

# **Continuous Structural Evolution of Calcium Carbonate Particles: A Unifying Model of Copolymer-Mediated Crystallization**

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## **Experimental**

The poly(ethylene oxide)-block-poly(sodium 4-styrenesulfonate) [PEO<sub>22</sub>-PNaStS<sub>49</sub>] diblock copolymer was prepared in an aqueous alcohol milieu via Atom Transfer Radical Polymerization (ATRP), as described previously.<sup>1</sup> The chemical structure of this copolymer is shown in Figure 1. The two subscripts are the mean degrees of polymerization for each block as determined by <sup>1</sup>H NMR spectroscopy. Aqueous gel permeation chromatography (GPC) analysis indicated an  $M_n$  of 14,300 g/mol and an  $M_w/M_n$  of 1.21 using near-monodisperse poly(sodium 4-styrenesulfonate) calibration standards. A second sulfonated diblock copolymer, PEO<sub>45</sub>-(PGMA:2SBA)<sub>48</sub> was prepared by treating a poly(ethylene oxide)-block-poly(glycerol monomethacrylate) diblock copolymer (previously prepared via ATRP in methanol at 20°C)<sup>2</sup> with excess 2-sulfobenzoic acid cyclic anhydride in dry pyridine at 20°C as described by Vo and co-workers.<sup>3</sup> This diblock copolymer is somewhat unusual in that it contains two aromatic sulfonate groups per methacrylic repeat unit (see Figure 1). The precursor copolymer prior to esterification had an  $M_n$  of 16,500 g/mol and an  $M_w/M_n$  of 1.30 respectively, as judged by DMF GPC using poly(methyl methacrylate) calibration standards. The two subscripts are the mean degrees of polymerization for each block as determined by <sup>1</sup>H NMR spectroscopy. These two copolymers were evaluated as crystal growth modifiers for

calcium carbonate, as described below.

One poly(sodium 4-styrenesulfonate) homopolymer, PNaStS<sub>79</sub>, was also briefly investigated and its structure is shown in Figure 1. This homopolymer was synthesized according to a previously reported protocol,<sup>1</sup> and its mean degree of polymerization was determined by <sup>1</sup>H NMR spectroscopy. Aqueous gel permeation chromatography (GPC) analysis indicated an  $M_n$  of 16,600 g/mol and an  $M_w/M_n$  of 1.71 using near-monodisperse poly(sodium 4-styrenesulfonate) calibration standards.

### ***Precipitation of CaCO<sub>3</sub> Crystals***

Calcium carbonate was precipitated in the presence of the sulfonate-functionalized block copolymers using an ammonium carbonate diffusion method. The Ca<sup>2+</sup> concentration in the solution was set at either 10 mM or 20 mM, and the block copolymer concentration was adjusted to give a [Ca]:[S] ratio (where [S] = number of moles of sulfonate groups) in the range 4:1 to 1:1000. Control experiments were also performed in the absence of the copolymer. CaCl<sub>2</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (ANALAR) were obtained from Aldrich and used without further purification. CaCl<sub>2</sub> solution was placed in the wells of a Nunc plate and a solution of the copolymer was added with stirring to give the desired Ca concentration and [Ca]:[S] molar ratio within a total volume of 2.5 ml. Glass slides previously cleaned with Piranha solution were then placed on the base of the wells. The plate was placed in a desiccator with a Petri dish containing 4 g of ammonium carbonate, covered with aluminium foil and pierced with 4 holes, and the system was left undisturbed for 2 days. The glass plates were finally removed from the wells, washed with Millipore water and allowed to dry at room temperature prior to analysis. Crystallization experiments were repeated at least five times to ensure that the observed crystals are common, representative and reproducible.

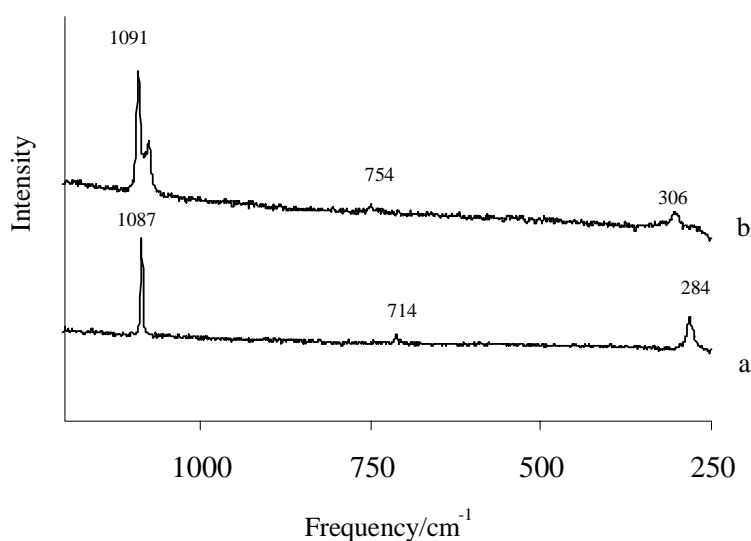
### *Analysis of CaCO<sub>3</sub> Crystals*

The morphology of the CaCO<sub>3</sub> particles was studied using Scanning Electron Microscopy (SEM). Glass slides supporting the crystals for analysis were mounted on SEM stubs with adhesive carbon pads and were sputter-coated with Pt/Pd using an Agar High Resolution Sputter Coater. SEM was carried out using a Jeol 6330 FEG-SEM operating at 10 kV. The crystal polymorph of individual particles was determined using Raman microscopy and for two selected samples by microbeam X-ray diffraction (see below). The crystals were examined on the glass slides using a Renishaw Raman 2000 System Microscope operating with a 785 nm laser. The quantity of polymer occluded within the particles was determined by thermogravimetric analysis (TGA). TGA samples were heated up to 800°C in air at a scan rate of 20°C min<sup>-1</sup> using a Perkin-Elmer TGA-7 instrument. Both copolymers are completely pyrolyzed under these conditions. Further information on the structure of the CaCO<sub>3</sub> particles was obtained from BET surface area analysis on 50 mg samples using a NOVA e4000 Surface Area Analyzer (Quantachrome Corp). Samples for BET were degassed at 120 °C for 3 hours prior to measurement.

The various crystal phases present in the samples were investigated using X-ray powder diffraction (XRPD), which was carried out using a Cu K $\alpha$ <sub>1</sub> source and an INEL CPS-120 curved position sensitive detector.<sup>4,5</sup> Data was collected between  $2\theta = 3.5^\circ$  and  $2\theta = 120^\circ$  in intervals of  $0.015^\circ$  at room temperature. Specimens were prepared by grinding 5-20 mg of sample in acetone and applying the dilute slurry to the surface of the zero background sample holder, thus ensuring a smooth and uniform layer of 10 to 20  $\mu\text{m}$ . Patterns were calibrated using correction curves produced from a mixture of silver behenate and yttria employed as a standard. A quantitative phase analysis of the XRPD patterns was performed by Rietveld refinement using the program GSAS.<sup>6</sup> Published structures for calcite,<sup>7</sup> and vaterite,<sup>8</sup> were used to initiate the refinements.

Microbeam X-ray diffraction experiments were performed at the  $\mu$ -Spot beamline at the synchrotron radiation source BESSY II in Berlin, Germany.<sup>9</sup> An X-ray wavelength of 0.14 nm was selected by a W/Si multilayer, and a microbeam of 15  $\mu$ m diameter was defined by a circular Fresnel-Zone-Plate. Diffraction patterns were collected with a Marmosaic 225 CCD-based area detector (Mar-USA) at a distance of 190 mm from the sample in on-line transmission geometry. The beamline setup enabled the small-angle scattering (SAXS) and wide-angle diffraction (XRD) signals to be collected simultaneously, without the need for a change of experimental configuration. The samples for microbeam diffraction were prepared on Si<sub>3</sub>N<sub>4</sub> membranes with thicknesses of 200 nm using the generic method described above. The membranes were mounted on brass-pins attached to an *x-y-z* scanning device at the beamline. An on-axis, high resolution optical microscope allowed single calcium carbonate particles to be selected for subsequent microbeam X-ray diffraction.

SI Figure 1: Typical Raman spectra of (a) calcite and (b) vaterite particle produced in the presence of PEO<sub>22</sub>-PNaSt<sub>49</sub>.



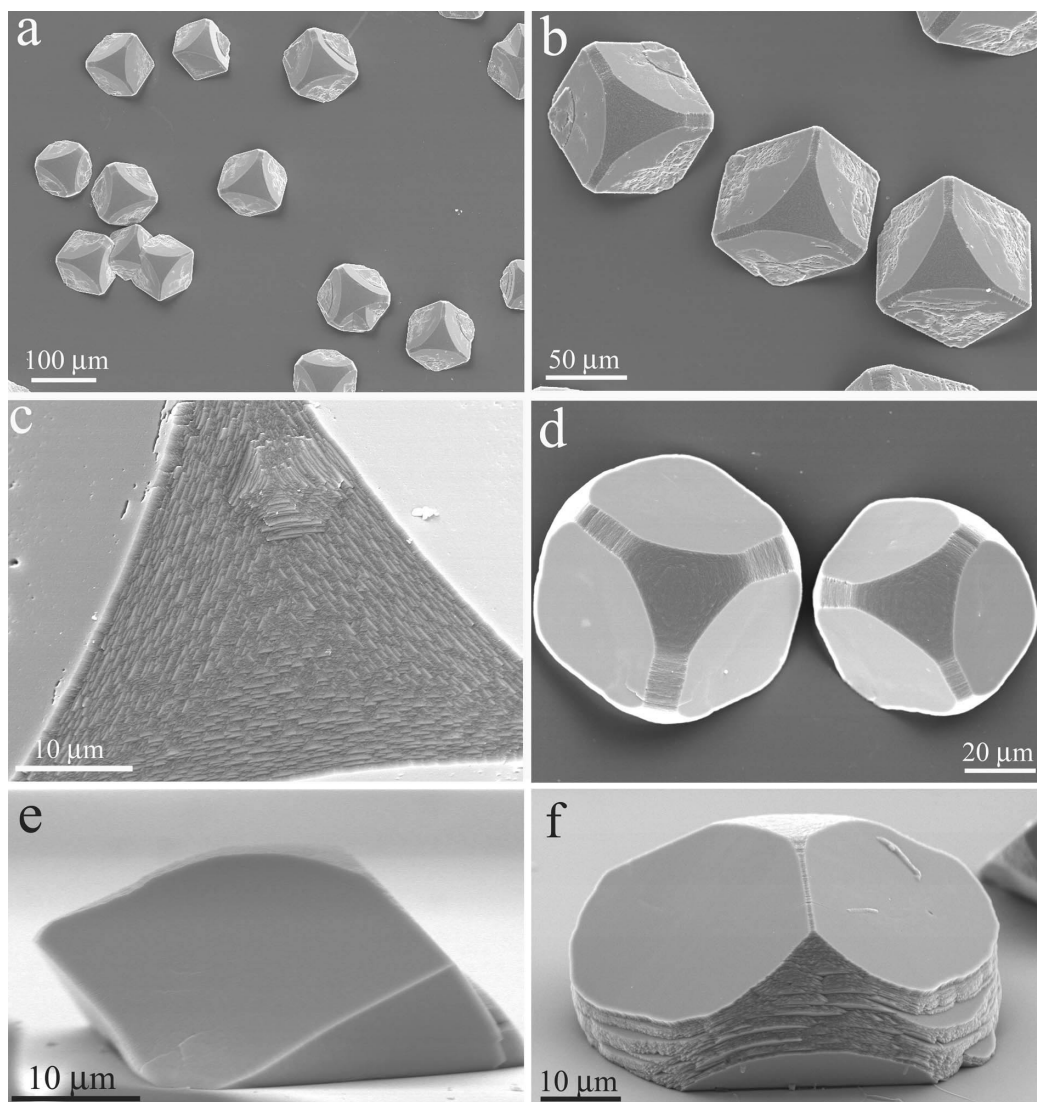
#### CaCO<sub>3</sub> crystallization in presence of PEO<sub>45</sub>-(PGMA:2SBA)<sub>48</sub>:

At  $[Ca] = 10 \text{ mM}$  and  $[Ca]:[S] = 1:1$  two closely-related particle morphologies were observed. Although all crystals were rhombohedral calcite, exhibited a truncated top corner and top edges and were oriented with the  $[001]$  direction perpendicular to the substrate (Figure SI 2), some particles exhibited truncation of the top corner only (Figures SI 2a and SI 2b), while others showed truncation of all of the corners of the rhombohedron (Figure SI 2d). The existence of these two morphological forms was confirmed by tilting the samples in the SEM, which enabled the side-faces to be imaged (Figures SI 2e and SI 2f). Notably, the top corner truncation was much larger than that observed for the PEO<sub>22</sub>-PNaStS<sub>49</sub> diblock copolymer and varied within a given sample, sometimes extending from each of the three corners bounding this face. The new truncated face was typically not entirely flat, as indicated by the curved interface between this face and the existing  $\{104\}$  faces (Figure 6e). Examination at high magnification showed that the new  $\{001\}$  face was very rough, comprising small  $\{104\}$  faces lying parallel to the external faces of the particles (Figure SI 2c). The  $\{104\}$  faces of the calcite rhombohedra were often highly roughened (Figure SI 2b), although particles were also observed which showed perfectly smooth  $\{104\}$  faces.

Lowering the copolymer concentration reduced its effect on the crystal habit, as expected. For example, at a  $[Ca]:[S]$  molar ratio of 1000:1, only a very small truncation of the top crystal face was observed. However, crystals were still predominantly  $[001]$  oriented. Increasing the copolymer concentration to  $[Ca]:[S] = 1:20$  caused a marked inhibition in crystal growth, and aragonite particles were produced in addition to unmodified calcite rhombohedra. Further experiments investigated a wide range of reagent concentrations and  $[Ca]:[S]$  molar ratios, varying from as high as 100 mM Ca to 0.2 mM Ca and for  $[Ca]:[S]$  molar ratios varying from 50:1 to 1:20. These experimental conditions resulted in variations in the size of the

characteristic face and edge truncations, but no transformation to mesocrystals or polycrystalline particles was observed under any of the conditions tested.

SI Figure 2: Calcium carbonate crystals precipitated from a solution containing 10 mM Ca and PEO<sub>45</sub>-(PGMA:2SBA)<sub>48</sub> at a [Ca]:[S] molar ratio of 1:1. Figures (e) and (f) show side views of typical crystals.



SI Table 1: Summary of vaterite structure from powder data obtained using PNaStS<sub>79</sub>.

|                                 |                  |             |            |          |             |
|---------------------------------|------------------|-------------|------------|----------|-------------|
| <b>Space Group</b>              | Pbnm             |             |            |          |             |
| <b>Unit cell parameters (Å)</b> | <b>a</b>         | <b>b</b>    | <b>c</b>   |          |             |
|                                 | 4.1285(5)        | 7.1463(6)   | 8.4669(4)  |          |             |
|                                 |                  |             |            |          |             |
| <b>Atom</b>                     | <b>Occupancy</b> | <b>x</b>    | <b>y</b>   | <b>z</b> | <b>Uiso</b> |
| <b>Ca</b>                       | 1.0              | 0.0         | 0.0        | 0.0      | 0.0252(7)   |
| <b>C</b>                        | 1.0              | 0.063(4)    | 0.646(4)   | 0.25     | 0.025(4)    |
| <b>O1</b>                       | 1.0              | 0.3767(28)  | 0.6004(13) | 0.25     | 0.0374(29)  |
| <b>O2</b>                       | 1.0              | −0.0518(16) | 0.6727(20) | 0.1185   | 0.0586(20)  |

## References

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