Low Molecular Weight Gelator Containing β-Diketonato Ligands: Stabilization of Gels by Metal Coordination

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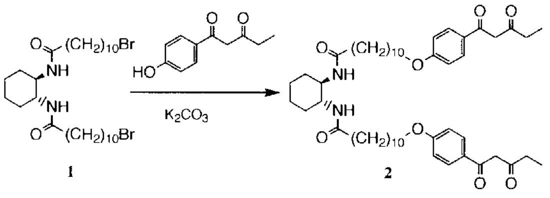
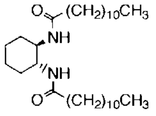
A low molecular weight gelator containing β-diketonato ligands was prepared from a derivative based on *trans*-(1*R*,2*R*)-diaminocyclohexane. Gels were converted to mechanically-robust and thermally-stable gels by complexation between β-diketonato ligands and divalent metal ions.

In the last decade, a number of reports have described the low molecular weight gelators that are capable of hardening liquids through non-covalent bonds.[1,2] Recently, there has been rising interest in not only the exploitation of gelators but also in their applications.[3] However, the thermal stability and mechanical strength of the formed gels must be further improved for practical use. Ferigna et al. reported the formation of thermally stable organogels by radical polymerization using a gelator containing two vinyl groups.[4] Shinkai et al. synthesized a robust gel by in situ cross-linking of the gel with tolylene diisocyanate[5] and also reported the preparation of robust gels by in situ photoradical polymerization of a gelator containing a bis(diacetylene) group.[6] We found that the gel strength was markedly increased, when polymer solutions were gelled by gelators.[7] In this communication, we report the physical gelation by a new gelator containing two ligands of β-diketone and the formation of mechanically-robust and thermally-stable gels by coordination with metal ions. Although there is precedence for gelation of solvents by organometallic compounds,[8] complexation with metal ions for the reinforcement of gels appears to be unprecedented.

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Compound **2** , which has two β-diketonato ligands, was prepared from *trans*-(1*R*,2*R*)-bis(10-bromodecylcarbonylamino)-cyclohexane (**1**) and 1-(*p*-hydroxyphenyl)pentane-1,3-dione in the presence of potassium carbonate. Results of gelation tests of compounds **1** and **2**, judged by test tube tilting method,[9] are summarized in Table 1. Compound **1** exhibited a very strong gelation ability, which was comparable to that of *trans*-(1*R*,2*R*)-bis(undecylcarbonylamino)cyclohexane (**3**).[10] Compound **2** having β-diketonato ligands also gels up many fluids, but not alcohols and *N*,*N*-dimethylformamide. Hydrophilic β-diketonato segments in **2** may destroy the hydrophilic and hydrophobic balance indispensable for good gelators. Although gelator **2** formed crystals from methanol instead of gels at the concentration of 5% gelator by weight (see Table 1), the mixture of **2** and **3** (molar ratio; 1:4), referred to as the mixed gelator, could gel up methanol at the concentration of 3% by weight. FT-IR spectrum of the methanol gels of the mixed gelator (30 mg cm^{-3}) is characterized by a strong band at 1635 cm^{-1} with a shoulder at 1649 cm^{-1}, which are assigned to hydrogen bonding stretching vibrations of C=O. It should be mentioned that gelator **2** in methanol (9.1 mg cm^{-3}) in the absence of **3** affords an isotropic solution, whose spectrum is characterized by a broad band at 1654 cm^{-1} indicative of non-hydrogen bonding. FT-IR spectra indicated that the molecules of **2** were completely integrated into molecular assemblies of gelator **3** through hydrogen bonding. In the present study, we focused on methanol gels by the mixed gelator and carried out the complexation with divalent metal ions.

Table 1. Results of gelation test[a]

Solvent	1	2	3
Methanol	S	C	G
Ethyl acetate	G	G	G
Acetone	G	G	G
2-Butanone	S	G	G
Benzene	G	l-G	G
Toluene	G	l-G	G
N,*N*-Dimethylformamide	G	S	G
Dimethyl sulfoxide	G	l-G	G
Kerosene	G	G	G
Light oil	G	G	G
Silicone oil	G	G	G
Soybean oil	G	G	G

[a]The warmed isotropic solution containing 5% gelator by weight was kept at 25 °C for 2 h. G = gel, l-G = loose gel, S = solution, C = crystallization.

Chelation was carried out by addition of triethylamine over the methanol gels containing $CuCl_2/2H_2O$, $NiCl_2/6H_2O$, or $CoCl_2/6H_2O$. When triethylamine was added, the colors of gels containing Cu^{2+}, Ni^{2+}, and Co^{2+} were changed from green to deep green, from pale green to green, and from pink to orange, respectively. Figure 1 shows the gel strength of Ni^{2+}-containing gels before and after chelation. The gel strengths were reproducible to about 5% on repeated runs. When the methanol containing $NiCl_2/6H_2O$ was gelled by the mixed gelator (30 mg cm^{-3}) and complexed by adding triethylamine, the gel strength was raised from 262 g cm^{-2} to 375 g cm^{-2}. Increasing the gel strength after chelation was also observed for gels containing $Cu^{2+}$and Co^{2+}. It was clarified that the reinforcement of molecular fibers through metal-complexation results in the formation of mechanically-robust gels.

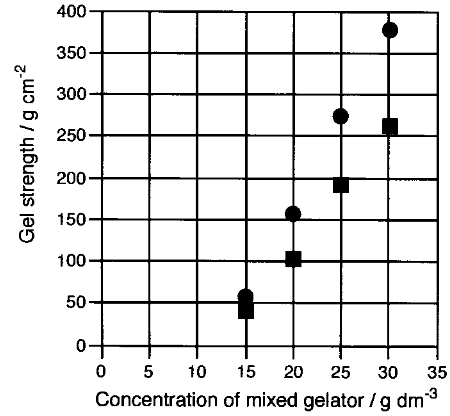

Figure 1. Strength of Ni^{2+}-containing methanol gels formed by mixted gelator (**2**+**3**; 1:4 molar ratio) before (■) and after adding triethylamine (●). The concentration of NiCl$_2$/6H$_2$O was adjusted to be equal to that of **2** in mixed gelator. The molar concentration of added triethylamine was 1.5 times that of **2**.

We determined sol–gel transition temperatures of gels reinforced by chelation using a ball-dropping method.[11] Figure 2 shows the sol–gel transition temperatures of gels before and after chelation. The transition temperature of the gel without metal ions was somewhat reduced by adding triethylamine. This can be explained by the action of triethylamine as a hydrogen bond acceptor. Triethylamine will partially destroy the intermolecular hydrogen bonds among the mixed gelator molecules. On the other hand, the sol–gel transition temperatures for the gel containing metal ions were drastically increased by adding triethylamine. Actually, the gels reinforced by chelation were too stable to change into the sol until 65 °C, which is the boiling point of methanol. Above the boiling point, the solvent was gradually released from the gels.

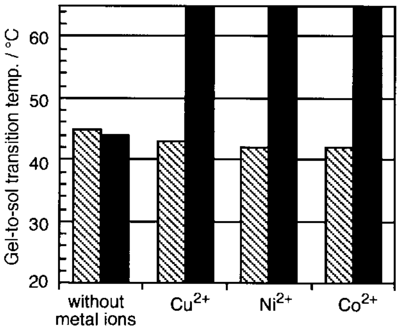

Figure 2. Gel-to-sol transition temperature of methanol gels formed by mixted gelator (**2**+**3**; 1:4 molar ratio). The concentration of mixed gelator is 25 g dm^{-3}, in which the concentration of **2** is 9.1 mM. The concentration of bivalent metal salt is 9.1 mM. Shaded bar: before adding triethylamine; black bar: after adding triethylamine (13.7 mM).

It is interesting to note that very contrasty TEM image was observed for Cu^{2+}-containing methanol gel after chelation, even if the sample was not treated with any stainers (Figure 3). Considering the fact that the reflection of electron beams is caused by heavy atoms, the contrasty image of aggregates is consistent with the view that the fibers were reinforced by cross-linking through the bis(β-diketonato)copper(II) complex.

Figure 3. TEM image of Cu^{2+}-containing methanol gel after chelation.

In conclusion, complexation with divalent metal ions leads to reinforce the weak gels of low molecular weight gelators, as a consequence providing mechanically-robust and thermally-stable gels.

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8 See five organometallic compounds described in page 246 of Ref. 1.

9 A tube tilting method is as follows: a weighed gelator was mixed with an organic liquid (2.0 mL) in a test tube with screw cap (inside diameter; 14 mm) and the mixture was heated until the solid was dissolved. The resulting solution was cooled at 25 °C for 2 h and then the gelation was checked visually. When upon inversion of the test tube no fluid ran down the walls of the tube, we judged it "gel". When the gel was formed, we evaluated quantitatively the gel-forming ability by minimum gel concentration (M.G.C.) which is the minimum concentration of gelator necessary for gelation at 25 °C.

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11 A steel ball (weight; 5.5 g, diameter; 11 mm) was placed on the surface of a gel and then the temperature was gradually increased. When the steel ball went down with a collapse of the gel, we determined the temperature as sol–gel transition one.