



# On the relation between the solvent parameters and the physical properties of methyl-4,6-*O*-benzylidene- $\alpha$ -D-glucopyranoside organogels

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## ABSTRACT

This paper reports the mechanisms of gel formation, the thermal properties and the microstructures of the networks of the gels composed of methyl-4,6-*O*-benzylidene- $\alpha$ -D-glucopyranoside and selected organic solvents: *p*-xylene, benzene, toluene, diphenyl ether and tetraethoxysilane. The Fourier transform infrared measurements together with simulation spectra, the air bath method and Polarized Optical Microscopy were employed in our studies. The experimental data show that the solvent has an influence on the microstructure of the gel network but there is no predictable influence of the solvent polarity on the shape of the formed gelator aggregates and correspondingly on the fibrous assemblies as revealed by the different microstructure of the gel network. Independently of the solvent polarity, the studied gelator, like other methyl-4,6-*O*-benzylidene derivatives of monosaccharides, formed gels through the formation of a hydrogen-bond network. The solvent parameters, such as the dielectric constant, Hildebrand solubility parameter, the polarity scale  $E_T$  and the Kamlet–Taft parameters were considered to quantify solvent effects on the gelation. The conclusions about the correlations are of interest but only to this particular sugar based gels.

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## 1. Introduction

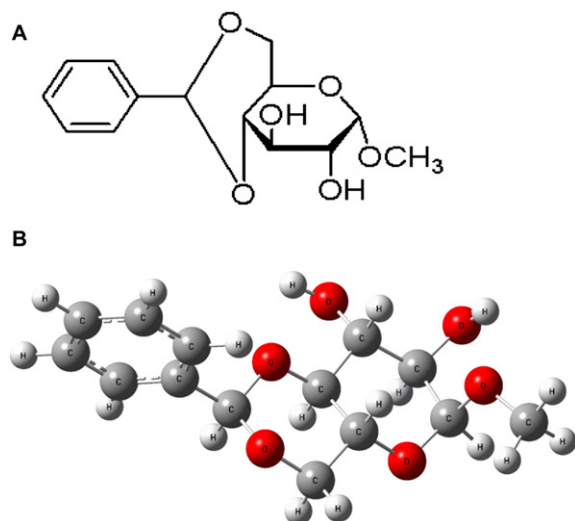
Organogels composed of low molecular-mass organic gelators (LMOGs) and solvents belong to the soft materials, which are receiving increasing interest due to numerous applications, such as, e.g., in tissue engineering, sensors, as viscosity modifiers or as templates for nanoparticles, and in drug delivery.<sup>1–3</sup> The gelation by the self-aggregation of the organogelators molecules is mediated only by physical interactions and thus the resulting gels are classified as physical gels. The aggregation leads to the formation of elongated fibrillar structures, which form an entangled three dimensional solid network. Such nanostructures are strong enough to block the flow of solvents.<sup>1,2</sup> The characteristic feature of the LMOGs is their ability to gel various organic solvents at a very low gelator concentration of less than 0.5% [wt %].<sup>4</sup> The gel network structure, the nature of physical interactions, the critical concentration values of the gelator, the change in the motion of the molecules, or thermodynamic parameters associated with the gel formation are widely studied by different methods: X-ray diffraction, small-angle neutron scattering and scanning electron

microscopy (SEM),<sup>5–10</sup> <sup>1</sup>H nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR),<sup>11–14</sup> or by rheology, and microscopy.<sup>1</sup> Understanding of organogel self-assembly and structure is essential for molecular design.

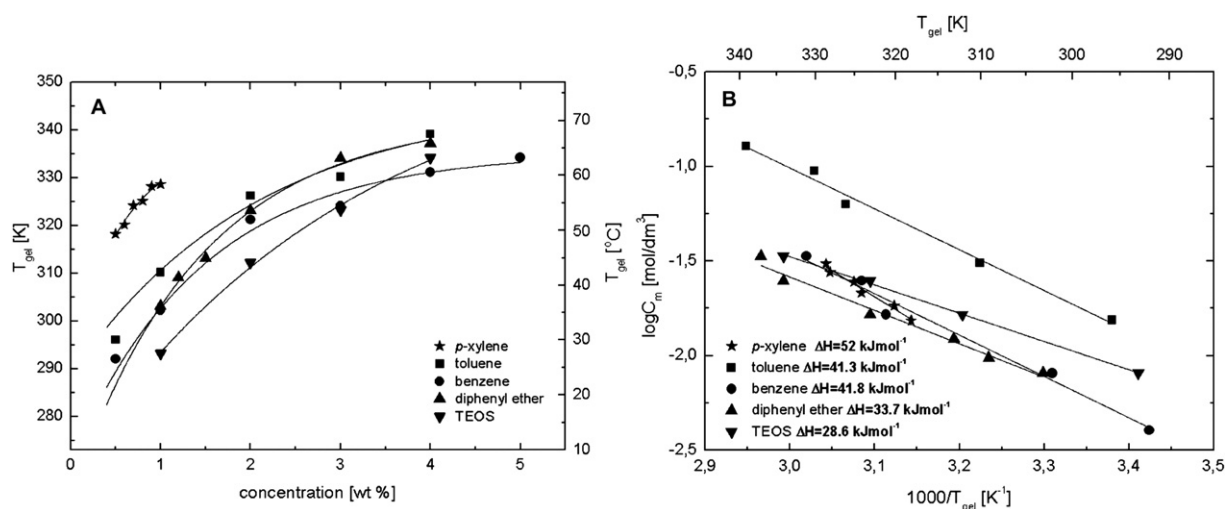
Despite the numerous studies performed on LMOG gels the design of a new gelator in a particular solvent is still a difficult task. Moreover, some questions concerning the gelation are still unfamiliar, e.g., the nature of the solvent–gelator interactions and why the same gelator forms such different microstructures of the gel network in different solvents. These important and still open questions are the subject of our work.<sup>15–19</sup>

In a large family of LMOGs, carbohydrates are attractive compounds because their structure can be easily modified to obtain different classes of gelators and because some of them are biocompatible and can have biological applications.<sup>4,7,14–28</sup> The methyl-4,6-*O*-benzylidene- $\alpha$ -D-glucopyranoside (gelator **1**, see Fig. 1), one of the representatives of this family of gelators, is the subject of our paper. While this sugar based gelator might seem old, it is actually still new and not yet fully explored gelator.<sup>4,21,27</sup> The structure of **1** has two unmodified hydroxyl groups 2-OH and 3-OH. The others hydroxyl groups are protected by a methyl group (1-OH group) and by a benzylidene group (and 4-OH and 6-OH).<sup>4,21,27</sup> In the solid state, **1** forms one-dimensional zigzag chains, in which molecules are connected by two hydrogen bonds using 2-OH and 3-

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**Fig. 1.** (A) Chemical structure of the organogelator, methyl-4,6-*O*-benzylidene- $\alpha$ -*D*-glucopyranoside ( $C_{14}H_{18}O_6$ ) used in this work and (B) the optimized geometrical structure of the gelator molecule.



**Fig. 2.** Dependence of the gel-sol phase transition,  $T_{gel}$ , upon the gelator concentration of methyl-4,6-*O*-benzylidene- $\alpha$ -*D*-glucopyranoside in *p*-xylene, benzene, toluene, diphenyl ether and TEOS gels (A) and plot of the logarithm of the unit mole fraction of gelator at temperature  $T$  versus  $1000/T_{gel}$ . (B). The solid lines on Fig. 2B are the best fits of Eq. 1 to the experimental points.

OH. In addition, the phenyl groups positioned at the edge of this one-dimensional chain can show a  $\pi$ - $\pi$  interaction with the phenyl groups arranged in other one-dimensional chains. Although this interaction is weaker than the hydrogen-bonding interaction, it may play an important role when the chain is grown as a bundle.<sup>27</sup> The following organic solvents: benzene, toluene, *p*-xylene, diphenyl ether, tetraethoxysilane (TEOS) and carbon tetrachloride have been tested to form a gel with gelator **1**.<sup>21</sup>

In the present work, we turned our attention to the mechanisms of gel formation, the thermal properties and the microstructure of the network of the gels composed by methyl-4,6-*O*-benzylidene- $\alpha$ -*D*-glucopyranoside and selected organic solvents. We also discussed the solvent effects on the physical properties of the gels employing different solvent parameters, such as the Hildebrand solubility parameter ( $\delta$ ), dielectric constant ( $\epsilon$ ), the polarity parameter  $E_T$  or the Kamlet-Taft parameters.<sup>14,29–33</sup>

## 2. Results and discussion

### 2.1. Thermal effects

The gelation of **1** was studied in five different solvents: *p*-xylene, toluene, benzene, diphenyl ether and tetraethoxysilane (TEOS). Like others LMOGs, gelator **1** gelatinized these solvents through non covalent interactions and thus the thermally reversible gel-to-sol phase transition is a characteristic feature of the resultant gels. To compare their thermal properties, the measured gel-sol phase transition temperatures ( $T_{gel}$ ) are plotted against the gelator concentration (in wt %) and presented in Fig. 2A. The data for some concentration of **1** with *p*-xylene, diphenyl ether, toluene and benzene were already published before.<sup>21,27</sup> In this paper we supplemented these results with more data of different concentrations of the gelator and particular solvent and performed measurements for TEOS gel of **1**, which had not been performed until now. The comparison of the five different gels of **1** enables us to discuss the solvent influence on the thermal properties and microstructure of the gel composed by **1** with different solvents.

The  $T_{gel}$  depends on the polarity, type of organic solvents and on the concentration of gelator. In all investigated gels  $T_{gel}$  increased with increasing gelator concentration. The experimental results for  $T_{gel}$  versus gelator concentration  $C$ , such as presented in Fig. 2 is

widely recognized for molecular gels and can be interpreted as a melting or dissolution of gelator crystals.<sup>34</sup> Therefore, the gelator concentration corresponds to the solubility of its crystals in a solution at the  $T_{gel}$  temperature and can be described by Schrader's equation<sup>35</sup> (also referred as Schroeder–van Laar equation<sup>36</sup>)

$$\log C = -\frac{\Delta H}{RT_{gel}} + \text{constant} \quad (1)$$

where  $C$  is the molar gelator concentration,  $\Delta H$  is the melting enthalpy of the neat gelator;  $R$  is the universal gas constant. Using Eq. 1 for describing the physical gel is perhaps oversimplified but is generally accepted.<sup>1,3,35,37</sup> The enthalpies  $\Delta H$  of the sol to gel transition for studied gels of **1** were determined from the fit of Eq. 1 to the experimental points of a specific representation of  $\ln$  of the unit mole fraction of gelator at temperature  $T$  versus  $1000/T_{gel}$ . The obtained values are presented in Fig. 2B and correspond well with

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