

NON-TYPICAL, INCLUDING STRUCTURAL TRANSITION, GELATION PROCESS OF MONOSACCHARIDES

H. Grigoriev

Institute of Nuclear Chemistry and Technology, Dorodna 14, 03-195 Warsaw, Poland

Keywords: structural transition, gelation, monosaccharide

e-mail: hgrigori.ichtj.pl

During gelation process, ruled by self-assembling, aggregates built of bonded and/of polymerized molecules are formed. Through the gelation process their size increases monotonically until a great supramolecular structure is formed.

The monosaccharide gelators can form physical, weak organogels of very low gelator concentration. The small, compact molecules of gelators can be held together only by weak, non-covalent interactions, and many aspects of these materials gelation are still unclear. One of the existing opinions, formed on the basis SEM pictures of the gels, is, that the gelator and solvent molecules form a homogenous mixture into sol phase, and, at the gelation point, they separate, forming an infinite fibril-like structure of the gelator in the medium. But SEM uses dried samples, and results of our study of these gels in wet and dried state showed that drying process caused a great structural changes in monosaccharide gels [1].

The experimental studies performed by us at SAXS beamlines of HasyLab and Elettra synchrotrons were as follows. (i) In situ studies of gelation of galactose-based gelator with benzene as a solvent, in room temperature, using time resolved mode [2]. (ii) Temperature influenced gelation of galactose-based gelator with diphenyl ether as a solvent, also using time-resolved mode [3]. (iii) Study of dependence of glucofuranose gels (with toluene as a solvent) structure on the gelator concentration [4]. The glucofuranose-based gelators molecules are larger, than galactose-based and each includes three (not two) free –OH groups.

The obtained experimental data, $I(q)$ [2-4], were analyzed using a row of methods:

a/ *Fractal structures* were identified for SAXS curves [$\log(I)$ vs $\log(q)$] through appearance of straight-line segments in q ranges related to one of fractal type: 1/ for larger q , after the Porod bend - to surface fractal of primary particle, of dimension $d_s = 6 - \text{segment slope}$, with values change from 2 - for smooth surface, to 3 - for very irregular and rough one, and 2/ for smaller q - to mass fractal of average aggregate, d_m , of dimension equal to value of the slope, not exceeding three.

b/ *Distance distribution function*, $p(r)$ in real space, which is connected with SAXS scattering data by Fourier transform (where $s = q$):

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty sr(I_s) \sin(sr) ds$$

c/ *Radius of gyration*, R_g . It is a shape-independent value, presented size of aggregate calculated from $p(r)$,

d/ *Aggregate model* built by Monte Carlo method through fitting its pair function with the experimental one.

The analyses results, obtained for sets of data in Refs. [2-4] were compared. The subsequent increase of gelator concentration [4] was compared with progressing stages of gelation [2, 3].

The run of gelation process of galactose-based gel with benzene as a solvent [2], showed in Fig. 1,2 and Table I, is as follows: for sol structure (Figs. 1a, 2a and Table I, meas. No. 2) aggregates exist, and are loose, of the largest size, oval-type shape, and without determined surface (lack d_s). At measurement No. 4, the big decreasing of R_g and rough but defined aggregate surface (Table 1) are detected. For the next measurements aggregate become denser, of rod-like shape (Fig. 1b and 2b) and mainly smoothness of the surface is more and more smooth (d_s in Table 1).

The similar run of structural changes during temperature-influenced galactose-based gelation, with diphenyl-ether as a solvent was registered [3].

During subsequent increase of glucofuranose-based gelator concentration [4], the structural changes registered in Table II are: for gel of the smallest concentration, the aggregate is the largest and, as above, only one fractal dimension is visible (Table 2). However, it is surface fractal. This seems to be caused by a change of two free –OH groups in galactose molecule for three such groups in glucofuranose one. Then, each gelator molecule can form 2twohydrogen bonds for galactose, *i.e.* one-dimensional chain, but 3 hydrogen bonds for glucofuranose can form 2-dimensional surface. In this way we found a confirmation, that hydrogen bonds are formed in these gels during gelation.

For increasing concentrations of glucofuranose can be observed: at 0.5 %—an appearance of second kind of aggregates with smooth surface, which become the only for biggest concentration (two d_s values). Also the gradual decrease in aggregate size is observed (Table II). Besides, the shape of aggregate change from the oval- like for the smallest concentration to rod-like for the largest one.

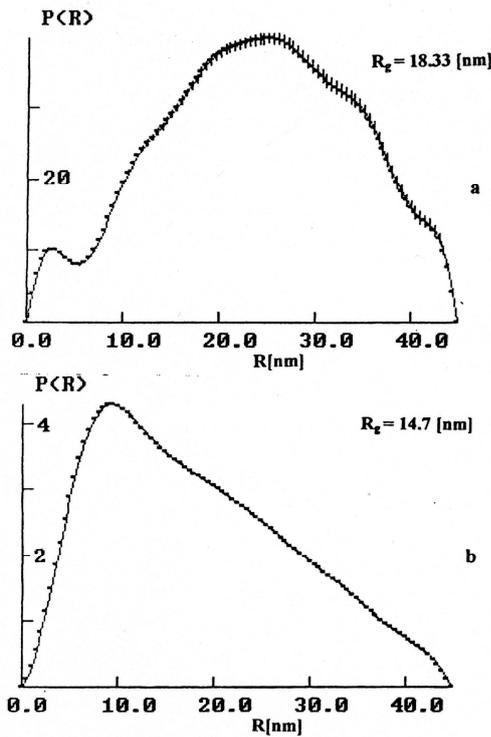


Figure 1. Pair curves, $p(r)$, for the sol (a) and the gel (b) [2].

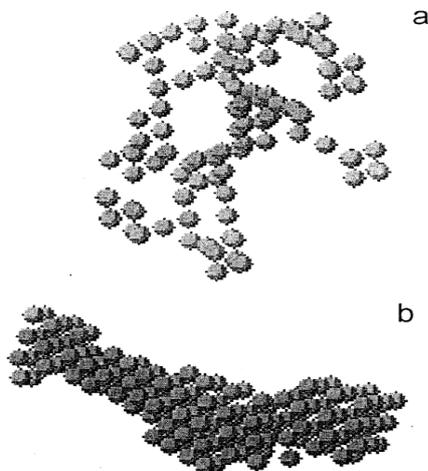


Figure 1. The aggregate model, for the sol (a) and the gel (b) [2].

Table 1. Structural parameters through gelation of galactose [2]

No. of	d_m	d_s	R_g
	Measurement		
2	1.58	-	18.33
3	1.79	-	17.72
4	1.79	2.90	14.88
10	1.84	2.29	14.56

Table 2. Structural parameters of concentration dependent glucofuranose gels [4].

Concentration %[g/mL]	d_m	d_s	R_g
0.1	-	2.9	61.9
0.5	2.7	2.2-2.7	60.7
1.0	2.6	2.2	57.4
3.0	2.8	2.2	49.7

The observed structural changes do not agree with aggregation ruled by self-assembling [5], and can be explained only by taking into account a structural transition, takes place after the initial stage of the aggregation.

Conclusions:

The gelator aggregates of fractal type exist also in a sol state. Supramolecular structure of studied sols and gels seems to be dependent on level of participation of the aggregates: i/ *small participation*- aggregates are of rounded, oval-type shape and loose, simple fractal structure including medium, ii/ *big participation* – aggregates are denser, partly occupy volume and are of rod-like shape and well-defined surface. The change of the aggregate structure from: i/ to ii/ is of structural transformation type.

The number of free –OH groups in the sugar molecule influences the formation of mass or surface fractals.

References

[1] H. Grigoriev, D. Chmielewska, J. Gronkowski, "SAXS structural study of Xerogels and Aerogels formed from small-molecule organic gelators", *J. Physics: Conf. Series*, in print.
 [2] H. Grigoriev, R. Luboradzki, S. Cunis, "In situ studies of monosaccharide gelation using the small-angle X-ray scattering time-resolved method", *Langmuir* **20** (2004) 7374-7377.
 [3] S. Bernstorff, H. Grigoriev, D. Chmielewska, "Structural change induced by temperature increase in monosaccharide gel", *Annual Report* (2006), SAXS beamline at ELETTRA, pp. 101-102.
 [4] H. Grigoriev, R. Luboradzki, J. Gronkowski, "USAXS studies of monosaccharide gels I. Dependence of glucofuranose-based gel structure on the gelator concentration", *J. Non-Cryst. Solids* **352** (2006) 3052-3057
 [5] H. Grigoriev, J. Gronkowski, "USAXS study of monosaccharide gels II. The common features of structural changes", *J. Non-Cryst. Solids* **352** (2006) 5492-5497

ISSRNS 2008 – abstracts