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Fluorescence Anisotropy in Sol-Gels: Microviscosities or Growing Silica Nanoparticles Offering a New Approach to Sol-Gel Structure Elucidation?

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It generally has been accepted that the addition of organic fluorophores to silica sols, before gelation, leads to the probe being located in two or multiple microdomains of different microviscosity (Fig. 1a) [1–4]. These microviscosities have been determined by assigning correlation times, obtained from the multi-exponential decay of time-resolved fluorescence anisotropy to dye molecules undergoing free Brownian rotational diffusion in their localization sites, and applying the classic Stokes-Einstein relation, $\tau_r = \eta V/kT$. Although this interpretation helps to monitor the sol-to-gel transition and structural changes, it does not reconcile fluorescence data with that of scattering techniques and offers no insight into silica clustering at nanometer resolution [1–5].

However, extensive studies by the authors on a variety of sol-gels [6–11] suggest an alternative interpretation of the fluorescence anisotropy data, one that describes the rapid partition of fluorophore between the aqueous sol and bound to growing (or aggregating) nanometer-size silica clusters (Fig. 1b). This interpretation, which is converse to that widely accepted, offers a new approach for providing fundamental information on the *self-assembly* processes of these discrete spherical silica colloids and subsequently sol-gel structure elucidation. This interpretation could therefore have important applications to the many silica products worldwide, where an understanding of the nanomorphology may enable improvements in the silica-based technologies.

We have recently suggested that the careful choice of a fluorescent probe can allow for the fluorescence anisotropy decay to provide both the growing mean silica particle size, as well as additional molecular viscosity information [8]. The addition of a suitable fluorescent probe to a hydrolyzed sol rapidly leads to its partitioning, where the fluorescence anisotropy function $R(t)$ can be best described in the simplest case 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_O is the initial anisotropy. 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. The fraction, f, has been interpreted as the fraction of fluorescence due to probe molecules bound to silica particles and hence $1\text{-}f$ the fraction due to free dye in the sol. However, the fractional intensities only give direct quantitative information when the anisotropies remain unassociated; that is, the quantum yield of the fluorophore remains similar when both free in the sol and bound to the growing silica nanoparticles.

Originally we applied our alternative interpretation to a variety of sodium silicate based hydrogels [8,9] at pH $<$ 1. More recently, our interpretation has taken on a wider application in studies on hydrogels at pH 1–2 [10] and $>$ pH 9 [11], as well as multiphoton excited low pH sols derived from acid catalyzed tetramethylorthosilicate [6,7]. In all cases the unassociated second rotational correlation time could be seen to correspond well to the silica nanoparticle sizes obtained by other independent techniques such as electron microscopy, neu-

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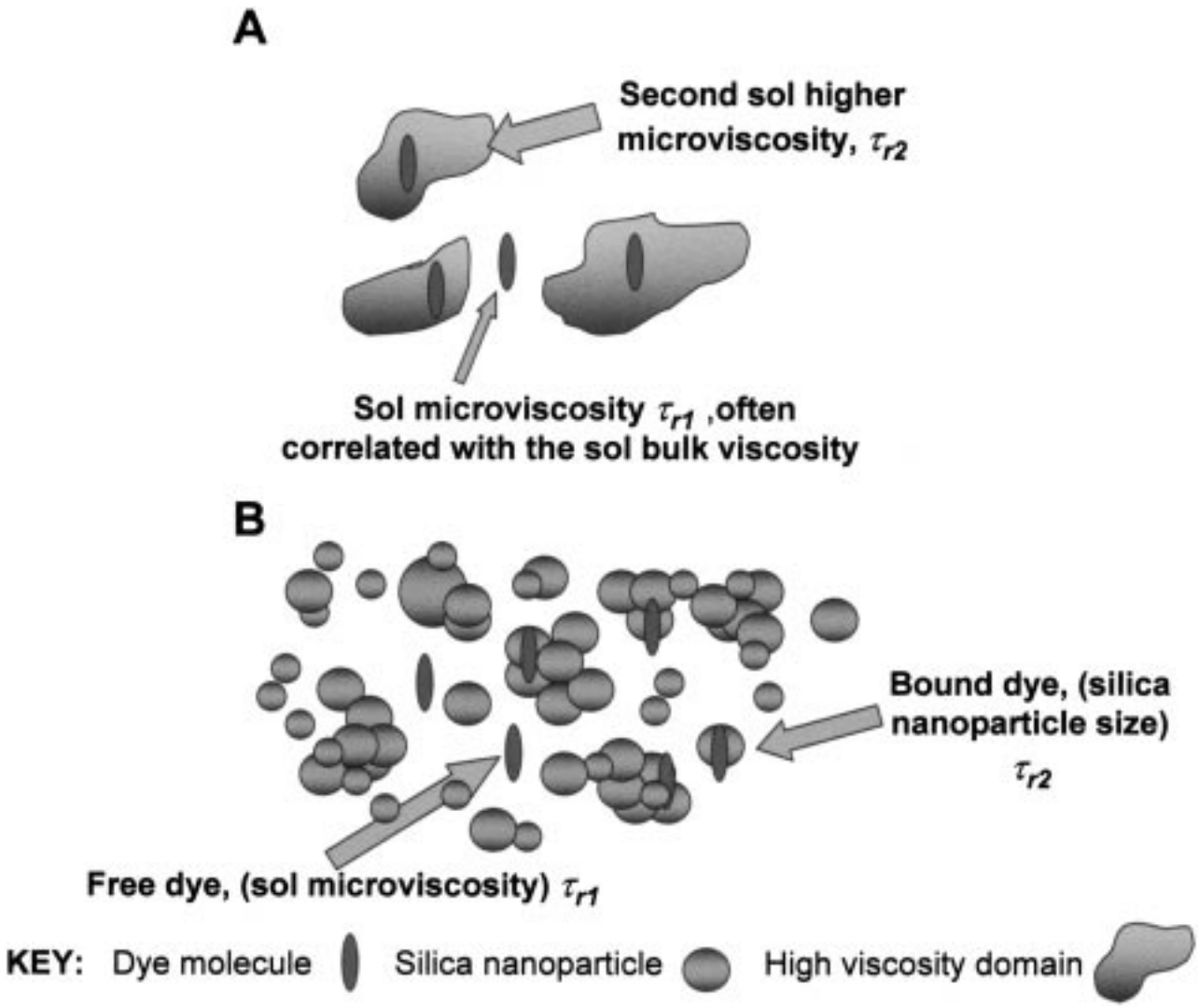

Fig. 1. (a) The fluorescent probe located in different viscosity domains. (b) The probe partitioned between the aqueous phase and bound to growing (or aggregating) silica nanoclusters.

tron, X-ray, and light scattering measurements [12–14], which all served to further confirm our interpretation.

In conclusion, our alternative explanation and therefore new approach to studying sol-gel metrology has many advantages, including the following:

- A more plausible explanation of the anisotropy decay of some doped sol-gel glasses, which is consistent with scattering techniques.
- One measurement (pair of polarized decays) enables both the sol microviscosity and silica nanoparticle size to be determined. Measurement times were typically < 2 min, although we have recently reported a *gated sampling approach*, which enables real-time resolution of the silica nanoparticles [15].
- A low-cost alternative to other fluorescence techniques that could be used to study micoviscosity, such as fluorescence recovery after photobleaching (FRAP) and fluorescence correlation spectroscopy, which requires a microscope and cannot be used on concentrated sols, because of dilution causing depolymerization.
- A low-cost alternative to scattering techniques for observing silica nanoparticle kinetics.
- An approach for understanding the tailoring of sol-gel materials at the molecular level. For exam-

ple, given that sol-gel pores are simply voids between particles, can one correlate pore size (volume) and particle size? Such an achievement may lead to specific "size in/exclusion" silicas.

In the context of fluorescence there can be few if any examples that demonstrate as well as sol-gels the power of anisotropy decay measurements in obtaining near Å resolution of continuously changing hydrodynamic radii.

REFERENCES

1. R. Winter, D. W. Hua, X. Song, W. Mantulin, and J. Jonas (1990) *J. Phys. Chem.* **94**, 2706–2713.
2. B. Dunn and J. I. Zink (1991) *J. Mater. Chem.* **1**(6), 903–913.
3. U. Narang, R. Wang, P. N. Prasad, and F. V. Bright (1994) *J. Phys. Chem.* **98**(1), 17–22.
4. G. D. Qian and M. Q. Wang (1999) *J. Phys. D: Appl. Phys.* **32**(18), 2462–2466.
5. B. Dunn and J. I. Zink (1997) *J. Chem. Mater.* **9**(11), 2280–2291.
6. J. Karolin, C. D. Geddes, K. Wynne, and D. J. S. Birch (2002) *Meas. Sci. Technol.* **13**, 21–27.
7. C. D. Geddes, J. Karolin, and D. J. S. Birch (2002) *J. Phys. Chem. B* **106**(15), 3835–3841.
8. C. D. Geddes and D. J. S. Birch (2000) *J. Non-Cryst. Sol.* **270**(1–3), 191–204.
9. D. J. S. Birch and C. D. Geddes (2000) *Phys. Rev. E.* **62**(2), 2977–2980.
10. C. D. Geddes and D. J. S. Birch (2002) *J. Non-Cryst. Sol.* (In preparation.)
11. D. J. S. Birch, C. D. Geddes, J. Karolin, R. Leishman, and O. J. Rolinski (2002) *Fluorescence Nanometrology in Sol-gels*, Springer series on the Methods and Applications of Fluorescence Spectroscopy. (In press.)
12. B. Himmel, T. Gerber, and H. Burger (1987) *J. Non-Cryst. Sol.* **91**(1), 122–136.
13. T. Matsoukas and E. Gulari (1988) Dynamics of growth of silica particles from ammonia-catalysed hydrolysis of tetra-ethyl-orthosilicate, *Jn. Coll. Interf. Sci.* **124**(1), 252–261.
14. T. Gerber, B. Himmel and C. Hubert (1994) WAXS and SAXS investigation of structure formation of gels from sodium-water glass, *Jn. Non-Cryst. Solids,* **175**(2–3), 160–168.
15. C. D. Geddes, J. Karolin, and D. J. S. Birch (2002) *J. Fluoresc.* **12**(1), 113–117.

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