DOI: 10.1002/ange.200600029

Crystallization in a Mixture of Solvents by Using a Crystal Modifier: Morphology Control in the Synthesis of Highly Monodisperse $CaCO_3$ Microspheres**

Xiao-Hui Guo, Shu-Hong Yu, and Guo-Bing Cai*

Bio-inspired morphosynthesis of inorganic and inorganic/organic composite materials by using a self-organized organic superstructure, organic additives, and/or templates with special functionalization patterns has attracted considerable attention.[1,2] One of the most intensively investigated systems is calcium carbonate, which is not only one of the most abundant biomaterials in nature but also has industrial application as a filler in paints, plastics, rubber, and paper.[3] Bio-inspired synthesis of crystals with complex forms that mimic natural biominerals in the presence of an organic template or additives has been intensively developed over the years.[2,4–6] Proteins were extracted from mollusc shell layers and used for the conformation-dependent control of the morphology of calcium carbonate.[6,7] Furthermore, self-assembled two-dimensional protein layers can play a key role in biomineralization. For example, a polypeptide structure may be associated with the $CaCO_3$ polymorph or morphology, in which the transformation of aragonite and calcite is coupled with the altering of a secondary structure of the polypeptide used.[8,9] Moreover, the sequences and conformation of proteins or mineral tissues were also used for the mediation of nucleation and crystal structure of calcium carbonate.[10]

In 1998, a class of so-called double-hydrophilic block copolymers (DHBCs) was introduced for the controlled crystallization of various compounds.[11] Nanocrystalline building blocks can be stabilized, at least temporarily, and

---

[*] X.-H. Guo, Prof. Dr. S.-H. Yu, G.-B. Cai
Division of Nanomaterials and Chemistry
Hefei National Laboratory for Physical Sciences at Microscale
School of Chemistry and Materials
University of Science and Technology of China
Hefei 230026 (P.R. China)
Fax: (+86) 551-360-3040
E-mail: shyu@ustc.edu.cn

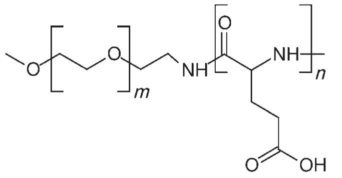
[**] We acknowledge the special funding support from the Centurial Program of the Chinese Academy of Sciences, the National Natural Science Foundation of China (NSFC, Nos. 20325104, 20321101, 50372065) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the Specialized Research Fund for the Doctoral Program (SRFDP) of Higher Education State Education Ministry, the Partner Group of the Chinese Academy of Sciences, and the Max Planck Society. We genuinely thank PD. Dr. habil. H. Cölfen and Prof. Dr. M. Antonietti for donating the block copolymers and for the long-standing and enjoyable collaboration in the area of biomimetic mineralization.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

then used for mesoscale transformation into complex morphologies.[5,12–14] The controlled synthesis and crystallization of $CaCO_3$ by using DHBCs has been intensively investigated.[15] Choi and Kim found in certain biological systems that the secondary structures of peptides can affect the structure of $CaCO_3$ as the transition from aragonite into calcite is related to the denaturing of an antiparallel β sheet.[16] Moreover, DHBCs with adjustable secondary structures, such as poly(ethylene glycol)-*b*-poly(L-glutamic acid), PEG(*m*)-*b*-pGlu(*n*), have been used to control the growth of $CaCO_3$ in aqueous solution.[17] Previously, crystallization of calcium carbonate under the control of DHBCs has been mainly carried out in nonionic water (NIW). DHBC-controlled crystallization in a mixture of solvents can lead to entirely new results because of the variation in mineral solubility, precipitation kinetics, solution properties, and aggregation of the polymer in the solvent mixture. However, this new system has not yet been thoroughly investigated.

Mineralization reactions in alcohol, ethanol, 2-propanol, and diethylene glycol have seldom been explored, and only $CaCO_3$ crystals with morphologies such as elongated spheres or inhomogeneous aggregated structures have been obtained.[5,18] In recent years, several research groups have focused on the use of the solvent to control the crystal growth of $CaCO_3$ and other compounds.[19] Vaterite microspheres can be produced in the presence of starburst dendrimers[20] and PEG(*m*)-*b*-pGlu(*n*),[17] but the vaterite spheres obtained thus far are not monodisperse. To date, a precisely controlled synthesis of highly monodisperse $CaCO_3$ spheres has not been achieved in a pure-water system.

Monodisperse particles have numerous important applications in ceramics, catalysis, pigments, recording materials, medical diagnostics, and many other areas. Thus, the exploration of rational routes for their synthesis has been a challenge.[21] Herein, we present a precisely controlled synthesis of highly monodisperse $CaCO_3$ microspheres by a slow gas–liquid diffusion reaction with an artificial peptide-type block copolymer, PEG(110)-*b*-pGlu(6), as a crystal-growth modifier in a mixture of solvents. The synergistic effect of PEG-*b*-pGlu and the solvent mixture on the growth of calcium carbonate has been investigated. The results demonstrate that the ratio of solvent used has significant influence on the morphology and polymorph of $CaCO_3$ crystals in the presence of this DHBC.



PEG (110)-*b*-pGlu(6), *m* = 110, *n* = 6

N,*N*-dimethylformamide (DMF) and other solvents, such as THF, *n*-propanol, ethanol, and 1,4-dioxane have been applied as the mineralization media for the crystallization of $CaCO_3$. The $CaCO_3$ samples obtained from different types of solvent mixtures are indexed as vaterite or a mixture of calcite and vaterite (see Supporting Information). Figure 1 a shows that the $CaCO_3$ particles crystallized in pure DMF are almost polyhedral. From a mixture of DMF and methanol, the formed particles are made up of layers of rectangles with small cavities at the center of each face (Figure 1 b). In a mixture of DMF and THF, there are calcium carbonate crystals similar in shape to those obtained in the DMF/methanol mixture (Figure 1 c). However, the $CaCO_3$ particles are mostly aggregates of oblong blocks with small cavities in the center of the crystal surfaces. Nearly spherical aggregates and spherical particles (vaterite phase) are obtained from a mixture of DMF and *n*-propanol (Figure 1 d). Relatively uniform microspheres with rough surfaces are obtained from a mixture of DMF and ethanol (Figure 1 e). Surprisingly, multibranched hierarchical structures form in a mixture of DMF and 1,4-dioxane (Figure 1 f). These results demonstrate that the combination of a block copolymer and a mixture of solvents can provide an effective tool for controlled morphogenesis of $CaCO_3$.

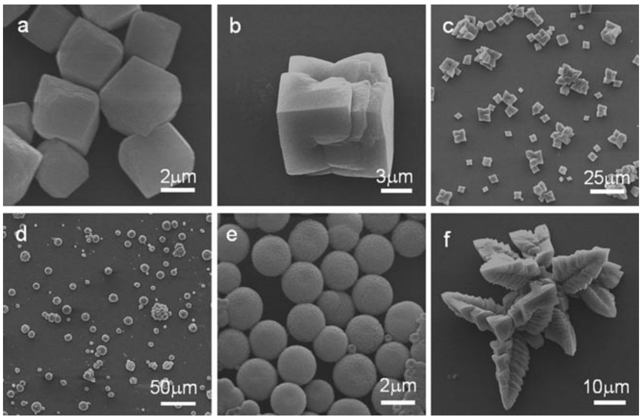


Figure 1. SEM images of $CaCO_3$ particles obtained from different solvent mixtures (volume ratios): a) Pure DMF; b) DMF:methanol = 5:1; c) DMF:THF = 5:1; d) DMF:*n*-propanol = 5:1; e) DMF:ethanol = 5:1; f) DMF:1,4-dioxane = 5:1. [PEG-*b*-pGlu] = 1 $g\,L^{-1}$. A solution of $CaCl_2$ was added to the solvent mixtures and the crystallization was allowed to proceed for 3 days at room temperature.

$CaCO_3$ microsphere arrays obtained from a DMF/NIW mixture with a polymer concentration of 1.0 $g\,L^{-1}$ are highly monodisperse (Figure 2 a). High-magnification SEM (Figure 2 b) reveals the smooth surface of the microspheres with diameters ranging from 5.3 to 6.0 μm. Similar results are obtained in a mixture of DMF and ethanol, as shown in Figure 2 c, but the vaterite microspheres obtained have a rough surface and are smaller and range from 1.5 to 2.4 μm in diameter (Figure 2 d). However, these microspheres are not stable and transform into rhombohedral calcite over prolonged reaction times (see Supporting Information).

To further examine the effects of DMF/NIW mixtures on controlled crystallization and modification of the $CaCO_3$ particles, a series of experiments was carried out by varying the volume ratio of the solvents, crystallization time, and polymer concentration (Figures 2 and 3). Decreasing the volume ratio of DMF:NIW to 1:7 results in the formation of

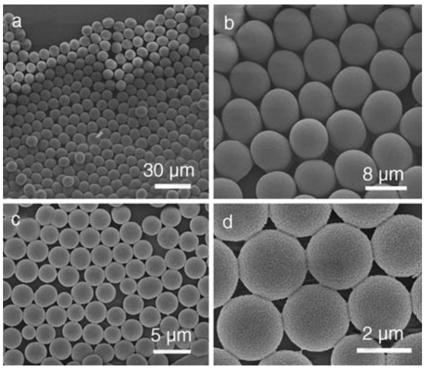


Figure 2. SEM images of $CaCO_3$ microspheres obtained from different solvent mixtures (volume ratios): a) DMF:NIW = 1:1; b) magnified SEM image of (a); c) DMF:ethanol = 5:1; d) magnified FESEM image of (c). [PEG-*b*-pGlu] = 1 g L^{-1}. A solution of $CaCl_2$ was added to the solvent mixtures and the crystallization was allowed to proceed for 3 days at room temperature.

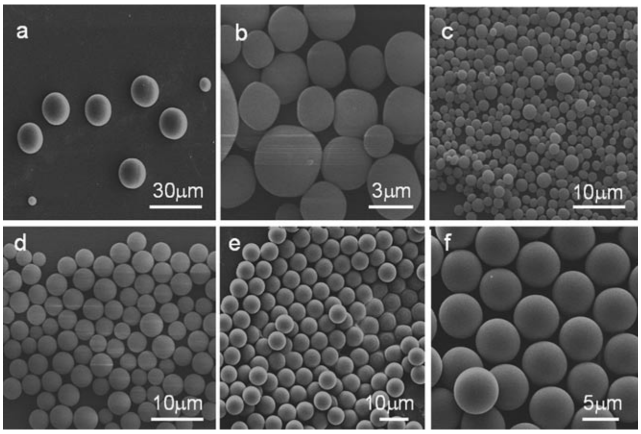


Figure 3. SEM images of $CaCO_3$ microspheres obtained in DMF/NIW with different volume ratios: a) 1:7; b) 1:3; c) 1:5; d) 1:2; e) 1:1.4; f) magnified SEM image of (e). [PEG-*b*-pGlu] = 1 g L^{-1}. A solution of $CaCl_2$ was added to the solvent mixtures and the crystallization was allowed to proceed for 3 days at room temperature.

$CaCO_3$ microspheres of mainly two sizes (Figure 3 a). There is a broad size distribution when the volume ratio of DMF:NIW is 1:3 (Figure 3 b). When the volume ratio of DMF:NIW is 1:5, $CaCO_3$ particles tend to transform into slightly deformed quasi-spheres or ellipsoids, which have a broad size distribution (Figure 3 c). Further decreasing the volume ratio of DMF:NIW to 1:2 results in the microspheres having a broader size distribution (Figure 3 d) A ratio of DMF:NIW of 1:1 results in the $CaCO_3$ particles being well-defined monodisperse spheres that tend to form an array similar to that shown in Figure 2 b and a similar result is found for a DMF:NIW ratio of 1:1.4 (Figure 3 e,f). Figure 4 shows the diameter distribution of microspheres obtained under different volume ratios of DMF to NIW. The microspheres obtained from DMF/NIW mixtures with volume ratios of 1:1.4 and 1:1 display narrow size distributions (Figure 4 c,d). However, changing the volume ratio of DMF:NIW from 1:7 to 1:2 results in a broadening of the size distribution (Figure 4 a,b and Table 1).

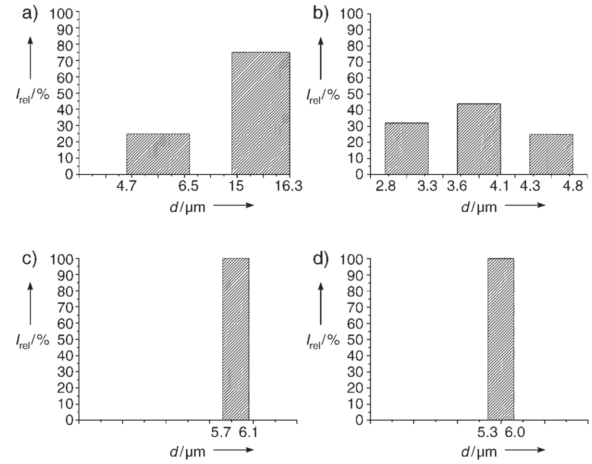


Figure 4. Size distributions of $CaCO_3$ microspheres produced under different conditions (*d*: diameter): The volume ratios of DMF:NIW are: a) DMF:NIW = 1:7; b) DMF:NIW = 1:2; c) DMF:NIW = 1:1.4; d) DMF:NIW = 1:1.

Table 1: Crystallization of vaterite particles.

DMF:NIW (v/v)	Polymorph	Particle distribution	Particle shape
1:7	vaterite	inhomogeneous	spheres
1:5	vaterite	inhomogeneous	spheres
1:3	vaterite	inhomogeneous	spheres and ellipsoids
1:2	vaterite	inhomogeneous	spheres
1:1.4	vaterite	monodisperse	spheres
1:1	vaterite + calcite[a]	monodisperse	spheres

[a] Trace of calcite phase present in this sample.

Figure 5 shows the X-ray diffraction (XRD) patterns of the as-prepared products obtained in DMF/NIW mixtures with different volume ratios when the other experimental

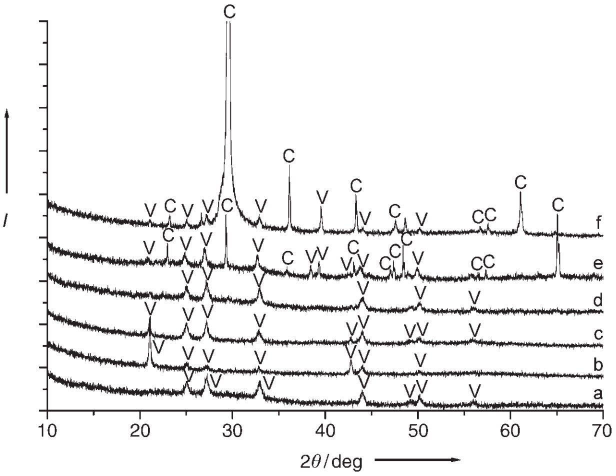


Figure 5. XRD patterns of $CaCO_3$ particles obtained in DMF/NIW with different volume ratios after mineralization for 7 days. a) 1:7; b) 1:5; c) 1:2; d) 1:1.4; e) 1:1; f) pure DMF. [PEG-*b*-pGlu] = 1.0 g L^{-1}. A solution of $CaCl_2$ was added to the solvent mixtures. V denotes vaterite and C denotes calcite.

conditions were kept constant. All reflection peaks of $CaCO_3$ particles can be easily indexed as vaterite for volume ratios ranging from 1:7 to 1:1.4 (Figure 5a–d). The broadening diffraction peaks indicate that the produced vaterite microspheres are composed of small nanoparticles. A trace amount of calcite phase is present when the volume ratio is 1:1 (Figure 5e). In pure DMF, the dominant phase is calcite although the vaterite phase is present (Figure 5 f). These data are different from those reported previously, which show that modification of calcite occurs only in pure water.[17b] Furthermore, metastable vaterite is stable for more than two months in a DMF/NIW mixture.

It was reported that a short block of glutamic acid, such as PEG-*b*-pGlu, can be used to precipitate a mixture of calcite and vaterite particles with irregular morphology, and that only the peptide block length of $n = 10$ produces vaterite spheres.[17] However, the results obtained here with mixtures of solvents are remarkably different from those reported previously for a pure-water system.[17]

The formation of monodisperse vaterite microspheres in a DMF/NIW mixture in the presence of PEG-*b*-pGlu is related to the secondary conformation of the polymer and its aggregated state adopted in the solvent mixture as well as to the effect of the solvent mixture itself.[16,19] Because of the different solvent properties of DMF and NIW, different volume ratios of them will have an influence on the polymer's solution properties, including the polymer conformation. A suitable mixture of DMF and NIW favors the dissolution of PEG-*b*-pGlu and alters its self-assembly process. The aggregates of PEG-*b*-PGlu in DMF/NIW mixtures are relatively uniform nanospheres with diameters of 100–150 nm as observed by TEM either in the absence or presence of Ca^{2+} ions (see Supporting Information). Clearly, such spherical aggregates of the block copolymer in the solvent mixture play a crucial role in controlling the nucleation and growth process of uniform vaterite microspheres.

Vaterite is transformed into thermodynamically stable calcite within a few days under the appropriate conditions.[22] Stable spherical vaterite particles can also be produced in the presence of a carboxylate-terminated dendrimer.[20] We propose that such particles can be stabilized by the aggregated framework of PEG-*b*-pGlu formed in DMF/NIW solution: PEG-*b*-pGlu associates with calcium ions to form strong Ca–O bonds thus preventing the dissolution of vaterite particles, as reported recently in the case of a mineralization reaction by using a native peptide, pelovaterin, extracted from eggshells of a soft-shelled turtle.[23] This viewpoint is also consistent with the recent findings that carboxylate block copolymers were able to initiate vaterite nucleation from stable supersaturated solutions through binding of the calcium ions at the ionized carboxylic groups.[20] However, the hydrogen-bonding interactions between peptide chains in PEG-*b*-pGlu and DMF/NIW mixed solvents, of PEG-*b*-pGlu itself, or between DMF and NIW could also attribute to the polymorph transformation from amorphous into vaterite as recently found by using acidic peptides that contain poly(carboxylate) ligands as crystal modifiers.[24]

Thermogravimetric analysis (TGA) was performed to examine the weight percentage of polymer in the superstructure microspheres, which was 5.7 wt% (see Supporting Information) and indicates that the polymer is enclosed within the microspheres. Time-dependent TEM observation in the early stage of the vaterite microsphere formation was performed and shows that after 10 min of mineralization, amorphous aggregated nanoparticles have formed, which grow and transform into single-crystalline spherical vaterite nanospheres within 30 min of mineralization (See Supporting Information). This growth process is different from the reported "sphere–rod–dumbbell–sphere" growth scenarios found in water with other DHBC additives, but has a similar aggregation-based mechanism.[12b] Microspheres were broken by ultrasound, and the broken parts were composed of small nanoparticles with diameters of about 15–20 nm (see Supporting Information), which is consistent with diameters calculated by the Scherer equation based on the broadening diffraction peaks of the XRD pattern (Figure 5d). SEM observation of the inner structure of a broken microsphere also revealed that they are indeed composed of small nanoparticles (see Supporting Information).

According to the LaMer model,[25] uniform particle growth occurs if the uniform primary particles form in solution below a critical supersaturation point. The size of the primary nanoparticles observed in the inner structures of the microspheres and the calculated size from the XRD pattern based on the Scherer equation are smaller than those observed in the early stage of mineralization, for example, after 30 min, which suggests either that the primary nanoparticles nucleate and then secondary nucleation occurs on the nanoparticle surface because it is energetically favored or that nanoparticles are nucleated in solution and then aggregate on the already existing seeds of about 100–200 nm in diameter (see Supporting Information).

We propose that polymer aggregates sequester Ca^{2+} ions and thus serve as localized nucleation centers due to the high local concentration of Ca^{2+} ions after the addition of a source of CO_3^{2-} ions, which is consistent with observations during hydroxyapatite whiskers growth in the presence of aggregates of PEO-*b*-PMAA-C_{12} [PEO is poly(ethylene oxide), PMAA is poly(methacrylic acid)].[11c] Important to the formation of highly monodisperse microparticles is the fact that the long solvating PEG blocks, with respect to the pGlu blocks, are mainly distributed on the outside of the aggregates and can stabilize the forming vaterite microparticles, thus preventing the microparticles from aggregating as demonstrated previously in a comprehensive study of PEO-*b*-PMAA and PMAA as additives for the mineralization of $CaCO_3$.[12a] Ostwald ripening also contributes to the formation of such uniform microspheres in the latter stages of mineralization.

In summary, we have demonstrated that PEG(110)-*b*-pGlu(6) can effectively mediate the controlled crystallization of $CaCO_3$ in a suitable mixture of solvents. Highly monodisperse vaterite microspheres can be produced by using a suitable volume ratio of DMF/NIW and by taking advantage of the synergistic effects of the block copolymer and the solvent mixture. Clearly, the solvent mixture plays a key role in controlling the growth, polymorphism, and shape of the $CaCO_3$ mineral. The detailed mechanism for the formation of such highly monodisperse vaterite microspheres mineralized in such a complex mixed-solvent system under the control of a block copolymer is not clear yet. The highly uniform $CaCO_3$ microspheres produced may have applications as an excellent template for polyelectrolyte multilayer capsules and biomimetic photon crystals in devices. Furthermore, this mixed-solvent approach may open a new general route for the crystallization of minerals with high quality and structure specialty.

Experimental Section

All chemicals were of analytical grade. Ammonium carbonate and calcium chloride were purchased from the Shanghai Chemical Reagent Company and used as received without further purification. PEG-*b*-pGlu ($PEG = 700\,g\,mol^{-1}$, $pGlu = 770\,g\,mol^{-1}$) was synthesized as described elsewhere.[17] The polymer was purified by exhaustive dialysis before being used in the crystallization of calcium carbonate.

All glassware (glass bottle and small pieces of glass substrates) was cleaned and subjected to ultrasound in a bath containing ethanol for 5–10 min, then rinsed with NIW ($18.2\,\Omega\,cm^{-1}$) and further soaked in a mixture of NIW/HNO_3(65 %)/H_2O_2 (volume ratio of 1:1:1), then rinsed with NIW, and finally dried with acetone. The mineralization experiments were carried out as described by Addadi et al.[26] The precipitation of $CaCO_3$ was carried out in a 10-mL glass bottle. A stock solution of $CaCl_2$ (0.1 M) was freshly prepared in boiled NIW.

In a typical synthesis, polymer (6 mg) was added to the solvent mixture (6 mL), then a solution of $CaCl_2$ (0.6 mL, 0.1 M) was injected into the vigorously stirring mixture. The reaction vessel was covered with parafilm, which was punctured with three needle holes, and placed in a closed desiccator at room temperature ((25 ± 3) °C). Three glass bottles (10 mL) filled with crushed ammonium carbonate and covered with parafilm punctured with three needle holes were also placed in the desiccator. After a set period of time, the parafilm was removed and the precipitate rinsed with NIW and ethanol and allowed to dry at room temperature. For the time-dependent crystallization experiments, copper TEM grids (3 mm in diameter) were put at the bottom of a glass bottle with the carbon film exposed to the solution. The copper grids and glass were then removed after a set period, allowed to dry in air, and directly used for TEM and SEM observation.

Samples on glass substrates were examined after being sputtered with gold for SEM on a BYBY-1010A microscope and field-emission SEM on a JSM-6700F microscope. The products were characterized by XRD, recorded on a (Philips X′ Pert Pro Super) diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.541874$ Å). TEM imaging and electron diffraction were performed with an H-800 electron microscope operating at 200 keV. TGA was carried out on a Diamond TG/DTA thermal analyzer (Perkin Elmer) with a heat rate of $10\,K\,min^{-1}$ in a nitrogen atmosphere.

Received: January 4, 2006
Revised: March 14, 2006
Published online: May 4, 2006

Keywords: block copolymers · crystal growth · peptides · polymorphism · solvent effects

---

[1] a) S. Mann, *Angew. Chem.* **2000**, *112*, 3532; *Angew. Chem. Int. Ed.* **2000**, *39*, 3392; b) L. A. Estroff, A. D. Hamilton, *Chem. Mater.* **2001**, *13*, 3227.

[2] D. B. Deoliveira, R. A. Laursen, *J. Am. Chem. Soc.* **1997**, *119*, 10627.

[3] E. Dalas, P. Klepetsanis, P. G. Koutsoukos, *Langmuir* **1999**, *15*, 8322.

[4] a) G. A. Ozin, *Acc. Chem. Res.* **1997**, *30*, 17; b) S. W. Weiner, L. Addadi, *J. Mater. Chem.* **1997**, *7*, 689; c) T. Kato, A. Sugawara, N. Hosoda, *Adv. Mater.* **2002**, *14*, 869; d) F. C. Meldrum, *Int. Mater. Rev.* **2003**, *48*, 187; e) H. Cölfen, S. Mann, *Angew. Chem.* **2003**, *115*, 2452; *Angew. Chem. Int. Ed.* **2003**, *42*, 2350.

[5] For reviews, see: a) S. H. Yu, H. Cölfen, *J. Mater. Chem.* **2004**, *14*, 2124, and references therein; b) H. Cölfen, S. H. Yu, *MRS Bull.* **2005**, *30*, 727, and references therein; c) H. Cölfen, *Macromol. Rapid Commun.* **2001**, *22*, 219.

[6] G. Falini, S. Albeck, L. Addadi, *Science* **1996**, *271*, 67.

[7] A. M. Belcher, X. H. Wu, R. J. Christensen, P. K. Hansma, G. D. Stucky, D. E. Morse, *Nature* **1996**, *381*, 56.

[8] N. J. Reeves, J. S. Evans, *J. Phys. Chem. B* **1997**, *101*, 6665.

[9] G. Falini, M. Gazzano, A. Ripamonti, *J. Cryst. Growth* **1994**, *137*, 577.

[10] G. K. Hunter, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 430.

[11] a) M. Sedlak, M. Antonietti, H. Cölfen, *Macromol. Chem. Phys.* **1998**, *199*, 247; b) H. Cölfen, M. Antonietti, *Langmuir* **1998**, *14*, 582; c) M. Antonietti, M. Breulmann, C. Göltner, H. Cölfen, K. K. Wong, D. Walsh, S. Mann, *Chem. Eur. J.* **1998**, *4*, 2493.

[12] a) H. Cölfen, L. M. Qi, *Chem. Eur. J.* **2001**, *7*, 106; b) S. H. Yu, H. Cölfen, M. Antonietti, *J. Phys. Chem. B* **2003**, *107*, 7396; c) S. H. Yu, H. Cölfen, A. W. Xu, *Cryst. Growth Des.* **2004**, *4*, 33; d) S. F. Chen, S. H. Yu, T. X. Wang, J. Jiang, H. Cölfen, B. Hu, B. Yu, *Adv. Mater.* **2005**, *17*, 1461; e) Y. X. Gao, S. H. Yu, H. P. Cong, J. Jiang, A. W. Xu, W. F. Dong, H. Cölfen, *J. Phys. Chem. B*, **2006**, *110*, 6432.

[13] a) S. H. Yu, H. Cölfen, K. Tauer, M. Antonietti, *Nat. Mater.* **2005**, *4*, 51; b) S. H. Yu, H. Cölfen, J. Hartmann, M. Antonietti, *Chem. Eur. J.* **2002**, *8*, 2937.

[14] a) D. B. Zhang, L. M. Qi, J. M. Ma, H. M. Cheng, *Chem. Mater.* **2002**, *14*, 2450; b) L. M. Qi, H. Cölfen, M. Antonietti, *Angew. Chem.* **2000**, *112*, 617; *Angew. Chem. Int. Ed.* **2000**, *39*, 604.

[15] a) T. X. Wang, H. Cölfen, M. Antonietti, *J. Am. Chem. Soc.* **2005**, *127*, 3246; b) H. Endo, D. Schwahn, H. Cölfen, *J. Chem. Phys.* **2004**, *120*, 9410; c) H. Cölfen, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 23.

[16] C. S. Choi, Y. W. Kim, *Biomaterials* **2000**, *21*, 213.

[17] a) P. Kašparová, *PhD Thesis*, Postdam, **2002**; b) P. Kašparová, M. Antonietti, H. Cölfen, *Colloids Surf. A* **2004**, *250*, 153.

[18] a) F. Manoli, E. Dalas, *J. Cryst. Growth* **2000**, *218*, 359; b) L. M. Qi, J. M. Ma, *Chem. J. Chin. Univ.* **2002**, *23*, 1595.

[19] a) S. R. Dickinson, K. M. Mcgrath, *J. Mater. Chem.* **2003**, *13*, 928; b) G. Falini, M. Gazzano, A. Ripamonti, *Chem. Commun.* **1996**, 1037; c) K. S. Seo, C. Han, J. H. Wee, J. K. Park, J. W. Ahn, *J. Cryst. Growth* **2005**, *276*, 680; d) S. F. Chen, S. H. Yu, B. Yu, *Chem. Eur. J.* **2004**, *10*, 3050; S. F. Chen, S. H. Yu, J. Jiang, F. Q. Li, Y. K. Liu, *Chem. Mater.* **2006**, *18*, 122.

[20] K. Naka, Y. Tanaka, Y. Chujo, *Langmuir* **2002**, *18*, 3655.

[21] For reviews, see: a) E. Matijević, *Chem. Mater.* **1993**, *5*, 412; b) E. Matijević, *Langmuir* **1994**, *10*, 8.

[22] a) A. Richter, D. Petzold, H. Hofmann, B. Ulrich, *Chem. Tech.* **1996**, *48*, 271; b) N. Nassrallah-Aboukais, A. Boughriet, J. Laureyns, A. Aboukais, J. C. Fischer, H. R. Langelin, M. Wartel, *Chem. Mater.* **1998**, *10*, 238.

[23] R. Lakshminarayanan, E. O. C. Jin, X. J. Loh, R. M. Kini, S. Valiyaveettil, *Biomacromolecules* **2005**, *6*, 1429.

[24] K. Takahashi, A. Kobayashi, M. Doi, S. Adachi, T. Taguchi, *J. Mater. Chem.* **2005**, *15*, 2178.

[25] V. K. LaMer, *Ind. Eng. Chem.* **1962**, *54*, 1270; V. K. LaMer, R. Dinegar, *J. Am. Chem. SOC.* **1950**, *72*, 4847.

[26] S. Weiner, S. Albeck, L. Addadi, *Chem. Eur. J.* **1996**, *2*, 278.