ESRF	**Experiment title:** In-situ study of aerogelation in a flame soot aerosol	**Experiment number:** SC 1961
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Report:

The aim of the present experiment was to investigate aerogelation of soot particles in an acetylene flame by (ultra) small-angle X-ray scattering [1]. As compared to previous studies, we have attempted to record the scattered intensity over a wider range of scattering wave vector (q), 10^{-3} nm^{-1} $\leq q \leq$ 0.5 nm^{-1}, by combining earlier experiments recorded at the ID2 pinhole SAXS instrument with Bonse-Hart USAXS measurements. The significantly reduced instrumental background of the Bonse-Hart setup using specially fabricated analyzer crystals facilitated this experiment [2]. Quantitative data analysis was performed using the unified scattering function involving up to three structural levels for primary particles, aggregates and agglomerates [3]. Each structural level provides corresponding radius of gyration (R_g), polydispersity (σ), number density (N), and fractal dimension (d_f).

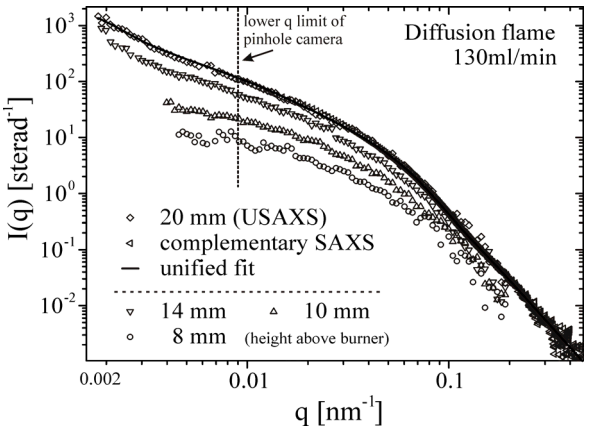

Figure 1. Comparison of Bonse-Hart USAXS and pinhole SAXS data for soot particles in a diffusion flame (acetylene, 130ml/min, $\varphi \sim 10^{-6}$) at different heights above the burner. The extended low q range of the USAXS data is essential for characterizing the structure of aggregates.

The diffusion flame was produced by a home-made stainless steel cylindrical burner fueled with acetylene. To stabilize the flame, a concentric flow of nitrogen gas was maintained around the acetylene stream by an outer concentric tube. The spatial stability of the flame was critical for the USAXS measurements which had a typical scanning time of 4 minutes. The flow rate of acetylene was varied between 90 ml/min and 340 ml/min, extending into the regime of aerogelation of soot [4]. The burner was mounted on a sample stage with motorized horizontal and vertical translations. The particle growth in the flame as a function of height above the burner (*HAB*) was probed by moving the burner in the vertical direction. The temperature profile of the flame was recorded using a miniature thermocouple. Using the measured temperature profile and assuming ideal gas behavior, *HAB* was converted to the residence time or kinetic time (t_R).

The size (R_{g1}) and polydispersity of compact primary particles and their fractal aggregates as a function of *HAB* was probed using the pinhole SAXS instrument. It is rather puzzling that the growth of primary particles follows an Avrami type beavior typical of classical nucleation and growth [5] resulting in a compact

morphology with terminal radius of gyration of $R_{g1}(\infty) \approx 27$ nm. In addition the growth exponent, n, was found to be 1, implying a linear growth of primary particles. This is suggestive of a scenario where primary particles are formed by the stacking of lower aspect ratio polycyclic aromatic hydrocarbons [6].

However, the limited low q range of the SAXS data recorded at a burner to detector distance of 10 m did not allow to fully characterize the aggregates and their final size. Therefore, SAXS results can only represent a lower limit of the aggregate R_{g2}.

During the present experiment, further details about the aggregation process of the primary particles could be monitored in the USAXS data which extends to the low q limit of about 0.001 nm^{-1}. Figures 1 shows the typical evolution of $I(q)$ at different HAB for a flow rate of 130 ml/min. For a comparison, corresponding SAXS data are also plotted. At lower HABs, only the scattering from the primary particles and the aggregates is observable. The low q upturn for $HAB \geq 14$ mm indicates the presence of agglomerates which can be described only by including a third structural level. The terminal R_{g2} of aggregates levels off at about 250 nm with $d_f \sim 1.96$. Similar features observed at a lower flow rate of 90 ml/min as a function of HAB and residence time t_R are shown in Figure 2.

Figure 3 presents the evolution of R_{g2} of the aggregates obtained from the SAXS and USAXS data. Within the error bars, the time dependence is consistent with $t_R^{1/2}$ growth law. The corresponding fractal dimension $d_f \sim 2$ without any systematic dependence on t_R signifies a constant mechanism of aggregation through the flame. In diffusion limited cluster-cluster aggregation, $R_g \sim t^{z/d_f}$, with z=1. Therefore, $t_R^{1/2}$ power-law growth presented in Fig. 3 is an indicative of the diffusion limited aggregation process.

Although the R_{g3} of agglomerates cannot be completely estimated from the USAXS data, the increased upturn at low q (see Figs. 2 and 3) indicates that the corresponding d_f is in the range of 2 to 2.4. This large value of d_f is attributed to shear flow effects and percolation of clusters. The size of the agglomerates is at least an order of magnitude larger than the aggregates but with a more compact morphology. The obtained structural parameters display similar dependence on the residence time for different flow rates investigated suggesting a constant growth mechanism.

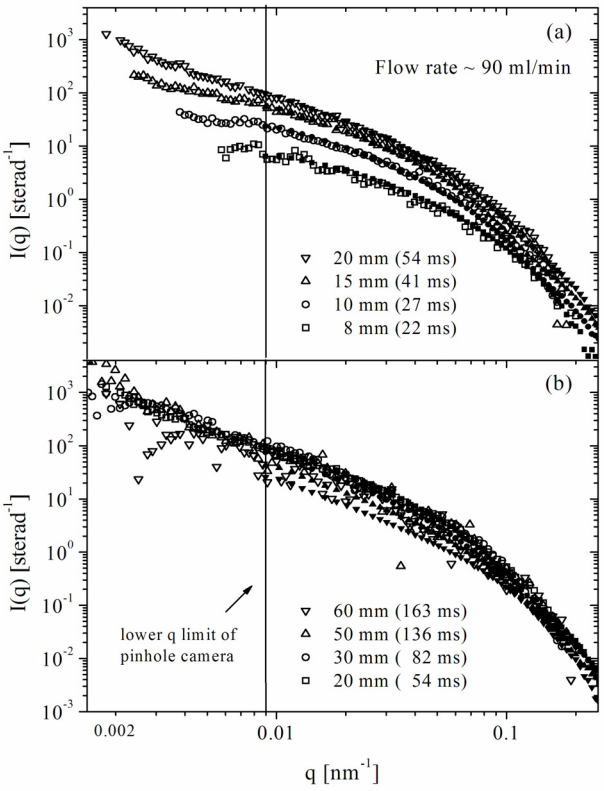

Figure 2. Typical evolution of scattered intensity as a function of HAB and residence time t_R for an acetylene flow rate of 90 ml/min. The overall features are similar to that shown in Fig. 2.

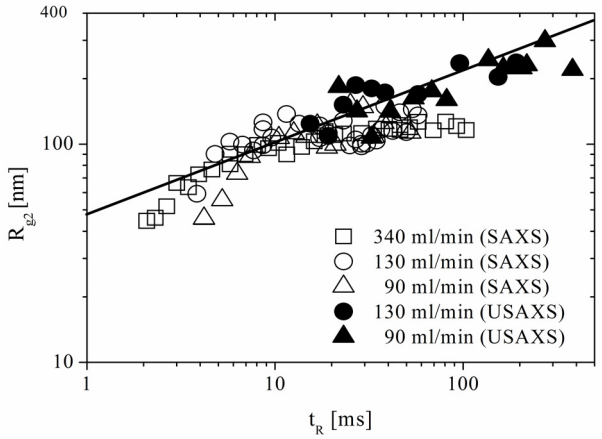

Figure 3. Radius of gyration of fractal aggregates as a function of the residence time in the flame for three different flow rates. R_{g2} has been deduced from independent fits to SAXS and USAXS data and the terminal value is more reliably deduced from USAXS. The solid line corresponds to $t^{1/2}$ behavior which is consistent with a diffusion limited growth.

Aerogelation was found to be a macroscopic phenomenon without significant changes in the aggregate or agglomerate level.

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