Supporting Information

Biomimetic Mineralization of Calcium Carbonate Mediated by a Polypeptide-based Copolymer

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1. Characterization of β-CD-*b*-PBLG and β-CD-*b*-PLGA copolymers by ^{1}H-NMR

^{1}H NMR spectra were recorded using Avance 550, Bruker. Figure S1 shows the ^{1}H NMR spectra of β-CD-*b*-PBLG and β-CD-*b*-PLGA block copolymers in DMSO-d_6 solvent. The PBLG segment has NMR peaks at (δ = 7.32, 5.04). The β-CD segment has peaks at (δ = 4.48, 3.72-4.17, 1.75-2.74). Compared with the ^{1}H NMR spectrum of β-CD-*b*-PBLG, the disappearance of the methylene proton peak (5.04 ppm) indicates the complete deprotection of the benzyl groups after the hydrolysis reaction.
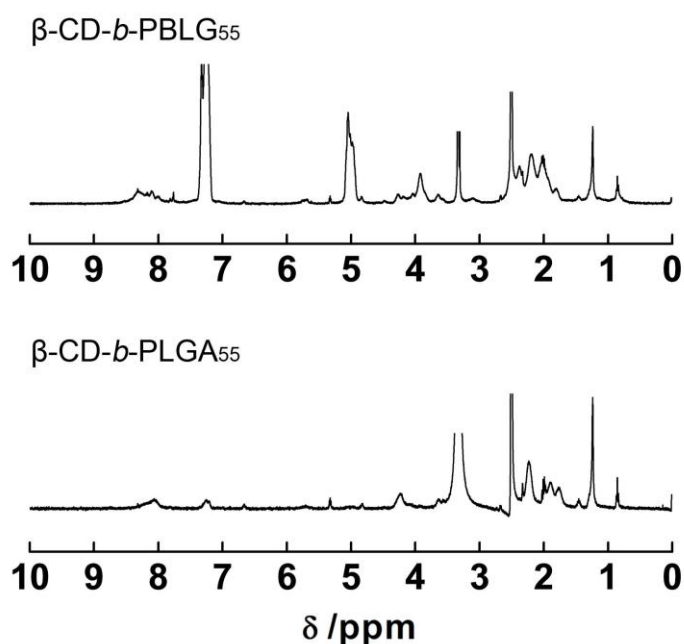

Figure S1 ^{1}H NMR spectra of β-CD-*b*-PBLG and β-CD-*b*-PLGA in DMSO-d_6 solvent.

2. Characterization of β-CD-*b*-PBLG copolymers by GPC

The β-CD-*b*-PBLG copolymers with various PBLG block lengths were measured by GPC (Polymer Lab, PL-GPC50 plus) using PBLG with narrow molecular weight distribution as standard, performed in LiBr/DMF solution. All the samples show a monomodal GPC curve and narrow molecular weight distribution.
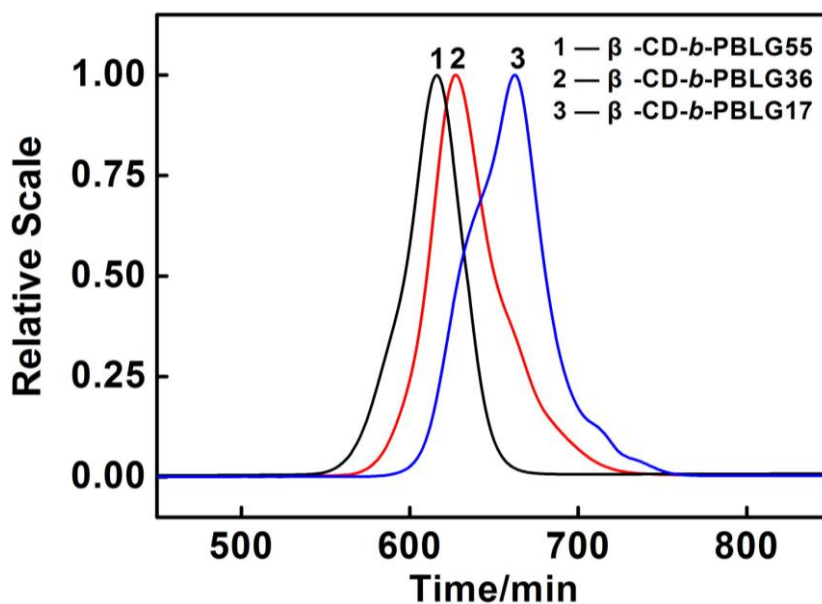

Figure S2 GPC traces of β-CD-*b*-PBLG copolymers.

3. Lattice fringe image of the pseudo-dodecahedral crystal

Interstice and mesopore are widely observed in the lattice fringe image of the pseudo-dodecahedral crystal (as white arrow shows). The defects originate from the interstitial voids of the packed primary nanoparticles, showing the feature of mesocrystal.
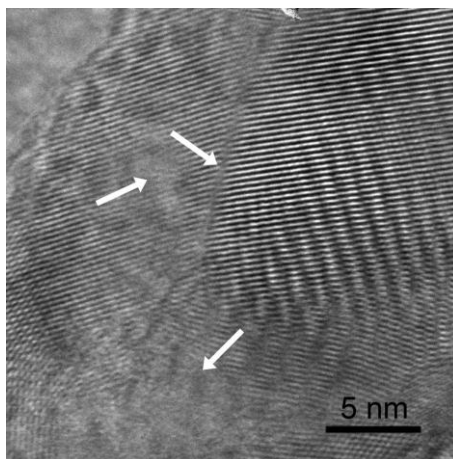

Figure S3 HR-TEM image of an ultra thin section of the pseudo-dodecahedral $CaCO_3$ crystal prepared in the presence of 2 mM calcium ions and 2.0 g/L CG1.

4. Thermal analysis of the CaCO₃ sample

Thermal analysis was applied to measure the content of the polymers in the $CaCO_3$ sample. TG curve shows two-step weight loss. The weight loss starting from 300 $^{\circ}$C is attributed to the decomposition of the CG1 copolymer. The weight loss of the second step is corresponding to the decomposition of $CaCO_3$.
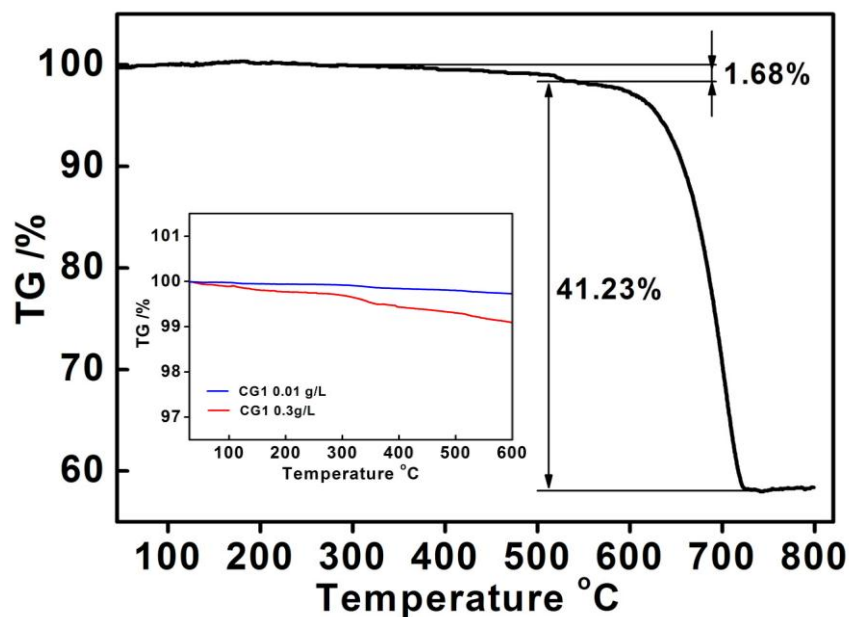

Figure S4 TG curve of the pseudo-dodecahedral crystals obtained in 2.0 g L^{-1} CG1 copolymer solution and the Ca^{2+} concentration is 2 mM. And the inset shows the TG curves of samples obtained in 0.3 and 0.01 g L^{-1} CG1 copolymer solutions. The sample formed in the presence of 0.3 g/L CG1 contains about 0.3 wt% of CG1. And in the case of 0.01 g/L CG1, there are very few polymers in the sample.

5. The influence of CG2 and CG3 on the mineralization behavior of CaCO$_3$

$CaCO_3$ crystals were prepared in the presence of CG2 and CG3 with various polymer concentrations respectively, (a) CG2, 0.1 g L^{-1}, (b) CG2, 2.0 g L^{-1}, (c) CG3, 0.1 g L^{-1}, (d) CG3, 2.0 g L^{-1}. At a polymer concentration of 0.1 g L^{-1}, rods were generated for both CG2 and CG3 (Figure S3a, b). While a high polymer concentration of 2.0 g L^{-1} leads to the formation of pseudo-dodecahedrons (Figure S3c, d).
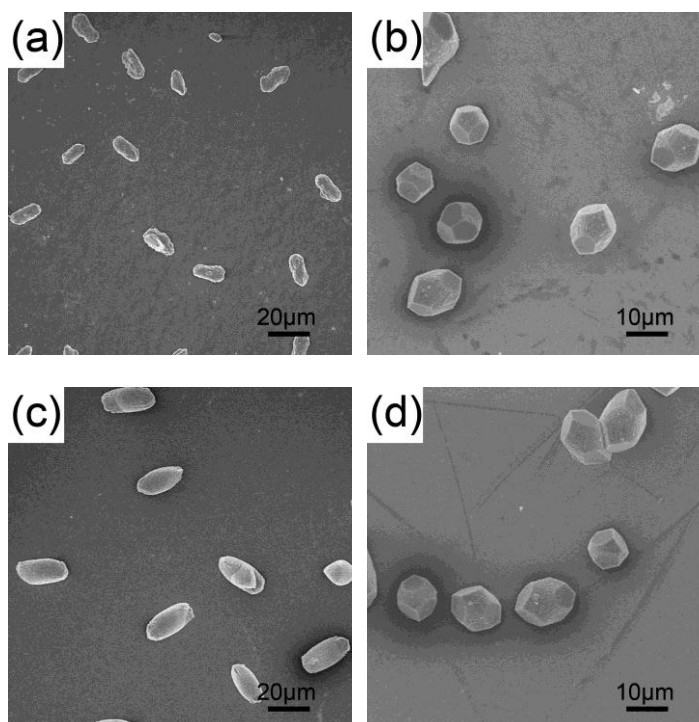

Figure S5 SEM images of CaCO$_3$ crystals obtained in the presence of CG2 and CG3 at various conditions (a) CG2, 0.1 g L^{-1}, (b) CG2, 2.0 g L^{-1}, (c) CG3, 0.1 g L^{-1}, (d) CG3, 2.0 g L^{-1}. The Ca^{2+} concentration is fixed at 2 mM.

6. CaCO$_3$ crystallization under control of β-CD and PLGA

In the presence of β-CD at a polymer concentration of 2.0 g L^{-1}, rhombohedral calcite was obtained (a). The crystals are mostly rod calcite crystals in PLGA$_{99}$ solution at a concentration between 0.1 to 3.0 g L^{-1}. Figure S4b shows the rod crystals formed in PLGA solution at a concentration of 2.0 g L^{-1}. The results indicate that the β-CD is a solvating block and the PLGA is a binding block.
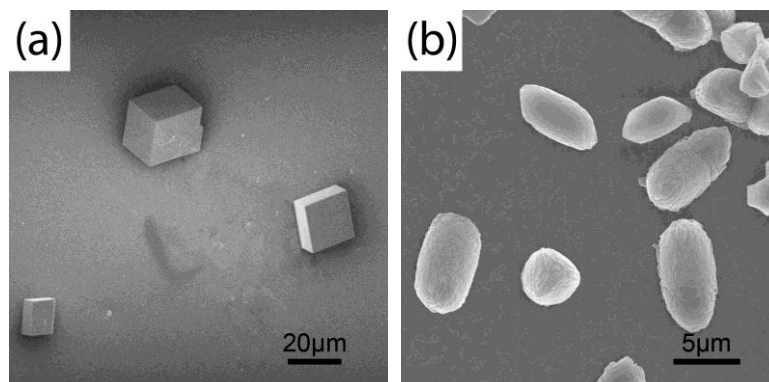

Figure S6 SEM images of CaCO$_3$ crystals prepared in the presence of β-CD and PLGA.