Spectral Characterization of Self-Assemblies of Aldopyranoside Amphiphilic Gelators: What is the Essential Structural Difference between Simple Amphiphiles and Bolaamphiphiles?

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Abstract: An aldopyranoside-based gelators (dodecanoyl-*p*-aminophenyl-β-D-aldopyranoside)s and [1,12-dodecanedicarboxylic-bis(*p*-aminophenyl-β-D-aldopyranoside)]s **1**–**4** were synthesized, and their gelation ability was evaluated in organic solvents and water. Simple aldopyranoside amphiphiles **1** and **2** were found to gelate organic solvents as well as water in the presence of a small amount of alcoholic solvents. More interestingly, not only extremely dilute aqueous solutions (0.05 wt%) of the bolaamphiphiles **3** and **4**, but solutions of **3** and **4** in several organic solvents could be gelatinized. These results indicate that **1**–**4** can act as versatile amphiphilic gelators. We characterized the superstructures of the aqueous gels and organogels prepared from **1**–**4** using SEM, TEM, NMR and IR spectroscopy, and XRD. The aqueous gels **1** and **2** formed a three-dimensional network of puckered fibrils diameters in the range 20–200 nm, whereas the aqueous gels **3** and **4** produced filmlike lamellar structures with 50–100 nm thickness at extremely low concentrations (0.05 wt%). Powder XRD experiments indicate that the aqueous gels **1** and **2** maintain an interdigitated bilayer structure with a 2.90 nm period with the alkyl chain tilted, while the organogels **1** and **2** take a loosely interdigitated bilayer structure with a 3.48 nm period. On the other hand, the aqueous- and the organogels **3** and **4** have 3.58 nm spacing, which corresponds to a monolayered structure. The XRD, ^{1}H NMR and FT-IR results suggest that **1**–**4** are stabilized by a combination of the hydrogen-bonding, π–π interactions and hydrophobic forces.

Keywords: amphiphiles · bolaamphiphile · gels · hydrogel · organogel · self-assembly

Introduction

Gels belong to the class of "soft" materials that neither flow freely like a true liquid nor take on the definite shape of a rigid solid. Owing mainly to this property, gels are among the most useful supramolecular systems with wide applications in photography, drug delivery, cosmetics, sensors and food processing, to name a few.[1] Nature itself has discovered the gel, protoplasm being of that ilk. Although gels are best known to arise from polymers, proteins and inorganics, low molecular-weight organic compounds can also exhibit gelating behaviour.[2–4] The organic gelators self-assemble into long fibrous structures that eventually entangle into three-dimensional networks. Solvents contained within the interstices of the network suffer impaired flow. Thus, a viscosity increase of ten times, induced by only one gelator molecule per 10^5 solvent molecules, are not uncommon.[5]

Supramolecular gels are based on the spontaneous, thermoreversible self-assembly of low molecular-weight molecules under nonequilibrium conditions. Noncovalent interactions like hydrogen bonding, solvophobic effects and π–π stacking give rise to the formation of fibres, which subsequently entrain and immobilize the solvent inside the interstices of a three-dimensional network.[6–10] In particular, "aqueous gels" are usually made of macromolecules (i.e., proteins and polymers) whose complicated intermolecular association modes are difficult to define. "Organogels" are reversible, one-dimensional aggregates of low molecular-weight compounds formed by self-assembly. However, to date only a limited number of "aqueous gels" composed of such aggregates have been reported.[11]

We have focused our research effort toward exploitation of sugar-based self-assemblies formed in water.[12] An advantage

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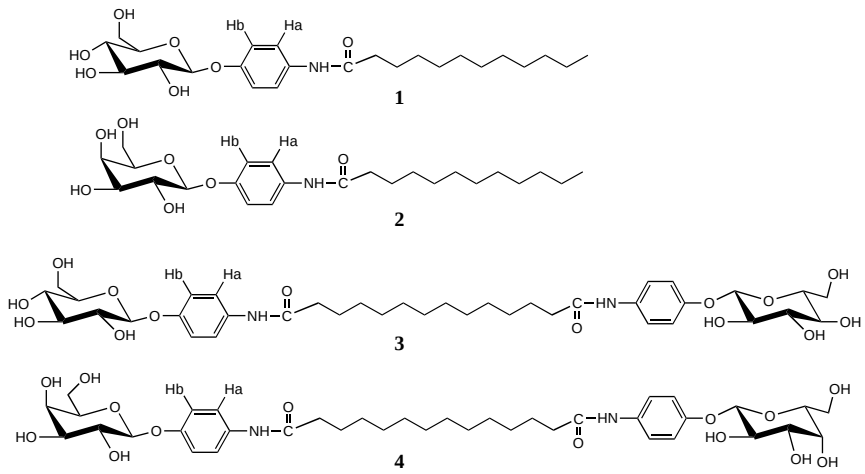
of this system is that one can systematically design various aggregates utilizing abundant basic skeletons in a carbohydrate family. In the research process, we found that glucoside or glucosamide derivatives can gelate water in the presence of a small amount of polar organic solvent or several organic solvents.[12a, 12d] In addition, simple aldopyranose amphiphilic gelator can gelate organic solvents as well as water.[12e] The findings imply that if we carefully search for sugars as well as for appropriate hydrophobic groups, several amphiphilic gelators may be further discovered; this may be useful to specify the basic structural requirements to design excellent amphiphilic gelators. With these objectives in mind, we designed new gelators bearing an aldopyranose moiety, an aminophenyl and a long alkyl chain group. The long alkyl chain of gelators not only enhances their solubility in organic solvents, but also promotes association among the fibres through van der Waals forces and eventual gel formation. Particularly, an aldopyranose moiety at both ends of the bolaamphiphiles should increase their solubility in water.



In the present work we turned our attention to the self-assembling behaviour and gelation capability of an aldopyranoside compounds. For example, it is most likely that an aldopyranose moiety, an aminophenyl group and a long alkyl chain group of an amphiphile can enjoy intermolecular hydrogen-bonding, $\pi-\pi$ stacking and interdigitated interactions and, therefore, should produce highly ordered layered structures. The possible gelation of water and organic solvents by aldopyranoside-based compounds will thus strengthen the concept of unidirectional interaction as a prerequisite for gelation. The second purpose of our research is to characterize the structural properties upon gel formation for the aldopyranoside amphiphilic gelators. During last years gel chemistry have mainly focused on synthesis and simple gelation properties of new gelators rather than detailed characterization for the gel formation.[2, 6–10] In particular we discuss the essential structural difference between simple amphiphiles and bolaamphiphiles. Here, we report on the synthesis of new powerful aldopyranoside-based compounds **1**–**4** as amphiphilic gelators and their self-assembling properties, such as gelation capability, morphologies and molecular packing in water and in organic solvents, examined by energy-filtering transmission electron microscopy (EF-TEM),[12c] SEM, CD, NMR and FT-IR spectroscopy, and XRD.

Results and Discussion

Gelation of organic solvents and water: The gelation ability of aldopyranoside-based compounds **1**–**4** for a range of organic solvents and water was examined by dissolving approximately 0.1–10 mg of compound in 1.0–2.0 mL of the desired solvent under heating. The solubility of these compounds at room temperature is very poor in most solvents. Upon cooling to room temperature, a gel, a precipitate or a clear solution was observed, depending on the solvent used. The results are summarized in Table 1 and show that 0.05–5.0 wt% of a gelator concentration range is enough to gelatinize. Compounds **1** and **2** can gelate seven out of ten organic solvents tested as well as water in the presence of a small amount of alcoholic solvents (ca. 1.0 wt%) (Figure 1a), owing to extremely low solubility in water; this indicates that they can act as versatile gelators of organic solvents and water. In addition, the bolaamphiphiles **3** and **4**, which possess two aminophenyl aldopyranoside moieties, can also gelate seven of the ten organic solvents tested. Particularly, they can gelate water in the absence of any organic solvents (Figure 1b). This feature will be due to the increased hydrophilicity of **3** and **4** with two aminophenyl aldopyranoside moieties in water. Very surprisingly, extremely dilute (0.05 wt%) aqueous solutions of the bolaamphiphiles **3** and **4** can gelate within several minutes at 25°C. Moreover, increasing the gelator concentration substantially reduces the gelation period. The gels given in Table 1 are stable for at least a few months at room temperature. The aqueous gels **1** and **2** are opaque (Figure 1a)

Table 1. The gelation ability of **1**–**4** in organic solvents and water.[a]

Solvent	**1**	**2**	**3**	**4**
methanol	S	S	S	S
ethanol	S	S	G	G
1-butanol	G	G	G	G
tert-butanol	G	G	G	G
tetrahydrofuran	G	G	G	G
acetic acid	G	G	G	G
n-hexane	I	I	I	I
ethylacetate	G	G	I	I
acetonitrile	G	S	G	G
acetone	G	S	G	G
water	G[b]	G[b]	G	G

[a] Gelator = 0.05–5.0 wt%; G = stable gel formed at room temperature; S = soluble; I = insoluble. [b] stable gel formed in the presence of a trace amount of methanol or ethanol.

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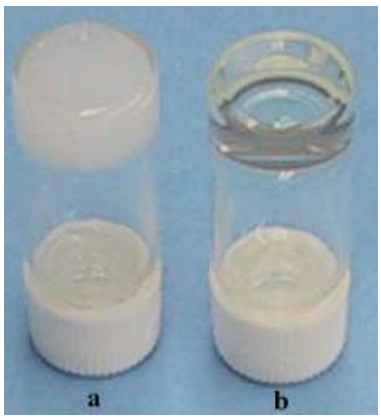

Figure 1. Two aqueous gels composed of **2** (0.2 wt%) (left) and **4** (0.05 wt%) (right), which are stable when inverted as shown.

and are destroyed by mechanical agitation, whereas the aqueous gels **3** and **4** are completely transparent (Figure 1b) and much more stable. In all cases gelation proved to be thermoreversible.

To obtain an insight into the chiral orientation of gelators in an aqueous gel system, circular dichroism (CD) of aqueous gels **2** in the presence of 10.0 wt% of methanol and **4** in the absence of any organic solvent was investigated (Figure 2).

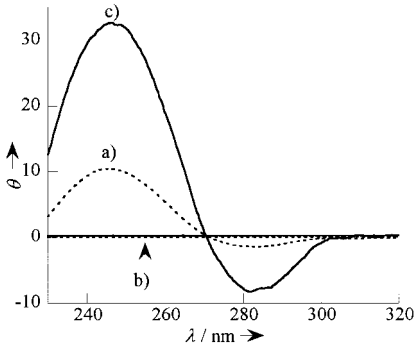

Figure 2. CD spectra of an aqueous gel a) **2** (0.1 wt%), b) methanol solution **2** (0.1 wt%) and c) an aqueous gel **4** (0.05 wt%) at 25.0 °C.

The λ_{max} value of **2** and **4** in UV absorption spectra appears at around 274 nm, ascribable to the phenyl group. In the CD spectra, the $\lambda_{\theta=0}$ value appears at 274 nm. One can therefore assign the CD spectra to the exciton coupling bands. The CD spectra of **2** and **4** exhibit a negative sign for the first Cotton effect, indicating that dipole moments orientate in an anticlockwise in the aggregate of their gels. No CD Cotton effect was observed for **2** in methanol solution. These data strongly support the view that an aqueous gel forms highly ordered chiral structure in comparison to the solution state. We also confirmed that the contribution of linear dichroism (LD) to the true CD spectra is negligible. On the other hand, the intensity of the CD signal of **4** [0.1 wt%; $T_{sol-gel}$ (sol–gel transition temperature): 53 °C] is much stronger than that of an aqueous gel **2** (0.1 wt%; $T_{sol-gel}$: 35 °C).[13] This spectral observation clearly indicates a highly ordered chiral structure of the aqueous gel **4**.

Electron microscopic observation: Molecular self-assembling features can be observed on an electron microscope, since the first stage of physical gelation is the self-aggregation of gelator molecules. Figure 3 shows SEM images of the aqueous gels and the organogels formed by **1** and **2**. The aqueous gels **1** and

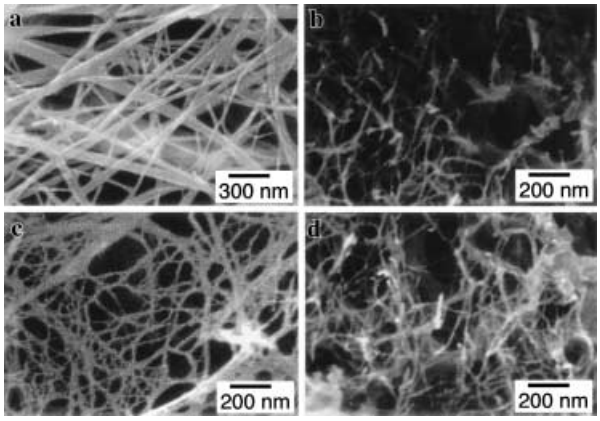

Figure 3. SEM pictures of the aqueous gels a) **1** and b) **2** obtained from water, and organogels c) **1** and d) **2** prepared from *tert*-butanol.

2 display linear fibre structures 140–200 nm in diameter and several μm in length (Figure 3a and 3b). In addition, TEM analysis of the chiral aggregate clearly showed that the fibres are twisted helical ribbons approximately 85 nm wide, about 315 nm pitch, and up to several micrometers in length (see graphic abstract). On the other hand, *tert*-butanol gels **1** and **2** show typical structures with three-dimensional networks of fibre bundles. The approximate diameters of the smallest aggregate in Figure 3c and 3d is 65–100 nm, several times larger than that observed with TEM (ca. 20 nm). Therefore, we assume that the gathering of numerous fibre bundles, observed from SEM measurements, forms the steric intertwined self-assembly that results in the immobilization of the isotropic liquid.

The aqueous gels **3** and **4**, which formed transparent gels, reveal the filmlike lamellar structures with 50–100 nm thickness at extremely low concentration (0.05 wt%) (Figure 4a and 4b); we do believe that these filmlike lamellae observed in this stage are the genuine structure in a swollen gel, and not a collapsed network induced by drying processes. In contrast, of particular interest is the xerogel **3** prepared from acetic acid. The spheres with 20–50 nm diameters are connected to one another like a pearl necklace at the initial stage of gel formation (not shown, but see arrows in Figure 4c); they turn out to grow into typical fibre structures with 20–40 nm diameters (Figure 4c). This phenomenon is a rare example as a morphology of organogel. The acetic acid gel **4** displays a three-dimensional fibre structure with diameters in the range 20–40 nm and up to several micrometers in length (Figure 4d). These findings imply that the bolaamphiphilic gelators, unlike the monohead amphiphile, satisfy both the solubility and the maintenance of intermolecular hydrogen-bond networks in water.

NMR and IR measurements: In general, NMR techniques can give a great deal of information on self-assembly process in

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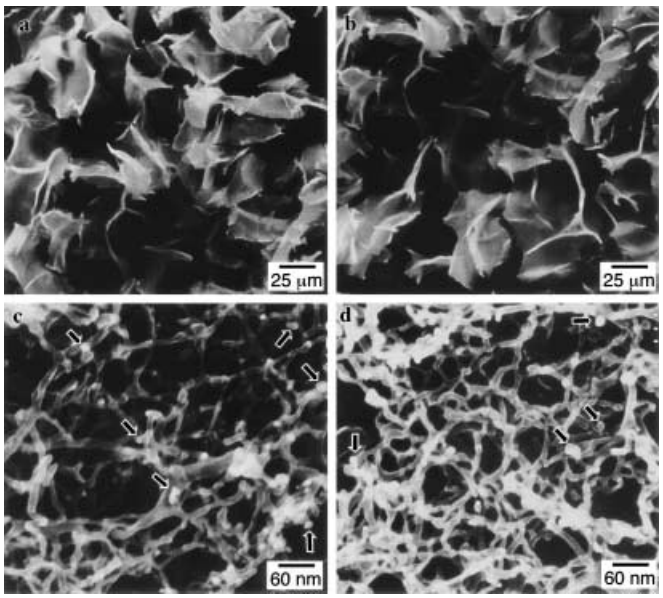

Figure 4. SEM pictures of the aqueous gels a) **3** and b) **4**, and the acetic acid gels c) **3** and d) **4**.

the gel state.[2, 6a, 7c, 14] Especially, ^{1}H NMR experiments may provide an insight into how molecules are orientated with respect to one another in a self-assembled state. In a previous NMR study, we have found that the amide proton of a cholesterol-based gelator is shifted to high-field in the gel state on heating, giving sharp peaks.[14] Therefore, we prepared loose aqueous gel samples for NMR measurements in D_2O/[D_4]methanol (1:1 v/v) or D_2O/[D_6]DMSO (9:1 v/v), since NMR signals of a rigid gel samples are gave generally quite broad.[11e, 11i] We thus studied the self-assembly behaviour of these compounds in aqueous gel states by using ^{1}H NMR spectroscopy. As shown in Figure 5a, aromatic proton signals of the self-assembled **1** in the gel phase appeared at $\delta = 7.43$ (d, $J =$ 8.61 Hz, H_b) and 7.38 ppm (d, $J = 8.61$ Hz, H_a) at 27 °C. Upon heating new peaks gradually appeared at $\delta = 7.60$ (d, $J =$ 8.61 Hz, H_b) and 7.28 ppm (d, $J = 8.61$ Hz, H_a) with gradual reduction in intensity of the original peaks at $\delta = 7.43$ and 7.38 ppm. The difference in chemical shift between the aromatic protons H_a and H_b may arise from π–π stacking and the hydrogen-bond interactions. A similar phenomenon was observed with the anomeric proton at the C-1 position of an aldopyranoside moiety. The appearance of the separate signals for the self-assembled and non-self-assembled species demonstrates that the chemical exchange is slow on the NMR timescale. These results afford noticeable evidence for the self-assembled structure stabilized by hydrogen-bonding and π–π stacking interactions in gel phase, and also strongly support the view that the aromatic units induce rigidity in the structure and form an aqueous gel with the help of linear arrangement.

On the other hand, original aromatic proton signals ($\delta =$ 6.77, $J = 8.0$ Hz and 6.58 ppm, $J = 8.0$ Hz) of the aqueous gels **3** and **4** displayed gradual downfield shift (δ7.27, $J = 8.0$ Hz and 6.97 ppm, $J = 8.0$ Hz) when heated (Figure 5b and 5d), but gave no new signals as with aqueous gel **1**. This behaviour is due to the fact that the chemical exchange between the self-assembled and non-self-assembled species is fast on the NMR timescale. Solutions of **3** in [D_6]DMSO revealed that the chemical shift change of the aromatic protons is less dramatic than those for the in the gel state. These data suggest that the bolaamphiphilic gelators **3** and **4** can form well-ordered monolayered structures through π–π stacking between phenyl groups in the gel state. Furthermore, NH peaks of the organogel **4** were gradually shifted upfield from $\delta = 8.97$ to 8.61 ppm upon heating (Figure 5c), an indication that the amide group of the bolaamphiphilic gelators participates in the intermolecular hydrogen-bond interaction in the gel state.[14]

Thus, we have observed evidence for the intermolecular hydrogen-bonding interaction in D_2O system. The amide absorption bands of **1**–**4** appeared at 1680–1690 cm^{-1} in organic solution; this is characteristic of non-hydrogen-bonded amide groups. On the other hand, the FT-IR spectra of the deuterated aqueous gels **1**–**4** are characterized by the absorption bands around 1639–1645 cm^{-1} (–C=O, amide-I).[12b–d] These spectral shifts are compatible with the presence of intermolecular hydrogen-bonded amide groups.

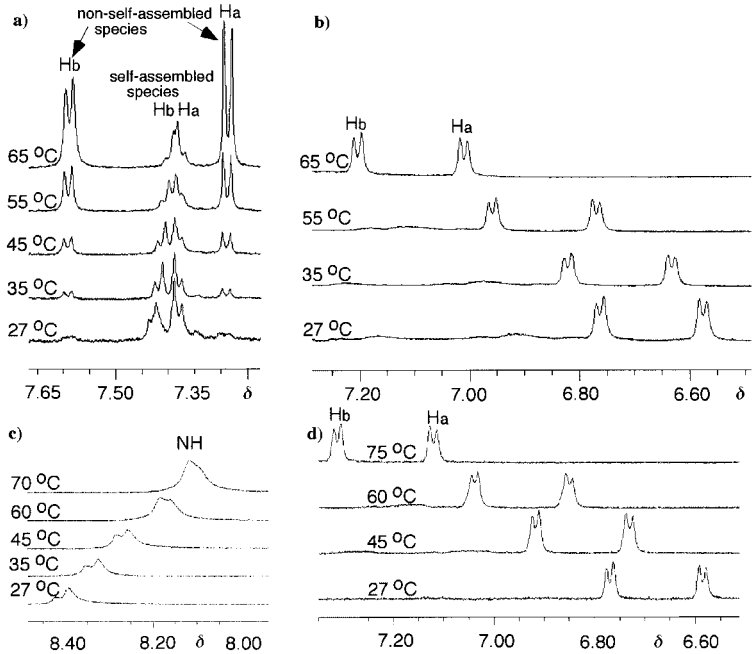

Figure 5. ^{1}H NMR spectra of a) aqueous gel **1** in D_2O and [D_4]methanol (1:1 v/v), b) an aqueous gel **3** in D_2O and [D_6]DMSO (9:1 v/v), c) the organogel **4** in [D_3]acetonitrile and d) an aqueous gel **4** in D_2O and [D_6]DMSO (9:1 v/v).

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XRD measurements: The xerogels **1**–**4** obtained from water and *tert*-butanol by a freezing method[6a] resulted in sponge-like aggregates, instead of a typical crystalline solid. The X-ray diffraction patterns of the xerogels **1** and **2** prepared from water show periodical reflection peaks (Figure 6a and 6b), an

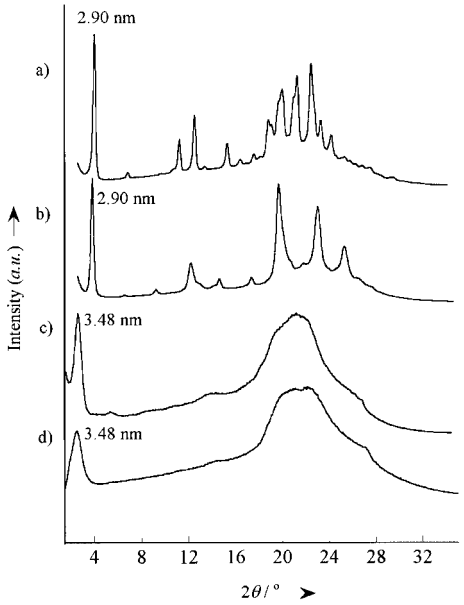

Figure 6. Powder XRD diagrams of the xerogels a) **1** and b) **2** prepared from water, the xerogels c) **1** and d) **2** prepared from *tert*-butanol.

indication that **1** and **2** indeed assemble into a lamellar organization. The obtained long spacings (*d*) of the xerogels **1** and **2** are 2.90 nm, 1.46 nm and 0.97 nm, corresponding to the ratio of 1:1/2:1/3. The 2.90 nm length is smaller than twice that of the extended molecular length of **1** and **2** (2.45 nm, by CPK molecular modeling), but larger than the length of one molecule. The aqueous gels **l** and **2**, thus, should maintain an interdigitated bilayer structure with a thickness of 2.90 nm (Figure 7a). This value is compatible with a bilayer structure with the alkyl chain tilting with respect to the normal to the layer plane. Long spacing of 2.90 nm was also observed for the aqueous gel state of **1** at high concentration. In addition, the wide-angle region of the X-ray diagram for the aqueous gels **1** and **2** revealed a series of sharp reflection peaks, supporting the view that presumably long alkyl chain groups form highly ordered layer packing through the interdigitated hydrophobic interaction.

In contrast, X-ray diffraction diagrams of the xerogels **1** and **2** obtained from *tert*-butanol are remarkably different from those obtained in water, with a single sharp peak appearing at $d = 3.48$ nm in the small-angle region and one broad reflection in wide-angle region (Figure 6c and 6d). However, it is unclear whether the broad band in the wide-angle region is based on the coexistence of different mesomorphic organizations or slightly disordered structure of the organogel.[15] The large difference in long spacing (*d*) implies that the molecular packing of the organogels **1** and **2** is quite different from those of obtained from water. On the basis of XRD experiments, there are two possible molecular packing structures that can form a bilayered structure with a period of 3.48 nm (Figure 7b

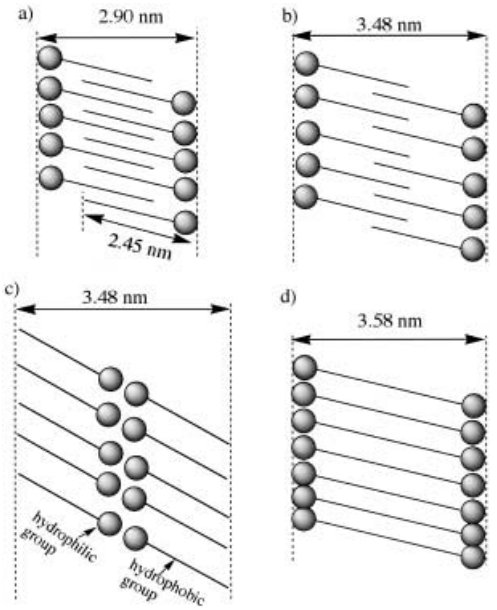

Figure 7. Possible molecular arrangement of a) the aqueous gels **1** and **2**, b) and c) the organogels **1** and **2**, and d) the aqueous gel **4**.

and 7c). The first one can be described in that the hydrophilic aldopyranoside moieties of **1** and **2** are exposed to the solvent, as shown in Figure 7b, with the formation of much weaker interdigitated hydrophobic interactions between long alkyl chain groups than that in Figure 7a. The second one is a molecular packing, in which hydrophilic aldopyranoside moieties and the hydrophobic long alkyl chains occupy the inner and outer parts of the bilayer membrane, respectively (Figure 7c). It needs to bear a head-to-head packing model with highly tilted alkyl chains relative to the bilayer normal. Although on the basis of these XRD results and CPK models the presence of the molecular packing in Figure 7c could not be completely ruled out, it would be very unlikely that the hydrophilic sugar moleties are shielded from the solvent. The gelation ability of the bolaamphiphiles **3** and **4** with *tert*-butanol also supports the molecular packing feature in Figure 7b, since they cannot form the packing as shown in Figure 7c. Hence, we propose a loosely interdigitated bilayer structure (Figure 7b) for the organogel of **1** and **2** with *tert*-butanol. In Figure 7b, the *tert*-butanol molecules might incorporate into the long alkyl chains. These results indicate that the hydrophobic interaction of the alkyl chains with the organogels **1** and **2** is relatively weaker than those the aqueous gels **1** and **2**. This feature can well explain the broadening in the wide-angle XRD for the xerogels **1** and **2**.

The powder XRD for the bolaamphiphiles **3** and **4** prepared from water display a single reflection peak with a long period of 3.58 nm (Figure 8); this is compatible with the fully extended molecular length of **3** and **4**, and suggests a layered structure with $\pi-\pi$ stacking between the aromatic groups, intermolecular hydrogen bounds between amide groups, and the intermolecular hydrogen-bonding interactions of the sugar moieties in aqueous phase (Figure 7d).[12c–d] Similar layered structures were also observable in the organogel systems.

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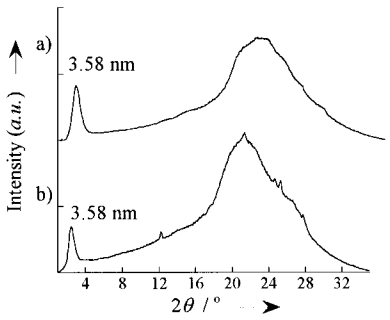

Figure 8. Powder XRD diagrams of the xerogels a) **3** and b) **4** prepared from water.

Conclusion

The aldopyranoside compounds proved to be effective gelators for various organic solvents and water. Particularly, **1** and **2** can gelate water in the presence of a small amount of alcoholic solvent, whereas **3** and **4** can gelate water in the absence of any organic solvent at extremely low concentrations (0.05 wt %). The gelation process was thermoreversible. Electron microscopy showed that gel formation is derived from the formation of long, intertwined fibres with widths of 20–200 nm and lengths of up to several micrometers. ^{1}H NMR and FT-IR experiments demonstrated that self-assembly of these aldopyranoside gelators is accompanied by formation of $\pi-\pi$ stacking and intermolecular hydrogen bonds.

According to powder XRD experiments, the aqueous gels **1** and **2** formed a highly intergiditated bilayer structure, whereas the organogels **1** and **2** maintained a loosely interdigitated bilayer structure. The bolaamphiphilic gelators **3** and **4** formed monolayered structures.

These aldopyranoside-based gelators **1**, **2** and **3**, **4** can form well-ordered bilayer and monolayered aggregates, respectively, by self-assembly, through intermolecular hydrogen-bonding interaction, $\pi-\pi$ stacking and interdigitated hydrophobic interaction in water. These findings mean that the combination of several difference forces is essential to successfully design the aqueous and the organic gel systems.

Experimental Section

Apparatus for spectroscopy measurements: ^{1}H NMR spectra were measured on a Jeol 600 spectrometer. FT-IR spectra were obtained in KBr pellets and KRS-5 windows cell using a Jasco FT-620 spectrometer, and MS spectra were obtained by Hitachi M-250 mass spectrometer. CD measurement was performed using a Jasco J-725 spectrometer.

TEM and SEM measurements: For energy-filtering transmission electron microscopy (EF-TEM) a piece of the gel was placed on a carbon-coated copper grid (400 mesh) and removed after 1 min, leaving some small patches of the gel on the grid. The grids were dried for 1 h at low pressure. The specimens were examined with Carl Zeiss EM902, with an accelerating voltage of 80 kV and a 16 mm working distance. Field emission scanning electron microscope (FE-SEM) was taken on Hitachi S-4500.

XRD: Powder XRD patterns were measured by a Rigaku diffractometer (Type 4037) by using graded *d*-space elliptical side-by-side multiplayer optics, monochromated $Cu_{K\alpha}$ radiation (40 kV, 30 mA) and an imaging plate (R-Axis). The typical exposure time was 10 min with a 150 mm camera length.

Gelation test of organic fluids: The gelator and the solvent were put in a septum-capped test tube and heated in an oil bath until the solid was dissolved. The solution was cooled at room temperature. If the stable gel was observed at this stage, it was classified as G in Table 1.

1,12-Dodecanedicarboxylic dichloride: A mixture of 1, 12-dodecanedicarboxylic acid (0.15 g, 0.58 mmol), oxalic chloride (0.50 g, 3.96 mmol) and DMF (1–2 drops) was dissolved in dichloromethane (5.0 mL), and the reaction mixture was then stirred for 10 h at room temperature. The residual oxalic chloride and solvent were removed by vacuum. The product was directly used for the coupling reaction without further purification.

***p*-Aminophenyl-*β*-D-glucopyranoside and *p*-Aminophenyl-*β*-D-galactopyranoside**: *p*-Nitrophenyl-*β*-D-glucopyranoside (1.0 g, 2.54 mmol) or *p*-nitrophenyl-*β*-D-galactopyranoside (1.0 g, 2.54 mmol) was dissolved in methanol (150 mL). Then, 10 % Pd/C (1.0 g) was added to the solution. Hydrogen gas was introduced into the mixed solution for 10 h at room temperature under a nitrogen atmosphere. The reaction mixture was filtered to remove Pd/C, and the filtrate was evaporated in vacuo to dryness. The residue was purified by column chromatography on silica gel with THF/chloroform (1/1 v/v). Yield 80–90 %; ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 3.4-4.1$ (s, 2H), 5.2–5.3 (m 3H), 5.6 (s, 1H), 6.7 (d, 2H), 7.37–7.46 (m, 5H); FT-IR (KBr): $\tilde{\nu} = 3312$, 2909, 1635, 1510, 1364, 1217, 1089, 1005, 1035, 999, 806, 706 cm^{-1}; MS (NBA): *m*/*z*: 360 [M^++H]; elemental analysis calcd (%) for $C_{19}H_{21}NO_6$: C 63.50, H 5.89, N 3.90; found: C 63.18, H 6.04, N 3.78.

Dodecanoyl-*p*-aminophenyl-*β*-D-glucopyranoside (1): A mixture of *p*-aminophenyl-*β*-D-glucopyranoside (0.30 g, 1.10 mmol), dodecanoyl choride (0.24g, 1.10 mmol) and triethylamine (0.536 g, 5.50 mmol) in dry THF (50 mL) was refluxed for 3 h under a nitrogen atmosphere. The solution was filtered after cooling to room temperature, the filtrate being concentrated to dryness by a vacuum evaporator. The residue was purified by column chromatography on silica gel with methanol/chloroform (1:6 v/v). Yield 40 %; m.p. 168–169 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta =$ 0.9 (t, 3H), 1.2–1.5 (m, 18H), 2.3 (m, 2H), 3.2–4.0 (m, 10H), 5.7 (d, 1H), 7.25 (d, 2H), 7.65 (d, 2H), 9.1 (s, 1H); FT-IR (KBr): $\tilde{\nu} = 3340$, 2912, 1630, 1510, 1364, 1217, 1089, 1005, 1035, 999, 806, 706 cm^{-1}; MS (NBA): *m*/*z*: 452.27 [M^++H]; elemental analysis calcd (%) for $C_{24}H_{37}NO_7$: C 63.84, H 8.26, N 3.10; found: C 63.84, H 8.25, N 3.15.

Related compounds (**2–4**) were synthesized according to a similar method. We thus describe only their analytical data.

Dodecanoyl-*p*-aminophenyl-*β*-D-galactopyranoside (2): Yield 80 %; m.p. 169–170 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 0.9$ (t, 3H), 1.2–1.5 (m, 18H), 2.3 (m, 2H), 3.2–4.0 (m, 10H), 5.7 (d, 1H), 7.25 (d, 2H), 7.65 (d, 2H), 9.1 (s, 1H); FT-IR (KBr): $\tilde{\nu} = 3340$, 2912, 1630, 1510, 1364, 1217, 1089, 1005, 1035, 999, 806, 706 cm^{-1}; MS (NBA): *m*/*z*: 452.27 [M^++H]; elemental analysis calcd (%) for $C_{24}H_{37}NO_7$: C 63.84, H 8.26, N 3.10; found: C 62.35, H 8.20, N 3.20.

1,12-Dodecanedicarboxylic-bis(*p*-aminophenyl-*β*-D-glucopyranoside) (3): Yield 50 %; m.p. > 300 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 1.0-1.5$ (m, 20H), 2.3 (m, 4H), 3.2–4.0 (m, 20H), 5.7 (d, 2H), 7.25 (d, 4H), 7.40 (d, 4H), 9.1 (s, 2H); FT-IR (KBr): $\tilde{\nu} = 3410$, 3340, 2912, 1630, 1510, 1364, 1217, 1089, 1005, 1035, 999, 806, 706 cm^{-1}; MS (NBA): *m*/*z*: 764.25 [M^++H]; elemental analysis calcd (%) for $C_{38}H_{56}N_2O_{14}$: C 59.67, H 7.38, N 3.66; found: C 60.02, H 7.20, N 3.60.

1,12-Dodecanedicarboxylic-bis(*p*-aminophenyl-*β*-D-galactopyranoside) (4): Yield 50 %; m.p. > 300 °C; ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 1.0-1.5$ (m, 20H), 2.3 (m, 4H), 3.2–4.0 (m, 20H), 5.7 (d, 2H), 7.25 (d, 4H), 7.40 (d, 4H), 9.1 (s, 2H); FT-IR (KBr): $\tilde{\nu} = 3410$, 3340, 2912, 1630, 1510, 1364, 1217, 1089, 1005, 1035, 999, 806, 706 cm^{-1}; MS (NBA): *m*/*z*: 750.25 [M^++H]; elemental analysis calcd (%) for $C_{38}H_{56}N_2O_{14}$: C 59.67, H 7.38, N 3.66; found: C 60.02, H 7.20, N 3.55.

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