**SAXS structural study of xerogels and aerogels formed from small-molecule organic gelators**

**H. Grigoriew**, **D. Chmielewska**, **J. Gronkowski**

1 Institute of Nuclear Chemistry and Technology, 03-125 Warsaw, Poland  
2 Institute of Experimental Physics, Warsaw University, 00-681 Warsaw, Poland  
E-mail: hgrigori@ichtj.waw.pl

**Abstract.** Structure of monosaccharide gels formed from glucose-based gelators with organic solvents were studied using SAXS method, in wet state and after drying as xerogels and aerogels. Fractal analysis of the scattering data was carried out. It occurred that these gels essentially change their structure during drying. The structure of the xerogels indicates a strong collapse. The aerogels produced from the apolar gel are also collapsed but, for the slightly stronger polar one, the mechanism of structural change probably includes Ostwald ripening. These results call in question the reasonableness of application of microscopic methods, requiring dry samples, like SEM and TEM, to structural investigations of gels of this type.

1. **Introduction**

   The processes of gel drying produce xero- or aerogels, depending on the method used. The method of xerogel production is lyofilization or frozen-drying, i.e. evaporation of the solvent at low pressure from the frozen gelator skeleton. The gelator structure, with enormous surface area and a very small pore size, is usually maintained, in spite of a shrinkage of the skeleton. The aerogel is produced by careful drying a wet gel in various environments, often in super-critical condition, and/or with solvent exchange. The gel does not shrink, so the fragile gelator network is unchanged and aerogel is highly porous. Both processes can be complex and many-staged [1].

   However, the investigated gels belong to the class of physical gels, which are weak and reversible, and, as it is known, can disintegrate upon touching. Therefore, the process of drying can be expected to have a more essential influence on their structure.

2. **Experimental**

   The first gel (G) was formed of methyl-4,6-O-benzylidene-α-D-glucopyranoside gelator with diphenyl ether as solvent. The gelator molecule is very small and apolar, similarly as the solvent. Therefore, very weak mutual interactions in the gel structure are expected. The next gelator molecule (P) was built of the previous one, but with the p-NO₂ group joined to it.
(Fig. 1), which introduced a polarity, and a polar solvent (water) was used as well. In this case the interactions between both gelator–gelator and solvent–gelator molecules are much stronger, so a stronger gel structure is expected.

Both gels were prepared in the same way, with the gelator concentration in the range from 1 to 1.5 % [g/mL]. Aerogels were produced by leaving obtained gels in open vessels till they became dry. Xerogels were produced by frozen-drying of the gels in Labconco lyph.lock 1l apparatus at about –50 °C and 10 mm Hg.

The measurements were carried out at the ULTRA-SAXS BW-4 wiggler beamline of Hasylab-DESY synchrotron. In order to obtain a wide size range of observed effects (USAXS–SAXS), each sample was measured at two different sample–detector distances (4 m and 12 m), and both measurements were joined. After their initial treatment, the $I(s)$ curves, where $I$ – the intensity of X-rays and $s = 2\pi \sin(\theta/2)/\lambda$, were obtained. The range of measurements transformed to real space was from 6 to 240 nm.

![Image](Figure 1. The molecule of the polar gelator. The molecule of the apolar one is similar but it does not have the $p$-NO$_2$ group.)

![Image](Figure 2. Schematic diagram of a part of the fractal curve indicating the Guinier, fractal and Porod ranges.)

3. Results and discussion

If the slope of the curve log$I$ vs. log$s$ forms straight-line segment(s), then it is a signal of a fractal-type structure. In our case the fractal analysis includes only some parts of the fractal (log–log) curve, as it is shown at the schematic sketch in Fig. 2. After the Guinier range for the smallest values of $s$, in the next fractal range the slope of 1–3 refers simply to the mass fractal dimension, $d_m$, but, after the Porod bend, the slope in the range of 3–4 is generated by the surface fractal of dimension $d_s = 6$–the slope value. Besides, the points of the slope change inform about the size of fractal clusters: $a$ – the primary cluster (at the Porod bend) and $R_g$ – the secondary one, between the fractal and Guinier range [2].

All numerical data are presented in Table I.

Apolar gel – G. Its fractal curves are shown in Fig. 3 and Table I. For the wet gel (Fig. 3a), the value of $d_m = 1.6$ is related to the mass fractal built in accordance to the DLCA (diffusion limited cluster aggregation) mechanism, and $d_s = 2.9$ means its uneven and developed surface [1]. The average size of the primary aggregate is $a = 10$ nm, and of the secondary one $R_g = 110$ nm (Table I). The essential change of the fractal curve observed for xerogel (Fig. 3b) and aerogel (Fig. 3c) in comparison with the one for the wet gel seems to be caused by a drying-induced shrinkage leading to a collapse. It results in formation of some large-scale morphological features, e.g. grains or other, of the micrometric length [3]. Their size is too large to be visible by X-rays, so the scattering is related only to surface fractal of $d_s \approx 2$, characteristic for smooth surfaces. This structure is of hierarchical type, because at larger angles, the slopes
related to primary aggregates are of \( d_m = 2.45 \) (Fig. 3b) and of \( d_m = 1.85 \) (Fig. 3c), i.e. characteristic for looser fractals. This collapse is similar for both dried gels, confirming a big weakness of the monosaccharide gel structure.

![Figure 3](image)

**Figure 3.** Fractal curves for weaker apolar gels: a) wet, b) xero, c) aero. The straight-line parts of the curves are marked by lines with their slopes.

**Polar gel – P.** Fractal curves are visible in Fig. 4 and Table I. For wet gel (Fig. 4a), the value of \( d_m = 2.9 \) is generated by a dense aggregate, according to RLCA (reaction limited cluster aggregation) mechanism. The value of \( a = 120 \) nm and then the slope from surface fractal of \( d_s = 2.05 \) [1] mean that the primary cluster is much greater than for the G gel and of smooth surface, which should be caused by the polarity of both of its constituents. The shape of the xerogel fractal curve (Fig. 4b and Table I) suggests a similar collapse as for the G xerogel. However, no collapse is observed for the aerogel (Fig. 4c, Table I) where the fractal curve consists of two parts: of mass fractal, \( d_m = 2.25 \), and of surface fractal, \( d_s = 3.0 \). The crossover between the parts corresponds to \( a = 70 \) nm. It is a new structure, not a modification of the wet gel structure. Such a structure can be caused by Ostwald ripening [1], including dissolutions and precipitations.

![Figure 4](image)

**Figure 4.** Fractal curves for stronger polar gels: a) wet, b) xero, c) aero. The straight-line parts of the curves are marked by lines with their slopes.

**Discussion of relation obtained results to SEM and TEM observations.** The commonly adapted view about the structure of physical, organic gels has been developed on the basis of their very frequently made microscopic (SEM and TEM) observations. This view apparently refers not to the structure of wet gel, but to other structure, formed during drying, because all microscopic methods use dry samples. The main feature of this view is the existence of fibrilar, not fractal,
structure of such gels [4,5]. Observations using scattering methods operating on wet gels [6,7] call in question this view, informing about fractal structures, formed according to typical gelation mechanisms, DLCA and RLCA. Results of the present work elucidate a reason of these differences and indicate the necessity to study such gels in the natural, wet state.

Table 1. Structural parameters of the monosaccharide gels determined from the fractal analysis.

| Gel                  | $d_m$  | $d_s$  | $d_m$  | $R_g$ [nm] | $a$ [nm] |
|----------------------|--------|--------|--------|------------|----------|
| weaker, apolar       |        |        |        |            |          |
| wet (Fig. 3a)        | 1.6    | 2.9    | –      | 110        | 10       |
| xero (Fig. 3b)       | –      | 2.05   | 2.45   | –          | –        |
| aero (Fig. 3c)       | –      | 2.05   | 1.85   | –          | –        |
| stronger, polar      |        |        |        |            |          |
| wet (Fig. 4a)        | 2.9    | 2.05   | –      | –          | 120      |
| xero (Fig. 4b)       | –      | 2.2    | –      | –          | –        |
| aero (Fig. 4c)       | 2.25   | 3.0    | –      | –          | 70       |

4. Concluding remarks

The lack of chemical bonds joining the gelator molecules, together with the reversibility of the small-molecule organic gels, cause the great weakness of their structure, which leads to fundamental structural differences after their drying, namely: (i) for xerogels – the frozen-drying process evidently favors the collapse of the gelator skeleton followed by rebuilding of the structure to much greater domains, (ii) for aerogels – an inclination to collapse was observed only for the weakest gel. For the slightly stronger one, the structure was also completely rebuilt, but in another way, probably by Ostwald ripening.

The results call in question the very popular opinion of the existence of fibrilar, not fractal structure of these gels, because this opinion was created mainly on the basis of their microscopic (SEM and TEM) observations and refers to dried gels.

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5. References

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