

Sol-Gel Nanometrology: Gated Sampling Can Reveal Initial Sol Formation Kinetics

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This report describes a gated sampling approach for studying the initial formation of sol-gel glasses prepared from sodium silicate solution (water glass) and sulphuric acid. Previously described were how changes in particle size and subsequently how sol-gel formation dynamics can be tracked using time-resolved fluorescence anisotropy, by labeling growing silica nanoparticles with suitable fluorescence probes. One limiting factor of this approach was the ≈ 2 minute measurement time, which limits this technique for studying the initial sol formation dynamics and limits the measurement precision. Using a continuous flow system and delaying sol flow through different tubing lengths overcomes this problem and allows monitoring of the very early stages of sol formation, second by second after sol preparation, irrespective of the anisotropy measurement time. This technique was applied to studying the initial formation dynamics, within the first 30 seconds, of a 12.01 % SiO₂ (w/w), pH 0.66 sol-gel, finding that silica particles of ≈ 1.5 nm mean radius are formed within 10 seconds of mixing the sol-gel.

KEY WORDS: Sol-gel; hydrogel; particle metrology; gated particle sampling; silica nanoparticles.

The kinetic life history of sol-gels is starting to be revealed by fluorescence techniques, and the influence of preparation parameters such as silicate concentration, temperature, and pH are now becoming realised [1–6]. Through the careful choice of a fluorescent probe, anisotropy decay has been shown to provide both the growing silica particle size and molecular viscosity information, which is the only technique currently providing hydrodynamic information on the self-assembly processes of silica particles at the molecular level [2,3]. It has been shown that under low pH conditions, an aqueous silicate can be polymerized by the simultaneous growth (Ostwald

Ripening) and diffusion limited aggregation of discrete silica spheroids, which eventually form the amorphous silica materials used in multifarious applications such as liquor refining, adhesives, and polishing, [7–9]. The addition of a fluorescent probe to a hydrolysed sol rapidly leads to its partitioning, where the fluorescence anisotropy function $R(t)$ can best be described by two rotational correlation times, τ_{r1} and τ_{r2} in the form:

$$R(t) = (1 - f)R_0 \exp\left(\frac{-t}{\tau_{r1}}\right) + fR_0 \exp\left(\frac{-t}{\tau_{r2}}\right) \quad (1)$$

where R_0 is the initial anisotropy. The fraction f has been interpreted as the fraction of fluorescence resulting from probe molecules bound to silica particles and hence $1-f$, the fraction resulting from free dye in the sol [2,3]. From the Stokes-Einstein relation, τ_{r1} , gives the sol microviscosity $\eta_1 = 3\tau_{r1}kT/4\pi r^3$, where r is the hydrodynamic radius of the dye and likewise using η_1 and τ_{r2} one obtains the average silica particle hydrodynamic radius (Fig. 1).

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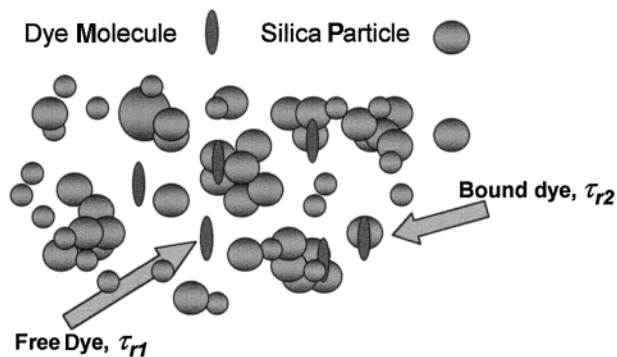


Fig. 1. Dye tracking sol-gel microviscosity, from τ_{r1} , and silica particle size, calculated from τ_{r2} .

However, observing the growth of silica nanoparticles <1 minute into the sol-gel polymerisation has previously not been considered using this technique because of the *relatively* long measurement time (typically 2 minutes [3]) needed to acquire both the vertically and horizontally polarised fluorescence decay curves, $F_V(t)$ and $F_H(t)$, orthogonal to pulsed and vertically polarised excitation, used to generate the anisotropy function $R(t)$, where:

$$R(t) = \frac{F_V(t) - F_H(t)}{F_V(t) + 2F_H(t)} \quad (2)$$

Here we have subsequently addressed this problem by using a continuous flow sol-gel preparation system and optical flow cell (Fig. 2), analogous to that reported previously for studying merocyanine isomers after irradiation of spiropyrans [10]. The different delay stages (times) for doped sol flow after initial mixing allow, in essence, *gated sampling* (in an analogous manner to an optical gate), which allows polarized fluorescence decays to be collected irrespective of the acquisition time, but more importantly, without the continued growth and aggregation of the silica nanoparticles.

Orthogonal polarised fluorescence decay kinetics were recorded using the time-correlated single-photon counting technique [11] (see Fig. 2). This incorporated a Hamamatsu PLP-02 diode laser for excitation and an EG&G CD2027 single photon avalanche diode for detection. The 650-nm diode laser generated 70-mW vertically polarised optical pulses of duration ≈ 50 ps at 1-MHz repetition rate. The overall instrumental response function was ≈ 350 ps FWHM. Fluorescence was selected using a 700-nm Kodak cut-off filter and a dichroic sheet polariser (Halbro Optics). For all measurements the sol remained optically transparent such that depolarisation resulting from multiple scattering from particles could be neglected.

Thirty percent H_2SO_4 was prepared by diluting 2750 cm^3 50% H_2SO_4 (Ineos Silicas) to 5307.87 cm^3 using doubly distilled deionised water. The addition of 85 mg rhodamine 700 produced a 30% H_2SO_4 , $3 \cdot 10^{-5}$ mol l^{-1} rhodamine 700 solution which after mixing ($\approx 1:3$ ratio of pump speeds) produced a 10^{-5} mol l^{-1} rhodamine 700 sol. Acid concentrations were confirmed by titration with 1 N NaOH.

Sodium silicate solution, 16.26% SiO_2 (w/w), was prepared by diluting 6000 cm^3 Crystal 79 (29.25% SiO_2 w/w, Ineos Silcas) to 12038.81 cm^3 again using doubly distilled deionised water and then sealed. After 24 hours (to allow the depolymerisation of initial silica species to reach equilibrium) the % (w/w) of Na_2O was confirmed by titration with HCl [Eq. (3)] and the % (w/w) SiO_2 confirmed by titrating the NaOH liberated from the reaction of $Si(OH)_4$ and NaF [Eq. (4)], with HCl.



Sodium silicate solution $Na_2O \times SiO_2 \cdot H_2O$, 16.26 % SiO_2 (w/w), $x = 3.14$, 1.198 specific gravity (SG) and sulphuric acid, 30% (w/w), 1.22 SG were peristaltically pumped using Marprene tubing (Watson Marlow), at a rate of 7.35 and 2.55 $ml s^{-1}$, respectively into a stainless steel mixing head and beaker, (Figs. 2 and 3), where the solutions were efficiently mixed by stainless steel mixing blades rotating at 1,200 rpm (Silverson) to produce a 12.01% SiO_2 (w/w), 0.44 N, pH 0.66 sol. Depending on preparation parameters such as reactant concentrations, temperature, pump speeds, and so on, sols differing in percentage weight of silica, excess acid normality, and pH can readily be produced by this procedure [12]. The sol output pump was *flow matched* to the sum of the rhodamine 700-doped sulphuric acid and sodium silicate solution pumps, (i.e., 9.9 $ml s^{-1}$), to maintain a system steady state, at which time a sol delay line was chosen, which, combined with the tubing length and bore size (0.8 mm diameter), gave the time of the anisotropy measurement (i.e., the gating time delay). The elevated temperature of the sol, resulting from the exothermic nature of the acid-base heat of neutralisation, was measured on the bulk sol directly after flowing through the flow cell and was found to be slightly dependent on the gate tubing length. This temperature (typically in the range 33–37°C) can then be used in calculating the silica particle sizes from the Stokes-Einstein relation. For the 12.01% SiO_2 (w/w), 0.44 N sol, vertically and horizontally polarized decays were measured using tubing lengths, measured from the bottom of the reaction beaker to the flow cell, of 139, 167, and 522 cm, corresponding to 7.02, 8.43,

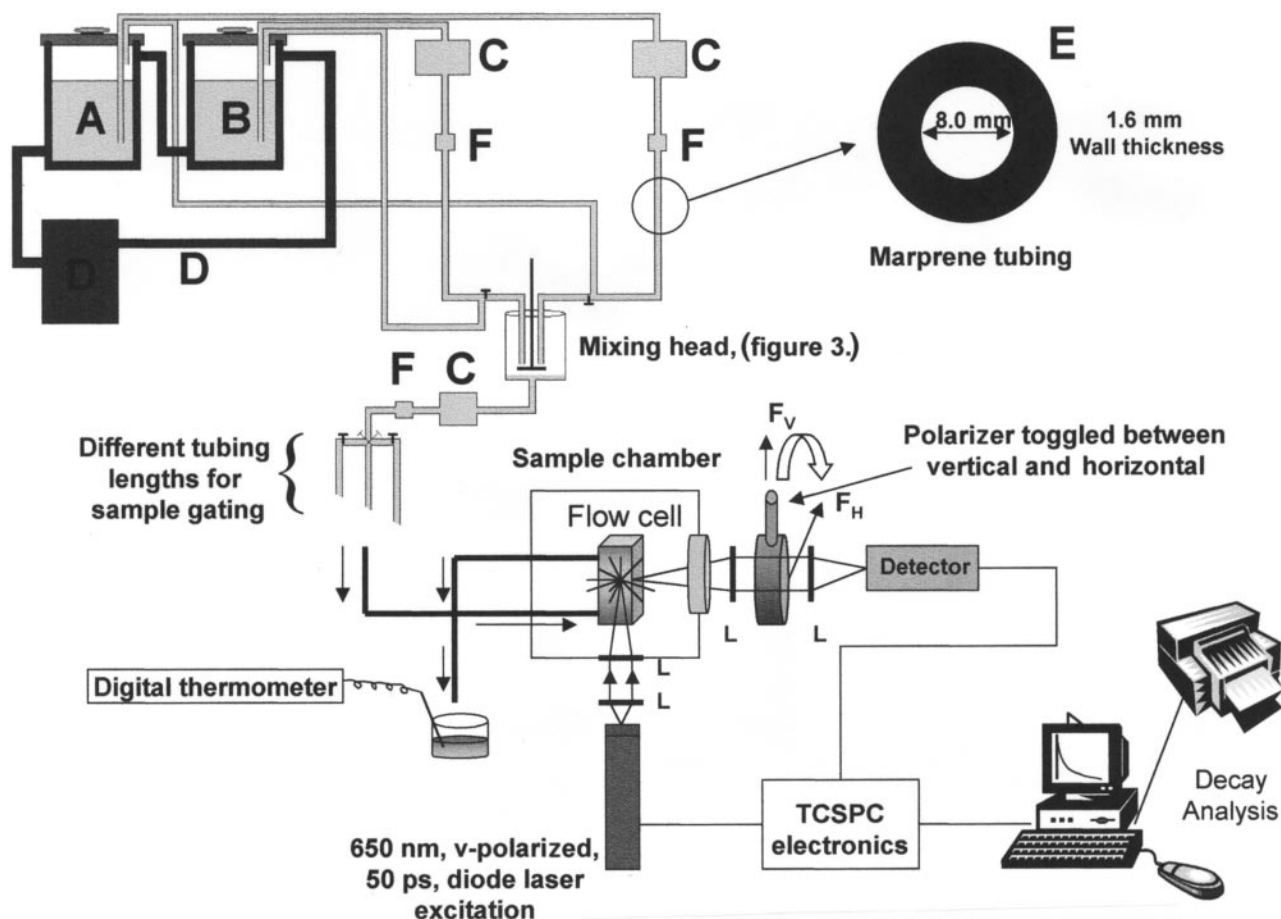


Fig. 2. Continuous flow sol-gel preparation system, flow cell, and time-correlated single-photon timing instrumentation. **A:** 5307 cm³ rhodamine 700-doped sulphuric acid; **B:** 12,038 cm³ sodium silicate solution; **C:** Watson Marlow 505S/RL peristaltic pumps; **D:** Recirculating cooling bath at 20°C. **E:** Marprene tubing. Ordinary tubing is not designed or suited for peristaltic pumping. The characteristics of the pump, including chemical suitability, suction lift, pressure, life, flow rate, and efficiency are largely determined by the tubing. 8.0-mm bore, 1.6-mm wall thickness tubing was used, which was a compromise between maximum tube life (using a large-bore tube at low speed) and maximum accuracy (using a small-bore tube at maximum speed). **F:** Digital flow meters.

and 26.36 seconds, respectively. Rhodamine 700 was the probe chosen to track particle growth because it was found to be stable in 30% (w/w) H₂SO₄, is relatively small ($r < 0.6$ nm), was rapidly *taken-up* by the growing silica nanoparticles in the acidic sol (similar behaviour to that observed under alkaline conditions [13]), as well as having a suitably short fluorescence lifetime, τ , in the sol to resolve silica nanoparticle formation and growth (i.e., $\tau \equiv \tau_r$). For rhodamine 700 in this sol, $\tau = 1.83$ ns, $\chi^2 = 1.24$, at a gating time of ≈ 1 minute.

Figure 4 shows the fluorescence anisotropy decay curves as a function of polymerization time (pt or gating time), for the 12.01% SiO₂, 0.44 N sol. Table I shows the corresponding rotational correlation times; bound dye fluorescence fraction, f ; and calculated silica nanoparticle radius. Differences in the decay curves can clearly be

seen, showing an increase in silica particle size as the polymerization proceeds. It is interesting to see from Table I that rhodamine 700 is initially unbound in the sol, evident by a very fast rotational correlation time ≈ 100 ps, very similar to that reported for aqueous (pH 7.0) rhodamine 700 [14]. At later gating delays, the probe is partitioned between the aqueous phase and bound to growing silica nanoparticles, where the fluorescence fraction, f , can be seen to increase to $\approx 32\%$ in < 27 seconds. It is interesting that the results show a silica particle radius of ≈ 1.5 nm, previously found after several minutes of polymerization [2,3], is in fact present within 10 seconds of a silica hydrogel being formed. Three gating times within 30 seconds of initial mixing are reported here; however, it is envisaged that many more measurements can be taken with even better *real-time resolution*

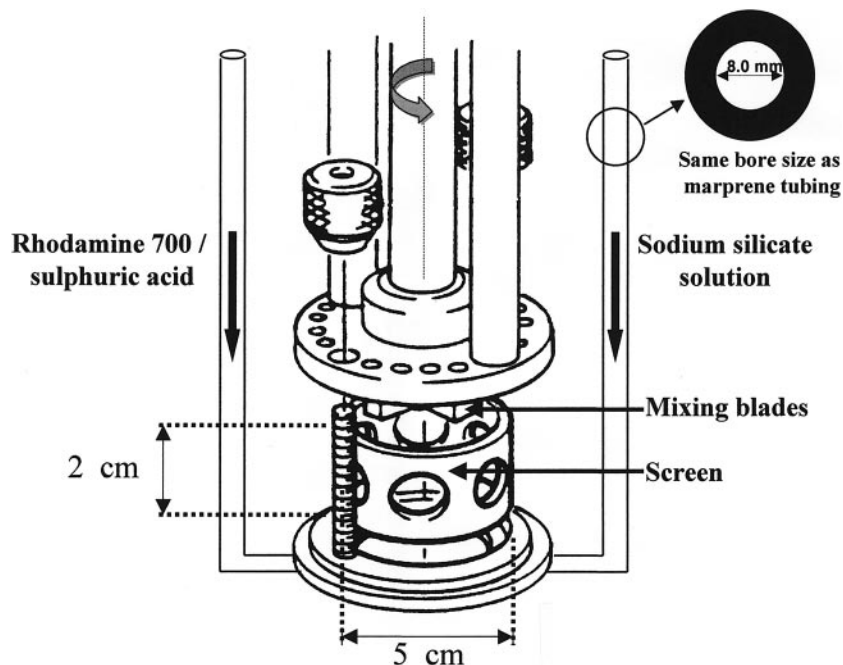


Fig. 3. Stainless steel mixing head. Both the rhodamine 700-doped sulphuric acid and sodium silicate solutions are pumped up into the rotating steel blades. A slight change in bore size and angled nozzles direct the solutions for maximum mixing efficiency, which can be verified by the consistency of the sol gelation time, t_g . For further mixing efficiency the screen mesh size can be changed depending on the viscosity of the sol.

by modifying the flow rates, tubing bore size, and sol viscosity, where the time resolution is independent of the sol mixing time, which was typically $\lll 1$ second.

In summary, this approach of gated fluorescence nanoparticle metrology:

- allows the early formation dynamics of sol-gels to be realised, including the possibility of being

able to distinguish discrete growth mechanisms such as Ostwald ripening or aggregation

- allows *real-time* silica nanoparticle measurements
- might allow *real-time* distributions of silica particles to be observed
- can be applied to any sol-gel system, including tetraalkoxysilanes which are readily used in sol-gel research and photonic applications because of their better defined reactants compared with sodium-, potassium-, or lithium-silicate-based hydrogels

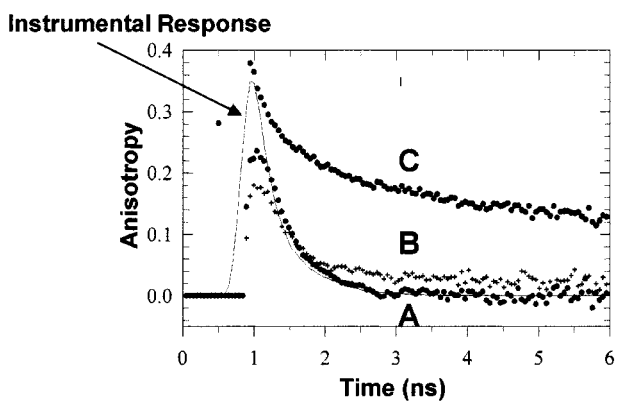


Fig. 4. Fluorescence anisotropy decay curves as a function of polymerisation time, (pt or gating time) for a 12.01% SiO_2 , 0.44 N sol. A: 7.02; B: 8.43; and C: 26.36 seconds, respectively.

Table I. Kinetic Analysis of the Gating Delay Data

Gating time/s	τ_{r1}/ps	τ_{r2}/ns	$f\%$	χ^2	R/nm
7.02	97.3 ± 3.0	—	—	1.16	—
8.43	55.6 ± 3.5	3.0 ± 1.2	9.4	1.07	1.45 ± 0.14
26.36	108 ± 2.4	4.5 ± 0.2	32.4	1.20	1.66 ± 0.03

A microviscosity of 1 cP was used in the silica particle radius (R) Calculation.—indicates that a suitable fit to the data could *not* be obtained. f is the percentage dye bound to growing silica nanoparticles, calculated from the amplitude of the second rotational correlation time, (c.f. Eq. (1)).

- can be used to measure other optical characteristics in *real time* (e.g., absorption or emission spectra, steady-state anisotropy, etc.) by mounting the flow cell in suitable instrumentation

Further studies of sol-gel evolution and the kinetic interpretation of the early growth of silica nanoparticles, which is beyond the scope of this text, will be reported shortly.

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