LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-CONF-825808

Optimization of Plastic Scintillators with Pulse-Shape Discrimination Capabilities

M. J. Ford, E. Aigeldinger, M. L. Carmen, N. P. Zaitseva

August 16, 2021

INMM & ESARADA Joint Annual Meeting
Remote, CA, United States
August 23, 2021 through September 1, 2021

Disclaimer

Optimization of Plastic Scintillators with Pulse-Shape Discrimination Capabilities

Michael J. Ford*, Elisabeth Aigeldinger, M. Leslie Carman, and Natalia P. Zaitseva
on behalf of the SANDD Working Group

* *Lawrence Livermore National Laboratory*
7000 East Avenue
Livermore, CA 94550
925-605-9793 *ford40@llnl.gov*

Abstract:

Plastic scintillators have recently reemerged as promising candidates for the detection and discrimination of nuclear materials. Relative to single crystal scintillators, plastic scintillators are cheap and straightforward to produce. Relative to liquid scintillators, plastic scintillators are easy to handle, easy to contain, and couple well with solid-state photosensors. However, there are challenges in light output, physical properties, and long-term stability of plastic scintillators. We have optimized and studied plastics capable of pulse-shape discrimination (PSD) to improve scintillation performance, physical properties, and long-term stability of these materials. We have also explored the addition of organic salts of lithium-6 to plastic scintillators to enable discrimination of thermal neutrons, which posed new challenges in materials processing. Our efforts have allowed us to produce large-scale plastic scintillators (≈0.5 m in length and larger). These plastics have great potential for any application that requires sensitivity to fast and/or thermal neutrons. These applications include multiplicity counting, neutron imaging, reactor antineutrino detection, and any system that currently uses PSD-capable liquid scintillators.

Introduction:

Organic scintillators are important for the detection and spectrometry of ionizing radiation. For applications like multiplicity counting, neutron imaging, and detection of antineutrinos to remotely monitor nuclear detectors, organic scintillators rely on their ability to identify neutrons in the presence of a gamma radiation background. This ability is referred to as pulse shape discrimination (PSD) since gamma rays and neutrons can be distinguished by the decay of the scintillation pulse.[1]

Liquid organic scintillators are commonly used for fast neutron detection; however, these materials may have challenges associated with storage and handling. Single crystals are promising as solid-state replacements for liquid scintillators; however, single crystals may be expensive, difficult

to transport, and limited in their operational temperature.[2] Plastic scintillators that are capable of PSD have been reestablished as promising alternatives to liquid and single crystal scintillators.[1,3,4]

As part of this exploration into plastic scintillators, we have studied lithium-loaded scintillators that are capable of distinguishing between fast and thermal neutrons.[5–7] This process relies on a capture reaction that emits ionizing radiation with a specific energy. For ^{6}Li, capture of a thermal neutron produces an alpha particle and triton with a reaction energy of 4.78 MeV. Polar lithium salts are insoluble in the monomers that comprise plastic scintillators (e.g., styrene or vinyl toluene), posing a challenge for the incorporation of ^{6}Li. However, polar solvents and/or monomers like dimethoxyethane or methyl methacrylate can coordinate with and/or dissolve ^{6}Li salts of carboxylic acids.[5,6] Thus, plastic scintillators that are loaded with ^{6}Li were synthesized, allowing for the "triple discrimination" of gamma rays, fast neutrons, and slow neutrons.

For remote detection, detectors with larger volumes are beneficial due to a greater probability of interaction with ionization radiation. Large, segmented detectors can also be useful for localized detection and multiplicity in particle identification.[8] Thus, large plastic scintillators (> 1 m in any dimension) are desirable. In exploring synthesis of large plastic scintillators, we've discovered a number of challenges that weren't obvious when studying smaller plastic scintillators. Defects like cracks and bubbles, discoloration, and opacity are more detrimental at larger scales due to attenuation of scintillation (**Figure 1a**).

There are many competing factors that result in defects, discoloration, and opacity. For example, lithium salts that have been explored thus far are not soluble in the precursors at room temperature. Plastic scintillators are opaque if insoluble compounds precipitate. High temperatures required for solubility can result in discoloration due to decomposition of the dyes and/or runaway polymerization that results in high internal temperatures (**Figure 1b**). These high temperatures increase the likelihood of defects. Other factors like chemical composition of the matrix, purification of materials, dye concentration and composition, and other processing parameters can all have influence on the properties of interest for scintillation. In this report, we outline recent results to improve processing by exploring aliphatic lithium salts and solubility in polar monomers. These improvements allow easier and more reproducible production of large plastic scintillators that are loaded with lithium.

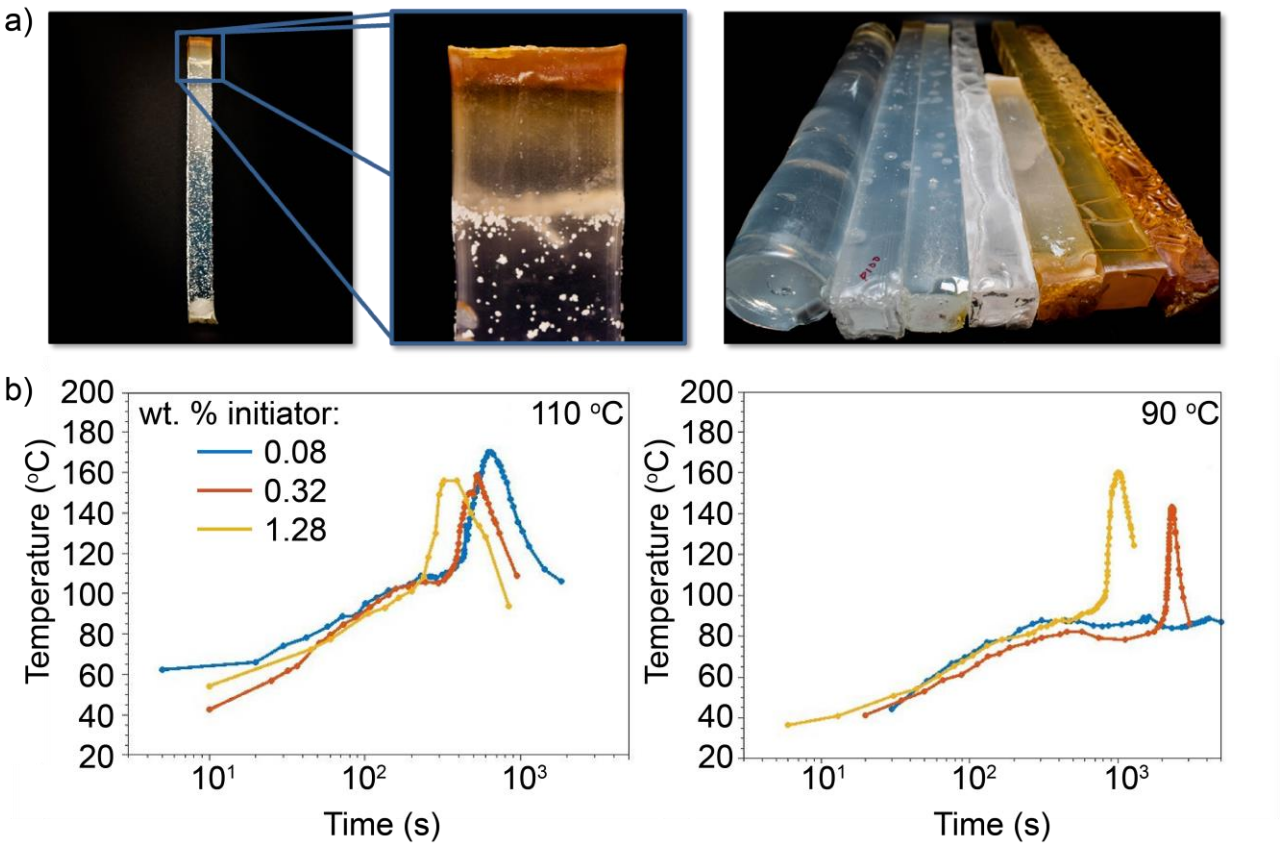


Figure 1. (a) Defects, discoloration, and opacity are major challenges for reproducibility of large plastic scintillators. These photographs highlight these challenges for large plastics (up to 45 cm in length). (b) Many factors can cause defects, discoloration, and opacity, including high temperatures during curing. These plots highlight the internal temperature of small plastics (about 17 mm in length) when curing with different initiator concentrations. The external temperature during curing was set to about 110 ^{o}C (left) or 90 ^{o}C (right). The internal temperature exceeded the external temperature due to exothermic polymerization for all cases except low initiator concentration at low temperatures. The exothermic reaction may have a greater impact for larger plastics if the surface area to volume ratio of the plastic decreases.

Results and discussion:

We have successfully synthesized multiple plastic scintillators that are loaded with lithium with lengths of about 0.4 m while minimizing defects and discoloration (**Figure 2a**). Smaller samples (17 mm in length) were cut for initial testing of scintillation properties. The average light yield was about 60% of a commercial scintillator (EJ-200). Gamma rays could be distinguished from neutrons,

and a spot consistent with the thermal neutron capture of lithium was observed (**Figure 2b**). While these results are promising, the yield of large plastics has been inconsistent due to the balance of solubility of lithium salts with temperature. In addition, optical clarity can be inconsistent.

One possibility is that the polar monomer that is used to dissolve lithium salts (methacrylic acid, MAA) can easily polymer prematurely during dissolution (**Figure 2c**). This opacity can be mitigated by diluting the MAA with the base monomer (styrene or vinyl toluene, VT). MAA introduces an additional issue: the scintillation properties are reduced upon addition of MAA to a greater extent than would be expected based on simple dilution rules. For example, we can compare the figure of merit (defined as the separation between the neutron and gamma peaks divided by the sum of the full widths at half max) of scintillators that incorporate MAA vs. those that incorporate methyl methacrylate (MMA). We observed a more precipitous decrease in the figure of merit as MAA content increased (**Figure 2d**). Given these observations, we sought a scintillator composition that would not require high temperatures for dissolution and that could minimize MAA content.

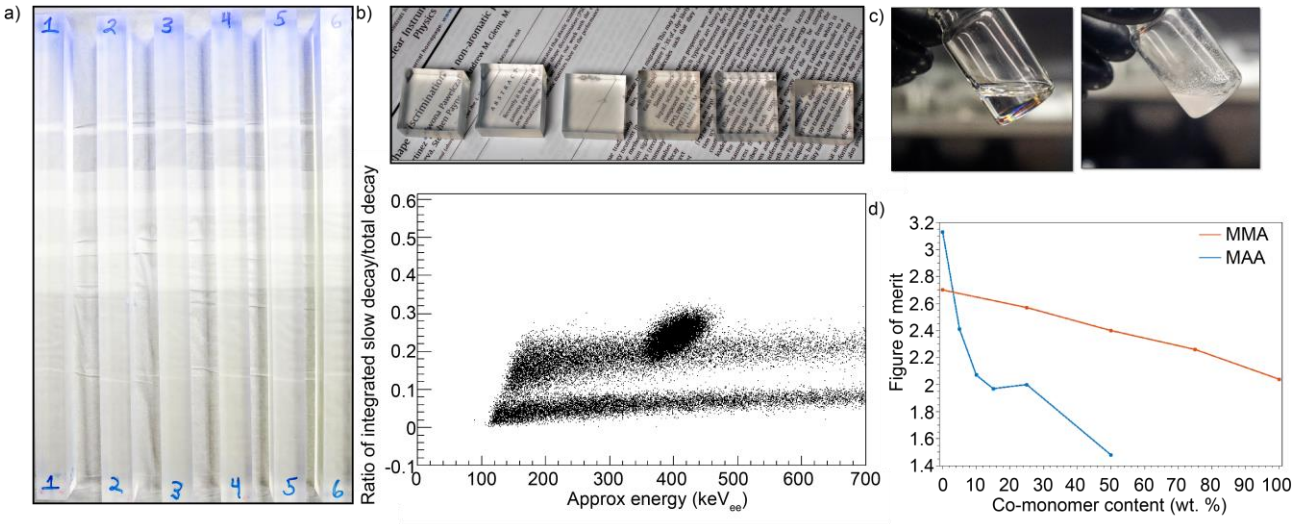
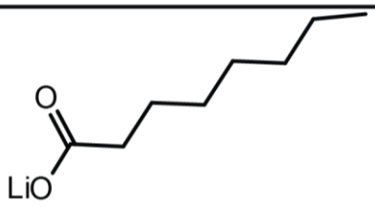
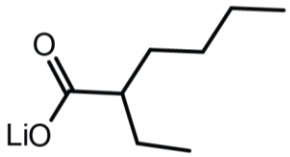
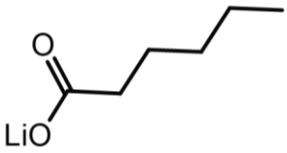
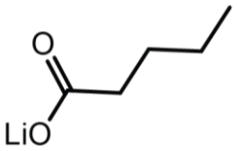
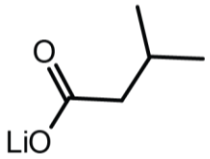
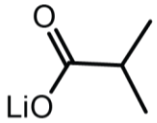


Figure 2. (a) Large plastic scintillators loaded with lithium can be fabricated with minimal defects and discoloration, as shown in this photograph, but the yield is low and opacity is still high in some of these plastics. These plastics are 0.4 m in length. (b) The plastics were cut to 17 mm lengths (top) and tested for PSD capabilities (bottom). (c) One possible cause of opacity is the co-monomer, MAA. While VT does not turn opaque upon heating to reflux (left image), MAA becomes opaque even before reflux (right image). (d) MAA also reduces scintillation performance more drastically than expected with simple dilution rules. When comparing to plastics that contain MMA, the figure of merit decreases more precipitously for plastics that contain MAA.

We explored aliphatic lithium salts (**Table 1**) and first investigated their solubility in the base monomers. First, we attempted to dissolve the lithium salts in the polar monomers MAA, MMA, and methacrylate (MA). Gentle heating (about 70 ^{o}C) was used to facilitate dissolution, and the solutions were allowed to cool over a period of about 24 h. For each lithium salt, we added an equivalent amount of salt such that the final plastic composition would contain 0.1 wt. % ^{6}Li. The amount of polar monomer used is relative to the amount of non-polar monomer (styrene).

Table 1. Information about lithium salts explored for this report.

No. of carbons	Acid precursor	Aliphatic Li salt (linear)	Aliphatic Li salt (branched)
8	Octanoic acid; 2-ethylhexanoic acid		
6	Hexanoic acid		
5	Pentanoic acid; 3-methylbutanoic acid		
4	Isobutyric acid		

For MMA and MA, all aliphatic lithium salts precipitated from solution (**Figure 3a,b**). For a final plastic composition that would contain 90:10 wt. content of styrene:MAA, lithium 3-methyl-butanoate was soluble at room temperature (**Figure 3b**). Lithium 3-methylbutanoate was also soluble at 95:5 styrene:MAA weight content. At 97:3 styrene:MAA weight content, the solution required heating to remain soluble. Interestingly, when using MMA and MAA as co-solvents, multiple lithium salts were soluble (**Figure 3c**). When adding the remaining constituents of the scintillator, which includes styrene, divinylbenzene, the primary dye, and the secondary dye, only compositions that contained lithium 3-methylbutanoate remained soluble at room temperature (**Figure 3d**).

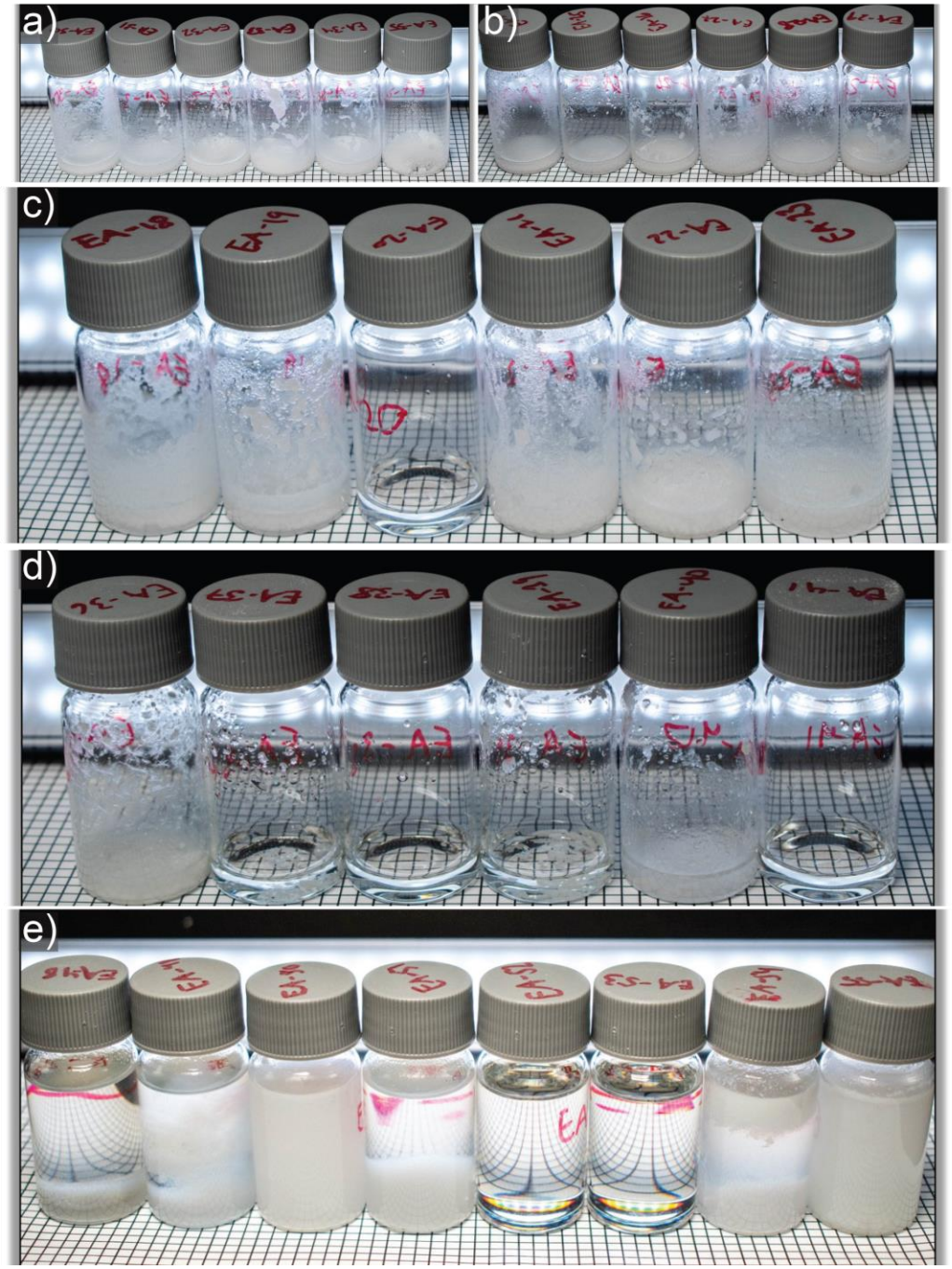


Figure 3. Photographs of solubility tests show that lithium salts are not soluble in MMA or MA (a,b). Lithium 3-methylbutanoate is soluble in MAA (c, 3rd from the left). Multiple salts are soluble in MMA:MAA mixtures that would result in a final composition of 90:5:5 styrene:MMA:MAA (d). However, once these mixtures are mixed with the remaining constituents of the plastic scintillators, only lithium 3-methylbutanoate is soluble at room temperature for compositions that contain 90:5:5 styrene:MMA:MAA and 90:10 styrene:MAA (5th and 6th from the left).

Conclusion:

We've developed a formulation that can be used for synthesis of large plastic scintillators. This composition will be useful as it doesn't require heating for solubility of the lithium salts. In preliminary experiments, the lithium 3-methylbutanoate remains indefinitely stable at room temperature. However, some formulations with lower MAA content precipitated for larger plastics, suggesting that these formulations are on the cusp of solubility. Gentle heating or more MAA can be amenable for proper curing of these formulations. Future work will continue developing formulations that reduce MAA content and finding curing conditions that will facilitate large plastic production. We will also focus on characterizing the transparency and scintillation properties of these plastics. By achieving minimal defects, discoloration, and opacity, we can produce plastic scintillators capable of PSD that will be useful for multiplicity counting, neutron imaging, reactor antineutrino detection, and any system that currently uses PSD-capable liquid scintillators.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References:

(1) Brooks, F. D. Development of Organic Scintillators. *Nucl. Instrum. Methods* **1979**, *162* (1), 477–505. https://doi.org/10.1016/0029-554X(79)90729-8.

(2) Zaitseva, N. P.; Glenn, A. M.; Mabe, A. N.; Carman, M. L.; Hurlbut, C. R.; Inman, J. W.; Payne, S. A. Recent Developments in Plastic Scintillators with Pulse Shape Discrimination. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2018**, *889*, 97–104. https://doi.org/10.1016/j.nima.2018.01.093.

(3) Zaitseva, N.; Rupert, B. L.; PaweŁczak, I.; Glenn, A.; Martinez, H. P.; Carman, L.; Faust, M.; Cherepy, N.; Payne, S. Plastic Scintillators with Efficient Neutron/Gamma Pulse Shape Discrimination. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2012**, *668*, 88–93. https://doi.org/10.1016/j.nima.2011.11.071.

(4) Bertrand, G. H. V.; Hamel, M.; Normand, S.; Sguerra, F. Pulse Shape Discrimination between (Fast or Thermal) Neutrons and Gamma Rays with Plastic Scintillators: State of the Art. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2015**, *776*, 114–128. https://doi.org/10.1016/j.nima.2014.12.024.

(5) Zaitseva, N.; Glenn, A.; Paul Martinez, H.; Carman, L.; Pawełczak, I.; Faust, M.; Payne, S. Pulse Shape Discrimination with Lithium-Containing Organic Scintillators. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2013**, *729*, 747–754. https://doi.org/10.1016/j.nima.2013.08.048.

(6) Mabe, A. N.; Glenn, A. M.; Carman, M. L.; Zaitseva, N. P.; Payne, S. A. Transparent Plastic Scintillators for Neutron Detection Based on Lithium Salicylate. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2016**, *806*, 80–86. https://doi.org/10.1016/j.nima.2015.09.111.

(7) Cherepy, N. J.; Sanner, R. D.; Beck, P. R.; Swanberg, E. L.; Tillotson, T. M.; Payne, S. A.; Hurlbut, C. R. Bismuth- and Lithium-Loaded Plastic Scintillators for Gamma and Neutron Detection. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2015**, *778*, 126–132. https://doi.org/10.1016/j.nima.2015.01.008.

(8) Li, V. A.; Classen, T. M.; Dazeley, S. A.; Duvall, M. J.; Jovanovic, I.; Mabe, A. N.; Reedy, E. T. E.; Sutanto, F. A Prototype for SANDD: A Highly-Segmented Pulse-Shape-Sensitive Plastic Scintillator Detector Incorporating Silicon Photomultiplier Arrays. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* **2019**, *942*, 162334. https://doi.org/10.1016/j.nima.2019.162334.