

Plastic scintillator with gadolinium phenylpropionate

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The paper is devoted to studies of scintillation efficiency of Gd-activated plastic scintillators. It is shown that during polymerization of Gd-loaded plastic, the quenching coloring centers are formed, preventing the energy transfer from the primary to the secondary luminescent additive, which could decrease the scintillator light yield. To weaken the quenching effect of coloring centers, it is proposed to use an auxiliary additive for plastic scintillators that absorbs in the absorption region of the primary luminescent additive and emits in the emission region of the secondary luminescent additive. Using such an additive enables to increase the Gd content in scintillator up to 2 %. The obtained scintillator showed light yield of 62 % with respect to the scintillator of standard content.

Изучена сцинтилляционная эффективность пластмассовых сцинтилляторов с добавкой гадолиния. Показано, что в процессе полимеризации Gd-содержащих пластмассовых сцинтилляторов образуются тушащие центры окраски, препятствующие переносу энергии возбуждения с первичной на вторичную люминесцентную добавку, что является причиной снижения световыхода сцинтиллятора. Для ослабления тушащего эффекта центров окраски предложено в составе пластмассовых сцинтилляторов использовать дополнительную люминесцентную добавку, которая поглощает в области первичной, а излучает в области вторичной люминесцентной добавки. Использование такой добавки позволило повысить содержание гадолиния в сцинтилляторе до 2 %. Полученный сцинтиллятор имеет световой выход 62 % относительно сцинтиллятора стандартного состава.

1. Introduction

Liquid scintillators with gadolinium additives are widely used in high energy physics. Because of extremely high neutron capture cross-section of gadolinium, this element is very efficient for neutron and neutrino detection. It is obvious that detection efficiency is increasing not only with larger cross-section, but also with higher Gd concentration in the scintillator. Usually Gd-containing substances are inserted in a liquid medium, forming, for example, liquid scintillators. But the practical use of liquid scintillators is related to many problems of

light collection, leak-proof design, fire safety and long-time stability of the detecting devices. Changing the base of a liquid scintillator to a solid or plastic can be a way of solving these problems.

But creating plastic scintillators (PS) with high level of neutron detection efficiency and high scintillation efficiency is a difficult and contradictory task. Indeed, to achieve high detection efficiency, Gd concentration is to be increased, which would lead to a significant decrease in PS scintillation efficiency. As it will be shown below, the main reason of scintillation efficiency degradation is the absorption band that ex-

ists in Gd-loaded PS and is located in the absorption region of the primary luminescent additive (LA1). This absorption prevents radiation transfer of excitation energy from the primary to the secondary luminescent additive (LA2). Moreover, to improve the registration efficiency, it is necessary to increase Gd concentration in the scintillator, which is difficult to realize because of poor solubility of most Gd-containing substances in aromatic polymers. There are only few reports about content and properties of Gd-loaded PS [1–4]. In these papers various compounds of Gd are presented that are inserted in a standard PS (polymer matrix and two luminescent additives). Described PS contain up to 2 wt.% of Gd and, due to above reasons, have markedly low scintillating efficiency. It is possible to insert Gd in a polymer matrix in the form of organic or inorganic compounds. The use of inorganic salts (e.g., gadolinium chlorides or nitrates) is restricted by their poor solubility in organic media. Therefore for their using it is necessary to add emulsifying agents or surfactants, which have hydrophilic and hydrophobic groups in a polymer composition. Moreover, the main characteristics of scintillators based on nitrates of metals are usually unstable [5]. The complexes with beta-diketones and carboxylates of gadolinium are often used as the organic compounds [6, 7]. All gadolinium complexes except carboxylates have distinctly expressed yellow color that makes the use of carboxylates more promising. Moreover, the salts of carboxylic acids have higher stability and better solubility in aromatic polymers. The advantage of carboxylic acids is that they are salt-forming agents, which practically excludes the ingress of foreign anions (Cl^- , NO_3^- etc.) into the organic phase causing an abrupt decrease in the scintillator light yield.

Basing on above advantages of carboxylic acids, we decided to use a gadolinium derivative of hydroxycinnamic acid — gadolinium phenylpropionat ($\text{Gd}(\text{OCO}(\text{CH}_2)_2\text{C}_6\text{H}_5)_3 \cdot 2\text{H}_2\text{O}$) as Gd-loaded substance. This salt, which was synthesized in our laboratory, has both aliphatic and aromatic fragments in its acid residual, which improves its solubility in aromatic polymers. We used polystyrene as a PS base. According to previous results we saw no need to use PS with a conventional three-component composition (aromatic base, activator (LA1), and wavelength shifter (LA2) [8]. The results obtained in [1, 4] and confirmed in the present work

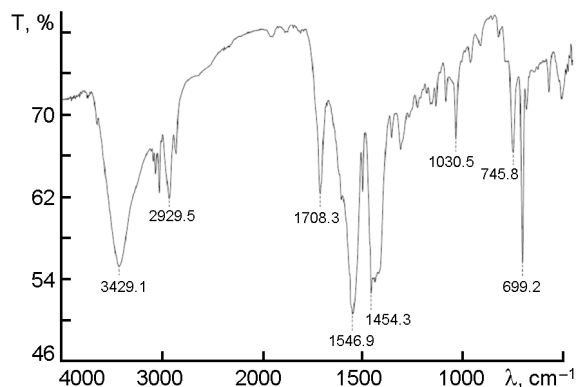


Fig. 1. IR spectrum of $\text{Gd}(\text{OCO}(\text{CH}_2)_2\text{C}_6\text{H}_5)_3 \cdot 2\text{H}_2\text{O}$.

showed that the radiative mechanism of excitation energy transfer from LA1 to LA2 is suppressed to a large extent in the presence of Gd-containing substances. Therefore, instead of the wave-length shifter, we have used a luminescent additive 1,4-dimethyl-9,10-diphenylanthracene (DMDPA), which absorbs in a LA1 luminescence region and emits in a LA2 emission region. In such a way the non-radiative transfer of excitation from the PS matrix is realized not affected by the presence of a Gd-containing complex.

2. Experimental

As raw materials, we used gadolinium oxide (99.998 %), phenylpropionic (hydroxycinnamic acid) (98 %, Merck). $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ complex was obtained by dissolving gadolinium oxide in nitric acid with further elimination of nitric acid and the solvent. The phenylpropionic acid was purified by recrystallization from isopropyl alcohol. The synthesis of $\text{Gd}(\text{OCO}(\text{CH}_2)_2\text{C}_6\text{H}_5)_3 \cdot 2\text{H}_2\text{O}$ complex ($\text{Gd}(\text{PPr})_3$) was carried out according to the previously described method [9] by means of interaction of gadolinium hydroxide with phenylpropionic acid in dry toluene under 75–85°C with simultaneous removing of water evolved as a result of the reaction. Then the reaction mass was cooled, and the obtained carboxylate was precipitated by hexane treated by isopropyl alcohol, with subsequent drying in air. The chemical content of Gd phenylpropionate was studied by means of IR spectroscopy using a Fourier IR spectrophotometer SPECTRUM ONE (Perkin Elmer). The spectra of phenylpropionic acid $\text{C}_6\text{H}_5(\text{CH}_2)\text{COOH}$ and Gd phenylpropionate ($\text{Gd}(\text{PPr})_3$) obtained from it were compared. In IR spectrum of $\text{Gd}(\text{PPr})_3$ (Fig. 1) the wide band at 3429.1 cm^{-1} ($\nu(\text{OH})$) was observed, indicating the presence of water molecules in the

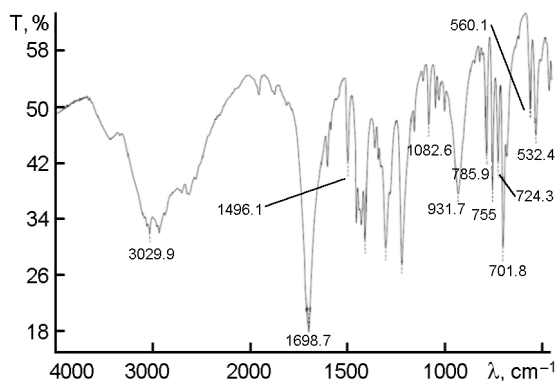


Fig. 2. IR spectrum of $C_6H_5(CH_2)COOH$.

obtained Gd phenylpropionate. Comparison of IR spectra of hydroxycinnamic acid (Fig. 2) and Gd carboxylate obtained from it (Fig. 1) have shown that, when we go from the acid to the Gd(III) complex, the absorption bands $\nu(C=O)/\nu_{as}(COO^-)$ are split and shifted towards lower frequencies. It is to be noted that water determination by Fisher method [10] has also shown the existence of two molecules of water in this compound.

Visually, the solution of 8 % $Gd(PPr)_3$ in toluene or styrene is transparent and has no yellow color. But after polymerization in styrene under $145^\circ C$ a yellow coloring occurs in it. This is illustrated in Fig. 3, where absorption spectra of 8 % $Gd(PPr)_3$ complex solution in styrene and polystyrene are presented. The spectra were measured in a layer of 1 cm thickness. It is seen that the complex synthesized by us shows insignificant absorption in near-UV, while the absorption spectrum of Gd-complex is extended up to 450 nm. The absorption maximum is at 340 nm, which coincides with luminescence bands of most primary luminescent additives. For example, luminescence maximum of the most frequently used LA1-*p*-terphenyl (*p*-TP) is at 340 nm [11].

So, it follows from the data presented that in Gd-loaded PS there will be absorption in the luminescence band of LA1 even if Gd-containing substance is colorless. Therefore, as noted before, to reduce the quenching influence of the absorption band that exists in Gd-loaded PS, it is reasonable to use a luminescent additive which absorbs as LA1 and emits as LA2. Such properties can be expected with molecules containing a phenyl group and a heavier aromatic fragment, for instance, anthracene, which emits in the luminescence region of LA2. Such a structure is, e.g., 1,4-dimethyl-9,10-diphenylanthracene (DMDPA) (Fig. 4). As it can be seen, DMDPA molecule contains di-

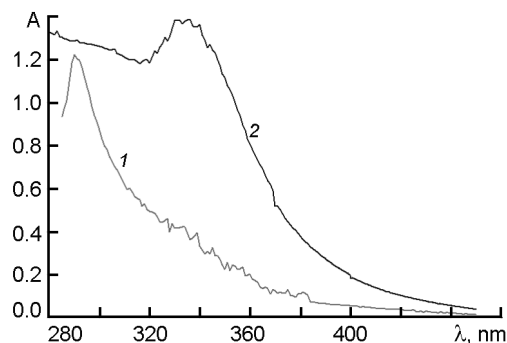


Fig. 3. Absorption spectra of 8 % solution of $Gd(PPr)_3$ complex in styrene (1) and polystyrene (2). Absorbing layer thickness is 1 cm.

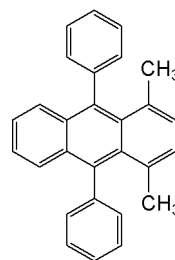


Fig. 4. Structural scheme of 1,4-dimethyl-9,10-diphenylanthracene (DMDPA).

methylanthracene core and two phenyl rings in 1 and 4 positions. DMDPA samples were obtained according to the procedure described in [12]. Luminescent properties of obtained DMDPA were studied using a Fluoromax-4 spectrofluorometer (HORIBA, Joben Ivon Inc.). In Fig. 5, the excitation (left) and emission (right) spectra of 1.5 % DMDPA solid solution in polystyrene are presented. As it follows from presented spectra, the DMDPA excitation (or absorption) band is in 240–430 nm range, overlapping the polystyrene emission band. The luminescent maximum at 465 nm is in the region of luminescence of typical luminescent additives. Due to the presence of two chromophore centers in DMDPA molecule, excitation energy transfer from polystyrene matrix is realized in a non-radiative manner on the "more short wave-length" phenyl fragment of DMDPA molecule, and luminescence occurs from the anthracene part of the molecule. It allows eliminating losses of excitation energy transfer from the first to the second luminescent additives that occur in the standard Gd-loaded scintillator.

Plastic scintillators were obtained by the known method of thermal bulk polymerization with further mechanical processing.

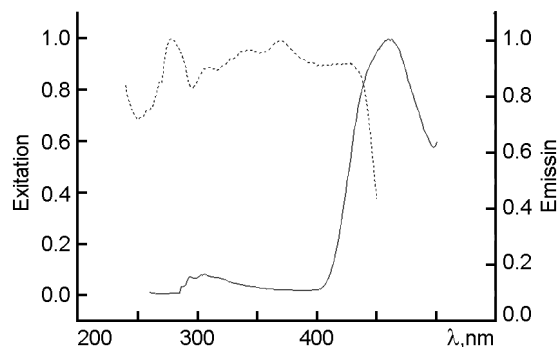


Fig. 5. Spectra of absorption (left) and luminescence (right) of 1.5 % DMDPA solution in polystyrene. Observation and excitation wavelengths are 461 and 255 nm, respectively.

1.5 g of $\text{Gd}(\text{PPr})_3$ (0.75 wt.% by Gd) and 0.75 g of DMDPA (1.5 wt.%) were put in an ampoule of heat-resistant glass. Then 50 g (55 ml) of fresh-distilled styrene was added. To ensure that the content was fully dissolved, the ampoule was heated to 85°C, then it was blown with nitrogen during 5 min for removal of oxygen. The ampoule was sealed off and placed in a thermostat. The polymerization process started with a preliminary storage at 135°C during 1 h; then the ampoule was kept at 150°C for 43 h. After that, the thermostat was cooled to room temperature, and PS blanks (ingots) were taken off the ampoule. These blanks were subject to machining and polishing. As a result, cylindrical samples of 16 mm diameter and 10 mm height were obtained. To determine the scintillating efficiency, PS samples were made with different content of luminescent additive DMDPA and Gd-containing complex $\text{Gd}(\text{PPr})_3$. Light yield measurements were made on a scintillation spectrometer. The spectrometrical section of the spectrometer consisted of a photomultiplier Hamamatsu R1306 and a charge-digit convertor LeCroy 2249A. The sample excitation was made by 0.975 MeV electrons from a Bi-207 source with collimator. The pulse height distribution on the PMT anode was measured. The light yield was determined by maximum of photopeak position corresponding to electrons with $E_e = 0.975$ MeV energy.

2. Results and discussion

To determine the optimal quantity of luminescent additive DMDPA, a set of PS samples was produced with different concentration of 1,4-dimethyl-9,10-diphenylanthracene but without Gd-complexes. Results

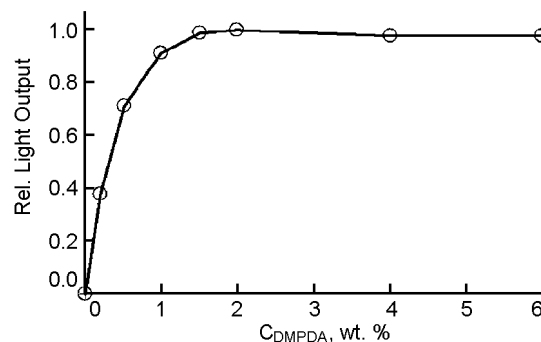


Fig. 6. Dependence of relative light yield on concentration of DMDPA in PS with 2 wt.% of $\text{Gd}(\text{PPr})_3$ complex.

of light yield $\eta(C)$ measurements on these samples are presented in Fig. 6. It can be seen that $\eta(C)$ rapidly grows when concentration of DMDPA increases up to 1.0 %. Then the growth slows down, and $\eta(C)$ achieves its maximum at DMDPA concentration about 2 %. Further increasing of concentration leads to some decreasing of light yield due to concentration quenching of luminescence. Therefore, the content of luminescent additive DMDPA within 1.5–2 % is optimal. So, all PS samples with different concentration of Gd-complex were made with 1.5 wt.% of DMDPA.

Results of relative light yield $\eta(C)$ measurements of PS samples with 1.5 % DMDPA and different concentrations of Gd-complex $\text{Gd}(\text{PPr})_3$ are presented in Table 1 and Fig. 7. It is seen from the data that increasing of $\text{Gd}(\text{PPr})_3$ concentration leads to decreasing of PS light yield. Thus, PS containing 0.5 wt.% Gd (2 wt.% $\text{Gd}(\text{PPr})_3$) have light yield of 0.88, while PS, containing 2.0 wt.% Gd (8 wt.% $\text{Gd}(\text{PPr})_3$) have light yield of 0.42 with respect to PS without Gd.

Polyvinyl-based PS described in [4] contains up to 14 % of Gd-complex ($\text{Gd}(\text{NO}_3)_3\text{TBP}_3$) (2 % Gd) and 1.2 wt.% of luminescent additive 2,5-diphenyloxazole (PPO). The data taken from this work and presented in Table 2 and Fig. 7 show that PS containing 0.68 wt.% of Gd have light yield of 0.62, while PS containing 1.93 wt.% of Gd have light yield of 0.42 with respect to PS without Gd.

Thus, PS with $\text{Gd}(\text{PPr})_3$ complex and luminescent additive DMDPA, described in the present work, showed relative light yield approximately 20 % higher (at the same Gd concentration) as compared to PS with $\text{Gd}(\text{NO}_3)_3\text{TBP}_3$ complex and PPO.

Table 1. Relative light yield $\eta(C)$ of PS samples with 1.5 wt.% of DMDPA and different content of Gd-complex $Gd(PPr)_3$

Gd(PPr) ₃ complex concentration, wt. %	Gd concentration, wt. %	Relative light yield
0	0	1
2	0.5	0.88
2.5	0.625	0.82
3	0.75	0.75
5	1.25	0.6
8	2	0.52

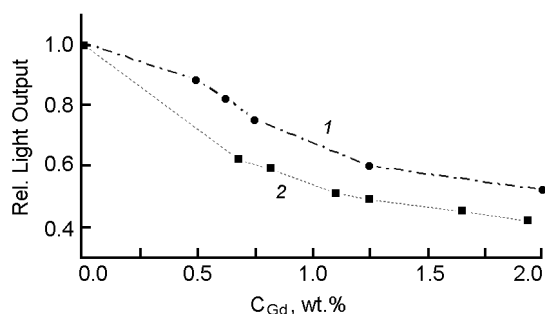


Fig. 7. Relative light yield of PS with different content of Gd. 1 — PS with $Gd(PPr)_3$ complex and 1.5 % DMDPA; 2 — PS with $Gd(NO_3)_3TBP_3$ complex and 1.2 % PPO [4].

4. Conclusions

Relative light yield of polystyrene-based PS with Gd phenylpropionate and luminescent additive DMDPA was shown to be higher comparing to known similar PS of other composition. The use of Gd-containing substances based on carboxylic acids is promising for design and development of new commercial PS. Also promising are the use of complicated phosphors (bifluorophores) for increasing PS light yield in the presence of Gd-containing substances.

Table 2. Light yield vs. concentration of $Gd(NO_3)_3TBP_3$ complex by Zane W.Bell [4]

Gd(NO ₃) ₃ TBP ₃ complex concentration, (wt. %)	Gd concentration (wt. %)	Relative light yield (Zane W.Bell [4])
0	0	1
5	0.68	0.62
6	0.82	0.59
8	1.10	0.51
10	1.25	0.49
12	1.65	0.45
14	1.93	0.42

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Пластмасовий сцинтилятор з фенілпропіонатом гадолінію

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Вивчено сцинтиляційну ефективність пластмасових сцинтиляторів з домішкою гадолінію. Показано, що в процесі полімеризації Gd-вмісних пластмасових сцинтиляторів утворюються гасячі центри забарвлення, які перешкоджають переносу енергії з первинної на вторинну люмінесцентну домішку, що є причиною зниження світлового виходу сцинтилятора. Для послаблення ефекту гасіння центрами забарвлення запропоновано у складі пластмасових сцинтиляторів використовувати допоміжну люмінесцентну добавку, яка поглинає в області первинної, а випромінює в області вторинної люмінесцентної добавки. Використання такої добавки дозволило підвищити вміст гадолінію у сцинтиляторі до 2 %. Отриманий сцинтилятор має світловий вихід 62 % відносно сцинтилятора стандартного складу.