

MACROPOROUS POLY(IONIC LIQUID)/IONIC LIQUID GELS VIA CO₂-BASED EMULSION-TEMPLATING POLYMERIZATION[†]

Kevin Mathieu, Christine Jérôme  and Antoine Debuigne *

Centre for Education and Research on Macromolecules (CERM), CESAM Research Unit, Department of Chemistry, University of Liège, Allée de la Chimie B6A, 4000 Liège, Belgium. E-mail: adebuigne@uliege.be

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/c7py01952a

Structuring poly(ionic liquid)s (PILs) into porous materials or swelling PILs with free ionic liquids (ILs) has received specific attention recently and contributed to the improvement of the performances of these materials used in a wide range of applications. The present work aims to take advantage of both approaches and produce macroporous PIL/IL gels in a single step through an innovative emulsiontemplated polymerization method based on supercritical carbon dioxide (scCO₂). More precisely, IL vinyl monomers and crosslinkers were polymerized in the presence of non-polymerizable ILs within the outer phase of a CO₂-in-IL high internal phase emulsion (HIPE). Specific macromolecular surfactants were synthesized using controlled radical polymerization techniques and tested for the stabilization of the CO₂-inIL emulsions. While optimizing the polymerization conditions, we found that adding a limited amount of water in the medium was beneficial for the emulsion stability. Overall, this straightforward process provided access to macroporous polyHIPEs composed of poly(vinyl imidazolium) networks swollen by ‘free’ vinyl imidazolium-based ILs having interesting properties such as switchable polarity upon a simple anion exchange reaction.

Introduction

Ionic liquids (ILs) are attracting much attention for applications in many fields of chemistry and industry, including gas capture,^{1,2} electrochemistry,³ catalysis,^{4,5} and porous polymer synthesis,^{6,7} and as green solvents,^{8,9} due to their unique combination of interesting physicochemical properties such as good chemical and electrochemical stability, low flammability, negligible vapor pressure, high ionic conductivity, etc.^{10,11} On the other hand, poly(ionic liquid)s (PILs), whose repeating unit bears an electrolyte group,^{12–14} is a fast growing research area because they combine some valuable features of ILs with the intrinsic characteristics of polymers.¹⁵ PILs can be synthesized either by the direct polymerization of IL-containing monomers or by the post-modification of existing polymers. Interestingly, PILs and ILs were also used as blends in order to combine their respective properties in a single material.^{16–19} For example, PIL/IL membranes with improved CO₂ capture ability were developed.^{20,21} In this case, the high CO₂ permeability and selectivity of ILs were associated with the good mechanical properties of PILs producing a membrane with high performance and excellent

integrity due to the strong electrostatic interactions between ILs and PILs. Gel polymer electrolytes (GPEs) made of PIL/IL mixtures were also used in the development of safer lithium ion batteries with improved electrochemical and mechanical properties.²²

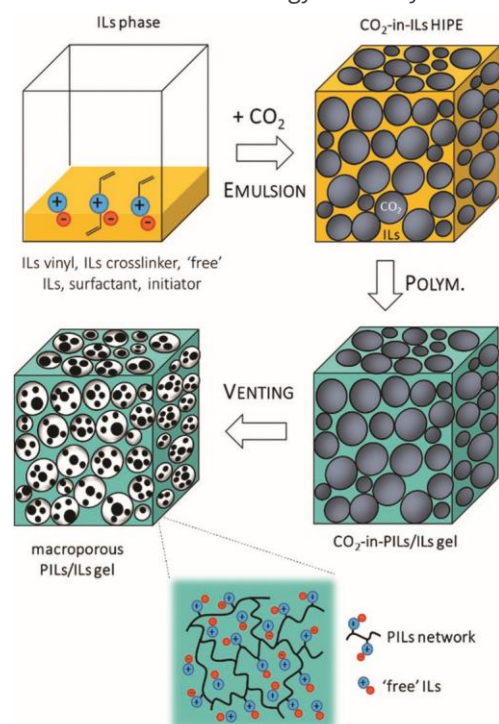
Structuring PILs into porous materials also attracted a lot of attention in the last few years and contributed to the expansion of the scope and increase the performance of these materials, especially for gas capture and catalysis.^{23–28} Some porous PILs are very promising sorbents for CO₂ uptake owing their high surface area and low density combined with their high thermal and chemical stability.²⁹ Mesoporous imidazolium-based networks having CO₂ sorption capabilities were notably prepared via hard-templating with silica nanoparticles¹⁵ and by the soft-templating pathway using Pluronic P123 as the sacrificial phase.^{30,31} The conventional radical copolymerization of alkylvinylimidazolium salts and divinylbenzene in different solvents also led to mesoporous PIL supports via the polymerization-induced phase separation process.³² Due to the excellent flow-through properties associated with materials with macropores, the design of macroporous PILs also raised a great interest, notably for chromatography or catalysis applications. For this purpose, silica colloidal crystal arrays were used as templates in the polymerization of alkylvinylimidazolium salts to obtain inverse opal structures of great promise in the field of sensors or photonic crystals.^{33–35} Recently, macroporous PIL monoliths dedicated to chromatography applications were synthesized via atom transfer radical polymerization (ATRP).³⁶

Another very popular method for the preparation of macroporous polymers, including PILs, is the high internal phase emulsion (HIPE) polymerization technique.^{37,38} A few years ago, fully interconnected poly(vinyl imidazolium)-based monoliths were produced via the polymerization of IL monomers and crosslinkers located in the external aqueous phase of a highly concentrated emulsion followed by the removal of the major internal dispersed phase, i.e. supercritical carbon dioxide (scCO₂).³⁹ The use of scCO₂ as the dispersed phase for polyHIPE synthesis affords several advantages as compared to traditional organic solvents, such as non-toxicity, non-flammability, abundance and easy removal via the simple depressurization of the reactor at the end of the process.^{40–42} Interestingly, CO₂-in-IL HIPE was also used as a template for the preparation of macroporous polyacrylamides⁴³ but no example of porous PILs has been reported in such a heterogeneous medium so far.

Given the huge potential of the PIL/IL combination and the valuable properties of macroporous structures, developing synthetic pathways towards macroporous PIL/IL monoliths appears as a strategic objective. Herein, we explored the radical copolymerization of IL monomers and crosslinkers in a CO₂-in-IL emulsion-templated approach for preparing innovative macroporous PIL/IL gels in a single step (Scheme 1). In this case, the ‘free’ IL serves as a solvent in the continuous internal phase of the emulsion and as a swelling agent for the formed PIL network whereas scCO₂ constitutes the dispersed phase of the emulsion used as a template for the preparation of porous PIL/IL gels. Indeed, at the end of the polymerization, the release of CO₂ should lead to porous PIL networks homogeneously swollen by ILs. This straightforward strategy favorably compares to the impregnation of a preformed porous PIL with a highly viscous non-polymerizable IL. A key point of our work consists of stabilizing the CO₂-in-IL emulsion. For this purpose, we considered fluorinated

molecular surfactants and also macromolecular surfactants including well-defined block copolymers composed of a CO₂-philic block and an ILphilic sequence produced by controlled radical polymerization (CRP). We also studied the effect of various parameters, including the CO₂ pressure or the addition of water in the IL phase, on the structure of porous PIL/IL gels and switched their nature and properties via simple ion exchange reactions.

Scheme 1 General strategy for the synthesis of PIL/IL macroporous gels.



Results and discussion

SURFACTANT-FREE SYNTHESIS OF PIL/IL GELS IN SCCO₂

Before considering the synthesis of macroporous PIL/IL gel monoliths using the CO₂-in-IL emulsion-templated method, it is necessary to select the 'free' IL as well as the IL monomer and crosslinker and also to carry out a preliminary polymerization study in the presence of scCO₂ without a surfactant in order to become familiar with this specific system. In this work, we decided to focus on the imidazolium-type ILs which are very popular and cover a large range of properties simply by varying the nature of the side chains of the imidazolium cation and the counteranion. For the selection, we also took into account the requirements of the targeted emulsions. First, the IL phase must be liquid at room temperature in order to enable its emulsification with scCO₂ without any additional solvent. Therefore, we exclusively focused on room-temperature ionic liquids (RTILs). Second, enough contrast is needed between the IL and the CO₂ phases in order to obtain proper emulsification. Although ILs are insoluble in scCO₂, CO₂ is partly soluble in some ionic liquids.^{44,45} This

characteristic is notably used in the field of CO₂ capture.^{16,46} In fact, the affinity of ILs for CO₂ depends on pressure, temperature, and nature of the cation, particularly the length of the side chains, but the most influential parameter is the counteranion.^{47–49} For example, fluorinated anions, like bis(trifluoromethylsulfonyl)amide (NTf₂[−]), favor CO₂ absorption^{50,51} and were thus discarded in our study. In contrast, IL derivatives with bromide or nitrate anions have a poor affinity for CO₂ and should offer a good phase contrast between ILs and the scCO₂ phase.

In light of the above considerations, we selected 1-vinyl-3-octylimidazolium bromide [OctVIm][Br] as the monomer, [C₆(Vim)₂][Br]₂ as the crosslinker and 1-methyl-3-octylimidazolium bromide [OctMelm][Br] as the ‘free’ IL partner (Table 1, entry 1). The above-mentioned IL mixture (IL comonomer/ ‘free’ IL 50/50 (v/v)) containing a radical initiator, i.e. V-50, was polymerized for 16 h at 65 °C under a CO₂ pressure of 300 bar in the absence of the surfactant. At the end of the process, the reactor was slowly vented and we recovered a crosslinked PIL/ IL material suggesting the effective initiation of the polymerization under these conditions. As expected, in the absence of the surfactant, the polymer occupied the bottom of the reactor indicating that CO₂ was not dispersed as discrete droplets in the IL phase, as expected.

Table 1 Copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ with ‘free’ ILs in scCO₂

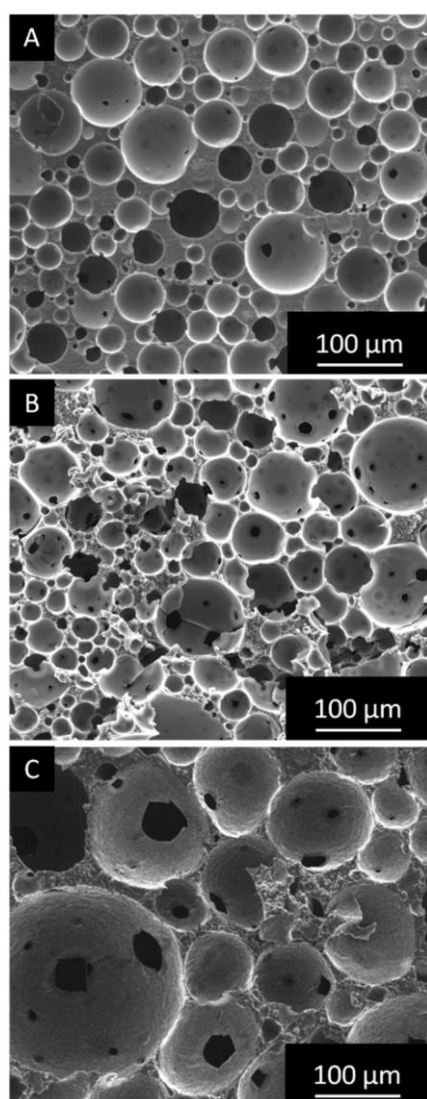
Entry	ILs	Temp. (°C)	P _{CO2} (bar)	Samples
1 ^a	[OctMelm][Br]	65	300	Non-porous
2 ^a	[OctMelm][NO ₃]	65	300	Non-porous
3 ^a	[BuMelm][NO ₃]	65	300	Porous (A)
4 ^b	[BuMelm][NO ₃]	40	200	Porous (B)
5 ^b	[BuMelm][NO ₃]	40	150	Porous ©

[OctVIm][Br] and [C₆(Vim)₂][Br]₂ were used as the monomer and crosslinker, respectively, in all cases. CO₂/IL 80/20 (v/v); monomer/free IL 50/50 (v/v), [OctVIm][Br]/[C₆(Vim)₂][Br]₂ 70/30 (v/v). ^a V-50 was used as the radical initiator (3.2 wt% based on monomers). ^b V-70 was used as the radical initiator (3.2 wt% based on monomers).

Inspired by a previous work describing the CO₂-in[BuMelm][NO₃] emulsion-templating polymerization of acrylamide,⁴³ we repeated the [OctVIm][Br] polymerization with ‘free’ ILs bearing a nitrate counterion and different alkyl chains, i.e. [OctMelm][NO₃] and [BuMelm][NO₃] (Table 1, entries 2 and 3). In both cases, the polymerization occurred and crosslinked PIL matrices swollen by ILs were recovered. Interestingly, the volume occupied by the polymer gel (sample A) formed in the presence of [BuMelm][NO₃] (Table 1, entry 3) was much higher than the sample obtained with [OctMelm][NO₃] (Table 1, entry 2). Scanning electronic microscopy (SEM) analysis of sample A revealed a porous structure (Fig. 1). This was quite unexpected in the absence of the surfactant and suggests that the [BuMelm][NO₃] possesses some surface activity at the CO₂/IL interface. Sample A possessed rather large cavities between 50 and 100 μm, which is consistent with a moderate stabilization of the CO₂-IL emulsion. It also showed a closed-cell structure in which cavities are separated by a wide polymer film preventing the formation of interconnecting pores. In order to

assess the influence of the CO₂ pressure and temperature, the copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ was repeated at 40 °C in the presence of [BuMelm][NO₃] at 200 and 150 bar leading to samples B and C, respectively (Table 1, entries 4 and 5). In this case, we replaced V-50 for V-70, a lower temperature radical initiator. As a result, the porous structures B and C were better interconnected than A. Although difficult to rationalize, this observation emphasizes the beneficial effect of the decrease in the temperature and pressure on the openness of the macroporous PIL/IL gel networks. Although encouraging, these porous materials are still far from the targeted structures in terms of the size of the cavities and connectivity. Moreover, additional experiments showed that a slight modification of the composition of the IL phase disturbed the stability of the emulsion and prevented the formation of the porous material. Nevertheless, this preliminary study allowed the identification of an interesting starting system that requires optimization, notably the addition of specific surfactants.

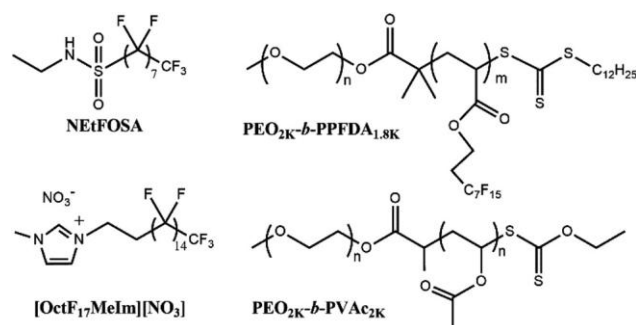
Fig. 1 SEM images of a PIL/IL gel obtained after the polymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ in the presence of [BuMelm][NO₃] at 300 bar/65 °C (sample A), 200 bar/40 °C (sample B) and 150 bar/40 °C (sample C).



SURFACTANT-ASSISTED CO₂-IN-IL EMULSION-TEMPLATED POLYMERIZATION

In order to improve the stability of the scCO₂-in-IL emulsion and the robustness of the corresponding emulsion-templated polymerization method, we added specific surfactants combining IL-philic and CO₂-philic parts. In this perspective, molecular and macromolecular surfactants (Fig. 2) were tested as stabilizers (150 mg) for the CO₂-in-IL emulsion-templated copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ in the presence of 'free' [BuMelm][NO₃]. The polymerization was invariably initiated with V-70 at 40 °C and 150 bar. As described below, the stabilizing CO₂-in-IL high internal phase emulsion was found to be really challenging.

Fig. 2 Molecular (left) and macromolecular (right) surfactants tested as stabilizers for the CO₂-in-IL emulsion-templated copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ in the presence of [BuMelm][NO₃] initiated with V-70 at 150 bar and 40 °C.



We first considered N-ethylperfluorooctane-1-sulfonamide (NETFOSA) that was previously used as a surfactant for the CO₂-in-IL emulsion-templated polymerization of acrylamide for the preparation of porous polyacrylamide matrices.⁴³ In this case, the sulfonamide head and the fluorinated tail of NETFOSA showed an affinity for the continuous IL phase and the internal CO₂ phase, respectively. Unfortunately, only nonporous PIL/IL gels were recovered when adding NETFOSA in our emulsion system combining CO₂ with a phase only containing IL derivatives. Even worse, the fragile emulsion formed without a surfactant and leading to the porous sample C seemed destabilized by the addition of NETFOSA.

In order to possibly reinforce the stabilization phenomena occurring in the presence of [BuMelm][NO₃], we prepared a fluorinated imidazolium-based molecule, i.e. 1-methyl-3-heptadecafluorooctylimidazolium nitrate ([OctF₁₇MeIm][NO₃]), whose perfluorinated tail should increase the affinity for the CO₂ phase. Note that several ionic liquids have already been used as surfactants in the past for preparing polymer nanoparticles, gels and open-cell porous materials.^{52–54} Briefly, [OctF₁₇MeIm][NO₃] was obtained via the quaternization of 1-methylimidazole with 1H,1H,2H,2H-perfluorodecyl bromide followed by an anion exchange to obtain the nitrate counterion. The structure was confirmed by ¹H NMR at 400 MHz (Fig. S1[†]). However, this modified imidazolium-based compound did not pave the way toward porous monoliths.

In previous studies, we synthesized by CRP a range of amphiphilic block copolymers with precisely controlled molecular parameters and compositions in order to ensure proper stabilization of the water-in-oil emulsion and tune the morphology of polyHIPEs.^{55–57} In a similar way, herein, we

designed a series of tailor-made copolymers dedicated to the stabilization of the CO₂-in-IL emulsion-templated copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂. As a CO₂-philic block, we selected poly(1H,1H,2H,2H-perfluorodecyl acrylate) (PFDA) and poly(vinyl acetate) (PVAc). The former fluorinated sequence enters the composition of several dispersion and emulsion polymerization stabilizers in scCO₂.^{58,59} The latter poly(vinyl ester) is inexpensive and biodegradable and has an uncommon high solubility in CO₂ for low molecular weight under conditions of practical relevance (P < 300 bar, T° < 100 °C).^{60,61} As an IL-philic block, we considered poly(ethylene)oxide (PEO) after verifying that it is soluble in the IL phase mixture composed of [OctVIm][Br], [C₆(Vim)₂][Br]₂ and [BuMelm][NO₃].

Without going into too many technical details, a PEO_{2k}-bPFDA_{1.8k} copolymer was prepared by the RAFT polymerization of FDA initiated from a PEO functionalized by a trithiocarbonate RAFT agent, following a procedure reported elsewhere.⁵⁸ The molar mass of the fluorinated block was determined by ¹H NMR based on the relative intensities of the signals corresponding to the methylene groups of PEO and the methylene -C₂F₂-CH₂-CH₂- of PPFDA (Fig. S2[†]). In a quite similar approach, a PEO_{2k}-b-PVAc_{2k} copolymer was prepared by the RAFT polymerization of VAc using xanthate as the RAFT agent, according to a well-established procedure.⁶² Briefly, PEO-OH (2000 g mol⁻¹) was functionalized with 2-bromopropionyl bromide followed by the reaction with potassium O-ethyl dithiocarbonate. The resulting PEO-xanthate was then used as the macroinitiator for the controlled polymerization of VAc in the presence of AIBN at 60 °C in THF. The overlay of the SEC chromatogram of the PEO precursor and the final copolymer ($M_{n,cal\ PEO} = 2700\text{ g mol}^{-1}$, $D = 1.32$) in Fig. S3[†] showed an almost complete chain extension. Based on the relative ¹H NMR intensities of the methylene groups of PEO and the methine groups of the VAc units, the M_n of the PVAc block was evaluated to be 2000 g mol⁻¹ (Fig. S4[†]), which is low enough to ensure its solubility in CO₂. Note that it is not necessary to remove the terminal RAFT agents from these copolymers because it will be located in the CO₂ phase of the emulsion and thus should not interfere with the polymerization of the IL monomers.

These macromolecular surfactants were tested as stabilizers (150 mg) for the CO₂-in-IL emulsion-templated copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ in the presence of [BuMelm][NO₃] at 150 bar and 40 °C using V-70 as the initiator. Note that all block copolymers were highly soluble in the IL continuous phase, which is essential to obtain a stable HIPE according to Bancroft's rule.⁵⁷ After the polymerization and depressurization of CO₂, crosslinked PIL/IL gels were obtained in all the cases but none of them was porous. This observation confirms that stabilizing HIPEs composed of a CO₂ phase and a phase containing ILs exclusively is much more challenging than stabilizing CO₂-in-water HIPE emulsions that are well documented.^{39,41,62}

MACROPOROUS PIL/IL GELS VIA CO₂-IN-IL/WATER EMULSION-TEMPLATED POLYMERIZATION

Until now, most emulsion-templating polymerization processes involving CO₂ as a dispersed phase and leading to porous monoliths used aqueous solution as the external phase.³⁶ In comparison with the CO₂-in-ILs considered in this study, the CO₂-in-water emulsions probably afford higher phase

contrast and lower viscosity of the external phase which might be favorable to the emulsification process. In light of these considerations, we decided to substitute [BuMelm][NO₃] for water in our standard HIPE polymerization procedure or add different proportions of water in our IL phase containing [OctVIm][Br] and [C₆(Vim)₂][Br]₂ (Table 2).

In these experiments, we tested various PEO-b-PVAc macromolecular surfactants which were successfully used for the preparation of polyHIPEs by the CO₂-in-water emulsion process.⁶² First, [OctVIm][Br], [C₆(Vim)₂][Br] and the PEO_{2k}-b-PVAc_{2k} macromolecular surfactant were dissolved in water instead of [BuMelm][NO₃] before the addition of V-70 and CO₂ pressurization under stirring (Table 2, entry 1). The polymerization was carried out at 40 °C and 150 bar. After several hours, the reactor was vented and a monolith occupied the whole volume of the reactor, suggesting an efficient emulsification process. At this stage, the obtained material still contained water and was thus lyophilized to provide the corresponding dry PIL polyHIPE D. The latter was observed by SEM (Fig. 3) and presented highly interconnected cavities of about 40 µm. Moreover, close examination of the wall of the cavities showed some roughness and the formation of microglobules probably due to the precipitation of the PILs within the continuous water phase. Such polymerization-induced phase separation created interstices between the particles after water removal.

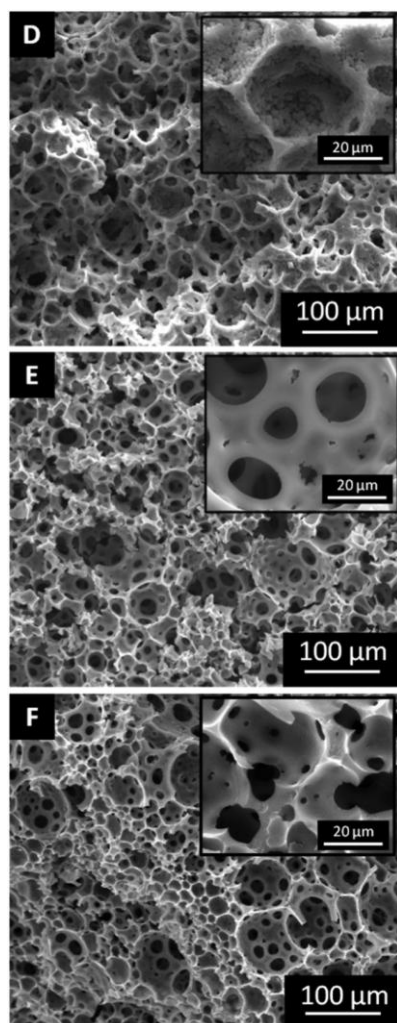
Although the previous experiment provides very nice porous PILs, it cannot provide access to the desired macroporous PIL/ IL gels. To achieve this, we repeated the same experiment except that a [OctMelm][Br]/water mixture (50/50: v/v) was used instead of water (Table 2, entry 2). Note that [OctMelm][Br] was selected as a 'free' IL in order to ensure an ideal homogeneity with the IL comonomers and the resulting PIL network. Under these conditions, a nice open-cell polyHIPE was recovered (Fig. 3, sample E). Moreover, the size of the cavities and interconnecting pores was almost unchanged as compared to sample D but in this case, the walls of polyHIPE were smoother even after the removal of water by lyophilization. This suggests that no precipitation occurred during the copolymerization of [OctVIm][Br] and [C₆(Vim)₂][Br] in the [OctMelm][Br]/water mixture. In this way, we also prepared the first macroporous PIL/IL gel via a single-step emulsion process. In order to prove that the PIL polyHIPE E was swollen by [OctMelm][Br] we performed an extraction treatment on E with deuterated chloroform and analyzed the extracts by ¹H NMR (Fig. 4). For the sake of comparison, sample D was subjected to an identical treatment. For both samples, typical signals of the PEO_{2k}-b-PVAc_{2k} surfactant were observed at 4.8 ppm for the methine group of PVAc and at 3.6 ppm for the methylene groups of PEO, suggesting an efficient extraction of the copolymer from the matrix. Aside from these peaks, in sample E, we clearly distinguished signals corresponding to [OctMelm][Br] which undoubtedly proves that E consisted of a macroporous PIL/IL gel before extraction.

Table 2 Synthesis of macroporous PILs and PIL/IL monoliths in the presence of water

Entry	[OctMelm][Br]/water (v/v)	CO ₂ pressure (bar)	Surfactant	Samples
1	0/100	150	PEO _{2k} -b-PVAc _{2k}	D
2	50/50	150	PEO _{2k} -b-PVAc _{2k}	E
3	50/50	300 ^a	PEO _{2k} -b-PVAc _{2k}	F
4	75/25	150	PEO _{2k} -b-PVAc _{2k}	—
5	50/50	150	PEO _{5k} -b-PVAc _{1.8k}	G
6	50/50	150	PEO _{2k} -b-PVAc _{5.2k}	—

[OctVIm][Br] and [C₆(Vim)₂][Br]₂ were used as monomers (70/30 (v/v)) and 7.5 wt% of surfactants compared to the continuous phase were used in all cases. CO₂/IL 80/20 (v/v); monomer/IL 50/50 (v/v). V-70 was used as the radical initiator (3.2 wt% based on monomers). The pressure was fixed at 80 bar at 20 °C before heating the medium at 40 °C and reaching 150 bar. ^aThe pressure was fixed at 150 bar at 20 °C before heating the medium at 40 °C and reaching 300 bar.

Fig. 3 SEM images of a PIL/IL macroporous monolith obtained after the polymerization of [OctVIm][Br] and [C₆(Vim)₂][Br]₂ in the presence of water (sample D), a mixture of [OctMelm][Br] and water at 150 bar (sample E) and 40 °C and at 300 bar (sample F).

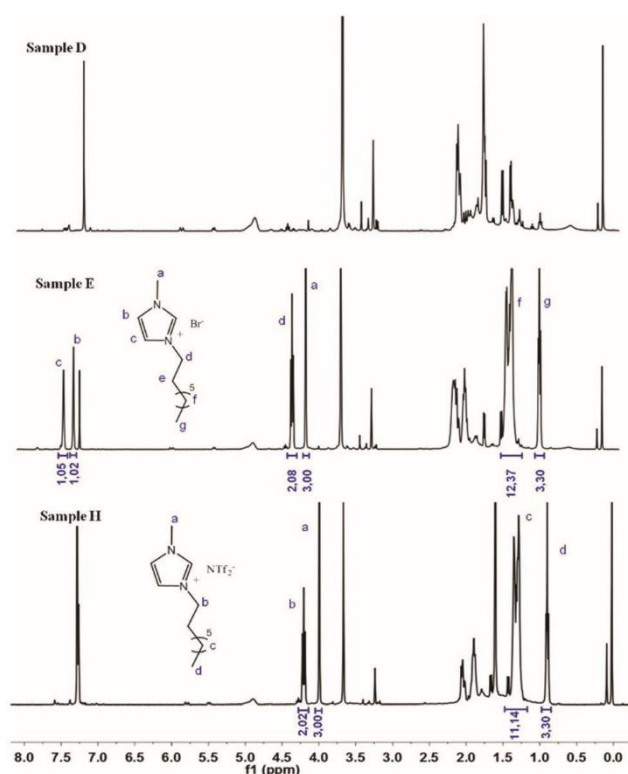


Increasing the CO₂ pressure from 150 to 300 bar (Table 2, entry 3) did not significantly change the structure of the macroporous PIL/IL gel (Fig. 3, sample F), confirming that 150 bar is enough to ensure the proper solubilisation of the PVAc segment of the surfactant in the scCO₂ dispersed phase.

Moreover, increasing the proportion of [OctMelm][Br] in the IL/water mixture (75/25 v/v) destabilized the HIPE emulsion and did not lead to porous monoliths (Table 2, entry 4). This further emphasized the necessity to incorporate a sufficient amount of water in the continuous phase to obtain stable CO₂-in-IL/water HIPE and the corresponding macroporous structures.

Finally, we changed the macromolecular parameters of the PEO-b-PVAc surfactant in order to emphasize their influence on the HIPE stabilization and the polyHIPE morphology (Table 2, entries 5 and 6). Following the above-mentioned synthesis strategy, the molar mass of PVAc and the PEO sequence was adjusted, i.e. PEO_{5k}-b-PVAc_{1.8k} (Fig. S5†) and PEO_{2k}-b-PVAc_{5.2k} (Fig. S6†). When using the copolymer with the longer PEO block, i.e. PEO_{5k}-b-PVAc_{1.8k}, the final PIL/IL monolith G did not occupy the whole reactor. The SEM analysis of G confirmed the less efficient emulsification process and the formation of a closed-cell material (Fig. S7†). The improved affinity of the surfactant for the continuous phase as well as the higher molecular weight associated with a lower mobility of the copolymer might account for this lack of stabilization. On the other hand, increasing the molar mass of the PVAc segment to 5200 g mol⁻¹ while keeping the PEO molar mass at 2000 g mol⁻¹ also had a detrimental effect on the emulsion templated process and no monolith was recovered. In this case, the absence of the stabilizing effect of the emulsion certainly originated from the poor solubility in the CO₂ of the PVAc segment as a result of its higher molar mass.

Fig. 4 ¹H NMR of the products obtained from the extraction of samples D, E and H with CDCl₃.



PRELIMINARY EVALUATION OF MECHANICAL AND SURFACE PROPERTIES OF THE PIL/IL POROUS GELS

The mechanical properties of the PIL polyHIPE D and the macroporous PIL/IL gel E were investigated (Fig. 5). Upon compression, D was irreversibly deformed. Moreover, a break in the stress–strain curve was clearly observed at low constraints (around 0.1 MPa) for D after lyophilization. This corresponds to the fracture of the monolith (picture in Fig. 5) and highlights the brittleness of the material anticipated based on the inhomogeneity of the walls of this polyHIPE (see sample D in Fig. 3). In contrast, a complete elastic deformation was observed for sample E. Indeed, even after 80% of deformation, the sample recovered its initial shape when the stress was released, as depicted by the picture in Fig. 5. In this case, no difference was noted before and after lyophilization. As expected for a gel, the Young's modulus values were as low as 4 MPa.

A very interesting feature of poly(ionic liquid)s, and in particular of poly(vinylimidazolium)s, is the possibility to drastically change their properties, including their solubility, by a simple anion exchange reaction.^{12,14,15} For example, the hydrosoluble poly(vinylethylimidazolium bromide) (PVI_mOctBr) can be easily converted into hydrophobic poly(vinylethylimidazolium bis(trifluoromethylsulfonyl)amide) (PVI_mOctNTf₂) upon treatment with NTf₂ salts.¹⁰ In this perspective, we tried to trigger the hydrophilicity/hydrophobicity of the macroporous PIL/IL gel E via a similar exchange reaction. In practice, E was immersed for one hour in an aqueous solution of LiNTf₂[−], washed with fresh water and lyophilized, leading the monolith H. Note that the amount of LiNTf₂[−] involved in the reaction was sufficient to replace the bromide anions of both the PIL matrix and [OctMelm][Br]. In order to confirm the anion exchange and verify that the ILs contained by the PIL network were not lost during the treatment, we performed an extraction on H with CDCl₃ and analyzed the deuterated solution by ¹H NMR. As expected, typical signals corresponding to [OctMelm][NTf₂] were detected (Fig. 4) which validates the ion exchange procedure and the formation of a novel macroporous PIL/IL gel H based on the NTf₂[−] counterion. The surface properties of these macroporous gels were then examined with a water drop deposition experiment (Fig. 6). The water droplet was instantaneously absorbed by the PIL/IL gel E containing bromide anions, confirming its high hydrophilicity. In sharp contrast, the water droplet remained on the surface of the NTf₂-based monolith H and showed a high contact angle (115°) typical of highly hydrophobic materials. This demonstrates the possible switch from highly hydrophilic to highly hydrophobic PIL/IL macroporous gels via a straightforward ion exchange strategy.

Fig. 5 Stress–strain curves for PIL polyHIPE D (full lines) and macroporous PIL/IL gel E (dotted lines) before (blue lines) and after lyophilization (red lines).

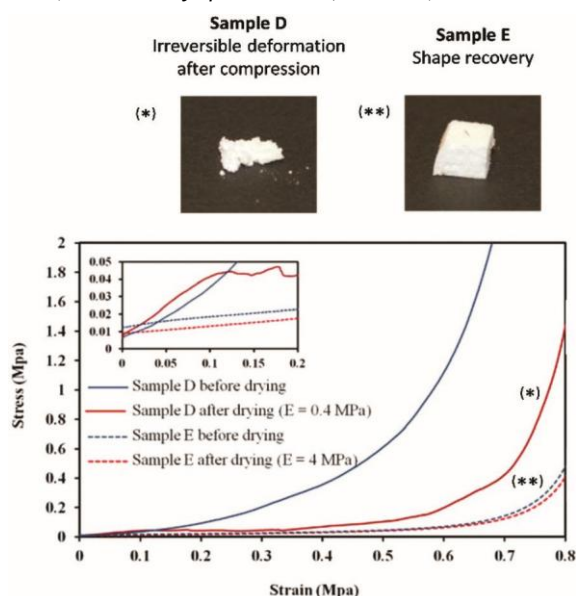
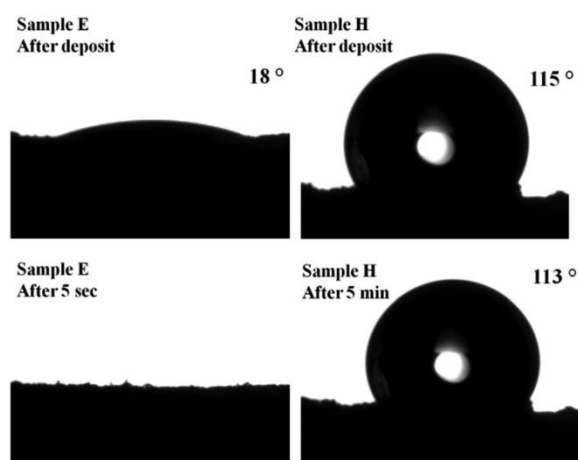


Fig. 6 Contact angle measurements of bromide-based PIL/IL macroporous gel E and NTf₂-based PIL/IL macroporous gel H.



Experimental

MATERIALS

1-Vinylimidazole, 1-bromooctane, 1-bromobutane, 1,6-dibromohexane, (α -methoxy, ω -hydroxy) poly(ethylene glycol) (PEO, 2000 g mol⁻¹), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (CTA), 1H,1H,2H,2H-heptafluorodecyl acrylate (FDA), 2-bromopropionyl bromide, potassium O-ethyl dithiocarbonate, 2,2'-azobis(2-methylpropionitrile) (AIBN) and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) were purchased from Aldrich and all were used as received. Silver nitrate (AgNO₃, Alfa Aesar), 1H,1H,2H,2H-perfluorodecyl bromide (ABCR),

perfluorooctanesulphonamide (NEtFOSA, ABCR), bis(trifluoromethane)sulfonimide lithium salt (LiNTf₂, ABCR) and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Chemicals) were also used as received. Vinyl acetate (>99%, Aldrich) was dried over calcium hydride, degassed by several freeze–thaw cycles before being distilled under reduced pressure and stored under argon. H₂O (18.2 mΩ cm⁻¹) was obtained from Millipore Milli-Q Plus. Carbon dioxide (CO₂) was pressurized into stainless steel reactors (12 cm³) using an Isco 260D syringe pump. The initial pressure in the reactor was measured with an Isco D-Series pump controller and on the reactor with a WIKA pressure gauge (0–600 bar). A PTFE poly(tetrafluoroethylene) coated magnetic bar was used to stir the reactor before polymerization.

CHARACTERIZATION

The relative molar mass (M_n) and the dispersity ($\bar{M}_w/\bar{M}_n$) of PEO-bPVAc were determined by size-exclusion chromatography (SEC) in THF at 45 °C at a flow rate of 1 mL min⁻¹ with a Viscotek 305 TDA liquid chromatograph equipped with 2 PSS SDV analytical linear M columns calibrated with poly(ethylene oxide) (PEO) standards. ¹H NMR analysis was performed using a 400 MHz Bruker spectrometer at 298 K.

The polyHIPE morphology was analyzed by scanning electron microscopy (SEM). SEM images of the polyHIPEs were obtained with a Jeol JSM 804-A apparatus after the metallization of the sample with Pt (30 nm) in order to estimate the size of voids and pore throats. The counteranion exchange performed on the polyHIPE surfaces was emphasized by static contact angle measurements with the sessile drop technique at 20 °C using a GBX Digidrop instrument (DGD Fast 60 contact angle meter) and the WinDrop software to analyze the shape of the drop. A 10 µL drop of distilled water was deposited on a piece of monolith previously dried. The contact angle was measured directly after the drop deposition and after 5 seconds. The mechanical properties of polyHIPEs were also characterized. The stress–strain curves were recorded at room temperature with an Instron tester (model DY24) equipped with a 10 N static cell at 1 mm min⁻¹ compression speed.

PROCEDURES

1,6-DI-(3-VINYLMIDAZOLIUM) HEXANE DIBROMIDE [C₆(VIm)₂][Br]₂. The synthesis of the crosslinker was carried out according to the procedure reported in the literature.³⁹ 1-Vinylimidazole (10 mL, 10.4 g, 110 mmol) and 1,6-dibromohexane (8.3 mL, 13.2 g, 54 mmol) were dissolved in acetonitrile (25 mL). The mixture was heated at 70 °C overnight under reflux. The solvent was then removed by filtration and the residue was washed with acetonitrile for 2 h at 70 °C in order to eliminate the residual reactants and the monoquaternized by-product. [C₆(VIm)₂][Br]₂ was obtained as a white solid and dried under reduced pressure.

1-VINYL-3-OCTYLMIDAZOLIUM BROMIDE [OCTVIm][Br]. 1-Vinylimidazole (19 mL, 19.7 g, 210 mmol) and 1-bromooctane (40 mL, 44.7 g, 230 mmol) were dissolved in acetonitrile (100 mL). After reflux at 80 °C for 24 h, the mixture was precipitated in cold diethyl ether. [OctVIm][Br] was recovered as a viscous liquid and washed three times with fresh diethyl ether in order to eliminate the residual reactants.

1-METHYL-3-OCTYLIMIDAZOLIUM BROMIDE [OCTMelm][Br]. 1-Methylimidazole (20 mL, 20.6 g, 250 mmol) and 1-bromooctane (50 mL, 55.9 g, 290 mmol) were dissolved in acetonitrile (100 mL). After reflux at 80 °C for 24 h, the mixture was precipitated in cold diethyl ether. [OctMelm][Br] was recovered as a viscous liquid and washed three times with fresh diethyl ether in order to eliminate the residual reactants.

1-METHYL-3-BUTYLIMIDAZOLIUM BROMIDE [BUMelm][Br]. 1-Methylimidazole (15 mL, 15.4 g, 190 mmol) and 1-bromobutane (40 mL, 51 g, 370 mmol) were dissolved in acetonitrile (40 mL). After reflux at 80 °C for 24 h, the mixture was precipitated in cold diethyl ether. [BuMelm][Br] was recovered as a white powder and washed three times with fresh diethyl ether in order to eliminate the residual reactants.

1-METHYL-3-OCTYLIMIDAZOLIUM NITRATE [OCTMelm][NO₃] AND 1-METHYL-3-BUTYLIMIDAZOLIUM NITRATE [BUMelm][NO₃]. Anion exchange was performed on [OctMelm][Br] and [BuMelm][Br] with AgNO₃. Typically, [BuMelm][Br] (15 g, 67 mmol) was dissolved in 30 mL of water and 10 mL of an aqueous solution of AgNO₃ (6.87 M, 70 mmol) was added dropwise under vigorous stirring for 30 minutes. The green precipitate (AgBr) was removed by centrifugation and the excess of AgNO₃ was reacted with a solution of [BuMelm][Br] until no precipitate was observed. The aqueous solution of [BuMelm][Br] was dried by lyophilisation and the product was recovered as a viscous liquid. The procedure was repeated for [OctMelm][Br].

1-METHYL-3-HEPTADEC AFLUORO OCTYLIMIDAZOLIUM NITRATE [OCTF₁₇Melm][NO₃]. 1-Methylimidazole (0.58 mL, 0.6 g, 7.3 mmol) and 1H,1H,2H,2H-perfluorodecyl bromide (4.6 g, 2.6 mL, 8.7 mmol) were dissolved in 4 mL of acetonitrile and the mixture was reacted under reflux at 80 °C for 24 h. The reaction mixture was precipitated in diethyl ether, washed three times and dried under vacuum. [OctF₁₇Melm][Br] (2 g, 3 mmol) was dissolved in 10 mL of water and 5 mL of a AgNO₃ solution (0.79 M, 0.04 mol) was added dropwise under stirring for 30 minutes. The solid was washed with MeOH in order to extract [OctF₁₇Melm][NO₃].

PEO-*B*-PFDA COPOLYMERS. Poly(ethylene oxide) macromolecular RAFT agent (PEO-CTA) was synthesized as previously described by reacting (α-methoxy, ω-hydroxy) poly(ethylene glycol) (2000 g mol⁻¹) with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid.^{57,58} PEO-CTA (1 g, 0.4 mmol), FDA (0.7 mL, 1.1 g, 2.1 mmol) and AIBN (0.014 g, 0.09 mmol) were placed into a Schlenk tube and dissolved in 6 mL of TFT. The mixture was degassed by bubbling argon for 5 min and heated at 80 °C under stirring. After 19 h, the conversion reached 87%. The solution was then cooled down and precipitated in cold diethyl ether. The copolymer was obtained by centrifugation and the molecular weight of the PFDA block was determined by ¹H NMR analysis in CDCl₃.

PEO-*B*-PVAC COPOLYMERS. According to the procedure by Tan et al.,⁶² (α-methoxy, ω-hydroxy) poly(ethylene glycol) (2000 g mol⁻¹, 10 g, 5 mmol) was dissolved in 30 mL of dry dichloromethane and placed in an ice bath. Pyridine (1.08 mL, 1.06 g, 13.4 mmol) and 2-bromopropionyl bromide (1.2 mL, 2.4 g, 11.3 mmol) were added in 5 mL of dry dichloromethane and the solution was transferred dropwise on PEO. The mixture was mixed at room temperature overnight and the salts were then filtered. The solution was washed with saturated ammonium chloride (3 × 30 mL), saturated sodium bicarbonate (3 × 30 mL) and water (3 × 30 mL) and finally dried over anhydrous magnesium sulfate.

After filtration, the product was dried under vacuum. The resulting bromopropionic acid poly(ethylene glycol) ester (2 g, 0.9 mmol) was dissolved in 10 mL of dichloromethane and reacted with pyridine (3.8 mL, 3.7 g, 47 mmol) and potassium O-ethyl dithiocarbonate (0.44 g, 2.7 mmol) overnight under stirring at room temperature. The solution was washed again with saturated ammonium chloride (3 × 30 mL), saturated sodium bicarbonate (3 × 30 mL) and water (3 × 30 mL) and dried over anhydrous magnesium sulfate. The solvents were then evaporated and PEO-xanthate was obtained. Finally, the polymerization of VAc was initiated. Typically, PEO-xanthate (0.8 g, 0.3 mmol) and AIBN (0.012 g, 0.07 mmol) were dissolved in 4 mL of THF and the solution was degassed. VAc (1.3 mL, 1.2 g, 13.8 mmol) was added and the mixture was immersed in an oil bath at 60 °C with stirring for 16 h. The resulting diblock was precipitated in cold n-hexane and dried under reduced pressure. The macromolecular characteristics of the copolymer were measured by SEC in THF (M_n of calibration PEO = 2700 g mol⁻¹, $\bar{D}$ = 1.32) and the molar mass of the poly(vinyl acetate) block was measured by ¹H NMR analysis in CD₂Cl₂ (M_n PVAc block = 2000 g mol⁻¹). A molecular weight of 5200 g mol⁻¹ for PVAc was targeted by adjusting the initial [VAc]₀/[PEO-xanthate]₀ molar ratio and a diblock PEO_{5k}-b-PVAc_{1.8k} was synthesized by using (α-methoxy, ω-hydroxy) poly(ethylene glycol) (5000 g mol⁻¹) according to the same procedure.

SURFACTANT-FREE SYNTHESIS OF PIL/IL GELS IN scCO₂. Typically, a mixture of [OctVIm][Br] (0.7 mL), crosslinker [C₆(VIm)₂][Br]₂ (300 mg, 0.007 mol) and [BuMelm][NO₃] (1 mL) was added in a stainless steel reactor (12 cm³) containing a magnetic stirrer. V-70 (65 mg) was added as the radical initiator and the vessel was purged for a few minutes with CO₂ under stirring at 400 rpm before pressurization with liquid CO₂ (20 °C, 80 bar). After 5 min, the temperature was increased gradually up to 40 °C to reach a pressure of 150 bar. After 16 h of polymerization, the reactor was cooled down to room temperature and slowly vented. The poly(ionic liquid) gel was obtained as a white crosslinked solid (sample C, Table 1). Other experiments were performed by using other free ILs ([OctMelm][Br] and [OctMelm][NO₃]) in the same amount, other pressures (300 bar and 200 bar), and another radical initiator and temperature (V-50 and 65 °C, respectively).

SURFACTANT-ASSISTED CO₂-IN-IL EMULSION-TEMPLATED POLYMERIZATION ASSAYS. The procedure was similar to the surfactant-free synthesis of PIL/IL gels in scCO₂ but the surfactants (150 mg of PEO-b-PVAc, PEO-b-PFDA, NEtFOSA or [OctF₁₇Melm][NO₃]) were added in the reaction vessel before pressurization.

SYNTHESIS OF MACROPOROUS PIL/IL GELS THROUGH CO₂-IN-IL/ WATER EMULSIONS. The procedure was similar to the surfactantfree synthesis of PIL/IL gels in scCO₂ except that 150 mg of PEO-b-PVAc with different macromolecular parameters and a mixture of water and ([OctMelm][Br]) (1 mL, 50/50 (v/v)) were used instead of [BuMelm][NO₃] (sample E, Table 2). The ratio of water/[OctMelm][Br] and the pressure in the reactor were also modified.

IL EXTRACTION FROM POLYHIPE. The macroporous PIL/IL gel E (100 mg) was reduced into powder before adding deuterated chloroform (CDCl₃, 1.4 mL) and mixed for two hours. The mixture was separated by centrifugation and the CDCl₃ solution was analyzed by ¹H NMR at 400 MHz to show the presence

of free ILs. The same procedure was applied on polyHIPE obtained after the anion exchange (sample H) and on polyHIPE without free ILs in the matrix (sample D).

ANION EXCHANGE ON PIL POLYHIPE. A piece (1 cm³) of PIL/IL macroporous gel monolith E was added in 30 mL of water containing LiNTf₂⁻ (0.7 g, 0.002 mol). The solution was stirred for 1 h and polyHIPE was washed with fresh water five times. The monolith was dried by lyophilisation and was observed by SEM. Contact angle measurement was also performed before and after the anion exchange.

Conclusions

In summary, macroporous PIL/IL gels were synthesized for the first time. For this purpose, we developed a CO₂-in-IL emulsion-templated copolymerization method of ionic liquid monomers and crosslinkers. A series of primary experiments was carried out in the presence of molecular and macromolecular surfactants specifically designed for stabilizing the CO₂-IL interface. Nevertheless, no porous monoliths were obtained when a pure IL phase was used, confirming that stabilizing a CO₂-IL HIPE is much more challenging than emulsifying CO₂ in water. Fortunately, the addition of water in the IL phase afforded a proper emulsification with CO₂ and the formation of highly interconnected macroporous monoliths. Lyophilisation of the latter allowed the removal of their water content without affecting the morphology of polyHIPE leading for the first time to macroporous PIL/IL gels in a single step. A preliminary mechanical study of these novel porous gels highlighted their complete shape recovery after strong deformation upon compression. Moreover, we took advantage of the intrinsic capacity of PILs to undergo ion exchange reactions and switched highly hydrophilic macroporous bromide-based PIL/IL gels into completely hydrophobic NTf₂-based macroporous gels. In the future, the presented pathway will be expanded to other PILs and ILs in order to cover a wide range of properties and applications, notably in the fields of gas capture and catalysis. Given the considerable interest on PILs, and more particularly on PIL/IL mixtures in numerous research fields as well as the increasing use of macroporous materials in many applications, this innovative CO₂-IL emulsion-templated method represents a unique opportunity to combine the advantages of the nature and structure of each material.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to the Belgian National Funds for Scientific Research (F.R.S.-FNRS) and the Belgian Science Policy (PAI VII-05) for funding. A. D. is a FNRS Research Associate.

Notes and references

1. M. Ramdin, T. W. De Loos and T. J. H. Vlugt, *Ind. Eng. Chem. Res.*, 2012, 51, 8149–8177.
2. E. Torralba-Calleja, J. Skinner and D. Gutiérrez-Tauste, *J. Chem.*, 2013, 1–16.
3. M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, 8, 621–629.
4. J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng and S. Zhang, *Catal. Today*, 2009, 148, 361–367.
5. Z. Zhang, F. Fan, H. Xing, Q. Yang, Z. Bao and Q. Ren, *ACS Sustainable Chem. Eng.*, 2017, 5, 2841–2846.
6. N. Shirshova, A. Bismarck and J. H. G. Steinke, *Macromol. Rapid Commun.*, 2011, 32, 1899–1904.
7. N. Shirshova, P. Johansson, M. J. Marczewski, E. Kot, D. Ensling, A. Bismarck and J. H. G. Steinke, *J. Mater. Chem. A*, 2013, 1, 9612–9619.
8. C. Le mericer, S. Acerbis, D. Bertin, F. Chauvin, D. Gigmes, O. Guerret, M. Lansalot, S. Marque, F. Le Moigne and H. Fischer, *Macromol. Symp.*, 2002, 247, 225–247.
9. L. Zhu and C. Hu, *Ionic Liq.: New Aspects Future*, 2013, 349–364.
10. R. Marcilla, J. A. Blazquez, J. Rodriguez, J. a. Pomposo and D. Mecerreyes, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, 42, 208–212.
11. J. Tang, H. Tang, W. Sun, M. Radosz and Y. Shen, *Polymer*, 2005, 46, 12460–12467.
12. J. Yuan, D. Mecerreyes and M. Antonietti, *Prog. Polym. Sci.*, 2013, 38, 1009–1036.
13. A. S. Shaplov, D. O. Ponkratov and Y. S. Vygodskii, *Polym. Sci., Ser. B*, 2016, 58, 73–142.
14. D. Mecerreyes, *Prog. Polym. Sci.*, 2011, 36, 1629–1648.
15. W. Qian, J. Texter and F. Yan, *Chem. Soc. Rev.*, 2017, 46, 1124–1159.
16. Z. Dai, R. D. Noble, D. L. Gin, X. Zhang and L. Deng, *J. Membr. Sci.*, 2016, 497, 1–20.
17. T. K. Carlisle, G. D. Nicodemus, D. L. Gin and R. D. Noble, *J. Membr. Sci.*, 2012, 397–398, 24–37.
18. J. E. Bara, R. D. Noble and D. L. Gin, *Ind. Eng. Chem. Res.*, 2009, 48, 4607–4610.
19. J. E. Bara, E. S. Hatakeyama, D. L. Gin and R. D. Noble, *Polym. Adv. Technol.*, 2008, 19, 1415–1420.
20. G. Zarca, W. J. Horne, I. Ortiz, A. Urtiaga and J. E. Bara, *J. Membr. Sci.*, 2016, 515, 109–114.
21. M. G. Cowan, D. L. Gin and R. D. Noble, *Acc. Chem. Res.*, 2016, 49, 724–732.
22. M. Safa, A. Chamaani, N. Chawla and B. El-Zahab, *Electrochim. Acta*, 2016, 213, 587–593.
23. S. Zhang, K. Dokko and M. Watanabe, *Chem. Sci.*, 2015, 6, 3684–3691.
24. S. Zulfiqar, M. I. Sarwar and D. Mecerreyes, *Polym. Chem.*, 2015, 6, 6435–6451.
25. X. Wang, Y. Zhou, Z. Guo, G. Chen, J. Li, Y. Shi, Y. Liu and J. Wang, *Chem. Sci.*, 2015, 6, 6916–6924.
26. J.-K. Sun, M. Antonietti and J. Yuan, *Chem. Soc. Rev.*, 2016, 45, 6627–6656.
27. Z. Guo, Q. Jiang, Y. Shi, J. Li, X. Yang, W. Hou, Y. Zhou and J. Wang, *ACS Catal.*, 2017, 7, 6770–6780.
28. Q. Wang, W. Hou, S. Li, J. Xie, J. Li, Y. Zhou and J. Wang, *Green Chem.*, 2017, 19, 3820–3830.

29. S. Soll, Q. Zhao, J. Weber and J. Yuan, *Chem. Mater.*, 2013, 25, 3003–3010.
30. Wilke, J. Yuan, M. Antonietti and J. Weber, *ACS Macro Lett.*, 2012, 1, 1028–1031.
31. Gao, G. Chen, X. Wang, J. Li, Y. Zhou and J. Wang, *Chem. Commun.*, 2015, 51, 4969–4972.
32. X. Feng, C. Gao, Z. Guo, Y. Zhou and J. Wang, *RSC Adv.*, 2014, 4, 23389–23395.
33. X. Hu, J. Huang, W. Zhang, M. Li, C. Tao and G. Li, *Adv. Mater.*, 2008, 20, 4074–4078.
34. J. Huang, C. Tao, Q. An, W. Zhang, Y. Wu, X. Li, D. Shen and G. Li, *Chem. Commun.*, 2010, 46, 967–969.
35. J. Huang, C. Tao, Q. An, C. Lin, X. Li, D. Xu, Y. Wu, X. Li, D. Shen and G. Li, *Chem. Commun.*, 2010, 46, 4103.
36. H. Zhang, L. Bai, Z. Wei, S. Liu, H. Liu and H. Yan, *Talanta*, 2016, 149, 62–68.
37. M. S. Silverstein, *Prog. Polym. Sci.*, 2014, 39, 199–234.
38. I. Pulko and P. Krajnc, *Macromol. Rapid Commun.*, 2012, 33, 1731–1746.
39. C. Boyère, A. Favrelle, A. F. Léonard, F. Boury, C. Jérôme and A. Debuigne, *J. Mater. Chem. A*, 2013, 1, 8479–8487.
40. W. Luo, S. Zhang, P. Li, R. Xu, Y. Zhang, L. Liang, C. D. Wood, Q. Lu and B. Tan, *Polymer*, 2015, 61, 183–191.
41. W. Luo, R. Xu, Y. Liu, I. Hussain, Q. Lu and B. Tan, *RSC Adv.*, 2015, 5, 92017–92024.
42. R. Butler, C. M. Davies, I. Hopkinson and A. I. Cooper, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 2002, 43, 744–745.
43. L. Peng, J. Zhang, J. Li, B. Han, Z. Xue and G. Yang, *Angew. Chem., Int. Ed.*, 2013, 52, 1792–1795.
44. F. Karadas, M. Atilhan and S. Aparicio, *Energy Fuels*, 2010, 24, 5817–5828.
45. C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke and E. J. Maginn, *J. Am. Chem. Soc.*, 2004, 126, 5300–5308.
46. J. L. Anderson, J. K. Dixon and J. F. Brennecke, *Acc. Chem. Res.*, 2007, 40, 1208–1216.
47. Y.-F. Hu, Z.-C. Liu, C.-M. Xu and X.-M. Zhang, *Chem. Soc. Rev.*, 2011, 40, 3802–3823.
48. D. Almantariotis, T. Gefflaut, A. A H. Pádua, J. Y. Coxam and M. F. Costa Gomes, *J. Phys. Chem. B*, 2010, 114, 3608–3617.
49. J. E. Bara, D. L. Gin and R. D. Noble, *Ind. Eng. Chem. Res.*, 2008, 47, 9919–9924.
50. R. S. Bhavsar, S. C. Kumbharkar and U. K. Kharul, *J. Membr. Sci.*, 2012, 389, 305–315.
51. J. E. Bara, S. Lessmann, C. J. Gabriel, E. S. Hatakeyama, R. D. Noble and D. L. Gin, *Ind. Eng. Chem. Res.*, 2007, 46, 5397–5404.
52. T. L. Merrigan, E. D. Bates, S. C. Dorman and J. H. Davis Jr., *Chem. Commun.*, 2000, 2051–2052.
53. F. Yan and J. Texter, *Chem. Commun.*, 2006, 2696.
54. Z. G. Asadov, G. A. Akhmedova, A. D. Aga-Zadeh, S. M. Nasibova, I. A. Zarbalieva, A. M. Bagirova and R. A. Ragimov, *Russ. J. Gen. Chem.*, 2012, 82, 1916–1927.
55. K. Mathieu, J. De Winter, C. Jerome and A. Debuigne, *Polym. Chem.*, 2017, 8, 1850–1861.

56. K. Mathieu, C. Jérôme and A. Debuigne, *Polymer*, 2016, 99, 157–165.
57. K. Mathieu, C. Jérôme and A. Debuigne, *Macromolecules*, 2015, 48, 6489–6498.
58. D. Alaimo, A. Beigbeder, P. Dubois, G. Broze, C. Jérôme and B. Grignard, *Polym. Chem.*, 2014, 5, 5273–5282.
59. D. Alaimo, D. Hermida Merino, B. Grignard, W. Bras, C. Jérôme, A. Debuigne and C. J. Gommès, *J. Phys. Chem. B*, 2015, 119, 1706–1716.
60. B. Tan and A. I. Cooper, *J. Am. Chem. Soc.*, 2005, 127, 8938–8939.
61. S. Zhang, W. Luo, W. Yan and B. Tan, *Green Chem.*, 2014, 16, 4408.
62. K. Chen, N. Grant, L. Liang, H. Zhang and B. Tan, *Macromolecules*, 2010, 43, 9355–9364.