

# Template synthesis of ordered mesoporous organic polymeric materials using hydrophobic silylated KIT-6 mesoporous silica†

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Porous organic materials can be synthesized *via* free-radical polymerization of crosslinkable olefinic monomers within the interstices of porous templates. The synthesis process has been employed to generate ordered mesoporous structures through use of a mesoporous silica template, KIT-6. The mesoporous silica features a bicontinuously mesoporous structure belonging to the cubic  $Ia\bar{3}d$  space group. Pore diameters of the silica could be varied over the range 3.6–7.3 nm by varying the synthesis conditions, while maintaining a constant pore wall thickness of 3.7 nm. The polymerization reaction proceeded with heating at 150 °C after initiation with  $\alpha,\alpha'$ -azobisisobutyronitrile. The resultant polymeric materials were characterized after template extraction using hydrofluoric acid. Characterization results demonstrated that the polymeric materials retained a cubic  $Ia\bar{3}d$  mesoporous structure only when the template pore diameters exceeded 5 nm, even if highly crosslinkable monomers, such as divinylbenzene, ethylene glycol dimethacrylate, and trimethylolpropane trimethacrylate, were incorporated. The polymeric structure collapsed unless the template pore diameters were sufficiently larger than the distance between crosslinking points. In addition, structural integrity was maintained only if the mesopore walls were hydrophobically functionalized *via* silylation. Under optimal replication conditions, the ordered mesoporous polymeric materials exhibited a very narrow pore size distribution and a high specific surface area (619 m<sup>2</sup> g<sup>-1</sup>) that reflected the qualities of the original silica template. Such mesoporous polymeric materials could be functionalized *via* copolymerization with other functional monomers or *via* organic reactions. The functionalized mesoporous polymers are suitable for catalytic and adsorption applications because the porous structures feature a high surface area and excellent functional group density.

## 1. Introduction

Mesoporous polymeric materials have gained much attention for the adsorption, separation, and catalysis of large molecules,<sup>1–3</sup> and also as dielectric materials,<sup>4</sup> due to their high specific surface area,<sup>5,6</sup> uniform pore diameter,<sup>7–10</sup> and chemical stability for recyclability.<sup>11,12</sup> Mesoporous polymers can be prepared by various routes, including phase separation,<sup>13–15</sup> controlled foaming,<sup>16,17</sup> imprinting with large molecules or nanoparticles,<sup>18,19</sup> ion track etching,<sup>20</sup> selective decomposition within a block copolymer assembly,<sup>21–26</sup> assembly of resin precursors by surfactants,<sup>7,9,10</sup> and polymerization inside a removable porous template<sup>27,28</sup> or with embedded template particles.<sup>29,30</sup> Among these methods, the porous template method is also referred to as ‘hard-templating’, ‘nanocasting’, or ‘template synthesis’.

In principle, the template synthesis technique is suitable for the preparation of highly-ordered mesoporous polymeric materials with a variety of structures. Various types of ordered mesoporous silica materials are available as templates. Since the discovery of MCM-41 mesoporous silica,<sup>31</sup> a large number of

mesoporous silica materials with controlled pore diameters and a variety of structures have been reported.<sup>32–35</sup> However, only two reports have described the synthesis of polymeric materials using ordered mesoporous silica templates. In the first report by Göltner *et al.*,<sup>27</sup> divinylbenzene was polymerized inside a mesoporous silica monolith, and the polymeric material was released from the template by HF treatment. The resultant polymeric material exhibited a broad peak by small angle X-ray scattering that indicated a fairly good structural correlation between the nearest neighboring mesopores although the pores were not completely ordered. In the second study involving this approach, Kim *et al.* used two types of ordered mesoporous silica,<sup>28</sup> MCM-48 and SBA-15, as templates for divinylbenzene. They reported that the polymeric materials released from the silica template exhibited very sharp and well-resolved peaks in X-ray powder diffraction (XRD) patterns below  $2\theta = 4^\circ$ , similar to the original silica templates. The XRD pattern was characteristic of a highly-ordered arrangement of uniform mesopores. Kim *et al.* measured the N<sub>2</sub> adsorption isotherm that indicated only a very small degree of capillary condensation in the 0.4–0.8 relative pressure range, which suggested the presence of mesopores.

As mentioned, the template synthesis technique using mesoporous silica would, in principle, be suitable for the preparation of highly-ordered mesoporous polymeric materials with a variety of structures. The resultant mesoporous polymeric material was expected to faithfully replicate the porous system of the template

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material. The pore diameters can be controllable *via* choice of a suitable template. Moreover, the polymeric pore walls would be functionalized through covalent bonding of organic functional groups or *via* copolymerization of crosslinkable monomers with functionalized monomers. Control over the structures with surface that could be coated with functional groups promised to provide many opportunities for advanced applications. With these expectations, we attempted to reproduce the templated synthesis reported by Kim *et al.* However, highly-resolved XRD patterns could not be obtained from the synthesized polymeric materials.

Template synthesis of inorganic materials using ordered mesoporous silica is much easier than the template synthesis of organic polymers. Several types of inorganic materials, including carbon,<sup>36–41</sup> silica, metal oxides,<sup>42–44</sup> and platinum metals,<sup>45</sup> have been synthesized *via* structural template synthesis in recent years. These materials retained ordered mesoporous structures, even after release from their templates. In contrast, structural template synthesis of organic polymers poses several challenges for achieving faithful replication of the template structure. Structural templating for organic polymeric materials is made difficult by the relatively long distance between crosslinking points in the organic polymers. In contrast, multiple bonds may form within very short distances between the nearest neighboring atoms in inorganic materials. In polymers, insufficient crosslinking across a template pore diameter produces a non-rigid architecture after template removal. In addition, the hydrophobic affinity between organic monomers and the template surfaces can affect the success of synthesis. However, no study has examined the physicochemical parameters that affect the synthesis of organic polymeric materials inside mesoporous silica templates.

The present work was undertaken to characterize the major synthetic factors that contribute to faithful replication of template mesopore system to organic polymeric systems. An ordered mesoporous silica, KIT-6, was chosen as the template. This silica contained a bicontinuously mesoporous structure belonging to the cubic  $Ia\bar{3}d$  space group, and was composed of enantiomeric pairs of interpenetrating mesoporous networks with uniform diameters. In principle, the three-dimensional (3D) pore connectivity was suitable as a template for the formation of a self-retaining replica. In addition, by varying the synthetic conditions, the pore diameters could be controlled over a range 4–12 nm. In this work, the KIT-6 template was tested both with the as-synthesized hydrophilic pore walls, and with hydrophobic functionalization *via* reaction with organosilanes. Several monomers, including the crosslinkable monomers divinylbenzene (DVB), ethyleneglycol dimethacrylate (EGDMA), and trimethylolpropane trimethacrylate (TMPTMA), were tested to generate polymers inside the silica template. Copolymerization between crosslinkable monomers and non-branching monomers was also performed to investigate the effects of crosslinking on faithful structural replication. The surfaces of the as-synthesized polymeric materials were functionalized *via* copolymerization with functional monomers or *via* organic reaction after completion of the template synthesis. The porous structure of the resultant polymeric material was analyzed by XRD and  $N_2$  adsorption to identify the major synthetic factors that affected the replication process. These results are described here to

improve methods for synthesizing functionalized mesoporous polymeric materials suitable for advanced applications in catalysis, separation, and other fields.

## 2. Experimental

### 2.1. Chemicals

Pluronic P123 triblock copolymer (EO<sub>20</sub>-PO<sub>70</sub>-EO<sub>20</sub>, MW = 5800, BASF), 1-butanol (99.4%, Aldrich), benzyl alcohol (99.0%, Aldrich), 1-hexanoic acid (99.0%, Aldrich), toluene (99.8%, Aldrich), trimethylsilylchloride (TMS-Cl, 98.0%, Aldrich),  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN, 98.0%, TCI), hydrochloric acid (35.0%, Daejung), dichloromethane (95.0%, Junsei) and tetraethylorthosilicate (TEOS, 95.0%, Junsei) were used as purchased. DVB (technical grade, 80.0%, Aldrich), EGDMA (98.0%, Aldrich), TMPTMA (technical grade, Aldrich), and 4-vinylbenzyl chloride (VBC, 98.0%, TCI) were purified by filtration through an Al<sub>2</sub>O<sub>3</sub> column prior to polymerization. Deionized water was used for all experiments.

### 2.2. Preparation of the KIT-6 silica template

KIT-6 mesoporous silica was synthesized following the procedures available in literature.<sup>35</sup> In a typical synthesis batch, a homogeneous solution was obtained by dissolving 32.0 g of P123 and 63.0 g of 35.0 wt% hydrochloric acid in 1150 g of deionized water under magnetic stirring for 8 h at 35 °C. 32.0 g of 1-butanol was added to this solution. After stirring for 1 h at 35 °C, 68.8 g of TEOS was added at once to the P123–butanol–HCl solution. This mixture was continuously stirred at 35 °C for 24 h, for the formation of KIT-6 silica phase. The mixture containing KIT-6 was then heated to 130 °C for 24 h, under static conditions in a Teflon-lined autoclave. This high-temperature aging process was applied to enlarge the silica pore diameters. The KIT-6 product after 24 h was filtered, and dried at 100 °C in air without washing. The product was washed with an HCl-ethanol mixture to extract as much P123 as possible, and was subsequently calcined at 550 °C in air.

### 2.3. Synthesis procedure for polymeric materials

After calcination, KIT-6 samples were either used immediately to avoid exposure to moisture or were degassed under vacuum at 250 °C. For silylation, 1.00 g of a degassed sample was added into 100 mL of toluene solution containing 1.89 g of TMS-Cl. The silylation reaction proceeded under toluene reflux condition (110 °C) for 3 h. The product was filtered, washed first with toluene then acetone, and dried at 80 °C for 2 h in air. The silylation process caused a 0.9 nm decrease in the pore diameter of the KIT-6 template (as confirmed by  $N_2$  adsorption).

In a typical experiment for polymerization, 0.960 mL of organic monomer (DVB, EGDMA or TMPTMA) and 0.0660 g of AIBN (3 mol% relative to total olefin groups) were dissolved in 1.00 mL of dichloromethane. AIBN was used as an initiator for free radical polymerization. The solution was added to 1.00 g of TMS-Cl-coated KIT-6. The mixture was rubbed with a spatula in a fume hood until most of the solvent had evaporated. The mixture was dried briefly at 40 °C, so that the dichloromethane solvent could be removed without significant

loss of the less volatile monomer. The sample was placed in a Pyrex cell, equipped with a vacuum stopcock and ground-glass joints. The sample was subsequently subjected to three freeze–vacuum–thaw cycles using a dry ice/acetone trap, to remove dissolved air and residual dichloromethane. The sample cell was maintained for 6 h at 35 °C, to achieve a uniform distribution of organic monomers prior to polymerization. The following temperature scheme was used for polymerization: 4 h at 60 °C, 1 h at 80 °C, and finally 1 h at 150 °C. After polymerization, the sample was exposed to air, washed with HF solution to remove the silica template, washed with dichloromethane to remove the remaining monomer, and dried at 80 °C.

#### 2.4. Functionalization methods

Functionalized polymeric materials were obtained *via* copolymerization of the functional monomers with crosslinkable monomers. The synthesis procedure was identical to that described as in Section 2.3, except for the use of mixed monomers. Alternatively, functionalization was carried out through organic reactions after the synthesis described in Section 2.3. For example, DVB was polymerized as in Section 2.3. This polymeric material was sulfonated as follows:<sup>46</sup> 1 g of sample was mixed with 10 mL of concentrated sulfuric acid at 90 °C with magnetic stirring for 2 h. After extensive washing with deionized water, the sample was dried at room temperature overnight under vacuum conditions. The sample was titrated with a standard NaOH solution, to determine the concentration of sulfonic acid groups.

#### 2.5. Catalytic reaction

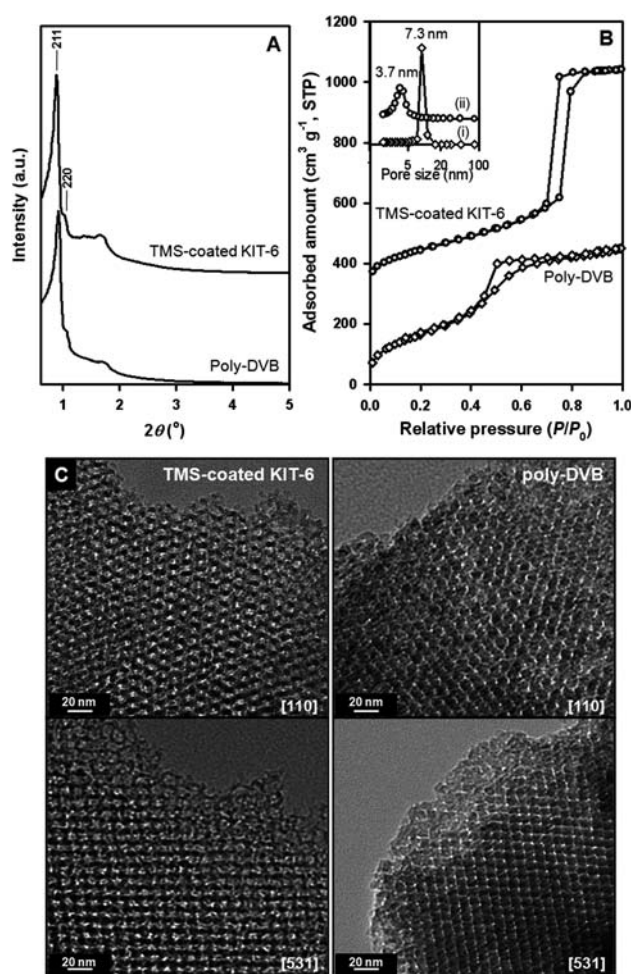
Esterification was carried out using a Pyrex batch reactor (EYELA Chemistation) with an equimolar ratio of benzyl alcohol and 1-hexanoic acid in dry toluene. The initial concentration of the two reactants was 0.5 M in both cases. The loading of the solid catalyst was 5 mol%, relative to the reactants, based on the sulfonic acid groups. The reactions proceeded by heating at 75 °C under stirring. The progress of the reactions was monitored by gas chromatography (GC, Younglin, Acme-6000 equipped with a flame ionization detector and a packed column with 10% SE-30) by regularly taking samples of the supernatant.

#### 2.6. Characterizations

Powder XRD patterns were obtained using a Rigaku Multiflex diffractometer equipped with Cu K $\alpha$  radiation (40 kV, 30 mA). XRD scanning was performed under ambient conditions at steps of 0.01° and an accumulation time of 3 s per step. N<sub>2</sub> adsorption isotherms were measured at 77 K with a Micromeritics TriStar II volumetric adsorption analyzer. Prior to the adsorption analysis, all samples were degassed for 6 h at 100 °C. The pore size distributions were analyzed by BJH algorithm. Transmission electron microscope (TEM) images were collected using a Tecnai G2 F30 with an accelerating voltage of 300 kV.

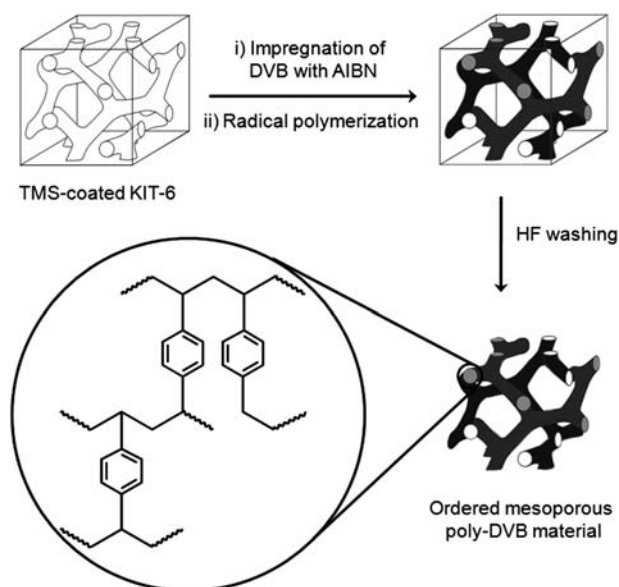
### 3. Results and discussion

The synthetic conditions and parameters were optimized by trial-and-error to yield faithful replication of the KIT-6-silica-pore system for the production of ordered mesoporous polymeric



**Fig. 1** Successfully synthesized ordered mesoporous poly-DVB material prepared by using TMS-coated KIT-6 as template: (A) powder XRD patterns, (B) N<sub>2</sub> adsorption isotherms, (B, inset) pore size distributions and (C) TEM images of (i) TMS-coated KIT-6 and (ii) poly-DVB materials. The (i) was prepared *via* coating of KIT-6 with TMS-Cl, and (ii) was done *via* free-radical polymerization of DVB inside KIT-6 as a template. The N<sub>2</sub> adsorption isotherm of (i) in (B) was offset by 300 cm<sup>3</sup> g<sup>-1</sup>. TEM images were taken along [110] and [531] incidences for both samples.

materials. Fig. 1 compares the powder XRD pattern, N<sub>2</sub> adsorption isotherm, and TEM image of a representative poly-DVB material, obtained according to the optimized synthesis procedures, with those obtained from the KIT-6 silica template. The KIT-6 silica sample showed a very narrow pore-size distribution centered at 7.3 nm. The pore walls of the silica template were coated with TMS-Cl *via* silylation treatment after synthesis. Note that the silica structure was initially formed at 35 °C, hydrothermally treated at 130 °C, and subsequently calcined at 550 °C. Thus, the organosilane coating was performed after calcination. The silylated mesopores were filled with DVB containing a small quantity of AIBN. Polymerization was initiated by AIBN at 60 °C inside the silane-coated mesopores. The reaction mixture was further heated to 150 °C to maximize crosslinking between the polymers prior to release from the template. The template-free polymeric material exhibited



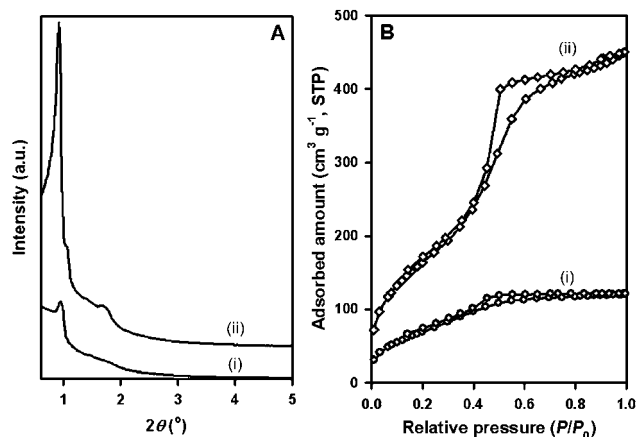
**Fig. 2** Schematic representation for the preparation of the ordered mesoporous poly-DVB materials using KIT-6 as a hard template.

well-resolved Bragg reflections in the small-angle XRD region, which were characteristic of a highly-ordered cubic  $Ia\bar{3}d$  structure similar to that of the original silica template. The TEM images in Fig. 1c showed that the poly-DVB sample assumed a structure that was inverted with respect to the silica template. Pore size analysis by  $N_2$  adsorption isotherm measurements showed that the poly-DVB sample had a very narrow distribution of mesopore diameters centered at 3.7 nm. The highly-ordered mesoporous polymeric material exhibited a BET surface area of  $619 \text{ m}^2 \text{ g}^{-1}$  and a total pore volume of  $0.69 \text{ mL g}^{-1}$ . The optimized template synthesis process is schematically described in Fig. 2.

The faithful replication of the cubic  $Ia\bar{3}d$  structure can be explained as follows: the cubic  $Ia\bar{3}d$  structure of KIT-6 silica was composed of two types of interpenetrating 3D porous networks. The pores belonging to the different systems were separated by a silica wall. The wall thickness varied typically in the range 2–5 nm, depending on the synthesis conditions. The KIT-6 silica could be synthesized with or without secondary pores (normally, 1–2 nm in diameter) within the pore wall.<sup>47</sup> The secondary pores were located in the center of a special flat point of the G-surface between two channel systems. In general, the diameter of the secondary pores increased as the  $\text{SiO}_2/\text{P123}$  ratio was lowered during synthesis.<sup>48</sup> When a KIT-6 silica sample without secondary pores was used as a structural template for platinum metals or carbon, the target material formed separate structures in the two mesoporous networks. When the silica wall was removed, the separated structures of the target material combined to form an  $I4_1/a$  structure. The pore diameter of the resultant product was described by the sum of the thickness of a silica wall and the cross-sectional diameter of the silica mesopore, and, therefore, the diameter was much larger than the silica wall thickness. On the other hand, when the silica template had sufficiently interconnected secondary pores, the target material formed in the secondary pores, building a bridge across the silica

wall. In this case, when the silica template was removed, the structural transformation to  $I4_1/a$  is prevented. This template synthesis led to the faithful replication of the cubic  $Ia\bar{3}d$  structure, and the pore diameter in the  $Ia\bar{3}d$  replica was equal to the silica wall thickness.

Good affinity between the monomers and the template walls was important for the synthesis of the polymer structures. The pore walls of mesoporous silica samples, such as KIT-6, MCM-41, and SBA-15 were hydrophilic due to the presence of silanol groups (Si-OH) on the surface. The silanol groups were difficult to remove completely, even by calcination at  $600 \text{ }^\circ\text{C}$ . The high surface tension of such hydrophilic surfaces prevented uniform pore-filling of most organic monomers. Hence, in the present work, it was necessary to increase the hydrophobic affinity of the pore walls *via* silylation with trimethylsilylchloride (TMS-Cl). Fig. 3 and Table 1 show the effects of surface coating by silylation. As these results show, the total pore volume of the KIT-6-templated poly-DVB material increased from  $0.19$  to  $0.69 \text{ mL g}^{-1}$  due to silylation treatment. The BET surface area increased from  $262$  to  $619 \text{ m}^2 \text{ g}^{-1}$ . The shape of the XRD pattern did not change noticeably, but the diffraction intensity changed dramatically. The XRD patterns were collected from same amounts of samples under identical measurement conditions. Therefore, the XRD



**Fig. 3** The effect of silylation of KIT-6 onto synthesis of ordered poly-DVB material: (A) powder XRD patterns and (B)  $N_2$  adsorption isotherms of poly-DVB materials prepared either by using (i) KIT-6 without any coating or (ii) TMS-coated KIT-6 as a hard template. Between two samples, poly-DVB material prepared by using TMS-coated KIT-6 silica exhibited highly ordered mesostructure with large pore volume.

**Table 1** Adsorption data calculated from  $N_2$  adsorption isotherms of poly-DVB materials<sup>a</sup>

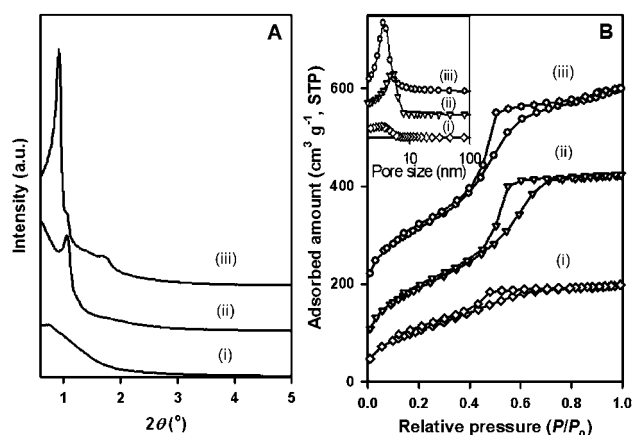
	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_t/\text{cm}^3 \text{ g}^{-1}$	$d_{\text{BJH}}/\text{nm}$
poly-DVB (TMS-coated KIT-6)	619	0.69	3.7
poly-DVB (KIT-6)	262	0.19	3.1

<sup>a</sup>  $S_{\text{BET}}$  is the apparent BET specific surface area deduced from the isotherm analysis in the relative pressure range 0.05–0.20.  $V_t$  is the total pore volume calculated at relative pressure of 0.95.  $d_{\text{BJH}}$  is the pore diameter calculated using the BJH method.

intensity could be used to compare the quality of the samples. Such XRD analysis indicated that without silylation, only a small portion of the sample possessed the ordered mesoporous structure. Most of the samples seemed to be disordered and, therefore 'X-ray amorphous'.

A sufficiently large pore diameter was required for the faithful replication of a template pore system, as demonstrated in Fig. 4. The results in Fig. 4 were obtained from polymerization of DVB using TMS-silylated KIT-6 templates with various mesopore diameters. The mesopore diameters were controlled by hydrothermal treatment during the silica synthesis. The synthesis was performed using a low SiO<sub>2</sub>/PI23 ratio to improve connectivity between the two types of mesoporous networks in the cubic *Ia3d* structure. The mesopore connectivity was confirmed by characterization of the faithful replication of the cubic *Ia3d* structure in the case of carbon synthesis.<sup>35</sup> Three samples of such TMS-functionalized KIT-6 silica exhibited XRD patterns characteristic of the cubic *Ia3d* structure. The mesopore diameters were 3.6, 5.0, and 7.3 nm, respectively. These samples were used as templates for the poly-DVB materials shown in Fig. 4. As the XRD patterns show, the poly-DVB obtained from the 3.6 nm template was completely X-ray amorphous, and the total pore volume was low. The poly-DVB from the 5.0 nm template produced a N<sub>2</sub> adsorption isotherm that indicated a sufficiently high pore volume and a sufficiently narrow distribution of pore diameters, although this sample displayed somewhat lower structural ordering than the product obtained from the 7.3 nm template.

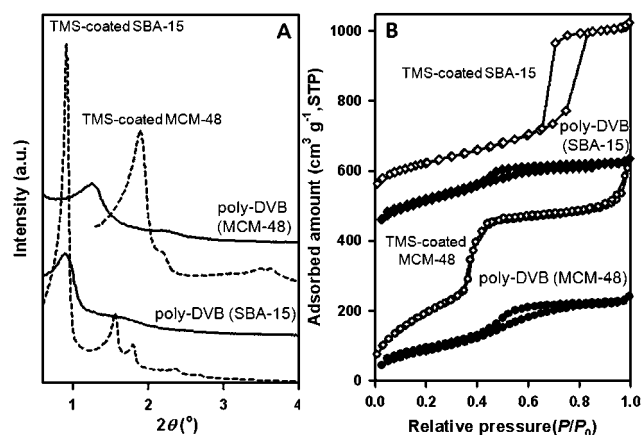
The three poly-DVB samples exhibited similar distributions of pore diameters centered at 3.5 nm ± 0.3 nm, despite differences in pore order, pore volume, and polymer framework thickness (Fig. 4b). This result implied that their KIT-6 templates had pore wall thicknesses of approximately the same size (3.5 nm ± 0.3 nm). That is, the wall thickness of the KIT-6 templates was uniformly maintained at 3.5 nm, whereas the pore diameters



**Fig. 4** The effect of pore diameter of KIT-6 silica onto synthesis of ordered poly-DVB material: (A) powder XRD patterns, (B) N<sub>2</sub> adsorption isotherms and (B, inset) pore size distributions of poly-DVB materials synthesized by using a series of KIT-6 having various pore diameters of (i) 3.6, (ii) 5.0 and (iii) 7.3 nm. The pore diameters of KIT-6 were varied by controlling the hydrothermal temperature during the synthesis. N<sub>2</sub> adsorption isotherms of (ii) and (iii) were offset by 50 and 150 cm<sup>3</sup> g<sup>-1</sup>, respectively.

varied over 3.6, 5.0, and 7.3 nm. As mentioned above, the template with 7.3 nm pores yielded a faithfully replicated structure of poly-DVB with an excellent pore-structural order. Pores that were 3.6 nm in size failed to replicate the ordered structure. Pores 5.0 nm in size produced borderline faithful replication with some loss of structural order. The pore size of the borderline structure was approximately 10 times the distance between the nearest possible crosslinking points, which was assumed to be the distance (0.59 nm) between the two olefinic carbon atoms bonded to the benzene ring in a DVB molecule. It was also possible to synthesize poly-EGDMA and poly-TMPTMA samples with highly-ordered mesoporosity using the 7.3 nm pore KIT-6 silica template (see the N<sub>2</sub> adsorption isotherms and XRD patterns given in Fig. S1, ESI†). The poly-EGDMA and poly-TMPTMA samples showed 10–30% lower BET area and pore volume as compared to poly-DVB (Table S1, ESI†). However, it was not clear whether this difference was significant or contributable to the higher densities of the poly-EGDMA and poly-TMPTMA materials. More rigorous studies using other monomers and a variety of templates would be necessary to extract the precise relationship between the crosslinking distance, crosslinking number, and pore diameter for faithful replication. Nevertheless, these results show that the crosslinking distances were longer in organic polymers than in inorganic materials. The distance between crosslinking sites appeared to facilitate the synthesis of ordered mesoporous inorganic materials, such as transition metal oxides, carbon, and noble metals, using mesoporous silica templates with pores as small as 2 nm in diameter.

Fig. 5 shows the XRD patterns and N<sub>2</sub> adsorption isotherms of three poly-DVB samples, synthesized using TMS-coated MCM-48 and SBA-15 silica templates. As shown, the MCM-48 and SBA-15 silica templates failed to produce faithful replicas. This can be explained as follows: MCM-48 silica had a cubic-*Ia3d* gyroid structure similar to the structure of the KIT-6 sample, but the mesopore diameters (4.0 nm) were insufficient for the formation of a rigid polymer framework. In SBA-15, the



**Fig. 5** The effect of kinds of silica template on the faithful replication to polymeric: (A) powder XRD patterns and (B) N<sub>2</sub> adsorption isotherms of various poly-DVB materials prepared by using various ordered mesoporous silica materials such as MCM-48 and SBA-15, as compared with their silica templates. All the template materials were used after silylation. N<sub>2</sub> adsorption isotherms of poly-DVB (SBA-15) and TMS-coated SBA-15 were offset by 400 and 500 cm<sup>3</sup> g<sup>-1</sup>, respectively.

**Table 2** Adsorption data calculated from N<sub>2</sub> adsorption isotherms of poly-DVB materials prepared by using various silica templates. Template materials were indicated in parenthesis

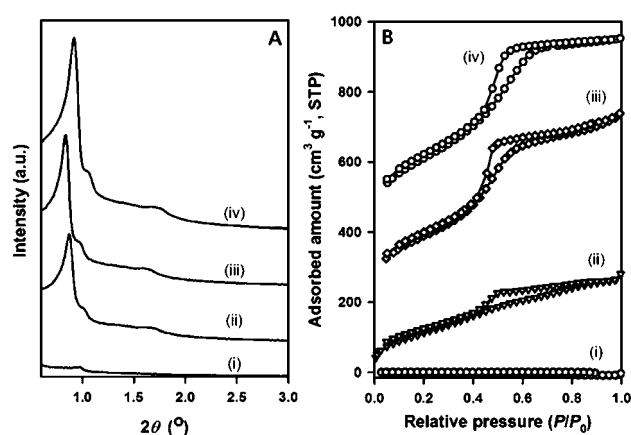
	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$V_t/\text{cm}^3 \text{ g}^{-1}$	$d_{\text{BJH}}/\text{nm}$
poly-DVB (KIT-6)	619	0.69	3.7
poly-DVB (SBA-15)	384	0.34	3.3
poly-DVB (MCM-48)	288	0.34	3.7

**Table 3** Total product conversion and ester/ether selectivity (mol mol<sup>-1</sup>) of the final products after 10 h reaction

Catalyst	Conversion (%)	Ester/ether/mol mol <sup>-1</sup>	Sulfur Density (m mol g <sup>-1</sup> )
Amberlyst-15	45.3%	7.3	4.54
Sulfonated poly-DVB	61.7%	7.6	2.15

mesopore diameters were sufficiently large (7.1 nm), but the mesopores were not fully interconnected. The SBA-15 silica had a 2D hexagonal *p6mm* structure, in which 1D mesoporous channels were hexagonally packed to form a bundle. The mesopores were interconnected through secondary pores (typically, 1–3 nm in diameter).<sup>49</sup> The secondary pores were not large enough to allow generation of rigid polymer bridges. Previously, it was reported that ordered mesoporous poly-DVB materials were successfully synthesized using MCM-48 and SBA-15 silica templates without silylation.<sup>28</sup> The structural order in those samples was characterized by highly-resolved XRD patterns, although the reported N<sub>2</sub> adsorption isotherms did not exhibit a distinct jump in adsorption quantity in the pressure region corresponding to mesopores (*i.e.*,  $P/P_0 = 0.4\text{--}0.8$ ). The materials shown in Fig. 5 contained much better mesoporosity (see Table 2), but did not yield highly-resolved XRD patterns, even after TMS-coating of the silica templates.

It was possible to synthesize ordered mesoporous polymers *via* copolymerization of DVB with non-crosslinking monomers in KIT-6. Fig. 6 shows the XRD patterns and N<sub>2</sub> adsorption isotherms for a series of DVB–VBC copolymer samples synthesized with various ratios of DVB/VBC. As this result shows, the copolymer at 50 mol% VBC content exhibited a very poor structural order and almost no accessible porosity. The copolymeric materials below 20 mol% VBC retained an ordered mesoporous structure similar to that of the poly-DVB homopolymer. A similar result was obtained when styrene (St) was used in place of VBC. We suggest that copolymerization in a silica template may be a suitable strategy for the preparation of ordered mesoporous polymeric materials containing various types of functional groups. For example, the DVB–VBC copolymeric material would be functionalized *via* substitution of Cl at the chloromethyl group. Various functional groups could be introduced at the aromatic rings in copoly-DVB–St *via* sulfonation, nitration, or Friedel–Crafts alkylation/acetylation for catalytic applications, such as acid, base, or metal-coordinating



**Fig. 6** Synthesis of ordered mesoporous DVB–VBC copolymeric materials synthesized using KIT-6 as template: (A) powder XRD patterns and (B) N<sub>2</sub> adsorption isotherms of various ordered mesoporous polymeric materials synthesized *via* co-polymerization of two different monomers (DVB and VBC) with various ratios. The loading of VBC was varied over (i) 50, (ii) 20, (iii) 10 and (iv) 0 mol% per total moles of monomers used here. The N<sub>2</sub> adsorption isotherms of (iii) and (iv) were offset by 200 and 400 cm<sup>3</sup> g<sup>-1</sup>, respectively.

catalysts. We confirmed that the DVB homopolymer could be sulfonated by sulfonic-acid functionalization, even without copolymerization with VBC. Sulfonation could be easily performed by stirring the mesoporous poly-DVB material in 98% sulfuric acid at 90 °C. The sulfonic acid group content was increased to 2.2 m mol g<sup>-1</sup> within a 2 h reaction time, without significant loss of structural order (see Fig. S2, ESI†).

Uniform mesoporosity in a highly crosslinked and rigid polymeric framework can provide remarkable advantages over ordinary porous polymeric materials with low degrees of crosslinking. With high crosslinking a high level of mesoporosity can be maintained in organic solvents, even in solvents in which shrinking or swelling is a serious problem for ordinary gel-type polymeric resins.<sup>50,51</sup> Therefore, template-synthesized polymeric materials with open mesopores may enhance catalytic activity when used as a catalyst support. This potential was tested for the esterification of benzyl alcohol with hexanoic acid in the present work. The catalytic activity of the sulfonated poly-DVB material was investigated at 75 °C and was compared with the activity of a commercially available catalyst, Amberlyst-15. The product yield and product selectivity are summarized in Table 3. As the results demonstrate, the ester/ether selectivity ratio was very similar for the two types of catalyst. However, the poly-DVB catalyst exhibited a 1.5-fold higher rate of conversion than did the Amberlyst-15. Because the catalysts were compared under the same conditions, the high catalytic activity of the silica-templated material was attributed to the more easily accessible acid sites available at the surfaces of the rigid pore walls.

## Conclusion

In this work, we have investigated the critical parameters that influence the synthesis of ordered mesoporous polymeric materials using porous silica templates. It was found that the most important factors are the hydrophobic coating of the silica pore

walls, crosslinking of the monomers, and sufficiently large pore diameters (>5 nm). The formation of highly crosslinked polymers inside the mesoporous silica template faithfully replicated the 3D pore system in the resulting rigid polymeric framework. The polymeric framework retained an ordered mesoporous polymeric structure after release from the template by HF. We demonstrated that such a highly mesoporous poly-DVB could be functionalized, and the material exhibited high catalytic activity and recyclability for an acid-catalyzed reaction.

A variety of methods<sup>7,9,10,13–26</sup> are currently available for the preparation of mesoporous polymeric materials in addition to the method discussed here, which used silica templates. No single method outperforms all the others, because each method presents different advantages, limitations, and area of applicability. Nevertheless, we have demonstrated that the most significant merit of the template method is versatility in terms of synthetic composition, through incorporation of a variety of monomers. Various crosslinking monomers, such as DVB, EGDMA, and TMPTMA, can be polymerized for the formation of rigid frameworks. The frameworks can be functionalized *via* organic reactions. The crosslinking monomers can also be copolymerized with non-crosslinking monomers for functionalization. In addition, quite a large number of ordered mesoporous silica materials with varying structures and pore diameters are currently available.<sup>32–35</sup> These mesoporous silicas can serve as templates for the synthesis of polymers with a variety of structures. Ordered mesoporous polymeric materials have potential applications in adsorption, purification, energy storage, and catalysis.

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## References

- 1 A. Derylo-Marczewska and J. Goworek, *Langmuir*, 2001, **17**, 6518.
- 2 Y. Wang, U. Gösele and M. Steinhart, *Chem. Mater.*, 2008, **20**, 379.
- 3 H. Deng, D. L. Gin and R. C. Smith, *J. Am. Chem. Soc.*, 1998, **120**, 3522.
- 4 J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Carter, W. Volksen, D. Y. Yoon and M. Trollsas, *Adv. Mater.*, 1998, **10**, 1049.
- 5 F. Zhang, Y. Meng, D. Gu, Y. Yan, C. Z. Yu, B. Tu and D. Y. Zhao, *J. Am. Chem. Soc.*, 2005, **127**, 13508.
- 6 Y. K. Takahara, S. Ikeda, K. Tachi, T. Sakata, T. Hasegawa, H. Mori, M. Matsumura and B. Ohtani, *Chem. Commun.*, 2005, 4205.
- 7 J. Jang and J. Bae, *Chem. Commun.*, 2005, 1200.
- 8 J. Jang and J. Bae, *J. Non-Cryst. Solids*, 2006, **352**, 3979.
- 9 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. Yang, Z. Li, C. Z. Yu, B. Tu and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2005, **44**, 7053.
- 10 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein and D. Y. Zhao, *Chem. Mater.*, 2006, **18**, 4447.
- 11 R. Drake, D. C. Sherrington and S. J. Thomson, *React. Funct. Polym.*, 2004, **60**, 65.
- 12 Z. M. Michalska, B. Ostaszewski, J. Zientarska and J. M. Rynkowski, *J. Mol. Catal. A: Chem.*, 2002, **185**, 279.
- 13 A. S. Zalusky, R. Olayo-Valles, J. H. Wolf and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2002, **124**, 12761.
- 14 J. Rzaev and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2005, **127**, 13373.
- 15 S. A. Jenekhe and X. L. Chen, *Science*, 1999, **283**, 372.
- 16 B. Krause, H. J. P. Sijbesma, P. Munuklu, N. F. A. van der Vegt and M. Wessling, *Macromolecules*, 2001, **34**, 8792.
- 17 B. Krause, G. H. Koops, N. F. A. van der Vegt, M. Wessling, M. Wubbenhorst and J. van Turnhout, *Adv. Mater.*, 2002, **14**, 1041.
- 18 H. P. Hentze and M. Antonietti, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 343.
- 19 G. Wulff, *Chem. Rev.*, 2002, **102**, 1.
- 20 C. R. Martin, *Chem. Mater.*, 1996, **8**, 1739.
- 21 R. C. Smith, W. M. Fischer and D. L. Gin, *J. Am. Chem. Soc.*, 1997, **119**, 4092.
- 22 B. A. Pindzola, B. P. Hoag and D. L. Gin, *J. Am. Chem. Soc.*, 2001, **123**, 4617.
- 23 A. S. Zalusky, R. Olayo-Valles, C. J. Taylor and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2001, **123**, 1519.
- 24 A. S. Zalusky, R. Olayo-Valles, J. H. Wolf and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2002, **124**, 12761.
- 25 M. Antonietti, R. A. Caruso, C. G. Göltner and M. C. Weissenberger, *Macromolecules*, 1999, **32**, 1383.
- 26 H. K. Lee, H. Lee, Y. H. Ko, Y. J. Chang, N. K. Oh, W. C. Zin and K. Kim, *Angew. Chem., Int. Ed.*, 2001, **40**, 2669.
- 27 C. G. Göltner and M. C. Weissenberger, *Acta Polym.*, 1998, **49**, 704.
- 28 J. Y. Kim, S. B. Yoon, F. Koolib and J. S. Yu, *J. Mater. Chem.*, 2001, **11**, 2912.
- 29 P. Jiang, K. S. Hwang, D. M. Mittleman, J. F. Bertone and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121**, 11630.
- 30 S. A. Johnson, P. J. Ollivier and T. E. Mallouk, *Science*, 1999, **283**, 963.
- 31 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 32 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- 33 Q. S. Huo, D. I. Margolese, U. Ciesla, P. Y. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth and G. D. Stucky, *Nature*, 1994, **368**, 317.
- 34 D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
- 35 T. W. Kim, F. Kleitz, B. Paul and R. Ryoo, *J. Am. Chem. Soc.*, 2005, **127**, 7601.
- 36 R. Ryoo, S. H. Joo and S. Jun, *J. Phys. Chem. B*, 1999, **103**, 7743.
- 37 J. Lee, S. Yoon, T. Hyeon, S. M. Oh and K. B. Kim, *Chem. Commun.*, 1999, 2177.
- 38 S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Oshuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712.
- 39 S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, 2001, **412**, 169.
- 40 J. S. Lee, S. H. Joo and R. Ryoo, *J. Am. Chem. Soc.*, 2002, **124**, 1156.
- 41 B. Tian, S. Che, Z. Liu, X. Liu, W. Fan, T. Tatsumi, O. Terasaki and D. Zhao, *Chem. Commun.*, 2003, 2726.
- 42 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 426.
- 43 P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152.
- 44 B. Z. Tian, X. Y. Liu, B. Tu, C. Z. Yu, J. Fan, L. M. Wang, S. H. Xie, G. D. Stucky and D. Y. Zhao, *Nat. Mater.*, 2003, **2**, 159.
- 45 H. J. Shin, R. Ryoo, Z. Liu and O. Terasaki, *J. Am. Chem. Soc.*, 2001, **123**, 1246.
- 46 M. Choi, F. Kleitz, D. Liu, H. Y. Lee, W. S. Ahn and R. Ryoo, *J. Am. Chem. Soc.*, 2005, **127**, 1924.
- 47 Y. Sakamoto, T. W. Kim, R. Ryoo and O. Terasaki, *Angew. Chem., Int. Ed.*, 2004, **43**, 5231.
- 48 T. W. Kim and L. A. Solovyov, *J. Mater. Chem.*, 2006, **16**, 1445.
- 49 R. Ryoo, C. H. Ko, M. Kr above, ntochshuk and M. Jaroniec, *J. Phys. Chem. B*, 2000, **104**, 11465.
- 50 D. J. Buckley and M. Berger, *J. Polym. Sci.*, 1962, **56**, 175.
- 51 B. H. Knox, H. D. Weigmann and M. G. Scott, *Textile Research Journal*, 1975, **45**, 203.