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*Ia*3*d* Cubic mesoporous silicas using $EO_{17}MA_{23}$ diblock copolymers made from ATRP

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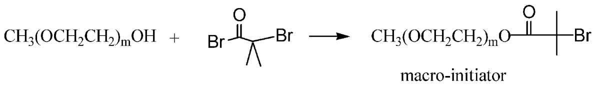
Poly(ethylene oxide)-*b*-poly(methyl acrylate) diblock copolymer (EO_mMA_n) prepared *via* an atom transfer radical polymerization (ATRP) approach was used as a template to synthesize *Ia*3*d* mesostructured silica with thick walls under acidic conditions.

Synthesis of mesoporous silica containing large pores (> 5.0 nm) with narrow size distribution and designed symmetry is rather difficult, particularly for the cubic *Ia*3*d* structure.[1] The usual approach uses commercially available amphiphilic block copolymers, such as Pluronic triblock polymers ($EO_mPO_nEO_m$), as templates.[2] However, the molecular weight distribution of the copolymers is rather polydisperse, which results the prepared mesoporous materials being much less ordered. In addition, the necessary acidic conditions in the preparation of such materials make the situation even worse because of the weaker silica–polymer interaction. In fact, most of the known 'mesoporous silicas' with pore size above 10 nm are either wormhole-like or foam-like in pore structure.[3,4] Therefore the search of amphiphilic copolymers with good monodispersity as templates for this purpose is a challenge.

The advent of the atom transfer radical polymerization (ATRP) method offers a synthetic method to obtain block copolymers with narrow molecular weight distribution.[5,6] Thus the hydrophilic–hydrophobic portion of the copolymer can be fine-tuned, which provides a better control in mesophases of polymer/silicate nanocomposites. Here, we perform the ATRP approach to prepare desired poly(ethylene oxide)-*b*-poly-(methyl acrylate) diblock copolymers (denoted as EO_mMA_n) and use these to synthesize a cubic *Ia*3*d* mesostructured silica, which is a difficult structure to construct, especially with a relatively large pore size (> 5.0 nm) and thick walls (> 3.0 nm) under acidic conditions.

Starting with the methyl-capped polyethylene oxide $Me(OCH_2CH_2)_mOH$, the macro-initiator poly(ethylene oxide)-2-bromoisobutyrate was prepared through an esterification process (eqn. (1)),[7] which was then subjected to connect the hydrophobic poly(methyl acrylate) units by ATRP. In the presence of CuBr/Me_6TREN (tris[2-(dimethylamino)ethyl]amine) as catalyst, polymerization of MA readily took place on the macro-initiator with the desired chain length *via* manipulation of the reaction conditions. Typically, reaction of macro-initiator (3 mmol) and methyl acrylate (60 mmol) at 26 °C for 10 min resulted in the formation of the desired $EO_{17}MA_{23}$ with M_n = 3100 (PDI = 1.14).



(1)

The $EO_{17}MA_{23}$–silica mesostructural composites were synthesized in acidic media similarly to that for SBA-15 silicas.[2] The as-synthesized mesoporous silica products were obtained after 1 day agitation at 25–50 °C. The final gel composition is: (0.3–0.5 g) EO_mMA_n : (20.0–25.0 g) H_2O : (4.0–6.0 g) 37% HCl : (1–2.5 g) TEOS. To increase the structural order and stability, 1.0 g of dried acid-made mesoporous silica was combined with 50.0 g water (pH ≈ 7.0) and then hydrothermally treated at 100 °C for 24 h.[8] The organic templates were removed by calcination at 500 °C in air for 6 h. Powder X-ray diffraction (XRD) patterns were recorded on Wiggler-A beamline (λ = 0.1326 nm) at the Taiwan Synchrotron Radiation Research Center. The TEM images of mesoporous silicas were taken using a Hitachi-7100 transmission electron microscope (TEM) with an operating voltage of 100 keV. N_2 adsorption–desorption isotherms were obtained at 77 K on a Micromeritics ASAP 2010 apparatus.

Fig. 1A shows the XRD patterns of the calcined mesoporous silica obtained from $EO_{17}MA_{23}$–TEOS–H_2O composite under acidic condition (pH < 1). Representative (211), (220), (420) and (332) peaks are observed indicative of the *Ia*3*d* cubic mesostructure.[9] The dimension of the unit cell (*a*) is 18.8 nm. To further confirm the *Ia*3*d* cubic mesostructure, TEM images of a microtomed sample taken along different axes, [111], [310] and [110], were examined for structural analysis (Fig. 1 B,C,D).[10] The observations are in a good agreement with XRD result, and the space group of the mesoporous silica was definitely determined to be *Ia*3*d*.

The N_2 adsorption–desorption isotherm for the calcined mesoporous silica is shown in curve I of Fig. 2. A sharp inflection at P/P_0 ~ 0.65 is attributed to capillary condensation within uniform nanochannels. Moreover, the existence of a hysteresis loop at P/P_0 of 0.6–0.7 can be ascribed to capillary condensation on large pore size. The pore size estimated by the Barrett–Joyner–Halenda method is 5.72 nm. The pore volume of this sample is comparatively high at 0.9 $cm^3 g^{-1}$, and the BET surface area is about 700 $m^2 g^{-1}$.

Combining the aforementioned results, well-defined *Ia*3*d* cubic mesoporous silica with large pore size and high surface area and porosity has been prepared by using an appropriate

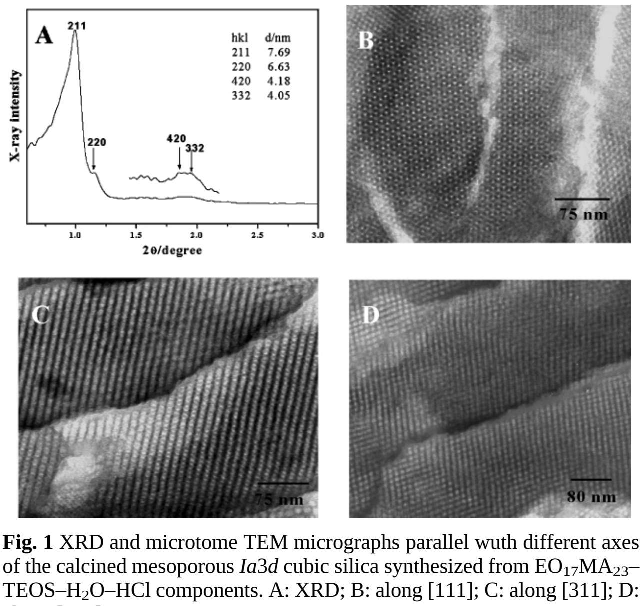


Fig. 1 XRD and microtome TEM micrographs parallel wuth different axes of the calcined mesoporous *Ia*3*d* cubic silica synthesized from $EO_{17}MA_{23}$–TEOS–H_2O–HCl components. A: XRD; B: along [111]; C: along [311]; D: along [110].

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diblock copolymer template of $EO_{17}MA_{23}$. According to previous literature, the mesoporous silicas synthesized from copolymer surfactants in acidic media possess good hydrothermal stability due to thick wall thickness. Correspondingly, curve II of Fig. 2 shows the pore size distribution is still excellent, with a small size expansion, after the calcined *Ia*3*d* mesoporous silica of $EO_{17}MA_{23}$ was treated in boiling water for two days. The excellent hydrothermal stability is in contrast to the other well-known *Ia*3*d* mesoporous structure MCM-48, which is synthesized by using the alkyltrimethylammonium halides under highly alkaline conditions (pH > 10.0) and cannot survive in boiling water for even 3 h.[1] This is due to our sample's extraordinarily thick walls of 3.2 nm relative to those of MCM-48 of 1.2–1.5 nm.[11] To our knowledge, this is the first time that hydrothermally stable, large pore-sized *Ia*3*d* cubic mesoporous silica has been synthesized in a dilute acidic condition rather than from a high-concentrated surfactant system[12] or alkaline media.[13, 14]

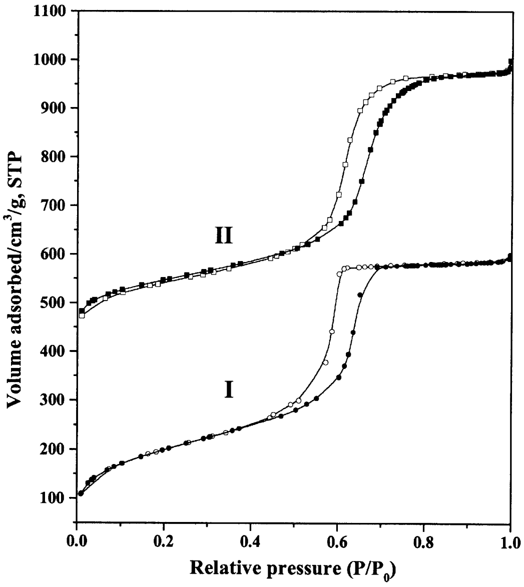

Fig. 2 N_2 adsorption–desorption isotherms of the calcined *Ia*3*d* cubic mesoporous silica before (curve I) and after (curve II) a two-day hydrothermal stability test.

It is well known that the *Ia*3*d* cubic mesophase exists in a diblock copolymer phase diagram. Therefore, with a careful tuning the composition (f) and combination parameter (χN) of copolymer,[15] the *Ia*3*d* cubic mesoporous silica could be synthesized by using a carefully chosen process and composition. Accordingly, we have a developed a method of polymerization based on ATRP which can make precisely controlled amphiphilic block copolymers.

Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.
3 J. S. Lettow, Y. J. Han, P. Schmidt-Winkel, P. Yang, D. Zhao, G. D. Stucky and J. Y. Ying, *Langmuir*, 2000, **16**, 8291.
4 C. G. Göltner, B. Berton, E. Krämer and M. Antonietti, *Adv. Mater.*, 1999, **11**, 395.
5 (*a*) J. Pyun and K. Matyjaszzewski, *Chem. Rev.*, 2001, **101**, 2921; (*b*) J. Pyun and K. Matyjaszzewski, *Chem. Mater.*, 2001, **13**, 3436.
6 M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.
7 E. J. Ashford, V. Naldi, R. O'Dell, N. C. Billingham and S. P. Armes, *Chem. Commun.*, 1999, 1285.
8 (*a*) H. P. Lin, S. B. Liu and C. Y. Mou, *Chem. Lett.*, 1999, **12**, 1341; (*b*) H. P. Lin, C. Y. Mou and S. B. Liu, *Adv. Mater.*, 2000, **12**, 103.
9 R. Ryoo, S. H. Joo and J. M. Kim, *J. Phys. Chem. B*, 1999, **103**, 7435.
10 M. Kaneda, T. Tsubakiyama, A. Carlsson, Y. Sakamoto, T. Ohsuna, O. Terasaki, S. H. Joo and R. Ryoo, *J. Phys. Chem. B*, 2002, **106**, 1256.
11 P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 2000, **16**, 2419.
12 S. A. El-Safty and J. Evans, *J. Mater. Chem.*, 2002, **12**, 117.
13 A. Sayari, *J. Am. Chem. Soc.*, 2000, **122**, 6504.
14 M. Widenmeyer and R. Anwander, *Chem. Mater.*, 2002, **14**, 1827.
15 F. S. Bates and G. H. Fredrickson, *Phys. Today*, 1999, **52**, 32.