# Supporting Information for: Self-catalysed coupling between Brønsted-acidic imidazolium salts and epoxy-based materials: a theoretical/experimental study

Magdalena Perchacz,<sup>a,b</sup> Libor Matějka,<sup>a</sup> Rafał Konefał,<sup>a</sup> Leandro Seixas,<sup>c</sup> Sebastien Livi,<sup>d</sup> Jérôme Baudoux, <sup>e</sup> Hynek Beneš<sup>a\*</sup> and Ricardo K. Donato<sup>a\*</sup>

<sup>a.</sup> Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Prague 6,Czech Republic.

<sup>b.</sup> Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland.

<sup>c.</sup> MackGraphe - Graphene and Nanomaterials Research Centre, Mackenzie Presbyterian University, Rua da Consolação 896, São Paulo - SP - 01302-907, Brasil.

<sup>d.</sup> Université de Lyon, F-69003, Lyon, France; INSA Lyon, F-69621, Villeurbanne, France; CNRS, UMR 5223, Ingénierie des Matériaux Polymères.

<sup>e.</sup> Laboratoire de Chimie Moléculaire et Thio-organique, ENSICAEN, Université de Normandie, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen, France.

# \* Corresponding authors:

Ricardo Keitel Donato; Phone: +420 296 809 293, E-mail: <u>donato@imc.cas.cz</u> Hynek Beneš; Phone: +420 296 809 313, E-mail: <u>benesh@imc.cas.cz</u>

This Supporting Information for publication contains 18 pages and 18 figures.

## Imidazolium salts

#### Synthesis protocols

# 1,3-bis(4-carboxyphenyl)imidazolium chloride (Benzoic)<sub>2</sub>ImCl) and 1,3-bis(3,5dicarboxyphenyl)imidazolium chloride (Isophtalic)<sub>2</sub>ImCl) synthesis

For the 1,3-bis(4-carboxyphenyl)imidazolium chloride ((Benzoic)<sub>2</sub>ImCl) synthesis, to a solution of 4-aminobenzoic acid (5.00 g, 36.5 mmol, 2.0 eq.) in dry methanol (20 mL) was added formic acid (2 drops) followed by dropwise addition of a 39 % aqueous solution of glyoxal (1.99 mL, 17.40 mmol, 1.0 eq.). The solution was stirred at ambient temperature for 24 h. The white solid formed was collected by filtration, washed with cold methanol, and dried in air. The product N,N'-bis(4-carboxyphenyl)ethylenediimine was obtained as a white solid (3.93 g, 79 %) and used for the next step without any purification. To a solution of N,N'-bis(4carboxyphenyl)ethylenediimine (3.93 g, 13.3 mmol, 1.0 eq.) in anhydrous THF (11 mL) under an argon atmosphere was added paraformaldehyde (498 mg, 16.6 mmol, 1.25 eq.) and 12 N HCl (1.65 mL, 20.00 mmol, 1.5 eq.) in dioxane (3.2 mL) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The precipitate formed was collected by filtration, washed with Et<sub>2</sub>O, and dried under vacuum. The product was obtained as a yellow solid (3.09 g, 75 %). (<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub> – Fig. S1) δ 13.42 (bs, 2H), 10.64 (s, 1H), 8.71 (d, J = 1.5 Hz, 2H), 8.24 (d, J = 8.7 Hz, 4H), 8.10 (d, J = 8.7 Hz, 4H). <sup>13</sup>C NMR (126 MHz, DMSO-d6 – Fig. S2) δ 166.2, 137.7, 135.5, 132.1, 131.2, 122.1, 121.9. IR (neat) cm<sup>-1</sup> 3124, 2974, 2810, 2599, 2456, 1704, 1556, 1392, 1231, 1175. Mp: > 400 °C. HRMS m/z (ESI): calculated for  $C_{17}H_{13}N_2O_4$  [M]+: 309.0875, found: 309.0878.)

For the 1,3-bis(3,5-dicarboxyphenyl)imidazolium chloride ((Isophtalic)<sub>2</sub>ImCl) synthesis, to a solution of 5-aminoisophtalic acid (5.26 g, 27.60 mmol, 2.0 eq.) in dry methanol (11 mL) was added formic acid (2 drops) followed by dropwise addition of a 39 % aqueous solution of glyoxal (1.62 mL, 13.80 mmol, 1.0 eq.). The solution was stirred at ambient temperature for 24 h. The white solid formed was collected by filtration, washed with cold methanol, and dried in air. The product N,N'-bis(3,5-dicarboxyphenyl)ethylenediimine was obtained as a white solid (3.33 g, 63 %) and used for the next step without any purification. To a solution of N,N'bis(3,5-dicarboxyphenyl)ethylenediimine (3.33 g, 8.66 mmol, 1.0 eq.) in anhydrous THF (5.13 mL) under an argon atmosphere was added paraformaldehyde (325 mg, 10.82 mmol, 1.25 eq.) and 12 N HCl (1.08 mL, 12.99 mmol, 1.5 eq.) in dioxane (2.05 mL) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The precipitate formed was collected by filtration, washed with Et<sub>2</sub>O, and dried in vacuum. The product was obtained as a yellow solid (3.00 g, 80 %). (<sup>1</sup>H-NMR (500 MHz, DMSO-d6 – Fig. S3)  $\delta$  13.93 (bs, 4H), 10.70 (s, 1H), 8.76 (d, J = 1.5 Hz, 2H), 8.68 (d, J = 1.3 Hz, 4H), 8.63(t, J = 1.3 Hz, 2H). <sup>13</sup>C-NMR (126 MHz, DMSO-d6 – Fig. S4)  $\delta$  165.5, 136.6, 135.4, 133.5, 130.8, 127.0, 122.3. Mp: > 400 °C. HRMS m/z (ESI): calculated for C<sub>19</sub>H<sub>11</sub>N<sub>2</sub>O<sub>8</sub> [M]-: 395.0515, found: 395.0510.



### NMR characterization

Fig. S1. <sup>1</sup>H-NMR of (Benzoic)<sub>2</sub>ImCl.



Fig. S2. <sup>13</sup>C-NMR of (Benzoic)<sub>2</sub>ImCl.



Fig. S3. <sup>1</sup>H-NMR of (Isophtalic)<sub>2</sub>ImCl.



Fig. S4. <sup>13</sup>C-NMR of (Isophtalic)<sub>2</sub>ImCl.



Fig. S5. MALDI-TOF spectra of the neat monofunctional ILs used in this study.



Fig. S6. MALDI-TOF spectra of the neat di- and tetrafunctional ILs used in this study.

# **Reaction systems**

# NMR characterization

The <sup>1</sup>H-NMR spectrum of the product obtained in the reaction between PGE and CH<sub>2</sub>CO<sub>2</sub>HMImCl at 100°C (Fig. S7) presents a total consumption of oxirane rings (lack of peak at  $\delta$  = 2.8 ppm related to unreacted epoxy ring).



**Fig. S7.** <sup>1</sup>H-NMR spectrum of PGE epoxide ring-opening at 100 °C, induced by CH<sub>2</sub>CO<sub>2</sub>HMImCl. Signals were assigned as n' when the same proton presented different field shifted signals between reactant and product or between different adducts.

The <sup>1</sup>H-NMR spectrum of the product obtained in the reaction between PGE and C<sub>3</sub>H<sub>6</sub>CO<sub>2</sub>HMImCl at 100°C (Fig. 8), demonstrates that the IL promoted the total consumption of PGE's oxirane rings (no signal at  $\delta$  = 2.8 ppm).



**Fig. S8.** <sup>1</sup>H-NMR spectrum of PGE epoxide ring-opening at 100 °C, induced by  $C_3H_6CO_2HMImCI$ . Signals were assigned as n' when the same proton presented different field shifted signals between reactant and product or between different adducts

The <sup>1</sup>H-NMR spectrum of the product obtained in the reaction between PGE and  $(CH_2CO_2H)_2$ MImCl at 100 °C indicated ~ 98 % of epoxide ring-opening. The two main products (mono- and di-substituted IL) of the reaction were found and their structure and signal assignment are presented (Fig. S9). The ratio between the mono- (6, 7, 8, 9, 10) and the di-substituted (6', 7', 8', 9', 10') products was calculated from the ratios of the integrals of peaks 8:8' and 6:6', and amounted to 30:70 respectively.



**Fig. S9.** <sup>1</sup>H-NMR spectrum of PGE epoxide-ring opening at 100 °C, induced by  $(CH_2CO_2H)_2MImCI$ . Signals were assigned as n' when the same proton presented different field shifted signals between reactant and product or between different adducts.

The <sup>1</sup>H-NMR spectrum of the product obtained in the reaction between PGE and  $(Benzoic)_2$ ImCl IL showed ~ 98% of epoxide ring-opening and the two main products of reaction were the mono- and di-substituted IL (Fig. S10). The ratio between mono- (7', 8', 9', 10') and di-substituted products (7, 8, 9, 10) was calculated from the rations between the integrals of the peaks 7':7, and amounted to 22:78 respectively.



**Fig. S10.** <sup>1</sup>H-NMR spectrum of PGE epoxide ring opening at 100 °C, induced by (Benzoic)<sub>2</sub>ImCl IL. Signals were assigned as n' when the same proton presented different field shifted signals between reactant and product or between different adducts

The <sup>1</sup>H-NMR spectrum of PGE epoxide-ring opening at 100 °C induced by (Isophtalic)<sub>2</sub>ImCl IL is shown in Fig. S11 and the chemical structure of tetra-substituted reaction product with signal assignment is depicted. In this case, about 30% of epoxide groups remained unreacted after the process (highlighted peaks around 3 ppm). Due to the large amount of signals in the  $\delta \approx 7.5$ -9 ppm area of the spectrum, it was assumed that the reaction produced a mixture of mono-, di-, tri- and tetra- substituted products, which, together with the neat IL, presented the characteristic peaks at the low field region.



**Fig. S11.** <sup>1</sup>H-NMR spectrum of PGE epoxide-ring opening at 100 °C, induced by (Isophtalic)<sub>2</sub>ImCl IL.

## **FTIR characterization**



**Fig. S12.** FTIR spectra (wide wavenumber) presenting the initial (black solid line) and final (red dashed line) state of the reaction between PGE and the different monofunctional ILs. In the spectrum of the reaction between PGE and  $C_3H_6CO_2HMImCl$  at 100°C, a green dotted line curve is presented for comparison with the initial state of this same reation at 25°C.



**Fig. S13.** FTIR spectra (wide wavenumber) presenting the initial (black solid line) and final (red dashed line) state of the reaction between PGE and the different bi- and tetrafunctional ILs.



**Fig. S14.** MALDI-TOF spectra of the final products obtained at 25°C after 48h ( $CH_2CO_2HMImCI$  and  $CH_2CO_2HMImNTf_2$ ) and at 100°C after 2h ( $CH_2CO_2HMImCI$ ) of the reaction between PGE and ILs.



**Fig. S15.** MALDI-TOF spectra of the final products obtained after 48h ( $C_3H_6CO_2HMImCl$  at 25°C) and 2h ( $C_3H_6CO_2HMImCl$  at 100°C) of the reaction between PGE and ILs.



**Fig S16.** MALDI-TOF spectra of the final products obtained after 48h ( $(CH_2CO_2H)_2$ ImCl at 25°C) and 12h ( $(CH_2CO_2H)_2$ ImCl at 100°C) of the reaction between PGE and ILs. Peaks assigned with (\*) are derived from the DHB matrix.



**Fig S17.** MALDI-TOF spectra of the final products obtained after 12h of the reaction between PGE and the ILs  $(Benzoic)_2$ ImCl and  $(Isophtalic)_2$ ImCl, at 100°C. Peaks assigned with (\*) are derived from the DHB matrix, and the peak assigned in red (880 m/z) could not be identified.



**Fig S18.** Correlation between the ILs' chemical hardness with the epoxy consumption kinetics (FTIR) and coupling product yield (MALDI-TOF) for their reaction with PGE at different temperatures.