Supplementary Information:

Thermosensitive polymer-controlled morphogenesis and phase discrimination of calcium carbonate

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Experimental Section:

Chemical: Anhydrous sodium carbonate (Mw = 105.99) and calcium chloride (Mw = 110.99) are commercially available and analytical grade used without further purification. In a typical experimental procedure, crystals of $CaCO_3$ were produced using a double-jet method. The double-jet experiments were carried out in a thermostated container. PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) was put into the vessel. Then, solution A and solution B (Solution A: 1.5 mL 100 mM [$CaCl_2$]; Solution B: 1.5 mL 100 mM [Na_2CO_3]) were injected into the vessel containing 10mL PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}) at a rate of 2mL h^{-1} under mild stirring. In addition, the vessel was covered with parafilm and the two injection needles were inserted, so the reaction was almost performed in a sealing system. Then, the crystals were collected for characterization. All experiments were repeated a minimum of three times to validate the method and results.

Characterization: X-ray power diffraction (XRD) analyses were carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation. Field emission scanning electron microscopy (FESEM) was carried out with a field emission scanning electron microanalyzer (JEOL-6700F). Transmission electron microscope (TEM) was performed on JEOL-2010 operated at an acceleration voltage of 200 kV.

Table S1 The average hydrodynamic radius, $\langle R_h \rangle$, and the average gyration radius, $\langle R_g \rangle$, of PEG-PNIPAM-PAMPS at 40°C, 50°C, 60°C. The ratios of $\langle R_g \rangle / \langle R_h \rangle$ indicate the formation of micelle nanoparticles in water.

Temperature/ °C	$\langle R_h \rangle$ / nm	$\langle R_g \rangle$ / nm	$\langle R_g \rangle / \langle R_h \rangle$
40	73.8	42.9	0.581
50	76.9	44.0	0.572
60	74.1	44.2	0.596

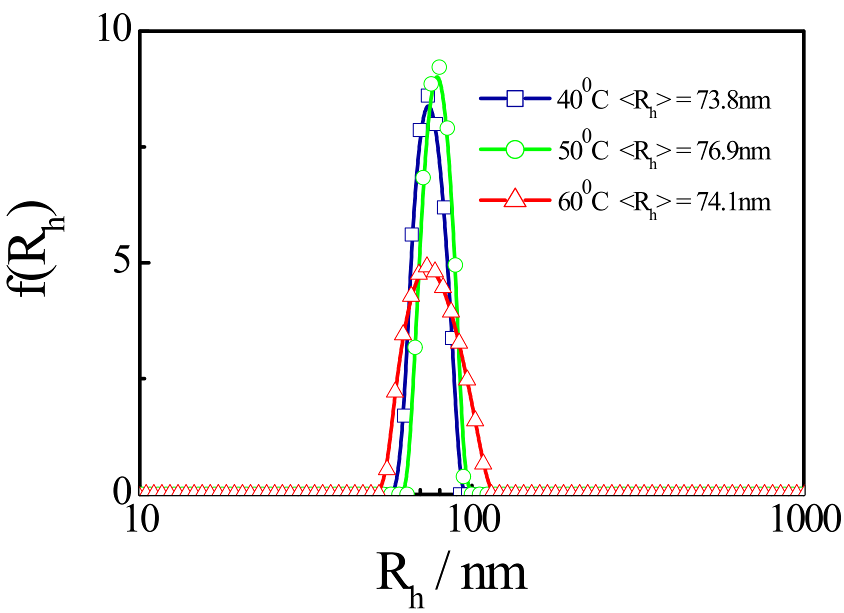

Fig. S1 Distributions of hydrodynamic radius of the PEG-PNIPAM-PAMPS at 40°C, 50°C, 60°C.

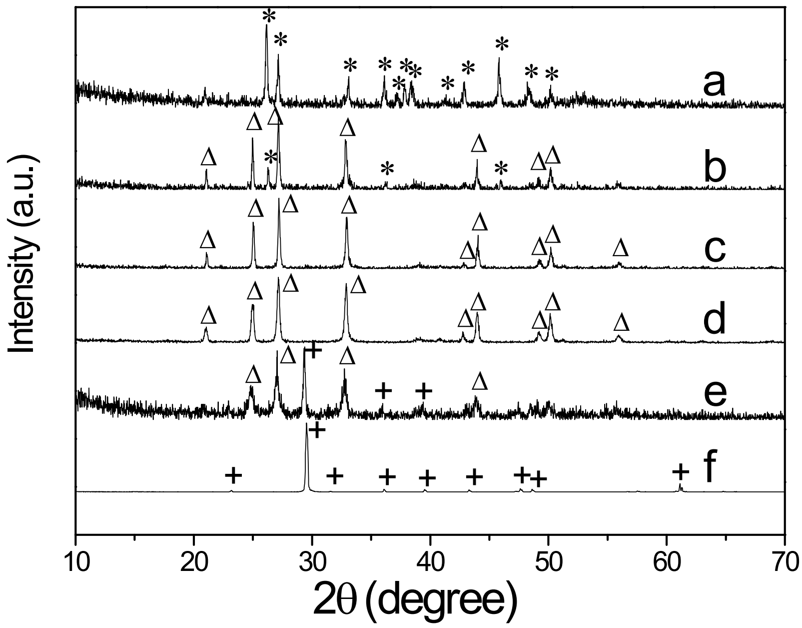

Fig. S2 XRD patterns of the $CaCO_3$ obtained by double-jet method at a rate of 2 $mL\cdot h^{-1}$. (a) 50 °C, pure aragonite. (b) 45 °C, a mixture of aragonite and vaterite. (c) 40 °C, pure vaterite. (d) 25 °C, pure vaterite. (e) 15 °C, a mixture of vaterite and calcite. (f) 0°C, pure calcite. [$CaCl_2$] = [Na_2CO_3] = 100 mM. The volume of both injected solutions was 1.5 mL, adding into PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel. Note: *, aragonite phase (JCPDS Card No. 41-1475); Δ, vaterite phase (JCPDS Card No. 33-0268); +, calcite phase (JCPDS Card No. 86-2340).

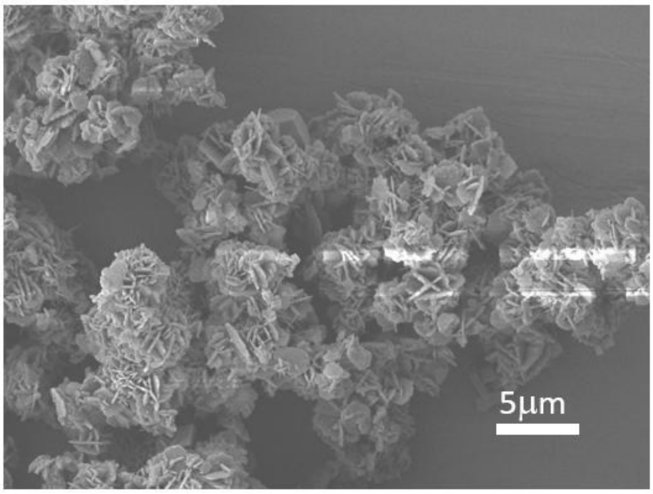

Fig. S3 Scanning electron microscopy (SEM) images of the $CaCO_3$ obtained by double-jet method at a rate of 2 mL/h at 25°C when the PEG-PNIPAM-PAMPS is absent, pure vaterite. [$CaCl_2$] = [Na_2CO_3] = 100 mM. The injected solutions was added into 10 mL water in the reaction vessel for 45 minutes.

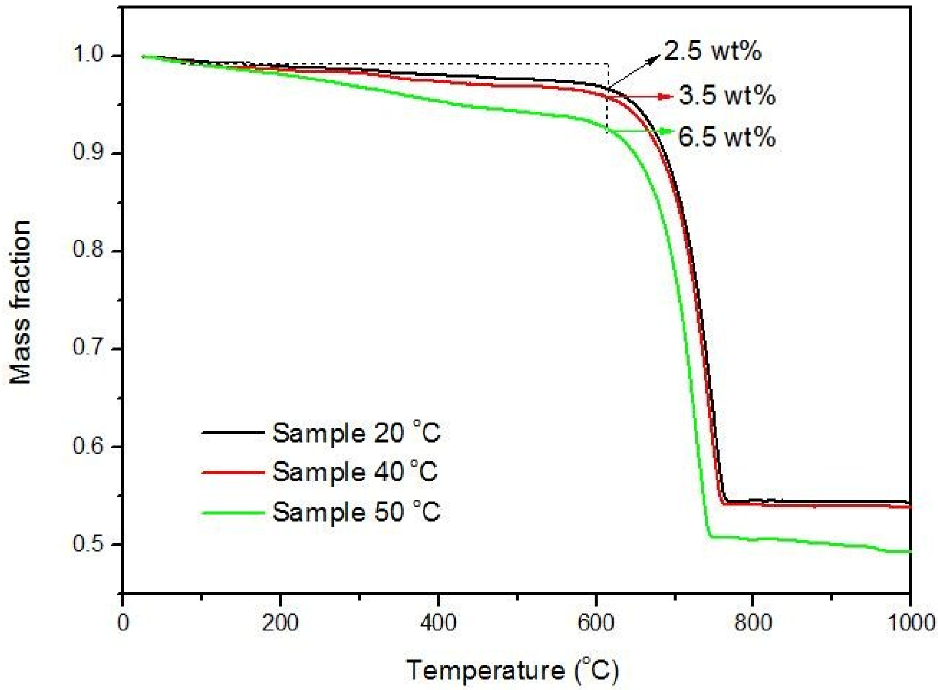

Fig. S4 Thermogravimetric curves of the obtained $CaCO_3$ at different temperature

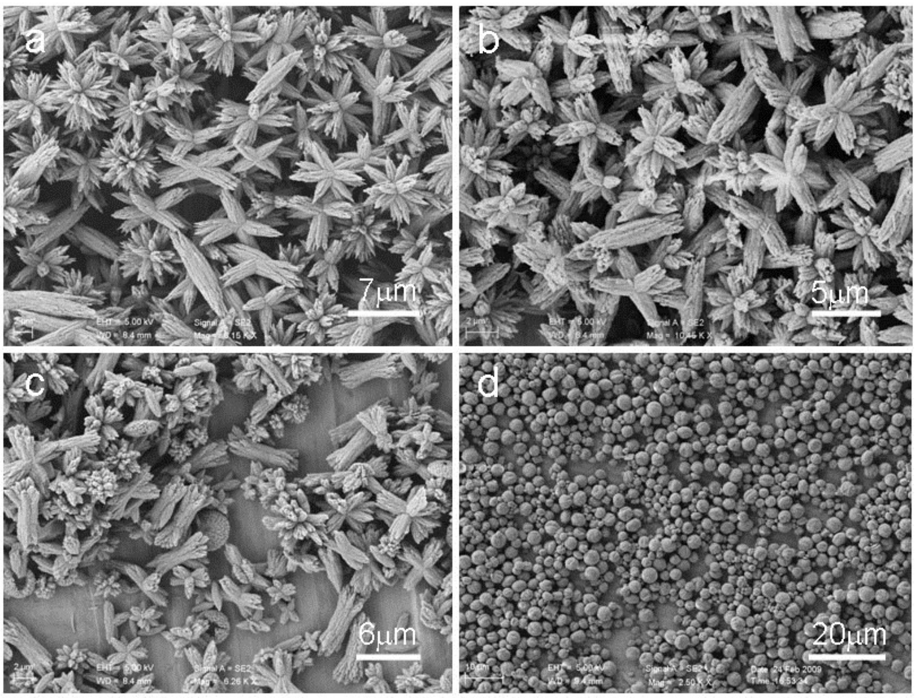

Fig. S5 Scanning electron microscopy (SEM) images of the $CaCO_3$ obtained at 50°C by double-jet method. (a) 4 mL·h^{-1}, pure aragonite; (b) 9 mL·h^{-1}, pure aragonite; (c) 18 mL·h^{-1}, a mixture of aragonite and vaterite (aragonite is dominant); (d) 1.5 mL·min^{-1}, a mixture of vaterite and calcite. [$CaCl_2$] = [Na_2CO_3] = 100 mM. The volume of each initial solution injected is 1.5 mL, adding into PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel.

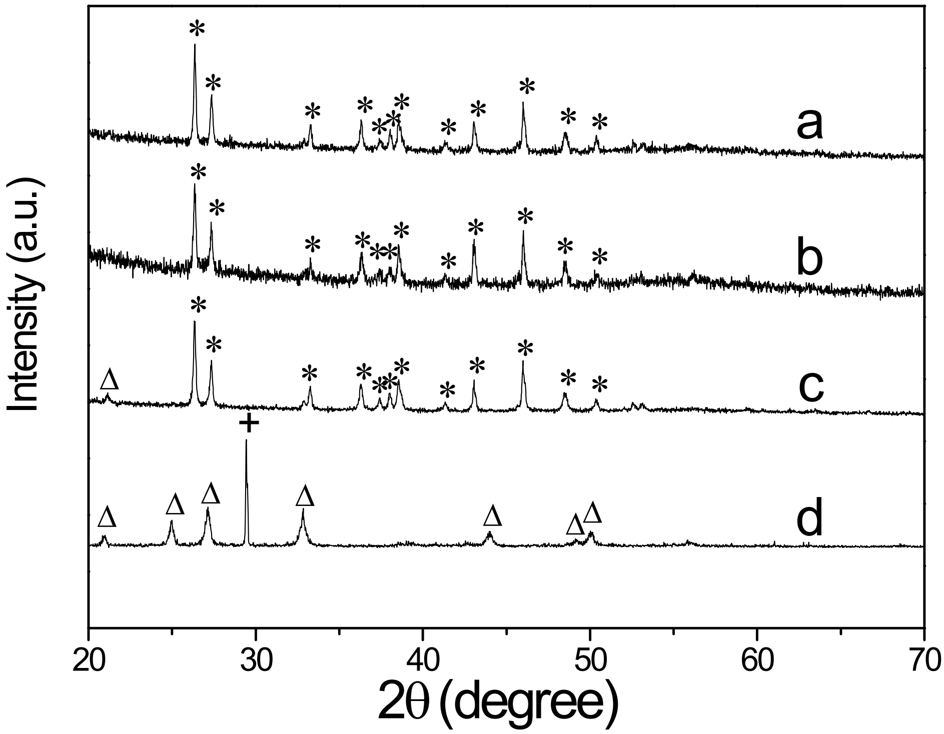

Fig. S6 XRD patterns of the $CaCO_3$ obtained at 50°C by double-jet method. (a) 4 $mL\cdot h^{-1}$, pure aragonite; (b) 9 $mL\cdot h^{-1}$, pure aragonite; (c) 18 $mL\cdot h^{-1}$, a mixture of aragonite and vaterite (aragonite is dominant); (d) 1.5 $mL\cdot min^{-1}$, a mixture of vaterite and calcite. $[CaCl_2]$ = $[Na_2CO_3]$ = 100 mM. The volume of each initial solution injected is 1.5 mL, adding into PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel. Note: ∗, aragonite phase (JCPDS Card No. 41-1475); Δ, vaterite phase (JCPDS Card No. 33-0268); +, calcite phase (JCPDS Card No. 86-2340).

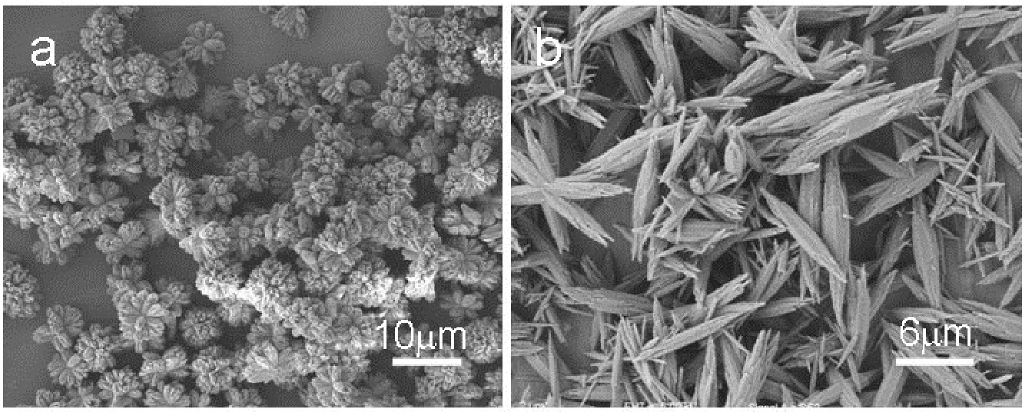

Fig. S7 SEM images of the $CaCO_3$ obtained by the double-jet method at a rate of 2 ml/h in presence of PEG-PNIPAM-PAMPS at 50°C. (a) [polymer] = 0.4 g L^{-1}, volume = 10 mL, aragonite; (b) [polymer] = 0.05 g L^{-1}, volume = 10 mL, aragonite. $[CaCl_2]$ = 100 mM, volume = 1.5 mL; $[Na_2CO_3]$ = 100 mM, volume = 1.5 mL.

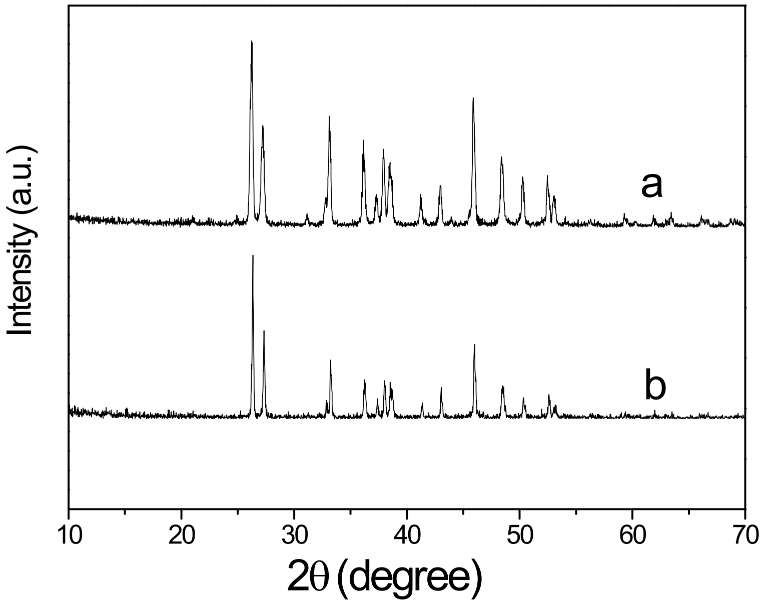

Fig. S8 XRD patterns of the $CaCO_3$ obtained by the double-jet method at a rate of 2 ml/h in presence of PEG-PNIPAM-PAMPS at 50°C: (a) [polymer] = 0.4 g L^{-1}, volume = 10 mL, aragonite; (b) [polymer] = 0.05 g L^{-1}, volume = 10 mL, aragonite. [$CaCl_2$] = 100 mM, volume = 1.5 mL; [Na_2CO_3] = 100 mM, volume = 1.5 mL.

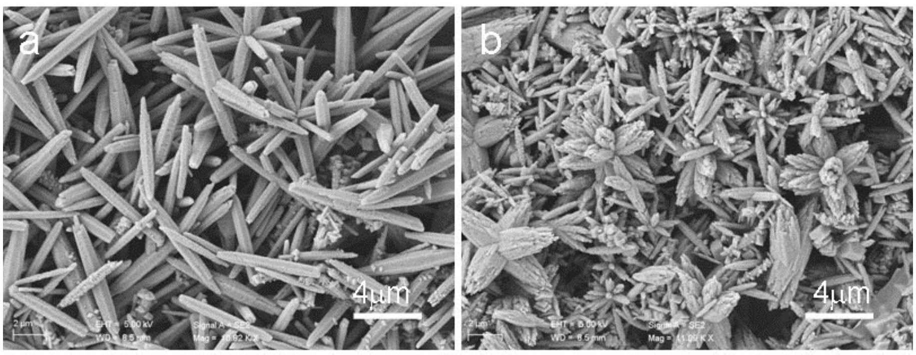

Figure S9. SEM images of the $CaCO_3$ obtained by single-jet method at a rate of 2 ml/h at 50 °C: (a) $CaCl_2$ ([$CaCl_2$] = 100 mM, volume = 1.5 mL) as the single-jet solution, Na_2CO_3 ([Na_2CO_3] = 100 mM, volume = 1.5 mL) is mixed with PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel, aragonite; (b) Na_2CO_3 ([Na_2CO_3] = 100 mM, volume = 1.5 mL) as the single-jet solution, $CaCl_2$ ([$CaCl_2$] = 100 mM, volume = 1.5 mL) is mixed with PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel, a mixture of aragonite and calcite.

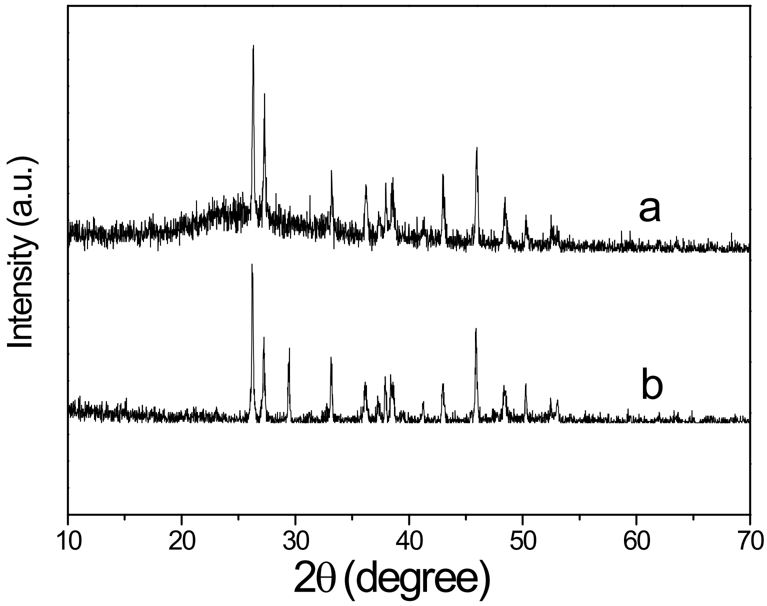

Figure S10. XRD patterns of the $CaCO_3$ obtained by single-jet method at a rate of 2 ml/h at 50 °C: (a) $CaCl_2$ ([$CaCl_2$] = 100 mM, volume = 1.5 mL) as the single-jet solution, Na_2CO_3 ([Na_2CO_3] = 100 mM, volume = 1.5 mL) is mixed with PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel, aragonite; (b) Na_2CO_3 ([Na_2CO_3] = 100 mM, volume = 1.5 mL) as the single-jet solution, $CaCl_2$ ([$CaCl_2$] = 100 mM, volume = 1.5 mL) is mixed with PEG-PNIPAM-PAMPS solution (0.2 g L^{-1}, 10 mL) in the reaction vessel, a mixture of aragonite and calcite.