Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information for:

Calcite nucleation on the surface of PNIPAM-PAAc micelles, studied by time resolved in situ PXRD

Anders C. S. Jensen,[a] Mogens Hinge[b] and Henrik Birkedal[a] ,

[a] Department of Chemistry & iNANO, Aarhus University, DK-8000 Aarhus C, Denmark.
[b] Department of Engineering, Aarhus University, DK-8000 Aarhus C, Denmark.

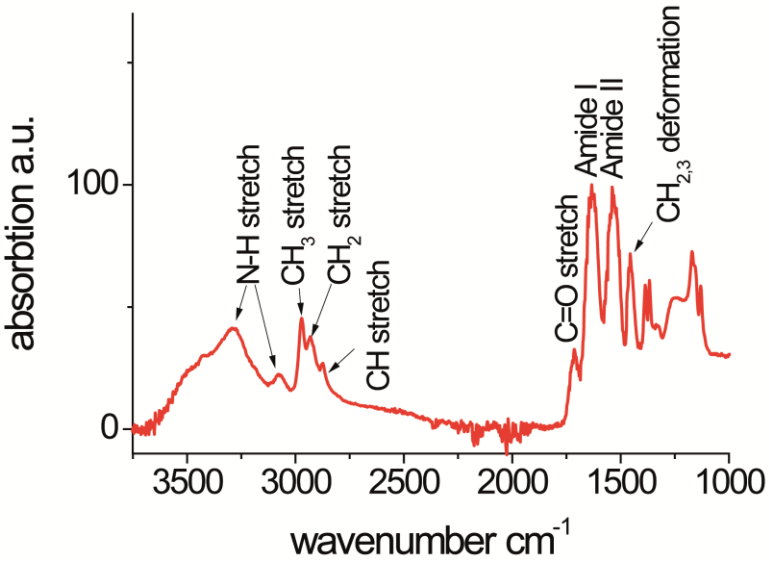

Figure S1 FTIR spectra of PNIPAM-b-PAAc polymer showing the characteristic band for the two monomers. Note that no bands from acrylic functionality are observed in the range from

3000 to 3030 , 980-995, or 905-915 cm^{-1} indicating that no unreacted carbon-carbon double bonds are left in the polymer.

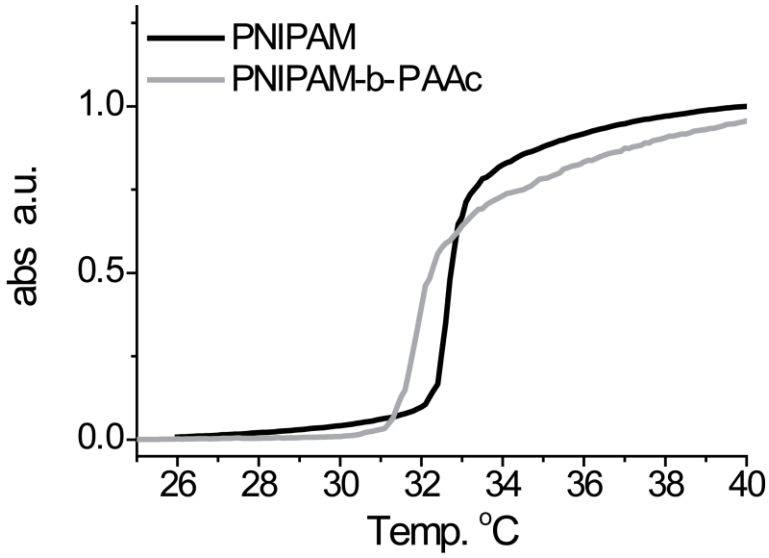

Figure S2 turbidity measurements of PNIPAM and PNIPAM-b-PAAc polymer showing the LCST transition of the PNIPAM and PNIPAM-b-PAAc are at 32 and 31 °C respectively.

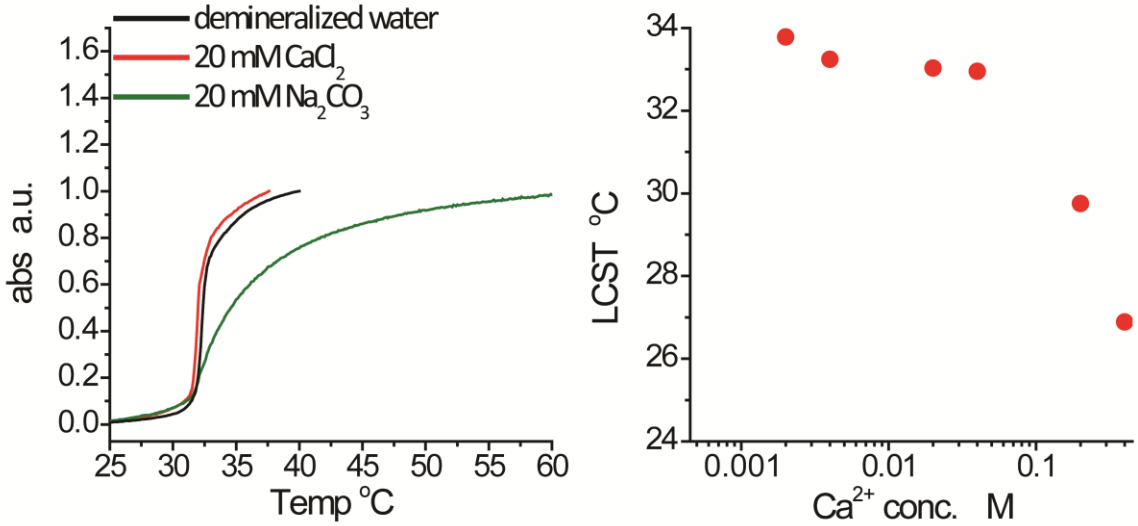

Figure S3 turbidity measurements of the LCST transition of PNIPAM-b-PAAc in the presence of the calcium and carbonate ions (left). As the polymer was mixed with the calcium ion turbidity measurements was also performed at concentration from 2 mM to 400 mM $CaCl_2$ (right).

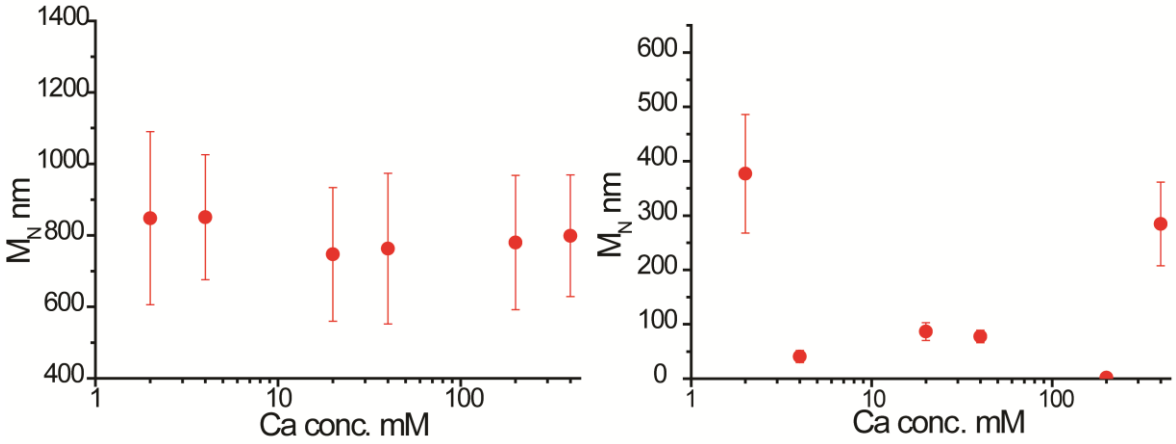

Figure S4 DLS measurements of the LCST transition of PNIPAM-b-PAAc in the presence of the calcium ions at concentrations ranging from 2 mM to 400 mM $CaCl_2$ at 25 C (left) and at 40 °C (right).

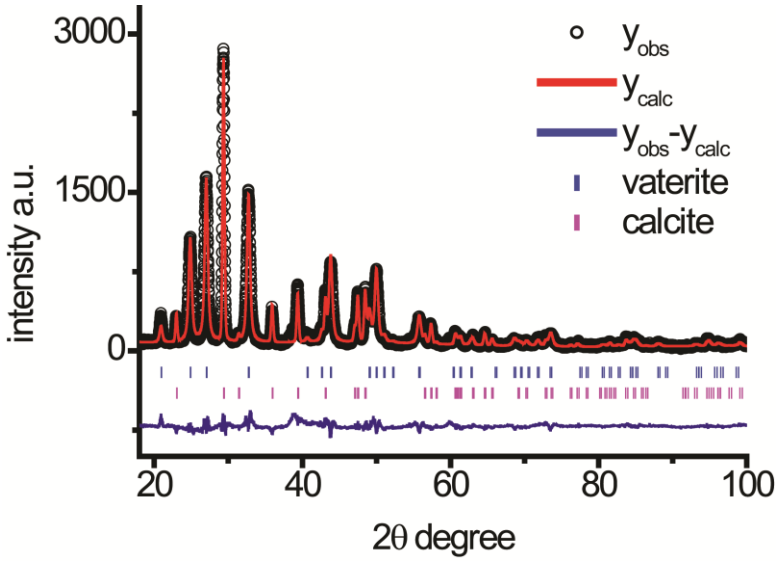

Figure S. 5 Example PXRD diffractogram with fit and difference curve. Reflection belonging to the vaterite and calcite phase are indicated.

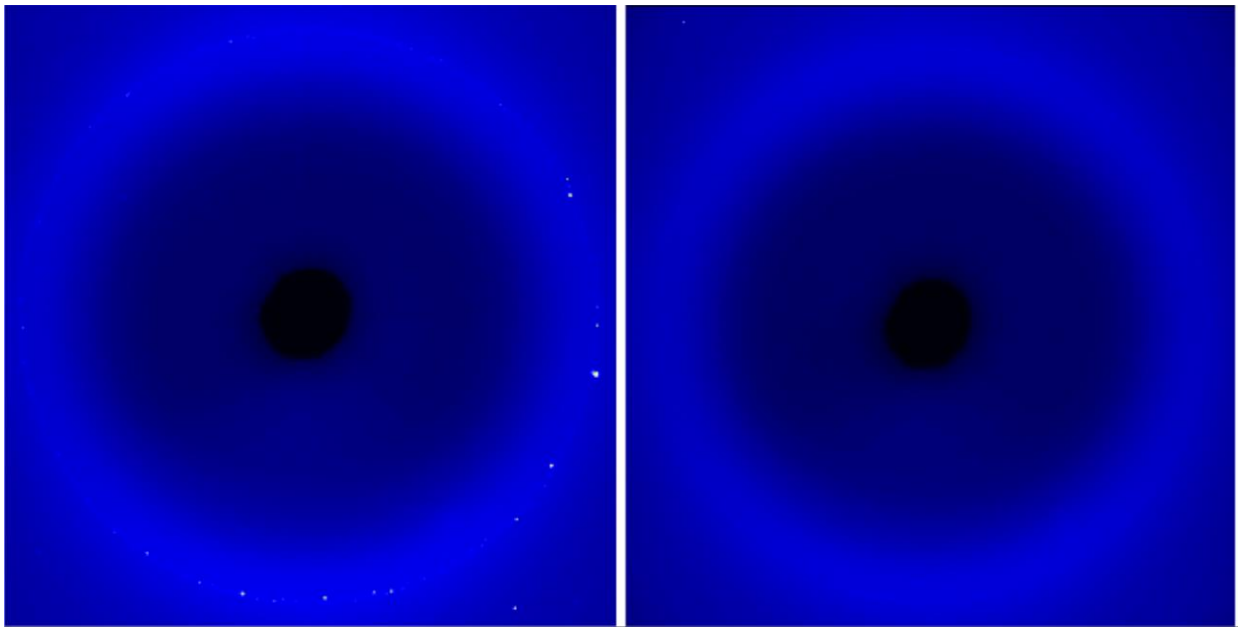

Figure S. 5 2D diffractograms measured under the formation of $CaCO_3$ at 25 °C after 5000 s. in the experiment without the polymer (left) and with the polymer (right), notice the localised high intensity peaks in the sample without polymer, that arise from large single crystal diffraction. Which is absent in the sample with polymer

Calculations of the ratio of the surface area of the swollen micelle (25 °C) and the collapsed micelle (35 °C)

The radius of the swollen and collapsed micelles are determined to be:

$$r_{m,swollen} = 425 * 10^{-9} m$$

$$r_{m,collapsed} = 250 * 10^{-9} m$$

The thickness of PAA shell is roughly estimated to be 20% of the micelle diameter as it will stretch more than the PNIPAM do to the charged side groups. This gives

$$l_{PAA} = 0.2 r_m, swollen$$

The volume of the PAA layer can now be calculated

$$V_{PAAswollen} = \frac{4}{3}\pi r_{m,swollen}^3 - \frac{4}{3}\pi\left(r_{m,swollen} - l_{PAA}\right)^3 = 1.569 * 10^8 (10^{-9})^3 m^3$$

$$V_{PAAswollen} = \frac{4}{3}\pi r_{m,collapsed}^3 - \frac{4}{3}\pi\left(r_{m,collapsed} - l_{PAA}\right)^3 = 4.663 * 10^7 (10^{-9})^3 m^3$$

This gives the ratio between the layer of PAA in its swollen and collapsed state, which is directly related to the charge density

$$ratio = 3.365$$

If the PAA layer is assumed to be 30% of the micelle diameter the ratio becomes 3.66 and as this is a rough estimate the value of 3.5 is given in the main text.