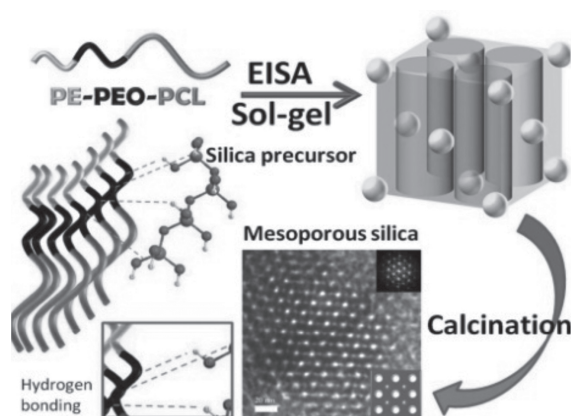


Hierarchical Mesoporous Silica Fabricated from an ABC Triblock Terpolymer as a Single Template

Jheng-Guang Li, Ruei-Bin Lin, Shiao-Wei Kuo*

Hierarchical mesoporous silicas containing two kinds of mesoporous size are successfully synthesized using the simple evaporation-induced self-assembly (EISA) strategy. Two blocks of hydrophobic segments (PE and PCL) in the poly(ethylene-*block*-ethylene oxide-*block*- ϵ -caprolactone) (PE-PEO-PCL) triblock copolymer are involved in the two types of mesopore after calcination, the PE segment being attributed to the face-centered cubic (fcc) morphology (spherical pores) and the PCL segment attributed to the tetragonal cylinder structure (cylindrical pores).



1. Introduction

Hierarchically ordered mesoporous materials at multiple length scales have recently been attracting considerable attention for both theoretical and practical aspects.^[1] Some synthetic methods have been reported for the fabrication of hierarchical porous structures,^[2] including opal and polymeric bead templating,^[3] sacrificial polymeric nanoparticle templates,^[4] controlled phase separation^[5] and mesoporous (hierarchical) particle assembly.^[6] These studies usually take two kinds of surfactant as templates to co-ordinate the forming ordered structures, use a cosolvent to induce pores with different length scales, or add polymeric beads (including organic or inorganic species) during the self-assembly process to achieve the goal of a hierarchical mesoporous morphology. However, there is

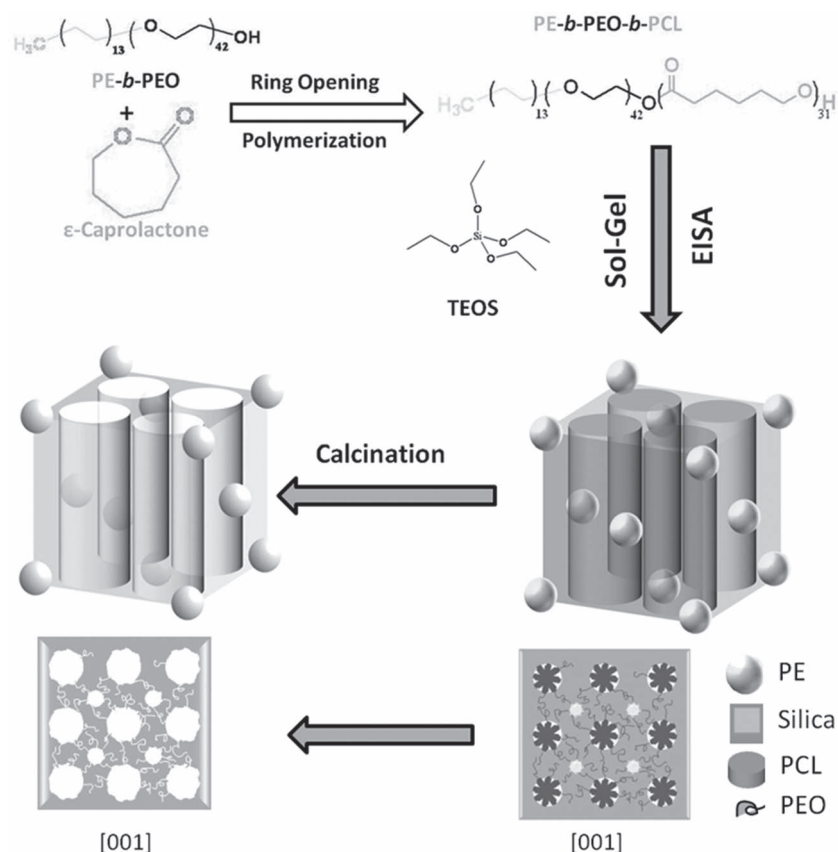
not an easy way to construct these hierarchical mesoporous structures using only one type of structure directing agent via a convenient evaporation-induced self-assembly (EISA) strategy. Self-assembled hierarchical nanostructures from ABC triblock copolymers have been attractive in recent years because they can form three-phase lamellae, core-shell cylinders and other hierarchical structures.^[7] Using ABC-type triblock copolymers as a template to prepare mesoporous materials was reported for the first time by Zhao's research group.^[8] A successful synthesis of highly ordered mesoporous carbon with large mesopores and tunable mesopore walls was introduced using the poly(ethylene oxide-*block*-methyl methacrylate-*block*-styrene) (PEO-PMMA-PS) triblock copolymer as a template and resol phenolic resin as a carbon source via the EISA strategy. However, the hydrophilic PEO segment was located at the chain end, and the two hydrophobic PMMA and PS segments were connected to each other. This kind of sequence distribution would cause production of only one type of mesoporous structure after calcination.

To achieve this goal of hierarchically mesoporous materials, we took a special, amphiphilic, ABC-type poly(ethylene-*block*-ethylene oxide-*block*- ϵ -caprolactone)

J.-G. Li, R.-B. Lin, Prof. S.-W. Kuo

Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan

E-mail: kuosw@faculty.nsysu.edu.tw



Scheme 1. Preparation of hierarchical mesoporous silica using the EISA procedure.

(PE-PEO-PCL) triblock copolymer as a single template for fabricating hierarchical mesoporous silica with two kinds of mesoporous size. PE-PEO-PCL, considered as the template, plays an important role in the fabrication of hierarchical mesoporous silica.

2. Results and Discussion

The PE-PEO-PCL triblock copolymer was composed of two hydrophobic segments, as terminal chains, and a hydrophilic segment, in the center; the specific compositions of the ABC-type triblock copolymer combined two kinds of morphology into hierarchical mesophases. Here, we utilized a commercial PE-PEO block copolymer ($\bar{M}_n = 2250 \text{ g mol}^{-1}$, PEO 80 wt%) as a macroinitiator and then synthesized the special ABC PE-PEO-PCL triblock copolymer through the convenient ring opening polymerization method. The PE-PEO-PCL triblock copolymer ($\bar{M}_n = 5700 \text{ g mol}^{-1}$) was easily prepared from this simple one-step ring opening polymerization method, as shown in Scheme 1. Gel permeation chromatography (GPC) results indicated a narrow polydispersity index (PDI) of 1.16 for the $\text{PE}_{13}\text{-PEO}_{42}\text{-PCL}_{31}$ triblock copolymer (Figure S1, Supporting

Information). The number-average molecular weights ($\bar{M}_n$) of the prepared copolymers were also determined using $^1\text{H-NMR}$ spectroscopy by comparing the peak intensity of the PEO segment in commercial PE-PEO macroinitiator (Figure S2, Supporting Information). Thermogravimetric analysis (TGA) of the PE-PEO-PCL showed a weight loss of approximately 98 wt% at a temperature of about 400°C in air (Figure S3–S6, Supporting Information). This result implies that the template can be removed easily by pyrolysis in both air and nitrogen.^[9]

Mesoporous silica was prepared using the EISA strategy in tetrahydrofuran (THF) with the PE-PEO-PCL triblock copolymer as the template and tetraethyl orthosilicate (TEOS) as the silica precursor.^[10,11] Prior to subsequent direct calcination, a hydrothermal treatment was adopted. In a typical synthetic procedure, 0.35 g of TEOS and 0.10 g of 0.1 M HCl solution were added to 5 g of a THF solution of the PE-PEO-PCL triblock copolymer (approximately 2.0 wt%) with stirring for 30 min to form a homogeneous solution following evaporation of the THF at room temperature for 48 h. The transparent

films were collected and ground into powders. The powders were treated by immersion into 30 mL of a HCl solution (1.0 M) and heating hydrothermally at 100°C for 3 d. The product was calcined in air at 600°C , with a heating rate of 1°C min^{-1} , to produce white mesoporous silica, as shown in Scheme 1.

Figure 1a shows the small-angle X-ray scattering (SAXS) pattern of the hierarchical mesoporous silica obtained from the silica/PE-PEO-PCL composite after calcination. The SAXS experiments were performed using the small- and wide-angle X-ray scattering (SWAXS) instrument at the BL17B3 beamline of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The X-ray beam had a diameter of 0.5 mm and a wavelength (λ) of 1.24 Å. The blend samples (thickness: 1 mm) were sealed between two thin Kapton windows (thickness = 80 μm) and analyzed at room temperature. (111) and (311) SAXS peaks were observed, indicating a face-centered cubic (fcc) structure.^[12] The other peaks could be indexed to the (10) and (20) reflections of a tetragonal cylinder mesostructure.^[13] These results indicate that the morphology of the hierarchical mesoporous silica was combined with the two kinds of morphology: a face-centered cubic structure and tetragonal cylinders.^[14] Among the reflection peaks,

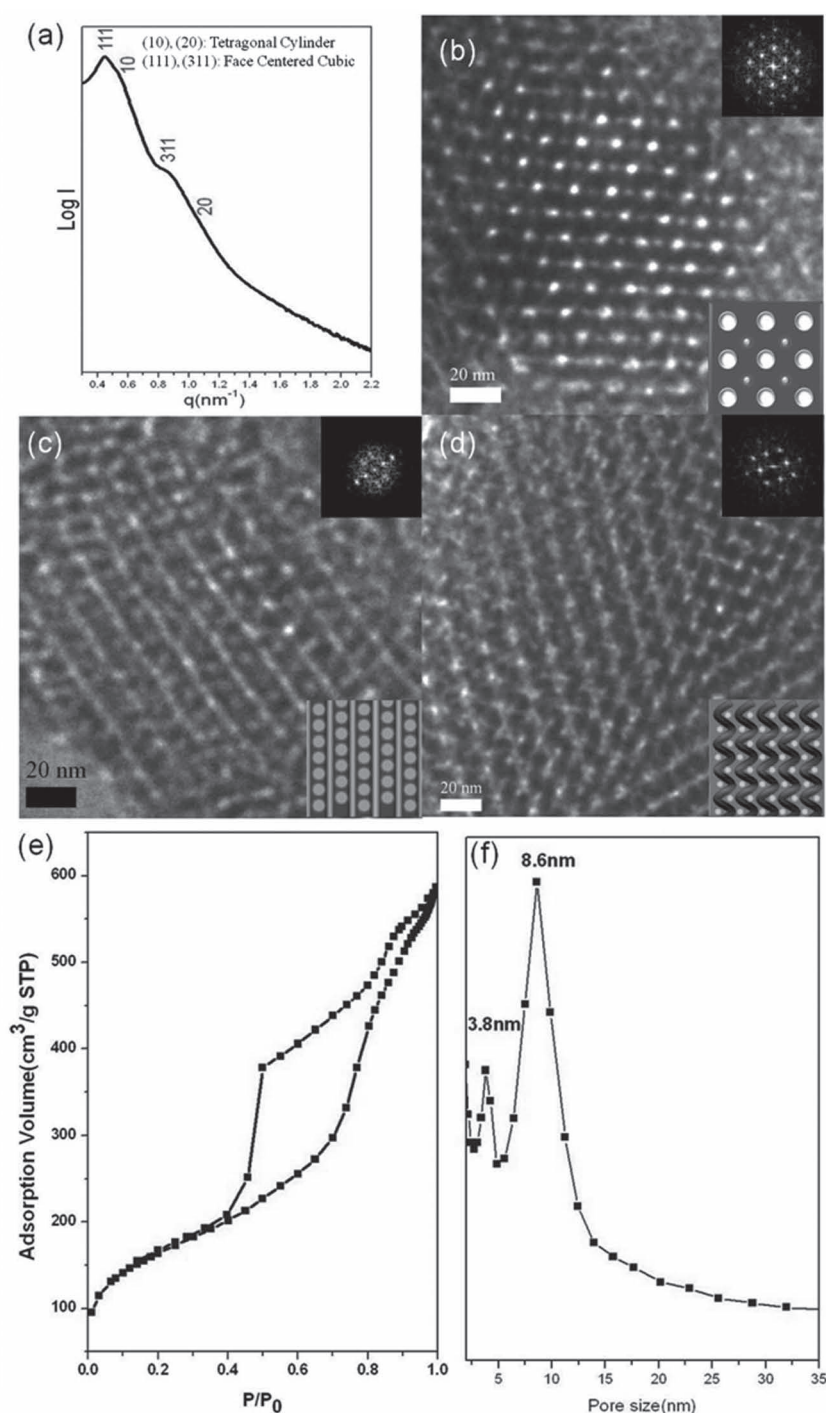


Figure 1. a–c) SAXS pattern (a) and microtomed TEM images of mesoporous silica templated by PE₁₃-PEO₄₂-PCL₃₁ viewed from the [001] (b), [10] (c), and [11] (d) directions. The insets are the corresponding FFT diffractograms. e–f) N₂ adsorption-desorption isotherms (e) and pore size distribution curves (f) of mesoporous silica templated by PE₁₃-PEO₄₂-PCL₃₁.

the q value of (10), attributed the tetragonal cylinder morphology, was located at the same position as the q value of (110) in the face-centered cubic structure. This fact helped

us to assign the relative SAXS patterns to the two separated morphologies. The mesophase and detailed hierarchical structure were characterized further by transmission electron microscopy (TEM) images and corresponding Fourier diffractograms. The TEM images were recorded using a JEOL-2100 transmission electron microscope, operated at an accelerating voltage of 200 kV. Ultrathin sections of the TEM samples (thickness ≈ 70 nm) were prepared using a Leica Ultracut UCT microtome equipped with a diamond knife. Figure 1b–d indicate that the hierarchical mesoporous silica had a high degree of periodicity, viewed from the [001], [10] and [11] directions. Figure 1b shows that there were two types of mesopore and both types of mesopore represent tetragonal packing along the [001] direction. Figure 1c shows spherical mesopores (fcc) included in the walls of the tetragonal-cylinder structure along [10] direction. On the other hand, when we turned the direction to [11], we observed spherical mesopores around the helix-like (zigzag, 21 helix) wall, shown in Figure 1d. The TEM images show that the texture of the mesoporous silica contained two distinguishable types of pore with different sizes. The small, spherical mesopores (≈ 3.8 nm) are attributable to the PE segment, and the large cylindrical mesopores (≈ 8.6 nm) are attributable to the PCL segment. The bimodal character of the mesoporous silica can clearly be appreciated in Figure 1b–d, in which two types of mesoporous order can be simultaneously observed. Nitrogen sorption isotherms of the hierarchical mesoporous silicas behaved like representative type-IV curves with two sharp capillary-condensation steps in the relative pressure ranges of 0.70 to 0.80 and 0.85 to 0.95, as shown in Figure 1e. This result indicates the generation of ordered mesopores with two kinds of pore size. For the same reason, the silica sample exhibited two hysteresis loops at $P/P_0 = 0.45$ to 0.80

(H₂-like loop) and $P/P_0 = 0.85$ to 0.95 (H₁-like loop), where P/P_0 is the relative pressure which are indicative of the two typical mesoporous structures: spherical pores and

cylindrical pores, respectively. Based on the Harkins and Jura model, the mean pore sizes measured from the adsorption branch were 3.8 nm (spherical pores) and 8.6 nm (cylindrical pores), as shown in Figure 1f. The two kinds of mesopore size, the surface area, pore volume and other textual properties, measured from Brunauer–Emmett–Teller (BET) analysis and SAXS, are presented (Table S1, Supporting Information) (sample E2H10).

To investigate the effects of the amounts of acid or TEOS, we designed a series of experiments, changing the amount of HCl in the TEOS/PE-PEO-PCL/HCl (Figure S7–S9 and Table S1, Supporting Information) and different TEOS/PE-PEO-PCL weight ratios at same amount of HCl (Figure S10–S12, and Table S2, Supporting Information). We found 3.5/1/1 to be the best TEOS/PE-PEO-PCL/HCl ratio for constructing an ordered mesophase (Figure S7–S8, Supporting Information). Two similar mesoporous sizes were observed by BET surface analysis. In addition, the SAXS peak of the tetragonal cylinders intensified on increasing the TEOS/E₁₃EO₄₂CL₃₁ ratio (Figure S10, Supporting Information). Hierarchically ordered mesoporous silicas were also observed (Figure S11, Supporting Information) by changing the TEOS/E₁₃EO₄₂CL₃₁ ratio. All of the pore size distribution curves presented two peaks, revealing the fact that two kinds of pore were still present on changing the TEOS/E₁₃EO₄₂CL₃₁ ratio (Figure S12, Supporting Information). All of the textual properties of these samples mentioned above were recorded (Table S1–S2, Supporting Information).

We also studied different molecular weights of PCL in the PE-PEO-PCL triblock copolymers. The nitrogen sorption isotherms of the hierarchical mesoporous silicas behaved like representative type-IV curves with

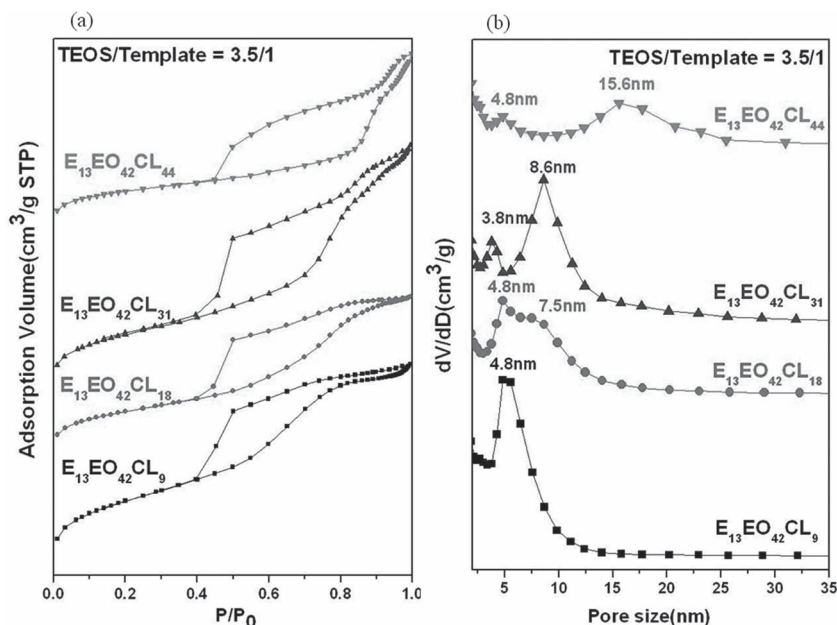


Figure 2. a–b) N₂ adsorption-desorption isotherms (a) and pore-size distribution curves (b) of mesoporous silicas templated by different molecular weight of PCL in PE-PEO-PCL triblock copolymers.

two sharp capillary-condensation steps, as shown in Figure 2A. Clearly, the mean pore sizes measured from the adsorption branch had two kinds of mesopore, as shown in Figure 2B. The smaller mesoporous sizes, attributable to the PE segment, almost did not change; however, the larger mesoporous size, attributable to the PCL segment, increased with increasing PCL molecular weight in the triblock copolymers. This result is consistent with the observations from the TEM images that the small spherical mesopores (≈ 3.8 nm) are attributable to the PE segments, and the large cylindrical mesopores (≈ 8.6 nm) to the PCL segments. The two kinds of mesopore size, the surface areas, the pore volumes and other textual properties measured from the BET analyses and SAXS measurements are presented in Table 1. Clearly, according to the position of the first-order scattering peaks in the SAXS

Table 1. Textual properties of mesoporous silicas templated by different PE-PEO-PCL copolymers at the same TEOS/PE-PEO-PCL weight fraction.

Template	d^a [nm]	Pore Size [nm]	S_{BET}^a [m ² g ⁻¹]	S_{M}^a [m ² g ⁻¹]	Pore Volume [cm ³ g ⁻¹]	Micropore Volume [cm ³ g ⁻¹]	TEOS/ Template
E ₁₃ EO ₄₂ CL ₉	12.6	4.8; 4.8	795	182	0.82	0.078	3.5/1
E ₁₃ EO ₄₂ CL ₁₈	13.9	4.8; 7.5	478	99	0.60	0.042	3.5/1
E ₁₃ EO ₄₂ CL ₃₁	14.0	3.8; 8.6	588	88	0.91	0.035	3.5/1
E ₁₃ EO ₄₂ CL ₄₄	21.0	4.8; 15.6	485	202	0.69	0.091	3.5/1

^aThe d -spacing values were calculated from the primary peak in Figure S13, Supporting Information. S_{BET} and S_{M} are the total BET surface area and the micropore surface area, calculated from the t -plots, respectively.

analyses, the average spacing between the neighboring microdomains, corresponding to the size of the mesoporous domains, systemically increases on increasing the PCL molecular weight in the PE-PEO-PCL triblock copolymers. The morphological transformations of the mesoporous structure, from TEM analyses of PCL with different molecular weights in PE-PEO-PCL triblock copolymers, are still under investigation.

3. Conclusion

In conclusion, we have successfully synthesized hierarchical mesoporous silica that comprised two types of morphology, using an unusual ABC-type triblock copolymer as the template. The appearance of the two kinds of mesopore came from the two hydrophobic segments of the PE-PEO-PCL. To the best of our knowledge, this is the first report to take amphiphilic ABC-type triblock copolymers as a single template to fabricate hierarchical mesoporous silica via the simple EISA method. This PE-PEO-PCL triblock copolymer can be obtained easily through the simple ring opening polymerization method using the cheap and commercially available PE-PEO block copolymer as a macroinitiator. In the future, we will apply our special hierarchical mesoporous silicas to some potential applications, such as catalysis, drug delivery, molecule sensing and separation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: This work was supported financially by the National Science Council, Taiwan, Republic of China, under Contract No. NSC 100-2221-E-110-029-MY3 and NSC-100-2628-E-110-001.

Received: December 19, 2011; Published online: February 21, 2012; DOI: 10.1002/marc.201100857

Keywords: hierarchical structures; mesoporous materials; self-assembly; silicas; triblock copolymers

- [1] a) H. Chen, J. Wydra, X. Zhang, P. S. Lee, Z. Wang, W. Fan, M. Tsapatsis, *J. Am. Chem. Soc.* **2011**, *133*, 12390; b) K. Möller, M. Bein, *Science* **2011**, *333*, 297; c) J. M. Lee, J. Kim, Y. Shin, C. E. Yeom, J. E. Lee, T. Hyeon, B. M. Kim, *Tetrahedron: Asymmetry* **2010**, *21*, 285; d) M. I. Kim, J. Kim, J. Lee, H. Jia, H. B. Na, J. K. Youn, J. H. Kwak, A. Dohnalkova, J. W. Grate, P. Wang, T. Hyeon, H. G. Park, H. N. Chang, *Biotechnol. Bioeng.* **2007**, *96*, 210.
- [2] P. Innocenzi, L. Malfatti, G. A. A. Soler-Illia, *Chem. Mater.* **2011**, *23*, 2501.
- [3] a) P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *282*, 2244; b) S. Tao, J. Yin, G. Li, *J. Mater. Chem.* **2008**, *18*, 4872; c) C. Oh, Y. Baek, S. Ihm, *Adv. Mater.* **2005**, *17*, 270; d) B. Lebeau, C. E. Fowler, S. Mann, C. Farcet, B. Charleux, C. J. Sanchez, *Mater. Chem.* **2000**, *10*, 2105; e) T. Sen, G. J. T. Tiddy, J. L. Casci, M. W. Anderson, *Chem. Mater.* **2004**, *16*, 2044; f) Y. Zhou, M. Antonietti, *Chem. Commun.* **2003**, 2564; g) M. Etienne, S. Sallard, M. Schroder, Y. Guillemin, S. Mascotto, B. M. Smarsly, A. Walcarius, *Chem. Mater.* **2010**, *22*, 3426; h) B. Mandlmeier, J. M. Szeifert, D. Fattakhova-Rohlfing, H. Amenitsch, T. Bein, *J. Am. Chem. Soc.* **2011**, *133*, 17274.
- [4] a) B. Zhao, M. M. Collinson, *Chem. Mater.* **2010**, *22*, 4312; b) D. Kuang, T. Brezesinski, B. Smarsly, *J. Am. Chem. Soc.* **2004**, *126*, 10534; c) O. Sel, S. Sallard, T. Brezesinski, J. Rathousky, D. R. Dunphy, A. Collord, B. M. Smarsly, *Adv. Funct. Mater.* **2007**, *17*, 3241; d) P. Falcaro, L. Malfatti, T. Kidchob, G. Giannini, A. Falqui, M. F. Casula, H. Amenitsch, B. Marmiroli, G. Greci, P. Innocenzi, *Chem. Mater.* **2009**, *21*, 2055; e) F. Guillemot, A. Brunet-Bruneau, E. Bourgeat-Lami, T. Gacoin, E. Barthel, J. P. Boilot, *Chem. Mater.* **2010**, *22*, 2822.
- [5] a) L. Malfatti, M. G. Bellino, P. Innocenzi, G. J. A. A. Soler-Illia, *Chem. Mater.* **2009**, *21*, 2763; b) M. C. Fuertes, G. J. A. A. Soler-Illia, *Chem. Mater.* **2006**, *18*, 2109; c) Z. Li, J. Ma, N. S. Lee, K. L. Wooley, *J. Am. Chem. Soc.* **2011**, *133*, 1228.
- [6] a) X. Li, X. Du, J. He, *Langmuir* **2010**, *26*, 13528; b) X. Guo, Y. Deng, B. Tu, D. Zhao, *Langmuir* **2010**, *26*, 702.
- [7] J. Rodriguez-Hernandez, F. Checot, Y. Gnanou, S. Lecommandoux, *Prog. Polym. Sci.* **2005**, *30*, 691.
- [8] J. Zhang, Y. Deng, J. Wei, Z. Sun, D. Gu, H. Bongard, C. Liu, H. Wu, B. Tu, F. Schuth, D. Zhao, *Chem. Mater.* **2009**, *21*, 3996.
- [9] a) J. G. Li, S. W. Kuo, *RSC Adv.* **2011**, *1*, 1822; b) J. G. Li, Y. D. Lin, S. W. Kuo, *Macromolecules* **2011**, *44*, 9295.
- [10] C. J. Brinker, Y. Lu, A. Sellinger, H. Fan, *Adv. Mater.* **1999**, *11*, 579.
- [11] Y. Deng, Y. Yu, Y. Wan, Y. Shi, Y. Meng, D. Gu, L. Zhang, Y. Huang, C. Liu, X. Wu, D. Zhao, *J. Am. Chem. Soc.* **2007**, *129*, 1690.
- [12] Y. Y. Huang, H. L. Chen, T. Hashimoto, *Macromolecules* **2003**, *36*, 764.
- [13] a) H. L. Chen, J. S. Lu, C. H. Yu, C. L. Yeh, U. S. Jeng, W. C. Chen, *Macromolecules* **2007**, *40*, 3271; b) W. S. Chiang, C. H. Lin, C. L. Yeh, B. Nandan, P. N. Hsu, C. W. Lin, H. L. Chen, W. C. Chen, *Macromolecules* **2009**, *42*, 2304.
- [14] M. Sugiyama, T. A. Shefelbine, M. E. Vigild, F. S. Bates, *J. Phys. Chem. B* **2001**, *105*, 12448.