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3-Hydroxyflavone *tert*-butyl fluorine derivative as activator of plastic scintillators

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An activator for plastic scintillators 2-(4-(*tert*-butyl)phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one (TBF-3-HF) with an increased solubility in polystyrene was synthesized in this work. A number of plastic scintillators with the TBF-3-HF content up to 3.0 wt. % were obtained. Their optical and scintillation properties have been studied.

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

Похідне третбутилфтор-3-гідроксифлавону як активатор пластмасового сцинтилятора. *П.М.Жмурін, Ю.О.Гуркаленко, Д.А.Єлісєєв, О.В.Єлісєєва, В.Д.Алексеєв*

Синтезовано активатор для пластмасових сцинтиляторів 2-(4-*трет*бутил)феніл-6-фтор-3-гідрокси-4H-хромен-4-он (TBF-3-HF) з підвищеною розчинністю у полістиролі. Отримано низку пластмасових сцинтиляторів із вмістом TBF-3-HF до 3,0 мас. %. Вивчено їх оптичні і сцинтиляційні властивості.

Синтезирован активатор для пластмассовых сцинтилляторов 2-(4-(*трет*бутил)фенил)-6-фтор-3-гидрокси-4H-хромен-4-он (TBF-3-HF) с повышенной растворимостью в полистироле. Получен ряд пластмассовых сцинтилляторов с содержанием TBF-3-HF до 3,0 масс. %. Изучены их оптические и сцинтилляционные свойства.

1. Introduction

The problem of increasing the radiation hardness of scintillation materials is associated with a significant increase in their irradiation dose. Previously, in CERN experiments, the maximum dose accumulated by polystyrene-based detectors did not exceed 2–5 Mrad. Today, the increased luminosity in such experiments as ATLAS [1], CMS [2], LHCb [3] requires an increase in the radiation hardness of plastic scintillators (PS) up to 30 Mrad. At the same time, the threshold of radiation hardness of traditional PSs based on polystyrene activated by paraterphenyl molecules does not exceed 2–3 Mrad [4, 5].

To date, the main ways of increasing the threshold of PS radiation hardness have been established. The first way is associated with an increase in the mobility of radicals formed in the polymer base under the action of high-energy radiation. For this, various diffusion enhancers are introduced into the polymer base of PS, which allow radicals to quickly restore the broken chemical bonds [6, 7]. However, it leads to a significant degradation of the mechanical properties of PS and to a decrease in long-term stability.

Another way to increase the radiation hardness is associated with the transfer of the PS main luminescence band to a longer wavelength range, where there are no absorption bands of various defects formed under the action of ionizing radiation. This method involves the use of molecules with a large Stokes shift as an activator, such as, for example, 3-hydroxyflavone (3-HF) and its fluorine derivatives. The use of these compounds as a PS activator makes it possible to increase the radiation hardness of the scintillators to 10–15 Mrad [8–10].

It is known that an increase in the concentration of activator molecules in the PS polymer base leads to a significant increase in the threshold of radiation hardness [11]. But the solubility of 3-hydroxyflavone and its fluorine derivatives in polystyrene usually does not exceed 1.5–2.0 wt. % [12], which limits the further improvement of the radiation hardness properties of plastic scintillators. An increase in the solubility of activator molecules in the PS polystyrene base can be achieved by modifying their structure by introducing alkyl substituents of various lengths. This modification, as a rule, leads to an increase in solubility and does not significantly affect the spectral-luminescent characteristics of the activator [13]. This allows us to hope for an increase in the radiation hardness of the PS by increasing the content of the activator in the scintillation composition.

This work describes the preparation of a fluorine derivative of 3-hydroxyflavone-2-(4- (*tert*-butyl)phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one (TBF-3-HF) (Fig. 1) with increased solubility in polystyrene. The scintillation properties of PS with this activator have been investigated.

2. Experimental

Synthesis of 2-(4-(tert-butyl) phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one

The solution of 2.4 g (0.0428 mol) KOH in 20 ml of methanol is added to a mixture of 3.0 g (0.0194 mol) of 5-fluoro-2-hydroxyacetophenone and 3.31 g (0.0204 mol) of 4-*tert*-butylbenzaldehyde in 30 ml of methanol at a temperature of 0–5°C. The resulting mixture then is stirred for 18 h at room temperature and for another 6 h at 40°C. The reaction mixture is neutralized with the 2N HCl solution. The resulting precipitate of 3-(4-*tert*-butyl)phenyl)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one is collected by filtration, washed on a filter with a small amount of methanol and water, squeezed thoroughly and dried at room temperature.

The resulting yellow chalcone in an amount of 3.24 g (0.0108 mol) is dissolved in a mixture of 40 ml of methanol and 1.22 g (0.0217 mol) of KOH. Then 4 ml of H_2O_2 (30 %) is slowly added dropwise to the orange-red solution at a temperature of 5–10°C. The mixture is stirred for 3 to 4 h at room temperature, then poured into cold water and acidified with the 2 N HCl solution. The precipitate is collected by filtration, washed with water, carefully squeezed out and dried at room temperature. For purification, the product is chromatographed on silica gel (eluent – cyclohexane), after which it is additionally sublimated under vacuum.

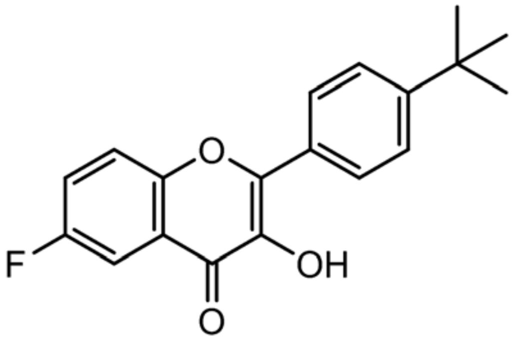

Fig. 1. Structural formula of a molecule 2-(4-(*tert*-butyl)phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one (TBF-3-HF).

The yield of 2-(4-*tert*-butyl) phenyl-6-fluoro-3-hydroxy-4H-chromen-4-one is 1.57 g (46.1 %); fine crystalline almost colorless product, melting point is 212–215°C.

Preparation of PS samples

The synthesized TBF-3-HF was used as an activator for the polystyrene base of a plastic scintillator. PS samples were obtained by thermally initiated bulk polymerization. For this, 0.01 wt. %, 0.5 wt. %, 1.0 wt. %, 2.0 wt. % and 3.0 wt. % of the activator were placed in glass ampoules, filled with an appropriate amount of styrene, purged with argon for 10 min, and polymerized at a temperature of 145°C for 72 hours. Samples in the form of cylinders 16 mm in diameter and 10 mm in height were cut from the obtained blanks; then they were polished to optical transparency.

The spectral-luminescent characteristics of PS samples were studied on a FluoroMax-4 spectrofluorimeter (Horiba Jobin Yvon, USA).

To measure the light yield, PS samples were mounted directly on the surface of the photocathode of a Hamamatsu R1307 PMT (optical contact was provided by means of an immersion liquid) and irradiated with a monoenergetic source of conversion electrons ^{207}Bi. The light yield was determined from the position of the maximum of the peak from electrons with energy of 975 keV.

The temporal characteristics were determined by the method of correlation single-photon counting [14] on a two-channel setup with two Hamamatsu 9800 PMTs in the Start and Stop channels. To measure the tem-

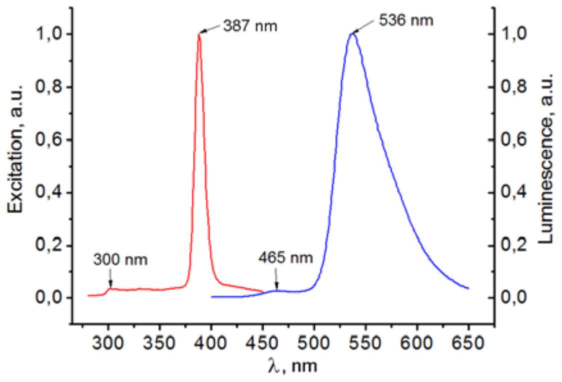

Fig. 2. Excitation (observation wavelength 535 nm) and luminescence (excitation wavelength 385 nm) spectra of TBF-3-HF molecules (0.01 wt. %) in polystyrene.

poral characteristics of the PS, we used a ^{90}Sr electron source. A Cherenkov radiation signal from a sample made of polymethyl methacrylate was used as a starting pulse.

3. Results and discussion

As expected, the presence of a *tert*-butyl group in the TBF-3-HF molecule led to an increase in their solubility in polystyrene, which made it possible to obtain PS with an activator content of up to 3.0 wt. %.

The luminescence spectrum of TBF-3-HF in polystyrene has a weakly pronounced peak at 465 nm and the main luminescence band with a maximum at 536 nm (Fig. 2). The observed luminescence spectrum is typical for molecules of 3-hydroxyflavone and its fluorine derivatives [15]. The excitation spectrum of TBF-3-HF molecules in polystyrene has a rather sharp peak at a wavelength of 385 nm and a very weak peak at a wavelength of 300 nm (Fig. 2). The luminescence and excitation spectra retained the indicated behavior in the entire available concentration range of TBF-3-HF molecules in polystyrene. Neither broadening of the luminescence band nor a change in its position was observed, which indicates the absence of any aggregation of TBF-3-HF molecules up to 3.0 wt. % in polystyrene.

The maxima of the luminescence spectra of polystyrene are located in the region of 290 nm (the maximum of the luminescence spectrum of phenyl groups of polystyrene) and 320 nm (the maximum of the luminescence spectrum of excimers of polystyrene molecules). In the observed excitation spectrum of TBF-3-HF molecules in polystyrene, there is only a weak excitation band (maximum at 300 nm), which coincides with the luminescence band of polystyrene. The maximum of the main excitation band of TBF-3-HF is located at 387 nm. This nature of the excitation spectrum indicates that TBF-3-HF molecules are not optimal for activating the polystyrene base, since they cannot efficiently collect the excitation energy from the polystyrene matrix through the mechanism of nonradiative energy transfer. But, despite this, polystyrene activated with TBF-3-HF demonstrates the necessary scintillation properties. The scintillation pulse time of the obtained PS is 6.53 ns (Fig. 3).

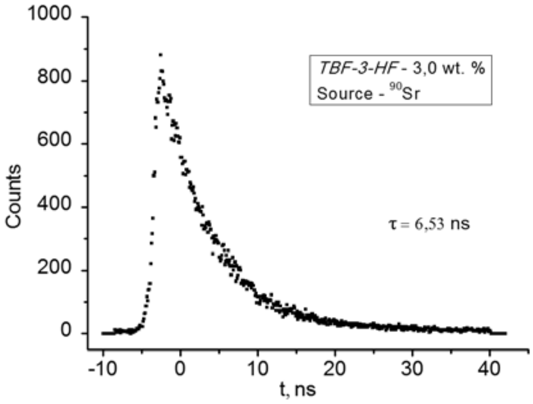

Fig. 3. Scintillation pulse decay curve of a PS based on polystyrene activated with 3.0 wt. % TFB-3-HF (source — ^{90}Sr).

In this case, the question arises about the path of the transfer of excitation energy from the polystyrene matrix to the activator molecules. It is traditionally considered that this is a nonradiative energy transfer due to the dipole-dipole interaction. However, the absence of overlap between the luminescence spectra of polystyrene and the absorption spectra of TBF-3-HF molecules indicates a low probability of such transfer mechanism. And in this case, the transfer of excitation energy, apparently, occurs due to the transfer of an electron from polystyrene to an activator molecule according to the mechanism described by the authors [16].

It should be noted that the decay curves remained identical in the entire studied range of concentrations of TBF-3-HF molecules in polystyrene up to 3.0 wt.%. This behavior of the decay curves also indicates the absence of aggregates of TBF-3-HF molecules capable to luminescence.

The relative light yield of the obtained scintillation compositions significantly depended on the concentration of activator molecules and varied from 11 % to 45 % of the light yield of the standard polystyrene

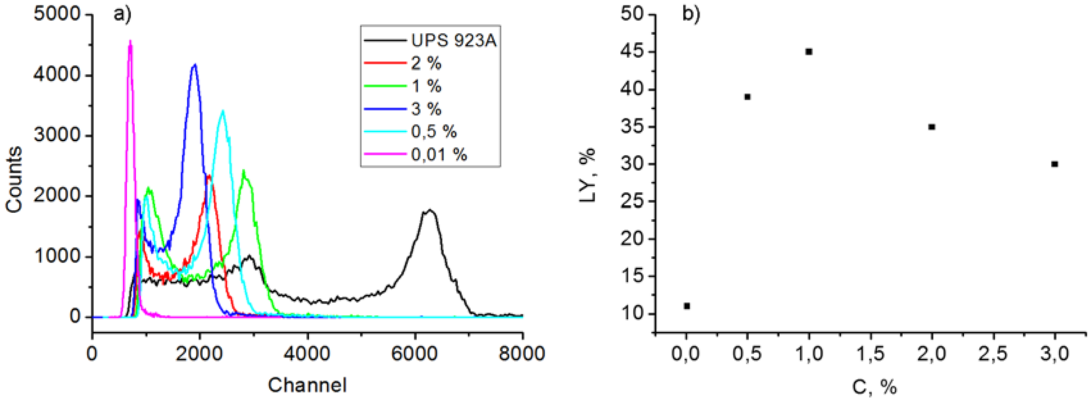

Fig. 4. Scintillation amplitude spectra of PSs with different TBF-3-HF concentrations (a); dependence of the light yield of polystyrene PSs on the TBF-3-HF concentration (b).

PS UPS 923A (Fig. 4). The maximum light yield was achieved at a TBF-3-HF concentration of 1.0 wt. % and was 45 % of the light yield of a standard PS.

The relative light yield was measured with an R1307 photomultiplier, the maximum sensitivity of which is about 420 nm, which corresponds to the scintillation wavelength of a standard PS. The scintillation maximum of PS with TBF-3-HF is located at a wavelength of 538 nm. In this region, the sensitivity of the PMT R1307 is almost two times lower than in the region of 420 nm. Considering the above, we can say that the light yield of new PS is at the level of the light yield of a standard PS.

With an increase in the concentration of TBF-3-HF more than 1.0 wt. %, the relative light yield of the PS starts to decrease. However, even with an activator content of 3.0 wt. %, the light yield of scintillation composition maintains at a level sufficient for practical use.

3. Conclusions

An alkyl fluorine derivative of 3-hydroxyflavone — 2-(4(*tert*-butyl)-phenyl)-6-fluoro-3-hydroxy-4H-chromene-4-one (TBF-3-HF) with increased solubility in polystyrene (up to 3.0 wt. %) has been synthesized. A number of PSs with TBF-3-HF use have been obtained and investigated. The spectral-luminescent properties of the new PSs remain unchanged over the entire range of investigated concentrations, which indicates the absence of aggregation of activator molecules. The maximum light yield was achieved at a TBF-3-HF concentration of 1.0 wt. %; however, with an activator content of 3.0 wt. %, the PSs keep the light yield at a level sufficient for practical use. It is hoped that the radiation resistance of scintillators activated by TBF-3-HF will increase by increasing its content in the scintillation composition.

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