



Functional mesoporous poly(ionic liquid)-based copolymer monoliths: From synthesis to catalysis and microporous carbon production



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ABSTRACT

Ionic liquid-functionalized mesoporous polymeric networks with specific surface area up to 935 m²/g have been successfully synthesized one pot by solvothermal copolymerization of divinylbenzene and monomeric ionic liquids. The as-obtained polymers exhibit a monolithic structure featuring large pore volumes, an abundant mesoporosity and an adjustable content of ionic liquids. The effect of the reaction conditions on the pore structure has been studied in detail. These poly(ionic liquid)-based porous networks (PILPNs) have then been employed as precursors in two distinct applications, namely organocatalysis and production of microporous carbon monoliths. Selected organocatalyzed reactions, including carbonation of propylene oxide by cycloaddition with carbon dioxide, benzoin condensation, and cyanosilylation of benzaldehyde have been readily triggered by PILPNs acting as crosslinked polymer-supported (pre)catalysts. The two latter reactions required the prior deprotonation of the imidazolium salt units with a strong base to successfully generate polymer-supported *N*-heterocyclic carbenes, referred to as poly(NHC)s. Facile recycling and reuse of polymer-supported (pre)catalysts was achieved by simple filtration owing to the heterogeneous reaction conditions. Furthermore, PILPNs could be easily converted into microporous carbon monoliths via CO₂ activation.

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1. Introduction

Ionic liquids (ILs) are well known for their exceptional physical properties, such as non-volatility, high thermal and chemical stability, superior ionic conductivity, non-flammability, wide electrochemical window and tunable solubility [1,2]. ILs bearing vinyl or other polymerizable groups can be polymerized *via* conventional or controlled/living radical polymerization, forming a new type of polyelectrolytes, referred to as poly(ionic liquid)s or polymerized ionic liquids (PILs). PILs can combine some of the unique properties of ILs with those characterizing polymeric materials [3,4]. This

synergy in chemical structure and property allows building up a versatile tool box of multifunctional polyelectrolytes for a wide range of applications [5–12].

Mesoporous materials have pore sizes between 2 and 50 nm [13–15]. Mesoporous polymers have attracted huge research interest in the last 5 years, and are currently still under intensive investigation as they provide sufficiently high surface area and meanwhile satisfactory mass/energy transfer, compared to microporous and macroporous systems. In addition, mesoporous polymers often outperform inorganic materials in some fields owing to their low density and their broad structural diversity provided by an appropriate monomer selection. The application scope of mesoporous polymers is very broad, encompassing separation, adsorption, gas storage, porous carbon production and catalysis [16–19]. There have been many reports on the synthesis of mesoporous polymers, each of which governs different structural and property aspects of the pores. The direct copolymerization utilizing a crosslinking comonomer is a straightforward method to achieve mesoporous polymers, the porous structure of which depends on

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initial polymerization parameters, such as temperature, time, solvent, nature and amount of crosslinker or initiator [20,21].

The incorporation of ILs into mesoporous polymers has received an increasing interest in recent years [22–24]. The high surface area provided by the porous polymer network and the functionality of the ILs can be synergistically combined in such a structure configuration. For example, Xiao et al. reported the synthesis of mesoporous polymers that were surface-decorated with IL molecules *via* post-polymerization modification. In their approach, divinylbenzene and *N*-vinylimidazole were firstly copolymerized under solvothermal conditions, forming a mesoporous network with Brunauer–Emmett–Teller specific surface area (S_{BET}) up to 670 m²/g. The IL species on the pore surface were subsequently introduced *via* a quaternization reaction of the surface imidazole groups with alkyl halide, which was followed by anion exchange [25]. Ionic porous polymers obtained in this way were shown to efficiently catalyze the transesterification reaction for biodiesel production. Recently, our group in Potsdam reported the synthesis of mesoporous polyelectrolyte networks with S_{BET} up to 310 m²/g, *via* interpolyelectrolyte complexation in organic solvents [26]. Their application as polymer-supported catalysts for aerobic oxidation of hydrocarbons, dye sorbent and CO₂ sorption and activation has been demonstrated.

The potential of porous PIL networks as a precursor for polymer-supported *N*-heterocyclic carbenes poly(NHCs) is of high interest. NHCs are known as versatile ligands for transition metals, but have also emerged as true organic catalysts for various organic reactions (such as benzoin condensation, cyanosilylation, etc.) [51–55]. The success of NHCs is due to both their steric and electronic properties which can be tuned through variation of their substituent pattern, allowing for a modulation of their reactivity towards various substrates. A common synthetic route to *in situ* generated NHCs is the deprotonation of the acidic C-2 proton of imidazolium IL salts by a strong base in an aprotic solvent [45,54–56]. The generation of NHC-functionalized porous polymer networks would allow for the heterogeneous catalysis, featuring easy separation and recycling.

Additionally, polymers and biopolymers are a class of important macromolecular carbon precursors [27,28]. As reported previously, microporous carbon monoliths can be prepared by physical activation of porous polymer monoliths [29–32]. CO₂ is commonly used as an activating agent. At the beginning, CO₂ reacts with the substrate, causing the pore opening and introducing large surface area. Following the activation, the *in situ* generated micropores continuously grow until they merge into bigger pores, thus decreasing the surface area [33].

Herein we describe a facile synthetic route to mesoporous copolymers in a monolithic form and possessing a tunable IL content and a controllable porosity (up to 935 m²/g), by direct copolymerization of an imidazolium-based ionic liquid monomer and divinylbenzene (DVB) as a crosslinker, under solvothermal conditions. The as-synthesized mesoporous copolymers, referred to as poly(ionic liquid)-based porous networks (PILPNs), were analyzed in detail *via* nitrogen sorption measurements and elemental analysis. We also show that such PILPNs can serve as polymer-supported organocatalysts, and as precursors as well in order to achieve microporous carbon monoliths *via* CO₂ activation at elevated temperatures.

2. Experiments

2.1. Materials

Divinylbenzene (DVB) (80% mixture of isomers), *N*-vinylimidazole (VI) (99%) and potassium bis(trimethylsilyl)amide (=hexamethyldisilazide, KHMDS) (95%) were purchased from

Sigma–Aldrich. 1-Bromobutane (98%), bromoethane (98%), and potassium hexafluorophosphate (KPF₆) (99%) were purchased from Alfa Aesar. Trimethylsilyl cyanide (TMSCN) (98%) was purchased from ABCR. 2,2'-Azobis(2-methylpropanitrile) (AIBN) (98%, Aldrich) was recrystallized from methanol. Propylene oxide (99%, Aldrich) was distilled over Na before use. Benzaldehyde (99.5%, Aldrich) was distilled before use. The two ionic liquid monomers were prepared according to our previous paper [1]. THF was distilled over Na/benzophenone prior to use. Solvents and other materials were used as received.

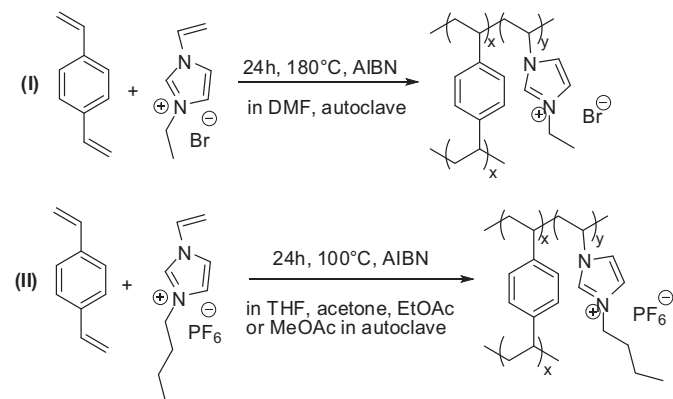
2.2. Copolymerization of IL monomers EVIBr and BVIPF₆ in presence of DVB

Targeted copolymers were designed as P(DVB-*y*IL) where *y* stands for the molar ratio of ionic liquid to DVB. Hydrophilic IL monomer, namely, 1-ethyl-3-vinylimidazolium bromide (EVIBr) and hydrophobic 1-butyl-3-vinylimidazolium hexafluorophosphate (BVIPF₆) were employed to demonstrate the applicability of this synthetic route to various IL compounds. The preparation of the porous monoliths is based on a modified Xiao method (Scheme 1) [34].

In a typical synthesis of mesoporous copolymers of P(DVB-0.1EVIBr), 2.0 g of DVB were added into a solution containing 0.05 g of AIBN and 20 mL of DMF, followed by addition of 0.31 g of IL-EVIBr. After stirring at room temperature for 3 h, the mixture was transferred into a Teflon autoclave and then solvothermally treated at 180 °C for 24 h. After cooling down, the monolith was immersed in a pure reaction solvent overnight to enable the extraction of any unreacted monomers. The purified monolith was dried in ambient conditions for 2–4 days to slowly evaporate the residual solvent, before it was completely dried at 80 °C under high vacuum. This drying procedure is crucial for the monolithic form conservation. Synthesis of mesoporous copolymer P(DVB-0.1BVIPF₆) was performed similarly, but carrying out the solvothermal polymerization at 100 °C due to the used solvents. For comparison purpose, DVB and *N*-vinylimidazole (VI) were polymerized in DMF and THF according to an already reported procedure [17].

2.3. Synthesis of the crosslinked copoly(*N*-heterocyclic carbene) P(DVB-0.1EV(NHC))

In a typical experiment, 1 g of P(DVB-0.1EVIBr) (0.50 mmol EVIBr units) (S_{BET} = 640 m²/g) was placed in a Schlenk tube that was previously flamed and dried under vacuum for 2 h and subjected to three Ar/vacuum cycles before adding 15 mL of dry THF. The



Scheme 1. Synthetic details of P(DVB-*y*EVIBr) (I) and P(DVB-*y*BVIPF₆) (II) under solvothermal conditions.

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