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|   | <b>Experiment title:</b><br>Impact of sodium polyacrylate on the formation of amorphous calcium carbonate | <b>Experiment number:</b><br>SC-2401               |
| <b>Beamline:</b><br>ID02  | <b>Date of experiment:</b><br>from: June 20 <sup>th</sup> 2008 to: June 23 <sup>rd</sup> 2008             | <b>Date of report:</b><br>Feb.2 <sup>nd</sup> 2009 |
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## Report:

### Introduction

The controlled formation of inorganic particles is relevant to industrial processes as well as to biomineralization. An understanding of the nucleation and initial growth of such inorganic particles from supersaturated solutions is of utmost importance for the design of new hybrid materials. An important step forward was provided by Ballauff et al., who performed time-resolved SAXS measurements on the formation of amorphous calcium carbonate (ACC). At  $[\text{CaCO}_3] \leq 4.5 \text{ mM}$ , monodisperse sphere-like ACC particles were observed.<sup>1,2</sup> At a carbonate concentration of 10 mM basic particles formed with a radius of 19 nm, which subsequently built aggregates with a broader size distribution than in the case of the lower concentrations.<sup>3</sup> Transformation of ACC to crystalline particles occurred via the solution state. Addition of a double-hydrophilic block-copolymer decreased the aggregation rate of the spherical building units significantly without preventing it though.<sup>3</sup> In order to shed further light on these processes, we performed time-resolved static light scattering experiments (TR-SLS)<sup>4</sup> on the same system. Although this recovered the essential features of ACC formation at  $[\text{CaCO}_3] = 4.5 \text{ mM}$ , our direct mixing procedure, denoted as **CM-method**, suffered from the lack of an appropriate stopped-flow device. We therefore applied an alternative process where the carbonate component was generated in situ by means of the hydrolysis of dimethylcarboxylate, leading to  $[\text{CaCO}_3] = 10 \text{ mM}$ . The gradual release of  $\text{CO}_3^{2-}$  requires a characteristic time to achieve the supersaturation necessary for ACC formation. Hence, the hydrolysis method denoted as **F-W-method**, introduces a lag-period of a few hundred seconds<sup>5</sup>, enabling excellent TR-SLS experiments. For the polymer free systems TR-SLS indicated an homogeneous ensemble of monodisperse spheres which either grow on the expense of monomers or basic small particles (the constituents). Addition of sodium polyacrylate (NaPA) with a molar mass of 80 kDa at a level of 2.5 – 12.5 ppm did not affect the lag-time.

Yet, the particle size had reached its final value already without any lag-time and the onset of ACC formation after the lag-time was only detectable by means of a steep increase of the averaged particle mass. Apparently, specifically interacting  $\text{Ca}^{2+}$  ions induce aggregation of the polyacrylates prior to ACC formation. The onset of the ACC formation after the lag-period then may occur as follows: The polymeric aggregates are domains of high local  $\text{Ca}^{2+}$  concentration which act as nucleation centers and/or as templates for the formation of ACC particles; once particles grow, polymers may adsorb on the particle surface or may be incorporated, thereby modifying the particle formation and particle morphology. However, TR-SLS set us into an excellent position to prepare SAXS experiments which are capable to extend significantly the knowledge provided by Ballauff et al.<sup>1,2</sup>. Three important questions shall be treated by the present proposal: (1) While the educts encounter instantaneously in the CM-method investigated by Ballauff et al.<sup>1-3</sup>, they occur gradually by the hydrolysis in the F-W-method. Do significant differences exist between the CM-method and the F-W-method applied in the present proposal? (2) Can the above postulated mechanism on the impact of standard sodium polyacrylate chains on the particle formation actually taking place at low levels of NaPA additives (< 15 ppm) be verified? (3) How do NaPA additives (considered to be model additives) modify particle formation in the CM-method and in the F-W-method? All three questions are crucial to a fundamental understanding of the controlled formation of inorganic particles.

### **Experimental method**

Formation of ACC particles was induced from supersaturated solutions of  $\text{CaCO}_3$  and the process was successively analysed by time-resolved SAXS at the ID02, equipped with a stopped-flow device. The wavelength was 0.995 Angstrom and the sample to detector distance 3 m. Acquisition time for a single frame was 50 ms. Two different procedures for particle formation were investigated. In a first procedure denoted as **CM-method**, a  $\text{CaCl}_2$  solution was mixed with a  $\text{Na}_2\text{CO}_3$  solution, both having identical concentrations. Evaluation of reproducible particle formation experiments with the stopped flow device turned out to be extremely difficult for the systems under consideration. First successive experiments with the CM-method were achieved with a final  $\text{CaCO}_3$  concentration of 5.0 mM. Hence, all further CM experiments were performed at this concentration. Two different flow rates - 2 ml/s and 5.7 ml/s - have been applied. After having established suitable experimental conditions, two NaPA samples were investigated at variable concentrations: sample Paa85k ( $M_w = 80$  kDa) was applied at final concentrations of 2.5 mg/L and 25 mg/L and sample PA20pn ( $M_w \sim 1$  kDa) was investigated at 2.5 mg/L, 12.5 mg/L, 25 mg/L and 50 mg/L respectively. All experiments with polymeric additives were performed at a flow rate of 2 ml/s. At least three runs have been carried out under each condition. In the alternative procedure denoted as **F-W-method**, an NaOH solution was added to a solution which includes  $\text{CaCl}_2$  and the dimethylester of carboxylic acid (DMC). The final concentration of the  $\text{Ca}^{2+}$  and DMC was 10 mM respectively, the final NaOH concentration was 20 mM. Unfortunately, no reproducible mixing experiments could be performed with this system, possibly due to an affection of the seals in the stopped flow device by the DMC or by NaOH.

### **Results**

Experiments with the CM method revealed spherically shaped particles of amorphous calcium carbonate (ACC) with a narrow size distribution. **Figure 1** illustrates the evolution of scattering curves by means of an example performed at a flow rate of 2 ml/s. The undulations are typical for compact particles with a regular (spherical) shape. Beyond 20 s, the scattering curve remain essentially unchanged. The size of the particles can be estimated by the location of the momentum transfer for the minimum  $q_{\min}$  of the first undulation according to

$$R = 3\pi/(2q_{\min})$$

which yields an outer sphere radius R. **Figure 2** compares this particle radius for the particle formation of all CM experiments without polymer. If the flow rate was 5.7 ml/s, particle formation was finished after 20 s where a particle size reached a value lying in the regime of  $30 \text{ nm} < R < 40 \text{ nm}$ . At the slower flow rate it took roughly 10 s to finish particle formation but the regime of particle size achieved at the end of the process

was in the regime of  $45 \text{ nm} < R < 85 \text{ nm}$ . This is much broader than at the faster flow rate and hence reproducibility in terms of the final particle size turned out to be better in the case of the faster flow rate. The slightly lower degree of reproducibility compared to the experiment by Balluff et al.<sup>1-3</sup> can easily be attributed to the slightly higher carbonate concentration applied in the present work (5.0 mM compared to 4.6 mM in the experiment by Ballauff et al.).

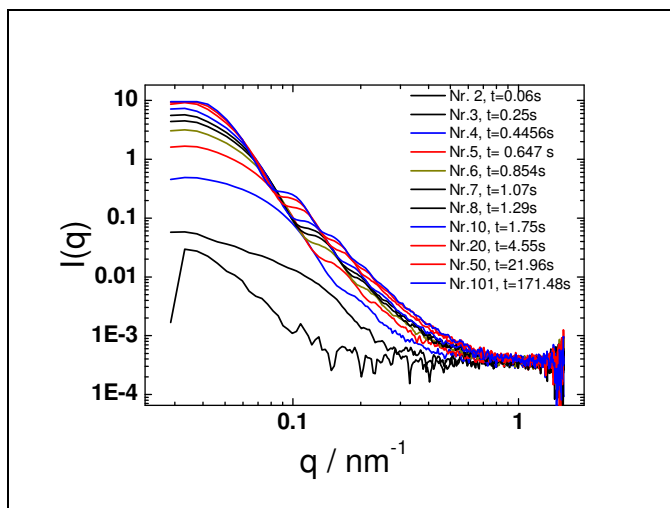
A detailed analysis of the scattering curves is under progress. If possible, the initial part of the scattering curves are evaluated according to Guinier analysis yielding an intercept related to the particle mass and a slope related to the mean squared radius of gyration  $R_g^2$ . An example is presented in **Figure 3**. For larger particles where a Guinier analysis is no longer possible, data will be analysed by means of a fit with the model formfactor of a polydisperse sphere.

As can be seen from **Figure 3**, a correlation of the resulting radius of gyration versus the apparent particle mass yields a power law behaviour of

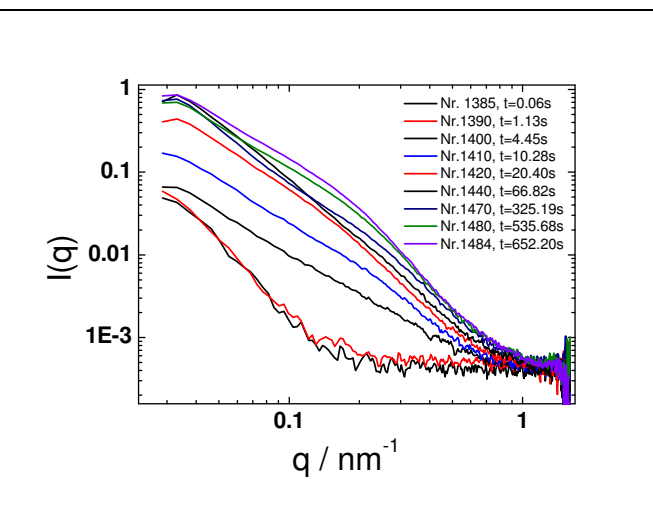
$$R_g = KM_w^a$$

The exponent is characteristic for the topology of the growing particles and the mechanism of the particle formation process.<sup>4</sup> For spheres, an exponent of  $1/3$  is expected if the mass contributing to the small angle scattering is constant. If there is an angular independent background contribution to the scattering from  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions, SAXS signals increases as the mass fraction of forward scatterers increases on the expense of the purely background generating ions which are decreasing in number. In such a case, the characteristic exponent has to be divided by 2, resulting in  $1/6 = 0.167$  for spherical particles.<sup>4</sup> The exponents observed for the particle formation experiments without polymer are all in the regime of  $0.17 < a < 0.19$  close to  $1/6$ . This is a strong indication for a “monomer” addition mechanism (with ionic species or small neutral  $\text{CaCO}_3$  clusters as “monomers”), which accomplishes final particles within 10 – 20 seconds. A coagulation of constituent particles in the size of a few nanometers can be ruled out.

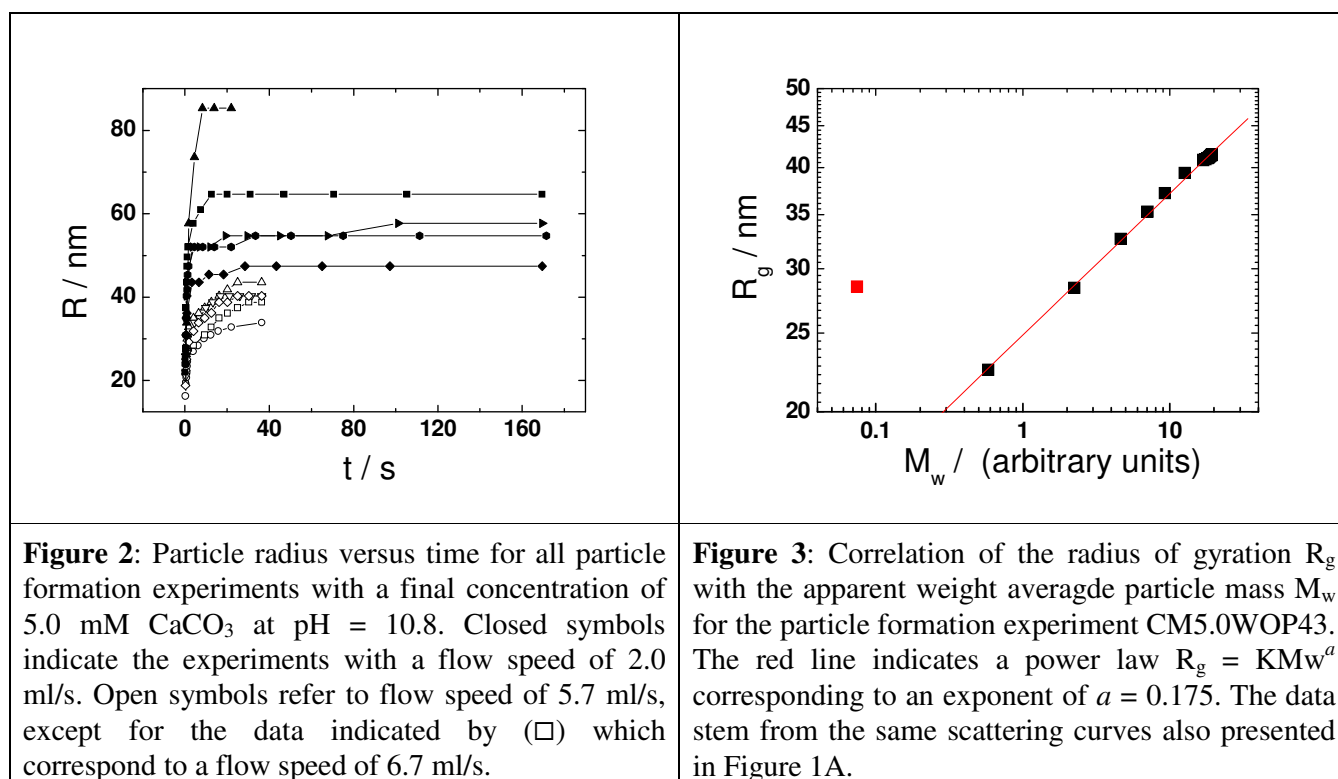
Analysis of particle formation in the presence of polymeric additives yields scattering curves, which differ strikingly from those recorded without polymer being present. **Figure 1B** shows a selection of curves, which includes 50 mg/L of the low molecular weight NaPA sample PA20pn.



**Figure 1A:** Scattering curves for particle formation experiment (CM5.0WOP43) with a final concentration of 5.0 mM  $\text{CaCO}_3$  at pH = 10.8. The time window corresponded to  $0 \text{ s} < t < 171 \text{ s}$ . The process is initiated by simply mixing the component solutions.



**Figure 1B:** Scattering curves for particle formation experiment (CM5.0WPA20PN\_50\_47) with a final concentration of 5.0 mM  $\text{CaCO}_3$  at pH = 10.8 in the presence of 50 mg/L of sodium polyacrylate (PA20pn). The time window corresponded to  $0 \text{ s} < t < 652 \text{ s}$ . The process is analogous to the one in Figure 1A.



From  $t = 100$  s on the particle size does not change any further. However, further changes are observed in the regime of  $0.1 \text{ nm}^{-1} < q < 0.5 \text{ nm}^{-1}$ . This may indicate incorporation of  $\text{CaCO}_3$  as ions and/or nanoparticles into a preformed microgel of aggregated NaPA chains. A more quantitative and extended interpretation of the data in terms of models is in progress.

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