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Tunable two-component saccharide-based gels: The effect of the co-operation of two glucofuranose-based compounds having different gelating abilities

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Addition of 1,2-*O*-(ethane-1,2-diyl)-α-D-glucofuranose, which is originally a poor organogelator, can support the gelating abilities of good glucofuranose-based organogelators. The properties of such two-component gels can be tuned by changing the proportion of the saccharides. The saccharide's ability to form two-component gels can be explained on the basis of its crystal structure, particularly, the way in which sugar molecules stack (or not) into hydrogen bond-based chains and the architecture of these chains. The thermal stability of the obtained two-component gels was characterised by measuring its T_{gel} temperature. SEM and XRD techniques were used to characterise the xerogels.

Keywords: gel; self-assembly; saccharide; X-ray structure

Introduction

In recent years, the development of new gelators of organic solvents, as well as the investigation of the gelating process and gel structure has received much attention (*1–10*). Gels derived from low-molecular-mass compounds have attracted special interest on account of their unique features, potential applications and relative simplicity of the gelator molecules. Low-molecular-mass gelators form gels that fall within the physical gels (in contradistinction to chemical gels) since, only non-covalent interactions between the gelator molecules are involved. The formation of the gel based on spontaneous self-assembly of gelator molecules under non-equilibrium conditions such as the cooling of oversaturated solutions is used as the typical preparation method. According to the type of driving forces of molecular aggregation, low-molecular-mass gelators can be classified into two categories: non-hydrogen bond-based and hydrogen bond-based gelators. The study saccharides having free OH groups fall within the latter group. The presence of intermolecular hydrogen bonds is responsible for self-assembling of the gelator molecules, which leads to the formation of a fibrous superstructure, as can be observed in the TEM and SEM pictures of xerogels. The structure of a particular fibril as well as the process of gel formation can be investigated by small angle X-ray scattering (*11*). Analysis of the crystal structure of the pure gelator can shed light on its gelating ability. Despite significant progress in this field during the last decade, the accurate design of a new gelator is still a hard task. The basic feature of the gelator molecules is their ability to stack into one-dimensional chains. Thus, the prediction of a new gelator can often be made per analogy according to the rule that if the molecule looks similar to already-known good gelators, it will stack in a similar way and thus also possess gelating abilities. Bis-urea compounds are excellent examples of this concept (*2*). The correlation between the hydrogen bond network in the bulk crystal and gelating ability was also shown for the class of pyranoside derivatives (*12–13*). On the other hand, saccharides having three free OH groups can form different hydrogen bond-based networks, even if the configuration of the saccharide ring remains unchanged: in other words, they look similar but can pack in quite a different manner that seems to be responsible for increasing the margin of unpredictability. Nevertheless, the 'crystallographic approach' still seems to be a useful tool, also for this class of gelators. Glucofuranose derivatives were chosen as they are one of the simplest, smallest and most efficient gelators. Moreover, having an unchanged furanose ring with three unprotected OH groups, they can be easily modified by changing the hydrophobic fragment connected to the dioxolane C-2′ carbon atom (Figure 1).

A two-component gel can be defined as a system in which an individual component can be present in an isotropic solution, and only the addition of the second component will actually form a gel. In some cases, however, systems containing a gelator and a second component that modifies its behaviour, and/or the

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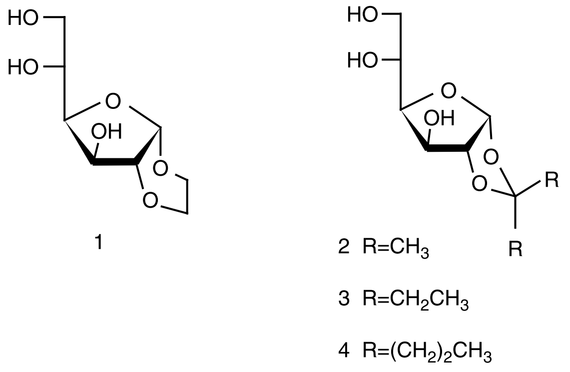
1

2 $R=CH_3$

3 $R=CH_2CH_3$

4 $R=(CH_2)_2CH_3$

Figure 1. Structure of monosaccharides **1**–**4**.

properties of the gel can also be assumed to be two-component gels (*14*). Different systems have been used to generate two-component gels, based on hydrogen-bonding interactions (*15*), π–π interactions (*16*), metal–ligand bonds (*17*), etc. The fact worth highlighting here is the necessity of co-operation on a molecular scale between two components for a new structure to form. From this point of view, even two good gelators can form a two-component gel.

Two-component gels are significantly rarer than single-component systems. On the other hand, two-component systems have a vast degree of tenability. This allows designing of gels towards a novel form of functional gel-phase materials.

Experimental

Materials

The saccharides were prepared according to the literature procedure (*19–20*). Solvents were purified and dried according to the literature methods.

Gelation test procedure

The gelation test was carried out as follows: the gelator was mixed in a closed capped tube with the appropriate amount of solvent to result in a concentration of 3% [g ml^{-1}] (about 15 mg of gelator and 0.5 ml of solvent was used). The mixture was heated until the solid was dissolved and then about one further minute. The solvent boiling point was usually reached by this procedure. The test tube was cooled in air to 20°C, left for 24 h at this temperature and then turned upside down. When the gel was formed, the whole procedure was repeated with the concentration below 1%. Once we had found by chance the gel formation in the concentration over 3% (while at 3% it was marked as 'S'), all the 'S'-marked systems (solution in 3%) were checked in higher concentration until we got either G (S → G) or P (S → P). In some cases, however, the solubility was so high and the amount of the gelator so limited that a final answer could not be given. In the case of 'I' at 3% starting concentration, lower concentrations were used in order to fully dissolve the saccharide, as the presence of crystals can influence gelation (to ultimately obtain either I → G or I → P). In addition to usual 'invert vial test', all the gels were examined using an optical microscope to exclude self-supporting precipitation.

Gel–sol transition temperature

The test tube containing the gel was put in a thermostated water bath. The temperature was raised at a rate of 2°C/min. Here, the T_{gel} was defined as the temperature at which the gel turned into sol phase. If, at the beginning, the gel started to leak solvent, this was defined as the start of the process that ran until the whole volume of the gel turned into sol.

SEM observations

SEM observations were performed using a scanning electron microscope-type DSM 942 (Zeiss, Jena, Germany) and Philips 515 in the secondary electron (SE) mode. The gel was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated by a vacuum pump for about 8 h. Samples were fixed with conductive glue to the SEM holder. Then the samples were coated with a thin layer of Au to protect them from heat destruction and to maintain the real parameters of the observed details.

XRD on xerogels

Xerogels were prepared using the same procedure as for SEM samples. The Bruker D8 Advance diffractometer was used, with Cu(K_α) radiation. The samples were measured in the 2θ range from 5° to 50°. Five scans were performed for each sample (each scan 12 h) showing no time-dependent changes in the XRD pattern.

Results and discussion

In addition to the previously reported class of saccharide-based gelators (*18–19*), we synthesised 1,2-*O*-(ethane-1,2-diyl)-α-D-glucofuranose (**1**) (*20*). The reason behind this is its molecular arrangement in a single crystal in which the molecules of **1** assembled in one-dimensional chains, as can be expected for a good gelator. Nonetheless, probably because of the relatively small hydrophobic part connected to O2 and O3, this compound was found to be a poor gelator, along with very low solubility in most organic solvents, as shown in Table 1.

Table 1. Organic solvents tested for gelation by **1**–**4**.

Solvent	Test results **1**	 **2**	 **3**	 **4**
Toluene	I → P	G	G*	G*
Benzene	I → P	G	G*	G*
p-Xylene	I → P	G	G*	G*
Carbon tetrachloride	I → P	G*	G*	P, PG
Nitrobenzene	P, SSP	G	G*	G*
Chloroform	I → P	G*	G	P, PG
Dibenzyl ether	I → P	G*	G*	G*
Cyclohexane	I → P	G*	P	P
n-Hexane	I → P	P	P	G*
n-Heptane	I → P	P	P	G*
Methanol	P	S	S	S
Ethanol	P	S	S → P	S → P
Acetonitrile	P	P	S → P	S
Ethyl acetate	I → P	P	P	S → G
1,4-Dioksane	P	S	S → P	S → P
THF	I → P	S	S	S → P
Water	P	S	S	S
Acetone	I → P	P	S	S → SSP

G, gel at 3.0 wt/vol%; G*, gel even under 1.0 wt/vol%; PG, partial gel; S, solution; P, precipitation; SSP, self-supporting precipitation; S → G, solution at 3.0 wt/vol% then gel at higher concentrations; S → P, solution at 3.0 wt/vol% then precipitation at higher concentrations; I → P, insoluble (not fully soluble at 3.0 wt/vol%) precipitation after dissolving at lower concentration.

On the other hand, the hydrogen bond-based chains in the bulk crystal of **1** are very similar to such chains observed in the crystal structure of a good gelator, namely 1,2-*O*-isopropylidene-α-D-glucofuranose (**2**) (Figure 2).

This inspired us to use compound **1** as a material that can 'support' gelation. Because of the perfect fit, the molecules of the gelator can be replaced by the molecules of **1**. Thus, the addition of **1** to the gelator–solvent mixture should lead (during the gelation process) to a larger number of gelator fibrils that should be reflected in the changed mechanical and thermodynamical properties of the gel. Moreover, the molar ratio of **1** can be changed smoothly, allowing these properties to be tuned quite well. The proposed mechanism is shown in Figure 3. In order to prove this concept, the samples of gels formed by **3** and **4** were prepared with the addition of different amounts of **1**, and the thermal stability of those gels was tested. The gelator concentration was fixed as 1 or 2% (wt/vol [g ml^{-1}]) and the concentration of **1** was 0, 0.01, 0.03, 0.06 and 0.12%, respectively. In some cases (mostly when CCl_4 was used), compound **1** tends to crystallise as a separated phase, which simply leads to a mixture of crystals and gel phase. However, in several cases (**3**/toluene, **3**/benzene, **4**/toluene, **4**/benzene), good transparent gels were obtained. The T_{gel} of such systems

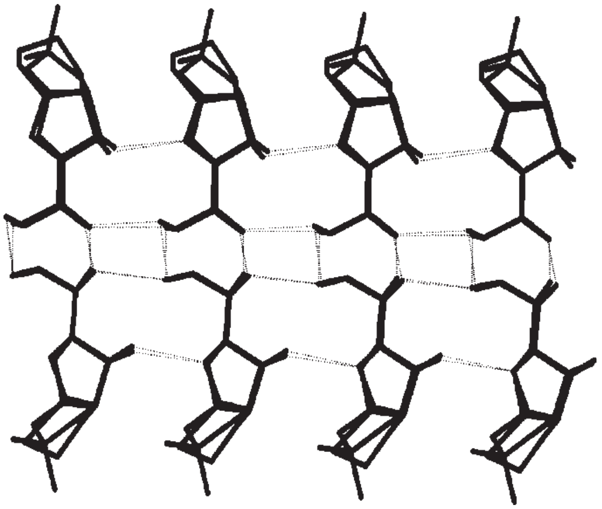

Figure 2. Least-squares fit of two fragments of hydrogen bond-based chains observed in the crystal structures of **1** and **2**. Fit based on all C4 atoms and hydrogen atoms have been omitted for clarity. H-bond lengths (donor···acceptor) range from 2.728 to 2.816 Å for **1** and from 2.758 to 2.878 Å for **2**, and may be assumed as typical.

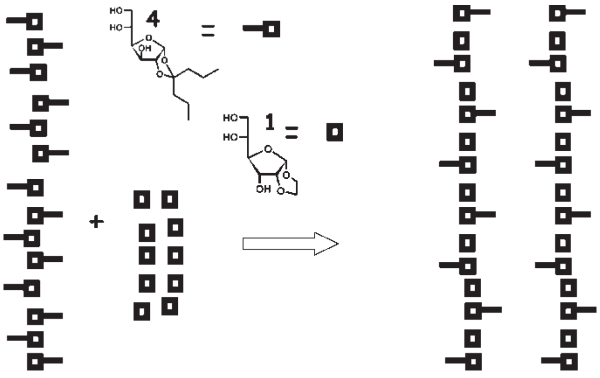

Figure 3. Possible mechanism of the way in which molecules of **1** can support the gelation of **4**.

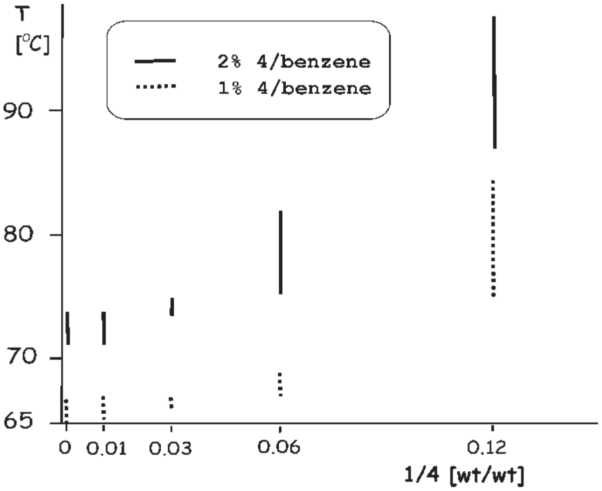

Figure 4. T_{gel} against **1**/**4** [wt/wt] (poor/good gelator) ratio in **4**/benzene gels. Higher concentrations of **1** usually could not be reached because of its low solubility, or the solution of **1** became so over-concentrated during cooling that **1** started to crystallise before compound **4** started to gelatinise the solvent.

depends strongly on the concentration of **1** and, as shown in Figure 4, can increase significantly once a certain concentration is exceeded. In addition, the temperature range from the start to the end of the process becomes wider, which may suggest that melting of such two-component gels is a more complicated process than in simple one-gelator systems. To obtain a visual insight into the aggregation mode, xerogels of **3**/benzene, **1**/**3**/benzene and dry **1**/benzene microcrystals were prepared by the freezing and pumping method. As expected, gelator **3** forms a three-dimensional network containing a large number of fibril–fibril junction points. A similar structure can be observed in **1**/**3**/benzene systems. Pure **1** also forms a fibrilar network, but the number of junction points is significantly lower and the fibrils are straight and longer. This picture may suggest self-supporting precipitation (which is compatible with data in Table 1), as the ability to form a fibre structure is not enough to act as a good gelator (*13*). Powder X-ray analysis was performed on dry samples of **3**/benzene, **1**/**3**/benzene and **1**/benzene. The **1**/benzene XRD pattern shows peaks that can also be observed for crystalline **1** or calculated from its crystal structure (*21*). The XRD patterns for **3**/benzene and **1**/**3**/benzene show a completely amorphic material. This confirms that **1**/**3**/benzene gel is not only a sum of two separate networks of **3** and **1** but is a genuine two-component gel, where poor gelator **1** modifies the thermal stability of the network formed by good gelator **3** and vice versa, and **3** modifies the behaviour of **1** (Figure 5).

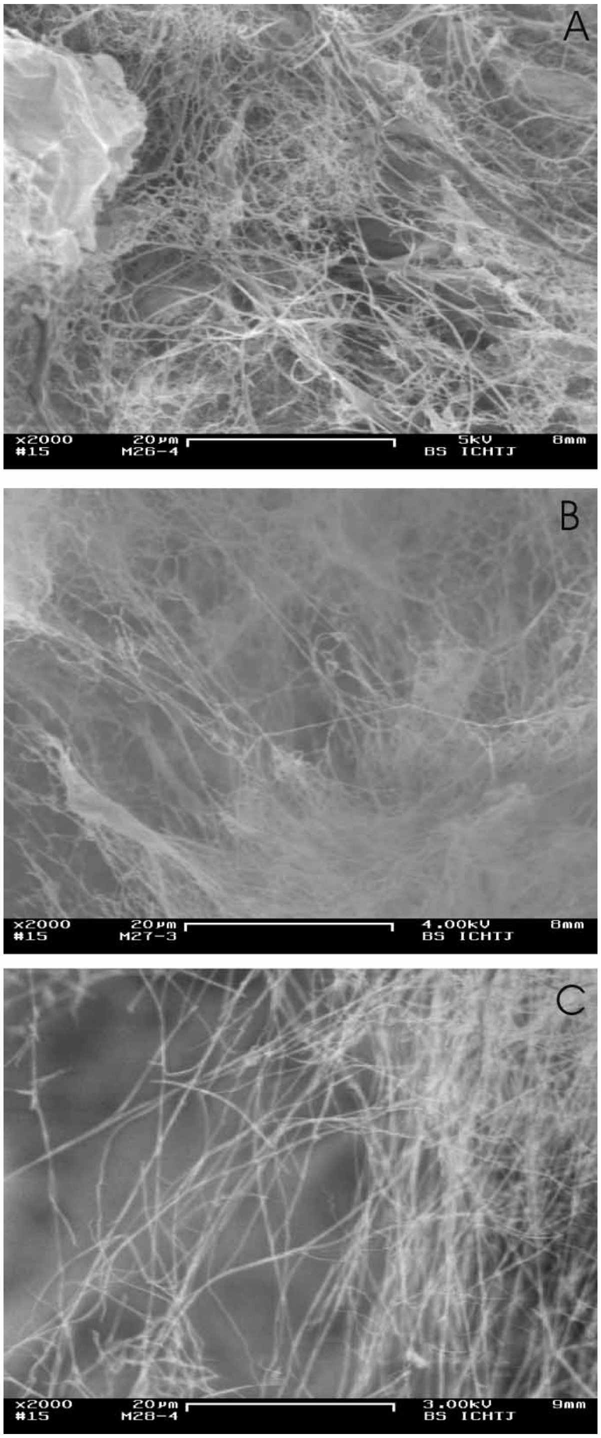

Figure 5. SEM pictures of dried samples of (A) **3**/benzene (0.5% wt/vol), (B) **1**/**3**/benzene (0.035 and 0.5%, respectively) and (C) **1**/benzene (0.02%).

Conclusion

In this paper, we demonstrated how the 'crystallographic approach' can help to design not only a particular gelator, but also a two-component gel. Based on the similarity in the crystal structure of different monosaccharides, we proposed two-component systems that can gelatinise different organic solvents. This tool seems to be particularly useful for two-component (+ solvent) systems – much more complicated than one-component typical gels.

Additionally, we introduced the new two-component gels whose properties can be continuously changed just by gently changing the concentration of one compound.

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