ISSN 1027-5495. Functional Materials, 24, No.3 (2017), p. 476-480.
doi:https://doi.org/10.15407/fm24.03.476

The plastic scintillator for n/γ-discrimination with alkyl-substituted PPO derivative.

P.N.Zhmurin, D.A.Eliseev, V.N.Pereymak, O.V.Svidlo, Yu.A.Gurkalenko

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Nauky Ave., 61001 Kharkiv, Ukraine

Received February 15, 2017

A new polystyrene-based plastic scintillator for pulse shape n/γ-discrimination is obtained by using alkyl-substituted PPO derivative as scintillation dopant. The microhardness and FOM of the new PS is measured. The microhardness is equal to 39 MPa, and FOM on 2 MeVee level is equal 2.12. Also it is established, the new PS has high long-term stability.

Keywords: plastic scintillator, pulse shape, n/γ-discrimination.

Получен новый пластмассовый сцинтиллятор на основе полистирола для n/γ-разделения по форме импульса. Измерены его микротвердость и FOM. Микротвердость равна 39 МПа, а FOM на уровне 2 МэВ равен 2,12. Установлено, что новый ПС обладает высокой долговременной стабильностью.

Пластмасовий сцинтилятор для n/γ-розділення з алкіл-заміщеною похідною PPO.
П.М.Жмурін, Д.А.Єлісєєв, В.М.Переймак, О.В.Свидло, Ю.А.Гуркаленко.
Отримано новий пластмасовий сцинтилятор на основі полістиролу для n/γ-розділення за формою імпульсу. Виміряно його мікротвердість та FOM. Мікротвердість дорівнює 39 МПа, а FOM на рівні 2 МеВ дорівнює 2,12. Встановлено, що новий ПС має високу довготривалу стабільність.

1. Introduction

Pulse shape discrimination is the main registration method of fast neutrons on γ-ray background with organic scintillators. Organic single crystals and liquid scintillators have very high n/γ-discrimination properties. Traditional PS show no n/γ-discrimination properties absolutely. However, in 1960 Brooks discovered that doping a standard plastic scintillator (e.g., polystyrene + *p*-terphenyl + POPOP) with a so-called "secondary solvent" (herein 4-isopropylbiphenyl) allowed to obtain a PS with fast neutrons and γ-rays discrimination properties [1]. Unfortunately, this PS was discarded after physical alterations appeared a few months after the production [2]. After this, several research groups tried to solve this problem in different ways. A chemical approach [3], use of geometry, allowing γ-rays rejection [4], and mathematical approaches with use of algorithms, identifying the difference between neutron and γ-pulses [5] were used.

In the work [6] a polyvinyltoluene-based PS with the FOM, comparable to liquid scintillators (LS), was obtained. The FOM of this PS is equal to 3.31, and for commercial LS EJ-301-3.21. The high n/γ-discrimination properties were reached by the high activator content in the PS material (30 wt.% 2,5-biphenyloxazole (PPO)), what

increases the triplet-triplet annihilation probability up to values, typical for LS.

However, the PS material, due to high PPO concentration in the polymeric matrix, has low mechanical hardness. This makes difficult its cutting and polishing, and after some time it becomes opaque [7, 8]. Also polymerization of this PS in big volumes is impossible. In order to overcome this disadvantage, in the work [9] a matrix, based on PMMA and its copolymers was proposed. It led to PS microhardness increase, because PMMA has higher rigidity relatively to polyvinyltoluene and polystyrene. However, our investigations have shown, that a PMMA-based PS with 40 wt.% PPO content becomes cloudy after one month since its polymerization, and after three months — almost opaque. So, matrix modification is not able to stop the dopant diffusion in the matrix and, as a result, PS material opacity. In the works [7, 8] PS, containing scintillation dopants with the depressed diffusion, are presented. The given PS have hardness, sufficient to their cutting and polishing, and they don't change their properties in course of time. Also they have the high FOM. For example, the best of the mentioned in [7, 8] PS with 40 wt.% TBPPD content has FOM = 2.0 on 2 MeVee level. This work is a continuation of [7, 8] series to obtain PS with high FOM and long-term stability by use of new scintillations dopants with depressed diffusion.

2. Experimental

To obtain a PS with long-term stability and high FOM, alkyl-derivatives of PPO could be used as the primary dopant. In particular, in this work 2-phenyl- 5-(4-tert-butylphenyl)-1,3-oxazole (TBPPO) was used. In Fig. 1 the TBPPO structure formula is presented.

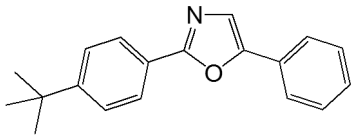

Fig. 1. The structure formula of 2-phenyl-5-(4-tert-butylphenyl)-1,3-oxazole (TBPPO).

Synthesis:

In Fig. 2 scheme of the synthesis is shown.

4-tert-Butylbenzoyl chloride (I): 35.6 g (0.2 mole) of tert-butylbenzoic acid, 70 ml of benzene, 17.4 ml (0.24 mole) of thionyl chloride, and 0.1 ml of pyridine is placed into a round-bottom 0.25 l flask equipped with a reflux condenser. The reaction mass is refluxed on water bath to full dissolution of the residue and end of significant gas products release. Benzene and excess of thionyl chloride are distillated off under vacuum of a water-stream pump. Obtained 4-tert-butylbenzoyl chloride is used in the next stage without additional purification.

N-(4-tert-butylbenzoyl)glycine (II): 20 g (0.24 mole) of glycine, 12 g (0.3 mole) NaOH in 300 ml of water are placed into a round-bottom 3-necked flask equipped with thermometer, ice-water bath and magnet stirrer. Solution of 0.2 mole 4-tert-butylbenzoyl chloride in 100 ml of benzene is added by small portions at intensive stirring and the temperature 5–10°C. Acid chloride addition is carried out for 1 h with keeping pH ≥ 7 by addition of 10 % NaOH solution. Then cooling is stopped and the reaction mass is stirred at the room temperature with keeping pH ≥ 7 by addition of 10 % NaOH solution in small portions, if it is necessary. When after alkali addition pH does not change for 15 min stirring goes on for 1 h and then benzene is distillated off from the mixture. The reaction mass is cooled and acidulated with concentrated

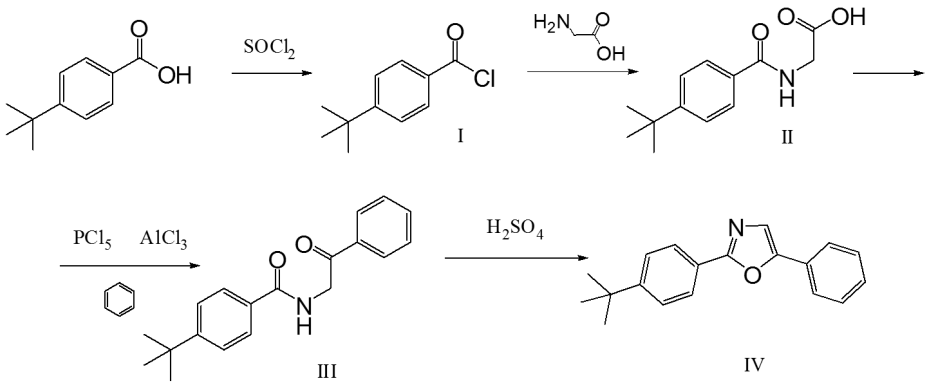

Fig. 2. The scheme of the 2-phenyl-5-(4-tert-butylphenyl)-1,3-oxazole (TBPPO) synthesis.

HCl. Precipitate solid is filtered, washed on the filter with cold water, pressed and dried at the temperature 90°C to the constant mass. Yield: 44 g, white powder, t_{melt} = 187°C.

4-tert-Butyl-N-(2-oxo-2-phenylethyl)benzamide (III): 47 g of N-(4-tert-butylbenzoyl)glycine, 300 ml of benzene, and few drops of pyridine are placed into a round-bottom 3-necked flask equipped with a reflux condenser, a thermometer, and a magnet stirrer. The reaction mass is cooled on an ice-water bath, and at the temperature 5–15°C 43 g of PCl_5 is added by small portions for 1 h. Then the reaction mass is stirred for 2 h at the same temperature. Then 80 g of $AlCl_3$ is added to the mixture for 1 h by small portions at intensive mixing at the temperature 10–15°C and stirred for 2 h at this temperature. Then the reaction mass is stirred at the room temperature for 2 h and the temperature is increased to 40°C, and stirring is continued to the end of significant HCl release. The reaction mass is cooled to the room temperature and poured on mixture of 300 g crushed ice and 30 ml concentrated hydrochloric acid. Then benzene is distillated off from the obtained mixture, a precipitate solid is filtered, washed on the filter with cold water, pressed and dried at the temperature 90°C to the constant mass. Yield: 58 g, crystalline light-beige powder, t_{melt} = 135°C.

2-(4-tert-Butylphenyl)-5-phenyloxazole (IV): Into 150 ml 100 % sulfuric acid at the room temperature and stirring is added by small portions 58 g of 4-tert-butyl-N-(2-oxo-2-phenylethyl)benzamide and the mixture is stirred to full residue dissolution. The reaction mass is left at the room temperature for 2 h and then it is poured on 700 ml of water with ice. The participated solid is filtered, washed on the filter with cold water, 5 % solution of Na_2CO_3 and cold water again and dried on the air at the room temperature. 56 g of technical product with t_{melt} — 60–65°C is obtained. Purification of the product is realized by column chromatography on aluminum oxide, eluent — petroleum ether. Yield: 42 g, colorless crystals, T_{melt} = 68°C.

TBPPO properties:

The solubility of the obtained activator was performed by the method of radical thermal polymerization of activator solution in styrene at the different activator concentration (the polymerization regimes are presented below). The activator solubility in the polystyrene matrix value was defined as the activator concentration, at which in PS volume origination of small single clusters started.

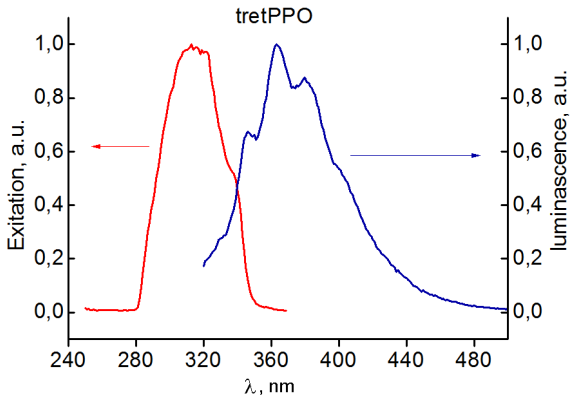

Fig. 3. The spectra of excitation and luminescence of 2-phenyl-5-(4-tert-butilphenyl)-1,3,4-oxazole (TBPPO).

TBPPO has the solubility in polystyrene equal to 50 wt.%, and the melting temperature equal to 68°C.

In Fig. 3 spectra of excitation and luminescence of the obtained scintillation dopant TBPPO are shown. The spectra were measured with a spectrofluorimeter Fluoromax4.

PS sample obtaining:

PS samples dummies were obtained by the method of thermal polymerization of previously deoxygenated solution of luminescent dopants in styrene. Into an ampoule of thermal-proof glass with 25 mm in diameter, the required quantity of the activator and the shifter was placed and fresh-distillated styrene was added to the general solution mass of 50 g. For full dissolution of the additives, the ampoule was heated to 80°C and purged with argon for 10 minutes in order to eliminate dissolved oxygen. Then the ampoule was sealed, placed to a thermostat, and was kep for 7 days at the temperature 155°C. Then the thermostat was cooled with the rate of 5°C/h to 40°C, after what the ampoule was taken out, cooled to the room temperature, and then the PS dummy was taken out. From the obtained dummies, the PS samples were obtained by mechanical manufacturing as polished cylinders 20 mm in diameter and 15 mm in height.

For investigations the PS ample was obtained with content of: PST + 40 wt.% TBPPO + 0.1 wt.% POPOP. At further activator content increase, softening and clouding of PS material is observed. Decrease of the activator content leads to

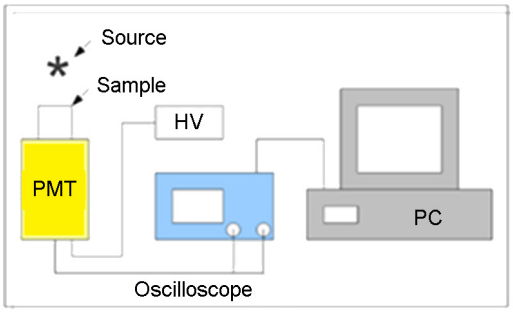

Fig. 4. The scintillation setup for n/γ-discrimination properties measurement.

rapid reduction of n/γ-discrimination properties reduction.

PS properties investigation:

The microhardness by Wickers (HV) of the PS sample was measured on a microhardnessmeter PMT-3 (Russian) at the load of 30 g.

The n/γ-discrimination parameter Figure Of Merit (FOM) was found by the method of pulse shape discrimination (PSD) by comparing charges of whole pulse (Q_{total}) and delayed component (Q_{slow}), similarly to [7, 8].

The scintillation setup for the n/γ-discrimination parameter measurement, showed in Fig. 4, consists of a photomultiplier tube (PMT) Hamamatsu R1307 and a digital oscilloscope Rigol DS 1302 CA (300 MHz, 2 GS/s, 8 bit), which is controlled by computer. The PS sample was set up with optical contact onto PMT input window. For light collection improvement, the sample was covered with an aluminum cone with a hole, closed with polytetrafluoroethylene light reflecting film 0.2 mm thick. The sample was irradiated with neutrons and γ-rays from a Pu–Be source through 6 mm of lead. The signal from PMT was fed to both inputs of the oscilloscope. The load resistance on the first input was of 50 Ohms, and on the second — of 1 MOhm. The amplification on the first channel was of 50 mV/div, and on the second — of 1mV/div. The oscilloscope scan was of 50 ns/div, sweep — single.

The oscilloscope digitized the input pulse from the PMT, and the data from the both channels were transferred to the computer. In the computer with special program, the signal shape was restored from two transmitted frames. Then the program, accordingly to the installed temporal gates, calculated the whole pulse value Q_{total}, and the slow component value Q_{slow} in mV·ns units. The temporal gates limits for Q_{total} were from −50 ns to 400 ns relatively to oscilloscope launch. And for Q_{slow} — from 70 ns to 400 ns respectively the maximum of the scintillation pulse, in order to account jitter influence to Q_{slow}. Then the obtained Q_{total} and Q_{slow} values were stored to a file. Then the program transmitted the command to launch to the oscilloscope and the cycle was repeated required times to acquire the necessary statistics. Then a distribution of pulse quantity on Q_{slow}/Q_{total} was built. The obtained distribution was approximated by sum of the two Gauss functions, and from obtained parameters of the approximation the FOM was calculated by formula:

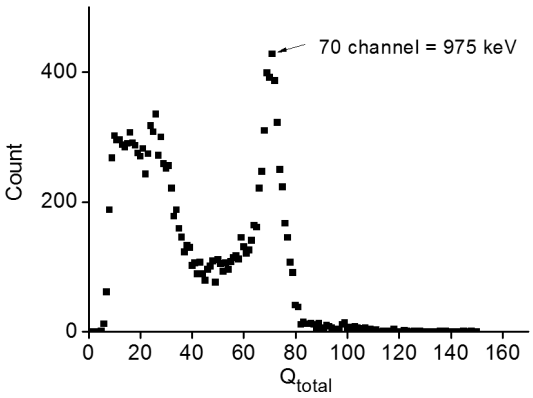

Fig. 5. Calibration of the electron-equivalent energy scale for the PS. The spectrum of electrons from a source Bi-207.

$$FOM = \frac{C_n - C_\gamma}{W_{\gamma L} + W_\gamma}, \quad (1)$$

where C_n and C_γ — the centers of gamma and neutron peaks, and W_n and W_γ — their full widths at the half maximum (FWHM). For determination of the energy, lost in scintillation material by registered particles, calibration is performed. Calibration procedure of electron-equivalent energy scale for the PS was performed on the same setup, that is used for FOM measurements, at the same geometry. For calibration, Bi-207, a source of conversional electrons with the energy 975 keV was used instead at Pu–Be. For light yield determination a special program was used, which determined Q_{total} for each pulse in the same time gates, as in FOM measurements. For each pulse Q_{total} was stored into a file. After the measurement, a distribution of pulse quantity on Q_{total} was built. The distribution is shown in Fig. 5. Relation between the Q_{total} scale and the energetic scale was determined by location of the peak of conversion electrons

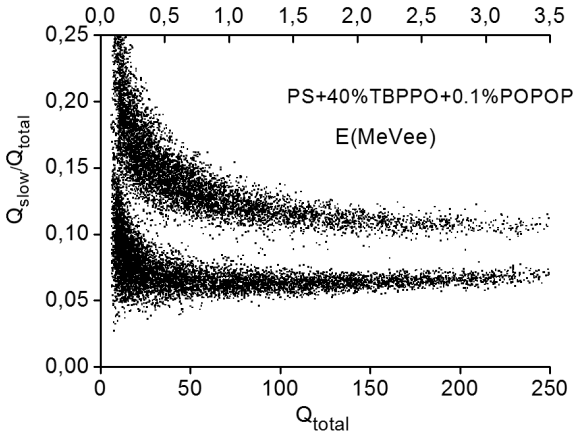

Fig. 6. The dependence of Q_{slow}/Q_{total} on Q_{total} and the electron-equivalent energy for fast neutrons and γ-rays from a Pu–Be source, registered with the PS with 40 wt.% TBPPO content.

with the energy of 975 keV. With help of the calibration, the energy of particles registered in FOM measurements was determined.

3. Results and discussion

In Fig. 6 a dependence of Q_{slow}/Q_{total} on electron-equivalent energy for particles from the Pu–Be source, registered with the obtained PS sample, is shown. In the figure it is seen, that the groups of dots, corresponding to neutrons and γ-rays, are clearly separated.

In Fig. 7 a distribution of pulses quantity on Q_{slow}/Q_{total} of fast neutrons with the energy more than 2 MeVee for the obtained PS sample is shown. This distribution clearly separates in two peaks, according to γ-rays and neatrons, respectively. The given distribution is approximated with sum of two Gauss functions. FOM for the PS sample was calculated accordingly to (1). The calculated FOM on the 2 MeVee level is equal to 2.12.

Also, the measured microhardness of the PS sample is equal to 39 MPa. At such low microhardness, the PS sample is not enough hard, but can remain its shape. So, for better reliability of its use, it can be used in a container. However, the container not necessarily must be hermetic, as in case with liquid scintillators, what makes the obtained PS convenient and safe.

Observations of the new PS have shown, that the new PS is long-term stable.

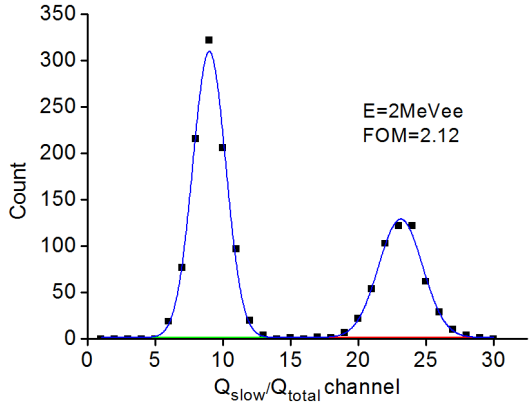

Fig. 7. The distribution of pulses quantity on Q_{slow}/Q_{total} of fast neutrons with the energy more than 2 MeVee for the obtained PS sample.

4. Conclusions

The new activator 2-phenyl-5-(4-tert-butilphenyl)-1,3,4-oxazole (TBPPO) has been synthesized. It is shown, that the new activator has the solubility in polystyrene more than 40 wt.%.

The new PS for *n*/γ-discrimination with 40 wt.% TBPPO content has been obtained. The *n*/γ-discrimination properties of the new PS are investigated. Based on the measurements, FOM on the 2 MeVee level has been calculated. FOM on the 2 MeVee level is equal to 2.12. For reliable *n*/γ-discrimination FOM must be more than 1.27 [6].

The obtained PS reliably discriminates signals from fast neutrons and γ-rays, is long-term stable, so it can be used to produce detectors of fast neutrons on γ-ray background.

References

1. F.D.Brooks, R.W.Pringle, B.L.Funt, *IRE Trans. Nucl. Sci.*, **NS-7**, 35 (1960).
2. D.L.Horrocks, *Rev. Sci. Instrum*, **34**, 1035 (1963).
3. M.Hamel, V.Simic, S.Normand, *React. Funct. Polym.*, **68**, 1671 (2008).
4. M.A.Kovash, B.Daub, J.French et al., Proc. of the IEEE Intern. Conf. on ANIMMA 2011, 2012.
5. Patent Application FR 2947344, 2009.
6. N.Zaitseva, B.L.Rupert, I.Pawelczak et al., *Nucl. Instr. Meth. A*, **668**, 88 (2012).
7. P.N.Zhmurin, V.N.Lebedev, V.D.Titskaya et al., *Nucl. Instr. Meth. Phys. Res. A*, **761**, 92 (2014).
8. P.N.Zhmurin, V.N.Lebedev, A.F.Adadurov et al., *Functional Materials*. **20**, 500 (2013).
9. H.P.Martinez, I.Pawelczak, A.M.Glenn et al., *Nucl. Instr. Meth. Phys. Res. A*, **771**, 28 (2015).