Macroporous polymer monoliths fabricated by using a metal–organic coordination gel template†

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We have found a new way, a metal–organic coordination gel template method, to generate polymer monoliths with an essentially macropore size, in which the pores are organized spontaneously into continuous networks; furthermore, the resulting macroporous monoliths have potential applications in high-throughput and high-efficiency separation of proteins.

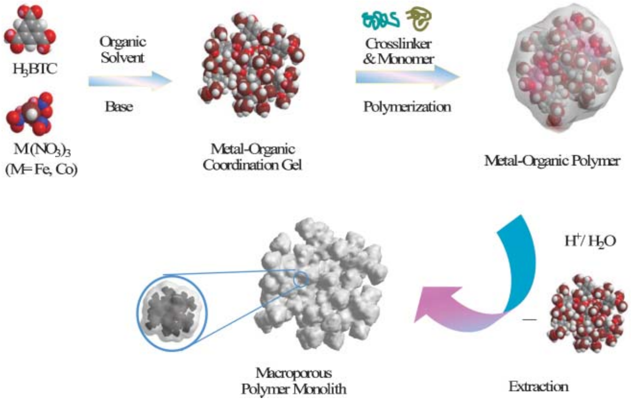
Macroporous materials prepared *via* soft chemistry (templated by surfactants, block copolymers, colloids) have overcome the restriction of the dimensions and accessibility of well-developed porous solids and, therefore, have sparked a wide spectrum of interest in areas such as chemical and biological separations, catalysis, photonic devices and drug delivery.[1–5] Among them, monolithic macroporous polymers are especially expected to have interesting and wide-ranging application in modern catalysis and separation sciences. Generally, these macroporous polymers are prepared using a typical radical polymerization of monomer(s) with cross-linker(s) in porogenic solvents. In traditional monoliths preparation, the pore structures are highly dependent on the monomer/porogen ratio, monomer/crosslinker ratio, and on the choice of porogenic solvents and the polymerization temperature.[6–9] A rigorous challenge in the preparation of macroporous monoliths for technological applications is to control both the size distributions and the relative positions of the pores. For the preparation of macroporous polymer materials with homogeneous and narrow-distributed pores and 3-D skeletons, polymerization protocols in the presence of templates (*e.g.* surfactants, silica spheres and gels) have been proposed in recent years.[10]

Metal–organic frameworks (MOFs) have attracted great excitement because of their controllable diverse structures and unique inclusion properties.[11–13] Many porous coordination materials with one-, two- and three-dimensional network structures have been intensively synthesized with a variety of properties such as catalysis, storage and conductivity.[14,15] However, exploitations of these MOFs (coordination polymers thereof) were generally investigated at the molecular level and characterized in the crystalline state. Much less is known about coordination polymer gels, despite their many possibilities for being endowed with complex behaviors by the presence of metal centers. Recently, Q. Wei and S. L. James fabricated a macroporous PMMA membrane using a metal–organic coordination gel as template.[16] Rigid polymer monoliths are more attractive than membranes for their versatile applications. Herein, we report a novel approach for fabricating macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) [P(GMA-co-EDMA)] monoliths using a metal–organic coordination gel as template (Scheme 1).

The metal–organic gel was prepared by reaction between 1,3,5-benzenetricarboxylic acid (H_3BTC) and $M(NO_3)_3{\cdot}xH_2O$ ($M = Fe^{III}$, Co^{III}, $x = 9, 6$) in a molar ratio of 2 : 3 in an appropriate organic solvent. Since H_3BTC can bind metal ions in different fashions, the multidentate type (which tends to form a 3-D structure) is more propitious to construct a porous three-dimensional network.[11] The dimensionality of the resulting metal–organic framework was dependent on the solvent and the base (which is a catalyst to deprotonate H_3BTC without binding to metal ions) employed in the reaction.

For preparation of the targeted M-BTC coordination gel, coordinating solvents (methanol, ethanol, acetone, acetonitrile, DMF and DMSO) and bases (pyridine and triethylamine) were tested (Fig. 1). Results indicated that methanol, ethanol, DMF and DMSO could rapidly give coordination gels in the presence of pyridine or triethylamine, whereas acetone and acetonitrile gave the precipitates.

We also found that triethylamine ($pK_b = 11.01$) tended to produce 3-D coordination frameworks, whereas pyridine ($pK_b = 5.21$) under the same conditions would lead to 2-D coordination frameworks. The reason may be that pyridine is a



Scheme 1 Preparation of macroporous polymer monolith by using a metal–organic coordination gel template.

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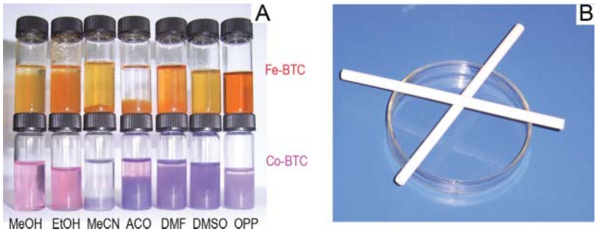

Fig. 1 Photographs of metal–organic coordination gels (A) and the macroporous monoliths prepared using this kind of gel template (B). Preparation of Fe^{III}-BTC gels (upper) and Co^{III}-BTC gels (lower) has been achieved using methanol (MeOH), ethanol (EtOH), acetonitrile (MeCN), acetone (ACO), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and organic polymer precursor (OPP) as coordinating solvents.

weak base. It could only partially deprotonate H_3BTC, but strongly bind to metal ions, thereby blocking extension of the structure into the third dimension.[11] Interestingly, the M-BTC gel could also be constructed in the presence of organic polymer precursors (OPP). Directly conducting the preparation in a mixture of ethanol, ethylene dimethacrylate (EDMA) and glycidyl methacrylate (GMA) gave M-BTC gel with a similar appearance. This gel was relatively stable in such an organic polymer precursors mixture if sealed and stored in a 4 °C refrigerator.

Macroporous poly(GMA-co-EDMA) monoliths were prepared by using an *in situ* polymerization with the as-prepared coordination gels (ESI†). The mixture of M-BTC gel (in ethanol), EDMA and GMA monomers (3 : 1 : 2, v/v) was thermally initiated at 60 °C in a stainless steel column mold (4.6 mm i.d. × 100 mm). After the polymerization, the resulting monoliths were flushed with 0.25 M sulfuric acid, followed by water, acetone and methanol to remove the M-BTC template, porogens and the possible unreacted monomers. Another poly(GMA-co-EDMA) membrane was synthesized in a similar way but using a UV initiation at 10 °C. As a control experiment, a macroporous monolith was also directly prepared in a mixture of methanol, dodecanol and triethylamine without M-BTC gels.

The morphological properties of the resulting macroporous P(GMA-co-EDMA) monolith were investigated by SEM and mercury intrusion porosimetry. SEM images (Fig. 2C–F) revealed their 3-D network skeletons with interconnected macropores in the size range of 200–450 nm. Obviously, the pore size of the monoliths synthesized by thermal initiation was much less than that of membranes synthesized by UV initiation at a lower temperature (Fig. 3). It was most likely because the M-BTC gel shrank at a higher temperature during the polymerization. This assumption was then confirmed by the apparent shrinkage of the M-BTC gel, which was observed by slowly heating the prepolymerization mixture to a higher temperature range of 45–75 °C. Mercury intrusion porosimetry gave surface areas of 86, 91, 136 and 128 m^2 g^{-1} for the rigid polymer monoliths C, D, E and F, in comparison to 45 and 27 m^2 g^{-1} for membrane A and monolith B (made without gel template), respectively.

Several approaches, such as changing the proportion of polymerization precursor and applying appropriate porogenic solvents, have been employed to tailor both the pore size and distribution of the conventional monolithic polymers.[8,17] In this experiment, however, the pore size and distribution were primarily controlled by M-BTC gels, which related to the metal and ligand types, as well as temperature. Coordinating solvents showed no apparent differences in the pore morphology of those monoliths. As can be seen from Fig. 2 and Fig. 3, pore sizes in polymer monoliths prepared with Fe^{III}-BTC gel were somewhat larger than those made by a Co^{III}-BTC gel template. This might be because the size of the Co^{III}-BTC gel was smaller than that of the Fe^{III}-BTC gel.

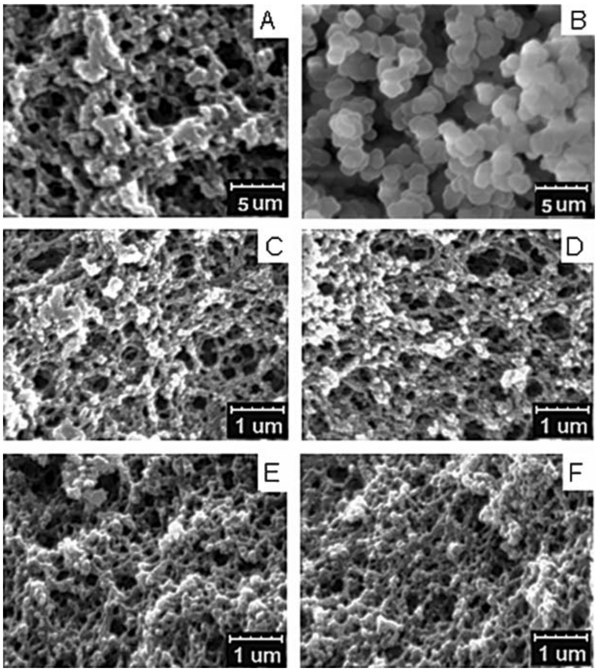

Fig. 2 SEM photographs of A) P(GMA-co-EDMA) membrane templated by Fe^{III}-BTC gel in ethanol, B) the control monolith made without coordination gel, and P(GMA-co-EDMA) monoliths templated by C) Fe^{III}-BTC gel in ethanol, D) Fe^{III}-BTC gel in DMF, E) Co^{III}-BTC gel in ethanol, and F) Co^{III}-BTC gel in DMF.

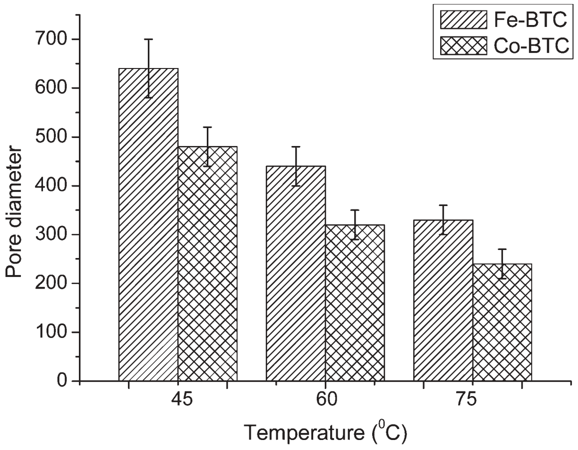

Fig. 3 Influence of temperature on the pore sizes of polymer monoliths.

The polymerization temperature was one of the most convenient factors to control pore size with no change of the composition of the prepolymerization mixture. Fig. 3 shows the pore size of the monoliths prepared at different polymerization temperatures, *i.e.* 45, 60, and 75 °C. An increase in polymerization temperature decreased the pore size through shrinkage of the templates, as well as through the higher number of nuclei in the polymeric mixture. But higher temperature, over 75 °C, led to a fast polymerization which tended to form irregular and particle-stacked structures.

The macroporous polymer monoliths have potential applications in separation and as supports. P(GMA-co-EDMA) monolith may serve its purpose only if provided with the surface chemistry required for the desired applications. A GMA epoxide moiety on the polymer monolith can be converted into diol groups, which can be used for hydrophobic interaction chromatography (HIC) or further modified to ion-exchange chromatography (IEC) materials.

As the separation media in high-performance liquid chromatography (HPLC), these polymer-based monoliths realized good separation efficiency with a low back-pressure drop due to a combination of a submicron or micron size polymer skeleton and relatively large macropores. The flow-through properties of P(GMA-co-EDMA) monoliths were evaluated by determining the chromatographic permeability (*K*) of the monolith, which is defined as

$$K = uL\eta/\Delta P$$

where u is the average linear mobile-phase velocity, L the length of the column, η the viscosity of the mobile phase, and ΔP the back-pressure. As expected, higher chromatographic permeability was observed and a typical K value for P(GMA-co-EDMA) monolith with 400 nm-pores was found to be *ca.* 1.1×10^{-13} m^2, which was about 3–5 times higher than that of a 10 μm particles packed column.

Macroporous polymer monoliths tolerate a fast flow rate, thus easily enabling high-throughput and high-efficiency separation of proteins. For instance, a mixture of bovine serum albumin (BSA), cytochrome C (Cyt-C), ribonuclease A (RNase-A), lysozyme (Lys), α-amylase (α-Amy) and insulin (Ins) was applied on this monolith in a typical HIC model. A chromatogram showed the proteins were rapidly and efficiently separated in only five minutes (Fig. 4).

The porous membranes exhibit both softness and friability, thus limiting their versatile applications in practice. Compared with a macroporous membrane, the prepared polymer monolith provided a rigid 3-D frame with narrowly-distributed macropores. Furthermore, the pore sizes of this rigid monolith were much smaller than those of the macroporous membrane (both in Ref. 16 and this study), less than 0.5 μm as compared to 2–10 μm, providing a relatively larger surface area for various applications. Besides their promise in chromatographic separations, the monoliths have potential applications as materials for solid catalysts and in drug delivery.

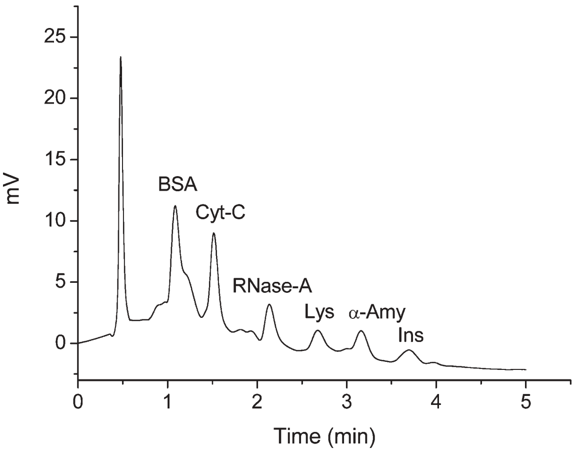

Fig. 4 Separation of proteins on the macroporous HIC monolith.

Notes and references

1 N. K. Mal, M. Fujiwara and Y. Tanaka, *Nature*, 2003, **421**, 350.
2 M. E. Davis, *Nature*, 2002, **417**, 813.
3 V. Bugarin, J. H. Clark, J. J. E. Hardy, R. Luque, K. Milkowski, S. J. Tavener and A. J. Wilson, *Angew. Chem., Int. Ed.*, 2006, **45**, 3782.
4 A. Imhof and D. J. Pine, *Nature*, 1997, **389**, 948.
5 X. He and D. Antonelli, *Angew. Chem., Int. Ed.*, 2002, **41**, 214.
6 C. Yu, M. H. Davey, F. Svec and J. M. J. Frechet, *Anal. Chem.*, 2001, **73**, 5088.
7 R. Mallik, T. Jiang and D. S. Hage, *Anal. Chem.*, 2004, **76**, 7013.
8 E. C. Peters, F. Svec and J. M. J. Fre'chet, *Adv. Mater.*, 1999, **11**, 1169.
9 F. Svec, *J. Sep. Sci.*, 2004, **27**, 747.
10 O. D. Velev and E. W. Kaler, *Adv. Mater.*, 2000, **12**, 531–534.
11 O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861.
12 O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096.
13 A. C. Sudik, A. P. Cote, A. G. Wong-Foy, M. O'Keeffe and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2006, **45**, 2528.
14 S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109.
15 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
16 Q. Wei and S. L. James, *Chem. Commun.*, 2005, 1555.
17 N. Tsujioka, N. Hira, S. Aoki, N. Tanaka and K. Hosoya, *Macromolecules*, 2005, **38**, 9901.