

Thin-Film Formation of Calcium Carbonate Crystals: Effects of Functional Groups of Matrix Polymers

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We report on the preparation of the thin films of calcium carbonate (CaCO_3) crystals on solid matrixes, i.e., cellulose, chitosan, and chitin in the presence of an acidic macromolecule. The crystal growth from CaCO_3 solution containing poly(acrylic acid) as a soluble acidic polymer results in the formation of CaCO_3 thin-film crystals about $0.8 \mu\text{m}$ in thickness on these solid matrixes. The crystallite size is estimated to be about 30 nm by X-ray measurements and SEM observation. The derivatives of these polysaccharides, whose functional groups of the OH and NH groups are protected, have been prepared and employed as insoluble solid matrixes. No precipitation is observed for the crystallization on the polysaccharide derivatives possessing no proton-donating group even in the presence of poly(acrylic acid). Rhombohedral calcite crystals are obtained from the solution in the absence of the acidic polymer. The infrared spectra for the solid matrixes soaked in the solution show that the acidic polymer is adsorbed on the solid matrixes. The thin-film crystals are obtained only when the acidic polymer exists both in the solution and on the solid matrixes. The balance of the crystallization by the acidic polymer adsorbed on the surface and the inhibition by the acidic polymer in the solution should be important for the thin-film formation because the films are obtained in certain ranges of the concentration of the acidic polymer. The thin films grown on cellulose and chitin consist of only calcite, while those grown on chitosan mainly consist of vaterite. The effects of the concentration and the molecular weight of poly(acrylic acid) on the polymorphs of the thin-film crystals have been examined. The polymorphs of the thin films developed on chitosan are dependent on the concentrations of poly(acrylic acid) in the solution. Poly(acrylic acid) with a higher molecular weight leads to the deposition of thin-film crystals consisting of less stable polymorphs on these polymer matrixes.

Introduction

In biological systems, a large variety of organisms form organic/inorganic composites with ordered structures by the use of biopolymers such as proteins, which have defined monomer sequences and controlled three-dimensional structures.^{1–9} The examples of such processes can be seen in the formation of bones, teeth, mollusc shells, and pearls. Bones and teeth comprise hydroxyapatite with small amounts of biopolymers. The major component of mollusc shells and pearls is CaCO_3 , in which a small quantity of biopolymers is contained. They have layered structures like bricks and mortar.^{2,3,7} Thin-film crystals of CaCO_3 represent the bricks, and the mortar consists of biological macromolecules. These characteristic structures result in the induction of mechanical stability and unique optical properties.

The biomacromolecules that participate in the fabrication of these composites can be classified into water-soluble proteins and water-insoluble macromolecules such as chitin and collagen which function as solid matrixes. These two classes of macromolecules play important roles in the control of morphology and polymorphs of CaCO_3 crystals.^{3,10}

Recently, the crystallization of inorganic compounds on solid organic templates has attracted a great deal of attention. For example, the use of organic biomolecules such as collagen,¹¹ cholesterol,¹² elastin,¹³ and chitin¹⁴ showed significant effects on the control of CaCO_3 crystallization. Synthetic compounds such as Langmuir monolayers,^{15–18} self-assembled monolayers,^{19,20} poly-

- (1) Calvert, P.; Mann, S. *J. Mater. Sci.* **1988**, *23*, 3801.
- (2) Addadi, L.; Weiner, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 153.
- (3) Weiner, S.; Addadi, L. *J. Mater. Chem.* **1997**, *7*, 689.
- (4) Mann, S. *Nature* **1988**, *332*, 119.
- (5) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313.
- (6) Sikes, C. S.; Wheeler, A. P. *CHEMTECH* **1988**, 620.
- (7) Watabe, N. *J. Ultrastruct. Res.* **1965**, *12*, 351.
- (8) Ozin, G. A. *Chem. Commun.* **2000**, 419.
- (9) Krampitz, G.; Graser, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1145.

- (10) Levi, Y.; Albeck, S.; Brack, A.; Weiner, S.; Addadi, L. *Chem. Eur. J.* **1998**, *4*, 389.
- (11) Falini, G.; Fermani, S.; Gazzano, M.; Ripamonti, A. *Chem. Eur. J.* **1998**, *4*, 1048.
- (12) Dalas, E.; Koutsoukos, P. G. *J. Colloid Interface Sci.* **1989**, *127*, 273.
- (13) Manoli, F.; Dalas, E. *J. Cryst. Growth* **1999**, *204*, 369.
- (14) Manoli, F.; Koutsopoulos, S.; Dalas, E. *J. Cryst. Growth* **1997**, *182*, 116.
- (15) Mann, S.; Heywood, B. R.; Rajam, S.; Birchall, J. D. *Nature* **1988**, *334*, 692.
- (16) Heywood, B. R.; Mann, S. *Chem. Mater.* **1994**, *6*, 311.
- (17) Litvin, A. L.; Valiyaveetil, S.; Kaplan, D. L.; Mann, S. *Adv. Mater.* **1997**, *9*, 124.

amide,²¹ peptidomimetic monolayers,²² and lyotropic liquid crystals²³ were also employed as organic templates for the deposition of inorganic compounds.

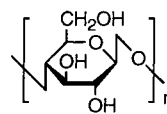
For water-soluble matrixes, biomacromolecules control the crystal habit, the polymorphs, and the morphology on the crystallization of CaCO₃ from its aqueous solution.²⁴ For example, proteins extracted from mollusc shell and sea urchin led to the growth of specific crystal planes of CaCO₃.^{25,26} Synthetic soluble polymers possessing functional groups also influenced crystallization.^{27–30}

Our approach has been to obtain new polymer/CaCO₃ composite materials by cooperation of insoluble and soluble polymers.^{30–34} The flat thin-film crystals of CaCO₃ were successfully developed on chitosan films³⁰ and chitin fibers³² in the presence of acidic macromolecules. Moreover, layered structures consisting of CaCO₃ crystals about 0.8–1.0 μm in thickness and polymer thin films about 60 nm in thickness have been obtained by the alternate repetition of the spin-coating of polysaccharides and the thin-film crystallization.³³ The thin films in the aragonite polymorph were deposited by using the effects of magnesium ion.³⁴ We expect that these organic/inorganic composites can be used as novel environmentally friendly materials exhibiting high mechanical strength and unique optical properties. The formation of CaCO₃ films on insoluble matrixes such as porphyrin monolayer³⁵ and chitosan³⁶ was also observed by the crystallization with acidic water-soluble polymers.

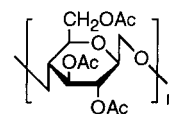
In the present paper, we report thin-film formation of CaCO₃ on solid polymer matrixes. The role of insoluble and soluble macromolecules has been examined to achieve controlled syntheses of CaCO₃/organic composite materials. Cellulose, chitosan, and chitin have been used as insoluble polymer matrixes for CaCO₃ crystallization from its aqueous solution with poly(acrylic acid). Polysaccharide derivatives of which the OH and NH groups are protected have been used as insoluble matrixes to examine what type of interactions is a key for the controlled CaCO₃ crystallization. The

Chart 1. Structures of Polymer Matrixes and Soluble Additives

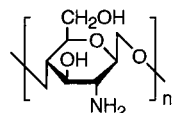
polymer matrixes



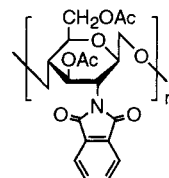
1a: cellulose



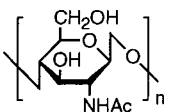
1b: cellulose derivative



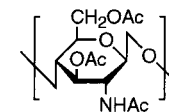
2a: chitosan



2b: chitosan derivative

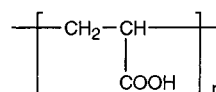


3a: chitin



3b: chitin derivative

soluble additives



poly(acrylic acid)

4a: $\overline{M}_w = 2.0 \times 10^3$

4b: $\overline{M}_w = 2.5 \times 10^5$

effects of the concentration and molecular weight of the soluble poly(acrylic acid) on the crystallization have also been studied to obtain information on the role of the polymers for the crystallization.

Results and Discussion

Approach to Cooperative Effects of Soluble and Insoluble Polymers for CaCO₃ Crystallization. Calcium carbonate was precipitated on a solid polymer matrix from its supersaturated solution containing a soluble additive. The morphology of these crystals was examined by optical and scanning electron microscopy. The polymorphs of the CaCO₃ crystals formed on the solid polymer matrixes were determined on the basis of powder X-ray diffraction patterns. The CaCO₃ crystal has three polymorphs: calcite; aragonite; vaterite. Calcite is the most stable, and vaterite is the least stable polymorph.

The molecular structures of insoluble polymer matrixes are given in Chart 1. Cellulose (**1a**), chitosan (**2a**), chitin (**3a**), and their derivatives **1b**, **2b**, and **3b** have been employed as solid polymer matrixes. Cellulose and chitin are polysaccharides that are abundant in nature. Chitosan is obtained by the deacetylation of chitin. Chitosan and chitin have two kinds of functional groups, i.e., OH and NH groups. In our previous work on CaCO₃

(18) Lahiri, J.; Xu, G.; Dabbs, D. M.; Yao, N.; Aksay, I. A.; Groves, J. T. *J. Am. Chem. Soc.* **1997**, *119*, 5449.

(19) Küther, J.; Seshadri, R.; Knoll, W.; Tremel, W. *J. Mater. Chem.* **1998**, *8*, 641.

(20) Aizenberg, J.; Black, A. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 4500.

(21) Ueyama, N.; Hosoi, T.; Yamada, Y.; Doi, M.; Okamura, T.; Nakamura, A. *Macromolecules* **1998**, *31*, 7119.

(22) Bekele, H.; Fendler, J. H.; Kelly, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 7266.

(23) Braun, P. V.; Osenar, P.; Tohver, V.; Kennedy, S. B.; Stupp, S. I. *J. Am. Chem. Soc.* **1999**, *121*, 7302.

(24) Belcher, A. M.; Wu, X. H.; Christensen, R. J.; Hansma, P. K.; Stucky, G. D.; Morse, D. E. *Nature* **1996**, *381*, 56.

(25) Addadi, L.; Weiner, S. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4110.

(26) Albeck, S.; Weiner, S.; Addadi, L. *Chem. Eur. J.* **1996**, *2*, 278.

(27) Gower, L. A.; Tirrell, D. A. *J. Cryst. Growth* **1998**, *191*, 153.

(28) Kawaguchi, H.; Hirai, H.; Sakai, K.; Sera, S.; Nakajima, T.; Ebisawa, Y.; Koyama, K. *Colloid Polym. Sci.* **1992**, *270*, 1176.

(29) Marentette, J. M.; Norwig, J.; Stöckelmann, E.; Meyer, W. H.; Wegner, G. *Adv. Mater.* **1997**, *9*, 647.

(30) Kato, T.; Suzuki, T.; Amamiya, T.; Irie, T.; Komiyama, M.; Yui, H. *Supramol. Sci.* **1998**, *5*, 411.

(31) Kato, T. *Adv. Mater.* **2000**, *12*, 1543.

(32) Kato, T.; Amamiya, T. *Chem. Lett.* **1999**, 199.

(33) Kato, T.; Suzuki, T.; Irie, T. *Chem. Lett.* **2000**, 186.

(34) Sugawara, A.; Kato, T. *Chem. Commun.* **2000**, 487.

(35) Xu, G.; Yao, N.; Aksay, I. A.; Groves, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 11977.

(36) Zhang, S.; Gonsalves, K. E. *Langmuir* **1998**, *14*, 6761.

crystallization,^{30–34} these polysaccharides were effective for thin-film formation. Cellulose has only OH groups as functional groups. In contrast to polysaccharides **1a**, **2a**, and **3a**, the derivatives of **1b** and **2b** have no proton-donating groups because the OH and NH groups are fully protected. Chitin derivative **3b** has only an NH group as a proton-donating group. Polymer matrixes **2b** and **3b** were synthesized by the acetylation of hydroxyl groups following the *N*-phthaloylation of the amino group of **2a**³⁷ and the acetylation of **3a**,³⁸ respectively. The crystallization on these polysaccharide derivatives **1b**, **2b**, and **3b** has been performed to examine the effect of the functional groups of the polymer matrixes on the formation of the CaCO₃ thin films.

Thin-Film Formation of CaCO₃. The polymers of **1–3** were spin-coated on the glass substrate. Poly-(acrylic acid)s with average molecular weights of ca. 2.0×10^3 (**4a**) and 2.5×10^5 (**4b**), which have carboxyl groups, have been used as acidic soluble additives to examine the effects of cooperation of these polymers with the solid polymer matrixes on the crystal growth.

Thin films of CaCO₃ are successfully developed on the surface of **1a** when the crystallization is performed in the presence of **4a** at the concentration of 2.4×10^{-3} wt %. Figure 1A,B shows the polarized optical micrograph and the scanning electron micrograph (SEM) of the thin films obtained by the crystal growth for 20 h with **4a**, respectively. A mosaic of connected spherulites with cross lines is observed in Figure 1A. The birefringence is observed even in those obtained by the crystallization for 10 h (Figure 1A, inset), suggesting that these films consist of polycrystals and that the nucleation occurs at the center of the spherulites. It should be noted that the thickness of the film, which is shown in Figure 1B, remains at about 0.8 μm. X-ray diffraction patterns of the crystals show that the thin-film crystals developed on **1a** consist of only calcite. The crystallite size that is estimated from the half-peak width of the X-ray diffraction patterns according to Scherrer's equation is about 30 nm. The crystallites are observed by the SEM at a higher magnification (Figure 1C). Particles with 30 nm in diameter, which is compatible with the crystallite size calculated from the X-ray diffraction peak, can be seen in the micrograph. In contrast, rhombohedral crystals of calcite are formed on **1a** in the absence of soluble polymer additive **4a**, and the crystallization is inhibited by **4a** without **1a**. These results suggest that **1a** alone in the solid-film state has no effect on the control of polymorphs and morphology and that the combination of **1a** and **4a** plays a significant role in the formation of the thin-film crystals.

To understand the role of **1a** and **4a** in the thin-film formation, we should know where polymer **4a** exists in the process of the thin-film crystallization. Infrared spectra have been obtained for the solid matrix of **1a** which is soaked in the supersaturated solution of CaCO₃ containing **4a** (1.0×10^{-2} wt %) and is removed from the solution before the crystallization occurs. In the initial stage of the crystallization, the pH of the supersaturated CaCO₃ solution with **4a** is 5.8. The *pK_a* of the

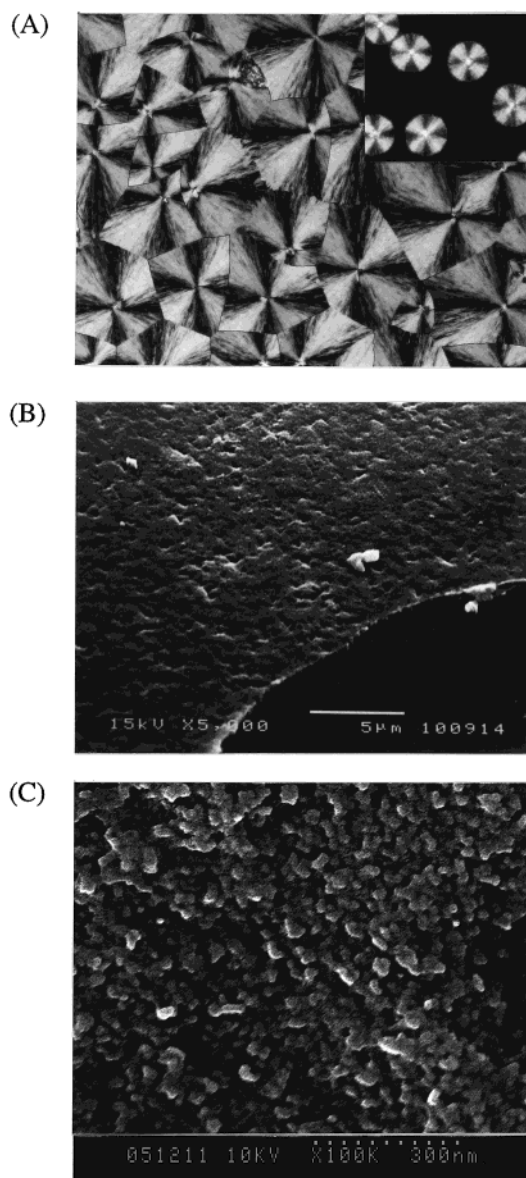


Figure 1. Micrographs of CaCO₃ thin films developed on **1a** by the crystallization for 20 h in the presence of 2.4×10^{-3} wt % of **4a**: (A) polarized optical micrograph; (B) scanning electron micrograph at lower magnification; (C) scanning electron micrograph at higher magnification. The inset of (A) shows the films developed by the crystallization for 10 h.

carboxylic acid of **4a** is 4.5. Figure 2A shows the infrared spectrum for the sample of **1a** soaked in the solution with **4a** for 3 h. The two bands at 1734 and 1419 cm⁻¹ correspond to the absorption of the carbonyl group and the COO⁻ ionic moiety of **4a**, respectively, whereas these bands are not observed in the spectrum for **1a** alone (Figure 2B). These results indicate that **4a** is adsorbed on the surface of **1a** in the solution containing **4a**.

Here we question whether only the complex of **1a** and **4a** can give the thin films of CaCO₃. The complex of **1a** and **4a** obtained by the soaking of **1a** in the aqueous solution with **4a** for 3 h has been placed in the CaCO₃ solution containing no polymer additive. Sporadic aggregates of CaCO₃ with irregular shapes are obtained on **1a**, and no thin-film formation is observed. This observation shows that not only **4a** adsorbed on the surface of **1a** but also **4a** that exists in the solution is

(37) Nishimura, S.; Kohgo, O.; Kurita, K.; Vittavatvong, C.; Kuzuhara, H. *Chem. Lett.* **1990**, 243.

(38) Nishi, N.; Noguchi, J.; Tokura, S.; Shiota, H. *Polym. J.* **1979**, 11, 27.

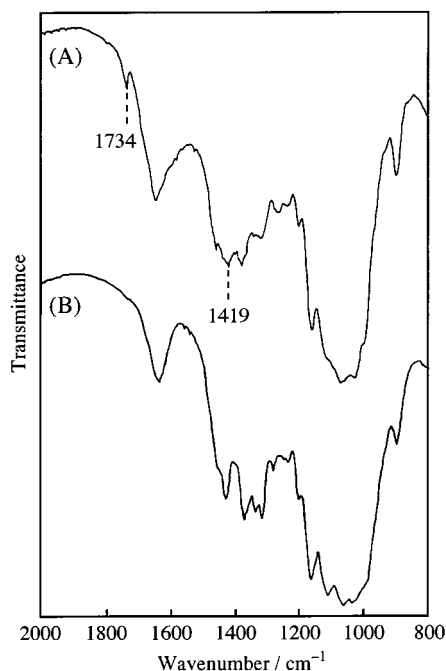


Figure 2. Infrared spectra of (A) **1a** soaked in the supersaturated solution of CaCO₃ containing **4a** (1.0×10^{-2} wt %) for 3 h and (B) **1a** without soaking.

important for the formation of the thin-film crystals of CaCO₃.

We assume that, in the process of the thin-film formation, polymer **4a** plays two kinds of roles in the solution and on the solid matrix. The adsorption of **4a** on the surface of **1a** leads to a local high concentration of the calcium ions by the interaction between the COO⁻ moiety and the calcium ion. This high concentration of the inorganic ions on the surface promotes the nucleation and the crystal growth of CaCO₃. For polymer **4a** remaining in the solution, it inhibits the crystallization of CaCO₃.^{30,35,36} The balance of the crystallization and the inhibition in a certain range of the concentration of **4a** should be important for the thin-film formation. The formation of the thin-film crystals on **1a** is observed at the concentration range of 7.2×10^{-4} to 2.0×10^{-2} wt %. In contrast, at concentrations lower than those for the thin-film formation, sporadic aggregates of CaCO₃ with irregular shapes are obtained, while at higher concentrations no crystal is formed.

For the CaCO₃ films reported by Gower and Tirrell,²⁷ they were formed on glass coverslips, and they contained bulky aggregates of CaCO₃. Our present results show that the suppression of the growth of the crystal aggregates and the resultant formation of flat films are achieved by using both of the soluble and insoluble organic polymers.

Effects of Functional Groups of Insoluble Polymers. It is expected that **4a** is adsorbed on the surface of **1a** by the hydrogen bonds between the OH groups of **1a** and the COO⁻ moieties of **4a**. To examine the role of the functional groups of the solid matrixes, polymers **2a** and **3a** containing the OH and NH groups and their derivatives **1b**, **2b**, and **3b** have been prepared and employed as solid matrixes. Polymers **1b** and **2b** have no proton-donating group. For **3b**, the hydroxyl groups are protected and only the NH group in the amide group acts as the proton-donating group.

Table 1. Morphology of CaCO₃ Crystals Grown on Insoluble Polymer Matrixes 1–3 in the Presence of 2.4×10^{-3} wt % of **4a**

polym matrixes	morphology	polym matrixes	morphology
1a	thin films	2b	<i>inhibited</i>
1b	<i>inhibited</i>	3a	thin films
2a	thin films	3b	thin films

In the absence of acidic soluble polymer **4a**, rhombohedral crystals of calcite are deposited on all of the polymer matrixes, as is observed for **1a**. Then, CaCO₃ crystallization has been performed with 2.4×10^{-3} wt % of acidic polymer **4a** for the polymer matrixes. No crystal growth is observed when **1b** and **2b** are used as the polymer matrixes. In contrast, the use of **2a**, **3a**, and **3b** as solid polymer matrixes results in the formation of CaCO₃ thin films. The thickness of the thin films and the size and shape of the crystallite forming the thin-film crystals on **2a**, **3a**, and **3b** are almost equal to those on **1a**. These results are summarized in Table 1 with the results of the crystallization on **1a**. The results for **1b** and **2b** indicate that the decrease of the interaction between the polymer matrixes and **4a** yields no concentration of calcium ions on the surface resulting in no nucleation of CaCO₃ on the polymer matrixes.

To make sure that the adsorption of **4a** on these polymer matrixes leads to the thin-film formation, the infrared spectra of all polymer matrixes that are soaked in the CaCO₃ solution containing **4a** have been obtained. The peaks corresponding to the functional group of **4a** are also observed for the samples of **2a**, **3a**, and **3b**, while no change is observed for the samples of **1b** and **2b**. These results show that **4a** is adsorbed by the interaction between the OH or NH groups of the polymer matrixes and the functional groups of **4a**.

Effects of the Concentration of the Soluble Additive. The effects of the concentration of **4a** on the thin-film deposition have been examined for the crystallization on **1a**, **2a**, and **3a**. The formation of the flat thin-film crystals on **1a** is observed at the concentration range of 7.2×10^{-4} to 2.0×10^{-2} wt %. The thin films on **2a** are obtained at the concentration range of 2.4×10^{-4} to 1.0×10^{-2} wt %, which is lower than that for **1a**. The use of **3a** as an insoluble matrix results in the thin-film formation at the concentration range of 2.4×10^{-3} to 7.2×10^{-3} wt %, which is narrower than those for **1a** and **2a**. Only calcite peaks are observed for the thin films developed on **1a** and **3a**. In contrast, the polymorphs of the thin-film crystals on **2a** switch from vaterite to calcite when the concentration of **4a** increases from 2.4×10^{-3} wt % to 1.0×10^{-2} wt % as shown in Figure 3. Figure 4 shows the plot of the calcite fraction in the thin-film crystals as a function of the concentration of **4a**. It is found that the calcite fraction increases significantly at the concentration of 4.8×10^{-3} wt %. These results show that the use of **2a** in the solid-film state for the CaCO₃ crystallization enables us to change the polymorphs by controlling the concentrations of **4a**. For all solid matrixes, sporadic aggregates of CaCO₃ with irregular shapes are obtained at lower concentrations than those for thin-film formation, while no crystal is formed at higher concentrations.

Effects of the Molecular Weight of the Soluble Additive. We have found that the polymorphs of thin-

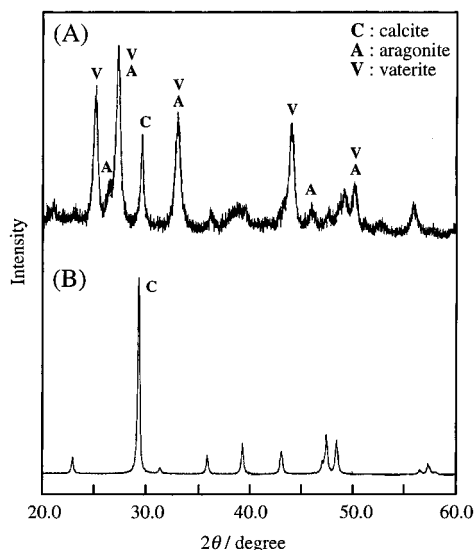


Figure 3. Powder X-ray diffraction patterns of CaCO_3 thin films developed on **2a** in the presence of **4a**: (A) 2.4×10^{-3} wt %; (B) 1.0×10^{-2} wt %.

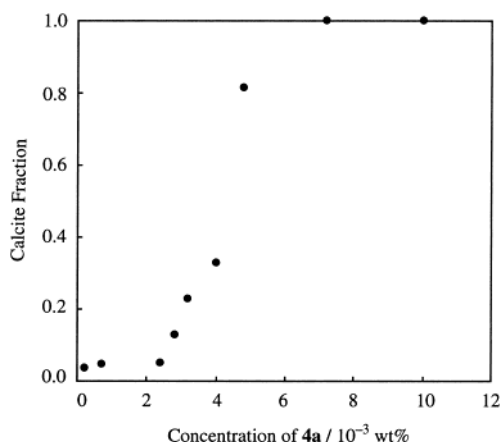


Figure 4. Plot of the calcite fraction in the CaCO_3 thin-film crystals developed on **2a** as a function of the concentration of **4a**.

Table 2. Polymorphs of CaCO_3 Thin-Film Crystals Grown on **1a, **2a**, and **3a** in the Presence of 2.4×10^{-3} wt % of **4a** or **4b****

polym matrixes	soluble additives	
	4a	4b
1a	calcite	calcite/vaterite/aragonite
2a	calcite/vaterite/aragonite	calcite/vaterite/aragonite
3a	calcite	calcite/vaterite

film crystals are dependent on the molecular weight of the soluble additive. Polymer **4b**, whose molecular weight is higher than **4a**, has been used for the crystallization on **1a**, **2a**, and **3a**. In the presence of 2.4×10^{-3} wt % of **4b**, flat thin-film crystals are obtained on **1a** and **2a**. The powder X-ray diffraction patterns of the thin films obtained by the cooperation of **4b** and **1a**, indicate the existence of three polymorphs: calcite; vaterite; aragonite. The thin films formed on **2a** in the presence of **4b** also contain three polymorphs. The crystallization on **3a** induces the formation of partial thin-film crystals consisting of calcite and vaterite. These results are summarized in Table 2 with those of the crystallization with **4a**. The crystal growth of CaCO_3 from the solution with **4b** results in the formation of

the thin-film crystals consisting of less stable polymorphs on these polymer matrixes in comparison with those obtained with **4a**.

Aksay and co-workers reported that porphyrin monolayers functioned as a template of the calcite thin-film crystallization.³⁵ They propose that the arrangement of the monolayers leads to the formation of calcite. In our system, we assume that the polymorphs of the thin films are dependent on a density of calcium ions on the surface of the polymer matrixes rather than the arrangement of the polymers. Recently, Falini et al. suggested that a higher calcium content induces precipitation of CaCO_3 with thermodynamically unstable polymorphs.¹¹ This is also the case for our system. The local higher concentration of the calcium ions is achieved by poly(acrylic acid) with higher molecular weight. Such an increase in the concentration may cause the kinetically controlled condition, which results in the preferred precipitation of less stable polymorphs in accordance with Ostwald's rule.

Conclusions

We have succeeded in the CaCO_3 thin-film formation by using the cooperative effects of the soluble additive and the solid polymer matrix. The soluble additive, poly(acrylic acid), is adsorbed on the surface of the polymer matrix by hydrogen bonds between the COO^- moieties of the soluble additive and the OH or NH groups of the polymer matrix. Both of the acidic polymer adsorbed on the solid matrix and the polymer remaining in the solution play key roles in the formation of the CaCO_3 thin-film crystals. The balance of the nucleation and the inhibition induced by the acidic polymer is important for the controlled crystallization. These results offer potential for the design of novel organic/inorganic composite materials with high performance and environmental benignancy.

Experimental Section

Materials. Cellulose (powder, $\sim 20 \mu\text{m}$, **1a**), cellulose acetate with $\overline{M}_w = 3.0 \times 10^4$ (**1b**), and poly(acrylic acid)s (**4a,b**) were obtained from Aldrich. Chitosan (**2a**), phthalic anhydride, and calcium carbonate (calcite) were purchased from Wako. Chitin (**3a**) was obtained from Tokyo Kasei. All reagents were of the highest grade and used without further purification.

Syntheses of **2b and **3b**.** Polymer matrixes **2b** and **3b** were synthesized using previously known methods.^{37,38} Polymer matrix **2b** was synthesized by stirring *N*-phthaloyl chitosan and acetic anhydride in pyridine at room temperature following the condensation of **2a** and phthalic anhydride in *N,N*-dimethylformamide at 130°C .³⁷ The product was obtained by reprecipitation in distilled water. $^1\text{H NMR}$ (CDCl_3 , 270 MHz): $\delta = 1.7\text{--}2.0$ (*O*-acetyl groups, 6H per monosaccharide residue), 7.6–7.9 (*N*-phthaloyl groups, 4H per monosaccharide residue). IR (KBr): 1770 and 1710 cm^{-1} (*N*-phthaloyl groups), 1750 and 1230 cm^{-1} (*O*-acetyl groups).

Polymer matrix **3b** was synthesized by the reaction of chitin and acetic anhydride in methanesulfonic acid at 0°C .³⁸ The product was obtained by reprecipitation in distilled water. Anal. Found: C, 48.67; H, 5.82; N, 4.92. Calcd for $\text{C}_8\text{H}_{11}\text{NO}_3 \cdot (\text{OCOCH}_3)_2$: C, 50.17; H, 5.96; N, 4.88. IR (KBr): 1750 and 1230 cm^{-1} (*O*-acetyl groups).

Preparation of Soluble Additives and Polymer Matrixes. Soluble additive **4a** or **4b** was dissolved in a supersaturated solution of CaCO_3 . Polymer matrixes **1–3** were used as the solid film on a glass substrate. Polymer matrix **1a** was dissolved in a mixture of aqueous ammonia and copper(II)

hydroxide. The solid film of **1a** obtained by spin-coating of the solution was washed with dilute hydrochloric acid. Polymer matrix **2a** was dissolved in water with acetic acid. The matrix of **2a** obtained by spin-coating was neutralized with dilute aqueous ammonia and washed with distilled water. The mixture of *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone containing lithium chloride was used as the spin-coating solvent of **3a**. The films were washed with alcohol and distilled water. Polymer matrixes **1b**, **2b**, and **3b** were dissolved in acetic acid, *N,N*-dimethylformamide, and formic acid, respectively. The matrixes of **1b** and **3b** obtained by spin-coating were neutralized with dilute aqueous ammonia and washed with distilled water. All the films were dried at 180 °C. Polymer matrixes were placed on the bottom of the vessels in the supersaturated solutions.

Preparation of CaCO₃ Crystals. Crystals were grown from supersaturated CaCO₃ solution. The preparation of supersaturated solution is as follows: Calcium carbonate (2.0 g/L) was suspended in water obtained from Milli-XQ (Millipore, relative resistivity: maximum $18 \times 10^6 \Omega \text{ cm}$; 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 CaCO₃ 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, $[\text{Ca}^{2+}] = 7.6 \times 10^{-3} \text{ mol/L}$) was transferred to vessels. The

system was kept at 30 °C in a water bath. The total amount 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 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 CaCO₃ crystals were performed using an X-ray diffractometer Rigaku RINT2400 with Cu K α radiation. The polymorphs of CaCO₃ were determined on the basis of powder X-ray diffraction patterns. The crystallite size was estimated from the half-peak width of X-ray diffraction patterns according to Scherrer's equation. FT-IR measurements were conducted on a JASCO FT/IR-8900 μ spectrometer.

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