Effect of Anionic Polyamidoamine Dendrimers on the Crystallization of Calcium Carbonate by Delayed Addition Method

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We examined the crystallization of $CaCO_3$ by changing the time of addition of the G1.5 and G3.5 poly(amidoamine) dendrimers to a calcium carbonate solution after incubation for several minutes (1, 3, 20, or 60 min) at 30°C. Based on the fact that the crystal phase obtained in the absence of the dendrimer was calcite, the dendrimers effectively stabilized the most unstable vaterite particles, even delaying the addition time of the dendrimer for 60 min. As the delayed addition time of the G1.5 dendrimer increased from 0 to 60 min, the particle size increased from 1.2 ± 0.5 to 4.7 ± 0.7 μm. As the generation number of the dendrimer increased from G1.5 to G3.5, the particle size of the spherical vaterite decreased under the same condition. The present results suggest that the anionic PAMAM dendrimers effectively modified the metastable vaterite surface and inhibited the further growth of vaterite particles by changing the addition time.

Biological inorganic materials have superior mechanical properties those of synthetic materials. The modelling of biomineralization is a promising approach to controlled crystal growth for seeking materials analogous to those produced by nature.[1,2] The majority of these efforts have focused on exploring the promoting effect of templates on crystal nucleation and growth. On the specific interactions, various synthetic polymers have been found to be potent inhibitors or habit modifiers for inorganic crystallization by adsorption onto the surfaces of the growing crystals, thus controlling their growth rate and habit through the strength and selectivity of this adsorption.[3–7] The final crystalline phase arises through a series of steps. By selectively interacting with the minerals at different stages during the crystal forming process, the organisms may choose manipulating both the polymorph and the orientation of the mineral to meet specific biological requirements. Although the presence of various synthetic additives has been studied for inorganic crystallization, selective interaction of an organic matrix with the mineral at different stages has been unexplored. Recently, we have reported a new concept for controlling crystal polymorphs of $CaCO_3$ by interaction of a synthetic additive at different nucleation stages.[8] We used sodium acrylate and a water-soluble radical initiator for selectively interacting with the mineral at different stages during the crystal-forming process. While sodium acrylate does not affect nucleation and growth of crystals, poly(acrylate) affects crystal morphology by inhibiting the growth of particular crystal faces.

Recently, dendrimers are receiving increasing attention because of their unique structures and properties.[9–11] Generally, dendrimers of lower generations tend to exist in relative open forms with high overall symmetries, which are different from linear polymers and classical micelles formed by intermolecular aggregation. The dendrimers are highly regular branched-structure and monodisperse macromolecules. The dendrimers also provide reaction sites including their interior or periphery. We previously showed that a crystallization of $CaCO_3$ in the presence of poly(amidoamine) (PAMAM) dendrimers with carboxylate groups at the external surface resulted in the formation of stable spherical vaterite crystals.[12,13] We speculated that the vaterite surface was stabilized by the carboxylate-terminated dendrimers in aqueous solution to prevent phase transformation. Furthermore, as the generation number of the PAMAM dendrimers increased from G1.5 to G3.5, the size of spherical vaterite particles was decreased from 5.5 ± 1.1 to 2.3 ± 0.7 μm, which may be due to differences of the coordination ability of the PAMAM dendrimers. These results suggest that the anionic PAMAM dendrimers act as effective protective agents for the vaterite crystals that are most unstable to supersaturated solutions of calcium carbonate. Here, we report specific polymorphological changes of vaterite particles by changing the addition time of the PAMAM dendrimers.

Experimental

Materials. The G1.5 and G3.5 poly(amidoamine) (PAMAM) dendrimers (these contain 16 and 64 structure carboxylate groups, respectively) and poly(acrylate) ($M_w = 1200$) were obtained from Aldrich. Calcium chloride and ammonium carbonate were purchased from WAKO Pure Chemical Industries, Ltd.

Crystallization of $CaCO_3$. The precipitation of $CaCO_3$ was carried out by a double jet method.[14] After 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 water, an aqueous solution of the PAMAM dendrimer was added to the reaction mixture after incubation at 30°C for several minutes (1, 3, 20, or 60 min). This solution was kept at 30°C under N_2 for 1 day with gentle stirring. The concentration of the calcium reactants was constant in all experiments. The crystalline part of $CaCO_3$ was collected and

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washed with water several times.

Measurements. The morphologies of $CaCO_3$ crystals were observed by scanning electron microscopy (SEM), JEOL JSM5310/LV at 15KV. The X-ray diffraction (XRD) was made on a Shimadzu XRD-6000 in $\theta/2\theta$ mode at room temperature. The 2θ scan data were collected at 0.02° intervals and the scan speed was 2° (2θ) min^{-1}. Fourier transform infrared (FT-IR) spectra were recorded by using a Perkin Elmer system 2000 employing a KBr pellet method.

Results and Discussion

Effect of Anionic Polyamidoamine Dendrimers on the Crystallization of Calcium Carbonate by Delayed Addition Method. Crystallization of calcium carbonate by changing the addition time of the G1.5 PAMAM dendrimer was studied. After each 4.95 mL of reactants (0.1 M $CaCl_2$ and 0.1 M $(NH_4)_2CO_3$) were injected via syringe into distilled water (180 mL), an aqueous solution of the G1.5 PAMAM dendrimer was added to the reaction mixture after incubation at 30°C for several minutes (1, 3, 20, or 60 min). For addition time of 0 min, the reactants were injected into an aqueous solution of the dendrimer. These solutions were kept at 30°C for 1 day. The critical point of a sudden increase in the turbidity of the solution was observed at 3–4 min after the addition of the calcium reactants. The experimental conditions and the results are summarized in Table 1.

At the high concentration of the G1.5 PAMAM dendrimer corresponding to 2.75 mM of –COONa, all five samples showed two bands at 877 and 746 cm^{-1} by FT-IR, indicating vaterite formation.[15,16] As the concentration of –COONa decreased to 1.37 mM, the obtained crystal phases were vaterite when the dendrimer was added after incubation for 0 and 1 min. However, the bands at 874 and 712 cm^{-1} assignable to calcite coexisted with vaterite when the dendrimer was added after incubation for 3 min. Although vaterite was predominantly formed even at the lower concentration of the G1.5 PAMAM dendrimer corresponding to 0.27 mM of –COONa, the amounts of calcite and aragonite forms were increased with increasing the delayed addition time of the dendrimer, as determined by FT-IR (Fig. 1). The crystal phase and the fraction of vaterite of the obtained products were further confirmed by XRD (Fig. 2).[17] The fraction of vaterite were increased by the earlier addition time compared with that found by the later addition time. Based on the fact that the obtained crystal phase in the absence of the dendrimer was calcite, the dendrimers effectively stabilized the most unstable vaterite crystal, even delaying the addition time of the dendrimer for 60 min. When the dendrimer was added after incubation for 120 min, calcite was predominantly formed.

Figure 3 shows SEM images of the samples of runs 11, 13,

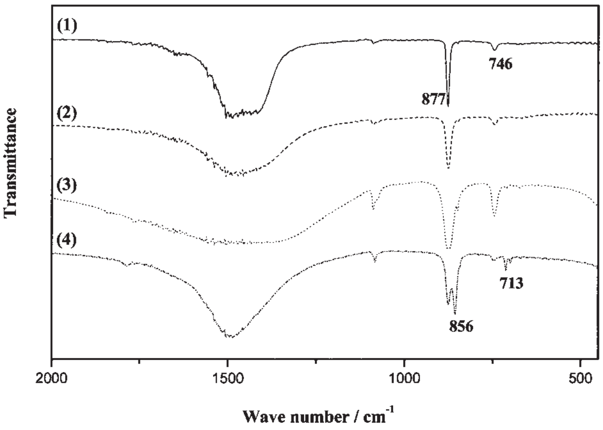

Fig. 1. FT-IR spectra of the products of (1) run 1, (2) run 2, (3) run 3, and (4) run 4 in Table 1.

Table 1. Formation of Crystalline $CaCO_3$ with the G1.5 Dendrimer at Different Addition Time and Different Feed Ratio of the Dendrimer to Calcium Ions at 30°C

Run	[–COONa] mM	[–COONa] /[Ca^{2+}]	Addition time min	Polymorphism[a)]	Particle size of vaterite[b)] μm	Yield %
1	0.27	0.1	0	Vaterite	2.3 ± 1.1	23
2			1	Vaterite (93%)[c)] + Calcite	2.8 ± 1.2	36
3			3	Vaterite (90%)[c)] + Calcite	2.1 ± 0.6	28
4			20	Vaterite + Calcite + Aragonite	9.1 ± 0.2	27
5			60	Vaterite + Calcite + Aragonite	6.7 ± 0.7	31
6	1.37	0.5	0	Vaterite	2.2 ± 1.6	26
7			1	Vaterite	1.7 ± 0.6	44
8			3	Vaterite (92%)[c)] + Calcite	2.4 ± 1.8	40
9			20	Vaterite (87%)[c)] + Calcite	4.6 ± 0.6	25
10			60	Vaterite + Calcite + Aragonite	6.9 ± 0.4	29
11	2.75	1	0	Vaterite	1.2 ± 0.5	22
12			1	Vaterite	1.3 ± 0.3	48
13			3	Vaterite	3.2 ± 0.9	44
14			20	Vaterite	3.8 ± 0.2	20
15			60	Vaterite	4.7 ± 0.7	47

a) Polymorphism was characterized by FT-IR. b) Particle size was measured by SEM. c) Vaterite content was determined by XRD.

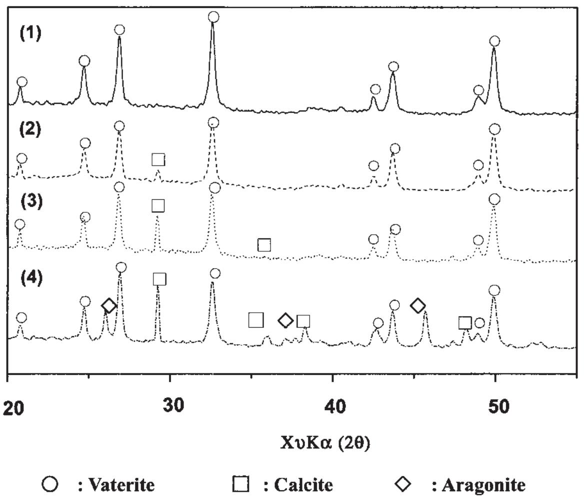

Fig. 2. X-ray diffraction patterns of the products of (1) run 1, (2) run 2, (3) run 3, and (4) run 4 in Table 1.

and 15 in Table 1. All the products show the vaterite. As the delayed addition time of the G1.5 PAMAM dendrimer increased from 0 to 60 min, the particle size of the vaterite increased from 1.2 ± 0.5 to 4.7 ± 0.7 µm. The shapes of vaterite were also changed by delay addition time of the G1.5 PAMAM. SEM of run 11 shows typical small spherical vaterite. However, the crystal of run 13 produced lentil shaped vaterite. Low energy surface {001} of vaterite might be due to the dendrimer absorbed on the smooth surface of growing vaterite.[18] This shape transferred to aggregated discs vaterite (run 15). The vaterite particle sizes of the other products are summarized in Table 1. We observed that the particle sizes of the vaterite increased with the delayed addition time of the G1.5 PAMAM dendrimer. Furthermore, as the concentration of –COONa decreased, the particle sizes of spherical vaterite increased. The mixtures of calcite and aragonite were also increased when the lower concentration of the PAMAM dendrimer was used under the same condition. This result indicates that the effect of the dendrimer as an inhibitor became weaker by decreasing the concentration of the PAMAM dendrimer.

Crystallization of $CaCO_3$ in the Presence of the G3.5 PAMAM Dendrimer under the Same Condition. The precipitations of $CaCO_3$ in the presence of the G3.5 PAMAM dendrimer were also carried out under the same condition; the results are summarized in Table 2. No calcite formation was observed in all the concentrations. As the generation number of the anionic PAMAM dendrimer increased from G1.5 to G3.5, the particle sizes of the spherical vaterite decreased under the same condition. These results suggest that the G3.5 dendrimer effectively stabilized the vaterite particles compared with the earlier generation of the dendrimer. It has already been reported that the adsorption of the G3.5 PAMAM dendrimer on the vaterite surface was higher than that of the G1.5 PAMAM dendrimer.[13]

Vaterite is the thermodynamically most unstable of the three crystal systems of $CaCO_3$; calcite, aragonite, and vaterite, and transforms into calcite when in contact with water. The complete phase transformation into the thermodynamically stable calcite occurs within 3 days. Previously, we have succeeded in surface modification of vaterite particles with the anionic PAMAM dendrimers[13] and a hydrophobic trisilanolate.[19] No transformation of the modified vaterites into thermodynamically more stable forms was observed in contact with water for more than 4 days. The present vaterite product of run 12 in Table 1 also kept vaterite form in an aqueous solution at room temperature for 4 days. This indicates that the vaterite surface was stablilized by the carboxylate-terminated dendrimer in aqueous solution to prevent the phase transformation. The contents of the G1.5 PAMAM dendrimer in the obtained crystalline $CaCO_3$ for runs 2, 7, and 12 in Table 1 measured by elemental analysis were 5.3, 6.4, and 6.9 wt %, respectively. Furthermore, the product of run 14, of which particle size was higher than those of runs 2, 7, and 12 in Table 1, contained below 0.6 wt % of the dendrimer. The spherical vaterite crystals were aggregates of vaterite nanoparticles with diameters of

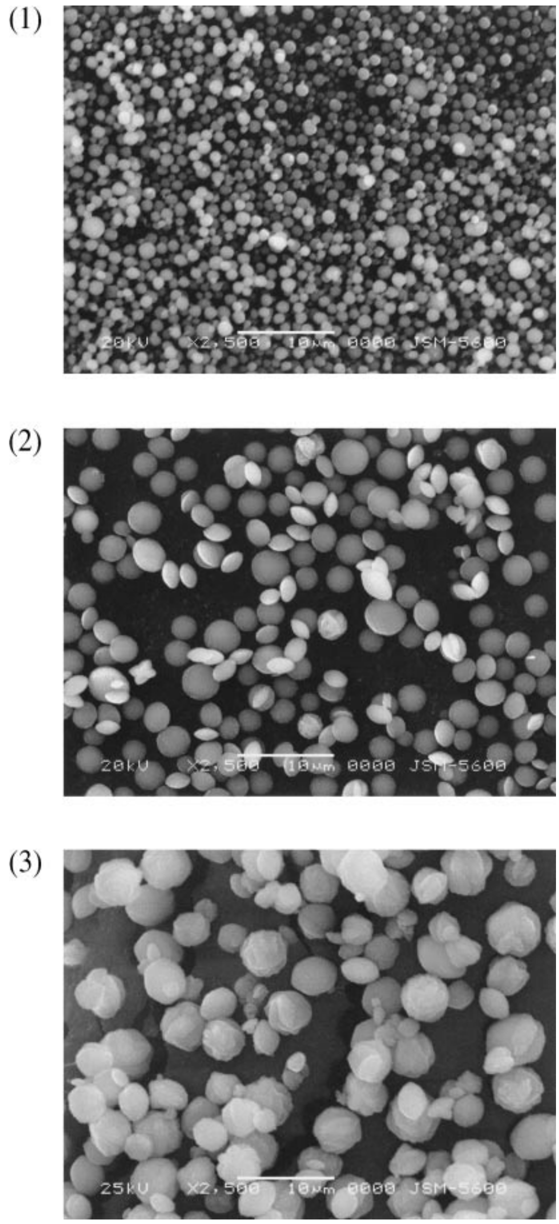

Fig. 3. Scanning electron micrographs of the products of (1) run 11, (2) run 13, and (3) run 15 in Table 1.

Table 2. Formation of Crystalline $CaCO_3$ with G3.5 Dendrimer at Different Time Addition and Different Feed Ratio of Dendrimer to Calcium Ions at 30°C

Run	[–COONa]	[–COONa]	Addition time	Polymorphism[a)]	Particle size of vaterite[b)]	Yield
	mM	/$[Ca^{2+}]$	min		μm	%
1	0.27	0.1	0	Vaterite	1.3 ± 0.2	27
2			1	Vaterite	1.4 ± 0.8	25
3			3	Vaterite	1.5 ± 0.8	29
4			20	Vaterite + Aragonite	6.2 ± 0.5	24
5	1.37	0.5	0	Vaterite	1.2 ± 0.7	24
6			1	Vaterite	1.4 ± 0.4	36
7			3	Vaterite	1.6 ± 0.3	28
8			20	Vaterite	5.5 ± 0.8	23
9	2.75	1	0	Vaterite	1.1 ± 0.6	17
10			1	Vaterite	1.1 ± 0.3	18
11			3	Vaterite	1.2 ± 0.5	23
12			20	Vaterite	3.1 ± 1.7	21

a) Polymorphism was characterized by FT-IR. b) Particle size was measured by SEM.

10 to 30 nm.[20] The surface of the nanosize metastable vaterite was modified with the higher amount of the PAMAM dendrimer at the earlier addition time and the aggregation of the vaterite nano crystals was inhibited by the earlier addition time.

The precipitation of $CaCO_3$ in the absence of any additives proceeded under comparable conditions. Crystalline products were immediately isolated after incubation for 3 min and 20 min by centrifugation. In the case of the product after 3 min incubation, vaterite and calcite coexisted, as found by FT-IR. The size of the vaterite particle was 4.2 ± 1.6 μm (Figure 4a). In the case of the product after 20 min, the size of vaterite particle was 10 ± 2.3 μm (Figure 4b). The size of spherical vaterite increased with increasing the incubation time. Aragonite and calcite crystals were also observed in the SEM images. The transformation of crystal phase might proceed during the isolation process without the dendrimers. After the calcium reactants were injected, the G3.5 dendrimer was added to the reaction mixture after incubation for 20 min and crystalline products were immediately isolated by filtration. The isolated products were spherical vaterite particles of which the sizes were the same as those of the products isolated after 1 day. These results suggest that the anionic PAMAM dendrimers quickly modified the vaterite surface and inhibited the further growth of the vaterite particles. Since the higher concentration of the PAMAM dendrimer effectively adsorbed on the vaterite particles, smaller size vaterite particles were produced compared with those found in the lower concentrations of the PAMAM dendrimer.

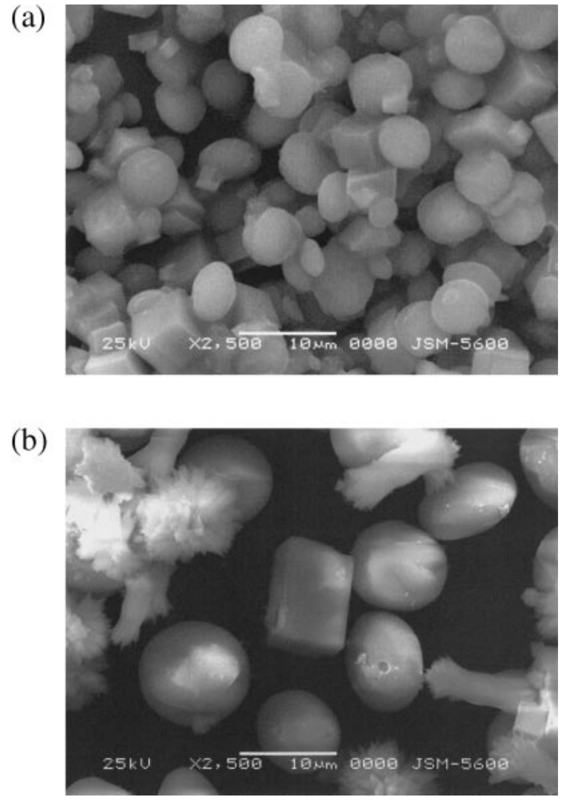

Fig. 4. Scanning electron micrographs of $CaCO_3$ isolated after incubation for 3 min (a) and 20 min (b) in the absence of any additives.

Conclusions

We examined the crystallization of $CaCO_3$ by changing the time of addition of the G1.5 and G3.5 PAMAM dendrimers to a calcium carbonate solution. The sizes of spherical vaterite crystals increased with increasing the delayed addition time. The present results suggest that the PAMAM dendrimers act as effective stabilizers for metastable vaterite phase, and the aggregation of vaterite crystals was quenched by changing the addition time of the dendrimer. The later generation of the dendrimer more effectively protected the vaterite particles than the earlier generation did. The present studies indicate that the final crystal shapes are highly sensitive to the presence of active additives at the very initial nucleation stage. The delayed addition method gives a new, simple process for controlling the $CaCO_3$ crystallization.

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