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In situ organogelation at room temperature: direct synthesis of gelators in organic solvents

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Organogels are formed through a conventional organogelation involving a heating process and an *in situ* organogelation at room temperature. The conventional organogelation is carried out by dissolution of gelators by heating, while the *in situ* organogelation is performed by mixing of highly reactive methyl 2,6-diisocyanatohexanoate (LDI) or 2-isocyanatoethyl 2,6-diisocyanatohexanoate (LTI) and alkylamines. The *in situ* organogelation produced the organogels within several seconds after mixing. The organogels prepared by the *in situ* organogelation showed quite similar FT-IR spectra and SEM photographs to those formed by conventional organogelation. Moreover, the *in situ* organogelation using LTI and octylamine as well as dodecylamine produced organogels of acetone, ethyl acetate, and acetonitrile that gelators **5** and **6** cannot gel through conventional organogelation.

Introduction

Organogels, in which organic solvents are gelled by low-molecular-weight compounds (organogelators), have attracted much interest due to their unique features and potential applications as new organic soft materials.[1] Many organogelators have been reported in the literature.[2] These organogelators create a three-dimensional network by the entanglement of nanofibers or nanoribbons formed by self-organization through noncovalent interactions such as hydrogen bonding, van der Waals, π-stacking, and coordination.

Organogelators have received much attention not only due to their organogelation properties but also for the formation of superstructures in organic solvents and organogels. One of the applications of organogelators is their use as organic templates for the fabrication of mesoporous polymer materials[3] and nano-scaled designed inorganic materials. Many organogelators have been used as organic templates.[4] The sol-gel polymerization of various metal alkoxides (Si, Ti, Ta, V, Ge, *etc*.) in solvents containing self-assembled organogelators forms hollow nanofibers of metal oxides followed by calcination. Other applications are their use in sensors,[5] gel electrolytes,[6] liquid crystallines,[7] and so on.[8] Furthermore, these organogelators have been used in industrial fields such as cosmetics, health care, textile, paper, foods, and oils.[1] As wide applications, organogelators that can be cheaply, simply, and effectively synthesized are desired. In addition, it is desirable that organogelators are environmentally friendly materials (having features such as biodegradiation).

In many cases, the organogelations of low-molecular-weight gelators need a heating-dissolution process. Especially, organogelation by excellent organogelators having a very low minimum gel concentration necessary for gelation require a longer heating time and higher heating temperature because they are difficult to dissolve in the organic solvents that can gel. Such a heating process is a disadvantage for the wide application as organogelators; if organogelations are achieved at room temperature, organogelators can be used in more fields. Recently, Weiss and George have developed a new method for the rapid formation of organogels at room temperature using amines and CO_2 gas.[9] Quite recently, we reported novel L-lysine based organogelators and organogelation at room temperature.[10] In this paper, we describe the synthesis of new tris-urea derivatives and their organogelation abilities and *in situ* organogelation at room temperature through the direct synthesis of gelators in organic solvents.

Results and discussion

Organogelation abilities of 1–7

The organogelation properties of **1**–**7** in organic solvents are listed in Table 1. The bis-urea derivatives, **1**–**4**, had good organogelation abilities for various organic solvents as reported previously.[10] Compared with the bis-urea derivatives, the tris-urea derivatives, **1**–**7**, were not necessarily good organogelators. Among **1**–**7**, **5** showed relatively good organogelation abilities for some organic solvents. Compounds **6** and **7** produced insoluble in solvents (Ins), viscous solutions (VS), and partial gels (PG) for some organic solvents due to their low solubilities in organic solvents.

Table 1 Organogelation properties of **1**–**7** in organic solvents[a]

Solvents	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Benzene	20	12	50	30	PG	PG	20
Toluene	20	15	50	35	VS	40	15
Chlorobenzene	30	25	50	40	5	5	5
Nitrobenzene	8	4	10	15	10	VS	VS
AcOEt	30	10	S	PG	Ins	Ins	Ins
Acetone	PG	35	15	Ins	Ins	Ins	Ins
c-Hexanone	35	25	15	15	12	20	35
THF	40	30	PG	15	P	VS	P
1,4-Dioxane	20	15	15	10	15	35	VS
DMF	S	S	28	PG	15	VS	P
DMSO	S	S	27	25	25	VS	VS
CH_3CN	20	PG	P	P	Ins	Ins	Ins
CCl_4	20	30	18	30	PG	VS	25
c-C_6H_{12}	PG	PG	15	7	P	PG	PG

[a] Values denote minimum gel concentration (MGC, g/L). P: precipitation at 2 wt%. VS: Viscous solution at 5 wt%. PG: Partial gel at 2 wt%. S: solution at 5 wt%. Ins: Almost insoluble.

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Table 2 Reaction conditions for *in situ* organogelation in bis-urea systems[a]

Solvents	LDI [b]: C_6NH_2 [c]	LDI [b] : C_8NH_2 [d]	LDI [b] : $C_{12}NH_2$ [e]	LDI [b] : $C_{18}NH_2$ [f]
Benzene	18.0 : 21.2	9.6 : 16.9	36.4 : 63.6	17.0 : 43.0
Toluene	18.0 : 21.2	11.8 : 21.1	36.4 : 63.6	19.8 : 50.0
Chlorobenzene	27.0 : 31.9	19.8 : 35.1	36.4 : 63.6	22.6 : 57.4
Nitrobenzene	7.2 : 8.5	3.2 : 5.6	7.3 : 12.7	8.5 : 21.0
AcOEt	27.0 : 31.9	7.9 : 14.0		**12.5 : 36.5** [g]
Acetone	**22.1 : 31.8** [g]	27.7 : 49.2	10.9 : 19.0	**12.5 : 36.5** [g]
c-Hexanone	31.5 : 37.1	19.8 : 35.1	10.9 : 19.0	8.5 : 21.5
THF	36.0 : 42.5	23.8 : 42.1	**15.7 : 31.5** [g]	8.5 : 21.5
1,4-Dioxane	18.0 : 21.2	11.9 : 21.1	10.9 : 19.0	5.7 : 14.3
DMF			20.4 : 35.5	**12.5 : 36.5** [g]
DMSO			19.7 : 34.3	14.1 : 35.8
CH_3CN	18.0 : 21.2	**19.4 : 34.8** [g]		
CCl_4	18.0 : 21.2	23.8 : 42.1	13.1 : 22.8	17.0 : 43.0
c-C_6H_{12}	**22.1 : 31.8** [g]	**19.4 : 34.8** [g]	11.0 : 19.0	4.0 : 10.0

[a] Final volumes were 2.0 ml. [b] Methyl 2,6-diisocyanatohexanoate (μl). [c] Hexylamine (μl). [d] Octylamine (μl). [e] Dodecylamine (mg). [f] Octadecylamine (mg). [g] Values correspond to 50 mg ml^{-1}.

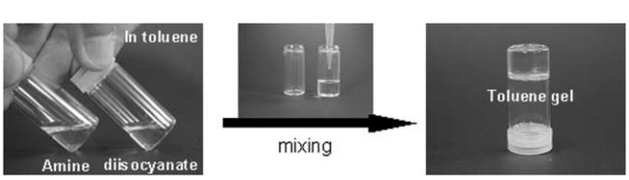
Table 3 Reaction conditions for *in situ* organogelation in tris-urea systems[a]

Solvents	LTI [b]: C_8NH_2 [c]	LTI [b] : $C_{12}NH_2$ [d]	LTI [b] : $C_{18}NH_2$ [e]
Benzene	**16.9 : 38.5** [g]	**13.0 : 33.3** [g]	8.0 : 30.0
Toluene		21.0 : 54.0	6.0 : 22.1
Chlorobenzene	3.3 : 5.5	2.6 : 6.7	2.0 : 7.6
Nitrobenzene	6.6 : 15.1		
AcOEt	**10.1 : 23.1** [g]	**13.0 : 33.3** [g]	**10.3 : 38.3** [g]
Acetone	**16.9 : 38.5** [g]	**13.0 : 33.3** [g]	**10.3 : 38.3** [g]
c-Hexanone	8.0 : 18.1	10.5 : 27.0	14.1 : 52.6
THF			
1,4-Dioxane	10.0 : 22.7	18.4 : 47.2	
DMF	10.0 : 22.7		
DMSO	16.6 : 37.8		
CH_3CN	**16.9 : 38.5** [g]	**13.0 : 33.3** [g]	**10.3 : 38.3** [g]
CCl_4	**16.9 : 38.5** [g]		10.1 : 37.6
c-C_6H_{12}		**13.0 : 33.3** [g]	**10.3 : 38.3** [g]

[a] Final volumes were 2.0 ml. [b] 2-Isocyanatoethyl 2,6-diisocyanatohexanoate (μl). [c] Octylamine (μl). [d] Dodecylamine (mg). [e] Octadecylamine (mg). [g] Values correspond to 50 mg ml^{-1}.

In situ organogelation

In order to omit a heating process during organogelation, we examined *in situ* organogelation at room temperature through the direct synthesis of gelators. Methyl 2,6-diisocyanatohexanoate (LDI) and 2-isocyanatoethyl 2,6-diisocyanatohexanoate (LTI) which are the precursors of **1**–**7** are liquids and are easily mixed in organic solvents. Hexylamine and octylamine are liquids, while dodecylamine and octadecylmine are solids at room temperature. The *in situ* organogelation by the direct addition of liquid amines to organic solvents containing isocyanate precursors often produces partial gels at room temperature even in solvents that can gel through conventional organogelation involving a heating process because of the rapid organogelation and heterogeneous mixing. Therefore, we carried out *in situ* organogelation through the mixing of amine solutions and isocyanate solutions. A typical procedure of *in situ* organogelation is shown in Scheme 1. First, alkyl amines and isocyanates were separately dissolved in 1.0 ml solvents, and then the amine solution was added to the isocyanate solution.[11]



Scheme 1 Typical procedure of *in situ* organogelation.

The reaction conditions of the *in situ* organogelation for the bis-urea and tris-urea (Fig. 1) systems are listed in Table 2 and Table 3, respectively. The concentrations of the isocyanates and alkylamines were calculated from the MGC values in Table 1. For all systems, the organogels were formed within several seconds after mixing the isocyanate and alkylamine solutions at room temperature. Fig. 2 shows the photographs of toluene gels and ethyl acetate gels of **2** prepared by conventional organogelation (A, C) and *in situ* organogelation (B, D). Both organogelation methods give visually similar organogels, transparent toluene gels and opaque ethyl acetate gels. Moreover, these

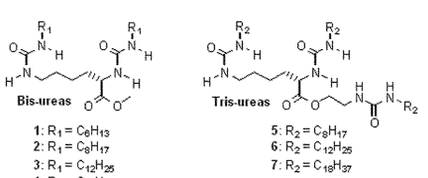


Fig. 1 Chemical structures of bis-urea and tris-urea derivatives.

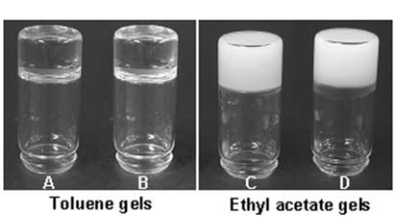


Fig. 2 Photographs of toluene gels and ethyl acetate gels of **2** prepared by ordinary organogelation (A, C) and *in situ* organogelation (B, D). [**2**] = 30 mg 2 ml^{-1} (A); [**2**] = 20 mg 2 ml^{-1} (C); [LDI] = 11.8 μl and [$C_8H_{17}NH_2$] = 21.1 μl in 2 ml toluene (B); [LDI] = 7.9 μl and [$C_8H_{17}NH_2$] = 14.0 μl in 2 ml ethyl acetate.

organogels show the same reversible gel–sol transition by heating and cooling as those obtained by conventional organogelation.

As mentioned above, gelators **1**–**7** cannot gel some solvents because of their low solubilities (PG) and insolubilities (Ins). In particular, the conventional organogelation of tris-urea compounds results in partial gels and insolubility in many solvents. We carried out *in situ* organogelation in such organic solvents. In Tables 2 and 3, the solvents represented by the bold values are those that produce partial gels and insolubilities with conventional organogelation using the corresponding gelators. Interestingly, *in situ* organogelation can gel these solvents. Fig. 3 shows photographs of samples after conventional organogelation and *in situ* organogelation in acetone. In the conventional organogelation, gelators **5** and **6** are almost insoluble in acetone even at 1 wt% (A and C). In contrast, the *in situ* organogelation using triisocyanates, $C_8H_{17}NH_2$ and $C_{12}H_{25}NH_2$ produces opaque acetone gels (B and D). The organogel formation is achieved for other solvents except for the $C_{18}H_{37}NH_2$ systems.[12]

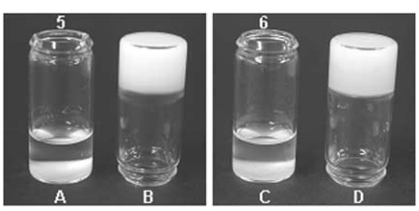


Fig. 3 Photographs of acetone solutions of insoluble **5** (A) and **6** (C) and acetone gels prepared by *in situ* organogelation (B, D). (A): [**5**] = 20 mg 2 ml^{-1}; (C): [**6**] = 20 mg 2 ml^{-1}; (B); [LTI] = 16.9 μl and [$C_8H_{17}NH_2$] = 38.5 μl in 2 ml acetone; (D); [LTI] = 13.0 μl and [$C_{12}H_{25}NH_2$] = 33.3 μl in 2 ml acetone.

FE-SEM

To evaluate visual insights into the aggregation mode of these gelators in organogels, we took FE-SEM images of the organogels prepared through conventional organogelation and *in situ* organogelation. Fig. 4 shows the FE-SEM photographs of dried gels prepared by conventional organogelation (A: toluene gel of **2** and C: dioxane gel of **5**) and *in situ* organogelation (B: toluene gel, D: dioxane gel, and E and F: acetone gels). The SEM photographs of A–D show a similar three-dimensional network entangling self-assembling nanofibers with fiber diameters of 20–60 nm. This fact indicates that the aggregation modes of the

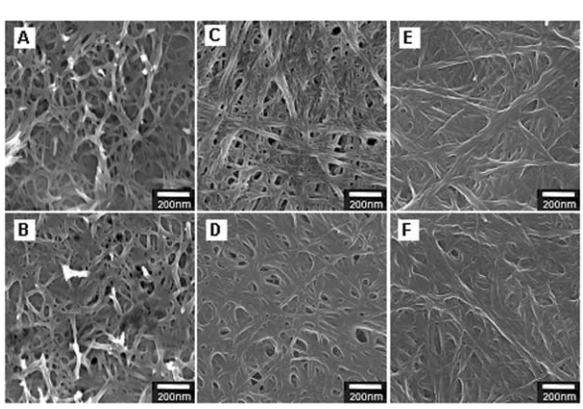


Fig. 4 FE-SEM photographs of dried gels prepared from: (A): toluene gel of **2** by ordinary organogelation (15 mg ml^{-1}); (B): toluene gel by *in situ* organogelation of LDI and octylamine ([LDI] = 11.8 μl and [$C_8H_{17}NH_2$] = 21.1 μl in 2 ml toluene); (C): dioxane gel of **5** by ordinary organogelation (15mg ml^{-1}); (D): dioxane gel by *in situ* organogelation of LTI and octylamine ([LTI] = 10.9 μl and [$C_8H_{17}NH_2$] = 22.7 μl in 2 ml dioxane); (E): acetone gel by *in situ* organogelation of LTI and octylamine ([LTI] = 10.1 μl and [$C_8H_{17}NH_2$] = 23.1 μl in 2 ml ethyl acetate); (F): acetone gel by *in situ* organogelation of LTI and dodecylamine ([LTI] = 13.0 μl and [$C_{12}H_{25}NH_2$] = 33.3 μl in 2 ml acetone).

gelators in organogels are independent of the organogelation methods; namely, the *in situ* organogelation produces almost the same organogels as conventional organogelation. It is noteworthy that the three-dimensional network structure of the self-assembled nanofibers is observed in acetone gels that cannot form through the conventional organogelation.

FT-IR and ^{1}H-NMR studies

It is well-known that hydrogen bonding is one of the driving forces for the self-assembly of organogelators in organic solvents.[1–2] IR spectroscopy is a powerful tool for studing hydrogen bonding interactions, thus we measured the FT-IR spectra. Fig. 5 shows the FT-IR spectra of organogels prepared by conventional organogelation and *in situ* organogelation. For all gels, the absorption bands, characteristic of the hydrogen bonded urea groups, were observed around 3330 cm^{-1} (νN–H), 1628 cm^{-1} (νC=O), and 1580 cm^{-1} (δN–H). Furthermore, the absorption bands of the antisymmetric (ν_{as}) and symmetric (ν_s) CH_2 stretching vibrational modes are observed around 2923 cm^{-1} (ν_{as}, C–H) and 2852 cm^{-1} (ν_s, C–H), indicating that the fluidity of the alkyl chains due to the strong organization of the alkyl groups *via* a van der Waals interaction.[13] These facts indicate that the driving forces for organogelation followed by entanglement of the self-assembled nanofibers are mainly hydrogen bonding and van der Waals interactions.

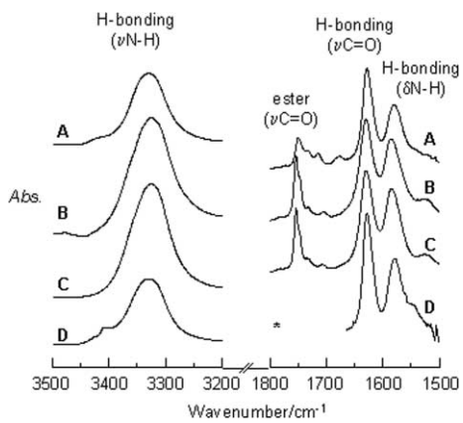


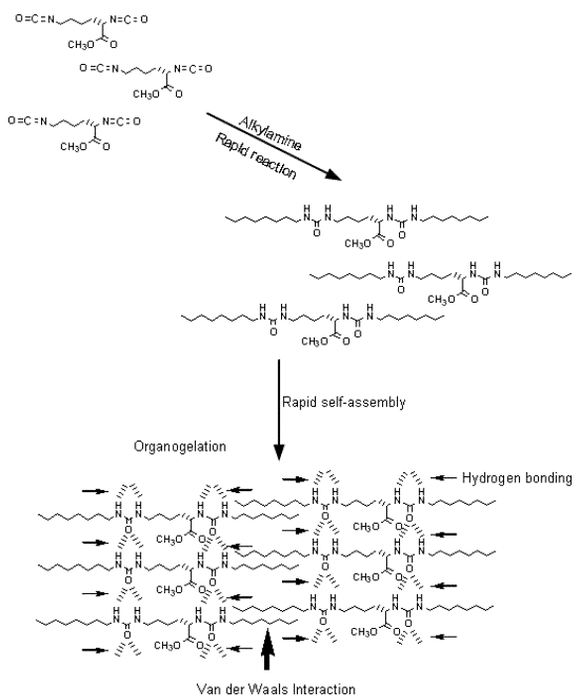
Fig. 5 FT-IR spectra of organogels prepared by ordinary organogelation and *in situ* organogelation. (A): acetonitrile gel of LDI/$C_6H_{13}NH_2$ by *in situ* organogelation ([LDI] = 18μl, [$C_6H_{13}NH_2$] = 21.1 μl in 2 ml); (B): acetonitrile gel of **1** by ordinary organogelation (20 mg ml^{-1}); (C): CCl_4 gel of LDI/$C_6H_{13}NH_2$ by *in situ* organogelation ([LDI] = 18 μl, [$C_6H_{13}NH_2$] = 21.1 μl in 2 ml); (D): acetone gel of LTI/$C_8H_{17}NH_2$ by *in situ* organogelation ([LTI] = 16.9 μl and [$C_8H_{17}NH_2$] = 38.5 μl in 2 ml).

On the other hand, the ^{1}H-NMR spectra of samples of (A), (C), and (D) in the FT-IR spectra show quite similar spectra for **1** [(A) and (C)] and **5** (D). Considering that the similar IR spectra are observed for the organogels prepared by both organogelation methods, it is clear that the gelators are formed by *in situ* organogelation.

Conventional organogelation and *in situ* organogelation

As mentioned above, a conventional organogelation involves a heating process because of dissolution into organic solvents. In order to gel an organic solvent by gelators, it first needs crystalline gelators to be dissolved in the organic solvents; thus, intermolecular interactions in the crystalline state are broken by heating. The organogel is then formed during self-organization of the gelator molecules dispersed in the solvent as nanofibers. Moreover, the cooling-down time to room temperature may make the organogelation time slow. In contrast, the *in situ* organogelation does not need a heating process because the gelators are never crystalline. We propose the gelation mechan-

ism for the *in situ* organogelation as illustrated in Scheme 2. The rapid reaction between isocyanate and alkylamine occurs just after the addition of alkylamine solution to the isocyanate solution, and then the gelators create a three-dimensional network followed by immediate self-assembly into nanofibers, which leads to rapid organogelation within several seconds. Therefore, the *in situ* organogelation cannot only omit a heating process but also shorten the organogelation time.



Scheme 2

Conclusion

We revealed the formation of organogels at room temperature through *in situ* organogelation. The *in situ* organogelation is an unique method in which the gelators are directly synthesized by mixing of isocyanates and alkylamines in organic solvents. Compared with conventional organogelation, the *in situ* organogelation has the following advantages: (i) a heating process is omitted, (ii) the organogelation is achieved at room temperature, (iii) the organogelation time is shortened, and (iv) it gels the solvents that cannot gel through conventional organogelation.

Experimental

Materials

Methyl 2,6-diisocyanatohexanoate (LDI) and 2-isocyanatoethyl 2,6-diisocyanatohexanoate (LTI) prepared from L-lysine were obtained from Kyowa Hakko Kogyo Co., Ltd. The other chemicals were of the highest commercial grade available and were used without further purification. All solvents used in the syntheses were purified, dried, or freshly distilled as required.

N^{α},N^{ε}-Bis(hexylaminocarbonyl)-L-lysine methyl ester (1)

To a dry toluene solution of methyl 2,6-diisocyanatohexanoate (20 mmol), hexylamine (41 mmol) was added. After heating the solution at 100 °C for 10 min, the resulting solution was evaporated to dryness. The product was obtained by recrystallization from ethyl acetate–methanol (97%). IR (KBr): 3336 cm^{-1} (νN–H, urea), 1733 cm^{-1} (νC=O, ester), 1631 cm^{-1} (νC=O, urea), 1577 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, J = 6.6Hz, 6H; CH_3), 1.27–1.30 (m, 18H; alkyl), 1.63–1.78 (m, 2H; CH_2CHNH(CO_2CH_3)), 3.09–3.21 (m, 6H, N^{ε}HCONHCH_2, N^{ε}HCH_2, N^{α}HCONHCH_2), 3.70 (s, 3H, OCH_3), 4.35–4.40 (m, 1H, CH), 5.01 (t, J = 5.5 Hz, 1H; N^{α}HCONH), 5.16 (t, J = 5.5 Hz, 1H; NHCON$^{\varepsilon}H$), 5.34 (t, J = 5.1 Hz, 1H; $N^{\varepsilon}H$), 5.76 (d, J = 7.8 Hz, 1H; $N^{\alpha}H$). Elemental analysis calcd (%) for $C_{21}H_{42}N_4O_4$ (414.58): C, 60.84; H, 10.21; N, 13.51. Found: C, 60.99; H, 10.42, N, 13.52%.

N^{α},N^{ε}-Bis(octylaminocarbonyl)-L-lysine methyl ester (2)

The product was obtained by the same procedure as **1** using octylamine (98%). IR (KBr): 3339 cm^{-1} (νN–H, urea), 1736 cm^{-1} (νC=O, ester), 1632 cm^{-1} (νC=O, urea), 1574 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ= 0.87 (t, J = 6.8 Hz, 6H; CH_3), 1.27–1.31 (m, 30H; alkyl), 1.65–1.75 (m, 2H; CH_2CHNH(CO_2CH_3)), 3.09–3.18 (m, 6H, CH_2NHCONH, CONHCH_2, NHCONHCH_2), 3.71 (s, 3H, OCH_3), 4.35–4.40 (m, 1H, CH), 4.98 (t, J = 5.3 Hz, 1H; NHCONH), 5.17 (t, J = 5.6 Hz, 1H; NHCONH), 5.31 (t, J = 4.9 Hz, 1H; NH), 5.74 (d, J = 7.6 Hz, 1H; NH). Elemental analysis calcd (%) for $C_{25}H_{50}N_4O_4$ (470.69): C, 63.79; H, 10.71; N, 11.90. Found: C, 63.89; H, 11.07; N, 11.91%.

N^{α},N^{ε}-Bis(dodecylaminocarbonyl)-L-lysine methyl ester (3)

The product was obtained by the same procedure as **1** using dodecylamine (97%). IR (KBr): 3344 cm^{-1} (νN–H, urea), 1736 cm^{-1} (νC=O, ester), 1625 cm^{-1} (νC=O, urea), 1568 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ = 0.87 (t, J = 6.8 Hz, 6H; CH_3), 1.25–1.31 (m, 34H; alkyl), 1.65–1.75 (m, 2H; CH_2CHNH(CO_2CH_3)), 3.11–3.15 (m, 6H, NHCONHCH_2, NHCH_2, NHCONHCH_2), 3.70 (s, 3H, OCH_3), 4.35–4.40 (m, 1H, CH), 5.02 (t, J = 5.5 Hz, 1H; NHCONH), 5.17 (t, J = 5.5 Hz, 1H; NHCONH), 5.36 (t, J = 5.1 Hz, 1H; NH), 5.77 (d, J = 7.8 Hz, 1H; NH). Elemental analysis calcd (%) for $C_{33}H_{66}N_4O_4$ (582.90): C, 68.00; H, 11.41; N, 9.61. Found: C, 68.10; H, 11.66; N, 9.61%.

N^{α},N^{ε}-Bis(octadecylaminocarbonyl)-L-lysine methyl ester (4)

The product was obtained by the same procedure as **1** using octadecylamine (98%). IR (KBr): 3344 cm^{-1} (νN–H, urea), 1736 cm^{-1} (νC=O, ester), 1625 cm^{-1} (νC=O, urea), 1576 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ= 0.87 (t, J = 6.8 Hz, 6H; CH_3), 1.25–1.31 (m, 68H; alkyl), 1.65–1.75 (m, 2H; CH_2CHNH(CO_2CH_3)), 3.11–3.15 (m, 6H, NHCONHCH_2, NHCH_2, NHCONHCH_2), 3.70 (s, 3H, OCH_3), 4.35–4.40 (m, 1H, CH), 5.02 (t, J = 5.5 Hz, 1H; NHCONH), 5.17 (t, J = 5.5 Hz, 1H; NHCONH), 5.36 (t, J = 5.1 Hz, 1H; NH), 5.77 (d, J = 7.8 Hz, 1H; NH). Elemental analysis calcd (%) for $C_{45}H_{90}N_4O_4$ (751.22): C, 71.95; H, 12.08; N, 7.46. Found: C, 72.03; H, 12.33; N, 7.46%.

N^{α},N^{ε}-Bis(octylaminocarbonyl)-L-lysine 2-(octylureido)ethyl ester (5)

To a dry toluene solution of 2-isocyanatoethyl 2,6-diisocyanatohexanoate (20 mmol), octylamine (62 mmol) was added. After heating the solution at 100 °C for 10 min, the resulting solution was evaporated to dryness. The product was obtained by recrystallization from ethyl acetate–methanol (95%). IR (KBr): 3338 cm^{-1} (νN–H, urea), 1733 cm^{-1} (νC=O, ester), 1626 cm^{-1} (νC=O, urea), 1578 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz,DMSO-d_6, TMS): δ = 0.86 (t, J = 6.8 Hz, 9H; CH_3), 1.25–1.35 (m, 40H; alkyl), 1.55–1.67 (m, 2H; CH_2CHNH(CO_2CH_2)), 2.95–3.00 (m, 8H, CH_2NHCONHCH_2, NHCH_2, NHCONHCH_2), 3.24–3.29 (m, 2H; CH_2CH_2NH), 3.99–4.05 (m, 2H, OCH_2), 4.12 (q, J = 5.5 Hz, 1H; CH), 5.71–5.76 (m, 2H; NHCONH, OCH_2CH_2NH), 5.89–5.94 (m, 3H; CH_2NHCO, CHNHCONH, NHCON$H$$CH_2$), 6.14 (d, J = 8.1 Hz, 1H; NH). Elemental analysis calcd (%) for $C_{35}H_{70}N_6O_5$ (654.97): C, 64.18; H, 10.77; N, 12.83. Found: C, 64.30; H, 10.94; N, 12.84%.

N^{α},N^{ε}-Bis(dodecylaminocarbonyl)-L-lysine 2-(dodecylureido)-ethyl ester (6)

The product was obtained by the same procedure as **5** using dodecylamine (95%). IR (KBr): 3340 cm^{-1} (νN–H, urea), 1736 cm^{-1} (νC=O, ester), 1625 cm^{-1} (νC=O, urea), 1580 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz, DMSO-d_6, TMS): δ = 0.87 (t, J = 6.8 Hz, 9H; CH_3), 1.25–1.35 (m, 64H; alkyl), 1.55–1.67 (m, 2H; CH_2CHNH(CO_2CH_2)), 3.06–3.12 (m, 8H, CH_2-NHCONHCH_2, NHCH_2, NHCONHCH_2), 3.41 (t, J = 5.1 Hz, 2H; CH_2CH_2NH), 4.12–4.20 (m, 2H, OCH_2), 4.28 (q, J = 4.8 Hz, 1H; CH), 5.50 (t, J = 5.3 Hz, 1H; $OCH_2CH_2NHCONH$), 5.56 (t, J = 5.6 Hz, 1H; $CH_2NHCONH$), 5.74 (t, J = 5.5 Hz, 1H; CHNHCONH), 5.78 (t, J = 5.5 Hz, 1H; CONHCH_2), 5.92 (t, J = 5.9 Hz, 1H; OCH_2CH_2NH), 6.15 (d, J = 7.5 Hz, 1H; CHNH). Elemental analysis calcd (%) for $C_{47}H_{94}N_6O_5$ (823.29): C, 68.57; H, 11.51; N, 10.21. Found: C, 68.66; H, 11.77; N, 10.22%.

N^{α},N^{ε}-Bis(octadecylaminocarbonyl)-L-lysine 2-(octadecyl-ureido)ethyl ester (7)

The product was obtained by the same procedure as **5** using octadecylamine (95%). IR (KBr): 3346 cm^{-1} (νN–H, urea), 1732 cm^{-1} (νC=O, ester), 1621 cm^{-1} (νC=O, urea), 1584 cm^{-1} (δN–H, urea). ^{1}H-NMR (400 MHz, DMSO-d_6, TMS): δ = 0.87 (t, J = 6.8 Hz, 9H; CH_3), 1.25–1.35 (m, 100H; alkyl), 1.55–1.67 (m, 2H; CH_2CHNH(CO_2CH_2)), 3.06–3.12 (m, 8H, CH_2-NHCONHCH_2, NHCH_2, NHCONHCH_2), 3.41 (t, J = 5.1 Hz, 2H; CH_2CH_2NH), 4.12–4.20 (m, 2H, OCH_2), 4.28 (q, J = 4.8 Hz, 1H; CH), 5.50 (t, J = 5.3 Hz, 1H; $OCH_2CH_2NHCONH$), 5.56 (t, J = 5.6 Hz, 1H; $CH_2NHCONH$), 5.74 (t, J = 5.5 Hz, 1H; CHNHCONH), 5.78 (t, J = 5.5 Hz, 1H; CONHCH_2), 5.92 (t, J = 5.9 Hz, 1H; OCH_2CH_2NH), 6.15 (d, J = 7.5 Hz, 1H; CHNH). Elemental analysis calcd (%) for $C_{65}H_{130}N_6O_5$ (1075.77): C, 72.57; H, 12.18; N, 7.81. Found: C, 72.66; H, 12.38; N, 7.82%.

Apparatus for measurements

The elemental analyses were performed using a Perkin-Elmer series II CHNS/O analyzer 2400. The FT-IR spectra were recorded on a JASCO FS-420 spectrometer. The FE-SEM observations were carried out using a Hitachi S-5000 field emission scanning electron microscope. The ^{1}H-NMR spectra were measured using a Bruker AVANCE 400 spectrometer with TMS as the standard.

Gelation test

A mixture of a weighed gelator in solvent (1 ml) in a sealed test tube was heated around the boiling point until a clear solution appeared. After allowing the solutions to stand at 25 °C for 6 h, the state of the solution was evaluated by the "stable to inversion of a test tube" method.[10]

Field emission scanning electron micrograph (FE-SEM)

The samples were dried overnight in a vacuum before the observation. The dried gels were sputtered using a gold target.

FTIR study

FTIR spectroscopy was performed using the spectroscopic cell with a CaF_2 window and 50 μm spacers operating at a 2 cm^{-1} resolution with 32 scans.

In situ organogelation

To a solution (1 ml) of LDI and LTI, alkylamine was added at room temperature.

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