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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Molecular Design of the Amphiphilic AB Diblock Copolymer toward One-Step Synthesis of Amino-group Functionalized Large Pore Mesoporous Silica

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Amino group functionalized mesoporous silica with large pore size were obtained by one-step self-assembling of amphiphilic AB diblock copolymer containing hydrophobic poly (styrene) (PS) tail and hydrophilic poly (acrylic acid) (PAA) head, the co-structure directing agent (CSDA) and the silica source. The mesoporous silica possessed hexagonal arranged ordered channels with large pore size at ca. 27.5nm, and 3.1 mmol/g amino group loading amount.

Introduction

Ordered mesoporous materials with large functionalized pores have received increasing attention owing to their in accommodating the immobilization of large-size guests such as biomacromolecules and metal nanoparticles¹⁻⁴ for further applications including catalysis, adsorption, separation, sensor design and drug delivery⁵⁻⁸. The functionalization methods of porous materials, especially mesoporous silica can generally be divided into two ways: the subsequent modification of the pore surface with various organic groups (post grafting)⁹, and the simultaneous condensation of the silica source and organosilane by one-step process (co-condensation)¹⁰. Both of the two strategies are commonly used for the synthesis of functional porous materials.

The synthesis of anionic surfactant templated mesoporous silica (AMS) materials¹¹ is one of the typical examples of the extremely convenient and highly efficient one-step process. Meanwhile, the electronic interaction between the anionic surfactant and the protonated co-structure directing agent (CSDA) can also result uniform distribution of the functional organic groups. However, most of these organically functionalized

mesoporous silicas only possess with small pore size ranging from 2.2 to 9.2 nm¹². The preparation of functionalized large-pore mesoporous material through CSDA route is still a big challenge.

Herein, we report a one-step synthesis of amino-group functionalized ordered mesoporous silica with large pores by using the co-structure directing¹³ route through the self-assembly of amphiphilic block copolymer template, CSDA and silica source in a mixture solvent. As well known, the pore size of mesoporous materials is mainly determined by the hydrophobic volume of the template molecules. Therefore the amphiphilic block copolymers with various long hydrophobic chains and hydrophilic poly (ethylene oxide) (PEO) block are usually applied as the templates to fabricate ordered mesoporous materials with large pores¹⁴⁻¹⁹. In order to meet the requirements of the CSDA route, a negatively charged hydrophilic block poly (acrylic acid) is designed here to connect with long hydrophobic polystyrene block (i.e. PS-*b*-PAA) as the template in this work. PAA block can interact with the CSDA 3-aminopropyltrimethoxysilane (APS) to functionalize the silica wall while the formation of mesoporous silica in one step; and PS can form ordered large pores through the phase separation with PAA and silica source in the mixed solvents.

Cite this: DOI: 10.1039/c0xx00000x

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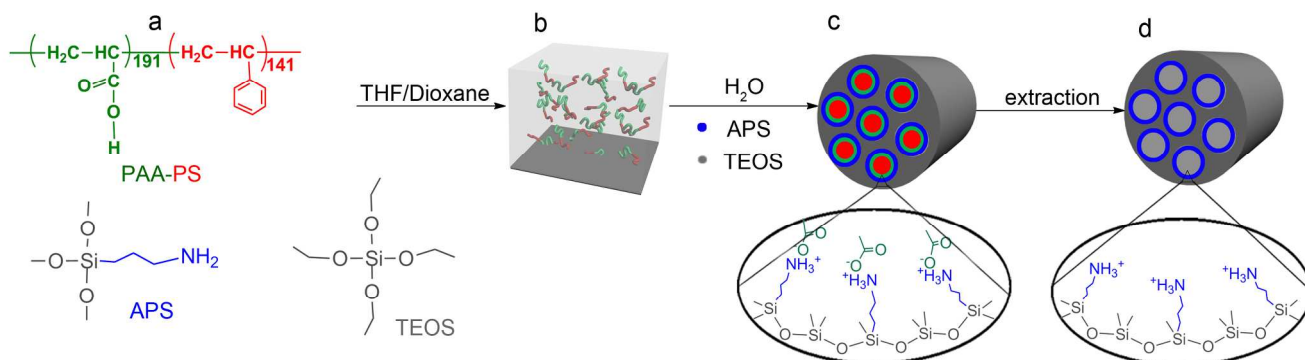


Fig. 1 Schematic illustration of the formation of amino groups modified on the pore surfaces via electrostatic interaction between the carboxylic groups of the PS-PAA and the amino groups of APSs.

5 Experimental

Chemicals

Ethyl 2-bromoisobutyrate (98%, TCI), Tetraethylorthosilicate (TEOS, 98%, TCI), 3-aminopropyltrimethoxysilane (APS, 98 % TCI), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%, TCI), copper bromide (CuBr, 97%, Sinopharm Chemical Reagent Co., Ltd), diethyl ether anhydrous (99%, Sinopharm Chemical Reagent Co., Ltd), hydrochloric acid (HCl, 36%, Sinopharm Chemical Reagent Co., Ltd), methanol (99%, Sinopharm Chemical Reagent Co., Ltd), petroleum ether (60-90, Sinopharm Chemical Reagent Co., Ltd), tetrahydrofuran (THF, 99%, Sinopharm Chemical Reagent Co., Ltd) and deionized water (Milli-Q, 18.2 MΩ·cm) were used as obtained without further purification. The polymerization inhibitor in tert-butyl acrylate (*t*BA) (97%, TCI) was removed by alkaline alumina column. The polymerization inhibitor in styrene (99%, Sinopharm Chemical Reagent Co., Ltd), was removed by 20% sodium hydroxide solutions, and dried with anhydrous magnesium sulfate, and then finally distilled under reduced pressure before using.

Synthesis of PS₁₄₁-Br

PS-Br was synthesized by the atom transfer radical polymerization (ATRP) of styrene at 110 °C using ethyl 2-bromoisobutyrate as the initiator, CuBr/PMDETA as the catalyst system. A 250 mL Schlenk flask containing 0.195 g (1 mmol) ethyl 2-bromoisobutyrate, 0.625 mL PMDETA (3 mmol) and 50.0 g styrene (0.288 mol) was purged thoroughly and then sealed with a rubber stopper. After the solution became clear with stirring, 0.144 g CuBr (1 mmol) was added into the solution. The bottle containing reactants was fully degassed with more than three freeze-pump-thaw cycles and sealed under vacuum. Then the flask was placed in an oil bath at 110 °C to allow the polymerization to take place. Eight hours later, the reaction mixture was cooled to room temperature and the polymerization was terminated by exposing the reaction mixture to air. The catalyst was removed by filtration through neutral alumina using methylene chloride as the eluent. The polymer was obtained by the precipitation of condensed organic phase in cold methanol

(500 mL). After being dried under vacuum, the polymer was characterized by GPC (gel permeation chromatography) and then used for the next step polymerization. The $M_{n, GPC}$ of PS-Br was about 1.48×10^4 g/mol with the PDI 1.13. The polymerization degree was 141 and the polymer was labeled as PS₁₄₁-Br. ¹H NMR (CDCl₃): δ(ppm): 1.30-1.55 (-CH₂CH(Ph)-), 1.70-1.90 (-CH₂CH(Ph)-), 6.30-6.70 and 6.90-7.20 (-C₆H₅).

Synthesis of PS₁₄₁-*b*-PAA₁₉₁

A 250 mL Schlenk flask containing 6 g PS₁₄₁-Br (0.4 mmol), 0.253 mL PMDETA (1.2 mmol), 30 mL DMF and 50.0 mL *t*BA was purged thoroughly and then sealed with a rubber stopper. After the solution becomes clear with stirring, 0.058 g CuBr (0.4 mmol) was added into the solution. Followed with three freeze-pump-thaw cycles and sealed under vacuum, the flask was placed in an oil bath at 70 °C with stirring for 18 hours. The mixture was cooled to room temperature and the catalyst was removed according to the synthesis of PS₁₄₁-Br. The copolymer was finally obtained by precipitation using cold ether (500 mL). After being dried under vacuum, the copolymer was characterized by GPC. The $M_{n, GPC}$ of the copolymer was about 3.93×10^4 g/mol with PDI 1.38, and the number of corresponding *t*BA segments was calculated as 191. (i.e. PS₁₄₁-*b*-*t*BA₁₉₁). ¹H NMR (CDCl₃): δ (ppm): 1.30-1.65 (-CH₂CH(Ph)- and -CH₂CH(CO)-), 1.35-1.50 ((CH₃)₃C-), 1.70-1.90 (-CH₂CH(Ph)-), 2.10-2.25 (CH₂CH(CO)-), 6.30-6.70 and 6.90-7.20 (-C₆H₅).

10 g of PS₁₄₁-*b*-*t*BA₁₉₁ and 10 mL trifluoroacetic acid (TFA) were dissolved in 50 mL of CH₂Cl₂ and stirred at room temperature for 36 h to prepare PS₁₄₁-*b*-PAA₁₉₁. The polymer was obtained by precipitation using cold ether (500 mL), and the pale gray residue was dried under vacuum for 24 h.

Synthesis of silica with *p6mm* structure

0.05 g of PS₁₄₁-PAA₁₉₁ was dissolved in a solvent mixture (4.0 g THF and 0.5 g dioxane). 1.0 g of water was added into the solution, and then stirred for about 0.5 h before 0.12 g of APS and 0.695 g TEOS were finally added. The final molar ratio was 1-COOH: 2APS: 10TEOS. The solution was kept stirring for another 2 h, and then allowed to be aged for 2 days. All the reactions were taken under ambient condition. The silica/template

composites were washed three times with water, and finally dried by lyophilization.

Extraction of the template

The diblock copolymer template was extracted three times in 200 mL THF solution with 20 mL of 2M HCl under reflux for 12 h. Then the samples were washed three times by deionized water, and finally dried under vacuum.

Characterization

The morphologies of the samples were observed with scanning electron microscopy (SEM, JEOL JSM-7401F) at 1.0 kV. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2100 microscope operated at 200 kV. The N_2 adsorption-desorption isotherm were obtained at 77 K on a Quadrasorb SI automated surface area and pore size analyzer. The pore-size distribution curves were calculated by the Barrett-Joyner-Halenda (BJH) method by using the adsorption branch of the isotherm. 1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian MERCURY plus-400 (400 MHz) spectrometer, and the chemical shifts are reported in ppm relative to the residual deuterated solvent and the internal standard tetramethylsilane. Small-angle X-ray scattering (SAXS) measurements were taken on a small-angle X-ray scattering station (BL16B1) with a long-slit collimation system in the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China, in which the third generation of synchrotron radiation light sources was employed. The experiments were carried out with the radiation of X-ray with the wavelength of $\lambda = 1.24 \text{ \AA}$ at room temperature (25 °C). Solid-state ^{13}C MAS NMR spectra of the large-pore mesoporous silica materials were collected on a Varian Mercury plus-400 NMR spectrometer at 100 MHz and a sample spinning frequency of 3 kHz. The elemental analysis of the materials was obtained from a Perkin-Elmer Series II CHNS/O Analyzer 2400.

Results and discussion

The total molar mass of the $PS_{141}\text{-}b\text{-}PAA_{191}$ is calculated as $2.86 \times 10^4 \text{ g/mol}$, and the volume fractions are of 55.3 % and 44.7 % for the PS and PAA block, respectively under the assumption that the tertbutoxy has been totally removed by TFA. Tetrahydrofuran (THF), dioxane and water were respectively used as the common and the selective solvents. As the self-assembly of the amphiphilic block-copolymers partly depends on solvents, the dielectric constant of the solvents should be considered for the aggregation behavior of the charged block, e.g. PAA²⁰. The electrostatic repulsion among the PAA chains is strongest in dimethyl formamide (DMF) and weakest in dioxane because the dielectric constant (ϵ) of the common solvents is decreased in the order of $DMF > THF > dioxane$, thus the curvature of the self-assembling structure of PS-*b*-PAA would be decreased in this order²⁰.

The $PS_{141}\text{-}b\text{-}PAA_{191}$ is highly soluble in THF and dioxane mixed solvents (Figure 1b). When the selective solvent water is added, microphase separation occurs. The common solvents (i.e. THF and dioxane) are mainly present in the hydrophobic PS aggregates regions to form large cavities, whereas water is driven out of the hydrophobic segments and mainly presented in the hydrophilic PAA region, which can give rise the microphase separation with the hydrophobic part (PS) in the core and the

hydrophilic part (PAA) in the shell (Figure 1c, with the two-dimensional hexagonal structure). Simultaneously, in the hydrophilic part, with the addition of 3-aminopropyltrimethoxysilane (APS) and tetraethylorthosilicate (TEOS), PAA and APS interact through the neutralization of the carboxylic acids ($pK_a=4.8$) of PAA and the amino group of APS ($pK_b \approx 3.4$), and couple electrostatically with each other. The alkoxy silane sites of APS are co-condensed with TEOS subsequently to form the silica framework. The trimethylene groups of the APS covalently tether the silicon atoms incorporated into the framework to the cationic ammonium groups (Figure 1c). After $PS_{141}\text{-}b\text{-}PAA_{191}$ was extracted by ion exchange, the large-pore-mesoporous silica with amino groups on the pore surface was finally obtained (Figure 1d). The interaction between PAA and APS produces a uniform distribution of amino groups, and a regular array of the amino groups will be formed on the surface of the mesopores following the arrangement of the

$PS_{141}\text{-}b\text{-}PAA_{191}$. Figure 2a represents small-angle X-ray scattering (SAXS) pattern of the extracted samples templated by $PS_{141}\text{-}b\text{-}PAA_{191}$ at room temperature. The two well-resolved peaks at q values of 0.15 and 0.26 nm^{-1} are indexed as the 10 and 11 reflections of hexagonal $p6mm$ (which is also confirmed by TEM later, vide post) respectively, indicating that the sample has a highly ordered hexagonal mesoscopic structure with the unit cell parameter of 49.7 nm. Nitrogen adsorption-desorption isotherms (Figure 2b) of the extracted sample show typical type IV isotherms with a sharp capillary condensation and hysteresis step in the relative pressure range of 0.75-0.98, which confirms the existence of uniform pores. The H1 hysteresis loop of the isotherms shows that the cylindrical pore system exists in the extracted sample. The Brunauer-Emmett-Teller (BET) specific surface area and the total pore volume of the sample are $54.9 \text{ m}^2\text{g}^{-1}$ and $0.25 \text{ cm}^3\text{g}^{-1}$, respectively. The pore size distribution (Figure 2c) calculated by the Barrett-Joyner-Halenda (BJH) method based on the adsorption branch of the isotherm reveals the mesopore size is 27.5 nm. The thickness of the pore wall is estimated to be 22.2 nm.

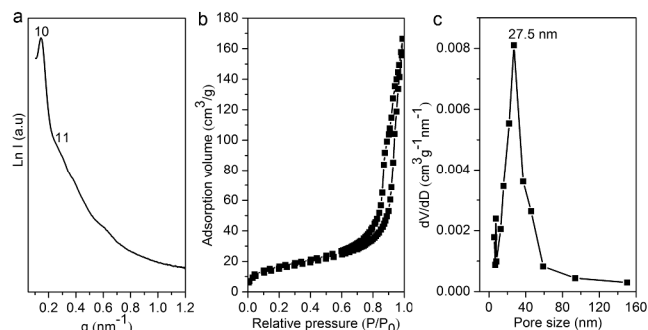


Fig. 2 SAXS pattern (a), N_2 adsorption-desorption isotherm (b) and pore size distribution (c) of the sample synthesized by $PS_{141}\text{-}PAA_{191}$. The synthesis molar compositions is: -COOH: 2APS: 10TEOS.

As shown in Figure 3a and 3b, SEM images show that the extracted mesoporous silica possess highly ordered hexagonal arrangement with two crystal faces (10 and 11) within a rather large domain, and obviously large pores. TEM images (Figure 3c and 3d) and fast fourier transformation (FFT) pattern (Figure 3c, inset) prove the existence of ordered two-dimensional hexagonal

p6mm mesostructure directly. The lack of long range order probably because of the fast interaction between PS-PAA and APS, which leads to the formation of the ordered structure in small domains and causes abundant defects in large area aggregation. The unit cell parameter calculated from the TEM image is about 50.8 nm, which is in correspondence with the result from SAXS pattern.

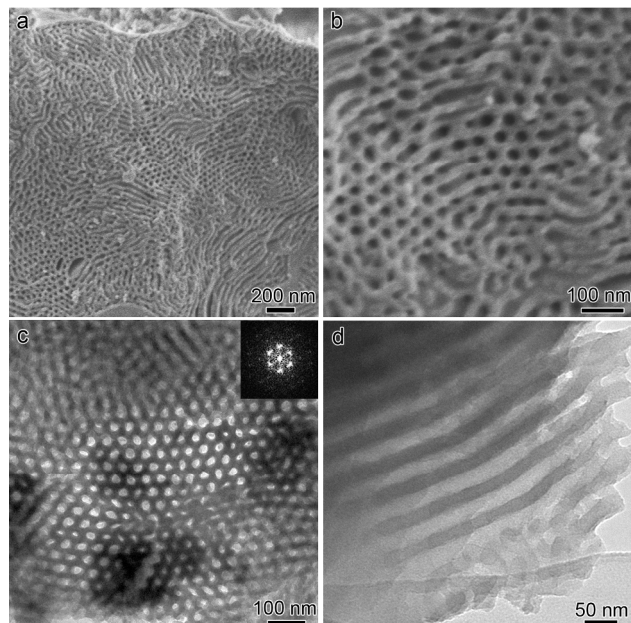


Fig. 3 SEM (a and b) and TEM images (c and d) of the sample shown in Fig. 2.

The removal of the block copolymer PS₁₄₁-b-PAA₁₉₁ and the remaining of the amino groups after the extraction are confirmed by the solid-state ¹³C NMR spectra of the large-pore silica (Figure 4). The NMR spectrum of the as-synthesized silica shows the signals both of the copolymer and the CSDA (APS). The chemical shift of the carboxyl groups (h) of PAA is at 183.3 ppm. The benzene ring carbon (d) which connect with the main chain is at 146.0 ppm, and the other carbons (e and f) of the benzene ring are at 126.3 ppm. The carbon (a) connect with benzene ring, carbon (g) connect with carboxyl groups, and carbon (C3) connect with amino group of the CSDA are at 42.4 ppm. The methylene carbons (b) of the main chain of PS and PAA (i) are at 28.2 ppm. The carbon (C2) of CSDA is at 22.2 ppm. The carbon (C1) of CSDA connect with silicon is at 10.3 ppm. The NMR spectrum of the extracted silica shows only three resonance signals at 9.6, 21.3 and 42.3 ppm that could be assigned to carbons (C1, C2 and C3) of the CSDA, respectively. These results demonstrated that the diblock copolymer was almost removed and the amino functional groups were retained on the surface of the large pores after the extraction.

The elemental analysis show that the samples are functionalized by amino groups with high loading amount of 3.1 mmol/g. The theoretical loading amount of the amino groups calculated from synthesis composition is 2.5 mmol/g. The higher actual loading amount is probably because the hydrolytic condensation conversion of TEOS is lower than APS. The strong interaction between PAA and APS would lead to high amount of

APS enter into the self-assembly system and converse to silica. With assuming that all the amino groups are on the pore surface, it has been calculated from the results of elemental analysis and surface area calculation that the amino group loading is ca. 34 molecules per nm², indicating that the large amount of amino groups were incorporated within the silica walls.

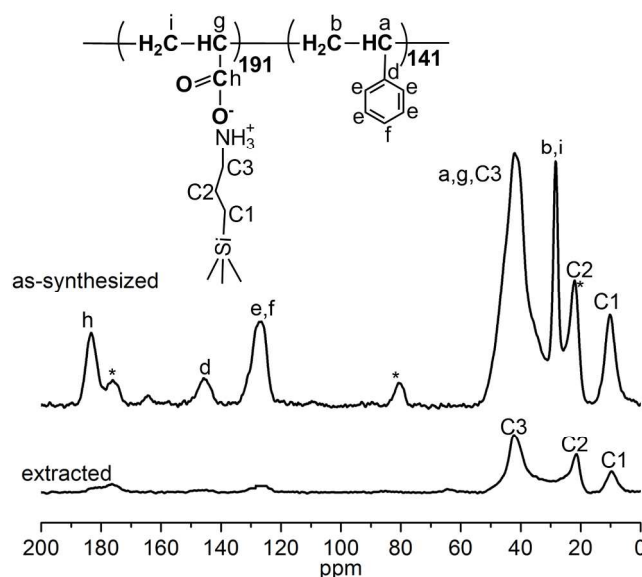


Fig. 4 Solid ¹³C NMR images of the extracted samples synthesized by PS₁₄₁ PAA₁₉₁. *Due to the productivity of the deprotection reaction, there are still some tertbutoxy groups on PAA block. (Supplementary Information Figure S3)

Conclusions

To the best of our knowledge, this is the first report on the synthesis of amino-group functionalized large-pore mesoporous silica by the self-assembly of amphiphilic AB diblock copolymer. The amphiphilic AB diblock copolymer PS₁₄₁-b-PAA₁₉₁ forms core-shell micelle through microphase separation when water is added into the mixed solution. The hydrophilic part PAA in the shell interacts electrostatically with APS, and the alkoxy silane sites of APS co-condense with TEOS to form the silica framework. The large pore mesoporous silica with amino groups loaded on the pore surface are finally obtained after the extraction of the PS₁₄₁-b-PAA₁₉₁.

This work was supported by the 973 project (2013CB934101), the National Natural Science Foundation (21201120, 21101106) of China, the Youth Natural Science Foundation of Shanghai (12ZR1445100) and Evonik industries. The authors thank the Shanghai Synchrotron Radiation Facility for the SAXS experiment at line 16B.

Notes and references

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