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LIGHT SCATTERING DYNAMIC STUDY OF THE GELATION PROCESS

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Light scattering is a choice method for studying the dynamic properties of fractal structures and growth processes. We present preliminary light scattering measurements to characterize the formation of small silica particles prepared in highly basic TMOS/methanol/water sols and the transformation of sol into gel employing digital clipped autocorrelation spectroscopy. The light scattering is due to gel clusters.

1. Introduction

Scattering techniques are choice methods for studying the aggregation processes, permitting the aggregates to be studied while they are growing without disturbing them. Silica sols obtained from a mixture of tetramethoxisilane (TMOS)/methanol/water are interesting candidates since they allow the preparation of either mono or polydisperse SiO_2 particles in suspension or humid gels. The small angle X-ray scattering technique (SAXS) have been recently used by us in order to study systematically and "in situ" the transformation of silica sols into humid gels [1]. These techniques are particularly useful in situations for which the product of the momentum transfer $|q|$ and the size of the scattering particles are smaller than 1, i.e, for particle size typically smaller than ~ 200Å. Due to their smaller q range, light scattering techniques allow the observation of aggregation having a characteristic scale of roughly a factor of 200 times larger. Moreover, modern equipment allows the study of the dynamic properties of such structures by measuring the electric field correlation function of light scattered from particles in suspension.

We present preliminary light scattering studies to:

(a) characterize the preparation of small particles using highly base-catalysed sols;
(b) characterize the cluster growth process in silica sols during the sol–gel transformation.

2. Preparation and characterization of small SiO_2 particles

Small silica particles can be easily prepared by the sol–gel technique using the Stöber method [2]. Typical sols have been prepared at room temperature by first mixing 65 ml of methanol in 34.4 ml bidistilled water and then adding 22 ml of NH_4OH and 3 ml of tetramethoxysilane TMOS (Fluka). Such sols have a pH of 12.3. The growing of the SiO_2 particles up to a certain size is extremely fast and due to the high pH values practically no skeleton aggregation is observed. The size of the particles has been observed by transmission electron microscopy using the Formvar film technique and examples are shown in fig. 1. Most of the particles appear spherical without aggregation although some of them seem to be superimposed to

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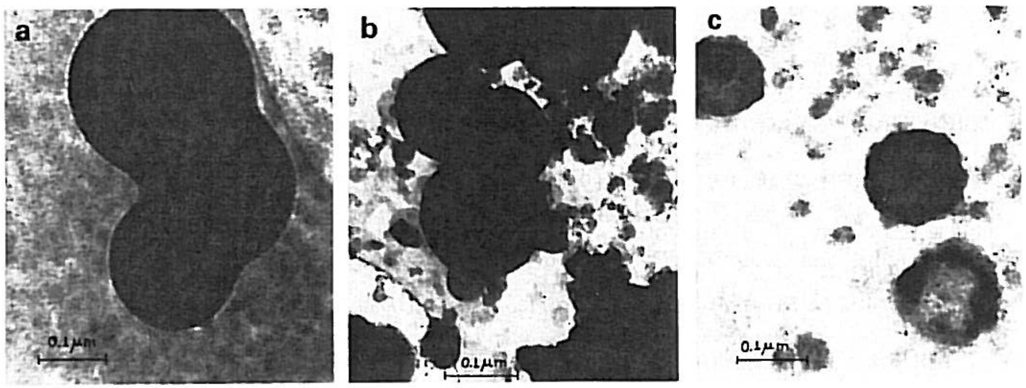

Fig. 1. Transmission electron microscopy of different volume proportions of TMOS/methanol/water base-catalysed sols showing SiO_2 spherical particles with mean diameters; (a) 0.23 μm (used in the photon correlation spectroscopy); (b) 0.16 μm; (c) 0.13 μm. The background of the micrographies is due to the Formvar film.

each other. The mean diameters have been found equal to 0.23 μm.

The technique of photon autocorrelation is another powerful method to study the dispersion of small particles in a liquid. A monochromatic light beam is scattered by the sol as a result of thermodynamic fluctuations accompanied by a variation of the dielectric susceptibility. The frequency spectrum of the light scattered at an angle θ is determined by the Fourier time transform of the normalized correlation function

$$G_n(t) = \frac{\langle \Delta\epsilon(-q)\, \Delta\epsilon(q, t)\rangle}{\langle \Delta\epsilon(-q)\, \Delta\epsilon(-q)\rangle}, \tag{1}$$

where $\Delta\epsilon(q, t)$ is the qth spatial Fourier component of the fluctuation in the dielectric susceptibility with $\Delta\epsilon(q) = \Delta\epsilon(q, 0)$ and $|q| = 4\pi n \lambda_0^{-1} \sin(\theta/2)$. Instead of measuring the frequency spectrum of the scattered light it is easier to measure the time fluctuations of the scattered intensity using an electronic digital clipped autocorrelator which measures a correlation function written as

$$R(t) = A + B\,|G_n(t)|^2, \tag{2}$$

where A and B are coefficients determined experimentally. Assuming that the fluctuations occur essentially in density and concentration we chose for $G_n(t)$ the following function:

$$|G_n(t)| = \exp\left[-(K_1 t)^{\beta}\right], \tag{3}$$

where $K_1 = 2/\tau_c$ with τ_c being called the optical time of coherence and β is an adjustable parameter.

The mean relaxation time of the system is given by

$$\langle\tau\rangle = \int_0^{\infty} |G_n(t)|\, dt = (\tau_c/\beta)\, \Gamma(1/\beta) \tag{4}$$

and we note that $\langle\tau\rangle = \tau_c$ for $\beta = 1$.

The mean translational diffusion coefficient of the particles involved in the scattering is given by

$$\langle D\rangle = 1/\tau_c q^2 \tag{5}$$

and introducing the viscosity η of the liquid in which the particles are diffusing we can determine their mean radius from the Stokes–Einstein relation

$$\langle R\rangle = k_B T / 6\pi\eta\langle D\rangle. \tag{6}$$

Photon correlation measurements have been performed using a 2 mW argon laser light beam ($\lambda_0 = 4880.8$ Å) whose scattered light was detected at $\theta = 90°$ and analysed by a Malvern digital autocorrelator Model K7023. The correlo-

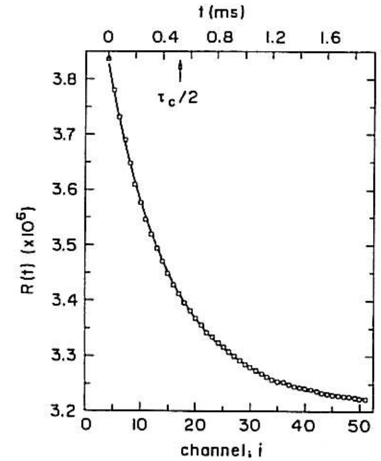

Fig. 2. Correlograms of SiO_2 particles measured at $\theta = 90°$ with a sampling time of 40 μs. The curve has been adjusted to the experimental points using the relation (2) for $\beta = 1$.

gram for these particles is shown in fig. 2 where the curve is the best fit of relation (2) with $\beta = 1$ for the experimental points. From this fit it was determined that $\tau_c = 0.92 \times 10^{-3}$s and using relations (5) and (6) we obtain, respectively:

$\langle D\rangle = 1.85 \times 10^{-8}$ cm^2 s^{-1},

$\langle R\rangle = 0.12$ μm.

We note that the fit is very good showing that the sol consists of essentially monodispersed SiO_2 particles and that the mean diameter obtained with this method is in good agreement with the results obtained by TEM (fig. 1).

3. Sol–gel transformation

The same technique has been tried for studying the growth of SiO_2 clusters prepared at 21°C by hydrolysis of a 50% vol. TMOS dissolved in methanol and a molar ratio $r = [H_2O]/[TMOS] = 4$ [1] under basic conditions (pH ~ 9). Preliminary data taken at a scattering angle of $\theta = 50°$ show that a correlation function with sampling time of 400 μs is only obtained after a certain time (5 h in our case) and disappears near the gelation time

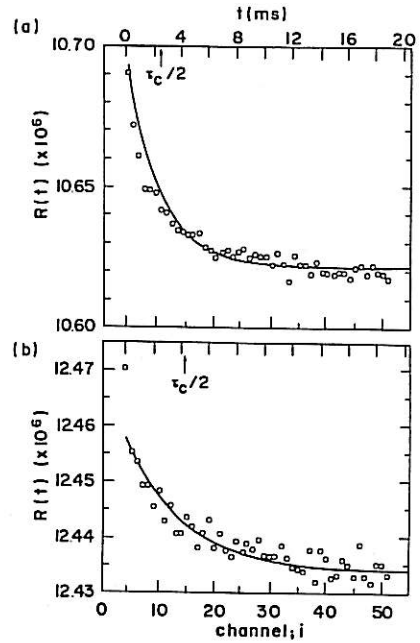

Fig. 3. Correlograms obtained at $\theta = 50°$ curing the sol–gel transformation for a TMOS/methanol/water sol ($r = 4$). The curves are the best fit of relation (2) with $\beta = 1$. (a) after 5 h; (b) after 7.5 h (near the gelation time).

(~ 8 h in this particular case). The results of two correlograms taken at $t = 5$ h and $t = 7.5$ h are shown in fig. 3. As before, the results have been best fitted with relation (2) with $\beta = 1$. Unfortunately it is not possible to obtain a good fit, showing that the clusters are probably polydisperse as already proposed by us from SAXS measurement, [1]. Other types of algorithms are now developped in order to study such results. The single exponential analysis is given here for a mere indication (variation observed during the lap of time in which autocorrelation has been observed):

$\tau_c \sim 4.5$–9.0×10^{-3} s,

$\langle D\rangle \sim 5$–10×10^{-9} cm^2 s^{-1},

$\langle R\rangle \sim 45$–75 μm.

We see that the translational diffusion coefficient is roughly 10 times smaller than for the small

SiO_2 spheres. This is an expected result since now the mean size $(2\langle R \rangle)$ of the clusters are much larger (90–150 μm). However a detailed analysis still remains to be done since clusters are without any doubt polydispersed.

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