



Transparent lithium-6 based polymer scintillation films containing a polymerizable fluor for neutron detection



Andrew N. Mabe^{a,*}, Matthew J. Urffer^b, Dayakar Penumadu^c, George K. Schweitzer^a, Laurence F. Miller^b

^a Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

^b Department of Nuclear Engineering, University of Tennessee, Knoxville, TN 37996, USA

^c Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, TN 37996, USA

HIGHLIGHTS

- A new transparent polymer scintillator containing 2.96 wt% ⁶Li has been synthesized.
- The scintillator is capable of detecting thermal neutrons.
- The scintillator demonstrates neutron/gamma-ray discrimination.
- The material comprises the matrix, ⁶Li, and fluor attached to a single molecule.

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ABSTRACT

A novel transparent polymer neutron scintillation material poly[styrene-co-lithium maleate-co-2-phenyl-5-(4-vinylphenyl)oxazole] has been synthesized and characterized for thermal neutron detection and neutron/gamma-ray discrimination. The terpolymer was synthesized using solution-based free radical polymerization and had a composition by mass of 60.64% styrene, 31.64% maleic anhydride, and 7.72% 2-phenyl-5-(4-vinylphenyl)oxazole. The maleic anhydride groups were hydrolyzed and titrated with ⁶LiOH to form the lithiated terpolymer, resulting in a ⁶Li content of 2.96% by mass. Monomer and polymer synthesis, film fabrication protocols, photoluminescence, and scintillation responses of this new scintillation material are reported. This approach demonstrates a novel method by which mechanically robust and transparent ⁶Li-based polymer films can be produced.

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1. Introduction

Thermal neutron detection is relevant to the fields of nuclear physics, nuclear power generation, medical imaging, and homeland security. Polymer scintillation detectors designed to detect thermal neutrons are commonly based on polymers such as polystyrene (PS), poly(vinyl toluene) (PVT), and poly(vinyl xylene) (PVX) or their modifications blended with fluors and neutron capture isotopes such as ⁶Li, ¹⁰B, or ¹⁵⁷Gd (Sen et al., 2011, 2012; Brudanin et al., 2001). In this study, ⁶Li was chosen as the neutron capture nuclide because of its high absorption cross section (940 b) and large reaction energy ($Q = 4.78$ MeV). After capturing a thermal neutron, ⁶Li fissions into an alpha particle (2.05 MeV) and a triton (2.73 MeV). These charged particles generate ionizations and

excitations in the surrounding matrix which are then collected by appropriate fluors that subsequently emit photons at target wavelengths which are tuned to match the spectral sensitivity of light collection devices such as photomultiplier tubes (PMTs).

Scintillation light is generated inside the scintillator volume and must be transported to the surface in order to be detected; hence, the ideal scintillation detector is one which is completely transparent such that it does not scatter or absorb its own scintillation light (Birks, 1964). There are a few examples of transparent composites that have been reported in the literature. For example, PVT can be loaded with either *o*-carborane (Brudanin et al., 2001) or gadolinium(III) isopropoxide (Ovechkina et al., 2009) to result in transparent composites. An independent previous report of a transparent lithiated scintillation detector utilized a styrene-lithium methacrylate copolymer (Breukers et al., 2013). Zaitseva and co-workers reported the use of a complex between lithium 3-phenylsalicylate and dimethoxyethane in polystyrene which produced a transparent

* Corresponding author. Circle Drive 552, Buehler Hall Knoxville, TN 37996, USA. Tel.: +1 865 974 3426.

E-mail address: amabe1@utk.edu (A.N. Mabe).

composite (Zaitseva et al., 2013). In our previous works, we investigated poly(2-vinyl naphthalene) (P2VN) containing lithium-6 salicylate (${}^6\text{LiSal}$) and organic dyes (Sen et al., 2011) as well as poly(ethylene naphthalate) and polystyrene (PS) containing lithium-6 fluoride (${}^6\text{LiF}$) and organic dyes (Sen et al., 2012; Mabe et al., 2013a) as potential thermal neutron detectors. However, the resulting composites were not transparent due to phase separation of the organic and inorganic components. We have also reported the use of thin polymer films based on poly(styrene-co-lithium maleate) as a transparent thermal neutron scintillation detector (Mabe et al., 2013b). The insolubility of this material in organic solvents precluded its use with common scintillation fluors. This was partially addressed in our previous work by implementing lithium salicylate as the fluor which has a quantum yield (QY) for fluorescence of only 36% and resulted in brittle composites (Pozdnyakov et al., 2008). The low QY of lithium salicylate resulted in low light yields for the material and the brittle nature of the resulting films precluded robust analyses. The present work seeks to overcome this challenge by synthesizing a polymerizable form of 2,5-diphenyloxazole (QY = 100%) (Berlman, 1971) and covalently incorporating it onto the backbone of the polymer matrix rather than implementing a fluor as a molecular inclusion. The compound chosen for this purpose is 2-phenyl-5-(4-vinylphenyl)oxazole (VPPO). To our knowledge, this is the first report of a polymer neutron scintillation detector containing all components (matrix, neutron capture nuclide, and fluor) on the same polymer chain. It has been reported that scintillators based on 2,5-diphenyloxazole exhibit pulse-shape discrimination (Zaitseva et al., 2012, 2013); however, we sought to implement pulse-height analysis to discriminate between neutron and gamma-ray events. Previous works have indicated that polymer films approximately 50 μm thick provide the best neutron/gamma-ray discrimination when using pulse-height discrimination methods (Mabe et al., 2013a), so this is the thickness at which current samples were fabricated.

The principle purpose of this work was to investigate polymer scintillation films for radiation portal monitor applications. Quantitative detection criteria for detectors implemented in radiation portal monitors are set forth and explained in detail elsewhere (ANSI, 2004) and are only briefly summarized here. Two important characteristics of neutron detectors are absolute neutron detection efficiency ($\epsilon_{\text{abs},n}$) and intrinsic gamma-neutron detection efficiency ($\epsilon_{\text{int},\gamma,n}$) which are defined in Equations (1) and (2), respectively. The absolute neutron detection efficiency is the fraction of neutrons emitted from a neutron source that are detected by the detector. The intrinsic gamma-neutron detection efficiency is the fraction of gamma-rays impinging on the detector surface that are misclassified as neutrons. The materials described herein are evaluated for performance only against the absolute neutron detection efficiency and the intrinsic gamma-neutron detection efficiency criteria.

$$\epsilon_{\text{abs},n} = \frac{\text{Number of pulses recorded}}{\text{Number of neutrons emitted from source}} \quad (1)$$

$$\epsilon_{\text{int},\gamma,n} = \frac{\text{Number of gamma-rays misclassified as neutrons}}{\text{Number of gamma-rays incident on the detector}} \quad (2)$$

2. Materials and methods

2.1. Materials

${}^6\text{LiOH} \cdot \text{H}_2\text{O}$, which was enriched to contain 97.6% ${}^6\text{Li}$, was dissolved in methanol at 10 g/L at room temperature, then filtered

with a 1 μm filter. The methanol was evaporated from the filtrate at 150 $^\circ\text{C}$ to give anhydrous ${}^6\text{LiOH}$ as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Tetrahydrofuran (THF) (Fisher), diethyl ether (Fisher), and toluene (Fisher) were fractionally distilled from anhydrous calcium chloride and passed through a 200 nm filter immediately before use. Styrene (Acros) was purified immediately before use by passing the monomer through a column containing activated basic alumina on top of silica gel to remove *t*-butyl catechol inhibitor and other impurities. Free radical initiator 2,2'-azobisisobutyronitrile (AIBN) (Aldrich), was recrystallized from methanol and stored at 5 $^\circ\text{C}$ under argon until needed. UVT-grade acrylic disks 3 mm thick with a diameter of 50.8 mm (Eljen Technologies) were cleaned with ethanol immediately prior to use. Maleic anhydride 99% (Acros), hippuric acid, acetyl chloride, phosphorus pentoxide, aluminum trichloride, phosphorus oxychloride, *N*-bromosuccinimide, benzoyl peroxide, carbon tetrachloride, triphenylphosphine, *p*-xylene, lithium methoxide, deuterated dimethylsulfoxide (DMSO-d_6), deuterated chloroform (CDCl_3), HSal (Fisher), ethanol (Fisher), methanol (Fisher), and Optima[®] LC/MS grade water (Fisher) were used as received. PS and PS-co-PLiMAN samples were fabricated as previously described (Mabe et al., 2013a,b).

2.2. Synthesis of VPPO

The strategy used to synthesize VPPO is illustrated in Fig. 1. Previous reports describing the experimental details of each step in the synthesis are rather incomplete so a precise description of each step is given below.

Step 1: Synthesis of hippuryl chloride (**1a**) (McInally et al., 1977; Phillips et al., 1983)

To a 500 mL flame-dried Erlenmeyer flask containing a magnetic stir bar, the following contents were added in this order: 250 mL (3.51 mol) acetyl chloride, 35.3 g (169.5 mmol) crushed phosphorus pentachloride, and 25.0679 g (139.9 mmol) hippuric acid. The mixture was covered with a rubber stopper and stirred for 30 min with periodic venting to release evolved HCl. After 30 min, a yellow precipitate formed which was collected by vacuum filtration, washed with acetyl chloride then anhydrous diethyl ether, and dried in a vacuum over P_2O_5 for 1 h. The resulting product had a single melting point at 124 $^\circ\text{C}$ with decomposition (lit. 125 $^\circ\text{C}$) indicating adequate purity for further use. A mass of 12.7156 g of **1a** was collected to give a 46.0% recovery.

Step 2: Synthesis of benzoyl aminomethyl *p*-tolyl ketone (**1b**) (McInally et al., 1977; Phillips et al., 1983; Frangopol et al., 1961; Lhoták and Kurfürst, 1993)

To a flame-dried 250 mL round bottom flask containing a magnetic stir bar, the following materials were added: 12.7156 g (64.3 mmol) **1a**, 125 mL (1.18 mol) dry toluene, 19.12 g (143.4 mmol) crushed anhydrous AlCl_3 . The flask was quickly stoppered and purged with argon. The solution was heated to 60 $^\circ\text{C}$ for 4 h with stirring. After approximately 30 min, the solution became black. After 4 h, the flask was cooled to room temperature, then the contents were poured into an HCl-ice bath and stirred for 30 min to quench the reaction. The product was then collected by vacuum filtration, washed with warm water and *n*-hexane, then dried in a vacuum overnight over P_2O_5 . Recrystallization from absolute ethanol gave **1b**. The identity of the product was confirmed by ${}^1\text{H}$ NMR analysis. The product had a single melting point at 116–118 $^\circ\text{C}$ (lit. 114–116 $^\circ\text{C}$). A mass of 4.3687 g (17.2 mmol) of **1b** was collected for a 26.8% recovery.

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