Using well-defined EO_nMA_m diblock amphiphilic copolymers as templates for synthesis of mesoporous silicas with different mesostructures

Yi-Tsu Chan^a, Hong-Ping Lin^b, Chung-Yuan Mou^{a,c}, Shiuh-Tzung Liu^{a,*}

^a Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

^b Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan

^c Center of Condensed Matter, National Taiwan University, Taipei 106, Taiwan

ARTICLE INFO

Article history:

Received 31 January 2009

Received in revised form 12 April 2009

Accepted 14 April 2009

Available online 19 April 2009

Keywords:

Diblock copolymer

Mesoporous silica

Amphiphilic polymer

Mesostructure

ABSTRACT

Highly ordered mesoporous silicas with large accessible pores have been prepared by using pre-synthesized poly(ethylene oxide)-*b*-poly(methyl acrylate) (EO_nMA_m) diblock copolymers as templates. Via adjusting the chain length of EO versus that of MA, a series of silica mesostructures, including two-dimensional (2-D) hexagonal, 3-D bicontinuous (*la3d*), and body-centered cubic (*Im3m*) symmetries, were prepared with the use of tetraethyl-orthosilicate (TEOS) as the silica precursor under acidic conditions. The mesostructures of all materials were characterized by small-angle X-ray scattering and transmission electron microscopy measurements. N_2 adsorption–desorption isotherms reveal that the pore size ranges from 4 to 30 nm with a narrow pore-size distribution and its dimension is proportional to the chain length of MA units.

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1. Introduction

Since the discovery of mesoporous silicas using cationic quaternary ammonium surfactants as templates [1], research concerning this subject has received much of attention due to its uniqueness in the high surface area, tunable pore size, uniform structures and hence suited to various applications. In order to fine-tune the properties of silicas, many synthetic protocols and chemical components have been employed to modify the micellar behaviors, i.e. the organic templates, among which amphiphilic polymers have received particular interest [2–32]. In this context, research using block copolymers as templates has increased enormously. Compared to ionic surfactant solubilized with hydrophobic molecules, polymer micelles have several advantages upon construction of porous silica; especially, they provide versatile but precise control over mesostructures and morphology through the interfacial curvature of copolymers [2–31]. As for a prototypical example, the pluronic copolymers have been exploited to prepare the mesoporous silicas with various pore sizes and mesostructures [13–18].

For AB diblock copolymers, it is believed that the degree of polymerization ($N = N_A + N_B$), the composition ($f_A = N_A/N$), and Flory–Huggins interaction parameter χ_{AB} are key factors to influence the mesostructure of their mesophase [31,32]. Although the meso-

structure is quite complicated for block copolymers, its corresponding phase diagram can be parameterized in terms of $\chi_{AB}N$ versus f , analogous to that of lyotropic liquid crystals. It is known that the assembled copolymers may form different ordered mesostructures, such as lamellae, cylinders or bicontinuous arrangement, which are found to be composition-dependent and have been verified via theoretical approaches under the strong segregation limit. In general, in templated sol–gel synthesis of mesoporous silica using the diblock copolymer, much of the 3-D structures as predicted in theoretical phase diagram could also be found if a enough set of sol conditions coupled with various designs in block ratios are employed.

In the previous communication, we found that with a careful tuning of f and $\chi_{AB}N$ of copolymer, *la3d* cubic mesoporous silica could be synthesized by using a proper process and composition of poly(ethylene oxide)-*b*-poly-(methyl acrylate) [denoted as EO_nMA_m] diblock copolymer ($\text{EO}_{23}\text{MA}_{17}$) [30]. Since the polydispersity of copolymers has dramatic effects on manipulating the formation of mesostructures in terms of structural ordering and uniformity, synthetic methodology leading to the well-defined copolymers becomes indispensable. With a careful tuning the composition and combination parameter of copolymer, one should be able to synthesize various structural mesoporous silicas. Herein, we reported details of the preparation of a series of well-defined diblock copolymers EO_nMA_m and their applications in the construction of mesoporous silica with various pore sizes ranging from 4.0 to 20.0 nm.

* Corresponding author. Tel.: +886 2 2366 0352; fax: +886 2 2363 6359.

E-mail address: stliu@ntu.edu.tw (S.-T. Liu).

2. Experimental section

2.1. General

Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone. Dichloromethane was dried with CaH_2 and distilled under nitrogen. Poly(ethylene glycol) methyl ethers $[\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OH}]$ with molecular weight 750, 2000 and 5000 were obtained from Acrôs and used without further purification. Tris(2-dimethylaminoethyl)amine (Me_6TREN) was prepared according to the method reported [33]. Tetraethoxysilane (TEOS), other chemicals and solvents were of analytical grade and were used as received.

Nuclear magnetic resonance spectra were recorded in CDCl_3 on a Bruker AM-300 spectrometer at 300 MHz under ambient conditions. Chemical shifts are given in parts per million relative to Me_4Si . 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 room temperature and polystyrene calibration curve for analyses.

2.2. Preparation of macro-initiators MI_{a-c}

A round-bottom flask was placed with poly(ethylene glycol) methyl ether (40.0 g) and was degassed. CH_2Cl_2 (100 mL), triethylamine (5.6 mL, 40 mmol) and 2-bromoisobutyl bromide (5.0 mL, 40.0 mmol) were syringed into the flask at ice-cooled temperature. After stirring at room temperature for 24 h, ether (200 mL) was poured into the reaction mixture and the ammonium salt precipitated. Upon removal of solids, the filtrate was concentrated to give the crude product. Re-precipitation of the product from CH_2Cl_2 /ether provided the pure MI_{a-c} in 80–85% yield. ^1H NMR (300 MHz, CDCl_3) δ 4.3 (t, $J = 4.8$ Hz, 2H), 3.6 (s, 4H, $-\text{OCH}_2\text{CH}_2-$), 3.3 (s, 3H, $-\text{OCH}_3$), 1.9 (s, 6H).

2.3. Preparation of EO_nMA_m diblock copolymers

The polymerization of methyl acrylate on the poly(ethylene oxide)-2-bromoisobutyrate(MI_n) were carried out by using the $\text{CuBr}/\text{Me}_6\text{TREN}$ as the catalyst. A typical procedure is as following: A mixture of MI_a (3.6 g, 4 mmol) and CuBr (114.8 mg, 0.8 mmol) in a 25 mL flask was degassed. Methyl acrylate (4.7 mL, 52.0 mmol) was syringed into the flask with stirring to form a homogeneous solution. $[(\text{Me}_2\text{NCH}_2\text{CH}_2)_3\text{N}]$ (0.23 mL, 0.8 mmol) was then added. After stirring at room temperature for 5 min, the reaction mixture was diluted with THF. The reaction mixture was passed through a column packed with silica gel to remove the copper complexes. The filtrate was concentrated to give the desired polymer (7.3 g). ^1H NMR (300 MHz, CDCl_3) δ 4.2 (br, 1H, $-\text{CHBrCOOMe}$), 4.1 (t, $J = 4.8$ Hz, 2H), 3.6 (br), 3.3 (s, 3H, $-\text{OCH}_3$), 2.25 (br, 1H), 2.0–1.3 (br, 2H), 1.11 (s, 3H, $-\text{CH}_3$), 1.08 (s, 3H, $-\text{CH}_3$). The detail analysis, chemical composites and reaction conditions of diblock copolymers are summarized in Table 1.

2.4. Preparation of mesoporous silicas

The EO_nMA_m -silica mesostructural composites were synthesized under acidic media as that for SBA-15 silicas [13–18]. The as-synthesized mesoporous silica products were obtained after 1 day agitation at 25–50 °C. The final gel composition (in g) is: (0.3–0.5 g) EO_nMA_m : (20.0–25.0 g) H_2O : (4.0–6.0 g) 37% HCl : (1–2.5 g) TEOS. In order to increasing the mesostructural orderness and stability, 1.0 g dried acid-made mesoporous silicas was com-

Table 1

Preparation of diblock copolymers EO_nMA_m .^a

Entry	Initiator (mmol)	MA (mmol)	Time	Temp. (°C)	Conv. (%)	M_N (PDI) ^d	$n:m$ ^e
1	MI_a (4)	52	5 min	26	93	2180 (1.13)	17:12
2	MI_a (3)	54	7 min	26	94	2700 (1.14)	17:18
3	MI_a (3)	60	10 min	26	96	3100(1.14)	17:23
4 ^b	MI_b (2)	70	4 min	31	91	5740 (1.11)	45:34
5	MI_b (1)	45	32 min	25	80	6500 (1.15)	45:42
6	MI_b (2)	147	40 min	25	78	9000 (1.14)	45:72
7	MI_b (1.9)	171	1.3 h	25	76	10,900 (1.10)	45:94
8	MI_b (2)	200	1.5 h	26	78	12,100 (1.14)	45:105
9 ^c	MI_c (0.75)	49	1 h	30	90	11,900 (1.13)	114:50
10 ^c	MI_c (0.5)	47	5 min	30	88	12,300 (1.13)	114:82
11 ^c	MI_c (0.5)	55	4 min	30	89	13,600 (1.16)	114:94
12 ^c	MI_c (0.5)	63	1 h	30	89	18,100 (1.12)	114:122

^a Reaction conditions: $[\text{Me}_6\text{Tren}]:[\text{CuBr}]:[\text{MI}_x] = 1:1:10$.

^b $[\text{Me}_6\text{Tren}]:[\text{CuBr}]:[\text{MI}_b] = 1:1:5$.

^c $[\text{Me}_6\text{Tren}]:[\text{CuBr}]:[\text{MI}_c] = 1:1:2$.

^d GPC analysis against linear polystyrene standards. PDI (polydispersity index) = M_w/M_n . M_w : weight average molecular weight; M_n : number average molecular weight.

^e Units (m) of MA were calculated by $(M_n - \text{molecular weight of } \text{MI}_x)/(\text{molecular weight of MA} = 86)$. Since this is determined by NMR integration, there is 5% of uncertainty for each determination.

bined with 50.0 g of water (pH $\approx$ 7.0) and then hydrothermally treated at 100 °C for 24 h [15].

2.5. Characterization of mesoporous silicas

The powder X-ray diffraction patterns (XRD) were taken on Wiggler-A beamline ($\lambda = 0.1326$ nm) of Taiwan Synchrotron Radiation Research Center, Hsin-Chu, Taiwan. The TEM images of the prepared mesoporous silicas were recorded on Hitachi S-7100 transmission electron microscope with an operating voltage of 75 keV. The N_2 adsorption-desorption isotherms were obtained at -196 °C 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

To avoid lots of try-and-error efforts on the synthesis of the designed EO_nMA_m surfactant for the mesoporous silica, the theoretical phase diagram of diblock copolymers gives us a guideline to follow [31,32]. Accordingly, for a A_mB_n diblock copolymer with a fixed composites at constant temperature (i.e. the fixed Flory-Huggins interaction parameter χ), the rich well-ordered mesostructural phases, including body-centered-cubic sphere (Q_{1m3m}), hexagonal cylinders (H), bicontinuous $1a3d$ cubic (Q_{1a3d}) and lamellar (L), generally occur in the diblock copolymer with relatively low molecular weight and vary with the block length ratio ($f = N_A/N$; $N = N_A + N_B$). Therefore, $\text{EO}_{17}\text{-OH}$, $\text{EO}_{45}\text{-OH}$ and $\text{EO}_{114}\text{-OH}$ were functionalized as the macro-initiator for the preparation of the various EO_nMA_m copolymers.

3.1. Synthesis of well-defined diblock copolymers

To prepare the amphiphilic block copolymers in the desired chain lengths is one of the primary works of this study. Among various synthetic methodologies, it appears that the method of atom transfer radical polymerization (ATRP) developed by Matyjaszewski provides an excellent approach to synthesize the polymers in well-defined units [34]. The methyl-capped polyethylene oxide, a commercial available reagent with well-defined units, is used for the hydrophilic portion of the polymer. Treatment of the alcohols with α -bromoiso-butanoyl bromide yielded the desired macro-initiator (**MI_{a-c}**), which was suitable for building the block of poly (methyl acrylate) (**Scheme 1**).

Without any solvent, methyl acrylate was polymerized in the presence of macro-initiator and copper(I) chloride and the amine ligand. By monitoring the reaction with GPC analysis, polymerization process was stopped by addition of tetrahydrofuran upon dilution. It appeared that all polymerizations proceeded smoothly with a high conversion of monomers. Reaction mixture was filtrated

through silica gel and the desired polymer with defined length was obtained. All polymers were analyzed by both gel permeation chromatographic and spectroscopic methods. Results of polymerization are summarized in **Table 1**. The obtained molecular weights for all copolymers are consistent with the theoretically calculated ones. In case of the macro-initiator with a higher molecular weight **MI_c**, the polymerization required the use of a large quantity of catalyst for the construction of a longer polyacrylate chain (entry 14). From the summary of **Table 1**, the polydispersity of these diblock copolymers are all in the range of 1.10–1.16, indicating a narrow molecular weight distribution of polymers. Such well-defined amphiphilic copolymers would meet the need for self-assembly of uniform mesostructures.

3.2. Mesoporous silicas with different mesostructures

3.2.1. Porous silica of P6mm hexagonal mesostructure

Although the high composition-flexibility (*N*) of the EO_{*n*}MA_{*m*} copolymers can be achieved using the ATRP, the χ value is still

Scheme 1. Preparation of diblock copolymers.

Fig. 1. XRD pattern, N₂ adsorption–desorption isotherm and TEM images of calcined **N1** (A) XRD, (B) and (C) TEM photography, and (D) N₂ adsorption–desorption isotherm.

unrevealed. From the analysis of the phase diagram of diblock copolymers, the hexagonal structure appears to be the most extensive mesophase. Therefore, the preparation of the hexagonal mesoporous with the diblock copolymer templates is relatively common to other mesostructures. Moreover, the characterization of 2-D hexagonal mesostructure is much more easily and clearly than those of the other 3-D mesostructures e.g. *Im3m* and *la3d*. Thus, the strategy of the first target for our study is to establish the conditions for the formation of silicas with hexagonal mesostructure via the template of the prepared EO_nMA_m diblock copolymers.

Fig. 1A demonstrates the representative XRD patterns of the mesoporous silica synthesized from the $\text{EO}_{17}\text{MA}_{12}$ -TEOS-HCl- H_2O compositions. Obviously, this mesoporous silica after calcination at 560 °C exhibits three sharp peaks at low-angles, which are the characteristic of the *P6mm* hexagonal mesostructure. TEM images of this sample (Fig. 1B–C) reveal the synthesized silica in the well-ordered hexagonal-array and parallel-channel of the 2-D hexagonal mesostructure, resembling to those from MCM-41 or SBA-15 silicas [15]. For the N_2 adsorption-desorption of the $\text{EO}_{17}\text{MA}_{12}$ -templated mesoporous silica (Fig. 1D) shows a sharp capillary condensation at P/P_0 of about 0.5. These data demonstrate that the mesoporous silicas are in uniform pore size with large porosity and surface area (pore volume $\approx 0.64 \text{ cm}^3/\text{g}$; BET surface area $\approx 709 \text{ m}^2/\text{g}$).

In addition to the copolymer of $\text{EO}_{17}\text{MA}_{12}$, the silica via $\text{EO}_{45}\text{MA}_{72}$ -templating possesses a hexagonal mesostructure as evidenced by three distinct (1 0 0), (1 1 0) and (2 0 0) XRD peaks at low angles but in a larger mesostructural dimension (see Supplementary data, Fig. S5). This material shows its pore dimension in ca. 12 nm and BET surface area of $566 \text{ m}^2/\text{g}$ (Table 2). However, the TEM image indicates that the orderliness of the channels in $\text{EO}_{45}\text{MA}_{72}$ -templated mesoporous silica is less orderly arranged, which is presumably attributed to the longer polymer chain. The orderliness decreases as the hydrophobic polymer chain length increases.

3.2.2. Porous silica of *la3d* cubic mesostructure

Accordingly, using the longer MA end of $\text{EO}_{17}\text{MA}_{23}$ as the template and under synthetic conditions described for

$\text{EO}_{17}\text{MA}_{12}$ -templated silica, the as-synthesized mesoporous silica (N3) has a representative XRD patterns ascribed to the 3-D *la3d* mesostructure. The characterization of this silica has been communicated previously [30]. It is known that the *la3d* cubic mesoporous silica could be synthesized by a careful tuning the composition (f) and combination parameter (χN) of copolymer. Thus, the f -value of copolymer $\text{EO}_{17}\text{MA}_{23}$ appears to be less than that of $\text{EO}_{17}\text{MA}_{12}$ in hexagonal phase because of the longer poly(methyl acrylate) chain.

3.2.3. Porous silica of *Im3m* cubic mesostructure

Theoretically the *Im3m* cubic mesostructure should be formed with the f -value of the diblock copolymer smaller than that of hexagonal. By using $\text{EO}_{45}\text{MA}_{42}$ as the template, the mesoporous silica product (N5) after calcination has a representative XRD patterns ascribed to the 3-D *Im3m* mesostructure (Fig. 2A). The low-angle peaks in the X-ray diffractograms are broad, but still these peaks at small angles with d spacings of 137.4, 98.6, 83.6 and 69.9 Å can be indexable as (1 1 0), (2 0 0), (2 1 1) and (2 2 0) reflections of the cubic *Im3m* mesostructure, respectively. This $\text{EO}_{45}\text{MA}_{42}$ -templated mesoporous silica is similar to that reported for the silica-based mesoporous counterpart SBA-16 [35,36]. This identification was further confirmed by the transmission electron microscopy (TEM) images shown in Fig. 2B–C, which were recorded along the [1 0 0] and [1 1 1] directions, respectively. Both micrographs clearly reveal the well-order domains of the 3-D cubic structures of this periodic mesoporous silica.

Nitrogen adsorption isotherms for the sample are of type IV with an H_2 -type hysteresis characteristic of large pore structure (Fig. 2D) [36]. Pore-size analysis gives the cavity in the range of 10 nm. The BET surface area and the pore volume of this sample were determined to be $604 \text{ m}^2/\text{g}$ and $0.75 \text{ cm}^3/\text{g}$, respectively.

3.2.4. Mesoporous silica templated with other diblock copolymers

In addition to the use of diblock copolymers described above, various chain lengths of EO_nMA_m prepared in this work were subjected for the preparation of mesoporous silicas as well. Some physical data of the silicas are summarized in Table 2. The $\text{EO}_{17}\text{MA}_{18}$ -templated silica sample (N2) contains binary mesophases of *la3d* cubic and 2-D hexagonal structures as revealed by the diffraction pattern. Besides the characteristic pattern resulted from the hexagonal phase, a weaker diffraction spot is indexed as the (2 0 0) at 1.2° , which is consistent with an *la3d* mesostructure.

For copolymer $\text{EO}_{45}\text{MA}_{94}$, small angle diffraction pattern of the as-synthesized sample N7 was quietly broad. Upon calcination, the first signal of the diffraction appeared at 0.4° . However, it was able to categorize its disordered mesostructure. TEM image of the calcined N7 (Fig. 3) clearly suggests the poor orderliness. Apparently, the change of composition (f), i.e. longer MA versus shorter EO, readily makes χ value in the range of disorder structure [31].

The templates of $\text{EO}_{114}\text{MA}_y$ series yield the disordered mesoporous silicas (N9–N12) rather than periodically ordered mesostructures. The broad XRD patterns can just provide the evidence of the mesostructure formation, but was not possible to identify the characteristic mesostructures of these series of silicas (Fig. 4). According to these results, it is noticed that the shorter chain of the copolymers as templating provides the highly ordered mesoporous silicas, whereas the longer chains gives disordered structures. This results is quite different from mesoporous silica obtained from the poly(ethylene oxide)₁₂₅-*b*-poly(styrene)₂₃₀ [$\text{EO}_{115}\text{ST}_{230}$] template [17]. Apparently, the hydrophobic chain interactions in the diblock copolymer $\text{EO}_{115}\text{ST}_{230}$ is quite different from that in the diblock copolymer $\text{EO}_{115}\text{MA}_y$.

Table 2
Properties of mesoporous silicas.

Sample	Surfactant	Meso-structure	d (Å) ^a	BET surface area (m^2/g)	Pore size ^b (Å)	Pore vol (cm^3/g)
N1	$\text{EO}_{17}\text{MA}_{12}$	Hexagonal	72.3 (65.1)	709	38	0.64
N2	$\text{EO}_{17}\text{MA}_{18}$	Mixture ^b	82.9 (74.9)	751	52	0.76
N3	$\text{EO}_{17}\text{MA}_{23}$	<i>la3d</i> cubic	86.6 (77.9)	699	57	0.88
N4	$\text{EO}_{45}\text{MA}_{34}$	Disordered	129.9 (114.6)	760	77	0.88
N5	$\text{EO}_{45}\text{MA}_{42}$	<i>Im3m</i> cubic	150.1 (139.4)	604	100	0.75
N6	$\text{EO}_{45}\text{MA}_{72}$	Hexagonal	185.9 (162.6)	566	120	0.71
N7	$\text{EO}_{45}\text{MA}_{94}$	Disordered	—(194.8)	266	190	0.89
N8	$\text{EO}_{45}\text{MA}_{105}$	Disordered	—	277	200	0.83
N9	$\text{EO}_{114}\text{MA}_{50}$	Disordered	205.5 (185.9)	603	153	0.92
N10	$\text{EO}_{114}\text{MA}_{82}$	Disordered	—(243.5)	533	188	1.01
N11	$\text{EO}_{114}\text{MA}_{94}$	Disordered	—(275.9)	512	222	0.95
N12	$\text{EO}_{114}\text{MA}_{122}$	Disordered	—	606	300	1.01

^a $d(100)$ Spacing or d value of characteristic reflection of as-synthesized products; the number inside brackets is the d value after calcinations at 560 °C for 6 h.

^b Mixture of hexagonal and cubic.

Fig. 2. (A) XRD, (B) [1 0 0] and (C) [1 1 1] TEM images, and (D) N₂ adsorption–desorption isotherm of N5 sample.

Fig. 3. TEM micrograph of calcined N7.

Fig. 4. XRD patterns of calcined N9–N12.

3.3. TGA study of organic/silica composites

The weight loss from TGA studies of the as-synthesized samples N1–N12 are shown in Table 3. All of the TGA curves were measured in air. A typical TGA curve of N12 is illustrated in Fig. 5, which includes four endothermic weight losses: <140 °C (region I), 140–230 °C (region II), 230–430 °C (region III) and >430 °C (region IV). These losses can be attributed to water desorption, decomposition

of EO units (~12%), decomposition of MA units (32%), and finally condensation of siloxy groups (~5%). By 600 °C, essentially all of the nonionic organic surfactants have been removed from the channels of the prepared silicas, and the remnant inorganic material exhibits a good thermal stability.

For all as-synthesized EO_nMA_m diblock copolymers-templated silicas, the total weight loss of the organic part is in the range of

Table 3
TGA analysis of as-synthesized **N1–N12**.^a

Sample	wt% Loss
N1	48
N2	54
N3	46
N4	62
N5	45
N6	53
N7	52
N8	56
N9	47
N10	47
N11	49
N12	50

^a The total weight loss before 430 °C.

Fig. 5. TGA diagram of the as-synthesized sample of **N12**.

45–60%, indicating that a large amount of organic templates are included in these silica matrices, which is quite similar to those of the mesoporous silica via other block copolymer templates [15].

3.4. Discussion

A well control on the pore size is an important subject in the preparation of mesoporous materials as well. Due to the high flexibility in the degree of polymerization in the hydrophobic MA chain, the pore size of the mesoporous silica could be fine-tuned. Fig. 6 illustrates a plot of pore size versus number of MA units. Under a constant EO unit number, the pore size increases with the increase of the MA length, and the pore size can be extended to 30.0 nm without the addition of hydrocarbons expanders (such as toluene, trimethylbenzene). From the analysis of the N₂ adsorption–desorption isotherms, it shows that the calcined mesoporous silicas obtained from this process possess the high surface area (500–800 m²/g) and uniform pores. In addition to the increase of pore size according to the MA units, the pore size is independent of chain length of EO_n part (Fig. 6), which indicates the channels formed by the self-assembly of the hydrophobic part, whereas the EO_n part (hydrophilic) cooperative assembly with the silica species to yield the composite aggregates. In other words, the use of various chain lengths of MA units is able to manipulate the preparation of various silicas with the accessible pore-size scale of these mesostructures.

Fig. 6. Correlation of pore size versus MA units of EO_nMA_m.

As for the wall thickness, the calculated values reach to 2.5–4.0 nm for these prepared mesoporous silicas [37]. This kind of thickness of wall readily makes these silicas in highly stable structures, except the one prepared by EO₄₅MA₉₄. For example, the EO₁₇MA₂₃ templated mesoporous silicas (**N3**) were stable under hydrothermal conditions for 48 h without apparent structural collapse. However, the mesoporous materials prepared via EO₄₅MA₉₄ (**N7**) and EO₄₅MA₁₀₅ (**N8**) templating are not in agreement with this series of silicas. Compared to others, these two are in low surface area (Table 2) with no distinctive peak on the X-ray diffraction upon the calcination, presumably due to the collapse of structures.

We noticed that the XRD patterns of silicas from the use of EO₁₁₄MA_y ($y = 50–112$) as templates do not have any distinctive signal for the well-defined mesostructural packing symmetries. Along with the TEM images, these mesopores are classified as disordered forms. However, the fraction of MA chain (f_{MA} in Table 4) in EO₁₁₄MA₈₂ is fairly close to that for EO₁₇MA₁₂, but the mesophases for both appear to be different, indicating that the ratio of hydrophobic to hydrophilic ends is not the main factor to direct the micelle-templated mesoporous silicas. According to the mesophase change via EO_nMA_m templated (Fig. 7), the packing param-

Table 4
Fraction (f_{MA}) of MA_x chain on the copolymers.

Surfactant	$f_{MA} = (N_{MA}/N)$	Surfactant	$f_{MA} = (N_{MA}/N)$	Surfactant	$f_{MA} = (N_{MA}/N)$
EO ₁₇ MA ₁₂	0.414	EO ₄₅ MA ₃₄	0.430	EO ₁₁₄ MA ₅₀	0.305
EO ₁₇ MA ₁₈	0.514	EO ₄₅ MA ₄₂	0.483	EO ₁₁₄ MA ₈₂	0.418
EO ₁₇ MA ₂₃	0.575	EO ₄₅ MA ₇₂	0.605	EO ₁₁₄ MA ₉₄	0.452
		EO ₄₅ MA ₉₄	0.676	EO ₁₁₄ MA ₁₂₂	0.516
		EO ₄₅ MA ₁₀₅	0.700

Fig. 7. Correlation of g value and EO_nMA_m.

ter g [$g = V/la_0$, where V : volume hydrophobic chain; l : chain length of copolymer; a_0 : effective area of hydrophilic head group at interface] increases in order of $\text{EO}_{45}\text{MA}_{42} < \text{EO}_{17}\text{MA}_{12} < \text{EO}_{45}\text{MA}_{72} < \text{EO}_{17}\text{MA}_{23}$ [32].

4. Conclusion

In brief, the ATRP synthetic method provides a convenient way to control the composition and combination of the neutral diblock or triblock copolymers. With a well tuning in the surfactant micellar properties and liquid-crystal phases, one can design the porosity, pore size, morphologies and mesostructures for extending the applications of mesoporous materials. The present contribution concerns a systematic study for the preparation of various mesostructural silicas in a large pore dimension. More theoretical consideration and experimental studies are currently under investigation.

Acknowledgment

This work was supported by National Science Council, Taiwan, ROC for the financial support.

Appendix A. Supplementary data

XRD of $\text{EO}_{17}\text{MA}_{18}$ -templated mesoporous silica **N2**, N_2 adsorption–desorption isotherm of **N2**, XRD of $\text{EO}_{45}\text{MA}_n$ -templated mesoporous silica **N4**, **N7** and **N8**, N_2 adsorption–desorption isotherm **N4**, **N7** and **N8**, XRD of $\text{EO}_{45}\text{MA}_{72}$ -templated mesoporous silica **N6**, TEM of $\text{EO}_{45}\text{MA}_{72}$ -templated mesoporous silica **N6**, TEM images of **N8**, N_2 adsorption–desorption isotherm **N9**, **N10**, **N11** and **N12**, and TEM image of **N12** are deposited as supporting materials. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micromeso.2009.04.019.

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