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3-hydroxyflavone derivatives as activators of radiation-resistant plastic scintillator

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The work is devoted to the development of radiation-resistant polystyrene based plastic scintillators, suitable for use in modern experiments in high-energy physics. The main attention is paid to the search and synthesis of radiation-resistant activators, derivatives of 3-hydroxyflavone. In the work, a number of fluoro-, phenyl-, fluorophenyl- and fluoroalkyl derivatives of 3-hydroxyflavone were obtained. With the obtained activators, radiation-resistant plastic scintillators were developed and their scintillation characteristics and radiation stability were investigated. The light output half-attenuation dose of the created scintillators reaches 49 Mrad.
Keywords: plastic scintillator, activator, fluoroderivatives of 3-hydroxyflavone, high-energy physics, radiation-resistant.

Похідні 3-гідроксифлавону як активатори пластмасового сцинтилятора. *О.В. Єлісєєва, Д.А. Єлісєєв, Ю.О. Гуркаленко, П.М. Жмурін, В.Д. Алексєєв*
Робота присвячена розробці радіаційностійких пластмасових сцинтиляторів на основі полістиролу, придатних для використання в сучасних експериментах з фізики високих енергій. Основна увага приділяється пошуку та синтезу радіаційностійких активаторів, похідних 3-гідроксифлавону. У роботі отримано ряд фтор-, феніл-, фторфеніл- та фторалкільних похідних 3-гідроксифлавону. З отриманими активаторами розроблені радіаційностійкі пластмасові сцинтилятори та досліджено їх сцинтиляційні характеристики і радіаційну стабільність. Доза половинного ослаблення світлового виходу створених сцинтиляторів досягає 49 Мрад.

1 Introduction

Plastic scintillators (PS) are widely used in various fields of science and technology as scintillation elements of ionizing radiation detectors. PS are easy to manufacture, have high sensitivity, high performance and relatively low cost. However, with the development of accelerator technology, the requirements for radiation resistance of materials used in the creation of various detectors are constantly increasing. In modern physical experiments, such as ATLAS [1], CMS [2] and LHCb [3], scintillators are subjected to significant radiation loads, which can reach tens of Mrad. At the same time, traditional PS based on polystyrene and polyvinyltoluene exhibit a low level of radiation resistance. In particular, for commercial SCSN-81T (Kuraray, Japan) [4], BC-408 (Bicron, USA) [5] and UPS-923A (Amcrys-H, Ukraine) [6] the half-attenuation dose of the light output is only 1–5 Mrad. Therefore, various attempts are being made to increase the radiation resistance of the PSs to adapt them to modern requirements.

Today, there are several ways to improve the radiation resistance of PS. One of them is the introduction of diffusion enhancers into the PS composition, which contribute to increasing the mobility of free radicals, which, in turn, accelerates their recombination and reduces damage to the polymer base. However, this method leads to a significant degradation of mechanical properties and a decrease in the long-term stability of PS [7, 8].

Another way involves the use of more radiation-resistant polymer bases, for example, polysiloxanes [9 – 11]. However, the main disadvantage of polysiloxanes as a PS base is their mechanical properties. Polymers based on polysiloxanes are jelly-like materials, which limits the scope of their practical application [12].

Another way to increase the radiation resistance of PS is to use luminescent additives with a large Stokes shift. Defects of the PS's vinylaromatic polymer base, formed under the action of ionizing radiation, have a wide absorption band, which extends from 280 nm to 520 nm [13, 14] (Fig. 1). The main luminescence band of traditional activator molecules is usually located in the range of 330–370 nm, and of shifter molecules – 390–430 nm. That is, the absorption band of defects completely overlaps the luminescence bands of both the activator and the shifter, which leads to a significant degradation of the scintillation properties of PS. Luminescent additives with a large Stokes shift allow to transfer the emission to a longer wavelength range, bypassing the absorption band of defects. Thus, their use allows to reduce the loss of excitation energy and increase the radiation resistance of PS.

One of the most radiation-resistant luminescent additives is considered to be 3-hydroxyflavone (3-HF). Its absorption maximum is at 350 nm, and its luminescence maximum is at 530 nm, i.e. the Stokes shift is 180 nm. Such a large Stokes shift allows to bypass most of the energy traps formed as a result of irradiation. The use of 3-HF as a PS activator allows to increase the radiation resistance of the material to 7 Mrad [15 – 17], however, in modern conditions this is no longer enough. It should be noted that for traditional PS an important factor in the degradation of scintillation characteristics is the formation of excitation energy traps as a result of damage to the polymer base itself. But in the case when it is possible to bypass these traps due to a large Stokes shift, one of the important factors becomes the radiation resistance of the activating additives themselves. Therefore, it is necessary to find ways to modify the activator molecules that will increase their radiation resistance and, accordingly, lead to an increase

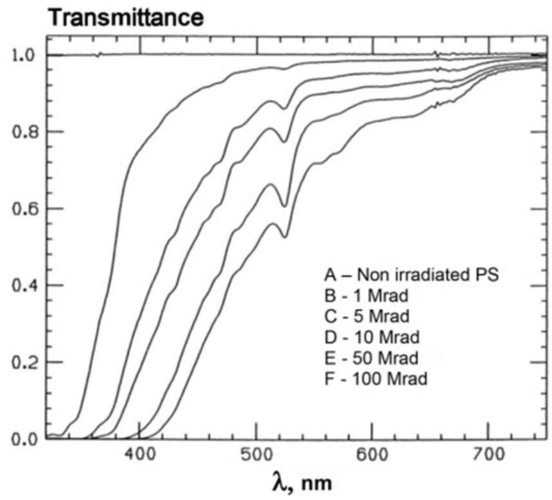


Figure 1 – Transmission spectra of pure polystyrene before irradiation (A) and after irradiation with doses of 1 Mrad (B), 5 Mrad (C), 10 Mrad (D), 50 Mrad (E) and 100 Mrad (F) [14]

in the radiation resistance of the PS where they will be used.

The work describes various 3-hydroxyflavone derivatives that were used to create radiation-resistant PS. The scintillation characteristics of the resulting scintillators were investigated, and their radiation resistance was determined.

2 Experimental

2.1 Synthesis of 3-hydroxyflavone derivatives. 3-HF derivatives are obtained by the interaction of equimolar amounts of the corresponding 2-hydroxyacetophenone derivatives and benzaldehyde in an alcoholic medium in the presence of alkali with the separation of chalcone and its subsequent oxidation with hydrogen peroxide according to the Algar-Flinn-Oyamada reaction. The scheme and generalized methodology for the synthesis of 3-HF derivatives of general formula **VI** are shown in Fig. 2.

Chalcone (III). To a solution of 0.2 mol of 2-hydroxyacetophenone (**I**) and 48 g (0.86 mol) of KOH in 300 ml of methanol at room temperature and stirring, 0.22 mol of aldehyde (II) is added. Stir for 22 h at room temperature, 8 h at 40 °C and then another 18 h at room temperature. Then pour onto the mixture 1 l of cold water and 100 ml of HCl (37 %). The resulting precipitate of chalcone (**III**) is collected by filtration, washed on the filter several times with 150 ml portions of hot water, squeezed thoroughly and dried at room temperature. The technical product is a yellow-orange powder.

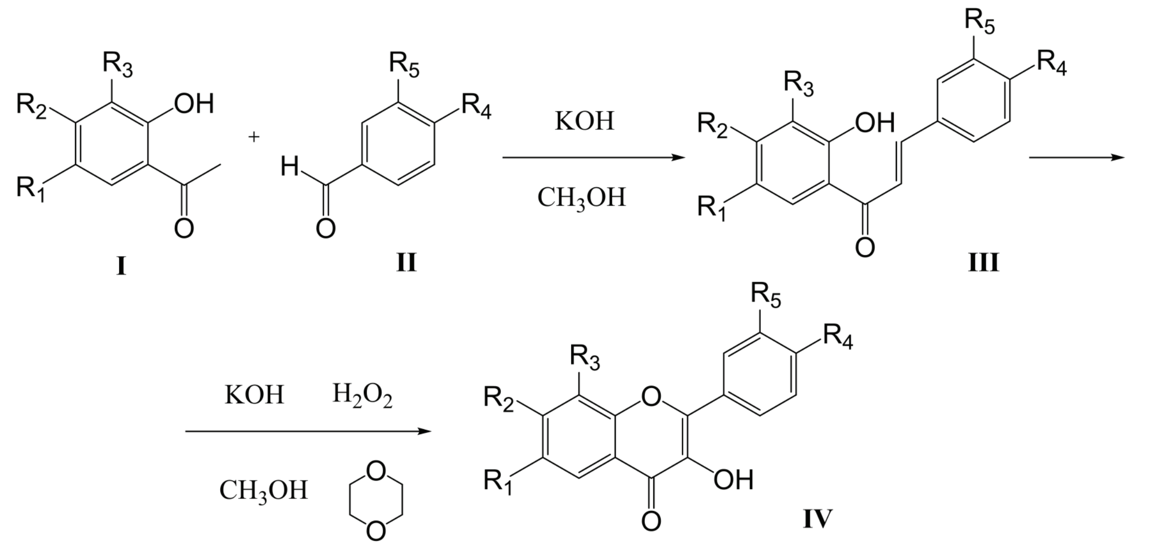


Figure 2 – Scheme of synthesis of 3-HF derivatives

Purification is carried out by recrystallization from benzene.

Derivative of 3-hydroxyflavone (IV). 0.1 mol of chalcone (**III**) is dissolved in a mixture of 200 ml of dioxane, 200 ml of methanol and 17.4 g (0.31 mol) of KOH. The orange-red solution is cooled to 5-10 °C and, with stirring, a mixture of 15 ml of H_2O_2 (30%) and 15 ml of methanol is slowly added dropwise. The reaction mass is stirred for 0.5 h at a temperature of 5-10 °C, after which the cooling is removed and stirring is continued at room temperature. After 1 h, another 4 ml of peroxide and 10 ml of methanol are added to the mixture. Stirring is carried out until the solution becomes clear and the red hue disappears. Then the reaction mass is poured into a mixture of 1 l of cold water and 50 ml of HCl (37 %). The precipitate of 3-hydroxyflavone (**IV**) formed is filtered, washed on the filter with water, thoroughly squeezed and dried at room temperature. The technical product is a finely dispersed powder of pale yellow color.

The technical product is purified by double chromatography on silica gel (eluent – cyclohexane), followed by recrystallization from benzene.

6-Fluoro-3-hydroxy-2-phenyl-4H-chromen-4-one or 6F-3HF (IV, R_1 = F; R_2, R_3, R_4, R_5 = H). Yield – 15.6 g (61 %), fine crystalline pale yellow powder, $T_{melt.}$ = 169–170 ºC. Elemental analysis: calculated for $C_{15}H_9FO_3$ (%): C – 70.31; H – 3.54; O – 18.43; found (%): C – 70,35; H – 3,50; O – 18,44. ^1H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H), 7.98 (ddd, J = 7.4, 1.6, 0.8 Hz, 2H), 7.56 (dd, J = 8.0, 1.5 Hz, 1H), 7.56–7.40 (m, 4H), 7.17 (ddd, J = 8.0, 7.5, 1.5 Hz, 1H).

2-(4-Fluorophenyl)-3-hydroxy-4H-chromen-4-one or 4′F-3HF (IV, R_4 = F; R_1, R_2, R_3, R_5 = H). Yield – 15.4 g (60 %), fine crystalline pale yellow powder, $T_{melt.}$ = 151–152 °C. Elemental analysis: calculated for $C_{15}H_9FO_3$ (%): C – 70.31; H – 3.54; O – 18.43; found (%): C – 70.28; H – 3.57; O – 18.25. ^1H NMR (400 MHz, DMSO-$d6$) δ 9.33 (s, 1H), 8.22–8.14 (m, 2H), 8.04 (dd, J = 7.4, 1.5 Hz, 1H), 7.75 (ddd, J = 7.5, 1.5 Hz, 1H), 7.53–7.43 (m, 2H), 7.31–7.22 (m, 2H).

6-Fluoro-2-(4-fluorophenyl)-3-hydroxy-4H-chromen-4-one or 6F4¢F-3HF, (IV, R_1, R_4 = F; R_2, R_3, R_5 = H). Yield – 17.4 g (64 %), fine crystalline pale yellow powder, $T_{melt.}$ = 190–193 ºC. Elemental analysis: calculated for $C_{15}H_8F_2O_3$ (%): C – 65.70; H – 2.94; O – 17.50; found (%): C – 65.73; H – 3.00; O – 17.47. ^1H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H), 8.21–8.12 (m, 2H), 7.58 (dd, J = 8.0, 1.5 Hz, 1H), 7.45 (dd, J = 7.5, 5.0 Hz, 1H), 7.31–7.22 (m, 2H), 7.18 (ddd, J = 8.0, 7.5, 1.5 Hz, 1H).

2-([1,1’-Biphenyl]-4-yl)-3-hydroxy-4H-chromen-4-one or 4′Ph-3-HF, (IV, R_1 = F; R_4 = Ph; R_2, R_3, R_5 = H). Yield – 25.1 g (80 %), fine crystalline pale yellow powder, $T_{melt.}$ = 222–224 ºC. Elemental analysis: calculated for $C_{21}H_{14}O_3$ (%): C – 80.24; H – 4.49; O – 15.27; found (%): C – 80.27; H – 4.50; O – 15.30. ^1H NMR (400 MHz, DMSO-d_6) δ 9.35 (s, 1H), 8.03 (td, J = 7.7, 1.8, 0.9 Hz, 1H), 7.80–7.71 (m, 3H), 7.71–7.60 (m, 4H), 7.52–7.42 (m, 4H), 7.41–7.33 (m, 1H).

2-([1,1'-Biphenyl]-4-yl)-6-fluoro-3-hydroxy-4H-chromen-4-one or 6F4′Ph-3-HF, (IV, R_4 = Ph; R_1, R_2, R_3, R_5 = H). Yield – 19.3 g (59 %), fine crystalline pale yellow powder, $T_{melt.}$ = 232–234 ºC. Elemental analysis: calculated for $C_{21}H_{13}FO_3$ (%): C – 75.90; H – 3.94; O – 14.4; found (%): C – 75.40; H – 3.90; O – 14.35. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21 (s, 1H), 7.76–7.59 (m, 6H), 7.59 (dd, J=8.0, 1.5 Hz, 1H), 7.52–7.34 (m, 4H), 7.20 (ddd, J=8.0, 7.5, 1.5 Hz, 1H).

6,8-Difluoro-2-(3,4-difluorophenyl)-3-hydroxy-4H-chromen-4-one or 6,8DF-3,4′DF-3HF (IV, R_1, R_3, R_4, R_5 = F; R_2 = H). Yield – 16.1 g (52 %), fine crystalline pale yellow powder, $T_{melt..}$ = 165–167 °C. Elemental analysis: calculated for $C_{15}H_6F_4O_3$ (%): C – 58.08; H – 1.95; O – 15.47; found (%): C – 58.12; H – 1.91; O – 15.55. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 7.82–7.78 (m, 1H), 7.58 (ddd, J = 8.1, 5.0, 1.5 Hz, 1H), 7.39 (dd, J = 8.0, 1.5 Hz, 1H), 7.25 (ddd, J = 8.0, 7.5, 5.0 Hz, 1H), 7.04 (td, J = 8.0, 1.5 Hz, 1H).

6,7-Difluoro-2-(3,4-difluorophenyl)-3-hydroxy-4H-chromen-4-one or 6,7DF-3,4′DF-3HF (IV, R_1, R_2, R_4, R_5 = F; R_3 = H). Yield – 17.1 g (55 %), fine crystalline pale yellow powder, $T_{melt..}$ = 225–128 °C. Elemental analysis: calculated for $C_{15}H_6F_4O_3$ (%): C – 58.08; H – 1.95; O – 15.47; found (%): C – 58.02; H – 1.95; O – 15.49. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 2H), 7.80 (ddd, J = 7.5, 5.0, 1.5 Hz, 2H), 7.72 (dd, J = 8.1, 5.0 Hz, 2H), 7.57 (ddd, J = 8.1, 5.0, 1.5 Hz, 2H), 7.27 (ddd, J = 8.1, 7.5, 5.0 Hz, 2H), 7.17 (dd, J = 8.0, 5.0 Hz, 2H).

2-(4-(tert-Butyl)phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one or 6F-4′TB-3HF (IV, R_1 = F; R_4 = *tert*-Bu; R_2, R_3, R_5 = H). Yield – 15.2 g (46 %), fine crystalline pale yellow powder, $T_{melt.}$ = 212–215 ºC. Elemental analysis: calculated for $C_{19}H_{17}FO_3$ (%): C – 73.06; H – 5.49; O – 15,37; found (%): C – 72.86; H – 5,47; O – 15.24. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.97–7.90 (m, 2H), 7.59 (dd, J = 8.0, 1.5 Hz, 1H), 7.48–7.39 (m, 1H), 7.43 – 7.36 (m, 2H), 7.24–7.15 (m, 1H), 1.36 (s, 9H).

2-(4-(tert-Butyl)phenyl)-6,8-difluoro-3-hydroxy-4H-chromen-4-one or 6,8DF-4′TB-3HF (IV, R_1, R_3 = F; R_4 = *tert*-Bu; R_2, R_5 = H). Yield – 12.9 g (39 %), fine crystalline, almost colorless product, $T_{melt.}$ = 180–182 ºC. Elemental analysis: calculated for $C_{19}H_{16}F_2O_3$ (%): C – 69.08; H – 4.88; O – 14.53; found (%): C – 69.09; H – 4.96; O – 14.49. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.97–7.89 (m, 2H), 7.46–7.36 (m, 3H), 7.04 (td, J = 8.0, 1.5 Hz, 1H), 1.36 (s, 9H).

2-(4-(tert-Butyl)phenyl)-6,7-difluoro-3-hydroxy-4H-chromen-4-one or 6,7DF-4′TB-3HF (IV, R_1, R_2 = F; R_4 = *tert*-Bu; R_3, R_5 = H). Yield – 8.3 g (25%), fine crystalline, almost colorless product, $T_{melt.}$ = 270–272 ºC. Elemental analysis: calculated for $C_{19}H_{16}F_2O_3$ (%): C – 69.08; H – 4.88; O – 14.53; found (%): C – 69.11; H – 4.91; O – 14.54. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 7.99–7.92 (m, 2H), 7.72 (dd, J = 7.9, 5.0 Hz, 1H), 7.45–7.38 (m, 2H), 7.15 (dd, J = 8.0, 5.0 Hz, 1H), 1.36 (s, 9H).

2-([1,1'-Biphenyl]-4-yl)-6,8-difluoro-3-hydroxy-4H-chromen-4-one or 6,8DF-4′Ph-3HF (IV, R_1, R_3 = F; R_4 = Ph; R_2, R_5 = H). Yield – 15.1 g (43 %), fine crystalline pale yellow powder, $T_{melt.}$ = 208–210 ºC. Elemental analysis: calculated for $C_{21}H_{12}F_2O_3$ (%): C – 72.00; H – 3.45; O – 13.70; found (%): C – 71.92; H – 3.44; O – 13.68. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (s, 1H), 7.77 – 7.71 (m, 2H), 7.71–7.61 (m, 4H), 7.52–7.43 (m, 2H), 7.43–7.34 (m, 2H), 7.04 (td, J = 8.0, 1.5 Hz, 1H).

2-([1,1'-Biphenyl]-4-yl)-6,7-difluoro-3-hydroxy-4H-chromen-4-one or 6,7DF-4′Ph-3HF, (IV, R_1, R_2 = F; R_4 = Ph; R_3, R_5 = H). Yield – 16.5 g (47 %), fine crystalline pale yellow powder, $T_{melt.}$ = 226–228 ºC. Elemental analysis: calculated for $C_{21}H_{12}F_2O_3$ (%): C – 72.00; H – 3.45; O – 13,70; found (%): C – 71,97; H – 3,39; O – 13,72. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 7.80–7.59 (m, 7H), 7.52–7.43 (m, 2H), 7.43–7.34 (m, 1H), 7.15 (dd, J = 8.0, 5.0 Hz, 1H).

6,8-Fluoro-2-(4-fluorophenyl)-3-hydroxy-4H-chromen-4-one or 6,8DF-4′F-3HF. Yield – 14,0 g (48 %), fine crystalline pale yellow powder, $T_{melt.}$ = 200–203 ºC. Elemental analysis: calculated for $C_{15}H_7F_3O_3$ (%): C - 61.66; H - 2.41; O - 16.43; found (%):C - 61.75; H - 2.43; O - 16.41 1H NMR (400 MHz, DMSO-d6) δ 8.85 (s, 1H), 8.22 – 8.13 (m, 2H), 7.38 (dd, J = 8.0, 1.5 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.04 (td, J = 8.0, 1.5 Hz, 1H).

2.2 Obtaining radiation-resistant PS based on polystyrene, activated with 3-hydroxyflavone and its derivatives. Glass ampoules are filled with 1–3 wt. % 3-HF (or its derivative) and poured with the appropriate amount of styrene to a total solution mass of 5 g. The mixture is purged with argon for 10 min to remove dissolved oxygen, after which the ampoules are hermetically sealed and placed in a heating cabinet at 145 ºC. At this temperature, the samples are kept for 72 h. The process is observed visually.

After holding, the temperature is reduced to 90 ºC at a rate of 5 °C/h, kept for 2 h, and cooling is continued at the same rate to room temperature.

After cooling, the ampoules are broken and the blanks are separated from the glass. The resulting blanks are subjected to mechanical processing – milling, grinding, polishing. The size of the finished PS samples: diameter 16 mm, height 10 mm.

2.3 Chemical structure confirmation. To confirm the composition and structure of the synthesized compounds, 1H NMR spectroscopy and elemental analysis were used.

1H NMR spectra were recorded on a Varian Mercury VX-400 (USA), operating frequency 400 MHz, solvent – deuterated dimethyl sulfoxide (DMSO-d_6), internal standard – tetramethylsilane (TMS).

Elemental analysis was performed on an Elementar Vario L cube device (Germany).

2.4 Measurement of excitation and luminescence spectra. Measurement of excitation and luminescence spectra of the obtained activators and PS samples was carried out at room temperature on a Fluoromax-4 spectrofluorimeter (HORIBA, Joben Ivon Inc.). The excitation and luminescence spectra of the obtained activators were measured in toluene at a concentration of 10^{-5} mol/l.

2.5 Measurement of light output. The light output of the PS is measured on a scintillation spectrometer made in the CAMAC standard. The signal from the anode of the Hamamatsu R1307 photomultiplier (PMT) is fed directly to the input of the digital charge converter QDC LeCroy 2249A. The PS samples are placed directly on the surface of the PMT photocathode, optical contact is provided using an immersion liquid. Irradiation is carried out with conversion electrons with an energy of 975 keV from a monoenergetic source of the radionuclide ^{207}Bi. The light output is determined by the position of the maximum peak of the amplitude scintillation spectrum. The relative light output of the obtained samples is set according to the light output of the standard plastic scintillator UPS-923A [18].

2.6 Measurement of time characteristics. Time characteristics were determined by the method of correlation single-photon counting [19] on a two-channel installation with two Hamamatsu 9800 PMTs in the "Start" and "Stop" channels. A ^{90}Sr electron source was used to measure the time characteristics of the PS. The Cherenkov radiation signal from a sample made of polymethyl methacrylate was used as a starting pulse.

2.7 Irradiation of samples. Irradiation of PS samples was carried out on a LUE-40 linear accelerator (electron energy – 41.2 MeV, dose rate – 135±9 Gy/s [20]) and in the radiation field of a ^{60}Co source with a dose rate of 12 Gy/h in air. Further in the work, in the case of irradiation of PS samples at a linear accelerator, the note (LUE-40) will be indicated along with the irradiation dose, and in the case of irradiation with a ^{60}Co source, the note (^{60}Co) will be indicated along with the irradiation dose.

2.8 Determination of radiation resistance. To characterize the radiation resistance of a PS in the literature, the ratio of the light output measured immediately after irradiation of the PS (L) and the unirradiated PS (L_0), i.e. L/L_0, is usually used. At the same time, different authors use different radiation doses and PS samples of different shapes. Therefore, for a more correct comparison of the radiation resistance values of the PS obtained by different authors, it is more convenient to use the dose of half attenuation of the light output ($D_{1/2}$, Mrad), which does not depend on the radiation dose and can be calculated if the value of L/L_0 and the radiation dose [21] are known. $D_{1/2}$ is the dose of ionizing radiation after irradiation at which the value of the light output of the PS decreases by 2 times:

$$L = L_0 \times \exp\left(-\alpha D\right), \qquad (1)$$

where L and L_0 are the light output of the PS sample before and after irradiation,

α is the degradation constant ($Mrad^{-1}$, kGy^{-1}),

D is the irradiation dose (Mrad, kGy).

The value of the degradation constant α is calculated by approximating experimental data, based on formula 1:

$$\alpha = \ln(L_0 / L) / D .$$

Since the dose of half attenuation of the light output $D_{1/2}$ is determined at L/L_0 = 1/2, the equation yields:

$$D_{1/2} = \left(\ln 2\right) / \alpha . \qquad (2)$$

It is the light output half attenuation dose that is used in this work as a parameter characterizing the radiation resistance of the material.

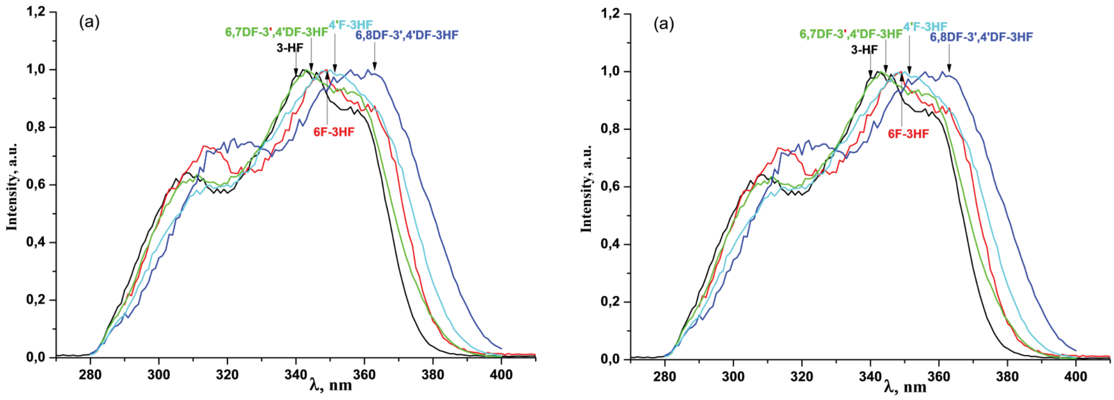


Figure 3 – Excitation (a) and luminescence (b) spectra of 3-HF molecules and its derivatives in toluene solution (10^{-5} mol/l)

It should be noted that when irradiated in the presence of oxygen, the polymer composition undergoes greater radiation damage than in the absence of oxygen. At low irradiation intensity (as in the case of ^{60}Co), the PS undergo greater damage than in the case of high-intensity irradiation (as in the case of high-energy electrons), since the same dose is accumulated over a longer period of time during which the oxygen contained in the air has time to diffuse into the depth of the sample. Therefore, at the same absorbed dose, the calculated value of $D_{1/2}$ will be higher under intense irradiation than under low-intensity irradiation. Given this, a correct comparison of the radiation resistance of materials by the parameter $D_{1/2}$ can only be made if the irradiation conditions of the samples coincide; otherwise, it is necessary to take into account the peculiarities of radiation damage to the material under different types and conditions of irradiation.

3 Results and discussion

In the works [14, 18, 22, 23], a study of PS based on polystyrene was conducted, in which 3-HF was used both as a shifter and as an activator. Two-component PS containing 3-HF as an activator demonstrated higher radiation resistance compared to three-component PS containing 3-HF as a shifter and p-terphenyl (p-TP) as an activator. That is, to eliminate the influence of radiolysis products, 3-HF is better used as an activator than as a shifter. Thus, the use of 3-HF as an activator allows to increase the radiation resistance of PS to 7 Mrad, but, as already noted, in modern conditions this is not enough.

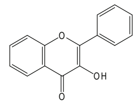
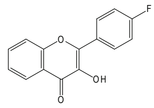
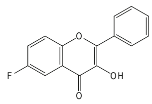
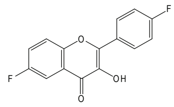
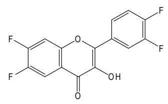
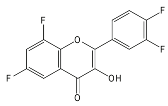
As is known, radiation degradation of PS is a long process that depends on a number of factors: the intensity of ionizing radiation, the nature of the polymer matrix, the concentration of luminescent additives and the presence of impurities. In the case when it is possible to avoid these traps by using an activator with a large Stokes shift, one of the important factors affecting the radiation stability of PS is the radiation stability of the activators themselves. An effective method of increasing the light stability of organic dyes is the introduction of fluorine atoms into their molecules [24, 25]. Given that the nature of damage to organic molecules under the action of light and under the action of ionizing radiation is in many ways similar, this approach was also applied to increase the radiation resistance of 3-HF.

3.1 PC with 3-hydroxyflavone derivatives containing one, two or four fluorine atoms

Fluorine derivatives of 3-HF with different numbers of fluorine atoms, both in the chromene fragment and in the phenyl part of the molecule, were synthesized. The structural formulas, names and symbols of the obtained compounds are presented in Table 1.

Fig. 3 shows the excitation (a) and luminescence (b) spectra of the 3-HF molecule and its fluorine derivatives in a toluene solution. It can be seen from Fig. 3b that the replacement of one or two hydrogen atoms by fluorine in the 3-HF molecule has practically no effect on the nature of its luminescence spectra. The maximum of the luminescence spectrum begins to shift somewhat to the long-wavelength region only after the replacement of four hydrogen atoms by fluorine. Therefore, the position of the main luminescence maximum in the region of 530 nm of fluoroderivatives of 3-HF, as in unsubstituted molecules, ensures a reduction in

Table 1 – Symbols, formulas and names of fluorinated derivatives 3-HF

Symbol	Structural formula	Name
3-HF		3-hydroxy-2-phenyl-4H-chromen-4-one
4′F-3HF		2-(4-fluorophenyl)-3-hydroxy-4H-chromen-4-one
6F-3HF		6-fluoro-3-hydroxy-2-phenyl-4H-chromen-4-one
6F4′F-3HF		6-fluoro-2-(4-fluorophenyl)- 3-hydroxy-4H-chromen-4-one
6,7DF-3′,4′DF-3HF		6,7-difluoro-2-(3,4-difluorophenyl)- 3-hydroxy-4H-chromen-4-one
6,8DF-3′,4′DF-3HF		6,8-difluoro-2-(3,4-difluorophenyl)- 3-hydroxy-4H-chromen-4-one

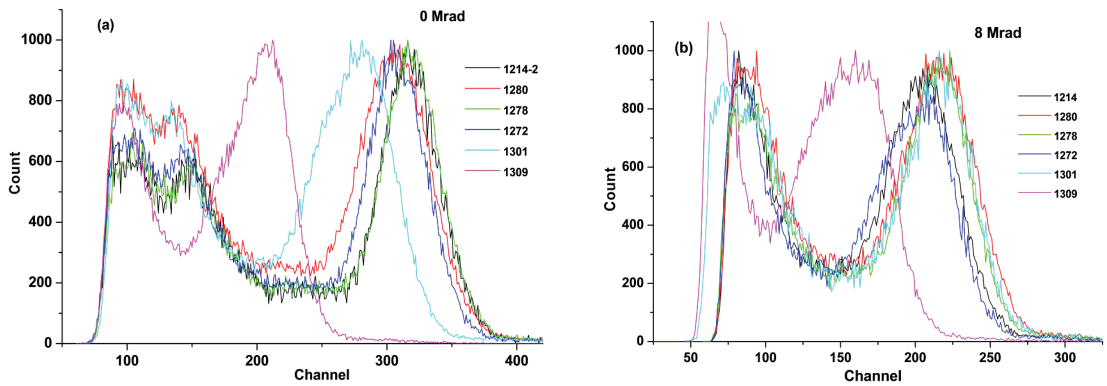


Figure 4 – Scintillation amplitude spectra of polystyrene-based PS containing 2 wt. % 3-HF and its fluoro derivatives, before (a) and after (b) irradiation with a dose of 8 Mrad

excitation energy losses on traps formed during irradiation of polystyrene.

Fluoro derivatives 3-HF were used as activators of polystyrene base PS. A series of PS with 2 wt. % of the corresponding activator was obtained. To determine the radiation resistance of PS samples, their relative light output before and after irradiation with a dose of 8 Mrad (LUE-40) was measured (Fig. 4). Table 5 presents the PS compositions, their light output before and after irradiation with a dose of 8 Mrad, as well as the $D_{1/2}$ values.

When analyzing the obtained light output values, it is necessary to take into account the fact that the maximum sensitivity of the used PMT [26] is in the region of 420 nm, while the maximum luminescence of 3-HF derivatives lies in the range of 530–550 nm. In this wavelength range, the sensitivity of the PMT is half as low (Fig. 5), which is proportionally reflected in the actually measured light output value.

The obtained data show that the new scintillation compositions demonstrate higher radiation resistance compared to PS, where unsubstituted 3-HF was used as an activator (Table 2, 1214). Replacing hydrogen with fluorine atoms in 3-HF molecules leads to an increase in the radiation resistance of PS activated by them. Depending on the position and number of fluorine atoms in the 3-HF molecule, it was

Table 2 – Composition of PS containing 3-HF and its fluoro derivatives, their relative light output (L_0) before and after (L) irradiation with a dose of 8 Mrad (LUE-40), light output half attenuation dose ($D_{1/2}$)

Sample number	Composition of polystyrenebased PS, wt.%	L_0, %	L, %	$D_{1/2}$, Mrad
1214	2 3-HF	31.5	20.3	12.6
1272	2 4′F-3HF	30.6	20.9	14.5
1278	2 6F-3HF	31.5	21.4	14.3
1280	2 6F4′F-3HF	30.4	21.4	15.8
1301	2 6,7DF-3′,4’DF-3HF	28.0	21.4	20.6
1309	2 6,8DF-3′,4’DF-3HF	20.9	16.1	21.3
UPS-923A	2 p-TP + 0,02 POPOP	100	-	-

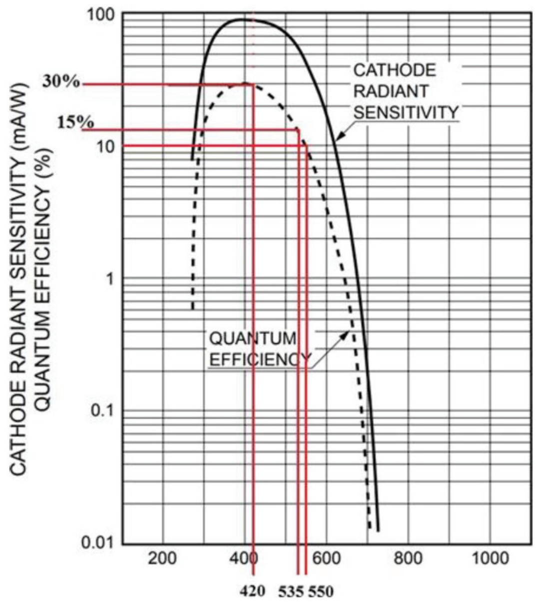


Figure 5 – Sensitivity of the Hamamatsu R1307 PMT [27]

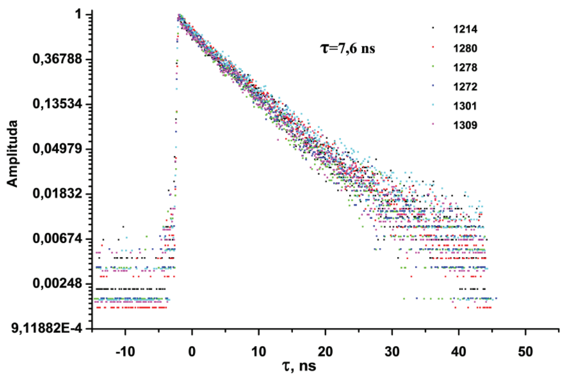


Figure 6 – Scintillation pulse decay of PS with fluorinated 3-HF derivatives

possible to achieve an increase in the radiation resistance of the material in the range from 15% to 69% (from 12.6 Mrad to 21.3 Mrad).

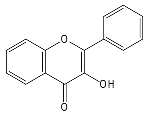
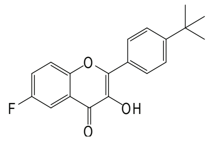
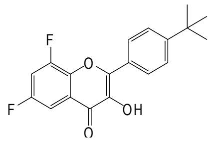
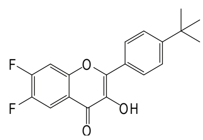
A study of the time characteristics of PS showed that they have almost the same scintillation pulse rise time – 0.9 ns (Fig. 6). This value is typical for PS on a polystyrene basis, since it is mainly associated with the time of charge absorption in the track created during the flight of a high-energy particle. From Fig. 6 shows that the modification of the 3-HF molecule does not lead to a change in the scintillation pulse decay time, the value of which is 7.6 ns. It should be noted that the decay spectra of the activator molecules did not change even after irradiation with a dose of 8 Mrad - both the exponential character and the numerical value are preserved. This indicates the absence of radiationless quenching of the luminescence of the activator molecules in the traps formed during irradiation.

Thus, it is shown that the replacement of hydrogen with fluorine atoms in 3-HF molecules leads to an increase in the radiation resistance of PS, where these compounds are used as activators. Depending on the position and number of fluorine atoms in the 3-HF molecule, it was possible to achieve an increase in the radiation stability of PS up to $D_{1/2}$ = 21.3 Mrad [27 – 30].

3.2 PS with tert-butylfluoroderivatives of 3-hydroxyflavone

It is known from previous studies that an increase in the concentration of the activator can lead to an increase in the radiation resistance of PS [17]. Therefore, it is relevant to check the possibility of increasing the radiation resistance of PS activated by 3-HF by increasing its concentration. However, the solubility of 3-HF and its derivatives in polystyrene usually does not exceed 1.5–2 wt. % [31], which limits further improvement of PS properties. To increase the solubility of 3-HF fluoroderivatives, a tert-butyl group was introduced into their molecules. Modification of activator molecules with a tert-butyl group, as a rule, does not significantly affect their spectral-luminescent characteristics [32, 33].

Table 3 – Symbols, structural formulas and names of tert-butyl fluoroderivatives 3-HF

Symbol	Structural formula	Name
3-HF		3-hydroxy-2-phenyl-4H-chromen-4-one
6F-4’TB-3HF		2-(4-(tert-butyl)phenyl)-6-fluoro-3-hydroxy-4H-chromen-4-one
6,8DF-4’TB-3HF		2-(4-(tert-butyl)phenyl)-6,8-difluoro-3-hydroxy-4H-chromen-4-one
6,7DF-4’TB-3HF		2-(4-(tert-butyl)phenyl)-6,7-difluoro-3-hydroxy-4H-chromen-4-one

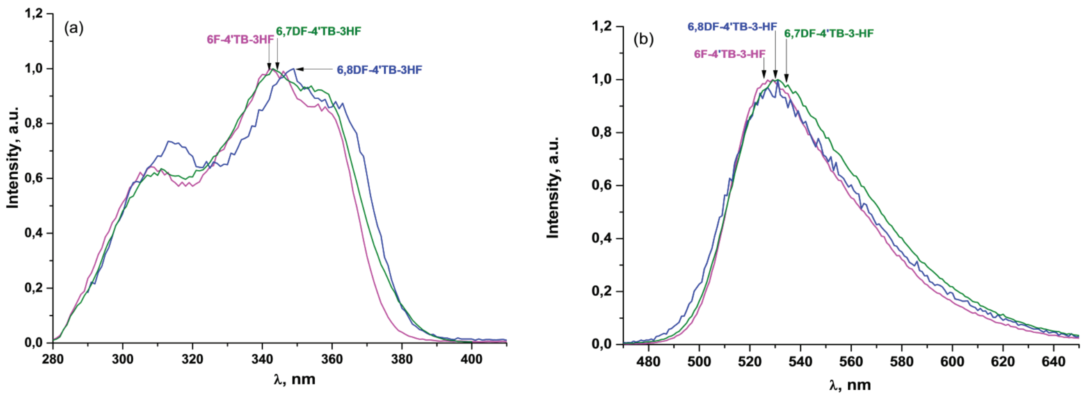


Figure 7 – Excitation (a) and luminescence (b) spectrum of 6F-4’TB-3HF at a concentration of 0.01 wt. % in polystyrene

Thus, fluoroderivatives of 3-HF were obtained, containing a tert-butyl substituent in position 4 of the phenyl fragment of the molecule. Table 3 presents the structural formulas, names and symbols of the obtained compounds.

As expected, the introduction of a tert-butyl group into molecules of 3-HF derivatives allowed to increase their solubility in polystyrene to 3 wt. %. This also did not cause a significant change in their spectral-luminescent characteristics. Thus, in the example of 6F-4′TB-3HF, it can be seen that the luminescence spectrum is practically identical to the luminescence spectrum of unsubstituted 3-HF (Fig. 7). This is also true for other fluoro-tert-butyl derivatives.

The luminescence and excitation spectra retained the specified form over the entire available concentration range of 6F-4′TB-3HF, 6,7DF-4’TB-3HF and 6,8DF-4’TB-3HF molecules in polystyrene. Neither broadening of the luminescence band nor change in its position were observed, indicating the absence of any aggregation of these activators in polystyrene.

The scintillation pulse decay curve of PS activated by 6F-4′TB-3HF is shown in Fig. 8. For PS samples containing 6,7DF-4’TB-3HF and 6,8DF-4’TB-3HF, the decay curves have a similar character, the scintillation pulse decay constant for all PS was 6.53 ns. It should be noted that the scintillation pulse decay curves retained an identical character in the entire investigated range of activator concentrations in polystyrene (from 1 wt. % to 3 wt. %). This behavior of the decay curves also indicates the absence of luminescent aggregates of 6F-4′TB-3HF, 6,7DF-4’TB-3HF and 6,8DF-4’TB-3HF.

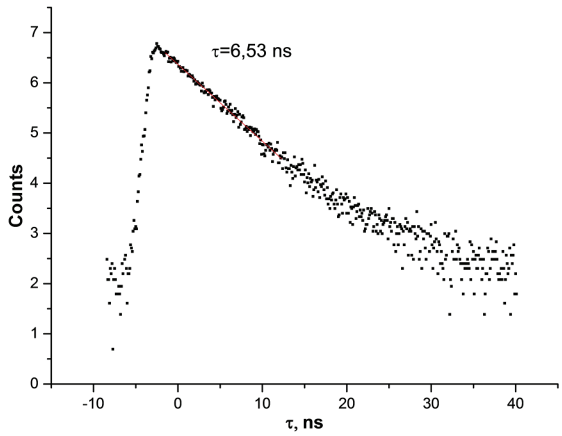


Figure 8 – Scintillation pulse decay curve of PS with 2 wt. % 6F-4′TB-3HF (source – ^{90}Sr)

The maximum luminescence of the 6F-4′TB-3HF PS is located at a wavelength of 538 nm. Considering the sensitivity of the PEP in this range, we can say that the light output of the new PS is at the level of the light output of the standard PS.

For PS samples activated by 6F-4′TB-3HF and 6,7DF-4’TB-3HF molecules, the maximum light output was observed at an activator concentration of 2 wt. %. At higher activator concentrations, the relative light output of PS begins to decrease, however, even at a content of 3 wt. %, the samples maintain the light output at a level sufficient for practical application.

PS activated by 6,8DF-4’TB-3HF demonstrated a gradual increase in light output with an increase in the activator content to 3 wt. %. The maximum light output was in the sample with 2 wt. % 6,7DF-4′TB-3HF. At the same time, it was almost 20 % higher than for PS with 2 wt. % unsubstituted 3-HF (Fig. 9, Table 3).

To determine the radiation stability of the obtained PS, the relative light output was measured before and after irradiation with a dose of 7 Mrad (^{60}Co). Table 4 shows the compositions of PS, their light output before and after irradiation, and the parameter $D_{1/2}$.

As can be seen from Table 4, the radiation resistance of PS activated by tert-butylfluoro derivatives of 3-HF is about 7 Mrad. This value is close to the radiation resistance of PS activated by unsubstituted 3-HF. That is, increasing the concentration of activators did not lead to an increase in the radiation resistance of PS. The obtained data indicate that the expected improvement in the radiation resistance of PS with increasing activator concentration is not universal. Probably, in this case, the radiation resistance depends on the properties and structure of the activator molecules themselves [34 – 36].

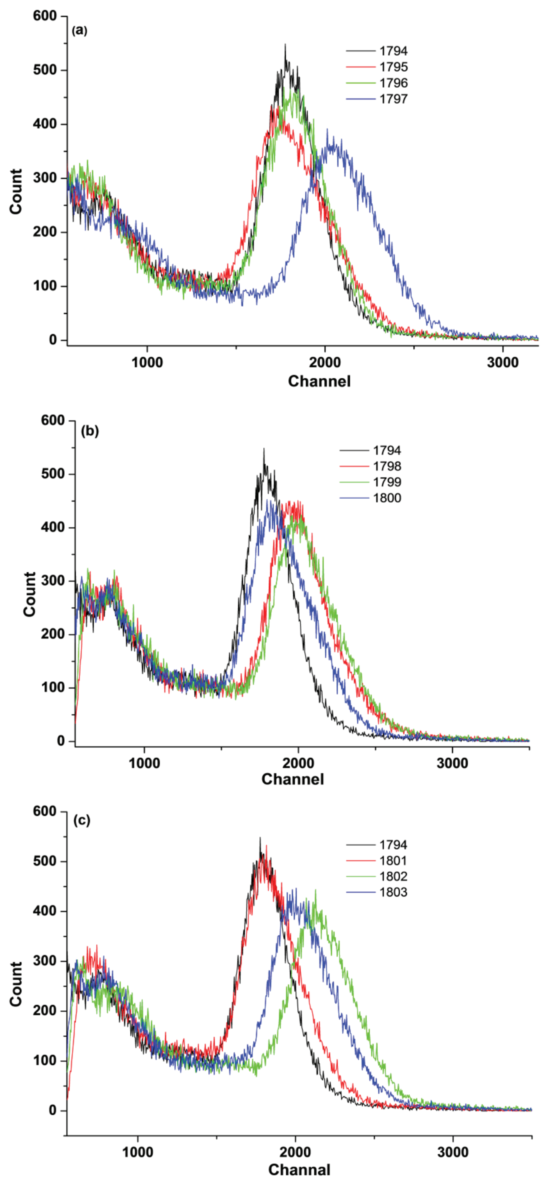


Figure 9 – Scintillation amplitude spectra of PS with different concentrations of tert-butyl fluoroderivatives 3-HF (source 207Bi): (a) 6,8DF-4′TB-3HF; (b) 6F-4′TB-3HF; (c) 6,7DF-4′TB-3HF

3.3 PS with fluoroderivatives of 4′-phenyl-3-hydroxyflavone

Also in the framework of the search for effective activators with a large Stokes shift, 4′-phenyl-3-hydroxyflavone (4′Ph-3-HF) was obtained and studied. In the work [37] it was found that the addition of a phenyl substituent at the 4′-position of the 3-HF molecule causes bathochromic and bathoflor shifts of the absorption and luminescence spectra (Fig. 10),

Table 4 – Composition of PS containing the obtained tert-butylfluoroderivatives 3-HF, their relative light outputs before (L_0) and after (L) irradiation with a dose of 7 Mrad (^{60}Co), $D_{1/2}$

Sample number	Composition of polystyrene based PS, wt. %	L_0, %	L, %	$D_{1/2}$, Mrad
1794	2 3-HF	100	49	6.9
1795	1 6,8DF-4′TB -3HF	97	51	7.5
1796	2 6,8DF-4′TB -3HF	101	47	6.6
1797	3 6,8DF-4′TB -3HF	115	53	6.4
1798	1 6F-4′TB-3HF	110	54	6.9
1799	2 6F-4′TB-3HF	110	43	5.4
1800	3 6F-4′TB-3HF	103	46	6.1
1801	1 6,7DF-4′TB-3HF	101	49	7.0
1802	2 6,7DF-4′TB-3HF	120	58	6.7
1803	3 6,7DF-4′TB-3HF	112	53	6.4

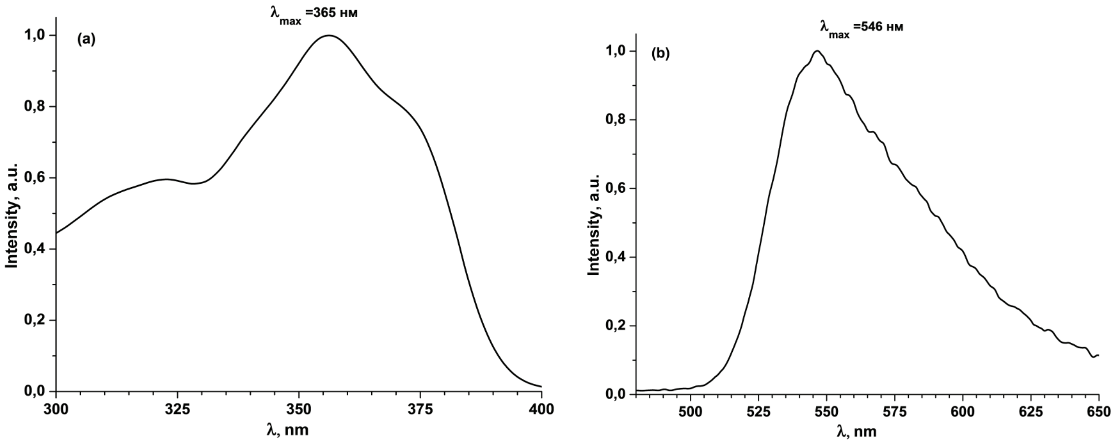


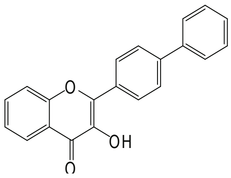
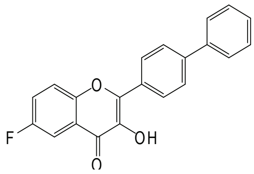
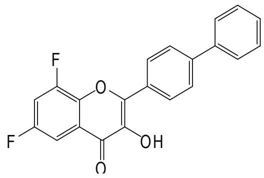
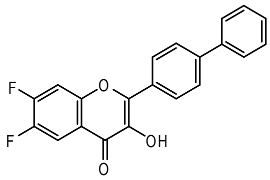
Figure 10 – Excitation (a) and luminescence (b) spectra of 4′-phenyl-3-hydroxyflavone in toluene (10^{-5} mol/L)

which more than doubles the absorption intensity, and also significantly increases the luminescence quantum yield [22]. The introduction of 2 wt. % 4′Ph-3-HF into the PS composition provides higher values of light output and radiation resistance compared to unsubstituted 3-HF and some of its derivatives. Also, as shown earlier the introduction of fluorine atoms in positions 6, 7 and 8 of 3-HF molecules increases the radiation resistance of PS, in which these fluorine derivatives were used as the primary luminescent additive. Taking into account these data, it was assumed that the simultaneous introduction of a phenyl substituent and fluorine atoms into the 3-HF molecule should lead to an even greater increase in radiation resistance. To test this assumption, a series of 4′Ph-3-HF fluorine derivatives containing different numbers of fluorine atoms in positions 6, 7, 8 of the chromene fragment of the molecule was obtained (Table 5).

The introduction of one or two fluorine atoms has practically no effect on the nature or position of the excitation and luminescence maxima of the fluorine derivatives compared to unsubstituted 4′Ph-3HF (Fig. 11). The excitation maxima of the obtained fluorine derivatives lie in the region of 360 nm, and the luminescence maxima remained in the region of 550 nm.

Fluorine derivatives 4’Ph-3HF were used to obtain samples of radiation-resistant polystyrene based PSs. The activator concentration was 1 wt. %. At higher concentrations, precipitation of the additive is possible due to their relatively low solubility in polystyrene. At lower concentrations of the additive, its amount is not enough to effectively convert the excitation energy of the polymer base into a scintillation signal, which leads to a drop in light output and a significant decrease in the efficiency of the scintillator.

Table 5 – Symbols, structural formulas and chemical names of the obtained fluoro-derivatives of 4′Ph-3-HF

Symbol	Structural formula	Name
4′Ph-3HF		2-([1,1’-biphenyl]-4-yl)-3-hydroxy-4H-chromen-4-one
6F-4′Ph-3HF		2-([1,1’-biphenyl]-4-yl)-3-hydroxy-6-methyl-4H-chromen-4-one
6,8DF-4′Ph-3HF		2-([1,1’-biphenyl]-4-yl)-6,8-difluoro-3-hydroxy-4H-chromen-4-one
6,7DF-4′Ph-3HF		2-([1,1’-biphenyl]-4-yl)-6,7-difluoro-3-hydroxy-4H-chromen-4-one

The spectral-luminescent and scintillation properties of the obtained PS were investigated, and their radiation resistance was determined.

The relative light output of the obtained PS was in the range from 22 % to 33 % of the light output of the standard UPS-923A PS [18] (Fig. 12). The maximum light output at an additive concentration of 1 wt. % was achieved for unsubstituted 4′Ph-3HF and was 33 %.

The maximum luminescence of PS with fluoroderivatives of 4′Ph-3HF is located at a wavelength of 550 nm. In this region, the sensitivity of the R1307 PMT is almost three times lower than in the region of 420 nm. Taking this into account, we can say that the absolute light output of the obtained PS is at the level of the light output of the standard PS. In Table 8 presents the compositions of PS, their relative light output before (L_0) and after irradiation with a dose of 15 Mrad (L) (LUE-40), and the calculated value of the light output half attenuation dose ($D_{1/2}$).

From the obtained data it is clear that the new compositions of PS demonstrate higher radiation resistance compared to PS, where unsubstituted 4′Ph-3HF was used as an activator (Table 8). Replacing hydrogen with fluorine atoms in 4′Ph-3HF molecules leads to an increase in the radiation resistance of the plastic scintillators activated by them. The introduction of one fluorine atom leads to an increase in radiation stability by only a few Mrad. In the case of replacing two hydrogen atoms with fluorine in the 6,7- or 6,8- position of the chromene fragment of the 4′Ph-3HF molecule, the radiation resistance of PS increases by two times. For PS with a content of 1 wt. % in the 6,8DF-4′Ph-3HF molecule, $D_{1/2}$ reaches 49 Mrad.

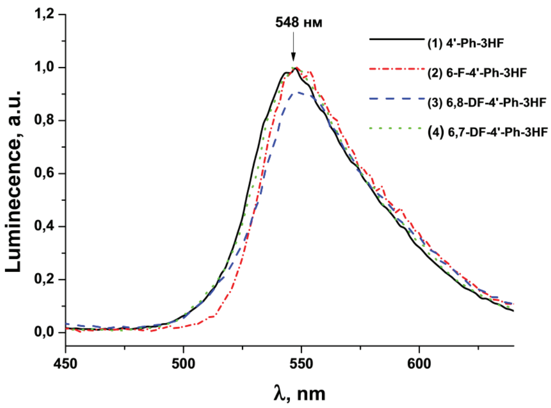


Figure 11 – Luminescence spectra in toluene (10^{-5} mol/L): 4’Ph-3HF (1); 6F-4’Ph-3HF (2); 6,8DF-4’Ph-3HF (3); 6,7DF-4’Ph-3HF (4)

Table 8 – Composition of PS containing 4′Ph-3HF obtained by fluorine derivatives, their relative light outputs before (L_0) and after (L) irradiation with a dose of 15 Mrad (LUE-40), $D_{1/2}$

Sample number	Composition of polystyrene based PS, wt.%	L_0, %	L, %	$D_{1/2}$, Mrad
1214	2 3-HF	30.5	18.1	13.8
3001	1 4′Ph-3HF	33.2	21.2	23.3
3002	1 6F-4′Ph-3HF	30.0	20.3	26.3
3003	1 6,8DF-4′Ph-3HF	22.6	18.3	49.0
3004	1 6,7DF-4′Ph-3HF	29.0	23.4	47.2
UPS-923A	2 p-TP + 0,02 POPOP	100	-	-

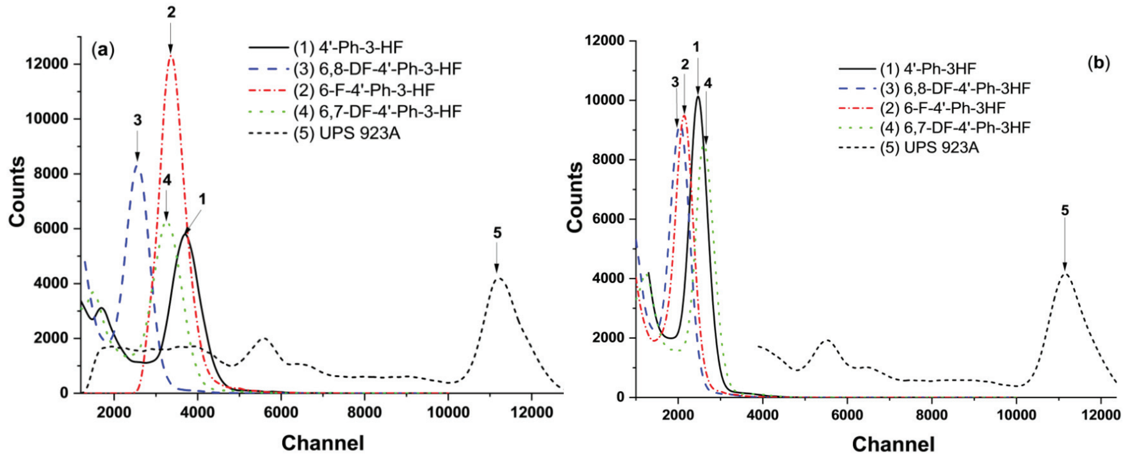


Figure 12 – Scintillation amplitude spectra of PS with fluorine derivatives of 4’Ph-3HF before (a) and after (b) irradiation with a dose of 15 Mrad

Thus, it was established that the replacement of hydrogen with fluorine atoms in 4′Ph-3HF molecules leads to an increase in the radiation resistance of the PS activated by them. Depending on the position and number of fluorine atoms in the molecule, it was possible to achieve an increase in the radiation resistance of the material from 23 Mrad to 49 Mrad [38].

3.4 PS with a 3-hydroxyflavone derivative containing three fluorine atoms

As can be seen, our team investigated 3-hydroxyflavone derivatives containing one, two or four fluorine atoms in different positions. It was shown that with an increase in the amount of fluorine in the 3-hydroxyflavone molecule, the radiation resistance of PSs, where these additives are used as activators, increases. To complete the work, it is relevant to obtain a 3-hydroxyflavone derivative with three fluorine atoms, develop PSs using it and investigate its radiation resistance. Thus, a derivative of 3-hydroxyflavone containing three fluorine atoms was synthesized – 6,8-fluoro-2-(4-fluorophenyl)-3-hydroxy-4H-chromen-4-one (Fig. 13).

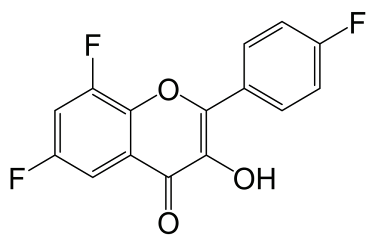


Figure 13 – Structural formula of 6,8-fluoro-2-(4-fluorophenyl)-3-hydroxy-4H-chromen-4-one (6,8DF-4′F-3HF)

Fig. 14 shows the excitation and luminescence spectra of the obtained derivative 6,8DF-4′F-3HF. It can be seen that, as in the case of replacing four hydrogen atoms with fluorine in the 3-hydroxyflavone molecule [28-30], when replacing three atoms, the luminescence maximum also shifts by 15 nm to the long-wavelength region (Fig. 14 b). In this case, a significant shift of the excitation maximum, almost

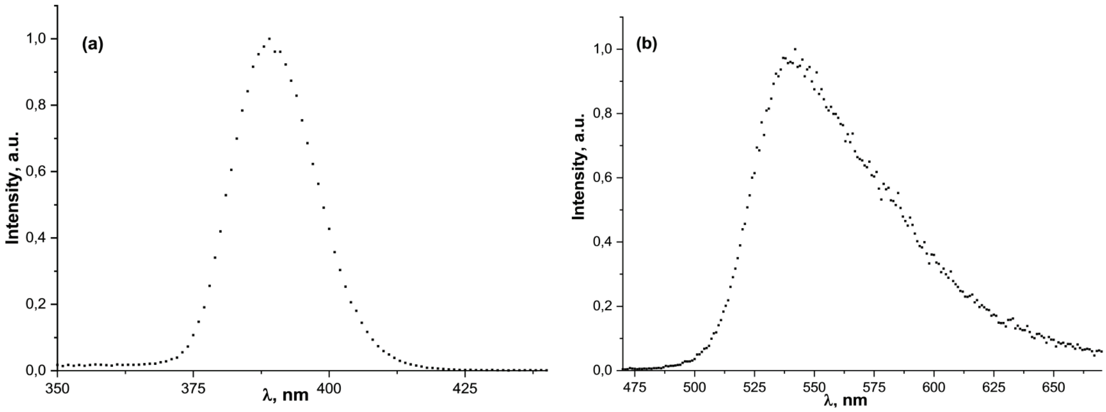


Figure 14 – Excitation (a) and luminescence (b) spectra of 6.8DF-4′F-3HF in toluene (10^{-5} mol/l)

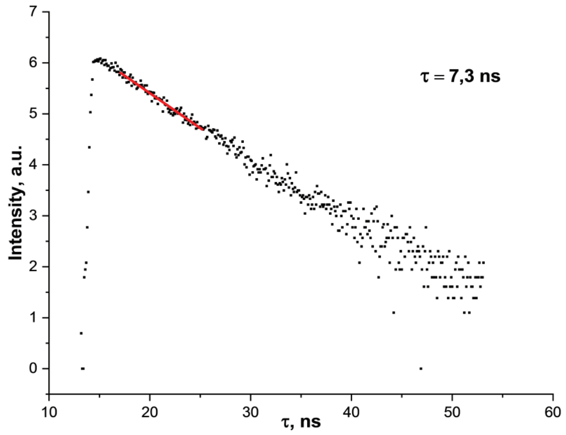


Figure 15 – Scintillation pulse decay curve of PS with 2 wt. % 6,8DF-4′F-3HF (source – ^{90}Sr)

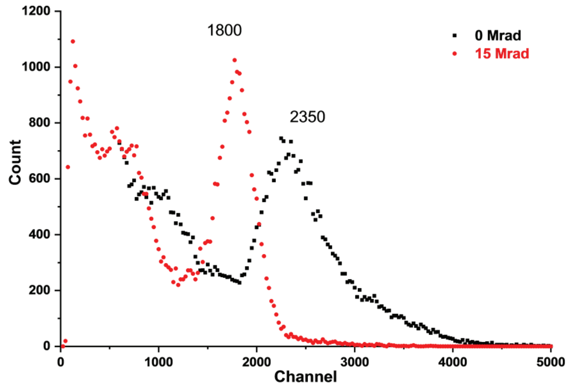


Figure 16 – Scintillation amplitude spectra of PS with 2 wt. % 6,8DF-4′F-3HF before (a) and after (b) irradiation with a dose of 15 Mrad

by 40 nm, to the long-wavelength region is also observed.

PS with 2 wt. % 6,8DF-4′F-3HF, a was obtained, its time characteristics were investigated, the relative light output was measured before and after irradiation with a dose of 15 Mrad (LUE-40) and the value of the half-attenuation dose of the light output was calculated (Fig. 16, Table 9).

Fig. 8 shows the scintillation pulse decay curve of a PS with 2 wt. % 6.8DF-4′F-3HF. It has a typical form for PS activated by 3-hydroxyflavone derivatives containing one, two or four fluorine atoms in different positions, while the scintillation pulse decay constant for the obtained PS was 7.3 ns.

For a correct comparison of the radiation stability of PS with 2 wt. % 6.8DF-4′F-3HF, PS samples with 2 wt. % unsubstituted 3-HF and its mono- and difluoro derivatives - 6F-3HF and 6F4′F-3HF were also obtained. PS samples were obtained and irradiated under the same conditions.

From Table 9 it is seen that PS with 6,8DF-4′F-3HF, a derivative of 3-hydroxyflavone containing three fluorine atoms, has higher radiation stability compared to PS with unsubstituted 3-HF.

Therefore, the obtained data once again confirm that an increase in the number of fluorine atoms in the 3-hydroxyflavone molecule leads to an increase in the radiation stability of PS, where these additives are used as activators.

4 Conclusions

The introduction of one or two fluorine atoms into any part of the 3-HF molecule has practically no effect on its spectral and luminescent properties. The introduction of three and four fluorine atoms into any part of the 3-HF molecule causes bathochromic and bathofloral shifts of the excitation and luminescence spectra by 15-20 nm compared to unsubstituted 3-hydroxyflavone. The time characteristics of PSs activated by fluoroderivatives of 3-HF containing one to four fluorine atoms do not change depending on the activator, while the

Table 9 – Composition of PS containing 3-HF and its fluoro derivative, their relative light output (L_0) before and after (L) irradiation with a dose of 15 Mrad (LUE-40), light output half attenuation dose ($D_{1/2}$)

Sample number	Composition of polystyrene based PS, wt.%	L_0, %	L, %	$D_{1/2}$, Mrad
1214	2 3-HF	30.5	18.1	13.8
1278	2 6F-3HF	34.7	20.7	20.0
1280	2 6F4′F-3HF	40	25.9	23.9
4000	2 6,8DF-4'DF-3HF	21.1	16.4	40.6
UPS-923A	2 p-TP + 0,02 POPOP	100	-	-

scintillation pulse decay time for all PSs is 7.3 - 7.6 ns. The replacement of hydrogen with fluorine atoms in 3-HF molecules leads to an increase in the radiation resistance of PSs, where these molecules are activators. Depending on the position and number of fluorine atoms in the 3-HF molecule, it was possible to achieve an increase in the radiation resistance of the material to 40.6 Mrad. Using fluoroderivatives 4′Ph-3HF, PS was obtained, the $D_{1/2}$ of which reaches 49 Mrad.

Modification of fluoroderivatives of 3-HF with a tert-butyl group increases their solubility in polystyrene. Increasing the activator concentration to 3 wt. % allowed obtaining PS with a light output 20% higher than the light output of PS activated by unsubstituted 3-HF. However, increasing the concentration of activators did not lead to an increase in the radiation resistance of PS. The obtained data indicate that the expected improvement in the radiation resistance of PS with an increase in the activator concentration is not universal. Probably, in this case, radiation resistance depends on the properties and structure of the activator molecules themselves.

The obtained results demonstrate that fluoro-, phenyl-, and fluorophenyl derivatives of 3-hydroxyflavone are effective activators for the creation of radiation-resistant PS.

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