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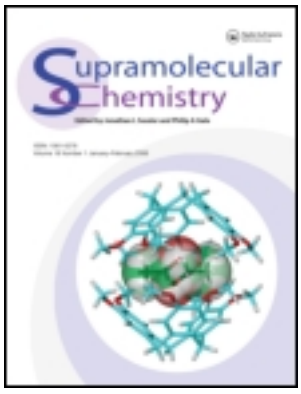

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Metal salt-induced regelation of acetone solutions of tris-urea low-molecular weight gelator and anions

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Metal salt-induced regelation of acetone solutions of tris-urea low-molecular weight gelator and anions

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A mixture of tris-urea **1** and acetone formed a gel on ultrasound irradiation. The gel-to-sol phase transition proceeded by adding halide ions as tetrabutylammonium (TBA) salts. The sols (solutions) were able to regel by mixing them with other metal salts followed by ultrasound irradiation. The regelation ability of various metal salts was tested. Anion selective and non-selective regelation was observed depending on the metal salt used. The mechanistic aspects of the sol-to-gel phase transition in the presence of metal salts were investigated using ^{1}H NMR employing a model compound.

Keywords: gel; phase transition; self-assembly; urea

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Introduction

Supramolecular gels are an attractive area of research, and many examples have been reported (*1–4*). Several interactions, such as hydrogen bonds, π–π, dipole–dipole and van der Waals interactions, form one-dimensional regulated assemblies of small molecules on gelation called low-molecular weight gelators (LMWGs) (*5–13*). Stimulus-responsive gel-sol phase transitions of supramolecular gels have the potential for use in intelligent materials. Shinkai and co-workers (*14*) reported on the photo-induced gel-sol phase transition of an azobenzene-introduced cholesteric-based LMWG as pioneering research. Today, various types of stimulus-responsive gel-sol phase transitions have been achieved as a result of rational design of LMWGs (*15–24*). Several strategies have been used to develop chemical stimulus-responsive LMWGs. Gel-sol phased transitions in response to changes in pH or redox are typical examples of them (*25*, *26*). It is also possible to synthesise a gel-sol phase transition system based on host–guest interactions, such as hydrogen bonds or metal–ligand coordination (*27*, *28*). Reversible gel-sol phase transitions are observed from physical, pH and redox stimulus-responsive LMWGs. In contrast, the exclusion of a host–guest interaction without damaging the entire system is difficult to achieve. Therefore, it is difficult to construct a reversible gel-sol phase transition system involving a host–guest interaction-responsive LMWG.

Recently, we have developed a reversible gel-sol phase transition system that is responsive to a chemical stimulus using a tris-urea LMWG (*29*, *30*). The acetone gel showed a selective gel-to-sol phase transition after the addition of anions. The obtained sols were reconverted to a gel either selectively or non-selectively by adding $BF_3{\cdot}OEt_2$ or $ZnCl_2$, respectively. Mechanistic investigations into the regelation process were not carried out at the time. Here, we report in detail experiments on our regelation system using various metal salts and discuss the mechanism using NMR data on a model compound.

Results and discussion

Gelation and phase transition (29)

Tris-urea LMWG **1** was synthesised in three steps from 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene. Ultrasound irradiation to a heterogeneous mixture of **1** and acetone afforded an opaque gel (Figure 1). The acetone gel changed into a homogeneous solution by adding various anions as a consequence of anion recognition by the ureide moiety of **1**. All of the halide ions used led to a gel-to-sol phase transition, and the amount required to complete the phase transition depended on the binding constant of the ions with **1**. The addition of 1.1, 1.7, 2.0 and 2.9 equiv. of fluoride, chloride, bromide and iodide ions as tetrabutylammonium (TBA) salts, respectively, was needed to attain the gel-to-sol phase transition of the acetone gel of **1** (Figure 1).

Regelation experiments

Interaction between the anions and ureide prevented the self-assembly of **1**. The removal of an anion may lead to intermolecular hydrogen bond aggregation of **1** for gelation. The results of the regelation experiments of an

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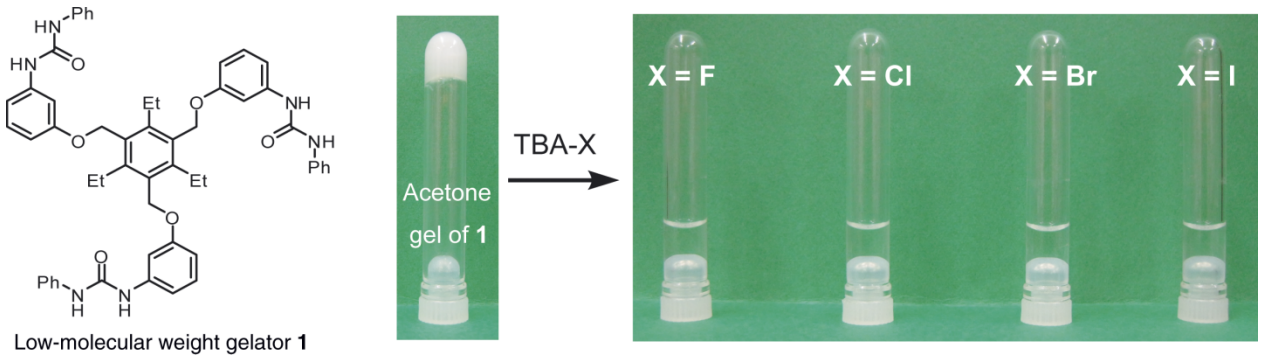

Figure 1. Chemical structure of LMWG **1** (left). Photographs of an acetone gel of **1** and anion-induced solutions of mixture of **1** and TBA-X in acetone (right).

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acetone solution of **1** and halide ions by adding various metal salts are summarised in Table 1. The solutions used in the regelation experiments were prepared by mixing **1** and halide ions (TBA-F and TBA-Cl = 2 equiv., TBA-Br and TBA-I = 3 equiv. for **1**) in acetone. Equimolar metal salts of the halide ions were added to the solutions, and then ultrasound was used to irradiate the solutions for a period of 30 min. Gelation was confirmed using the inverted test tube method. $BF_3{\cdot}OEt_2$ acted as a fluoride ion selective regelation reagent (entry 1) (*29*). In the mixture, $BF_3{\cdot}OEt_2$ and fluoride ions formed tetrafluoroborate ions (*31*) which have little capability to form a gel-to-sol phase transition of the acetone gel of **1**. Zinc salts, such as $ZnCl_2$, $ZnBr_2$ and ZnI_2, are effective for the regelation of halide ions containing solutions of **1** in a non-selective manner (entries *2–4*). Homologous $CdCl_2$ also worked as a non-selective regelation reagent for the above solutions, as well as the zinc salts (entry 5). The addition of 1 equiv. of bivalent copper chloride ($CuCl_2$) for the anions showed a unique selectivity on their regelation (entry 6). Chloride and iodide ion-containing solutions of **1** were gelled, but fluoride and bromide ion-containing solutions of **1** were unchanged. Excess amounts of $CuCl_2$ (more than 2 equiv. for anions) afforded gels in all halide ion-containing solutions of **1** (entry 7). In contrast with $CuCl_2$, the addition of monovalent copper chloride (CuCl) did not form a gel, and unidentified precipitates were obtained (entry 8). Monovalent copper iodide (CuI) showed a selective regelation capability for acetone solutions of **1** and halide ions (entry 9). An acetone mixture of **1**, fluoride ions and CuI gave a heterogeneous suspension, but the addition of CuI to solutions of **1** containing chloride, bromide or iodide ions formed gels after ultrasound irradiation. The selective regelation nature was unchanged on increasing the amount of CuI used. Regelation experiments by adding 1 equiv. of $FeCl_3$, $SnCl_2$ or $BiCl_3$ showed irreproducible results. By fixing the amount of the metal salts to 2 equiv. of the anions, non-selective and reproducible regelation was achieved (entries *10–12*). These sol-gel phase transitions, in general, could be repeated several times. The addition of other metal salts, such as $MgCl_2$ (entry 13), $CoCl_2$, $NiCl_2$, $LaCl_3$ and $PbCl_2$ did not form a gel. Xerogel prepared from an acetone gel of **1** showed intertwining nanosized fibres under a scanning electron microscope (SEM). In contrast, a halide ion-containing solution of **1** showed no significant structure under SEM observation. Most of the xerogels prepared from regelled samples of **1**, halide ions and metal salts showed fibrous aggregates in an SEM. As a typical example, an SEM image of a xerogel prepared from an acetone gel of **1**, TBA-Cl and CuI is shown in Figure 2.

Table 1. Regelation experiment using metal salts[a].

		State[b]			
Entry	Metal salt	TBA-F	TBA-Cl	TBA-Br	TBA-I
1	$BF_3{\cdot}OEt_2$	G	S	S	S
2	$ZnCl_2$	G	G	G	G
3	$ZnBr_2$	G	G	G	G
4	ZnI_2	G	G	G	G
5	$CdCl_2$	G	G	G	G
6	$CuCl_2$	S	G	S	G
7	$CuCl_2$[c]	G	G	G	G
8	CuCl	P	P	P	P
9	CuI	P	G	G	G
10	$FeCl_3$[c]	G	G	G	G
11	$SnCl_2$[c]	G	G	G	G
12	$BiCl_3$[c]	G	G	G	G
13	$MgCl_2$	S	S	S	S

[a] Gelation was confirmed after 30 min sonication of a mixture of **1** (2 wt%), TBA-X (X = F and Cl: 2 equiv. of **1**, X = Br and I: 3 equiv. of **1**) and metal salt (1 equiv. of TBA-X) in acetone.
[b] G: gel; S: solution; P: precipitation.
[c] 2 equiv. metal salt of anion was used.

NMR studies

We carried out the NMR experiments using a model compound of an LMWG to elucidate the mechanistic aspects of the metal salt-induced regelation of **1** and an

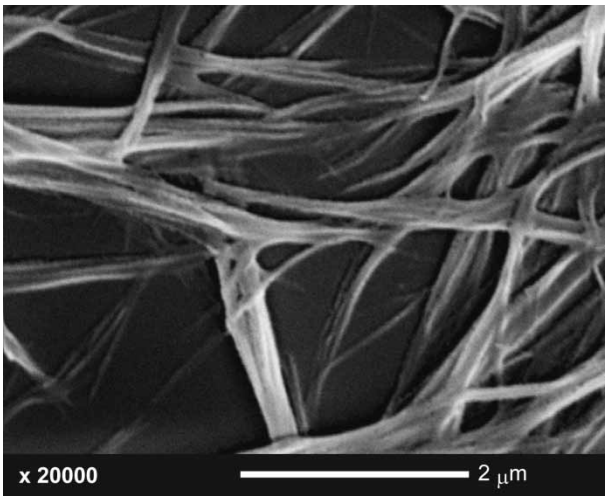

Figure 2. SEM image of a xerogel prepared from an acetone gel of **1**, TBA-Cl and CuI.

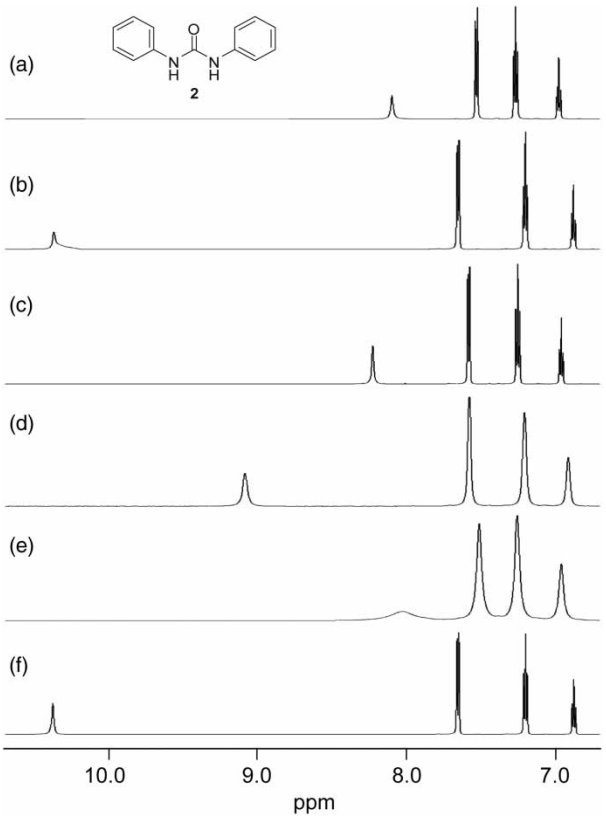

Figure 3. Partial ^{1}H NMR spectra of (a) [**2**] = 60 mM; (b) [**2**] = [TBA-Cl] = 60 mM; (c) [**2**] = [TBA-Cl] = [$ZnCl_2$] = 60 mM; (d) [**2**] = [TBA-Cl] = [$FeCl_3$] = 60 mM; (e) [**2**] = [TBA-Cl] = 60 mM, [$FeCl_3$] = 120 mM; and (f) [**2**] = [TBA-Cl] = [$MgCl_2$] = 60 mM in acetone-d_6.

anionic solution. The ureide groups of **1** play an important role in the gelation and phase transitions. Mono-urea **2**, which is simply an extracted structure of **1**, was used in the NMR experiments as a model compound, given its solubility in acetone. The ureide N—H protons of **2** were observed at 8.10 ppm in the ^{1}H NMR spectrum (60 mM in acetone-d_6) (Figure 3(a)). The addition of an equimolar amount of TBA-Cl to the solution resulted in a change in the ^{1}H NMR spectrum, given the ureide–anion interaction (Figure 3(b)). In particular, a significant downfield shift of the ureide N—H (δ = 10.37 ppm) was observed. Addition of an equimolar amount of $ZnCl_2$, which was a fine regelation reagent of **1**, and an anionic solution to an acetone-d_6 solution of **2** and TBA-Cl led to a change in the ^{1}H NMR spectrum (Figure 3(c)). The spectrum became similar to that of **2** alone, and the N—H protons appeared at 8.23 ppm. This meant that $ZnCl_2$ would prevent the interaction between **2** and anions. In the regelation process, **1** released from an interaction with anions by metal salts such as $ZnCl_2$ would self-assemble and gel. The irreproducible regelation results of **1** and an anionic solution using 1 equiv. of $FeCl_3$ were explained by these ^{1}H NMR experiments. The ureide N—H protons of **2** appeared at 9.09 ppm in an equimolar mixture of **2**, TBA-Cl and $FeCl_3$ in acetone-d_6 (Figure 3d). By adding 2 equiv. of $FeCl_3$ to a solution of **2** and TBA-Cl, the N—H protons of **2** shifted to 8.03 ppm (Figure 3(e)). One equivalent of $FeCl_3$ was not enough to prevent an interaction with the anions, and therefore, the regelation results were uncertain. Complete dissociation of ureide and the anions

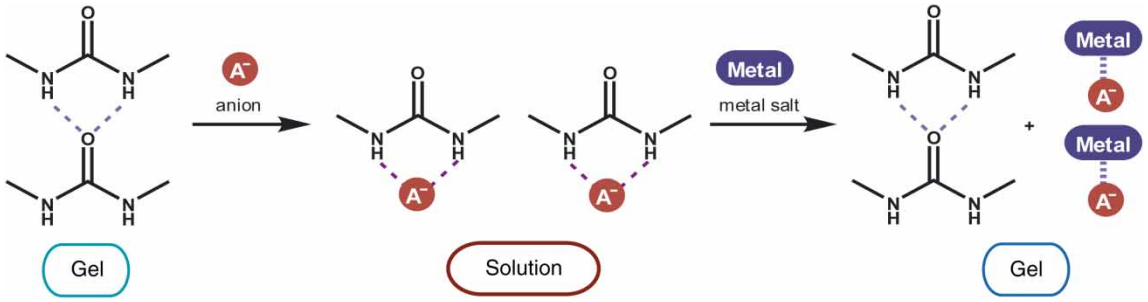

Figure 4. Schematic representation of plausible mechanism of metal salt-induced regelation.

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was accomplished by adding 2 equiv. of $FeCl_3$. As a result, positive regelation was attained. In contrast, the addition of $MgCl_2$, which showed no regelation capability for **1** and an anion solution, to an acetone-d_6 solution of **2** and TBA-Cl led to a small shift in the ^{1}H NMR spectrum (Figure 3(f)). The metal salt was not able to cancel the ureide–anion interaction and could not act as a regelation reagent. Similar results were also observed in the ^{1}H NMR experiments of **2** in the presence of various halide ions and metal salts. These results suggest that the prevention of the ureide–anion interaction resulted from an anion–metal salt interaction that revived the self-assembly of LMWG **1** (Figure 4).

Conclusions

Acetone gels of tris-urea **1** showed a gel-to-sol phase transition on addition of halide anions. The solutions were able to regel on ultrasound irradiation in the presence of some metal salts. Metal salts, such as $ZnCl_2$ and $CdCl_2$, showed a non-selective regelation of anions containing solutions of **1**. $BF_3{\cdot}OEt_2$ acted as a fluoride ion selective regelation reagent. As a complementary result, regelation with $CuCl_2$ showed chloride, bromide and iodide ion selectivity. ^{1}H NMR experiments using **2** as a model compound indicated that the prevention of a ureide–anion interaction was the key process for regelation.

Experimental

Regelation experiments

A weighed amount of tris-urea **1** (2 wt%) and TBA-X were placed in a test tube, and acetone was added. Metal salt was added to the solution, and the closed test tube was sonicated for 30 min. The gelation was confirmed by the inverted test tube method.

Acknowledgements

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