On the Delicate Influence of a Minute Amount of Water on the Organogel Stability Comprised of a Sugar-Integrated Gelator

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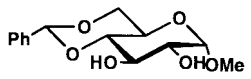
It was found that the stability of organogel of methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**1**) is sensitively affected by a minute amount of concomitant water: the maximum stability is observed at $[H_2O]/[\mathbf{1}] = 1.0$. The effect of water molecules on the organogel stability is well understood in relation to its crystal structures. Thus, this paper has provided an important admonition for the stability of hydrogen-bond-dependent organogels.

The development of new gelators of organic solvents has recently received much attention.[1] 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.[2–12] The gelators can be classified mainly into two categories, namely hydrogen-bond-based gelators and non-hydrogen-bond-based gelators. The typical examples for the former category bear amide or urea groups which can enjoy sufficient intermolecular hydrogen-bonding interactions. The typical examples for the latter category are cholesterol derivatives which tend to form one-dimensional molecular stacks. In addition, a new class of gelators in which both a cholesterol moiety and a hydrogen-bonding site are combined within a molecule has been exploited toward molecular design of universal gelators.[13] In these studies we have been wondering whether the stability of organogels in the former category is affected by a small amount of water concomitant in aprotic solvents, because such hydrogen-bonding sites should also act as good binding sites for water molecules. More recently, we found that certain saccharide derivatives can act as hydrogen-bond-based gelators[14,15] and the gelation ability is predictable, not entirely but to considerable extent, on the basis of the crystal structure.[16] For example, methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**1**) results in the single crystal which features one-dimensional array of two hydrogen-bonds (Figure 1) and acts as an excellent gelator of many organic solvents.[16] In contrast, some saccharide derivatives featuring zero-dimensional (intramolecular hydrogen-bonds only) or two-dimensional hydrogen-bonding array show the very poor gelation ability. The clear difference establishes that to form the one-dimensional hydrogen-bonding array is one of the prerequisites for good gelators. Surprisingly, we have found that when the crystal of **1** is grown up from wet *p*-xylene, it is composed of $\mathbf{1}:H_2O = 1:1$ stoichiometry. This unexpected finding prompted us to solve the X-ray structure of this single crystal and to assess the influence of a minute amount of water on the organogel stability.

The water-containing single crystal was obtained by slow recrystallization of **1** from wet *p*-xylene. The crystal structure was successfully solved as shown in Figure 2.[17] It is seen from Figure 2A that **1** molecules form one-dimensional hydrogen-bonding array using the 2-OH···1-OMe hydrogen bonds. This array is further crosslinked by water molecules using the 3-OH···HOH···3-OH hydrogen bonds (Figure 2B). In total, this crystal is classified into the two-dimensional one which is characteristic of poor gelators.[15]



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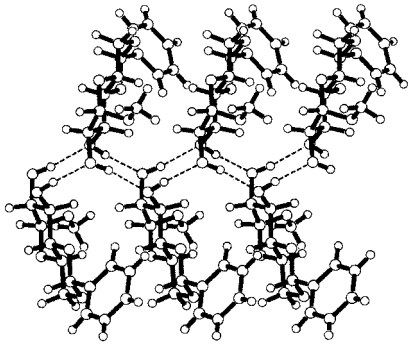

Figure 1. ORTEP drawing for the chain fragment in **1** crystallized from "dry" ethyl acetate.[16]

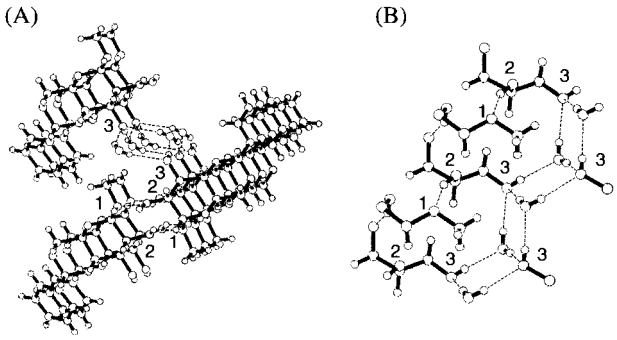

Figure 2. (A) ORTEP drawing for the chain fragment in $\mathbf{1}\cdot H_2O$ and (B) that around water molecules crystallized from "wet" *p*-xylene.

To correlate the crystal structure with the gel fiber structure, we determined the water content in the xerogel obtained from the wet toluene gel. The xerogel was prepared by vacuum dry of the frozen sample at –10 °C. This was dissolved into anhydrated $CHCl_3$ and the solution was subjected to Karl–Fischer titration. Substracting the background water concentration in $CHCl_3$, the molar ratio of $\mathbf{1}/H_2O$ was estimated to be $1.0/0.7 \pm 0.1$. The molar ratio was also determined by the ^1H NMR spectroscopic measurement of the $CDCl_3$ solution: $\mathbf{1}/H_2O = 1.0/0.9 \pm 0.1$. These results consistently support the view that the organogel fibers contain approximately one mole of water per one mole of **1**, like the stoichiometry of the single crystal.

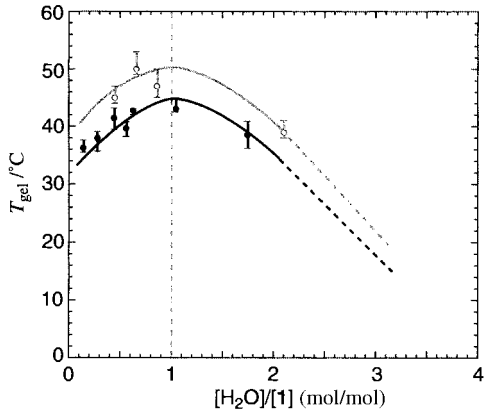

Figure 3. Influence of $[H_2O]$ on T_{gel}: [**1**]=1.2 wt/vol% in toluene (●), [**1**]=3.0 wt/vol% in *p*-xylene (○).

Thus, the next concern is the influence of the water concentration on the gel stability. We determined T_{gel} (sol–gel phase-transition temperature) as a function of $[H_2O]$ in toluene and *p*-xylene ($[H_2O]$ was estimated by Karl–Fischer titration). As shown in Figure 3, T_{gel} values increase in low $[H_2O]$ region and then decrease in high $[H_2O]$ region, giving rise to a maximum at around $[H_2O]/[\mathbf{1}] = 1.0$. Above $[H_2O]/[\mathbf{1}] > 2.8$, in the case of the toluene gel, solvent leaked out of the gel in the tilted sample tube, indicating that the gel is very unstable. These results establish that these wet organogels are most stabilized at $[H_2O]/[\mathbf{1}] = 1.0$.

Then, why does the **1** + H_2O system provide such a stable organogel in spite of the two-dimensional hydrogen-bonding array? Weiss and we have already noticed that in general, organogel fibers are not so "wet" with solvent molecules.[7,8,10,18] However, this proposal is apparently incompatible with the fact that the organogel stability is very dependent upon the solvent. According to recent AFM study by Whitten et al.,[19] "fiber bundles" result from assembly of "unit fibers" initially formed and solvent molecules are preserved in the interfiber channels. This observation can reasonably explain the facts that organogel fibers are not so "wet" but the stability is solvent-dependent. In the present study, hydrogen-bonds among **1** molecules primarily result in one-dimensional unit fibers, which are secondarily crosslinked by water molecules present in the channels as "adhesive solvent molecules". One may thus regard that water molecules do not disturb one-dimensional hydrogen-bonding array of **1** but rather facilitate the bundle formation from unit fibers.

In conclusion, the present study has provided an important admonition that the stability of organogels formed from "hygroscopic" hydrogen-bonding gelators can be affected by a minute amount of concomitant water molecules. It is also worthwhile to mention that the influence can be well understood in relation to the crystal structures.

Reference and Notes

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17 $C_{14}H_{20}O_7$, M_r = 300.31, monoclinic, space group $P2_1$ (#4), a = 9.0195(6), b = 4.8798(4), c = 17.462(1) Å, β = 103.929(3) °, V = 745.67(10) Å^3, $F(000)$ = 320.00, ρ_{calcd} = 1.337 g cm^{-3}, Z = 2, μ(Cu Kα) = 9.15 cm^{-1}, crystal dimension 0.1 × 0.1 × 0.2 mm, 473 reflections collected, $2\theta_{max}$ = 136.5 °, 1421 independent reflections, R_1 = 0.039 for 1170 reflections with $I>2\sigma(I)$, wR = 0.106 (for all data), S = 0.98. Data collected at room temperature, Rigaku RAXIS-RAPID Imaging Plate diffractometer, structural solution by direct methods, full-matrix least-squares refinement on F^2. Hydrogen atoms refined as isotropic. Calculations were performed using teXsan package.

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