

## Layer-by-layer coated imidazolium – Styrene copolymers fibers for improved headspace-solid phase microextraction analysis of aromatic compounds

David J.S. Patinha<sup>a,b</sup>, Nallepalli Pothanagandhi<sup>c</sup>, Kari Vijayakrishna<sup>c</sup>, Armando J.D. Silvestre<sup>b</sup>, Isabel M. Marrucho<sup>a,d,\*</sup>

<sup>a</sup> Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. Da República, 2780-157 Oeiras, Portugal

<sup>b</sup> CICECO - Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>c</sup> Department of Chemistry, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu, India

<sup>d</sup> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal



### ARTICLE INFO

#### Keywords:

Solid phase microextraction  
SPME  
Poly(ionic liquids)  
Layer-by-layer  
Spray coating  
BTEX extraction

### ABSTRACT

The design of poly(ionic liquids) (PILs) and their application as solid phase microextraction (SPME) fibers has been attracting enormous attention mainly due to the need for new SPME coating materials with improved analytical sensitivity. In this work, the tunability of PILs is explored by preparing different imidazolium monomers bearing benzyl, naphthylmethyl or pentyl pending groups that were subsequently co-polymerized, by reversible addition–fragmentation chain transfer (RAFT) polymerization with styrene. The obtained co-polymers showed excellent thermal stability up to 275 °C, with no melting point up to 250 °C. SPME fibers were prepared by an innovative approach based on layer-by-layer spray coating. The thin (< 10 μm) SPME coatings were tested in GC-FID for the detection of volatile aromatic compounds such as benzene (B), toluene (T), ethylbenzene (E) and xylene (X) present in aqueous samples and the extraction parameters optimized. Superior results were obtained when comparing these LbL PILS-based SPME fibers with a commercial fiber composed of poly(dimethylsiloxane), with an increase in the detectable areas of 83%, 69%, 57% and 58% for B, T, E and X, respectively. Low relative standard deviations were obtained for the same fiber (< 5.6%) and also for different fibers (< 9.8%). Furthermore, a spiked soil sample was used to mimic a real contaminated soil sample and excellent recovery results, ranging from 67.0% to 102.2%, were obtained.

### 1. Introduction

During the past few years, huge attention has been paid to the development of new high performance materials for solid phase microextraction. The urge for fast analysis, precise results and low detection limits is gaining increasing attention as industries need to comply with increasingly restrictive regulations for hazardous contaminants in their products. Due to its easy operation, non-invasive/destructive character, robustness and quickness, solid phase microextraction (SPME) is one of the most studied pre-concentration techniques for the analysis of volatile organic compounds [1,2]. SPME was introduced by Pawliszyn in the 90's [3] and since then, countless studies concerning the detection of chemicals in demanding conditions or in trace concentrations, the identification and detection of new chemicals or the development of new methods of analysis have been published [4–7]. However, a less explored subject is the development of new coating materials that can

be used as sorptive media in SPME. Nowadays, a limited range of coatings is commercially available, being poly(dimethylsiloxane) (PDMS), poly(acrylate) (PA) or poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) the most used [8]. Other coatings, where mixtures of these polymers are used aiming to impart different polarities to the same fiber, have also been reported [9]. Regardless of their good performances for a large range of chemically diverse analytes, new fiber coatings are needed to overcome new challenges in analytical chemistry posed by the complex nature of the samples and the large difference in concentrations between analytes [8]. Moreover, *in-vivo* analysis or metabolomics monitoring [10–13] also demand special attention, specifically in the development of biocompatible polymers to be used directly under skin or muscle, for continuous health monitoring or the detection of specific biomarkers for diagnosis of early stage diseases.

Poly(ionic liquids) (PILs), a subclass of polyelectrolytes, are versatile materials since they display some of the ILs monomers remarkable

\* Corresponding author at: Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal.  
E-mail address: [isabel.marrucho@tecnico.ulisboa.pt](mailto:isabel.marrucho@tecnico.ulisboa.pt) (I.M. Marrucho).

characteristics, in particular the easy tuning of their physical and chemical properties. In addition, PILs also combine the advantageous thermal and mechanical properties of polymers, which opens the door to a versatile platform of engineered functional polymeric materials. Some successful examples of their use include batteries [14], CO<sub>2</sub> separation [15], analytical chemistry [16] or as sensors [17]. In what concerns their application as SPME fiber coatings, PILs have been studied since 2008 for the detection of several types of analytes, such as CO<sub>2</sub>, alcohols and amines, benzene derivatives, polycyclic aromatic hydrocarbons, genotoxic impurities, fatty acids, among others [18,19]. Despite the diversity of analytes, and their successful detection and quantification, only one polycation based on imidazolium core has been used to develop the SPME fibers. The tunability of the prepared PILs was afforded mostly by the introduction of alkyl side chains of different length in the nitrogen positions of the imidazolium group. The preparation of PIL-based SPME fibers typically encompasses three steps: i) design and preparation of the IL monomer; ii) polymerization of IL monomer to obtain the PIL; iii) preparation of the SPME PIL-coating. The last step is the most challenging since a homogeneous coating with < 100 μm thickness needs to be produced. Several approaches have been proposed, being the dip-coating method the most used, due to its easiness [20–23]. However, other methods such as electro-deposition [24] or *in situ* surface polymerization using thermal or UV initiated polymerization have also been used [25–30].

Spray-coating is a simple and fast technique that allows the easy preparation of thin films by controlling processing parameters such as the solution concentration, gas/liquid ratio, nozzle diameter, distance from substrate and nozzle or working temperature [31]. This technique has been mainly used in the preparation of layer-by-layer (LbL) polymeric films [32], in detriment of dip-coating that is time-consuming and difficult to scale-up. These LbL films with well-defined properties have found applications in optoelectronic devices [33], solar cells [34] or transistors [31]. The advantages of preparing of SPME fibers through spray-coating, using silica based octadecyl particles and polyacrylonitrile (C18-PAN), over dip-coating or brush coating have already been put forward: coatings prepared by dip and brush coating peeled off from the metallic support over 70 experiments, whereas the spray coated fibers were stable over the same number of experiments [35]. Due to the small thickness of the consecutive layers obtained by spray coating, the adhesion between them is stronger than what is observed when other coating methods are used, thus resulting in very stable materials. Another advantage of the LbL method is that different polymers can be used to form layers of different compositions. Putting together the PILs tunable nature and the LbL approach, a great diversity of SPME fibers can be created by producing consecutive layers of different polycations, polyanions or polycations with polyanions to meet specific needs. Spray coating has already showed excellent results in the preparation of PIL films for other purposes, such as, for example, the creation of super hydrophobic surfaces (> 165°), using poly [(1-vinyl-3-ethylimidazolium) bis (trifluoromethanesulfonyl)imide] and poly (sodium 4-styrenesulfonate) sprayed onto a glass surface [36]. The easiness of handling, the low amounts of solvents and polymeric material required, and mostly, the high finishing quality makes spray coating extremely appealing for the preparation of SPME fibers.

The main goal of this work is the easy and speedy development of SPME fibers using spray coating. For that purpose, vinylimidazolium cation units functionalized with benzyl, naphthylmethyl and a pentyl alkyl chain were copolymerized with styrene and used to prepare SPME fibers by spray coating. Giving the aromatic nature of the prepared copolymers, a reference mixture of aromatic compounds composed by benzene, toluene, ethylbenzene and xylene (BTEX) mainly found in gasoline, but also in adhesives, inks, dyes, lacquers and degreasers, was used to test the efficiency of the prepared SPME fibers. These aromatic hydrocarbons when in contact with humans, either by direct contact through product application or indirect contact due to spills in soil or water [37–40], can easily enter the body through skin or lungs. These

substances can cause several neurological diseases or cancer [41,42]. To demonstrate the potential of the prepared SPME fibers, aqueous solutions containing a BTEX mixture were prepared and the performance of the fibers was accessed by head-space-SPME coupled with gas chromatography (HS-SPME-GC). Also, to demonstrate the potential of the fabricated fibers on a real sample, spiked soil samples with BTEX were prepared and recovery studies carried out.

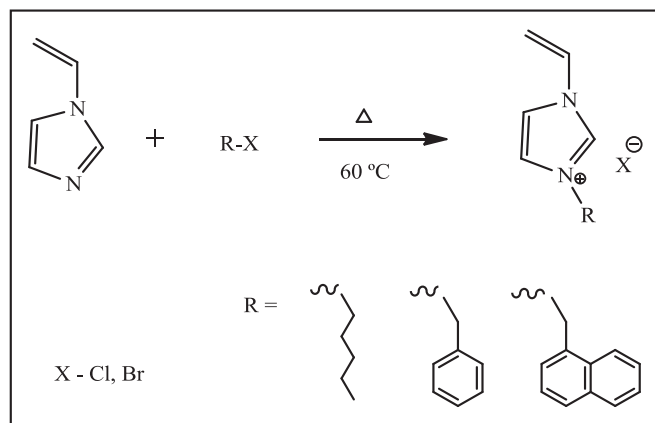
## 2. Experimental

### 2.1. Materials

Source and grade of the used chemicals and reagents were as follows: 2,2'-Azobis(2-methylpropionitrile) (AIBN) (> 98%), 1-Vinylimidazole (> 99%), n-bromopentane (> 98%), benzyl bromide (C<sub>7</sub>H<sub>7</sub>Br) (> 98%), styrene (> 99%), ethyl-2-bromopropionate (99%), 1-(chloromethyl)naphthalene (C<sub>11</sub>H<sub>9</sub>Cl) (> 97%), potassium ethyl xanthogenate (96%), acetone (99.5%), dry dimethylformamide (99.8%), diethyl ether (99.8%), dichloromethane (99.9%), ethyl acetate (99.8%) and methanol (99.8%) were purchased from Sigma-Aldrich. Acetonitrile (99.8%) was supplied by Carlo Erba Reagents. Lithium bis (trifluoromethanesulfonyl)imide salt (LiTFSI) (99%) was purchased from IOLITEC. Benzene (99%) was provided by Riedel-de Haen. Steel wire was purchased in a local store. Ethylbenzene (99%), toluene (99%) and p-xylene (99%) were obtained from Merck. Chloroform-*d* (CDCl<sub>3</sub>) (≥ 99.8) and dimethyl sulfoxide *d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) (99.8%) were supplied by Cambridge Isotope Laboratories, Inc. The commercial fiber PDMS (7 μm) (PDMS7) and the Supelco SPME fiber holder were purchased from Supelco (Aldrich, Bellefonte, PA, USA). All reagents were used as received. Double distilled water, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment, was used in all experiments.

### 2.2. Synthesis of ionic liquid monomers

Three different vinylimidazolium based monomers, having different side chains such as pentyl, benzyl and naphthylmethyl, were synthesized as shown in Scheme 1 [43]. Briefly, 2 g of 1-vinylimidazole (21.25 mmol) and 4.81 g of *n*-bromopentane (31.87 mmol) were mixed in a round bottom flask and heated at 60 °C for 3 h. Afterwards, the reaction mixture was dissolved in minimum amount of methanol and precipitated in 50 mL of ethyl acetate, to wash out unreacted starting materials. This procedure afforded 1-vinyl-3-pentyl imidazolium bromide (ViPenIm)Br in quantitative yields. 1-Vinyl-3-benzyl imidazolium bromide (ViBnIm)Br was synthesized as follows: 2 g of 1-vinylimidazole (21.25 mmol) were dissolved in 5 mL of methanol and 5.4 g (32 mmol) of benzyl bromide were added dropwise and kept under reflux for 3 h.



Scheme 1. Synthesis of substituted vinyl imidazolium monomers.

Download English Version:

<https://daneshyari.com/en/article/7826341>

Download Persian Version:

<https://daneshyari.com/article/7826341>

[Daneshyari.com](https://daneshyari.com)