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## **Final LDRD Report: Advanced Plastic Scintillators for Neutron Detection**

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# Final LDRD Report: Advanced Plastic Scintillators for Neutron Detection

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## Abstract

This report summarizes the results of a one-year, feasibility-scale LDRD project that was conducted with the goal of developing new plastic scintillators capable of pulse shape discrimination (PSD) for neutron detection. Copolymers composed of matrix materials such as poly(methyl methacrylate) (PMMA) and blocks containing *trans*-stilbene (tSB) as the scintillator component were prepared and tested for gamma/neutron response. Block copolymer synthesis utilizing tSBMA proved unsuccessful so random copolymers containing up to 30% tSB were prepared. These copolymers were found to function as scintillators upon exposure to gamma radiation; however, they did not exhibit PSD when exposed to a neutron source. This project, while falling short of its ultimate goal, demonstrated the possible utility of single-component, undoped plastics as scintillators for applications that do not require PSD.

## **ACKNOWLEDGMENTS**

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## NOMENCLATURE

|             |  |
|-------------|--|
| PMT         | photomultiplier tube   |
| PSD         | pulse shape discrimination   |
| tSB         | <i>trans</i> -stilbene   |
| PtSBMA-PMMA | poly( <i>trans</i> -stilbene methacrylate)-poly(methyl methacrylate) copolymer |

## 1. Introduction

New materials could benefit the homeland security mission to detect fissionable material, and organic scintillators represent an area of opportunity for significant advances. The goal of this one-year, feasibility-scale project was the creation of a new class of plastic scintillators with pulse shape discrimination (PSD) capabilities. Current neutron detection devices typically feature neutron counters such as  $^3\text{He}$  tubes, liquid scintillators or lithium-loaded fibers. PSD is an especially useful capability for neutron detection because it allows for the detection of neutrons in the presence of significant background gamma radiation and is a requirement for successful neutron spectrometers. It would be advantageous for the production of more robust neutron detectors to be able to use solid scintillators in place of liquids or  $^3\text{He}$  tubes; however, existing solid scintillators have distinct limitations. Solid organic scintillators capable of neutron detection fall into two general classes: single crystals and plastics. Single crystals, such as *trans*-stilbene (tSB), offer the advantage of exhibiting PSD for gamma-neutron differentiation; however, they are costly, fragile, and difficult to grow in sizes greater than 2" diameter. Plastic scintillators are readily available in a variety of formulations and can be easily made in different shapes and sizes; however, they do not exhibit PSD. While plastic scintillator materials have remained essentially unchanged over decades, significant advances have been made in the field of polymer science that should enable a new class of scintillator materials to emerge. One recent attempt was reported in the literature using fluorescent 1,8-naphthalimide-containing polymers as potential PSD plastic scintillators; however, the authors reported their materials did not show neutron-gamma discrimination.<sup>1</sup> In this work, we proposed to prepare block copolymers based on a functionalized tSB and test the materials for PSD.

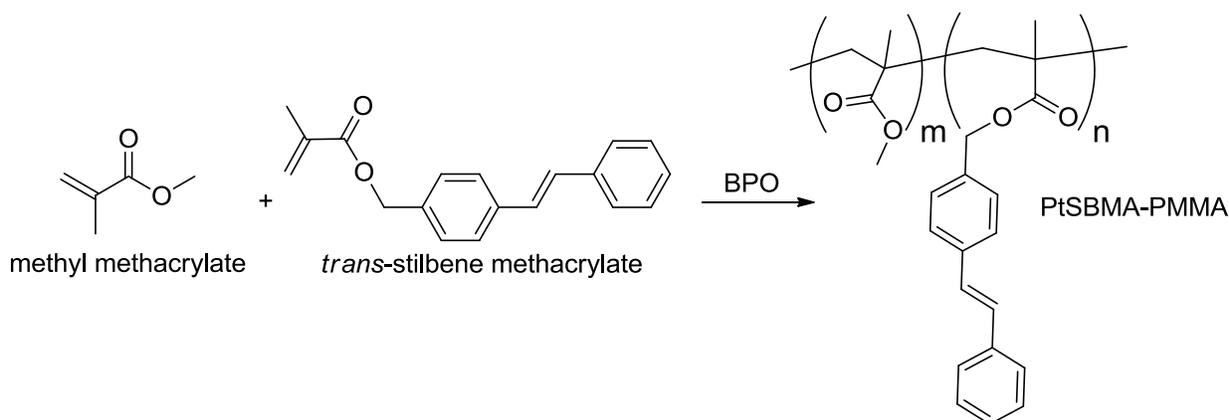
Earlier examples of tSB-containing polymers have appeared in the literature as candidates for electroluminescent polymers.<sup>2,3,4,5</sup> In those systems, it was found that the tSB functional group retained the fluorescence properties of the monomer, and that emission resulted from a fluorescent dimer. Most interesting, however, was the observation of Karasz and coworkers that the tSB-functionalized polymer absorbed energy at solution concentrations where the monomer did not. They attributed this behavior to "...the fact that when attached to a polymeric backbone the localized concentration of the chromophores will be much higher than in the non-bound state..."<sup>3</sup>. So-called "stilbenoid dimers" have also been studied and found to exhibit emission indicative of bimolecular interactions.<sup>6</sup> Another recent report of interest noted that crystalline tSB particles on the order of 1–2 mm embedded in an optical silicone matrix exhibit PSD, although scintillation signals for this material are lower than single crystal tSB for neutrons with energies above 2 MeV.<sup>7</sup>

In tSB, the fluorescent process that leads to PSD is well-established to be bimolecular, in which one excited triplet state decays by transferring energy to another molecule generating a delayed fluorescence that would not be seen if the molecule decayed directly to the ground state.<sup>8</sup> The bimolecular nature of the fluorescence that gives rise to PSD and the observations cited above that tSB can be modified to control its fluorescent properties formed the basis for the proposed use of tSB-containing polymers as PSD scintillators. The goal was to show that a single polymeric material containing nanoscale stilbene-rich domains could exhibit pulse shape discrimination. This report will summarize experiments carried out in FY2010 and discuss the results and potential paths forward.

## 2. Results and Discussion

### 2.1 Polymer Synthesis

Polymers containing pendant tSB groups were prepared using *trans*-stilbenemethanol (tSBMeOH) obtained from Aldrich Chemical. The first step in preparing the tSBMeOH for polymerization is esterification with methacryloyl chloride or acryloyl chloride to give the polymerizable tSB-methacrylate (tSBMA) or acrylate (tSBA). The products were purified by flash column chromatography and characterized by  $^1\text{H-NMR}$ . Fig. 1 shows an example of a potential route to a tSB-copolymer using tSBMA.

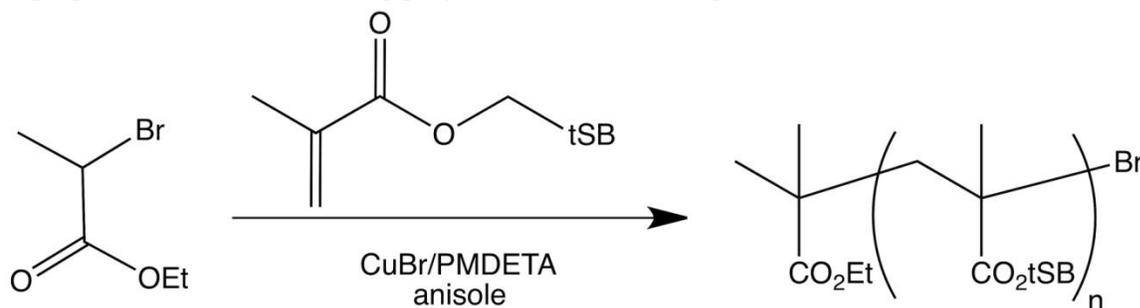


**Figure 1.** Example of synthetic scheme to produce tSB-containing polymer.

Initial polymerizations were carried out using radical initiators such as benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) with tSBMA in solution to give homopolymers of tSBMA. The tSBMA homopolymer was then blended with poly(methylmethacrylate) (PMMA) homopolymer at a concentration of 10 wt% PtSBMA to give a polymer blend material in powder form. The PtSBMA-PMMA polymer blend was heat pressed at the PMMA melt temperature of 160 °C in a circular mold to give a polymer disc. The disc was unfortunately opaque at this concentration due to phase separation, and was therefore unsuitable for radiation detection. The opaque color and difficulties with associated heat pressing to produce uniform polymer discs necessitated a different approach.

To avoid macro phase separation and maintain transparency of bulk materials, a strategy was developed to produce microdomains of tSB rich polymer within a PMMA or polystyrene (PS) matrix. The goal of preparing microdomains of polymer containing tSB segments can be realized by preparing a conjugated block-copolymer of PtSBMA and PMMA. Conjugated copolymers like a polymer blend can phase separate, but such separation is controlled to produce microdomains of polymer segments via covalent attachment and control of polymer block length. Uncontrolled radical polymerization was shown to be successful for polymerization of tSBMA and therefore an approach to make a living polymer block of PtSBMA by atom transfer radical polymerization (ATRP) conditions was attempted (ratio of initiator 2-ethylbromopropionate:  $\text{CuX}_n$  copper (I) bromide: ligand PMDETA; 1:1:1; temperature 75 °C). Living polymerization differs from uncontrolled polymerization by inhibiting radical side

reactions to give nearly monodisperse polymeric materials (polymers with uniform chain length). An advantage of living polymerization is that the initiator is incorporated at the chain end and provides a means to reinitiate polymerization and prepare block copolymers. A revised strategy to prepare PtSBMA containing polymers is shown in Fig. 2.

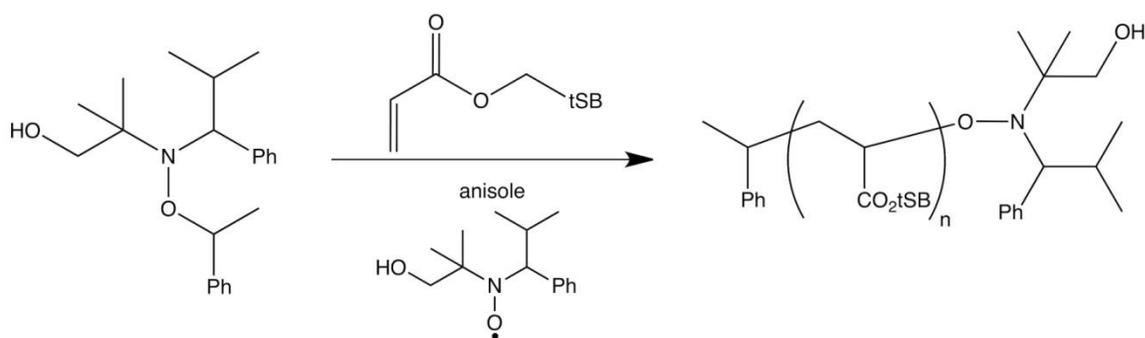


PMDETA = *N,N,N',N',N''*-pentamethyldiethylenetriamine

**Figure 2.** Standard ATRP conditions for homopolymer preparation of PtSBMA.

The attempted ATRP of tSBMA resulted in no appreciable conversion of monomer to polymer as determined by proton NMR analysis. Initial thoughts for lack of polymerization were insufficient radical initiation for the polymerization kinetics from using 2-ethylbromopropionate as the initiator. Therefore  $\alpha$ -ethylbromoisobutyrate was employed as the initiator using standard ATRP conditions (initiator: $\text{CuX}_n$ :ligand; 1:1:1). Unfortunately no conversion was observed by NMR. In this instance standard ATRP conditions were not providing conversion of the methacrylate monomer tSBMA to homopolymer. Therefore a special ATRP system known as activators regenerated by electron transfer (ARGET)<sup>9</sup> was employed, which takes advantage of using a highly active ATRP ligand such as tris(2-pyridinylmethyl)amine (TPMA) and an oxidized copper complex ( $\text{CuCl}_2$ ) with the addition of a reducing agent such as citric acid or stannous octoate ( $\text{SnEH}_2$ ) to actively regenerate the active ATRP copper (I) catalyst. An advantage of the ARGET conditions is utilization of low copper concentrations to minimize contamination variables for future radiation detection studies on sample materials. The ARGET ATRP polymerization resulted in virtually the same outcome observed with standard ATRP conditions.

A third living polymerization technique known as nitroxide mediated polymerization (NMP)<sup>10</sup> was employed which takes advantage of the reversible dissociation of an *N*-alkoxyamine radical initiator. Due to steric limitations of NMP, an acrylate monomer must be used in place of the previously prepared methacrylate, therefore the synthesis of the monomer was adjusted to produce *trans*-stilbene acrylate (tSBA) by employing *t*-SBMeOH and acryloyl chloride. Polymerization of the acrylate monomer by NMP was carried out by first degassing a solution of the monomer, an *N*-alkoxyamine initiator (2-methyl-2-((2-methyl-1-phenylpropyl)(1-phenylethoxy)amino)propanol), and 5% of the parent nitroxide (with respect to the initiator) dissolved in anisole and then heating to 120 °C under argon (Fig. 3). As with the ATRP based polymerization reactions, the NMP of tSBA was followed by proton NMR, which unfortunately again displayed no conversion of the monomer to polymer.



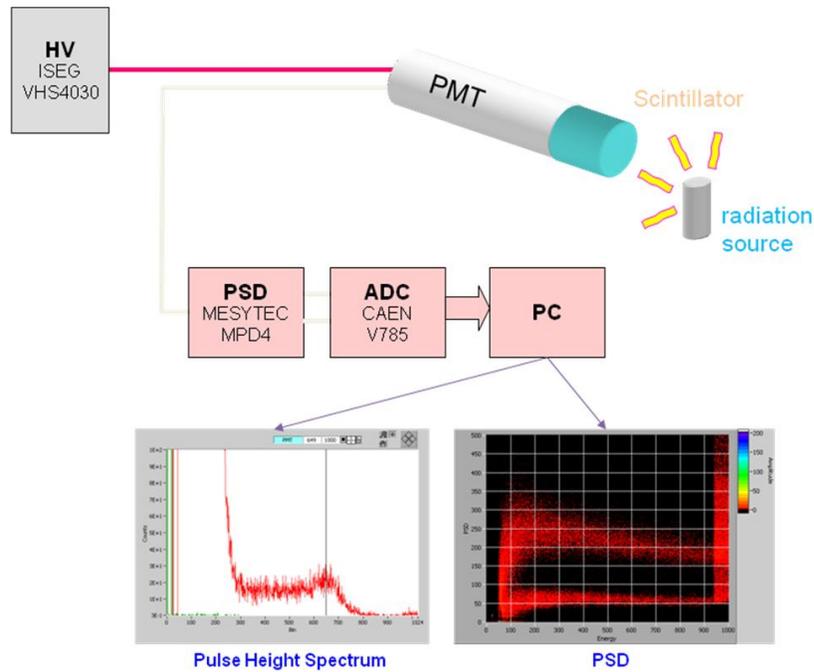
**Figure 3.** Nitroxide mediated polymerization of tSBA.

Since the standard radical polymerization conditions returned a polymeric tSB containing material, it is hypothesized that not enough radical concentration is built up during living radical polymerization to overcome the byproducts obtained from addition of an initiator to the stilbene olefin. Although this type of addition is generally considered a negligible effect for radical polymerizations due to steric interactions, it is possible that for a living radical process a slight amount of addition product shuts down the initiation kinetics due to the controlled quantities of radical initiator present.

Foregoing the designed approach to prepare conjugated diblock copolymers, another strategy was employed to give random copolymers with the aim of adding enough PtSBMA monomeric segments into a matrix material to afford a scintillation effect. Previously prepared tSBMA monomer was dissolved in a matrix monomer of MMA at four weight percentages: 5, 10, 20, and 30. The solutions were degassed and placed under argon. Traditional radical polymerization was carried out by addition of BPO as the radical initiator. The solutions were heated to 50 °C for three days to complete curing of the solution as a solid polymer monolith. The polymeric materials were indeed transparent and only a slight discoloration was observed at concentrations higher than 10 wt% tSBMA.

## 2.2 Scintillator Testing

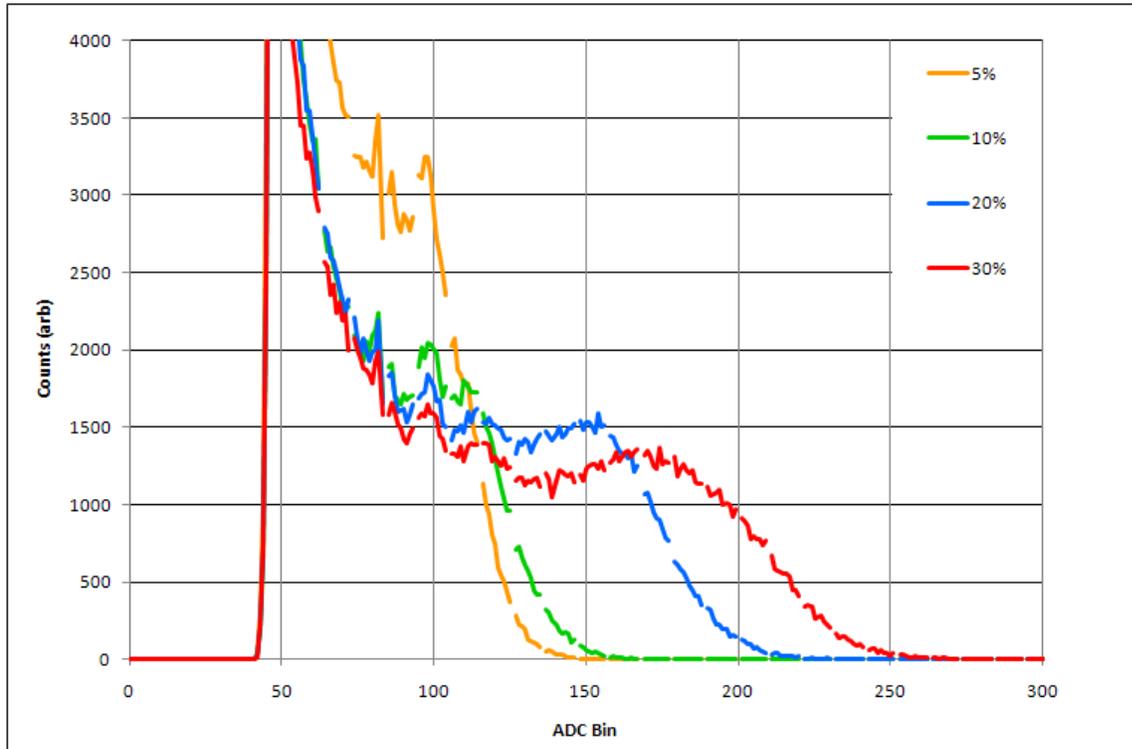
Samples were tested using the setup shown in Fig. 4. Reference spectra were collected using a standard liquid PSD scintillator (Eljen 301). Gamma exposure was conducted using a Cesium 137 source, and neutron exposure was conducted with an AmBe source. Pulse height responses of the samples were compared to the Eljen 301 reference liquid scintillator in a 2” diameter X 2” tall cylindrical cell. Likely due to the fact that the plastic samples were smaller than the liquid scintillator, pulse heights for the plastics were lower than for the liquid. As seen in Fig. 5, the tSB-containing polymers responded to gamma irradiation, with pulse heights increasing with higher tSB content. These tSB-containing plastics are clearly displaying scintillation in response to gamma exposure. This is of interest because plastic scintillators typically have one or more dopants added to provide light yield visible to the PMT.



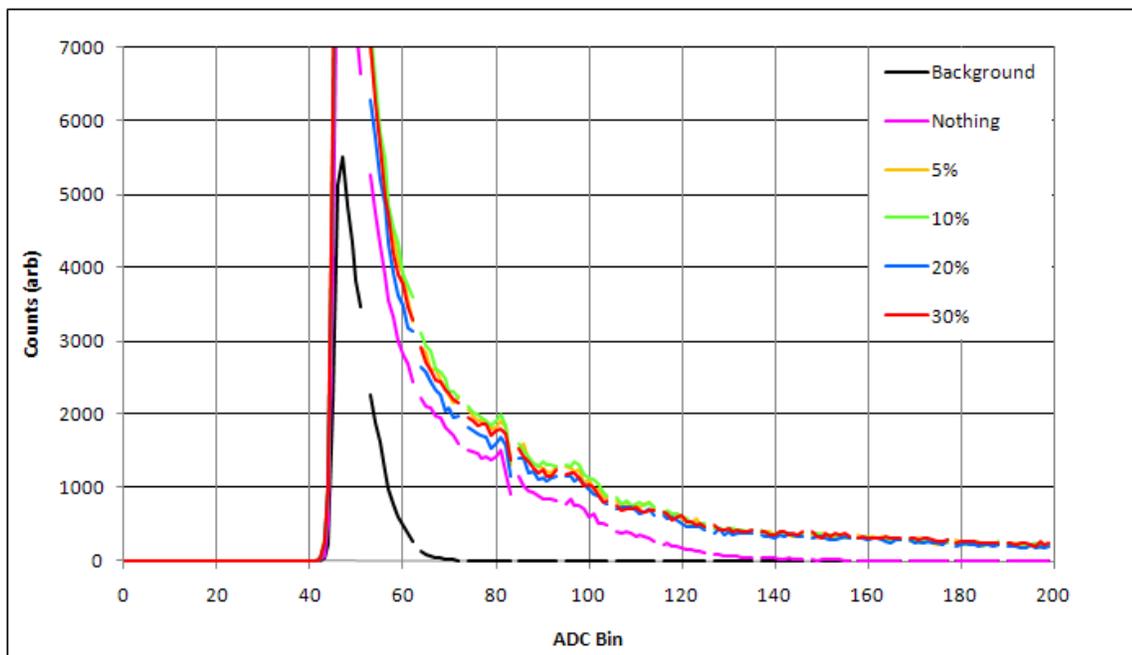
**Figure 4.** Scintillator test setup.

Equally interesting results were not obtained upon exposure of the plastic samples to the AmBe neutron source. As seen in Fig. 6, the responses of the 5-30% tSB samples are very similar and only slightly higher than no sample on the PMT.

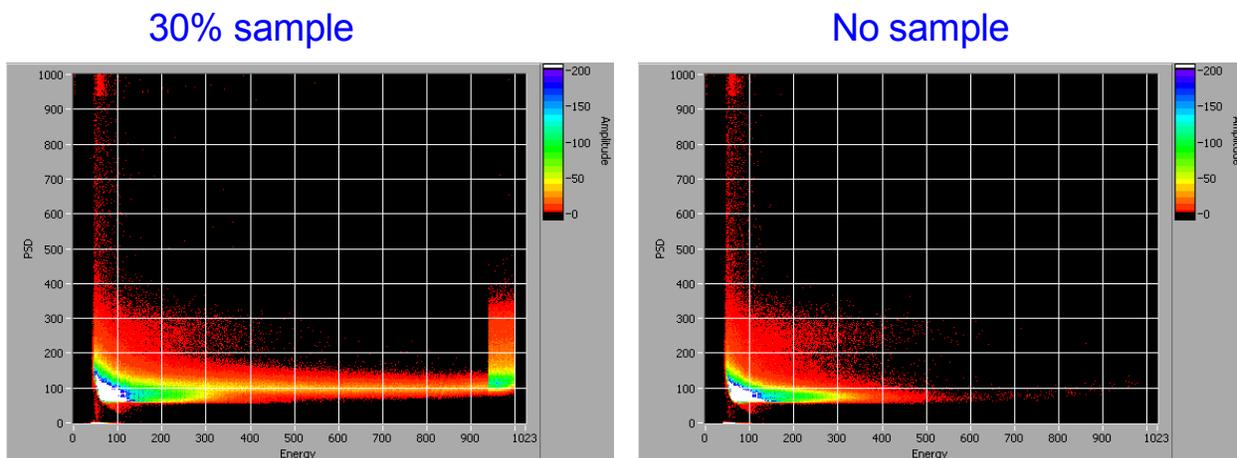
The 30% tSB sample was tested for PSD response. As shown in Fig. 7, it did not provide evidence of PSD but did give exhibit a clear response at higher energies, indicating it functioned as a gamma-sensitive scintillator. For comparison, Fig. 8 shows the response of the known PSD liquid scintillator E301. The stratified structure along the PSD axis shows the typical appearance of a PSD scintillator.



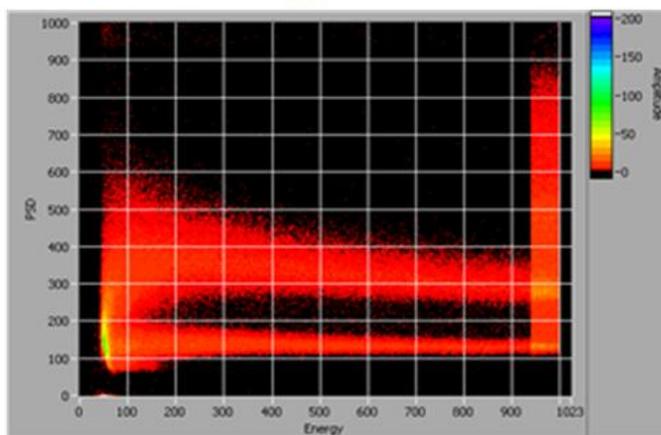
**Figure 5.** Pulse height spectra for tSB- plastics exposed to Cs 137 source ( $\gamma$ /x-ray 662 KeV, 89.9%).



**Figure 6.** Pulse height spectra of tSB-plastics exposed to AmBe neutron source ( $\sim 4.5$  MeV neutron,  $\gamma$ /x-ray 13.9 KeV, 42.7% and 59.5 KeV, 35.9%).



**Figure 7.** Response of 30% tSB-plastic to AmBe source compared to no sample.



**Figure 8.** Response of E301 liquid scintillator to AmBe source showing PSD signal.

### 3. Conclusions

The project goal of demonstrating a PSD-capable plastic was not realized; however, the new plastics that were prepared and tested functioned as scintillators. In addition, as a result of this project, the test setup for evaluation of plastic scintillators for gamma/neutron detection was restarted. This project demonstrated that increased tSB loading of the copolymers provided an improved scintillation response to gamma radiation. This class of materials may be of interest because they are single-component plastic scintillators that do not require the addition of dopants or wavelength shifters to produce a measureable light yield. It may be possible to tailor copolymers to specific applications. Additional studies could be pursued to further explore copolymers as plastic scintillators for applications that do not require PSD.

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