



## Poly(ionic liquid)-based aerogels for continuous-flow CO<sub>2</sub> upcycling

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### ABSTRACT

The atmospheric concentration of CO<sub>2</sub> is rising at an alarming pace, creating a pressing need for new and sustainable materials capable of capture and conversion. Poly(ionic liquid)s (PILs) are particularly effective catalysts for processes at or near atmospheric pressure. PILs industrial application poses challenges due to the low porosity of PIL, the limited batch conversion capacity, and the difficulties in reuse. To overcome these limitations, we herein propose the use of *AEROPILs* catalysts obtained from the integration of PILs in chitosan-based aerogels. These cost-effective highly porous materials have unique and tuneable porous properties making them not only ideal sustainable CO<sub>2</sub> sorbents but also promising heterogeneous catalysts. While *AEROPILs* show moderate yields for CO<sub>2</sub> conversion in batch mode, high catalytic activity was achieved when *AEROPILs* were used to catalyse the CO<sub>2</sub> cycloaddition reaction to epoxides in packed-bed reactors operated under continuous flow. The catalytic activity and stability were maintained over 60 h without activity loss, and high productivity (space-time yield of 21.18 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup>). This research reveals the pioneering use of *AEROPILs* to efficiently upcycle CO<sub>2</sub> into cyclic carbonate under a continuous flow setup.

### 1. Introduction

Global warming demands the globalisation of CO<sub>2</sub> capture and utilisation (CCU) technologies [1]. The use of CO<sub>2</sub> as a C1 building block for synthesising alternative chemical products, such as cyclic carbonates, using epoxides is regarded as an environmentally sound and proficient strategy. Cyclic carbonates can be used as polymer precursors, aprotic polar solvents, fuel additives, or electrolytes in batteries [2–6]. In recent times, there has been a notable emergence of poly(ionic liquid)

(PILs), which combine the attributes of ionic liquids (ILs) and the features of polymers. ILs are salts encompassing organic cations conjoined with organic or inorganic anions, with melting points below 100 °C. PILs feature a substantial macromolecular architecture that imparts augmented mechanical robustness, heightened manipulability in processes, increased durability, and precise governance of meso to nanostructural attributes. The elevated processability exhibited by these compounds holds pertinence in industrial domains encompassing electrochemistry, analytical chemistry, biosciences, catalysis, sensors,

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magnetism, energy conversion, and environmental applications [7–10]. PILs have been found to increase CO<sub>2</sub> sorption capacity, but materials with tailored porosity remain a significant challenge. Therefore, porous PILs emerged as promising materials for CO<sub>2</sub> capture (CC) and catalysis due to their high surface area, tuneable pore size, and selective functional groups [11–17]. The development of porous substrates derived from PILs has predominantly revolved around ionic porous organic polymers (IPOP)s and, more contemporarily, molecularly imprinted polymers and aerogels. This progression has generated the formulation of innovative substances merging PILs with porosity, thereby enhancing efficacy and selectivity. Recent advances in developing porous PILs highlight their potential for addressing environmental and energy-related challenges [18–22].

Solid catalysts can be easily applied in fixed-bed reactors, continuous flow systems, or others suitable for large-scale processes [2,23]. In contrast to batch processes, continuous flow catalytic systems offer several advantages. They favour mixing, handle heat transfer more effectively, optimise catalytic performance by enhancing phase interactions, and boost productivity through continuous reagent feeding and product removal from the reactor. Overall, they offer a more reliable, scalable, secure, and efficient approach for conducting chemical reactions, making them a highly appealing technology for industrial applications [24–28].

In previous works, Iglesias *et al.* [6] and Valverde *et al.* [28] reported cycloadditions of CO<sub>2</sub> to produce cyclic carbonates using 3D printed reactors and PILs in continuous flow. However, the reported reactors lack porosity, and catalysis only occurs on the surface of the material. In the present work, AEROPILs were optimized to catalyse CO<sub>2</sub> not only at the surface but also on the core, exhibiting an increased catalytic load with high stability. Chitosan-based aerogels were envisioned to achieve this.

Aerogels are lightweight nanostructured materials with high porosity and specific surface area. Silica aerogels are already being used for CC [29,30]. However, formulating aerogels from biopolymers such as chitosan is advantageous as it has basic nitrogen groups that can enhance the interactions with acidic CO<sub>2</sub> [31]. Besides being biodegradable, chitosan has the advantage of using biomass residue from processed seafood products as a starting material, increasing profitability by recycling waste [32–34]. Chitosan aerogels and their composites are innovative and eco-friendly materials characterized by significant porosity, extensive specific surface area, excellent

biodegradability, biocompatibility, and widespread availability. The synthesis of chitosan aerogels takes advantage of the polymer's functional groups to improve physicochemical properties, usually through colloidal formation from molecular precursors, or the use of particle-based precursors. Both methods impact the aerogel's properties and factors such as precursor concentration, crosslinkers, and drying procedures play crucial roles, which are vital for applications ranging from catalysis to wastewater treatment [22]. The amine groups in chitosan's structure contribute to its versatility, allowing for functionalization through graft reactions and ionic interactions due to their basic nature. While surface area and porosity are crucial for CO<sub>2</sub> capture and fixation, chitosan itself has a limited surface area and a crystalline structure. Therefore, chitosan composites with porous materials having high specific surface area enhance the effectiveness in CO<sub>2</sub> capture and fixation. This is supported by research indicating that the abundant amine groups in chitosan facilitate the adsorption of CO<sub>2</sub> molecules, but its lower surface area limits the adsorption capacity [35,36].

Previously, we described for the first time a simple and economically viable methodology for producing AEROPILs (composite aerogel beads with PILs and chitosan), and tested them for CC [37]. Here, we report, for the first time, the use of AEROPILs (Fig. 1) in continuous flow packed-bed reactors in an automatised flow platform that enabled the fast screening of different conditions. AEROPILs produced a highly efficient catalytic system for CO<sub>2</sub> cycloadditions to epoxides, moving a step closer to industrial applications.

## 2. Materials and methods

### 2.1. Material

Chitosan (deacetylation degree 75–85 %, viscosity 20–300 mPa.s, Mw 50–190 kDa), glutaraldehyde solution (grade II, 25 wt % in H<sub>2</sub>O), 1-vinylimidazole (≥99 % purity), 4-vinylbenzyl chloride (90 % purity), 2-bromoethylamine hydrobromide (99 % purity), poly(diallyldimethylammonium) chloride (P2) solution (20 wt % in H<sub>2</sub>O, viscosity 250–500 mPa.s, average Mw 100–200 kDa), triethylamine (≥99.5 % purity), tributylphosphine (≥93.5 % purity), styrene oxide (97 % purity) and epichlorohydrin (≥99 % purity) were supplied by Sigma-Aldrich (St. Louis, MO, USA). Ethylene glycol diglycidyl ether (EGDE) mixture and 1,2-butylene oxide (99 % purity) were acquired

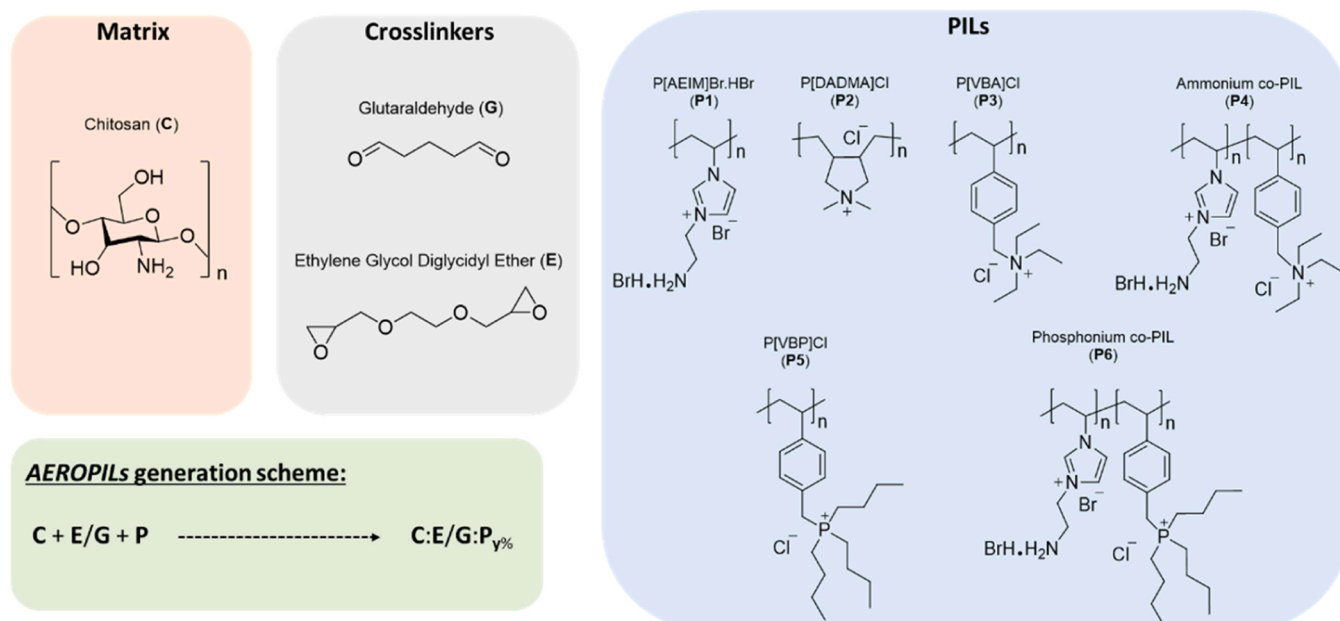


Fig. 1. Chemical structures of the matrix (C), crosslinkers (E or G) and PILs (P) in AEROPILs formulations.

from TCI Chemicals (Tokyo, JP). 2,2'-Azobis(2-methylpropionitrile) (AIBN) was acquired from Glenthams Life Sciences (Corsham, UK). Glacial acetic acid, isopropanol (IPA), and absolute ethanol (EtOH) were acquired from VWR (Radnor, PA, USA). NaOH (98 % purity) was acquired from Panreac (Barcelona, Spain). DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub> were acquired from Euriso-top (Saint-Aubin, France). Water was purified using reverse osmosis (resistivity > 18 MΩ.cm, Milli-Q, Millipore®, Madrid, Spain). Carbon dioxide (99.8 % purity) was supplied by Nippon Gases (Madrid, Spain). Carbon dioxide (99.998 % purity) supplied by Air Liquid was used in the catalytic reactions. He 4.6 and CO<sub>2</sub> 4.5, supplied by Linde Portugal, were used in the thermogravimetric analysis (TGA) and CO<sub>2</sub> capture experiments. All chemicals were used without further purification.

## 2.2. IL and PIL synthesis

ILs *p*-vinylbenzyltriethylammonium chloride ([VBA]Cl), *p*-vinylbenzyltributylphosphonium chloride ([VBP]Cl) and 1-aminoethylimidazolium bromide hydrobromide ([AEIM]Br.HBr) were synthesised and characterised as outlined in Section 1 (Figure S.1) and Section 4 of the Supporting Information. PILs poly(1-aminoethylimidazolium bromide hydrobromide) (**P1**), poly(*p*-vinylbenzyltriethylammonium) chloride (**P3**), poly(*p*-vinylbenzyltributylphosphonium) chloride (**P5**) and copolymer<sub>50/50</sub> poly(*p*-vinylbenzyltriethylammonium chloride-co-aminoethylimidazolium bromide hydrobromide) (**P4**) and copolymer<sub>50/50</sub> poly(*p*-vinylbenzyltributylphosphonium chloride-co-aminoethylimidazolium bromide hydrobromide) (**P6**) were synthesised and characterised as outlined in Section 2 (Figure S.2) and Section 4 of the Supporting Information.

## 2.3. Chitosan aerogel beads formulation

### 2.3.1. Chitosan hydrogels formulation

Hydrogel particles were synthesised using the sol-gel approach, following the methodology delineated in López-Iglesias *et al.* [32] and Barrulas *et al.* [37]. Initially, a 2.5 % w/v chitosan solution was prepared by dissolving chitosan in Milli-Q water with a 1 % (v/v) acetic acid content, resulting in a 30 mL solution volume. The mixture underwent mechanical agitation for 8 h, after which it was allowed to settle until the cessation of gas bubble formation occurred during the stirring process.

Chitosan (C) solutions were then prepared with several crosslinkers. The addition of either glutaraldehyde (G) or EGDE (E) was evaluated, as well as the use of heating after the crosslinker addition (50 °C). Glutaraldehyde was added at a concentration previously reported in the literature – 0.30 % w/w (glutaraldehyde/chitosan) to avoid leakage of the PILs [37]. Chitosan solutions with different loadings of PILs: **P1**, **P2**, **P3**, and **P4** (30 %, 50 % and 80 % w/w with respect to chitosan), and glutaraldehyde (0.30 %) were used to produce beads. Also, chitosan solutions with different loadings of **P4**, **P5**, **P6**, and **P2** (50 % and 80 % w/w with respect to chitosan) and with EGDE 32 % w/w (EGDE/chitosan) directly incorporated were used to produce beads. The solutions were then stirred for 15 min at 50 °C according to the procedure described by Martucci *et al.* [38] to activate the crosslinker. Chitosan solutions with different loadings of PILs **P1**, **P2** and **P4** (30 % w/w with respect to chitosan) and without crosslinker directly incorporated were also used to produce beads. In all instances, PILs were previously solubilised within a 3 mL aqueous volume, which was subsequently subtracted from the overall water volume employed in the chitosan solution formulation. Following this, aliquots of the resultant chitosan solution (ranging from 15 to 18 mL) were incrementally introduced via a plastic syringe (with a nozzle diameter of 2 mm) into a 100 mL gelation bath containing 1 mol L<sup>-1</sup> NaOH. The infusion was maintained at a constant flow rate of 0.65 mL min<sup>-1</sup>, facilitated by a syringe pump (AL-1000, World Precision Instruments, Sarasota, FL, USA). The vertical distance from the syringe to the bath's surface was approximately 16.5 cm. The

droplets solidified upon contact with the NaOH solution, producing hydrogel beads. The time between the addition of the crosslinker and the prilling process to prepare the beads in the NaOH solution was approximately 15 min. These beads were retained within the gelation bath for either 24 h without subsequent treatment or for 2 h when subsequent steps of crosslinking or heating were administered. So, after gelation, some sample variations were subjected to heating with a water bath (blanks) or with an aqueous EGDE solution (ratio 1:1 EGDE:NH<sub>2</sub>) at 50 °C for 3 h, according to procedures described in the literature [39–41]. The complete table with the prepared *AEROPILs* is outlined in Section 6 (Tables S.2 and S.3) of the Supporting Information.

### 2.3.2. Solvent exchange

The gel beads were gently decanted from the beaker containing the gelation bath and promptly supplanted with 100 mL of absolute EtOH. Following a duration of 4 h, a subsequent solvent substitution was enacted utilising a comparable volume of EtOH to eliminate residual water content from the gel matrices.

### 2.3.3. Supercritical extraction of the gel solvent

The alcogel particles were inserted into Whatman paper cartridges and subsequently introduced either into the 400 mL autoclave module of the supercritical drying apparatus from Eurotechnica GmbH, Barga-teheide, Germany or into the 300 mL autoclave module of a custom-made equipment from Paralab, Valbom, Portugal (Figure S.12). Previously, 100 mL of EtOH were introduced into the chamber, ensuring the prevention of premature EtOH evaporation from the alcogels before the achievement of supercritical conditions within the CO<sub>2</sub>-EtOH mixture [32,42]. A continuous flow of scCO<sub>2</sub> at a rate of 15 g min<sup>-1</sup> was directed through the autoclave housing the gels, which were maintained at an operational temperature of 40 °C and a pressure of 120 bar for a duration of 3.5 h.

Herein, *AEROPILs* samples are addressed as in the general symbology: **C:G:Mx:P<sub>y</sub>%** (where x is the methodology used for extra processing procedures and y is the percentage of PIL added with respect to chitosan); the terms **M1** (methodology associated with the crosslinker EGDE, represented as E, directly incorporated), **M2** (E incorporated into the aqueous bath), **M3** (aqueous bath subjected to heat) or **M4** (E incorporated into the aqueous bath subjected to heat) also appear related to extra processing procedures.

A compilation of the *AEROPILs* abbreviations in use throughout the manuscript is presented in Table 1.

**Table 1**  
List of abbreviations.

Abbreviations	Meaning
C	Chitosan
E and EGDE	Ethylene glycol diglycidyl ether
G	Glutaraldehyde
Mx	Methodology for extra processing, where x = 1, 2, 3, or 4
M1	Methodology associated with the crosslinker EGDE directly incorporated
M2	Methodology with EGDE incorporated into the aqueous bath
M3	Methodology with aqueous bath subjected to heat
M4	Methodology with EGDE incorporated into the aqueous bath subjected to heat
p	PIL
P <sub>y</sub> %	y% w/w with respect to chitosan
<b>P1</b>	Poly(1-aminoethylimidazolium bromide hydrobromide)
<b>P2</b>	Poly(diallyldimethylammonium) chloride
<b>P3</b>	Poly( <i>p</i> -vinylbenzyltriethylammonium) chloride
<b>P4</b>	Copolymer <sub>50/50</sub> poly( <i>p</i> -vinylbenzyltriethylammonium chloride-co-aminoethylimidazolium bromide hydrobromide)
<b>P5</b>	Poly( <i>p</i> -vinylbenzyltributylphosphonium) chloride
<b>P6</b>	Copolymer <sub>50/50</sub> poly( <i>p</i> -vinylbenzyltributylphosphonium chloride-co-aminoethylimidazolium bromide hydrobromide)

## 2.4. Batch catalytic cycloaddition of CO<sub>2</sub> to epoxides

**AEROPILs – Reaction conditions.** In a typical experiment, the epoxide substrate (1.4 mmol, 100 mg - 1st condition – or 829 mg to 1382 mg depending on the substrate, 11.5 mmol - 2nd condition) and the AEROPIL (100 mg) was added in a stainless-steel reactor (45 mL), which was flushed with CO<sub>2</sub> for three times before stirring under the appointed CO<sub>2</sub> atmosphere (10 bar). The reaction mixture was stirred under a CO<sub>2</sub> atmosphere at 135 °C for 72 h. The yield was determined by the <sup>1</sup>H NMR data (Section 8.2 of the Supporting Information).

## 2.5. Continuous flow catalytic cycloaddition of CO<sub>2</sub> to epoxides

In a typical catalytic reaction, the reaction mixture consisted of a solution of 1 M of epichlorohydrin in IPA. The reaction was conducted using a Vapourtec flow system, which comprised several key components: the 'R-4 Flow Reactor Heater' module, the 'R2S Pumping Module' equipped with two peristaltic pumps, and the 'R2C Pumping Module' featuring two HPLC type pumps. Additionally, the system was connected to an autosampler to facilitate automated sample collection. All these modules and systems were remotely controlled via a UA-OPC communication protocol, utilizing software developed in Python for this purpose. This mixture was pumped at 0.05 mL min<sup>-1</sup> using an HPLC pump. Simultaneously, CO<sub>2</sub> was pumped at a nominal flow rate of 0.20 mL min<sup>-1</sup> and mixed with the liquid phase using a T-mixer. The actual CO<sub>2</sub> flow rate was determined to be 41 μL min<sup>-1</sup>, considering factors such as gas compression and solubility calculations in the solvent at a temperature of 25 °C. The CO<sub>2</sub> was directly pumped into a back pressure regulator operating at a nominal flow rate of 0.20 mL min<sup>-1</sup>. This regulator aimed to maintain a constant gas flow into the T-mixer, ensuring a consistent pressure line for the gas-liquid mixture. The experimental flow rate of CO<sub>2</sub> was determined to be 41 μL min<sup>-1</sup> by calculating the difference between the total flow rate (of the gas-liquid mixture) and the flow rate of the incompressible liquid in a known tubing volume and selected time. Considering the system's pressure conditions, this calculation yielded the actual CO<sub>2</sub> inlet flow rate. The reaction was conducted within a packed bed reactor containing the catalysts with C:E:M1:P2<sub>80%</sub>, C:E:M1:P5<sub>50%</sub>, C:E:M1:P6<sub>50%</sub>, C:G:P4<sub>30%</sub> and the control aerogel, operating at 120 °C and 6 bar pressure, with a residence time ranging from 98 to 104 min. The conversion and selectivity of CO<sub>2</sub> cycloaddition reactions were calculated by <sup>1</sup>H NMR spectra (using styrene as an internal standard). Residence time (RT) was calculated using Eq. 1:

$$\text{Residence time (RT)} = \frac{Vr(\text{mL})}{Q\left(\frac{\text{mL}}{\text{min}}\right)} \quad (1)$$

Where Vr represents the volume of the reactor according to different catalysts (C:E:M1:P2<sub>80%</sub> = 7.78 mL; C:E:M1:P5<sub>50%</sub> = 7.61 mL; C:E:M1:P6<sub>50%</sub> = 7.84 mL; C:G:P4<sub>30%</sub> = 8.04 mL; P0 control = 7.95 mL), and Q is the flow rate obtained by adding the experimentally determined gas flow rate to the liquid flow rate. Productivity was determined to understand the applicability of these catalysts at an industrial level by considering the space-time yield (STY) using Eq. 2:

$$\text{STY} = \frac{\text{product weight}}{\text{volume reactor} \times \text{residence time}} = \frac{g_{\text{prod}}}{L \cdot h} \quad (2)$$

## 3. Results and Discussion

### 3.1. Morphological and textural properties of the chitosan aerogels

A library of stable chitosan aerogels with different PILs (P1, P2, P3, P4, P5 and P6) was obtained. The presence of crosslinker and heating during the preparation were also assessed, being the general approach of the AEROPILs preparation procedure depicted in Figure S.13. Also, the

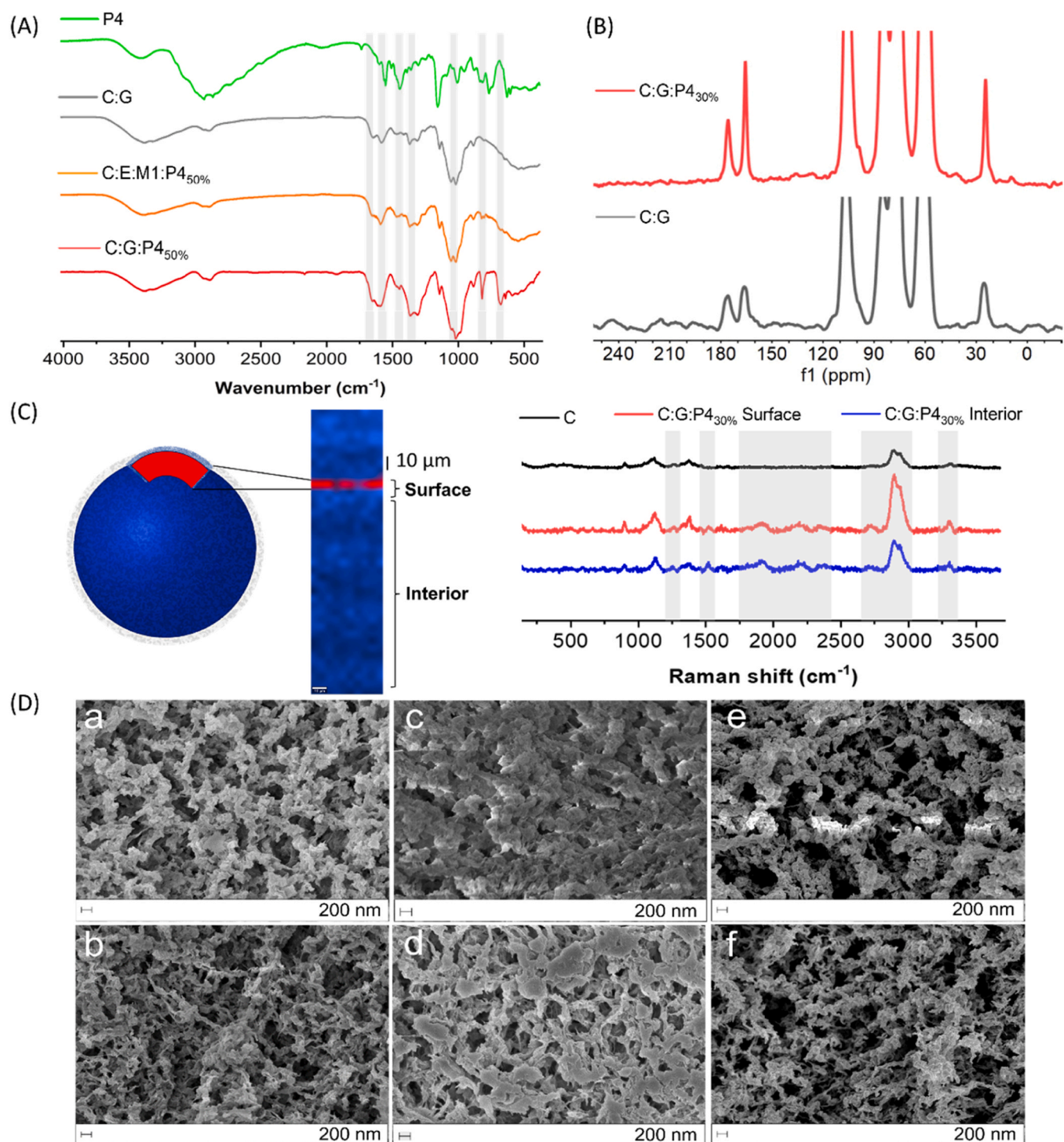
respective physicochemical (Table S.2) and textural properties (Table S.3) are presented in Section 6 of Supporting Information. The overall porosity exhibited a notable elevation, surpassing 88.1 % for all cases. Being that the lowest overall porosities were observed in the cases where the direct incorporation of EGDE occurred within the chitosan solution (Table S.2, entries 6, 8 and 11). The crosslinking reaction with EGDE can be achieved by reacting the epoxide groups in the crosslinker with the amino groups (-NH<sub>2</sub>) on the chitosan backbone and PIL [43–45]. In this case, with the increased percentage of crosslinker and PIL, the structure of the aerogel's fibres became denser and therefore, the overall porosity diminished. Relatively to the specific surface area, it has generally increased with a higher amount of P4 and/or the use of EGDE directly in the chitosan solution, being a<sub>BET</sub> values in the 173–748 m<sup>2</sup> g<sup>-1</sup> range (Table S.3).

Through the characterisation by ATR-FTIR spectroscopy, it is possible to infer that when glutaraldehyde was used, P4 was successfully incorporated into the aerogel beads (Fig. 2 (A)). The sample without P4 exhibited differences in the regions at 1615 cm<sup>-1</sup> (aromatic), 1328 cm<sup>-1</sup> (N-containing aromatic ring), 831 cm<sup>-1</sup> (C=C) and 697 cm<sup>-1</sup> (aromatic). Also, the vibration band at 1750 cm<sup>-1</sup> corresponding to the C=O carbonyl group of free glutaraldehyde was absent [37,46]. Analysing the differences arising from the crosslinkers, more PIL was incorporated in the structure when glutaraldehyde is added. When P4 was used, the same trend was obtained, as this PIL contains terminal -NH<sub>2</sub> groups that can be crosslinkable with chitosan. The main differences were observed in the following regions: 1658 (-NH stretching vibration), 1584 (C=N bond formed between the amine residues of chitosan and the aldehyde terminals of the glutaraldehyde, adding to the amide II vibration from chitosan), 1476 (characteristic vibration of imidazolium N heterocycle cation), 1337 (-CH<sub>3</sub> deformation), 1024 (C-N bend), 831 (C=C) and 688 cm<sup>-1</sup> (aromatic) [37,41,46,47].

Regarding the use of heating during the bead's preparation, there are no significant differences in the FTIR spectra (Figure S.4), which can be indicative of the hydrophilic PIL P2 lixiviation when the beads are in the aqueous solution of the crosslinker EGDE. Therefore, this analysis shows no apparent advantage in using this heating step.

<sup>13</sup>C CP-TOSS NMR spectra (Fig. 2 (B)) confirmed P4 incorporation in the structure when glutaraldehyde was used with the chemical shifts that appear at 10 ppm, 43 ppm and between 120 and 142 ppm. The same was verified for P2, as shown in Figure S.11.

Samples were analysed using Raman confocal microscopy to determine the extent of the modification with PILs. This technique allows the mapping of the composition of the polymer with a penetration depth of approximately 10 μm. Fig. 2 (C) depicts the mapping obtained for the AEROPIL C:G:P4<sub>30%</sub> using different penetrations for the incident laser light. The analysis clarified that the PIL P4 is present both at the surface and the interior of the bead, with apparently a higher amount at the surface. The mapping shows two different components, one in red corresponding to the chitosan and one in blue corresponding to a crystalline component compatible with the PIL. The blue region above the red line corresponds to air, the red region corresponds to the bead modification with P4, and the blue region below the red line corresponds to the interior of the bead, which is inaccessible to the analysis. Additionally, the Raman spectra of the different components can be observed on the right side of Fig. 2 (C). The Raman spectrum of a bead with chitosan only reveals the presence of bands in the range of 2813–3000 cm<sup>-1</sup> (-CH stretching), 1365 cm<sup>-1</sup> and 1109 cm<sup>-1</sup> (polysaccharide backbones), which is in accordance with the literature [48–50]. The analysis of the spectra of the interior and surface of the AEROPIL bead reveals new peaks assignable to imidazolium in the 1517–1384 cm<sup>-1</sup> region where the C=C and C=N bond stretching bands of imidazolium appear [28]. There are also other bands at 3294 cm<sup>-1</sup> (typically associated with -OH stretching vibration), 2192 cm<sup>-1</sup> and 1911 cm<sup>-1</sup> (often assigned to C=C stretching vibration of aromatic rings, such as those found in benzene derivatives). These results are consistent with the other characterisations that could help explain the possible CO<sub>2</sub> capture and



**Fig. 2.** (A) ATR-IR spectra of P4 (green), C:G (grey), C:E:M1:P4<sub>50%</sub> (orange) and C:G:P4<sub>50%</sub> (red). (B) <sup>13</sup>C CP-TOSS NMR spectra of C:G:P4<sub>30%</sub> beads (red) and C:G (grey). (C) (Left) Schematic representation of the area of the bead C:G:P4<sub>30%</sub> observed and the corresponding mapping for the outer 10 μm depth of the bead. The blue region above the red line represents air, the red region represents the bead modification with P4, and the blue region below the red line corresponds to the bead interior that is impossible to see. (Right) Raman spectra correspond to the surface and interior of the AEROPIL bead compared to the C bead. (D) Textural appearance of the (a, c, e) surface of beads C:G, C:G:P4<sub>30%</sub>, C:G:P1<sub>30%</sub>, respectively, and (b, d, f) interior of beads C:G, C:G:P4<sub>30%</sub>, C:G:P1<sub>30%</sub>, respectively, by SEM imaging (scale bar: 200 nm).

catalytic activity since the active moiety for these PILs is effectively distributed into the final material.

The most promising beads were analysed through SEM microscopy. Fig. 2 (D) shows some images of AEROPIL beads from P1 and P4 with glutaraldehyde as a crosslinker, which presents high specific surface areas, especially when the amount of PIL is increased. Chitosan beads

with the same amount of crosslinker are also provided for comparison. There is a dual porous structure in the inner and outer structure of the particles, as reported previously [37]. It is also possible to observe that according to the PIL identity, different changes were induced, both in the interior and surface of the beads. The beads with P4 ((D) c and d) presented more structured fibres than those with P1 ((D) e and f).

### 3.2. Batch catalytic activity of AEROPILs

The characterization of AEROPILs' efficacy towards CO<sub>2</sub> capture and the assessment of their affinity for this gaseous substrate, was done as elucidated by Barrulas et al. [37] and expounded upon in Section 7 of the Supporting Information. The CO<sub>2</sub> capture capacity ( $n_{\text{CO}_2}$ ) varies between 0.41 and 0.62 mmol g<sup>-1</sup>, being C:E:M1:P2<sub>80%</sub> the best AEROPIL capturing CO<sub>2</sub>. No direct correlation was observed between the AEROPIL porosity and CO<sub>2</sub> capture. Their performance is most likely a compromise of the textural and morphological properties and the respective PIL structure and dosage. The PIL addition percentage seems to be a determining factor since it can be observed in Figures S.14 and S.15 in Supporting Information that for the same PILs, increasing  $\gamma$  enhances the CO<sub>2</sub> adsorption capacity. Afterwards, their catalytic activity was assessed in terms of conversion and selectivity.

To identify optimal candidates, a comprehensive screening process was conducted within batch reactions to advance their utilisation in continuous flow reactions, aligning with prospective industrial applications. The batch tested AEROPILs were selected for their textural and morphological properties, their ability to capture CO<sub>2</sub>, and also to evaluate the performance of the different moieties that compose the PILs.

The outcome of these reactions was calculated by integrating the <sup>1</sup>H NMR signals in the spectrum of the crude mixture in CDCl<sub>3</sub>. The results are summarised in Table 2.

As it is possible to verify, when PIL was present in the bead, there was a substantial enhancement in the catalytic activity compared to chitosan alone. However, although the conversion is high, there is a significant diol formation indicating the presence of water competing with the CO<sub>2</sub> reaction. The selectivity of the reaction for cyclic carbonates is relatively low in AEROPILs from P1, P2 and P3 (Table 2, entries 3–5, 9). Even, when considering a higher PIL content as in C:E:M1:P2<sub>80%</sub> (Table 2, entry 9), there is no further increase in the cyclic carbonate yield under this condition. Being that P4 has crosslinkable moieties like P1 but is less hydrophilic due to the presence of the vinylbenzyl derivative, the selectivity of P4 was enhanced when highly crosslinked with EGDE (Table 2, entry 8). Therefore, a balance between the presence of crosslinkable moieties and the hydrophobicity of the PIL should be further

pursued.

Due to suspicion of oligoether carbonates formation in AEROPILs from P4 (Table 2, entry 7), GC-MS analysis of the reaction product was performed (Figure S.16), being the possible chemical structures of the additional products stated in Table S.4.

Alternative approaches were undertaken to enhance the selectivity for cyclic carbonates by increasing the substrate-to-catalyst ratio. This strategy aimed to facilitate the optimal impregnation of AEROPILs with the liquid substrate, thereby envisaging a substantial improvement in the reaction process. These innovative endeavours yielded favourable outcomes, specifically with butylene oxide and epichlorohydrin substrates, as demonstrated by the results outlined in Table 2, entries 10–13, 15. Styrene oxide (Table 2, entry 14) exhibits a lower conversion and selectivity, possibly due to being less reactive and bulkier. In the literature, several works neglect to provide data on selectivity (Table S.5). This level of scrutiny is significant, particularly when considering the prospective industrial implementation of these materials. Despite the present conversion occurring at 135 °C, the pressure is relatively low (10 bar). It is of relevance that reaction occurs in the absence of a co-catalyst and solvent and is also a metal-free catalytic reaction, which poses an environmental and economic advantage regarding some works in the literature [51–53]. Some good examples of using highly effective porous PILs as catalysts in CO<sub>2</sub> conversions have been reported [54,55], however, these materials are mainly described as powders.

The regenerative capability of the catalyst holds paramount significance, given its fundamental role in attaining a durable and sustainable material over an extended period. Consequently, within the boundaries of the present study, the utilisation of aerogel beads offers an additional reusability advantage, which has been refined through a progressively optimised protocol, as delineated in Section 8.3 of the Supporting Information. AEROPIL beads were completely rinsed with diethyl ether two consecutive times and subjected to moderate vacuum drying at 60 °C for at least 48 h until the next catalytic cycle under the same reaction conditions. Figure S.20 presents the CO<sub>2</sub> cycloaddition catalysed by AEROPIL C:E:M1:P2<sub>80%</sub> without co-catalyst and solvent. Five consecutive reactions were carried out at 135 °C and 10 bar of pressure for 72 h using approximately 10 wt % of catalyst (100 mg of catalyst and

**Table 2**  
Batch CO<sub>2</sub> cycloaddition catalysed by AEROPILs in the absence of co-catalyst and solvent.

Entry	Catalyst	R	Catalyst amount (wt %)	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>b</sup>
1	C	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	26	37
2	C:G	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	19	25
3	C:G:P3 <sub>30%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	92	11
4	C:G:P1 <sub>30%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	91	37
5	C:E:M2:P1 <sub>30%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	83	38
6	C:G:P4 <sub>30%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	94	44
7	C:G:P4 <sub>50%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	93	34 <sup>a</sup>
8	C:E:M1:P4 <sub>50%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	74	75
9	C:E:M1:P2 <sub>80%</sub>	CH <sub>2</sub> CH <sub>3</sub>	100 <sup>c</sup>	98	22
10	C:E:M1:P2 <sub>80%</sub>	CH <sub>2</sub> CH <sub>3</sub>	10 <sup>d</sup>	59	80
11	C:E:M1:P5 <sub>50%</sub>	CH <sub>2</sub> CH <sub>3</sub>	10 <sup>d</sup>	22	80
12	C:E:M1:P6 <sub>50%</sub>	CH <sub>2</sub> CH <sub>3</sub>	10 <sup>d</sup>	32	81
13	C:G:P4 <sub>30%</sub>	CH <sub>2</sub> CH <sub>3</sub>	10 <sup>d</sup>	77	88
14	C:G:P4 <sub>30%</sub>	Ph	10 <sup>d</sup>	4	26
15	C:G:P4 <sub>30%</sub>	CH <sub>2</sub> Cl	10 <sup>d</sup>	81	90

<sup>a</sup> Possible formation of oligoether carbonates detected.

<sup>b</sup> Conversion determined by integration of <sup>1</sup>H NMR signals of epoxide, diol, and cyclic carbonate on the reaction mixture with CDCl<sub>3</sub>; selectivity for cyclic carbonates when diol is a by-product. The error of measurement is 6 %.

<sup>c</sup> 100 mg of catalyst, 100 mg (1.4 mmol) of epoxide.

<sup>d</sup> 100 mg of catalyst, 11.5 mmol (829 mg to 1382 mg) of epoxide.

11.5 mmol of butylene oxide). The catalyst was reused through the previously mentioned diethyl ether protocol between cycles. During these cycles, an increase in the conversion from the initial 59–72 % in the 3rd cycle and the selectivity enhancement from 80 % to 94 % led to the attempt to start the initial reaction with a similar diethyl ether pre-treatment. Indeed, when the 1st cycle started with pre-treated *AEROPIL*, the conversion enhanced from 59 % to 68 % and the selectivity from 80 % to 91 %. This could be due to the creation of new active sites with the washings and the vacuum drying. TGA thermograms (Section 4.4 in [Supporting Information](#)) show the presence of structural water that could be released with this treatment, enhancing the selectivity. Additionally, SEM and N<sub>2</sub> sorption results indicated that the morphology and porosity of *AEROPIL C:E:M1:P2<sub>80%</sub>* changed after catalysis. This might be due to residual cyclic carbonate trapped within the bead (Figure S.19), resulting in pore blockage. However, despite the loss of overall porosity, the average pore size increased ( $a_{\text{BET}} 30 \pm 2 \text{ m}^2 \text{ g}^{-1}$ ;  $V_{\text{P, BJH}} 0.19 \pm 0.01 \text{ cm}^3 \text{ g}^{-1}$ ;  $D_{\text{P, BJH}} 24.8 \pm 1.2 \text{ nm}$  – Table S.9, entry 1), the catalyst activity remained, and it was considered as a renewable and stable catalyst (Figure S.21). As observed for CO<sub>2</sub> capture, no direct correlation was found between the porosity and the catalytic activity of *AEROPILs* in these conditions.

Regardless of the reusability of the aerogel beads, they require washing processes with vacuum drying which entails energy and time costs. This makes the continuous flow catalysis even more advantageous as stated in the following section.

### 3.3. Continuous flow catalytic activity of *AEROPILs*

The catalysts that exhibited the best performance in batch were selected for the CO<sub>2</sub> cycloaddition experiments under continuous flow [6]. The following conditions were systematically optimised: temperature (80, 100 and 120 °C); CO<sub>2</sub> flow rate (0.10, 0.15 and 0.20 mL min<sup>-1</sup>); liquid flow rate (0.05, 0.10, 0.15 and 0.20 mL min<sup>-1</sup>); concentration variation of the epoxide (0.5, 1 and 2 M of epichlorohydrin in IPA); stability tests (liquid flow rate of 0.05 mL min<sup>-1</sup>; CO<sub>2</sub> flow rate of 0.15 mL min<sup>-1</sup>; 1 M of epichlorohydrin in IPA; 120 °C). First, the CO<sub>2</sub> flow rate and the liquid flow rate were fixed at 0.20 mL min<sup>-1</sup> and 0.05 mL min<sup>-1</sup> respectively and then the temperature was varied. With the temperature optimised and the liquid flow rate fixed at 0.05 mL min<sup>-1</sup>, the CO<sub>2</sub> flow rate was then varied. The same principle was applied for the liquid flow rate and the concentration variation of the epoxide.

Optimisation efforts were undertaken using the *C:E:M1:P2<sub>80%</sub>* catalyst, while other catalysts, namely *C:E:M1:P5<sub>50%</sub>*, *C:E:M1:P6<sub>50%</sub>* and *C:G:P4<sub>30%</sub>*, were evaluated under the identified optimal reaction conditions. These *AEROPILs* were selected to understand the difference between ammonium and phosphonium, thus having different families of compounds. Additionally, a control aerogel (devoid of PIL) was tested for reference purposes, demonstrating a lack of catalytic activity.

The liquid phase, epichlorohydrin in IPA, was pumped with an HPLC pump into a T-mixer and mixed with CO<sub>2</sub> driven by a peristaltic pump. A back-pressure regulator (BPR) was added between the peristaltic pump and the T-mixer to ensure control over the gas flow rate (Fig. 3 (A)). The reaction mixture entered the reactor packed with the *AEROPILs* at a temperature of 120 °C (after optimisation), where the cycloaddition takes place. The BPR controlled the pressure of the reactor at 6 bar. After reaching a steady state, which was achieved in a time equivalent to three times the bed volume, the products were collected in triplicate vials using an automated fraction collector. The samples were analysed integrating the <sup>1</sup>H NMR signals in the spectrum of the reaction mixture in CDCl<sub>3</sub>, using styrene as an internal standard. The results are herein presented in Fig. 3 (B–E).

According to the tests performed, the optimal reaction conditions were set at a temperature of 120 °C, a liquid flow rate of 0.05 mL min<sup>-1</sup> and a CO<sub>2</sub> flow rate of 0.15 mL min<sup>-1</sup> (Figure S.22). When analysing Fig. 3 (B), it can be observed that the conversion decreases with

increasing substrate concentration. The concentration of 1 M epichlorohydrin in IPA was selected. Although it presents an intermediate conversion, this concentration has a higher productivity, yielding sufficient sample as required for NMR analysis. A trade-off decision therefore had to be made.

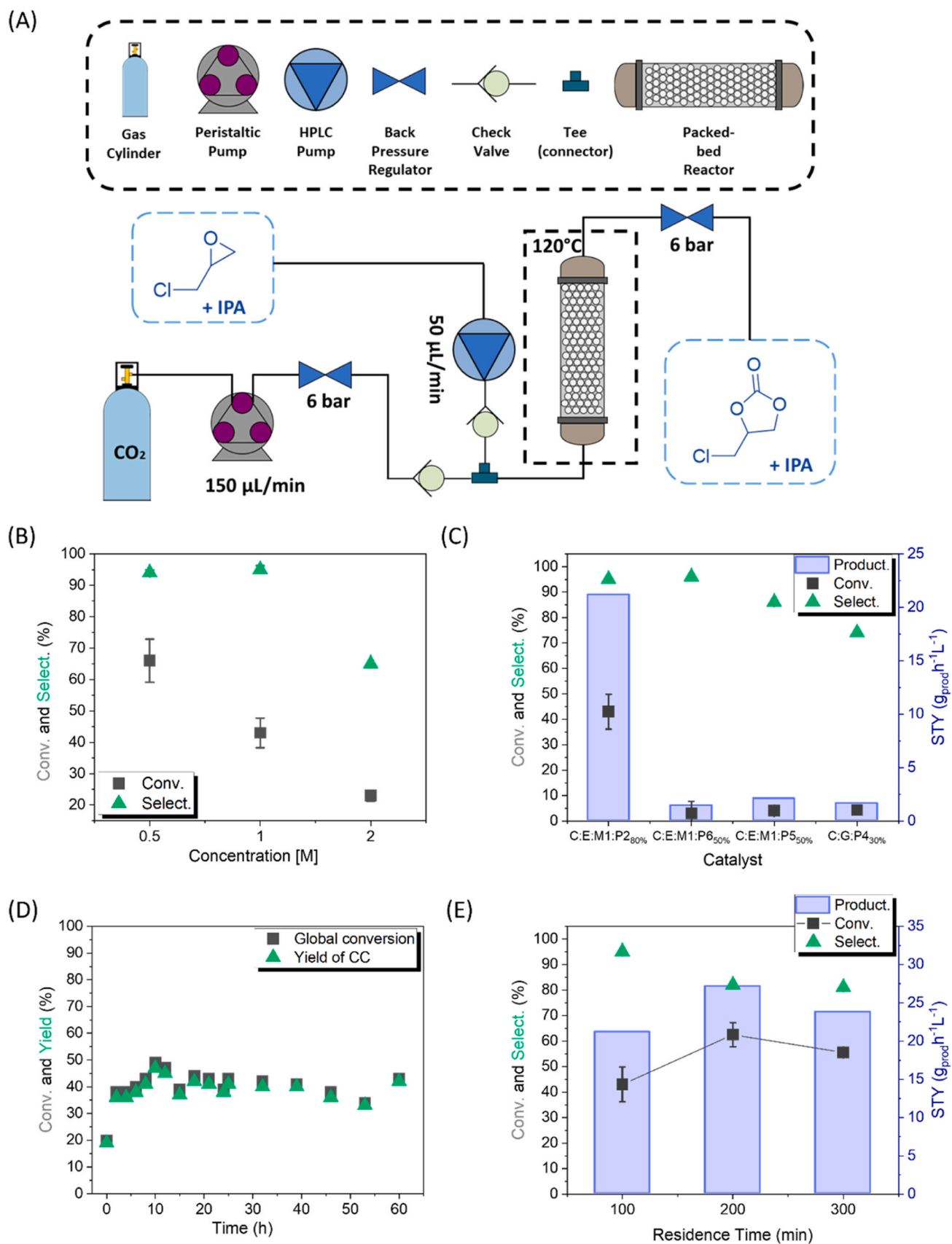
From Fig. 3 (C) and (D) we can conclude that the catalyst *C:E:M1:P2<sub>80%</sub>* was the more efficient one, with a productivity of 21.18 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup>, compared to the other catalysts whose productivity values were substantially lower (*C:E:M1:P6<sub>50%</sub>* 1.43 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup>; *C:E:M1:P5<sub>50%</sub>* 2.07 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup>; *C:G:P4<sub>30%</sub>* 1.62 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup>). *C:E:M1:P2<sub>80%</sub>* was stable for more than 60 h maintaining its structure (Figure S.23–S.25). Considering that all the optimisations were made with the same catalyst, the total durability was higher than 300 h. Also, when doing the reactions simulating a 2nd column or more residence time (Fig. 3 (E)), it was observed that the productivity reached a maximum of 27.14 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup>. Therefore, a promising material for an industrial application was successfully achieved. Due to the novelty of this methodology, existing literature data regarding this reaction with epoxides is scarce. This work also presents relative advantages to the CO<sub>2</sub> pressure applied, which is substantially lower than the data from the literature, the same for the stability time comparable to the data, and the moderate temperature used [56–62].

The catalyst *C:E:M1:P2<sub>80%</sub>* stabilised around 40 % of conversion (96 % selectivity), after 10 h of activity at 6 bar and 120 °C. This work presents advantages relatively to other works in the literature for CO<sub>2</sub> cycloaddition to epoxides under continuous flow, especially regarding the pressure used. Wang et al. [57] reported 45 % of conversion at 20 bar and 130 °C after approximately 35 h of activity, and then it stabilized around 41 %. Sun et al. [61] reported 57.1 % of conversion at 20 bar and 90 °C, after continuous reaction for 2 h, however the catalyst could only be used up to 24 h since stabilization was not achieved. Valverde et al. [58] reported 53 % of conversion after stabilization at 140 bar and 150 °C for 10 days of continuous use. Although the conversion is important, comparing different process conditions, namely substrate concentration, flow, temperature, and catalysts, requires calculating productivity parameters, the STY. Iglesias et al. [6] obtained a productivity of 4.38 g<sub>prod</sub><sup>-1</sup> h<sup>-1</sup> L<sup>-1</sup> using styrene oxide and TBA-Br, a pressure of 6 bar at 100 °C. The present work used epichlorohydrin instead, without using a co-catalyst, and achieved a substantially higher productivity of 21.18 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup> at 6 bar and 120 °C.

Ultimately, the catalyst with PIL **P2** was the most efficient. This is probably due to the increased amount of PIL present in the bead compared to the other catalysts, since there was an increment of 30 % and 50–80 % w/w concerning chitosan. As **P2** is a commercial PIL, it probably has a higher molecular weight and is more controlled than **P4**, **P5** and **P6**, which are synthesised on a small scale in the laboratory. Consequently, **P4**, **P5** and **P6** can be more easily leached during the formation of beads due to the acid-base interactions. Also, the cation moiety in **P2** is less sterically hindered, facilitating interactions with the substrate and CO<sub>2</sub>. The fact that the catalyst with a commercial PIL was the most efficient and productive represents an economic advantage, and it is also easier to apply a material with these characteristics on an industrial scale.

Also, comparing batch with flow catalysis, it is safe to say that the flow presents several advantages, as stated in Fig. 4. After batch catalysis, the SEM and N<sub>2</sub> sorption results indicated that the morphology and porosity of *AEROPIL C:E:M1:P2<sub>80%</sub>* were lost. On the contrary, when used in flow, this same catalyst exhibited a smoother decrease in surface area and pore volume, while the average pore size increased, probably due to the blockage of smaller pores were, and therefore the remaining wider pores led to increase in the average pore size ( $a_{\text{BET}} 118 \pm 6 \text{ m}^2 \text{ g}^{-1}$ ;  $V_{\text{P, BJH}} 0.66 \pm 0.03 \text{ cm}^3 \text{ g}^{-1}$ ;  $D_{\text{P, BJH}} 22.2 \pm 1.1 \text{ nm}$  – Table S.9, entry 2), reinforcing the possibility of implementing this process at an industrial scale.

Based on theoretical and experimental knowledge, a mechanism can be proposed for *AEROPILs* (Figure S.26). First, mediated by the



**Fig. 3.** (A) Schematic representation of continuous-flow system. (B) Different epichlorohydrin concentrations with the optimal reactional conditions. (C) Productivity of C:E:M1:P2<sub>80%</sub>, C:E:M1:P6<sub>50%</sub>, C:E:M1:P5<sub>50%</sub> and C:G:P4<sub>30%</sub>. (D) Stability test of C:E:M1:P2<sub>80%</sub>. (E) Conversion and productivity of C:E:M1:P2<sub>80%</sub> according to the residence time.











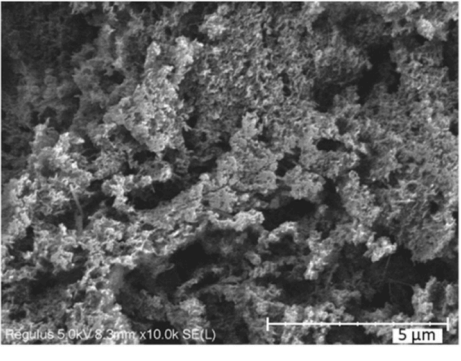
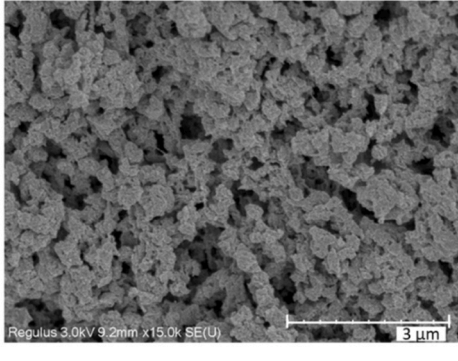
Batch	Flow
  conversion	  conversion
 Multi-step recycling	 One-step recycling
 11x smaller ( $a_{\text{BET}} 30 \text{ m}^2 \text{ g}^{-1}$ )	 2.8x smaller ( $a_{\text{BET}} 118 \text{ m}^2 \text{ g}^{-1}$ )
	

Fig. 4. Comparison between batch and continuous flow catalysis with the textural appearance of the *AEROPIL* C:E:M1:P2<sub>80%</sub> interior after catalysis by SEM imaging.

structural water contained in the *AEROPIL*s, there is a hydrogen-bond donor activation between the oxygen atoms from the epoxide and -NH groups, which leads to the activation of the epoxy ring. After some time, the free halide anion, as the nucleophilic reagent, attacks the less sterically hindered carbon atom of epoxide to open the epoxy ring. The resulting oxyanion attacks a CO<sub>2</sub> molecule, forming an intermediate carbonate anion upon CO<sub>2</sub> addition. However, a competing water addition to the oxyanion can lead to a diol by-product, decreasing the reaction selectivity. When there is an intramolecular cyclisation of the oxyanion, the cyclic carbonate is formed, and the resulting free active sites can undergo the next catalytic reaction.

#### 4. Conclusions

Efforts to combat climate change have spurred the development of new materials for efficiently capturing and converting CO<sub>2</sub>. In this regard, PILs have shown promise as CO<sub>2</sub> sorbents, but challenges remain in tailoring their properties for optimal performance. Here, we report on successfully using optimized *AEROPIL*s for CO<sub>2</sub> upcycling. *AEROPIL*s with high porosity and surface area were tested as metal-free heterogeneous catalysts for CO<sub>2</sub> conversion in the absence of solvent and co-catalysts for the first time. We found that the combination of PILs with chitosan aerogels typically potentiates the CO<sub>2</sub> conversion into cyclic carbonates in a cost-effective and reusable process. Regarding batch reactions, the catalysts C:E:M1:P2<sub>80%</sub> and C:G:P4<sub>30%</sub> exhibited the highest CO<sub>2</sub> conversion capability with high selectivity, being that C:E:M1:P2<sub>80%</sub> remained active for 5 consecutive cycles, bringing these materials closer to the reuse that is crucial for industrial applications. Applying *AEROPIL*s to continuous flow systems was explored as a stepping stone to scaling-up processes. The optimum reaction conditions were determined to be a temperature of 120 °C, a liquid flow rate of 0.05 mL min<sup>-1</sup>, and a CO<sub>2</sub> flow rate of 0.15 mL min<sup>-1</sup>. The catalyst with the highest efficiency, C:E:M1:P2<sub>80%</sub>, exhibited a significant productivity of 21.18 g<sub>prod</sub> h<sup>-1</sup> L<sup>-1</sup> and remained stable for over 60 h. In the end, the catalyst maintained the morphology and porosity, emphasising

the advantage of implementing this process on an industrial scale.

#### CRediT authorship contribution statement

**Raquel V. Barrulas:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Cristopher Tinajero:** Writing – review & editing, Software, Investigation. **Diogo P. N. Ferreira:** Writing – review & editing, Investigation. **Carlos Illanes-Bordomás:** Writing – review & editing, Investigation. **Victor Sans:** Writing – review & editing, Resources, Methodology. **Manuela Ribeiro Carrott:** Writing – review & editing, Resources, Methodology. **Carlos A. García-González:** Writing – review & editing, Resources, Methodology. **Marcileia Zanatta:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Marta C. Corvo:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### Appendix A. Supplementary data

**Supporting Information.** The supporting information is available free of charge at (...)

- Procedures for the synthesis of IL monomers and PILs, BJH-pore size distribution, nitrogen adsorption-desorption isotherm, elemental analysis, FTIR spectra, TGA curves, supporting NMR spectra, GC-MS analysis and supporting experimental data on CO<sub>2</sub> capture and catalysis.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2024.102771](https://doi.org/10.1016/j.jcou.2024.102771).

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