Self-organization of Patterned $CaCO_3$/Polymer Composite Films: Tuning of Their Morphologies by the Change of Molecular Weights of Acidic Polymers

Takeshi Sakamoto, Akira Oichi, Ayae Sugawara, and Takashi Kato*
Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113-8656

(Received December 26, 2005; CL-051570; E-mail: kato@chiral.t.u-tokyo.ac.jp)

Calcium carbonate ($CaCO_3$) thin films with periodic surface patterns are formed on thin film matrices of a polysaccharide derivative from a solution containing poly(acrylic acid) (PAA). The morphologies of the patterned films have been tuned by the change of molecular weights of the PAA.

Natural inorganic/organic composites called biominerals form self-organized and hierarchical structures, which provide them with outstanding material properties such as mechanical toughness and unique optical properties.[1] Organisms produce these elaborate structures using organic matrices interacting with inorganic substances. Synthetic approaches inspired by biomineralization to morphological control of $CaCO_3$ crystals have been performed and a variety of shapes were obtained in the presence of organic substances.[1–8]

Herein, we present $CaCO_3$/polymer composite films with regularly patterned structures with periodicities from submicrometer to micrometers in width. These self-organized structures can be tuned by the change of molecular weight and concentration of an acidic polymer used as a soluble additive.

$CaCO_3$ thin film composites with smooth surfaces have been obtained by cooperative effects of insoluble thin film matrices having OH groups and soluble acidic polymers.[3a–3e] Recently, we have reported that the use of modified polysaccharides as thin film matrices has resulted in the formation of thin film crystals of $CaCO_3$ with regular surface-relief structures.[3f] The submicrometer scale structures are spontaneously formed[3f] on the matrix of cholesterol-bearing pullulans (CHP)[9] (Figure 1) in the presence of poly(acrylic acid) (PAA) with average molecular weight of 2.0×10^3 (PAA2k). However, it is not easy to control the periodicity of the relief structures. We expected that the molecular weight of PAA affects the morphologies of the patterned surfaces.

In the present study, we have examined the effects of PAAs with different average molecular weights on the formation of the patterned $CaCO_3$ grown on the matrices of CHP that has four cholesteryl groups per 100 glucose units of pullulan.[10] The molecular weights of 2.0×10^3 (PAA2k), 3.8×10^3 (PAA4k), and 2.9×10^4 (PAA30k) were used for this study.[11] $CaCO_3$ crystallization was performed by slowly diffusing ammonium carbonate vapor into a 10 mM of calcium chloride solution containing PAAs for two days at 20 °C.[12]

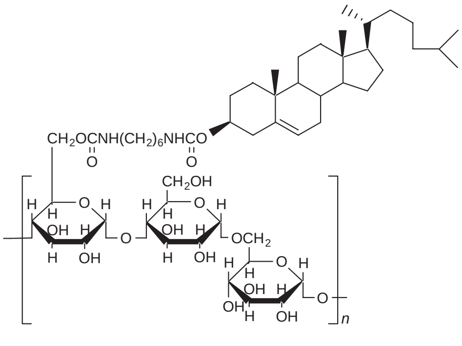

Figure 1. Structure of cholesterol-bearing pullulan (CHP).

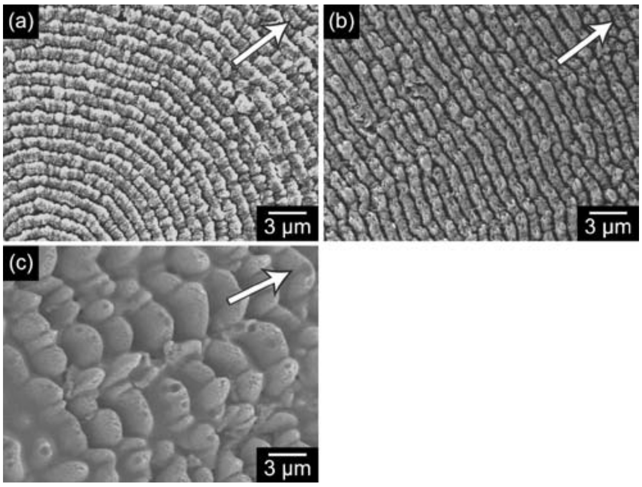

Figure 2. SEM images of $CaCO_3$ crystals grown on the CHP matrices in the presence of PAAs (2.4×10^{-3} wt %): a) PAA2k, b) PAA4k, and c) PAA30k. The white arrows indicate crystal growth directions.

Figure 2 shows the SEM images of the $CaCO_3$ thin films obtained in the presence of PAAs with three different molecular weights. The concentration of PAA was 2.4×10^{-3} wt % because in our previous study[3f] PAA2k at this concentration gave the most regular structures. These PAAs have induced the formation of $CaCO_3$ films with periodic surface grooves that align perpendicular to the crystal growth direction. The molecular

Table 1. Morphology and the distances between the surface grooves for the patterned $CaCO_3$ formed in the presence of PAA

Polymer	Concentration/10^{-3} wt %			
	1.0	2.4	5.0	12.0
PAA2k	⊥[a], 1–2[b,c]	⊥[a], 1[b]	⊥[a], 0.8[b]	—[d]
PAA4k	⊥[a], 1–3[b,c]	⊥[a], 1[b]	⊥[a], 1–3[b,c]	—[d]
PAA30k	random	⊥[a], 2–3[b,c]	⊥[a], 2[b]	‖[e], 0.4[b]

[a]The surface grooves align perpendicular to the crystal growth directions. [b]The distances between the surface grooves (μm). [c]The distances for several samples vary in the range indicated. However, the same sample shows the same distance. [d]No precipitation. [e]The surface grooves align parallel to the crystal growth directions.

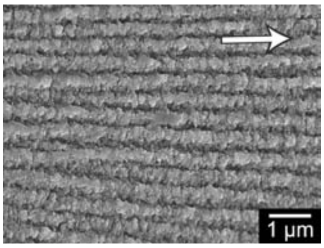

Figure 3. SEM image of $CaCO_3$ crystals grown on the CHP matrix in the presence of PAA30k (1.2×10^{-2} wt %). The arrow indicates crystal growth direction.

weight of PAA has exerted effects on the periodicity of the patterned $CaCO_3$. The use of PAA2k has resulted in the formation of regularly patterned $CaCO_3$ with a periodicity of about 1.0 μm (Figure 2a). These films are spherulites of calcite. PAA4k has also induced the formation of patterned films with 1.0 μm periodicity (Figure 2b). In the presence of PAA30k, the patterned crystals with 2–3 μm periodicity between grooves with more rough shapes have been formed on the matrices (Figure 2c).

The effects of the concentrations of these PAAs on the periodically patterned $CaCO_3$ have also been studied. The results are summarized in Table 1. In the presence of PAA2k, $CaCO_3$ films with periodic surface grooves which align perpendicular to the crystal growth directions have developed at the concentration range of 1.0×10^{-3} to 5.0×10^{-3} wt %. The most regularly patterned crystals are obtained at the concentration of about 2.4×10^{-3} wt %. For higher concentrations (more than 6.0×10^{-3} wt %), no crystals are obtained because the inhibition of PAA becomes more effective.[3] The morphologies with PAA4k are basically very similar to that observed for PAA2k. It is of interest that in the presence of PAA30k, the directions of the patterned surface grooves on $CaCO_3$ films are parallel to the direction of the crystal growth at higher concentration. Figure 3 shows the SEM image of the $CaCO_3$ films obtained from the solution containing a higher concentration of PAA30k (1.2×10^{-2} wt %). Formation of $CaCO_3$ crystals at this concentration of PAA30k indicates that the inhibiting effect of PAA30k on the crystallization is weaker than those of PAA2k and PAA4k. Imai et al. reported that higher molecular weights of PAA showed different effects on the morphologies of $CaCO_3$ crystals.[6] The periodicity of the surface grooves on the films is about 400 nm (Figure 3), which is the shortest that we have ever obtained in that of patterned $CaCO_3$ crystals.

We assume that the pattern formation in this study belongs to a self-organization process in the reaction–diffusion systems, in which competition between precipitation and ion diffusion occurs.[3f] It was reported that various kinds of patterned structures such as concentric rings and dense branching morphology occurs in these reaction–diffusion systems.[13] Differences in molecular weights and concentrations of PAA may change the parameters such as the level of supersaturation and diffusion of ions,[3d,6,14] which has resulted in modification of self-organized structures based on $CaCO_3$.

In conclusion, for the formation of novel regularly patterned $CaCO_3$ crystals, their regular structures have been tuned by changing the molecular weight and concentrations of PAAs that are present in aqueous solution. These results suggest that morphology and hierarchical structures of self-organized inorganic/organic materials obtained by solution processes can be controlled by change of the chemical structures and molecular weights of soluble polymers.

This study was partially supported by Grant-in-Aid for the 21st Century COE Program for Frontiers in Fundamental Chemistry (TK and AS) and for Exploratory Research (No. 17655048) (TK) from the Ministry of Education, Culture, Sports, Science and Technology.

References and Notes

1 a) *Biomineralization*, ed. by E. Bäuerlein, Wiley-VCH, Weinheim, **2000**. b) E. Dujardin, S. Mann, *Adv. Mater.* **2002**, *14*, 775. c) S. Weiner, L. Addadi, *J. Mater. Chem.* **1997**, *7*, 689.

2 a) T. Kato, A. Sugawara, N. Hosoda, *Adv. Mater.* **2002**, *14*, 869. b) F. C. Meldrum, *Int. Mater. Rev.* **2003**, *48*, 187. c) H. Cölfen, *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 23.

3 a) T. Kato, *Adv. Mater.* **2000**, *12*, 1543. b) T. Kato, T. Suzuki, T. Amamiya, T. Irie, M. Komiyama, H. Yui, *Supramol. Sci.* **1998**, *5*, 411. c) T. Kato, T. Suzuki, T. Irie, *Chem. Lett.* **2000**, 186. d) N. Hosoda, T. Kato, *Chem. Mater.* **2001**, *13*, 688. e) N. Hosoda, A. Sugawara, T. Kato, *Macromolecules* **2003**, *36*, 6449. f) A. Sugawara, T. Ishii, T. Kato, *Angew. Chem., Int. Ed.* **2003**, *42*, 5299. g) A. Sugawara, T. Kato, *Compos. Interfaces* **2004**, *11*, 287.

4 a) S. Zhang, K. E. Gonsalves, *Langmuir* **1998**, *14*, 6761. b) G. Xu, N. Yao, I. A. Aksay, J. T. Groves, *J. Am. Chem. Soc.* **1998**, *120*, 11977.

5 a) L. A. Gower, D. A. Tirrell, *J. Cryst. Growth* **1998**, *191*, 153. b) X. Xu, J. T. Han, K. Cho, *Chem. Mater.* **2004**, *16*, 1740. c) D. Volkmer, M. Harms, L. Gower, A. Ziegler, *Angew. Chem., Int. Ed.* **2005**, *44*, 639.

6 A. Kotachi, T. Miura, H. Imai, *Chem. Mater.* **2004**, *16*, 3191.

7 a) K. Naka, Y. Tanaka, Y. Chujo, *Langmuir* **2002**, *18*, 3655. b) T. Sugawara, Y. Suwa, K. Ohkawa, H. Yamamoto, *Macromol. Rapid Commun.* **2003**, *24*, 847. c) A.-W. Xu, Q. Yu, W.-F. Dong, M. Antonietti, H. Cölfen, *Adv. Mater.* **2005**, *17*, 2217.

8 a) J. Aizenberg, *Adv. Mater.* **2004**, *16*, 1295. b) D. Walsh, S. Mann, *Nature* **1995**, *377*, 320. c) R. J. Park, F. C. Meldrum, *Adv. Mater.* **2002**, *14*, 1167. d) D. Ogomi, T. Serizawa, M. Akashi, *J. Controlled Release* **2005**, *103*, 315.

9 K. Akiyoshi, S. Deguchi, N. Moriguchi, S. Yamaguchi, J. Sunamoto, *Macromolecules* **1993**, *26*, 3062.

10 CHP used as thin film matrices was synthesized according to literature procedures.[9] The substitution degree was determined by ^1H NMR. CHP matrices were prepared by spin coating of their 2 wt % DMSO solution on glass substrates. They were annealed for 1 h at 180 °C to remove the solvent.

11 PAA2k was obtained from Aldrich. PAA4k and PAA30k were purchased from Wako. Molecular weights of PAAs were determined through a size exclusion chromatography (SEC) following methyl esterification. *N*,*N*-Dimethylformamide containing 0.1 M LiBr was used as the eluent. The molecular weight calibration curve was obtained with standard polystyrenes (Nishio).

12 Calcium chloride aqueous solution containing PAA was transferred to vessels that contained CHP matrices. The vessels were then placed in a closed desiccator together with a vial of ammonium carbonate.[3f]

13 a) G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418. b) K. Iwamoto, S. Mitomo, M. Seno, *J. Colloid Interface Sci.* **1984**, *102*, 477. c) H.-J. Krug, H. Brandtstädter, *J. Phys. Chem. A* **1999**, *103*, 7811.

14 J. E. Loy, J. Guo, S. J. Severtson, *Ind. Eng. Chem. Res.* **2004**, *43*, 1882.