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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 hydrolised $Si(OCH_3)_4$ - Methanol mixture and about the effect of the subsequent steps of the processes leading to the obtention of amorphous silica on the structure and fractal behavior of humid gels, hypercritically dried aerogels and the gel → glass transformation [1-4].

The SAXS measurements have been performed at the LURE synchrotron facilities (Orsay, France) using the DC-1 position storage ring X-ray source which provides a point-like beam cross-section at $\lambda = 1.55$ 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.

$$I(q) \sim AQ^{-\alpha} \qquad (1)$$

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where $Q = 4\pi\sin\Theta/\lambda$, 2Θ being the scattering angle; the exponent α can be related to the fractal caracteristics of the particles |5|: $\alpha = D$, the fractal dimensionality for mass fractal and equal to $6-D_S$ for surface fractals of dimension D_S. A particle having a smooth non fractal surface follows the classic Porod's behavior $I(q) \sim Q^{-4}$.
At low scattered angles the mean radius of aggregation R_G was determined from the relation

$$I(Q) \sim A \exp\left(-\frac{1}{3} R_G^2 Q^2\right) \qquad (2)$$

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 TMOS - Methanol solutions having a composition C = 50 vol % TMOS. To this solution various amounts of bidistilled water, base (pH$\tilde{=}$9) or acid (pH $\tilde{=}$ 2) catalysed have been added in the molar ratio $[H_2O]/[TMOS]$ r=1, 2 or 4. Similar sols have been let to gel at 55°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 ($P_c \tilde{=}$ 200 bar, $T_c \tilde{=}$300°C) by addition of methanol in an autoclave |6|. The sintering process performed on gel not previously aged has been studied as a function of the heat treatment time at fixed temperatures 530°C, 660°C, 810°C, 912°C and 1080°C. For SAXS measurements the dry samples have been sawed into thin slices and polished on both faces; their thicknesses have been adjusted for optical 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 $\alpha \tilde{=} 2$; for base catalysed sols the values are found slightly higher. The corresponding Guinier plots shows rather well defined limiting slopes allowing the determination of R_G. Figure 2 shows that the aglomeration occurs via a diffusion-controlled process. The interpretation of α in term of fractal indicates that, far from the gelation time, the growing aggregates are mass fractal for both series of sols ($\alpha = D$). However another explanation is possible if one take into account the polydispersity of the sols. Martin et al |7| showed that α may represent a polydispersity-smeared fractal dimension and that the dimensionality $D > |\alpha|/(3-\tau)$, where τ is the classic exponent of the mass distribution law $N(M) = M^{-\tau}$which must be extracted from a separate determination. Admitting for the acid series the values D = 2,5 and τ = 2,2 of percolation clusters we found $|\alpha| = 2$ as shown by the experiment. The increase of the exponent α observed for the basic sols is interpreted as due to an increase of the polydispersity.

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 vol % TMOS and r = 1, 2 and 4.
For acid catalysed gels the curves exhibit linear behavior as described by relation (1) with $\bar{\alpha} \tilde{=} 2.3$ (mass fractal). No cross over point is observed; therefore the structural units which build the structure are small (< 4 Å).

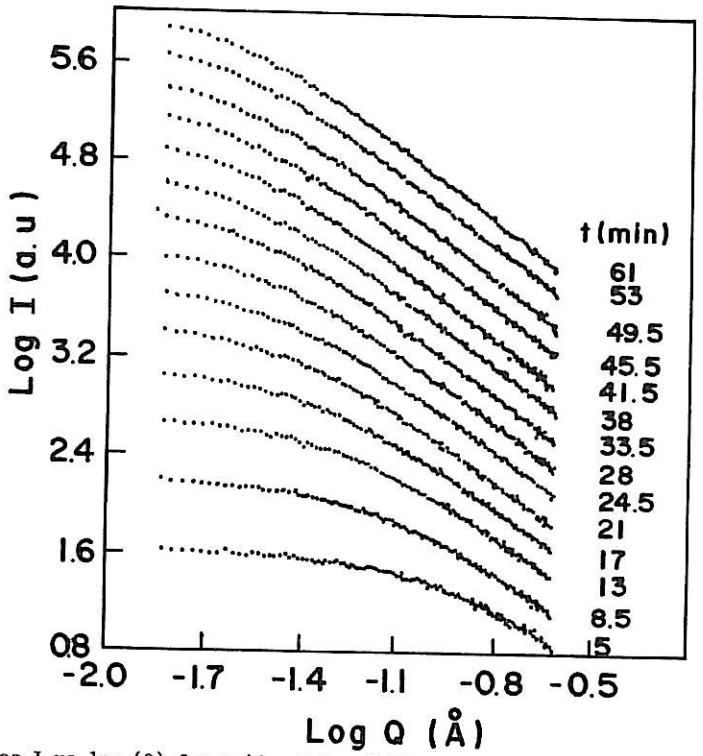

Fig. 1: Log I vs log (Q) for acid-catalysed TMOS - Methanol - H_2O sol having c = 50 % vol. TMOS and r = 2 measured in situ for different time t(min) well before the gelation time ($t_g \tilde{=}$ 500 h).

For base-catalysed gels two linear regions are observed defining three parameters. At low Q values $\alpha_1 \tilde{=} 2.4$ (almost independent of r and c) implying a mass fractal of dimensionality 2.4; at high Q values α_2 = 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 ($\alpha_1 = D \tilde{=} 2.15$) with smooth interface at larger length scale ($\alpha_2 = 4$). At higher concentration (c > 70 vol %) 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 $\alpha_1 < 3$ at low Q values. The size of the structural units are in the sequence $r_{acid} < r_{neutral} < r_{basic}$. The structures have been analysed in term of a two density system |8| and visualised as a light SiO_2 matrix of apparent density ρ_a containing essentially closed micro-

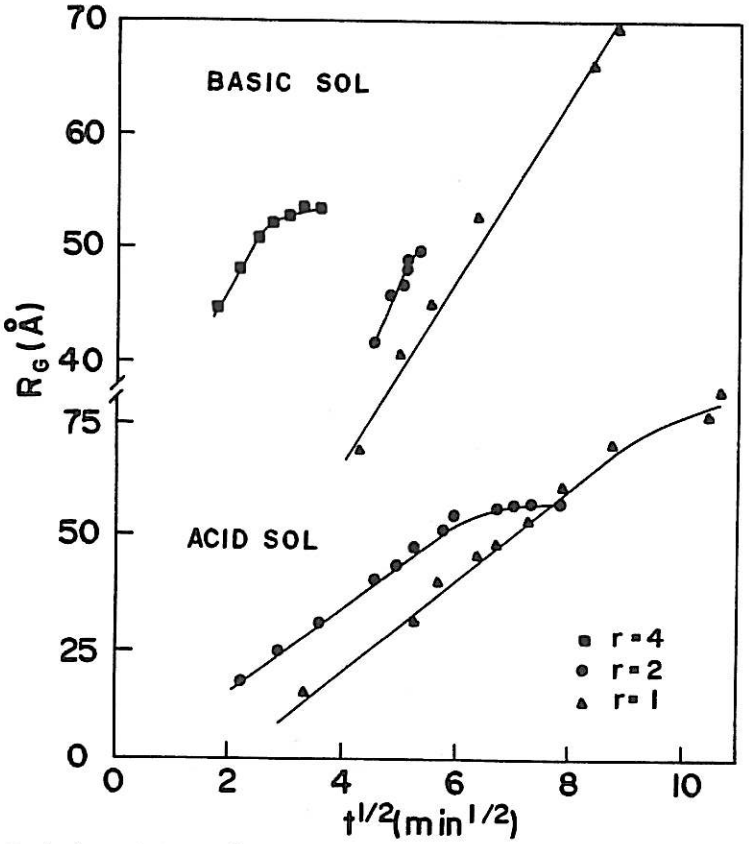

Fig. 2: Variation of the radius of gyration for basic and acid-catalysed sol in the early time of the sol-gel transformation ($t \ll t_g$).

pores (5-10 Å) reducing drastically its skeletal density ρ and meso and macropores which are the scattering entities of volume fraction Φ and mean radius $\langle R_G \rangle$ (table 1).

d) DENSIFICATION OF AEROGELS (4,8,9)

The SAXS curves obtained after heat treatment at 500 < T < 1080°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°C and increases for T > 900°C reflecting a coalescence of the pores due to Ostwald ripening or an expansion due to bloating.

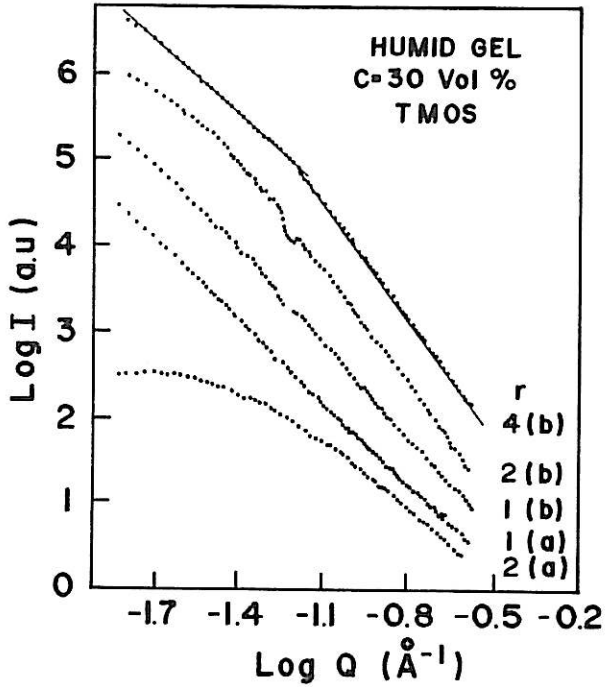

Fig. 3: Log I vs log Q for humid gels base (b) and acid-catalysed (a) having c = 30 % vol TMOS and r = 1, 2, 4.

c (vol %)	α = D	ρ_a(g/cm³)	ρ(g/cm³)	R_G(Å)	r(Å)	Φ(%)
30	2.23	0.21	0.24	159	7	9
40	2.28	0.35	0.42	100	8	16
50	2.17	0.43	0.53	81	7	20
30	2.25	0.15	0.16	180	8	6
40	2.29	0.23	0.25	147	8	10
50	2.23	0.28	0.32	118	8	13
30	2.67	0.14	0.14	114	12	6
40	2.42	0.17	0.18	96	14	7
50	2.39	0.20	0.22	90	14	8

Table 1: Parameters obtained for acid, neutral and basic aerogel (from top to botton) (see text for their definitions).

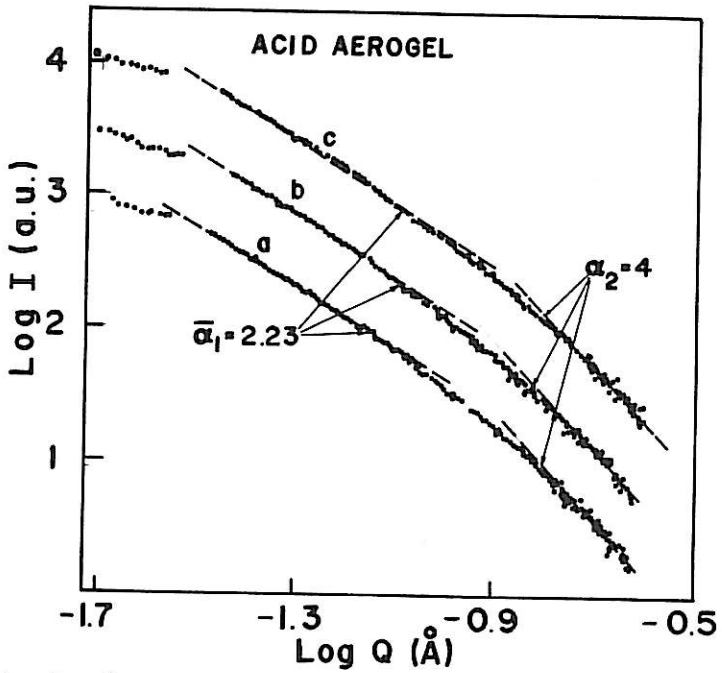

Fig. 4: Log I vs log Q for aerogels prepared from acidic sols for TMOS concentration (vol %) - a) 30 b) 40 c) 50.

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