Shaped Silicas Transcribed from Aggregates of Four-Armed Star Polyethyleneimine with a Benzene Core

Ren-Hua Jin* and Jian-Jun Yuan

Synthetic Chemistry Lab, Kawamura Institute of Chemical Research, 631 Sakado, Sakura,
Chiba 285-0078, Japan

Received March 5, 2006. Revised Manuscript Received April 30, 2006

The formation of shaped silicas directed by a star poly(ethyleneimine) (**sPEI4−200**, with benzene core, four arms, and 200 repeated units per arm) was reported. The resulting silicas were characterized with scanning electronic microscope, optical/fluorescence microscope, and UV−vis and fluorescence spectrometers. We found that the silicas could be controlled into a rich variety of shapes and structures, including nanofiber-based bundles, flowers, films, or plates and continuous silica films, depending on the modulations of polymer concentrations and methanol and tetrakis(4-sulfonylphenyl)porphyrin (TSPP) addition. We further found that the silica directed by the star is remarkably star-specific in comparison with the linear counterpart. Star architecture enhances the parallel aggregation of unit silica fibers and also promotes the ability to form nanofibers. This aggregation enhancement was tentatively proposed to be intramolecular interaction of ethyleneimine segments in star structure associated with a specific conformation distribution of PEI arms tethered at a small benzene core. For silica formation, TSPP-modulation route facilely afforded the porphyrin-functionalized and shaped silicas that are potentially applicable in medical, photonic, electronic, and catalytic fields.

Introduction

Microscale controlled generation with nanostructured inorganic materials or organic/inorganic hybrid composites from the as-formed organized organic templates presents a very promising approach to the fabrication of advanced materials.[1] A good organic template should be rich in developing shapes and structures but also highly efficient in catalytic and/or scaffold functions on template domains for inorganic deposition. The nanofabrication of silicas is intensively attractive, such as mesoporous silicas,[2] organic gelator-directed silica fibers, or tublular[1] as well as hierarchical silicas.[3] However, these controlled syntheses of nanostructured silicas, generally performed at extremes of temperatures, pressures, or pH, face increasing challenges from the view of environmentally benign process. Therefore, biomimetic processing of silicas featuring benign conditions such as ambient temperatures and pressures, as well as near-neutral pH, caused increased attention.[4] One of the most significant challenges currently is how to control biomimetic silicas into precise and multiple shapes and patterns, which has been elegantly accomplished in natural organisms on large scale, such as diatoms and sponges.[5] Most successful works on biomimetic silicas involve the preparation of silica spheres or particles mediated by various organic molecules.[6] By using the polyamines from *Stephanopyxis turris* consisting of 15−21 *N*-methylpropyleneimine repeating units attached to putrescine, Sumper et al.[7] found that the diameters of silica spheres could be controlled from 30 to 700 nm by phosphate concentrations. Knecht et al.[8] are able to control the dimensions of silica spheres from 30 to 300 nm by using amine-terminated dendrimers as templates. Furthermore, some approaches have been developed for the preparation of complex silicas. Cha et al. reported that silica columns[9] could be formed by designing the peptides into block architecture and silica fibers[10] could be formed by using silicatein filaments and subunits. Stone et al.[11] and Clarson et al.[12] demonstrated the formation of complex silicas by applying physical fields, using additives, or changing the size

---

* To whom correspondence should be addressed. Fax: +81-43-498-2202. E-mail: jin@kicr.or.jp.

(1) van Bommel, K. J. C.; Friggeri, A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980−999.

(2) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712. (b) Zhao, D. Y.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka B. F.; Stucky, G. D. *Science* **1998**, *279*, 548−552.

(3) (a) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692−695. (b) Ozin, G. A. *Acc. Chem. Res.* **1997**, *30*, 17−27. (c) Sokolov, I.; Yang, H.; Ozin, G. A.; Kresge, C. Y. *Adv. Mater.* **1999**, *11*, 636−642. (d) Wang, J. C.; Tsung, K.; Hayward, R. C.; Wu Y.; Stucky, G. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 332−336, and references therein.

(4) (a) Morse, D. E. *Trends in Biotechnol.* **1999**, *17*, 230−232. (b) Sumper M.; Kroger, N. *J. Mater. Chem.* **2004**, *14*, 2059−2065. (c) Sun, Q.; Vrieling, E. G.; van Santen R. A.; Sommerdijk, N. A. J. M. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8*, 111−120.

(5) Muller, W. E. G., Ed. *Silicon Biomineralization: Biology-Biochemistry-Molecular-Biology-Biotechnology*; Springer: Berlin, 2003.

(6) (a) Knecht, M. R.; Wright, D. W. *Chem. Commun.* **2003**, 3038−3039. (b) Coradin, T.; Durupthy, O.; Livage, J. *Langmuir* **2002**, *18*, 2331−2336. (c) Patwardhan, S. V.; Clarson, S. J. *Silicon Chemistry* **2002**, *1*, 207−214. (d) Knecht, M. R.; Wright, D. W. *Langmuir* **2004**, *20*, 4728−4732. (e) Belton, D.; Paine, G.; Patwardhan, S. V.; Perry, C. C. *J. Mater. Chem.* **2004**, *14*, 2231−2241. (f) Vrieling, E. G.; Beelen, T. P. M.; van Santen R. A.; Bieskes, W. W. C. *Angrew. Chem., Int. Ed.* **2002**, *41*, 1543−1546.

(7) Sumper, M.; Lorenz, S.; Brunner, E. *Angrew. Chem., Int. Ed.* **2003**, *42*, 5192−5195.

(8) Knecht, M. R.; Sewell S. L.; Wright, D. W. *Langmuir* **2005**, *21*, 2058−2061.

(9) Cha, J. N.; Stucky, G. D.; Morse D. E.; Deming, T. J. *Nature* **2000**, *403*, 289−292.

(10) Cha, J.; Stucky, G. D.; Morse, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 361−365.

10.1021/cm060533s CCC: $33.50

of the polypeptides. In addition, the studies from the Sumper group[13] showed the formation of roughly hexagonal silica structures when using polyamine-stabilized sol as silicon source in place of silicic acid.

Synthetic polymers with defined architectures are very useful in self-assembly for developing shaped and patterned structures[14−19] and have been exploited for the controlled fabrication of various inorganic materials.[18,19] Star polymers are of particular interest among tailored polymers, as they show attractive and mysterious architecture-dependent behavior in bulk and solution.[20,21] Recently, a wealth of self-assembled objects have been obtained by virtue of the star architecture with various polymer backbones.[22−28] However, it is rare that the self-assembled star polymers was used for synthesis of shape-controlled inorganic materials. We have shown that a silica−poly(oxazoline) composite with nano-sized hollows and porphyrin moieties could be fabricated via mediation of a star poly(oxazoline) possessing porphyrin core.[29] Our interest in biomimetic silica is to develop a self-organized polymer system for silica deposition featuring both ambient-condition processing and controlled generation of multiple shapes and hierarchical structures. In the biomimetic silica synthesis, one important event is how to promote species-specific function of organic amine molecules for silica deposition. Although many synthetic polyamines are utilizable for rapid silica deposition, they are not effective in silica architecture, because the polyamines do not show special conformations in aqueous media. Different from the many synthetic polyamines, including randomly branched polyethyleneimine (b-PEI), linear polyethyleneimine (PEI) possessing only secondary amine residues in the backbone has specific all-trans zigzag conformation in aqueous media and thus easily forms ordered aggregates.[28] We found that the organized aggregates of linear PEI are capable of directing silicas into multiple morphologies with hierarchical structures, in which the hydrolytic condensation of alkoxysilane occurred exclusively and rapidly around the PEI aggregates under ambient conditions.[30,31] This process seems to mimic to the biosilica formation. It was found that various parameters, including polymer architectures, concentrations, media, additives, and physical fields, could be facilely used for the shape and structure control of silica.[30,31] One of fascinating results is that star-architecture PEI could direct remarkably different silica compared with the linear counterparts.[30] The silica shapes are strongly dependent on the parameters of star architectures, such as the number of arms and core size. Four-armed porphyrin-core PEI produces asterlike silica, while six-armed benzene-core PEI gives silica with fiber−sponge morphology.[30] When using linear PEI as mediator for silica deposition, the photofunctional additive such as tetrakis(4-sulfophenyl)porphyrin (TSPP) can effectively switch the resulting silica morphology via association between PEI and TSPP to give particularly shaped silica with fluorescency.[31] To further exploit the formation of shaped silicas by virtue of star architecture in detail, herein, we selected a four-armed star PEI (**sPEI4−200**) with a small benzene core and adopted such factors as polymer concentrations, methanol modulation, and TSPP additives to control silica shapes and structures with additional photofunctional feature. We found that the star polymer is capable of self-organizing into aggregates with multiple and controllable shapes and structures under various conditions, and thus, the self-organized aggregates directed shaped silica along the programmed code.

Results and Discussion

Silicas directed by organized PEIs could be controlled into a wide variety of structures and morphologies at ambient conditions. One of the important merits of this unique approach is that various silicas are available through simple modulations such as polymer concentrations, media, and

---

(11) (a) Rodriguez, F.; Glawe, D. D.; Naik, R. R.; Hallinan, K. P.; Stone, M. O. *Biomacromolecules* **2004**, *5*, 261−265. (b) Naik, R. R.; Whitlock, P. W.; Rodriguez, F.; Brott, L. L.; Glawe, D. D.; Clarson S. J.; Stone, M. O. *Chem. Commun.* **2003**, 238−239. (c) Naik, R. R.; Brott, L. L.; Rodriguez, F.; Agarwal, G.; Kirkpatrick, S. M.; Stone, M. O. *Prog. Org. Coatings* **2003**, *47*, 249−255.

(12) Patwardhan, S. V.; Mukherjee, N.; Steinitz-Kannan, M.; Clarson, J. *Chem. Commun.* **2003**, 1122−1123.

(13) Sumper, M. *Angrew. Chem., Int. Ed.* **2004**, *43*, 2251−2254.

(14) (a) Discher, D. E.; Eisenberg, A. *Science* **2002**, 297, 967−973. (b) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525−557.

(15) Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, *277*, 1225−1232.

(16) (a) Fischer, M.; Vogtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (b) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449−452. (c) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Moller M.; Sheiko, S. S. *Nature* **1998**, *391*, 161−164. (*d*) Tomioka, N.; Takasu, D.; Takahashi T.; Aida, T. *Angew. Chem., Int. Ed.* **1998**, *37*, 1531−1534. (*e*) Jang, W.-D.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **2000**, *122*, 3232−3233.

(17) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039−4070.

(18) Liu, T.; Burger, C.; Chu, B. *Prog. Polym. Sci.* **2003**, *28*, 5−26.

(19) (a) Lazzari, M.; López-Quintela, M. A. *Adv. Mater.* **2003**, *15*, 1583−1594. (b) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195−217.

(20) (a) Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453−571. (b) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747−3792.

(21) (a) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484−485. (b) Robello, D. R.; Yamaguchi, N.; Blanton, T.; Barnes, C. *J. Am. Chem. Soc.* **2004**, *126*, 8118−8119.

(22) (a) Widawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387−389. (b) Stenzel-Rosenbaum, M. H.; Davis, T. P.; Fane, A. G.; Chen, V. *Angew. Chem., Int. Ed.* **2001**, *40*, 3428−3432. (c) Connal, L. A.; Gurr, P. A.; Qiao, G. G.; Solomon, D. H. *J. Mater. Chem.* **2005**, *15*, 1286−1292.

(23) Li, Z.; Kesselman, E.; Talmon, Y.; Hillmyer, M. A.; Lodge, T. P. *Science* **2004**, *306*, 98−101.

(24) (a) Genson, K. L.; Hoffman, J.; Teng, J.; Zubarev, E. R.; Vaknin, D.; Tsukruk, V. V. *Langmuir* **2004**, *20*, 9044−9052. (b) Peleshanko, S.; Jeong, J.; Gunawidjaja, R.; Tsukruk, V. V. *Macromolecules* **2004**, *37*, 6511−6522. (c) Peleshanko, S.; Gunawidjaja, R.; Jeong, J.; Shevchenko, V. V.; Tsukruk, V. V. *Langmuir* **2004**, *20*, 9423−9427. (d) Peleshanko, S.; Jeong, J.; Shevchenko, V. V.; Genson, K. L.; Pikus, Y.; Ornatska, M.; Petrash, S.; Tsukruk, V. V. *Macromolecules* **2004**, *37*, 7497−7506.

(25) Tsitsilianis, C.; Alexandridis, P.; Lindman, B. *Macromolecules* **2001**, *34*, 5979−5983.

(26) Yu, X.; Fu, J.; Han, Y.; Pan, C. *Macrom. Rapid Commun.* **2003**, *24*, 742−747.

(27) (a) Jin, R.-H. *Adv. Mater.* **2002**, *14*, 889−892. (b) Jin, R.-H. *ChemPhyChem* **2003**, *4*, 1118−1121. (c) Jin, R.-H. *Macromol. Chem. Phys.* **2003**, *204*, 403−409. (d) Jin, R.-H. *J. Mater. Chem.* **2003**, *13*, 672−675.

(28) Yuan, J. J.; Jin, R.-H. *Langmuir* **2005**, *21*, 3136−3145.

(29) (a) Jin, R.-H. *Chem. Commun.* **2002**, 198−199. (b) Jin, R.-H. *J. Mater. Chem.* **2004**, *14*, 320−327.

(30) (a) Jin, R.-H.; Yuan, J. J. *Chem. Commun.* **2005**, 1399−1401. (b) Jin, R.-H.; Yuan, J. J. *Macromol. Chem. Phys.* **2005**, *206*, 2160−2170. (c) Yuan, J.-J.; Zhu, P.-X.; Fukazawa, M.; Jin, R.-H. *Adv. Fucnt. Mater.*, accepted for publication.

(31) Yuan, J. J.; Jin, R.-H. *Adv. Mater.* **2005**, *17*, 885−888.

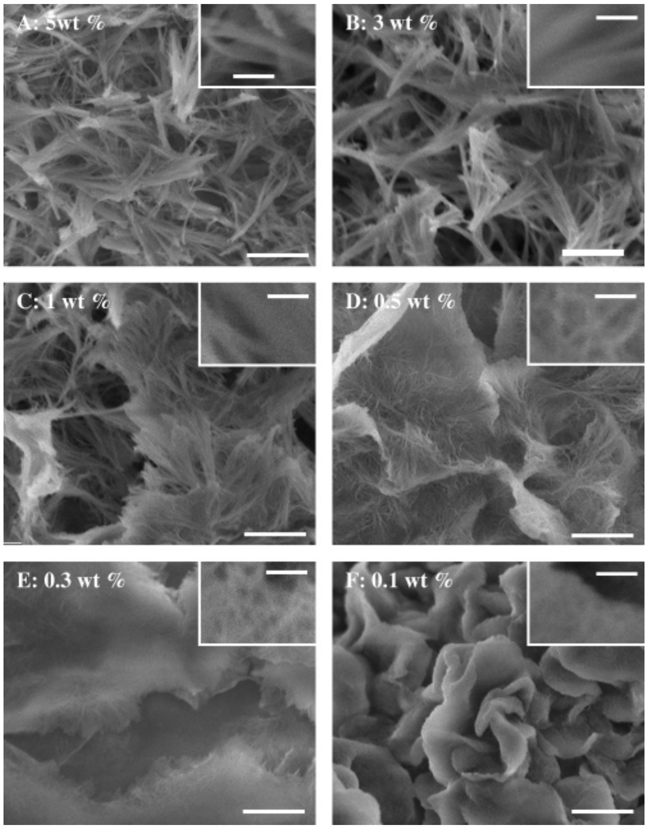

Figure 1. SEM images of silicas mediated from various concentrations of **sPEI4−200** in neat water as media. The silicas of A, B, C, D, E, and F were mediated from the polymer concentrations of 5, 3, 2, 1, 0.5, 0.3, and 0.1%, respectively. The bars are 5 μm (500 nm for inset).

additives.[30,31] These modulation routes, originating from the adjustment of PEI crystalline and/or aggregation, enable a facile availability to multiply shaped silicas by using only simple PEI macromolecule. For **sPEI4−200**-mediated hydrolytic condensation of TMOS (tetramethoxysilane), the three typical and high-efficiency modulation methods, polymer concentrations, methanol participation, and TSPP addition, were employed for examining the shape-controlled silica formation.

Polymer Concentrations. PEI concentration is a very simple factor to regulate the silica shapes. As shown in Figure 1, the morphologies and structures of the silica obtained from hydrolytic condensation of TMOS depend clearly upon **sPEI4−200** concentrations. The silicas produced under concentrations of 5, 3, and 1% showed bundle shape with unit nanofiber structure (Figure 1A−C and insets, respectively). The silica mediated from the lower concentration of the star (1%) has the bundles with an increasing expanding degree relative to that from higher concentrations of the star (3 and 5%). As the concentration of **sPEI4−200** decreased to 0.5%, very large and curved silica films appeared (Figure 1D), and these films are clearly composed of unit nanofibers (Figure 1D inset). Furthermore, 0.3% concentration of the star also resulted in filmlike silica (Figure 1E), but the unit nanofibers became less clear (Figure 1E and inset) in comparison with that from the 0.5% concentration (Figure 1D and inset). In addition, we found that very low concentration, i.e., 0.1% **sPEI4−200**, still was able to aggregate and deposit silica into thick films with highly fused and aggregated form (Figure 1F). These films seem to be thicker than that from the higher concentrations (0.3 and 0.5%), and we did not observe unit fiber structure in the thicker films (Figure 1F inset). We assume that the lower concentration of the star elevates the quantity of brushlike free PEI segments on the surface of the crystalline PEI fiber (free PEI to crystalline PEI)[30c] and thus would result in loose PEI aggregates that lead to the silica films with increased thickness. The similar tendency was also observed when using a simple linear PEI for the investigation of silica shape dependence on polymer concentrations.[31]

However, it is worthy to note that **sPEI4−200** exhibits a prominent difference of silica shape dependence on polymer concentrations as compared with the linear counterpart. For example, the silicas from 1% **sPEI4−200** have fiber bundle shape (Figure 1C), whereas the linear PEI-directed silicas with the same concentration expand to leaf- or filmlike shape.[31] Moreover, the silica bundles from 3% **sPEI4−200** (Figure 1B) appear dense in their structures in comparison with those from linear PEI.[31] Obviously, **sPEI4−200** with a star architecture has a relatively higher tendency to form silica with the fiber bundle shape with dense structure, which would be resulted from the parallel aggregation of the unit nanofibers. It should be quite interesting to address why such star-specific organization appears. Different than linear PEI, the PEI arms in **sPEI4−200** are closely tethered on a very small benzene core. This chain architecture may give rise to a specific conformational distribution of PEI arms, a rigid rodlike region near the core center, followed by a flexible-rod region, and then a continuous random-polymer region.[27d,32] Therefore, the monomer unit density is very high near the benzene core center. Here, for **sPEI4−200**, we propose that the conformational distribution due to star architecture imparts a specific intramolecular interaction between arms, which probably enhances the nanofiber aggregation in parallel when the polymer organizes.

Methanol Modulation. Among normal solvents, it was observed that only methanol is capable of dissolving hydrate crystalline PEI at room temperature. Mixing a methanol solution of PEI with water with an appropriate volume ratio and polymer concentration allows PEI to organize into controlled shapes and structures and subsequently directs the corresponding silicas under ambient conditions.[30b,31] This methanol-modulation approach enriched the shape generation of silicas and also is potentially valuable in terms of ambient processing of PEI aggregates, which would be of particular interest in view of applications such as bioactive component immobilization and surface patterning of silicate-based materials.

Selecting three polymer concentrations, 0.5, 0.3, and 0.1%, we comparatively examined the effect of methanol modulation on the silica shapes from **sPEI4−200**. Figure 2 shows the SEM images of the resulting silicas. When polymer concentration is 0.5%, a medium with 50% methanol content gave rise to fanlike silicas with very close aggregation structure of unit fibers (Figure 2A,B). This shape is in sharp contrast to that formed in neat water (Figure 1D). Decreasing

---

(32) Ronis, D. *Macromolecules* **1993**, *26*, 2016−2024.

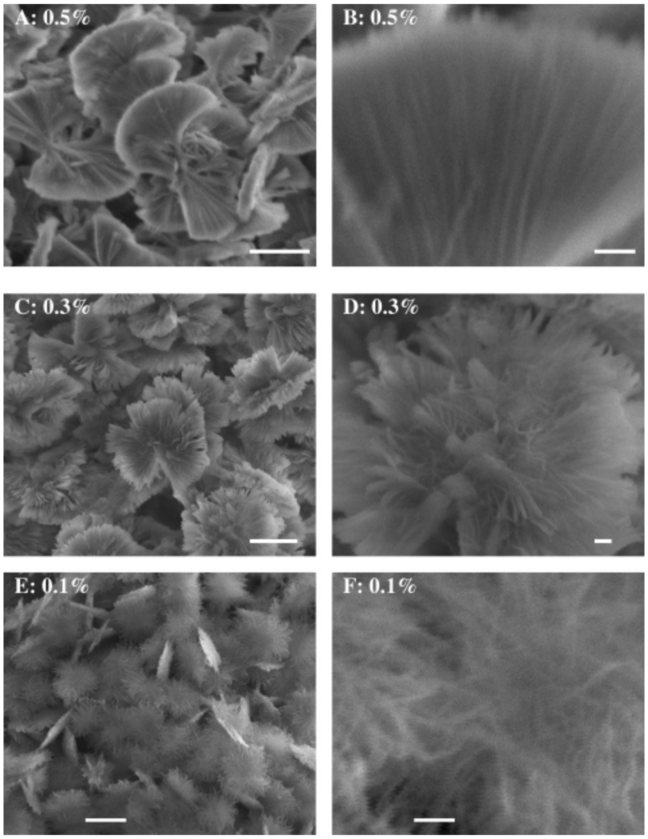

Figure 2. SEM images of silicas from the modulation of methanol. The silicas of A/B, C/D, and E/F were mediated from the polymer concentrations of 0.5, 0.3, and 0.1% and the methanol content in media of 50, 30, and 10%, respectively. B, D, and F are magnified versions of A, C, and E, respectively. The bars are 5 μm for A, C, and E and 500 nm for B, D, and F.

the polymer concentration to 0.3%, **sPEI4−200** in a medium with 30% methanol content directed fanlike silicas with relatively looser aggregation structures and flowerlike shape with looser petals (Figure 2C,D). In contrast, only fiber-based silica films formed when using neat water as media (Figure 1E). The silica that resulted from a medium of 10% methanol and 0.1% concentration of **sPEI4−200** showed plates with clear elemental fibers (Figure 2C,D). This is different than the case of the neat water media, which caused the thicker silica films with invisible fibrous structures (Figure 1F). To confirm the precise transcription of silica shapes from the polymeric aggregates, we visualized the star aggregates by optical microscopy. As shown in Figure 3, the polymer aggregates changed their shapes from fanlike to flowerlike upon decreasing the polymer concentrations from 0.5 to 0.1%. These shape changes are highly consistent with the corresponding silicas. Accordingly, it is conclusive that the preorganized aggregates of the star determine the corresponding silica structures. This tendency seems very strong for the star polymer.

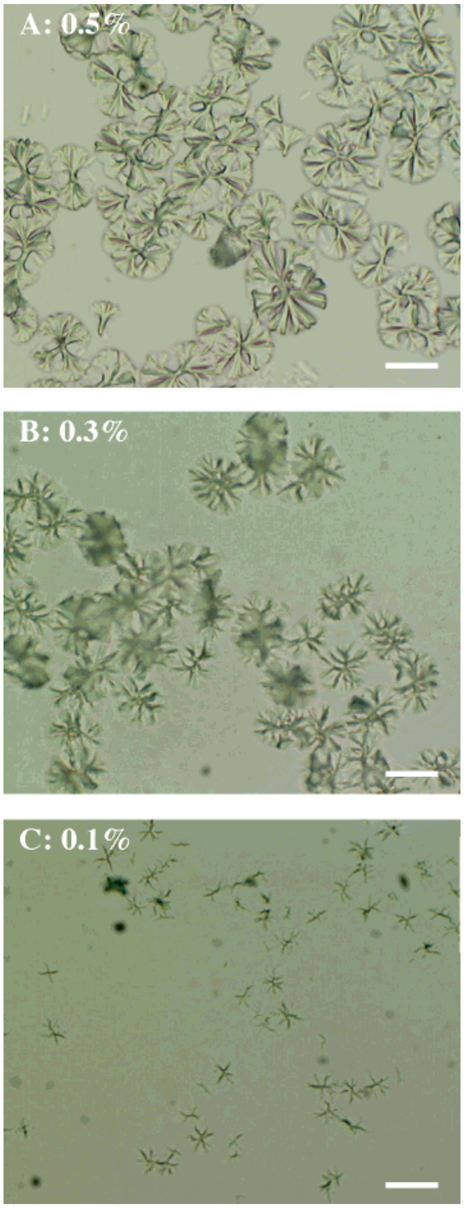

Figure 3. Optical microscope images of **sPEI4−200** aggregates from the modulation of methanol before silica deposition. The aggregates of A, B, and C are from the polymer concentrations of 0.5, 0.3, and 0.1% and the methanol content in media of 50, 30, and 10%, respectively. The bars are 10 μm.

The above comparative results of silica morphologies clearly suggest that the methanol modulation prominently enhances the radial and/or parallel aggregation of unit fibers. Perhaps, the nucleation of the PEI crystalline was retarded greatly due to the presence of methanol and thus the growth of the crystalline was suppressed within smaller domains. This slow and suppressed aggregation and/or crystallization process would be favorable to exclusively form a quite ordered morphology. Experimentally, aggregate formation in neat water media took several minutes when cooling the hot solution of **sPEI4−200**, whereas the complete aggregation in the methanol-modulation process usually takes several hours, especially for those systems with higher methanol contents (e.g., 50%).

In the methanol modulation, the polymer concentrations and methanol contents are two important factors to regulate the silica formation. To further examine these two factors, we performed silica deposition from the aggregates with 0.3% concentrations of **sPEI4−200** in the media containing 50% methanol. This system has a low polymer concentration relative to the silica formation shown in Figure 2A,B (0.5% concentration and 50% methanol content) and has a raised methanol content compared with silicas in Figure 2C,D (0.3% concentration and 30% methanol content). As seen in Figure 4, thinner and closer fiber bundles were observed, and some

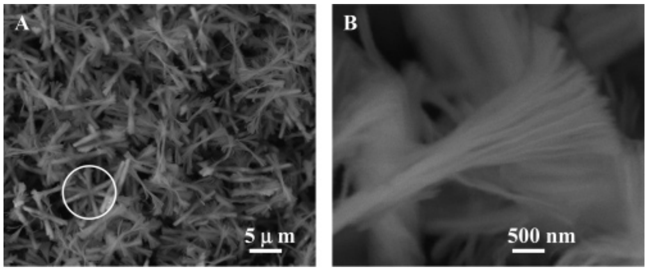

Figure 4. SEM images of silicas from a precursor solution containing 0.3% polymer concentration and 50% methanol. B is a magnified image of the circled region of A.

bundles aggregated into dendritic shape (circular mark in Figure 3A). It is likely that decreasing polymer concentrations from 0.5% (Figure 2A,B) to 0.3% (Figure 3A,B) or increasing methanol content from 30% (Figure 2C,D) to 50% (Figure 3A,B) make silica bundles thinner and smaller. This probably arises from a slower crystalline process due to lower polymer concentration or higher methanol content.

TSPP Modulation. Incorporation of porphyrin residues with **sPEI4−200** for silica formation is of particular interest in terms of the acquirement of both photofunctionalization and direction of silica shape. Compared with using porphyrin-cored star PEI, the synthesis of which is costly,[33] promoting a template by association of TSPP with **sPEI4−200** through hydrogen-bonding interaction is a facile approach to constructing functionalized and shaped silica. By selecting polymer concentrations and methanol contents the same as the above-mentioned methanol modulation, we are able to validate the roles of TSPP in the silica formation. Figure 5 shows fluorescent microscope images of aggregates of the star incorporated with TSPP in different polymer concentrations and methanol content. The aggregates with a shaped morphology are nicely luminescent under fluorescent microscope due to the porphyrin moieties, and no fluorescence appeared from the solution phase. This strongly indicates that TSPP was efficiently embedded in the PEI aggregates. These morphologies seem similar to those that appeared without TSPP, as shown in Figure 3. We performed silica deposition on these TSPP-associated aggregates. The silica obtained showed clear variation in shapes (Figure 6). The case of higher polymer concentration (0.5%) and methanol content (50%) resulted in larger silica particles in which some of particles are in fan- or flowerlike shapes (Figure 5A,B). Decreasing polymer concentration and methanol content to 0.3% and 30%, respectively, led to the formation of silicas with platelike and flowerlike shape (Figure 5C,D). As the polymer concentration and methanol content further decreased to 0.1% and 10%, respectively, relative uniform silica plates were observed (Figure 5E,F). Compared with the silica formation without TSPP (Figure 2), the TSPP regulation decreased the uniformity of silica formation; this can be seen especially in the system with higher methanol content (e.g., 50%). Also, the order of the radial or parallel aggregation deteriorated upon the TSPP encapsulation. On the other hand, in contrast to the TSPP-modulated silica deposition by a linear PEI that resulted sphere-based silica network under the conditions of 0.5% polymer concentration and 50% methanol content,[31] **sPEI4−200** directed the complexly structured silica particles under same conditions, in which some were observed to be composed of unit nanofibers (Figure 5A,B). It is remarkable that the star architecture prominently promotes the formation of fibrous silica structure. This is further proof that PEI star architecture is favorable to form polymeric unit fibers that grow into radial and/or parallel aggregates due to the specific conformation distribution of star PEI.[27d,32]

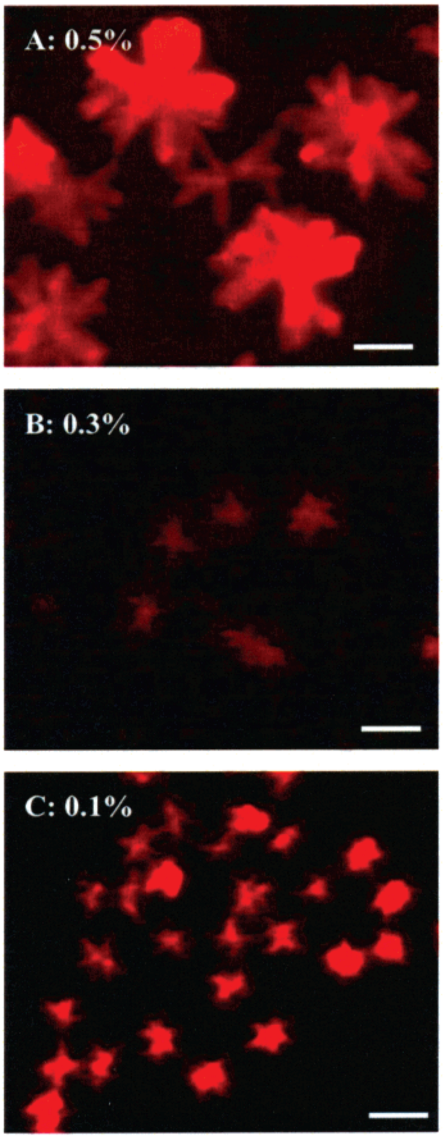

Figure 5. Fluorescence micrographs of **sPEI4−200** aggregates from the modulation of TSPP. The aggregates of A, B, and C were from the polymer concentrations of 0.5, 0.3, and 0.1% and the methanol content in media of 50, 30, and 10%, respectively. The molar ratio of ethyleneimine units to TSPP is 1200/1 for the three cases. The bars are 2 μm.

In addition to the shape-directed feature of TSPP modulation, another important feature of these shaped silicas is that they are simultaneously functionalized with chromophore, due to the entrapment of porphyrin residues. The silicas are luminescent and observable by fluorescent microscope (insets of Figure 5A,C,E). By casting the silica particles dispersed in ethanol on quartz substrate, we measured their fluorescence spectra. As can be seen in Figure 7, three silicas show

---

(33) Jin, R.-H.; Motoyoshi, K. *J. Porphyrins Phthalocyanines* **1999**, *3*, 60−64.

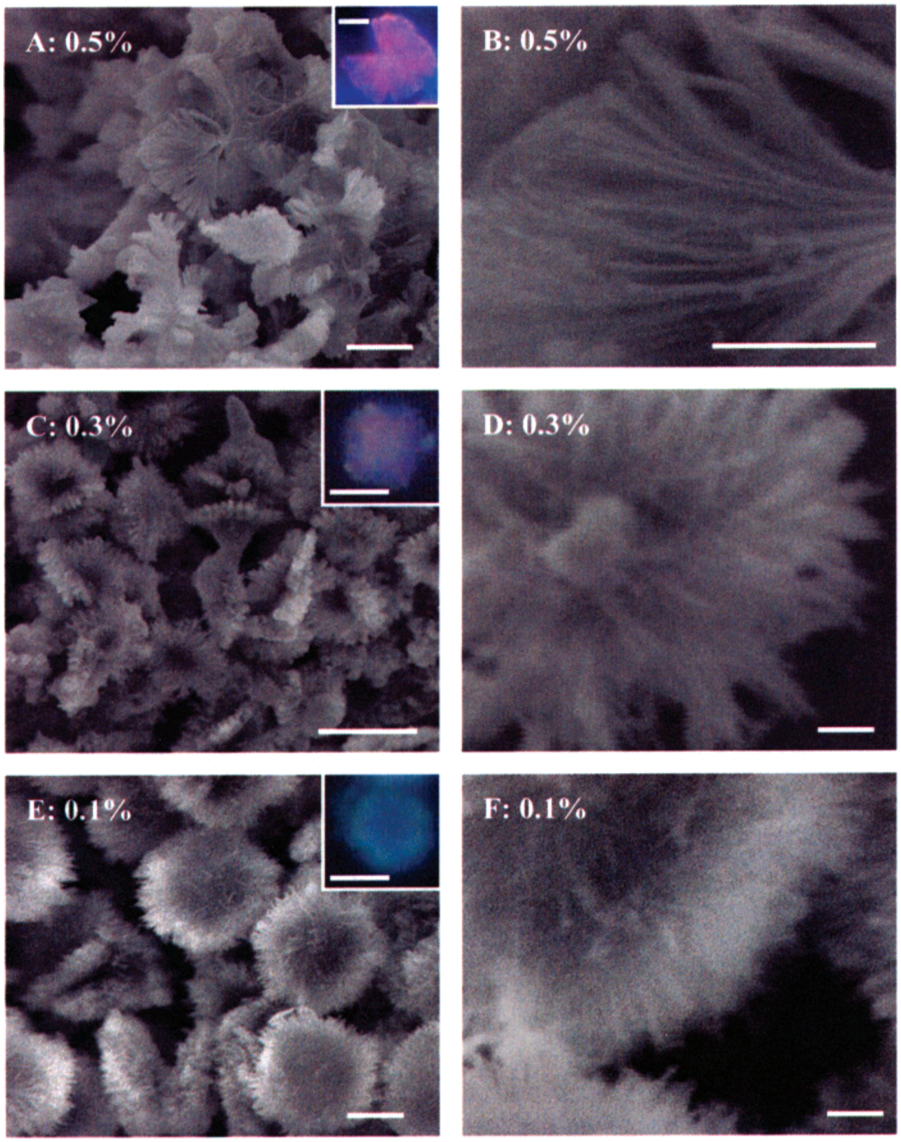

Figure 6. SEM images of silicas from the modulation of TSPP. The molar ratio of ethyleneimine units to TSPP is 1200/1 for three cases. The silicas of A/B, C/D, and E/F were mediated from the polymer concentrations of 0.5, 0.3, and 0.1% and the methanol content in media of 50, 30, and 10%, respectively. B, D, and F are magnified versions of A, C, and E, respectively. The insets are fluorescence micrographs of the corresponding silicas. The bars are 5 μm for A, C, and E; 500 nm for B, D, and F; and 2 μm for insets, respectively.

the typical emission at ~653 nm under excitation at 410 nm due to porphyrin moieties. To elucidate the state of TSPP in the resulting silicas, we compared the UV−vis spectra between the silica and the methanol solution containing TSPP and **sPEI4−200** (Figure 8). It is obvious that the spectroscopic line from the TSPP-trapped silicas appears without remarkable changes compared to that from the methanol solution. This is very different than the case of the TSPP-entrapping silica obtained from linear PEI, in which the Soret band became broader with a slight red shift and the Q-bands also shifted toward longer wavelength.[31] We think that TSPP entrapped in the star-directed silica exists in an isolated state but not in the π−π stacked form. Probably, the interaction fashion of TSPP with the star PEI is strong, so that the initial location of TSPP in the star aggregates remained even as the silica deposition proceeded around the aggregates' domain. The fact that the shapes of the aggregates containing TSPP retain entirely after silicification also means that the

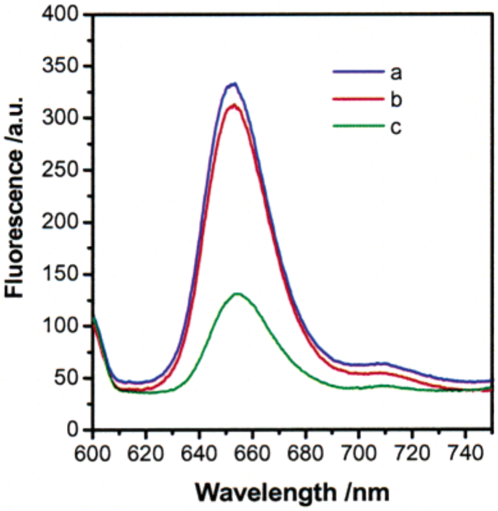

Figure 7. Fluorescence spectra of shaped silicas. Spectra a, b, and c correspond to the silicas shown in Figure 6, parts A, C, and E, respectively.

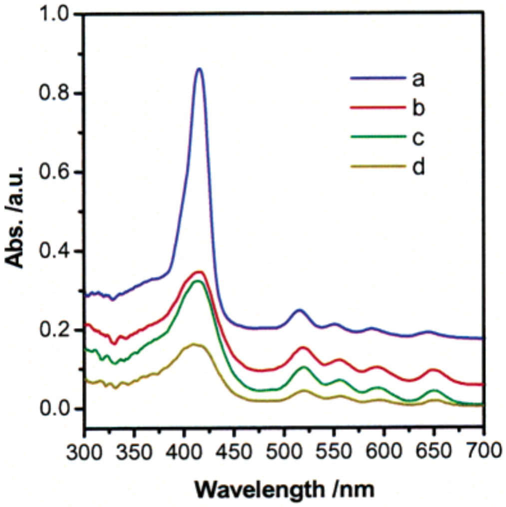

Figure 8. UV−vis spectra of porphyin residues (a) from the methanol solution of **sPEI4−200** and TSPP and (b, c, and d) from the silicas shown in Figure 6, parts A, C, and E, respectively.

TSPP is capable of fixing its state in silica as in the aggregates.

Conclusions

In summary, we have demonstrated that the star **sPEI4−200** is capable of directing the biomimetic formation of silicas with a rich spectrum of shapes and structures by the facile modulations of polymer concentrations, methanol, and TSPP addition. The silicas could be shaped into the nanofiber-based bundles, flowers, films or plates, and continuous films. The comparative examination of silica shapes and structures between linear and star PEIs indicates that the silica formation remarkably exhibits the star-specific character. The star architecture dramatically enhances the parallel aggregation of unit fibers and also promotes the fiber aggregation ability as compared with the linear architecture. This interesting enhancement of aggregation may result from the intramolecular interaction of ethyleneimine segments in a star structure, probably arising from the specific conformation distribution of PEI backbone tethered to a small benzene core.[27d,32] For silica deposition, the methanol-modulation route enables both the processing of precursor aggregates and silicification to be performed under ambient conditions, which is potentially important for bioactive component immobilization as well as silicate−materials patterns. Moreover, TSPP-modulation silicas are simultaneously functionalized with porphyrin moieties, affording composite materials applicable in medical, photonic, electronic, and catalytic fields.

Experimental Section

Synthesis of sPEI4−200. The four-armed star **PEI** was produced from hydrolysis of the corresponding poly(oxazoline) precursor in the presence of HCl. The precursor four-armed star poly(methyloxazoline) (PMOZ) was prepared by performing a ring-opening living polymerization of 2-methyl-2-oxazoline (MOX, Aldrich) in DMA (*N*,*N*-dimethylacetamide) using 1,2,4,5-tetrakis(bromomethyl)benzene (TKBB, Aldrich) as a initiator. Typically, TKBB (0.068 g, 0.15 mmol) was first added to a flask equipped with a three-way stopcock and a magnetic bar, and the flask was vacuumed for 2 h and purged with dried N_2. Then, 10 mL of MOX (120 mmol) and 20 mL of DMA were subsequently added by syringe under N_2 flow. The reaction mixture was first stirred at 60 °C for 1 h for dissolution of initiator, and then the polymerization was carried out at 100 °C for 24 h. The ^{1}H NMR measurement of a small amount of polymerization mixture in $CDCl_3$ showed that MOX completely converted into the corresponding polymer. After polymerization, the mixture was poured into ethyl acetate (500 mL) for precipitation. The obtained polymer was dried under vacuum at 60 °C. The polymerization degree of per arm was estimated to be 200 from quantitative polymerization by feeding ratio. The GPC trace showed M_w 11 800 and M_w/M_n 1.48 relative to PEG/PEO standard using a solution of 0.1 M NaCl in MeOH/H_2O (5/5 vol) as eluent.

For hydrolysis reaction, 5 g of the above star PMOZ was dissolved into 38 mL of 5 M HCl, and the mixture was stirred at 100 °C for 12 h. The white precipitate (associated with HCl) that appeared was filtered and washed by acetone. The obtained solid was dissolved into water and subsequently dialyzed against an ammonia solution (pH = 11−12) for 3 days upon changing the ammonia solution three times. The crystalline **sPEI4−200** (free base) was washed with acetone and then dried. Typically, this procedure resulted in hydrated crystalline PEI containing about 16−20 wt % water estimated from TGA measurement.

Preparation of sPEI4−200 Aggregates. Aggregates formed in pure aqueous media were prepared by dissolving a definite amount of **sPEI4−200** into 1 mL of distilled water at 80 °C and then cooling the hot solutions to room temperature naturally. For methanol or methanol/TSPP modulations, a stock solution containing **sPEI4−200**, methanol, and/or TSPP was prepared first. The stock solution of **sPEI4−200** in methanol was prepared by dissolving polymer in methanol at room temperature with desired concentrations. The stock solution containing the desired quantity of **sPEI4−200** and TSPP in methanol was prepared by heating the mixture at 80 °C for 3 h. Polymer aggregates were made by mixing the stock solution with distilled water with a desired volume ratio. The mixture was kept under room temperature and static conditions for 24 h for the organization of **sPEI4−200** aggregates before silica deposition.

Silica Deposition. The silica deposition was facilely performed by adding the silica source into the aggregate solution. Typically, a solution (1 mL) of as-prepared PEI aggregates was suspended into a mixture (2 mL) containing TMOS and ethanol with 1/1 volume ratio, and the mixture was placed at room temperature for 40 min. For aggregates formed in water with polymer concentrations of >2% (e.g., 3, 4, and 5%), 4 mL of silica source containing 2 mL of TMOS and 2 mL of ethanol was used. The silica particles were washed three times with ethanol and centrifuged (16 000 rpm for 5 min). After being dried, final silica powders were obtained.

Characterization. The silica morphologies were viewed by a Keyence VE7800 scanning electron microscope (SEM). The morphology of **sPEI4−200** aggregates and fluorescence images of porphyrin-encapsulated silicas was visualized with a video-enhanced optical microscope (Olympus BX-60 equipped with a CB-300Z/OL digital camera). For imaging the PEI aggregate, a small volume of aggregate dispersion was softly pasted on a glass slide and observation was performed the in wet state. The electrospectroscopic properties of porphyrin residues under various environments were characterized with a Hitachi U-3500 UV−vis spectrometer and Hitachi F4500 fluorescence spectrometer. The UV−vis spectra were recorded with an integration spherical attachment.

CM060533S