Template Effect of Crystalline Poly(vinyl alcohol) for Selective Formation of Aragonite and Vaterite $CaCO_3$ Thin Films

Naoya Hosoda,† Ayae Sugawara, and Takashi Kato*

Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received November 23, 2002; Revised Manuscript Received June 11, 2003

ABSTRACT: Aragonite thin films of calcium carbonate are selectively formed on crystalline poly(vinyl alcohol) matrices in the presence of poly(acrylic acid) in $CaCO_3$ solution. For thin film formation, this is the first example in which aragonite is formed selectively by cooperation of only synthetic organic macromolecules. In contrast, the addition of poly(glutamic acid) results in the formation of vaterite thin films on the crystalline poly(vinyl alcohol) matrices. These results show that crystalline poly(vinyl alcohol) matrices can be used to select the polymorph from aragonite and vaterite by changing the soluble additive.

Introduction

A large number of organisms are capable of exerting remarkable control over the fabrication of biominerals by using interactions between inorganic substances and biomacromolecules.[1] Although the processes of biomineralization are not fully understood, approaches to mimicking these processes may result in the fabrication of new organic/inorganic hybrid materials.[1,2] For example, the nacre of mollusc shells, which has a layered structure of aragonite crystals of $CaCO_3$ and organic macromolecules, is an interesting example for research into mimicking its hybrid structure.[1,3] $CaCO_3$ crystals have three polymorphs: calcite, aragonite, and vaterite. In the synthetic approach, selective formation of $CaCO_3$ polymorph is important. Calcite and vaterite $CaCO_3$ crystals are selectively formed in the presence of a variety of synthetic functionalized polymers and molecular assemblies.[4−6] On the other hand, polymorph control for aragonite crystals in vitro is not easy and the examples are limited.[7−13] Template effects of Langmuir monolayers[8] and SAMs[9] resulted in the formation of aragonite $CaCO_3$ crystals. The addition of Mg^{2+} also induces aragonite deposition.[10] Recently, we have reported that aragonite thin films are obtained by cooperative effects of Mg^{2+} and randomly oriented chitosan adsorbing poly(aspartate).[11] A biofabrication method involving the mantle and shell of red abalone led to the formation of aragonite flat crystals.[13] However, to our knowledge, no aragonite thin film was induced by only organic molecular templates.

Here we report the first example in which aragonite thin film crystals are selectively formed on a designed synthetic organic matrix. We chose poly(vinyl alcohol) (PVA) as a polymer matrix for the aragonite thin film formation because the distance between the hydroxyl groups of crystalline PVA[14] is almost equal to that between calcium ions in the *ab* plane of aragonite, as shown in Figure 1. We expected that poly(acrylic acid) (PAA) adsorbed on the crystalline state of PVA can partially form aligned carboxylic acid moieties. For the thin film formation of $CaCO_3$, polysaccharides such as cellulose, chitosan, and chitin were used as solid polymer matrices.[15−17] However, no aragonite thin film could be obtained by the effects of only organic macromolecules because of random arrangement of the hydroxyl groups which adsorb polyacids.

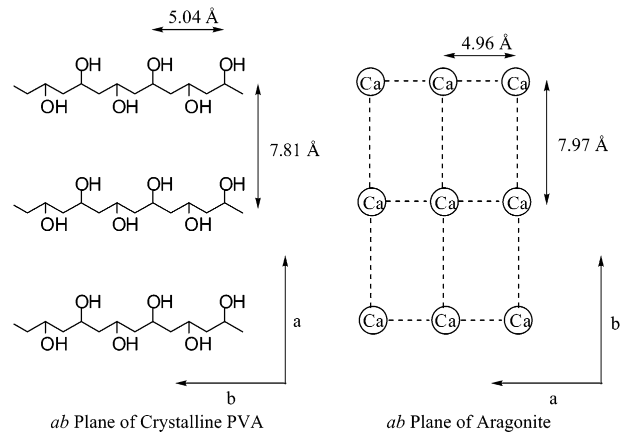

Figure 1. Schematic representation of the spatial relationship between the *ab* plane of crystalline PVA and the *ab* plane of aragonite.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA, $\bar{M}_w = 8.9 \times 10^4$ to 9.8×10^4) and poly(acrylic acid) (PAA, $\bar{M}_w = 2.0 \times 10^3$) were obtained from Aldrich. Calcium carbonate (calcite) was purchased from Wako. Poly(glutamic acid) (PGA, $\bar{M}_w = 1.4 \times 10^4$) was obtained from Sigma. All reagents were of the highest grade and used without further purification.

Preparation of the Polymer Matrix. PVA was dissolved in distilled water. The film of PVA was formed by spin-coating of the solution on a glass substrate. It was annealed at 200 °C for 0.5 h to obtain the insoluble crystalline PVA matrix.

Preparation of $CaCO_3$ Crystals. Crystallization of $CaCO_3$ has been performed from supersaturated $CaCO_3$ solution. The preparation of the supersaturated solution is as follows: Calcium carbonate (2.0 g/L) was suspended in water obtained from Auto pure WT100 (Yamato, relative resistivity: maximum 1.8×10^7 Ω cm; organic compounds concentrated; below 0.1 ppm). Carbon dioxide gas (99.7%) was bubbled into a stirred suspension for 3 h at 30 °C. The remaining solid $CaCO_3$

* To whom correspondence should be addressed. E-mail: kato@chiral.t.u-tokyo.ac.jp.
† Current address: Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

10.1021/ma025869b CCC: $25.00
Published on Web 07/24/2003

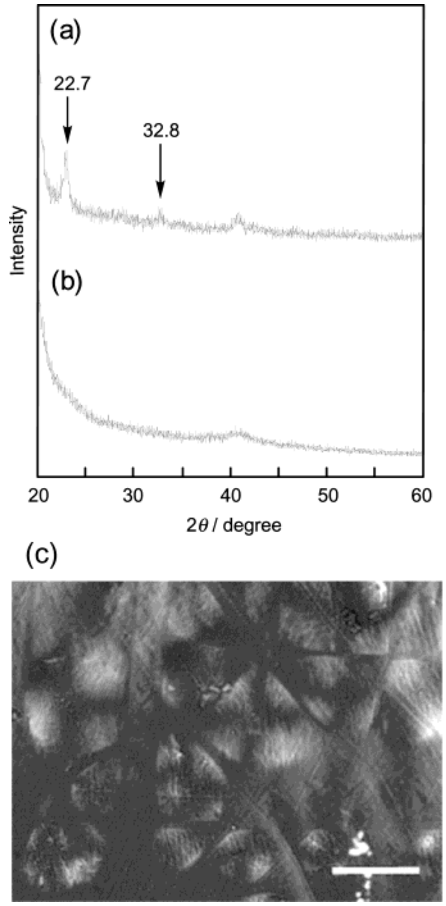

Figure 2. (a) X-ray diffraction pattern of the PVA matrix after annealing at 200 °C for 0.5 h. (b) X-ray diffraction pattern of the PVA matrix before annealing. (c) Polarizing optical photomicrograph of the PVA matrix after annealing at 200 °C for 0.5 h. Bar = 50 μm.

was then removed by filtration. After the addition of a soluble additive and further bubbling of carbon dioxide gas for 1 h, the resulting solution (pH = 5.8, $[Ca^{2+}] = 7.6 \times 10^{-3}$ mol/L) was transferred to vessels. The system was kept at 30 °C in a water bath. The concentration of calcium ion dissolved in the system was determined by EDTA titration. Calcium carbonate crystals were collected after 20 h.

Characterization. Visual observation was performed by polarizing optical microscopy (Olympus BH2). The SEM pictures were obtained by a JEOL JSM-5400/LV and a HITACHI S-900S scanning electron microscopes. X-ray measurements of $CaCO_3$ crystals were performed using an X-ray diffractometer Rigaku RINT2400 with Cu Kα radiation. The polymorphs of $CaCO_3$ were determined on the basis of powder X-ray diffraction patterns. The average crystallite size was estimated from the half-peak width of X-ray diffraction patterns according to Scherrer's equation. The aragonite fractions were calculated from the diffraction peak areas using a calibration curve obtained from crystal mixtures with known ratios of the polymorphs. The vaterite fractions were estimated by Rao's equation.[18]

Results and Discussion

The crystalline PVA matrix for $CaCO_3$ crystallization was prepared by annealing of a spin-coated PVA film. The X-ray diffraction pattern of the PVA matrix after annealing shows sharp peaks at $2\theta = 22.7$ and 32.8° (Figure 2a), which correspond to secondary reflections from *cb* and *ab* planes, respectively. On the other hand, no sharp peak appears for the diffraction pattern of the film before annealing (Figure 2b). These observations

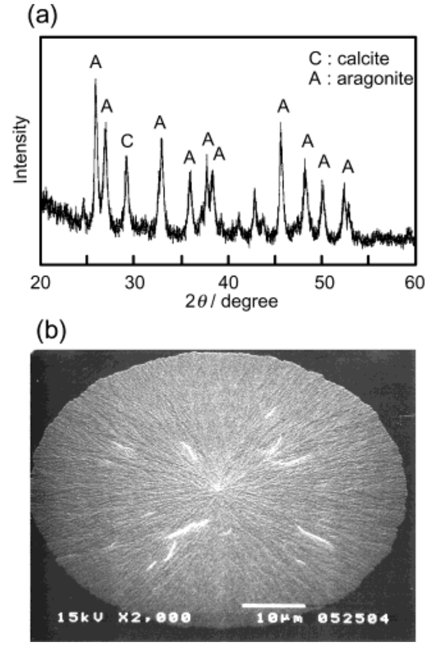

Figure 3. (a) Powder X-ray diffraction pattern and (b) scanning electron micrograph of $CaCO_3$ thin film crystals developed on the crystalline PVA matrix in the presence of 2.4×10^{-3} wt % of PAA.

show that the PVA matrix changes from an amorphous state to a partially crystalline state by annealing. A polarizing optical photomicrograph of the annealed PVA matrix is shown in Figure 2c. The film is partially birefringent because of the induction of partial crystallization, whereas no birefringence is observed before annealing.

Thin film crystals of $CaCO_3$ have been developed on the surface of the annealed PVA matrix when the crystallization is performed with PAA at the concentration of 2.4×10^{-3} wt %. The powder X-ray diffraction pattern of the crystals shows that aragonite $CaCO_3$ thin films are preferably formed on the crystalline PVA (Figure 3a), whereas the major polymorphs of the thin film crystals on the polysaccharides were vaterite and/or calcite.[15−17] Figure 3b shows the scanning electron micrograph of the aragonite thin film crystals grown on the PVA. These thin films show circular symmetry around the center of nucleation. It should be noted that the thickness of the films is observed to be about 0.3 μm, which is thinner than those (0.8−1.0 μm) formed on the polysaccharides.[15−17] In contrast, rhombohedral crystals of calcite are formed on the PVA in the absence of soluble polymer additives, and the crystallization is inhibited by PAA without the PVA matrix. These results suggest that the PVA alone in the solid-film state has no effect on the control of the polymorphs and morphology of $CaCO_3$ and that the thin films in the aragonite polymorph are formed by the cooperative effects of only organic templates, PVA and PAA.

The thin film aragonite crystals with a homogeneous thickness are obtained at the concentration range of 7.2×10^{-4} to 1.0×10^{-2} wt %. For example, the aragonite fraction of the thin film crystals is 93 wt % at the concentration of 2.4×10^{-3} wt %. At concentrations lower than those for the thin film formation, aggregates of the mixture of calcite, aragonite, and vaterite with irregular shapes are obtained, while the thin films sporadically form at higher concentrations. The average crystallite size of the aragonite thin films has been

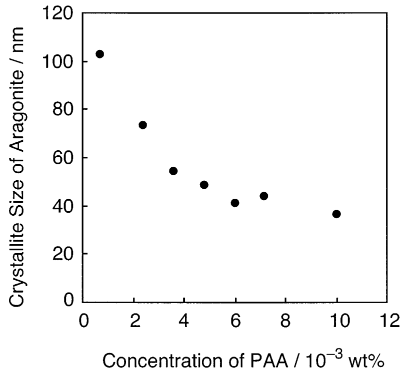

Figure 4. Plot of the crystallite size of the aragonite thin films developed on the crystalline PVA matrices as a function of the concentration of PAA.

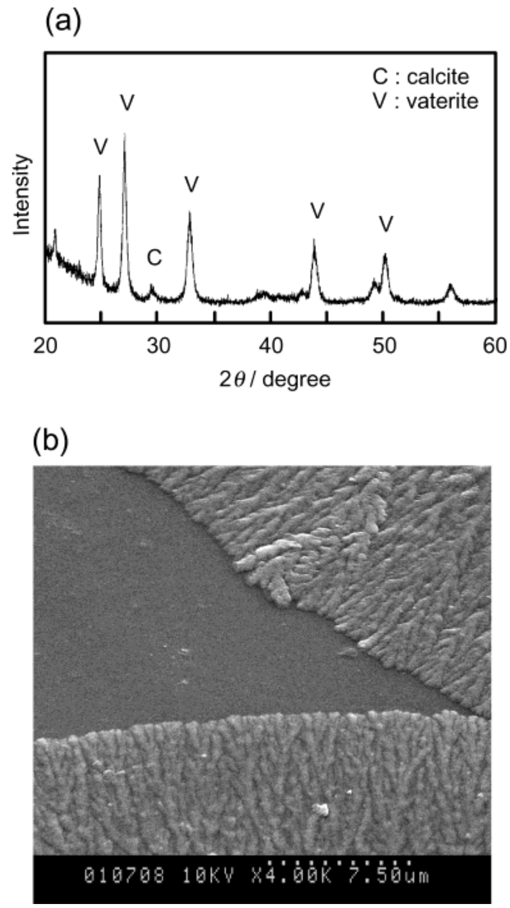

Figure 5. (a) Powder X-ray diffraction pattern and (b) scanning electron micrograph of $CaCO_3$ thin film crystals developed on the crystalline PVA matrix in the presence of 1.5×10^{-3} wt % of PGA.

calculated from the half-peak width of the X-ray diffraction patterns according to Scherrer's equation. The increase of the concentration of PAA from 7.2×10^{-4} to 1.0×10^{-2} wt % results in the decrease of the crystallite size of aragonite from 100 to 40 nm as shown in Figure 4.

In contrast to the aragonite formation in the presence of PAA, the addition of poly(glutamic acid) (PGA) to the solution leads to the deposition of vaterite thin film crystals on the crystalline PVA (Figure 5a). Figure 5b shows the scanning electron micrograph of the vaterite thin film crystals grown on the PVA. The thickness of the thin films is about 0.3 μm, which is almost equal to that formed in the presence of PAA. The thin films are

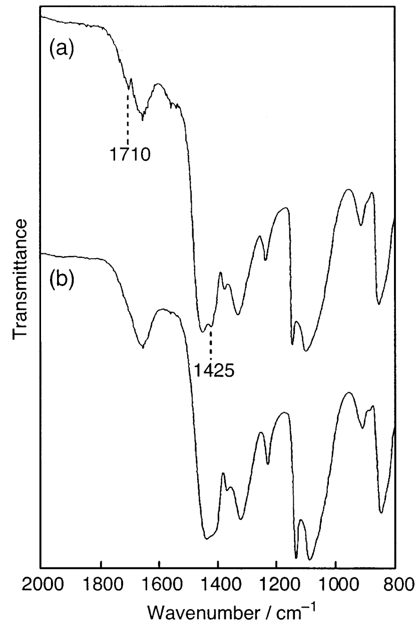

Figure 6. Infrared spectra of the PVA matrices soaked in the supersaturated solution of $CaCO_3$ (a) containing PAA (1.0×10^{-2} wt %) and (b) without PAA for 3 h.

obtained at the concentration range of 5.0×10^{-4} to 5.0×10^{-3} wt %, whereas aggregates of vaterite and calcite are formed at lower concentrations. In this concentration range, the vaterite fractions are over 90 wt %, which indicates that the cooperation of PVA and PGA provides the selective formation of vaterite thin film crystals. The average crystallite size of vaterite decreases slightly from 20 to 15 nm as the concentration of PGA increases.

PAA is adsorbed on the PVA matrix by the interaction between the COO^- moieties of PAA and the OH groups of PVA. Figure 6a shows the infrared spectrum of the PVA matrix soaked in the supersaturated solution of $CaCO_3$ containing PAA. Two bands at 1710 and 1425 cm^{-1} are observed in the infrared spectrum. These peaks correspond to the absorption of the carbonyl group and the COO^- ionic moiety of PAA, respectively, whereas these bands are not observed in the spectrum for PVA soaked in the solution without PAA (Figure 6b). This was also observed for the cellulose/PAA system in our previous study.[17] The PVA matrix forms partial crystalline region by annealing as shown in Figure 1. This crystalline structure may induce locally aligned two-dimensional structures of the COO^- moieties by the adsorption of PAA on the matrix. We assume that aragonite crystals nucleate at these regions by the template effects of the PVA matrix that aligns the COO^- moieties, leading to the crystal growth of aragonite thin films without template effects on the disordered matrix.

Gower and Odom reported that polymer-induced liquid-precursor process induced single-crystalline films of calcite.[6] The films were obtained on an amorphous glass substrate from solution containing a polypeptide. In their process, amorphous precursor was formed first on the amorphous substrate, and then it transformed into the crystalline film of calcite. On the other hand, amorphous to crystalline transformation is not observed in our process. Our $CaCO_3$ films are polycrystalline materials, which are directly formed by the cooperative effects of the polymer additive and the crystalline polymer substrate.

Conclusions

We have succeeded in the preparation of aragonite thin film crystals by the cooperative effects of crystalline PVA and PAA. In contrast, the use of PGA as a soluble polymer results in the formation of vaterite thin film crystals on PVA. These approaches can be applied to the syntheses of novel composites whose morphology is controlled by template effects of the crystalline polymer matrices.

Acknowledgment. Partial financial support of a Grant-in-Aid for Scientific Research and The 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science, and Technology is gratefully acknowledged.

References and Notes

(1) Mann, S. *Nature (London)* **1988**, *332*, 119. Addadi, L.; Weiner, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 153. Krampitz, G.; Graser, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1145.
(2) Kato, T.; Sugawara, A.; Hosoda, N. *Adv. Mater.* **2002**, *14*, 869.
(3) Watabe, N. *J. Ultrastruct. Res.* **1965**, *12*, 351. Addadi, L.; Weiner, S. *Nature* (*London*) **1997**, *389*, 912. Smith, B. L. *Chem. Ind.* **1998**, 649. Smith, B. L.; Schäffer, T. E.; Viani, M.; Thompson, J. B.; Frederick, N. A.; Kindt, J.; Belcher, A.; Stucky, G. D.; Morse, D. E.; Hansma, P. K. *Nature (London)* **1999**, *399*, 761.
(4) Heywood, B. R.; Mann, S. *Adv. Mater.* **1994**, *6*, 9. Berman, A.; Ahn, D. J.; Lio, A.; Salmeron, M.; Reichert, A.; Charych, D. *Science* **1995**, *269*, 515. Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature (London)* **1999**, *398*, 495. Ueyama, N.; Hosoi, T.; Yamada, Y.; Doi, M.; Okamura, T.; Nakamura, A. *Macromolecules* **1998**, *31*, 7119.
(5) Kato, T.; Suzuki, T.; Amamiya, T.; Irie, T.; Komiyama, M.; Yui, H. *Supramol. Sci.* **1998**, *5*, 411. Gower, L. A.; Tirrell, D. A. *J. Cryst. Growth* **1998**, *191*, 153. Naka, K.; Tanaka, Y.; Chujo, Y. *Langmuir* **2002**, *18*, 3655. Cölfen, H.; Antonietti, M. *Langmuir* **1998**, *14*, 582.
(6) Gower, L. B.; Odom, D. J. *J. Cryst. Growth* **2000**, *210*, 719.
(7) Heywood, B. R.; Mann, S. *Chem. Mater.* **1994**, *6*, 311. Falini, G.; Gazzano, M.; Ripamonti, A. *J. Cryst. Growth* **1994**, *137*, 577. Wada, N.; Yamashita, K.; Umegaki, T. *J. Colloid Interface Sci.* **1999**, *212*, 357. Sims, S. D.; Didymus, J. M.; Mann, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1031. Belcher, A. M.; Wu, X. H.; Christensen, R. J.; Hansma, P. K.; Stucky, G. D.; Morse, D. E. *Nature (London)* **1996**, *381*, 56. Wang, W.; Wang, G.; Liu, Y.; Zheng, C.; Zhan, Y. *J. Mater. Chem.* **2001**, *11*, 1752. Valiyaveettil, S.; Lakshminarayanan, R. *Polym. Mater. Sci. Eng.* **2001**, *84*, 798.
(8) Litvin, A. L.; Valiyaveettil, S.; Kaplan, D. L.; Mann, S. *Adv. Mater.* **1997**, *9*, 124.
(9) Küther, J.; Seshadri, R.; Knoll, W.; Tremel, W. *J. Mater. Chem.* **1998**, *8*, 641.
(10) Kitano, Y. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1973.
(11) Sugawara, A.; Kato, T. *Chem. Commun.* **2000**, 487.
(12) Kato, T. *Adv. Mater.* **2000**, *12*, 1543.
(13) Fritz, M.; Belcher, A. M.; Radmacher, M.; Walters, D. A.; Hansma, P. K.; Stucky, G. D.; Morse, D. E.; Mann, S. *Nature (London)* **1994**, *371*, 49.
(14) Bunn, C. W. *Nature (London)* **1948**, *161*, 929.
(15) Kato, T.; Amamiya, T. *Chem. Lett.* **1999**, 199.
(16) Kato, T.; Suzuki, T.; Irie, T. *Chem. Lett.* **2000**, 186.
(17) Hosoda, N.; Kato, T. *Chem. Mater.* **2001**, *13*, 688.
(18) Rao, M. S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1414.

MA025869B