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Tuning the decay time of plastic scintillators

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Abstract

In the field of nuclear physics, plastic scintillators are popular and efficient radiation detectors thanks to the following properties: they can be prepared in large volumes, are cheap and various properties can be afforded to the material. However, peculiar applications might require plastic scintillator with unusual scintillation decay times, such as laser beam positioning or detectors stacking. In the case of the scintillation decay time, commercial suppliers do not propose many choices, as only the range 0.7 – 10 ns is usually covered, along with a long decay time – 285 ns – material. Herein we propose a new concept and associated formulations where the scintillation decay time can be finely chosen and tuned in a range starting at 2.5 ns and finishing around 90 ns. These materials are presented, synthesized and characterized.

Keywords

Plastic scintillators; decay time; time-correlated single photon counting

Highlights

- New plastic scintillators are presented, showing an unusual decay time
- A combination of two different primary fluorophores allows tuning the photoluminescence decay time of the material
- The plastic scintillators are fully characterized

Introduction

Plastic scintillators are known since the beginning of the 1950's.¹ They are fluorescent materials that are able to emit light while exposed to ionizing radiations. Traditionally composed of a polymer matrix (usually polystyrene or poly(vinyltoluene)) and two fluorescent molecules acting as primary and secondary fluorophore, most of their chemical developments was performed during the years 1950 – 1970.² Usually, the chemical modifications were used to change the emission wavelength (green- or red-emitting plastic scintillators). More importantly, adding chemical additives to the material allocates the material "special" properties, such as (in a non-exhaustive way) boron or lead loading for thermal neutron detection and low energy gamma spectroscopy, respectively. The 2000's have seen an infatuation in the chemical modifications of plastic scintillators,³ but so far, only fast neutron/gamma discriminating materials have led to two commercialized products from Eljen Technology and Amcrys, as well as a new green-emitting scintillator from Nuvia a.s..

In this context, a new set of formulations is proposed herein, where the key step is the careful choice of different primary fluorophores with their respective concentrations, which leads to plastic scintillators showing photoluminescence decay times that can be finely tuned in the range 2.5 up to 87 ns. Such scintillators' modulation decay might be interesting when coupling pulse shape analysis with a moderately fast digitizer, which could be unable to capture the fastest component. This decay range lies in a place where no products are commercially available, at least for the popular ≈ 420 nm emitting materials. For example, the two biggest scintillator providers offer materials with decays in the range 0.7 – 3.3 ns, and a slow material with a 285 ns decay also exists. Our research thus allows choosing the most appropriate decay time for the experiment, and works not only for 420 nm emitting scintillators, but also with 500 nm (green) or for even 560 nm (red) emitting scintillators. Their synthesis and characterization will be described.

Experimental

All the chemicals were purchased from Sigma-Aldrich and used as received unless otherwise stated. Styrene was vacuum-distilled over calcium hydride prior to the experiment. EJ-200 and EJ-244 plastic scintillators were obtained from Eljen Technology.

Fluorescence spectra were recorded at 90° angle with a Horiba Jobin Yvon Fluoromax-4P device, monitored with FluorEssence software. The light decay characteristics of the plastic scintillators were investigated with the Time-Correlated Single Photon Counting (TCSPC) module available on the Fluoromax-4P spectrofluorometer, with excitation laser diodes operating either at 274 nm or at 368 nm. Decay spectra were fitted using DAS6 software (Horiba Jobin Yvon). Radioluminescence spectra were acquired by using the following procedure. In the Fluoromax 4P spectrofluorometer, the excitation light was shut down. In the center of the experimenter chamber, a $^{90}\text{Sr}/^{90}\text{Y}$ β emitting source (37 MBq) was placed in close contact with the scintillator which opposite side faces the detection cell. Spectra were acquired with integration time 0.1 s/nm and were compared to a reference spectrum (EJ-200 sample).

Beta scintillation yields were recorded as follows: the sample was optically coupled to a Hamamatsu R7724-100 photomultiplier operating at negative voltage. A 4π , 6 kBq ^{36}Cl radioactive source was used to excite the material. Pulses coming from the PMT were sorted and treated with a CAEN DT5730B electronic board. The high voltage was kept constant during the experiments as well. Determination of the Compton edge (CE) position was evaluated from the top of the full energy peak. The relative scintillation yield was calculated using a reference spectrum (EJ-244 sample). This comparison was possible due to the fact that the tested scintillators emit in the same wavelength range as the reference material.

Results and discussion

In the context of designing a new plastic scintillator, several parameters have to be correctly fulfilled:

- the composition, typically a matrix and one or several fluorophores,
- the preparation method, which has an influence on the photophysical quality of the scintillator,
- the light yield, crucial for almost all the applications,
- the potential ageing of the material,
- the photophysical properties and photoluminescence decay time.

In addition, some parameters or chemicals may affect the whole formulation, leading to trade-offs. Varying the decay time of a scintillator can be achieved in two ways: either by adding supplementary molecules or changing the nature of the primary or the secondary fluorophore. Traditionally, the first method is used to prepare ultra-fast plastics (usually less than 1 ns) with photoluminescence quenchers inside.⁴ Adding such nature of molecule leads invariably to a strong decrease of the light output, giving thus only 1700 ph/MeV for a < 1ns fast plastic scintillator. An example of the second method is typically the use of iridium^{5,6,7} or europium⁸ organometallics whose luminescence decay falls in the microsecond range; usually these decays are too long regarding to the given application. The concentration of the primary fluorophore may also affect the decay time, but to a smaller extent. In this study, we wish to introduce a third and new concept to achieve decay time tuning. To the best of our knowledge, this strategy has never been applied in the field of plastic scintillator chemistry.

Plastic scintillator compositions were modified to include two molecules, both used as a primary fluorophore, with each having strongly different photoluminescence decay times. Therefore, their relative concentration leads to materials with different decay times, usually less than 100 ns. As this composition is proprietary, we will refer to these molecules as molecule *A* and molecule *B*. The first one (*A*) can be considered as slow-decaying (a little less than 100 ns) and the other (*B*) as fast-decaying (in the range of a few ns). Acting as primary fluorophores means that their absorption spectrum match the emission of the polymer (around 320 – 330 nm), while their emission spectrum maximum is located around 350 – 360 nm, for *A* and *B*. One can note that here we do not exploit optical quenching to modulate lifetime decay as this phenomenon intrinsically decreases the total quantum yield. However, we rather use a carefully chosen mixture of fluorophores to achieve such modulation using energetically neutral phenomena such as Dexter, Förster or reabsorption, to modulate the decay time of the system. Furthermore, the mixture of molecules should have a resulting emission wavelength compatible with scintillation application, constraining further the choice of molecules. In order to achieve concentration decay tuning we need to identify and investigate the crosstalk between excited states of *A* and *B*.

In a first scenario, this overlap could be due to radiative crosstalk (emission of *A/B* absorbed by *B/A*), so a decay time component that is the sum of the *A/B* system would be observed. The tuning would hence come from the statistic implied by *A/B* concentration ratio, their respective molecular scintillation yields and two self-absorption coefficients (*A* towards *B* and *B* towards *A*). This assumption is supported by the theory given by Böhmer *et al.* with their method presented in Time-resolved fluorescence correlation spectroscopy.⁹

In the case of a second scenario, this overlap could be due to non-radiative crosstalk (Förster or Dexter energy transfer), then we could have a tunable decay time component as the photoluminescence decay time. Here the tuning would come from the statistic implied by *A/B* concentration ratio, their respective scintillation yield and four energy transfer efficiency coefficients (*A* towards *B* and *B* towards *A*, for both Dexter and Förster interactions). However, our concentration range leads us to discard Dexter energy transfer that is highly efficient at low distance only.

In the case these effects are either negligible or balance each other, we would obtain a proportional function between *A/B* concentration and decay time. In practice these overlaps are always present and not balanced, consequently we have a nonlinear relationship, as showed in Figure 1. The shape of the graphic also shows that the imbalance is towards the fast fluorophore.

Figure 1 presents the decay time evolution of a polystyrene-based scintillator along the *A* and *B* concentration ratio, the mixture containing also a 420 nm emitting secondary fluorophore at low concentration. Its decay time should be faster than or as fast as the fastest primary fluorophore.

Usually the Time Correlated Single Photon Counting (TCSPC) measurements give the results as biexponential decays; for the sake of clarity the results presented in this Figure are the mean decay time, following the Equation $\tau_{\text{mean}} = \tau_{\text{fast}} (\%_{\text{fast}}) + \tau_{\text{slow}} (\%_{\text{slow}})$. The percentages represent the relative weights of each exponential decay when fitting the TCSPC result. A 274 nm pulsed LED was used as the excitation source, allowing therefore to excite the polystyrene matrix, followed by the full fluorophores deexcitation. A mean exponential decay trend is followed along the A/B molar ratio, with a value starting around 2.5 ns and reaching 87 ns. On a TCSPC side experiment, each scintillator was excited at 368 nm, thus in the excitation wavelength of the secondary fluorophore, and only the residual decay time of this molecule was observed, proving undoubtedly that the tunable decay time value is accessible from the choice of the A/B molar ratio.

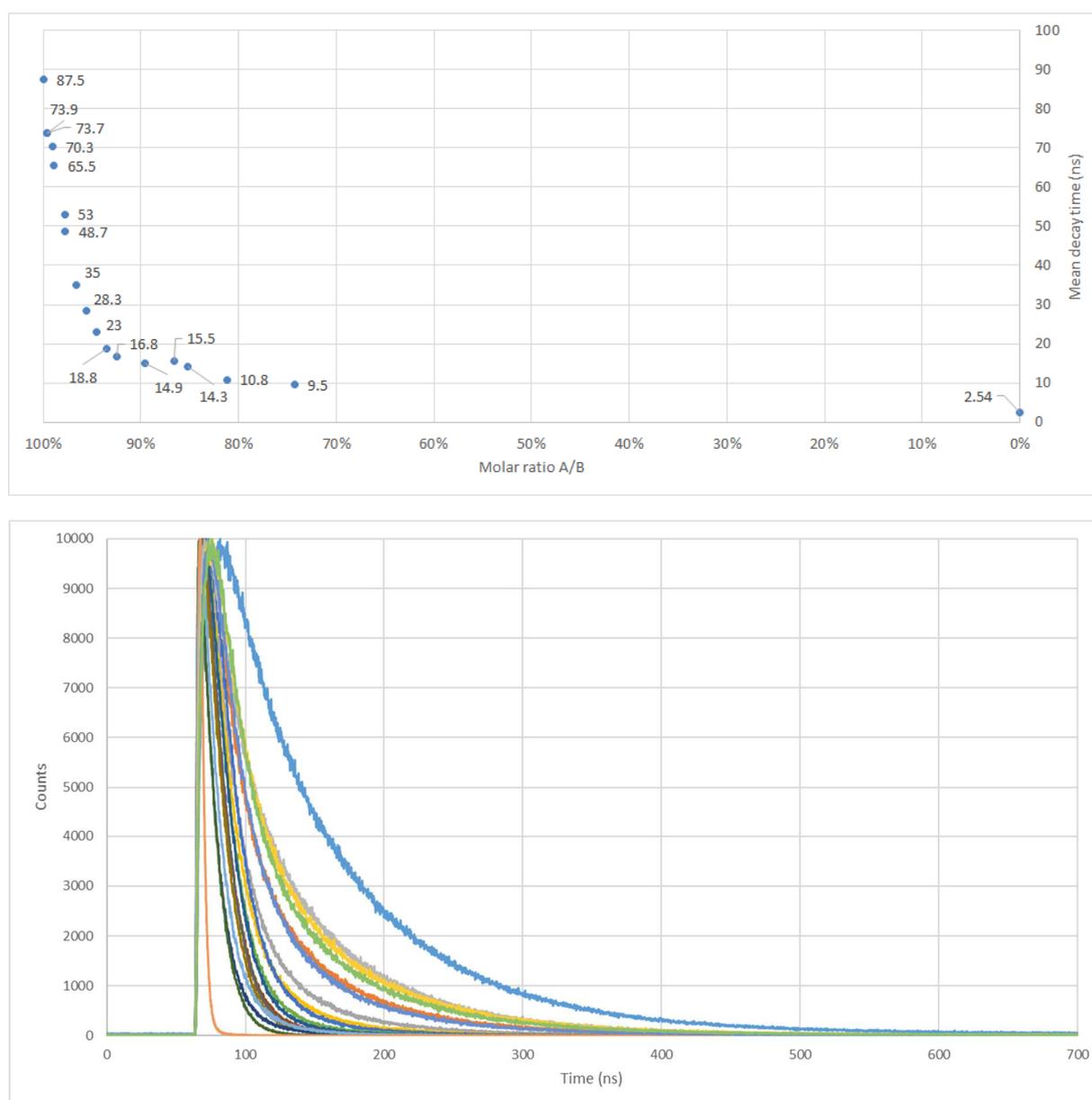


Figure 1. Top: mean value decay time of the 420 nm emitting plastic scintillators. Bottom: photoluminescence decay time of the same 18 samples. TCSPC conditions: $\lambda_{\text{ex}} = 274 \text{ nm}$; $\lambda_{\text{obs}} = 420 \text{ nm}$.

Table 1 shows the influence of the concentration of molecule A on a cross-linked polystyrene/9,10-DPA system, where 9,10-DPA stands for 9,10-diphenylanthracene. A slight increase of the decay time is observed along with [A]. For all six samples, the light yield was evaluated against an EJ-244 plastic scintillator. A moderate light yield was observed, starting around 20 % and reaching a plateau around 30 %.

Table 1. Influence of the concentration of molecule A on the decay time and the light yield. $\lambda_{ex} = 274 \text{ nm}$; $\lambda_{obs} = 420 \text{ nm}$.

Ref.	[A] (wt%)	τ_{fast} (%)	τ_{slow} (%)	τ_{mean} (ns)	β light yield (vs. EJ-244, %)
Sample 1	1	19.8 (15)	82.7 (85)	73.3	18
Sample 2	2	26.7 (13)	84.2 (87)	76.7	25
Sample 3	3	24.3 (15)	82.4 (85)	73.7	27
Sample 4	4	25.1 (13)	82.1 (87)	74.7	29
Sample 5	5	30.8 (13)	83.8 (87)	76.9	31
Sample 6	6	31.8 (11)	84.0 (89)	78.3	30

Various secondary fluorophores suitable for an efficient energy transfer with the A/B primary fluorophores were also considered. Based on a mixture containing polystyrene and 3 wt% of primary fluorophore A only, 4 different molecules were tested: 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP), 1,4-bis-2-(4-methyl-5-phenyloxazolyl)benzene (diMePOPOP), 9,10-diphenylanthracene (9,10-DPA) and bis-methylstyrylbenzene (bis-MSB). The concentration of the secondary dye was kept equal. Varying this molecule had little or no impact on the global photoluminescence decay time, as can be seen on the Table 2. Only 9,10-diphenylanthracene gives a slower scintillator, but this molecule is already known to be slower than the three other tested molecules. When confronted to the EJ-244 plastic scintillator, the $^{90}\text{Sr}/^{90}\text{Y}$ radioluminescence spectra were about 30% the intensity of the commercial sample for both samples, giving thus about 2500 ph/MeV as the light yield.

Table 2. Influence of the secondary dye on a polystyrene/A system. $\lambda_{ex} = 274 \text{ nm}$; $\lambda_{obs} = 420 \text{ nm}$.

Ref.	2 nd dye	τ_{fast} (%)	τ_{slow} (%)	τ_{mean} (ns)	λ_{em}^{max} (nm)	Radioluminescence integral (vs. EJ-244)
Sample 7	POPOP	14.6 (12)	76.1 (88)	68.7	422	29
Sample 8	diMePOPOP	14.5 (13)	75.8 (87)	67.8	438	32
Sample 9	9,10-DPA	24.3 (15)	82.4 (85)	73.6	434	28
Sample 10	bis-MSB	16.0 (13)	75.1 (87)	67.4	426	37

Since our strategy works with various secondary fluorophores that emit around 420 nm, we therefore tested other dyes able to shift the scintillation spectrum towards longer wavelengths. Especially, green and red scintillators are usually of interest as well. Thus, nine plastic scintillators with different A/B ratio were prepared and the secondary fluorophore was changed to afford either 420 nm, 500 nm or 560 nm emitting materials. The green dye shows a maximum of emission close to 500 nm and a monoexponential decay time of 4.57 ns in polystyrene ($\lambda_{ex} = 368 \text{ nm}$), whereas the red dye has a maximum of emission close to 560 nm and a monoexponential decay time of 11.94 ns in polystyrene ($\lambda_{ex} = 368 \text{ nm}$). The results are given in the Figure 2. It is seen the good trend for each composition, except only for the fastest, red material where a 12 ns decay time is observed instead of less than 5 ns, due to the intrinsic lifetime of the red shifter used in this experiment. The independence of the decay time tuning from the wavelength is also another argument granting the tuning coming only from the choice of A and B molecules and their respective concentrations, and can be capped by a slower wavelength shifter.

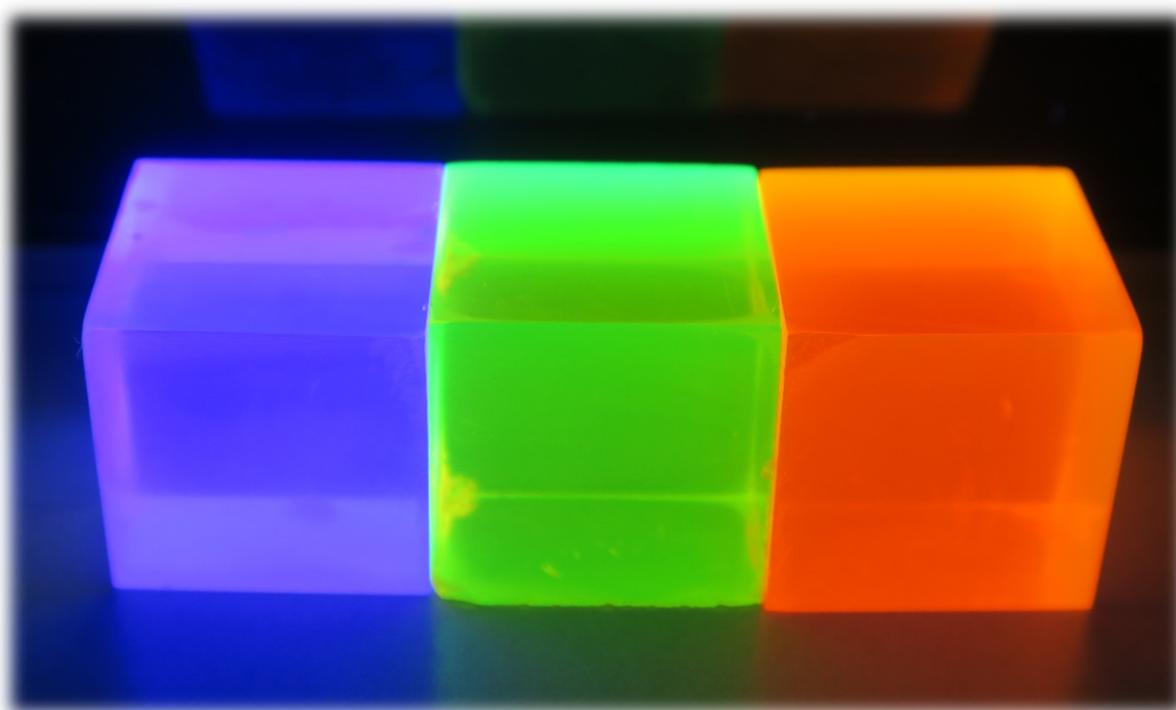
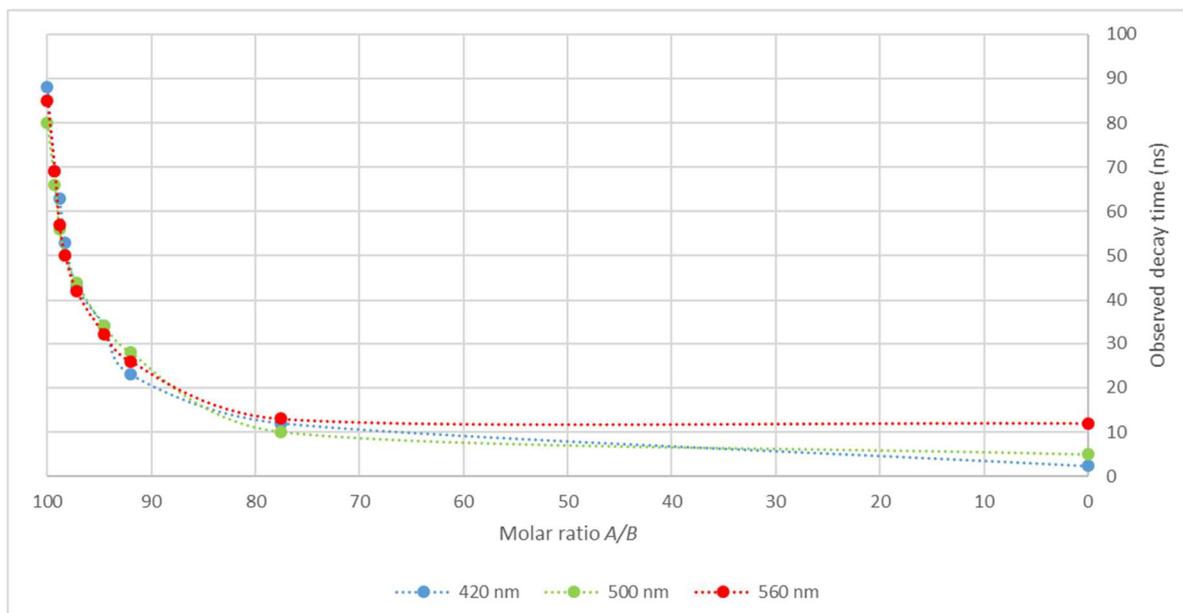


Figure 2. Top: observed decay time vs. A/B molar ratio for violet, green and red-emitting plastic scintillators ($\lambda_{ex} = 274 \text{ nm}$; λ_{obs} at the corresponding wavelength). Bottom: picture of the three materials with different emission wavelength under UV lamp excitation.

Ultimately, the stability of the blue materials was checked; both light yield and photoluminescence decay time were kept homogenous over a five months monitoring.

Conclusion

An important achievement in the choice of plastic scintillators was reached in our study, where the end user may choose the most suitable scintillation decay time for its experiment, at least in the range

2.5 – 90 ns. Since these materials are neither fast neither slow, we introduce the concept of *tunable* plastic scintillator. In addition, this tuning has been proven for three different emission wavelengths. The main drawback is probably the scintillation yield, which is rather weak for the slowest compositions. Future experiments will be conducted to fix this issue. We would be glad to share with the scientific community these materials for further testing and collaboration.

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