



Plastic scintillators with efficient neutron/gamma pulse shape discrimination

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ABSTRACT

A possibility of manufacturing plastic scintillators with efficient neutron/gamma pulse shape discrimination (PSD) is demonstrated using a system of a polyvinyltoluene (PVT) polymer matrix loaded with a scintillating dye, 2,5-diphenyloxazole (PPO). Similarities and differences of conditions leading to the rise of PSD in liquid and solid organic scintillators are discussed based on the classical model of excited state interaction and delayed light formation. First characterization results are presented to show that PSD in plastic scintillators can be of the similar magnitude or even higher than in standard commercial liquid scintillators.

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1. Introduction

Pulse shape discrimination (PSD) is one of the major techniques used for detection of high-energy neutrons in the presence of a gamma radiation background. The method is based on the difference in the shapes of the scintillation signals due to excitation by neutrons (recoil protons) and γ -rays (recoil electrons) in organic scintillators. According to a commonly accepted mechanism [1,2], both gamma- and neutron-induced pulses contain a short decay (prompt) and a long decay (delayed) fluorescence components. The prompt component results from the direct radiative de-excitation of excited singlet states (S_1), while the slow component is determined by the kinetics of the triplet (T_1) exciton diffusion process preceding the triplet–triplet interaction and annihilation: $T_1 + T_1 \rightarrow S_0 + S_1$, which leads to the excitation of additional singlet states decaying with the same spectral distribution, but over a longer and delayed time scale. The short range of energetic protons produced from neutron collisions yields a high concentration of triplets, leading to the enhanced level of delayed emission in neutron-induced pulses in comparison to those produced by the longer range of the electrons from gamma interactions. The different proportions of the prompt and delayed components in scintillation pulses produced by neutron and gamma interactions give the basis for the pulse separation used in PSD techniques. The mechanism of triplet–triplet annihilation was first discovered and demonstrated [3–7] in a number of

unitary systems of organic single crystals (anthracene, trans-stilbene, p-terphenyl, and p-quaterphenyl), among which stilbene became known for its superior discrimination properties. Similar discrimination properties were also found in organic liquid scintillators, which typically are binary or ternary systems composed of highly efficient fluorescent dyes (e.g. p-terphenyl, PPO, PBD, or POPOP) dissolved in aromatic solvents (e.g. toluene or xylene) [1]. A good level of PSD known for liquid scintillators reveals that the mechanisms of delayed light formation via excitation migration and triplet–triplet annihilation must also work in amorphous systems, meaning that crystallographic structure is not a necessary condition for PSD. In this respect, it has never been clear why scintillating plastics, which differ from crystals only by the absence of the crystallographic arrangement, have been historically found to exhibit much poorer discrimination properties. Typical compositions of scintillating plastics are similar to those used for the liquid scintillators, with the difference that liquid solvents are replaced by aromatic polymers, such as polystyrene or polyvinyltoluene (PVT). However, despite this similarity, PSD in plastics has been always reported to be absent, negligible, or significantly inferior to that in crystals or liquids [8–10], leading to an established opinion that plastics are materials unsuitable for efficient detection of fast neutrons via neutron/gamma discrimination methods [1,11].

Recent studies conducted with organic crystals [12] showed that the main reason for the absence of PSD in mixed systems results from the excitation traps formed by a lower-band-gap fluorescent impurity (dye) present in the host material (solvent) at low concentration. It was demonstrated that increasing the concentration of the dye can provide conditions suitable for

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formation of a network for excitation energy migration and triplet annihilation, and may lead to the appearance of PSD comparable to that of typical for pure single crystals of the dye. The present paper introduces the results of similar studies conducted with mixed liquid and plastic scintillating systems. Analysis of the results shows that explanations of the conditions leading to the formation of PSD in crystals, and liquids can be similarly applied to the mixed plastic systems. The properties of the first plastics scintillators fabricated with efficient neutron/gamma discrimination are discussed in comparison with commercially available liquid and single crystal organic scintillators.

2. Experimental methods

All chemicals for sample preparation were purchased from Sigma-Aldrich. Liquid scintillator mixtures were made using anhydrous p-xylene (> 99%), 2,5-diphenyloxazole (PPO, 99%), and 9,10-diphenylanthracene (DPA, > 98%) in the oxygen-free atmosphere of a nitrogen-filled glovebox. PPO was used as received, DPA was stirred for 0.5 h in warm acetone, collected by filtration, dried, and stored in nitrogen atmosphere prior to sample preparations. The liquid mixtures of required concentrations were transferred into sealed Ø50 mm × 10 mm cylindrical quartz cuvettes used for further measurements. For the plastic preparation, methylstyrene was filtered through a chromatographic support material to remove inhibitor prior to polymerization. Filtered methylstyrene and a radical initiator were sparged with nitrogen for 40 min and stored in sealed containers in a glovebox refrigerator at −20 °C. To conduct polymerization, required amounts of PPO and DPA were weighed in a glovebox into 20 mL scintillation vials, radical initiator (1% by weight with respect to monomer) and methylstyrene were then added to make up the final weight proportions of polymer parts. The vials were tightly sealed, removed from the glovebox, and placed in an oven until polymerization was complete. After cooling to room

temperature the glass was scored and broken with a mallet to remove the bare scintillator part.

Photoluminescence (PL) spectra were measured under UV excitation using a commercial Spex Fluoromax-2 spectrometer. The scintillation light yield efficiency was evaluated from the position of the Compton edge in the ^{137}Cs spectra, in which 480 keVee (electron-equivalent energy) was defined by 50% of the Compton edge peak. Neutron detection properties of samples were studied using a ^{252}Cf source shielded with 5.1 cm of lead, which reduced the gamma rates to the same order of magnitude as neutrons, to irradiate liquid or plastic samples coupled to Hamamatsu R6231-100-SEL photomultiplier tube (PMT). The signals collected at the PMT anode were recorded using a 14-bit high-resolution waveform CompuScope 14200 digitizer with a sampling rate of 200 MS/s, for offline analysis. The ability of scintillators samples to discriminate between the neutrons and gamma rays emitted from the ^{252}Cf source was evaluated using the charge integration method. The waveforms were numerically integrated over two time intervals: Δt_{Total} and a subinterval Δt_{Tail} , corresponding to the total charge (Q_{Total}) and the delayed component (Q_{Tail}) of the signal, respectively. The value of the ratio of charge $R = Q_{\text{Tail}}/Q_{\text{Total}}$ for the two time intervals indicated whether the considered event was likely produced by a neutron (high R value) or a gamma ray (small R value). Quantitative evaluation of PSD was made using figures of merit $\text{FOM} = S/(\delta_{\text{gamma}} + \delta_{\text{neutron}})$, where S is the separation between gamma and neutron peaks, and δ_{gamma} and δ_{neutron} are full width at half maximum (FWHM) of the corresponding peaks (Fig. 1A). The separation S was calculated as a difference between the mean delayed light fraction, $Q_{\text{Tail}}/Q_{\text{Total}}$, for neutrons and gammas taken as a normal distribution in PSD over a specified energy range. In total, 40,000 events were collected for each scintillator sample, with approximately 20% of the statistics used for FOM calculation in the energy range near the Compton edge. Considering that a reasonable definition for well separated Gaussian distributions of similar population sizes is $S > 3(\sigma_{\text{gamma}} + \sigma_{\text{neutron}})$, where σ is the standard deviation for each corresponding peak,

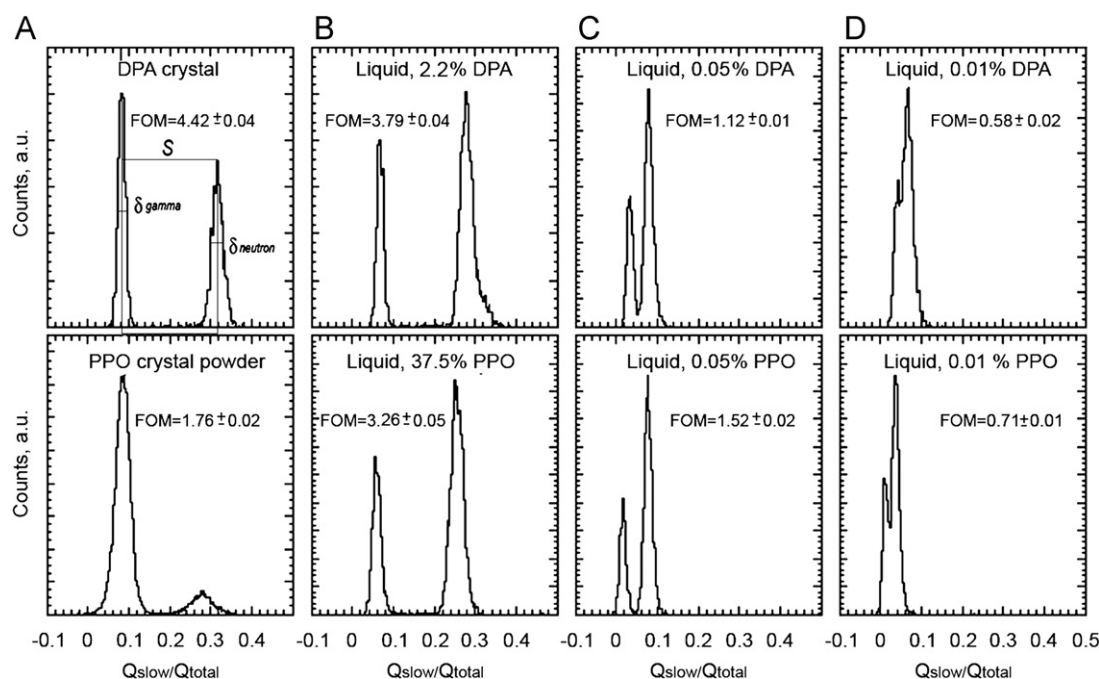


Fig. 1. PSD patterns obtained with organic scintillators containing DPA and PPO dyes: (A) crystals; (B) close-to-saturation solutions with excellent PSD; (C) solutions of intermediate concentration with deteriorating PSD; and (D) low concentration solutions with near complete absence of PSD. Concentration shown in weight % of dyes in p-xylene solutions. All results obtained with ^{252}Cf source in a 480 ± 75 keVee energy range, with the exception of the PPO crystalline powder, for which the distribution is integrated over all events, because of the small size of crystals.

and noting that $\text{FWHM} \approx 2.36\sigma$, $\text{FOM} \geq 3(\sigma_{\text{gamma}} + \sigma_{\text{neutron}})/2.36(\sigma_{\text{gamma}} + \sigma_{\text{neutron}}) \approx 1.27$ was used as a reference parameter to define efficient PSD in the tested samples.

3. Results and discussion

PPO and DPA are well-known fluorescent compounds traditionally used as fluorescent dyes in composition of different organic scintillators. Measurements made in a PSD survey of many organic crystals [13,14] showed that both PPO and DPA exhibit neutron–gamma discrimination properties in their pure crystalline state (Fig. 1A). It should be noted here that a much smaller value of the PSD FOM calculated for solid PPO in comparison to DPA is most likely due to the fact that the measurements were made with commercial PPO micron-scale crystallites instead of difficult-to-grow PPO single crystals needed for energy calibration. Both DPA and PPO are soluble in xylene, although at very different solubilities of about 2.5 wt% for DPA and 42 wt% for PPO at the room temperature. As shown by Fig. 1B, liquid solutions containing DPA or PPO dyes at the concentration close to their solubility limits exhibit high levels of PSD (FOM $\gg 1.27$) similar to that of single crystals. However, at decreasing concentrations, the separation of the peaks gradually decreases (Fig. 1C) leading at the end to a nearly complete overlap of the neutron and gamma pulse distributions (FOM $\ll 1.27$ in Fig. 1D). Fig. 2 A presents the dependence of PSD on the dye concentration measured in DPA and PPO solutions through the entire range of their solubility in xylene. For both types of

solutions, there is a region of very low dye concentrations ($< 1 \mu\text{mole/g}$ solution, or $\sim 0.02 \text{ wt}\%$) with negligibly small PSD. Increasing the concentration leads to a gradual enhancement of PSD which, despite the large difference in the solubility, has the same slope for both dyes up to a molecular concentration of about $10 \mu\text{mole/g}$ solution. It is interesting to note that the separation of the PSD curves occurs at the molecular concentration ($\sim 10 \mu\text{mole/g}$ solution), which corresponds to the maximum in the light yield (Fig. 2B) for both PPO and DPA. Since the decrease of the scintillation light efficiency at increasing concentration (concentration quenching, [1]) is typically ascribed to the formation of excimers, S_0S_1 , it can be suggested that the separation of the PSD curves may relate to different kinetics of these processes for different types of the molecules.

A rise of the PSD to efficient values above some certain concentration threshold measured in DPA and PPO solutions is similar to that observed recently in the mixed crystal systems [12], for which the interpretation of the PSD behavior was given on the basis of a simple model of energy transfer and triplet–triplet annihilation mentioned above. It is well known that binary or ternary organic liquid scintillators are prepared in a way that the excitation received by the solvent can be efficiently transferred to the lower band gap solute (dye) molecules. Excitation of the solute singlet states via the energy transfer results in the prompt fluorescence from the individual solute molecules. Formation of the delayed light, which involves excitation of triplet states, is a bi-molecular process which depends upon the intermolecular overlap of carbon $2p\pi$ molecular orbitals. The process of the triplet annihilation, $T_1 + T_1 \rightarrow \text{S}_0 + \text{S}_1$, which gives rise to PSD phenomena, requires physical proximity of interacting molecules [15]. At very small concentrations, excited singlet states of the solute molecules still produce scintillation light, while excited triplets behave more like energy traps, since direct fluorescence from the triplets is effectively forbidden. At relatively large intermolecular distances and low probability of collisions in dilute solutions, dye molecules cannot interact, thus leading to a quenched triplet migration, recombination, and absence of PSD. At higher concentrations, the increased probability of triplet–triplet collisions leads to the enhancement of the delayed light and a rise of the PSD above a certain concentration threshold corresponding to the establishment of a continuous network of interacting dye molecules. The much lower dye concentrations needed for the appearance of efficient PSD in liquid scintillators (0.01–0.02 wt %), in comparison with those found previously in mixed single crystals ($\sim 20\%$) [12], can be easily explained by the high degree of molecular diffusion facilitating interactions of excited states in liquid solutions.

Assuming that similar processes can take place in plastic scintillators, one can expect that, due to the fixed position of molecules in a polymer matrix, the concentration of a dye required for efficient PSD should be closer to that in mixed crystals rather than in liquid solutions. An unfortunate fact is that most of the known efficiently scintillating dyes, such as DPA, POPOP, PBD, bis-MSB, etc., have very low solubility in aromatic solvents which include vinylstyrene and vinyltoluene used to obtain polystyrene or polyvinyltoluene (PVT)-based plastic scintillators. Among the exceptions is PPO, which being highly soluble in toluene, can also be used for the preparation of plastics with a high dye load up to $\sim 30 \text{ wt}\%$. Fig. 3 shows examples of experimental PSD pattern measured in selected PVT-based plastics containing different concentrations of PPO. Similar to the results presented in Fig. 1, the neutron–gamma separation, hardly detectable at low concentrations, becomes clearly pronounced in plastics containing larger fractions of the dye. More detailed measurements made with a large number of plastic samples prepared with a broad range of PPO concentrations (Fig. 4) confirmed an increase of the neutron–gamma peak separation in a range of 10–30 wt% which

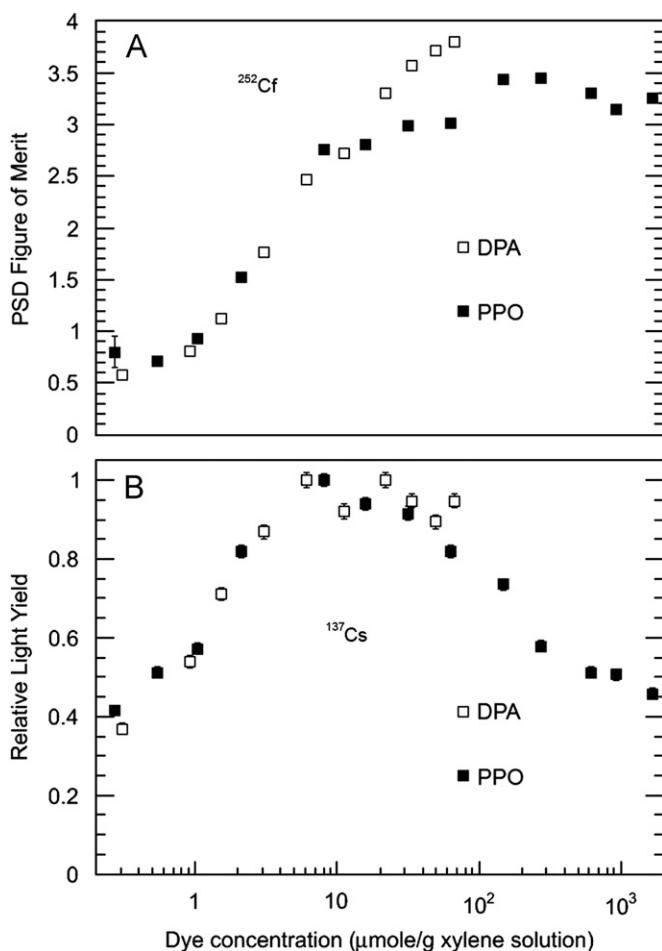


Fig. 2. PSD FOM (A) and ^{137}Cs light yield and (B) dependences on concentration of DPA and PPO in p-xylene solutions. The data show increase of PSD in the region corresponding to the maximum LY. FOM statistical errors are within the points.

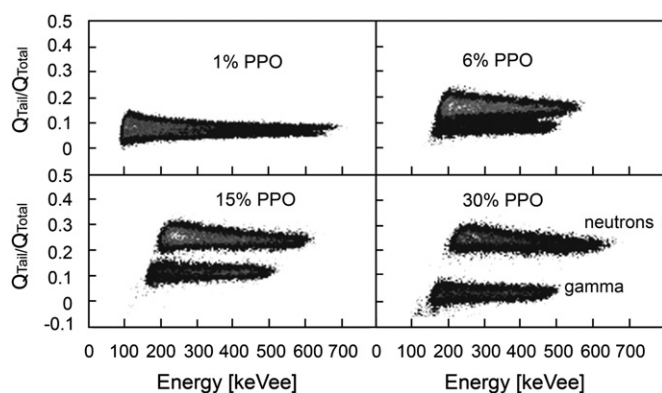


Fig. 3. Examples of experimental PSD patterns showing increase of neutron–gamma peak separation at increasing PPO concentration in a PVT polymer matrix.

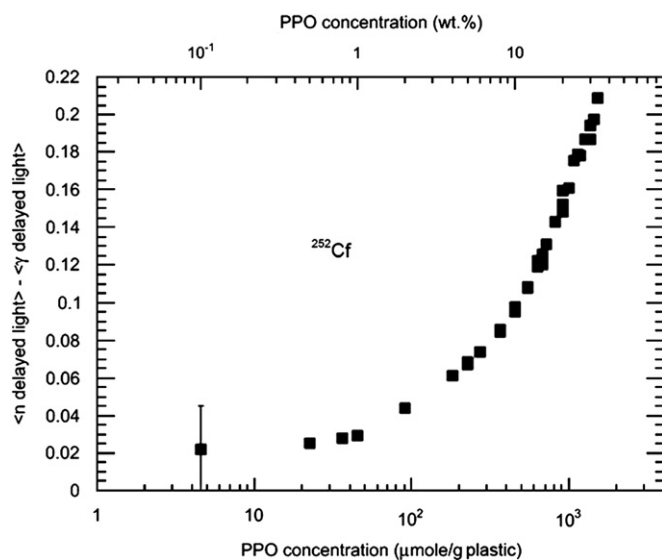


Fig. 4. General dependence of neutron–gamma separation measured in the whole range of concentrations up to the limit of the PPO solubility. Statistical error bars are within the points, except for the lowest concentration point, where larger uncertainty is introduced by the overlap of the two distributions.

gives rise to efficient PSD with FOMs > 1.27 (Fig. 5A). As expected, the increase of PSD in plastics occurs at much larger PPO concentrations, more than two orders of magnitude higher than in corresponding liquid solutions. It should be noted that the optimal dye concentration used in practical preparation of mixed scintillators has been traditionally selected based on the highest scintillation efficiency. The fact that in liquids both the maximum LY and the efficient PSD correspond to the same region of low concentrations (Fig. 2) could explain the easy preparation of liquid scintillators with PSD. In plastics, the scintillation with the most efficient light output still occurs at relatively low dye concentrations ($\sim 1\%$ weight in Fig. 5B), while efficient PSD appears in a different region, in which increasing PPO concentration leads to about 20% LY loss, due to the concentration quenching. It might be that this decline in the light efficiency contributed to the fact that the region of high dye concentration was not sufficiently explored in the previous studies of plastic scintillators.

A noticeable decrease of the light yield at high PPO concentrations can negatively influence the final performance of PSD scintillators. The problem can be corrected by the use of ternary systems traditionally designed to increase the light efficiency by addition of secondary dyes with lower band gap and higher quantum efficiency. Fig. 6A presents one of the first results

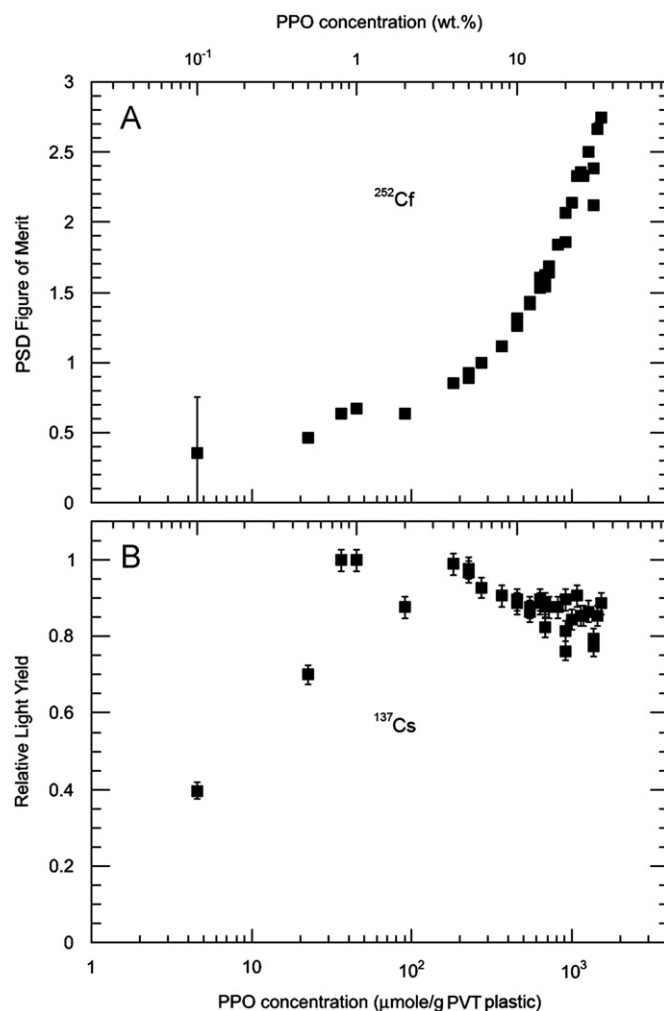


Fig. 5. Dependence of neutron/gamma PSD FOM obtained in PPO–PVT plastic scintillators. Comparison with the ^{137}Cs LY measured in the same samples shows that the noticeable increase of PSD starts in the region of the declining LY. All measurements were done with $\varnothing 25 \text{ mm} \times 10 \text{ mm}$ samples.

showing a more than 50% LY increase obtained with the addition of only 0.2% DPA, in this case, used as a secondary dye in a PPO–PVT plastic. The concentration of the secondary dye is too low to affect the triplet–triplet interaction, still occurring mainly between the PPO molecules. At the same time, the fact that fluorescence in the ternary system is dominated by emission from the DPA molecules (Fig. 6B) indicates that singlet excitation is efficiently transferred from PPO to DPA molecules. As a result, the final neutron/gamma peak separation determined by the process of T_1 – T_1 interaction does not show any noticeable difference in the final PSD patterns of binary and ternary samples. On the contrary, increasing light output determined by the high quantum efficiency and low concentration of DPA, leads to the narrowing of the FWHMs of both peaks, ultimately resulting in the increase of PSD in plastics with the secondary dye (Fig. 7A and B).

Tests of the first samples showed that plastic scintillators can provide PSD comparable to the PSD of the best commercially available liquid scintillators (Fig. 7B and C). This important result permits replacement of liquid scintillators by plastics for applications challenged by the well-known problems of liquids, including toxicity, flammability, high freezing points, and difficulties in handling large amounts of organic liquids in field conditions. With respect to single crystals, more research is required to understand if the better performance of stilbene (Fig. 7D) or other single crystals

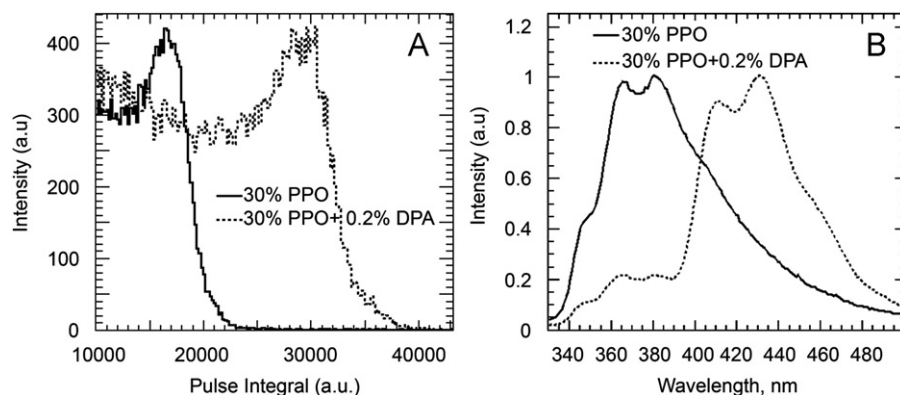


Fig. 6. (A) Comparison of the ^{137}Cs light yield in two Ø25 mm \times 25 mm PPO-PVT plastic samples showing more than 50% increase upon a small addition of DPA used as a secondary dye and (B) corresponding photoluminescence spectra showing that the light emission from PPO molecules in the binary PPO-PVT plastic changes to the spectrum of DPA in the ternary system; excitation wavelength is 273 nm.

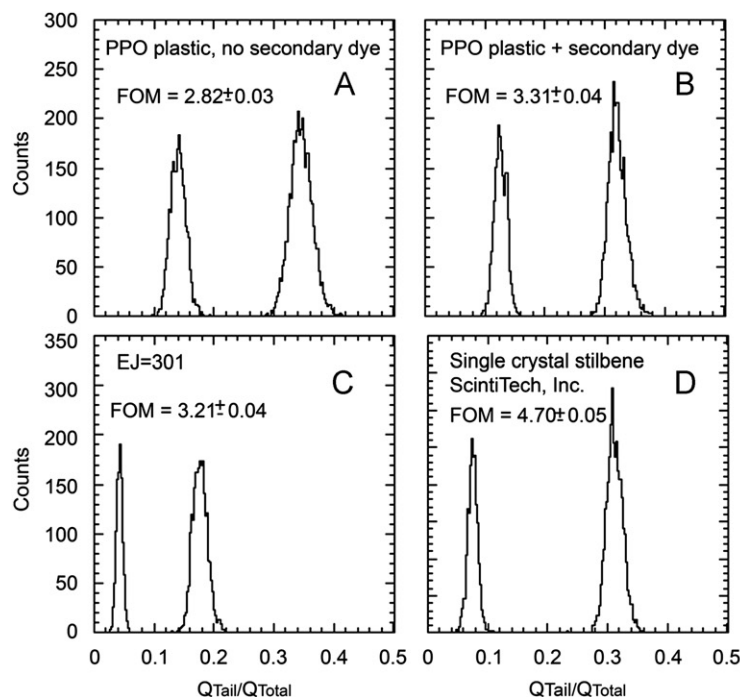


Fig. 7. Neutron/gamma PSD FOMs for (480 ± 75) keVee energy range obtained with (A) binary and (B) ternary plastics in comparison with commercial (C) liquid, and (D) single crystal scintillators; and (E)-measurements made with the same size samples of Ø25 mm \times 25 mm using ^{252}Cf source.

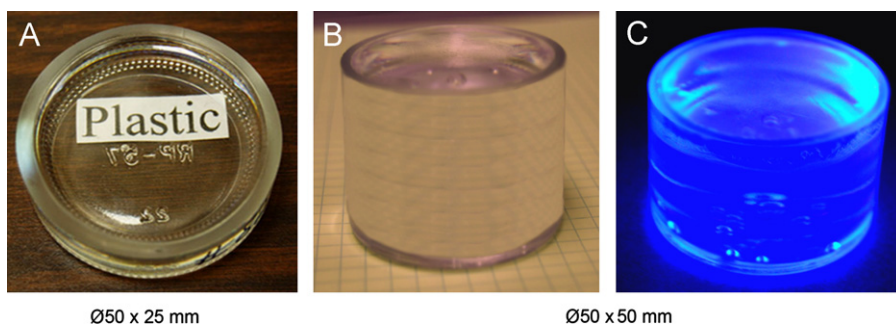


Fig. 8. Photographs of first PSD plastics taken under white (A and B) and UV (C) illumination. The label “Plastic” placed under the bottom of the sample (A) shows high optical transparency typical for the tested scintillators.

(e.g. the DPA single crystal in Fig. 1) is fundamental, and due to the high degree of structural order. It is possible that the crystallographic arrangements which introduce conditions enhancing triplet migration and hence PSD, lead to the better performance of crystals

in comparison to the amorphous plastics where excitation transport is fundamentally inferior. At the same time, methods of combining different, including currently unknown, fluorescent compounds in plastics to control self-absorption, may ultimately lead to future

efficient plastic scintillators offering performance comparable to the best single crystals.

The described PPO–PVT plastics have high optical transparency (Fig. 7E and Fig. 8A). They are adequately hard for cutting and polishing using regular equipment for plastic scintillators. Since preparation procedures to obtain new materials do not have any principle differences from the manufacturing methods of standard plastic scintillators, the scaling process can easily produce larger samples (Fig. 8B and C) comparable to the sizes of the most commonly employed liquid scintillators. At the same time, the plastics described above are only the first examples of this new class of scintillators. Future studies may introduce more efficient systems obtained by replacement of PPO by other highly soluble compounds combined with different secondary dyes, opening broader opportunities for understanding of the PSD phenomena and their practical application for production of low-cost and high-availability new materials for wide-spread use in radiation detection.

4. Conclusion

The first plastic scintillators have been synthesized with efficient neutron/gamma pulse shape discrimination (PSD) comparable to that of commonly used organic liquid scintillators. The composition of PSD plastics is based on a combination of the polyvinyltoluene (PVT) matrix loaded with traditional fluorescent compounds, 2,5-diphenyloxazole (PPO) and 9,10-diphenylanthracene (DPA) used as a primary and a secondary dyes. Studies conducted with the new scintillators showed that the physical processes giving rise to PSD phenomena in plastics are similar to those occurring in mixed organic liquids and crystals. The results of characterization results obtained with varying concentrations of PPO confirm a similar increase of PSD with the dye concentration in all three types of scintillators. The roughly three order of magnitude lower dye concentrations needed for efficient PSD in liquid scintillators (0.01% vs 10–20% in plastics and crystals) is consistent with a higher degree of the triplet–triplet interaction facilitated by the molecular

motion in liquids in comparison to solid matrixes. Efficient PSD combined with easy fabrication and advantages in deployment of plastics over liquids may lead to widespread use of new PSD materials as large-volume and low-cost neutron detectors.

Acknowledgments

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