

Control Crystallization of Calcium Carbonate in Aqueous Solution with In-Situ Radical Polymerization of Sodium Acrylate as a Latent Inductor for Crystal Nucleation and Growth

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Crystallization of $CaCO_3$ with in-situ radical polymerization of sodium acrylate in aqueous solution was carried out by a double jet method to prevent heterogeneous nucleation at glass walls. The concentration of sodium acrylate was 1.71 mM and the feed ratio of sodium acrylate to calcium ions was 0.62. After addition of the calcium reactants into the aqueous solution of sodium acrylate was completed, an aqueous solution of potassium peroxodisulfate as a water-soluble radical initiator was added to the reaction mixture after incubation at 30 °C for several minutes (1, 3, or 20 min). Three different crystal polymorphs of $CaCO_3$ (aragonite, vaterite, and calcite) were selectively induced by changing the time for adding the radical initiator to a calcium carbonate solution with sodium acrylate. Formation of crystalline $CaCO_3$ in the presence of sodium acrylate with the radical initiator at different feed ratio of sodium acrylate to calcium ions was also studied. The higher concentration of sodium acrylate increased sizes of vaterite spherical particles. The present results indicate that the final crystalline phases are highly sensitive to the presence of the active additives at the very initial nucleation stage (within several minutes).

In nature, biological organisms produce polymer–inorganic hybrids. These hybrids have superior mechanical properties to those of synthetic hybrids. The abalone shell, a composite of calcium carbonate with a few per cent of the organic component, is 3000 times more fracture resistant than a single crystal of the pure mineral.[1] In these mineralized tissues, crystal morphology, size, and orientation are determined by local conditions and, in particular, by the presence of "matrix" proteins or other macromolecules.[2] The processes and materials that control such crystal growth are of great interest to materials scientists who seek to make composite materials and crystalline forms analogous to those produced by nature. Due to the complexity of the natural biomineralization systems, however, the mineralization research has been conducted on model organic interfaces.[3] These studies have been focused on the main fundamental question how inorganic crystallization can be controlled in aqueous solution. The major inorganic produced in natural organisms is calcium carbonate. Calcium carbonate makes an attractive model mineral for studies in the laboratory, since its crystals are easily characterized. The particular interest in this system is due to the polymorphism of calcium carbonate, which has three anhydrous crystalline forms: vaterite, aragonite, and calcite, in order of decreasing solubility and increasing stability. Morphological control can also be accomplished by adsorption of soluble additives onto specific faces of growing crystals, altering the relative growth rates of the different crystallographic faces and leading to different crystal habits. Since these processes usually take place at an organic–inorganic interface, the organic portion providing the initial structural information for the inorganic part to nucleate on and grow outwards in the desired manner. However, there remain many unknowns as to how the matrix affects the crystallization process in nature, especially the initial nucleation.

The final crystalline phase could arise through a series of steps, initiated by the formation of an amorphous phase that undergoes subsequent phase transformations. The existence of several phases would enable organisms to control mineralization through intervention with the kinetics. By selectively interacting with the mineral at different stages during the crystal forming process, the organisms could choose to manipulate both the polymorph and the orientation of the mineral to meet specific biological requirements. Although crystallization of $CaCO_3$ in the presence of various synthetic polymers has been investigated as a model of biomineralization, selective interaction of organic matrix with the mineral at different stages has not been examined. Very recently, we have introduced a new concept for controlling a polymorph of calcium carbonate as schematically shown in Fig. 1.[4] The key point of the method is using a "latent inductor" for crystal nucleation. The latent inductor at inactive state does not affect a nucleation and growth of a crystal. After the inactive state is transferred to an active state by a stimulus, the active inductor can control the nucleation and growth of the crystal. We used sodium acrylate as a latent inductor for this purpose and potassium peroxodisulfate was used as a stimulus. Sodium acrylate may not affect the nucleation and growth of the crystal.[5] On the other hand, poly(acrlylate) acts as an inhibitor for crystal formation.[6,7] Sodium acrylate can be transferred to poly(acrylate) by adding the radical initiator. In the previous communication,[4] we showed that three different crystal polymorphs of $CaCO_3$ (aragonite, vaterite, and calcite) were selectively induced by changing an time when the radical initiator was added to a calcium carbonate solution with sodium acrylate. In this paper, we describe detailed studies of crystallization of $CaCO_3$ with in-situ radical poly-

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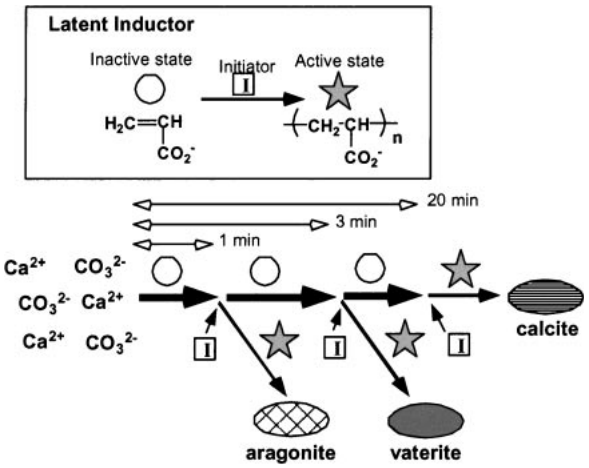

Fig. 1. Schematic depiction for the control of crystal polymorph by a latent inductor.

merization of sodium acrylate in aqueous solution. It should be noted that crystallization of calcium carbonate with in-situ polymerization of anionic monomers in aqueous solution has not been reported so far.

Experimental

Materials. Poly(acrylic acid)s (PAA) (M_w = 5100 and 1200) were obtained from Aldrich. Calcium chloride and ammonium carbonate were purchased from WAKO Pure Chemical Industries, Ltd. Potassium peroxodisulfate (KPS) was crystallized from distilled water and dried at 50 °C in a vacuum desiccator. Acrylic acid was purified by vacuum distillation. An aqueous solution of sodium acrylate was prepared by mixing the same molar ratios of acrylic acid and sodium hydroxide for 12 h at 30 °C under N_2.

Characterization. Scanning electron microscopic (SEM) measurements were carried out with a JEOL JSM-5310/LV at 15 kV. The X-ray diffraction was recorded on a Shimadzu XRD-6000. The ^{1}H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin Elmer 1600 spectrometer, respectively. TGA was made on a Shimadzu DT-30 instrument (10 °C/min). Gel permeation chromatography was carried out on a TSKgel α-3000 column by using 0.2 M $NaNO_3$ aqueous solution as an eluent at 40 °C.

Crystallization of $CaCO_3$. The precipitation of $CaCO_3$ was carried out as follows. A solution of sodium acrylate in 180 mL of distilled water was adjusted to pH 8.5 with aqueous NH_3. The solution was degassed with N_2 for 10 min. The 0.1 M $CaCl_2$ aqueous solution (adjusted to pH 8.5) and 0.1 M $(NH_4)_2CO_3$ aqueous solution (adjusted to pH 10.2) were injected via syringe into the reaction mixture at 30 °C under N_2 with stirring and with the reactant being supplied at 1 mL/min. After 4.95 mL of each reactant was added, 2.5 mol% of potassium peroxodisulfate in aqueous solution (0.2 mL) was added. After a sudden increase in the turbidity of the solution, this solution was then kept at 30 °C under N_2 for 1 day with gentle stirring. The crystalline $CaCO_3$ was washed with water several times. Crystallization of $CaCO_3$ in the absence of the additive was carried out using 180 mL of aqueous solution containing 2.50 mmol of NaCl.

Results and Discussion

Crystallization of Calcium Carbonate with In-Situ Radical Polymerization of Sodium Acrylate. The precipitation of $CaCO_3$ was carried out by a double-jet method to prevent heterogeneous nucleation at the glass walls.[3,8] The two capillary ends were joined together so that a high local reactant concentration and thus extreme supersaturation is achieved at the moment when the two reactants leave the capillaries, which provides an immediate nucleation of $CaCO_3$. The nuclei are then immediately transported to regions of lower $CaCO_3$ concentration and can grow further. If each 4.95 mL of reactants (0.1 M $CaCl_2$ and 0.1 M $(NH_4)_2CO_3$) were injected via syringe into 180 mL of the solution in the absence of additives, the turbidity of the solution suddenly spread over the whole solution. Thus, 4.95 mL of each of the reactants (0.1 M $CaCl_2$ and 0.1 M $(NH_4)_2CO_3$) were added to the aqueous solution of sodium acrylate, which was adjusted to pH 8.5 by aqueous NH_3. The concentration of calcium ions was constant at 2.75 mM in all the following experiments. The concentration of sodium acrylate was 1.71 mM and the feed ratio of sodium acrylate to calcium ions was 0.62. After addition of the calcium reactants into the aqueous solution of sodium acrylate was completed, an aqueous solution of potassium peroxodisulfate as a water-soluble radical initiator was added to the reaction mixture after incubation at 30 °C for several minutes (1, 3, or 20 min). This solution was then kept at 30 °C under N_2 with gentle stirring and the critical point of the sudden increase in the turbidity of the solution was observed at 3 to 4 min of stirring after the addition of the calcium solution. This delay of the $CaCO_3$ crystal formation compared with the case in the absence of the additives indicates that sodium acrylate acts as an inhibitor for crystal formation. When the radical initiator was added to the calcium solution with sodium acrylate after incubation for 1 min, no turbidity of the solution was observed. These solutions were kept at 30 °C under N_2 for 1 day with gentle stirring. The crystalline $CaCO_3$ was collected and washed with water several times. The yields of the crystalline products obtained when the radical initiators were added to the reaction mixture after incubation for 1 min (for product A), 3 min (for product B), and 20 min (for product C) were 33, 35, and 54%, respectively.

The crystal phase of the obtained $CaCO_3$ was characterized by FT-IR analysis (Fig. 2).[6,9,10] A strong absorption occurring around 1414 cm^{-1} was characteristic of calcium carbonate.

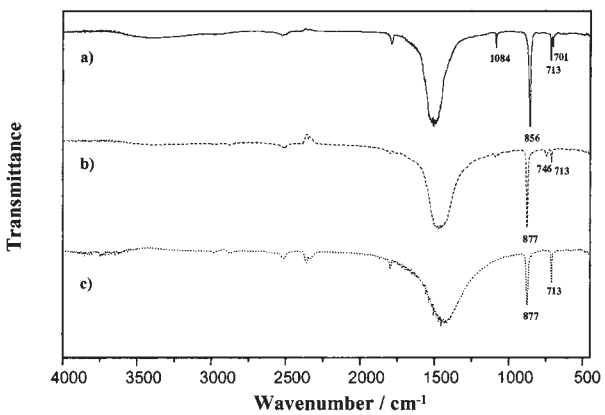

Fig. 2. FT-IR spectra of $CaCO_3$ of (a) product A, (b) product B, and (c) product C. The concentration of sodium acrylate and a feed ratio of sodium acrylate to calcium ions were 1.71 mM and 0.62, respectively.

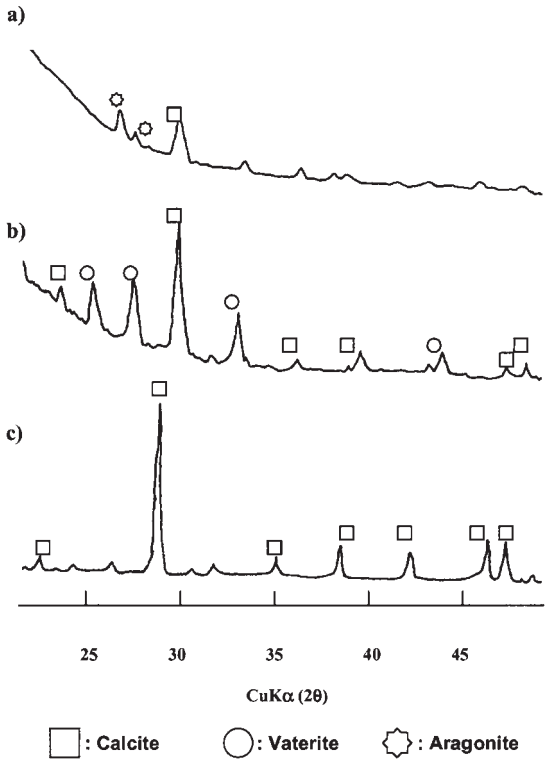

Fig. 3. X-ray diffraction patterns of $CaCO_3$ of (a) product A, (b) product B, and (c) product C.

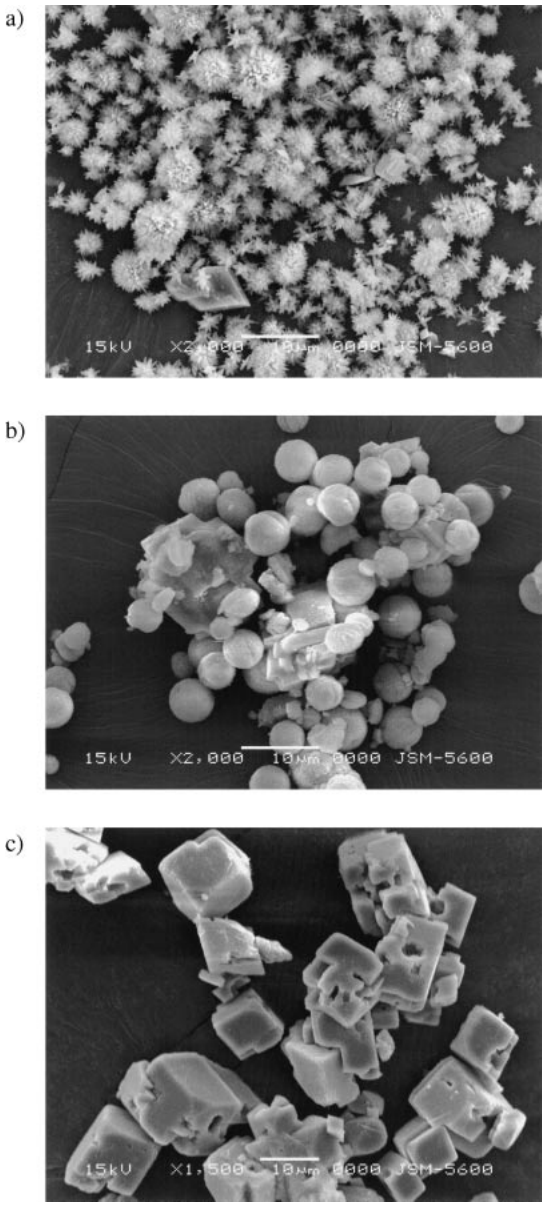

Fig. 4. Scanning electron micrographs of $CaCO_3$ of (a) product A, (b) product B, and (c) product C.

Product A displays a characteristic symmetric carbonate stretching vibration at 1084 cm^{-1}, a carbonate out-of-plane bending vibration at 856 cm^{-1}, and a pair of peaks at 701 and 713 cm^{-1}, while the band at 877 cm^{-1} assignable to calcite was almost invisible. This indicates aragonite formation. When the radical initiator was added after incubation for 3 min, product B showed several bands corresponded to a carbonate out-of-plane bending vibration. A band at 746 cm^{-1} indicated a vaterite formation and the bands at 877 and 713 cm^{-1} assignable to calcite coexisted. The crystal phase of product C was determined to be calcite by IR. Only the two bands at 877 and 713 cm^{-1}, assigned to the ν_4 and ν_2 absorption bands of CO_3^{2-} in calcite, respectively, were recognized.

The crystal phase of the obtained $CaCO_3$ was further confirmed by XRD (Fig. 3). The reflections of product C were characteristic for calcite. The fraction of vaterite in the crystalline phase of product B was 63% as determined by Rao's equation.[11] Although a strong peak at 33° assigned to calcite is observed in product A (Fig. 3a), the aragonite XRD reflections were observed. Figure 4 shows the scanning electron micrographs (SEM) of the three crystalline products. Each SEM micrograph shows different crystal modifications. Most crystals of product A were efflorescent bundles of needles (Fig. 4a), which is a typical aragonite crystal morphology. Product B consisted of two different crystal modifications: spherical vaterite and rhombs of calcite (Fig. 4b). The crystal of product C was rhombohedral (Fig. 4c). Each shape of $CaCO_3$ is a typical morphology for each polymorph. The thermogravimetric analysis showed that organic additives were not built-in into the crystals obtained to any significant degree after washing with water. At above 600 °C, a weight loss due to CO_2 was observed, as is normal for all calcium carbonate.[5,12]

After precipitates were filtered by suction and washed with water, the combined water phases were evaporated. Formation of poly(acrylate) was confirmed by IR analysis and GPC measurements of the residues. Number-average molecular weights of the products were higher than 30000 by GPC analysis.

Control Experiment for Crystallization of Calcium Carbonate. The yields of the crystalline products obtained with sodium acrylate without addition of the radical initiator, in which feed ratios of sodium acrylate to calcium ions were 0.37, 0.75, 0.87, and 1.0 under the same condition described above, were 40, 43, 59, and 53%, respectively (Table 1). The crystal phases of the $CaCO_3$ obtained were all determined to be calcite by IR, in which the bands at 876 and 712 cm^{-1} assignable to calcite were recognized. The mono-carboxylic acid did not exert any influence for the nucleation and crystal growth

Table 1. Formation of Crystalline $CaCO_3$ in the Presence of Sodium Acrylate with Radical Initiator at Different Feed Ratio of Sodium Acrylate to Calcium Ions at 30 °C for 1 d

Run	[acrylate]/[Ca^{2+}]	Addition time of KPS/min	Yield/%	Polymorphism[a)]
1	0.37	1	47	calcite
2	0.37	3	61	calcite
3	0.37	20	98	calcite
4	0.50	1	45	calcite
5	0.50	3	59	calcite
6	0.50	20	78	calcite
7[b)]	0.62	1	33	aragonite + calcite (trace)
8[b)]	0.62	3	35	vaterite (63%) + calcite
9[b)]	0.62	20	54	calcite
10	0.75	1	19	calcite + aragonite (trace)
11	0.75	3	33	vaterite (38%) + calcite
12	0.75	20	47	calcite
13	0.87	1	14	calcite
14	0.87	3	25	calcite > aragonite
15	0.87	20	27	vaterite (89%) + calcite
16	1.00	3	36	calcite
17	1.00	20	41	calcite + aragonite (trace)
18	0.37	—[c)]	40	calcite
19	0.75	—[c)]	43	calcite
20	0.87	—[c)]	59	calcite
21	1.00	—[c)]	53	calcite

a) Polymorphism was characterized by FT-IR. The fraction of vaterite in the crystalline phase was determined by XRD. b) The products of runs 7, 8, and 9 were product A, product B, and product C, respectively. c) The precipitation of $CaCO_3$ was carried out without addition of KPS.

of $CaCO_3$ even upon increasing the feed ratio of acrylic acid and calcium to 1.0. Calcite is thermodynamically more stable than the other two crystalline structures, namely, aragonite and vaterite. The crystal phase of $CaCO_3$ obtained without any additives was also calcite under the same conditions as described above. Sodium acrylate was regarded as an inactive form for induction of metastable $CaCO_3$ crystalline phases (vaterite or aragonite). In addition, the crystal phase of product C was also thermodynamically stable calcite. The final crystalline phase was not affected by the polymerization of sodium acrylate after incubation for 20 min.

The precipitation of $CaCO_3$ in the presence of sodium-salt of poly(acrylic acid) (PAA) ($M_w = 5100$) was prevented under the same nucleation condition.[13] Here a feed ratio of a repeating unit of acrylate to calcium ions was 0.62. Little crystalline $CaCO_3$ was collected after incubation at 25 °C under N_2 for 4 days. The IR spectrum of the $CaCO_3$ obtained with less than 1% yield in the presence of PAA showed amorphous character. This indicates that the initial presence of PAA acts as an inhibitor for crystal formation.

Effect of Sodium Acrylate Concentration. Formation of crystalline $CaCO_3$ in the presence of sodium acrylate with the radical initiator at different feed ratios of sodium acrylate to calcium ions was studied. The molar ratios of the calcium reactants to the carboxylic acid were varied from 0.37 to 1.0. The concentrations of the calcium reactants and the radical initiator were constant in all experiments. After addition of the calcium reactants into the aqueous solution of sodium acrylate was completed, an aqueous solution of the water-soluble radical initiator was added to the reaction mixture after incubation at 30 °C for several minutes (1, 3, or 20 min). The experimental condition and the results are summarized in Table 1. When a feed ratio of sodium acrylate to calcium ions was reduced to 0.37 or 0.5, all the crystal phases obtained when the radical initiator was added after incubation for 1, 3, and 20 min were calcite. Lower concentration of sodium acrylate did not influence the nucleation and crystal growth of $CaCO_3$. These results also suggest that the presence of the radical initiator was not a main factor for controlling the final crystal phase of $CaCO_3$.

When the feed ratio of sodium acrylate to calcium ions increased from 0.62 to 0.75, the crystal obtained when the radical initiator was added after incubation for 3 min was a mixture of vaterite and calcite. The fraction of vaterite in the crystalline phase of the product was 38%, as determined by XRD analysis. Although the crystal phase obtained when the radical initiator was added after incubation for 1 min was calcite, a trace amount of aragonite formation was detected by IR.

When the feed ratio of sodium acrylate to calcium ions further increased to 0.87, the crystal phases obtained when the radical initiator was added after incubation for 1 or 3 min were calcite. The crystal phase obtained when the radical initiator was added after incubation for 20 min was vaterite. The fraction of vaterite in the crystalline phase of the product was 89%, as determined by XRD. When a feed ratio of sodium acrylate to

calcium ions further increased to 1.0, the crystal phases obtained when the radical initiator was added after incubation for 3 or 20 min were calcite. The supersaturated concentration of calcium ions in the presence of sodium acrylate might increase compared with that in the absence of the additive. Indeed, a sudden increase in the turbidity of the solution was observed after incubation of the homogeneous solution for about 5 minutes.

Figure 5 shows SEM micrographs of calcite in the different sodium acrylate concentrations (runs 2, 5, and 14 in Table 1). The sizes of the calcite crystals depend on the concentration of sodium acrylate. As the concentration of sodium acrylate increased, sizes of the calcite crystals increased from 3 ± 0.7 μm (Fig. 5a) to 12 ± 0.6 μm (Fig. 5c). The crystallization of calcium carbonate involves two processes, that is, the nucleation and the growth of the crystal. In general, fast nucleation relative to growth results in a formation of small crystals. The higher concentration of sodium acrylate might decrease the nucleation rate, resulting in larger calcite crystals. Sizes of the vaterite spherical particles of run 8 and run 11 in Table 1 are 5.3 ± 0.7 μm (Fig. 4b) and 5.2 ± 0.5 μm (Fig. 6a), respectively. This indicates that the sizes of the vaterite spherical particles are independent of the concentration of sodium acrylate. However, the size of the vaterite particles of run 15 increased to 9.2 ± 0.8 μm (Fig. 6b). This may be due to the permission of the growth of vaterite particles by delayed addition of the radical initiator.[14]

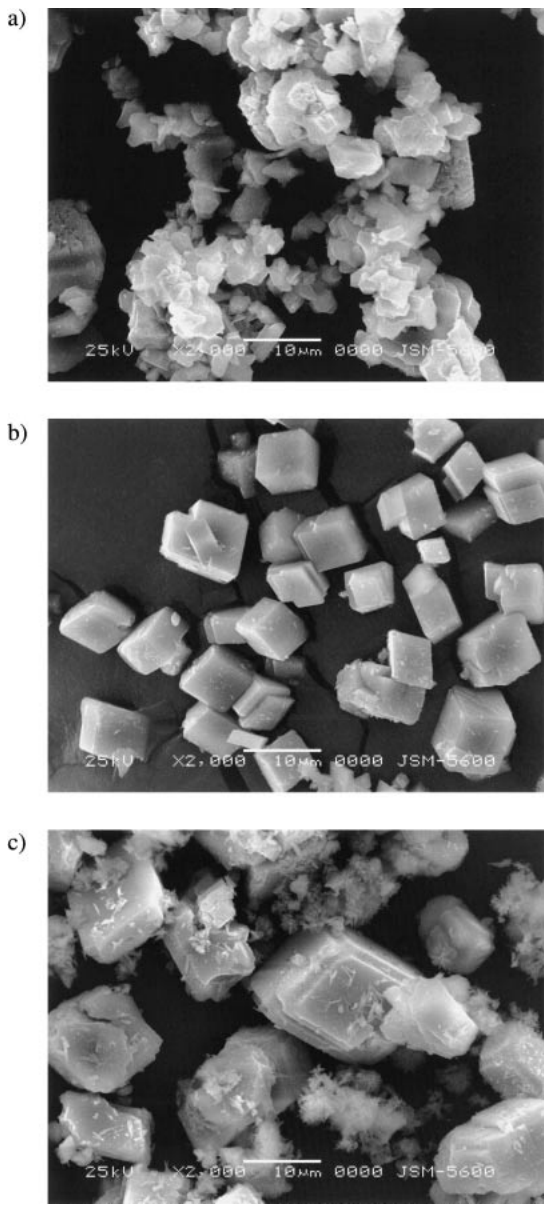

Fig. 5. Scanning electron micrographs of $CaCO_3$ of run 2 (a), run 5 (b), and run 14 (c) in Table 1.

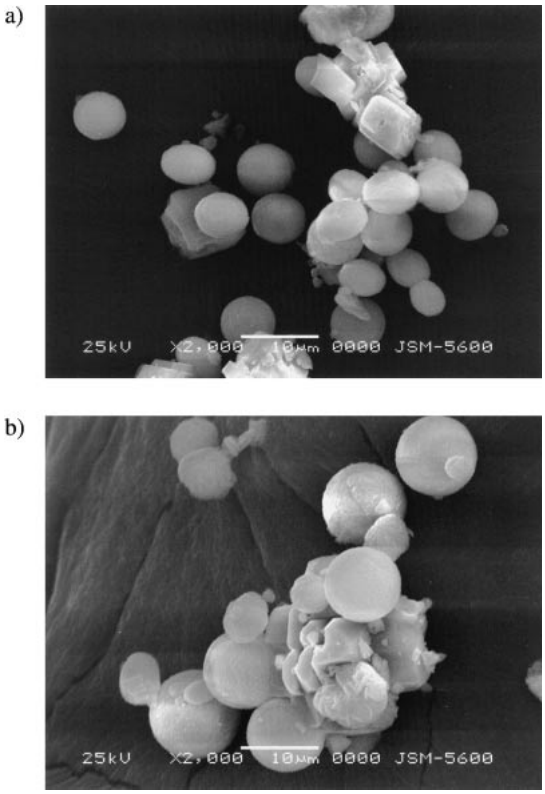

Fig. 6. Scanning electron micrographs of $CaCO_3$ of run 11 (a) and run 15 (b) in Table 1.

Control Polymorphs. It was reported that alkaline pH and relatively high supersaturations at room temperature favor the precipitation of vaterite.[15] Vaterite transforms easily and irreversibly into thermodynamically more stable calcite when in contact with water.[16] The complete phase transformation into the thermodynamically stable calcite occurs within 80 h, usually much faster under the conditions described above. Without any additives, it is well known that vaterite transforms into stable calcite via a solvent-mediated process. The crystal polymorph of product B did not change when the solution was kept for 2 days. We speculate that the vaterite surfaces were stabilized by the resulting poly(acrylate) in aqueous solution to prevent phase transformation. The vaterite crystal, however, was transformed to calcite when the solution was incubated for 3 days. In the previous reports,[13,17] we have shown that spherical vaterite crystals were stabilized by an anionic poly(amidoamine) (PAMAM) dendrimer in aqueous solution for more than 7 days. These results indicate that the Ca–O bonds to poly(acrylic acid) are relatively weaker than that to the anionic

Table 2. Formation of Crystalline $CaCO_3$ in the Presence of Sodium Acrylate with Radical Initiator at Different Feed Ratio of Sodium Acrylate to Calcium Ions at 35 °C for 1 d

Run	[acrylate]/[Ca^{2+}]	Addition time of KPS/min	Yield/%	Polymorphism[a)]
1	0.62	1	<1	amorphous
2	0.62	3	29	aragonite
3	0.62	20	21	aragonite
4	0.75	3	26	aragonite
5	0.87	20	19	aragonite

a) Polymorphism was characterized by FT-IR.

PAMAM dendrimer. Thus, the resulting poly(acrylic acid) might detach from the vaterite surfaces by washing with water.

The formation of aragonite is usually achieved at higher temperature than 50 °C using a solution method of preparation.[18,19] In our present results, aragonite can be formed at 30 °C when the radical initiator was added to the calcium solution with sodium acrylate after incubation for 1 min, in which the $CaCO_3$ crystal formation was not started. After 4 days incubation in water, aragonite in product A still existed. It is possible that aragonite is rapidly nucleated at the very beginning of the nucleation process, resulting in being kinetically induced by poly(acrylate). Since aragonite is a metastable structure, aragonite crystallization under mild conditions in homogeneous nucleation was achieved only in the presence of extraneous molecules such as Mg^{+} or Li^{+}.[20,21] Our present result provides a new method for aragonite formation at ambient temperature in homogeneous nucleation system. This result may provide a new clue to consider how the organisms control the crystallization process.

A higher temperature of 35 °C was employed for crystallization of calcium carbonate with radical polymerization of sodium acrylate in aqueous solution. A sudden increase in the turbidity of the solution was observed after incubation of homogeneous solution for about 1 to 2 min, indicating the crystallization rate was faster than that at 30 °C under the same condition. The experimental condition and the results are summarized in Table 2. When the concentration of sodium acrylate was 1.71 mM, the polymorphs of the products obtained when the radical initiators were added to the reaction mixture after incubation for 1 min (run 1) and 3 min (run 2) were amorphous and aragonite, respectively. Aragonite formation was also observed when the radical initiators were added to the reaction mixture after incubation for 20 min. These results suggest that higher temperature tends to induce aragonite formation due to reduced activation energy for aragonite nucleation. It should be emphasized again that the present method produced aragonite at ambient temperature in homogeneous nucleation system.

After addition of the calcium reactants into an aqueous solution, an aqueous solution of sodium-salt of PAA ($M_w = 1200$) (74 mg) was added to the reaction mixture after incubation at 30 °C for several minutes (1 or 20 min). A feed ratio of a repeating unit of PAA to calcium ions was 0.62. Little crystalline $CaCO_3$ was collected after incubation at 30 °C under N_2 for 1 day when sodium-salt of PAA ($M_w = 1200$) was added to the reaction mixture after incubation at 30 °C for 1 min. When sodium-salt of PAA ($M_w = 1200$) was added to the reaction mixture after incubation for 20 min, a very small amount of vaterite was obtained. Although the concentration of the additive should be an important parameter, these results indicate that the final crystalline phases are highly sensitive to the presence of the active additives at the very initial nucleation stage. Further detailed studies are currently underway, and will be reported in due course.

Conclusions

We show that three different crystal polymorphs of $CaCO_3$ (aragonite, vaterite, and calcite) were selectively induced by changing the time of addition of the radical initiator to the calcium carbonate solution with sodium acrylate. The present results indicate that the final crystalline phases are highly sensitive to the presence of the active additives at the very initial nucleation stage (within several minutes). During the phase transformation, resulting PAA may kinetically and thermodynamically induce a crystal nucleation at each stage. Our current data have provided a new concept for controlling the crystal polymorphs of calcium carbonate. Sodium acrylate was inactive for nucleation and growth of the crystal. After the radical initiator was added, acrylate was transferred to poly(acrylate), which could interact with nucleation and growth of $CaCO_3$. Sodium acrylate was regarded as a latent active ligand for induction of the crystal phase. For controlling the polymorph of $CaCO_3$, we believe that the initial nucleation processes play an important role in controlling the final crystal.

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