Periodic mesoporous silicas via templating of new triblock amphiphilic copolymers

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Abstract

By using atom transfer radical polymerization method, triblock copolymers $[(MA)_x(EO)_{77}(MA)_x]$ (MA = methyl acrylate) with the hydrophilic chain (PEO) in the center part of the polymers were prepared in a narrow molecular weight distribution. Thus the hydrophilic–hydrophobic portion of the copolymer can be fine-tuned, which provides the use of these polymers as structure directing agents to synthesize highly ordered hexagonal mesoporous silicas. Under acidic conditions, polymers of $[(MA)_x(EO)_{77}(MA)_x]$ ($x = 33–70$) provided the synthesis of a 2D hexagonal array of mesopores in uniform orderliness.

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1. Introduction

During the past decade, syntheses of periodic mesoporous silica have received much of attention from both fundamental and application points of view [1]. Although the process of self-assembly of surfactant silicate leading to porous materials is quite complicated, both structure of surfactants and reaction conditions are two major factors to influence the mesostructure and morphologies of silicas. Recently, a large variety of block copolymers were used as mesostructural directing agents in preparation of SBA materials [2]. In this context, versatile in these syntheses are the triblock copolymers Pluronics ($EO_m-PO_n-EO_m$) [3,4], few other triblock copolymers are known for this purpose [5].

In general, these triblock copolymers have a central polypropylene block surrounded by polyethylene blocks $((EO)_x-(PO)_y-(EO)_x)$, i.e. the hydrophilicity at both ends

of the polymer. For silica structures prepared via these templates under acidic conditions, water depletion within the corona–core interface was observed during the mesophase assembly, and believed that the PEO chains are embedded in micropore [6]. However, the use of a triblock copolymer with hydrophilic part in the center of polymer has never been investigated. Herein we report on the preparation of triblock copolymer $[(MA)_x(EO)_y(MA)_x]$ and the use of these polymers as structure directing agents to synthesize highly ordered hexagonal mesoporous silicas (denoted as NTU- x).

2. Experimental section

2.1. General

All reaction steps for polymerization were performed under a dry nitrogen atmosphere. Dichloromethane was dried with CaH_2 and distilled under nitrogen. Poly(ethylene glycol) methyl ethers $[H(OCH_2CH_2)_nOH]$ with molecular weight 3400 were obtained from Acrôs and used without further purification. Tris(2-dimethylaminoethyl)amine

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Table 1
Results of the polymerization of methyl acrylate with macro-initiator A^a

Entry	Initiator A (mmol)	Monomer (mmol)	CuBr (mmol)	Ligand ^b (mmol)	<i>t</i> (min)	<i>M_n</i> /PDI ^c	Ratio ^d MA:EO:MA
B1	1.09	57.8	0.22	0.22	40	7800/1.16	21:77:21
B2	0.82	77.9	0.33	0.33	8	9500/1.23	33:77:33
B3	0.82	24.5	0.49	0.49	120	11,000/1.25	39:77:39
B4	0.82	98.4	0.49	0.49	120	16,400/1.20	70:77:70
B5	0.54	108.0	0.54	0.54	60	22,400/1.27	108:77:108

^a Reaction temperature 30 °C.

^b Tris(2-dimethylaminoethyl)amine (Me₆TREN).

^c Determined by GPC; PDI = *M_w*/*M_n*.

^d Calculated ratio.

(Me₆TREN) was prepared according to the method reported [7]. Tetraethoxysilane (TEOS), other chemicals and solvents were of analytical grade and were used as received.

Nuclear magnetic resonance spectra were recorded in CDCl₃ on either a Bruker AC-E 200 or AM-300 spectrometer. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets. Gel permeation chromatography (GPC) data were obtained from a Waters Model 590 liquid chromatograph installed with a Lab Alliance RI 2000 detector using THF as eluant (at the rate 1 ml/min) at 40 °C and polystyrene calibration curve for analyses.

2.2. Preparation of triblock copolymers

2.2.1. Macro-initiator A

To a 250 ml round bottom flask was placed with poly(ethylene glycol) [MW = 3400, 40.0 g, 11.8 mmol]. The flask was degassed and re-filled with dry nitrogen gas. Anhydrous dichloromethane (70 ml) and triethylamine (4.9 ml, 35.4 mmol) was added, and the mixture was then cooled to ice-bath temperature. 2-Bromo-2-methylpropionyl bromide (4.4 ml, 35.4 mmol) was added dropwise to the flask. After stirring for 24 h, the reaction mixture was filtered to remove the ammonium salt. The filtrate was concentrated and re-dissolved in a small amount of THF. The desired product was precipitated out from the solution by addition of ice-cooled ether. The white solid was obtained (34.0 g, 79%) by filtration. IR(CH₂Cl₂) 1729 cm⁻¹; ¹H NMR δ 3.70–3.60 (br, –COOCH₃), 3.62 (s, –OCH₂CH₂–), 2.40–2.10 (br, –CH), 2.00–1.30 (br, –CH₂–), 1.14 (s, –C(CH₃)₂). Anal. Calcd. for C₁₆₉H₃₃₄Br₂O₈₀: C, 53.33; H, 8.84. Found: C, 53.01; H, 8.48.

2.2.2. Preparation of triblock copolymers (B1–B5)

A mixture of macro-initiator A (3.0 g, 0.82 mmol), CuBr (46.8 mg, 0.33 mmol) in 50 ml flask was capped with septum and was degassed. Methyl acrylate (7.0 ml, 77.9 mmol) was syringed into the flask under nitrogen atmosphere. The flask was immersed into water-bath at 30 °C. [(Me₂NCH₂CH₂)₃N] (93 μl, 0.33 mmol) was then added. After stirring at 30 °C for 8 min, the reaction mixture was diluted with THF. The reaction mixture was filtered

through silica gel to remove the catalyst. Upon concentration and re-precipitation in ether/methanol, the obtained copolymer was dried under vacuum overnight. The desired copolymer was obtained in a white solid form (6.6 g, 80%): ¹H NMR δ 3.70–3.60 (br, –COOCH₃), 3.62 (s, –CH₂CH₂–), 2.40–2.10 (br, –CH), 2.00–1.30 (br, –CH₂–), 1.14 (s, –C(CH₃)₂). Other chain length of MA was prepared by the same manner but with various amount of monomers (Table 1).

2.3. Synthesis of mesoporous silicas

The MA_{*n*}EO₇₇MA_{*n*}-silica mesostructural composites were synthesized in acidic media as that for SBA-15 silicas [3]. The as-synthesized mesoporous silica products were obtained after 1 day agitation at 20 °C. The final gel composition (in gram) is: (0.5 g) MA_{*x*}EO₇₇MA_{*x*}: (25.0 g) H₂O: (5 g) *n*-PrOH: (4.0 g) 37% HCl: (1.5 g) TEOS. The dried acid-made mesoporous silicas (1.0 g) in 50.0 g water (pH ≈ 7.0) was hydrothermally treated at 100 °C for 24 h to increase its structural stability. Calcination of the sample was carried at 560 °C in air for 6 h.

2.4. Characterization of the mesoporous silicas

The powder X-ray diffraction patterns (XRD) were taken on Wiggler-A beamline (λ = 0.1326 nm) of Taiwan National Synchrotron Radiation Research Center, Hsin-Chu, Taiwan. The TEM mesostructural images of mesoporous silicas were recorded on Hitachi S-7100 transmission electron microscope (TEM) with an operating voltage of 75 keV. The N₂ adsorption-desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus, and the pore size distribution was calculated from the adsorption isotherms using the Barrett-Joyner-Halenda (BJH) method.

3. Results and discussion

3.1. Synthesis of triblock copolymers and mesoporous silicas

Starting with the polyethylene oxide H(OCH₂CH₂)₇₇OH, the macro-initiator A was obtained by the esterification with 2-bromoisobutyryl chloride (Scheme 1),

Scheme 1. Preparation of triblock copolymers.

which was then subjected to connect the poly(methyl acrylate) chain (hydrophobic part) by atom transfer radical polymerization (ATRP) method [8,9]. By the manipulation of the reaction conditions, polymerization of MA readily took place on the macro-initiator with the desired chain length **B1–B4**. Typically, reaction of macro-initiator (0.33 mmol) and methyl acrylate [MA] (78 mmol) at 30 °C for 8 min resulted in the formation of the desired $\text{MA}_{33}\text{EO}_{77}\text{MA}_{33}$ (**B2**) in $M_N = 9500$ (PDI = 1.23) (Table 1).

The silica mesostructural composites via $[(\text{MA})_x(\text{EO})_{77}(\text{MA})_x]$ templates were synthesized in acidic media as that for SBA-15 silicas [3]. Copolymer and HCl were dissolved in water and propyl alcohol with stirring. The silica mesostructural composites were synthesized in acidic media. The as-synthesized mesoporous silica products were obtained after 1 day agitation at 20 °C and then hydrothermally treated at 100 °C for 24 h. The organic templates were removed by a calcination at 560 °C in air for 6 h. The obtained silicas by various copolymers **B1–B4** are abbreviated as NTU-11–NTU-14, respectively.

3.2. Characterization of mesoporous silicas

All the samples obtained were analyzed by powder X-ray diffraction (XRD), TEM and N_2 adsorption–desorption. Fig. 1(II) shows the XRD patterns of the calcined mesoporous silica NTU-12. It is easily find the representative (100), (110) and (200) peaks indicating of the 2D hexagonal mesostructure. The dimension of the unit cell (a_0) is 10.9 nm. To further confirm its mesostructure, The micro-tome TEM images of the sample taken along different axes, [100] and [110], were examined (Fig. 2a and b), which is consistent with the XRD result. The highly ordered arrangement of mesopores could be observed over the entire particle in all cases, indicating the highly mesostructural orderliness of the sample.

N_2 adsorption–desorption isotherm for the calcined mesoporous silica is shown in Fig. 3. A sharp inflection at $P/P_0 \sim 0.7$ is attributed to the capillary condensation within uniform nanochannels, whereas the existence of a hysteresis loop at P/P_0 of 0.7–0.75 is ascribed to the capillary condensation on large pore size. The pore size estimated by Barrett–Joyner–Halenda method is 9.8 nm,

Fig. 1. XRD pattern of as-synthesized (NTU-11–14) from templates **B1**-(I), **B2**-(II), **B3**-(III) and **B4**-(IV), respectively. Fig. 2. TEM images of calcined silica synthesized from **B2**-TEOS- H_2O -PrOH-HCl (a) along [100] and (b) along [110].

which is in good agreement with value determined from the TEM measurement. The pore volume of NTU-12 is fairly high at $0.90 \text{ cm}^3/\text{g}$, and BET surface area is about $500 \text{ m}^2/\text{g}$. A relative thicker wall (2.7 nm) for NTU-12 sample is observed. From the isotherm study, the β plot yields the non-zero value with the value less than $0.02 \text{ cm}^3/\text{g}$. Such a small value indicates that the microporosity in NTU-12 is significant as compared to SBA-15 obtained from P123 templating (Table 2) [10].

Other physical properties of NTU- x samples are summarized in Table 2. Notable is pore size increasing with the chain length of MA unit. In case of $\text{MA}_{70}\text{EO}_{77}\text{MA}_{70}$, the pore size reaches to 19.6 nm. From the XRD analysis, the calcined NTU-11 sample is adopted into an irregular morphology, whereas NTU-13 and NTU-14 samples are in a 2D hexagonal array of mesopores. This outcome might be due to the lower MA/EO ratio of **B1** copolymer, which destabilizes the core consisting of hydrophobic block during the self-organization in aqueous solution. The thickness of wall for NTU-12 and NTU-13 are 2.7 and 1.9 nm, respectively, but is quite thin for NTU-14. For the longer hydrophobic chain of copolymer **B5**, it

Fig. 3. N₂ adsorption-desorption BET isotherm plot for the calcined silica prepared from templates **B1**-(I), **B2**-(II), **B3**-(III) and **B4**-(IV), respectively.

became insoluble in the aqueous system as described for **B1**–**B4**. The shrinkage degree of SBA-15 was about 13% [12], while NTU-*x* (*x* = 11–14) showed a slightly lower shrinkage (ranging 8–11%) upon calcination. One factor might be caused by a partial condensation of the silica wall during the hydrothermal treatment. Another factor might be due to the less effect on the temperature dependent structural rearrangement in our system. Consequently, the fur-

ther condensation during the calcination contributed less than that of SBA-15 and gave a lower degree of shrinkage.

The solid-state one-pulse ²⁹Si MAS NMR spectrum of the as-synthesized NTU-*x* (*x* = 11–14) showed two broad peaks at 99 and 109 ppm corresponding to Q³ and Q⁴ silica species, respectively. These data are similar to those of the reported samples [4c]. Like that of SBA-15, the broad signals of these samples are also consistent with a locally disordered silica framework. For these hydrothermally treated materials of as-synthesized NTU-11–14, the ratio Q³/Q⁴ are about 1.10, 0.84, 0.79 and 0.64, respectively, indicating an incomplete silica condensation. The values appeared to be higher in NTU11-12 and a slightly lower in NTU13-14 than that of SBA-15 prepared at 35 °C [4c]. This may be caused possibly by the loop formation of triblock copolymers (MA)_{*x*}(EO)_{*y*}(MA)_{*x*} in the inorganic-organic composite.

3.3. Discussion

There have been many studies on the mesophase formation of the triblock **ABA** type copolymers in aqueous solution where **A** is the hydrophilic block and **B** is the hydrophobic block. In contrast, there is very few reports on the self-assembly of the reverse **BAB** type copolymers [11]. There is no report on mesoporous silica templated by **BAB** type amphiphiles. Besides difficulties in synthesis of the copolymer, there is thermodynamic reason against the formation of mesostructures in **BAB** type copolymers. For the hydrophilic **A** block in **BAB**, there are three possible configurations in mesophase formation: loop (Fig. 4A),

Fig. 4. Schematic picture of the organization of silicates with (A) NTU-*x* in loop, (B) NTU-*x* in bridging, (C) NTU-*x* in dangling form, and (D) P123.

Table 2
Physical properties of porous silicas prepared via MA_{*x*}EO₇₇MA_{*x*} templates

Sample	Copolymer	<i>d</i> (Å) ^a	Pore size (Å)	Pore vol. (cm ³ /g)	Surface area (m ² /g)	Micropore vol. (cm ³ /g)	Wall thickness (Å)	(Q ³ /Q ⁴) ^c
NTU-11	MA ₂₁ EO ₇₇ MA ₂₁	106 [119]	73	0.86	740	0.05	—	1.08
NTU-12	MA ₃₃ EO ₇₇ MA ₃₃	109 [123]	98	0.90	500	0.02	27	0.84
NTU-13	MA ₃₉ EO ₇₇ MA ₃₉	141 [153]	144	1.13	510	0.05	19	0.79
NTU-14	MA ₇₀ EO ₇₇ MA ₇₀	165 [173]	196	0.82	330	0.03	—	0.64
SBA-15 ^b	EO ₂₀ PO ₇₀ EO ₂₀	104 [105]	89	1.17	850	not detectable	31	—

^a *d*-Value of characteristic reflection is measured with the sample after calcinations at 560 °C for 6 h; numbers given in brackets are values of as-synthesized materials (after hydrothermal treatment).

^b Refs. [4c,10].

^c Q³/Q⁴ determined by ²⁹Si NMR.

bridge (Fig. 4B) and dangling (Fig. 4C). Dangling of the portion **A** would lead to the portion of **B** highly exposed to the hydrophilic silicates through the electrostatic interaction, which is energetically unfavorable (Fig. 4C). Bridging configuration (Fig. 4B) would lead to either a non-uniform distribution of the micellar size or to the uninteresting lamellar phase (structure collapse after calcination). Loop formation (Fig. 4A), necessary for micelle formation, has its entropic penalty. Thus one expects templating well-ordered mesoporous silica would be difficult. However, this study illustrates that the uniform mesoporous silica can be achieved by using the triblock copolymers [(MA)_x(EO)_y-(MA)_x] templates. The hydrophobicity of poly(methyl acrylate) was reflected on the pore size of the silica. Thus the longer of the chain length on (MA)_x provides the larger of the pore.

It is known that the PEO chains are hydrophilic whereas the poly(propylene oxide) (PPO) chains are hydrophobic in Pluronic copolymers. Such copolymers would assemble each other to form the cylindrical micelles with the PEO chains on the outside (Fig. 4D). Consequently, the PEO chains of the Pluronics may be deeply included within the silica walls and give the micropore upon calcination [11]. Unlike the Pluronics, the PEO blocks appear in the center part of the designed copolymers (NTU-*x*), which form a loop shape outside the hydrophobic core (Fig. 4A). This kind of arrangement should decrease the freedom of the PEO, which is also elucidated the formation of micropores along the mesopores in these materials. It is noticed that these micropores remain even after the hydrothermal treatment, unlike the Pluronic copolymers, i.e. the microporosity resulting from PEO–PPO–PEO trends to shrink upon the hydrothermal treatment.

4. Conclusion

In summary, uniform large-pore mesoporous silicas have been synthesized by non-ionic triblock copolymer surfactants with the hydrophilic groups at the center part of chain. These uniform large mesopores may have potential use as templates for the generation of 3 D nanoobjects or supporting for ligands in catalysis.

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Appendix A. Supplementary data

TEM images of calcined silica synthesized from NTU-3 and NTU-4 along [100] and [110] (1 page) is available from authors. Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.micromeso.2005.11.034.

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