	Experiment title: **Time-resolved SAXS study on the formation and growth of calcium carbonate in the presence of a polypeptide**	**Experiment number**: SC-1147
Beamline: ID02	**Date of experiment**: from: 06-mars-03 to: 09-mars-03	**Date of report**: 18-august-04
Shifts: 9	Local contact(s): Dr. D. Pontoni, Dr. T.Narayanan	

Names and affiliations of applicants (* indicates experimentalists):

Dr. S. Rosenfeldt, Physikalische Chemie I, University of Bayreuth, Germany*

M. Patel, MSc., Physikalische Chemie I, University of Bayreuth, Germany*

Dr. J. Bolze, Polymerinstitut, University of Karlsruhe, Germany*

Prof. Dr. M. Ballauff, Physikalische Chemie I, University of Bayreuth, Germany

Report:

This experiment was a continuation of the experiment about time-resolved SAXS-studies of the formation of calcium carbonate where we found out that the precursors of the crystalline modifications of calcium carbonate are colloidal amorphous particles (SC 786, results published in [1]). During this beam time TR-SAXS/WAXS studies were conducted in combination with the stopped flow device to investigate the formation and growth of calcium carbonate without and in the presence of polypeptide. Our data validate our previous findings concerning the amorphous character of the initially formed colloidal particles (cf. fig. 1). The transforming of the amorphous $CaCO_3$ particles proceeds via dissolution/sedimentation and subsequent heterogeneous nucleation of the crystalline modification on the wall of the capillary. This can be concludes from the decrease of the intense isotropic SAXS signal, the appearance of streaks in the SAXS pattern and from the appearing spots in the WAXS signal (cf. fig. 1). Our results are published in [2].

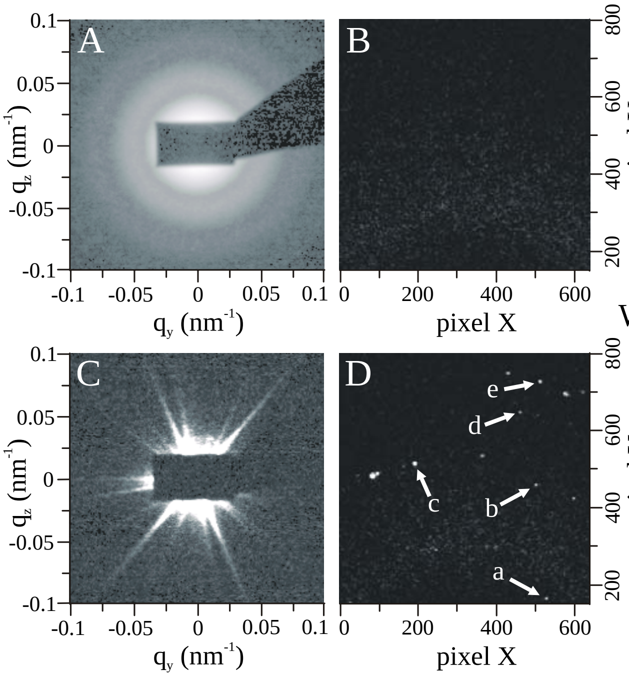

Fig 1. Top: Simultaneous SAXS (A) and WAXS (B) 2d images acquired 30 seconds after mixing 9 mM solutions of Na_2CO_3 and $CaCl_2\cdot 2H_20$. The pH was 11. The typical modulation of the isotropic SAXS intensity indicates the formation of colloidal spheres with a diameter of ca. 200 nm. The absence of Bragg diffraction spots in the WAXS data confirms that these spheres are made of *amorphous* calcium carbonate. **Bottom**: Simultaneous SAXS (C) and WAXS (D) 2d images acquired 1 hour after mixing 50 mM reagent solutions. The streaks in the SAXS pattern indicate the presence of microcrystallites nucleating on the capillary wall. The corresponding WAXS image shows diffraction spots which can be assigned to the various crystalline modifications of calcium carbonate. The spots indicated by arrows correspond to the following Bragg reflections: [a] calcite (012); [b] vaterite (004); [c] aragonite (032); [d] aragonite (310); [e] aragonite (302).

Furthermore the effect of a double-hydrophilic block-copolymer additive as polyaspartic acid and polyethyleneglycol on the initial formation of calcium carbonate from a supersaturated salt solution has been studied (fig.2). In reference measurements without polymer additive the very rapid formation of primary, overall spherical $CaCO_3$ particles with a radius of ca. 19 nm and a size polydispersity of ca. 26 % was observed within the first 10 ms after mixing. A subsequent, very rapid aggregation of these primary particles was evidenced by a distinct upturn of the SAXS intensity at smallest angles. During the aggregation process the size of the primary particles remained unchanged. Upon adding 200 pm of the block-copolymer no influence on the size, the size polydispersity and morphology of the primary particles, nor on the kinetics of their formation and growth was found. On the other hand, the subsequent aggregation and precipitation process is considerably slowed down by the additive and smaller aggregates result. The crystalline morphology of the sediment was studied *in situ* by WAXS ca. 50 minutes after mixing the reactants. Several diffraction rings could be detected, which indicate that a transformation of the metastable, amorphous precursor particles to randomly oriented vaterite nano-crystallites has taken place. All results have been published [3].

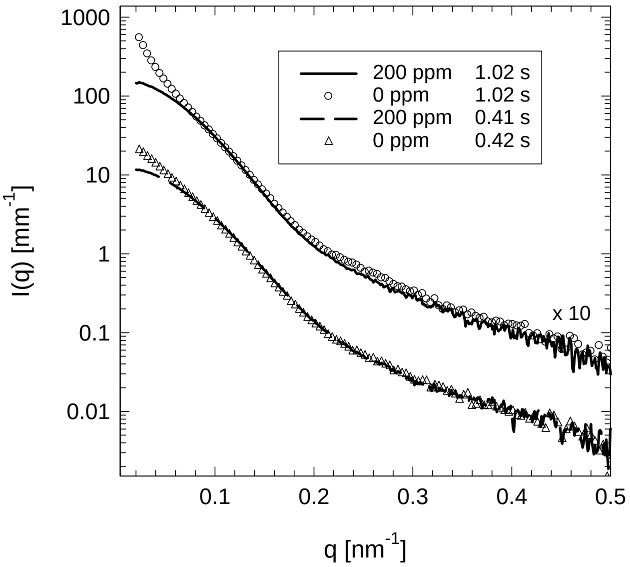

Fig. 2: Effect of the added block-copolymer (200 ± 40 ppm) on the scattering curves that were measured after mixing 20 mM salt solutions at two selected points of time *t*. For the sake of clarity two intensities are multiplied by factor 10. At each point of time the respective curves superimpose at $q > 0.1$ nm^{-1}. It is concluded that the primary particles have the same size, size polydispersity and mass density, irrespective of the added polymer. On the other hand, at *q* smaller than 0.1 nm^{-1} the upturn of the scattering curves measured in the presence of polymer is much less pronounced. This indicates that the polymer slows down the aggregation process of the primary particles.

Publications:

1. J. Bolze, B. Peng, N. Dingenouts, P. Panine, T. Narayanan, M. Ballauff, *Formation and growth of amorphous colloidal $CaCO_3$ precursor particles as detected by time-resolved SAXS*, Langmuir 2002, **18**, 8364

2. D. Pontoni, J. Bolze, N. Dingenouts, T. Narayanan, M. Ballauff; *Crystallization of calcium carbonate observed in-situby combined small- and wide-angle X-ray scattering*, J. Phys. Chem. B. 2003, **107**, 5133.

3. J. Bolze, D. Pontoni, M. Ballauff, T. Narayanan, H. Cölfen, *Time-Resolved SAXS-Study on the Effect of a Double Hydrophilic Block-Copolymer on the Formation of $CaCO_3$ from a Supersaturated Solution*, J. Colloid Interf. Sci. 2004, **277**, 84