



	<b>Experiment title:</b> <b>Time-resolved SAXS-study of the formation of Calciumcarbonate</b>	<b>Experiment number:</b> <b>SC-786</b>
<b>Beamline:</b> ID02	<b>Date of experiment:</b> from: 6.5. 2001 to: 9.5. 2001	<b>Date of report:</b> 22.02.2002
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## Report:

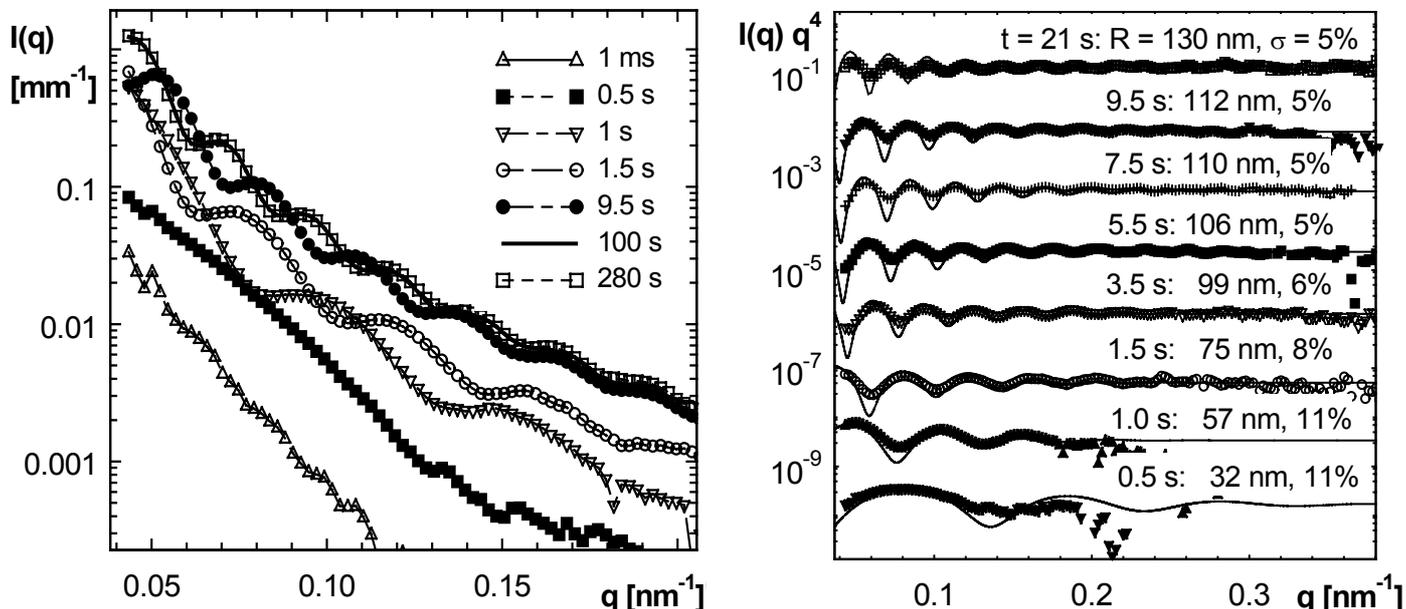
Time-resolved SAXS studies were conducted to investigate the formation and growth of calcium carbonate particles. Equimolar aqueous solutions (7 - 9 mM) of  $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  were rapidly mixed in a stopped-flow apparatus. SAXS-data were recorded with exposure times of 50 - 200 ms using a CCD detector equipped with an image intensifier. We also studied the influence of various block copolymer additives on particle formation as a function of their chemical composition and concentration.

As shown in Fig. 1 and 2 the formation of well-defined, spherical particles with colloidal dimensions and a remarkable uniformity in size could be observed. After a short nucleation period (below 500 ms in case of Fig. 1) the number and mass density of the growing particles remain constant. There is no indication for a phase transition within the time frame studied here. The absolute intensities were evaluated to yield the mass density of the particles which was determined to ca.  $1.55 \text{ g/cm}^3$ . The calculated intensities for any crystalline modification of calcium carbonate (such as calcite or vaterite) are considerably higher than the observed ones. Our data thus point to the observation of colloidal, amorphous particles which are expected to be a precursor modification of the thermodynamically stable calcite. This is supported by Ostwald's rule of stages, which states that during a solid phase precipitation from solution, the first precipitate may be a metastable phase of high solubility as long as its solubility is exceeded in solution. This precursor may subsequently transform stepwise into a more stable phase and then into a final reaction product. According to Brecevic and Nielsen (*J. Cryst. Growth* 98 (1998) 504) the water solubility of amorphous calcium carbonate is 1.7 mM/l at room temperature and thus non-negligible compared to the initial concentrations used here. Upon lowering the concentration of the educts, particle formation and growth is considerably slowed down and smaller particles are being formed (cf. Fig. 3).

Adding a few ppm of block copolymers (such as MAA-bloc-PEO) in all cases resulted in the formation of smaller particles with a higher size polydispersity. Higher polymer concentrations led to smaller particles. This may be understood because the polymers are expected to cover the particle surfaces thus lowering their surface energy. On the other hand, for a given initial concentration of  $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$  and

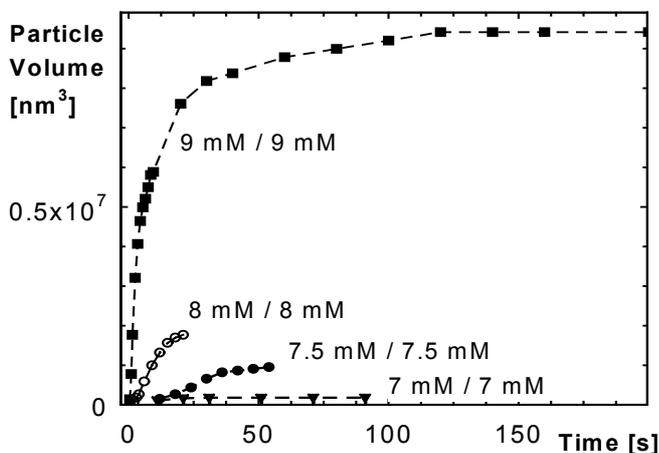
$\text{Na}_2\text{CO}_3$ , the integrated scattering intensity (scattering invariant  $Q$ ) in first approximation was found to be independent of the amount of added polymers. This indicates, that the modification of the particles is not influenced by the polymers.

In these experiments, we could demonstrate for the first time, that time-resolved SAXS is an excellent method to study the growth of calcium carbonate particles *in situ* with an excellent time resolution. In a continuation of those experiments we would like to investigate the mechanism of particle formation.



**Fig. 1 (left):** Time-resolved SAXS data measured after rapidly mixing 9 mM  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and 9 mM  $\text{Na}_2\text{CO}_3$  solutions using a stopped-flow apparatus. The observed oscillations of the spherically averaged images indicate that uniform  $\text{CaCO}_3$  particles are growing rapidly. The data also show that the particle growth was completed within 100s.

**Fig. 2 (right):** Plot of  $I(q)q^4$  vs.  $q$  of the experimental data displayed in Fig. 1. For sake of clarity, the curves were vertically offset using arbitrary factors. The data show a plateau region at high  $q$  and thus follow Porod's Law. This indicates the existence of well-defined particles with sharp surfaces. The solid lines are fit curves with the form factor of homogeneous spheres. The fit parameters show the increase in particle radius  $R$  and the concomitant decrease of size polydispersity  $\sigma$  as a function of time. All data could be fitted with the same particle and electron density.



**Fig. 3:** Increase of the particle volume as a function of time for various initial concentrations of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$ . Particle size and growth rate were found to be strongly concentration-dependent.

In the presence of small amounts of copolymer additives (not shown here) particle growth is markedly slowed down and considerably smaller particles are formed.