

Supporting Information

Effect of a Thermo-Responsive Polypeptide-Based Copolymer on Mineralization of Calcium Carbonate

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1. $^1\text{H-NMR}$ analysis of the PNIPAM-*b*-PBLG and PNIPAM-*b*-PLGA

^1H NMR spectra were recorded using Avance 550, Bruker. Figure S1 shows the ^1H NMR spectra of PNIPAM-*b*-PBLG and PNIPAM-*b*-PLGA block copolymers in CDCl_3/TFA mixed solution. Since the degree of polymerization of the PNIPAM block is known, the molecular weight can be calculated by comparing the integral value of the characteristic peak of PNIPAM at $\delta = 3.9$ ppm with that of PBLG at $\delta = 5.1$ ppm (Figure S1a). The disappearance of the peak at 5.1 ppm indicates that the benzyl groups were completely removed after hydrolyzation (Figure S1b).^{1,2}

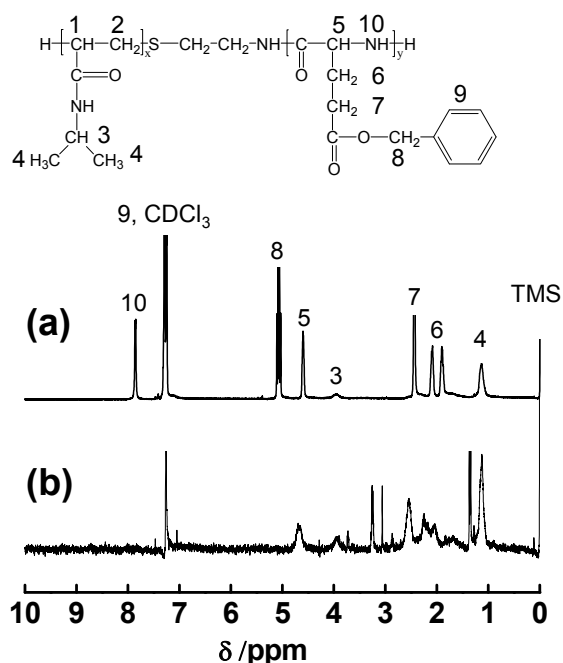


Figure S1 ^1H NMR spectra of PNIPAM₄₅-*b*-PBLG₁₉₂ (a) and PNIPAM₄₅-*b*-PLGA₁₉₂ (b) in CDCl_3 and TFA mixed solvent (5/1, v/v).

2. The thermo-responsive behavior of NG192 studied by static light scattering (SLS)

SLS was employed to characterize the thermo-responsive behavior of NG192, since the copolymers aggregated and the solution turned cloudy when the temperature was raised from below the LCST to above the LCST. As shown in Figure S2, the scattered intensity is very weak at lower temperatures and dramatically increased above 33 °C. Above 50 °C, the scattered intensity basically remains constant.

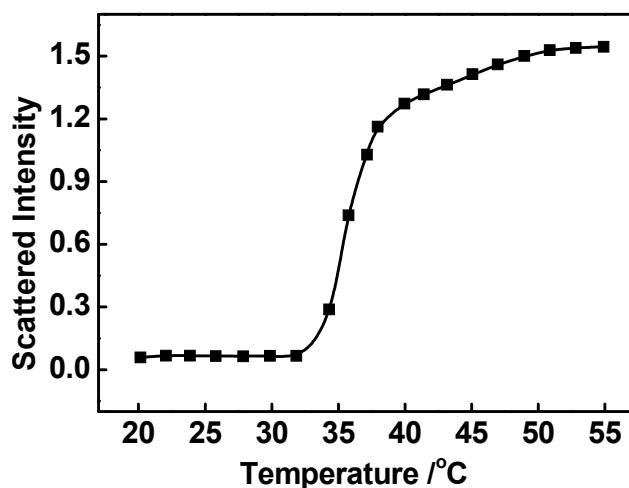


Figure S2 Plot of scattered intensity as a function of temperature of the NG192 at the concentration of 2.0 g/L.

3. CaCO₃ crystallization controlled by PNIPAM and PLGA homopolymers

The influence of PNIPAM and PLGA homopolymers on CaCO₃ crystallization were studied as a control experiment. The degrees of polymerization of PNIPAM and PLGA homopolymers are 45 and 274 respectively. Rhombohedra crystals and rosette-like crystals were obtained in the presence of PNIPAM and PLGA respectively. The images indicate that the PNIPAM and PLGA homopolymers do not change their influences on CaCO₃ mineralization at different temperatures (Figure S3). The crystals are all calcite as indicated by the FT-IR measurement (Figure S4).³

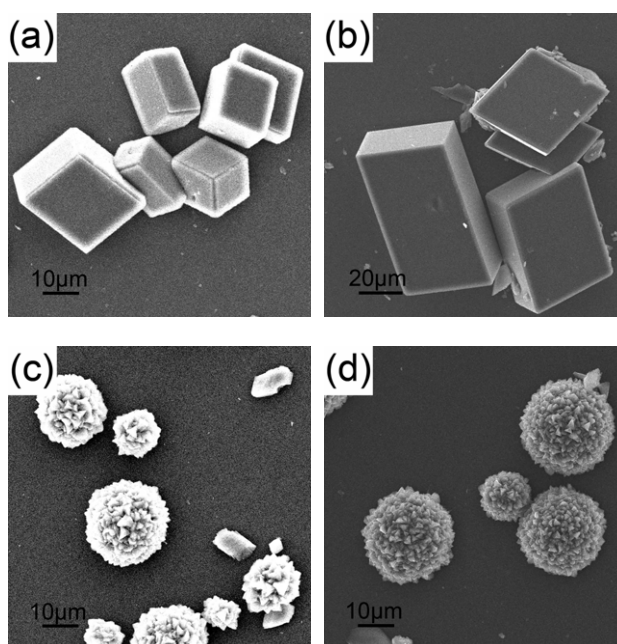


Figure S3 SEM images of CaCO₃ crystals formed in the presence of PNIPAM and PLGA homopolymers at different temperatures. (a) PNIPAM, 25°C; (b) PNIPAM, 50°C; (c) PLGA, 25°C; (d) PLGA, 50°C. The polymer concentration is fixed at 1.0 g/L in each case.

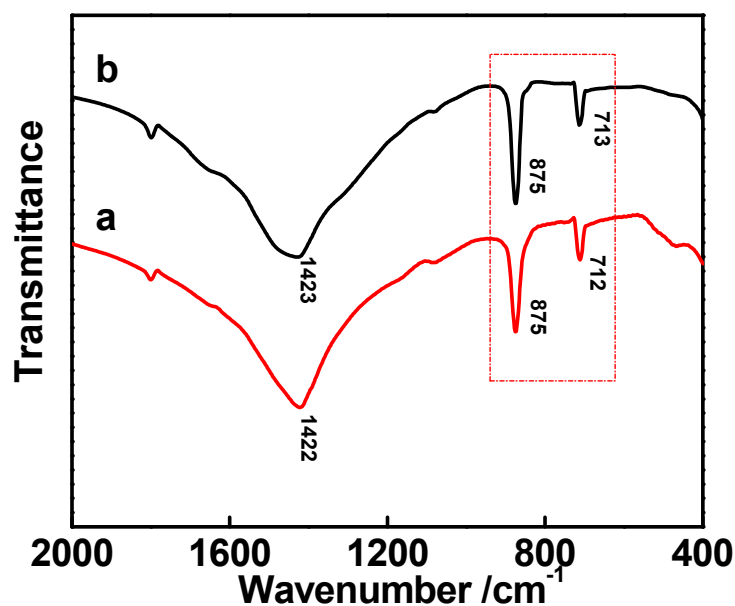


Figure S4 FT-IR spectra of CaCO_3 crystals formed in the presence of NG192 unimers with different copolymer concentrations at 25°C : (a) 1.0 g/L; (b) 0.1 g/L. The bands at 874 and 712 cm^{-1} indicate the calcite formation.

4. CaCO_3 crystallization in the micelle solution at 40°C

Figure S5 shows the SEM images of CaCO_3 samples in the micelle solution at 40°C . The samples are mainly in the form of fibers, similar to the samples obtained at 50°C .

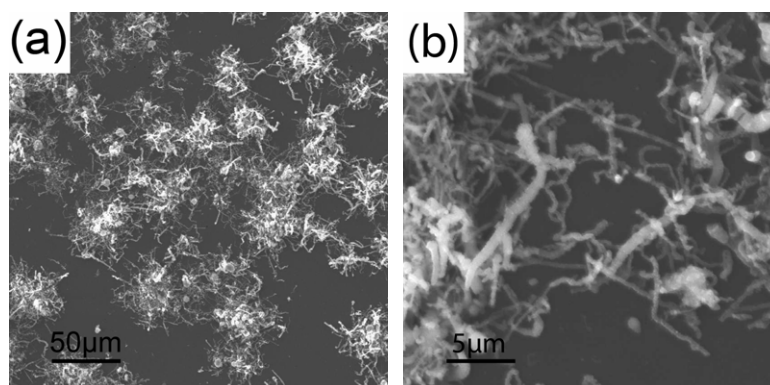


Figure S5 SEM images of CaCO_3 crystals in the presence of 2.0 g/L NG192 micelle solution at 40°C after 24 hour reaction.

Figure S6 shows FT-IR spectra of CaCO_3 samples in the micelle solution at 40°C . In the FT-IR spectra, the absorption bands at 858, 712 cm^{-1} are the characteristic bands of aragonite. The bands at 877 and 745 cm^{-1} are assigned to the characteristic bands of vaterite. The result indicates that both aragonite and vaterite exist in the crystals.

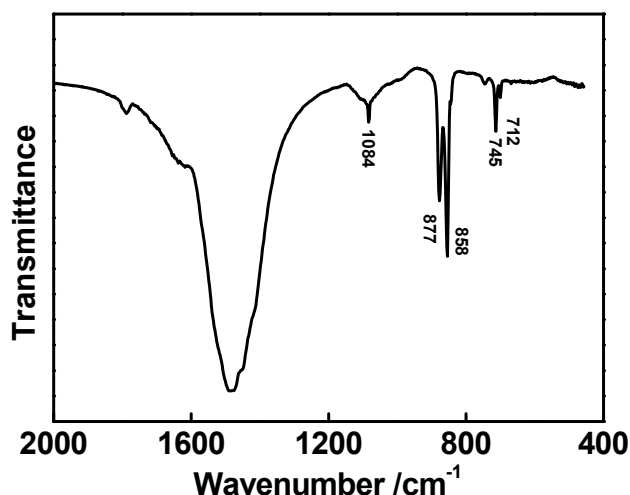


Figure S6 FT-IR spectra of CaCO_3 crystals formed in the presence of 2.0 g/L NG192 micelle solution at 40°C after 24 hour reaction.

5. FT-IR measurement of CaCO_3 crystals in the presence of NG12 and NG42 micelles

Figure S7 shows FT-IR spectra of CaCO_3 crystals formed in the presence of NG12 and NG42 micelles. The absorption bands at 858, 712 cm^{-1} are the characteristic bands of aragonite. And the bands at 877 and 745 cm^{-1} are the characteristic bands of vaterite. In both cases, aragonite and vaterite exist in the samples.

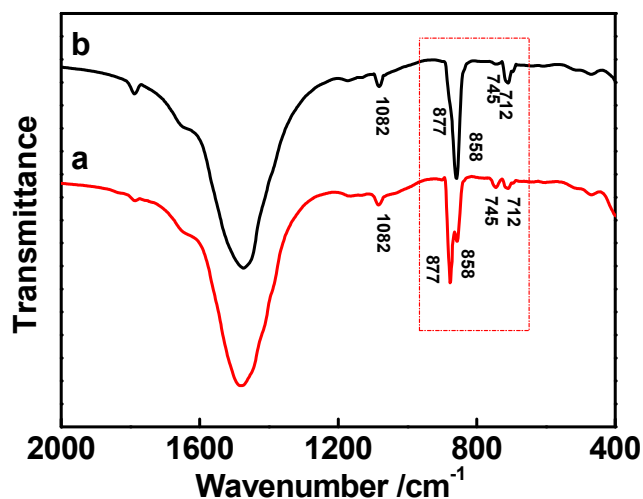


Figure S7 FT-IR spectra of CaCO_3 crystals formed in the presence of NG12 (a) and NG42 (b) micelles.

References

- (S1) C. Cai, L. Zhang, J. Lin, L. Wang, *J. Phys. Chem. B.* 2008, **112**, 12666-12673.
(S1) J. Rodríguez-Hernández, S. Lecommandoux, *J. Am. Chem. Soc.* 2005, **127**, 2026-2027.
(S2) F. A. Andersen, L. Brecevic, *Acta Chim. Scand.* 1991, **45**, 1018.