Binary Supramolecular Gels Based on Bismelamine·Cyanurate/Barbiturate Noncovalent Polymers

Shiki Yagai,* Masatsugu Higashi, Takashi Karatsu, and Akihide Kitamura*

Department of Materials Technology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
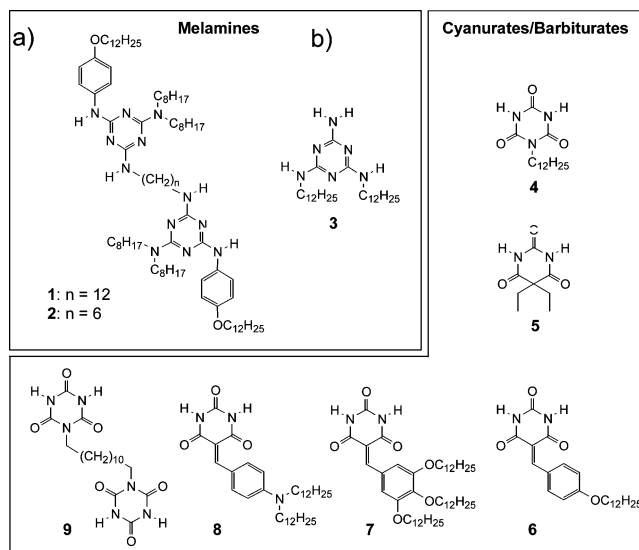
Gel formation of low molecular mass self-assembling molecules in organic fluids is a prominent phenomenon that shows usefulness of supramolecular chemistry in practical materials science.[1] For example, there are a few recent reports which pertain to the design of functional gel, based on conjugated dye molecules, and their use as light harvesting gel materials.[2] Though a diverse kind of self-assembling molecules that can gelate organic fluids by oneself (by single component) has been developed, the examples of a binary organogelator[3] are limited due to its difficulty in practical application. In the binary systems, however, once one component, the structure of which is crucial for gelation, is established, large supramolecular libraries become available by changing the other component, which is hoped to be less crucial for gelation. This endows the binary systems with facile modulability in the physical property and the function of the gel.

Complementary hydrogen-bonding interaction between the diaminopyridine-type DAD hydrogen-bonding surface and imide ADA hydrogen-bonding surface is one of the most useful intermolecular glues and has been widely used to create a diverse kind of supramolecular structures.[4] Use of this interaction in organogel formation was first accomplished by Hanabusa et al., using linear tapelike aggregates formed from amphiphilic

Chart 1

melamine and barbiturate derivatives.[3a] The main disadvantage in this system is its low gelation ability (minimum concentration for gelation (*mcg*) is approximately 2−5 wt % in cyclohexane). This is most likely due to the rigid and flat structure of the tapelike aggregates, unfavorable for three-dimensional entanglement with large void volume.[5] Shinkai et al. improved the gelation ability of this binary system by conjugating the cholesteryl functionality.[3b,c] Here, we report a versatile binary organogelator system based on DAD·ADA hydrogen-bonding complexation between melamine and cyanurate or barbiturate.

As components crucial for gelation, bismelamines **1** and **2** were prepared by tethering two monotopic melamines by a flexible aliphatic linkage (Chart 1). These components are expected to form quasi-one-dimensional supramolecular polymers[6] through the complementary hydrogen bonding with ditopic cyanurate **4** or barbiturates **5**−**8**. Melamine **3** is a reference aggregator to form linear tapelike assembly.[3a] Biscyanurate **9** may act as a cross-linker for the one-dimensional supramolecular polymers, facilitating gelation as well as enhancing stability of the gel.

Bismelamine **1** alone did not gelate any organic solvents examined, whereas successful gelation was observed in the presence of an equimolar amount of complementary partners **4**, **6**, and **7** in nonpolar organic solvents even at the concentrations less than 5 mM (Table 1 and Figure 1a).[7] This demonstrates that gelation is a

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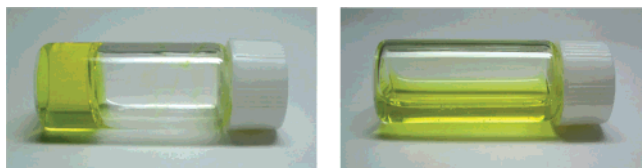
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(7) Gelation test was conducted as follows. A solid mixture of bismelamine and cyanurate/barbiturate (1:1 molar ratio) was completely dissolved in appropriate organic solvent (1 mL) by heating in a sealed vial (φ = 16.5 mm), and the resulting homogeneous solution was cooled to room temperature and kept at 20 °C for 1 h. Gelation was judged by the appearance of gravitational flow in the resulting homogeneous materials.

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Table 1. Gelation Properties of the Binary Organogelators at 20 °C[a]

	1·4	1·5	1·6	1·7	1·8
cyclohexane	G (0.21)	I	G (0.22)	G (0.26)	VF
hexane	TG	I	G (0.34)	G (0.98)	VF
benzene	P	P	G (0.41)	S	S
toluene	G (0.19)	C	G (0.25)	TG	S
chloroform	P	S	VF	S	S
CCl$_4$	VF	I	G (0.56)	G (0.56)	S

[a] [Gelator] = 5 mM (0.5−1.5 wt %); G: gel, C: crystal, S: solution, P: precipitates, TG: turbid gel, VF: viscous fluid. For the gelators showing successful gelation, their *mcg* values are shown in parentheses (wt %).

Figure 1. Photographs of cyclohexane gel of **1·7** (5 mM) before agitation (a) and after agitation (b).
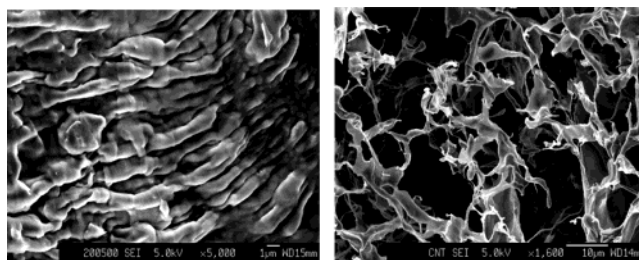
consequence of DAD·ADA hydrogen-bonding complexation.[8] Remarkably, in all pairs, *mcg* values in cyclohexane at 20 °C could be decreased up to 1.0 mM (0.21 wt % for **1·4**, 0.22 wt % for **1·6**, and 0.26 wt % for **1·7**). For the **1·6** pair, this value shows that approximately 10000 cyclohexane molecules are immobilized by one **1·6** pair. These *mcg* values are considerably lower than that of the **3·7** pair in cyclohexane (15 mM, 2.6 wt %) and can categorize these gelators as supergelators. The dramatic improvement of the gelation ability must come from the looser association of the one-dimensional aggregates, accommodating large void volume that can entrap solvent molecules therein.

The cyclohexane gels obtained from **1·4**, **1·6**, and **1·7** are jelly-like and showed thixotropic property;[9] i.e., mechanical agitation makes them completely isotropic fluids (Figure 1b). Aging the resulting fluids at ambient temperature for 1 week did not recover the original gel but gave inhomogeneous loose gel. Recovery of the original gel state requires a heating−cooling procedure. This indicates that the mechanical agitation breaks the gel networks into the soluble supramolecular polymer level, not into a molecularly dissolved state. Since gelation is a result of crystallization of gelator molecules, such soluble supramolecular polymers obtained by mechanical agitation are supposed to no longer have optimum structures required to form the stable gel network.

Microscopic structure of the present gel was investigated by scanning electron microscopy (SEM). The xerogel of the cyclohexane gel of **1·4** obtained by air-drying exhibited bundles with a diameter of ca. 1 μm (Figure 2, left). These bundles must be hierarchically created from fibrous assembly in the air-drying process.

Figure 2. SEM images of the dried cyclohexane gel of **1·4** obtained via air-drying (left) and freeze-drying (right).

Thus, the freeze-dried gel visualized submicrometer fibrous entities entangled in a three-dimensional manner (Figure 2, right).

Gel-to-sol transition behavior of the cyclohexane-d_{12} gel of **1·4** (2 mM), apparent gel-to-sol transition temperature (T_{gel}) of which had been determined as 33 °C in the "dropping ball method",[10] was assessed by variable temperature ^{1}H NMR measurements. At 25 °C, only the resonances of monomeric **1** were observed as unresolved peaks with significantly low sensitivity (Figure 3). As reported previously, the resonances of the gelator molecules in a rigid gel state are too broad to be observed due to the long correlation time.[11] Therefore, the observed resonances are derived from monomeric **1** dissolved in the solvent entrapped *between the fibers of the gel*. With increasing the temperature (30−50 °C), the resonances of the monomeric **1** became sharper. Interestingly, the resonances of the monomeric **4** were not observed until the temperature reached 55 °C. This might be due to the low solubility of **4** in cyclohexane: **4** would be embedded *within the fiber of the gel*.[12] Further increase of the temperature allowed observation of the resonance of the N−CH$_2$ protons of **4** at 3.97 ppm, indicating the collapse of the fibers of the gel (55−70 °C). Concomitantly with the appearance of the resonances of **4**, the resonances of **1** again became unresolved and this condition continued until the temperature reached 75 °C. Unresolution of the peaks at this temperature range (55−70 °C) strongly suggests the release of soluble (NMR-detectable) large aggregates from the gel network. Finally, at 75 °C, the spectrum became well-resolved, indicating the presence of molecularly dissolved **1** and **4**. Thus, the VT NMR investigation of the present gel demonstrated stepwise collapse of the gel, i.e., gel fiber → soluble large aggregates → monomers.

The length of the linker moiety connecting the two melamine functionality in a bismelamine component proved critical for gelation. In sharp contrast to **1**, the equimolar mixture of hexamethylene-tethered bismelamine **2** and **4−8** did not gelate any organic solvents even at high concentrations over 150 mM. An analogous effect of aliphatic linker moiety connecting the two interactive sites on gelation has been reported in bisurea gelators[9a] and dendritic binary gelators.[3d] In the present system, however, lack of the gelation ability in **2** can

(8) FTIR spectrum of the cyclohexane gel of **1·4** showed a broad NH stretching band at 3323 cm^{-1} and a broad C=O stretching band at 1694 cm^{-1}. These bands are considerably different from the solid samples (self-aggregated) of the individual components (NH stretching bands of **1** at 3449, 3423, and 3269 cm^{-1}; NH stretching band of **4** at 3205 cm^{-1}; C=O stretching bands of **4** at 1743, 1712, and 1694 cm^{-1}).

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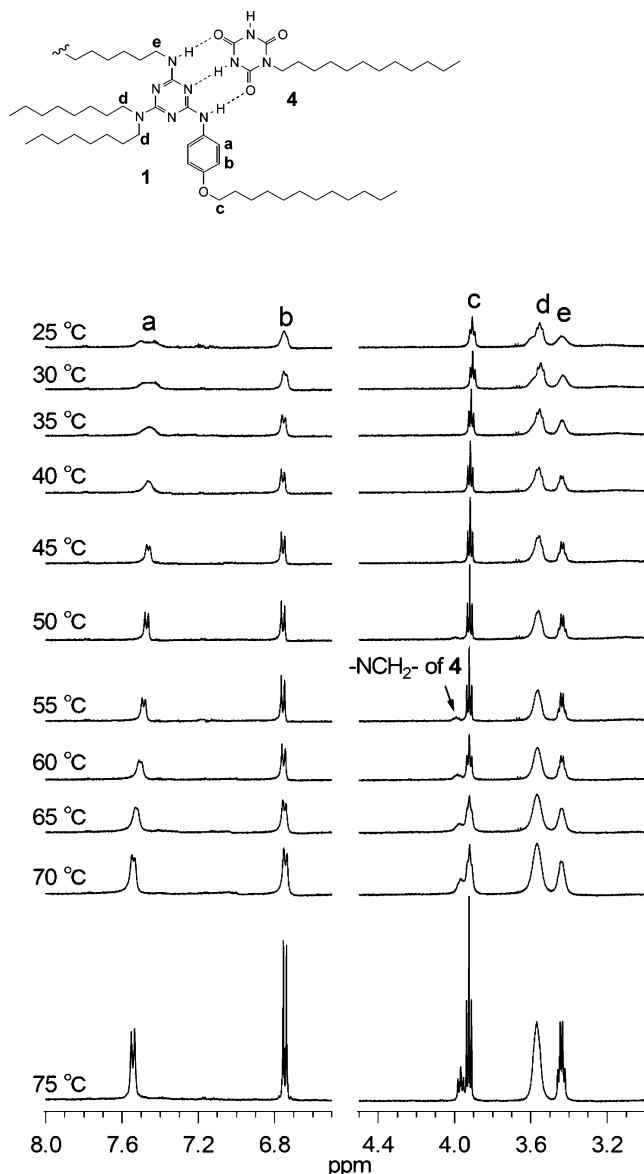
Figure 3. Variable temperature ^{1}H NMR spectra of cyclohexane-d_{12} gel of **1·4** (2 mM).

Figure 4. ^{1}H NMR spectrum of a 1:1 mixture of **2** and **4** (5 mM) in cyclohexane-d_{12} at 25 °C.

be explained from the ^{1}H NMR investigation (Figure 4). The equimolar mixture of **2** and **4** in cyclohexane-d_{12} (5 mM) exhibited a well-resolved spectrum with the resonance of the hydrogen-bonded NH protons of **2** (signal e) at δ 9.65 ppm and the imide NH protons of **4** at δ 15.5 ppm, indicating the formation of well-defined aggregates. Together with the high solubility of these complexes in cyclohexane (over 150 mM), it seems likely that **2** acts as a Hamilton-type receptor[13] for guests **4**–**8** to form closed aggregates shown in Figure 4.

Cross-linking of one-dimensional fibrous aggregates enhances the gel network as well as facilitates propagation of the gel network. In the present binary system, biscyanurate **9** can act as a cross-linker. The 2:1 solid mixture of **1** and **9** (**1₂·9**, equivalent based on the number of hydrogen-bonding sites) is scarcely soluble in cyclohexane even at refluxing temperature, but it could be dissolved, to some extent, in the cyclohexane
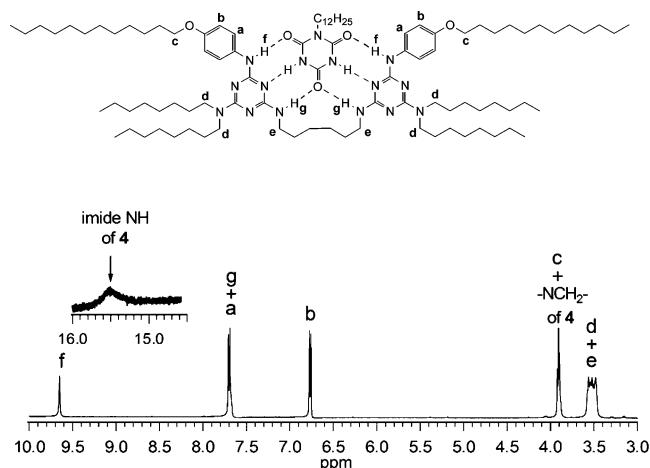
gel of **1·4** by a heating–cooling procedure, giving transparent gel. The maximum mixing ratio of **1₂·9** into **1·4** gel (7 mM) is 20%, above which precipitation occurred after cooling to room temperature. The resulting **1·4·9** ternary gel showed a slight increase in T_{gel} (0%, 37 °C; 10%, 40 °C; 20%, 43 °C). In the concentration range near *mcg* (1 mM), we could not observe the difference in T_{gel} between the binary and the ternary systems. Instead, the aging period required for complete gelation was markedly improved in the ternary system. At 20 °C, the ternary system completely gelated cyclohexane within minutes whereas the **1·4** binary system required 1-h aging for gelation. This result clearly demonstrates the promoted propagation of the gel network by the cross-linking molecule.

Finally, it is worthwhile to focus on the structural effect of cyanurate/barbiturate components on gelation (Table 1). Successful gelation of **1** with amphiphilic cyanurate **4** and barbiturates **6** and **7** indicates the requirement of sufficiently long aliphatic chains for gelation. Of great interest is the low gelation ability of **1·8** despite the structural similarity of **8** to **6** and **7**. In the low-concentration range (1–5 mM), **1·8** in cyclohexane exists as a viscous fluid at ambient temperature. However, in a sufficiently high concentration range (>16 mM, 3.6 wt %), **1·8** affords stable gel without thixotropic property, which is quite different from jelly-like gel obtained in other pairs. This may originate from stronger D-π-A character of **8** than **6** and **7**, enhancing the dipole–dipole aggregation of dye.[14] If such a dipole–dipole aggregation cooperatively occurs between the dyes embedded in one-dimensional supramolecular polymers, they should be bundled up more densely and strongly. This is in good agreement with the high *mcg* value (16 mM) of **1·8** in cyclohexane and the stability of the resulting gel against mechanical stress. This point is highly intriguing in view of enhancing the stability of gel by the cooperation of hydrogen bond and dye aggregation as well as the control of dye aggregation by hydrogen-bonded supramolecular scaffold.[15] Further investigation into such aspects is now in progress.

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In conclusion, we have demonstrated a novel binary organogelator system based on melamine·cyanurate/barbiturate hydrogen-bonded supramolecular polymers. The gelation abilities of the present binary systems are remarkably high as compared to those of the linear tapelike aggregates reported previously.[3a] Physical properties of the gel could be facilely adjusted by changing

the cyanurate/barbiturate components. Bismelamine **1** is a versatile molecule providing functional gels featuring imide-functionalized dye molecules such as barbiturate-type merocyanine[15c] and perylene bisimide dyes.[15a] We are currently creating photofunctional organogels by the use of such photofunctional chromophores possessing imide functionality.

Supporting Information Available: Characterization data of **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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