

STRUCTURAL STUDY OF FRACTAL SILICA HUMID GELS

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The structures of gels of silica obtained from solutions of TMOS, methanol and water have been studied by small angle X-ray scattering (SAXS) using synchrotron radiation. The SAXS results indicate that all the gels studied exhibit fractal structures. It is inferred that gels obtained under basic conditions are volume fractals built up by surface and volume fractal units for high and low water content, respectively. The gels obtained under acidic conditions are all volume fractals having structural units much smaller than those of basic gels. The influence of aging on the structure of basic gels has also been established.

1. Introduction

The silica sols obtained by hydrolysis and polycondensation of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) and $\text{Si}(\text{OCH}_3)_4$ (TMOS) in the liquid phase are formed by particles which can be described as volume or surface fractals [1,2]. These particles grow by the classical diffusion mechanism and after a critical time the system gelifies.

The aim of this work is the study of the structural features of silica gels obtained from liquid solutions of TMOS–methanol–water under acidic and basic conditions in their humid state (before the drying process used to obtain aerogels).

Gels obtained from solutions with different TMOS/methanol contents (c), and water/TMOS ratios (r), have been studied by SAXS [3]. This technique has been chosen because it allows the relevant structural parameters of fractal materials to be obtained, namely the fractal dimensionalities and the cut-off length scale of fractality.

2. Samples

The gel samples were obtained from solutions of tetramethoxysilane (TMOS) (Fluka) in metha-

nol, for compositions of 30 and 50% volume TMOS for the base-catalysed series and of 30, 50 and 70% volume TMOS for the acid-catalysed series. HNO_3 was added to the solutions corresponding to the acid-catalysed series ($\text{pH} = 2$) and NH_4OH to the base-catalysed series ($\text{pH} = 9$). Bidistilled water was added to all these solutions in order to obtain ratios r (mol H_2O /mol TMOS) equal to 1, 2 and 4.

The additions of water and catalysers were done during the stirring of solutions at 25°C . After these additions the solutions were transferred into 1 mm thick Lyndemann tubes, sealed and kept at 25°C for time periods much longer than that needed for gelation.

3. Experimental

The gelified samples were studied by SAXS in one of the experimental stations of the LURE Synchrotron Radiation Laboratory (Orsay). The white incoming beam was monochromatized by a bent single crystal silicon monochromator providing a beam of wavelength $\lambda = 1.61 \text{ \AA}$. The beam was collimated by two sets of slits defining a pin-hole geometry. This provides SAXS curves

which are free from beam cross-section size effects, eliminating the frequently troublesome de-smearing process of the experimental curves which are obtained by using X-ray beams with linear cross-section. The parasitic scattering from air and slits is constant (independent of the scattering angle) and negligible over the angular domain of SAXS measurements, except for the high q region where the scattering from samples approaches zero. This parasitic scattering intensity has been suppressed by subtracting from the total SAXS intensity the scattering from non-hydrolysed solutions having an equivalent TMOS/methanol concentration.

The SAXS intensities from the different samples have been measured as functions of the modulus of the scattering vector, q , which is given by $q = 4\pi \sin \theta / \lambda$, where θ is half the scattering angle. The function $I(q)$ contains the maximum amount of information which can be obtained from an ordinary SAXS experiment on isotropic samples like the studied gels.

The SAXS intensity $I(q)$ which is expected from fractal structures presents a potential dependence on q [4]:

$$I(q) \propto q^{-\alpha_1}, \quad (1)$$

where α_1 is equal to the dimensionality D_v for volume fractals ($1 < D_v < 3$). For surface fractals the exponent of eq. (1) is given by:

$$\alpha_1 = 6 - D_s, \quad (2)$$

where D_s is the surface fractal dimensionality. The q -domain over which eq. (1) holds is limited by a minimum q_m value, which corresponds to the reciprocal of the structural correlation length, R_c , and by a maximum value q_M related to an average radius, R_u , of the structural units which build up the fractal structure. R_u is determined from q_M by

$$R_u = 1/q_M. \quad (3)$$

For $q > q_M$ the q dependence of $I(q)$ is given by

$$I(q) \propto q^{-\alpha_2}. \quad (4)$$

When the external surfaces of the structural units are non-fractal, as for example "smooth" groups of molecules or Ludox particles, their dimensionality is $D_s = 2$. Since α_2 , like α_1 , is also related

to D_s by eq. (2), $\alpha_2 = 4$ results and consequently the asymptotic behavior of $I(q)$ ($\propto q^{-4}$) corresponds to the well known Porod's law [3].

4. Results

SAXS has been measured for a series of base-catalysed gels having TMOS/methanol concentrations of $c = 30$ and 50% , each of them containing water in H_2O /TMOS ratios of $r = 1, 2$ and 4 . For acid-catalysed gels SAXS results were obtained from samples having $c = 30, 50$ and 70% and $r = 1$ and 2 . SAXS intensities from acidic gels with $r = 4$ are very weak and no clear conclusion could be inferred from the obtained experimental results.

All SAXS intensities were plotted as a function of q in a log-log scale, in order to visualise the linear behavior on the q domain over which eqs. (1) and (4) are obeyed.

Clear differences were found between the SAXS curves from acid and base-catalysed gels. Therefore the two series of SAXS curves are discussed separately.

4.1. Acid-catalysed gels

The SAXS curves from acid-catalysed gels are shown in fig. 1 in double-logarithmic plots. The SAXS intensities $I(q)$ obtained for the various TMOS/methanol concentrations and water/TMOS ratios, exhibit linear behaviors which are predicted by eq. (1) over a rather large q domain for $r = 1$ and over a smaller one for $r = 2$. At low q the expected deviations from linearity associated with finite correlation lengths are apparent. The values of the slopes α_1 of the different curves of fig. 1 are given in table 1A for every concentration c and ratio r . As every slope is lower than 3, we conclude that all acid-catalysed humid gels are volume fractals.

No cross-over between two linear regions is observed in fig. 1. This means that the structural units which build up the volume fractal structures in acidic gels, are small enough to prevent the presence of a cross-over along the q domain investigated.

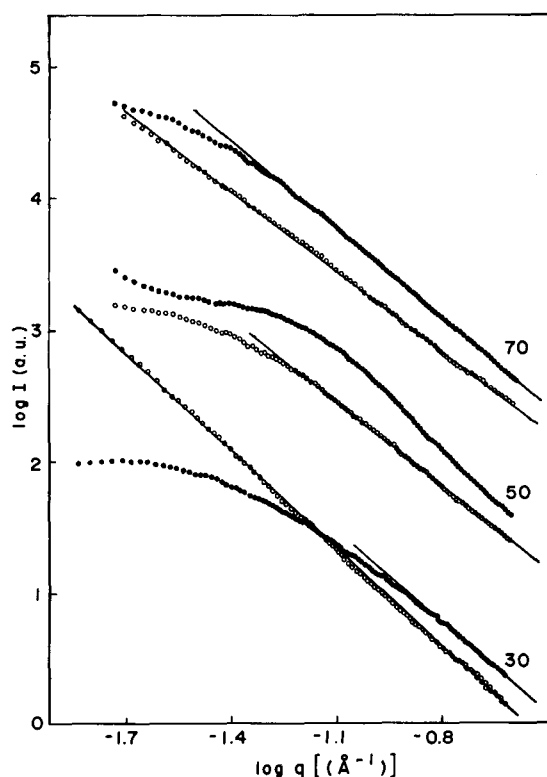


Fig. 1. SAXS from acid-catalysed gels. Molar water/TMOS ratio $r=1$ (○) and $r=2$ (●). The TMOS/methanol (Vol%) concentrations are indicated in the figure.

The fractal dimensionalities corresponding to acidic gels with different TMOS concentrations and $H_2O/TMOS$ ratios are given in table 1A. The average fractal dimensionality is $D_v = 2.3$. A decrease in D_v is observed for increasing TMOS content in samples with $r=1$. This tendency is not so apparent in samples with $r=2$.

The SAXS intensity from gels with $r=4$ is much weaker than those from gels with $r=1$ and 2. This prevented us from drawing any conclusion about these gels. In order to explain the peculiar results concerning the gels with $r=4$ additional experimental work is required.

4.2. Base-catalysed gels

The general features of the SAXS curves of the base-catalysed gels differ clearly from those of the acid-catalysed ones. The SAXS intensity curves

Table 1

Structural parameters of acid-catalysed (A) and base-catalysed gels (B) and variation of the parameters for different aging times for a basic gel with $c=50\%$ and $r=2$ (B*). The fractal dimensionalities are $D_v = \alpha$ if $\alpha < 3$ and $D_s = 6 - \alpha$ if $\alpha > 3$. The symbol $\sim$ indicates less precise slopes which correspond to SAXS curves exhibiting a rather narrow domain of linearity

Table 1A

c (%TMOS)	$(H_2O/TMOS)$	t (h)	α_1
30	1	25	2.40
30	2	25	2.32
50	1	27	2.17
50	2	26	~ 2.4
70	1	25	2.05
70	2	25	2.26

Table 1B

c (%TMOS)	r ($H_2O/TMOS$)	t (h)	α_1	α_2	R_u (Å)
30	1	14	2.46	2.84	26
30	2	14	2.45	3.48	21
30	4	14	2.36	3.55	16
50	1	11	2.44	2.91	24
50	2	11	~ 2.2	3.20	17
50	4	8	2.20	3.42	15

Table 1C

c (%TMOS)	r ($H_2O/TMOS$)	t (h)	α_1	α_2
50	2	5	2.40	3.16
50	2	11	~ 2.2	3.20
50	2	17	—	3.46

from the basic gels are plotted in fig. 2 in a double logarithmic scale. They present two linear regions with different slopes. This type of curves defines three parameters: α_1 (eq. (1)), R_u (eq. (3)) and α_2 (eq. (4)). The values of α_1 for the basic gels imply that $D_v \approx 2.4$ for $c=30\%$ and $D_v \approx 2.3$ for $c=50\%$. The fractal dimensionality is approximately independent of the water/TMOS ratio, although a weak decrease in D_v is suggested by the values given in table 1B for increasing water/TMOS ratios.

The q_M values associated with the cross-over points range from $R_u \approx 15$ Å for $r=4$ up to $R_u \approx 25$ Å for $r=1$. This should represent the approximate average size of the structural units

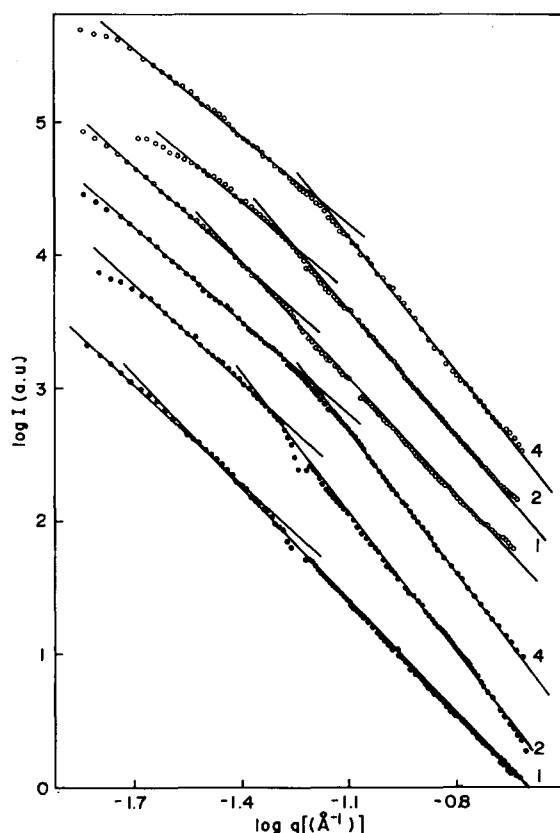


Fig. 2. SAXS from base-catalysed gels. Vol% TMOS/methanol concentration $c = 30\%$ (●) and 50% (○). The molar water/TMOS ratios are indicated in the figure.

which build up the volume fractal structure of basic gels.

The slopes of the outer parts ($q > q_M$) of the scattering curves in log-log scale (fig. 2) deviate clearly from -4 which would be expected from Porod's law for euclidean (non fractal) units. The parameter α_2 of eq. (4) exhibits a clear dependence on the water/TMOS ratio, being the average value of α_2 over all TMOS concentrations, equal to 2.8 for $r = 1$, 3.3 for $r = 2$ and 3.5 for $r = 4$. This implies that the structural units are volume fractals for $r = 1$ ($\alpha_2 < 3$) and surfaces fractals for $r = 2$ and 3 ($3 < \alpha_2 < 4$).

The existence of two different fractal structures over different length scales leads us to name them as primary (intra units) and secondary (inter units) fractal structures. The average radius of the units,

determined from the q value associated with the cross-over points, are about $20 \text{ \AA}$.

Fig. 3 shows the SAXS results from a base-catalysed gel with $c = 50\%$ and $r = 2$ and different aging times. The linear regions of the outer (high q) part of the curves (associated with the primary fractal structure) have α_2 values which increase with aging time (table 1B*). Another feature which is apparent in fig. 3 is the decrease in the width of the q domain of linearity of the inner (low q) linear part of the SAXS curves in logarithmic scale, associated with the secondary fractal structure.

The approximately constant value of $I(q)$ over the small angle side of the studied q domain for $t = 11 \text{ h}$ and 17 h implies that the structures of the gels have low correlations lengths. The cross-over between the constant intensity region and the domain where $I \propto q^{-\alpha_1}$, defines q_M and its reciprocal R_c value which corresponds to the corre-

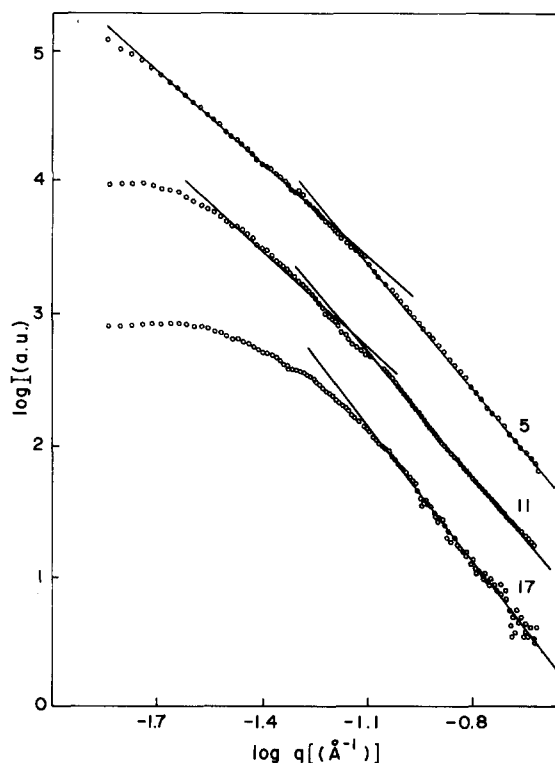


Fig. 3. SAXS from base-catalysed gels ($c = 50\%$ and $r = 2$) for different aging times (h) indicated in the figure.

lation length. The parameter R_c represents the upper limit of fractal scaling of the studied structure.

The values of R_c obtained from the curves of fig. 3 are $R_c > 80 \text{ \AA}$, $R_c = 40 \text{ \AA}$ and $R_c = 20 \text{ \AA}$ for 5, 11 and 17 h of aging, respectively. The value of the correlation length for 17 h of aging is closely associated with the radius of the structural units (table 1B). Therefore the SAXS results indicate that aging produces two types of changes of the structural units: (a) it decreases the fractal dimensionality D_s from 2.8 for 5 h to 2.5 for 17 h of aging time, and (b) it markedly decreases the correlation length.

5. Conclusions

The main conclusions of this study concerning the structure of TMOS-methanol-water humid gels, are the following:

(i) Acid-catalysed humid gels exhibit volume fractal structures with a fractal dimensionality of about 2.3. The structural units of the fractal object are very small and their average radius is lower than $4 \text{ \AA}$.

(ii) Base-catalysed humid gels present a secondary volume fractal structure, with nearly the same dimensionality as that of acid-catalysed gels. They are built up of units with fractal structure. These structural units are volume fractals for $r = 1$ and surface fractals for $r = 2$ and 4.

(iii) The aging of humid basic gels decreases the dimensionality of the structural units (which can be understood as a "smoothing" effect) and decreases the correlation length. The decrease in correlation length implies that aging progressively

suppresses the fractal nature of the secondary structure. Then the macroscopic volume contraction associated with aging is related to microscopic modifications in both the primary and the secondary fractal structures.

These conclusions support the idea that the formation of basic gels is a composite process involving (a) a primary aggregation of monomers leading to fractal particles, (b) a subsequent aggregation of these particles leading to a secondary fractal structure and (c) an aging mechanism which modifies either the primary and the secondary fractal structure. Probably the process of gel formation in acidic sols is essentially the same but involves much smaller structural units.

In a recent study of base-catalysed silica aerogels [6] double-log plots of SAXS intensity present two linear domains with slopes -2.1 and -4 , and a cross-over for $q = 1/14 \text{ \AA}^{-1}$. This suggests that the drying process of gels not aged preserves the secondary fractal structure and smoothes the surface of the structural units which are fractal in the humid state.

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