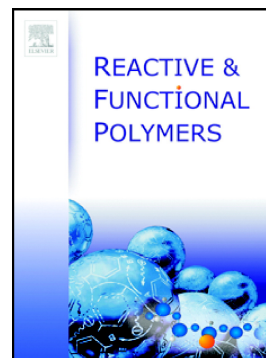


## Accepted Manuscript

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

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**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 copolymerized, 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.

Keywords: solid phase microextraction; SPME, poly(ionic liquids); layer-by-layer; spray coating. **BTEX extraction**

## 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 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 less than 100  $\mu\text{m}$  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 electrodeposition [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 ( $>165^\circ$ ), 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.

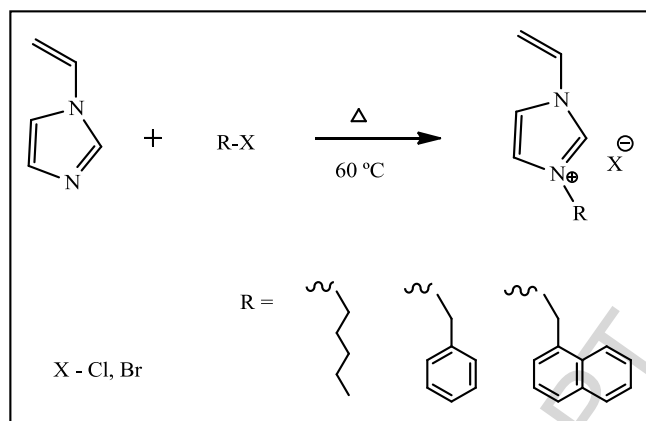
The main goal of this work is the easy and speedy development of SPME fibers using spray coating. For that purpose, vinylimidazolium cation units functionalized with benzyl, naphthylmethyl and a pentyl alkyl chain were copolymerized with styrene and used to prepare SPME fibers by spray coating. Giving the aromatic nature of the prepared co-polymers, 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. The reaction mixture was then precipitated in 50 mL of ethyl acetate, to wash out unreacted starting materials, producing (ViBnIm)Br in quantitative yields. The same procedure was followed for the synthesis of 1-vinyl-3-naphthylmethyl imidazolium bromide (ViNapIm)Br. The NMR data are provided in supporting information, from Figure S1 to S6.



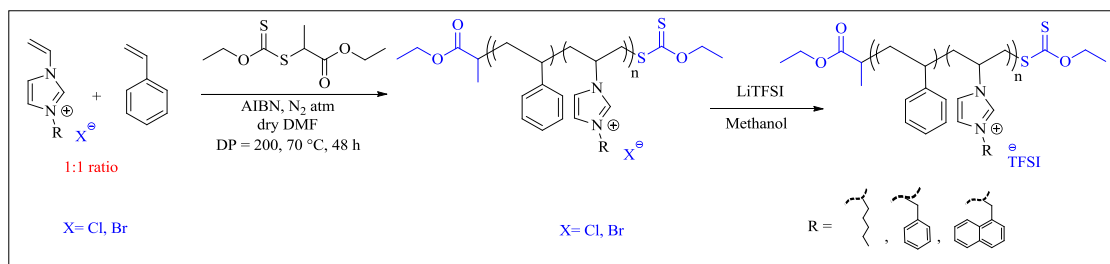
Scheme 1. Synthesis of substituted vinyl imidazolium monomers.

### 2.3 Synthesis of Co-poly(ionic liquids)

The imidazolium based co-poly(ionic liquids) were synthesized by RAFT copolymerization of vinylimidazolium monomers with styrene as co-monomer, using a xanthate based chain transfer agent, namely 2-ethoxythiocarbonylsulfanyl-propionic acid ethyl ester (CTA) [44,45]. Briefly: 1-vinyl-3-pentyl imidazolium bromide ((ViPenIm)Br), 4 g (16.3 mmol) and 1.7 g (16.3 mmol) of styrene (Sty), 36.22 mg of CTA (0.163 mmol) and 5.35 mg of AIBN (0.059 mmol) were taken in a flame dried Schlenk flask and dissolved in 10 mL dry dimethylformamide. Three freeze-thaw cycles were performed to remove dissolved gases. Then the reaction mixture was heated up to 70 °C for 48 h. The obtained co-PIL was purified by the precipitation in cold chloroform and dried under vacuum, yielding 5.51 g of poly(ViPenIm-co-Sty)Br (89 % yield). The remaining co-PILs, namely poly(ViBnlm-co-Sty)Br (88 % yield) and poly(ViNaplm-co-Sty)Br (89 % yield), were synthesized with the same procedure, as described in Scheme 2.

The counter halide anions, bromide or chloride, of synthesized co-PILs were exchanged with lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) [44]. For that purpose, 7.29 g (25.41 mmol) of LiTFSI dissolved in distilled water were added dropwise to 5 g (12.7 mmol) of poly(ViPenIm-co-Sty)Br and kept at room temperature, under stirring, until the reaction was complete, yielding poly(ViPenIm-co-Sty)TFSI. The product was filtered and washed carefully several times with water and dried over vacuum. The same procedure was used to obtain poly(ViBnlm-co-Sty)TFSI and poly(ViNaplm-co-Sty)TFSI.





**Scheme 2.** Synthesis of poly(ViR-co-Sty)X through polymerization of (ViRIm)X and styrene and subsequent anion exchange.

## 2.4 TGA, DSC and GPC analysis

The thermal stabilities and decomposition temperatures of the prepared materials were measured using a thermogravimetric analyzer (TGA) Q50, while the glass transition temperatures were determined using a DSC Q200 differential scanning calorimeter, both from TA Instruments. The TGA experiments were performed under  $N_2$  atmosphere using aluminum pans by performing one heating ramp from room temperature up to  $600\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$ . The DSC experiments were also performed in aluminum pans and under  $N_2$  atmosphere. Three temperature cycles from  $-70\text{ }^\circ\text{C}$  to  $210\text{ }^\circ\text{C}$  and  $210\text{ }^\circ\text{C}$  to  $-70\text{ }^\circ\text{C}$  at a heating/cooling rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  were performed. NMR spectra were recorded on a Bruker AC-400 MHz spectrometer in appropriate deuterated solvents. Molar masses of PILs were determined by a Waters gel permeation chromatography (GPC) instrument with Styragel columns equipped with refractive index (RI) detector using tetrahydrofuran (THF) as solvent at an elution rate of  $1\text{ mL}/\text{min}$ .

## 2.5 SPME Fiber spray coating preparation

For the preparation of fiber coatings, straight steel wires, with  $0.2\text{ mm}$  of outer diameter, were cut into  $9\text{ cm}$  length, cleaned with methanol, acetone and dichloromethane, and kept at  $60\text{ }^\circ\text{C}$  during 8 hours, to remove all solvents. Each wire was glued to a step by step rotational motor and the area to be coated ( $1\text{ cm}$ ) carefully adjusted. For the spray coating procedure (Figure 1), a solution containing  $0.5\text{ g}$  of the desired co-polymer in  $25\text{ mL}$  of acetone was prepared. The solution was transferred into an air-brush spray coater and, with the wire rotating at a constant speed, a series of 20 layers were deposited. Between each spray coating layer,  $10\text{ s}$  interval was taken to allow acetone evaporation. To speed up the evaporation process, the spray coating

procedure was carried out inside of an oven at  $40 \pm 1$  °C. The distance between the fiber support and the air-brush nozzle was set to 20 cm.

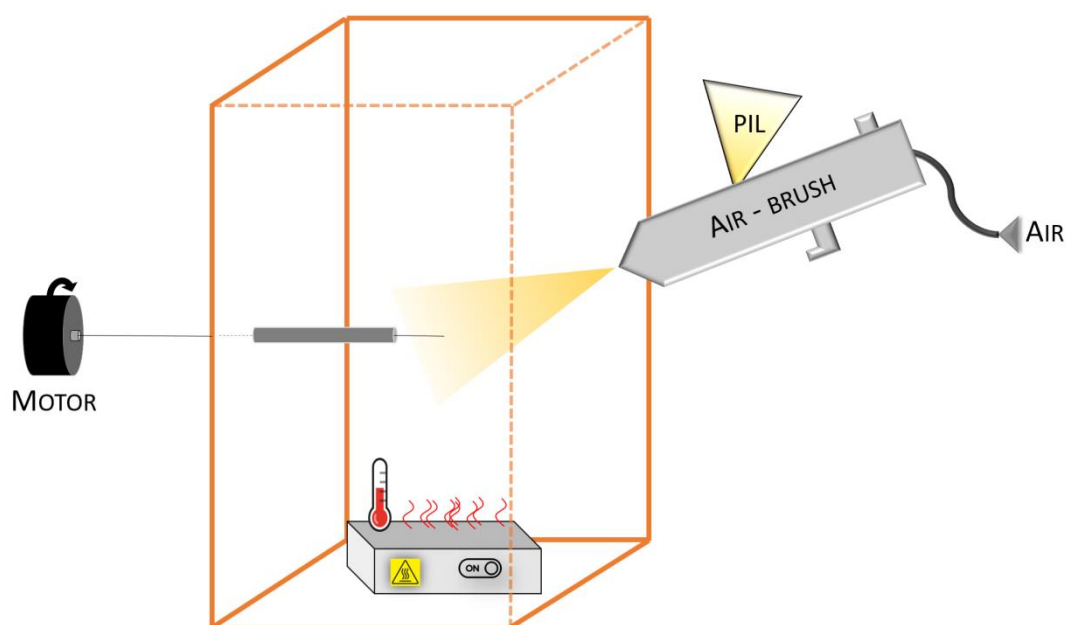


Figure 1 – Illustration of the spray coating of the steel wires with the prepared PIL.

## 2.6 HS-SPME methodology

To evaluate the HS-SPME performance of the prepared fibers, extractions of standard aqueous solutions composed of benzene, toluene, ethylbenzene and xylene (BTEX) at different concentrations (as discussed for each experiment in part 3 – Results and discussion) were carried out using the SPME fibers developed in this work. The results were compared with those of a commercial fiber. All PIL fibers were preconditioned/annealed prior their first use during 1 h at 220 °C. For the HS-SPME procedure, 5 mL of each standard solution were transferred into 10 mL glass vials and HS-SPME parameters such as stirring rate, extraction temperature, salt addition or extraction time were studied (details are described in point 3.3 of Results and discussion). After extraction, the fibers were immediately inserted in the GC injector and kept there for 3 min. Between each set of experiments, a blank injection was performed to confirm the absence of analytes from previous extractions (carryover). All

the experiments were done in triplicate to estimate uncertainties. The GC analyses were performed in a Trace 1300 gas chromatograph from Thermo Scientific equipped with a flame ionization detector (FID). Helium was used as carrier gas at  $1.0 \text{ mL}\cdot\text{min}^{-1}$ . The GC injector was kept at  $220 \text{ }^{\circ}\text{C}$  with a splitless time of 3 min and FID was kept at  $250 \text{ }^{\circ}\text{C}$ . A Trace TR-V1 ( $30 \text{ m} \times 0.250 \text{ mm} \times 1.40 \text{ }\mu\text{m}$ ) capillary column from Thermo Scientific was used with the following temperature program: initial temperature of  $50 \text{ }^{\circ}\text{C}$  during 1 min, followed by a ramp at  $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  to  $80 \text{ }^{\circ}\text{C}$ , held during 5 min and then increased to  $250 \text{ }^{\circ}\text{C}$  at a ramp of  $50 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ .

### 2.7 Matrix effect, validation and recovery tests

The analytical performance of the prepared fibers was evaluated using the following conditions:  $T = 30 \text{ }^{\circ}\text{C}$ ,  $t = 15 \text{ min}$ ,  $50 \text{ mg/mL}$  of NaCl and 400 RPM, using standard solution concentrations varying from  $0.4$  to  $500 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ . Linearity was studied the same range of concentrations for all the analytes. Limits of detection (LOD) were determined by decreasing the concentration of the standard solution until the signal to noise ratio (S/N) of 3 was attained. The recovery tests were accessed by spiking real soil samples with known amounts ( $50 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  and  $10 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ ) of the analytes under study. The soil was dried at  $60 \text{ }^{\circ}\text{C}$  during 24 h, and  $0.5 \text{ g}$  of dried soil was added to a glass vial and spiked with  $1 \text{ mL}$  of standard solution. The prepared vials were homogenized using a magnetic stirrer and then kept at  $4 \text{ }^{\circ}\text{C}$  during 8 hours before analysis.

### 3 Results and discussion

#### 3.1 Polymer synthesis

Imidazolium based co-poly(ionic liquids) bearing three different side chains (pentyl, benzyl and naphthylmethyl) were synthesized by RAFT polymerization using 2-ethoxythiocarbonylsulfanyl-propionic acid ethyl ester as chain transfer agent. These RAFT derived hydrophilic co-PILs bearing bromide or chloride counter anions were converted into hydrophobic co-PILs-TFSI by simple anionic metathesis reaction with LiTFSI salt. The synthesized co-PILs were characterized by TGA, DSC, GPC and NMR analysis. The thermal stability of these three co-polymers was studied using TGA. The co-polymers showed thermal stability up to 275 °C and a steady decomposition pattern (see Figure S7-S9). The DSC thermograms show that the three copolymers, poly(ViPenIm-co-Sty)TFSI, poly(ViBnIm-co-Sty)TFSI and poly(ViNapIm-co-Sty)TFSI, have  $T_g$  values of 47.6 °C, 76.9 °C and 95.3 °C, respectively (see Figure S10-S12), indicating that they are all suitable to be used as SPME fibers, provided that desorption/cleaning takes place below 275 °C. All polymers are in the vitreous state at the extraction temperature. This fact possibly hinders the sorption of the analytes, leading to extraction efficiencies lower than the expected.

The molecular weights of co-PILs were analyzed with GPC and data is depicted in Table 1 and Figure S13. The three polymers have relatively high  $M_w$ , which favors film formation. Although the polymer with the pentyl pendant group has the highest  $M_w$ , it also has the highest polydispersity index (PDI). The lowest PDI was obtained for the benzyl substituted polymer that has also the lowest  $M_w$  co-PIL. The amount of styrene (52-57%) present in the copolymers was calculated from  $^1\text{H}$  NMR data of co-PILs (see supporting information from Figure S14 to Figure S16).

**Table 1** – Results from GPC analysis of Homo and Co-PILs used in this work.

S. No	PILs	$M_n$	$M_w$	PDI
1	poly(ViBnIm-co-Sty)TFSI	34100	44600	1.31
2	poly(ViNapIm-co-Sty)TFSI	35200	50850	1.45
3	poly(ViPenIm-co-Sty)TFSI	41200	62800	1.52

### 3.2 Preparation of co-PIL fibers

PIL co-polymers were here used for the first time to prepare homogeneous fiber coatings by spray-coating. The co-polymers were coated on a previously cleaned steel wire (> 83 % of Fe by EDS tests) using an air-brush gun with an adjustable nozzle (Figure 1). The nozzle allows the control of the quantity of sample that is sprayed out and, depending on the polymer solution concentration and nozzle aperture, different coatings can be obtained. For example, when using high concentration and large nozzle aperture, the coatings are unevenly distributed on the surface due to the high viscosity of the polymer solution. However, a thinner layer can be obtained using less concentrated/less viscous polymer solutions. Acetone was chosen as solvent due to its low boiling point and good co-PIL solvent capacity. Using a spray-chamber with controlled temperature, the layer-by-layer deposition is quicker and the formation of irregularities is avoided due to quick solvent evaporation. All our coatings were prepared using a 20 mg/mL polymer-acetone solution, which allows very thin layers of about 0.4  $\mu\text{m}$  each, resulting in highly homogeneous fibers, with less than 10  $\mu\text{m}$ , containing around 20 coatings (Figure 2b and 2c). To achieve the best coating homogeneity, the steel wire was attached to a rotary motor, at a constant speed of 10 revolutions per second, ensuring an excellent polymer distribution over the substrate (see Figure S17 on supporting information). After the spray-coating process, all the fibers were cured in an oven at 230  $^{\circ}\text{C}$  for 2h, to improve the adhesion of the coatings to the steel wires [36].

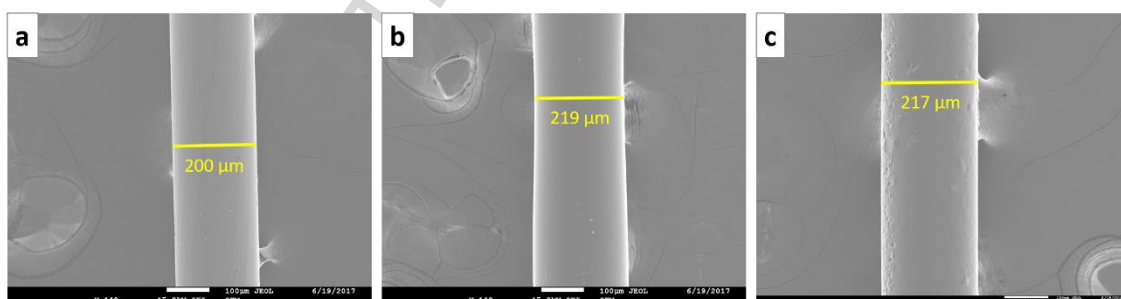


Figure 2 – SEM image of: a) steel uncoated wire; b) poly(ViBnIm-co-Sty)TFSI c) poly(ViPenIm-co-Sty)TFSI based fibers revealing coating thicknesses between 8 and 10  $\mu\text{m}$ .

### 3.3 Co-PIL based fibers HS-SPME extraction parameters influence

Several experimental parameters such as extraction time, temperature, salt addition, desorption temperature and stirring effect were taken into account in the optimization of SPME extraction efficiencies of the newly developed fibers. Other

parameters, such as pH ( $\approx 7$ ) and headspace ratio of 50 %, were kept fixed. For these studies, the fiber composed of poly(ViBnlm-co-Sty)TFSI was chosen due to the similar structure between the IL- benzyl pendant group and the styrene co-monomer with the BTEX compounds under study. Furthermore, this fiber showed the best thermal stability in the TGA analysis.

### 3.3.1 Extraction time

HS-SPME extractions of BTEX mixture from aqueous solutions ( $400 \mu\text{g}\cdot\text{L}^{-1}$ ) were carried out at different times (5, 10, 15, 20 and 60 min) maintaining temperature at  $30^\circ\text{C}$ , stirring rate at 450 RPM, using 50 mg/mL of NaCl throughout the experiences. The chromatographic areas of BTEX mixture using the fiber composed of poly(ViBnlm-co-Sty)TFSI are shown in Figure 3. The chromatographic areas of the analytes reached the **maximum extraction** in about 15 min, mainly due to their small thickness. Working at equilibrium conditions in SPME is advantageous since it minimizes variability and the resulting quantification errors. Consequently, the extraction time was fixed at 15 min. Although similar sorption times were already reported by other authors [46], longer times were also observed [47,48] when performing direct immersion studies and using thicker coatings.

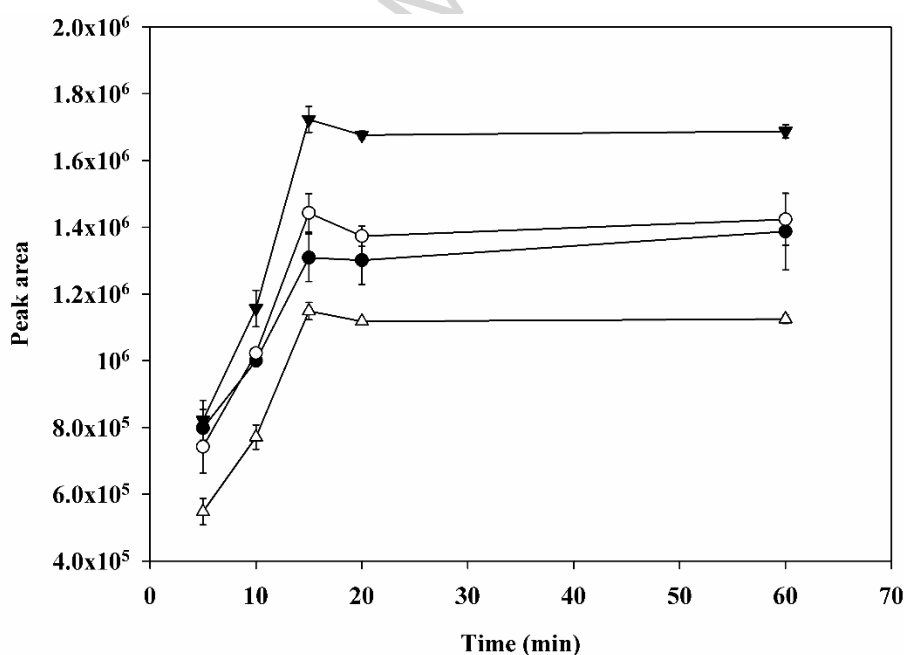


Figure 3 – Sorption time profiles of the BTEX mixture using the fiber composed of poly(ViBnlm-co-Sty)TFSI; ● benzene, ○ toluene, ▼ ethylbenzene and △ xylene. ( $T = 30^\circ\text{C}$ , stirring 400 RPM, 50 mg/mL of NaCl and concentration:  $400 \mu\text{g}\cdot\text{L}^{-1}$ ;) )

### 3.3.2 Extraction temperature

Temperature usually plays a very important role in the efficiency of HS-SPME. As the temperature increases, the partition coefficients between the head-space and both the liquid phase and the fiber coating change also increases [28]. Thus, a careful optimization of this parameter is required. A comparison of the chromatographic peak areas obtained at 30, 40, 50 and 60 °C (Figure 4a) shows that the optimum extraction temperature for all compounds was 50 °C, since for higher temperatures a decrease in the detected area was observed. This decrease is mainly linked to the effect of temperature in partition coefficients as mentioned above, although the presence of higher water content in the headspace, which competes with the analytes for active sites on the fiber cannot be excluded [49].

### 3.3.3 Salt concentration

Using NaCl as salting out agent, maximum peak areas were obtained by adding between 50 and 150 mg/mL of salt to the aqueous solutions. Given the poor solubility in water of the selected analytes (152-1780 mg·L<sup>-1</sup>) [50], the salt addition promotes their higher concentration in the headspace by decreasing their solubility, resulting in better extraction efficiencies. As can be seen in Figure 4b, the extraction efficiencies for the four analytes benefit from the addition of 50 mg/mL of NaCl. However, for higher NaCl concentrations, a decrease in the efficiency is generally noticed. Although this is not a typical behavior of this type of systems, similar observations have been previously reported by other authors [46,51–53] and tentatively explained by Pawliszyn [54]. Therefore, 50 mg/mL of salt was selected to be used onwards.

### 3.3.4 Desorption temperature

The extraction efficiency can also be affected by the injector temperature (Figure 4c). In this work, the extraction efficiency was studied using desorption temperatures of 200, 220 and 240 °C. The best results were obtained for a temperature of 220 °C and therefore, this desorption temperature was used in the rest of the study.

### 3.3.5 Stirring effect

The stirring speed also influences the extraction efficiency in SPME [55]. In this study, the effect of three RPM's, 100, 450 and 800, on the extraction efficiency was evaluated (Figure 4d). The obtained results show that the maximum extraction efficiency was reached at 450 RPM and thus, 450 RPM was used in all the experiments.

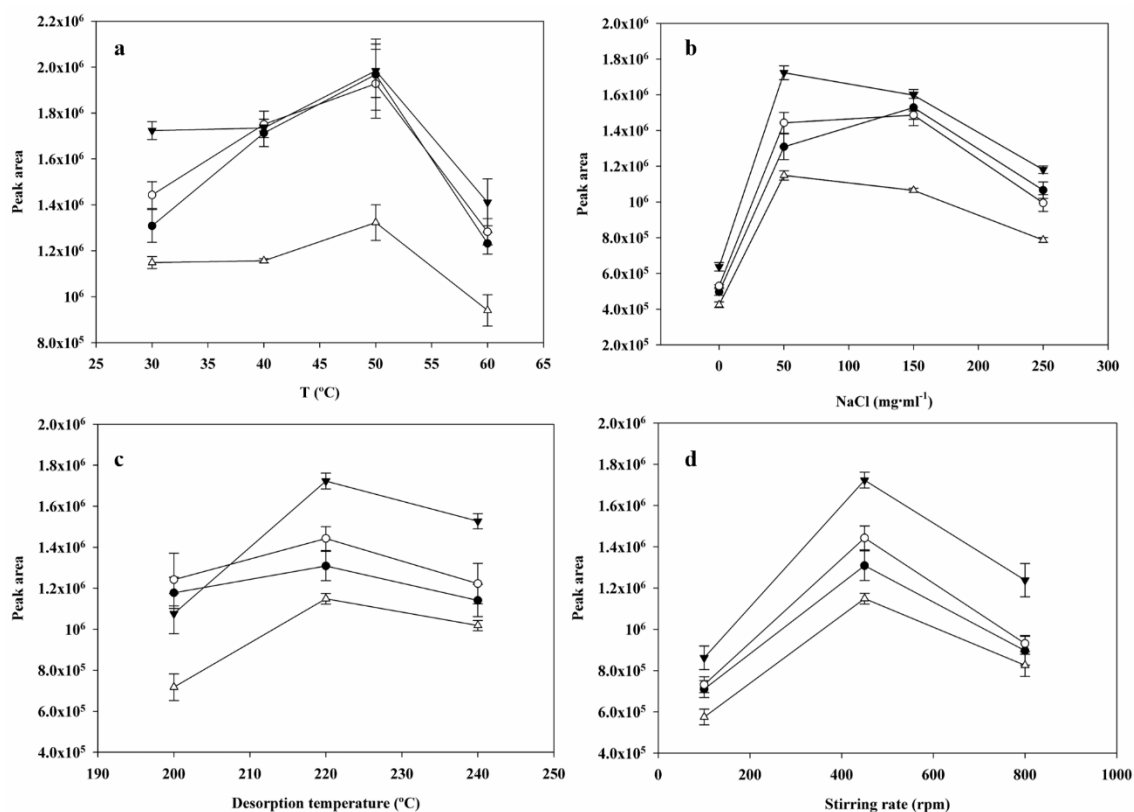


Figure 4 – Extraction efficiency of the poly(ViBnIm-co-Sty)TFSI fiber when varying (a) - extraction temperature ( $t = 15$  min, 400 RPM, 50 mg/mL of NaCl); (b) - salt concentration ( $T = 30$  °C, 400 RPM,  $t = 15$  min); (c) – desorption temperature and (d) – stirring rate ( $T = 30$  °C,  $t = 15$  min, 50 mg/mL of NaCl); ● benzene, ○ toluene, ▼ ethylbenzene and △ xylene at a concentration of  $400 \mu\text{g}\cdot\text{L}^{-1}$ .

### 3.4 Comparison of the homemade fibers with commercial fibers

Concerning the comparison of PIL-based SPME fiber with the commercial PDMS fiber, the coating thickness is an important parameter that needs to be taken into account. Since the coating thickness of homemade spray-coated fibers was of  $7 \mu\text{m}$ , a PDMS fiber of the same thickness was selected. The comparison of the extraction efficiencies, based on the chromatographic peaks areas, of the three co-PIL-based fibers prepared by spray-coating with the commercial fiber, at the optimized conditions,  $T = 50$  °C with 15 min of extraction at 400 RPM with 50 mg/mL of NaCl using an aqueous mixture of BTEX with concentration of  $400 \mu\text{g}\cdot\text{L}^{-1}$ , is presented in Figure 5. All polymers, namely poly(ViPenIm-co-Sty)TFSI poly(ViBnIm-co-Sty)TFSI and poly(ViNapIm-co-Sty)TFSI, show superior results than PDMS for the extraction of



benzene and toluene, whereas for ethylbenzene and xylene only poly(ViPenIm-co-Sty)TFSI showed better results than PDMS.

While benzene showed very similar affinity for poly(ViBnIm-co-Sty)TFSI and poly(ViPenIm-co-Sty)TFSI, affording chromatographic areas of the same order of magnitude, for the remaining analytes the latter is substantially better yielding area increments of 1.6, 3.2 and 3.2 for toluene, ethylbenzene and xylene respectively. As generally observed in Figure 5, the  $\pi$ - $\pi$  interactions between aromatic groups result in an improved packed structure of the material and a decrease in free volume [56,57], favoring the efficiency of the poly(ViPenIm-co-Sty)TFSI-based fiber, however, this trend is not observed for benzene. On the other hand, the higher affinity of toluene, ethylbenzene and xylene for the latter fiber when compared to that of benzene could also be related with the pending methyl groups that increase the affinity with the pentyl moiety.

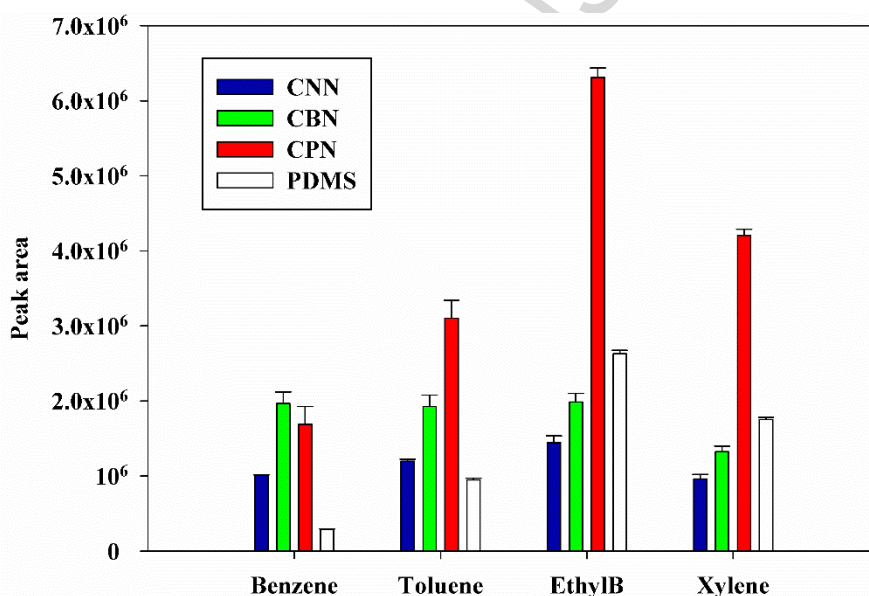


Figure 5 - Comparison of the performance of the prepared co-PILs-based fibers against the commercial PDMS fiber in terms of individual compound area. ( $T = 50^{\circ}\text{C}$ ,  $t = 15\text{ min}$ , 400 RPM, 50 mg/mL of NaCl and concentration:  $400\ \mu\text{g}\cdot\text{L}^{-1}$ ).

### 3.5 Validation, matrix effect and demonstration using poly(ViBnIm-co-Sty)TFSI fiber

The analytical performance of the poly(ViBnIm-co-Sty)TFSI SPME fiber in the HS-SPME analysis of 50 mg/mL BTEX aqueous solution is represented in Table 2. Linear regions with  $r^2$  varying from 0.9985 to 0.9993 were obtained between  $0.4$  and  $50\ \mu\text{g}\cdot\text{L}^{-1}$ .

The LODs using poly(ViBnIm-co-Sty)TFSI SPME fiber varied between 0.01 and 0.09  $\mu\text{g}\cdot\text{L}^{-1}$ . Superior results were obtained for HS-SPME of BTEX mixtures using poly(ViBnIm-co-Sty)TFSI SPME fiber here prepared compared to those reported in the literature for fibers made of mixtures of poly(1-vinyl-3-hexylimidazolium) and poly(1-vinyl-3-hexadecylimidazolium) with TFSI<sup>-</sup> and Cl<sup>-</sup> anions [58]. Also, lower LODs were obtained for ethylbenzene and xylene using the newly prepared poly(ViBnIm-co-Sty)TFSI fiber compared to those reported in the literature using poly 1-vinyl-3-octylimidazolium hexafluorophosphate [25]. Concerning the comparison of PILs versus ILs, such as [C<sub>8</sub>MIMPF<sub>6</sub>] [59], in HS-SPME, the use of PILs always results in a marked decrease of the overall LODs, proving their high potential as materials for HS-SPME. The fiber to fiber repeatability was studied under two different conditions: using the same fiber to analyze the same standard solutions in different days, and using different fibers to analyze equivalent standard solutions. The obtained results show variability values always lower than 10 %, even when using different fibers, confirming the high reproducibility of the spray-coating method.

Table 2 – Analytical results obtained for the poly(ViBnIm-co-Sty)TFSI SPME fiber ( $T = 30^{\circ}\text{C}$ ,  $t = 15\text{ min}$ , 400 RPM, 50 mg/mL of NaCl)

Sample name	Linear range $\mu\text{g}\cdot\text{L}^{-1}$	$r^2$	slope	LOD $\mu\text{g}\cdot\text{L}^{-1}$ (S/N=3)	Repeatability %		Recovery (% , n=3)	
					Same fiber	Different fiber	Spiked level $\mu\text{g}\cdot\text{L}^{-1}$	
							50	10
Benzene	0.4-500	0.9986	12115	0.09	5.6	8.2	102.2	101.2
Toluene	0.4-500	0.9985	12683	0.05	4.0	9.8	98.2	89.0
Ethylbenzene	0.4-500	0.9993	8013	0.01	4.7	7.3	72.1	67.0
Xylene	0.4-500	0.9993	5342	0.01	4.9	6.9	78.4	70.1

The efficiency of the poly(ViBnlm-co-Sty)TFSI SPME fiber was further demonstrated in the HS-SPME analysis of a BTEX spiked soil sample (no signals of the compounds under study were detected in the studied raw soil sample). Recoveries were accessed by performing extractions from the soil sample spiked with two different analytes concentrations,  $50 \mu\text{g}\cdot\text{L}^{-1}$  and  $10 \mu\text{g}\cdot\text{L}^{-1}$  ( $10 \mu\text{g}\cdot\text{g}$  and  $2 \mu\text{g}\cdot\text{g}$ ). Recoveries ranging from 72.1% to 102.2% for the sample with highest analyte concentration, and from 67.0% to 101.2% for the sample with the lowest analyte concentration, were obtained. A comparison with literature, where the presence of BTEX in soil was evaluated using a PDMS fiber with  $100 \mu\text{m}$  [60], reveals that poly(ViBnlm-co-Sty)TFSI fiber yields similar results, in terms of LODs and repeatability, compared with the commercial fiber used, that is 10 times thicker than ours. The lower recoveries obtained for ethylbenzene and xylene when compared to those of benzene and toluene, can be attributed to the high affinity of these analytes for the soil sample, in agreement with the higher octanol/water ( $\text{Log } K_{\text{ow}}$ ) values for ethylbenzene and xylene [50], that hampers their release from the soil.

#### 4 Conclusions

In this work, novel PILs based co-polymers were synthesized and SPME thin coatings were successfully prepared using a layer-by-layer expedite easy to use technique. The PIL structures were carefully designed to detect volatile aromatic compounds, namely benzene, toluene, ethylbenzene and xylene. Thus, imidazolium-based monomers were quaternized with aromatic and non-aromatic moieties, which were subsequently co-polymerized with styrene. The use of LbL technique to prepare SPME fibers allowed to prepare highly homogeneous very thin ( $<10 \mu\text{m}$ ) coatings. Excellent efficiencies were obtained for the newly prepared fibers in comparison with commercial PDMS fibers, emphasizing the role coating's chemical structure design to meet specificity in SPME. The high reusability of the fibers was attributed not only to the high thermal stability of the PIL co-polymers, but also to the fact that LbL technique produces coatings with high adhesion, making the whole fiber highly stable. In conclusion, PILs represent a highly tunable platform of polymers that clearly deserves to be further explored to prepare selective SPME fibers.

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ACCEPTED MANUSCRIPT

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