

# Salt effects on the early stages of formation of Stöber silica particles

H. Boukari, D. Green, and M.T. Harris

*Chemical Engineering Department, University of Maryland, College Park, MD 20742 USA*

## Introduction

The Stöber route of synthesis of silica particles is known to produce highly monodisperse spherical particles [1]. Understanding the mechanisms of formation and growth that yield such monodispersity is of prime interest for fundamental research in colloidal science. Recent time-resolved small-angle x-ray scattering (SAXS) investigations have revealed that under basic conditions the first entities formed from hydrolysis and condensation of tetraethylorthosilicate (TEOS) in several low-molecular alcoholic solvents are sizable, polymeric-like, mass fractals [2, 3]. The entities then undergo further densification and growth to become the well-known spherical, compact, stable particles. These results are not accounted for in the growth models proposed so far, in which an elusive primary particle is assumed but not proven with solid experimental evidence.

The present experiment was performed as a follow-up at the Advanced Photon Source (APS) facilities using a Bonse-Hart type instrument [4] to investigate the role of LiCl salt on the dynamics of the nanostructure during the formation and growth of these particles. Our goal is to acquire further information that elucidates the role of ionic charges on the stability and kinetics of the particles. Particularly, we are focusing on the early stages (prenucleation to nucleation) and attempting to identify and characterize the so-called primary particle. For this purpose, we measured the scattering profiles from the entities formed in the sample at various times immediately following the mixing of the appropriate chemical components. The high intensity of the x-ray beam and the low wavevector ( $q$ ) range covered by the instrument are ideal for the full characterization of the structure of the scattering entities as a function of time. We analyzed the scattering profiles and determined the size distribution of the particles.

## Methods and Materials

Solute concentrations of 0.5 M of TEOS (Aldrich Chemical Company), 2.2 M of highly purified water, and 0.1 M ammonia base (Aldrich Chemical) in methanol solvent were used to obtain reaction conditions as close to those of the Stöber method as possible. Three samples were prepared with 1) no salt added, 2)  $10^{-4}$  M of LiCl salt, and 3)  $10^{-3}$  M of LiCl salt. With these concentrations, the reaction kinetics were slow enough to probe the changes in the nanostructure of the growing particles and to obtain good statistics from the ultra-small-angle x-ray scattering measurements.

The reacting solution was sandwiched between two Kapton windows that formed the optical path of the x-ray sample cell. All of the reactions occurred at room temperature. The scattering profiles were collected within 10 minutes following the mixing of the components. The angle scan of

the camera takes about 15 minutes, which represents the limiting smallest time accessible by the technique. All the scattering profiles were corrected for background and calibrated.

## Results

The scattering profiles showed the following characteristics: increasing intensity profiles as a function of time, a sharply decreasing intensity versus the wavevector into the background around  $1 < q < 2$  (1/nm), and a flat intensity at the low- $q$  on the log-log scale. The increasing intensity with time is the signature of either an increase in the number or size of particles or a combination of both. As a preliminary observation, the steep decrease in the scattering profile may be correlated with the sphericity and the narrowness of the size distribution. We estimate the size of the particles to be larger than 8 nm as already noticed in [3] for methanol. The flattening of the data at low  $q$  indicates that the Guinier region of the spectrum is well defined, allowing a good determination of the size of the scattering particles.

Comparison of the scattering profiles among the samples shows: 1) adding salt tends to speed up the formation and growth kinetics; and 2) at high concentration  $[\text{LiCl}] = 10^{-3}$  M and late times ( $\sim 900$  min) a power-law behavior in the log-log scale of the intensity profiles appears at low- $q$  values, indicating the possible formation of aggregates. These aggregates are likely to be made from the formed particles. At this point we are attempting to separate the growth kinetics of the aggregates from the continuous formation of particles using a particular model of aggregating spherical particles.

## Discussion

Preliminary analysis of the data indicates that salt has no significant effects on the early stages of the formation of the Stöber silica particles. The size of the first observable particles in the solutions with or without salt is about 8 nm. This size appears to depend on the solvent. In ethanol and butanol, it is about 16 nm [2, 3]. Addition of salts, however, speeds up the kinetics of the reaction, which results in the rapid formation of the spherical particles. So, limited by the experimental time scan, it is difficult to measure and characterize the fractal nature of the initial scattering entities as in the SAXS experiment [2, 3]. At later times, the presence of salt appears to help the aggregation of the formed particles. It is interesting to note that the aggregation process occurs after the formation and growth of the particles although the salt is added from the beginning as a part of the hydrolyzing TEOS.

## Acknowledgments

We would like to acknowledge the help of P. Jemian and J. Ilavsky in setting up the experiment. The UNI-CAT facility of the APS is supported by the University of Illinois at Urbana-Champaign, the Oak Ridge National Laboratory, the National Institute of Standards and Technology, and UOP LLC. The APS is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

## References

- [1] W. Stöber, A. Fink, and E. Bohn, *J. Colloid Interface Sci.* **26**, 62 (1968).
- [2] H. Boukari, J.S. Lin, and M.T. Harris, *J. Colloid Interface Sci.* **194**, 311 (1997).
- [3] H. Boukari, J.S. Lin, and M.T. Harris, *Chem. Mater.* **9**, 2376 (1997).
- [4] G.G. Long, P.R. Jemian, J.R. Weertman, D.R. Black, H.E. Burdette, and R. Spal, *J. Appl. Cryst.* **24**, 30 (1991).