ORIGINAL ARTICLE

Palladium ion-induced supramolecular gel formation of tris-urea molecules

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A multicomponent supramolecular gel constructed from the self-assembly of pyridyl-substituted tris-urea 1 and Pd(OAc)$_2$ is reported. A mixture of 1 and Pd(OAc)$_2$ in dimethyl sulfoxide provided a supramolecular gel after brief ultrasound irradiation. The supramolecular gel changed into a sol/solution upon addition of chelating agents such as diamines and bidentate phosphine ligands. Dissociation of the coordination bonds between 1 and the palladium ion via addition of a chelating agent caused the phase transition. The Wacker oxidation of styrene was performed in the supramolecular gel. The reaction in the gel phase required a longer induction period to produce acetophenone than did the reaction in the homogeneous solution.

INTRODUCTION

Supramolecular gels have potential applications in a wide range of fields in materials science.[1,2] The development of supramolecular gels through the self-assembly of a small molecule, called a low-molecular-weight gelator (LMWG), has attracted significant attention in recent decades.[3–6] LMWGs self-assemble by noncovalent interactions, such as hydrogen bonding, π–π interactions, dipole–dipole interactions and solvophobic interactions, to form three-dimensional networks that immobilize fluids. Intermolecular hydrogen bonds of ureide groups are the common driving force for the formation of supramolecular gels.[7] A variety of LMWGs with mono-urea,[8,9] bis-urea,[10–15] tris-urea[16,17] and tetrakis-urea[18] structures have been reported. We have also developed C_3-symmetric tris-urea LMWGs.[19–22]

Supramolecular gels are generally constructed from a single component of LMWGs; however, some are formed from multiple types of small molecules.[23] A metal–ligand coordination bond is a common aspect of the multicomponent supramolecular gels; the advantage in this case is that gel formation can be easily controlled by controlling the formation and dissociation of the metal–ligand coordination bond. Moreover, the metal center of the resulting gel can potentially function as a catalyst for organic reactions.[24–29] We have previously reported multicomponent supramolecular gels of tris-urea, in which the gelation ability of phenyl-substituted tris-urea was increased by the addition of a small amount of pyridyl-substituted tris-urea and metal ion or bis-carboxylic acid.[30] In this paper, we report supramolecular gel formation from pyridyl-substituted tris-urea in the presence of palladium ions in dimethyl sulfoxide (DMSO). The supramolecular gel underwent a gel to sol/solution phase transition upon the addition of chelating agents for palladium ions. The palladium-catalyzed Wacker oxidation of styrene was performed in the gel phase.

EXPERIMENTAL PROCEDURE

Materials and measurements

Pyridyl-substituted tris-urea 1 was synthesized according to a previously published protocol.[30] All chemicals and solvents required were obtained from commercial suppliers. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA600 spectrometer (JEOL, Tokyo, Japan). Ultrasound irradiation was performed using a BRANSON B2510J ultrasonic cleaner. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer (Danbury, CT, USA). Scanning electron microscope (SEM) studies were carried out on a JEOL JSM-6300 spectrometer (JEOL).

Gelation experiment

Weighed amounts of tris-urea 1 and Pd(OAc)$_2$ were placed in a test tube, and solvent was then added. The closed test tube was sonicated for a few minutes. Gel formation was evaluated by the inverted tube test. The mixture remaining at the top of an inverted test tube was defined as the gel.

Wacker oxidation in supramolecular gel

Tris-ureas 1 (0.55 mg, 0.62 μmol), Pd(OAc)$_2$ (0.42 mg, 1.86 μmol), styrene (3.9 mg, 37.2 μmol) and DMSO-H$_2$O (7:1, 100 μl) were placed in a test tube, which was closed and then sonicated for a few minutes to achieve gel formation. The gel was maintained at ambient temperature for the duration of the reaction. Afterwards, CDCl$_3$ was added to the test tube, and the mixture was centrifuged (14 500 g) for 10 min. The supernatant was analyzed by ^{1}H-NMR, using 1,1,2,2-tetrachloroethane as the internal standard. The yield of the produced acetophenone was calculated from the integration ratio of the ^{1}H-NMR spectrum.

RESULTS AND DISCUSSION

Formation of supramolecular gel

C_3-symmetric tris-urea 1, prepared via the condensation of 4-pyridyl isocyanate and a triamine derivative, has two interactive functional groups, namely, ureide and pyridyl (Figure 1).[30] The self-assembly of 1
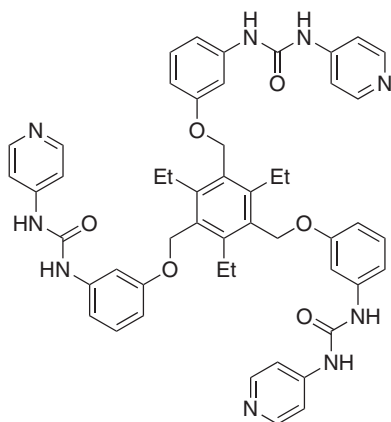
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Figure 1 Chemical structure of tris-urea **1**.

Table 1 Gelation experiments of 1 with additives

Entry	*1* (mM)	Additive (mM)	Solvent	State
1	6.2	none	DMSO	Solution
2	6.2	Pd(OAc)$_2$ (6.2)	DMSO	Solution
3	6.2	Pd(OAc)$_2$ (9.4)	DMSO	Gel
4	6.2	Pd(OAc)$_2$ (19)	DMSO	Gel
5	6.2	Pd(OAc)$_2$ (62)	DMSO	Suspension
6	6.2	PdCl$_2$ (9.4)	DMSO	Suspension
7	6.2	Cu(OAc)$_2$ (9.4)	DMSO	Solution
8	6.2	AgOAc (9.4)	DMSO	Solution
9	6.2	Pd(OAc)$_2$ (9.4)	DMSO-H$_2$O	Gel
10	6.2	Pd(OAc)$_2$ (9.4)	DMF-H$_2$O	Gel

can be controlled by controlling the interactions of these functional groups. Pyridyl-substituted tris-urea **1** is essentially insoluble in most organic solvents, such as acetone, acetonitrile, chloroform and hexane; however, DMSO was found to be a good solvent for **1**, and a mixture of **1** and DMSO gave a clear solution. Nevertheless, the ^{1}H-NMR spectrum of **1** (6.2 mM) in DMSO-d_6 with an internal standard (1,2-dichloroethane) indicated that less than 50% of **1** appeared as signals. This suggests that more than 50% of **1** formed a DMSO-soluble aggregate with a long relaxation time. This result encouraged us to investigate the supramolecular gel formation of **1** and DMSO in the presence of an additive to catalyze the formation of three-dimensional networks.

A broad survey revealed that palladium(II) acetate [Pd(OAc)$_2$] is a suitable additive for the formation of a supramolecular gel of **1**. The gelation experiments are summarized in Table 1. As mentioned above, tris-urea **1** (6.2 mM = 0.5 wt%) in DMSO gave a clear solution (entry 1). A mixture of **1** (6.2 mM), Pd(OAc)$_2$ (6.2 mM) and DMSO gave a slightly turbid yellow solution (entry 2). A yellow supramolecular gel was formed by ultrasound irradiation of a mixture of **1** (6.2 mM), Pd (OAc)$_2$ (9.4 mM), and DMSO for 3 min (Figure 2a and entry 3). Because the typical thermal treatment (heating and cooling) was ineffective for gelation, ultrasound irradiation was critical.[31,32] The minimum gelation concentration of **1** in DMSO was estimated to be 6.2 mM. The molar ratio of **1** and Pd(OAc)$_2$ (2:3) was sufficient for bidentate coordination of the palladium ion to the tridentate ligand. Even a 1:3 mixture of **1** (6.2 mM) and Pd(OAc)$_2$ (19 mM) in DMSO afforded a supramolecular gel (entry 4). The use of a large excess of Pd (OAc)$_2$ had an adverse effect on the gelation, resulting in an insoluble suspension (entry 5). Similar divalent palladium complexes, for example, PdCl$_2$, were ineffective additives for the gelation of **1** (entry 6). Other metal acetates such as Cu(OAc)$_2$ and AgOAc, were also ineffective for gelation (entries 7 and 8). In addition, no gel formation was observed when using a combination of **1** and Pd(OAc)$_2$ with other solvents such as acetone, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) and H$_2$O; instead, insoluble suspensions were obtained from these mixtures. A mixture of **1** (6.2 mM) and Pd(OAc)$_2$ (9.4 mM) could cause gelation in a DMSO/H$_2$O (7:1) solvent (entry 9). Notably, a mixed solvent of DMF and H$_2$O (DMF:H$_2$O = 7:1) formed a yellow gel with a mixture of **1** (6.2 mM) and Pd(OAc)$_2$ (9.4 mM), although neither solvent afforded the gel individually (entry 10). Pyridyl groups of **1** played an important role in this gelation; an analog without pyridyl groups[19] never formed any gel under the standard conditions.

Infrared spectra analyses were carried out to investigate the mechanism of self-assembly (Figure 2b). The C=O stretching
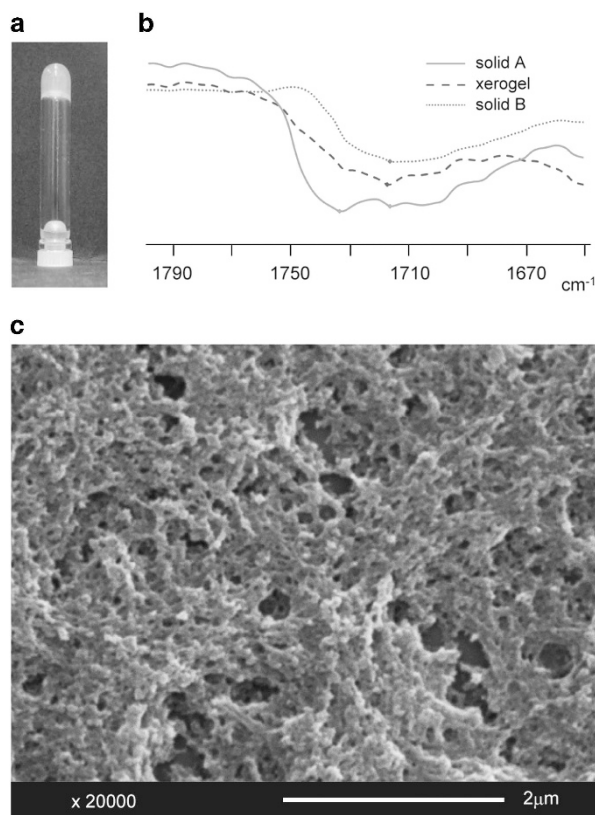

Figure 2 (**a**) Photographs of DMSO gel of **1** (6.2 mM) and Pd(OAc)$_2$ (9.4 mM), (**b**) infrared (IR) spectra of **1** solid A (solid line) and solid B (dotted line) and xerogel of **1** and Pd(OAc)$_2$ (dashed line) and (**c**) scanning electron microscope (SEM) image of xerogel **1** and Pd(OAc)$_2$. A full color version of this figure is available at *Polymer Journal* online.

vibrations of solid **1** (solid A), obtained by reprecipitation from a THF–Et$_2$O mixture, appeared at 1734 and 1716 cm^{-1}. Multiple peaks resulted from the partial aggregation of **1** during purification. By contrast, the C=O stretching vibration of the xerogel of **1** and Pd (OAc)$_2$ was resolved at 1716 cm^{-1}. Another type of solid **1** (solid B) was prepared by the following procedure. A mixture of **1** and DMSO was subjected to ultrasound irradiation for a few minutes, and DMSO was then removed *in vacuo*. The C=O stretching vibration of solid B appeared at 1716 cm^{-1}, which is similar to the infrared spectrum obtained from the xerogel. This indicated that self-assembled

precursors of the supramolecular gel were formed in the DMSO solution of **1** following ultrasound irradiation. It is hypothesized that Pd(OAc)$_2$ interconnects the aggregates of **1** to afford the supramolecular gel.

An SEM image of the xerogel of **1** and Pd(OAc)$_2$ showed a porous spongiform nanostructure (Figure 2c). The small components observed in the SEM image may be because of the self-assembly of **1**, and Pd(OAc)$_2$ may link these together; however, such types of aggregates were not found in the SEM images of **1** itself (Supplementary Figure S1).

Stimuli responsive gel to sol/solution phase transition

Supramolecular gels constructed from weak noncovalent interactions can be easily transformed into a sol/solution in response to external stimuli such as light, mechanical stress and chemical stimuli.[33–35] The molecular design of LMWGs can strongly reflect their responsiveness. For instance, hydrogen-bonded supramolecular gels are typically changed to sols/solutions by the addition of anions, which form host–guest complexes with the gelators.[35]

In the construction of the supramolecular gel of **1** and Pd(OAc)$_2$, the coordination bonds between **1** and the palladium ion play an important role. Dissociation of these coordination bonds can cause a phase transition of the supramolecular gel into sol/solution. A chelating agent seems to be a suitable additive for this phase transition. To test this hypothesis, the addition of ethylene diamine was examined for the phase transition of a supramolecular gel of DMSO prepared from **1** (6.2 mM) and Pd(OAc)$_2$ (9.4 mM). The addition of an equimolar amount of ethylene diamine (9.4 mM) relative to Pd(OAc)$_2$ showed a partial phase transition of the supramolecular gel after 24 h. Complete gel to sol/solution phase transition of the supramolecular gel was achieved by adding 2 equiv. of ethylene diamine relative to Pd(OAc)$_2$ (Figure 3a); this phase transition required 12–24 h, during which time penetration and diffusion would occur. The phase transition was accelerated by ultrasound irradiation. Reconstruction of the gel from the sol/solution was examined by adding excess Pd(OAc)$_2$. The addition of an equimolar amount of Pd(OAc)$_2$ relative to ethylene diamine to the sol/solution [**1** = 6.2 mM, Pd(OAc)$_2$ = 9.4 mM and ethylene diamine = 19 mM] gave a gel after brief

Figure 3 Photographs of mixtures. (**a**) DMSO gel [**1** (6.2 mM) and Pd(OAc)$_2$ (9.4 mM)] with ethylene diamine (19 mM), (**b**) (**a**)+Pd(OAc)$_2$ (19 mM), (**c**) DMSO gel [**1** (6.2 mM) and Pd(OAc)$_2$ (9.4 mM)] with 1,3-diphenylphosphino propane (9.4 mM) and (**d**) (**c**)+Pd(OAc)$_2$ (9.4 mM). A full color version of this figure is available at *Polymer Journal* online.

ultrasound irradiation (Figure 3b). However, the reconstructed gelatinized object was less stable than the original gel and easily collapsed even under weak mechanical stress. The addition of 1,3-diaminopropane to the supramolecular gel of **1** and Pd(OAc)$_2$ showed results almost identical to those with the addition of ethylene diamine. By contrast, the addition of benzyl amine, a monodentate ligand, was less effective in promoting the phase transition, and the gel partially remained even after the addition of 4 equiv. of benzyl amine relative to Pd(OAc)$_2$.

Bidentate phosphine ligands were also effective as additives for the gel to sol/solution transition of the supramolecular gel of **1** and Pd (OAc)$_2$. Complete gel to sol/solution phase transition was achieved by adding only 1 equiv of 1,3-bis(diphenylphosphino)propane (dppp) relative to Pd(OAc)$_2$ (Figure 3c). Reconstruction of the gel from the sol/solution of **1**, Pd(OAc)$_2$, and dppp was not achieved even after adding excess Pd(OAc)$_2$, and an insoluble suspension was obtained (Figure 3d). The analogous 1,2-bis(diphenylphosphino)ethane (dppe) and 1,4-bis(diphenylphosphino)butane (dppb) were less effective, and 4 equiv. of dppe or dppb relative to Pd(OAc)$_2$ were required to complete the phase transition.

Wacker oxidation of styrene in the supramolecular gel

Organic reactions are generally performed in organic solvents. Collisions of the substrates and the catalyst in the bulk solvent play an important role in determining the reaction kinetics. The manner in which the reaction kinetics is influenced by changing the reaction phase from a solution to a gelatinized matrix is a simple question to be answered. Some supramolecular gel catalysts that catalyze the oxidation of alcohols, hydrolysis of esters, aldol reactions and intramolecular cycloaddition of alkynoic acids have recently been reported.[25,36–38] These reports showed the potential applicability of supramolecular gels as catalysts, although they did not mention the differences between the reaction kinetics in the gel phase and in solution. The supramolecular gel of **1** with an excess amount of Pd (OAc)$_2$ contains free Pd(OAc)$_2$ in the supramolecular gel phase. Therefore, palladium-catalyzed reactions in the absolute gel phase could be accomplished using this system, and it might be possible to compare the reaction kinetics in gel and in solution. To test this hypothesis, we selected the Wacker oxidation of styrene to produce acetophenone as a model system.[39]

A supramolecular gel was prepared from the ultrasound irradiation of a mixture of **1**, Pd(OAc)$_2$, styrene and DMSO-H$_2$O (7:1). The supramolecular gel retained its form for more than a month without melting or crystallizing. Centrifugation of the supramolecular gel with CDCl$_3$ made it possible to extract the unreacted styrene, and acetophenone was concentrated in the supernatant (Figure 4 and Supplementary Figure S2). The chemical yield of acetophenone produced in the gel-phase reaction was determined by the integration ratio of the ^{1}H NMR spectrum of the supernatant with the internal standard. The oxidation reaction of styrene (37.2 µmol) in the DMSO-H$_2$O gel of **1** and Pd(OAc)$_2$ (1.86 µmol) at room temperature was monitored (Figure 5). As a control experiment, the Pd(OAc)$_2$ (1.86 µmol) catalyzed oxidation of styrene (37.2 µmol) in DMSO-H$_2$O solution was performed. Typically, an oxidant such as benzoquinone would be added to the reaction to oxidize palladium(0) to palladium(II); however, in the present case, no oxidant was added, so that the reaction conditions would be simple. In the case of the reaction in DMSO-H$_2$O solution (control), the amount of acetophenone gradually increased after the initial stage. After 5 days, the amount of acetophenone reached a saturation value at 2.38 µmol, and remained unchanged thereafter. This amount corresponded to a yield of 126%,
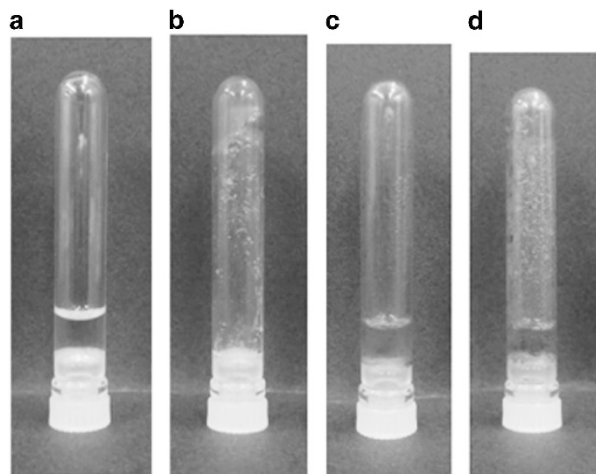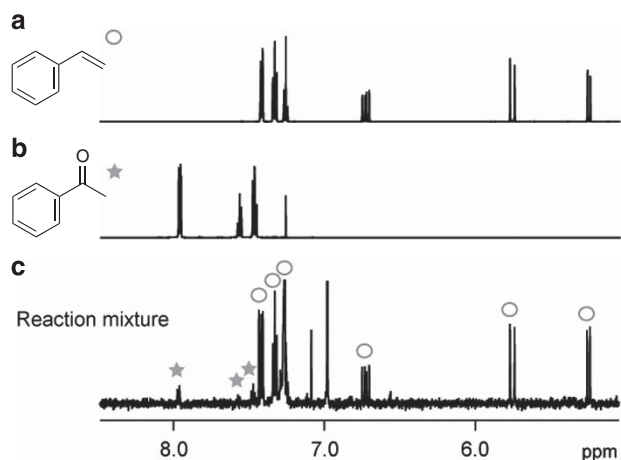
Figure 4 ¹H nuclear magnetic resonance (NMR) spectra of (**a**) styrene, (**b**) acetophenone and (**c**) extracted supernatant of the reaction mixture [DMSO-H_2O gel of **1**, Pd(OAc)$_2$, and styrene] in CDCl$_3$.
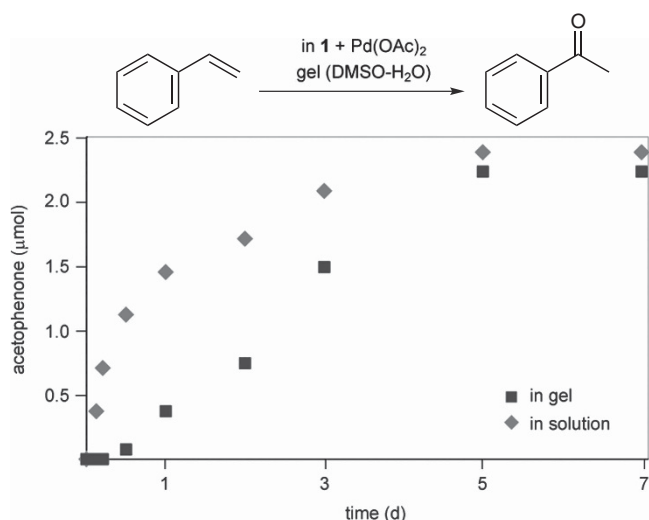

Figure 5 Reaction scheme for the Wacker oxidation of styrene (top) and the amount of acetophenone versus reaction time in gel and in solution phase (bottom). A full color version of this figure is available at *Polymer Journal* online.

based on the amount of Pd(OAc)$_2$. The Wacker oxidation of styrene in the supramolecular gel of **1** and Pd(OAc)$_2$ also reached a saturation point after 5 days, similar to the reaction in solution. At the saturation point, the reaction mixture contained 2.23 µmol of acetophenone (120% yield based on the amount of Pd(OAc)$_2$). However, the time profiles of the amount of acetophenone formed were considerably different between the reaction in the gel and that in solution. Acetophenone was not formed in the supramolecular gel reaction mixture at 3 h or at 6 h, which suggests that a long induction period is required to perform the reaction in the supramolecular gel phase. After 1 day of the gel phase reaction, the amount of acetophenone was 0.37 µmol (20% yield based on the amount of Pd(OAc)$_2$), which was identical to that in the solution-phase reaction at 3 h. Appropriate dispersion of substrate and catalyst in the gel would take a longer time than that in homogeneous solution. As a result, the reaction in the gel phase required a long induction period. After the induction period, however, the reaction in the gel proceeded at a rate similar to that of

the reaction in solution. In the later stage of the reaction, the rate of the reaction in the gel phase was faster than that in the solution. It is well known that aggregation of palladium catalysts decelerates the reaction rates of homogeneous solutions.[40] Aggregation of the catalyst might be inhibited in the gel phase. This result demonstrates the potential applicability of the supramolecular gel as a novel reaction phase.

CONCLUSION

A supramolecular gel was formed by tris-urea **1** in the presence of an appropriate amount of Pd(OAc)$_2$. SEM image of the xerogel revealed a porous spongiform nanostructure. Gel to sol/solution phase transitions of the supramolecular gel were induced by adding chelating agents to prevent the formation of coordination bonds between **1** and the palladium ion. A supramolecular gel of **1** and Pd(OAc)$_2$ offered a unique reaction phase. The Wacker oxidation of styrene was performed in the supramolecular gel, and the reaction kinetics were compared with those in a typical bulk solution.

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