

# The effect of an anionic starburst dendrimer on the crystallization of $\text{CaCO}_3$ in aqueous solution

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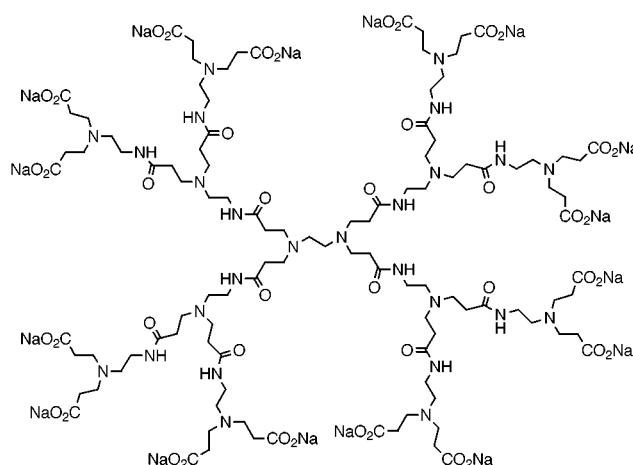
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**Crystallization of  $\text{CaCO}_3$  in the presence of poly(amidoamine) (PAMAM) dendrimer containing carboxylate groups at the external surface resulted in the formation of spherical vaterite crystals whereas rhombohedral calcite crystals were formed in the absence of additive.**

In nature, biological organisms produce polymer–inorganic hybrids which have superior mechanical properties as compared to synthetic hybrids.<sup>1</sup> Small amounts of acidic-rich proteins play a major role in forming such hybrids by influencing mineral crystal nucleation and growth.<sup>2</sup> On the basis of specific interactions, ‘matrix’ proteins or other macromolecules affect crystal morphology by inhibiting the growth of particular crystal faces. The processes and materials that control such crystal growth are of great interest in the field of material chemistry, in particular in the construction of composite materials analogous to those produced by nature. Crystallization of inorganics in the presence of various synthetic polymers has been investigated as a model of biomineralization. Synthetic anionic polypeptide analogues and anionic non-peptide polymers have also been found to be potent inhibitors or habit modifiers of inorganic crystallization.<sup>3–5</sup> Studies of inorganic crystallization in the presence of soluble polymers, modeled on biogenic proteins, have shown that the selectivity for certain crystal faces appears to be highly dependent on the secondary structure of the macromolecules. For example, poly-L-aspartate, with a predominantly  $\beta$ -sheet conformation, produces more aragonite than poly-L-glutamate, which has a random conformation.<sup>3</sup>

Poly(amidoamine) (PAMAM) dendrimers with carboxylate groups at the external surface, denoted half-generation or  $G = n.5$  dendrimers have been proposed as mimics of anionic micelles or proteins.<sup>6</sup> The starburst structures are disklike shapes in the early generations, whereas the surface branch cell becomes substantially more rigid and the structures are spherical for later generations.<sup>7</sup> Owing to their unique and well defined secondary structures, anionic starburst dendrimers should be good candidates for studying inorganic crystallization. Although the interaction of the negative surface of the dendrimers with metal ions has been extensively examined,<sup>8</sup> the effect of dendrimers on inorganic crystallization in aqueous solution has not been reported. Here we studied crystallization of  $\text{CaCO}_3$  in the presence of anionic PAMAM dendrimers and found that the anionic starburst dendrimer was a habit modifier which affected the crystal morphology upon crystallization. We used calcium carbonate ( $\text{CaCO}_3$ ) as the inorganic phase, since its crystals are easily characterized, and since the morphology of  $\text{CaCO}_3$  has been shown to be subject to control in biomineralization processes.<sup>9</sup>

The precipitation of  $\text{CaCO}_3$  in the presence and the absence of the PAMAM dendrimer ( $G = 1.5$ ) was carried out under the same conditions as used by Cölfen *et al.*<sup>10</sup> to prevent heterogeneous nucleation at the glass walls.†  $\text{CaCO}_3$  crystal formation occurring after addition of the reactants was readily



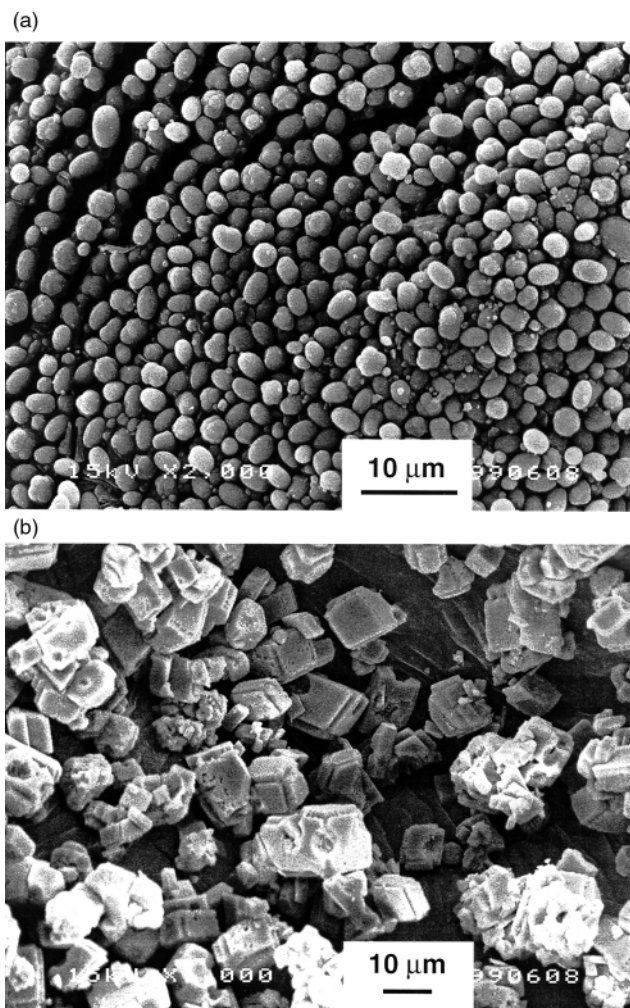
PAMAM dendrimer ( $G = 1.5$ )

observed from a sudden increase in the turbidity of the solution. This solution was then kept at 25 °C under  $\text{N}_2$  for 4 days with gentle stirring. Owing to the complexation of the dendrimer with calcium ions, the saturated concentration of calcium ions in the presence of PAMAM dendrimer ( $G = 1.5$ ) was 1.3 times higher than that in the absence of the additive. The crystalline  $\text{CaCO}_3$  was washed with water to remove contaminating dendrimers that were not involved in the crystals. The yields of the crystalline products in the absence and presence of the dendrimer were 51 and 61%, respectively. The dendrimer content in the crystalline  $\text{CaCO}_3$  was 33 wt% as determined by elemental analysis. These results indicate that the anionic dendrimer was bound to the crystalline  $\text{CaCO}_3$ .

The precipitation of  $\text{CaCO}_3$  in the presence of the Na salt of poly(acrylic acid) (PAA) ( $M_n = 5100$ ) was also carried out under the same conditions as above. The concentration of calcium ions in the presence of the Na salt of PAA was twice that in the absence of the additive before a sudden increase in the turbidity of the solution was observed. In the presence of the Na salt of PAA, the formation of crystalline  $\text{CaCO}_3$  was prevented and amorphous  $\text{CaCO}_3$  was collected after incubation at 25 °C under  $\text{N}_2$  for 4 days. This indicates that PAA acts as an inhibitor for crystal formation.<sup>11</sup>

The crystal phase of  $\text{CaCO}_3$  obtained in the presence of the PAMAM dendrimer was characterized by FTIR analysis.<sup>12</sup> Bands at 877 and 746  $\text{cm}^{-1}$  indicated the formation of vaterite while bands at 874 and 712  $\text{cm}^{-1}$  characteristic of calcite were scarcely observable.

By contrast, according to IR spectroscopy, the crystal phase of  $\text{CaCO}_3$  obtained in the absence of dendrimer was calcite. The IR spectrum of  $\text{CaCO}_3$  obtained in the presence of the Na salt of PAA suggested an amorphous character. Crystal phases  $\text{CaCO}_3$  were further confirmed by XRD; in the presence of dendrimer,



**Fig. 1** Scanning electron micrographs of calcium carbonate in the presence (a) and the absence (b) of PAMAM dendrimer ( $G = 1.5$ ).

the precipitate consisted entirely of vaterite (>99%) while in the absence of dendrimer, the reflections were characteristic for calcite.

SEM observations showed that the vaterite particles were spherical [Fig. 1(a)] with an average particle diameter of 1–2  $\mu\text{m}$ . SEM also showed that calcite crystals obtained in the absence of the polymer were rhombohedral [Fig. 1(b)]. Vaterite transforms readily and irreversibly into thermodynamically more stable forms when in contact with water and complete phase transformation into the thermodynamically stable calcite form occurs within 80 h and usually much faster under the conditions described above.<sup>10</sup> It is well known that vaterite transforms into the stable calcite form *via* a solvent-mediated process.<sup>13</sup> Stable spherical vaterite crystals have already been reported in the presence of various divalent cations,<sup>14</sup> a surfactant [bis(2-ethylhexyl)sodium sulfonate (AOT)],<sup>15</sup> and double-hydrophilic block copolymers.<sup>10</sup> We speculate that the vaterite surface is stabilized by the carboxylate-terminated dendrimer in aqueous solution to prevent phase transformation. If the Ca–O bonds to a polymer ligand are easily dissociated by

water, then the polymer is thought not to be occluded in the  $\text{CaCO}_3$  crystal, and solvent-mediated vaterite–calcite transformation would occur. Strong Ca–O bonds are thus required to alter the obtained polymorph of  $\text{CaCO}_3$ .<sup>‡</sup> In the presence of the PAMAM dendrimer, further washing of the vaterite crystal with water did not change the crystal morphology. Although a template mechanism involving dendrimers appears to be of a complex nature since simultaneous  $\text{CaCO}_3$  nucleation and interaction with the polymer is expected, the complexation properties of PAMAM dendrimers may be a major factor in the mineralization of calcium ions.

In conclusion, we present the first example of crystallization of  $\text{CaCO}_3$  in the presence of an anionic starburst dendrimer. Whereas a linear poly(carboxylic acid), PAA, acts as an inhibitor for crystal formation, the dendrimer was a habit modifier and affected the crystal morphology upon  $\text{CaCO}_3$  crystallization. The complexes of anionic starburst dendrimers with calcium ions are considerably stronger for higher generations than for lower generations. Investigations are now underway on crystallization of  $\text{CaCO}_3$  in the presence of anionic starburst dendrimers of even higher generations.

## Notes and references

† PAMAM dendrimer ( $G = 1.5$ ) (16 surface carboxylate groups) was purchased from Aldrich.  $\text{CaCO}_3$  crystallization was carried out as follows. A solution of  $1.56 \times 10^{-1}$  mmol of the dendrimer (corresponding to 2.50 mmol of  $-\text{CO}_2\text{Na}$ ) in 300 ml distilled water was adjusted to pH 8.5 with  $\text{NH}_3$  (aq). Then 0.5 M  $\text{CaCl}_2$  aqueous solution (adjusted to pH 8.5) and 0.5 M  $(\text{NH}_4)_2\text{CO}_3$  aqueous solution (adjusted to pH 10.2) were injected *via* syringe into the reaction mixture at 25 °C under  $\text{N}_2$  with stirring. After a sudden increase in the turbidity of the solution, this solution was then kept at 25 °C under  $\text{N}_2$  for 4 days with gentle stirring.  $\text{CaCO}_3$  crystallization in the absence of the dendrimer was carried out using a 300 ml aqueous solution containing 2.50 mmol of NaCl instead of the dendrimer solution. ‡ Stoichiometric exchanges of alkali-metal ions with divalent cations such as  $\text{Ca}^{2+}$  have been reported for anionic PAMAM dendrimers.<sup>6</sup>

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