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Optical and scintillation properties of polystyrene based plastic scintillators activated by *trans*-stilbene alkyl derivative

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In this work, a series of plastic scintillators with the content of 4-*tert*-butylstilbene activator up to 40.0 wt. % was obtained. Their optical and scintillation properties were studied. The suitability of new scintillators for creating neutron-sensitive detectors has been evaluated.

Keywords: plastic scintillator, activator, *trans*-stilbene, polystyrene.

Получен ряд пластмассовых сцинтилляторов с содержанием активатора 4-*трет*-бутилстильбена до 40.0 масс. %. Изучены их оптические и сцинтилляционные свойства. Оценена пригодность новых сцинтилляторов для создания нейтрончувствительных детекторов.

Оптичні і сцинтиляційні властивості полістирольних пластмасових сцинтиляторів, активованих алкілпохідним *транс*-стильбену. *П.М.Жмурін, Д.А.Єлісєєв, О.В.Єлісєєва, В.Д.Алексєєв, Ю.А.Гуркаленко.*

Отримано низку пластмасових сцинтиляторів з вмістом активатора 4-*трет*-бутилстильбену до 40.0 мас. %. Вивчено їх оптичні і сцинтиляційні властивості. Оцінено придатність нових сцинтиляторів для створення нейтрончутливих детекторів.

1. Introduction

Despite the long history, the task of finding new effective scintillation media for neutron registration remains relevant and sow day. It is known that the most effective media for detecting fast neutrons are organic media, due to the high specific content of hydrogen atoms. The mass of a hydrogen atom practically coincides with the neutron mass; as a result, the neutron energy is efficiently exchanged. The resulting recoil protons create a scintillation pulse, which is used to register neutrons. The main problem that arises during the registration of neutrons is associated with the need to separate the neutron created scintillation pulse from gamma background pulses. For organic scintillation media, the scintillation yield of protons is almost an order of magnitude smaller than the scintillation yield created by gamma rays; and the spectra of amplitudes of scintillations from fast neutrons and photons of gamma radiation overlap significantly. Therefore, it is impossible to produce a discrimination of pulses in amplitude. But organic solutions of phosphors are characterized by the presence of delayed luminescence associated with the effect of triplet-triplet ($T-T$) annihilation [1]. The presence of the delayed luminescence is also characteristic for organic single crystals [2]. Analysis of the intensity of the slow luminescence allows you to discriminate the scintillation signal generated by the recoil proton from the

scintillation signal generated by the gamma quantum, by the form of the pulse. But production of organic crystals for high-performance large-sized detectors is associated with considerable difficulties, as is the exploitation of liquid organic scintillators. And as an alternative, plastic scintillators (PS) can be used.

But, unfortunately, in traditional plastic scintillators, in which polystyrene or polyvinyltoluene is used as a polymer base, there are no long-lived triplet excited states. Therefore, the implementation of the $T-T$ annihilation mechanism is difficult and the delayed luminescence is practically not observed. Therefore, to create neutron-sensitive (from the point of view of the possibility of discrimination of scintillation pulses) scintillation polymer media, it is necessary to modify their composition by dissolving various kinds of scintillation additives with long-lived excited triplet states. In addition, it is necessary to ensure the energy exchange of triplet excited states between the dissolved molecules in order to realize the effect of triplet-triplet annihilation. Since the transfer of the excitation energy of triplet states is possible only due to the exchange interaction, the efficiency of which decreases exponentially with increasing distance between molecules; thus, the number of the dissolved molecules in the polymer medium should be significant. As a rule, these are few dozens of weight percent. Unfortunately, there are very few molecules with the required spectral-luminescent properties and capable of dissolving in polystyrene in such quantities. PPO molecules are suitable for these tasks. With their use, neutron-sensitive PSs were created [3]. However, the resulting polymeric medium for several reasons limits the possibility of wide distribution of such scintillators. Therefore, the problem is to find new scintillation additives capable to improve neutron sensitivity of polymeric media.

All organic single crystals widely used today (stilbene, anthracene, *p*-terphenyl) have a high n/γ-discrimination ability [4]. Most of the works on the n/γ-discrimination in organic single crystals refer to stilbene. Apparently, this is due to the fact that it has the best discrimination ability. Therefore, there is an interest in studying the properties of a neutron-sensitive plastic scintillator enriched with stilbene molecules. To date, there is no description of the scintillation properties of such plastic scintillators. This is due to the fact that it is impossible to dissolve stilbene molecules in polystyrene in sufficient quantities. A known method of modifying luminophore molecules in order to increase their solubility in a polystyrene medium is the introduction of a *tert*-butyl group into their structure [5].

In this paper, the *tert*-butylstilbene molecules as the object of research were selected. Their solubility in a polystyrene medium in an amount that leads to the implementation of the effect of delayed luminescence was determined. The optical and scintillation properties of plastic scintillators containing modified stilbene molecules were studied.

2. Experimental

Synthesis of 4-tert-butylstilbene (tBuSt)

Synthesis of tBuSt was performed according to the scheme shown in Fig. 1. To this end, in the first stage, *tert*-butyl toluene (1) was brominated with liquid bromine in a tetrachloromethane medium. Then, the obtained *tert*-butylbenzyl bromide (2) reacted with triphenylphosphine in a benzene solution; as a result, *tert*-butylbenzyltriphenylphosphonium bromide (3) was obtained. Next, the phosphonium salt was introduced into the Wittig reaction with benzaldehyde in a methanol solution in the presence of sodium methoxide. The *tert*-butylstilbene (4) thus obtained was precipitated with water, extracted with methylene chloride, the organic layer was separated, dried, and the solvent was distilled off. Technical tBuSt was purified by three-fold chromatography on alumina, eluent — hexane.

Preparation of scintillation samples

Polystyrene samples containing molecules of both stilbene and 4-*tert*-butylstilbene were prepared by the method of thermally initiated bulk polymerization. For this purpose, 0.01, 5, 10, 20, 30, 40 and 45 wt. % of activator was placed in glass ampoules and filled with the appropriate amount of styrene. The mixture was purged with argon for 10 min; then the ampoules were sealed. The samples were polymerized at 150°C for 6 days. The 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 they were polished to optical transparency.

The samples of plastic scintillators containing 10, 20, 30, 35, 40 and 45 wt. % of molecules of 4-*tert*-butylstilbene were obtained in a similar way using 0.05 wt.% of diphenylanthracene as a shifter.

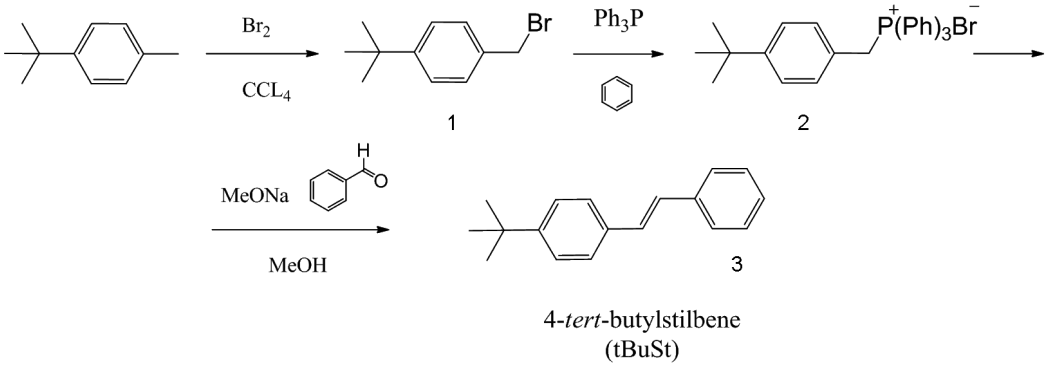

Fig. 1. Synthesis scheme of 4-*tert*-butylstilbene (tBuSt).

The excitation and luminescence spectra of the samples were measured at room temperature using a FluoroMax-4 spectrofluorimeter (HORIBA JOBIN YVON-EDISON, USA).

The luminescence decay time characteristics were determined by the method of time correlated single photon counting [6] 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 light output of polystyrene scintillators was measured on a scintillation spectrometer. The device consisted of a Hamamatsu R1307 photomultiplier and a LeCrou 2249A charge converter. To measure the light output, the PS samples were installed directly on the surface of the photocathode of the photomultiplier (optical contact was provided by means of an immersion liquid) and irradiated with a monoenergetic source of conversion electrons. Bi^{207} radionuclide was used as an electron source. The light output was determined by the position of the maximum peak of the scintillation amplitude spectrum.

The n/γ-discrimination parameter FOM was determined by comparing the total signal charge (Q_{total}) and its relationship to the slow component (Q_{total}/Q_{slow}) [7, 8].

3. Results and discussion

The introduction of a *tert*-butyl substituent into the stilbene molecule leads to a significant increase of the substance solubility in polystyrene. In the case of unsubstituted stilbene, transparent samples were obtained with an additive content up to 10 wt. %; at higher concentrations, a significant opacity of the samples was observed. In the case of tBuSt, it was possible to obtain transparent samples with an additive content up to 40 wt. %.

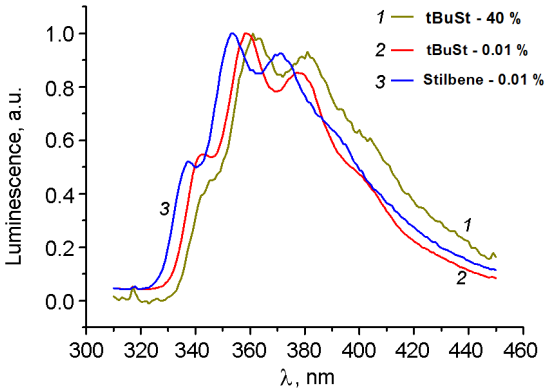

Fig. 2. Luminescence spectra of stilbene and 4-*tert*-butylstilbene molecules in a polystyrene matrix. Luminescence excitation wavelength is 300 nm.

As can be seen from Fig. 2, the luminescence spectra of tBuSt molecules in a polystyrene medium undergo only minor modifications as compared to stilbene molecules.

The luminescence spectrum of stilbene molecules in a polystyrene matrix is characterized by the presence of three clearly distinguishable maxima at 337 nm, 354 nm, and 372 nm. Modification of the stilbene molecule with a *tert*-butyl group does not change the nature of the luminescence spectrum. Three characteristic maxima (342 nm, 359 nm, and 378 nm) are also clearly visible, but they are shifted by 5 nm to the long-wavelength range compared to stilbene molecules. This suggests that the presence of a *tert*-butyl group leads to some polarization of the π-conjugated system of the stilbene molecule. With increasing concentration, the luminescence spectrum practically does not undergo significant changes, and only when the concentration of the additive reaches 40 wt. %, there is a slight shift of the luminescence bands to the long-wavelength range (Fig. 2). This fact can be associated with intermolecular inter-

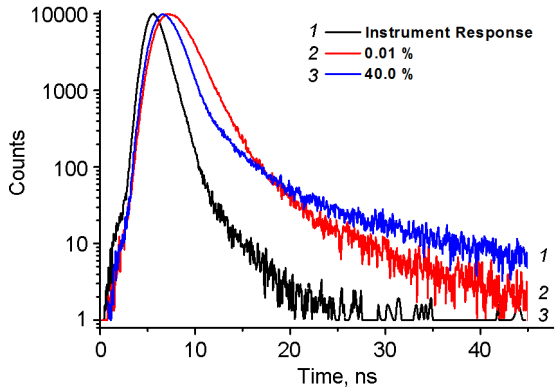

Fig. 3. Luminescence decay curves of 4-*tert*-butylstilbene molecules in polystyrene at different concentrations. Excitation wavelength is 300 nm, observed value is 375 nm.

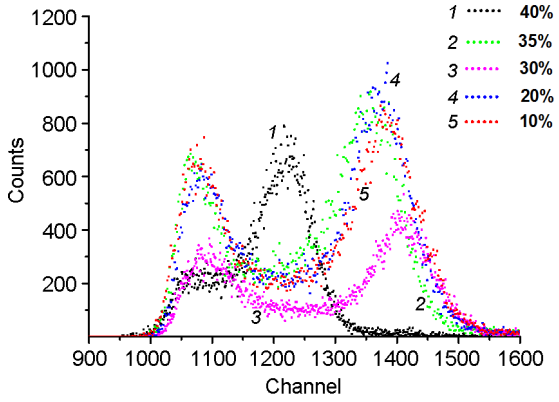

Fig. 4. Scintillation amplitude spectra of PS with different concentrations of tBuSt.

action, which, as is well known, can lead to the splitting of the initial molecular states. This is also clearly seen in the observed luminescence decay curves of tBuSt molecules in polystyrene (Fig. 3).

As seen from Fig. 3, at low concentrations, the decay curve is described quite well by the monoexponential dependence with a decay time of 2.5 ns. The presence of a non-exponential "tail" may be due to the imperfection of the luminescence excitation function. But with an increase in the concentration of tBuSt molecules in polystyrene, a qualitative change in the attenuation curve is observed; it is associated with a substantial delayed part, the presence of which indicates delayed luminescence. This is usually associated with the transformation of triplet states of excitation energy into singlet states through the effect of triplet-triplet annihilation. To realize this effect, two conditions are necessary — the presence of excited triplet states and the possibility of exchange interaction between molecules. The second condition with an activator concentration of about 40 wt. % is almost guaranteed due to the small mutual distance between the molecules. To provide a sufficient number of excited triplet states with the help of ordinary low-intensity optical excitation is not always a feasible task, due to the low probability of intercombination conversion. But in the existence of an exchange interaction, the singlet excitation of a single molecule can be distributed among the excited triplet states of two nearby molecules. For the possibility of such exchange, it is necessary that the energy of the excited singlet state exceeds the double energy of the triplet states. And in order to observe the delayed luminescence, it is necessary that the energy of the sum of two triplet excited states exceeds the energy of the singlet excited state. Apparently, for tBuStF molecules in polystyrene, some coincidence of the energy of the singlet state with the doubled excitation energy of triplet states occurs. And such a coincidence is not the optimal condition for the realization of discrimination of a scintillation pulse from neutrons and gamma rays. A possible conversion of the excitation energy from singlet excited states to triplet states can greatly affect the ratio of the fast and slow components of the scintillation signal.

To create scintillation compositions based on tBuSt molecules, diphenyl anthracene molecules were added to the polystyrene matrix as a shifter in an amount of 0.05 wt. %. The light output of the scintillation compositions obtained on the polystyrene base is shown in Fig. 4 and in Table 1.

From Fig. 4 it is seen that the light output of the obtained plastic scintillators at concentrations greater than 10 wt. % practically does not change, and only slightly decreases with 40 wt. % of tBuSt. But at the same time, the level of light output does not reach even 50 % of the light output of a standard plastic scintillator with the poly-

Table 1. Relative light output of PS with different concentrations of tBuSt

Concentration of tBuSt, wt.%	Relative light output, %
40	39.7
35	44.1
30	45.7
20	44.4
10	44.9
UPS-923A [8]	100.0

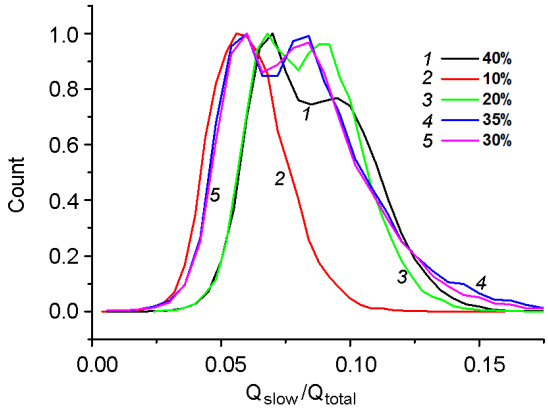

Fig. 5. *n*/γ-Discrimination based on the ratio of fast and slow scintillation components for PS activated by tBuSt molecules.

styrene base activated by *p*-terphenyl molecules. Apparently, the reason lies in the specificity of the interaction of molecules with each other; this opens up new channels for the loss of excitation energy. For tBuSt molecules, this can be the channel for exchanging the excitation energy of singlet states to triplet excitation.

The presence of additional channels for the distribution of the excitation energy of tBuSt molecules in polystyrene results in the fact that the scintillators obtained do not demonstrate good *n*/γ-discrimination parameters, although signs of such discrimination in PS with tBuSt are observed (Fig. 5, Table 2). From the data obtained, it follows that tBuSt molecules are not really suitable for creating neutron-sensitive PS.

4. Conclusions

It was shown that the modification of the stilbene molecule by the introduction of a branched alkyl substituent contributes to a significant increase of its solubility in a polystyrene medium. Based on these molecules, it is possible to create scintillation compositions with an activator contents in a wide concentration range. The found features of the singlet states excitation energy relaxation of tBuSt molecules in polystyrene do not allow us to achieve the desired characteristics of the *n*/γ-discrimination. However, for other polymer bases, tBuSt molecules can be more efficient.

Table 2. FOM values for PS activated by tBuSt molecules

Concentration of tBuSt, wt. %	FOM
40	0.512
35	0.467
30	0.45
20	0.491

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