

Controlled Crystallization of Hierarchical and Porous Calcium Carbonate Crystals Using Polypeptide Type Block Copolymer as Crystal Growth Modifier in a Mixed Solution **

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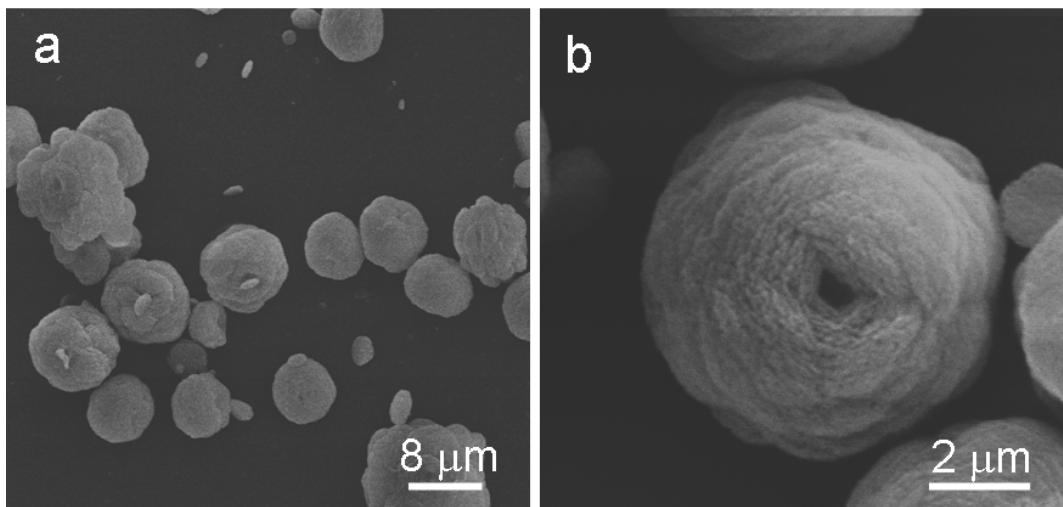


Fig. S1 SEM images of calcium carbonate particles formed in the presence of polymer (1.0 g L^{-1}) at R value of ~ 0.5 after crystallization for 7 days. The initial concentration of calcium chloride was 10 mM.

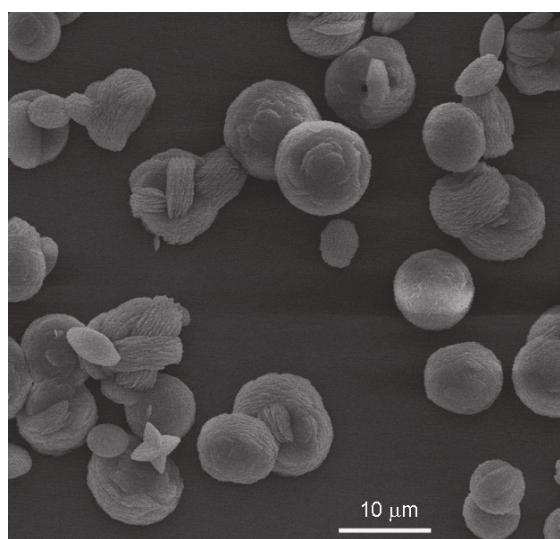


Fig. S2 SEM image of calcium carbonate sample prepared in the presence of polymer (1.0 g L^{-1}) in pure cyclohexanol solution after crystallization for 10 days. $[\text{Ca}^{2+}] = 10 \text{ mM}$.

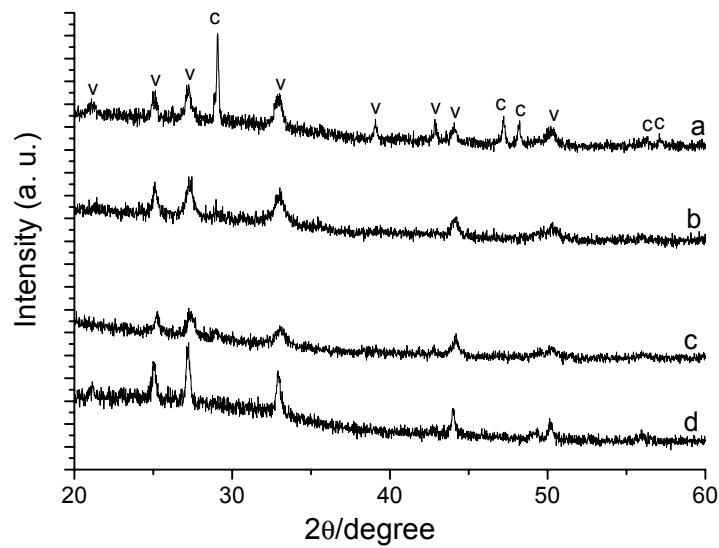


Fig. S3 XRD patterns of the samples prepared using different polymer concentration (g L^{-1}) and at R value of ~ 1 after crystallization for 7 days: (a) 1.0; (b) 0.5; (c) 2.0; (d) 0.25. $[\text{Ca}^{2+}] = 10 \text{ mM}$. Herein, C denoted calcite (JCPDS no: 86-0174), V denoted vaterite (JCPDS no: 33-0268).

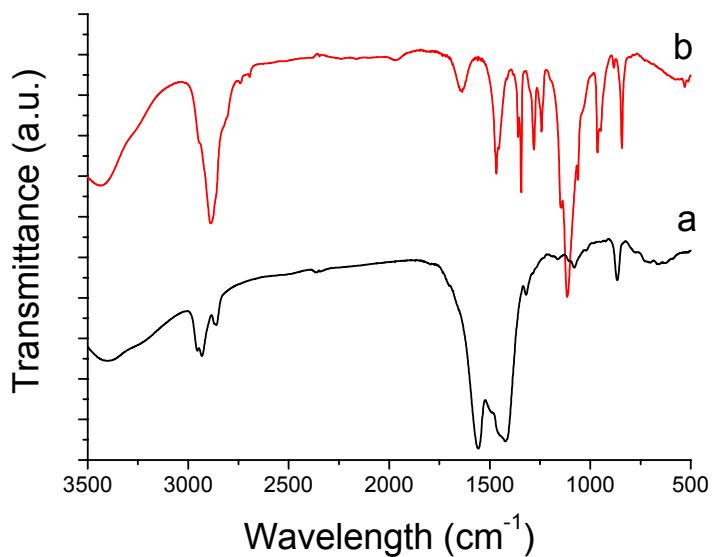


Fig. S4 FTIR spectra of (a) the sample prepared after crystallization for 7 days in the case of $R \sim 5$, $[\text{polymer}] = 1.0 \text{ g L}^{-1}$, $[\text{Ca}^{2+}] = 10 \text{ mM}$. (b) pure PEG-*b*-pAsp.

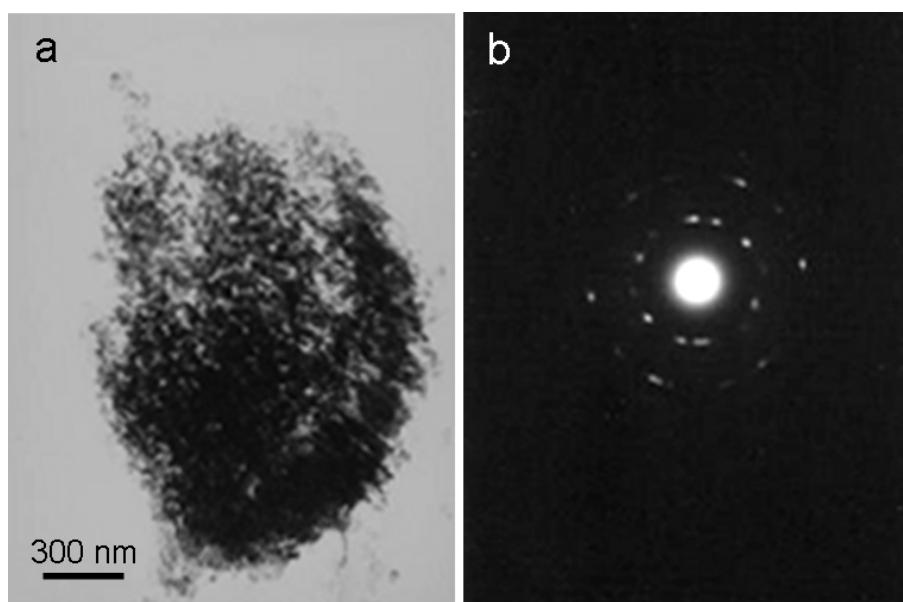


Fig. S5 TEM image and ED image of the calcium carbonate crystals after grinding and sequent ultrasonic treatment. The sample was prepared at R value of ~ 1 , in the presence of 0.5 g L^{-1} polymer, and the concentration of calcium ion was 10 mM . The samples were prepared by crystallization for 7 days.

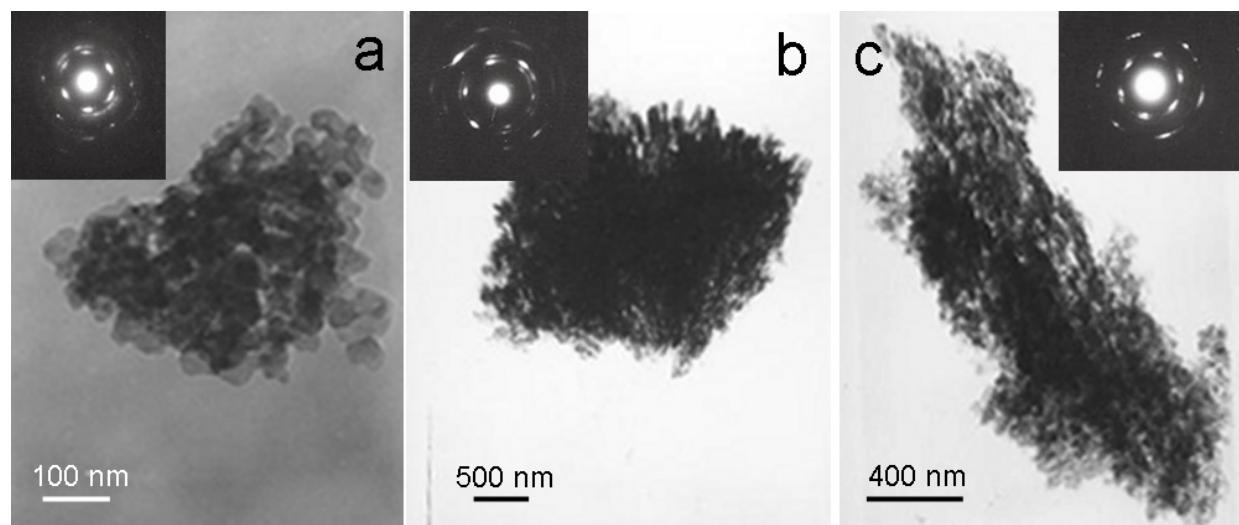


Fig. S6 TEM and SAED images of CaCO_3 particles formed at different R value. (a) $R = 0.5$; (b) $R = 0.5$; (c) $R = 5$. The concentrations of polymer and calcium ion are 1 g L^{-1} and 10 mM , respectively.

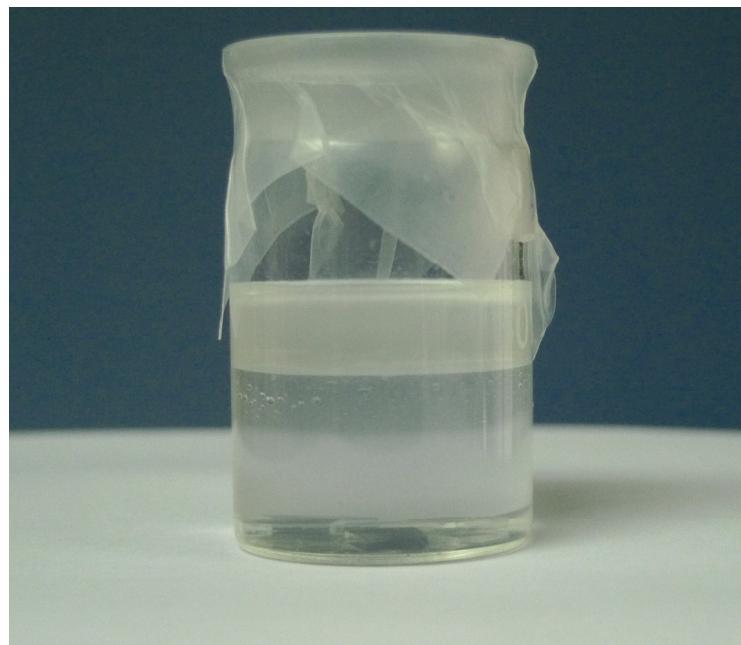


Fig. S7 The optical microscope image of the micro-emulsion liquid-drop formed in DMF/cyclohexanol solution after aging for 6 h.

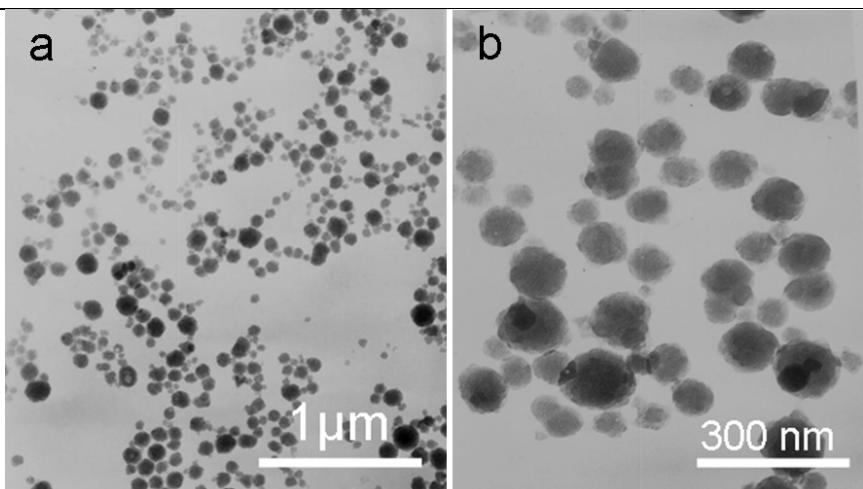


Fig. S8 TEM images of calcium carbonate crystals obtained in the case of $R \sim 1$ after crystallization for about 3 days. The polymer concentration and calcium ion were 2 g L^{-1} and 10 mM, respectively.