Supramolecular organogel formation triggered by acid–base interaction in two-component system consisting of L-lysine derivative and aliphatic acids†

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The formation of supramolecular organogels using an acid–base interaction was investigated in organogelation systems consisting of N^{ε}-lauroyl-L-lysine ethyl ester and aliphatic acids. Although the L-lysine derivative and aliphatic acids hardly had any organogelation abilities for organic solvents and oils, the mixing of both solutions led to the formation of organogels. This is induced by the formation of organic salts. The organic salt compounds of N^{ε}-lauroyl-L-lysine ethyl ester and aliphatic acids also exhibited a good organogelation property for oils. The transmission electron microscopic analysis demonstrates these gelators formed a helical nanofiber and created a three-dimensional network in organogels. The FT-IR studies indicate that the formation of organic salt compounds through an acid–base interaction is an important step for the organogelation.

Introduction

Gels are formed through the initial assembly of the gelator molecules into nanofibers which are then further organized into a three-dimensional network, trapping the solvent within the free space of the network. The gels formed by low-molecular-weight organic molecules in organic solvents are often called physical gels or supramolecular gels.[1,2] Supramolecular organogels have received considerable attention recently on account of their unique features and potential applications for new soft organic materials,[3] template synthesis,[4] drug delivery,[5] and separations and biomimetics.[6] Well-known organogelators including, for example, certain derivatives of carbohydrates,[7] amino acids,[8] urea[9] and cholesterols[10] have been prepared and their self-assembling properties have been well studied. Most organogelators have functional groups that can undergo non-covalent intermolecular interactions; *e.g.*, amide, urea, hydroxy and carboxy groups for hydrogen bonding, linear and cyclic alkyl chains for van der Waals interaction, aromatic groups for π-stacking and polypyridine groups for coordination interaction.[1–10] Interestingly, research efforts have been focused on two-component gelators formed through hydrogen bonding,[11] donor–acceptor interaction,[12] metal ion coordination[13] and acid–base interactions,[14] which offer the potential of developing soft materials with highly tunable microscopic and macroscopic properties. Although the two compounds forming two-component gelators do not have organogelation properties by themselves, they can function as an organogelator by the formation of a two-component compound. In this paper, we describe the gelation behavior of organic salt-type organogelators consisting of N^{ε}-lauroyl-L-lysine esters and aliphatic acids.

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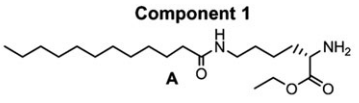
Results and discussion

Organogelation properties

N^{ε}-Lauroyl-L-lysine ethyl ester (**A**)[8a] and commercially available aliphatic acids (**1–8**) were used as component 1 and 2, respectively (Fig. 1). The organogelation abilities of **A** and **1–8** were first examined. **1–8** did not form an organogel in various organic solvents and oils. **A** did not gel organic solvents, while it showed organogelation ability for some oils such as silicone oils and liquid paraffin. For the two-component system, the organogelation properties are listed in Table 1, where the values denote minimum gel concentration (MGC, g L^{-1}) necessary for organogelation. In the present case, the organogelation was examined by two methods as shown in Scheme 1: one is simultaneous dissolution of **A** and **1–8** in solvents by heating (Procedure 1), the other is mixing of solutions of **A** and **1–8** at room temperature (Procedure 2). After simultaneous dissolution of **A** and aliphatic acid at 80 °C, the organogel was formed by storing the resulting solution at 25 °C for 2 h. On the other hand, when the solutions of **A** and aliphatic acid were mixed at 25 °C with vigorous stirring (from **A** to acid or from acid to **A**), the organogel was formed within 5 minutes. Because the organogelation using Procedure



1: Octanoic acid; **2**: Nonic acid; **3**: Lauric acid; **4**: Tridecanoic acid; **5**: Tetradecanic acid; **6**: Pentadecanoic acid; **7**: Palmitic acid; **8**: Stearic acid

Fig. 1 Components 1 and 2.

Table 1 Organogelation properties of two-component systems at 25 °C[a]

	A	1 + A 1A	2 + A 2A	3 + A 3A	4 + A 4A	5 + A 5A	6 + A 6A	7 + A 7A	8 + A 8A	9	10
Oleic acid	—[g]	—	—	—	—	—	—	—	—	—	10
Salad oil	—	25	30	30	25	20	20	10	15	—	6
Linseed	—	—	—	—	—	—	—	30	30	—	15
OMCTS[b]	—	25	—	10	2	2	2	0.8	0.8	—	—
DMCPS[c]	—	10	—	10	2	2	2	0.8	0.8	—	—
IPM[d]	—	—	—	—	—	—	—	20	6	—	20
Paraffin	15	8	8	6	1	1	1	0.8	1	30	4
Si oil-1[e]	15	5	6	15	5	4	4	2	1	8	3
Si oil-2[f]	15	10	15	20	5	4	4	2	1	8	4
Triolein	—	—	—	—	—	—	—	—	—	—	6
$^{n}C_{12}H_{26}$	—	6	10	15	5	5	2	2	2	—	20
Squalane	—	25	20	12	8	0.7	1	1	1	30	6
Diesel oil	—	15	15	20	30	20	20	7	6	—	20
Kerosene	—	15	30	20	10	10	8	5	5	—	20

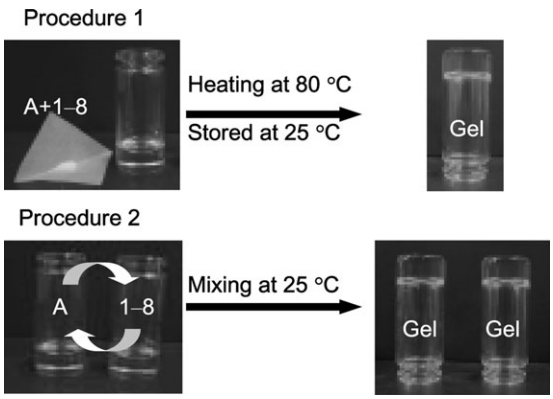
[a] Values denote minimum gel concentration (MGC, g L^{-1}) necessary for organogelation (**A** + **1**–**8**). [b] Octamethylcyclotetrasiloxane. [c] Decamethylcyclopentasiloxane. [d] Isopropyl myristate. [e] Silicone oil KF-54 (Shin-Etsu Chemical Co., Ltd). [f] Silicone oil KF-56 (Shin-Etsu Chemical Co., Ltd). [g] —: No gelation at 30 g L^{-1}.

2 is conducted at 25 °C, the organogelation time is fast. In contrast, Procedure 1 is first carried out at 80 °C and then it needs the cooling process; as the result, the organogelation is slower than that by Procedure 2. Both procedures showed almost the same results that produced an organogel. Although **A** + **1–8** did not form an organogel in organic solvents,[15] they showed good organogelation abilities for many oils that formed an organogel at low MGC; especially, **7** + **A** and **8** + **A** were able to form transparent gels of cyclic silicone oils (OMCTS and DMCPS), liquid paraffin, silicone oils, and squalane below 1 mg mL^{-1}. An organogelator which can gel cyclic silicone oils is relatively rare among our organogelators. In addition, because **A** and **1–8** are dissolved by heating to less than 100 °C, the two-component system is very useful. Why is the organogelation induced by a mixing of two compounds that have no organogelation abilities? After mixing of two components, component 1 (amine) reacts with component 2 (carboxylic acid) through an acid–base interaction and they form the organic salts, which leads to the formation of the organogels, followed by the self-assembly into nanofibers.

In order to elucidate the formation of organic salts, organic salt compounds, **1A–8A**, were prepared and their organogelation properties were examined (Fig. 2). The organic salt compounds were prepared by very simple synthetic procedures using **A** and **1–8** and these compounds were obtained with a high yield (total yield > 95%). As expected, these organic salt compounds functioned as organogelators, and interestingly, their organogelation behavior is identical with the results listed in Table 1. These results imply that the organogelation in the two-component systems is induced by the formation of organic salt compounds; namely, one of the important driving forces for the organogelation is an acid–base interaction.

We have previously reported that the L-lysine-based organogelators, **9** and **10**, function as organogelators; especially, **10** is a powerful organogelator that can gel many organic solvents and oils.[16] **9** has a little organogelation ability for oils and **10** can gel oils except for cyclic siloxanes. Their organogelation abilities are less than those of two-component systems and organic salt compounds. In addition, the organic salt compounds are dissolved in oils at a lower temperature.

The organogelation abilities of **A** + **1–8** significantly depended on the alkyl chain length of the aliphatic acids. For example, for linseed oil and IPM, **A** + **1–6** ($\leq C_{15}$) gave no organogelation, but (**7** + **A**) and (**8** + **A**) formed an organogel. The organogelation abilities increased with increasing length of the alkyl chains in the aliphatic acids. In general, a lyophilic–lyophobic balance of an organogelator molecule is very important for the organogelation property.[1,2] The lyophilic–lyophobic balance of **A** and aliphatic acids is not suitable for the formation of an organogel, while the organic salt compounds formed by mixing of **A** and aliphatic acids have a good balance, leading to the organogelation.



Scheme 1 Organogelation procedures for two-component system.

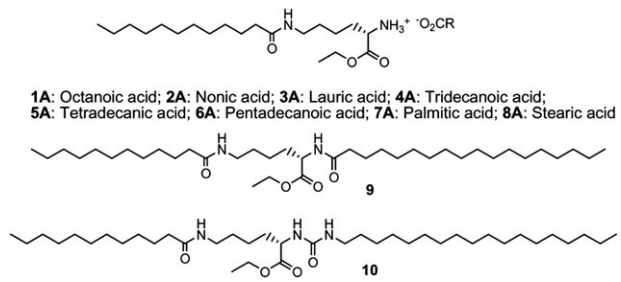


Fig. 2 Organic salt compounds and L-lysine-based organogelators.

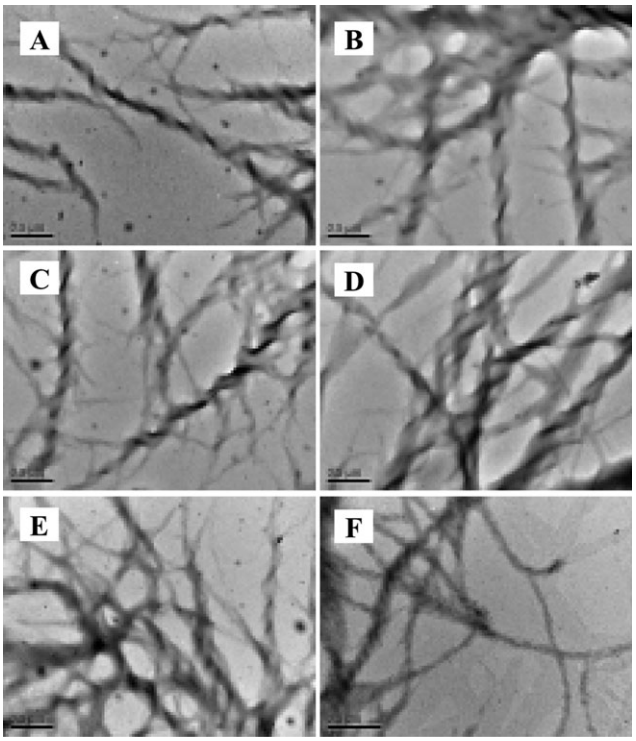


Fig. 3 TEM images of samples prepared from organogels based on **7** + **A** and **7A** (5 mg mL^{-1}). (A): Si oil-1 gel of **7** + **A**; (B): Si oil-1 gel of **7A**; (C): liquid paraffin gel of **7** + **A**; (D): liquid paraffin gel of **7A**; (E): DMCPS gel of **7** + **A**; (F): DMCPS gel of **7A**.

TEM study

It is well-known that organogelators construct a three-dimensional network by entanglement of the self-assembled nanofibers in the organogels.[1] The morphologies of the nanofibers in the organogels were observed using an electron microscopic technique. Fig. 3 shows the transmission electron microscope (TEM) images of samples prepared from various organogels based on **7** + **A** and **7A**. In these organogels, no clear difference was observed between the nanostructures formed by **7** + **A** (two-component system) and by **7A** (organic salt). Interestingly, these organogelators formed a helical nanofiber (120–180 nm) entangling thin nanofibers with a diameter of 30–60 nm. Similar electron microscopic images were observed for other organogels. No peaks were observed in the CD spectra of **A** in DMCSP and **7A** in MeOH (solution), while the CD spectrum of **7A** in DMCSP (gel) showed a negative Cotton effect at 198 nm and a positive one at 220 nm.[17] The CD result indicates that **7A** (or **7** + **A**) forms a chiral aggregate in the gel and this is supported by the result of TEM observation. It is not clear why these organogelators form a helical nanofiber, but the chirality of the L-lysine segment may have an effect.

FT-IR study

IR spectra at room temperature. In order to analyze the organogelation mechanism, IR spectroscopy was used. Fig. 4 shows the FT-IR spectra of **A** (solution), **7** (solution), **7** + **A** (gel) in DMCPS and $CHCl_3$ solution of **7** + **A** in DMCPS at 25 °C. For **7**, the IR peak, arising from the stretching vibration

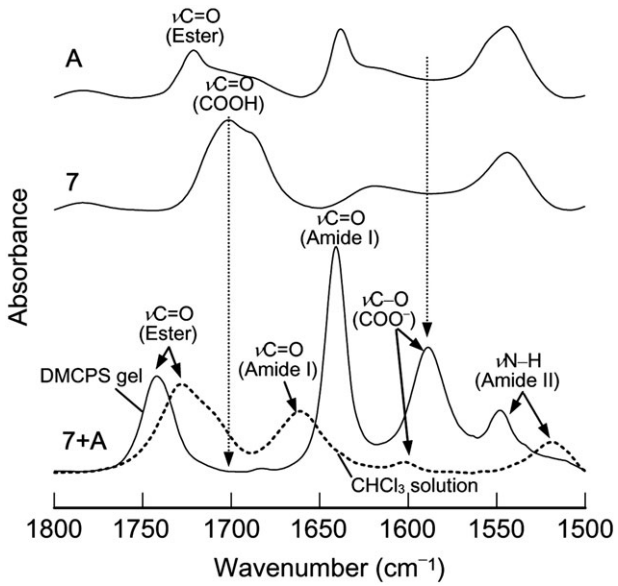


Fig. 4 FT-IR spectra of **A**, **7** and **7** + **A** in DMCPS and $CHCl_3$ (dotted line) at 25 °C. $>$**A**] = [**7**] = 10 g L^{-1}, [**7** + **A**] = 10 g L^{-1}.

of carboxylic acid, was observed around 1700 cm^{-1} (νC=O). The IR spectra of **A** showed the typical absorption bands at 1721 cm^{-1} (νC=O of ester), 1638 cm^{-1} (νC=O of amide I) and 1544 cm^{-1} (δN–H of amide II). Because **A** has organogelation ability for DMCPS and forms the organogel at 15 g L^{-1}, it shows the IR peaks of hydrogen bonded amide I and II at 10 g L^{-1} in which no organogelation occurs. In contrast, although the FT-IR spectrum of the DMCPS gel formed by mixing of **7** + **A** is the same as that formed by **7A**, it is quite different from the IR spectrum simulated from **7** and **A**; the IR bands were observed at 1721 cm^{-1} (νC=O of ester), 1641 cm^{-1} (νC=O of hydrogen bonded amide I), 1589 cm^{-1} (νC–O of carboxylate, COO^-), and 1548 cm^{-1} (δN–H of hydrogen bonded amide II). Very interestingly, the IR peak of the carboxylic acid of **7** disappeared and a new peak of carboxylate appeared. This fact indicates that **A** reacts with **7** through an acid–base reaction and an organic salt compound is formed. In addition, hydrogen bonding interaction between the amide groups was observed. On the other hand, the IR spectrum of **7** + **A** in $CHCl_3$ solution showed peaks at 1729 cm^{-1} (νC=O of ester), 1660 cm^{-1} (νC=O of non-hydrogen bonded amide I), 1602 cm^{-1} (νC–O of carboxylate, COO^-), and 1519 cm^{-1} (δN–H of non-hydrogen bonded amide II). Although **7** and **A** form an organic salt compound in $CHCl_3$, the compound never forms a gel because it does not have an intermolecular hydrogen bonding interaction. Furthermore, the IR peaks of the antisymmetric and symmetric stretching vibrations of C–H were observed at 2927 cm^{-1} (ν_{as}C–H) and 2855 cm^{-1} (ν_sC–H) for $CHCl_3$ solution as well as at 2919 cm^{-1} (ν_{as}C–H) and 2850 cm^{-1} (ν_sC–H) for DMCPS gel. Therefore, the organogelation occurs through the formation of an organic salt compound by an acid–base interaction in addition to hydrogen bonding and van der Waals interactions.

Temperature-controlled FT-IR. Further experiments for the elucidation of the organogelation mechanism were conducted

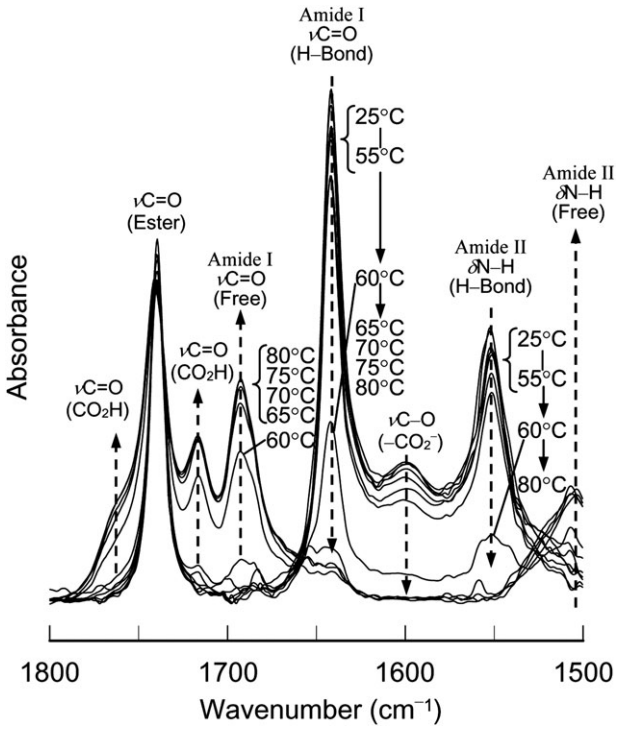
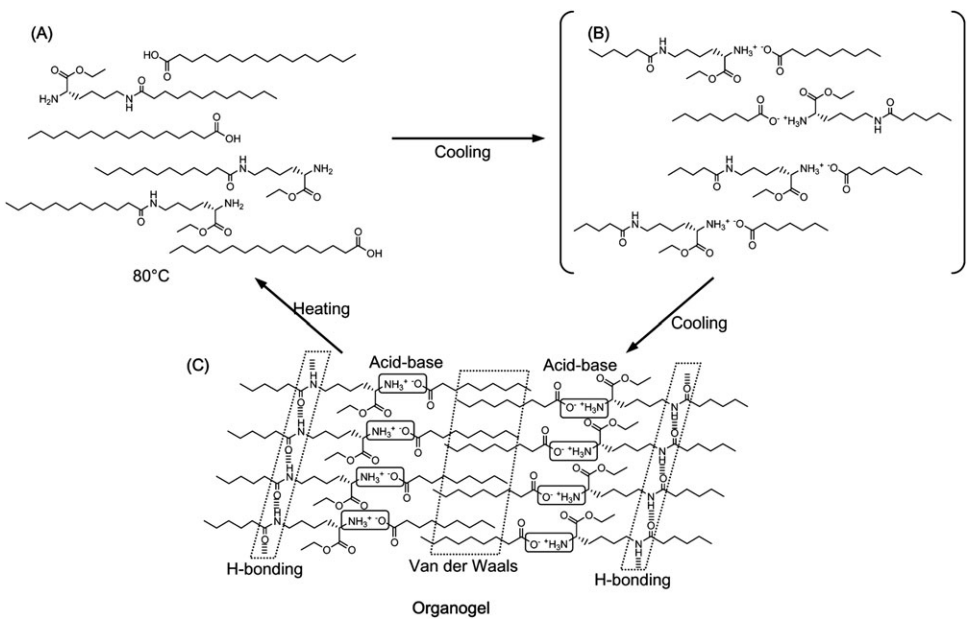


Fig. 5 Temperature-controlled FT-IR spectra of **7** + **A** in DMCPS (10 g L^{-1}).

by the estimation of a gel to sol transition temperature (T_{gel}) and measurement of a temperature-controlled FT-IR spectrum. The T_{gel} value of the DMCPS gel formed by **7** + **A** (10 g L^{-1}) was 56 °C. Fig. 5 shows the FT-IR spectra of **7** + **A** in DMCPS at various temperatures. Although the FT-IR spectra hardly changed in the temperature ranges of 80–60 °C and 55–25 °C, they drastically changed around the T_{gel} (from 60 °C to 55 °C). Just after the dissolution of **7** and **A** at 80 °C into DMCPS, IR peaks arising from both **7** and **A** were observed at 1760 cm^{-1} and 1715 cm^{-1} (–CO_2H) in **7** as well as at 3456 cm^{-1} (νN–H, free amide A), 3400 cm^{-1} (νN–H, free –NH_2), 1693 cm^{-1} (νC═O, free amide I), 1506 cm^{-1} (δN–H, free amide II) in **A**. This fact indicates that the **A** and **7** have no interaction at the high temperature (80–65 °C). With the decreasing temperature (65 °C → 55 °C), the IR peaks of the carboxylic acid, amine and free amide groups disappeared and new peaks were observed at 3327 cm^{-1} (H-bonding amide A), 1641 cm^{-1} (H-bonding amide I), 1553 cm^{-1} (H-bonding amide II) and 1600 cm^{-1} arising from a carboxylate group. Furthermore, the IR peaks of the νC–H shifted from 2915 cm^{-1} (< 60 °C) to 2927 cm^{-1} (> 55 °C) and from 2849 cm^{-1} (< 60 °C) to 2857 cm^{-1} (> 55 °C).[17] Very interestingly, the temperature-controlled FT-IR spectrum of **7A** in DMCPS was identical with those of **7** + **A**. These results indicate that the acid–base interaction (the formation of organic salt) in addition to hydrogen bonding and van der Waals forces plays an important role in the organogelation. Based on the IR results, we propose an organogelation mechanism. When an L-lysine derivative and aliphatic acid are dissolved in an oil by heating, their molecules are dispersed in the hot oil. During the cooling to 25 °C, organic salt compounds are formed through an acid–base interaction, and then they self-assemble into nanofibers through hydrogen bonding and van der Waals interactions, which leads to the formation of an organogel. Similarly, an organic salt organogelator dissolved in a hot oil is decomposed to L-lysine derivative and aliphatic acid. During the cooling process, their molecules form the organic salt compounds again and these then self-assemble into nanofibers.

Organogelation mechanism

The FT-IR results allow us to propose the organogelation mechanism illustrated in Scheme 2. Just after the dissolution of L-lysine ester and aliphatic acid at 80 °C, both components are dispersed and have no interaction (A). During cooling to 25 °C, the organic salt compound is formed through an



Scheme 2 Tentative illustration of organogelation mechanism.

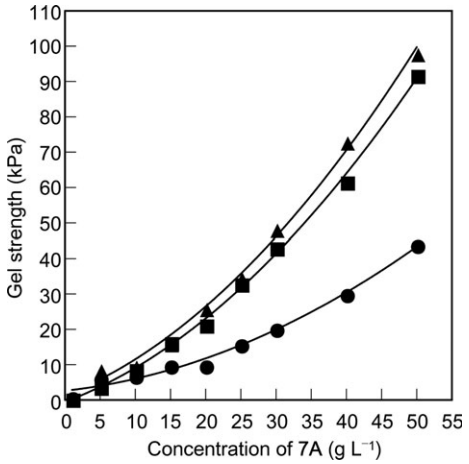


Fig. 6 Strength of organogels based on **7A**: (●) DMCPS gel; (■) paraffin gel; (▲) Si oil-2 gel.

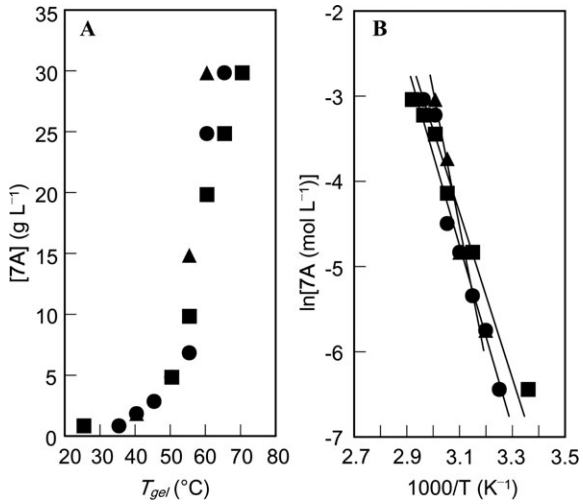


Fig. 7 Plots of concentration of **7A** against T_{gel} (A) and van't Hoff plots (B) for organogels based on **7A**: (●) DMCPS gel; (■) paraffin gel; (▲) Si oil-2 gel.

acid–base interaction (B), and then it self-assembles into nanofibers; these grow into a three-dimensional network through hydrogen bonding and van der Waals interactions (C) , which leads to the formation of an organogel. On the other hand, the mixing of the solutions of L-lysine ester and aliphatic acid at 25 °C induces fast self-assembly into nanofibers, followed by the formation of organic salt. At 25 °C, L-lysine ester has no hydrogen bonding and van der Waals interactions and aliphatic acids disperse in solvents. However, the organic salt compounds undergo hydrogen bonding and van der Waals interactions. Therefore, the acid–base interaction plays a key role in the organogelation.

Gel strength and thermal behavior

Gel strength, which is an important factor in the application of gels, has been evaluated by measuring the elastic storage modulus and loss storage modulus values.[18] In our study, however, gel strength is evaluated as the stress necessary to sink a cylindrical bar (10 mm in diameter) 4 mm deep in the gels. Fig. 6 shows the dependence of gel strengths of DMCPS gel, paraffin gel and Si oil-2 gel of **7A** on the concentration of **7A**. It is clear that gel strength increases with increasing concentration of gelators. The paraffin gel and Si oil-2 gel had almost the same gel strength at various concentrations, while the DMCPS gel was softer than them over 10 g L^{-1}. The strengths of paraffin gel and Si oil-2 gel are more than twice as large as that of DMCPS gel. In the paraffin gel and Si oil-2 gel, **7A** would form a more effective interpenetrated network.

As mentioned above, the formed organogels show thermally reversible gel-to-sol transition because they are physical gels in which the three-dimensional networks are constructed by non-covalent interactions. Fig. 7 shows the plots of the concentration of **7A** against T_{gel} of DMCPS gel, paraffin gel and Si oil-2 gel. The T_{gel} values increased with increasing concentration of **7A**. Over 70 °C, **7A** lost its organogelation ability and could not form an organogel even at 70 g L^{-1}. This is the reason why **7A** cannot maintain its organic salt structure over 70 °C and dissociates to **7** and **A**. Therefore, the increase in temperature promotes the dissociation of organic salt compound to carboxylic acid and amine, leading to the increase in MGC. As listed in Table 2, the Si oil-2 gel showed the lowest T_{gel} value and most thermal stability.

Table 2 Physical parameters for organogels based on **7A**

	DMCPS	Paraffin	Si oil-2
Gel strength (kPa)[a]	6.8	8.7	9.7
T_{gel} (°C)[a]	56	57	53
ΔH_{gel} (kJ mol^{-1})	99.5	100.6	118.8

[a] [**7A**] = 10 g L^{-1}.

The thermodynamic analysis for the gel-to-sol transition was carried out using a van't Hoff relationship.[19] From the relationship between T_{gel} and MGC, the gel-to-sol transition enthalpy (ΔH_{gel}) was determined from the slope of ln[**7A**] *versus* $(T_{gel})^{-1}$ (Fig. 7B). For these organogels, the plots gave a linear relationship. The Si oil-2 gel had the highest ΔH_{gel} value.

Conclusions

In summary, we have revealed novel organogelation systems using the formation of organic salt compounds of an L-lysine derivative and aliphatic acids. The L-lysine derivative and commercially available aliphatic acids formed an organic salt compound in solvents. These organic salt organogelators have good organogelation abilities for oils; especially, they can form an organogel in cyclic siloxanes, silicon oils, paraffin and squalane below 0.1 wt%. The FT-IR studies imply that the organogelation takes place through an acid–base interaction in addition to hydrogen bonding and van der Waals interactions. Furthermore, organic salt gelators form a thermally stable gel and relatively rigid gel.

Experimental

Materials

N^{ε}-Lauroyl-L-lysine was obtained from the Ajinomoto Co., Inc. N^{ε}-Lauroyl-L-lysine ethyl ester and dodecyl ester were

prepared according to the literature.[1] 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.

Syntheses: typical synthesis

All two-component organogelators were prepared according to a synthetically simple procedure. N^{ε}-Lauroyl-L-lysine alkyl ester (10 mmol) and aliphatic acid (10 mmol) were dissolved in methanol (50 mL) by heating, and then the reaction mixture was stirred at room temperature for 15 min. The resulting solution was evaporated to dryness. The product was obtained by recrystallization from methanol–ether.

$C_2AmiNH_3O_2CC_7$ (1A). 99%. IR (KBr): 3311, 1738, 1645, 1590, 1543 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 7.1 Hz, 6H), 1.25–1.30 (m, 27H; alkyl), 1.40–1.46 (m, 2H), 1.50–1.55 (m, 2H), 1.58–1.81 (m, 6H), 2.15 (t, J = 7.3 Hz, 2H), 2.31 (t, J = 7.3 Hz, 2H), 3.25 (q, J = 6.3 Hz, 2H), 3.45–3.48 (m, 1H), 4.18 (q, J = 7.3 Hz, 2H), 4.37 (br, 3H), 5.62 (br, 1H). Elemental anal. Calcd. for $C_{28}H_{56}N_2O_5$ (500.75): C, 67.16; H, 11.27; N, 5.59. Found: C, 67.33; H, 11.56; N, 5.60%.

$C_2AmiNH_3O_2CC_8$ (2A). 99%. IR (KBr): 3312, 1740, 1645, 1592, 1543 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 6.8 Hz, 6H), 1.26–1.30 (m, 29H; alkyl), 1.40–1.49 (m, 2H), 1.51–1.57 (m, 2H), 1.59–1.82 (m, 6H), 2.16 (t, J = 7.3 Hz, 2H), 2.30 (t, J = 7.6 Hz, 2H), 3.25 (q, J = 6.1 Hz, 2H), 3.46–3.49 (m, 1H), 4.18 (q, J = 7.3 Hz, 2H), 4.86 (br, 3H), 5.68 (br, 1H). Elemental anal. Calcd. for $C_{29}H_{58}N_2O_5$ (514.78): C, 67.66; H, 11.36; N, 5.44. Found: C, 67.78; H, 11.51; N, 5.46%.

$C_2AmiNH_3O_2CC_{11}$ (3A). 99%. IR (KBr): 3305, 1745, 1645, 1594, 1543 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 7.1 Hz, 6H), 1.25–1.38 (m, 35H; alkyl), 1.40–1.46 (m, 2H), 1.51–1.55 (m, 2H), 1.57–1.80 (m, 6H), 2.15 (t, J = 7.8 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 3.25 (q, J = 6.0 Hz, 2H), 3.44–3.47 (m, 1H), 3.97 (br, 3H), 4.18 (q, J = 7.3 Hz, 2H), 5.59 (br, 1H). Elemental anal. Calcd. for $C_{32}H_{64}N_2O_5$ (556.86): C, 69.02; H, 11.58; N, 5.03. Found: C, 69.74; H, 11.89; N, 5.04%.

$C_2AmiNH_3O_2CC_{12}$ (4A). 99%. IR (KBr): 3312, 1744, 1644, 1595, 1543 cm^{-1}. ^{1}H–NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 6.6 Hz, 6H), 1.26–1.28 (m, 37H; alkyl), 1.40–1.46 (m, 2H), 1.49–1.58 (m, 2H), 1.59–1.82 (m, 6H), 2.16 (t, J = 7.6 Hz, 2H), 2.30 (t, J = 7.3 Hz, 2H), 3.25 (q, J = 6.1 Hz, 2H), 3.46–3.50 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.89 (br, 3H), 5.67 (br, 1H). Elemental anal. Calcd. for $C_{33}H_{66}N_2O_5$ (570.89): C, 69.43; H, 11.65; N, 4.91. Found: C, 69.64; H, 11.73; N, 4.91%.

$C_2AmiNH_3O_2CC_{13}$ (5A). 99%. IR (KBr): 3317, 1744, 1644, 1595, 1542 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 6.6 Hz, 6H), 1.26–1.29 (m, 39H; alkyl), 1.40–1.46 (m, 2H), 1.51–1.53 (m, 2H), 1.55–1.82 (m, 6H), 2.16 (t, J = 7.6 Hz, 2H), 2.31 (t, J = 7.6 Hz, 2H), 3.25 (q, J = 6.3 Hz, 2H), 3.46–3.49 (m, 1H), 4.18 (q, J = 7.0 Hz, 2H), 4.60 (br, 3H), 5.67 (br, 1H). Elemental anal. Calcd. for $C_{34}H_{68}N_2O_5$ (584.91): C, 69.82; H, 11.72; N, 4.79. Found: C, 70.00; H, 11.88; N, 4.81%.

$C_2AmiNH_3O_2CC_{14}$ (6A). 99%. IR (KBr): 3320, 1748, 1644, 1595, 1540 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 6.6 Hz, 6H), 1.25–1.32 (m, 41H; alkyl), 1.40–1.45 (m, 2H), 1.49–1.56 (m, 2H), 1.53–1.82 (m, 6H), 2.16 (t, J = 7.6 Hz, 2H), 2.30 (t, J = 7.6 Hz, 2H), 3.25 (q, J = 6.3 Hz, 2H), 3.46–3.49 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.52 (br, 3H), 5.67 (br, 1H). Elemental anal. Calcd. for $C_{35}H_{70}N_2O_5$ (598.94): C, 70.19; H, 11.78; N, 4.68. Found: C, 70.33; H, 11.99; N, 4.69%.

$C_2AmiNH_3O_2CC_{15}$ (7A). 99%. IR (KBr): 3323, 1751, 1644, 1598, 1536 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 6.6 Hz, 6H), 1.25–1.30 (m, 43H; alkyl), 1.40–1.45 (m, 2H), 1.49–1.55 (m, 2H), 1.57–1.80 (m, 6H), 2.16 (t, J = 7.6 Hz, 2H), 2.29 (t, J = 7.6 Hz, 2H), 3.25 (q, J = 6.1 Hz, 2H), 3.47–3.50 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 5.00 (br, 3H), 5.75 (br, 1H). Elemental anal. Calcd. for $C_{36}H_{72}N_2O_5$ (612.97): C, 70.54; H, 11.84; N, 4.57. Found: C, 70.54; H, 11.99; N, 4.58%.

$C_2AmiNH_3O_2CC_{17}$ (8A). 99%. IR (KBr): 3316, 1748, 1643, 1596, 1542 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.88 (t, J = 6.6 Hz, 6H), 1.25–1.29 (m, 47H; alkyl), 1.39–1.46 (m, 2H), 1.49–1.55 (m, 2H), 1.57–1.81 (m, 6H), 2.15 (t, J = 7.6 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 3.25 (q, J = 6.0 Hz, 2H), 3.43–3.46 (m, 1H), 3.64 (br, 3H), 4.18 (q, J = 7.1 Hz, 2H), 5.57 (br, 1H). Elemental anal. Calcd. for $C_{38}H_{76}N_2O_5$ (641.02): C, 71.20; H, 11.95; N, 4.37. Found: C, 71.57; H, 12.21; N, 4.38%.

Instrumentation and techniques

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 transmission electron microscope (TEM) images were obtained using a JEOL JEM-2010 electron microscope at 200 kV. The field emission scanning electron microscope (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. The circular dichroism spectra were measured using a JASCO Circular Dichroism J-600 spectrometer. The gel strengths of the hydrogels were measured using a Sun Science Sun Rheo Meter CR-500DX.

Gelation test. The formation of an organogel was evaluated by the tube inversion method.

Procedure 1 in two-component systems. Weighed L-lysine derivative and aliphatic acid (mol/mol) in an organic solvent (1 mL) in a sealed test tube was heated at 80 °C until a clear solution appeared, and then the sample was allowed to stand at 25 °C for 2 h.

Procedure 2 in two-component systems. Two solutions of **A** and aliphatic acid (equivalent molar) were mixed in a vial (15 mm in diameter) with vigorous stirring at 25 °C, and then the capped vial was allowed to stand at 25 °C for 2 h.

Two-component organogelators. A weighed two-component organogelator in an organic solvent (1 mL) in a sealed test tube was heated at 80 °C until a clear solution appeared, and then the test tube was allowed to stand at 25 °C for 2 h.

Transmission electron microscope (TEM). Samples were prepared as follows: the organogels were added to hexane with vigorous stirring, and the white precipitate was filtered,

washed with hexane, and then dried in vacuum for 24 h. The white precipitate was dispersed into hexane, and the hexane dispersion was dropped on a collodion and carbon coated 400 mesh copper grid and dried in vacuum for 12 h. After negative staining by osmic acid overnight, the grids were dried under reduced pressure for 2 h.

FT-IR study. The FT-IR spectroscopy was performed using a spectroscopy cell with a CaF_2 window and 50 μm spacers operating at a 2 cm^{-1} resolution with 32 scans. The temperature-controlled FT-IR spectra were measured using 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.

CD study. The CD spectra were measured in DMCPS gel and MeOH solution of **7** + **A** (10 mg mL^{-1}) at 25 °C.

Gel strength. Samples were prepared as follows: a mixture of a weighed gelator in solvent (2 mL) in a sealed sample tube (15 mm in diameter) was heated until a clear solution appeared. The resulting 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.

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