

# Synthesis of polystyrene–silica hybrid mesoporous materials *via* the nonsurfactant-templated sol–gel process

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The first synthesis of polymer–silica hybrid mesoporous materials has been achieved *via* the acid-catalyzed sol–gel reactions of tetraethyl orthosilicate with poly(styrene-*co*-styrylethyltrimethoxysilane), containing 90 mol% of styrene, in the presence of dibenzoyltartaric acid (DBTA) as a nonsurfactant template or pore-forming agent, followed by extraction with EtOH–H<sub>2</sub>O (2:1 v/v) to remove the DBTA molecules. At low DBTA concentrations, both micropores and mesopores contribute to the porosity of the materials. At high DBTA concentrations ( $\geq 45$  wt%), mesopores become dominant and the hybrid materials exhibit high surface area of  $\sim 800$  m<sup>2</sup> g<sup>-1</sup>, pore volume of  $\sim 0.6$  cm<sup>3</sup> g<sup>-1</sup> and pore diameters of  $\sim 3$ –5 nm with relatively narrow size distributions. Polymer chains are covalently bonded to the silica network through the cross-condensation of the alkoxy groups in both the inorganic and polymer precursors. Thermal treatment at 130 °C results in appreciable changes in the pore parameters, attributable to polymer chain motions in the hybrid framework.

## Introduction

In 1992, Kresge *et al.*<sup>1,2</sup> first reported the synthesis of the M41S family of mesoporous silicate and aluminosilicate materials *via* the surfactant-templated sol–gel process. Since then, numerous mesoporous materials with different compositions and pore structures have been obtained by modifying the synthesis conditions, such as type of surfactant templates, inorganic precursors and other reaction parameters.<sup>3–12</sup> These new materials have a wide variety of potential applications in the areas of catalysis, selective membranes, and molecular recognitions.<sup>13</sup> Recently, research in this area has been extended to mesoporous organic polymers<sup>14–17</sup> and to organic–inorganic hybrid mesoporous materials with incorporation of small organic moieties, such as alkyl, aryl and vinyl groups, into the inorganic framework.<sup>18–28</sup> The organic-modified materials could have desired combinations of the features of both organic and inorganic components. The inorganic species usually have good mechanical and thermal stabilities as well as optical properties. The organic moiety would provide the materials with interesting new properties such as flexibility, toughness, and hydrophobicity.

Several approaches have been developed for the synthesis of organic-modified mesoporous materials.<sup>25</sup> In 1996, Burkett *et al.*<sup>18</sup> described a cocondensation of tetraethoxysilane (TEOS) with phenyl- or octyl-triethoxysilane, imbedding the organic moieties into the mesoporous channel wall. Other functional groups, including amine, thiol, epoxide, *etc.*, have also been incorporated into the mesoporous hosts.<sup>19,20</sup> In an effort to probe the internal pore structure, Lim *et al.*<sup>21</sup> prepared a hybrid mesoporous material with vinyl functionality. Subsequent bromination of the C=C bonds demonstrated that most vinyl groups were attached to the internal pore surface and hence accessible to bromination. Moller *et al.*<sup>22</sup> recently reported the cocondensation of 3-(trimethoxysilyl)propyl methacrylate (TMSiPMA) and tetramethyl orthosilicate (TMOS). The encapsulated methacrylate groups were also readily accessible for further bromination addition. Organic modifications have also been achieved through the post-synthesis technique.<sup>23,24</sup> For example, thiol groups have been introduced into the preformed M41S type of mesoporous silica.<sup>23</sup> The resultant

materials exhibit high efficiency in removing mercury and other heavy metals from waste water. However, no report has appeared in the literature on mesoporous hybrid materials containing organic polymers or oligomers.

We report here the first successful synthesis of polymer-modified mesoporous hybrid materials *via* the nonsurfactant templating sol–gel route.<sup>29,30</sup> The method involves the hydrolysis and cocondensation of inorganic precursors such as TEOS with sol–gel reactive polymer precursors such as poly(styrene-*co*-styrylethyltrimethoxysilane) [P(ST-STMS)]<sup>31</sup> under acidic conditions using dibenzoyl tartaric acid (DBTA) as the templating or pore-forming compound. Removal of the template molecules was easily achieved by solvent extraction, resulting in mesoporous P(ST-STMS)–silica hybrid materials. The new materials were characterized by means of infrared spectroscopy, thermogravimetric analysis, nitrogen sorption measurements and transmission electron microscopy.

## Experimental section

### Materials and synthesis

Styrene (ST, Aldrich) was washed with 1 M NaOH aqueous solution to remove inhibitors and distilled under a reduced pressure. Styrylethyltrimethoxysilane (STMS, Gelest) was freshly distilled under a reduced pressure prior to use. Benzoyl peroxide (BPO, Fisher) was recrystallized from ethyl alcohol. Tetraethyl orthosilicate (TEOS, Aldrich), dibenzoyltartaric acid (DBTA, Aldrich), ethyl alcohol (Pharmco) and HCl (Fisher) were used as received without further purification. The polymer precursor [P(ST-STMS)] was synthesized *via* free radical copolymerization of ST with STMS ([ST]:[STMS]=9:1 molar ratio) using BPO as initiator (1 mol% based on the monomers) and benzene as solvent at 70 °C, following the literature procedures.<sup>31</sup>

To prepare mesoporous hybrid materials, the alkoxy groups containing polymer precursors were hydrolyzed and cocondensed (*i.e.*, sol–gel reactions) with TEOS in the presence of DBTA as the templating or pore-forming agent and HCl as catalyst, following similar procedures as reported previously.<sup>29</sup> The amount of DBTA used was varied from 20 to 60 wt%

based on the weight of final dry product before the removal of DBTA. Regardless of the DBTA concentrations used, the solutions (sols) and gels, *i.e.*, the reaction systems before and after gelation, were homogeneous without visible macroscopic phase separations. The gelation and subsequent aging and drying of the DBTA-containing hybrid gels proceeded at room temperature. Porous polystyrene-silica materials were obtained upon removal of DBTA by exhaustive extraction with a mixed solvent (*i.e.* EtOH-H<sub>2</sub>O, 2:1 v/v). A schematic diagram for the synthesis of the hybrid mesoporous materials is illustrated in Fig. 1.

In a typical procedure for preparing the hybrid mesoporous materials, TEOS was prehydrolyzed at room temperature for 2–3 h in a mixture of tetrahydrofuran (THF) and 0.2 M HCl at a [TEOS]: [THF]: [HCl] molar ratio of 1:1:0.01 to afford sol A. The polymer precursor (0.018 g, *i.e.* 3 wt% of the final product after the template removal) was dissolved in THF to make a 1.8 wt% solution, denoted as sol B. The molar ratio of TEOS to the polymer precursor based on the repeating units was 64:1. An appropriate amount of DBTA based on the desired compositions in the products was dissolved in 1.0 g THF to make sol C. Finally, sol A was added dropwise to the mixture of sol B and sol C under vigorous stirring. The resultant transparent and homogeneous solution was cast into a 25 mL beaker covered with a paraffin film and was stirred magnetically. After about 20 h, 15–20 pin-holes were punched on the film to allow the evaporation of volatile molecules, *i.e.*, solvents and byproducts of the sol-gel reactions. Upon gelling and drying in air for three to seven days, a transparent and monolithic DBTA-containing polymer-silica hybrid gel was obtained. This as-synthesized sample was further evacuated in a vacuum oven at room temperature until a constant weight was reached. To remove DBTA after drying the sample in vacuum, 0.2 g of the as-synthesized sample was ground into fine powder and was placed in a test tube containing 15 mL of EtOH-H<sub>2</sub>O (2:1 v/v). The test tube was then sealed with

paraffin film and was kept under constant agitation. After about 1 h, the mixture was centrifuged; the solvent was decanted; and another 15 mL mixed solvent was added. The above extraction procedures were repeated at least four to five times plus an additional overnight extraction. Such a solvent extraction by EtOH-H<sub>2</sub>O mixture should have little effect in plasticizing or swelling the crosslinked polymer component in the product, because both EtOH and H<sub>2</sub>O are nonsolvent for the polymer. The sample was then dried at 65–80 °C in an oven for 2–3 days to afford porous polymer-silica hybrid materials. The completion of the DBTA removal was monitored with infrared spectroscopy. A control sample (HMD0) was made in the absence of DBTA under otherwise identical conditions.

### Characterization and instrumentation

Gel permeation chromatography (GPC) of the copolymer (0.2 wt% solution in THF) was performed on a Waters Model IIA GPC equipped with a Model 590 solvent delivery module, a refractometer as detector, and an Ultrastaygel<sup>TM</sup> linear column using THF as eluant at 25 °C at a flow rate of 1.0 mL min<sup>-1</sup>. The number-average molecular weight of P(ST-STMS) was estimated to be 18800 based on the standard polystyrene calibration. Infrared spectra of the samples as powder-pressed KBr pellets were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer (Norwalk, CT). Brunauer-Emmett-Teller (BET) characterizations were performed on a Micromeritics ASAP 2010 micropore analysis system (Micromeritics, Inc., Norcross, GA) at -196 °C using the nitrogen adsorption-desorption isotherm method. The samples were degassed at 80 °C and 1 Pa overnight prior to the measurement. Transmission electron microscopy (TEM) was performed on a JEOL 100CX2 microscope using an accelerating voltage of 100 kV. The samples were prepared by allowing an ethyl alcohol suspension of the finely ground polymer-silica hybrid to evaporate on a Cu grid coated with a holey C film. The silica contents in the sol-gel hybrid materials were determined from the weight loss at 600 °C in air using thermogravimetric analysis (TGA) on a DuPont 2000 thermal analyzer equipped with a TGA 950 module.

### Results and discussion

Polymer-modified mesoporous hybrid materials have been made *via* the sol-gel reactions of TEOS with P(ST-STMS) in the presence of DBTA as the nonsurfactant template or pore-forming agent at room temperature, followed by solvent extraction to remove the DBTA molecules. The compositions and pore parameters of the materials are summarized in Table 1. The SiO<sub>2</sub> contents calculated from the reactant stoichiometry and found by TGA experiments before the extraction are in reasonably good agreement. The differences might result from incomplete hydrolysis of TEOS and/or incomplete removal of the volatile solvents and by-products (*e.g.*, water and ethanol) that were bound tightly to the inorganic matrix. Some templates, such as D-glucose, D-fructose and D-maltose used in the original method by Wei *et al.*,<sup>29</sup> seemed not to be easily applicable to template this polymer-silica system since it was difficult to find a common cosolvent that could yield a homogeneous solution prior to the gelation. These sugar molecules exhibited limited solubility in THF which is an excellent solvent for the polymer precursor. Even though water could dissolve the sugar compounds, addition of aqueous solutions resulted in immediate precipitation of the alkoxy silane-containing polymer precursors.

Similar to the nonporous polymer-modified inorganic sol-gel materials,<sup>31–33</sup> covalent bonds between the organic and inorganic components are introduced conveniently through the cross-condensation of the alkoxy silyl groups in the polymer precursors with those in the inorganic precursors. After

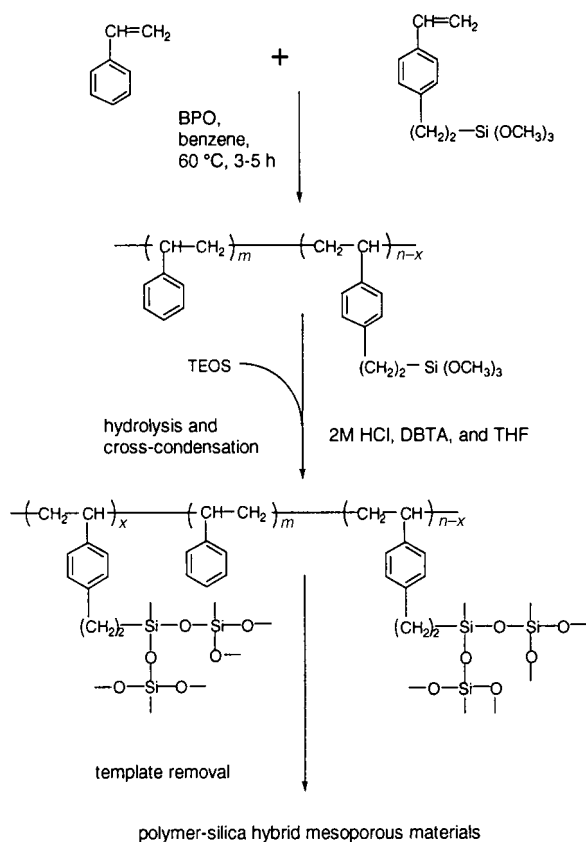


Fig. 1 Schematic synthesis of the polymer-silica hybrid mesoporous materials ( $m/n=9$ ).

**Table 1** Compositions and pore parameters of the polymer (3 wt%)-silica hybrid mesoporous materials after removal of the template

Sample code <sup>a</sup>	SiO <sub>2</sub> (wt%)		$S_{\text{BET}}/$ $\text{m}^2 \text{g}^{-1}$	$V_{\text{PORE}}/$ $\text{cm}^3 \text{g}^{-1}$	$D_{\text{BJH}}/$ $\text{\AA}$	$D_{\text{BET}}/$ $\text{\AA}$	Micropore vol./ $\text{cm}^3 \text{g}^{-1c}$
	calc.	found <sup>b</sup>					
HMD0	97.0	86	4	0.01			
HMD20	77.6	66	493	0.30	<17	24	0.18
HMD35	62.8	55	651	0.38	<17	23	0.14
HMD45	53.4	47	832	0.52	35	25	0.13
HMD55	43.6	42	761	0.61	36(44) <sup>d</sup>	32	0.10
HMD60	38.8	39	606	0.64	37(50) <sup>d</sup>	42	0.08

<sup>a</sup>The numerical figure in the sample code denotes the template concentration (wt%) in the materials before the solvent extraction. <sup>b</sup>Values from the TGA weight loss at 600 °C, which represent the total contents of nonvolatile molecules. <sup>c</sup>Values determined from the *t*-plot analysis. <sup>d</sup>Bimodal pore size distribution.

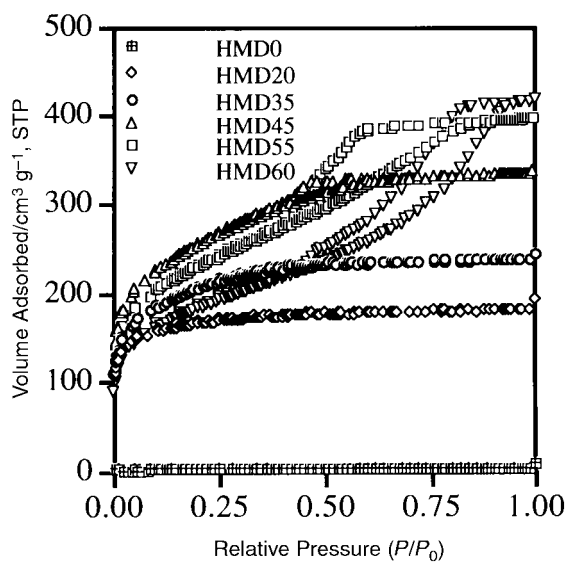
removing DBTA from as-synthesized sol-gel materials by extraction with mixed solvents, further extraction with THF, a good solvent for the polymer, showed little change in either the polymer or SiO<sub>2</sub> content, suggesting covalent bonding of the polymer chains to the silica network. Such a strong bonding would compensate the thermodynamic repulsion between the hydrophobic polymer and the hydrophilic inorganic component, thus avoiding macroscopic phase separation.

Fig. 2 shows the N<sub>2</sub> adsorption-desorption isotherms at -196 °C for all the samples after the template removal. As the template concentration is increased, the characteristic isotherm transforms from that of nonporous solids (*e.g.*, sample HMD0) to microporous (*e.g.*, HMD20) and then to mesoporous (*e.g.*, HMD55) materials. The microporosity is manifested by the completely reversible type I isotherms<sup>34</sup> observed for the samples prepared at low concentrations of DBTA. At the DBTA concentrations of 45 wt% and higher, the samples exhibit type IV-like isotherms with H2 hysteresis, typical of mesoporous materials. There is also a well-defined plateau at relative pressures above 0.8, suggesting the presence of framework confined mesopores and the lack of secondary interparticular porosity. As demonstrated in Table 1, the BET and BJH pore diameters ( $D_{\text{BET}}$  and  $D_{\text{BJH}}$ , respectively) as well as the pore volumes ( $V_{\text{PORE}}$ ) tend to increase with the template concentration. Both micropores and mesopores contribute to the resultant BET surface areas ( $S_{\text{BET}}$ ) and pore volumes. However, as the DBTA concentration is increased, the relative contribution from mesopores becomes dominant while microporosity becomes negligible. All these trends are similar to

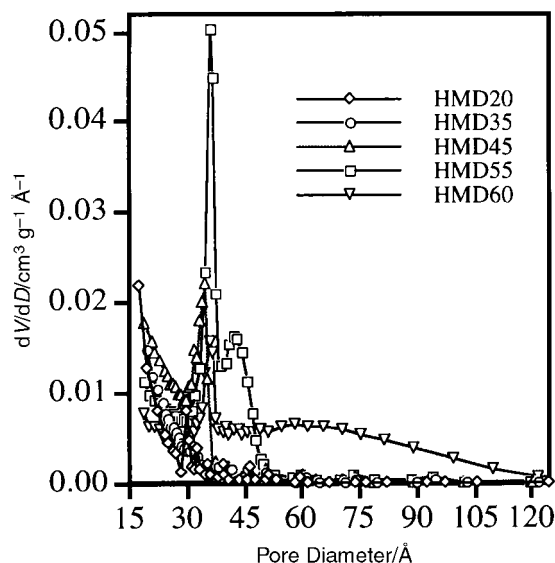
those reported for the pure mesoporous silica.<sup>29</sup> It should be noted that all of the as-synthesized samples before the removal of DBTA exhibit little porosity with typical BET surface area of  $\sim 5 \text{ m}^2 \text{ g}^{-1}$  and pore volume of  $\sim 0.005 \text{ cm}^3 \text{ g}^{-1}$ . This suggests that the pores were generated from the vacancies left by DBTA molecules after the solvent extraction. The formation mechanism of this nonsurfactant templated mesostructures has been discussed and postulated in our previous reports.<sup>29</sup>

Fig. 3 shows the pore size distributions of the hybrid materials after the template removal, according to the Barrett-Joyner-Halenda (BJH) method using the Halsey equation for multilayer thickness. At the template concentrations of 45–60 wt%, the dominant pore diameters are in the mesopore range with major peaks at 3.2–3.5 nm. The samples containing 55 and 60 wt% template show a bimodal distribution with a second and rather broad peak at  $\sim 4.4$  and 5.0 nm, respectively. The underlying mechanism for such a bimodal distribution is not yet fully understood. TEM image of the mesoporous sample prepared with 55 wt% of DBTA is shown in Fig. 4. There are numerous interconnecting pores or channels with regular diameters of around 5 nm, which is in reasonable agreement with the results from the nitrogen isotherm measurements. Similar to the pure mesoporous sol-gel silica templated with the neutral surfactants<sup>5</sup> or nonsurfactants,<sup>29</sup> there is no clearly identifiable structural order or packing of the mesoporous channels.

We have also investigated the possibility of controlling internal structure of the hybrid mesoporous materials. The



**Fig. 2** N<sub>2</sub> adsorption-desorption isotherms at -196 °C for the P(ST-STMS) (3 wt%)-silica hybrid mesoporous materials prepared in the presence of 0, 20, 35, 45, 55 and 60 wt% of DBTA.



**Fig. 3** BJH pore size distributions obtained from N<sub>2</sub> desorption isotherms for the P(ST-STMS) (3 wt%)-silica hybrid mesoporous materials.

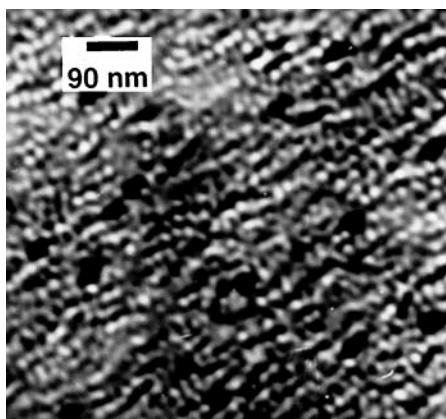


Fig. 4 TEM image of mesoporous P(ST-STMS) (3 wt%)-silica hybrid sample prepared in the presence of 55 wt% DBTA.

samples were heated in an oven at 130 °C for 15 hours after the first nitrogen sorption measurement, and were then characterized by the nitrogen sorption measurement for the second time. The second BET data show decreased surface areas and pore volumes for all the heated samples. For example, the surface area and pore volume of sample HMD45 decreases, respectively, to 585 m<sup>2</sup> g<sup>-1</sup> and 0.361 cm<sup>3</sup> g<sup>-1</sup> after the thermal treatment. It is known that at temperatures above  $T_g$  (for polystyrene: ~100 °C), large-scale, cooperative segmental motions of polymer chains take place, which could lead to increased blockage of the mesopore channels to a certain extent. On the other hand, the inorganic silica component should not be affected by the thermal treatment at 130 °C. This has been confirmed by a series of control experiments. Thus, mesoporous silica samples were prepared under identical conditions except for the absence of the polymer precursor and were subjected to the same thermal treatment. These control samples are found to have little change in both the BET surface areas and pore volumes. Therefore, the observed changes in the pore parameters of the hybrid materials upon thermal treatment are attributed by the polymer component.

Fig. 5 shows the IR spectra of the P(ST-STMS)-silica hybrid materials containing 3, 8 and 17 wt% of the polymer after the removal of template, along with the spectrum of the sample containing 3 wt% of the polymer before the template removal. The strong C=O band at 1720 cm<sup>-1</sup> (Fig. 5a) from DBTA disappears after the solvent extraction (Fig. 5b), indicating a complete removal of the template. Characteristic bands for the polymer precursor remain unchanged by the extraction, further suggesting that the polymer chains are covalently bonded to the silica component. For example, the bands at 700 and 790 cm<sup>-1</sup> can be assigned to the out-of-plane bending vibrations of the aromatic C-H bonds, and that at ~2900 cm<sup>-1</sup> to the aliphatic C-H stretching. The intensity of these bands increases as the polymer content is increased. The appearance of a shoulder at ~1160 cm<sup>-1</sup> indicate the presence of non-hydrolyzable Si-C bonds in the mesoporous hybrid materials. A similar assignment for such a Si-C band was reported for the organic-modified silica materials.<sup>18,22</sup> Transparent and monolithic hybrid products could be obtained with polymer contents up to 17 wt% in the presence of 40 wt% of DBTA template. However, after the removal of DBTA, the materials exhibit mainly microporous properties based on the nitrogen adsorption-desorption isotherm measurements. Again, this might be attributed to the relatively high mobility of the polymer chains in comparison with the rigid silicate component. Further investigation is in progress to evaluate the effects of structure and molecular weight of the polymer component on the pore structures and to explore the possibilities of reversible fine tuning of the pore parameters by simple physical means such as temperature change.

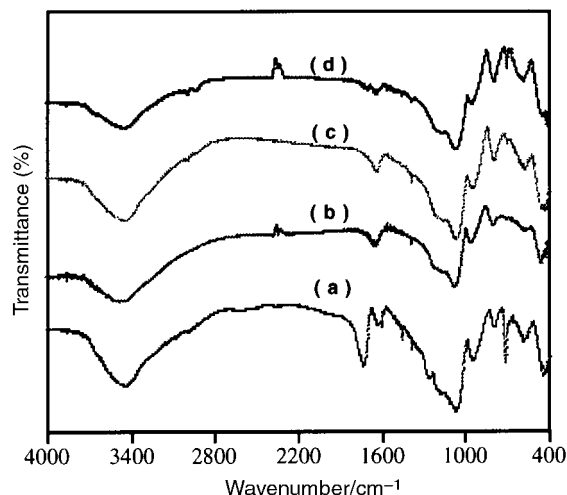


Fig. 5 FT-IR spectra of the P(ST-STMS)-silica hybrid materials (a) before the template removal with the polymer content of 3 wt%, and after the template removal with the polymer contents of (b) 3, (c) 8 and (d) 17 wt%. The amount of DBTA template was fixed at 40 wt% in the preparation of all the samples.

## Summary and conclusions

We have described the synthesis and characterization of mesoporous P(ST-STMS)-silica hybrid materials. The synthesis has been achieved by the HCl-catalyzed sol-gel reactions of TEOS with trialkoxysilyl-functionalized polystyrene precursor (3 wt%) in the presence of DBTA as the nonsurfactant template or pore-forming agent at various concentrations, followed by solvent extraction to remove the DBTA molecules. Both pore volume and pore size tend to increase with the DBTA concentration. At low DBTA concentrations, both micropore and mesopore contribute to the porosity of the materials. At high DBTA concentrations ( $\geq 45$  wt%), mesopores become dominant. The hybrid materials exhibit high surface area of ~800 m<sup>2</sup> g<sup>-1</sup>, pore volume of ~0.6 cm<sup>3</sup> g<sup>-1</sup> and pore diameters of ~3-5 nm with narrow size distributions. The polymer chains are covalently bonded to the inorganic silica network. Thermal treatment at 130 °C results in a decrease in the pore parameters, which could be attributed to the polymer chain segmental motions. Further modifications of the polymer chains in the hybrid materials such as sulfonation, chloromethylation, *etc.* are currently under investigation for chromatography, solid phase biosynthesis and biosensor applications. Using the same approach, we are also preparing the hybrid mesoporous materials containing other polymer and inorganic components.

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