

Influence of electron-donor additive on properties of plastic scintillator

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The main goal of the work is to study the influence of electron-donor additives of a polymer matrix on scintillation properties of plastic scintillators. Molecules of triphenylamine were chosen as the additives which have substantially lesser than styrene ionization. The use of this compound leads to distinct improving of the scintillator properties, namely, to increasing the light yield on 15 % and cutting in half the rise time.

Изучено влияние электронодонорных наполнителей полимерной матрицы на сцинтилляционные свойства созданных на ее основе пластмассовых сцинтилляторов. В качестве таких добавок выбраны молекулы трифениламина, которые имеют значительно меньший по сравнению со стиролом потенциал ионизации. Использование этого соединения приводит к существенному улучшению свойств пластмассового сцинтиллятора, а именно, повышению световыхода на 15 % и уменьшению времени нарастания почти вдвое.

Властивості пластмассового сцинтилятора з електронодонорними домішками.
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Вивчено вплив електронодонорних наповнювачів полімерної матриці на сцинтиляційні властивості створених на її базі пластмассових сцинтиляторів. У якості таких домішок вибрано молекули трифеніламіну, які мають значно менший у порівнянні зі стиролом потенціал іонізації. Використання цієї сполуки призводить до суттєвого поліпшення властивостей пластмассового сцинтилятора, а саме, підвищення світлового виходу на 15 % і зменшення часу наростання майже вдвічі.

1. Introduction

Plastic scintillators (PS) are widely used for registration of high energy particles with low energy losses. Their composition was chosen and optimized as early as in mid-1950ies and since then has been practically unchanged. A standard scintillation composition consists of polystyrene or polyvinyltoluene base with *p*-terphenyl (*p*-Tp) as an activator and *p*-bis[(2-(5-phenyloxazolyl)]benzene (POPOP) as a wavelength shifter [1]. Such a composition provides

light yield of about 10000 photons/MeV for polyvinyltoluene-based PS and ~8000 photons/MeV for polystyrene-based PS [2, 3]. But a modern physical experiment imposes new requirements to PS-based detectors — higher light output and shorter scintillation pulse are needed now.

Mechanisms of interaction of a high-energy particle with a polymer medium are well understood now. An electron passing through the polymer medium creates a track consisting of primary ionization centers. Simulations of observed processes have

shown that the average energy loss by an 1 MeV electron in a single act of interaction with polymer medium does not exceed 30 eV [4]. As a rule this energy is transferred to a secondary electron which, ionizing the medium, can produce electrons of a next generation, and so on. The secondary electron of above energy cannot be displaced on a distance larger than 0.5 nm. As far as Onsager radius is 25 nm under room temperature, it is obvious that the born electron cannot overcome the Coulomb potential of the produced ion and will necessarily recombine with it. As the result, a set of excitation centers is created along the trajectory. The excitation energy is efficiently collected by the activator molecules. So, the scintillation process can be conditionally divided into two stages. The first stage is connected with the leading edge of a scintillation pulse and is directly determined by diffusion time of the charges formed in the track. The second stage is the excitation decay which is determined by life times of activator and shifter molecules.

The main methods of changing the temporal characteristics of plastic scintillators were based, as a rule, on changing de-excitation conditions of scintillating additives of the plastic scintillator. Usually these methods were based on adding different fluorescence quenchers to the polymer medium. They indeed decrease the decay time of scintillation but also noticeably decrease the PS light yield. It is to be noted that these methods do not affect the rise time of scintillation pulse because it is determined by diffusion of charges in a polymer medium. So, a promising way to decrease the rise time is to change the charge mobility in the polymer base of a plastic scintillator. This mobility is determined first of all by donor-acceptor properties of the polymer medium molecules and, as the result, by their ionization potentials. For polystyrene molecules the ionization potential 9.2 eV is determined by the ionization potential of phenyl groups [5]. But molecules with lower ionization potential in a polymer medium can increase the total number of electron-ion pairs in a track of a high-energy particle and accelerate the recombination processes determined by the rate of charges diffusion in a polymer medium. All these can increase the PS light yield and reduce the rise time of a scintillation pulse [6].

The main goal of the present article is to study the influence of electron-donor additives in a polymer matrix on scintillation

properties of plastic scintillators. As electron-donor additives, molecules of triphenylamine were chosen, which have much lower (as compared to styrene) ionization potential — 6.8 eV. This substance is widely used as organic *p*-type semiconductor [7, 8].

2. Experimental

Triphenylamine was obtained from Aldrich and used without any additional purification.

Triphenylamine presence in a polymer scintillating system noticeably affects the polymerization process and scintillators properties. We have determined the triphenylamine solubility in styrene and effects of its concentration on the polymerization process. The optimal concentration of triphenylamine appears to be 40 wt. %.

Selected optimal concentration of triphenylamine (40 wt. %) was used for polystyrene-based scintillators with 2,5-dimethyl-1,4-distyrylbenzene (DMDSP) luminescent additive.

DMDSP was obtained according to the method described in [10]. On the first stage, after interaction of 1,2,4,5-tetramethylbenzene (durene) with *N*-bromosuccinimide in carbon tetrachloride, in the presence of benzoyl peroxide, 2,5-dimethyl-1,4-dibrombenzene is obtained (I). On the stage II, the obtained semi-product reacts with triethylphosphite. As the result a semi-product II is obtained which in the presence of nucleophilic condensing agent (sodium-methoxide) is converted into compound III. Its interaction with benzaldehyde gives the required 2,5-dimethyl-1,4-distyrylbenzene (stage IV).

Solution of triphenylamine and DMDSP in styrene was made under 78°C followed by sparging by argon during 6 min. Experimental samples were made by mean of bulk radical polymerization under 155°C during 96 h. Transparent fluorescent blanks were obtained which then were cut to obtain 8×10×15 mm³ samples.

Spectrofluorometer Fluoromax-4 (HORIBA, Joben Ivon Inc.) was used for fluorescence spectra measurements.

The light pulse shape studies were performed by the time-correlated single-photon counting method. The time spectrometer had two Hamamatsu R9800 PMT. One PMT registered a signal from a Cherenkov counter and was used to generate a trigger signal. The second PMT was used to detect single photons from the samples. Measurements were performed using β -particles of collimated ⁹⁰Sr source.

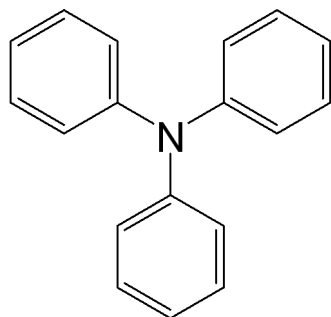


Fig. 1. Structural scheme of triphenylamine.

3. Results and discussion

A triphenylamine molecule (Fig. 1) is a typical molecule with donor electron properties because of high oxidative property of the central nitrogen atom and possibility of transferring the positive charge to outer cations radicals. As it can be seen in the Table 1, triphenylamine has fluorescence band with the maximum at 355 nm wavelength and small quantum yield $\Phi_{fluor} = 5\%$. Polymer based on polystyrene with 30 wt. % of triphenylamine has low fluorescent band with maximum at 370 nm (Fig. 2) and a distinct excitation band with maximum at 340 nm. At high concentration of the additive, the excitation maximum is somewhat shifted to the long-wave side compared to data of Table 1 [9]. It is to be noted that in the spectrum presented in Fig. 2 a peak in the 280 nm region (excitation of polystyrene chromophore groups) is practically absent. This points to the fact that there is no efficient channel of energy transfer from polystyrene to triphenylamine.

Triphenylamine, having the absorption peak at 320 nm, effectively quenches the fluorescence of the standard plastic scintillator with *p*-TP as the first luminescent additive (Table 1) and, as the result, significantly reduces its light yield. Indeed, adding only 1 wt. % of triphenylamine in a standard scintillation composition abruptly (actually, by three times) decreases the light yield of a plastic scintillator. Further increasing of triphenylamine content in a

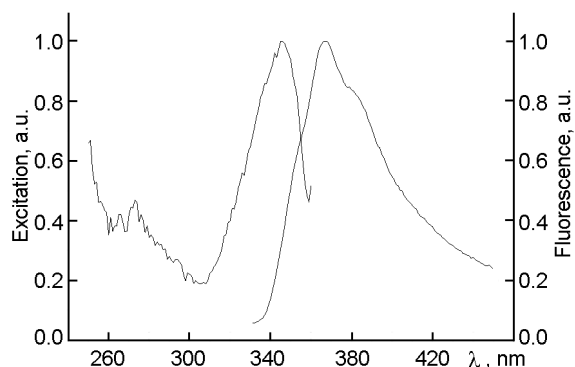


Fig. 2. Excitation and fluorescence spectra of a polystyrene (70 wt.%) with triphenylamine (30 wt %).

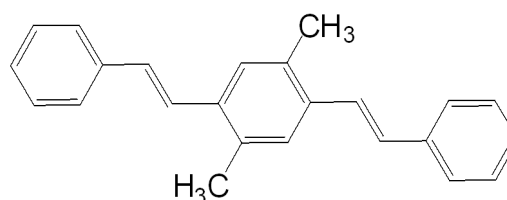


Fig. 3. Structural scheme of DMDSP molecule.

standard plastic scintillator leads to even more light yield losses (Table 2). So, the standard scintillation composition with *p*-TP activator does not suite for operating with triphenylamine. Therefore, to transfer efficiently the excitation energy from a polymer with triphenylamine additive, another activator is needed, which can collect excitation energy at 370 nm (triphenylamine emission). 2,5-Dimethyl-1,4-distyrylbenzene, which structural scheme is presented in Fig. 3, was selected for this purpose. The DMDSP solution in toluene has absorption maximum at 355 nm, and fluorescence maximum at 425 nm with 0.75 quantum yield. As it seen in Fig. 4, these properties of the activator are retained in polystyrene with 40 wt. % of triphenylamine and 2 wt. % of DMDSP.

Table 1. Fluorescent characteristics of triphenylamine and the standard activator of a plastic scintillator — *p*-terphenyl

Activator	λ_{max} abs., nm	E , 10^4 l·Mol ⁻¹ cm·m ⁻¹	λ_{max} fluor., nm	Φ_{fluor}
<i>p</i> -TP	275	3.3	340	0.93
TPA	300	2.37	355	0.05

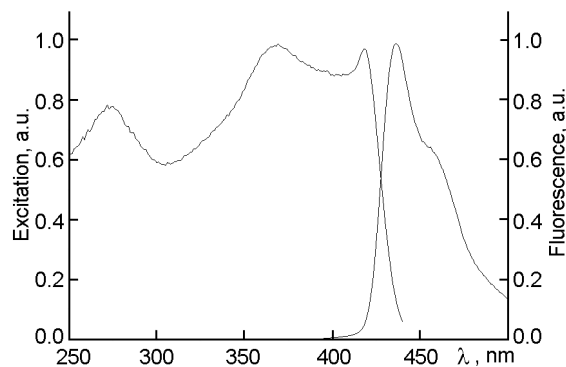


Fig. 4. Excitation and fluorescent spectra of scintillation composition with (60 % PS +40 % TPA + 2 % DMDSP).

Table 2. Dependence of plastic scintillator efficiency on the content of triphenylamine

Content	Scintillating efficiency
PS+2 % <i>p</i> -TP + 0.05 % POPOP	1
PS+2 % <i>p</i> -TP + 0.05 % POPOP + 1 % TPA	0.34
PS+2 % <i>p</i> -TP + 0.05 % POPOP + 5 % TPA	0.2
PS+2 % <i>p</i> -TP + 0.05 % POPOP + 10 % TPA	0.15

Scintillation properties of obtained polymers were studied on a composition of the following content — 60 % PS + 40 % TPA + 2 % DMDSP. Light yield was estimated by means of amplitude analyzer relative to a standard sample under irradiation by ²⁰⁷Bi 0.975 MeV electrons. As shown in the Fig. 5, the light yield of polystyrene-base PS with TPA and DMDSP exceeds that of the standard sample almost on 15 %. Note that this result is obtained without using any wave-length shifter for putting scintillation pulses into the same spectral region.

So, reducing the total ionization potential really increases the scintillator light yield. This result can be attributed to increasing of total number of electron-ion pair in a track. But in addition, the presence of triphenylamine must increase the charge mobility. It is known that the liquid solutions of triphenylamine have semiconductor properties. Increasing the mobility of the charges must accelerate their dispersal in a track. It must affect the rising edge of a scintillating pulse. To check this we made time-domain measurements of scintillation pulse development in a standard scintillator and the scintillation composition

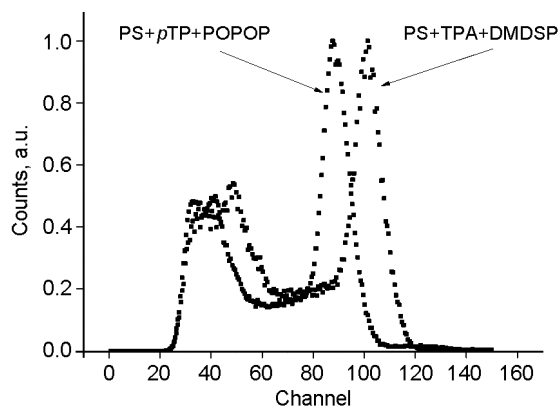


Fig. 5. Amplitude spectra of 60 % PS + 40 % TPA + 2 % DMDSP scintillation composition and the standard scintillator.

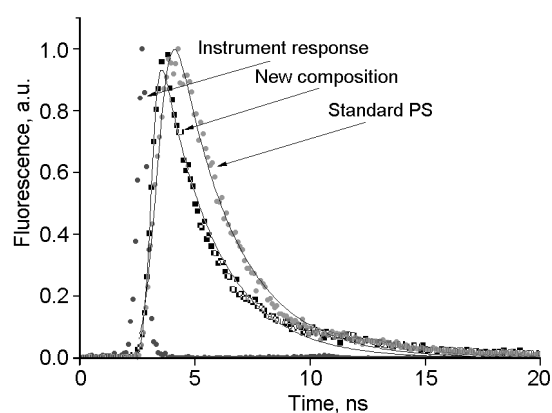


Fig. 6. Time-domain decay curves of scintillation pulse in plastic scintillators. Solid lines — fitting by convolution integral (1).

with 60 % PS + 40 % TPA + 2 % DMDSP. Results are presented in Fig. 6.

It is seen in the figure that the half width at half maximum of the instrument response function is not more than 400 ps and, therefore, it can not be considered in the following analysis. It is known that time dependence of a scintillation pulse is described by the convolution integral [11–13]:

$$I(t) = \int_0^{\infty} F_{rise}(t - \tau) \cdot \exp(-\tau/\tau_{decay})d\tau, \quad (1)$$

where F_{rise} — pulse response of the entire system, τ_{decay} — lifetime of an excited state.

To determine time characteristics of the charges diffusion it is needed to reconstruct the pulse response of the entire system according to (1) [12].

Table 3. Fitting parameters for (1) and (2)

Scintillator	A	σ	τ_{decay}
Standard	2.97	0.49	2.51
PS+TPA+DMDSP	4.267	0.26	2.36

In our case the pulse response of the entire system can be described by a Gaussian distribution with dispersion σ^2 :

$$F_{rise}(t) = A \exp(-t^2/2\sigma^2). \quad (2)$$

Fitting experimental data presented in the Fig. 6 we obtained rising functions for polymer mediums of the standard scintillator and for scintillator with triphenylamine. Fitting parameters are presented in Table 3.

Since rise time of the Gaussian (from 10 % to 90 %) becomes 1.69σ , than it can be said that the emission rise time of the scintillator with polystyrene and TPA is reduced to 0.49 ns compared to that of the standard PS — 0.85 ns. So the change of conducting properties promotes acceleration of charge relaxation processes in a track of a plastic scintillator's polymer base.

Conclusions

The presented results apparently demonstrate that modification of a plastic scintillator properties by means of changing charge mobility in its polymer base can significantly change its scintillation characteristics. These changes can be related to the total number of electron-ion pairs in a track due to lowering of the total ionization potential of the medium, which can significantly affect the temporal characteristics of a plastic scintillator. And if using such a

simple compound as triphenylamine leads to a clear improvement of the scintillator properties, namely, to increasing the light yield by 15 % and making the rise time 2 times shorter, the search for new more efficient additives with lower ionization potential can allow us to improve scintillation properties in a greater degree.

References

1. J.B.Birks, *The Theory and Practice of Scintillation Counting*, Pergamon Press, Oxford, London, New York, Paris (1964).
2. N.Z.Galunov, O.A.Tarasenko, V.A.Tarasov, *Functional Materials*, **20**, 304 (2013).
3. V.G.Senchishin, V.L.Vasilchuk, A.Yu.Borisenko et al., *Semicond. Phys., Quant. Electron. Optoelectron.*, **3**, 223 (2000). @SPLIT = 4. A.M.Mitrev, *Uspekhi Fizicheskikh Nauk*, **172**, 1131 (2002).
5. A.J.Swallow, *Radiation Chemistry of Organic Compounds*, Pergamon Press, Oxford, London, New York, Paris (1960).
6. G.Zhang, J.K.Thomas, *J. Phys. Chem.*, **100**, 11438 (1996).
7. Kwangsoek Doa, Chulwoo Kima, Kihyung Songb et al., *Solar Energy Mater. Solar Cells*, **115**, 52 (2013).
8. Wei Shi, Suqin Fan, Fei Huang et al., *J. Mater. Chem.*, **16**, 2387 (2006).
9. I.B.Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed, Academic Press, London (1971).
10. R.A.Minakova, S.A.Verezubova, L.Ya.Malkes, A.I.Bedrik, *J. Appl. Spectrosc.*, **38**, 506 (1983).
11. J.R.Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York (2006).
12. E.N.Matveeva et al., *Nucl.Instr.and Meth., Phys. Res.***179**, 277 (1981).
13. Yasunobu Arikawa, Mitsuo Nakai, Takeshi Watari et al., <http://www.researchgate.net/publication/242398588>.