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Crosslinked plastic scintillators: A new detection system for radioactivity measurement in organic and aggressive media

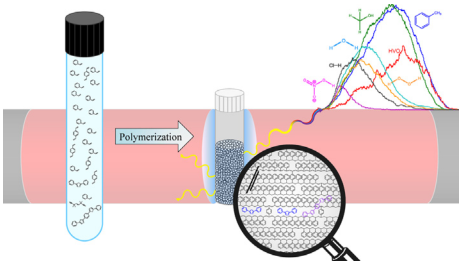
Héctor Bagán [a,*], Alex Tarancón [a], Lei Ye [b], José F. García [a]

[a] Departament de Química Analítica, Universitat de Barcelona, Diagonal 645, Barcelona E-08028, Spain
[b] Department of Pure and Applied Biochemistry, Lund University, POB 124, Lund SE-22100, Sweden

HIGHLIGHTS

- A crosslinked plastic scintillatior for radioactivity measurement was developed.
- The effect of C-PS composition in the detection efficiency was evaluated.
- C-PS permits the measurement of radioactivity in organic and aggressive media.
- C-PS exhibits high detection efficiency in water and even higher in organic media.
- C-PS exhibits good reproducibility under different polymerisations with elevated yield.

GRAPHICAL ABSTRACT



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ABSTRACT

The measurement of radioactive solutions containing organic or aggressive media may cause stability problems in liquid and plastic scintillation (PS) techniques. In the case of PS, this can be overcome by adding a crosslinker to the polymer structure. The objectives of this study are to synthesise a suitable crosslinked plastic scintillator (C-PS) for radioactivity determination in organic and aggressive media. The results indicated that an increase in the crosslinker content reduces the detection efficiency and a more flexible crosslinker yields higher detection efficiency. For the polymer composition studied, 2,5-diphenyloxazole (PPO) is the most adequate fluorescent solute and an increase in its concentration causes little change in the detection efficiency. The inclusion of a secondary fluorescent solute 1,4-bis-2-(5-phenyloxazolyl) benzene (POPOP) improves the C-PS radiometrical characteristics. For the final composition chosen, the synthesis of the C-PS exhibits good reproducibility with elevated yield. The obtained C-PS also displays high stability in different organic (toluene, hydrotreated vegetable oil (HVO) and methanol) and aggressive media (hydrochloric acid, nitric acid and hydrogen peroxide). Finally, the C-PS exhibits high detection efficiency both in water and in aggressive media and can also be applied in organic media showing similar or even higher detection efficiency values.

1. Introduction

The measurement of radioactivity is important in many fields, such as energy production in nuclear power plants, medicine in diagnosis and treatment, industrial processes (e.g. tracers) and

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* Corresponding author. Tel.: +34 934 021 281; fax: +34 934 021 233.
E-mail address: hector.bagan@ub.edu (H. Bagán).

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research (e.g. marker or environmental studies). Due to this wide range of uses, many radioactivity determinations are performed to obtain information regarding the processes that are being studied as well as to evaluate the environmental impacts [1,2]. Many of the samples are analysed in aqueous media but some other important groups of samples have organic matrices or are present in very aggressive aqueous media [1,3–6]. The routine technique for the measurement of beta and alpha emitters in these types of samples is liquid scintillation (LS). LS is a consolidated and robust technique for the analysis of aqueous samples with a high detection efficiency. However, LS exhibits some challenges when it is applied to the measurement of strong salt matrices due to phase separation, strong acid media due to luminescence, or strong oxidative media due to the degradation of the scintillator cocktail [1,7,8].

Plastic scintillation in the form of microspheres (PS) is an alternative to the LS technique for the measurement of alpha and beta emitters with the advantages of not producing radioactive mixed wastes. In addition, the plastic scintillator can be used as support for the separation steps and due to the intrinsic heterogeneity of the PS – sample mixture, it can be used for the measurement of samples with a high salt content [9–12]. However, this technique also exhibits some drawbacks, such as a low detection efficiency when low energy beta emitters are measured (^{3}H) due to the higher distance between the sample and the scintillator. As in LS, PS also suffers degradation problems when strong aggressive or organic media are used [13].

Most PS materials are polymers composed of a linear chain that can be dissolved or degraded in the above mentioned media. This problem can be overcome with the addition of a crosslinker that transforms the polymer structure into a three-dimensional network that confers polymer solvent resistance and rigidity, with divinyl benzene (DVB) being one of the most commonly used crosslinker [14]. However, some attempts made to produce these types of polymers, for high activity detectors, have resulted in an important reduction in the detection efficiency of the final PS [15,16].

The objectives of this study are to evaluate the effect of changing the polymer composition on the detection efficiency to establish the appropriate composition and to synthesise and evaluate a crosslinked plastic scintillator (C-PS) that can be used in organic and aggressive media with high detection efficiency. The C-PS will be the starting point for new fields of application of the PS technique including the measurement of organic samples containing labelled molecules, biological samples [3] or industrial organic compounds such as biodiesels [4], for samples containing aggressive media from the strong acid dissolution of soils or tissue samples [1,5], for the preparation of imprinted polymers [17,18] or scintillation proximity assay polymers [19] and for developing high activity detectors.

2. Experimental

2.1. Reagents and solutions

All of the reagents were of analytical grade. The initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) was purified by recrystallisation from methanol, and the crosslinkers and monomer were purified prior to use by passing through an alumina oxide column. Deionised water was used to prepare the calibration and test solutions. A $133 \pm 2\,\mathrm{Bq\,g^{-1}}$ ^{14}C active stock solution was prepared from a $44.7 \pm 0.5\,\mathrm{kBq\,g^{-1}}$ standard in a water solution containing glucose ($50\,\mu\mathrm{g\,g^{-1}}$) and formaldehyde ($1\,\mathrm{mg\,g^{-1}}$) (CERCA-LEA). An $47.4 \pm 0.5\,\mathrm{Bq\,g^{-1}}$ ^{241}Am active stock solution was prepared from a $924 \pm 9\,\mathrm{kBq\,g^{-1}}$ standard in a 1 M HNO_3 water solution (CERCA-LEA). A $38.5 \pm 0.2\,\mathrm{Bq\,g^{-1}}$ ^{90}Sr/^{90}Y active stock solution was prepared from a $4.07 \pm 0.02\,\mathrm{kBq\,g^{-1}}$ standard in an aqueous solution containing strontium ($100\,\mu\mathrm{g\,g^{-1}}$) and yttrium ($100\,\mu\mathrm{g\,g^{-1}}$) in 0.1 M HCl (Amersham International). A $271 \pm 5\,\mathrm{Bq\,g^{-1}}$ ^{14}C active stock solution in benzene was prepared from a $3700 \pm 67\,\mathrm{kBq\,g^{-1}}$ standard in toluene (DuPONT). A ^{3}H active stock solution (i.e. $4425 \pm 29\,\mathrm{Bq\,g^{-1}}$) was prepared from a $69.8 \pm 0.5\,\mathrm{kBq\,g^{-1}}$ standard in dead water (Eckert & Ziegler). These stock solutions were used to prepare the different active solutions.

For the LS measurements, Optiphase Supermix cocktails from Wallac PerkinElmer were used. The measurement solutions were contained in 6 and 20 mL polyethylene vials (Packard Instruments Co.).

Ac-PPO ((2,5-diphenyloxazol-4-yl) methyl acrylate) was synthesised in 5 steps according to previously published protocols [20]. The obtained products were characterised by 400 MHz NMR.

2.2. Apparatus

A Beckman J2-HS was used to centrifuge the PS vials. A P-Selecta ultrasonic bath was used to apply ultrasonic waves to the PS vials. A Quantulus liquid scintillation spectrometer (EG & G Wallac) with logarithmic amplification, multichannel analyser (MCA) (4096 channels distributed in four segments of 1024), alpha/beta discrimination and background reduction using active guard were used for the scintillation measurements. Secondary electron images were obtained using a field emission scanning electron microscopy (FE-SEM) (Jeol-7100).

2.3. Procedure

2.3.1. Preparation of the polymers

Depending on the polymer design, different reagents were used to achieve the desired composition. The components were as follows: styrene (St) as the monomer (acting as solvent in the PS); DVB and ethylene glycol dimethacrylate (EGDMA), which were used as a crosslinker, 2,5-diphenyloxazole (PPO), *p*-terphenyl (TP), Ac-PPO as the fluorescent solute, 1,2-diisopropylnaphthalene (DIN) as the secondary solvent, and 1,4-bis-2-(5-phenyloxazolyl) benzene (POPOP) as the secondary fluorescent solute. The compositions of the various synthesised polymers are summarised in Table 1. The quantities of the different components were chosen to obtain a theoretical final polymer amount of 865 mg (only St and DVB were taken into account) except for the final C-PS which gave a theoretical yield of 8.91 g.

The different components were placed in a test tube, and the solution was saturated with dry nitrogen for 2 min, except for the final polymer, which was saturated for 10 min before being sealed. The polymerisation was thermally induced at 62 °C for 24 h and at 75 °C for an additional period of 24 h. The obtained polymer was repeatedly washed with ethanol and dried in air. For the bulk polymerisations, the final polymer block was ground with a mechanical mortar. For all of the polymerisations where microparticles were obtained, these microparticles ranged from 5 to 15 μm. For the ground bulk polymers, the size of the particles was between 20 and 70 μm.

2.3.2. Preparation of radioactive solutions (active solutions)

For the water, hydrochloric acid, nitric acid, hydrogen peroxide and ^{3}H solutions as well as the ^{14}C toluene solution, these active solutions were prepared by diluting a small known amount of the active stock solution in the corresponding medium. For the other ^{14}C solutions, an aliquot of the active stock solution was evaporated to dryness and redissolved in the corresponding organic medium. For the other ^{90}Sr/^{90}Y and ^{241}Am solutions, the isotope was extracted from the aqueous active stock solution using a tri(*n*-octyl) phosphine oxide at 4% in the corresponding organic medium.