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# Synthesis of highly ordered mesoporous polymer networks

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**Synthesis of highly ordered three-dimensionally interconnected mesoporous hydrocarbon polymer networks exhibiting Bragg X-ray diffraction is reported by replicating the mesoporous MCM-48 and SBA-15 channel frameworks.**

Microporous and mesoporous materials have very high surface areas occurring from their regular open frameworks with a narrow pore size distribution. These materials can be used as hosts in the template synthesis, providing a confined space for controlled intrapore inclusion chemistry including metals[1] and carbons.[2,3] Hydrocarbon polymer replicas were also reported in such porous materials. In this case, polymerization of preadsorbed ordinary monomers in the pores of the template and subsequent dissolution of the template framework leave macromolecular hydrocarbon replicas. The polymerization and pyrolysis of several monomers were demonstrated in different zeolites.[4] However, the extracted hydrocarbon polymer replicas were X-ray amorphorous, indicating that the pore ordering was not well maintained in the polymer replicas due to nonrigidity of polymer frameworks formed in the narrow pores of zeolites. Recently, several studies on polymer synthesis were reported using mesoporous materials as templates. The mesoporous materials have an advantage over microporous zeolites for the inclusion of larger molecules. Polymerization of aniline and acrylonitrile was conducted within the mesoscopic silica channel of MCM-41.[5] Poly(methyl methacrylate)[6] and poly(phenolformaldehyde) fibers[7] with a high aspect ratio were obtained using MCM-41 as a mould. Polyethylene linear nanofibers were fabricated by extrusion polymerization with a titanocene complex supported in fibrous mesoporous silica.[8] Ring-opening polymerization of preadsorbed silaferrocenophane was also reported in the hexagonal channels of MCM-41.[9] To the best of our knowledge mesoporous template-assisted polymerization has been conducted mainly with hexagonal MCM-41 except for the synthesis of a poly(methyl methacrylate)–MCM-48 composite.[6] Few studies have been described on the extraction of the resulting polymers and their *ex situ* structural characterization.[7,8] Most studies have focused on the fabrication of organic nanofibers representing a cast of the mesopores in confined spaces as a primary structure of resulting polymers. Thus none of them belong to a mesoporous polymer network. In practice, the first mesoporous organic polymers were reported through replication of hexagonal-type mesoporous materials with a three-dimensional continuity by Goltner *et al.*[10,11] The work described the extracted polymer networks using various characterizations including small angle X-ray scattering. Since then, there has been no report on the fabrication of a mesoporous polymer network through casting of mesoporous hosts. In this work, we present for the first time the synthesis of highly ordered three-dimensionally interconnected mesoporous hydrocarbon polymer networks using pure silica MCM-48 and SBA-15 as templates and divinylbenzene as a polymer precursor. Particularly, this work shows the first example of template-free mesoporous polymers exhibiting Bragg X-ray diffraction patterns characteristic of a highly ordered mesopore network resulting from the MCM-48 and SBA-15 templates.

High quality silica MCM-48 was prepared using hexadecyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$, HTMABr) and Brij 30 (polyoxyethylene(4) lauryl ether, $C_{12}(EO)_4$) as surfactants and colloidal silica Ludox HS40 as a silica source based on modification of the literature procedure.[12] Mesoporous SBA-15 silica was prepared by using tetraethyl orthosilicate (TEOS) as a silica source and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (Aldrich, $M_{avg.} = 5{,}800$, $EO_{20}PO_{70}EO_{20}$, P123) as a structure-directing surfactant.[13] To completely remove the surfactants, as-synthesized mesoporous materials were stirred in an ethanol–hydrochloric acid mixture (0.1 mole HCl per liter of ethanol) for 1 h, filtered, dried in an oven at 150 °C and calcined in flowing oxygen at 550 °C for 5 h. The calcined MCM-48 and SBA-15 exhibited surface areas of 1140 $m^2 g^{-1}$ and 780 $m^2 g^{-1}$ and total pore volumes of 1.20 ml $g^{-1}$ and 0.92 ml $g^{-1}$, respectively. The calcined mesoporous materials were wetted with drops of ethanol and pressed into pellets with pressure at 1.0 ton per $cm^2$, at which the mesoporous silica frameworks were almost intact as determined by powder X-ray diffraction. This pelletization maximized the proportion of the organic polymer to be formed in the templating pores instead of the particle surface. The pelletized templates were dehydrated in vacuum at 200 °C overnight, and then a precursor solution of divinylbenzene (DVB) with a free radical initiator, azoisobutyronitrile (AIBN) (DVB–AIBN mole ratio $\cong$ 24) was added dropwise into the pores in the pelletized hosts at ambient temperature. Dissolved oxygen was removed by several freeze–pump–thaw cycles. Polymerization was performed by heating to 70 °C for overnight. The resulting polymer is heavily crosslinked in the template pores. Template-free polymer replicas were obtained after subsequent dissolution of the silica framework in 48% aqueous HF, followed by filtering, washing with deionized water and drying at ambient temperature. For comparison purposes, the bulk form of polyDVB was also prepared under identical conditions without the use of mesoporous hosts.

The polymerization of DVB was confirmed by infrared spectroscopy. A decrease of bands near to 1650 $cm^{-1}$ and 3090 $cm^{-1}$ corresponding to vinyl groups and a concomitant development of bands near to 2930 $cm^{-1}$ and 1465 $cm^{-1}$ attributed to $-CH_2-$ groups in the resulting polyDVB were observed.[14] Low angle powder XRD patterns were measured at various stages during the course of the synthesis (Fig. 1). Fig. 1c

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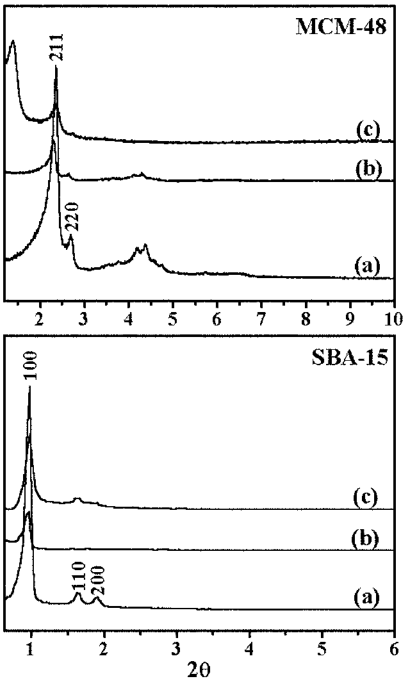

**Fig. 1** Ambient temperature low angle powder X-ray diffraction patterns using Cu K$\alpha$ radiation of (a) calcined pure silica forms of MCM-48 and SBA-15 hosts, (b) poly(divinylbenzene)–host composites and (c) template-free polyDVB replicas of MCM-48 and SBA-15.

shows two peaks at $2\theta = 1.3$ and 2.4 in the resulting polymer replica of MCM-48, indicating highly ordered uniform mesopores with long-range ordering. It is interesting to note that the first intense peak was not seen in the parent MCM-48 template (Fig. 1a). This peak was the result of the phase transition of a cubic MCM-48 with $Ia3d$ space group to a new cubic with $I4_{1}32$ upon removal of the silica host.[2,3] Interestingly, however, the polymer replica of SBA-15 maintained the symmetry of the parent SBA-15 template as seen in the XRD patterns. It is the first time that polymer replicas of MCM-48 and SBA-15 showing such Bragg X-ray diffraction patterns characteristic of a highly ordered uniform mesopore network are reported in this work. Elemental analysis showed C : H molar ratios of about 0.94 (C 87.37 wt% and H 7.75 wt%) and 0.96 (C 85.25 wt% and H 7.40 wt%) for MCM-48 and SBA-15 hydrocarbon polymer replicas, respectively, with some undissolved Si (3.0–6.0 wt%). These C : H molar ratios are close to the theoretical value of 1.0. Energy dispersive X-ray spectrophotometer analysis determined by field emission scanning electron microscope indicated also a predominantly strong carbon signal at 0.273 keV with a weak residual silicon signal at 1.746 kev. The C : Si intensity ratios of about 50 were in agreement with C : Si molar ratios from the elemental analysis.

TEM (transmission electron microscope) images from the thin edges of the extracted mesoporous polymer networks show a regular array of fine lines and patterns (Fig. 2) despite a poor resolution due to the low contrast of polymer materials. The corresponding carbon replicas obtained by further pyrolysis of polyDVB embedded in the mesoporous silica host at 900–1000 °C under argon gas flow and subsequent removal of the silica framework showed much clearer and better resolved TEM images. These regular arrays of lines and patterns were found along the thin edge of the entire particles. The widths of the lines or fibers, as determined through the micrographs, were found to be *ca.* 3.0 nm and 6.0 nm for MCM-48 and SBA-15 replicas, respectively. These values are comparable to the pore diameters of the host mesoporous MCM-48 and SBA-15 materials used in this work. In particular, the arrays of polymer and carbon mesofibers that can image the length of the mesoporous channel were recovered in the hexagonal mesoporous SBA-15 silica host. The array displayed extensive lengths comparable to the particle sizes which were in the range of 1–10 μm. The aspect ratios of the extracted polymer fibers of SBA-15 were found to exceed to $10^3$. Regular arrays of the polymer and carbon fibers suggest that the pores are interconnected to each other in the SBA-15 host. In the case of MCM-41, known to have a non-interconnecting one dimensional channel network, the resulting polymer and carbon replica fibers look rather disordered.[15] The interconnecting pores which will be filled with polymer in the replication process will bind the pore replica fibers to each other in SBA-15.

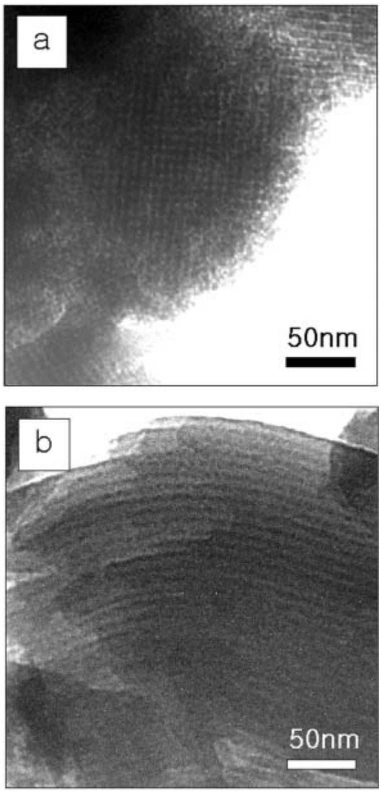

**Fig. 2** Transmission electron microscope (TEM) images of thin sections of mesoporous polyDVB networks obtained by replication of calcined silica (a) MCM-48 and (b) SBA-15 as templates.

The BET surface areas of the resulting MCM-48 and SBA-15 polymer replicas were found to be about $610\ \mathrm{m^2\,g^{-1}}$ and $410\ \mathrm{m^2\,g^{-1}}$, respectively. These values are lower compared to the corresponding host mesoporous templates. The MCM-48 and SBA-15 polymer replicas showed broader pore size distribution centered at $1.7 \pm 0.1$ nm and $3.4 \pm 01$ nm, respectively (see an insert in Fig. 3). However, the host MCM-48 and SBA-15 templates showed a narrow distribution centered at $3.4 \pm 0.1$ nm and $6.3 \pm 0.1$ nm, respectively. The pore size changes occurred from morphological alterations during the replication process, in which the pores and walls of the host silica templates were transformed to the walls and pores in the resulting polymer networks, respectively. The wall thickness of several silica SBA-15 hosts was in the range 2.0–2.9 nm from lattice parameters and pores sizes.[16] This is consistent with BJH pore measurement of $3.4 \pm 01$ nm for the corresponding polymer replica. The silica wall thickness of 1.3 nm for MCM-48 determined from the electron diffraction[17] is close to the value deduced from the pore size distribution data of MCM-48 polymer replica. The pore sizes of the polymer replicas are expected to be slightly bigger compared to the wall thickness of the corresponding host materials due to the shrinkage of the polymer wall. In the case of bulk DVB polymer prepared without the use of host templates, the low angle powder XRD

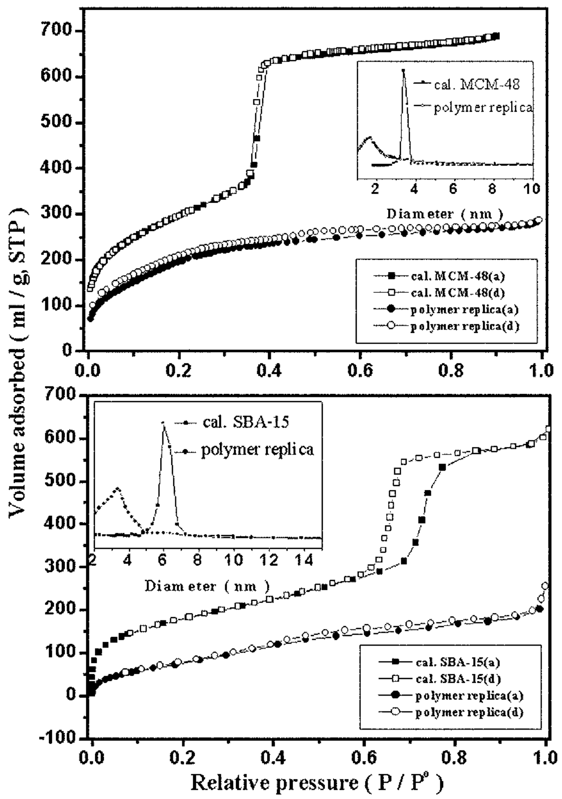

**Fig. 3** $N_2$ adsorption (a) and desorption (d) isotherms of calcined MCM-48 and SBA-15 templates and their corresponding polymer replicas. (insert) The corresponding pore size distribution curve calculated from the adsorption branch of the nitrogen isotherm by the BJH method. The isotherms were measured at 77 K on a Micromeritics ASAP 2000 Gas Adsorption Analyzer after the silica templates and polymers were degassed at 200 °C and 65 °C, respectively to 20 μTorr for 4–6 h.

showed no signals below $2\theta$ equal to 10. The regular array in TEM pictures and porosity above 1 nm were also not observed in the bulk DVB polymer. These facts indicate that the uniform mesopores in the polymer network formed with the templates originated from the templating effect of the MCM-48 and SBA-15 hosts.

In conclusion, the polymerization of preadsorbed DVB monomer in the channel structures of calcined silica MCM-48 and SBA-15 hosts, followed by subsequent dissolution of the template framework produced free-standing hydrocarbon polymer networks with highly ordered regular mesopore arrays. This novel method provided the first example of polymer networks obtained from cubic MCM-48 and hexagonal SBA-15 molecular sieves, which exhibit characteristic mesoporous Bragg X-ray diffraction patterns. The mesoporous polymer replica obtained from MCM-48 was found to have a new cubic phase different from that of the parent MCM-48. Unlike the MCM-48 replica, the SBA-15 polymer replica maintained the symmetry of the host SBA-15 molecular sieve with a hexagonal phase. Various functional groups can be introduced into the benzene rings of the polyDVB. This can alter the properties of the polymer networks. The highly ordered mesoporous polymer networks will find many advanced applications such as in catalysis, ion-exchange and separation, chemical sensing and host–guest chemistry.

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