

*Supporting information*

## Expanding the applicability of poly(ionic liquids) in solid phase microextraction: pyrrolidinium coatings

David J. S. Patinha,<sup>1,2</sup> Liliana C. Tomé,<sup>1</sup> Mehmet Isik,<sup>3</sup> David Mecerreyes,<sup>3,4</sup> Armando J. D. Silvestre,<sup>2\*</sup> and Isabel M. Marrucho,<sup>1,2\*</sup>

<sup>1</sup> Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. Da Repúblida, 2780-157, Oeiras, Portugal; [davidpatinha@itqb.unl.pt](mailto:davidpatinha@itqb.unl.pt) (DJSP), [liliana.tome@itqb.unl.pt](mailto:liliana.tome@itqb.unl.pt) (LCT)

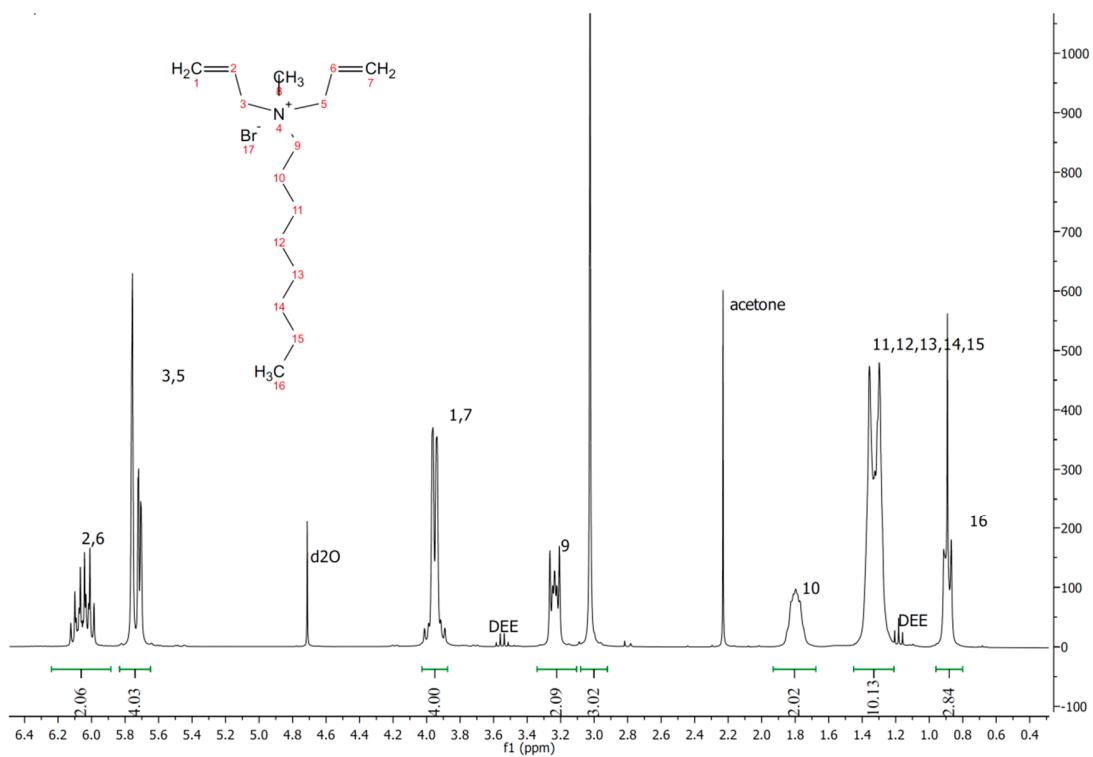
<sup>2</sup> CICECO - Aveiro Institute of Materials and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; [armsil@ua.pt](mailto:armsil@ua.pt) (AJDS)

<sup>3</sup> POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastian, Spain; [isik.mehmet@ehu.eus](mailto:isik.mehmet@ehu.eus) (MI), [david.mecerreyes@ehu.es](mailto:david.mecerreyes@ehu.es) (DM)

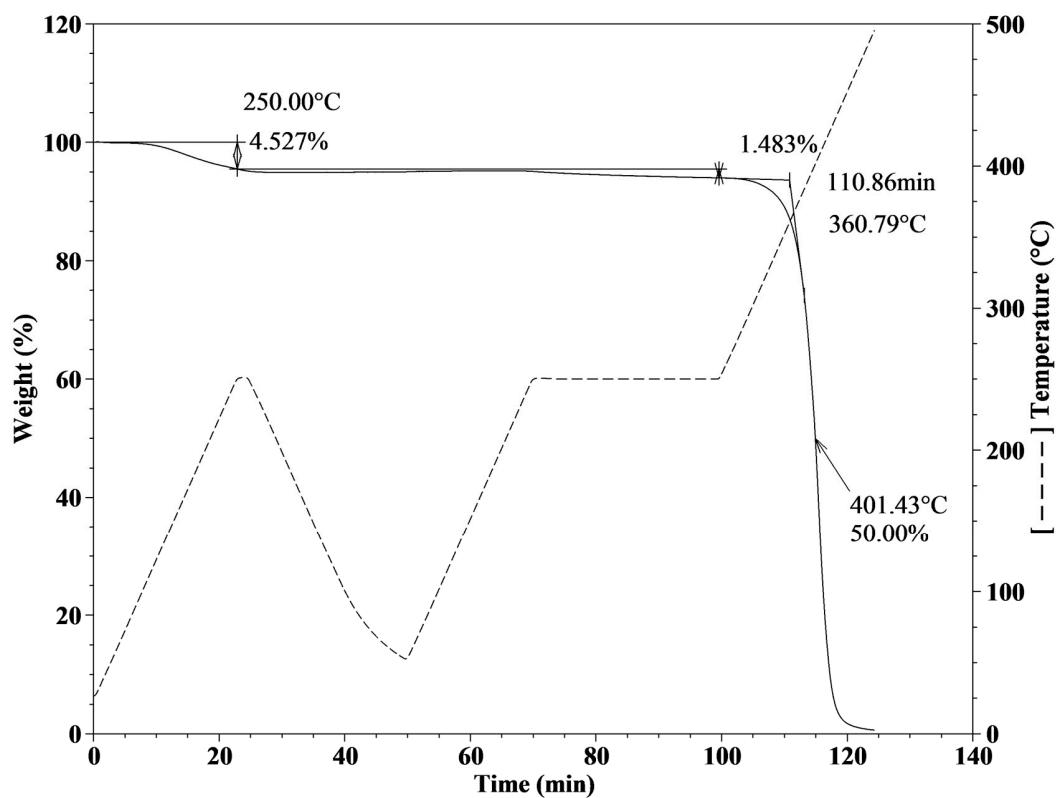
<sup>4</sup> IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain

<sup>5</sup> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal; [isabel.marrucho@tecnico.ulisboa.pt](mailto:isabel.marrucho@tecnico.ulisboa.pt) (IMM)

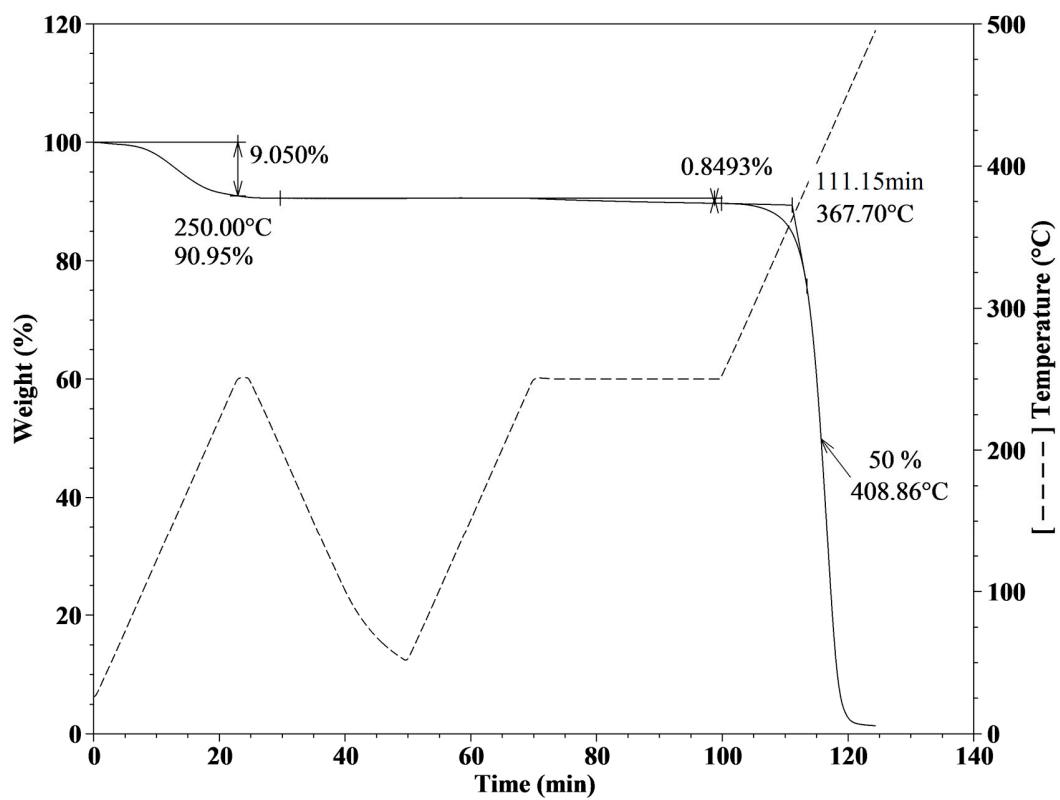
\* Correspondence: [armsil@ua.pt](mailto:armsil@ua.pt), Tel: +351 234 370711; [isabel.marrucho@tecnico.ulisboa.pt](mailto:isabel.marrucho@tecnico.ulisboa.pt); Tel: +351 21-4469724; fax: +351-21-4411277



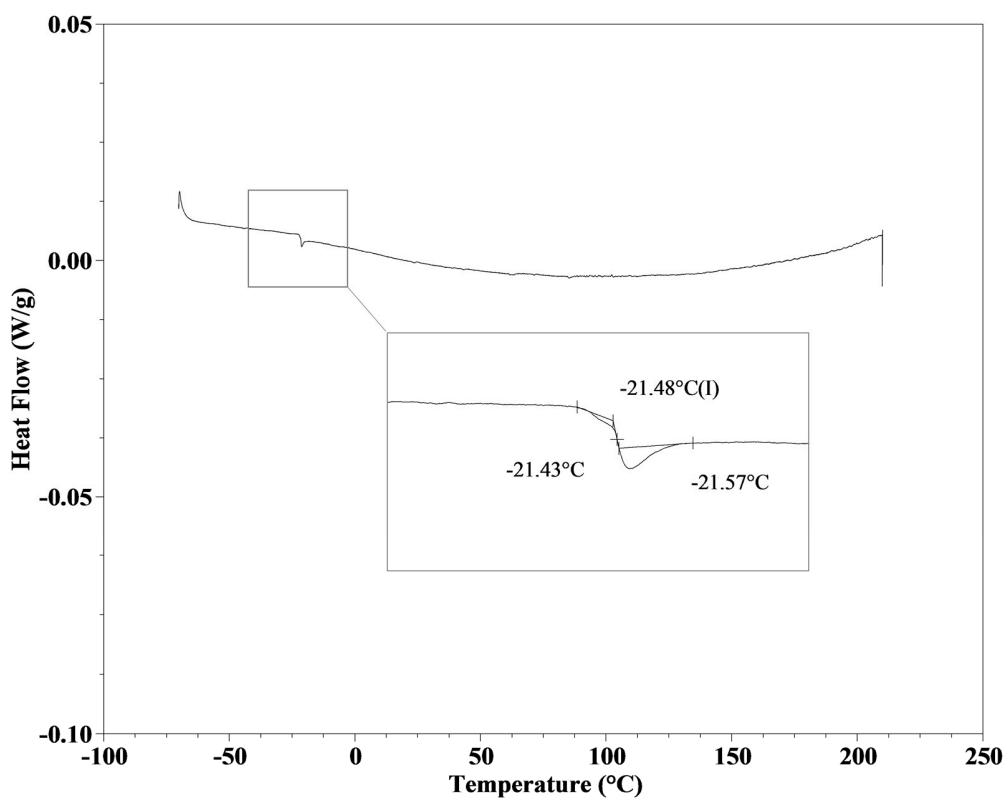
**Figure S1**  $^1\text{H}$  NMR data example of the synthesized diallylmethyoctyl bromide ( $[\text{DAMC}_8]\text{Br}$ ) ionic liquid monomer.  $\text{H}^1$  NMR assignments data for the three monomers: **[DAMC<sub>14</sub>][Br]** -  $^1\text{H}$  NMR (400 MHz, deuterated dimethyl sulfoxide ( $d_6\text{-DMSO}$ )):  $\delta$  0.67-0.89 (t, 3H),  $\delta$  1.01-1.37 (m, 22H),  $\delta$  1.56-1.81 (q, 2H),  $\delta$  3.06-3.22 (s, 3H),  $\delta$  3.22-3.37 (t, 2H),  $\delta$  4.05-4.29 (d, 4H),  $\delta$  5.56-5.70 (dd, 4H) and  $\delta$  5.84-6.05 (m, 2H). **[DAMC<sub>8</sub>][Br]** -  $^1\text{H}$  NMR (400 MHz, Deuterium oxide ( $D_2\text{O}$ )):  $\delta$  0.80-0.95 (t, 3H),  $\delta$  1.20-1.40 (m, 10H),  $\delta$  1.70-1.91 (q, 2H),  $\delta$  2.90-3.10 (s, 3H),  $\delta$  3.15-3.25 (t, 2H),  $\delta$  3.90-4.10 (d, 4H),  $\delta$  5.70-5.85 (d, 4H) and  $\delta$  5.90-6.20 (m, 2H). **[DAMC<sub>2</sub>][Br]** -  $^1\text{H}$  NMR (400 MHz,  $D_2\text{O}$ ):  $\delta$  1.25-1.35 (t, 3H),  $\delta$  2.85-2.95 (s, 3H),  $\delta$  3.25-3.35 (q, 3H),  $\delta$  3.75-3.90 (d, 4H),  $\delta$  5.56-5.70 (d, 4H) and  $\delta$  5.84-6.05 (m, 2H).



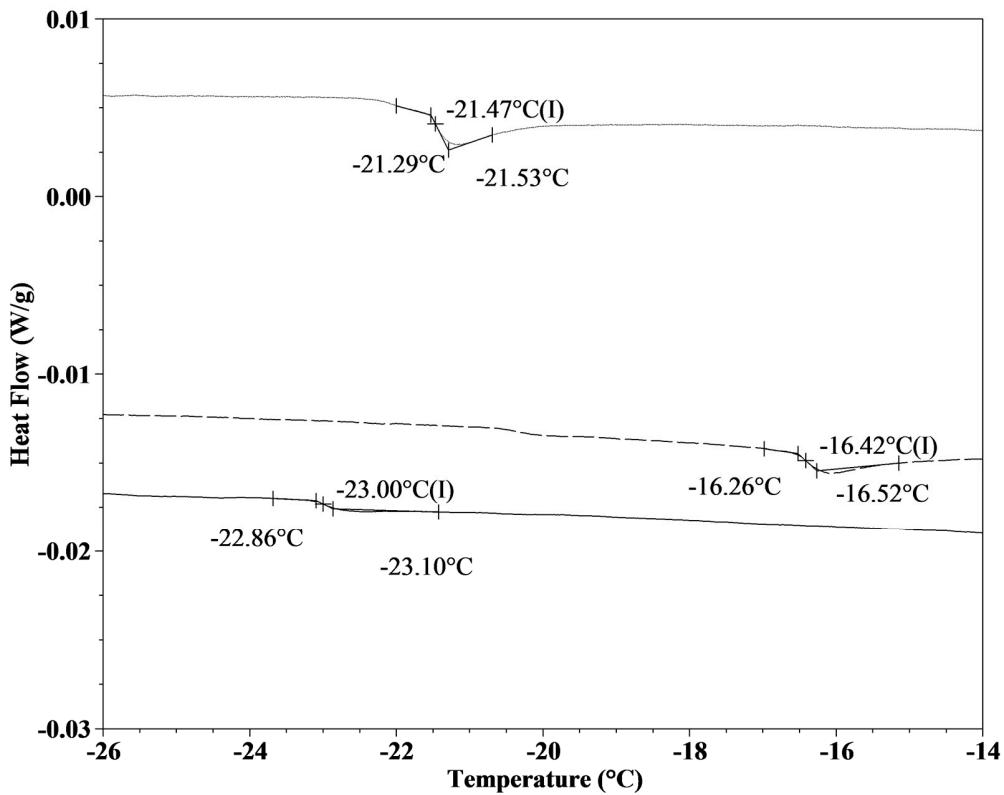
**Figure S2** – Thermo gravimetric analysis data of the crosslinked poly(methyloctyl pyrrolidinium) TFSI (pD8) under N<sub>2</sub> atmosphere.



**Figure S3** – Thermo gravimetric analysis data of the crosslinked poly(methylethyl pyrrolidinium) TFSI (pD2) under N<sub>2</sub> atmosphere.



**Figure S4** – Differential Scanning Calorimetry data of the crosslinked poly(methyltetradecyl pyrrolidinium) TFSI (pD14).



**Figure S5** – Differential Scanning Calorimetry data of the crosslinked polymers. From top to bottom: pD14, pD8 and pD2.

**Table S1** – Glass transition temperatures and decomposition temperatures obtained for the three crosslinked polymers.

Polymers	$T_g / ^\circ C$	$T_d / ^\circ C$
pD14	-21.47	368
pD8	-16.42	361
pD2	-23.00	355

**Table S2** – Representation of the linear range and limits of detection for the analytes under study for the pD14 fiber. ( $T = 45 ^\circ C$ ,  $t = 15$  min, 2.5 wt. % of NaCl, 200 rpm).

Sample name	$\mu g \cdot L^{-1}$ ( $\times 10^3$ )	$r$	slope	LOD	
				$\mu g \cdot L^{-1}$	
				pD14	PDMS
1-butanol	5-100	0.999	55±0.7	200	200
3-pentanone	2.5-100	0.989	281±11	200	200

<i>2-hexanone</i>	0.02-100	0.993	595±15	2	2
<i>cyclopentanone</i>	2.5-100	0.991	72±2.4	200	200
<i>2-heptanol</i>	0.25-100	0.996	387±7.9	5	20
<i>2-heptanone</i>	0.02-100	0.994	1332±29	1	2
<i>1-octanol</i>	0.02-100	0.993	1866±44	1	2
<i>benzyl alcohol</i>	0.5-100	0.999	134±1.2	20	50
<i>DL-menthol</i>	0.25-100	0.987	1044±32	0.2	2
<i>(1R)-(+)-camphor</i>	0.02-100	0.998	441±5.8	0.5	2
<i>(S)-(-)-β-citronellol</i>	0.02-100	0.999	1322±12	0.2	2