

The plastic scintillator for n/γ -discrimination

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A method for modifying activator molecules is described. A series of plastic scintillators with the different content of the activator 2,5-bis(4-(tert-butyl)phenyl)oxazole (DtBuPPO) up to 40.0 wt. % has been obtained. Their scintillation characteristics and physico-mechanical properties were studied. The possibility of using the new scintillators for n/γ -discrimination tasks is shown.

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

Получен ряд пластмассовых сцинтилляторов с содержанием активатора 2,5-бис(4-(трет-бутил)фенил)оксазола (DtBuPPO) вплоть до 40.0 масс. %. Изучены их сцинтилляционные характеристики и физико-механические свойства. Показана возможность использования новых сцинтилляторов для задач n/γ -разделения.

Пластмассовий сцинтилятор для n/γ -розділення. *П.М.Жмурін, Д.А.Єлісеєв, О.В.Єлісеєва, В.М.Переїмак, Ю.А.Гуркаленко, В.Д.Олексєєв.*

Отримано ряд пластмассових сцинтиляторів з вмістом активатора 2,5-бис(4-(трет-бутил)феніл)оксазолу (DtBuPPO) до 40.0 мас. %. Вивчено їх сцинтиляційні характеристики та фізико-механічні властивості. Показана можливість використання нових сцинтиляторів для задач n/γ -розділення.

1. Introduction

Plastic scintillators (PS) are widely used to create various types of detection devices. It can be used to register high-energy electrons, protons, gamma quanta, and alpha particles [1, 2]. By the reason of a high level of hydrogen atoms content in PS, a quite effective exchange of neutron energy takes place due to the creation of recoil protons. The energy recoil protons create a scintillation pulse which is registered well enough. The main problem of neutron registration by a plastic scintillator is the difficulty to discriminate a scintillation signal produced by the recoil proton from a scintillation signal produced by background gamma radiation.

For the sure registration of neutrons, it is necessary that the scintillation pulse created by the neutron be different from the scintillation pulse created by a gamma quantum. Such a difference is observed in organic crystals and it is associated with the different distributions of the excitation energy between the triplet and singlet states in the tracks with different densities of excitation energy which are created during the passage of the gamma quantum and neutron in crystal medium. Also, due to the different lifetime of the excited states of the triplet and singlet states of organic molecules, there is a difference in the temporal shape of scintillation pulses produced by the gamma quantum and neutron. For a fast neutron in organic crystals, a signifi-

cant enhancement of the long-lived component of the scintillation signal is observed due to the effect of triplet-triplet annihilation [3]. By the discrimination of the scintillation pulse into the "fast" and "slow" components and analyzing them, you can clearly identify the particle that created the scintillation pulse.

Usually as the base of plastic scintillators, polystyrene or vinyltoluene which have a short lifetime of the excitation energy of the triplet states are used. For this reason, the described scenario for the scintillation pulse evolution is not realized in a plastic scintillator. In order to provide the n/γ -discrimination property for PS, it is necessary to create conditions for the manifestation of the effect of triple-triplet annihilation. For this purpose, various additives (activators) are introduced into the polymer base. Since the effect of triplet-triplet annihilation is realized due to the short-range exchange interaction, its efficiency will increase with decreasing of the average distance between the molecules introduced into the polymer base. The necessary reduction in the distance between molecules is achieved by increasing their concentration sometimes to several tens of percent. This approach was implemented for a neutron sensitive plastic scintillator [4].

However, there is a number of problems within the framework of this approach. To ensure a high concentration of activator molecules in the polymer medium, it is necessary to use small organic molecules with good solubility (for example, 2,5-diphenyloxazole — PPO). Such compounds usually have a rather low melting point (the melting point of PPO is 73°C). This immediately

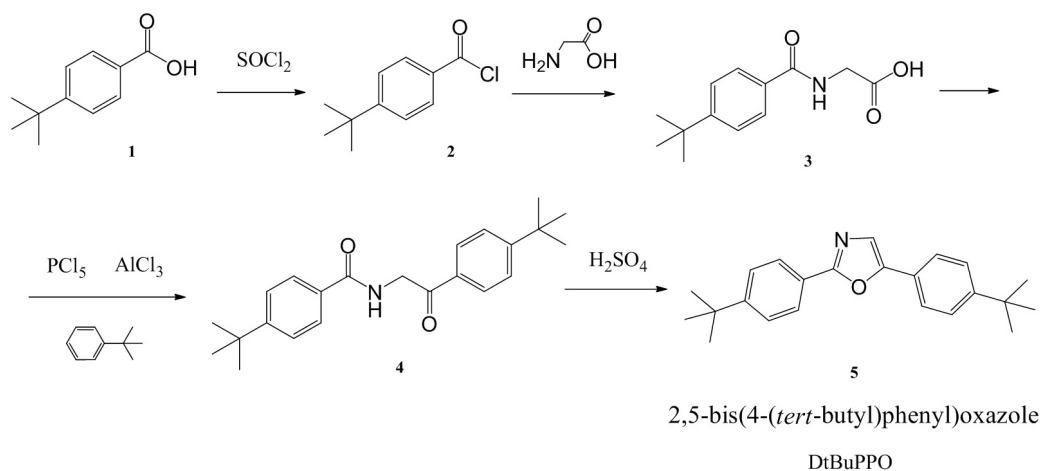
results in degradation of the mechanical properties of PS. The low melting point of the activator causes a significant decrease in the glass transition temperature of the polymer composition, and the small size of the molecules leads to a significant diffusion of the activator to the surface of the polymer with time. In addition, on the one hand, molecules in a polymeric medium should be close enough to each other, and on the other hand, they should not form (at least a "significant" amount) various kinds of associates capable to extinguish significantly the luminescence of the molecules themselves. These disadvantages can be avoided by modifying the molecules introduced into the polymer base of PS. It was shown that the introduction of branched alkyl substituents into the structure of activator molecules can reduce their diffusion in the polymeric medium [5, 6]. It should be noted that such substituents also prevent the molecules aggregation which can suppress the effect of the triplet-triplet annihilation.

This paper describes the properties of a plastic scintillator based on PPO molecules modified with alkyl substituents.

2. Experimental

Synthesis of 2,5-bis(4-(*tert*-butyl)phenyl)oxazole (DtBuPPO)

Synthesis of DtBuPPO was performed according to the Scheme 1. For this purpose, *p*-*tert*-butylbenzoic acid (1) was converted into the corresponding acyl chloride (2) by the action of thionyl chloride. Amino-acetic acid was N-acylated with acyl chloride, and *tert*-butyl hippuric acid (3) was obtained. Next, the resulting acid in the *tert*-butylbenzene medium was transferred to the cor-



Scheme 1. Synthesis of 2,5-bis(4-(*tert*-butyl)phenyl)oxazole (DtBuPPO).

Table 1. Microhardness of polymer samples with different content of DtBuPPO molecules

Content DtBuPPO, wt. %	Microhardness, MPa
5	324
10	324
20	328
40	224
UPS-923A [10]	336

responding acyl chloride by the action of phosphorus pentachloride. Then the Friedel-Crafts acylation was carried out in the same reaction mass by adding aluminum chloride, and 4-(tert-butyl)-N-(2-(4-(tert-butyl)phenyl)-2-oxoethyl) benzamide (4) was obtained. The cyclodehydration of the intermediate product was carried out by the action of concentrated sulfuric acid; as a result, DtBuPPO (5) was obtained directly. Technical DtBuPPO was purified by three-fold chromatography on alumina, eluent — hexane.

Preparation of scintillation samples

Polystyrene samples containing DtBuPPO molecules were prepared by the method of thermally initiated bulk polymerization. For this, appropriate amounts (5.0, 10.0, 20.0 and 40.0 wt. %) of the activator were placed in glass ampoules and filled with the corresponding amount of styrene. The mixture was purged with argon for 10 minutes, after which the ampoules were sealed. The samples were polymerized at 150°C for 6 days. Samples in the form of cylinders with a diameter of 16 mm and a height of 10 mm were cut out from the obtained blanks, and then polished to optical transparency.

Samples of plastic scintillators containing 5.0, 10.0, 20.0 and 40.0 wt. % of DtBuPPO molecules were obtained in a similar way using 0.5 wt. % diphenylanthracene as a shifter.

Measurement

The spectral and luminescent characteristics of the samples were measured with a Horiba Jobin Yvon Fluoromax-4 spectrofluorimeter.

To measure the light output, the PS samples were installed directly on the photocathode surface of a photomultiplier (optical contact was provided by an immersion liquid) and irradiated with a ^{207}Bi monoenergy source of conversion electrons. The light output was determined by the position of

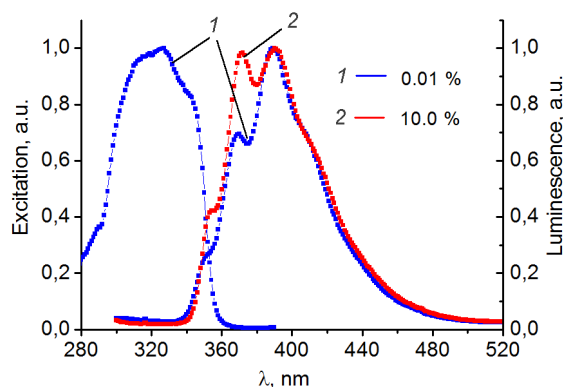


Fig. 1. Spectra of luminescence and excitation of DtBuPPO molecules in polystyrene at concentrations of 0.01 wt. % and 10.0 wt. %.

the maximum peak from electrons with energy of 975 keV.

The luminescence decay time characteristics were determined by the method of time correlated single photon counting [7] with two Hamamatsu 9800 PMTs in the Start and Stop channels. The Sr-90 electron source was used. As a starting pulse, the signal of the Cherenkov radiation from a sample made of polymethylmethacrylate was used.

The n/γ -discrimination parameter FOM was determined by comparison of the total signal charge (Q_{total}) and its relationship with the parameters of the slow component (Q_{total}/Q_{slow}) [8, 9].

3. Results and discussion

The DtBuPPO is a modified PPO molecule, the structure of which includes two tert-butyl substituents (Scheme 1). The presence of branched alkyl substituents practically doesn't affect the spectral-luminescent properties, but it significantly improves the solubility of the compound in non-polar media and significantly suppresses the diffusion of the activator from the polymer volume, i.e., the exit of the activator to the surface of the polymer. And, indeed, DtBuPPO dissolves quite well in polystyrene up to 60.0 wt. % and forms transparent polymer compositions. In addition, the polystyrene base, even with significant concentrations of the activator, sufficiently retains the mechanical properties (Table 1).

As can be seen from the Table 1, even at 40 % enrichment of polystyrene with DtBuPPO molecules, the polymer composition retains its mechanical properties sufficiently so that problems do not arise during the mechanical processing of the samples or

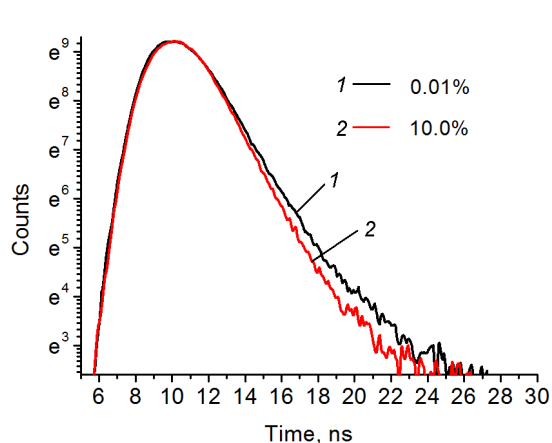


Fig. 2. Luminescence decay curves of DtBuPPO molecules in polystyrene at concentrations of 0.01 wt. % and 10.0 wt. %.

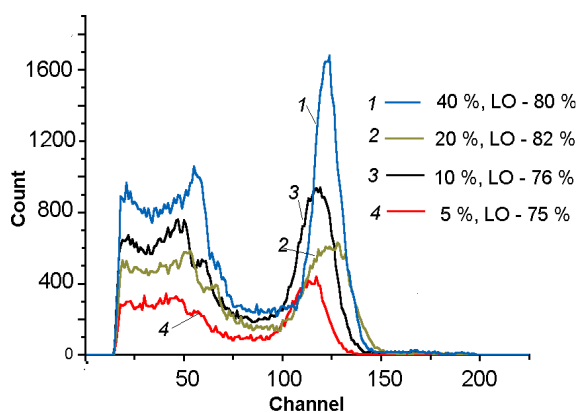


Fig. 3. Scintillation amplitude spectra and light output (LO, relative to UPS923A) PS with various concentrations of DtBuPPO.

during maintenance of the finished product. This suggests that the modification of activator molecules of various kinds of alkyl branched substituents can not only suppress the diffusion of molecules to the surface of the polymer, but also help to preserve the "rigidity" of the polymer composition. If using the PPO molecules at a concentration of 40 wt. %, the microhardness of the scintillation composition was only about 25 MPa [11]; then when using the DtBuPPO molecules at the same concentration, the microhardness of the samples was almost an order of magnitude higher. This suggests that by modifying only the activator molecules, it is indeed possible to significantly improve the mechanical properties of PS.

The DtBuPPO molecules in polystyrene have a wide, practically unstructured excitation band with a maximum in the region of 320 nm, and a structured luminescence band with the positions of maxima at

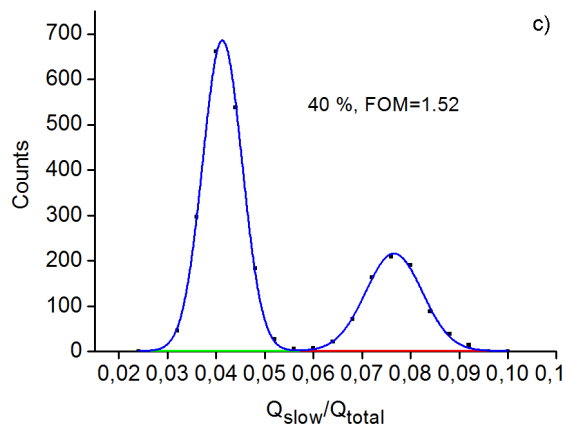
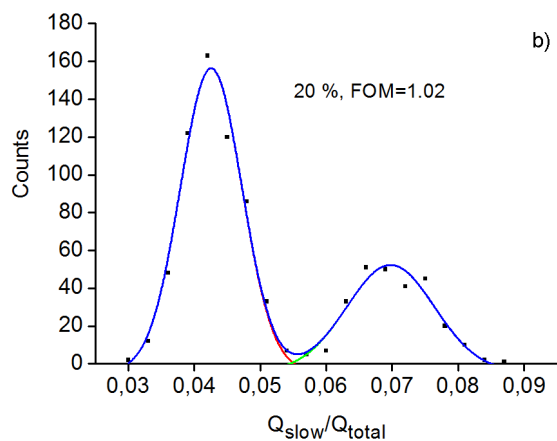
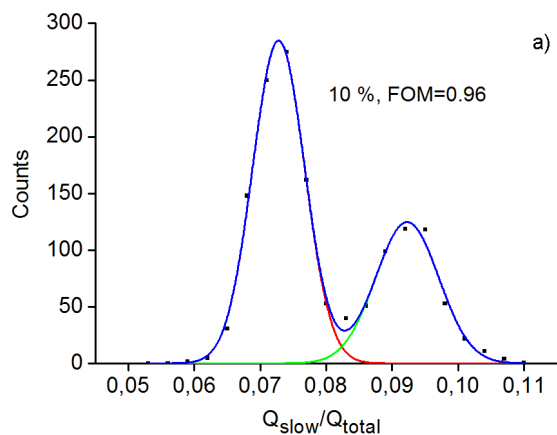


Fig. 4. FOM for plastic scintillators with different concentrations of DtBuPPO.

354 nm, 372 nm and 391 nm, respectively (Fig. 1). As can be seen from Fig. 1, the luminescence band of the DtBuPPO molecules remains almost unchanged when the concentration of the additive in polystyrene significantly changes. This fact indicates the absence of any aggregation of molecules in the polymeric medium. Also the curves of luminescence decay may be a confirmation of the absence of the aggregation of molecules (Fig. 2). These curves remain practi-

cally unchanged also with increasing concentration. Thus, as expected, the presence of tert-butyl fragments of the DtBuPPO molecule actually prevents the aggregation of molecules in the polystyrene medium.

Since the main luminescence band of the activator DtBuPPO molecules in polystyrene is located in the region of 390 nm, then to create a scintillation composition, diphenylanthracene (0.05 wt.%) was used as the shifter most suitable for spectral-luminescent characteristics.

Fig. 3 shows the light output of scintillation compositions containing different amounts of DtBuPPO. As can be seen from the presented data, the light output of the obtained samples practically does not change with an increase in the activator concentration from 5.0 wt. % to 40.0 wt. % and is about 80 % of the light output of a standard plastic scintillator.

As mentioned earlier, the ability of the plastic scintillators to discriminate the neutron and gamma-quantum scintillation pulses is determined by the average distance between the activator molecules. Therefore, the n/γ -discrimination factor (FOM) should depend on the concentration in proportion to the cub root of the ratio, which is observed in our case.

As can be seen from the Fig. 4, already at an activator concentration of 10.0 wt. % you can quite clearly discriminate the peak of neutrons from gamma-peaks (Fig. 4a). Although, there is a small region of the peaks overlap. When the concentration of the activator is 20.0 wt. %, the peak areas are practically separated (Fig. 4b) and this trend continues at a higher level of activator content. Fig. 4c shows that the samples with 40.0 wt. % of DtBuPPO are able to clearly separate the peaks from neutrons and gamma-quanta.

4. Conclusions

The compound 2,5-bis(4-(tert-butyl)phenyl)oxazole (DtBuPPO) has been obtained, which is a modified 2,5-diphenyloxazole molecule (PPO) with a structure including two branched alkyl substituents. It has been shown that the DtBuPPO molecules can be used as an activator for the creation of neutron-sensitive plastic scintillators. It has been demonstrated that the polymer scintillation compositions with a high concentration of DtBuPPO are able to maintain their physical and mechanical properties at a sufficient level.

As a result of DtBuPPO application, a plastic scintillator with the n/γ -discrimination parameter $FOM = 1.52$ has been created. The mechanical properties of the new PS are found to be almost at the level of the standard plastic scintillator.

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