

-Supporting Information-

Bioinspired fabrication of macroporous calcium carbonate crystals mediated by
thermoresponsive copolymers

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1. Characterization of PNVCL- β -CD block copolymers

Fourier Transform Infrared (FT-IR) spectra were recorded in transmission mode on a Spectra One FT-IR spectrometer (USA PE Company). Fig. S1 shows the FT-IR spectra of PNVCL-C \equiv CH, N₃- β -CD and PNVCL2- β -CD block copolymer. The peaks of alkyl in 2118 cm⁻¹, azido in 2105 cm⁻¹ and 2038 cm⁻¹ were disappeared in PNVCL2- β -CD, the peak of 2104 cm⁻¹ in PNVCL2- β -CD was the character of triazole, the peak of 1631 cm⁻¹ was the character of PNVCL and 1031 cm⁻¹ was the character of β -CD, all those indicated the successfully reaction of alkyne and azide.

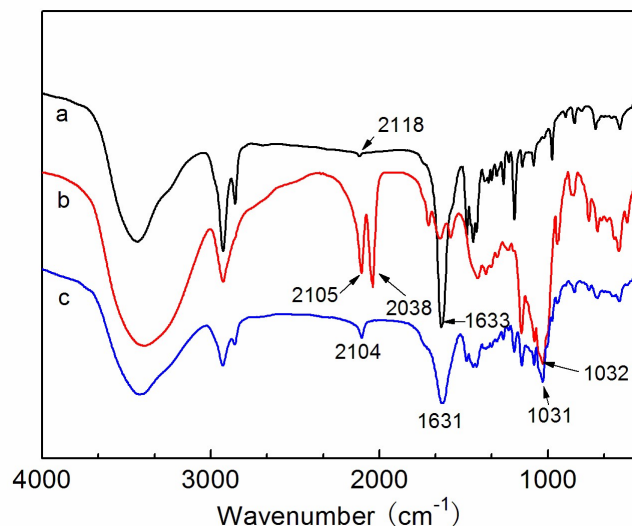


Fig. S1 FT-IR spectra of PNVCL-C \equiv CH (a), N₃- β -CD (b) and PNVCL2- β -CD (c).

The ¹H NMR spectrum was recorded on a Varian Mercury-300 NMR spectrometer using DMSO-*d*₆ as a solvent. Chemical shifts (δ) were given in ppm using tetramethylsilane (TMS) as an internal reference. Fig. S2 shows the ¹H NMR

spectrum of PNVCL2- β -CD block copolymer. The peak at 7.95 ppm was assigned to triazole.

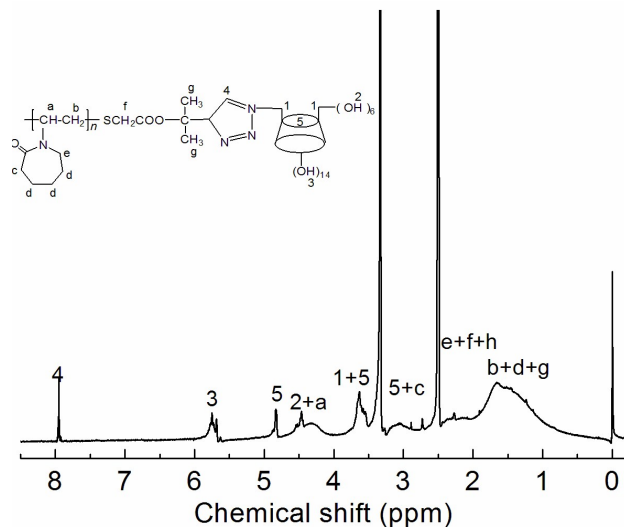


Fig. S2 ^1H NMR spectrum of PNVCL2- β -CD in $\text{DMSO-}d_6$.

The PNVCL2- β -CD copolymers with various PNVCL block lengths were measured by the gel permeation chromatography (GPC) measurement with a Waters 1515 GPC instrument and a 2414 differential refractive index detector. THF was used as eluent at the flow rate of 1.0 mL/min at 30 $^\circ\text{C}$, and the molecular weights were calibrated with polystyrene standards. All samples show a unimodal GPC curve.

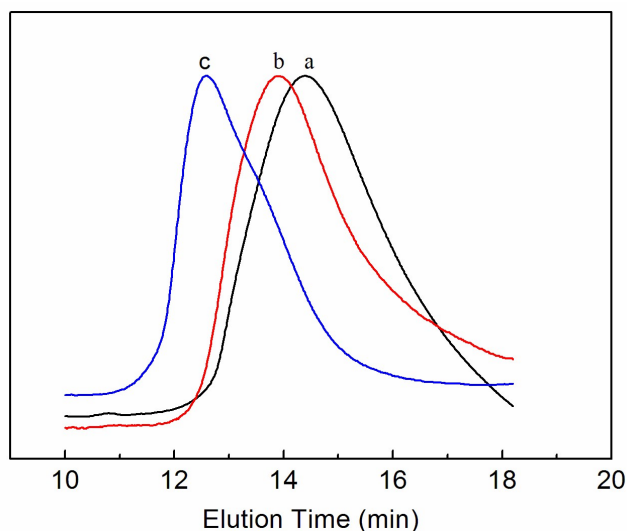


Fig. S3 GPC curves of the copolymers.

(a) PNVCL1- β -CD (b) PNVCL2- β -CD (c) PNVCL3- β -CD

2. Formation of micelles

The micellar structures of PNVCL- β -CD were confirmed by fluorescence technique using pyrene as a probe. A pyrene solution (in acetone) was added into a series of volumetric flasks in such an amount that the final concentration of pyrene in each solution was 6.0×10^{-7} mol/L, thereafter acetone was removed completely. The polymer solution was added into the volumetric flasks and diluted till the calibration mark using ultrapurified water to obtain the desired copolymer concentrations ranging from 1.0×10^{-4} g/L to 1.0 g/L. The samples were stored at room temperature overnight to equilibrate pyrene and micelles. Steady-state fluorescence excitation spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer at 390 nm emission wavelength and 5.0 nm slit width. The scan rate was 120 nm/min. The fluorescence excitation spectra of pyrene in the presence of PNVCL- β -CD at various concentrations are shown in Fig. S4. A red shift from 334 to 338 nm is observed with increasing concentration of PNVCL- β -CD, indicating that micellization takes place for the PNVCL- β -CD copolymer. Such results can be attributed to the transfer of pyrene molecules from water to a hydrophobic environment within the micelles core.

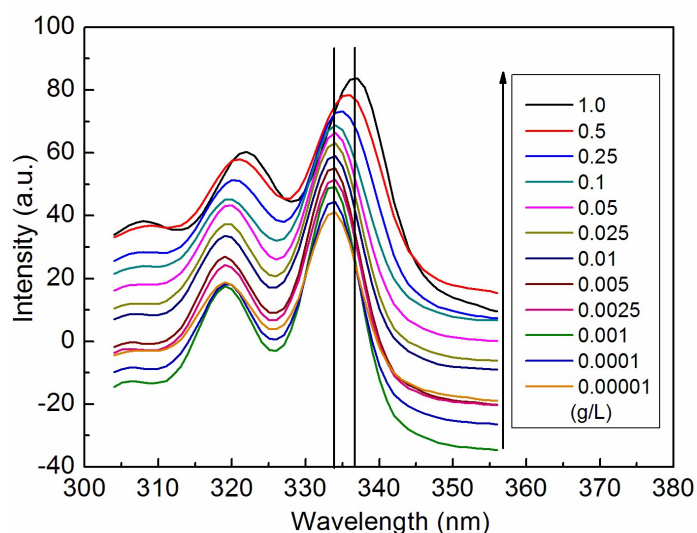


Fig. S4 Excitation spectra of pyrene as a function of PNVCL- β -CD concentration in water.

The onset of micellization and the critical micelle concentrations (CMC) can also be obtained from the studies of excitation spectra. For the copolymer PNVCL- β -CD, 334 and 338 nm are chosen as the peak wavelength of the (0, 0) band in the pyrene excitation spectra in the aqueous phase and in the entirely hydrophobic core of

polymeric micelle, respectively. The pyrene fluorescence intensity ratios (I_{338}/I_{334}) are plotted against the logarithm of copolymer concentration. The plots are shown in Fig. S5. Below a certain concentration, I_{338}/I_{334} is constant, above this concentration, I_{338}/I_{334} increases with increasing $\lg C$. From this plot, CMC were obtained from the intersection of two straight lines: the base line and the rapidly rising I_{338}/I_{334} line. The CMC values in Table 1 reduced with the increasing of the proportion of PNVCL segment.

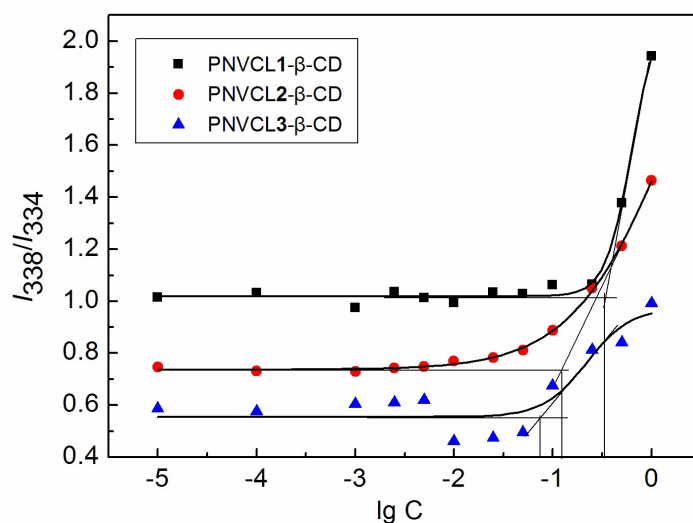


Fig. S5 Plots of I_{338}/I_{334} versus logarithm of block copolymers concentrations.

3. Thermosensitivity of copolymers

Fig. S6 is a typical photograph of aqueous solutions of PNVCL-β-CD. Below the LCST, PNVCL-β-CD copolymers are amphiphilic, consisting of a hydrophilic block (PNVCL) and hydrophobic block (β-CD). The solution was transparent and colorless (Fig. S6a). However, when heated closed to the LCST, the solution gradually turned into a semitransparent emulsion (Fig. S6b), then above the LCST, the copolymers are hydrophobic and the solution became a white opaque suspension (Fig. S6c), and finally the polymers precipitated from water if the solution was kept at a high temperature for enough time. When cooled, the semitransparent emulsion and transparent colorless solution were gotten again. Evidently, PNVCL-β-CD showed a reversible LCST phase transition in water. This phenomenon takes place due to the different solvation of PNVCL chains by water molecules at the temperatures below

and above the phase transition temperature¹.

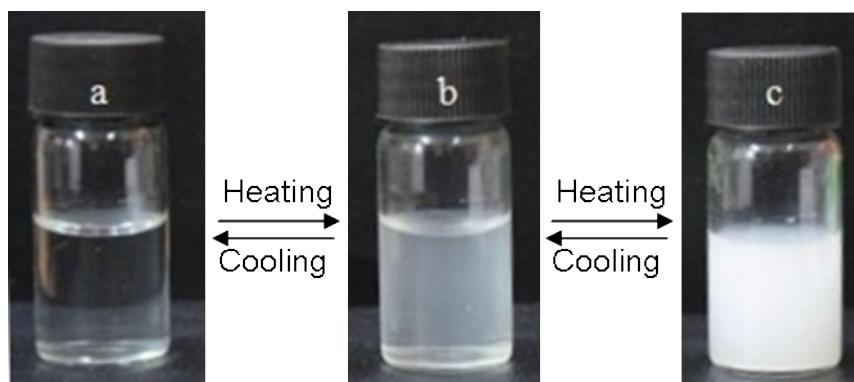


Fig. S6 The photos of PNVCL2- β -CD aqueous solution in different temperature (C=1.0 g/L).

(a) 25.0 °C (b) 38.5 °C (c) 42.0 °C

The transmittance of aqueous solutions of polymer was recorded on a Perkin-Elmer Lambda Bio 20 UV-vis spectrophotometer (Fig. S7). Briefly, the polymers were dispersed (5.0 g/L) in ultrapurified water (Aquaplast 18.2 M Ω). The transmittance of aqueous solutions of polymer at $\lambda=500$ nm was recorded in a 1.0 cm path length quartz cell. The rate of heating was set at 1 °C/min with hold steps of 10 min at each temperature. Values for the LCST of aqueous solutions of the polymers were determined at a temperature with a half of the optical transmittance between below and above transitions.

It is reported that the LCST of thermoresponsive polymers can be controlled by compositions of hydrophobic and hydrophilic units². In this study, the LCST transition behaviors of the PNVCL- β -CD block copolymers were tuned by changing the lengths of the thermoresponsive PNVCL block: the larger the PNVCL content of the copolymer, the lower the LCST. Fig. S7 shows the temperature dependence of optical transmittance of micellar solutions of copolymers with different PNVCL block lengths. The transmittance decreased significantly at a specific temperature on heating solutions of all of the copolymers. The LCST were evaluated as 39.7, 38.5 and 34.9 °C for PNVCL1- β -CD, PNVCL2- β -CD and PNVCL3- β -CD respectively, thus showing a decreasing trend with increasing PNVCL block length.

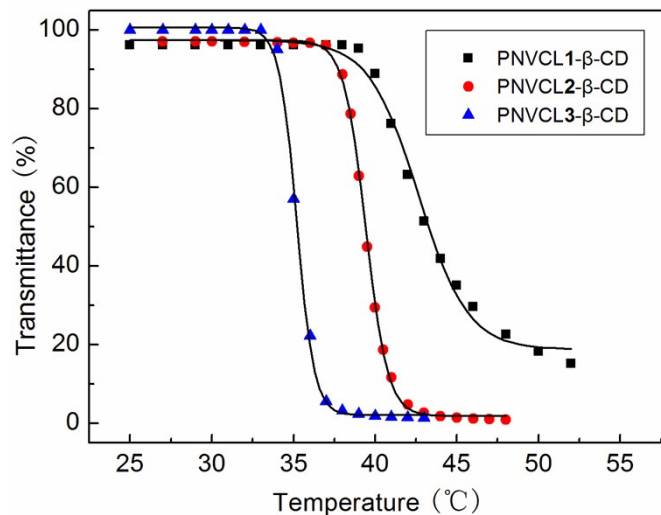


Fig. S7 PNVCL- β -CD aqueous solutions transmittance curves with the temperature change ($C=0.5$ g/L).

The hydrodynamic diameter of the aggregates at 50 °C was determined by dynamic light scattering (DLS) using a Malvern Nano ZS instrument (Fig. S8).

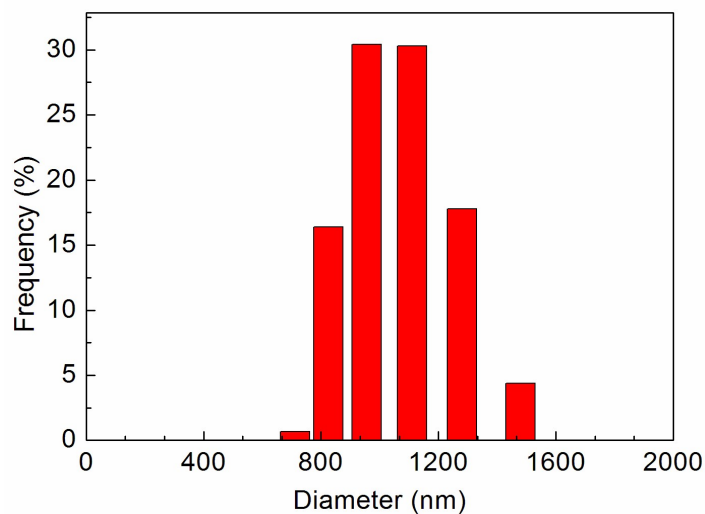


Fig. S8 The size distribution of PNVCL2- β -CD copolymer aggregates at 50 °C in aqueous solution measured by DLS.

4. The polymorphs of the crystal in the presence of PNVCL- β -CD below the LCST

Fig. S9A shows the FT-IR spectra of the crystals. The peaks of 712 cm^{-1} and 876 cm^{-1} can be attributed to the in-plane bending mode and out-of-plane bending mode bands of calcite, and the peak of 855 cm^{-1} was the out-of-plane bending mode of

aragonite. XRD measurements also demonstrated that the crystals obtained in the presence of PNVCL- β -CD are all mixtures of calcite and a small amount of aragonite (see Fig. S9B).

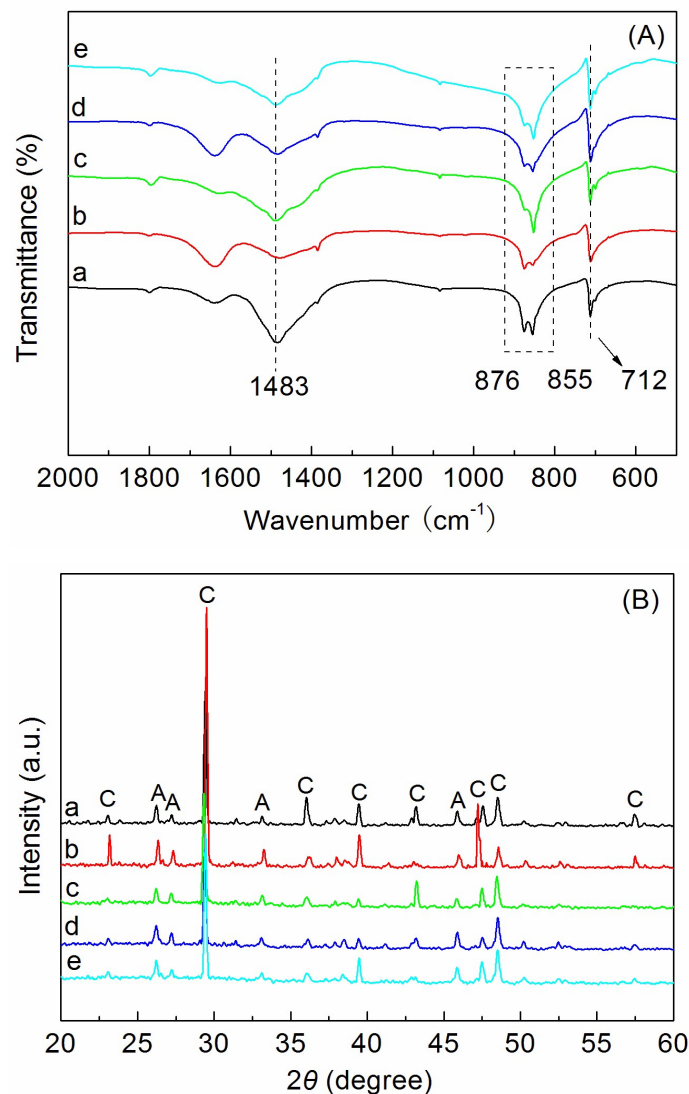


Fig. S9 FT-IR spectra (A) and XRD patterns (B) of CaCO₃ crystals formed in the PNVCL- β -CD solution with various concentrations. (a) 0.01, (b) 0.1, (c) 0.5, (d) 1.0, (e) 2.0 g/L ([Ca²⁺]=20 mM, T=25 °C).

5. CaCO₃ crystallization under the control of PNVCL-C \equiv CH and β -CD below the LCST

With PNVCL-C \equiv CH or β -CD as the additive, the formed crystals exhibit a typical rhombohedral calcite (see Fig. S10b-e), which is similar to the crystals formed without any additive (see Fig. S10a).

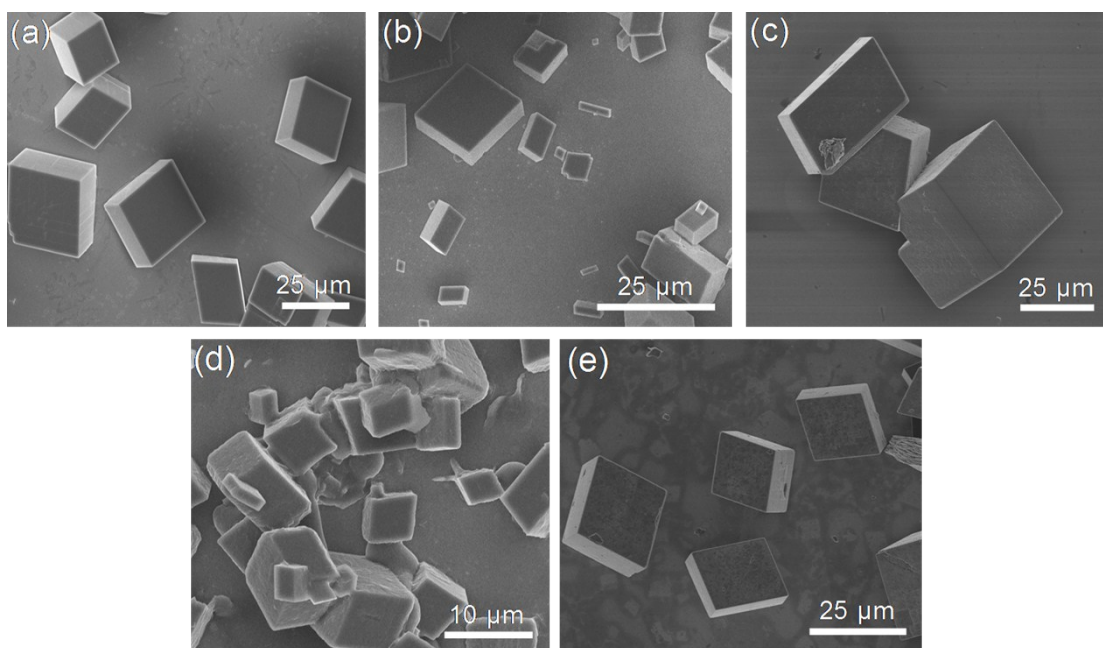


Fig. S10 SEM images of the samples prepared without any additive (a), in 1.0 g/L of PNVCCL-C≡CH (b), 2.0 g/L of PNVCCL-C≡CH (c), 1.0 g/L of β-CD (d) and 2.0 g/L of β-CD (e) ($[Ca^{2+}] = 20 \text{ mM}$, $T = 25 \text{ }^\circ\text{C}$).

6. Magnified TG curve of CaCO₃ particles in PNVCCL2-β-CD solution

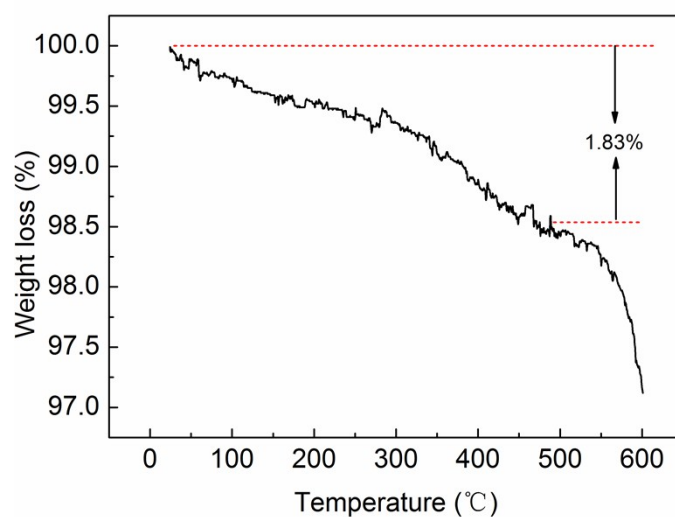


Fig. S11 Magnified TG curve of CaCO₃ particles in PNVCCL2-β-CD solution at 50 °C.

- 1 J. Hain, M. Schrunner, Y. Lu, A. Pich, *Small*, 2008, **4**, 2016-2024.
- 2 Y. Chang, Y. Hyun, U. Kang, J. H. Youk, *Colloid Polym Sci.*, 2012, **290**, 1107-1113.