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Pulse shape discrimination properties of plastic scintillators incorporating a rationally designed highly soluble and polymerizable derivative of 9,10-diphenylanthracene

Tibor Jacob Hajagos, David Kishpaugh, Qibing Pei *

UCLA Department of Materials Science & Engineering, 420 Westwood Plaza, Los Angeles, CA 90095, USA

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ABSTRACT

A highly soluble and polymerizable derivative of 9,10-diphenylanthracene was designed and synthesized specifically to be capable of achieving very high loadings (at least 50 wt.%) when copolymerized with a polyvinyltoluene (PVT) matrix. The resulting heavily crosslinked plastics are mechanically hard and robust, and were found to have exceptional clarity with no sign of dye precipitation. Samples of these plastics both with and without added wavelength shifter were characterized for light yield, scintillation decay, and pulse shape discrimination (PSD) performance for α/γ discrimination, and the results were compared to that of a commercially available PSD plastic, EJ-299-34. The best performing formulation, with a primary dye loading of 50 wt.%, had a measured light yield of 9950 photons/MeV, and achieved a PSD figure-of-merit (FOM) of 1.05, the latter indicating that while the present material is not suited for practical applications, the overall approach demonstrates a proof-of-concept of PSD in highly loaded plastics stabilized through copolymerization of the primary dye, and suggests that further improvements through better dye choice/design may yet be achievable.

1. Introduction

The variation in pulse shape originating from excitation from different high-energy particles is the origin of the technique of pulse shape discrimination (PSD), a technique that can be used to actively identify the type of the detected particle. In contrast to inorganic scintillators, which are among the best materials for γ-ray detection and spectroscopy, organic materials are among the most widely used materials for PSD applications [1], a primary example of which is the use of PSD based detection methods for fast-n/γ discrimination, which is of particular interest for the detection of special nuclear material (SNM). The PSD properties of organic scintillators have a long history dating back to the 1950's [2]. Organic crystals are among the highest performing materials for n/γ PSD, with single crystal *trans*-stilbene being readily considered as having the best known PSD performance [2,3]. On the other hand, PSD is readily achievable in conventional liquid scintillator solutions, which have distinct advantage over organic crystals in terms of cost, scalability, and ease of manufacture and handling. There are some distinct disadvantages of organic liquids, including concerns over toxicity, flammability, the potential for leaks, and the necessity of maintaining strict oxygen free conditions of the solution throughout its life, all of which are even more problematic in the context of very large detector sizes. Despite these shortcomings, liquid scintillator solutions are among the most widely used detector materials for fast neutron spectroscopy and n/γ discrimination.

For other types of detection, plastic scintillators offer many distinct advantages over organic or even inorganic crystals and liquid scintillator solutions, most notably low cost, very good scalability, and great ease of use and handling, with complex geometries being readily attainable due to the good machinability of typical plastic formulations. Despite all these advantages, plastic materials have until only recently long been regarded as unsuitable for PSD applications due to their inferior discrimination properties. A notable exception to this, however, is the development by Brooks et al. in 1960 of a PSD capable plastic scintillator dubbed as “Plastic 77” by the authors [4], whose commercialization was attempted under the trade name NE-150 but which was eventually abandoned due to issues with the material's long-term stability [5]. Only in last few years has the demonstration of commercial plastic scintillators with efficient PSD properties been fully realized. The recent breakthrough was made in 2012 when Zaitseva et al. first reported the use of polyvinyltoluene (PVT) based scintillators with a high loading $(\geq 30\%)$ of 2,5-

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* Corresponding author.
E-mail addresses: tiborhaj@ucla.edu (T.J. Hajagos), dkishpaugh@ucla.edu (D. Kishpaugh), qpei@seas.ucla.edu (Q. Pei).

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diphenyloxazole (PPO) as the first plastic scintillator since Brooks' that was capable of achieving efficient n/γ discrimination [6]. The necessity for a high primary dye loading in plastic scintillators was hinted at in their previous work, which established the requirement in PSD capable mixed crystals of a high concentration of primary solute states in order to facilitate triplet–triplet annihilation leading to emission of delayed fluorescence [7]. Since then, the material has been developed into two different commercial materials from Eljen Technology, EJ-299-33A, which has better performance but is relatively soft for a scintillating plastic, and EJ-299-34, which has better mechanical properties but decreased discrimination performance [8]. As an example of the difference in their mechanical properties, in our hands, EJ-299-33A was found to be very difficult to machine using our protocol for fabricating small disks (typically ø10 mm × 2–5 mm) from regular sheet stock, which we developed initially for conventional plastic scintillator formulations (e.g., EJ-212). While EJ-299-34 was much more easily machined via the same process, some additional care was needed to achieve good finish prior to polishing, and some additional complications were encountered when attempting to affix the samples for polishing with low melting point adhesives ($T_M \sim 55\,°\text{C}$, actual working temp. ~60–80 °C), namely some deformation and surface hazing. While alternative and more optimized machining techniques quite probably can achieve good results with either material, it would be advantageous to have a PSD capable plastic that in general has as good if not better machinability than traditional scintillating plastic formulations so that costs associated with the processing of the material can be minimized. The mechanical properties of the all these materials are directly related to the high dye loading that enables them to be efficient at pulse shape discrimination. With such high loadings, the dye molecules act as effective plasticizing agents, rendering the resulting material softer than either the base plastic alone or conventional plastic scintillator formulations. Martinez et al. have shown that substitution of the aromatic polymer matrices with a non-aromatic material such as poly(methyl methacrylate) (PMMA) can be advantageous due to its higher hardness, but the discrimination performance was again diminished [9].

Another potential problem arising from the use of high primary dye loading is the long term stability of the material, which is a principal issue needing to be addressed with regards to the current generation of PSD capable plastics. The failure of Brook's "Plastic 77" to be fully realized as the NE-150 commercial material was largely due to the dramatic loss of transparency and whitening which took place over time [5], presumably due to precipitation of the highly loaded dye components. Blanc et al. have experimented further with the Plastic 77 composition and demonstrated that both incorporating polymerizable additives and cross-linking of the polymer matrix were effective means of preventing precipitation of the dye components [10]. In general, with no other means of fundamentally preventing dye crystallization, a high dye loading will quite likely lead to precipitation, either during fabrication or upon aging, since it will be quite likely that the dye will be above its solubility limit in the cured plastic. The reason for this is at the elevated polymerization temperature with which plastics are typically cured, the dye will typically have a significantly higher solubility than in the monomer at room temperature. If a plastic is cured with a dye content at or near the high temperature solubility limit, upon cooling to room temperature there will be a significant degree of supersaturation of the dye, which can lead to precipitation either during the cooling itself, leading to an opaque material, or slowly over time, leading to a gradual loss of transparency. Additionally, the thermodynamic solubility limit of the dye in a polymer may be fundamentally lower than in the liquid monomer at any given temperature, which again would lead to a situation of supersaturatiion of the dye in the cured plastic. Lower dye loadings can be utilized to improve long term stability of the material, but not without some sacrifice in PSD performance (at least for presently known PSD-capable dyes). As such, development of new approaches to stabilization of high dye loadings remains a key objective for the development of new PSD capable plastics.

In this work, we address several key factors to the design of novel primary dyes to specifically address all of the issues associated with the high dye loading method. First and foremost is the need for a primary dye with high solubility to achieve loadings capable of effecting good PSD performance, but without leading to precipitation of the dye or loss of mechanical properties, especially at timescales corresponding to the expected useful lifetime of the material. While PPO has been shown to be a PSD capable dye in plastic scintillators, it is anticipated that there are a number of other possible candidates, some of which may be able to achieve significantly better performance than even the best commercial PSD plastic. However, there are very few if any efficient and common scintillating dyes other than PPO or its derivatives that have solubilities in aromatic solvents high enough to achieve decent PSD performance [6,11]. With all this in mind, our main approach was to identify a candidate scintillating dye with overall good properties and good PSD performance, and then functionally derivatize the parent molecule to overcome the shortcoming of solubility and stability in the final plastic. To achieve the former, the introduction of long, flexible, and/or branched alkyl chains can greatly enhance solubility while simultaneously lowering the compounds melting point, while for the latter, the introduction of polymerizable groups can allow for direct bonding of the dye to the polymer backbone, eliminating the ability of the dye to precipitate from the plastic upon cooling. It is worth noting that at least one previous attempt has been made, albeit unsuccessfully, to directly incorporate a scintillating dye via copolymerization into a PSD-capable plastic. In their report, O'Bryan et al. demonstrated PMMA-based plastic scintillators loaded up to 30 wt.% with a polymerizable *trans*-stilbene derivative, but the resulting material failed to demonstrate any performance for n/γ PSD [12].

With all of these factors in mind, we set out to synthesize an entirely new primary dye that was rationally designed to fulfill each of these key requirements. Our specific approach reported herein is based upon the derivatization of 9,10-diphenylanthracene (DPA), a scintillating dye known in single crystal form to posses both good PSD and overall scintillator performance [13–15], and Fig. 1 details the chemical structure of our proposed primary dye (DPA-DHS, where DHS = 'dihexylstyrene'). Functionalization of the DPA core by introduction of aryl ether linkages onto the pendant phenyl rings introduces the flexible hexyl spacer groups, whose primary intended function is to enhance the solubility of the dye while simultaneously lowering its melting point, both of which are critical factors in allowing for the required high loading content. At the distal end of the spacer chains are styrenyl groups, which are purposefully included in our proposed structure over other potential polymerizable groups in an attempt to achieve optimal incorporation of the dye into the overall polymer matrix. In addition, the presence of two polymerizable groups per dye molecule was intended to allow the dye to simultaneously act as a cross-linker for the matrix, and since high loadings are sought after, such a high degree of cross-linking would lead to a material that is quite hard and tough, potentially more so than the current generation of PSD plastics.