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# SEARCHING FOR NEW GREEN WAVELENGTH SHIFTERS IN POLYSTYRENE

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## ABSTRACT

A series of commercially available fluorescent compounds was tested as wavelength shifters in polystyrene for the tile/fiber SDC calorimeter. The objective was to find a green-fluorescing compound with short decay time (3–7 ns). Transmittance, fluorescence, and decay time measurements were performed in order to characterize each compound in polystyrene. These samples were also studied for radiation-induced damage.

## 1. Introduction

A scintillating tile/fiber design has been selected for the SDC calorimeter. It consists of scintillator plates embedded with a wavelength shifting (WLS) fiber which is spliced to a clear fiber. In order for this system to perform properly, the absorption spectrum of the WLS fiber must match the emission spectrum of the scintillating tile. Based on the results from previous radiation damage studies on different scintillating materials, SCSN38 has been chosen for the scintillating tile and BCF91 or Y7 for the WLS fiber. SCSN38 is a blue-emitting scintillator. (SCSN38 and SCSN81 were both tested with similar results.) Both WLS fibers use K-27, a green-emitting compound, as dopant. K-27 has a decay time of approximately 12 ns which is long in comparison to that of most blue-emitting materials (2–3 ns). Of all the factors that affect the speed of the scintillator tile/fiber calorimeter, the lifetime of the green-emitting dopant is the dominant component. To increase the speed of the calorimeter, it would be desirable that the green WLS fibers utilized had lifetimes between 3–5 ns. However, currently available green WLS fibers exhibit decay times between 7–12 ns. Development of new green-emitting WLS fibers with short decay times must be investigated.

The goal of this project is to search for commercially available fluorescent compounds with  $\lambda_{abs}=400-450$  nm,  $\lambda_{em}=450-550$  nm,  $\tau=3-7$  ns, and quantum efficiency of minimum 0.7 (current K-27 baseline). Large Stokes shift and low self-absorption are not important requirements since the optical pathlength for the shifted light is small. Characterization of the fluorescence properties of these compounds after styrene polymerization is important since this is an essential part of

the manufacturing of WLS fibers.

## 2. Experimental Section

All fluorescent compounds meeting the specifications listed above were purchased from Aldrich, Exciton, Lambda Physics, and Eastman Kodak. Polystyrene samples with a 0.02% (by weight) dopant concentration were prepared following the procedure previously described [1]. Transmittance, fluorescence, and decay time determinations were performed using samples of 2.2-cm diameter and 1-cm thick. The setup for the decay time measurements is depicted in Figure 1. Radiation damage studies were carried out using a  $^{60}\text{Co}$  source. The samples were irradiated in air to a total dose of 10 Mrad and at a dose rate of 1 Mrad/h.

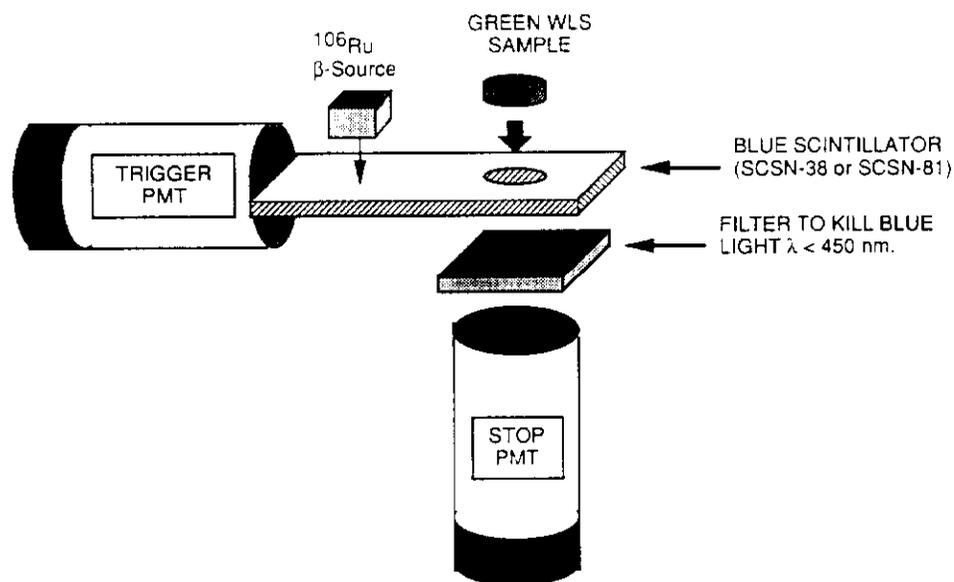


Figure 1. Scheme of the decay time determination setup.

## 3. Results and Discussion

Approximately 80 different fluorescent compounds were tested. The compounds considered belonged to a wide range of chemical families such as coumarins, rhodamins, stilbenes, fluoresceins, cyanines, and acridines, among others. Absorption and emission data were available for many of these compounds since they are often utilized as laser dyes. This information was used to select the compounds matching the absorption and emission wavelength range of interest for this project. Nevertheless, these data present an important drawback since they are based on measurements recorded in polar solvents such as methanol and DMSO. Because

polystyrene is not as polar as those solvents, shifts towards shorter wavelengths in the absorption and fluorescence spectra should be expected, in addition to changes in the emission lifetimes.

A few compounds such as bis-MSB and DMPOPOP which emit in the blue region of the visible spectrum, were included as reference to check our instrumentation since they were already well characterized in polystyrene. Samples doped with K-27 were prepared, characterized, and used as baseline in the measurements of the other compounds, for the current green WLS fibers are based on K-27.

Many compounds were eliminated as possible candidates after the styrene polymerization. Simple visual observations indicated that some dopants were reacting during polymerization. In such cases, the final samples exhibited little or no fluorescence. Other compounds presented solubility problems since they had an ionic character. A crown-ether was added to enhance their solubility. However, these samples also showed little fluorescence. Due to solvent effects, some compounds gave rise to blue-emitting WLS samples although they had a green emission in polar solvents. Among the compounds tested, coumarins seemed to be the most likely candidates to outperform K-27. Table 1 presents the spectroscopic characteristics of these dopants relative to those of K-27. Coumarins were easily dissolved in styrene and stable during polymerization. Some coumarins listed in Table 1 emit between 420–450 nm which is below the targeted wavelength range. But the majority of the compounds fluoresce in the desired region. Several coumarins show higher light output and shorter lifetime than K-27. Nonetheless, these decay times represent only a minor improvement over that of K-27 and are far from the original goal. Since some of these compounds could still be of interest for plastic scintillation applications, this sample set was tested for radiation stability. The results from this study are listed in Table 2. The samples were exposed to a total dose of 10 Mrad in air, at 1 Mrad/h. The light yield of the samples was measured before irradiation, after irradiation, and after annealing. After irradiation, the samples were annealed in oxygen to accelerate the recovery process. Although the samples were irradiated in air, they underwent annealing in oxygen atmosphere because the dose rate had been high enough that the oxygen diffusion rate was smaller than its consumption rate. The final results are similar to those of an irradiation under inert atmosphere, with the exception of the formation of oxidation products on the surface of the samples [2]. The performance under radiation of the coumarins is significantly inferior to that of K-27. The losses in transmission of the coumarins are larger than those of K-27.

#### 4. Conclusions

Due to differences in the polarity of the solvents, the compounds tested in polystyrene experienced hypsochromic shifts (to shorter wavelengths) in the absorption and emission bands, in comparison to the data reported in catalogs and handbooks. Many compounds presented problems either prior to or during polymere-

**Table 1. Spectroscopic characteristics of the best dopants studied.**

Dopant <sup>a</sup>	Threshold <sup>b</sup> (nm)	FS Emission <sup>c</sup> (nm)	BS Emission <sup>d</sup> (nm)	Lifetime <sup>e</sup> (ns)	Brightness <sup>f</sup> (%)
K-27	480	468,496,530	496,530	11.8	100
C153LP	470	478	480	10.8	99
C314T	460	456	468	9.6	106
C338	460	460	472	9.7	105
C35/C481	450	456	460	9.1	95
C478	420	422	428	6.9	65
C480	430	424	428	7.2	63
C485	450	452	456	9.3	107
C487	420	426	430	7.2	62
C490	420	426	430	6.9	52
C498	470	456	470	9.5	109
C500	440	440	444	8.0	85
C503	440	442	446	8.1	88
C504	470	458	468	8.5	-
C510	480	478	484	7.6	119
C515	480	478	492	7.5	100
C519	490	474	488	10.0	100
C521	490	476	490	10.3	106
C522	460	466	472	9.4	113
C523	490	470	484	10.0	95
C525	520	508	518	8.1	82
C535	500	504	508	7.7	85
C540	510	510	514	7.4	90
C545	520	526	528	8.4	76

<sup>a</sup>Concentration of dopant in polystyrene is 0.02% by weight. <sup>b</sup>Absorption threshold for 1-cm thick samples. <sup>c</sup>Emission spectrum using Front Surface excitation,  $\lambda_{exc}=436$  nm. <sup>d</sup>Emission spectrum using Back Surface excitation,  $\lambda_{exc}=436$  nm. It documents self-absorption in a 1-cm pathlength. <sup>e</sup>Estimated measurement error is of  $\pm 0.2$  ns. <sup>f</sup>Light yield results are relative to K-27, when being used as WLS under side illumination by a samples of SCSN38 (blue) scintillator.

rization which rendered them unsuitable for our application. Several coumarin derivatives exhibited the right spectroscopic characteristics and seemed possible substitutes to K-27 in the WLS fibers. However, the radiation damage study of these compounds indicated that they are not as resilient under radiation as K-27. The differences in transmission losses due to radiation damage among the compounds tested are small, but a correlation with the structure of the compounds can be observed. Coumarins containing a “quinolizine” fragment seem more susceptible to radiation damage than the rest. An improvement in radiation stability may be achieved by preparing coumarin derivatives with the third and fourth positions blocked by substituents [3].

**Table 2. Radiation Damage Studies.**

Dopant <sup>a</sup>	Light Yield <sup>b</sup> (%)			T Loss <sup>c</sup> (%)
	Before Irradiation	After 10 Mrad	After Annealing	
K-27	84	43	71	1
C153LP	83	18	45	10
C314T	89	24	56	14
C338	88	24	53	17
C35/C481	82	22	53	4
C478	55	6	28	14
C480	53	5	23	11
C485	90	22	23	2
C487	52	6	24	8
C490	44	8	35	8
C498	92	23	49	13
C500	71	22	42	*
C503	74	17	42	5
C504	-	21	50	15
C510	100	22	54	12
C515	84	18	47	19
C519	84	25	55	12
C521	89	28	54	12
C522	95	18	45	9
C523	80	27	51	15
C525	69	18	49	15
C535	71	23	50	7
C540	76	30	56	8
C545	64	18	49	9

<sup>a</sup>Concentration of dopant in polystyrene is 0.02% by weight. <sup>b</sup>Light yield results before irradiation are relative to C510. <sup>c</sup>Radiation-induced transmission losses. \*This sample presents a 2% gain in transmission.

## 5. Acknowledgements

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