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# A family of low-molecular-weight organogelators based on $N^{\alpha}$,$N^{\varepsilon}$-diacyl-L-lysine: effect of alkyl chains on their organogelation behaviour

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ABSTRACT

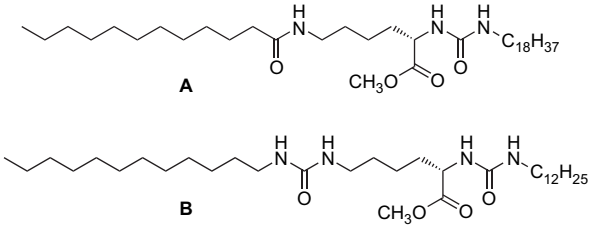
A family of low-molecular-weight organogelators based on $N^{\alpha}$,$N^{\varepsilon}$-diacyl-L-lysine was synthesized by acylation of $N^{\varepsilon}$-dodecyl-L-lysine with acyl chlorides through the one-pot synthetic procedure and their organogelation properties were examined. These compounds functioned as an organogelator; especially, L-lysine derivatives possessing the branched alkyl groups are a better organogelation property. The NMR and IR studies demonstrate that the organogelation occurred through hydrogen bonding interactions between the amide groups and between the carboxy groups.



## 1. Introduction

Supramolecular gels, which are a quasi-solid containing much solvents and made by low-molecular-weight gelators, have attracted much interest because of their unique properties and potential applications as new soft materials.[1–8] A supramolecular gel is formed by entrapping solvents into a three-dimensional network created by entanglement of non-covalently self-assembled nanofibers, so-called supramolecular polymers and called organogels for organic solvents and oils as well as hydrogels for aqueous solutions.[1–9] Recently, the academic research results have been reported in various fields; the use as organic templates for the fabrication of mesoporous polymer materials[10] and nano-scaled designed inorganic materials,[11–14] and the application to liquid crystalline,[15–19] photochemistry[20–29] and electrochemistry.[30–33]

On the other hand, low-molecular-weight gelators have developed not only in academic interests but also in industrial fields such as cosmetics, health care, textile, foods and oil.[1–8] For example, 12-hydroxystearic acid is one of the most famous gelators[34] and has been used for the treatment of domestic waste oils. *N*-Lauroyl-L-glutamic acid-α,γ-bis(*n*-butylamide) is in practical use for the treatment of oil spill. Furthermore, for cosmetics, paints and foods, some low-molecular-weight gelators are used as gelators and thickeners. The gelators used in academic researches generally have a complex structure and are prepared via multi-synthetic steps. Such gelators are not suitable for large-scale applications (industrial applications). In contrast, some gelators, which can be simply and cheaply prepared, have been reported and they show a good gelation ability for many organic solvents and oils.[35–40] As wide applications to industrial fields, it is desirable that gelators can be simply, cheaply and effectively synthesized and are environmentally friendly materials (having features such as biodegradiation and non-toxicity). We have already reported some easily preparable L-lysine based organogelators (Scheme 1).[39,41,42] Gelator A was synthesized through a two-step procedure and an all-powerful organogelator that formed the organogels in many organic solvents and oils.[41] Gelator B was easily prepared by mixing of the isocyanated L-lysine derivative and alkyl amine and functioned as a good organogelator.[39,42] For both systems, isocyanate derivatives were used in the synthetic procedures although they were commercially available (relatively cheap). In this paper, we describe that the one-step preparation of $N^{\alpha}$,$N^{\varepsilon}$-bis(acyl)-L-lysine from commercially available $N^{\varepsilon}$-lauroyl-L-lysine in aqueous solutions and their organogelation behaviour.




**Scheme 1.** L-Lysine based organogelators.

## 2. Results and discussion

All diacyl-L-lysine derivatives were prepared by mixing of commercially available $N^{\varepsilon}$-lauroyl-L-lysine and alkanoyl chloride

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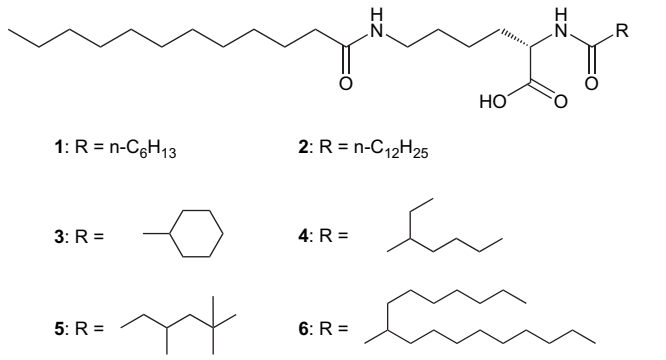



**Figure 1.**

with a relatively high reaction yield. In addition, because these syntheses were one-pot synthetic procedure and can also be carried out at the large scale, it is suitable for industrial applications. In these procedures, the reaction yield for each step was very high (>98%) and total reaction yield was above 96% (Fig. 1).

The orgenogelation properties of **1**–**6** are listed in Table 1. These compounds were readily soluble in alcohols and $CHCl_3$. The organogelation properties significantly depended on the alkyl groups linking to the $N^{\alpha}$ position; the compounds, **3**–**6**, having the branched alkyl chains, showed the better organogelation ability[43] than those of the linear alkyl chains (**1** and **2**). For **1** and **2**, having the linear alkyl chains, **1** had a relatively good organogelation ability, and **2** (having long alkyl group) barely formed the organogels. It is well-known that the organogelation ability depends on a hydrophobic–hydrophilic balance of the molecule, namely, the balance of polar hydrogen bonding units and non-polar alkyl chains or that of strengths between hydrogen bonding and van der Waals interaction.[1–7,39,44] Because the difference of molecular structures is the alkyl chain at the $N^{\alpha}$ position in the present cases, the gelation ability depends on the feature of their alkyl chains. Compound **1** has the suitable balance for organogelation, while the alkyl chain length of **2** may be too long and tend to precipitate. Compounds **3**–**6** formed organogels in many organic solvents and oils such as hydrocarbone, esters, ketones, cyclic ethers, aromatic solvents,

**Table 1**
Organogelation properties of **1**–**6** at 25 °C

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| *n*-Hexane | Ins | Ins | Ins | Ins | 20 | 3 |
| *c*-Hexane | — | — | — | 1 | 13 | 7 |
| EtOH | — | — | — | — | — | — |
| AcOEt | 15 | — | 30 | 30 | 18 | 15 |
| Acetone | 45 | P | 20 | 25 | 35 | 15 |
| THF | — | — | 20 | 10 | — | 30 |
| 1,4-Dioxane | — | 7 | 25 | 15 | 30 | 15 |
| Toluene | 45 | 35 | 40 | 10 | 3 | 20 |
| Nitrobenzene | 3 | 10 | 40 | 35 | 6 | 10 |
| DMSO | — | — | — | — | — | 15 |
| $CH_3CN$ | P | P | P | P | P | P |
| $CCl_4$ | 3 | PG | 45 | 2 | 4 | 20 |
| PC | 5 | P | 25 | 15 | 20 | 8 |
| γ-BL | 25 | P | P | 30 | 10 | 4 |
| Oleic acid | 30 | 40 | 30 | — | — | 20 |
| Linseed oil | 10 | — | 45 | 10 | 30 | 8 |
| IPM | 15 | P | 10 | 10 | 2 | 8 |
| Liquid paraffin | — | — | P | — | — | 6 |
| Triolein | — | — | 30 | 15 | 6 | 6 |
| Silicone oil (KF56) | 10 | 15 | 10 | 40 | 40 | 5 |
| D4 | Ins | Ins | Ins | Ins | — | 7 |
| Diesel oil | 40 | — | 40 | 6 | 1 | 5 |
| TEG | — | — | — | — | — | 3 |
| PEG400 | — | 45 | 30 | 30 | 30 | 15 |
| MePEG550 | 45 | 45 | 40 | 20 | — | 15 |
| PPG700 | 20 | 45 | 15 | 20 | — | 3 |

Values denote minimum gel concentration (MGC, g/L). Ins: insoluble; P: precipitate after dissolution; PG: partial gel consisting of gel and solution; —: no gelation at 40 g/L; PC: propylene carbonate; γ-BL: γ-butyrolactone; IPM: myristic acid isopropyl ester; D4: octamethylcyclotetrasiloxane; TEG: tetraethylene glycol; PEG400: polyethylene glycol (MW≈400); MePEG550: polyethylene glycol monomethyl ether (MW≈550); PPG700: polypropylene glycol (MW≈700).

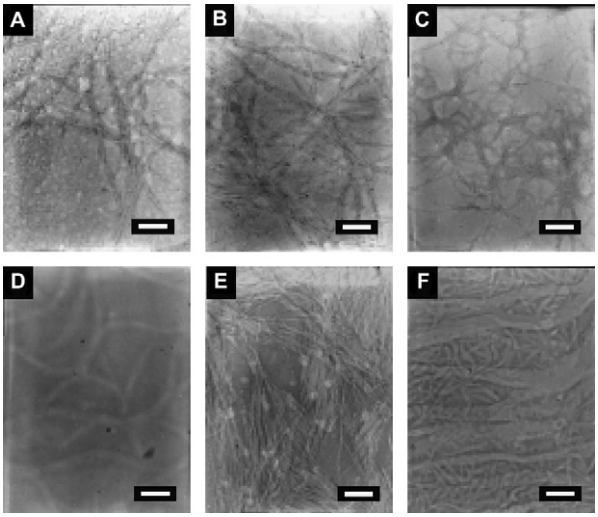



**Figure 2.** TEM images of xerogels prepared from ethyl acetate gel of **1** (A) and 1,4-dioxane gels of **2**–**6** (B–F).

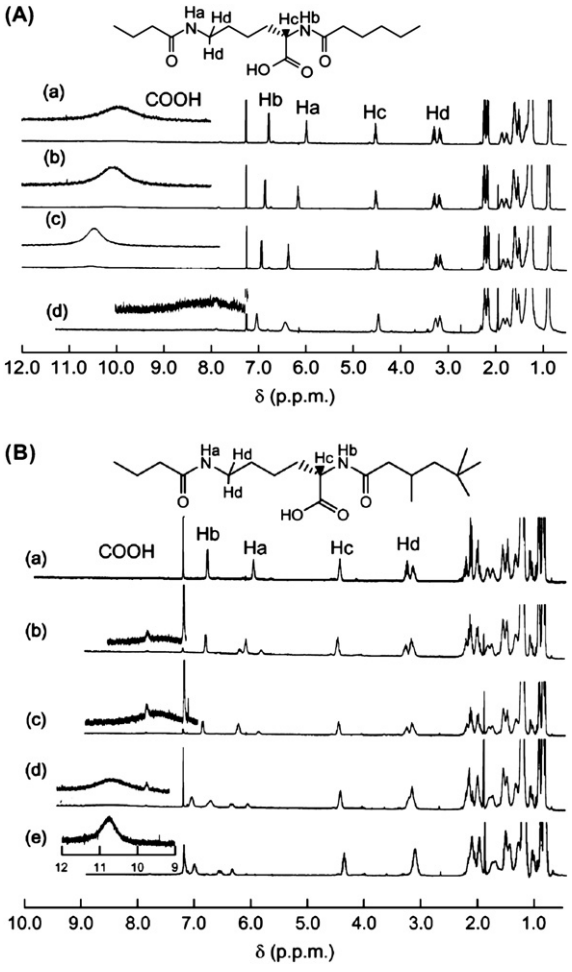



**Figure 3.** $^1H$ NMR spectra of **1** (A) and **5** (B) in a mixture of $CDCl_3$ and $CCl_4$; $CDCl_3/CCl_4$ (vol/vol)=100:0 (a), 70:30 (b), 50:50 (c), 30:70 (d) and 10:90 (e); [**1**]=10 g/L, [**5**]=5 g/L.

**Table 2**
$^1$H NMR data of **1** and **5** in $CDCl_3/CCl_4$

| | $CDCl_3/CCl_4$ | COOH | $N^{\alpha}$–H | $N^{\varepsilon}$–H |
|---|---|---|---|---|
| **1** | 100:0 | 9.91 | 6.79 | 6.00 |
| | 70:30 | 10.03 | 6.86 | 6.16 |
| | 50:50 | 10.53 | 6.94 | 6.30 |
| | 30:70 | 8.00 | 7.03 | 6.42 |
| **5** | 100:0 | — | 6.83 | 6.01 |
| | 70:30 | 7.90 | 6.85 | 6.24 |
| | 50:50 | 7.90 | 6.90 | 6.29 |
| | 30:70 | 8.50 | 7.10 | 6.78 |
| | 90:10 | 10.74 | 7.23 | 7.07 |

propylene carbonate and γ-butyrolactone, vegetable and mineral oils and glycols; especially, **6**, which has the isostearic acid group (2-heptylundecanoyl group), showed the best organogelation ability among **1**–**6**. For gelators having the linear alkyl chains, the hydrophobic–hydrophilic balance of the gelator molecule is important for the organogelation. However, the organogelation ability for **3**–**6** increased with the increasing carbon numbers of the branched alkyl chains. These results imply that the formation of supramolecular gels (molecular aggregation) depends on not only the hydrophobic–hydrophilic balance of the gelator molecule but also other factors such as the size of alkyl chains, van der Waals radius and steric hindrance for aggregation.

It is well-known that a gelator molecule constructs nanoscale superstructures such as nanofibers, nanoribbons and nanosheets in a supramolecular gel.[1] Figure 2 shows the transmission electron microscopic (TEM) images of xerogels prepared from ethyl acetate gel of **1** and 1,4-dioxane gels of **2**–**6**. In all supramolecular gels, these gelators formed a supramolecular nanofiber with a diameter of 10–40 nm, and their entanglements created a three-dimensional network. Similar images were observed for other organogels such as acetone and toluene. Therefore, the organogelation occurs by immobilizing solvents in the nanospaces in the three-dimensional networks.

The hydrogen bonding and van der Waals interactions are main driving forces for self-assembly of the gelators into nanofibers.[1,45,46] The NMR spectra can reveal hydrogen bonding interaction. Figure 3 shows the typical $^1$H NMR spectra of **1** and **5** in a mixture of $CDCl_3$ and $CCl_4$, and the NMR data are listed in Table 2. Here, **1** and **5** are soluble in $CDCl_3$ and forms an organogel in $CCl_4$. Two NMR signals of the amide protons were observed at 6.79 and 6.00 for **1** as well as at 6.83 and 6.01 for **5** in the $CDCl_3$ solution, corresponding to the free amide proton. With the increasing content of $CCl_4$, these peaks shifted to the lower field and broadened. Such lower field shift and broadening of the NMR resonance peaks can be interpreted as an indication of restricted freedom of motion; therefore, it indicates the presence of hydrogen bonding interaction.[29,47–49] The similar results were obtained for other compounds. In addition, the proton of the carboxy group showed the similar shift; therefore, the interaction of carboxy groups play an important role in the gelation. Unfortunately, $^1$H NMR of an organogel cannot be measured, because of its long relaxation time of amide protons.

Further detailed study was carried out using FTIR spectropscopy. FTIR spectroscopy is extensively used to investigate the organogelation because the IR spectrum of the gel state in addition to solution and solid states can be obtained. Figure 4 shows the FTIR spectra of **1** and **5** in $CHCl_3$ solution and $CCl_4$ gel and these data are listed in Table 3. In the $CHCl_3$ solution, the typical IR bands were observed around 3445 $cm^{-1}$, 1658 $cm^{-1}$ and 1520 $cm^{-1}$, arising from the non-hydrogen bonded amide groups. In contrast, the IR peaks of the hydrogen bonded amide groups appeared around 3300 $cm^{-1}$, 1640 $cm^{-1}$ and 1550 $cm^{-1}$ in the $CCl_4$ gels. These results indicate the presence of hydrogen bonding interaction between the amide groups in the organogel. In the $CCl_4$ gels, the IR peak of the hydrogen bonded amide I was observed at 1637 $cm^{-1}$ for **1** and at 1650 $cm^{-1}$ for **5**. The branched alkylated gelators have a different hydrogen bonding pattern from the linear alkylated gelators. Probably, this is induced by steric effect of the branched alkyl chain. In addition, the FTIR measurements also provide information on the alkyl groups, and we obtained interesting results. For **1**–**3**, the absorption bands of the asymmetric ($\nu_{as}$) and symmetric ($\nu_s$) $CH_2$ stretching vibrations in the $CCl_4$ gel were observed around 2920 $cm^{-1}$ and 2851 $cm^{-1}$, while these bands appear at a low frequency compared with those of free alkyl chains in $CHCl_3$ [2929 $cm^{-1}$ ($\nu_{as}$, C–H) and 2856 $cm^{-1}$ ($\nu_s$, C–H)]. Such a low frequency shift shows the strong interaction between the alkyl chains (van der Waals interaction).[43] On the other hand, the IR bands of the $CH_2$ stretching vibration of **4**–**6**, having the branched alkyl chains, were independent of solvents (almost the same band in the $CHCl_3$ solution as that in the $CCl_4$ gel). Compared with those of the solid states, these bands appear at high frequency. This fact implies that the branched alkyl chains are relatively fluidic in the $CCl_4$ gel and their molecular packing is more random than that of the solid state; i.e., van der Waals interaction between the branched alkyl chains is weak (or non). The fluidity of the branched alkyl chains may give large spaces for trapping of solvent molecules, which leads to a more effective organogelation than **1**–**3**.

As mentioned above, the NMR study showed the change in the proton of the carboxy group when increasing $CCl_4$ content, and the contribution of the carboxy group to the organogelation (self-assembly into nanofibers) was indicated. Therefore, we focus also the IR bands of the carboxy group. As shown in Figure 4, the IR peaks

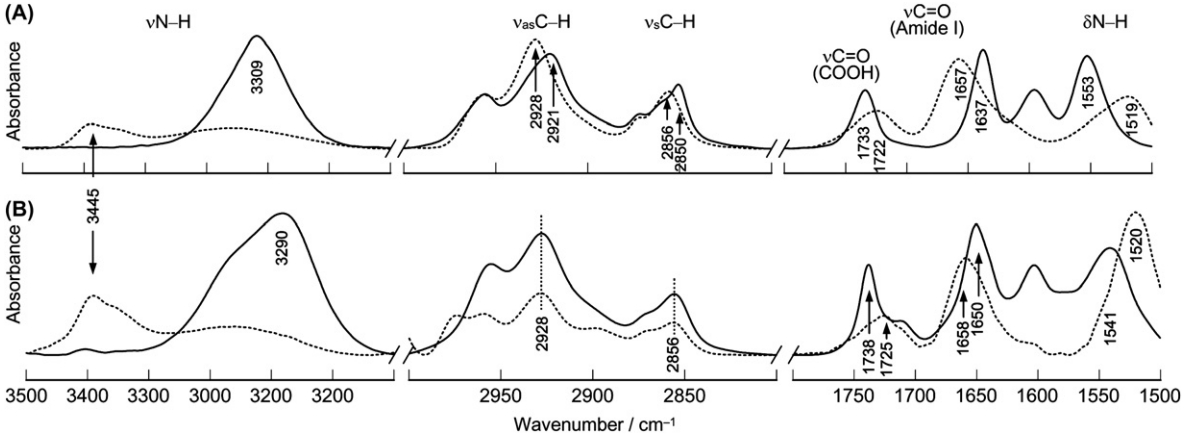



**Figure 4.** FTIR spectra of **1** (A) and **5** (B) in $CHCl_3$ solutions (dotted line) and $CCl_4$ gels (solid line); [**1**]=[**5**]=10 g/L.

**Table 3**
FTIR data of **1** and **5** in $CHCl_3$ solution and $CCl_4$ gels

| | **1** | | **5** | |
|---|---|---|---|---|
| | $CHCl_3$ | $CCl_4$ | $CHCl_3$ | $CCl_4$ |
| Amide A ($\nu$ N–H) | 3445 | 3309 | 3446 | 3290 |
| $\nu_{as}$ C–H | 2928 | 2920 | 2928 | 2928 |
| $\nu_s$ C–H | 2856 | 2850 | 2856 | 2855 |
| COOH ($\nu$ C=O) | 1722 | 1733 | 1725 | 1738 |
| Amide I ($\nu$ C=O) | 1657 | 1637 | 1658 | 1650 |
| Amide II ($\nu$ C=O) | 1519 | 1553 | 1520 | 1544 |

were observed at 1722 $cm^{-1}$ for **1** and 1725 $cm^{-1}$ for **5** in the $CHCl_3$ solution, while they shifted to high frequency in the $CCl_4$ gel; i.e., 1733 $cm^{-1}$ for **1** and 1738 $cm^{-1}$ for **5**. These bands are almost the same as those in the solid state. This result indicates that the hydrogen bonding pattern between the carboxy groups in the $CHCl_3$ solution is different from that in the $CCl_4$ gel and the solid state; namely, the hydrogen bonding becomes weak in the $CCl_4$ gel compared with that in $CHCl_3$ solution. It is assumed that the formation of intermolecular hydrogen bonding interaction inhibits the interaction of the carboxy groups. In contrast, for **6**, the IR bands of the carboxy group in $CHCl_3$ solution and $CCl_4$ gel hardly change (1721 $cm^{-1}$ in $CHCl_3$ and 1718 $cm^{-1}$ in $CCl_4$ gel), indicating that they have almost the same hydrogen bonding pattern of the carboxy groups.

The NMR and IR studies led us to propose the gelation mechanism. For **1** and **2** having a linear alkyl chain, the hydrogen bonding between the amide groups, relatively weak hydrogen bonding between the carboxy groups and van der Waals interactions are the driving forces for self-assembly into the nanofibers and then organogelation. This is similar to the results reported previously.[1,39,44] On the other hand, for **4**–**6**, the carboxy groups undergo a relatively strong hydrogen bonding interaction because the amide groups do not have the hydrogen bonding interaction in the $CHCl_3$ solution. After dissolution of the gelators (**4**–**6**) in $CCl_4$, hydrogen bonding interactions between the amide groups and between the carboxy groups lead to the formation of three-dimensional networks by the self-assembled nanofibers. In this case, the steric effect of the branched alkyl chains hinders the van der Waals interaction of the alkyl chains and provides large spaces; as a result, the effective organogelation is achieved (Scheme 2).

## 3. Conclusions

In conclusion, we reveal the preparation of a family of $N^{\alpha}$,$N^{\varepsilon}$-diacyl-L-lysine based organogelators and effect of the alkyl chains on their organogelation behaviour. These compounds are prepared by acylation of $N^{\varepsilon}$-dodecyl-L-lysine with acyl chlorides through the one-pot synthetic procedure with low cost and high reaction yield. L-Lysine organogelators possessing the branched alkyl groups are a better organogelation property, especially, **6** is excellent gelator that form organogels in many organic solvents and oils. The NMR and IR studies demonstrate that the driving forces for the organogelation are mainly hydrogen bonding interactions between the amide groups and between the carboxy groups. It is found that the introduction of the branched alkyl chain into L-lysine decreases the van der Waals interaction between the alkyl chains due to its large van der Waals radius and gives large spaces in the three-dimensional networks. Because these gelators can simply and cheaply be synthesized with high reaction yield and the synthetic procedure can undergo in large scale, it is expected the application for many industrial fields.

## 4. Experimental

### 4.1. General

#### 4.1.1. Materials

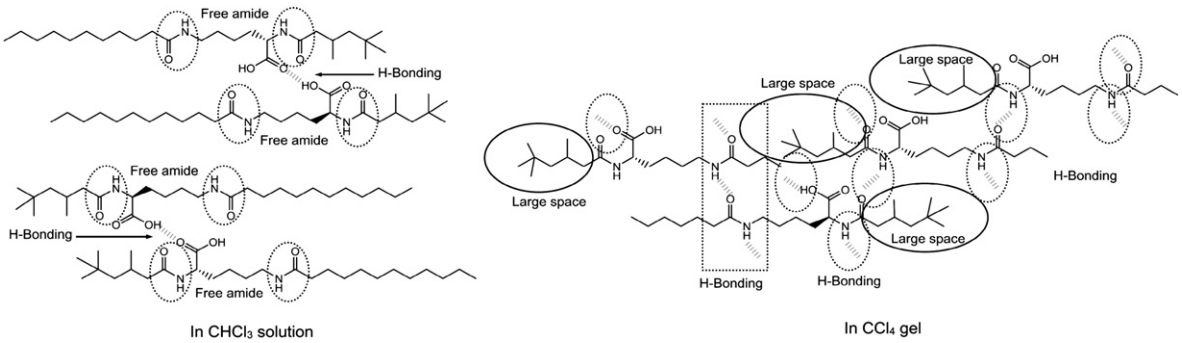
$N^{\varepsilon}$-Lauroyl-L-lysine was kindly supplied from Ajinomoto Co., Inc. The other chemicals were of the highest commercial grade available and were used without further purification. All solvents used in the syntheses were purified, dried or freshly distilled as required.

#### 4.1.2. Typical synthetic procedure

$N^{\varepsilon}$-Lauroyl-L-lysine (65.7 g, 0.2 mol) was dissolved in NaOH aq solution (80 g/700 mL) and ethyl ether (500 mL) was added. Alkanoyl chloride (0.3 mol) was slowly added to the ether layer. The biphasic solution was vigorously stirred at 0 °C for 4 h and then at room temperature for 20 h. The resulting solution was carefully acidified by concd HCl to ca. pH=1. White precipitate was filtered, washed with water and then dried. The crude product was purified by recrystallization from EtOH/ether.

*4.1.2.1. $N^{\alpha}$-Hexanoyl-$N^{\varepsilon}$-lauroyl-L-lysine (**1**).* Yield 88%. IR (KBr): $\nu$=3311 $cm^{-1}$ ($\nu$ N–H, amide A), 1733 $cm^{-1}$ ($\nu$ C=O, –COOH), 1638 $cm^{-1}$ ($\nu$ C=O, amide I), 1555 $cm^{-1}$ ($\delta$ N–H, amide II); $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): $\delta$=0.86–0.90 (m, 6H, C$H_3$), 2.18 (t, $J$=7.3 Hz, 2H, C$H_2$CONH), 2.24 (t, $J$=7.0 Hz, 2H, NHCOC$H_2$), 3.19–3.26 (m, 2H, NHC$H_2$), 4.42–4.47 (m, 1H, C$H$NH), 6.30 (t, $J$=5.6 Hz, 1H, N$^{\alpha}H$CO), 6.85 (d, $J$=7.3 Hz, 1H, CON$^{\varepsilon}H$), 9.37 (br, 1H; COO$H$). Elemental analysis calcd (%) for $C_{24}H_{46}N_2O_4$ (426.63): C, 67.57; H, 10.87; N, 6.57. Found: C, 67.88; H, 10.99; N, 6.58.

*4.1.2.2. $N^{\alpha}$,$N^{\varepsilon}$-Bis(lauroyl)-L-lysine (**2**).* Yield 96%. IR (KBr): $\nu$=3307 $cm^{-1}$ ($\nu$ N–H, amide A), 1713 $cm^{-1}$ ($\nu$ C=O, –COOH), 1645 $cm^{-1}$ ($\nu$ C=O, amide I), 1557 $cm^{-1}$ ($\delta$ N–H, amide II); $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): $\delta$=0.88 (t, $J$=6.3 Hz, 6H, C$H_3$), 2.18 (t, $J$=7.6 Hz, 2H, C$H_2$CONH), 2.24 (t, $J$=7.6 Hz, 2H, NHCOC$H_2$), 3.17–3.29 (m, 2H, NHC$H_2$), 4.51 (q, $J$=4.8 Hz, 1H, C$H$NH), 6.22 (t, $J$=5.6 Hz, 1H, N$^{\alpha}H$CO), 6.82 (d, $J$=7.6 Hz, 1H, CON$^{\varepsilon}H$), 10.63 (br, 1H, COO$H$).




**Scheme 2.** Organogelation mechanism.

Elemental analysis calcd (%) for $C_{30}H_{58}N_2O_4$ (510.79): C, 70.54; H, 11.45; N, 5.48. Found: C, 70.66; H, 12.01; N, 5.55.

*4.1.2.3. $N^{\alpha}$-Cyclohexylcarbonyl-$N^{\varepsilon}$-lauroyl-L-lysine (**3**).* Yield 92%. IR (KBr): $\nu$=3312 $cm^{-1}$ ($\nu$ N–H, amide A), 1725 $cm^{-1}$ ($\nu$ C=O, –COOH), 1639 $cm^{-1}$ ($\nu$ C=O, amide I), 1545 $cm^{-1}$ ($\delta$ N–H, amide II); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25 °C): $\delta$=0.88 (t, $J$=6.6 Hz, 6H, C*H*$_3$), 2.17–2.25 (m, 3H, C*H*$_2$CON$_H$, 1H, NHCOC*H*), 3.16–3.28 (m, 2H, NHC*H*$_2$), 4.49 (q, $J$=4.8 Hz, 1H, C*H*NH), 6.33 (t, $J$=5.6 Hz, 1H, N$^{\alpha}$*H*CO), 6.74 (d, $J$=7.6 Hz, 1H, CON$^{\varepsilon}$*H*), 10.23 (br, 1H, COO*H*). Elemental analysis calcd (%) for $C_{25}H_{46}N_2O_4$ (438.64): C, 68.45; H, 10.57; N, 6.39. Found: C, 68.49; H, 11.00; N, 6.34.

*4.1.2.4. $N^{\alpha}$-2-Ethylhexanoyl-$N^{\varepsilon}$-lauroyl-L-lysine (**4**).* Yield 86%. IR (KBr): $\nu$=3308 $cm^{-1}$ ($\nu$ N–H, amide A), 1736 $cm^{-1}$ ($\nu$ C=O, –COOH), 1641 $cm^{-1}$ ($\nu$ C=O, amide I), 1546 $cm^{-1}$ ($\delta$ N–H, amide II); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25 °C): $\delta$=0.84–0.90 (m, 9H, C*H*$_3$), 2.18 (t, $J$=7.7 Hz, 2H, C*H*$_2$CONH), 3.23 (t, $J$=6.2 Hz, 2H, NHC*H*$_2$), 4.51–4.55 (m, 1H, C*H*), 6.34–6.38 (m, 1H, N$^{\varepsilon}$*H*), 6.74–6.78 (m, 1H, N$^{\alpha}$*H*), 9.29 (br, 1H, COO*H*). Elemental analysis calcd (%) for $C_{26}H_{50}N_2O_4$ (454.69): C, 68.68; H, 11.08; N, 6.18. Found: C, 68.77; H, 11.22; N, 6.19.

*4.1.2.5. $N^{\alpha}$-3,5,5-Trimethylhexanoyl-$N^{\varepsilon}$-lauroyl-L-lysine (**5**).* Yield 94%. IR (KBr): $\nu$=3312 $cm^{-1}$ ($\nu$ N–H, amide A), 1734 $cm^{-1}$ ($\nu$ C=O, –COOH), 1638 $cm^{-1}$ ($\nu$ C=O, amide I), 1553 $cm^{-1}$ ($\delta$ N–H, amide II); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25 °C): $\delta$=0.86–0.91 (m, 15H, C*H*$_3$), 2.16–2.22 (m, 2H, C*H*$_2$CONH), 3.18–3.29 (m, 2H, NHC*H*$_2$), 4.50 (br, 1H, C*H*), 6.19 (br, 1H, N$^{\varepsilon}$*H*), 6.83 (d, $J$=7.3 Hz, 1H, N$^{\alpha}$*H*), 8.23 (br, 1H, COO*H*). Elemental analysis calcd (%) for $C_{27}H_{52}N_2O_4$ (468.39): C, 69.19; H, 11.18; N, 5.98. Found: C, 69.22; H, 11.55; N, 5.98.

*4.1.2.6. $N^{\alpha}$-2-Heptylundecanoyl-$N^{\varepsilon}$-lauroyl-L-lysine (**6**).* Yield 94%. IR (KBr): $\nu$=3303 $cm^{-1}$ ($\nu$ N–H, amide A), 1736 $cm^{-1}$ ($\nu$ C=O, –COOH), 1638 $cm^{-1}$ ($\nu$ C=O, amide I), 1544 $cm^{-1}$ ($\delta$ N–H, amide II); $^1H$ NMR (400 MHz, $CDCl_3$, TMS, 25 °C): $\delta$=0.85–0.89 (m, 9H, C*H*$_3$), 2.12–2.20 (m, 3H, C*H*$_2$CONH, NHCOC*H*), 3.23 (q, $J$=6.8 Hz, 2H, NHC*H*$_2$), 4.51 (q, $J$=6.7 Hz, 1H, C*H*), 6.20 (br, 1H, N$^{\varepsilon}$*H*), 6.65 (d, $J$=6.8 Hz, 1H, N$^{\alpha}$*H*), 8.31 (br, 1H, COO*H*). Elemental analysis calcd (%) for $C_{36}H_{70}N_2O_4$ (594.95): C, 72.68; H, 11.86; N, 4.71. Found: C, 72.99; H, 12.11; N, 4.77.

*4.1.3. Instrumentation and techniques*

The elemental analyses were performed using a Perkin–Elmer series II CHNS/O analyzer 2400. The VT-IR spectra were recorded on a JASCO FS-420 spectrometer. The TEM observations were carried out using a JEOL JEM-2010 electron microscope at 200 kV. The FE-SEM observation was carried out using a Hitachi S-5000 field emission scanning electron microscope. The $^1H$ NMR spectra were measured using a Bruker AVANCE 400 spectrometer with TMS as the standard. The UV–vis spectra were measured using a JASCO V-570 UV/VIS/NIR spectrophotometer with a temperature-controller (JASCO ETC-505T). The gel strength measurements were performed using a Sun Science Sun Rheo Meter CR-500DX.

*4.1.4. Gelation test*

A weighed gelator in solvent (1 ml) in a sealed test tube was heated until the gelator dissolved. After allowing the solutions to stand at 25 °C for 6 h, the state of the solution was evaluated by the 'test tube inversion' method.

*4.1.5. Transmission electron microscope (TEM)*

Samples of organogels were prepared as follows: benzene, 1,4-dioxane or tetrachloromethane of the gelators were dropped on a collodion- and carbon-coated 400 mesh grid and quickly dried in vacuo for 24 h. After negative staining by osmic acid overnight, the grids were dried under reduced pressure for 2 h.

*4.1.6. Gel strength*

Samples were prepared as follows: a mixture of a weighed gelator in water (2 mL) in a sealed vial (15 mm in diameter) was heated at 90 °C for 5 min. The resulting opaque solution was allowed to stand at 25 °C for 6 h. The gel strength was evaluated as the force necessary to sink a cylinder bar (10 mm in diameter) 4 mm deep in the gel.

*4.1.7. FTIR study*

The 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 for solution and gel states and KBr method for solid states.

*4.1.8. VT-IR study*

An automatic temperature-control cell unit (Specac Inc., P/N 20730) with a vacuum-tight liquid cell (Specac Inc., P/N 20502, path length 50 μm) fitted with $CaF_2$ windows was used to measure the IR spectra at different temperatures.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.061.

## References and notes

1. *Molecular Gels: Materials with Self-assembled Fibrillar Networks*; Weiss, R. G., Terech, P., Eds.; Springer: Dordrecht, 2006.
2. *Low Molecular Mass Gelators: Design, Self-assembly, Function*; Fages, F., Ed.; Topics in Current Chemistry; Springer: New York, NY, 2005; vol. 256.
3. Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133–3159.
4. van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2263–2266.
5. Estroff, L. A.; Hamilton, A. D. *Chem. Rev.* **2004**, *104*, 1201–1217.
6. Sangeetha, N. M.; Maitra, U. *Chem. Soc. Rev.* **2005**, *34*, 821–836.
7. de Loos, M.; Feringa, B. L.; van Esch, J. H. *Eur. J. Org. Chem.* **2005**, 3615–3631.
8. George, M.; Weiss, R. G. *Acc. Chem. Res.* **2006**, *39*, 489–497.
9. *Low Molecular Weight Organic Gelators, Special Issue*; Smith, D. K., Ed.; Tetrahedron; 2007; 63, 7285–7494.
10. Suzuki, M.; Sakakibara, Y.; Kobayashi, S.; Kimura, M.; Shirai, H.; Hanabusa, K. *Polym. J.* **2003**, *34*, 474–477.
11. Kobayashi, S.; Hamasaki, N.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *J. Am. Chem. Soc.* **2002**, *124*, 6550–6551.
12. Llusar, M.; Roux, C.; Pozzo, J.-L.; Sanchez, C. *J. Mater. Chem.* **2003**, *13*, 442–444.
13. Jung, J. H.; Shinkai, S.; Shimizu, T. *Chem. Mater.* **2003**, *15*, 2141–2145.
14. Yang, Y.; Suzuki, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Chem. Commun.* **2004**, 1332–1333.
15. Kato, T. *Science* **2002**, *295*, 2414–2418.
16. van Bruggen, M. P. B.; Lekkerkerker, H. N. W. *Langmuir* **2002**, *18*, 7141–7145.
17. Camerel, F.; Faul, C. F. J. *Chem. Commun.* **2003**, 1958–1959.
18. Tong, X.; Zhao, Y.; An, B.-K.; Park, S. Y. *Adv. Funct. Mater.* **2006**, *16*, 1799–1804.
19. Mizoshita, N.; Kato, T. *Adv. Funct. Mater.* **2006**, *16*, 2218–2224.
20. de Jong, J. J. D.; Lucas, L. N.; Kellogg, R. M.; van Esch, J. H.; Feringa, B. L. *Science* **2004**, *304*, 278–281.
21. Ryu, S. Y.; Kim, S.; Seo, J.; Kim, Y.-W.; Kwon, O.-H.; Jang, J.-D.; Park, S. *Chem. Commun.* **2004**, 70–71.
22. Ikeda, M.; Takeuchi, M.; Shinkai, S. *Chem. Commun.* **2003**, 1354–1355.
23. George, M.; Weiss, R. G. *Chem. Mater.* **2003**, *15*, 2879–2888.
24. Koshima, H.; Matsusaka, W.; Yu, H. *J. Photochem. Photobiol., A: Chem.* **2003**, *156*, 83–90.
25. Tsou, C.-C.; Sun, S.-S. *Org. Lett.* **2006**, *8*, 387–390.
26. Yagai, S.; Iwashita, T.; Kishikawa, K.; Nakahara, S.; Karatsu, T.; Kitamura, A. *Chem.—Eur. J.* **2006**, *12*, 3984–3994.
27. Tam, A. Y.-Y.; Wongm, K. M.-C.; Wang, G.; Yam, V. W.-W. *Chem. Commun.* **2007**, 2028–2030.
28. Yang, H.; Yi, T.; Zhou, Z.; Zhou, Y.; Wu, J.; Xu, M.; Li, F.; Huang, C. *Langmuir* **2007**, *23*, 8224–8230.
29. Xue, P.; Lu, R.; Chen, G.; Zhang, Y.; Nomoto, H.; Takafuji, M.; Ihara, H. *Chem.—Eur. J.* **2007**, *13*, 8231–8239.
30. Hanabusa, K.; Hiratsuka, K.; Kimura, M.; Shirai, H. *Chem. Mater.* **1999**, *11*, 649–655.

31. Kubo, W.; Kambe, S.; Nakade, S.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2003**, *107*, 4374–4381.
32. Shibata, Y.; Kato, T.; Kado, T.; Shiratuchi, R.; Takashima, W.; Kaneto, K.; Hayase, S. *Chem. Commun.* **2003**, 2730–2731.
33. Li, X.-Q.; Stepanenko, V.; Chen, Z.; Prins, P.; Siebbeles, L. D. A.; Würthner, F. *Chem. Commun.* **2006**, 3871–3873.
34. Tachibana, T.; Mori, T.; Hori, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1714–1720.
35. Bhattacharya, S.; Krishnan-Ghosh, Y. *Chem. Commun.* **2001**, 185–186.
36. Ballabh, A.; Trivedi, D. R.; Dastidar, P. *Chem. Mater.* **2003**, *15*, 2136–2140.
37. George, M.; Snyder, S. L.; Terech, P.; Glinka, C. J.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10275–10283.
38. Kiyonaka, S.; Shinkai, S.; Hamachi, I. *Chem.—Eur. J.* **2003**, *9*, 976–983.
39. Suzuki, M.; Nakajima, Y.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Org. Biomol. Chem.* **2004**, *2*, 1155–1159.
40. D'Aléo, A.; Pozzo, J.-L.; Fages, F.; Schmutz, M.; Mieden-Gundert, G.; Vögtle, F.; Caplar, V.; Zinic, M. *Chem. Commun.* **2004**, 190–191.
41. Hanabusa, K.; Nakayama, H.; Kimura, M.; Shirai, H. *Chem. Lett.* **2000**, 1070–1071.
42. Suzuki, M.; Nakajima, Y.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Langmuir* **2003**, *19*, 8622–8624.
43. In the present case, the gelation ability is regarded as the ability of the gelator that can gel many kinds of organic fluids.
44. Suzuki, M.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Chem.—Eur. J.* **2003**, *9*, 348–354.
45. Timioka, K.; Sumiyoshi, T.; Narui, S.; Nagaoka, Y.; Iida, A.; Miwa, Y.; Taga, T.; Nakano, M.; Handa, T. *J. Am. Chem. Soc.* **2001**, *123*, 11817–11818.
46. Sumiyoshi, T.; Nishimura, K.; Nakano, M.; Handa, T.; Miwa, Y.; Timioka, K. *J. Am. Chem. Soc.* **2003**, *123*, 12137–12142.
47. Dunchan, D. C.; Whitten, D. G. *Langmuir* **2000**, *16*, 6445–6452.
48. Makarević, J.; Jokić, M.; Raza, Z.; Štefanić, Z.; Kojić-Prodić, B.; Žinić, M. *Chem.—Eur. J.* **2003**, *9*, 5567–5580.
49. Suzuki, M.; Yumoto, M.; Kimura, M.; Shirai, H.; Hanabusa, K. *Helv. Chim. Acta* **2004**, *87*, 1–10.