dose of 10 Mrad. During the irradiations, the sample temperature was held constant to approximately 5 °C. All the samples developed some coloration during the exposure, some of which disappeared with time when the samples were exposed to oxygen. For this study, the samples were kept under a 40 psig. oxygen atmosphere for 10 days after their irradiation.

Transmittance and Fluorescence Spectra

Transmittance and fluorescence spectra were recorded with a Hewlett-Packard model 8451A diode array spectrophotometer. All transmittance measurements used pure (undoped) polystyrene as the reference. The fluorescence spectra were measured using an external Hg lamp whose light was brought into the spectrophotometer by means of a quartz fiber. An excitation wavelength of 313 nm or 450 nm could be selected with the use of bandpass filters. For these measurements, the quartz fiber was positioned so that the UV light excited the sample surface facing the spectrophotometer optics. In this case, the fluorescence is viewed directly, not through the sample. The angle of incidence was 45°. The measurements using the 313-nm excitation wavelength were made in order to calculate the fluorescence of each dopant relative to that of HBT, since at these excitation wavelengths polystyrene does not absorb. The 450-nm excitation wavelength was used to observe fluorescence from new radiation-induced absorption bands in some of the HBT derivatives.

Light yield measurements

Scintillators doped with HBT, 4CNHBT, and 3HF were excited by 1 MeV conversion electrons from a ^{207}Bi source. The scintillation light yield measurements used a Hamamatsu R669 photomultiplier as the photo-detector. This PMT has a relatively constant quantum efficiency from 430 nm to 600 nm. An optical cone of polymethylmethacrylate was used as adapter to couple the scintillator disc to the PMT. Immersion oil for optical contact was used between the cone and the disc. The pulse height spectra were recorded with a LeCroy qVt multi-channel analyzer and then light yield values obtained from these measurements were corrected for the quantum efficiency variations of the photomultiplier tube over the fluorescence wavelength region of the scintillator studied.

RESULTS AND DISCUSSION

Because of an intramolecular proton transfer process (Fig. 2), HBT exhibits a large separation between its absorption and emission spectra (Cohen and Flavian, 1967; Barbara *et al.*, 1980). The proton transfer causes a structural rearrangement, which is indicated by the large separation between the absorption and fluorescence bands.

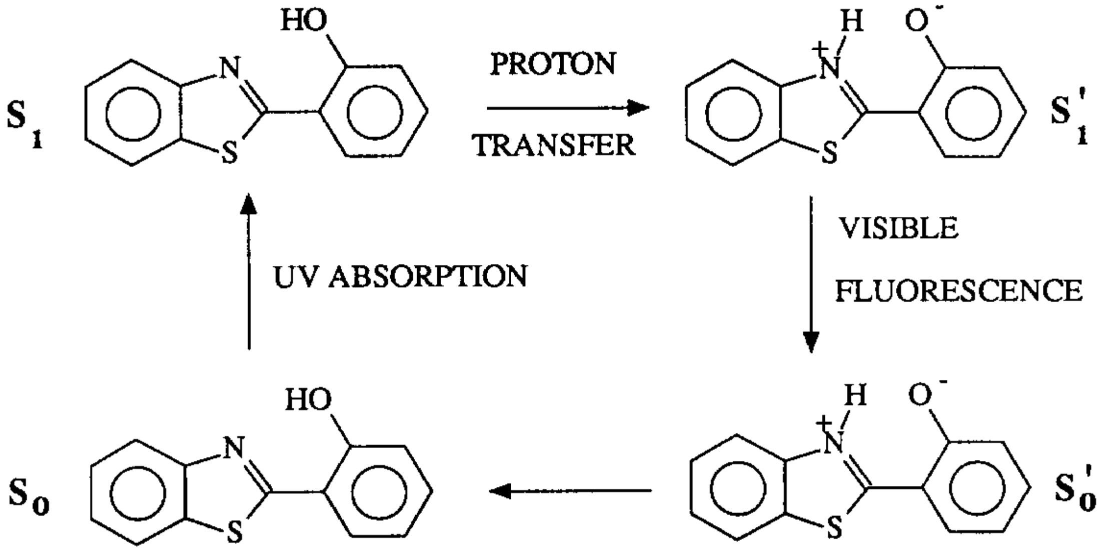

Figure 2. Excited-state intramolecular proton transfer process.

The proton transfer in the excited state is favored because of an increase in the N basicity and the O acidity in the excited state and, in addition, it is aided by a pre-existing hydrogen bond. HBT absorbs at approximately 340 nm and fluoresces at 530 nm in polystyrene. The quantum yield of HBT varies considerably from measurements in solution (1.5±0.5% in tetrachloroethylene (Elsaesser and Kaiser, 1986)) in the solid (31% (Williams and Heller, 1970) and 38% (Anthony *et al.*, 1984)), and no data are available for its quantum yield in polystyrene. Relative quantum yield measurements performed at Fermilab, considering the area underneath the fluorescence curve, indicated that the quantum yield is larger in polystyrene than in an ethanol solution. However, it can be expected that the quantum yield in polystyrene will not be larger than that in the solid phase where, because of the crystalline structure, vibrations and rotations are more restricted than in a polymer matrix. Substitution in the 2-phenyl ring was studied as a way to increase the quantum yield of HBT. Initially electron-withdrawing groups in the third and fifth position were considered, for they would mesomerically stabilize the negative charge formed after proton transfer (Fig. 2). Large substituents were also studied because they favor certain conformations and tend to freeze some rotational and vibrational modes, thus decreasing the non-radiative relaxation of the compound. Only two substituents were placed in the fourth position. As presented in Table 2, substitution does not significantly alter the magnitude of the Stokes shift. For instance, the phenyl group shifts both the absorption and fluorescence towards longer wavelengths, thus maintaining the Stokes shift at approximately the same value. With the exception of the cyano group, the other substituents have little effect towards significantly increasing the quantum yield of the compound.

Radiation damage studies were performed on these scintillator samples. In the first test, they were irradiated to a total dose of 1 Mrad in a nitrogen atmosphere. Transmittance and fluorescence measurements were recorded before, immediately after, and two weeks after irradiation. All samples presented an increase in absorption immediately after irradiation which partially disappeared after the annealing process in oxygen. However, with the exception of the 4CNHBT, all samples showed the formation of a new absorption band at longer wavelengths. New HBT and 4CNHBT scintillator samples were prepared and irradiated to two different doses (10 and 50 Mrad). Figure 3 shows the changes in transmittance for two irradiated HBT samples. Immediately after irradiation, both samples present a large absorption which is partially annealable. However, after the annealing period in oxygen both samples show the formation of a new absorption band at longer wavelengths. Fluorescence measurements were carried out using a 450-nm excitation wavelength. Figure 4 indicates that no fluorescence is observed before irradiation using this long wavelength excitation. Nonetheless, a significant emission was recorded from both samples after the annealing period.

This radiation-induced absorption band does not disappear over an extended oxygen annealing period or under usual sample handling procedures after irradiation. However, studies carried out by Kang *et al.*, 1988; showed that this second absorption band could be bleached out under certain specific conditions. The formation of this second absorption band can be explained by considering all possible HBT conformers (Fig. 5). The ionic enol form presents cis- and trans-ionic enol forms through rotation around the σ-bond. These forms, in turn, can be represented as cis- and trans-keto or quinoid forms. Based on the current results, it can be understood that some trans-keto isomer will be formed in high radiation environments. The molecules remain locked in that conformation until enough energy is provided to overcome the energy barrier to go back to the cis-ionic form. For instance, if the HBT scintillator sample is heated to 90 °C and left overnight at this temperature, this absorption band will disappear.

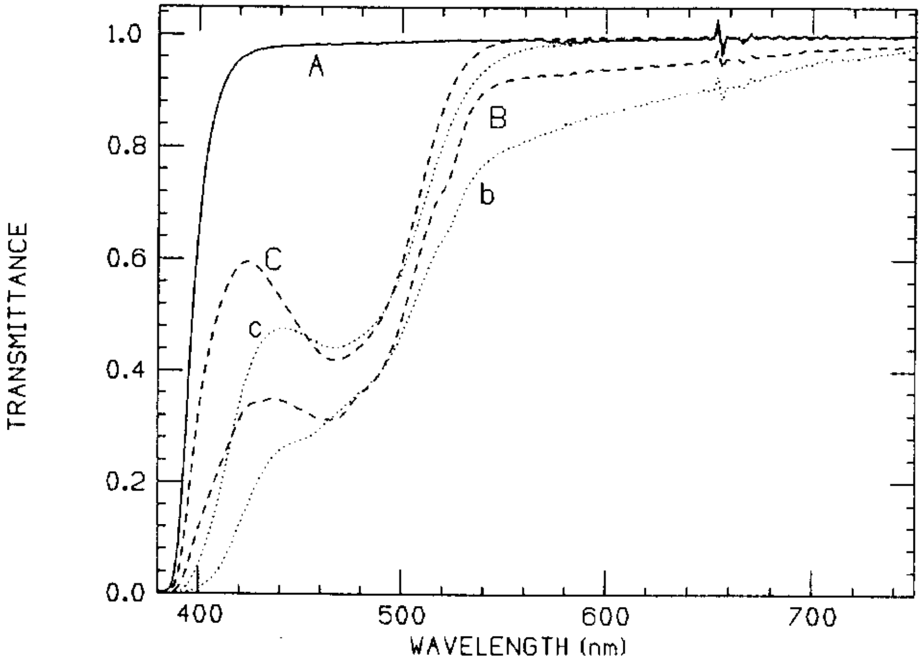

Figure 3. Transmittance spectra for 1% HBT in polystyrene scintillator samples irradiated at 10 Mrad (B, C)and 50 Mrad (b, c): before (A), immediately after (B, b), and two weeks after irradiation (C, c).

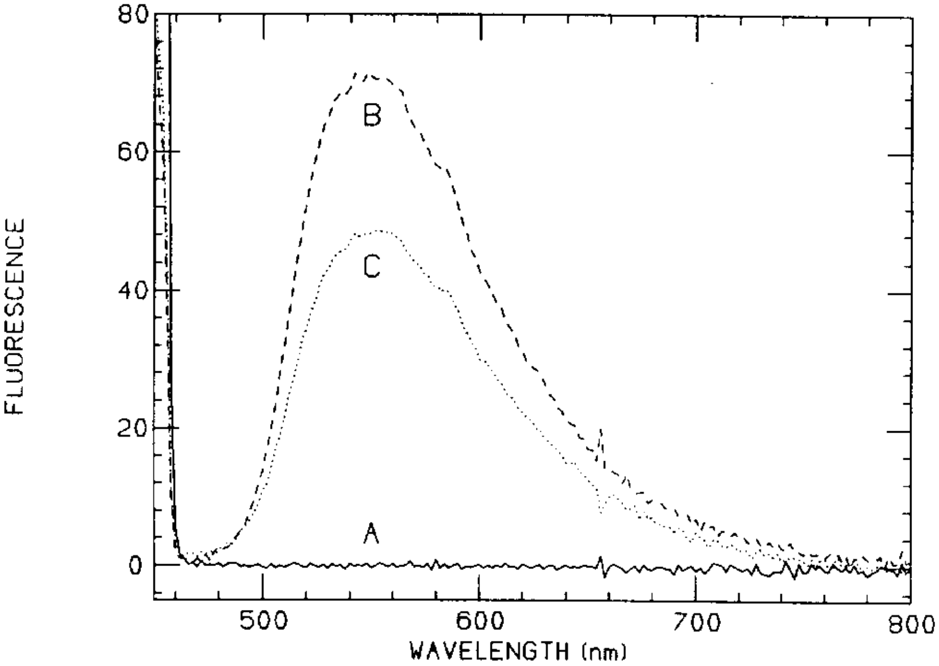

Figure 4. Fluorescence spectra using 450-nm excitation wavelength for 1% HBT in polystyrene scintillator samples: before (A) and two weeks after irradiation (B, 10 Mrad and C, 50 Mrad).

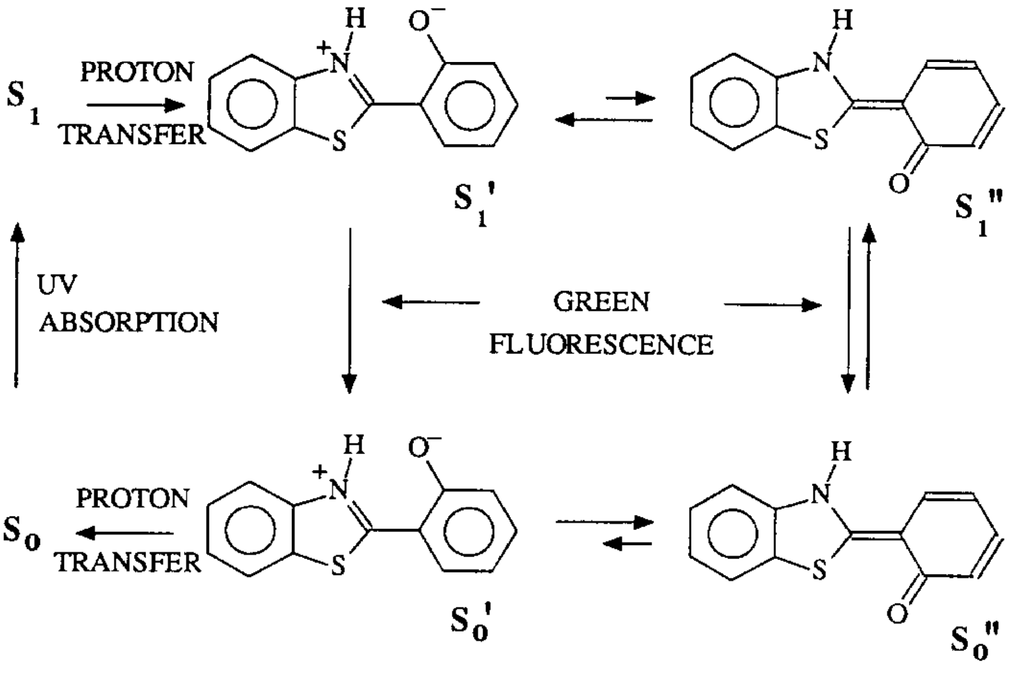

Figure 5. Formation of the trans-keto HBT isomer.

The samples doped with 4CNHBT were also irradiated at 10 and 50 Mrad. Transmittance and fluorescence measurements were performed before, immediately after and two weeks after the respective irradiations (Figs. 6 and 7). The 4CNHBT derivative does not present the formation of a second absorption band at longer wavelengths. Of all the HBT derivatives tested, this is the only one that does not behave as the parent compound. The 4CNHBT derivative presents a resonant form that the other compounds can not (Fig. 8). This new form introduces a certain restriction to the σ-bond rotation.

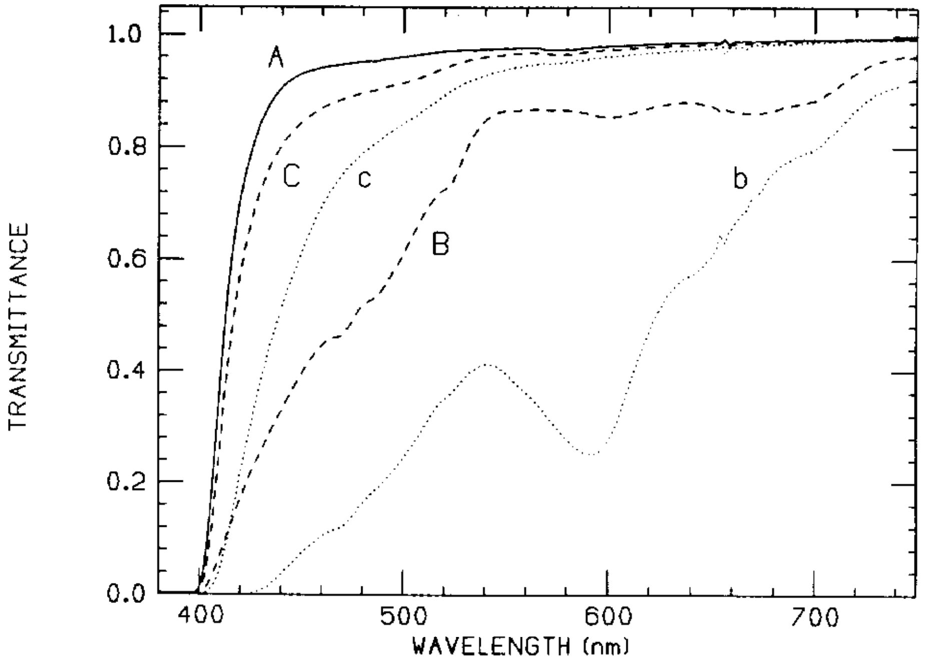

Figure 6. Transmittance spectra for 1% 4CNHBT in polystyrene scintillator samples irradiated at 10 Mrad (B, C) and 50 Mrad (b, c): before (A), immediately after (B, b), and two weeks after irradiation (C, c).

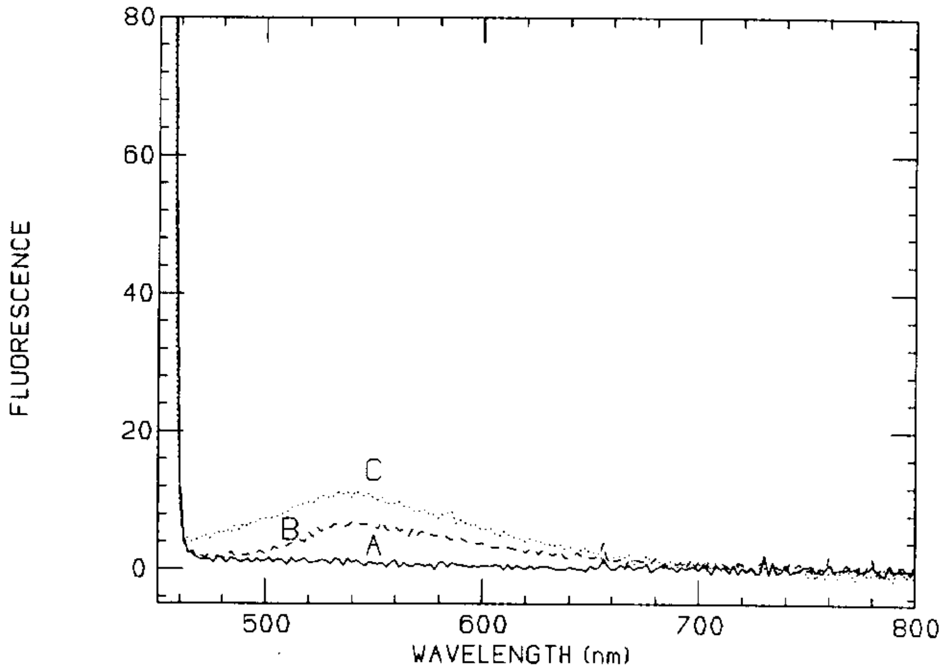

Figure 7. Fluorescence spectra using 450-nm excitation wavelength for 1% 4CNHBT in polystyrene scintillator samples: before (A) and two weeks after irradiation (B, 10 Mrad and C, 50 Mrad).

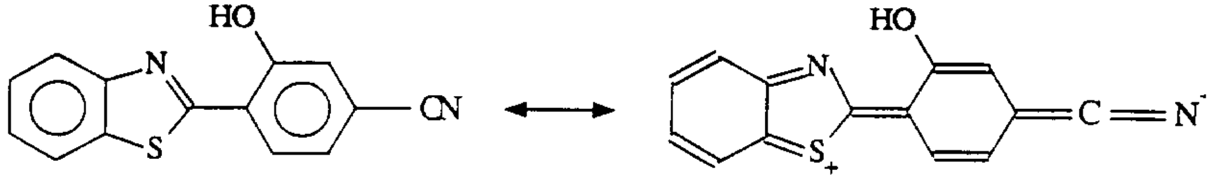

Figure 8. A different resonant contribution in 4CNHBT.

Among the HBT derivatives tested, only the 4CNHBT derivative presents an improvement in quantum yield and radiation resistance. In fact, 4CNHBT has characteristics similar to those of 3HF which is probably the most widely used green-emitting dopant in plastic scintillation applications. The 4CNHBT derivative can also be used as a secondary dopant. Table 3 lists the decay time and relative quantum yield of 3HF, HBT, and 4CNHBT in both intrinsic and ternary scintillators.

Table 3. Decay time and relative light yield of polystyrene-based scintillators containing HBT, 4CNHBT, or 3HF.

Scintillator[a]	Decay time τ (ns)	Light yield[b] ^{207}Bi β-source	UV 313 nm
1% HBT	3.90±0.2	1	1
1% 4CNHBT	6.47±0.2	2.31	2.45
0.75% 3HF	8.77±0.2	2.35	2.50
1.25% PT + 0.01% HBT	3.87±0.2	1.13	-
1.25% PT + 0.01% 4CNHBT	6.83±0.2	2.07	-
1.25% PT + 0.01% 3HF	7.88±0.2	2.35	-

[a]Concentration of the derivatives is in percent by weight. [b]Light yield results using different excitation sources are relative to HBT. The experimental error in these measurements is ±5%.

CONCLUSIONS

HBT is not a suitable compound for many scintillation detector applications because of its low light yield and the formation, under radiation, of an isomer which induces a new absorption band. The latter is a more severe effect in intrinsic plastic scintillators where HBT is used in high concentration. The HBT derivatives studied exhibit the same characteristics of the parent compound and, therefore, the same disadvantages. The only exception is the 4CNHBT derivative. The 4CNHBT derivative has significantly higher light output and does not form the trans-keto isomer under radiation. In comparison to 3HF, the 4CNHBT derivative gives similar light output and radiation resistance, and has a faster decay time (6.5±0.2 ns at 1% by weight concentration and 6.8±0.2 ns at 0.01% by weight concentration). Although 3HF remains a good candidate for plastic scintillation applications, 4CNHBT may become a better dopant for both intrinsic and standard plastic scintillators once its long-term photostability and oxidation resistance properties become known.

ACKNOWLEDGEMENTS

We thank Fermilab and Northern Illinois University for their financial support. The work performed at Fermilab was supported by the U.S. Department of Energy under contract No. DE-AC02-76CHO3000. We wish to extend our appreciation to C. J. Kelley and R. Pai for providing us with the 4CNHBT derivative. The synthesis of this compound forms part of R. Pai's Ph.D. research project.

REFERENCES

Anthony, K., R. G. Brown, J. D. Hepworth, K. W. Hodgson, B. May and M. A. West (1984) Solid-state fluorescent photophysics of some 2-substituted benzothiazoles. *J. Chem. Soc. Perkin Trans. 2*, 2111.

Barbara, P. F., L. E. Brus and P. M. Rentzepis (1980) Intramolecular proton transfer and excited-state relaxation in 2-(2-hydroxyphenyl)benzothiazole. *J. Am. Chem. Soc.*, 102, 5631.

Birks, J. B. (1964) *The Theory and Practice of Scintillation Counting*, Pergamon Press, The MacMillan Co., New York.

Bross, A. D. (1990) Development of intrinsic IPT scintillator. *Nucl. Instr. Meth.*, A235, 315.

Bross, A. D., A. Pla-Dalmau and C. W. Spangler (1992) New fluorescent compounds for plastic scintillator applications. *Nucl. Instr. Meth.*, submitted.

Cohen, M. D. and S. Flavian (1967) Topochemistry. Part XXIV. The luminescence properties of N-salicylideneaniline and related anils in solution. *J. Chem. Soc. (B)*, 317.

Elsaesser, T. and W. Kaiser (1986) Visible and infrared spectroscopy of intramolecular proton transfer using picosecond laser pulses. *Chem. Phys. Lett.*, 128, 231.

Kang, T. J., P. F. Barbara, A. Pla-Dalmau and A. D. Bross (1988) *Proceedings of the Workshop on Scintillator Fiber Detector Development for the SSC.* Fermi National Accelerator Laboratory, Batavia, IL, pp. 769–782.

Pai, R. (in preparation) Massachusetts College of Pharmacy and Allied Health Sciences, Boston, MA, Ph.D. Dissertation.

Pla-Dalmau, A. (1990) *Design of Fluorescent Compounds for Scintillation Detection*, Northern Illinois University, DeKalb, IL, Ph.D. Dissertation.

Williams, D. L. and A. Heller (1970) Intramolecular proton transfer reactions in excited fluorescent compounds. *J. Phys. Chem.*, 74, 4473.

Zorn, C. (1992) Fast scintillators for high radiation levels. Part II: Plastic and liquid organic scintillators. In: *Instrumentation in high energy physics* (F. Sauli, ed.) World Scientific Publishing Co. Pte. Ltd. In press.