SAXS MEASUREMENTS ON AEROGELS

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SAXS studies have been performed at LURE facilities during the sol → gel transformation on solutions prepared by hydrolysis of TMOS - Methanol of various compositions and pH values, on humid gel, on hypercritically dried aerogels and during the gel → glass densification process. The effect of the various steps of the processes on the structure and fractal behavior of these materials has been determined.

INTRODUCTION

We have undertaken systematic SAXS studies in order to obtain detailed informations about the kinetics of the sol → gel transformation of hydrolysed Si(OCn)4 - Methanol mixture and about the effect of the subsequent steps of the processes leading to the obtention of amorphous silicas on the structure and fractal behavior of humid gels, hypercritically dried aerogels and the gel → glass transformation [1-5].

The SAXS measurements have been performed at the LURE synchrotron facilities (Irancy, France) using the DC-1 position storage ring X-ray source which provides a point-like beam cross-section at λ = 1.55 Å. The scattered X-ray intensity was detected by a one-dimensional position sensitive detector and all data including parasitic background scattering correction due to the cell and slits have been computer processed.

SAXS METHOD

The X-ray intensity scattered at high angles have been analysed in term of a power law in log-log plots.

\[ I(q) \propto q^{-\alpha} \quad (1) \]

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where \( Q = 4 \pi \sin \theta / \lambda \), \( 20 \) being the scattering angle; the exponent \( \alpha \) can be related to the fractal characteristics of the particles [5]: \( \alpha = D - D_F \), the fractal dimensionality for mass fractal and equal to \( 6 - D_F \) for surface fractals of dimension \( D_F \).

A particle having a smooth non-fractal surface follows the classic Porod's behavior \( I(Q) \sim Q^{-6} \).

At low scattered angles the mean radius of aggregation \( R_g \) was determined from the relation

\[
I(Q) = A \exp\left(-\frac{1}{3} R_g^2 Q^2\right)
\]

using log \( I(Q) \) vs \( Q^2 \) plots.

**PREPARATION OF THE SAMPLES**

The kinetics of aggregation was studied in situ, well before the gelation time with samples prepared from TMS - Methanol - H₂O sol having a composition C = 50 vol% TMS. To this solution various amounts of bidistilled water, base (pH9) or acid (pH < 2) catalysed have been added in the molar ratio \( [\text{TMS}] / [\text{TMS}] = 1, 2, 4 \).

Similar sols have been let to gel at \( 55^\circ \text{C} \) in hermetically closed Pyrex tube and studied just after the gelation or after several days of aging. Dry aerogels have been prepared by hypercritical solvent evacuation \( (T = 200 \text{ bar}, \text{P} = 500^\circ \text{C}) \) by addition of methanol in an autoclave [6].

Sintering process performed on gel not previously aged has been studied as a function of the heat treatment time at fixed temperatures \( 530^\circ \text{C}, 660^\circ \text{C}, 810^\circ \text{C}, 912^\circ \text{C} \) and \( 1080^\circ \text{C} \). For SAXS measurements the dry aerogels have been sawn into thin slices and polished on both faces; their thicknesses have been adjusted for optimal X-ray transmission <1mm>.

**RESULTS AND DISCUSSION**

**a) SOL-GEL KINETICS (1)**

Figure 1 shows an example of the sequence of SAXS intensity curves in log-log plot for acid-catalysed sols with \( r = 2 \). The curves show a progressive evolution with a limiting slope \( \alpha = 2 \); for base catalysed sols the values are slightly higher. The corresponding Guinier plots shows rather well defined limiting slopes allowing the determination of \( R_g \).

**b) HUMID GEL (2)**

The SAXS curves for acid and base-catalysed humid gel measured just after the gelation show clear differences. Figure 3 shows an example of gels prepared with \( c = 30 \text{ vol% TMS} \) and \( r = 1, 2, 4 \).

For acid catalysed gels the curves exhibit linear behavior as described by relation (1) with \( \alpha = 2.3 \) (mass fractal). No cross over point is observed; therefore the structural units which build the structure are small \(< 4 \AA\).

**SAXS MEASUREMENTS**

Fig. 1: Log 1 vs log (Q) for acid-catalysed TMS - Methanol - H₂O sol having \( c = 50 \text{ vol% TMS} \) and \( r = 2 \) measured in situ for different time \( t(\text{min}) \) before the gelation time \( t_g = 300 \text{ h} \).

For base-catalysed gels two linear regions are observed defining three parameters. At low Q values \( q = 2.4 \) (almost independent of \( r \) and \( c \)) implying a mass fractal of dimensionality 2.4; at high Q values \( q = 2.8 \) (\( r = 1 \), 3.25 (\( r = 2 \)) and 3.6 (\( r = 4 \)) implying that the structural units are mass fractals at low water content and surface fractals at high water content. The average radius of the units determined from the cross-over points are of the order of 15 Å. We also found that aging decreases the dimensionality of the structural units and the correlation length.

**c) AEROGELS (3)**

Figure 4 shows an example of SAXS curves for dry aerogels prepared from acidic sols. For low concentration two linear regions are seen and interpreted as mass fractal at low Q (\( q = 2.15 \)) with smooth interface at larger length scale \( (q = 4) \).

At higher concentration \( c = 70 \text{ vol% TMS} \) the SAXS curves follow the Porod law in the whole Q range. Neutral or basic gels present also two linear regions with a slope = 4 at high Q and \( q = 3 \) at low Q values. The size of the structural units are in the sequence \( \text{acid} < \text{neutral} \) = \text{basic} \). The structures have been analysed in term of a two density system [8] and visualised as a light SiO₂ matrix of apparent density \( \rho_a \) containing essentially closed micro-
The SANS curves obtained after heat treatment at \(500 < T < 1080^\circ C\) show that the Porod's behavior is always obeyed during the sintering indicating well defined interfaces which can only undergo further smoothing as the thermal treatment proceeds. However, the Guinier plots show that the radius of gyration decreases as a function of the heat treatment time for \(T < 800^\circ C\) and increases for \(T > 900^\circ C\) reflecting the coalescence of the pores due to Ostwald ripening or an expansion due to bloating.
Fig. 4: Log I vs log Q for aerogels prepared from acidic sols for TMOS concentration (vol %) - a) 30 b) 40 c) 50.

REFERENCES


