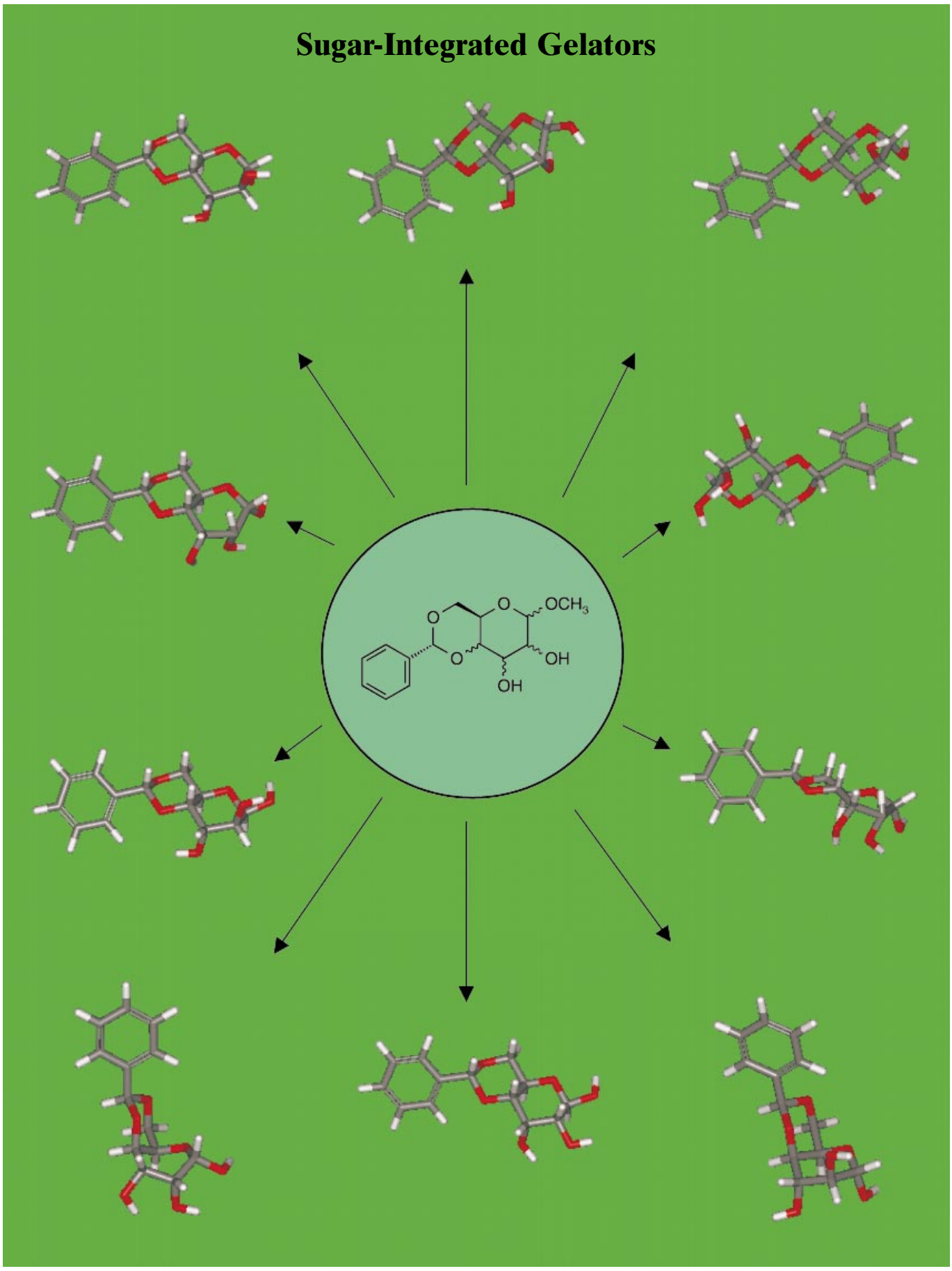

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Sugar-Integrated Gelators of Organic Solvents

Oliver Gronwald[a] and Seiji Shinkai*[a, b]

Abstract: Some methyl 4,6-*O*-benzylidene monosaccharides can act as strong low molecular weight gelators for various organic solvents. As they are accessible in a variety of homologues, each with a unique molecular architecture, they can be used for systematic studies of gelation phenomena. Structural details of their hydrogen-bond-based fiber network in the gel phase can be resolved by small angle X-ray scattering (SAXS). Analysis of the molecular arrangement in a single crystal can be a valuable tool for the prediction of gelation ability presupposing that the elongated shape of the gel fibers arises from an anisotropic assembly of the gelator molecules into one-dimensional aggregates. It is found that some derivatives act as "supergelators", which can gelate hydrocarbon solvents with 0.03 – 0.05 wt %. The recent results emerging from these investigations will be outlined in this article.

Keywords: carbohydrates · hydrogen bonds · sol – gel processes · X-ray diffraction

Introduction

Motivated by the numerous applications for gels, formed by dilute solutions of polymers, proteins, and inorganic substances,[1] the development of new low molecular weight gelators for organic solvents and investigation of their particular self-assembly properties have recently received much attention. They not only gelate various organic solvents but also create novel networks with fibrous superstructures, which can be characterised by scanning electron microscopy (SEM) pictures of xerogels.[2–13] The self-assembly of these gelling agents to fiber-like structures, which entangle to form a three-dimensional (3D) network, prevents the solvent from flowing similar to their macromolecular and inorganic counterparts.[14] Gelators can be classified according to their driving forces for molecular aggregation into two categories: nonhydrogen-bond-based gelators and hydrogen-bond-based gelators. Cholesterol derivatives[7–10] are typical examples of the former group whereas aliphatic amide derivatives[2–5] and saccharide-containing gelators[9, 15–17] are the main representatives of the latter group. As general guidelines for the design principles are accepted: i) the presence of strong self-complementary and unidirectional interactions to enforce one-dimensional self-assembly; ii) control of the fiber-solvent interfacial energy to control solubility and to prevent crystallisation; and iii) some factor to induce fiber cross-linking for network formation.[18] Despite the recent achievements elucidating the molecular prerequisites for gelation ability, the control of this aggregation phenomena is still a challenging goal. Recent studies demonstrated that methyl 4,6-*O*-benzylidene derivatives of monosaccharides are well-suited to study the structural prerequisites for gelation ability.[17] In gels these monomers establish rigid, strong, and highly directional hydrogen bonds. Their unique and well-defined molecular architecture added to the easy accessibility of a wide variety of isomers, each of which can be obtained as a single enantiomer and allows systematic studies to connect monomer structure and gelation ability. No other gelator discovered so far shows such a variety in its homologues: undoubtely, this mechanistic view utilising a rich carbohydrate library is one of the largest merits of sugar-integrated gelators. Here we give a brief description of their gelation properties and recent results of structural studies in gel state by small angle X-ray scattering (SAXS). The concept of unidirectional interactions as prerequisite for gelation ability is strengthened by correlation of the monomer structure with the molecular arrangement in single crystal and gel.

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Results and Discussion

Gelation properties: Methyl 4,6-*O*-benzylidene derivatives of monosaccharides belong to a well-established class of compounds, though they have yet not been fully explored as gelators. Also well known to form strong and highly directional hydrogen bonds, this type of compounds meets the requirements for systematic studies. Their features are i) un-

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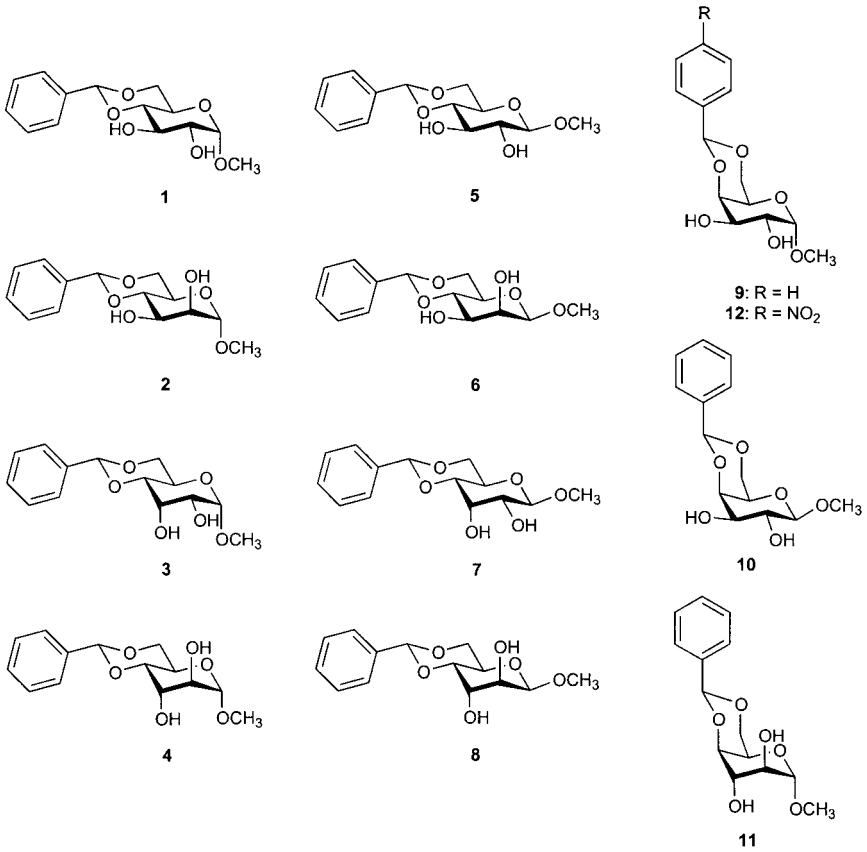
modified 2-OH and 3-OH group; ii) protection of the 1-OH group by a methyl group; and iii) protected 4-OH and 6-OH group with a benzylidene group, whereas their different abilities to gelate solvents are solely due to configurational isomerism. So far, eleven methyl 4,6-benzylidene derivatives of the monosaccharides D-glucose, D-mannose, D-allose, D-altrose, D-galactose, and α-D-idose (**1**–**11**) have been investigated (Scheme 1).

Among the criteria that have to be taken into account when the monosaccharides derivatives should be classified according their "quality" as gelators are: i) versatility of gelating solvents, ii) stability of the gel, including T_{gel} and other physico-chemical properties, iii) minimum gelator concentration (C_{min}).

A comparison of the gelation potential for 34 different solvents reveals the versatility of gelated solvents for the different methyl 4,6-benzylidene derivatives (Table 1):[17b, d, e] Among the α-monosaccharides **1**, **2**, **3**, **4**, **9**, and **11** only the *gluco* **1**, *manno* **2**, and *galacto* **9** isomers act as gelators. The widest variety of solvents is gelled by the α-*galacto* isomer **9**. The range of gelated solvents covers apolar hydrocarbon and aromatic solvents (entries 1–8), carbon tetrachloride, carbon disulfide, diethyl ether, diphenyl ether, *n*-octanol, triethylamine, triethylsilane, and tetraethoxysilane. The α-*manno* **2** isomer is able to gelate the similar range with the exception of cyclohexane, benzene, carbon tetrachloride, diethyl ether, *n*-octanol, triethylamine, and tetraethoxysilane. Additionally, **2** can gelate water at 3 wt% which is very uncommon for gelators. Compared with α-*galacto* and α-*manno* isomers, the α-*gluco* **1** shows a reduced gelation ability since it gels only benzene, toluene, *p*-xylene, carbon tetrachloride, diphenyl ether and tetraethoxysilane.

In contrast, the α-allo- **3**, α-altro- **4** and α-idopyranoside **11** tend to be insoluble in or precipitate out of solvents in group I. Most α-compounds dissolve in the more polar solvents of group II. On the other hand, among the β-isomers only the *manno* **6** and *galacto* **10** isomers can be considered as gelators. Both gelate nearly a similar range of solvents as their anomeric counterparts. In contrast to its α-anomer **9**, the β-anomer **10** forms a partial gel (Gp) in nitrobenzene, ethyl formate, and methyl acetate but precipitates in diethyl ether and tetraethoxysilane (**9**: both G*). Compared with its opposite anomer, β-*manno* **6** exhibits additional gelation ability for benzene and carbon tetrachloride but no gelation potential for water. The β-gluco- and allopyranosides (**5**, **7**) tend to form mainly gel-like solids as denoted by the numerous "P_S" marks. Similarly, the β-altropyranoside **17** exhibits a low solubility in the major part of the solvents tested, reflected by the "P" and "P_S" marks.

In order to compare the gel qualities, the gel–sol phase transition temperatures (T_{gel}) of gels of **1**, **2**, **6**, **9**, and **10** in *p*-xylene estimated by the oil-bath method are plotted against the gelator concentration (Figure 1). For the same concentration the T_{gel} values always appear in the order of: **10** > **6** > **9** > **1** > **2**. In other solvents similar results are obtained. Together with the results from Table 1 this confirms the conclusion that the *galacto* derivative tends to be more efficient than the *manno* derivative and that the α-anomer is inferior to the β-anomer. Consequently, α-*gluco* occupies an intermediate position between gelators and non-gelators because it forms P_s as well as gels. Therefore, the optimal requirements for a compound to be classified as a gelator are fulfilled only by methyl 4,6-*O*-benzylidene derivatives of D-mannose and D-galactose. Compared with other low molecular weight gelators these saccharides gelate a broader range of solvents. Especially, α-*manno* **2** reveals highly flexible gelation properties. Few other gelators are capable to gelate a broad variety of organic solvents *and* water at the same time.[19] Not only the variety of solvents but also the C_{min} reveals a further characteristic of sugar-based-gelators. Methyl 4,6-*O*-*p*-nitrobenzylidene-α-D-galactopyranoside (**12**) and methyl 4,6-benzylidene-α-D-mannopyranoside



Scheme 1. Methyl 4,6-*O*-benzylidene monosaccharides as gelators.

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Table 1. Organic solvents tested for gelation by **1**–**11**.[a]

	Organic solvent	**1**	**2**	**3**	**4**	**9**	**11**	**5**	**6**	**7**	**8**	**10**
					α-series					β-series		
group I												
1	*n*-hexane[b]	P_S*	G*	P*	I*	G*	P*	P_S*	G*	P_S*	P*	G*
2	*n*-heptane[b]	P_S*	G*	P*	I*	G*	P*	P_S*	G*	P_S*	P*	G*
3	*n*-octane[b]	P_S*	G*	P	P*	G*	P	P_S*	G*	P_S*	P*	G*
4	cyclohexane[b]	P_S*	P_S*	P	P*	G*	P*	P_S*	G*	P_S*	P_S*	G*
5	methylcyclohexane[b]	P_S*	G*	P	P_{PS}*	G*	P	P_S*	G*	P_S*	P*	G*
6	benzene[b]	G	P_S*	P_{PS}	P_{PS}	G*	S	P_S*	G*	P_S	P_{PS}	G*
7	toluene[b]	G*	G*	P_{PS}	P_{PS}	G*	S	P_S*	G*	P_S*	P_S	G*
8	*p*-xylene[b]	G*	G*	P_{PS}	P_{PS}	G*	S	P_S*	G*	P_S*	P_S	G*
9	nitrobenzene[b]	S	S	S	S	S	S	P_S	S	S	S	Gp
10	carbon tetrachloride[b]	G*	P	P	P*	G*	P	P_S*	G*	P_S*	P	G*
11	carbon disulfide[c]	P*	G*	P*	P*	G*	P_{PS}	P_{PS}*	G*	P_S*	P_S	G*
12	diethyl ether[b]	S*	S*	P	P*	G*	S*	P_S*	S*	P*	P*	P
13	diphenyl ether[b]	G	G	P_{PS}	P_{PS}	G*	S	P_S*	G	P_S	P_{PS}	G*
14	ethyl formate[b]	S	S	S	S	P	S	P*	S	S	S	Gp
15	methyl acetate[b]	S	S	S	S	S	S	P_S	S	S	P	Gp
16	*n*-octanol[b]	S	S	S	S	G	S	P_S	P	P_S	P	G
17	triethylamine	S*	S	S*	S*	G	P	P*	S	S	P	G
18	triethylsilane	P_S*	G*	P	S*	Gp	P*	P_S*	G*	P_S*	P*	G
19	tetraethoxysilane	G*	S	P	P_{PS}*	G*	P	P*	P	P	P	P
20	water	P_S	G	S	S	S	P	P*	S	P_S	P	S
group II												
21	1,2-dichloroethane	S	S	S	S	S	S	P_S*	S	S	P	S
22	dichloromethane[b]	S	S	S	S	S	S	P_S	S	S	P	S
23	chloroform	S	S	S	S	S	S	P_S	S	S	S	S
24	ethyl acetate[b]	S	S	S	P	P	S	P_S	S	P	P	S
25	ethyl malonate[b]	S	S	S	S	S	S	P_S	S	S	S	S
26	acetone[b]	S	S	S	S	S	S	P	S	S	S	S
27	methyl ethyl ketone[b]	S	S	S	S	S	S	P_S	S	P	P	S
28	acetonitrile[b]	S	S	S	S	S	S	P	S	P	P	S
29	ethanol[b]	S	S	S	S	S	S	P	P	P	S	S
30	*n*-propanol[b]	P	S	S	S	P	S	P_S	P	P	S	P
31	*n*-butanol[b]	P	S	S	S	S	S	P_S	P_S	P_S	S	P
32	hexanoic acid	S	S	S	S	P	S	P_S	P	P_S	P	P
33	acetic anhydride	S	S	S	S	S	S	P_S	S	S	S	S
34	glycerol	S	S	S	S	S	S	P_S	S	S	S	S

[a] 3.0 wt/vol %, * = 1.0 wt/vol %, G = gel, P_S = self-supporting precipitate (gel-like solid which is unstable to inversion), P_{PS} = partial self supporting precipitate, P = precipitation, S = solution, I = insoluble. [b] Dried over molecular sieves 4 Å. [c] Dried over anhydrous magnesium sulfate.

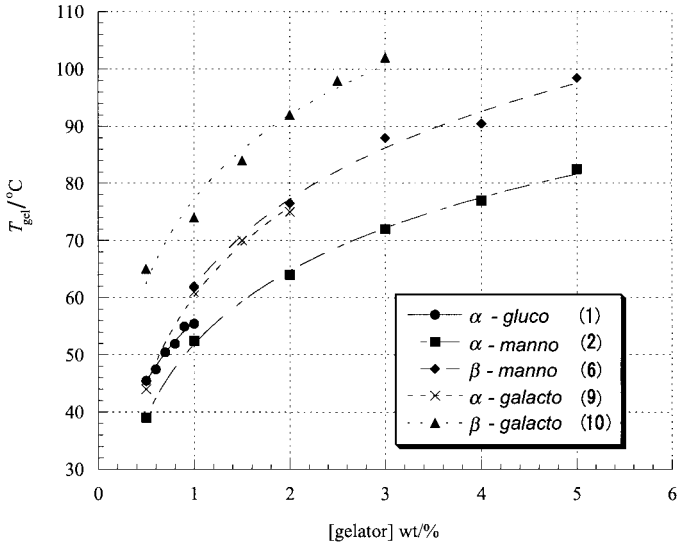

Figure 1. Plots of T_{gel} against gelator concentration in *p*-xylene.

(**2**) act as "supergelators" for apolar solvents. Both saccharides can gelate hydrocarbons (*n*-hexane, *n*-heptane, *n*-octane, *n*-decane, and cyclohexane) in concentrations around 0.03–0.05 wt/vol %.[17c] Compared with the typical gelator concentration range of 3–15 mM[12c] the C_{min} of 0.9–1.22 mM for **12** and 1.77–2.48 mM for **2** represent the lowest concentrations reported for organic solvents so far. Especially, the drastically lowered minimum gelation concentration of **12** compared with its non-*p*-nitro-analogue **9** opens new perspectives for certain solvents. Through preparation of further *p*-nitro-analogues, lower C_{min} might be obtained, which can facilitate further SAXS investigations since higher diluted systems provide clearer scattering pattern.

Mode of aggregation: Methyl glycosides of 4,6-*O*-benzylidene derivatives of monosaccharides aggregate the solvents through formation of a hydrogen-bond-based gel network. The evidence is given by FT-IR and temperature dependent ^{1}H NMR spectroscopy.[17a,b] Due to intermolecular and intramolecular hydrogen-bonding interactions, no $\tilde{\nu}_{OH}$ peak for a free OH group (around 3600 cm^{-1}) could be detected for the solid samples (KBr) of all monosaccharides. In the gel state all signals are more broadened and the $\tilde{\nu}_{OH}$ values for the OH groups appear in two groups between 3220–3475 cm^{-1} and 3573–3588 cm^{-1} (0.15–0.60 wt % in toluene) and can there-

fore be assigned to the intermolecular hydrogen bonds and free OH groups, respectively. The peak intensity ratio (R) of hydrogen-bonded OH to free OH abruptly decreases at the gel–sol transition temperature (T_{gel}), indicating that the gel network is primarily stabilised by intermolecular hydrogen bonding.[17b]

Additionally, the gels provided by sugar-integrated gelators offer the unique possibility to probe their thermal stability by monitoring the change of intermolecular aggregation near the T_{gel} region by temperature dependent ^{1}H NMR spectroscopy[20] by observing the chemical shift values for δ_{OH}.[17b] Due to the formation of strong intermolecular bonds at T_{gel}, the chemical shifts have their maximum downfield values at T_{gel}. Since the molecular motion of gelators drastically changes at T_{gel}, this phenomenon is reflected by the line broadening effect in the ^{1}H NMR spectrum.[17b] In the gel phase the mobility of gelator molecules is significantly suppressed, whereas in the sol phase it is comparable to that of a homogeneous solution. Therefore the width of the peak at half its height, $\delta_{1/2}$ of the PhCH methine proton is nearly constant above T_{gel}, while it increases with falling temperature below T_{gel}.

Molecular arrangement in single crystal and gel state: The above-mentioned results highlight that variations in the saccharide configuration result in a drastical change of the gelation properties. In an attempt to elucidate the origin of these differences, we turned our attention to the molecular arrangement in a single crystal. The question whether solid-state properties actually reflect solution properties has lead to contradictory results in the history of gel research. Crystal structures of gelator molecules have been scarcely reported up to now. Weiss et al.[6] proved that the gel fiber morphology of cholesterylanthrachion-2-carboxylate differs from the molecular packing of single crystals. For one urea-based hydrogen-bonded gelator Feringa[12b] demonstrated that its crystal structure does not account for low-angle reflections observed in toluene gels of this compound. Both studies suffer the disadvantage that each of them is based on only one example. Moreover, the fact that both investigated compounds showing polymorphism, limits the significance of the obtained results. In contrast, a very recent study demonstrated the successful design of efficient aryl-L-cystine hydrogelators based on the analysis of the crystalline "fibrous" molecular orientation of the non gelator-analogue di(*p*-toluoyl)-L-cystine.[19a] Since methyl 4,6-*O*-benzylidene monosaccharides are not prone to polymorphism and their organogel fibers are not so "wet" with solvent molecules,[6, 8, 10, 21] we expected them to display more or less crystal-like character, although the organogel fiber structure is somewhat more disordered than the crystal structure.[10] This implies, that the X-ray structure can make an important contribution to explain the mechanism of the organogel fiber formation.

Since the examined saccharide gelators tend to grow as needles, only some single crystals suitable for X-ray analysis have been isolated so far. The crystal structures of **1**,[17d] **3**,[22] **4**,[23] and **11**[24] have been determined or are available from the Cambridge Structural Database. As shown by Hanabusa et al.[2] and Feringa et al.,[12] amide-based- and urea-based-gelators tend to form one-dimensional hydrogen-bond arrays. In the solid state **1** forms one-dimensional zigzag chains, in which molecules are connected by two hydrogen-bonds using 2-OH and 3-OH (Figure 2). In addition, 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 chains grow up as a bundle. Since these characteristics of **1** seem to satisfy the prerequisites for a gelator, these results match with the observed gelation ability in aromatic solvents, carbon tetrachloride, and tetraethoxysilane.

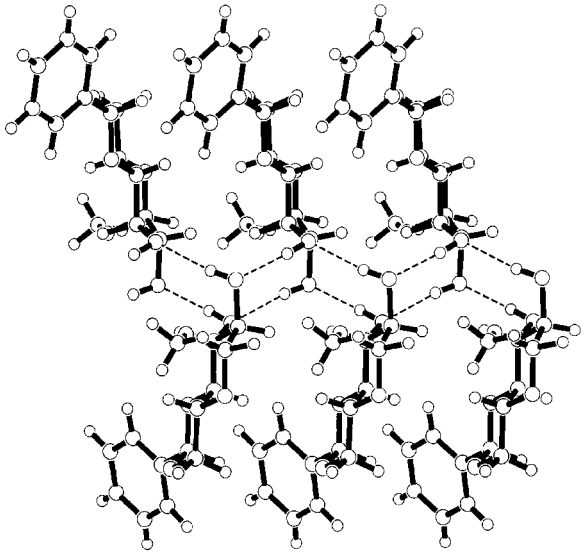

Figure 2. Molecular packing in methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**1**).

Compound **3** (Figure 3) also exhibits a one-dimensional chain structure. In this case, however, the molecular packing is supported by only one intermolecular hydrogen bond and the second one is used for the intramolecular interaction between the 3-OH and the 1-OMe. Hence, **3** basically satisfies the primary prerequisite to be one-dimensional. In the gel phase

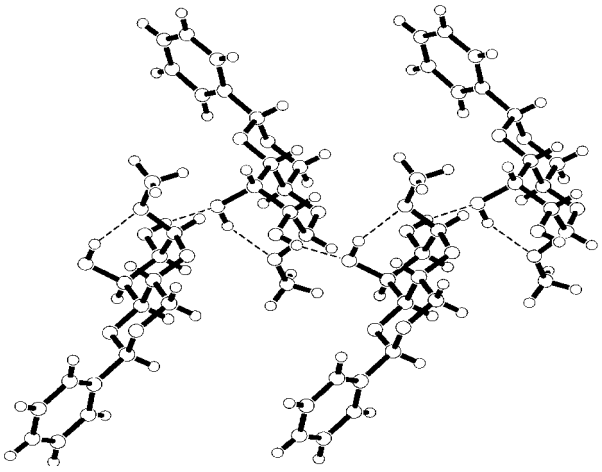

Figure 3. Molecular packing in methyl 4,6-*O*-benzylidene-α-D-allopyranoside (**3**).

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where the intermolecular hydrogen-bonding interaction must compete with solvation, however, the fibrous structure cannot be as stabilised as that of **1**. The instability gives rise to the disordered structure including free OH groups, the hydrogen bonds of which eventually result in the formation of three-dimensional, insoluble aggregates. This situation is reflected by many P and P* marks for which **1** has G and G* marks.

The crystal structure of compound **4** features saccharide molecules connected by hydrogen bonds between two OH groups and the 5-ether oxygen into two-dimensional layers (Figure 4). As a result, **4**, cannot construct a one-dimensional hydrogen-bonding array. In the crystal of compound **11**, on the other hand, two OH groups are both used to form the intramolecular hydrogen bonds and no significant intermolecular hydrogen bonding is found in the crystal structure (Figure 5). This may be called a zero-dimensional hydrogen-bonding array. As expected, compound **11** is very soluble in many organic solvents.

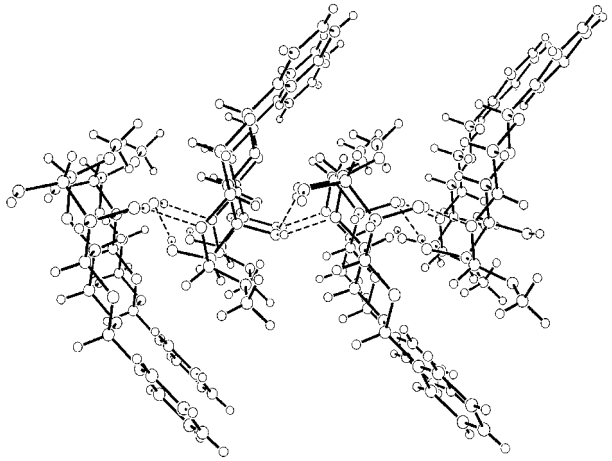

Figure 4. Molecular packing in methyl 4,6-*O*-benzylidene-α-D-altropyranoside (**4**).

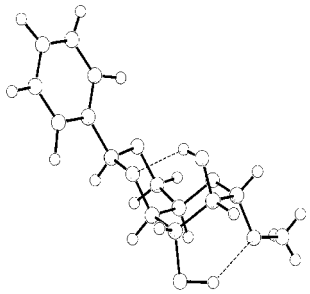

Figure 5. Molecular packing in methyl 4,6-*O*-benzylidene-α-D-idopyranoside (**11**).

Although not fully clear, these results underline that the molecular arrangement in the single crystal can be relevant for the ability of monomers to assemble in one-dimensional aggregates. The concept of unidirectional interactions as prerequisites for gelation ability is therefore strengthened as derived from investigations of the affluent saccharide library.

Investigation of the gel structure: To obtain visual insight in these structures, dry samples of organic gel fibers have been investigated by SEM.[25] Although in general the observed three-dimensional fiber network has been ascribed to the gel structure, the shrinking step induced by the freeze-drying procedure can result in collapses of the frail three-dimensional network. Thus, SEM might focus on general shapes and morphologies rather than on absolute quantities such as diameters, lengths, or topologies. To overcome these problems, synchrotron small angle X-ray scattering (SAXS), a powerful method to explore directly the supramolecular structure, can be used. Since the synchrotron X-ray is almost 10^6 times stronger than conventional X-rays, it has great a advantage for diluted systems such as organogels. Terech et al.[26] analyzed SAXS from different non-sugar-based organogelators. We measured SAXS with a BL-15A SAXS station at the Photon Factory High Energy Research Organization in Japan[27] from the sugar-based organogelators for the first time.[17e] The typical temperature dependent scattering profile of **6** (1.5 wt% in *p*-xylene) displays at 50 °C two broad peaks at $q = 0.018$ and 0.11 Å^{-1} (Figure 6). With increasing temperature (60 °C) the position of these peaks remains unchanged, however, the intensity of the peak at $q = 0.018$ Å^{-1} decreases about 50% and it disappears completely at 70 °C. Because the sol–gel transition temperature (T_{gel}) of this system was estimated by the oil-bath method to be 70 °C, this result supports the assumption that this peak can be assigned to the supramolecular structure of the gel.

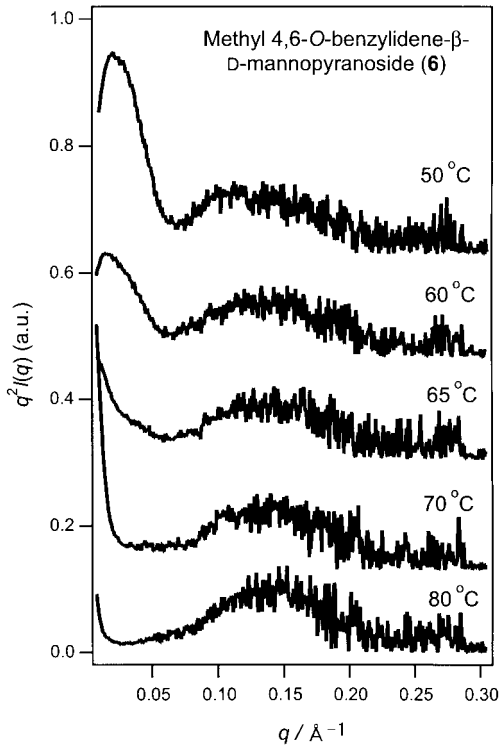

Figure 6. Temperature dependence of the SAXS profiles for **6** (1.5 wt% in *p*-xylene).

Recently, further investigations carried out at the BL45XU biophysics beam line at SPring8 in Japan[28] gave an improved scattering quality for gels of **2**, **6**, **9**, and **10** in *p*-xylene due to the higher S/N ratio. The fit of the scattering profiles with a

solid cylinder model indicated that all gels consist of fibers with an approximate diameter of 60 Å. For α-manno-saccharide **2** the SAXS investigation provided four peaks. The ratio of their position gives strong evidence that the cylinders assemble in a hexagonal packing mode.[29] These results clearly suggest that organogels of methyl 4,6-*O*-benzylidene derivatives of glycosides can be resolved at nanoscopic scale by SAXS. Current investigations are ongoing to correlate the molecular structure with the SAXS and SEM results.

Outlook

The aforementioned results clearly demonstrate that methyl 4,6-*O*-benzylidene monosaccharides serve as excellent library compounds for the investigation of the gelation phenomenon based on the formation of hydrogen bonds. Preliminary results suggest that these compounds provide a possible correlation of the molecular structure to the different gelation properties by analysis of the molecular arrangement in single crystal. Furthermore, structural details of their gel network can be deduced from the analysis of SAXS data. Both strategies to approach the gelation phenomenon from a microscopic and macroscopic viewpoint contribute to a better understanding of the process how small molecules gelate solvents. Additional studies of the sugar-integrated gelators must be useful for the discovery and design of new gelators. We believe that the saccharide library provided by nature can be applied further, in particular to the design of molecular assemblies, such as macrocycles, DNA mimics, monolayers, bilayer membranes, liquid crystals.

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