Control of crystal polymorphs by a 'latent inductor': crystallization of calcium carbonate in conjunction with *in situ* radical polymerization of sodium acrylate in aqueous solution

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Three different crystal polymorphs of $CaCO_3$ (aragonite, vaterite and calcite) have been selectively induced by changing the time of addition of a radical initiator to a calcium carbonate solution containing sodium acrylate.

In nature, biological organisms produce polymer–inorganic hybrids. In these mineralized tissues, crystal morphology, size, polymorph, and orientation are determined by local conditions and, in particular, the presence of 'matrix' proteins or other macromolecules.[1] However, there remain many unknowns as to how the matrix affects the crystallization process, especially the initial nucleation. A final crystalline phase might arise through a multistage crystallization process.[2,3] 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 may choose to manipulate both the polymorph and the orientation of the mineral to meet specific biological requirements. Although crystallization of minerals in the presence of various additives and synthetic polymers has been investigated as a model of biomineralization,[4–6] selective interaction of synthetic additives with the minerals at different stages during the nucleation process has not been examined.

Here, we report a new concept for controlling crystal polymorphs of $CaCO_3$ by addition of a synthetic additive. The key point of our method is using a 'latent inductor' for crystal nucleation as shown in Fig. 1. The latent inductor at its inactive state does not affect nucleation and growth of the crystal. After the inactive state is transferred to an active state by a stimulus, the active inductor can induce nucleation and growth of the crystal. We used sodium acrylate as a latent inductor for this purpose and a water-soluble radical initiator was used as a stimulus. While sodium acrylate does not affect nucleation and growth of crystals[7] poly(acrylate) affects crystal morphology by inhibiting the growth of particular crystal faces.[3,8] Indeed, the precipitation of $CaCO_3$ in the presence of the sodium salt of poly(acrylic acid) (PAA) (M_n = 5100) was prevented under the nucleation conditions applied here.[6] Sodium acrylate can be transformed to poly(acrylate) by adding a radical initiator. In the present system, aqueous solutions of $CaCl_2$ and $(NH_4)_2CO_3$ were initially added to an aqueous solution of sodium acrylate and then subjected to polymerization by adding the radical initiator at 30 °C after incubation for several minutes. Crystallization of calcium carbonate with *in situ* polymerization of anionic monomers in aqueous solution has not been reported.

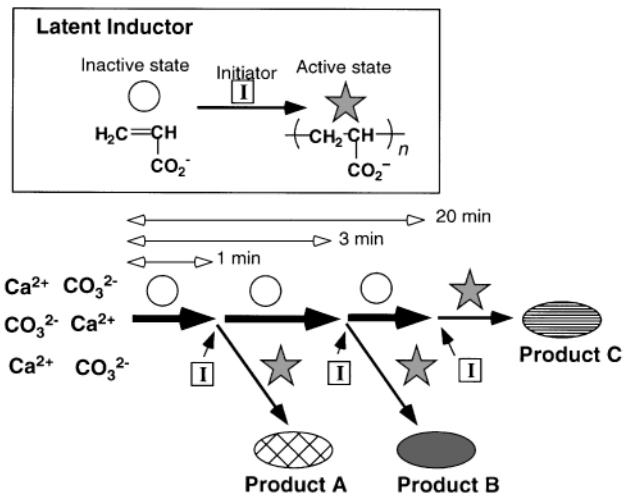

Fig. 1 Schematic depiction for the control of crystal polymorph growth by a latent inductor.

The precipitation of $CaCO_3$ was carried out under the same conditions as reported by Cölfen *et al.*[9,10] 4.95 ml of each reactant [0.1 M $CaCl_2$ and 0.1 M $(NH_4)_2CO_3$] were injected *via* syringe into 180 ml of an aqueous solution of sodium acrylate which was adjusted to pH 8.5 by NH_3(aq). The ratio of sodium acrylate to calcium ions was 0.62 : 1. After addition of the reactants was complete, an aqueous solution of $K_2S_2O_8$ 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). A sudden increase in the turbidity of the solution was observed after incubation for several minutes. The 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 (product A), 3 min (product B) and 20 min (product C) were 33, 35 and 54%, respectively.

The crystal phases of the obtained $CaCO_3$ were characterized by FTIR analysis.[3,11,12] Product A displayed 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} indicating aragonite formation. When the radical initiator was added after incubation for 3 min, product B showed several bands corresponding to a carbonate out-of-plane bending vibration. A band at 746 cm^{-1} indicated vaterite formation and bands at 877 and 713 cm^{-1} assignable to calcite were also present. The crystal phase of product C was calcite according to IR with only two bands at 877 and 713 cm^{-1} observed.

Fig. 2 shows scanning electron micrographs (SEM) of the three crystalline products. Each SEM micrograph shows different crystal modifications. The aragonite crystals (product A) were efflorescent bundles of needles [Fig. 2(a)], typical of the phase. Product B consisted of two different crystal modifications, spherical vaterite and rhombs of calcite [Fig. 2(b)]. Stable spherical vaterite crystals have already been reported in the presence of various bivalent cations,[13] double-hydrophilic block copolymers[9] and anionic PAMAM dendrimers.[6] Crystals of product C were rhombohedral [Fig. 2(c)]. The crystal phases of the obtained $CaCO_3$ samples were further confirmed by powder X-ray diffraction (XRD) analysis. The reflections of products A and C were characteristic for aragonite and calcite, respectively. The fraction of vaterite in product B

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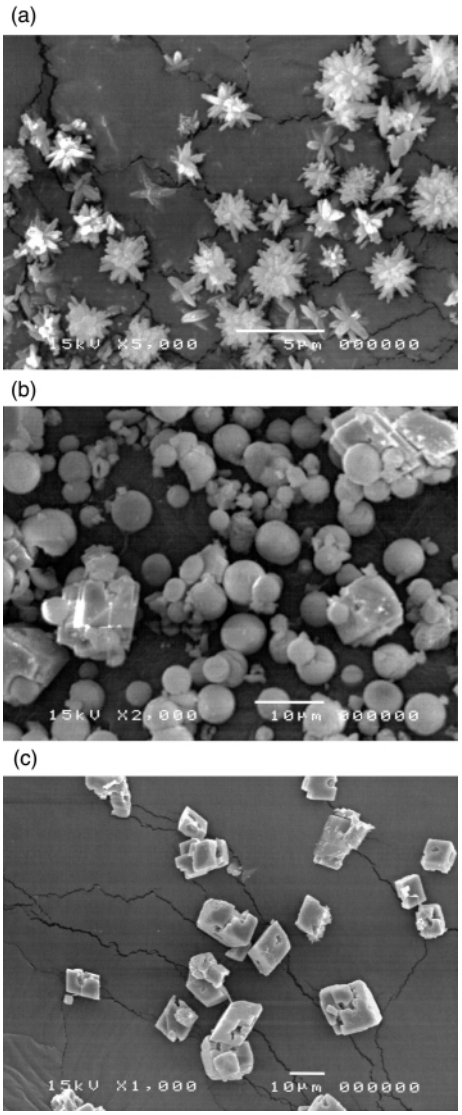

Fig. 2 Scanning electron micrographs of (a) product A, (b) product B and (c) product C.

was 63% as determined by Rao's equation.[14] These results indicate that the three different polymorphs of $CaCO_3$ were controlled simply by changing the addition time of the radical initiator to the calcium carbonate supersaturated solution containing sodium acrylate at ambient temperature. When the ratio of sodium acrylate to calcium ions was reduced to 0.37, the crystal phase obtained when the radical initiator was added after incubation for 1, 3 and 20 min was always calcite. This result suggests that the presence of the radical initiator was not the main factor for controlling the final crystal phase of $CaCO_3$.

Calcite is thermodynamically more stable than the other two crystalline modifications, aragonite and vaterite. The crystal phase of $CaCO_3$ obtained without any additives or with sodium acrylate in the absence of radical initiators was calcite under the same conditions as described above. Sodium acrylate is thus inactive for induction of metastable $CaCO_3$ crystalline phases (vaterite or aragonite). Since the crystal phase of product C was also thermodynamically stable calcite, the final crystalline phase was not affected when the polymerization of sodium acrylate was started *via* radical initiation after incubation of the reaction mixture containing calcium reactants and sodium acrylate for 20 min.

Aragonite is usually obtained at temperatures > 50 °C using a solution method of preparation.[4,11] In our present results, aragonite can be obtained at 30 °C when the radical initiator is added to the calcium ion solution with sodium acrylate after incubation for 1 min, during which time $CaCO_3$ crystal formation has not started. It is possible that aragonite is rapidly nucleated at the very beginning of the nucleation process, resulting in it being kinetically induced by the poly(acrylate). When the initiator was added to the reaction mixture after incubation for 3 min, crystals of calcite and vaterite were formed. These results indicate that the final crystalline phases are highly sensitive to the presence of the active additives at the very initial nucleation stage (first few minutes). During the phase transformation, the poly(acrylate) may kinetically and thermodynamically induce a crystal nucleation at each stage. In the absence of any additives, it is well known that vaterite transforms into stable calcite *via* a solvent-mediated process.[15] Although the crystal polymorph of product B did not change when the solution was kept for 2 days, vaterite crystals were transformed to calcite when the solution was incubated for 3 days. We speculate that the vaterite surfaces were stabilized by the resulting poly(acrylate) in aqueous solution so slowing phase transformation.

After the crystalline $CaCO_3$ was filtered off and washed with water, the combined water phase was evaporated under reduced pressure. GPC and FTIR analyses of the residue indicated the formation of poly(acrylate). Although we do not fully understand the mechanistic implication of the effect of *in situ* radical polymerization of sodium acrylate in aqueous solution for nucleation and growth of calcium carbonate, our current results have provided a new concept for controlling the crystal polymorphs of calcium carbonate. While sodium acrylate is inactive for nucleation and growth of crystals, addition of a radical initiator leads to poly(acrylate), which can influence nucleation and growth of $CaCO_3$. Sodium acrylate can be regarded as a latent active ligand for induction of crystal phases. We believe that the initial nucleation processes play an important role in controlling the final crystal modifications of $CaCO_3$ obtained. Further investigations are in progress.

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