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# Scaling and branching in wet sonogels as a function of the volume fraction of the liquid phase

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## Abstract

The structural properties of wet silica sonogels prepared with different volume fractions of the liquid phase were studied by small-angle x-ray scattering (SAXS) and thermogravimetry (TG). The SAXS intensity curves of aged wet gels were all found to be well fitted by the form factor for scattering from non-randomly branched polymers in solution. The radius of gyration ( $R_g$ ) of the polycondensates and the branching density were found to increase with the volume fraction of the liquid phase of the wet gels. The molecular weight ( $M$ ) of the branched polycondensates was found to scale as  $M \sim R_g^\alpha$  with  $\alpha$  quite close to 2 in the studied range.

## 1. Introduction

A wide variety of silica-based glasses and glass ceramics have been obtained by a sol–gel process from the hydrolysis of tetraethoxysilane (TEOS) [1]. The overall sol–gel process of silicon alkoxides comprises hydrolysis and polycondensation reactions of the precursors through a series of possible events that lead to the evolution of the gelling system from the initial homogeneous sol of silicon oligomers up to the final gel. The structural evolution of the gelling system has been discussed on the basis of chemical mechanisms [2], mainly at the beginning of the process, and of physical restructuring [3–5] which can take the form of a phase separation.

Different structures for gels have been reported depending on the starting materials, the initial conditions of preparation such as pH, alcoxide/water molar ratio, type of catalyst, temperature and method employed for hydrolysis (ultrasound or conventional), and also on the conditions of gelation and subsequent treatments for ageing and drying of the gels [6–12]. It is generally accepted that hydrolysis under acid conditions and excess of water leads to the formation of wet gels with a structure that can be described as mass-fractal [3, 7, 11, 12], probably formed by clustering of branched polycondensates of liner chains.

Most of the structural properties of the gels are even defined at the early gelation and ageing period in which the gels are yet in wet conditions. Knowledge of the

structural parameters of the wet gels is naturally important for understanding the basic processes of aggregation and branching in the formation of the gels. The structuring of silica sols and gels in various chemical conditions has been studied by means of small-angle x-ray scattering (SAXS) using classical particle scattering factors [3]. The results have been interestingly discussed from the point of view of branching, aggregation and phase separation during the gelation of TEOS-derived systems. In this work, we study, using mainly small-angle x-ray scattering (SAXS), the basic structural modifications in aged wet silica sonogels prepared with different volume fractions of the liquid phase. High purity silica sonogels have been considered, for instance, as supports for materials with interesting linear and nonlinear optical properties [13, 14]. The aim of the present work is to study the effects of the dilution, throughout the increase of the volume fraction of the liquid phase of the gels, on the structural characteristics of the aged wet sonogels, considering classical particle scattering factors of some branched and linear chain polymers in solution [15].

## 2. Experimental procedure

Samples of wet gels were prepared from sono-hydrolysis of mixtures of TEOS, distilled and deionized water, and 0.1N HCl as a catalyst. The hydrolysis was promoted at pH = 2

**Table 1.** Measured and evaluated properties of the wet gel.

| $r_w$ | $\rho$ (g cm <sup>-3</sup> ) | $(m_L/m_0)_{TG}$ | $\rho_L$ (g cm <sup>-3</sup> ) | $\phi_L$      | $(m_L/m_0)_{calc}$ | $\rho_{calc}$ (g cm <sup>-3</sup> ) |
|-------|------------------------------|------------------|--------------------------------|---------------|--------------------|-------------------------------------|
| 5.5   | 1.01 ± 0.02                  | 0.703 ± 0.007    | 0.835 ± 0.008                  | 0.872 ± 0.009 | 0.721 ± 0.007      | 1.02 ± 0.02                         |
| 7.7   | 1.01 ± 0.02                  | 0.727 ± 0.007    | 0.854 ± 0.008                  | 0.884 ± 0.009 | 0.748 ± 0.007      | 1.02 ± 0.02                         |
| 9.9   | 1.01 ± 0.02                  | 0.744 ± 0.007    | 0.870 ± 0.009                  | 0.895 ± 0.009 | 0.764 ± 0.008      | 1.03 ± 0.02                         |
| 14.3  | 1.02 ± 0.02                  | 0.792 ± 0.008    | 0.892 ± 0.009                  | 0.902 ± 0.009 | 0.790 ± 0.008      | 1.02 ± 0.02                         |
| 18.7  | 1.02 ± 0.02                  | 0.824 ± 0.008    | 0.908 ± 0.009                  | 0.914 ± 0.009 | 0.814 ± 0.008      | 1.02 ± 0.02                         |

for 10 min under a constant power ( $\sim 0.7$  W cm<sup>-3</sup>) of ultrasonic radiation. The pH was increased to 4.5 by addition of NH<sub>4</sub>(OH) before the sols were cast in sealed containers and kept for 30 days at 40 °C for gelation and ageing. Monolithic wet gels with equivalent water/TEOS molar ratios ( $r_w$ ) varying according to  $r_w = 5.5, 7.7, 9.9, 14.3$  and  $18.7$  were then obtained. The wet gels were analyzed for density measurements, thermogravimetry (TG) and SAXS.

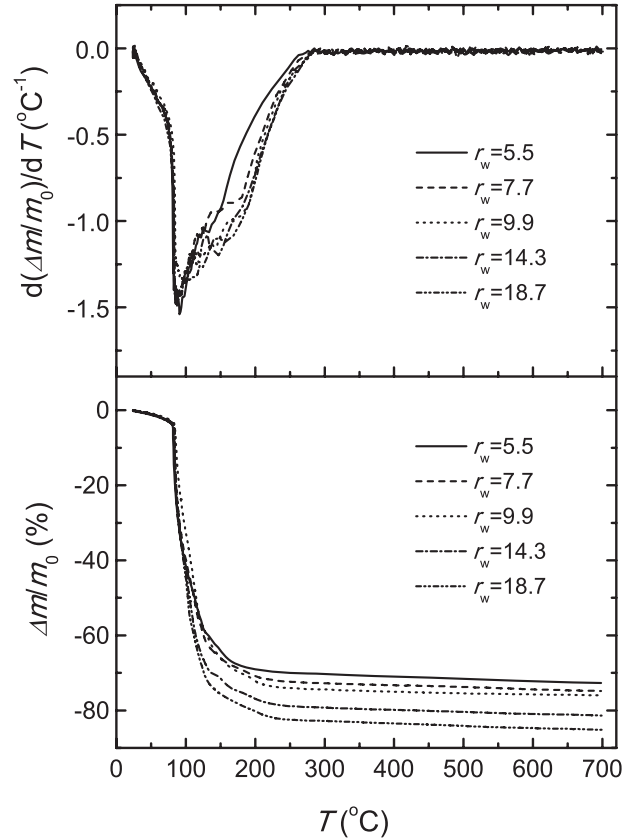
The TG tests were carried out with a heating rate of 10 °C min<sup>-1</sup> in the temperature range from 25 up to 700 °C.

The SAXS experiments were carried out using synchrotron radiation with a wavelength  $\lambda = 0.1608$  nm. The beam was monochromatized by a silicon monochromator and collimated by a set of slits defining a pin-hole geometry [16]. A one-dimensional position sensitive x-ray detector was used to record the SAXS intensity,  $I(q)$ , as a function of the modulus of the scattering vector  $q = (4\pi/\lambda) \sin(\theta/2)$ , where  $\theta$  is the scattering angle. The experimental setup allowed us to obtain SAXS data from  $q_0 = 0.069$  nm<sup>-1</sup> to  $q_m = 3.27$  nm<sup>-1</sup> at intervals of  $\Delta q = 2.56 \times 10^{-3}$  nm<sup>-1</sup>. The data were corrected by sample attenuation and parasitic scattering, and normalized with respect to the beam intensity and the logarithm of the attenuation, which is proportional to the thickness of the sample.

### 3. Results

Table 1 shows the density of the wet gels  $\rho$  as determined from direct volume and mass measurements. Figure 1 (bottom) shows the relative mass loss ( $\Delta m/m_0$ ) for the wet gels as determined by thermogravimetry (TG). As expected, the total mass loss increases with  $r_w$ . Almost the whole of the mass loss occurs up to about 300 °C, as can be inferred from the derivate of the TG signal in figure 1 (top). This means that the mass loss can be attributed almost exclusively to the evaporation of the liquid phase of the gels. Table 1 shows the fraction of the mass loss up to 300 °C, labeled as  $(m_L/m_0)_{TG}$ . The TG results suggest that the hydrolysis and polycondensation reactions were practically 100% complete after the ageing of the gels at 40 °C.

Assuming 100% hydrolysis and polycondensation under perfectly sealed conditions, we expect the liquid phase of the wet gels to be a mixture of ethanol and water with a molar ratio equal to  $4:(r_w - 2)$ . The density of the liquid phase  $\rho_L$  was then estimated (table 1) by assuming an ideal liquid mixture with that composition. The volume fraction of the liquid phase  $\phi_L$  was evaluated by the equation  $\phi_L = (\rho_S - \rho)/(\rho_S - \rho_L)$ , where  $\rho_S$  is the density of the solid particles (silica) of the wet gels assumed as 2.2 g cm<sup>-3</sup> as frequently quoted for fused silica. The volume fraction of solid particles (silica)  $\phi_S$ , which

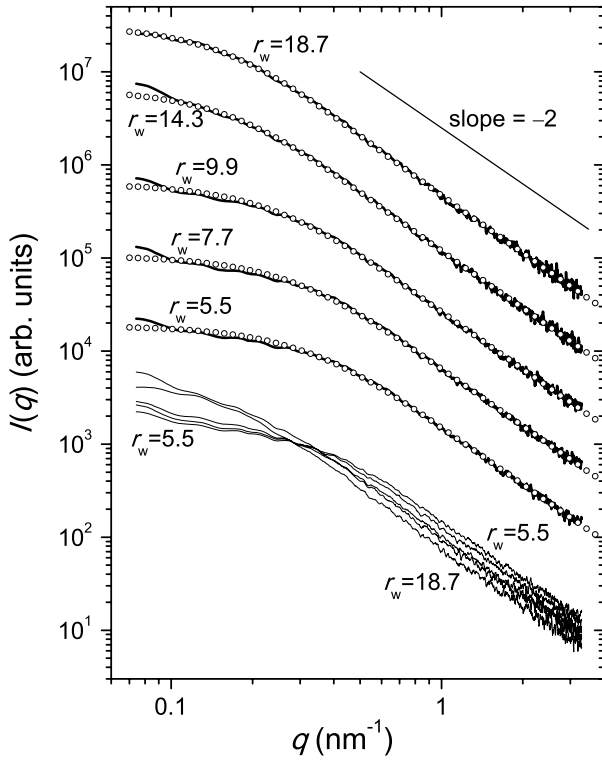


**Figure 1.** Bottom: thermal gravimetric (TG) tests carried out under a heating rate of 10 °C min<sup>-1</sup> for the wet gels as a function of the water/alkoxide molar ratio  $r_w$ . Top: derivative of the TG signal.

is proportional to the silica concentration in the wet gels, was naturally evaluated by  $\phi_S = (1 - \phi_L)$ .

To check the validity of these assumptions in evaluating  $\rho_L$  and  $\phi_L$  for the wet gels, we evaluated the theoretical mass fraction of the liquid phase as  $(m_L/m_0)_{calc} = (\rho_L/\rho)\phi_L$  and the theoretical density of the wet gels as  $\rho_{calc} = \phi_L\rho_L + \phi_S\rho_S$  in order to compare them with the respective experimental ones ( $(m_L/m_0)_{TG}$  and  $\rho$ ) (table 1). The results were found to be in good agreement in both cases.

Figure 2 shows the SAXS intensity  $I(q)$  for the wet gels. The curves exhibit a plateau at small  $q$  and a power law decay  $I(q) \sim q^{-\alpha}$  at large  $q$ , with the exponent  $\alpha$  being quite close to 2 for all the wet gels, independently of  $r_w$  or of the volume fraction of the liquid phase in the gel. Figure 3 shows the corresponding Kratky plots  $q^2I(q)$  versus  $q$ . A maximum appears in the Kratky plots at low  $q$ . The appearance of the maximum is more perceptible as  $r_w$  is increased, while the position of the maximum is shifted towards the low- $q$  region.

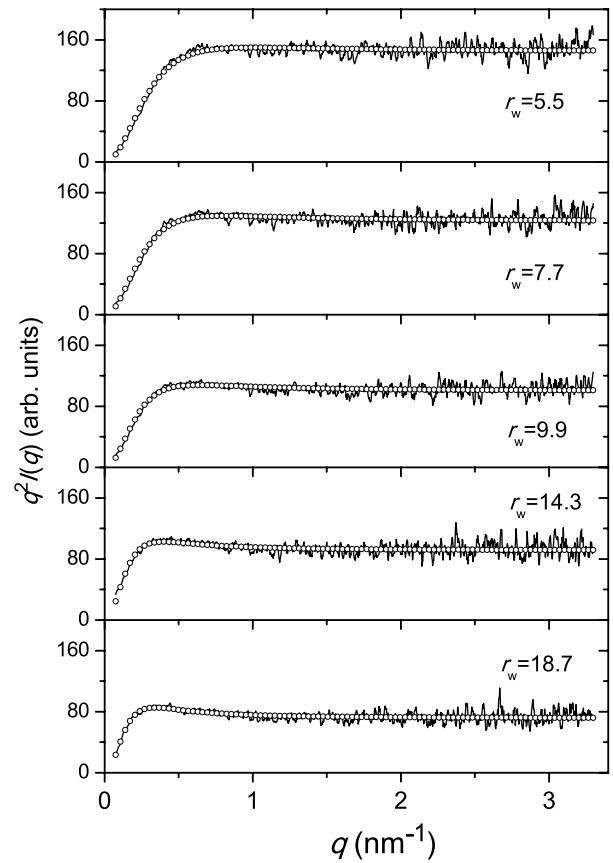


**Figure 2.** SAXS intensity for the wet gels as a function of the water/alkoxide molar ratio  $r_w$ . For the sake of clarity, the curves were plotted once more after being shifted vertically by different factors. The small circles are plots of equation (1) from the fitted parameters in table 2.

The presence of a maximum in the Kratky plots is characteristic of branched polymers in solution [15]. The SAXS data were analyzed with a particle scattering factor that is valid either for non-randomly branched polycondensates or for star molecules with polydisperse rays. That approach can be cast as [15]

$$I(q) = I(0)[1 + C(qR_g)^2/3]/[1 + (1 + C)(qR_g)^2/6]^2, \quad (1)$$

where  $I(0)$  is the intensity at  $q = 0$ ,  $R_g$  is the radius of gyration of the macromolecules and  $C$  is a dimensionless constant, which is a function of the link probability for the formation of a chain and the link probability for the formation of a branching point in a given macromolecule. When  $C = 1$ , equation (1) becomes the form factor for the scattering from either polydisperse coils of linear chains or branched polycondensates of random  $f$ -functional elements [15], but no maximum is expected in the Kratky plots. The maximum in the Kratky plots is sensitive to the parameter  $C$ . The SAXS data were thus fitted by equation (1), using a nonlinear least squares routine (Levenberg–Marquardt algorithm), to obtain the parameters  $I(0)$ ,  $R_g$  and  $C$  that minimize the difference between  $q^2I(q)$  in the Kratky plots with respect to the experimental ones. Table 2 shows the results of the fitting process.



**Figure 3.** Kratky plots for the wet gels as a function of the water/alkoxide molar ratio  $r_w$ . The small circles show the fitting of the function  $q^2I(q)$ , with  $I(q)$  given by equation (1), to the experimental data.

**Table 2.** Structural parameters of the wet gels as determined by SAXS.

| $r_w$ | $I(0)$ (arb. units) | $R_g$ (nm)      | $C$               |
|-------|---------------------|-----------------|-------------------|
| 5.5   | $188 \pm 3$         | $5.03 \pm 0.06$ | $0.258 \pm 0.005$ |
| 7.7   | $212 \pm 4$         | $5.68 \pm 0.07$ | $0.238 \pm 0.004$ |
| 9.9   | $253 \pm 5$         | $6.75 \pm 0.09$ | $0.226 \pm 0.004$ |
| 14.3  | $526 \pm 9$         | $9.8 \pm 0.1$   | $0.201 \pm 0.004$ |
| 18.7  | $515 \pm 9$         | $10.5 \pm 0.2$  | $0.176 \pm 0.003$ |

#### 4. Discussion

The most striking feature of the SAXS intensity for this set of wet gels is the appearance of a maximum in the Kratky plots and a constant plateau value at high  $q$ , characteristic of a power law decay  $I(q) \sim q^{-2}$ . These characteristics are expected for the scattering factor of branched polycondensates in solution. The presence of the maximum becomes more evident as the dilution  $r_w$ , or the volume fraction of the liquid phase  $\phi_L$ , is increased.

Neither monodisperse nor polydisperse (most probable distribution) coils of linear chains exhibit a maximum in the Kratky plots. Instead, the quantity  $q^2I(q)$  asymptotically reaches a plateau at high  $q$ . The same behavior is expected for randomly branched  $f$ -functional polycondensates ( $A_f$ -type monomer) [15]. A maximum in the Kratky plots is

also expected for non-randomly branched ( $f + 1$ )-functional polycondensates (AB<sub>f</sub>-type monomer), but a constant plateau value for the quantity  $q^2 I(q)$  is not expected at high  $q$ , because the particle scattering factor follows a Debye–Bueche form as  $I(q) = 1/[1 + (1/6)R_g^2 q^2]$  [15], which goes to a Porod's law  $I(q) \sim q^{-4}$  behavior as  $q \rightarrow \infty$ . So, the scattering produced by the aged wet gels seems to be more properly described in terms of the scattering factors from either star molecules with  $f$ -polydisperse rays (most probable distribution) or non-random polycondensates of the A  $\prec_C^B$  type monomers [15].

For large degrees of polymerization and not such a high branching probability, the scattering factors of both mentioned structures (star molecules with  $f$ -polydisperse rays and non-random polycondensates of the A  $\prec_C^B$  type monomers) are equally given by equation (1), except by the meaning of the parameter  $C$  [15]. In this case, the quantity  $1/C$  represents the number of branching points per macromolecule in non-random polycondensates while  $f = 1/C$  represents the number of rays in the star molecules. In the particular case of  $C = 1$ , equation (1) coincides with the scattering factor of either polydisperse coils of linear chains or randomly branched  $f$ -functional polycondensates, but no maximum should appear in the Kratky plots. Rigorously, a maximum in the Kratky plots could also be observed for star molecules with regular monodisperse rays, although the scattering factor of such a structure is different from that of equation (1) [15]. The maximum in the Kratky plots for a macromolecule scattering as equation (1) should occur at  $q_{\max} = (1/R_g)[6/(1 - 3C)]^{1/2}$ . Thus the greatest value for  $C$  able to display a real maximum in the Kratky plots is  $1/3$ , in which case the maximum would be at  $q = \infty$ , which corresponds to the asymptotic behavior of the quantity  $q^2 I(q)$  as expected for polydisperse linear chains or randomly branched polycondensates ( $C = 1$ ). Therefore, it is very critical to decide between randomly branched polycondensates, non-randomly branched polycondensates and polydisperse coils of linear chains when the maximum in the Kratky plots is not so apparent, as was found for the samples with low  $r_w$  in the present work.

The diminution of the parameter  $C$  (or increase of  $f$ ) with the dilution of the system (table 2) is a clear indication that branching is a process facilitated by the increase of free space originating naturally from the increase in the volume fraction of the liquid phase in the gel. The increase in the radius of gyration  $R_g$  with the dilution (table 2) suggests that the growth of the macromolecules also depends on the branching process, not only on the coiling of linear chains. The number of macromolecules in the unit volume of the sample should diminish with increase in their size ( $R_g$ ), because of mass conservation. The internal structure of the macromolecules, however, produces approximately the same scattering law  $I(q) \sim q^{-2}$  in the domain of high- $q$  (figure 2), given roughly by  $q \gtrsim R_g^{-1}$ . That is the same law for the scattering from a mass-fractal structure with dimensionality equal to 2 [17].

For a two-phase system, like the present wet gels built up by silica, with a volume fraction  $\phi_S$  and a liquid phase with complementary volume fraction  $\phi_L$ , the SAXS intensity integrated over the reciprocal space  $q$ , a property known as

invariant  $Q$ , is given by [18]

$$Q = \int_0^\infty q^2 I(q) dq = 2\pi^2 (\Delta\rho)^2 \phi_S \phi_L V, \quad (2)$$

where  $(\Delta\rho)$  is the difference in the electronic density of the phases (silica and liquid phase) and  $V$  is the irradiated volume of the sample.

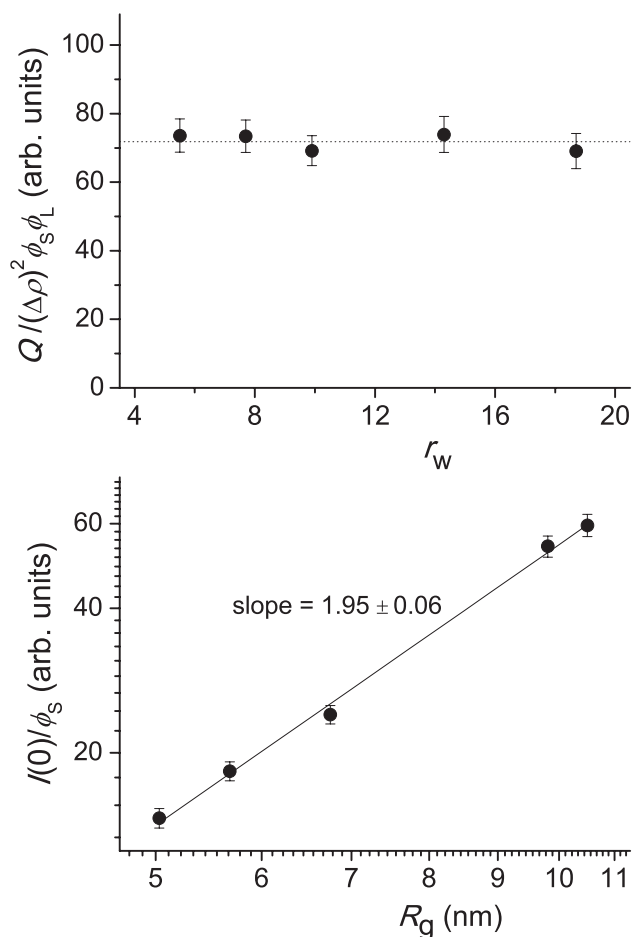
The values for  $Q$  were numerically determined in the experimentally accessible range from  $q_0$  to  $q_m$ . The contribution to the integral  $Q$  due to the range from  $q = 0$  to  $q_0$  was evaluated by extrapolation of the intensity fitted by equation (1), using the parameters of table 2; that due to the range above  $q_m$  was evaluated by  $I(q_m)q_m^3$ , which results from the assumption that the intensity follows Porod's law  $I(q) \sim q^{-4}$  above the maximum experimentally measured value  $q_m$ . The contrast in the electronic density of the phases  $(\Delta\rho)$  is expected to change with  $r_w$  due to the difference in the composition of the liquid phase. The electronic density of the liquid phase of the wet gels was estimated as  $N_A \sum n_i z_i / \sum n_i V_i$ , where  $N_A$  is the Avogadro number and  $z_i$ ,  $V_i$  and  $n_i$  are, respectively, the number of electrons per molecule, the molar volume, and the number of moles of the component  $i$  in the liquid, a mixture of 4 mol of ethanol and  $(r_w - 2)$  mol of water, resulting from 100% hydrolysis and condensation reactions in completely sealed conditions, as mentioned. The electronic density of silica was estimated simply as  $N_A z_S / V_S$ , using for  $z_S$  and  $V_S$  the number of electrons per molecule and the molar volume of the solid phase, the values corresponding to fused silica. Thus, the square of the difference in the electronic density of the phases  $(\Delta\rho)^2$  was evaluated for the wet gels. Figure 4 (top) shows that the quantity  $Q/(\Delta\rho)^2 \phi_S \phi_L$  is accordingly a fairly constant value for all the wet gels.

The striking similarity of the scattering law  $I(q) \sim q^{-2}$  produced by the macromolecules in the domain of high- $q$  suggests that the structure behaves as a mass-fractal structure with dimensionality close to 2. Then, the molecular weight  $M$  of the macromolecule in solution should scale as  $M \sim R_g^2$  [17]. The intensity  $I(0)$  scattered at  $q = 0$  is proportional to the mass concentration  $c_0$  and to the molecular weight  $M$  [18], or  $I(0) \sim c_0 M$ . Since  $M \sim R_g^2$  and  $c_0 \sim \phi_S$ , we should have  $I(0)/\phi_S \sim R_g^2$ . Figure 4 (bottom) shows the plot of the data  $I(0)/\phi_S$  versus  $R_g$  in a log–log scale, together with the plot of the linear fitting to the data. The slope of the linear fitting was found accordingly to be quite close to 2.

## 5. Conclusions

The structural characteristics of the aged wet silica sonogels were studied as a function of the volume fraction of the liquid phase, considering classical particle scattering factors of some branched and linear chain polymers in solution. The scattering produced by the aged wet gels is more properly described in terms of the scattering factors from either star molecules with  $f$ -polydisperse rays (the most probable distribution) or non-random polycondensates of A  $\prec_C^B$  type monomers, although it was found to be very critical to decide between randomly branched polycondensates, non-randomly branched





**Figure 4.** Properties of the invariant  $Q$  and of the intensity  $I(0)$  extrapolated to  $q = 0$  as determined by SAXS for the wet gels. Top: the constancy of the quantity  $Q / (\Delta\rho)^2 \phi_S \phi_L$  as the water/alkoxide molar ratio  $r_w$  is varied. Bottom: log–log plots of  $I(0) / \phi_S$  ( $\sim M$ ) versus  $R_g$  together with the linear fitting to the data with a slope quite close to 2, suggesting an approximate scaling law  $M \sim R_g^2$ .

polycondensates and polydisperse coils of linear chains in the case of gels prepared with low water/alkoxide molar ratio. The radius of gyration ( $R_g$ ) of the polycondensates and the

branching density were found to increase with the volume fraction of the liquid phase of the wet gels. The molecular weight ( $M$ ) of the branched polycondensates scales as  $M \sim R_g^\alpha$  with  $\alpha$  quite close to 2 in the studied range.

## Acknowledgments

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