ESRF	**Experiment title:** Multiscale characterisation of organic gels, aerogels and carbon aerogels by SAXS.	**Experiment number**: SC-678
Beamline: BM2	**Date of experiment**: from: April 12, 2000 to: April 15, 2000	**Date of report**: May 2001
Shifts: 21	**Local contact(s)**: Erik Geissler	Received at ESRF:

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Report:

These experiments aimed at characterizing multiscale morphology of monolithic silica aerogels (prepared by supercritical CO_2 drying of gels synthesised in a two-step catalysis with polyethoxydisiloxane precursor in ethylacetoacetate under HF catalysis) in the context of a European JOULE III project (HILIT - "Highly insulating and light transmitting aerogel glazing for windows", Contract JOR3-CT97-0187) and in the framework of a programme funded by the French Environmental and Energy Agency (PACTE Aerogel ADEME). The influence of the number of water molecules (n*) used to synthesize the precursors, as well as their volume fraction in solution during the second step (x_{Prec}) were investigated. The second series of parameters investigated dealt with strengthening of the silica aerogels by washing and aging processes before drying. The third and fourth ones focused on conditions and scale effects of the supercritical CO_2 drying. Information obtained by SAXS was compared to results obtained with standard methods for measuring surface area and pore size distribution.

USAXS measurements were made at the BM2 beamline. The incident beam section was limited by the defining slits at 10 m to 200µm×200µm, the curvature of the second mirror and the monochromator being adjusted to provide a mildly focused beam in both the sagittal and the vertical directions to 100µm×100µm at the sample. The incident energy was 7.8 keV. To reduce unwanted scattering from windows, a differential pumping system was employed, with a 10m long window-free path for the beam between the second mirror and the sample. Specimens were held in cells fixed on a sample changer open to the atmosphere, the air gap being less than 5 cm. To measure the scattered intensity over a broad range of q values, two distances between sample and detector were used (2.3 m and 0.54 m). The beamstop, a small pillar of 1 mm diameter gold wire, was fixed to a Kapton foil just upstream of the flight tube exit window. An indirect illumination CCD detector (Princeton Instruments) was used. In this configuration the minimum value of the transfer wave vector q was close to 2×10^{-3} Å^{-1}.

Among the many experimental results, we note the following, both for the gel synthesis (sol-gel and ageing treatments) and its supercritical drying (liquid or direct supercritical CO_2 washing before extraction).

1) Comparison of different series of aerogels dried in the same conditions had shown that increasing the number of water molecules used to synthesize the precursors (n*) and their volume fraction in solution during the second step (x_{Prec}) lead to a decrease of the particle and cluster sizes as shown in the figures below. Corresponding optical

measurements on those samples confirmed that the transmission of visible light increased simultaneously. Increasing n* and x_{Prec} induces a decrease in the size of the nanometric objects, which may be correlated with the experimentally observed shift of the Rayleigh scattering from the visible range to the ultra-violet domain. The changes in nanostructure observed in those SAXS experiments were thus a counterpart of larger-scale structural modifications that occurred with increasing n* and x_{Prec}. It is important to note that measurements at lower q-value may be interesting.
This part of the experimental work was presented by poster at the 6th International Symposium on Aerogels (Albuquerque, 8-11 October, 2000) and the corresponding paper has been accepted by the Journal of Non-Crystalline Solids.

2) The influence of the wet gel washing and aging processes performed before drying at the laboratory scale was also investigated. Gels were washed in water solution (to increase their permeability) and then soaked in a solution of polyethoxydisiloxane precursor (to strengthen and stiffen their structure). The low and intermediate q-value regions of the scattering curves showed that the structures of the as-prepared, washed and/or aged samples were very similar. The washing and ageing treatment seemed to have a larger impact in the large q-value domain. The results extracted from the global q-value domain showed that washing and aging treatments tended to increase both the cluster and particle dimensions, but treatments performed at elevated temperatures were more effective in doing so. Regarding optical measurements, for the opposite reason as explained above in point (1), washing and aging processes induced a slight degradation of the optical properties. From the process point of view, such phenomena were counterbalanced by the increase in permeability and mechanical properties which might enhance the whole drying step. It is important to note that measurements at larger q-value may be interesting.
This part of the experimental work was presented orally at the 6th International Symposium on Aerogels (Albuquerque, 8-11 October, 2000). The corresponding paper will appear in the Journal of Non-Crystalline Solids.

3) As published in the Proceedings of the 7th Meeting on Supercritical Fluids (Antibes, 6-8 December, 2000), it had also been observed during those SAXS experiments that the two different drying routes performed - liquid CO_2 washing before supercritical extraction or direct supercritical CO_2 washing - did not induce significant textural changes for the characterised nano-objects (particle and cluster sizes, mass fractal exponent, …). The lower aerogel densities observed for the direct supercritical path is consistent with the reduction of the capillary stresses at larger pressure and may be correlated with textural changes involving objects larger than those observed during these experiments.

4) In parallel, the influence of the scale of the drying process had also been investigated. Indeed, one of the goals of the HILIT project is to demonstrate experimentally the feasibility of making large silica aerogel plates on a pre-industrial pilot scale. The observed results showed that, within the q-value region studied, no significant difference appeared. This applied result confirms the reasonably successful technology transfer from laboratory to pilot scale, involving autoclaves of 19 and 500 litres respectively.