

## Mesoporous zwitterionic poly(ionic liquid)s: intrinsic complexation and efficient catalytic fixation of CO<sub>2</sub>†

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Mesoporous poly(ionic liquid)s with zwitterionic structures have been successfully prepared. This synthesis made use of a facile template-free approach *via* precipitating an organic solution of an imidazolium-based poly(ionic liquid) homopolymer in a straightforward manner into ammonia-containing organic solvents. The complex products have a specific surface area up to 260 m<sup>2</sup> g<sup>-1</sup>, and exist in a robust nanoparticle form. They could serve as active catalysts for the chemical fixation of CO<sub>2</sub>.

Recently poly(ionic liquid)s or polymerized ionic liquids (PILs) as an innovative type of polyelectrolyte have attracted rapidly increasing attention in the field of polymer and materials science.<sup>1–6</sup> They are commonly prepared by conventional or controlled radical polymerization of monomeric ionic liquids (ILs).<sup>2,7,8</sup> The presence of an IL moiety in the repeating unit of the polymer chains integrates some IL properties (IL chemistry and physics) into the polymeric architecture. The synergistic effect can positively enable new functions and improve the performance of some polymer materials. This expands the traditional application spectrum of classical polyelectrolytes studied so far. Some application examples of PILs have already been demonstrated very recently, such as polymeric electrolytes, CO<sub>2</sub> capture and separation, stationary phases in chromatography, carbon precursors, catalysis, model systems for block copolymer self-assembly, *etc.*<sup>9–19</sup> Among them, the major efforts have been devoted to the chemical design of specific PILs that can deliver superior performance in the bulk and solution.

Porous PILs with enlarged surface area can in principle accelerate the interfacial mass and energy transport, thus representing a

promising pathway to amplify material functions even without modifying the chemical structure. Many porous PILs reported to date are macroporous (pore size >50 nm) with specific surface area up to 37 m<sup>2</sup> g<sup>-1</sup>.<sup>20–25</sup> Recently *via* a hard-templating method we synthesized a mesoporous (pore sizes between 2 and 50 nm) PIL with specific surface area up to 220 m<sup>2</sup> g<sup>-1</sup>. This mesoporous PIL demonstrated enhanced CO<sub>2</sub> adsorption dynamics and capacity compared to its nonporous bulk counterpart.<sup>12</sup> Despite this merit, an obvious drawback associated with the hard-templating method is the inevitable template (usually silica) preparation and removal, which is often time-consuming and hard to scale up. In addition, it involves hazard chemicals, such as fluoride to etch away silica. Therefore, a template-free method to synthesize mesoporous PIL materials was highly desired. This has been recently introduced by us in a simple dissolution–precipitation approach: (1) mixing a PIL with poly(acrylic acid) in DMF to reach a homogeneous blend solution; (2) precipitating the blend solution into NH<sub>3</sub>-containing organic solvents to trigger the *in situ* interpolyelectrolyte complexation that subsequently built up porous PIL complexes (denoted as PILCs) with a specific surface area up to 310 m<sup>2</sup> g<sup>-1</sup>.<sup>26</sup> It was found that the specific surface area values peaked at a molar ratio of imidazolium cation to carboxylate anion at exactly 1 : 1. The porous structure of the as-synthesized PILC was proven to be highly stable in some organic solvents and was employed as a robust catalyst support. In the follow-up work, we further found that even multi-acid organic compounds could crosslink PILs into porous polyelectrolyte frameworks.<sup>27</sup>

Herein we describe a simplified version of this template-free synthetic route towards mesoporous PILCs (mesoPILCs) from a zwitterionic PIL homopolymer as a single structural building component *via* intrinsic inter-/intrapolyelectrolyte complexation, which features an absolute and favorable 1 : 1 ratio of the imidazolium cation to carboxylate anion. In addition, the configuration of the imidazolium cation and the COOH group in the same repeating unit guarantees the molecular homogeneity in the chemical structure all through the porous matrix. One of the as-synthesized mesoPILCs was employed as an efficient and recyclable catalyst in the CO<sub>2</sub> cycloaddition reaction.

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The synthetic strategy for the preparation of mesoPILCs is illustrated in Scheme 1. A room temperature IL monomer (compound A in Scheme 1) was first prepared by quaternization of 1-vinyl imidazole with *tert*-butyl-2-bromoacetate (step i in Scheme 1). The homopolymer PIL (compound B in Scheme 1) was prepared *via* free radical polymerization of the IL monomer in DMSO at 80 °C using 2,2'-azobis(2-methylpropionitrile) (AIBN) as an initiator (step ii in Scheme 1). The *tert*-butyl protecting group was detached in the sequential step *via* trifluoroacetic acid (TFA) treatment (step iii in Scheme 1), introducing the carboxylic acid functionalized PIL (compound C in Scheme 1, denoted as PIL-COOH). Precipitation of the DMF or DMSO solution of PIL-COOH into ammonia-containing non-/low polar solvents (here exemplified with diethyl ether) produced insoluble PILCs (step iv in Scheme 1). It should be mentioned that the present PILC formation process differs itself from previously reported systems, in which always two components were required.<sup>26,27</sup>

The success in each synthetic step was confirmed by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy. As shown in Fig. 1B, after quaternization of 1-vinyl imidazole, an intense peak at 1.4 ppm appeared which was assigned to the 9 protons in the *tert*-butyl group. The full quaternization was verified by the integration ratio (9 : 1) of the *tert*-butyl protons (peak h in spectrum B) to the well-resolved single vinyl proton (peak c in spectrum B) at 5.8 ppm. Following the polymerization, all vinyl protons (peaks a, b and c in spectrum B) eventually vanished and two new broad peaks at 2.6 and 4.1 ppm (spectrum C in Fig. 1) were observed, which could be assigned to the two types of backbone protons (–CH<sub>2</sub>–C(H)–). The cleavage of the *tert*-butyl group proceeded quantitatively, as the strong peak at 1.4 ppm disappeared, leaving the remaining peaks actually untouched. All products until this step have good solubility in organic solvents, like DMF or DMSO. The intrinsic inter-/intrapolyelectrolyte complexation occurred when the PIL-COOH solution was dropped into ammonia-containing organic solvents. In this process, the COOH function was immediately deprotonated, which triggered the *in situ* complexation between the carboxylate anion and the imidazolium cation and built up an ionically crosslinked polymer network. What is very unique

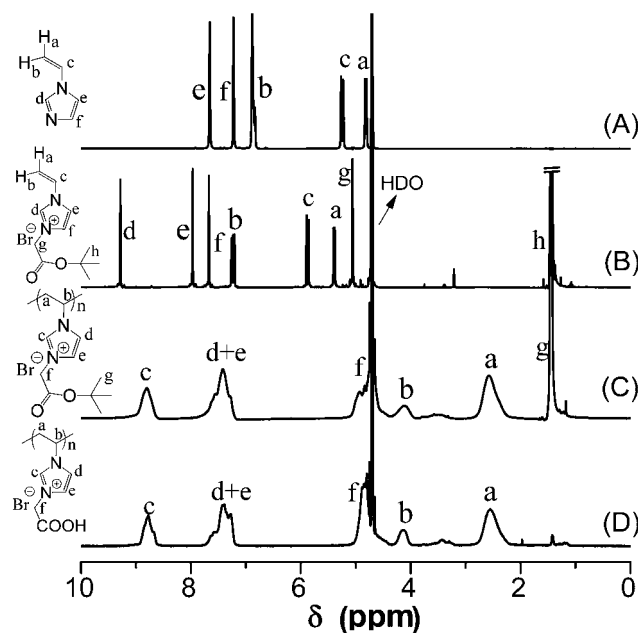
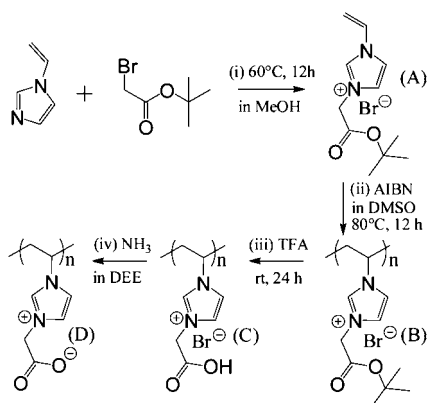


Fig. 1 <sup>1</sup>H-NMR spectra (in D<sub>2</sub>O) of 1-vinyl imidazole (A), monomeric IL (B), corresponding PIL (C) and the deprotected form PIL-COOH (D).

in this system is, PIL-COOH acts as the only building component, therefore the complexation takes place only among different PIL-COOH chains (interpolyelectrolyte complexation) or within the same PIL-COOH chain (intrapolyelectrolyte complexation). After the charge neutralization, the polymer became insoluble in many organic solvents and was only partially swollen in DMSO under heating.

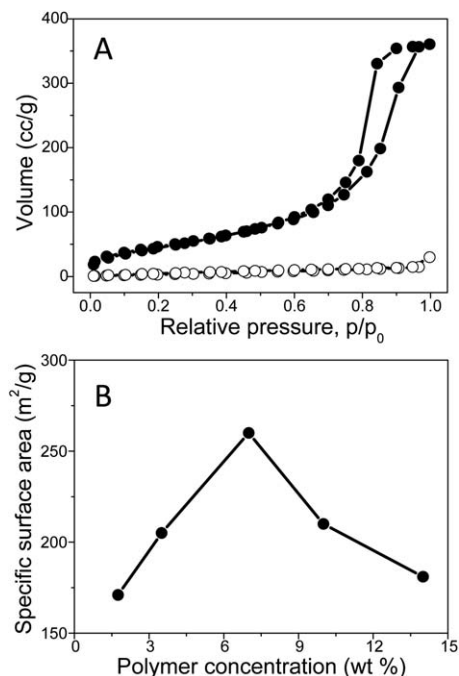
Fig. 2A shows a typical nitrogen sorption isotherm of the PILC sample prepared by precipitation of a PIL-COOH solution (7 wt%) in DMSO into NH<sub>3</sub>-containing (0.5 wt%) diethyl ether. It exhibits unambiguously a type-IV isotherm with a hysteresis loop in the *p/p*<sub>0</sub> range from 0.7 to 0.9. The pore size distribution curve (Fig. S1†) indicates that the material is essentially made up of mesopores (6–20 nm in size). The pore structure is robust in organic solvents, such as acetone, THF or acetonitrile, even after several cycles of wet-drying or refluxing, as its characteristics in gas sorption measurements changed little. This is actually expected for such a densely and ionically crosslinked system, in good accordance with other PILC systems prepared previously.<sup>26,27</sup> The specific surface area calculated from Brunauer-Emmett-Teller equation (*S*<sub>BET</sub>) is 260 m<sup>2</sup> g<sup>-1</sup>.

It should be noted that ammonia played a central role in controlling the inter-/intra-polyelectrolyte complexation and pore generation. Without adding ammonia, no porous product formed (Fig. 2A) and the precipitating solid in diethyl ether could be re-dissolved in DMF or DMSO because of no network formation in PIL-COOH. Furthermore, in the case of NH<sub>3</sub>-containing complexation solvents (in which the complexation takes place), such as diethyl ether as in this case, the *S*<sub>BET</sub> values were able to be modulated between 160 and 260 m<sup>2</sup> g<sup>-1</sup> *via* the PIL-COOH concentration in DMSO. As shown in Fig. 2B, the highest *S*<sub>BET</sub> value was obtained at a PIL-COOH concentration of 7 wt%. Below or above this concentration, the *S*<sub>BET</sub> value



Scheme 1 Chemical structure and synthetic route towards a mesoporous zwitterionic PILC from a homopolymer PIL possessing a COOH function. DEE: diethyl ether.



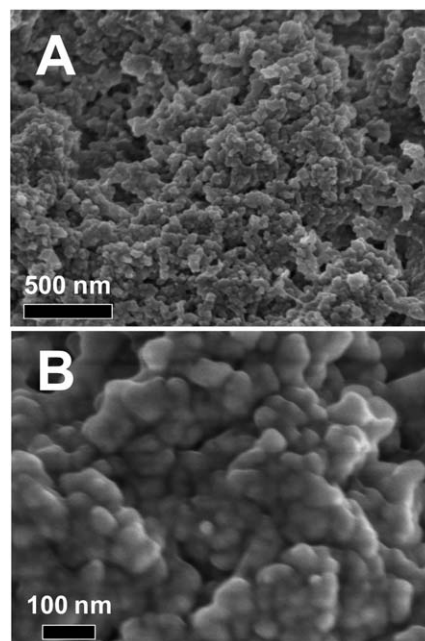


**Fig. 2** (A) Nitrogen sorption isotherms of the mesoPILC product prepared via precipitation of 7 wt% of the PIL-COOH solution in DMSO into diethyl ether with (solid dots) and without ammonia activation (open circles). (B) Plot of specific surface area of the formed mesoPILC products vs. the PIL-COOH concentration in DMSO.

drops. Besides, the complexation solvent quality also plays an important role. Porous materials come up only when the PIL-COOH solution was precipitated into organic solvents of low polarity, such as diethyl ether, hexane ( $150 \text{ m}^2 \text{ g}^{-1}$ ) and cyclohexane ( $174 \text{ m}^2 \text{ g}^{-1}$ ). Compact and nonporous products were received when complexation was conducted in water, methanol or DMSO in the presence of  $\text{NH}_3$ . Therefore, a poor or non-solvent of PIL-COOH seems to be the prerequisite for preparing mesoPILCs in the current system.

Scanning electron microscopy (SEM) characterization (Fig. 3) provides additional information on the morphology of the mesoPILC product. As can be clearly observed, it exhibits distinctive round-shaped particles stacking onto each other. The particles are 30 to 50 nm in size and exist as a secondary structure motif of the primary aggregates of the ionically locked PIL backbones. Thermogravimetric analysis (TGA) indicated that the first thermal decomposition step took place at  $250 \text{ }^\circ\text{C}$  (Fig. S2†). Because of its nanoparticle shape and good thermal stability, we investigated whether the as-synthesized mesoPILC could work directly as a catalyst. The cycloaddition reaction of  $\text{CO}_2$  to epoxides, a reaction related to the chemical storage of  $\text{CO}_2$  by capturing it as a building block in C1 chemistry, was selected as a model reaction. It is worth noting that several halide-containing crosslinked PIL nanoparticles have been recently tested by Xiong *et al.* and showed active catalytic activity for this reaction.<sup>28–31</sup>

The catalytic tests were conducted in an autoclave at  $160 \text{ }^\circ\text{C}$  under 1 MPa  $\text{CO}_2$ . Propylene oxide, styrene oxide and epichlorohydrin were chosen as exemplary substrates. The results are summarized in Table 1. As can be seen, all three substrates



**Fig. 3** SEM images of the mesoPILC product prepared from precipitation of PIL-COOH solution (7 wt% in DMSO) into ammonia-containing diethyl ether. (B) Enlarged view of (A).

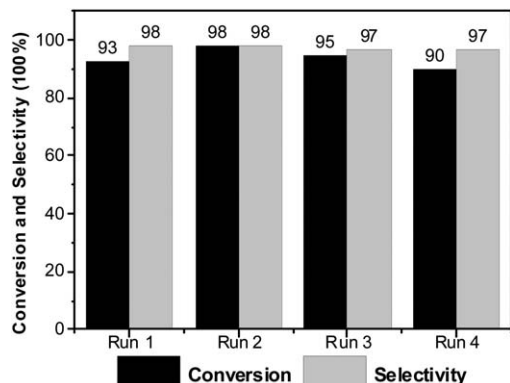
can be smoothly transformed into cyclic carbonates with satisfactory conversion ( $\geq 93\%$ ) when using the mesoPILC nanoparticles as a catalyst. A high selectivity ( $\geq 97\%$ ) was obtained in the cycloaddition of  $\text{CO}_2$  with propylene oxide and epichlorohydrin, while a relatively lower one of 87% was found for styrene oxide, which is possibly caused by the enhanced steric hindrance due to the large phenyl ring.

Further experiments were conducted to examine the recyclability of the porous PILC nanoparticles in the  $\text{CO}_2$  cycloaddition by using propylene oxide as a model substrate. As shown in Fig. 4, the PILC catalyst could be reused for at least four runs without significant loss of the catalytic activity, which is a prerequisite for practical applications. The average conversion

**Table 1** Cycloaddition reaction of various epoxides with  $\text{CO}_2$  catalysed by mesoPILC (prepared by precipitation of 7 wt% of PIL-COOH solution in DMSO into ammonia-containing diethyl ether). Reaction conditions: epoxide (3 mL), catalyst: 50 mg, 1 MPa  $\text{CO}_2$ ,  $150 \text{ }^\circ\text{C}$

Entry	Epoxide	Product	T/h	Conv.	Sel.
1			6	93%	98%
2			24	94%	87%
3			8	99%	97%





**Fig. 4** The reusability of a mesoPILC catalyst. Reaction conditions: propylene epoxide (3 mL), catalyst: 50 mg, 1 MPa CO<sub>2</sub>, 150 °C, *t* = 6 h.

of these four runs is 94%, and a slight deviation (4% in 2<sup>nd</sup> and 4<sup>th</sup> runs) is within the experimental error. Meanwhile the catalytic selectivity remains constantly high ( $\geq 97\%$ ). The overall superior catalytic activity, high selectivity and excellent recyclability of mesoPILCs as a heterogeneous catalyst could be attributed to their excellent structural stability and unique nanoscale morphology. The reaction temperature (160 °C) is far below the thermal decomposition threshold temperature (Fig. S2†). The nanoparticle form and the porous state allow for a rapid diffusion of the reactants easily into the reactive center. At the same time the ionic crosslinking firmly holds the particle structure together in the organic liquid product, facilitating the easy separation by simple filtration from the liquid products.

In summary, we have developed a facile synthetic route to convert a zwitterionic PIL homopolymer into a mesoporous PIL complex *via* precipitating the PIL solution into organic solvents of low polarity. The obtained porous polyelectrolyte networks have nanoparticle morphology and are structurally stable in some organic solvents even under reflux treatment. In addition, they were successfully used as catalysts for the cycloaddition of CO<sub>2</sub> to epoxides. From a viewpoint of the chemical structure and application potential, this single-component zwitterionic mesoporous PILC might broaden the current research scope of poly(ionic liquid)s, which is mostly polycation-based.

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