Sugar-Integrated “Supergelators” Which Can Form Organogels with 0.03–0.05% [g mL^{-1}]

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It was found that methyl-4,6-*O*-*p*-nitrobenzylidene-α-D-galactopyranoside (**1**) and methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**2**), which are scarcely soluble in apolar solvents, act as “supergelators” when they are enforcedly dissolved above their bp’s in a sealed tube. The minimum gelator concentrations (C_{min}) were 0.03–0.07% [g mL^{-1}] which are one of the lowest concentrations achieved so far. The coupled study of TEM observation with partial solvent exchange established that the organogel stability is related to the superstructure in the fibril network constructed in specific solvents.

The development of new gelators of organic fluids has recently received much attention. They not only gelate various organic solvents but also create novel fibrous super-structures which can be characterized by TEM pictures of the organogels and SEM pictures of xerogels.[1–11] Most gelators developed so far have long aliphatic chains in order to acquire the “moderate” solvent affinity. More recently, we found that certain saccharide derivatives can act as gelators even though they do not have any long aliphatic chains.[12] The finding implies that the intrinsic quality of the organogel formation is associated not only with the solvent affinity but with the aggregation mode forming one-dimensional molecular packing.[13] In this context, sugar-integrated gelators have an advantage exceeding others because one can design a variety of gelators easily derived from affluent saccharide library and find out an appropriate gelator structure most suitable to each solvent.

At least three different criteria may be taken into account when some compound is described as a “good” or “excellent” gelator. Those are (1) versatility of gelating solvents, (2) stability of the gel, including T_{gel} and other physico-chemical proprieties, and (3) minimum gelator concentration (C_{min}). It is known that the solubility of saccharide derivatives is drastically changed by a slight difference in their absolute configuration.[12] Among them, there are several saccharide derivatives which are scarcely soluble in most organic solvents or frequently result in the precipitate.[12] We have found, accidentally, that when they are forcibly dissolved above the solvent boiling point (bp) in a sealed tube, the solutions frequently provide the stable organogels.

Now, we have found that methyl-4,6-*O*-*p*-nitrobenzylidene-α-D-galactopyranoside (**1**) and methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**2**) (Figure 1) form gels with alkane solvents at very low concentration about 0.05% [g mL^{-1}] or less. Only a few similar results showing the comparable C_{min} values were previously obtained for nonhydrogen-bond-based gelators[14,15] and for hydrogen-bond-based ones.[16] Usually, the reported C_{min} is much higher and varied about 0.2% [g mL^{-1}]. All gels obtained from **1** and **2** prepared at around 0.1% were turbid, however at the lower concentration the most transparent gels were observed. The C_{min} values are given in Table 1. All gels are obtained by heating the mixture of the solvent and the gelator in a closed capped tube until the solvent start boiling and than a few further minutes. By this procedure the solvent bp becomes higher than that in the normal conditions. This process is indispensable to dissolve the almost insoluble saccharide in the solvent. No gels were obtained when an open bottle was used: only in the case of *n*-decane the result may be classified as a partial gel.

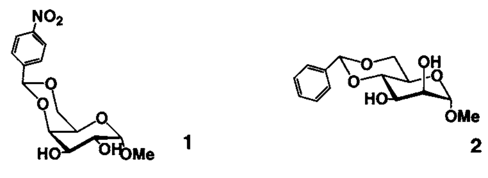

Figure 1. Structure of gelators.

Table 1 . C_{min} and solubility for gels made by **1** and **2** (g mL^{-1} × 100%)

	1		**2**
Solvent[a]	C_{min}	Solubility[b]	C_{min}[c]
n-Hexane	0.03	0.005	0.05
n-Heptane	0.05	0.0025	0.05
n-Octane	0.05	0.0025	0.05
n-Decane	0.04	0.0025	0.07
Cyclohexane	0.04	0.0025	0.2
Methylcyclohexane	P[d]		0.05
Carbon tetrachloride	0.07	0.03	P[d]
Carbon disulfide	0.08	0.04	0.3

[a]Solvent included in the table if C_{min} is lower than 0.1% [g mL^{-1}] for either **1** or **2**. [b]Solubility measured at 20 °C by cooling the hot solution. [c]Solubility not measured. [d]P = precipitation.

To obtain a visual insight into superstructural morphology in the organogels we took TEM pictures. The TEM pictures for *n*-hexane-**1** gel show a characteristic fibril structure with fibril diameter varied from 15 to 100 nm (Figure 2).

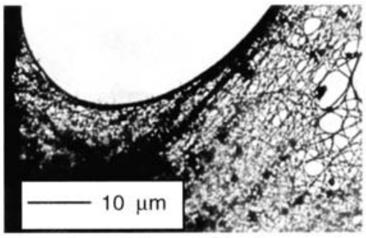

Figure 2. TEM picture of **1** *n*-hexane gel, not stained.

It is undoubted that in the present study the major driving-force for gelation is the hydrogen-bonding interaction. This force should be intensified in less polar solvents. Since the sol–gel phase-transition temperature (T_{gel}) increases with increasing gelator concentration,[7,12] the organogel should be further stabilized at higher gelator concentration. Because of the low saccharide solubility, however, the more concentrated gels with alkanes cannot be prepared. This inspired us to incorporate an aliphatic solvent into the already prepared gel network. Preliminary investigations showed that this idea cannot be realized by simply mixing the solvent with the xerogel. We thus tested the following procedure: that is, about 0.5 mL of 0.5% [g mL^{-1}] benzene gel of **1** were prepared and then the twice volume of *n*-hexane was added. The sample which consists of an upper homogenous solution layer and a lower gel layer was left for 7 days. The two layers were separated and each solvent composition was analyzed by using gas chromatography. In both cases *n*-hexane : benzene = 2:1 (v/v) proportion was found. This suggests that the partial solvent exchange runs unexpectedly smooth. The TEM pictures of the gel layers were taken for the starting benzene gel, the gel after partial solvent exchange, and the gel obtained directly from *n*-hexane : benzene = 2:1 (v/v) mixture (Figure 3).

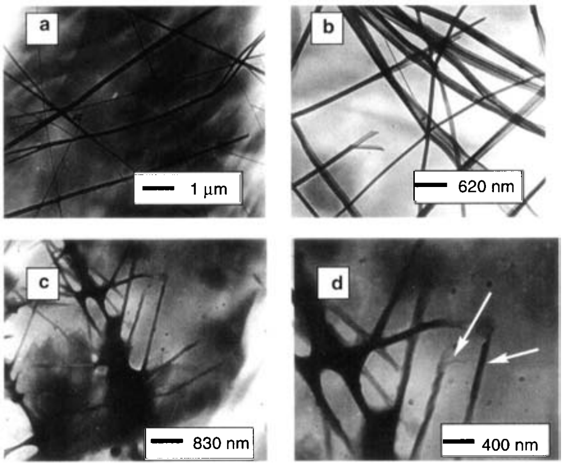

Figure 3. TEM pictures of **1** gels obtained from (a) benzene, (b) benzene partially exchanged to *n*-hexane (1:2), (c) benzene – *n*-hexane mixture (1:2), and (d) enlarged fragment of the picture c. The arrows show the helical fibers, not stained.

In the first two cases the pictures seem to be almost identical: the network consists of long straight fibers. The finding strongly suggests that the basic benzene gel fibril network is kept during the partial solvent exchange. Moreover, the TEM picture for the gel obtained directly from the mixed solvent is significantly different. Especially, the helical fibril structure can be observed, which is not present either in pure benzene or *n*-hexane gels. The T_{gel} measurements also support the differences between the gel prepared by using partial solvent exchange and that obtained directly from the mixture (Table 2). Very interestingly, it is seen from Table 2 that the T_{gel} values for the "exchanged" gels are higher than those for both the "original" gels and the "mixture" gels: in particular, the difference of ca. 30 °C is achieved in a $CCl_4 \leftrightarrow$*n*-hexane exchange system. Once the "exchanged" gel was melt during the T_{gel} measurement, its T_{gel} became identical to that measured for the "mixture" gel. The results suggest that at least two parameters are responsible for the thermal gel stability (T_{gel} value): they are the gel fibril structure and the solvent used for gel preparation. This conclusion has become evident only by using a novel solvent exchange method which has allowed us for the first time to separate these two factors.

Table 2. T_{gel} for gels formed by **1**

Solvent and gel preparation method	T_{gel}/°C
Benzene (0.5%)	68-71
Benzene (0.5%) exchanged with *n*-hexane (1:2 (v/v))	118-125
Mixture of benzene + *n*-hexane (1:2 (v/v))	105-108
p-Xylene 0.5%	80-90
p-Xylene (0.5%) exchanged with *n*-hexane (1:2 (v/v))	120-130
Mixture of *p*-xylene + *n*-hexane (1:2 (v/v))	115-124
CCl_4 (0.5%)	94-99
CCl_4 (0.5%) exchanged with *n*-hexane (1:2 (v/v))	127-131
Mixture of CCl_4 + *n*-hexane (1:2 (v/v))	98-115

In conclusion, the present paper reports an accidental but very interesting finding that when certain poorly-soluble gelators are enforcedly dissolved above the solvent normal bp's in a sealed tube, they act as novel "supergelators". The partial solvent exchange procedure established that this high stability is related to the superstructure of the fibrils which are specifically obtained in poor solvents. The novel findings indicate that the organogel stability is profoundly affected by the dynamic preparation process, which will give us the further chance to discover "hypergelators".

References and Notes

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