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Radiation hardness of plastic scintillators activated by *tert*-butylfluoro derivatives of 3-hydroxyflavone

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Activators for a radiation-resistant plastic scintillator with increased solubility in polystyrene, *tert*-butylfluoro derivatives of 3-hydroxyflavone, have been synthesized. A series of plastic scintillators containing up to 3.0 wt. % of the new activators have been obtained. The optical and scintillation properties of the obtained plastic scintillators have been studied, and their radiation hardness has been determined.

Keywords: plastic scintillator, radiation hardness, degradation, 3-hydroxyflavone, activator.

Радіаційна стійкість пластмасових сцинтиляторів, активованих *трет*-бутилфторпохідними 3-гідроксифлавону. *П.М.Жмурін, Д.А.Єлісєєв, Ю.О.Гуркаленко, О.В.Єлісєєва, В.Д.Алексєєв*

Синтезовані активатори з підвищеною розчинністю в полістиролі для радіаційностійкого пластмасового сцинтилятора — *трет*-бутилфторпохідні 3-гідроксифлавону. Отримано ряд пластмасових сцинтиляторів, що містять до 3.0 мас. % нових активаторів. Вивчено оптичні та сцинтиляційні властивості отриманих пластмасових сцинтиляторів, визначена х радіаційна стійкість.

1. Introduction

A modern experiment in high-energy physics imposes new requirements on the materials used to create various types of detectors. Often, these requirements are associated with the need to increase the threshold of radiation hardness, due to a significant increase in the luminosity of the experiments [1–3]. Plastic scintillators (PS) are widely used as components for creating various calorimetric and veto systems [4, 5]. It is not possible to find a replacement for them in the near future due to their availability, ease of processing and, of course, cost. Therefore, various attempts to increase the threshold of radiation hardness of PS are being made.

A plastic scintillator usually consists of a polymer base (usually polystyrene or polyvinyltoluene), and luminescent additives — an activator and a shifter. Under the action of high-energy irradiation, the properties of all PS components are degraded. The defects formed under the action of irradiation in the PS polymer base have a broad absorption band extending from 280 to 500 nm [6]. The main luminescence band of the activator molecules is located in the range of 330–370 nm, and of the shifter molecules — from 390 to 430 nm. Thus, the absorption band of defects completely overlaps the luminescence bands of both the activator and the shifter; this leads to a significant degradation of the scintillation properties of PS. For example, the radiation hardness threshold of a standard PS based on poly-

styrene with an activator *p*-terphenyl and a shifter 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP) does not exceed 3 Mrad [7].

To date, there are several ways to increase the radiation hardness threshold of PS. This is, first of all, the search for a new polymer base that is more resistant to high-energy radiation. And although it is not difficult to find polymers that are more resistant to radiation (for example, polysiloxanes [8, 9]), but, for a number of reasons, it is currently not possible to create effective scintillation media for PS on their basis. Therefore, the main path to increase the radiation hardness is associated with the search for PS polymer base activators capable of shifting the main radiation band to the long-wavelength range beyond the main absorption band of radiation traps, formed in the polystyrene medium under the action of irradiation.

Another way is to look for ways to modify activator molecules to increase their own radiation hardness. Thus, the use of 3-hydroxyflavone (3HF) as an activator with a luminescence band maximum located in the region of 530 nm makes it possible to increase the radiation resistance of PS to 7 Mrad [10]. And the introduction of fluorine into 3HF molecules makes it possible to achieve a level of radiation hardness up to 14 Mrad [11].

In addition to these methods, the authors of [12] showed that, for some activators, an increase in their concentration in the polymer base leads to an increase in the radiation hardness of PS. Therefore, it is important to check the possibility of increasing the radiation resistance of PS activated by 3HF derivatives by increasing the concentration of the activator.

The solubility of unsubstituted 3HF molecules in polystyrene does not exceed 1.5 wt. % [13]. There is a need to modify the structure of 3HF molecules with substituents that increase their solubility. As a result, 3HF fluorine derivatives with a tert-butyl group were obtained, the presence of which made it possible to increase their solubility in polystyrene. PSs containing up to 3.0 wt. % of new activators were obtained, and their scintillation properties and radiation hardness were studied.

2. Experimental

Fluorine derivatives of 3-hydroxyflavones were synthesized using the well-known Algar-Flynn-Oyamada reaction by oxidation of o-hydroxyphenylstyryl ketones to flavones with hydrogen peroxide [14]. For this, equimolecular amounts of p-*tert*-butylbenzaldehyde and fluorine-containing o-hydroxyacetophenones were dissolved in methanol and mixed with 10 % sodium hydroxide solution. The resulting chalcone was oxidized with a solution of hydrogen peroxide in an alcohol-alkaline medium, followed by neutralization by the dilute mineral acid. The resulting *tert*-butylfluoro derivatives of 3-hydroxyflavone were purified by chromatography of benzene solution on silica gel.

PS samples containing tert-butylfluoro derivatives of 3HF were obtained by bulk polymerization. For this, 1.0, 1.5, 2.0 and 3.0 wt. % of the corresponding activator and the required amount of styrene were placed in a glass ampoule, purged with argon for 15 minutes, hermetically sealed and polymerized at a temperature of 150°C for 72 hours. Samples in the form of cylinders with a diameter of 16 mm and a height of 10 mm were cut from the obtained blanks, after which they were polished to optical transparency.

The spectral and luminescent characteristics of the samples were obtained on a Horiba JobinYvon Fluoromax-4 spectrofluorimeter. To measure the light yield, the PS samples were mounted directly on the surface of the photomultiplier photocathode (optical contact was provided by means of an immersion liquid) and irradiated with a ^{207}Bi monoenergetic source of conversion electrons. The light yield was determined from the position of the maximum peak in the amplitude scintillation spectrum from electrons with energy of 975 keV.

The time characteristics were determined by the single-photon correlation method on a two-channel setup with two Hamamatsu 9800 PMTs in the Start and Stop channels. The ^{90}Sr electron source was used to measure the time characteristics of the PS. The signal of Cherenkov radiation from a sample made of poly(methyl methacrylate) was used as the starting pulse.

To determine the radiation hardness, PS samples were placed in the radiation field of a ^{60}Co source with a dose rate of 1.2 Krad/h in air and kept up to an irradiation dose of 7 Mrad. The light yield of the samples was measured immediately after irradiation and after 2 weeks.

3. Results and discussion

Structural formulas, names, symbols of the obtained compounds and PS's codes are

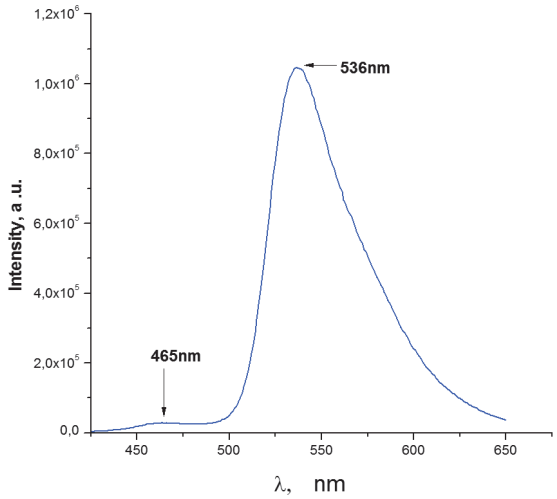

Fig. 1. Luminescence spectrum of 0.01 wt. % 3HF in polystyrene (excitation wavelength 385 nm).

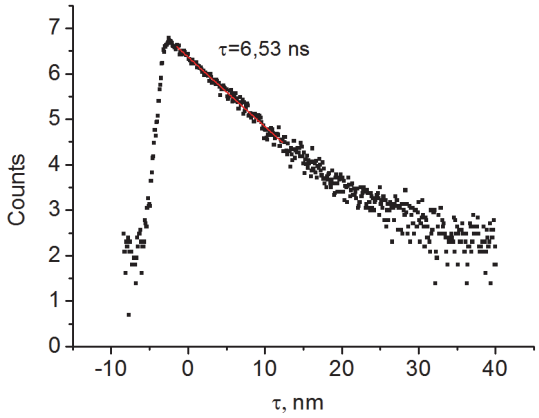

Fig. 2. Scintillation pulse decay curve of polystyrene based PS activated with 2.0 wt. % 3HFTB2 (source — ^{90}Sr).

presented in Table 1. The presence of the *tert*-butyl group in the molecules of 3HF derivatives made it possible to increase their solubility in polystyrene to 3.0 wt. %, which is almost two times higher than the solubility of unmodified 3HF molecules. The synthesized activators have a luminescence spectrum with a main band maximum around 536 nm. These spectra are almost identical and coincide with the luminescence spectrum of unsubstituted 3-hydroxyflavone molecules (Fig. 1). With an increase in the activator concentration in polystyrene, the nature of the luminescence spectra of the samples practically did not change.

A typical view of the scintillation flash of PS samples with synthesized activators is shown in Fig. 2. The observed duration of the scintillation pulse was 6.5 ns. It should be noted that the decay curves retained an identical character throughout the available range of activator concentrations in polystyrene.

For PS samples activated by 3HF, 3HFTB2, and 3HFTB3 molecules, the maximum light yield was observed at an activator concentration of 1.5 wt. %. PS activated with 3HFTB1 showed an increase in light yield up to concentration 3.0 wt. %, and its light yield was almost 20 % higher than for PS with 1.5 wt. % unsubstituted 3HF (Fig. 3, Table 2). The relative light yield was determined from the position of the maximum in the amplitude-scintillation spectrum (channel number) (Fig. 3).

To determine the radiation hardness of the obtained PSs, their light yield was measured before and after irradiation with a dose of 7 Mrad. Table 2 presents PS code, their relative light yield before (L_0) and after irradiation (L), as well as the ratio of

Table 1. PS with *tert*-butylfluoroderivatives of 3HF

Code PS	Structural formula and activator name	Activator designation	Activator concentration, wt. %
1794	3-hydroxy-2-phenyl-4H-chromen-4-one	3HF	1.5 %
1795	2-(4-(tert-butyl)phenyl)-6,8-difluoro-3-hydroxy-4H-chromen-4-one	3HFTB1	1.0 %
1796			2.0 %
1797			3.0 %
1798	2-(4-(tert-butyl)phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one	3HFTB2	1.0 %
1799			2.0 %
1800			3.0 %
1801	2-(4-(tert-butyl)phenyl)-6,7-difluoro-3-hydroxy-4H-chromen-4-one	3HFTB3	1.0 %
1802			2.0 %
1803			3.0 %

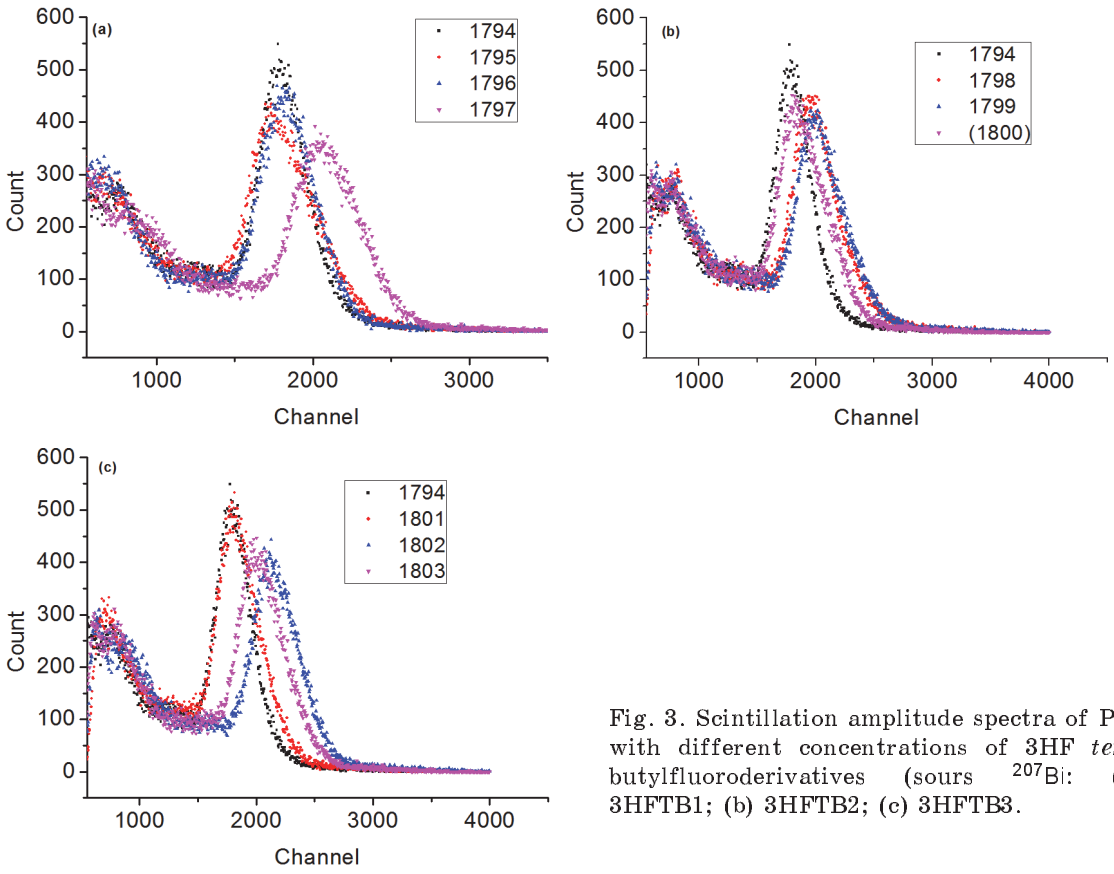

Fig. 3. Scintillation amplitude spectra of PSs with different concentrations of 3HF *tert*-butylfluoroderivatives (sours ^{207}Bi: (a) 3HFTB1; (b) 3HFTB2; (c) 3HFTB3.

light yields after and before irradiation (L/L_0), which characterizes the degree of influence of irradiation on PS scintillation characteristics. The dose value for half attenuation of the light yield ($D_{1/2}$) was obtained by extrapolation of the available data.

As can be seen from the Table 2, the radiation hardness of PS activated by *tert*-butylfluoro derivatives of 3HF is about 7 Mrad. This value is close to the radiation hardness of the PSs activated with unsubstituted 3HF. A slight increase in the radiation hardness is observed only for the activator 3HFTB1 (Table 2). An unexpected de-

Table 2. Scintillation characteristics of the obtained PS before and after irradiation with a dose of 7 Mrad

Code PS	L_0	L	L/L_0	$D_{(1/2)}$, Mrad	$D_{(1/2)}$, Mrad +2 weeks
1794	100	49	0.49	6.9	7,2
1795	97	51	0.53	7.5	7.6
1796	101	47	0.47	6.6	7.7
1797	115	53	0.46	6.4	7.12
1798	110	54	0.49	6.9	7.23
1799	110	43	0.39	5.42	6.3
1800	103	46	0.45	6.1	6.8
1801	101	49	0.49	7.0	7.8
1802	120	58	0.48	6.7	7.5
1803	112	53	0.47	6.4	6.1

crease in the threshold of radiation resistance with an increase in the concentration of activator molecules was found for all PS samples. This result contradicts the original premise of the study. The data obtained and the fact that the observed deviations in radiation hardness vary within 15 % indicate that the expected improvement in the properties of PS radiation hardness with increasing activator concentration is not universal. Apparently, the change in radiation hardness with a change in the activator concentration largely depends on the properties and structure of the activator molecules themselves. First of all, it depends on the ability of the ability of the decomposition products of the activator molecules to effectively absorb scintillation radiation of PS polymer base. In this case, it can be assumed that the higher the concentration of the activator, the more degradation products that can adversely affect the light yield of PS after irradiation. It is difficult in practice to distinguish the absorption band of such products against the background of the main absorption of activator molecules.

4. Conclusions

The introduction of a *tert*-butyl group into the molecules of 3HF fluorine derivatives significantly increased their solubility in the PS polystyrene base. The increase in the concentration of the activator to 3.0 wt. % made it possible to obtain PS with a light yield 20 % higher than the light yield of PS activated with unsubstituted 3HF. Contrary to expectations, an increase in the concentration of activators did not lead to an increase in the radiation hardness of PS.

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