Organogel Formation by Self-assembly of Ag(I) and Mono-urea Derivatives Containing Pyridyl Group

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The mono-urea derivative **3** derived from 4-(2-aminoethyl)-pyridine and dodecyl isocyanate gelled aromatic solvents, such as *p*-xylene, tetralin, and benzene, in the presence of Ag(I). The complex formation by the coordination of two equivalents of mono-urea **3** to Ag(I) and the intermolecular hydrogen bonding between urea groups plays important roles for the fibrous self-assembly followed by the gelation.

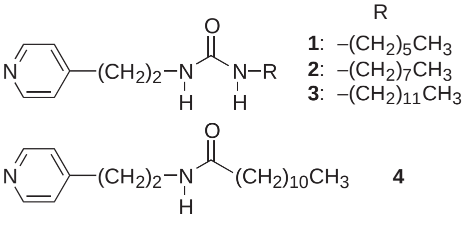
In recent years, low-molecular-weight organic compounds, which form thermoreversible physical gels in various organic solvents and water, have received much attention because of their potential applications, such as cosmetics, drug delivery systems, and catalysis.[1]

These gelators self-assemble by multiple noncovalent intermolecular interactions like hydrogen-bonding interactions, van der Waals forces, π–π stacking, donor–acceptor interactions, electrostatic interactions, and solvophobic effects to form one-directional alignment of gelator molecules. The resulting strands subsequently assemble into supramolecular fibrous structures, which in turn entangle to form extended three-dimensional (3D) networks and immobilize the solvent molecules. The hydrogen-bonding interactions play an important role in these aggregation processes, and the typical examples of this class of organogelators are amide compounds,[2] urea derivatives,[3] and sugars.[4]

Although metal coordination has been used to prepare supramolecular polymers,[5] the application for gelators is still limited.[6] We now report the organogel formation by the self-assembly of the silver(I) ion and mono-urea compounds containing the pyridyl group.[7]

Mono-urea derivatives **1**–**3** were prepared by the reaction of the corresponding isocyanates with 4-(2-aminoethyl)pyridine (Scheme 1). All compounds were isolated as white powders and characterized by ^{1}H and ^{13}C NMR, APCI mass spectroscopy, and elemental analyses.[8]

The gelation ability of the mono-urea derivatives **1**–**3** was tested in twelve different solvents with $20\,\mathrm{g\,dm^{-3}}$ as the standard concentration. A mixture of the gelator and the solvent was placed in a sealed test tube and heated until the solid dissolved. The test tube was stored for two hours at room temperature and its state was evaluated by the "stable-to-inversion of a test tube" method.[9] The results are summarized in Table 1. Compounds **1**–**3** did not gel any of the tested solvents. It has been reported that bis-urea derivatives possessing aromatic groups have more effective gelation properties than the mono-urea derivatives.[10] Since the pyridyl nitrogen atoms can interact with the silver(I) ion to yield the two-coordinate, linear complexes,[11] the complexation of compounds **1**–**3** with the silver(I) ion could afford the bis-urea type complexes.[12] The addition of silver(I) pentafluoropropionate, $AgC_2F_5CO_2$, to the benzene solution of the mono-urea **3** afforded a thermoreversible opaque gel (see Graphical Information). Table 1 shows that in the presence of $AgC_2F_5CO_2$, the mono-urea **3** gelled the aromatic solvents. The counter anion of the Ag(I) salts affected the gelation of **3**; benzene was also gelled by $AgClO_4$, however, $AgCF_3SO_3$ and $[Ag(CH_3CN)_4]BF_4$ produced soft benzene gels.



Scheme 1.

In order to evaluate the driving forces for gelation, we measured the ESI-MS spectra. Figure 1 shows the ESI-MS spectra of the sample obtained from *p*-xylene gel formed by **3** and $AgC_2F_5CO_2$. The spectrum shows peaks at $m/z = 773$ and 775 corresponding to the 2:1 complex $[\mathbf{3}\cdot\mathbf{3} + Ag]^+$. We also found that the sol–gel phase-transition temperature (T_{gel}) of *p*-xylene gel increased with increasing the ratio of [Ag(I)]/[**3**]

Table 1. Gelation ability of compounds **1**–**3** in organic solvents[a]

Solvent	State[b]					
	1	**1** + Ag(I)	**2**	**2** + Ag(I)	**3**	**3** + Ag(I)
Butyl ether	I	I	P	I	P	I
p-Xylene	I	I	P	P	P	G
Tetralin	I	PG	S	G	SG	G
Benzene	S	P	S	S	S	G
Ethyl acetate	S	P	S	P	S	P
Butyl acetate	I	P	P	P	S	P
Chloroform	S	I	S	S	S	S
Cyclohexanone	S	I	S	S	S	S
Acetone	S	I	S	P	S	P
Acetonitrile	S	I	S	P	P	P
Ethanol	S	I	S	S	S	S
2-Octanol	S	I	S	S	S	S

[a] $[\text{gelator}]/[AgC_2F_5CO_2] = 2$. [b] G: gel; SG: soft gel; PG: partial gel; I: insoluble at solvent reflux temperature; P: precipitation.

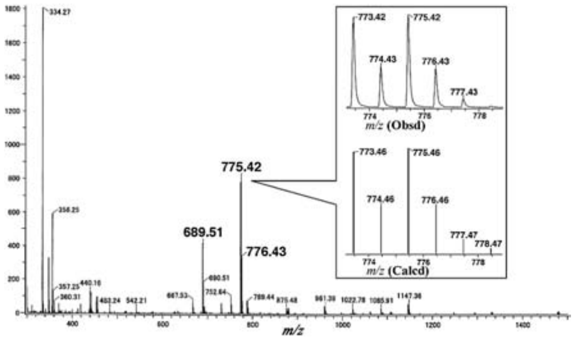


Figure 1. ESI-MS spectra of a *p*-xylene solution formed by **3** ($0.5\,\mathrm{g\,dm^{-3}}$) with 0.5 equivalent of $\mathrm{AgC_2F_5CO_2}$.

to a maximum around [Ag(I)]/[**3**] = 0.5–0.6 and then slightly decreased at higher ratios. These results indicate that the gel is stabilized by the formation of the 2:1 complex.

The amide-type compound **4**, synthesized from 4-(2-aminoethyl)pyridine and dodecanoyl chloride, failed to gel in the absence or presence of Ag(I) under the same conditions. These results suggest that the urea group also plays an important role in the gelation process.

The relationship between the gelation ability and intermolecular hydrogen bonding was studied by FT-IR spectroscopy. In the spectrum of the benzene solution of **3** ($20\,\mathrm{g\,dm^{-3}}$) in the absence of Ag(I), the urea absorption bands were observed at 3360, 1684, and $1560\,\mathrm{cm^{-1}}$. These results indicate the presence of non-hydrogen-bonding urea groups.[10,13] On the other hand, the spectrum of the benzene gel containing Ag(I) showed that the urea absorption bands were observed at 3342, 1618, and $1583\,\mathrm{cm^{-1}}$. These spectral shifts are characteristic for the presence of hydrogen-bonded urea group,[10,13] and apparently indicate that the formation of a gel is accompanied by the formation of intermolecular hydrogen bonds between the urea groups.

To obtain a visual image of the assemblies of the complexes, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were measured after evaporation of the solvent as shown in Figure 2. The TEM image showed many long thin fibers. The diameter of the smallest fibers is approximately 30 nm. The SEM picture of the xerogel resulted in bundles of fibers and a sheet-like structure.

In conclusion, we have demonstrated the organogel formation by the self-assembly of Ag(I) and pyridine-containing mono-urea derivatives. The pyridyl units interact with Ag(I) to form the 2:1 complex, and the gelators also interact by intermolecular hydrogen bonding of the urea groups that forms the fibrous structure and then forms the organogels. Further studies of the metal induced gelation are in progress in our laboratory.

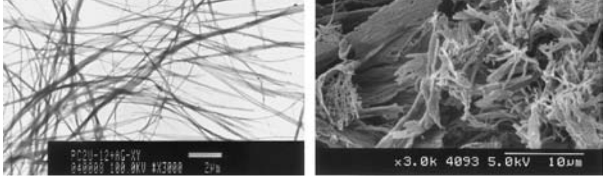


Figure 2. Electron micrographs. (A): TEM image of the dried sample obtained from **3** ($5.0\,\mathrm{g\,dm^{-3}}$) and 0.5 equivalent of $\mathrm{AgC_2F_5CO_2}$ in *p*-xylene. (B): SEM image of the xerogel obtained from **3** ($20\,\mathrm{g\,dm^{-3}}$) and 0.5 equivalent of $\mathrm{AgC_2F_5CO_2}$ in *p*-xylene.

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8 Selected data for **3**, Yield 19%; mp 80.0–80.5 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.87 (t, $J = 6.6$ Hz, 3H), 1.16–1.32 (m, 18H), 1.38–1.51 (m, 2H), 2.80 (t, $J = 6.6$ Hz, 2H), 3.11 (q, $J = 6.9$ Hz, 2H), 3.46 (q, $J = 6.8$ Hz, 2H), 4.81 (m, 2H), 7.10 (d, $J = 6.0$ Hz, 2H), and 8.40 (d, $J = 6.0$ Hz, 2H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 14.1, 22.6, 26.9, 29.3, 29.6, 30.2, 31.9, 35.9, 40.4, 40.5, 124.3, 148.8, 149.6, 158.2; APCI MS: 334 ($\mathrm{MH^+}$); Anal. Found: C, 71.94; H, 10.39; N, 12.67%; Calcd for $\mathrm{C_{20}H_{35}N_3O}$: C, 72.03; H, 10.58; N, 12.60%.

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