

SYNTHESIS OF HYBRID MESOPOROUS POLYSTYRENE-SILICA MATERIALS WITH NON-SURFACTANT CITRIC ACID AS TEMPLATE VIA SOL-GEL PROCESS*

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Abstract Hybrid mesoporous polystyrene-silica materials were successfully prepared through HCl-catalyzed sol-gel reactions of tetraethyl orthosilicate (TEOS) and triethoxysilyl-functionalized polystyrene obtained via atom transfer radical polymerization (ATRP) of styrene, in the presence of citric acid (CA) as non-surfactant template or pore-forming agent and followed by ethanol extraction to remove template molecules. The materials were characterized by infrared spectroscopy (IR), N₂ adsorption-desorption measurements, powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The results indicate that the materials prepared with 50 wt%–60 wt% template contents have average pore sizes of 2–3 nm and large surface areas (ca. 886 m²/g) as well as high pore volumes (ca. 0.53 cm³/g). The mesoporosity arises from interconnected channels and pores with disordered arrangements. The pore diameters and pore volumes increase as the template content is increased. The pore diameters show a little change upon heating at 200°C overnight. However, the materials do not have good hydrothermal stability.

Keywords Atom transfer radical polymerization, Hybrid material, Mesoporous, Polystyrene, Silica

INTRODUCTION

In 1992, researchers at Mobil Company achieved an exciting breakthrough in the synthesis of mesoporous materials^[1, 2]. By removing the surfactant molecules from surfactant-silica composites via calcination, they obtained mesoporous silica and alumina materials. Since the surfactant molecules have assembling function, they were widely used as templates to direct the formation of different pore structures and pore sizes. Such a surfactant-templated process has been extensively studied and numerous mesoporous silica and metal oxides have been synthesized using various ionic or neutral surfactants as templates.

After that, a nonsurfactant-templated sol-gel route used to prepare mesoporous materials has been developed^[3–5], in which nonsurfactant small organic molecules such as *D*-glucose, *D*-maltose, *etc.*, were employed as templates or pore-forming agents to direct the formation of mesopores. Upon removal of the organic molecules by solvent extraction, mesoporous silica^[3, 4] and alumina materials^[5] were obtained with large surface areas and pore volumes as well as narrow pore size distributions.

The synthesis of hybrid organic-inorganic mesoporous materials with narrow pore size distributions has already attracted much attention. There are many reports on the modification of mesoporous materials by

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incorporating small organic moieties, such as alkyl, aryl and thiol groups, into the inorganic framework^[6–11]. In 2000, Wei and Qiu^[12] reported the synthesis of vinyl polymer-inorganic hybrid materials, for example: styrene (St)^[13, 14] and methyl methacrylate (MMA)^[15] were introduced into the framework of silica through copolymerization with 3-(trimethoxysilyl)propyl methacrylate (MSMA) or other alkoxyisilyl vinyl monomers to give polymer precursors containing reactive alkoxyisilyl pendant groups. Then polymer-modified silica composites can be achieved via HCl-catalyzed hydrolysis and condensation reactions (*i.e.*, sol-gel reactions) of tetraethyl orthosilicate (TEOS) with these polymer precursors. Wei *et al.*^[16] for the first time reported that when the above sol-gel reaction was carried out in the presence of non-surfactant templates, such as dibenzoyl-*L*-tartaric acid (DBTA), polymer-silica hybrid mesoporous materials were obtained. Qiu *et al.*^[17] utilized poly(styrene-*co*-maleic anhydride) to react with 3-aminopropyltriethoxysilane (APTES), a coupling agent, via the aminolysis reaction of anhydride groups with the amino groups of APTES to obtain a polymer precursor containing reactive alkoxyisilyl pendant groups^[18]. Mesoporous polymer-silica hybrid materials were then prepared using this polymer precursor with TEOS via a non-surfactant templated sol-gel process. Till now, only a few papers concern the nonsurfactant-templated method to synthesize organic polymer-inorganic mesoporous materials.

In order to expand the synthesis of organic polymer-silica mesoporous materials prepared through nonsurfactant-templated sol-gel process, we present a novel method to synthesize hybrid mesoporous polystyrene (PS)-silica materials, in which PS precursor bearing triethoxysilyl end groups was obtained via atom transfer radical polymerization (ATRP). Generally, ATRP is used to conduct a controlled/living polymerization and it is optimal to control the molecular weight, molecular weight distribution, and the structure of resulting polymer. The inclusion of well-defined polymers to inorganic substrates is of significance, because the functionality, composition, and dimensions of these macromolecules enable the design of specific properties into the resulting hybrid^[19, 20]. In this paper, the ATRP of St was conducted by using 2-(4-chloromethylphenyl)ethyltriethoxysilane (CTES) as initiator and CuCl/2,2'-bipyridine (bipy) as catalyst system. Then the acid catalyzed co-hydrolysis and co-condensation of TEOS and PS precursor were processed in the presence of citric acid (CA) as non-surfactant template or pore-forming agent. After the formation of transparent and monolithic composite gel products, CA molecules were removed by ethanol extraction to afford hybrid porous PS-silica materials.

EXPERIMENTAL

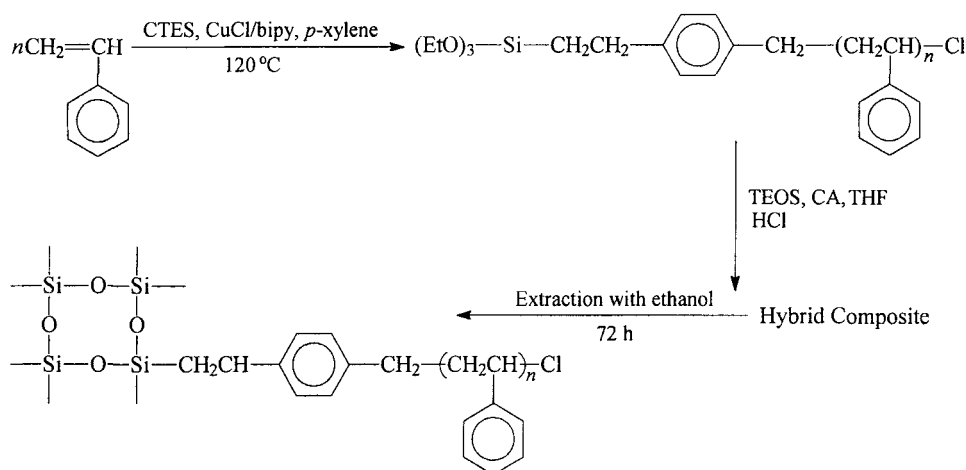
Polymerization

CTES was prepared by the catalytic hydrosilylation of 4-vinylbenzylchloride (Aldrich, 90%) and triethoxysilane (Aldrich, 99%)^[21]. The polymer precursor PS with triethoxysilyl end groups was prepared through typical ATRP of St initiated by CTES in conjunction with CuCl/bipy at 120°C. 0.5 mL St was added in a dry glass tube together with 0.0033 g CTES, 0.0041 g CuCl, 0.0129 g bipy and 0.24 mL *para*-xylene used as solvent. The molar ratio of this system is [St]: [CTES]: [CuCl]: [bipy] = 417:1:4:8. The mixture was immediately degassed by three freeze-pump-thaw cycles and sealed under vacuum. Then it was immersed in an oil bath thermostated at 120°C. After 24 h, the polymerization was quenched by cooling the tube in ice water. The resulting polymer was dissolved in 10 mL THF, then precipitated with 100 mL methanol and dried. The conversion (0.1688 g PS, 49.5%) of polymerization was determined gravimetrically. The number-average molecular weight (M_n) and polydispersity (M_w/M_n , M_w is weight-average molecular weight) of PS determined by GPC were 46 100 and 1.27, respectively.

Preparation of Hybrid Mesoporous PS-SiO₂ Materials with Non-Surfactant Template

The procedure for the preparation of hybrid mesoporous PS-silica material was similar to the literature^[16]. In a typical procedure (PS-3-50 in Table 1), 2.0 g (9.6 mmol) TEOS (Acros, 98%) was prehydrolyzed in a mixture of 0.8 g THF and 0.34 g of 0.28 mol/L HCl (*aq.*) at room temperature for 4 h to afford a clear solution as solution A. The molar ratio of [TEOS]:[HCl]:[H₂O] in solution A was 1:0.01:2. The polymer precursor PS (0.018 g, 3 wt% of the final product after the removal of template molecules) containing triethoxysilane end groups was dissolved in 1.887 g THF to obtain solution B. Solution C was prepared by dissolving 0.06 g CA into 1.0 g THF.

The amount of CA was determined by the desired template content (*i.e.*, 0 to 60% by weight) in the final dry composite gels. Solution A was then added drop-wise to a beaker containing the mixture of B and C under vigorous stirring. The beaker was then sealed with cellophane film. After standing at room temperature till gelation, a number of pinholes were made in the cellophane film to allow the slow evaporation of the solvents and by-products. Upon drying at ambient temperature for 10–15 days, transparent and monolithic template-containing hybrid composite was obtained. However, it always broke into several pieces during the later drying process. In order to remove the template molecules, the sample was ground to fine powder and extracted by ethanol in a Soxhlet apparatus for 72 h, followed by drying under an infrared lamp till constant weight. The composition of the polymer, as presented as 3 wt%, was determined by thermogravimetric analysis (TGA) through the weight loss of PS at 350–450 °C. The incorporation of higher content polymer was also tried, but there existed serious phase separation. The whole process for the synthesis of hybrid mesoporous PS-silica materials is shown in Scheme 1.



Scheme 1

Measurements

Morphologies of the porous materials were examined on a Hitachi H-9000NAR HREM transmission electron microscope (TEM) operated at an accelerating voltage of 300 kV. The samples for TEM measurement were prepared by dipping an ethanol suspension of the finely ground hybrid powders onto a Cu grid coated with a holey C film. The IR spectra of the samples before and after ethanol extraction were measured in the form of KBr powder-pressed pellets on a Bruker Vector22 IR spectrometer. The surface area, pore volume, pore diameter and pore size distribution were obtained from the nitrogen adsorption-desorption measurements examined on a Micromeritics ASAP2010 analyzer at 77 K. Before each measurement, the sample was degassed at 353 K overnight. Powder X-ray diffraction (XRD) pattern was recorded on a Rigaku DMAX2400 diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm, 40 kV, 100 mA) at the scan rates of 1 ($^\circ$)/min and 8 ($^\circ$)/min in the 2θ ranges of 0.6–10 $^\circ$ and 10–70 $^\circ$, respectively. ^1H -NMR spectra were recorded using a Bruker ARX400 (400 MHz) spectrometer in CDCl_3 at 298 K, in which tetramethylsilane (TMS) was used as an internal reference. Thermogravimetric analysis was performed on a SDT2960 Simultaneous TG-DTA at a heating rate of 10 K/min and 100 mL/min nitrogen flow.

RESULTS AND DISCUSSION

Synthesis of Triethoxysilyl-Functionalized Polystyrene

Recently some papers reported the ATRP of St and MMA, which were initiated by silica surface-modified with ATRP initiators, such as CTES^[21], 2-(4-chloromethylphenyl)ethyldimethylethoxysilane^[22] and 2-(4-

chlorosulfonylphenyl)ethyltrimethoxysilane^[23]. In this article, we used CTES as the initiator and CuCl/bipy as the catalyst to conduct ATRP of St at 120 °C, and triethoxysilyl-terminated PS was then synthesized. End group analysis of the resulting PS carried out by ¹H-NMR spectroscopy is shown in Fig. 1. The signal “a” at $\delta = 4.35$ is ascribed to the proton of the $-\text{CH}_2\text{C}(\text{Ph})\text{H}-\text{Cl}$ group. It reveals that the obtained PS is functionalized with an ω -Cl end group that shows the polymerization is processed according to ATRP mechanism. The signal “b” at $\delta = 3.93$ is assigned to the protons of the $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$ group. It shows that the resulting PS has a triethoxysilyl group on the other end, which can be used in the co-hydrolysis and co-condensation reactions with TEOS.

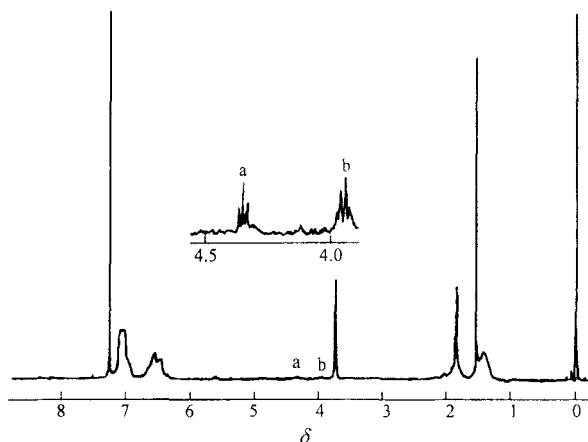


Fig. 1 ¹H-NMR spectrum of triethoxysilyl-terminated PS ($M_n = 23200$) obtained with CTES/CuCl/bipy initiating system

Synthesis of Hybrid Mesoporous PS-SiO₂ Materials

Hybrid mesoporous PS-SiO₂ materials have been synthesized via the sol-gel reaction of TEOS and triethoxysilyl-functionalized PS in the presence of CA as a non-surfactant template followed by removal of the template molecules with ethanol extraction. The complete removal was monitored by IR analysis. Figure 2 shows the IR spectra of the hybrid material, sample PS-3-50, before (a) and after (b) ethanol extraction. There is a strong absorption band at 1734 cm⁻¹ which is corresponding to the C=O stretching vibration of carboxylic group of CA molecules. However, this characteristic C=O absorption band disappears completely after solvent extraction, indicating the complete removal of the template molecules. The characteristic 698 cm⁻¹ absorption band corresponding to the C—H out-of-plane deformation vibration of monosubstituted benzenes and the 3000 cm⁻¹ absorption band corresponding to the C—H stretching vibration of benzenes of PS are not affected by extraction.

Characterization of Hybrid Mesoporous PS-SiO₂ Materials

The pore parameters of the hybrid materials after the removal of template molecules are summarized in Table 1. The obtained hybrid mesoporous materials have average pore sizes about 2–3 nm. And the samples prepared with 50 wt%–60 wt% template contents have large Brunauer-Emmett-Teller (BET) surface areas (*ca.* 886 m²/g) and Barrett-Joyner-Halenda (BJH) total pore volumes (*ca.* 0.53 cm³/g). Moreover, as the template content increases, the pore volume and pore diameter display a clear increase tendency.

The N₂ adsorption-desorption isotherms obtained at various relative pressures (P/P_0) are shown in Fig. 3. The samples prepared in the absence of CA or at low concentrations of CA (*e.g.*, PS-3-20) exhibit reversible type I isotherms, typical for microporous materials^[24]. At high CA concentrations (*e.g.*, PS-3-50), the samples are predominantly mesoporous materials evidenced by the type IV isotherms with H2 hysteresis loops. The BJH pore size distributions for samples at various CA concentrations are given in Figure 4.

Sample PS-3-50W was subjected to hydrothermal treatment by heating in boiling water for 6 h. Collapse of its framework happened, which led to the increase of pore diameter up to 5.98 nm. Sample PS-3-60H underwent thermal treatment at 200 °C higher than the glass transition temperature of PS (105 °C). Polymer chains have diffusive segmental motions or relaxations at temperatures above T_g , which lead to partial blockage of pores.

However, after heating this sample at 200°C overnight, its BET surface area, BJH total pore volume and pore diameter values showed little change. Compared with the greater changes in literature^[16], these changes are insignificant because the polymer precursor in this paper bears only one triethoxysilyl group at each polymer chain terminus, with the result that every chain is connected to the silica framework only by one end, so the motions of polymer chains can hardly have a great influence on the framework and the pores.

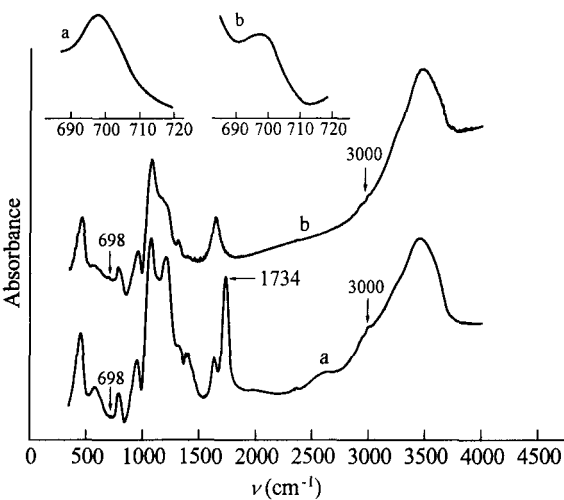


Fig. 2 IR spectra of hybrid material PS-3-50 before (a) and after (b) ethanol extraction
The two insets on the top is the magnifications of (a) and (b) between 680 and 720 cm⁻¹ respectively

Table 1. Sorption properties of the porous PS-silica materials after removal of CA by ethanol extraction

Sample code ^a	Template content (wt%) ^b	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter	
				BET ^c (nm)	BJH ^d (nm)
PS-3-0	0	15	0.0089	1.90	2.20
PS-3-20	20	470	0.23	1.95	3.14
PS-3-35	35	641	0.31	1.95	2.93
PS-3-50	50	886	0.46	2.09	2.66
PS-3-50W ^e	50	319	0.48	5.98	5.78
PS-3-60	60	878	0.53	2.41	2.90
PS-3-60H ^f	60	869	0.51	2.35	2.83

^a The first number “3” means that the content of polymer precursor PS is 3 wt% of the final product after the removal of template molecules. The second number is the template content (0 to 60 by weight) in the final dry composite gel.
^b Designed template concentration in the template-containing composite, calculated by the feed composition under the assumption that TEOS transformed into SiO₂ completely.
^c The average pore diameter is calculated from 4 *V*/*A*, where *V* is the total pore volume, and *A* is the BET surface area with the assumption that the materials contain regular cylindrical channels or pores.
^d The average pore diameter is calculated from the BJH absorption branch of the isotherm with the Halsey equation.
^e Sample was heated in boiling water for 6 h.
^f Sample was degassed at 200°C overnight.

Figure 5 exemplifies the XRD pattern of sample PS-3-50. There is a diffraction peak centered at 2θ value of 0.94°, which corresponds to a *d*-spacing of 9.39 nm calculated from the Bragg equation. Based on the worm-like pore structure, the *d*-spacing could be approximated as the repeated distance of the material. From the difference

between the repeated distance and the pore diameter (2.09 nm), it can be estimated^[25, 26] that this mesoporous material has a pore wall thickness of 7.30 nm. The broadness of the single peak and the absence of additional peaks at higher angles suggest that this material lacks long range ordering arrangements. There is a typical amorphous silica diffraction peak at a 2θ value of 23° that indicates the amorphous nature of the obtained hybrid PS-silica framework.

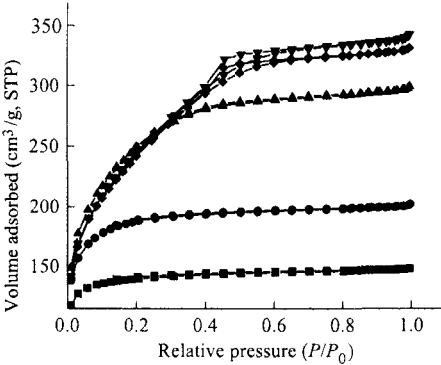


Fig. 3 N₂ adsorption-desorption isotherms for the afforded porous materials with various CA contents
■ PS-3-20; ● PS-3-35; ▲ PS-3-50;
▼ PS-3-60; ◆ PS-3-60H

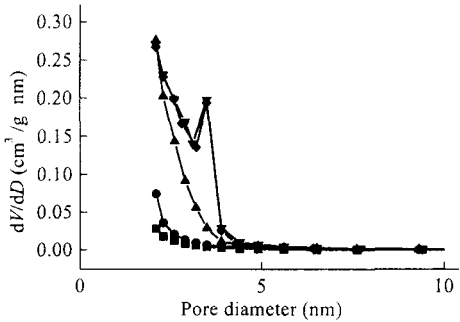


Fig. 4 BJH pore size distributions for the afforded porous materials with various CA contents
■ PS-3-20; ● PS-3-35; ▲ PS-3-50;
▼ PS-3-60; ◆ PS-3-60H

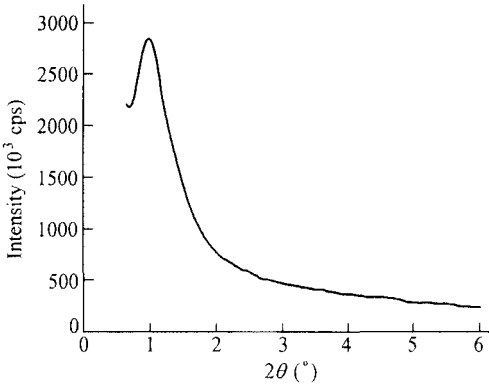


Fig. 5 Powder XRD pattern for hybrid mesoporous material PS-3-50

The mesoporosity of the hybrid materials is further established by the results of transmission electron microscopy (TEM). The TEM image of hybrid mesoporous material PS-3-50 is shown in Fig. 6. It is visible that there are numerous interconnected worm-like channels or pores, which are relatively regular in diameter but largely disordered in channel arrangements.

Figure 7 shows the TG curve of hybrid mesoporous material PS-3-50. The weight loss at the beginning is due to the elimination of ethanol and water. The lost weight (0.1286 mg, 3.04 wt%) from 350°C to 450°C is the PS content in hybrid material. This result agrees quite well with the polymer content we designed.

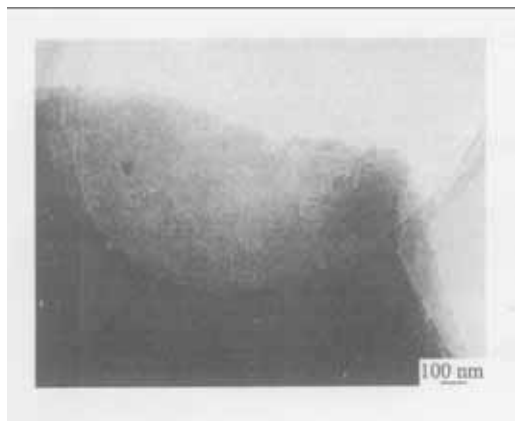


Fig. 6 TEM image for hybrid mesoporous material PS-3-50

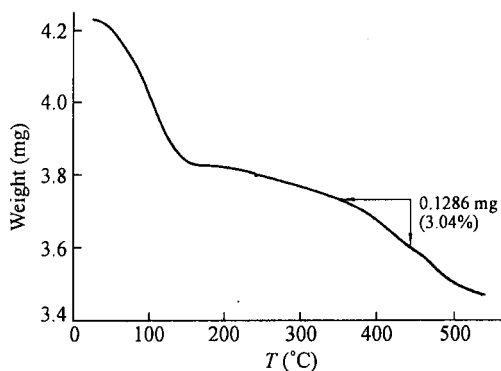


Fig. 7 TG curve of hybrid mesoporous material PS-3-50

CONCLUSIONS

We successfully present a new method to synthesize hybrid mesoporous polystyrene-silica materials with non-surfactant citric acid as template or pore-forming agent via HCl-catalyzed co-hydrolysis and co-condensation of TEOS and PS precursor bearing triethoxysilyl end groups at room temperature. ATRP is applied in the synthesis of PS precursor. The hybrid mesoporous materials prepared with high template contents exhibit type IV isotherms with H2 hysteresis loops, and they possess large surface areas (*ca.* 886 m²/g) and pore volumes (*ca.* 0.53 cm³/g). The average pore diameter and pore volume generally increase with template content. The XRD pattern and TEM image suggest that the hybrid mesoporous materials lack long-range ordering channel arrangements. The mesoporosity appears to arise from the interconnecting channels with diameters of 2–3 nm.

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