New sugar-based gelators with an amino group, the gelation ability of which is remarkably reinforced by the hydrogen bond and the metal coordination

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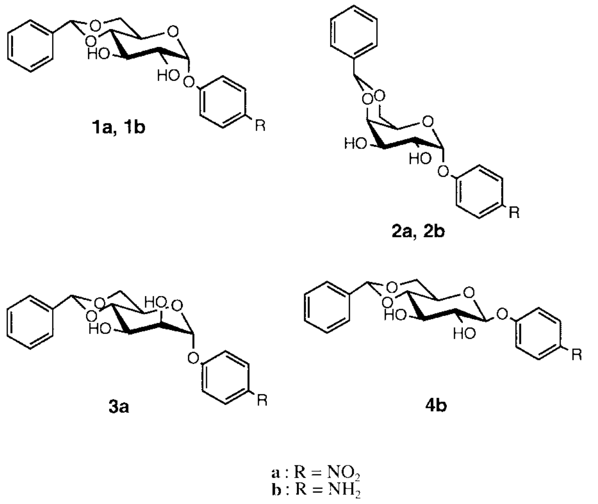
Three sugar-integrated gelators bearing a *p*-aminophenyl group which are expected to exert a hydrogen-bonding effect and a metal coordination effect on the gelation ability were synthesised. α-D-Galactose-based **2b** was only soluble or precipitated and β-D-glucose-based **4b** gelated only two of 15 solvents tested herein whereas α-D-glucose-based **1b** acted as an excellent gelator which could gelate 8 solvents. The sol–gel phase-transition temperature (T_{gel}) values for **1b** were higher by 41–78 °C than those for α-D-glucose-based **1a** bearing a *p*-nitrophenyl group. The spectral studies indicated that this gel reinforcement is due to the hydrogen-bonding interaction including the amino group. The T_{gel} values for the ethanol gel of **1b** were markedly improved by the addition of $AgNO_3$, $CoCl_2$ or $CdCl_2$. The detailed examination of a **1b** + $CoCl_2$ gel system in ethanol showed that the gel is stabilised by the ‘cross-link’ of **1b** molecules by the Co(II)–amino group interaction. This is the first and a convenient method for the metal reinforcement of organic gels.

Introduction

The development of new gelators of organic solvents has recently attracted much attention. They not only gelate various organic solvents but also create novel fibrous superstructures which can be characterised by SEM observation of the xerogels.[1–12] These organic gels are of particular interest in that being different from polymer gels, fibrous aggregations of low molecular-weight compounds formed by non-covalent interactions are responsible for such gelation phenomena. The gelators can be classified into two categories according to the difference in the driving force for the molecular aggregation: *viz.* hydrogen-bond-based gelators and nonhydrogen-bond-based gelators. In the former category, aliphatic amide derivatives which feature efficient hydrogen-bonding interactions among the amide groups have been widely studied.[1–4] The SEM observations of these derivatives showed that various superstructures can be created by a slight difference in the intermolecular hydrogen-bonding network.[5–9,13] These results stimulated us and others to use saccharides as a hydrogen-bond-forming segment in the gelators, because one can easily introduce a variety of hydrogen-bond-forming segments (including chiral ones) into gelators by appropriate selection from a saccharide library.[8,14–17] Thus, we previously synthesised **1a**–**3a** with a *p*-nitrophenyl chromophore (Scheme 1) and found that their gelation ability is profoundly affected by the slight structural difference in the saccharide moiety.[16] Here, it occurred to us that the cross-linking of gelators by the metal cation might enhance the gelation ability. In fact, a few studies have indicated that the gel network is reinforced by polymerisation or three-dimensional cross-links.[18,19] In the present system, this idea can be readily tested with **1b**, **2b** and **4b** which are derived from **1a**, **2a** and **4a** by reduction of the nitro group to the amino group.[20] In 1997, Sohna and Fages explored a similar idea with bipyridine-containing gelators.[4] They found that the metal (Fe(II)) complexation with the bipyridine moieties enforces a structural change in the gel fibers and lowers the gelation ability. Here, we address the fact that among **1b**, **2b** and **4b**, the organic gels prepared from D-glucose-based **1b** are efficiently stabilised not only by hydrogen-bonding interactions between the amino groups but also by metal coordination (particularly to Co(II), Cd(II) and Ag(I)). This is a new and convenient method of reinforcing the organic gels.

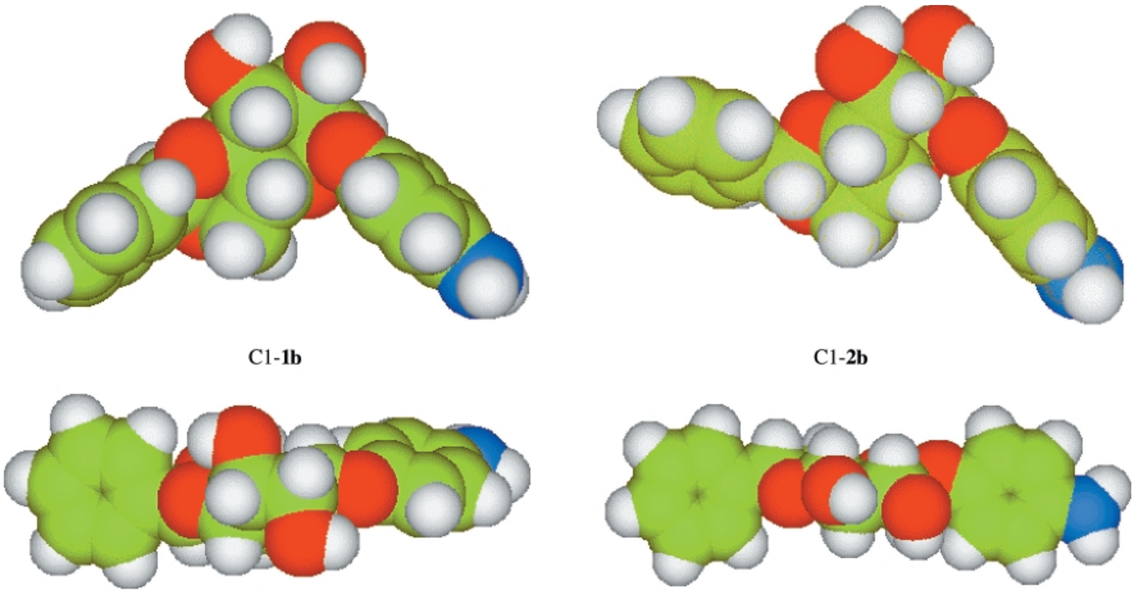


Scheme 1 Structure of sugar-based gelators: R = NO_2 for **1a**, **2a** and **3a** and R = NH_2 for **1b**, **2b** and **4b**.

Results and discussion

Gelation test

Compounds **1b**, **2b** and **4b** were synthesised from **1a**, **2a** and **4a** by catalytic reduction with H_2 and Pd on charcoal. The products were identified by ^1H NMR and MS spectral evidence and elemental analyses (see Experimental). The gelation test in the absence of the metal cation was carried out for 15 solvents (Table 1). The gelator (**1b**, **2b** or **4b**; 3.0 mg) was mixed with solvent (0.10 ml) in a septum-capped test tube and the mixture


C1-**1b**

C1-**2b**

1C-**2b**

C1-**4b**

Fig. 1 Energy-minimised structures of **1b**, **2b** and **4b** predicted from MM3: note that C1-**1b** (a good gelator) has an L-shaped structure which is unfavourable to intermolecular stacking aggregation whereas 1C-**2b** and C1-**4b** have a flat structure which is favourable to it.

Table 1 Organic solvents tested for gelation by **1b**, **2b** and **4b**

	Organic solvent	1b	2b	4b
1	Carbon disulfide	G	R	R
2	Carbon tetrachloride	G	I	I
3	Benzene	I	I	I
4	Toluene	G(S)	R	I
5	Diphenyl ether	G(S)	R	R
6	Methylcyclohexane	I	I	I
7	*n*-Octanol	G	R	G
8	Tetraethoxysilane	G	I	R
9	Pyridine	S	S	S
10	Aniline	S	S	S
11	Acetic acid	S	S	S
12	Dimethyl sulfoxide	S	S	S
13	Methanol	S	S	S
14	Ethanol	G	R	G
15	Ethyl acetate	G	R	I

G = gelation ([gelator] = 3.0 (wt/vol)%), G(S) = ([gelator] = 1.0 (wt/vol)%), I = insoluble, R = recrystallisation.

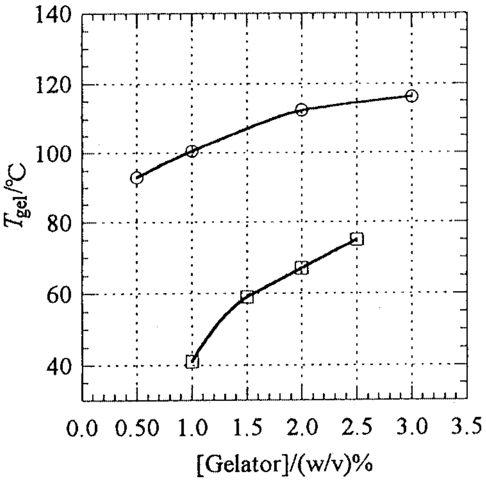


Fig. 2 Plots of T_{gel} *vs.* [gelator] in diphenyl ether: (□) for **1a** and (○) for **1b**. The data for **1a** are cited from ref. 17.

was heated until the solid had dissolved. The solution was cooled to room temperature and left for 1 h (G in Table 1 denotes that a gel was formed at this stage). Some solutions gelated at a gelator concentration below 1.0 (wt/vol)% [G(S) or super-gelator; Table 1].

It is clear from Table 1 that α-D-glucose-based **1b** acts as an excellent gelator which can gelate 8 solvents and behaves as a super-gelator for two of those. It is really surprising that even though the major driving-force for gelation in this system is the hydrogen-bonding interaction, **1b** can gelate even ethanol. On the other hand, α-D-galactose-based **2b** was only soluble or precipitated and β-D-glucose-based **4b** gelated only two solvents (*n*-octanol and ethanol). In the previous study, we found that α-D-glucose-based **1a** shows a high gelation ability for various organic solvents whereas α-D-galactose-based **2a** shows poor solubility in most organic solvents. This trend is commonly observed for **1b** and **2b**, indicating that the saccharide structure plays a central role in the aggregation process. The stable structures energy-minimised by MM3 are illustrated in Fig. 1. The minimised energies are 39.02, 30.63, 28.57 and 29.66 kJ mol^{-1} for C1-**1b**, C1-**2b**, 1C-**2b** and C1-**4b**, respectively (the initial structures are either C1 or 1C of the corresponding pyranose forms). It has been pointed out that the gelators adopting an L-shaped, folded conformation tend to hamper the stacking aggregation mode and to afford a stable organic gel, whereas the gelators adopting a flat conformation tend to aggregate according to a regular orientation and consequently precipitate.[16,17] Compound **1b** which can adopt only a C1 structure belongs to the former group and in fact acts as a good gelator. Compound **2b** has a similar L-shaped structure in the C1 structure with an axial 4-OR and an equatorial $5\text{-CH}_2\text{OR}$ but can be inverted into its 1C structure with an equatorial 4-OR and an axial $5\text{-CH}_2\text{OR}$. As shown in Fig. 1, 1C-**2b** has a flat conformation, which could be the reason why this compound tends to precipitate. It is also seen from Fig. 1 that **4b** which can adopt only the C1 structure shows a flat conformation. Again, this compound does not act as a good gelator.

Fig. 2 shows plots of T_{gel} (sol–gel phase transition temperature determined by a test-tube-tilting method) *vs.* [gelator] for **1a** and **1b**. It is clear that **1b** bearing an amino group provides a diphenyl ether gel that is more stable by 41–78 °C than **1a** bearing a nitro group. We consider that this stabilisation effect is brought about by hydrogen-bonding interactions involving the amino group (*vide post*).

Previously, we derived eqn. (1) from the Schrader's relation

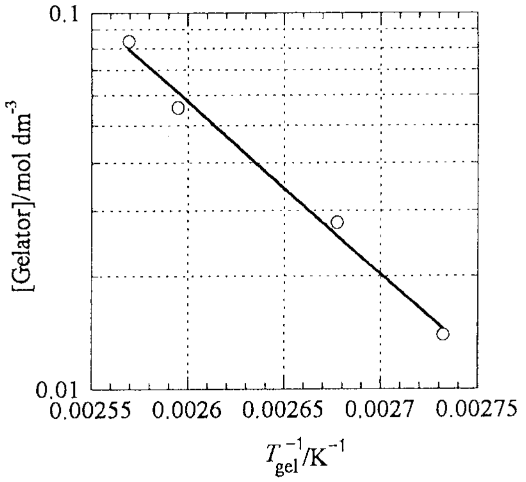


Fig. 3 Plots of [**1b**] *vs.* T_{gel}^{-1}/K^{-1}.

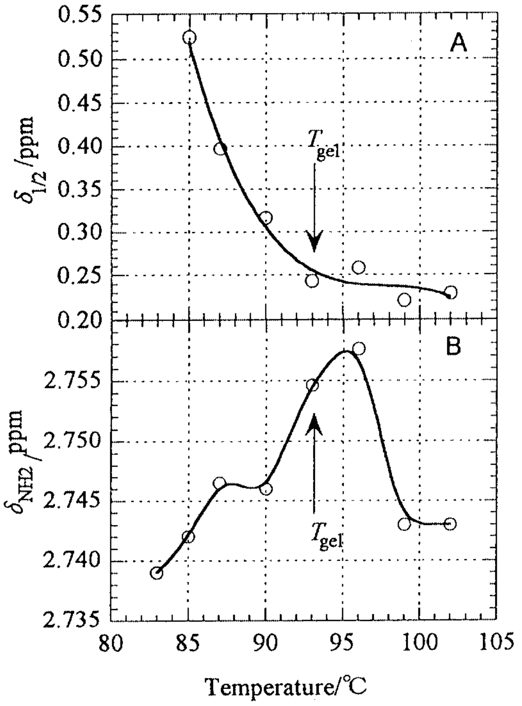


Fig. 4 Plots of (A) $\delta_{1/2}$ (half-height peak-width of the peak) against temperature and (B) δ_{NH_2} (chemical shift of an NH_2 group): [**1b**] = 0.50 (wt/vol)%, toluene-d_8.

$$\log[\text{gelator (in mol dm}^{-3})] = -\frac{\Delta H}{2.303R}\frac{1}{T_{\text{gel}}} + \text{constant} \quad (1)$$

frequently used for dissolution of solid compounds into organic solvents.[7] ΔH can be determined from the slope of log[gelator (in mol dm^{-3})] *vs.* T_{gel}^{-1}. It is known that the ΔH values are comparable with or slightly larger than ΔH_f values determined from differential scanning calorimetry (DSC) measurements at the melting point of the solid.[7,16,17] This might indicate that the ΔH reflects the heat released at the sol–gel phase-transition temperature. This implies (although as indirect evidence) that a change occurring at the sol–gel phase transition temperature is basically similar to dissolution of crystals into solution and the gelator fibers formed in organic solvents are not well wetted by solvent molecules.[7,16,21]

As shown in Fig. 3, a plot of log[gelator] *vs.* T_{gel}^{-1} afforded a straight line with γ (correlation coefficient) > 0.99. The ΔH value estimated on the basis of eqn. (1) was 43 kJ mol^{-1}. The ΔH_f value at the mp determined by the DSC measurement was 31.7 kJ mol^{-1}. The similarity of these two values suggests that the gel fibers are scarcely wetted by diphenyl ether molecules.[7,16,21] On the other hand, these values are larger than the corresponding ΔH (32 kJ mol^{-1}) and ΔH_f (22.1 kJ mol^{-1}) for **1a**. We believe that this difference reflects the hydrogen-bonding interaction with the amino group.

Spectral examination of the amino group participation

It is known that the hydrogen-bonding interaction among OH groups operating in the gelation process can be monitored by FT-IR spectroscopy.[1,16,17] In the present system, however, the ν_{NH} band seriously overlaps with the ν_{OH} band and any useful information to characterise hydrogen-bond formation was not obtained. Instead, we noticed that the ^{1}H NMR spectra change with the measurement temperature. It is expected that the molecular motion of gelators drastically changes at the T_{gel}. This change can be conveniently monitored by the line-broadening effect observed for the ^{1}H NMR peaks. In fact, such a phenomenon has already been reported for related gel systems.[17,22] We measured the ^{1}H NMR spectra of a **1b** [0.50 (wt/vol)%] + toluene system at 83–102 °C. In this system, the T_{gel} was 93 °C. As shown in Fig. 4A, the half-height peak-width ($\delta_{1/2}$) of the NH_2 (at around 2.7 ppm) is nearly constant above the T_{gel} while it increases when the temperature drops below the T_{gel}. The results imply that the amino group is significantly involved in the formation of the gel network and the mobility of gelator molecules is significantly suppressed in the gel phase whereas in the sol phase it is comparable with that of the homogeneous solution. On the other hand, a plot of δ_{NH_2} *vs.* temperature for **1b** tends to give the lowest chemical shift at the T_{gel} (Fig. 4B). In general, the formation of strong hydrogen bonds with OH groups induces the down-field shift of δ_{OH}.[23,24] This should be applicable to the chemical shift of NH_2 groups. Hence, the hydrogen bonds with NH_2 groups should also intensify with lowering of the medium temperature from the sol phase to the T_{gel} region. This change can be explained by the relation of the intermolecular aggregation with the gel formation. In contrast, it is difficult to explain why the hydrogen bonds are gradually weakened with lowering of the medium temperature in the gel phase. Probably, at the T_{gel} temperature region the formation of the 'soft gel' is predominantly governed by the intermolecular hydrogen-bonding interaction but at temperatures much lower than the T_{gel} the formation of the crystal-like 'hard gel'[7,16,21] is governed not only by intermolecular hydrogen-bonding interactions but also by other intermolecular forces such as π–π interactions, van der Waals interactions, *etc.*[10] In case the latter forces interfere with the hydrogen-bonding interaction because of the steric mismatching, it may be weakened with lowering of the medium temperature even in the gel phase. Anyhow, it is clear that ^{1}H NMR spectroscopy is a potential tool to estimate organic gel formation.

SEM observations of xerogels

In order to obtain visual insights into the aggregation mode in the gel phase, we have prepared dry samples of organic gel fibers for SEM studies.[25] Fig. 5A shows a typical picture obtained from the xerogel of **1b** in carbon tetrachloride. It is clear that the gelator forms a three-dimensional network with 20–120 nm frizzled fibrils. The fibrils obtained from other solvents are more or less similar. We expected that the hydrogen-bonding interactions among chiral saccharide moieties might create a helical fiber structure, but such a periodical, regular structure was not found in these SEM pictures.

Influence of added metal salts on the gelation ability

As mentioned in the Introduction, a few studies have demonstrated that organic gels which are held together by the fibrous network comprised of intermolecular aggregates are reinforced

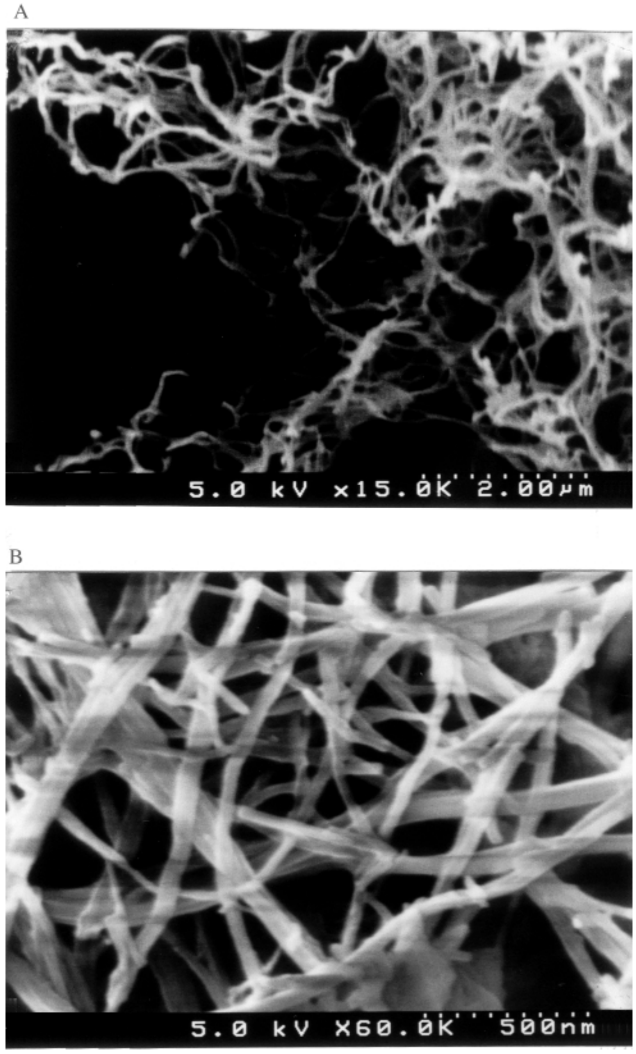


Fig. 5 SEM pictures of (A) **1b** [1.0 (wt/vol)%] prepared from carbon tetrachloride and (B) **1b** [1.0 (wt/vol)%] + $CoCl_2$ ([**1b**]/[$CoCl_2$] = 1.0) prepared from ethanol.

by polymerisation or three-dimensional cross-linking.[18,19] We expected that the cross-linking should be readily accomplished by coordination bonds formed between ligands and metal cations. A similar concept has been applied to cross-link arginic acid by Ca(II) in order to prepare arginic acid fibers. This 'salt bridging' is applied to enzyme immobilisation.

We have tested $AgNO_3$, $FeCl_3$, $CoCl_2$, $CdCl_2$ and $CaCl_2$. Among these, the organic gel of a **1b** [1.0 (wt/vol)%]–ethanol system was markedly stabilised by $CoCl_2$ and $CdCl_2$. The T_{gel} in the absence of the metal cation was −10 °C, but this was enhanced up to 71 °C and 72 °C in the presence of an equimolar amount of $CoCl_2$ and $CdCl_2$, respectively. Since the addition of tetra-*n*-butylammonium chloride showed no effect on the gelation ability, this change is ascribed to the metal–amino group interaction and not to a simple salting-out effect. $AgNO_3$ was also effective to enhance the T_{gel} for the ethanol gel of **1b**, but a brown solid gradually precipitated from this gel system (even kept in the dark). Fig. 5B shows the SEM picture of the xerogel prepared from a 1 : 1 molar mixture of **1b** [1.0 (wt/vol)%] and $CoCl_2$ in ethanol. These gel fibers are straighter than those obtained in the absence of $CoCl_2$ (Fig. 5A). This means that although the fiber structure is somewhat changed by metal complexation, it does not induce an unfavourable destruction of the intermolecular aggregates as in the previous example[4] but rather reinforces them.

The TEM pictures of the **1b** [1.0 (wt/vol)%] + $CoCl_2$ system in ethanol are shown in Fig. 6. From Fig. 6A which exhibits an ethanol gel of [**1b**]/[$CoCl_2$] = 1.0, it is clear that the micro-particles of $CoCl_2$ are adsorbed to the gel fibers. In Fig. 6B which shows an ethanol gel of [**1b**]/[$CoCl_2$] = 6.0, such micro-particles are scarcely seen, indicating the homogeneous dispersion of $CoCl_2$ into the amino-group-containing gel fibers.

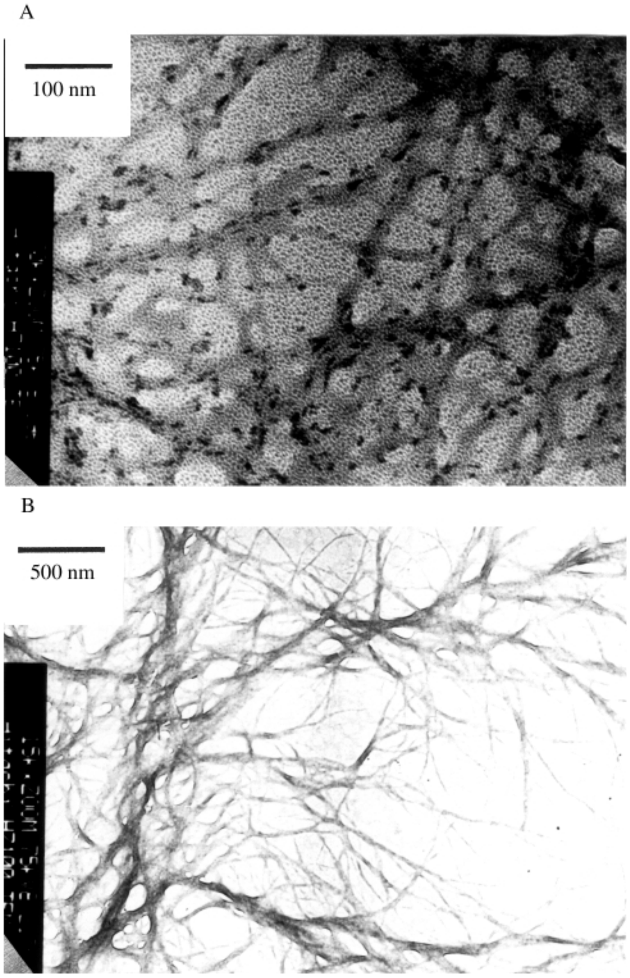


Fig. 6 TEM pictures of (A) **1b** [1.0 (wt/vol)%] + $CoCl_2$ ([**1b**]/[$CoCl_2$] = 1.0) and (B) **1b** [1.0 (wt/vol)%] + $CoCl_2$ ([**1b**]/[$CoCl_2$] = 6.0) prepared from ethanol.

Then, does $CoCl_2$ really bridge multiple **1b** molecules in the gel fibers? According to the stability constant table, the logarithmic values of K_1(=[ML]/[M][L]) and K_2(=[ML_2]/[ML][L]) for *p*-anisidine are 1.85 and 1.65, respectively.[26] In a homogeneous ethanol solution at [**1b**] = 0.02 mol dm^{-3} and [$CoCl_2$] = 0.01 mol dm^{-3}, therefore, the concentrations are 0.0042 mol dm^{-3} for free Co(II), 0.0037 mol dm^{-3} for Co(II)·*p*-anisidine (ML) and 0.0021 mol dm^{-3} for Co(II)·(*p*-anisidine)$_2$. This suggests that the Co(II)–**1b** complex is also not so stable in ethanol. The ethanol gel of **1b** containing $CoCl_2$ was apparently blue, indicating that the major species has a tetrahedral structure.[27] The solid samples were prepared from a 1 : 1 and a 1 : 6 Co(II)–**1b** ethanol gel by evaporating them to dryness and their KBr disks were subjected to the absorption spectral measurements. The 1 : 6 mixture, the visible region absorption band of which should mainly reflect the Co(II)·(**1b**)$_2$ 1 : 2 complex, gave λ_{max} at 641 nm and a shoulder peak at 600 nm (Fig. 7). In contrast, the 1 : 1 mixture gave a broad absorption spectrum at 650–700 nm, suggesting that it should mainly consist of Co(II)·**1b** with a λ_{max} at around 670 nm. The ethanol gel of **1b** [1.0 (wt/vol)%] + $CoCl_2$ ([**1b**]/[$CoCl_2$] = 1.0) gave λ_{max} at 660 nm and two shoulder peaks at 570 and 620 nm. These results suggest that the gel contains both Co(II)·**1b** and Co(II)·(**1b**)$_2$. We believe that in the Co(II)·(**1b**)$_2$ complex two **1b** molecules are connected by Co(II) and this bridging effect acts as the origin of the gel reinforcement.

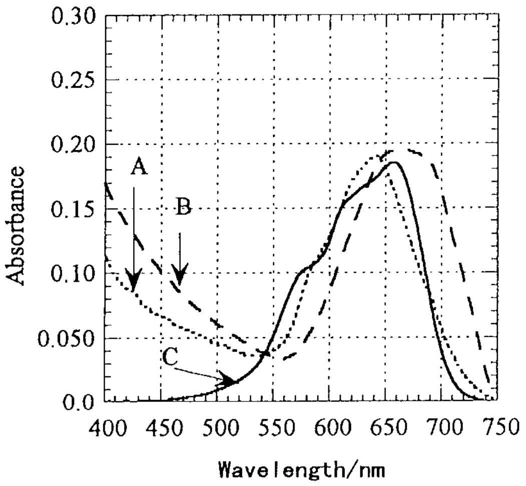


Fig. 7 Absorption spectra of (A) the 1 : 6 Co(II)–**1b** solid sample, (B) the 1 : 1 Co(II)–**1b** solid sample and (C) the ethanol gel of the 1 : 1 molar mixture ([**1b**] = 1.0 (wt/vol)%). The ordinate for (A) and (B) is an arbitrary unit. The absorption band at 400–500 nm for (A) and (B) is due to aquation of $CoCl_2$ in the KBr disk.

Conclusion

The present study has demonstrated that saccharides are promising building-blocks for new gelators with different gelation abilities and different three-dimensional network structures. In addition, it was found that the introduction of an amino group and the metal-bridging of these amino groups are effective in the reinforcement of these organic gels. We believe that the convenient synthesis and the diversity of the products and facile gel reinforcement cannot be attained in a more simple fashion than with amino-containing saccharides as building-blocks. It is not yet clear, however, what the essential factors are that govern the matching (as in the present system) or the mismatching (as in ref. 4) between the gel-forming segments and the metal-complexation sites. Further investigations are currently continuing in our laboratories.

Experimental

1-*O*-(*p*-Aminophenyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (1b)

Compound **1b** was synthesised from **1a** as follows; **1a** (reported previously[17]) (500 mg, 1.29 mmol) was added to a mixture of methanol (40 ml) and THF (5 ml) and stirred until the solid was dissolved. Then, 10% Pd-C (500 mg) was added to the solution. Hydrogen gas was introduced into a mixed solution at room temperature under a nitrogen atmosphere until the starting material disappeared. The reaction was traced by TLC (silica gel–chloroform–methanol = 9 : 1 (v/v); $R_f = 0.1$). The reaction mixture was filtered to remove 10% Pd-C, which was washed with methanol. The combined reaction solution was evaporated to dryness. The solid obtained was purified by column chromatography (silica gel–chloroform–methanol = 9 : 1 (v/v); $R_f = 0.1$); 1-*O*-(*p*-aminophenyl)-4,6-*O*-benzylidene-α-D-glucopyranoside (112 mg, 24.2%), mp 199.7–200.1 °C; ^{1}H NMR (DMSO-d_6) δ 3.46–3.80 [m, 6H, sugar-CH (H-2 ~ H-6)], 4.76 (s, 2H, NH_2), 5.22 (t, 2H, OH × 2), 5.30 [d (*J* = 5.13), 1H, sugar-CH (H-1)], 5.59 (s, 1H, PhCH), 6.51 [d (*J* = 8.7), 2H, *o*-Ph-NH_2], 6.78 [d (*J* = 8.7), 2H, *p*-Ph-NH_2], 7.37 (t, 3H, *o*, *p*-Ar-H), 7.45 (t, 2H, *m*-Ar-H); *m*/*z* 360 (M + H^+); Found: C, 63.18; H, 6.04; N, 3.78. Calc. for $C_{19}H_{21}O_6N$: C, 63.50; H, 5.89; N, 3.90%.

1-*O*-(*p*-Aminophenyl)-4,6-*O*-benzylidene-α-D-galactopyranoside (2b)

Compound **2b** was synthesised from **2a** according to a similar method used for **1b**; 1-*O*-(*p*-aminophenyl)-4,6-*O*-benzylidene-α-D-galactopyranoside (142 mg, 30.8%), mp 239.1–239.6 °C; ^{1}H NMR (DMSO-d_6) δ 3.17–4.22 [m, 6H, sugar-CH (H-2 ~ H-6)], 4.88 [d (*J* = 7.5), 1H, sugar-CH (H-1)], 5.43 (s, 1H, PhCH), 5.58 [d (*J* = 5.7), 2H, OH × 2], 6.15 (s, 2H, $PhNH_2$), 6.64 [d (*J* = 8.7), 2H, *o*-$PhNH_2$], 6.83 [d (*J* = 12), 2H, *p*-$PhNH_2$] 7.36–7.39 (m, 3H, *p*, *m*-Ar-H), 7.42–7.71 (m, 2H, *o*-Ar-H); *m*/*z* 360 (M + H^+); Found: C, 63.18; H, 5.91; N, 3.89. Calc. for $C_{19}H_{21}O_6N$: C, 63.50; H, 5.89; N, 3.90%.

1-*O*-(*p*-Aminophenyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (4b)

Compound **4b** was synthesised according to a method similar to that used for **1b**. 1-*O*-(*p*-Nitrophenyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (**4a**)[28] used as a starting material was synthesised from 1-*O*-(*p*-nitrophenyl)-β-D-glucopyranoside and benzaldehyde in a manner similar to the literature:[15,17] 1-*O*-(*p*-aminophenyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (203.5 mg, 44.1%), mp 169.6–170.0 °C; ^{1}H NMR (DMSO-d_6) δ 3.17–4.22 [m, 6H, sugar-CH (H-2 ~ H-6)], 4.88 [d (*J* = 4.5), 1H, sugar-CH(H-1)], 5.43 (s, 1H, PhCH), 5.57–5.59 (m, 2H, OH × 2), 6.15 (s, 2H, NH_2), 6.63–6.66 (m, 2H, *o*-ArH in $PhNH_2$), 6.81–6.85 (m, 2H, *m*-ArH in $PhNH_2$), 7.36–7.42 (m, 3H, *p*,*m*-Ar-H), 7.43–7.71 (m, 2H, *o*-Ar-H); *m*/*z* 360 (M + H^+); Found: C, 63.21; H, 6.02; N, 3.87. Calc. for $C_{19}H_{21}O_6N$: C, 63.50; H, 5.89; N, 3.90%.

Solvent effects on gelation in the absence of metal salts

The gelator and solvent were put in a septum-capped sample tube and heated until the solid was dissolved. The solution was cooled to 25 °C for 1 h. If the stable gel was observed, it was classified as G [it was shown as G(S) if the concentration of gelator was under 1.0 (wt/vol)%].

Gelation test in the presence of metal salts

The gelator (4.0 mg, 11.1×10^{-6} mol) was added to an ethanol solution (400 μl) containing metal salt (11.1×10^{-6} mol) in a septum-capped sample tube and heated until the solid was dissolved. The solution was cooled to 25 °C for 1 h. If the stable gel was observed, it was classified as G.

Gel–sol phase transition temperatures

The test tube containing the gel was immersed inversely in a thermostatted oil bath. The temperature was raised at a rate of 2 °C min^{-1}. Here, the T_{gel} was defined as the temperature at which the gel disappeared.

SEM observations

A Hitachi S-900S scanning electron microscope was used for taking the SEM pictures. The thin gel was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated by a vacuum pump for 3–5 h. The dry sample thus obtained was shielded by gold. The accelerating voltage of SEM was 5 kV and the emission current was 10 μA.

TEM observations

A Hitachi H-7100 transmission electron microscope was used for taking the TEM pictures. A carbon-supported grid was pressed against the gel sample. This grid was dried for one night at room temperature. The sample on the grid was observed without staining by TEM. The accelerating voltage of TEM was 75 kV.

Computational methods

Energy-minimization was carried out by a MM3 program using AccuModel 1.0 (Microsimulation L.A. Systems Inc.) on a Macintosh computer.

Apparatus for spectral measurements

^{1}H NMR spectra were measured on a Bruker ARX 300 apparatus. UV spectra were obtained by using a JASCO V-570 spectrometer.

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