

Neutron-sensitive plastic scintillator

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A new activator for plastic scintillators 2-([1,1'-diphenyl]-4-yl)-4-isobutyl-5-(2,4,5-trimethylphenyl) oxazole (*i*BuTMeBPO) has been synthesized. A number of plastic scintillators with an activator content of up to 50.0 wt.% have been obtained. Their optical and scintillation properties were studied. The possibility of using new scintillators for n/γ -discrimination tasks is shown.

Keywords: plastic scintillator, activator, light yield, n/γ -discrimination.

Нейтроночутливий пластмасовий сцинтилятор. *П.М.Жмурін, Д.А.Єлісеєв, О.В.Єлісеєва, Ю.О.Гуркаленко, В.Д.Алексєєв*

Синтезовано новий активатор для пластмасових сцинтиляторів 2-([1,1'-дифеніл]-4-іл)-4-ізобутил-5-(2,4,5-триметилфеніл)оксазол (*i*BuTMeBPO). Отримано ряд пластмасових сцинтиляторів з вмістом активатора до 50.0 мас.%. Вивчено їх оптичні та сцинтиляційні властивості. Показано можливість використання нових сцинтиляторів для задач n/γ -розділення.

Синтезирован новый активатор для пластмассовых сцинтилляторов 2-([1,1'-дифенил]-4-ил)-4-изобутил-5-(2,4,5-триметилфенил)оксазол (*i*BuTMeBPO). Получен ряд пластмассовых сцинтилляторов с содержанием активатора до 50.0 масс.%. Изучены их оптические и сцинтилляционные свойства. Показана возможность использования новых сцинтилляторов для задач n/γ -разделения.

1. Introduction

Traditionally, detectors based on organic crystals are widely used to register fast neutrons, while detectors based on helium-3 counters are most widely used to register thermal neutrons [1, 2]. However, taking into account the problem of producing the required amounts of helium-3, it becomes more and more urgent to search for an alternative to such detectors. The use of organic crystals for these tasks is also limited due to the difficulty of obtaining large samples to achieve the required level of registration of the neutron flux. The relatively recent development of neutron-sensitive plastic scintillators (PS) has given rise to the hope of obtaining of detectors of the required size as an

alternative to helium-3 counters and organic crystals. To register neutrons in such PSs, as in organic crystals, the method of discrimination of scintillation signals by the pulse shape is used [3, 4]. The method uses the dependence of the population of triplet states in the organic base of the scintillator on the density of energy losses created by a high-energy particle. By analyzing the fast and slow parts of the scintillation pulse, it is possible to determine the type of particle that created this type of pulse.

As a rule, the polymer base of traditional PS is polystyrene or polyvinyltoluene containing a phenyl group as the main chromophore. In such systems, due to mutual quenching at a high concentration of chro-

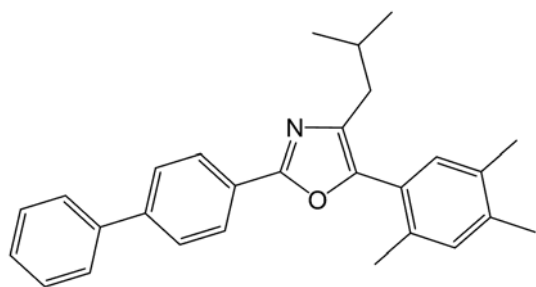


Fig. 1. Structural formula of 2-([1,1'-biphenyl]-4-yl)-4-isobutyl-5-(2,4,5-trimethylphenyl)oxazole (iBuTMeBPO).

mophores, the lifetimes of triplet states are significantly reduced, sometimes to the complete disappearance of triplet radiation [5, 6]. Therefore, to impart the property of neutron sensitivity, a large amount (up to 40 wt. %) of molecules with a triplet excitation lifetime which sufficient for the manifestation of triplet-triplet annihilation (TTA) is introduced into the polymer base of PS.

Today, the main additive (activator) used in commercially available neutron-sensitive PS is 2,5-diphenyloxazole (PPO) [7, 8]. However, the introduction of such significant amounts of PPO into the polymer composition leads to both a degradation of mechanical properties and to a significant deterioration in long-term stability [9]. Almost 10 years have passed since the creation of neutron-sensitive PSs, but the list of proposals for the use of other molecules as an activator for the polymer base of such PS is still limited. Therefore, the search for new activators capable of dissolving in the polymer base of PS in quantities sufficient for the manifestation

of the TTA effect, which is responsible for the appearance of delayed luminescence, remains urgent.

This paper discusses a new activator of neutron-sensitive PS 2-([1,1'-biphenyl]-4-yl)-4-isobutyl-5-(2,4,5-trimethylphenyl)oxazole (iBuTMeBPO) with solubility in polystyrene up to 50 wt.% (Fig. 1). The scintillation properties of PSs with the new activator have been investigated.

2. Experimental

2.1. Synthesis of 2-([1,1'-biphenyl]-4-yl)-4-isobutyl-5-(2,4,5-trimethylphenyl)oxazole

iBuTMeBPO was synthesized according to the scheme shown in Fig. 2. For this purpose, 4-diphenylcarboxylic acid (1) was converted into the corresponding acid chloride (2) by the action of thionyl chloride. Leucine was N-acylated with resulting acid chloride to obtain ([1,1'-biphenyl]-4-carbonyl) leucine (3). Then ([1,1'-biphenyl]-4-carbonyl) leucine was converted to the corresponding acid chloride in a pseudocumene medium by the action of phosphorus pentachloride. Then, in the same reaction mass, Friedel-Crafts acylation was carried out by adding aluminum chloride to obtain N-(4-methyl-1-oxo-1-(2,4,5-trimethylphenyl)pentan-2-yl)-[1,1'-biphenyl]-4-carboxamide (4).

Cyclodehydration of the intermediate product (4) was carried out by the action of concentrated sulfuric acid; as a result, iBuTMeBPO (5) was obtained directly. Technical iBuTMeBPO was purified by chromatography on alumina using hexane as eluent.

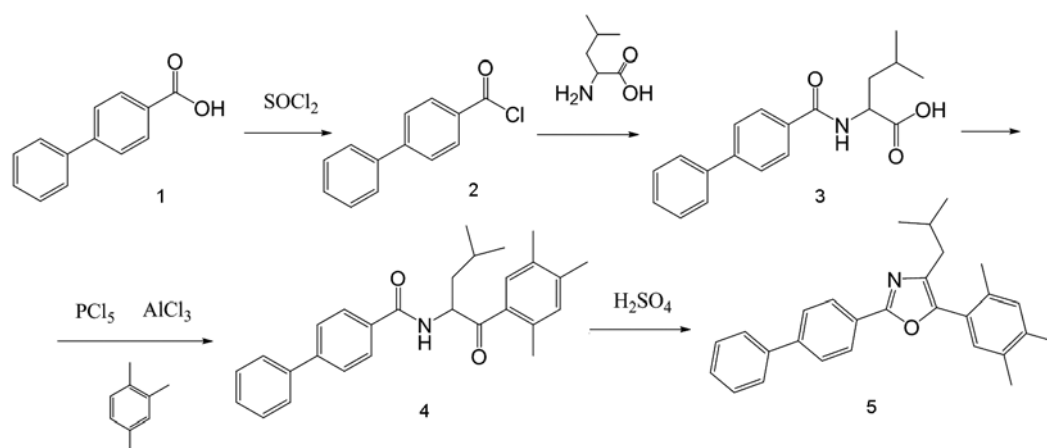


Fig. 2. Scheme of 2-([1,1'-biphenyl]-4-yl)-4-isobutyl-5-(2,4,5-trimethylphenyl)oxazole (iBuTMeBPO) synthesis.

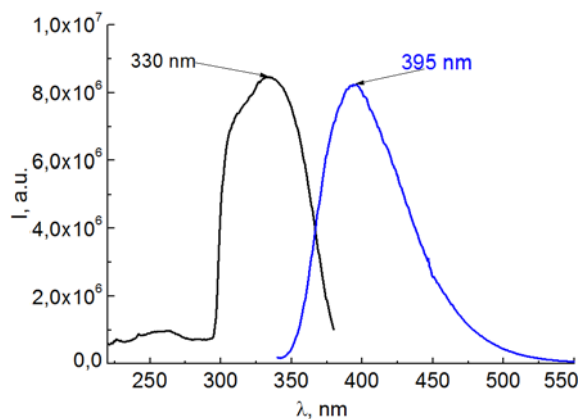


Fig. 3. Excitation and luminescence spectra of polystyrene sample containing 0.01 wt. % of iBuTMeBPO ($\lambda_{ex} = 335$ nm, $\lambda_{em} = 395$ nm).

2.3. Obtaining and measurements PS samples

PS samples were obtained by the method of thermally initiated bulk polymerization. We used 0.1 wt. % 9,10-diphenylanthracene and X ($X = 10.0, 20.0, 40.0$ and 50.0 wt. %) iBuTMeBPO and the corresponding amount of styrene. The vials were purged with argon for 10 minutes and then sealed. The substances were polymerized at 140°C for 6 days. Samples in the form of cylinders 16 mm in diameter and 10 mm in height were cut from the obtained blanks, and then polished to optical transparency.

A sample based on polystyrene containing 0.01 wt. % iBuTMeBPO was obtained in a similar way.

The excitation and luminescence spectra of the obtained samples were studied at room temperature on a FluoroMax-4 spectrofluorometer (Horiba Jobin Yvon-Edison). The time characteristics were determined by the method of correlated single-photon counting on a two-channel setup with two Hamamatsu 9800 photomultipliers in the Start and Stop channels. A ^{90}Sr electron source was used. The starting pulse was a Cherenkov radiation signal from a sample made of polymethylmethacrylate.

The device for determining the light yield of the PS consisted of a Hamamatsu R1307 photomultiplier and a LeCrou 2249A charge converter. 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 monoenergetic source of conversion electrons. Radionuclide Bi-207 was used as a source of electrons. The light yield was determined from the position of

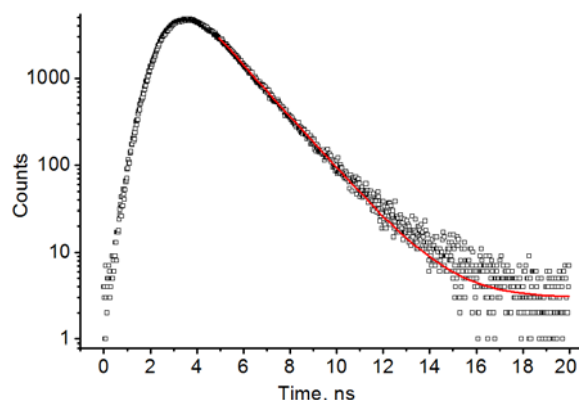


Fig. 4. Luminescence decay curve of polystyrene sample containing 0.01 wt. % of iBuTMeBPO.

the maximum of the amplitude scintillation spectrum peak.

The n/γ -discrimination parameter FOM was determined by comparing the total charge of the signal (Q_{total}) and its ratio to the slow component (Q_{total}/Q_{slow}). For this, PS samples were irradiated with fast neutrons and γ -quanta from a plutonium-beryllium source ($^{239}\text{Pu}-\text{Be}$) through a lead plate of 20 mm thick. After digital processing, the pulse shape and the value of the areas of the slow component (Q_{slow}) in the range from 50–70 ns to 200 ns and the entire pulse (Q_{total}) were saved in the original file for each recorded pulse. The choice of the initial integration time point for calculating Q_{slow} was selected for each sample individually. Then, for each event, the ratio $D = Q_{slow}/Q_{total}$ was calculated and the distribution of the number of events over D was constructed, from which the FOM was determined. The method is described in more detail in [10].

3. Results and discussion

To study the spectral-luminescent properties of iBuTMeBPO molecules in a polystyrene matrix, a sample with an activator content of 0.01 wt. % was obtained. Excitation and luminescence spectra, as well as the luminescence decay curve of a polystyrene sample containing 0.01 wt. % iBuTMeBPO are presented in Fig. 3 and 4.

As can be seen from Fig. 3, the maximum of the luminescence band is located at a wavelength of 395 nm, while the maximum of the excitation spectrum is at 335 nm. The iBuTMeBPO activator differs from the traditionally used scintillation additive 2-(4-diphenyl)-5-phenyloxazole (BPO) by the presence of three methyl groups in the phenyl fragment and an is-

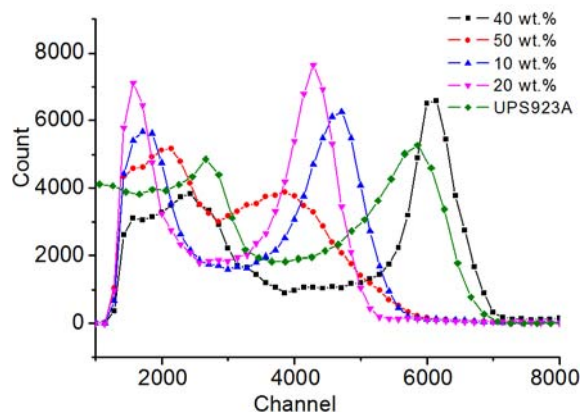


Fig. 5. Scintillation amplitude spectra of polystyrene scintillators with various *iBuTMeBPO* concentrations and 0.1 wt. % of DPA.

obutyl substituent in the oxadiazole fragment of the molecule. The introduction of alkyl substituents designed to increase the solubility of the compound in a non-polar polystyrene medium led to insignificant changes in the spectral-luminescent properties of the molecule: a bathochromic shift of 10 nm and a bathochromic shift of 5 nm are observed compared to the unsubstituted BPO molecule [11]. The lifetime of *iBuTMeBPO* molecules in a polystyrene matrix is about 1.5 ns (Fig. 4). For the creation of a scintillation composition, the observed spectral-luminescent characteristics of *iBuTMeBPO* make it possible to select 9,10-diphenylanthracene (DPA) as a shifter with an absorption maximum at 395 nm [12].

A series of PS samples with different concentrations of the *iBuTMeBPO* activator and 0.1 wt. % of DPA were obtained. When the concentration of the activator is above 40 wt. % after the completion of polymerization, a slightly noticeable turbidity of the samples is observed, which is associated with exceeding the solubility threshold in polystyrene and crystallization of the activator. For all samples, the scintillation properties were studied and the relative light output was determined (Fig. 5, Table).

As can be seen from Table, with an increase in the concentration of the activator in the scintillation composition, an increase in the light yield is observed, which reaches its maximum at 40 wt. % of the activator. In this case, the light yield of PS containing *iBuTMeBPO* slightly (by 5 %) exceeds the light yield of the UPS923A standard sample [13]. A further increase in the concentration leads to a deterioration of the scintillation properties, which is associated with the crystallization of *iBuTMeBPO* from a solid

Table 1. Relative light yield (LY) and n/γ -discrimination parameter (FOM) of PSs with various contents of *iBuTMeBPO* molecules and 0.1 wt. % of DPA

<i>iBuTMeBPO</i> concentration, wt. %	Relative light yield (LY), %	FOM
UPS923A	100	
10	80	1.02
20	74	1.05
40	105	1.65
50	6	1.72

solution and, as a consequence, to lowering the transparency of the sample.

All the samples demonstrated the ability to discriminate the signal from neutrons and gamma by the pulse shape (Fig. 6).

From Fig. 6 and Table, it can be seen that with an increase in the concentration of *iBuTMeBPO* molecules, the n/γ -discrimination property of PS improves. This confirms once again that the main factor affecting the n/γ -discrimination ability of PS is the spatial distribution of molecules. An increase in the concentration of the activator leads to a decrease in the average distance between molecules; this leads to an increase in the exchange interaction, which, as is known, decreases exponentially. Thus, an increase in the concentration and a decrease in the intermolecular distance contribute to an increase in the migration rate of triplet excitation and, as a consequence, an increase in the probability of triplet-triplet annihilation. The highest value of the n/γ -discrimination factor was obtained at an *iBuTMeBPO* concentration of 50 wt. % (Fig. 6), although the light yield of the sample at this concentration decreases sharply. FOM was 1.72 at an *iBuTMeBPO* concentration of 50 wt. % (Fig. 7). The optimal ratio of light yield and discrimination ability is observed at an activator concentration of 40 wt. %. At this concentration of the activator, FOM is slightly lower than the maximum — 1.65, and the light yield of this scintillator is 5 % higher than the light yield of the standard sample UPS923A. It should be noted that the introduction of more than 30 wt. % PPO usually after some time leads to the release of the activator to the sample surface. This is associated with the easy migration of the activator from the bulk to the surface of the polymer composition. In the case of *iBuTMeBPO*, this effect

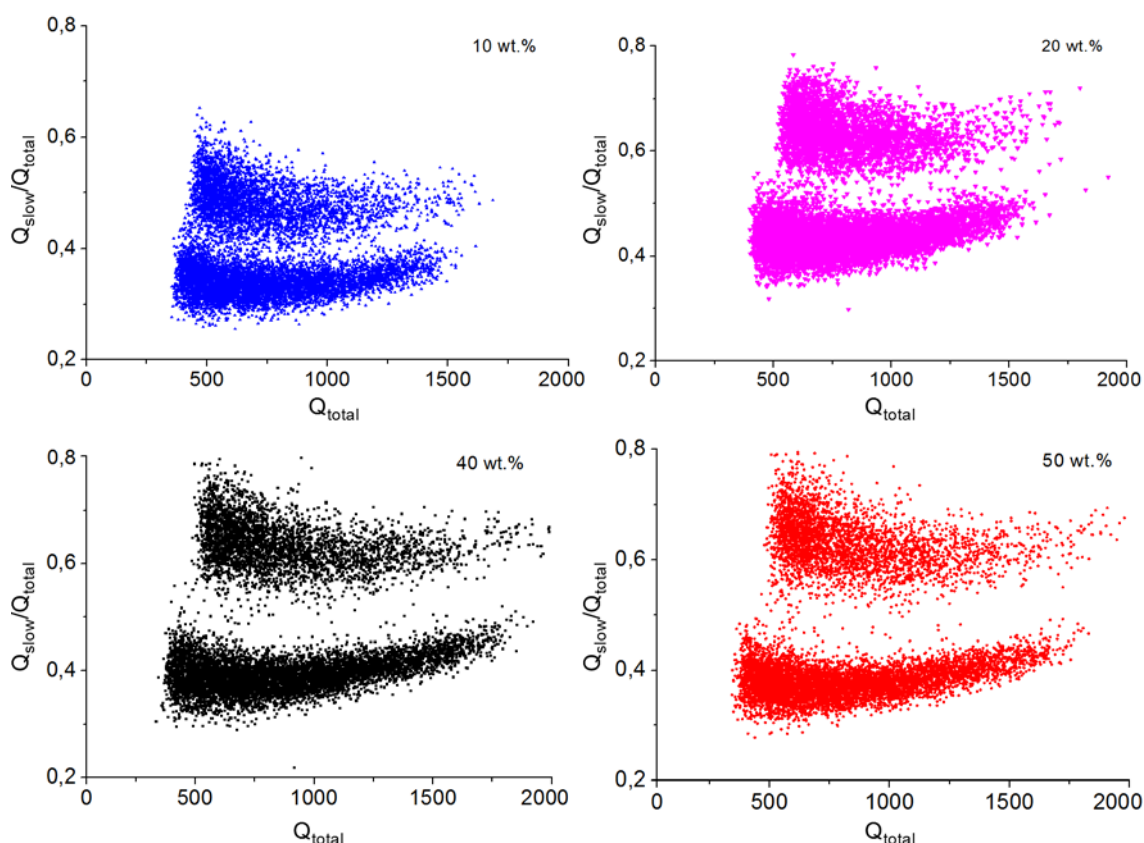


Fig. 6. n/γ -discrimination of scintillators with various concentrations of *i*BuTMeBPO molecules.

was not observed even at an activator concentration of 50 wt. %. This fact indicates an insignificant migration of the new activator in the polymer and allows us to hope for an increase in the long-term stability of scintillation compositions with *i*BuTMeBPO in comparison with similar PSs with PPO.

4. Conclusions

Compound 2-([1,1'-biphenyl]-4-yl)-4-isobutyl-5-(2,4,5-trimethylphenyl)oxazole (*i*BuTMeBPO) was synthesized, which can be used as an activator of neutron-sensitive plastic scintillators. The high solubility of the new activator in polystyrene makes it possible to obtain scintillation compositions with its concentration of up to 50 wt. %. PSs with *i*BuTMeBPO exhibit good n/γ -discrimination properties and relatively high light yield. The insignificant migration of the additive in the polymer allows us to hope for an increase in the long-term stability of scintillation compositions with *i*BuTMeBPO in comparison with similar PSs containing PPO.

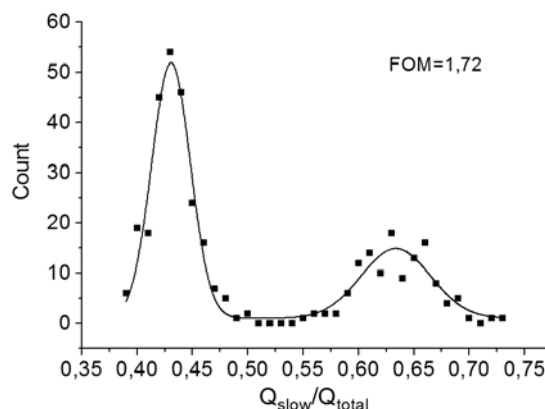


Fig. 7. n/γ -Discrimination form factor of PS at 50 wt. % concentration of *i*BuTMeBPO.

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