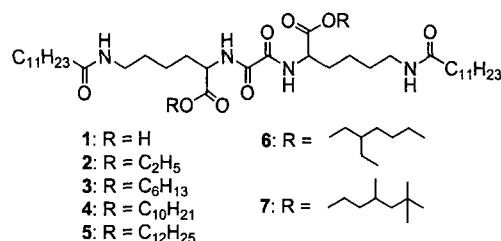


Self-Assembly of L-Lysine Derivatives into Nanofibers and Formation of Gels

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ABSTRACT

New gemini organogelators linked by an oxalyl amide that can be easily, effectively, and cheaply synthesized have good organogelation abilities and their cyclohexane gels have superior thermal stabilities; especially **7** possessing the branched alkyl ester can gel at 0.7 wt% cyclohexane even at 70 °C.



INTRODUCTION

A number of low-molecular-weight organic compounds have been found to be organogelators that can gel various organic solvents at relatively small concentrations. Most organogels consist of long nanofibers that are self-assembled as a result of the usual array of noncovalent forces such as hydrogen bonding, van der Waals, π -stacking, electrostatic, and charge-transfer interactions. Noncovalent cross-links among the nanofibers and/or mechanical entanglements create a three-dimensional network. Solvent is entrapped within the interstices, therefore leading to gelation.

Organogelators have received much attention not only for organogelation but also for the formation of superstructures in solvents and organogels. Many organogelators have been used as organic templates for designing inorganic materials, and used for sensors, molecular recognition as well as in industrial fields such as cosmetics, health care, textile, paper, foods, and oil. For these applications, the development of organogelators that can be cheaply, simply, and effectively synthesized is important. We now describe the easy and effective synthesis of new gemini organogelators and their organogelation properties.

Results and Discussion

Compounds **1-7** were easily and effectively synthesized from commercially available N^ε-

Table 1 Gelation Properties of **1-7** in organic solvents^a

	1	2	3	4	5	6	7
c-C ₆ H ₁₂	PG	I	4	25	6	10	4
MeOH	45	28	20	P	S	25	20
EtOH	PG	25	20	PG	S	25	40
1-PrOH	PG	26	30	PG	S	25	40
1-BuOH	S	20	20	PG	S	30	S
AcOEt	15	25	25	35	PG	50	35
Acetone	18	50	40	PG	I	35	30
c-Hexanone	35	30	30	40	PG	PG	40
Dioxane	18	20	20	45	40	30	30
Ph-H	35	20	8	35	45	25	12
Ph-CH ₃	35	12	8	25	30	20	18
Ph-Cl	12	12	8	30	45	20	20
Ph-NO ₂	38	PG	15	26	35	40	10
DMF	30	28	30	PG	S	30	35
DMSO	15	S	15	PG	S	20	10
CHCl ₃	8	S	S	S	S	S	S
CCl ₄	25	15	6	15	PG	25	40
CH ₃ CN	I	30	25	P	I	25	22

^aValues denote minimum gel concentration (MGC) necessary for gelation (mg/ml). I: almost insoluble; PG: partial gel; S: solution at 5 wt%; P: precipitate

lauroyl-L-lysine (Ajinomoto Co., Ltd.) according to a synthetically simple procedure: the one-step acylation for **1** and two-step esterification and acylation for **2-7**.

The organogelation abilities of **1-7** are listed in Table 1. **1**, the dicarboxylic acid type, can gel many organic solvents; particularly it is noteworthy that it can gel CHCl₃ generally acting as a cosolvent. The diester types **2-7** also function as good organogelators. Among **2-5** having linear alkyl ester groups, **3**, possessing a hexyl ester group, had the best

gelation ability. With the increasing alkyl chain length, the organogelation ability decreased due to enhancement of their solvophilicity. In contrast, the organogelation abilities of **6** and **7** possessing the branched alkyl ester groups compared to **2** were higher than those of **3** and **4**.

TEM pictures reveal that the gels consist of a three-dimensional network structure formed by entanglement of the self-assembled nanofibers with a diameter of 20 – 40 nm. Therefore, the organogels are formed by entrapping the solvent molecules in the spaces of the three-dimensional networks.

To help understand the organogelation mechanism, we measured the FT-IR and ¹H-NMR spectra of **2** in chloroform and CCl₄. In the ¹H-NMR spectra, the chemical shift of N^ε-H in CDCl₃ shifts down field with the addition of CCl₄ (5.61→5.84 ppm), indicating the presence of the intermolecular hydrogen bonding. In contrast, the chemical shift of N^α-H only slightly changes (7.81→7.84ppm). Considering that the chemical shift of the non-interacted N^α-H appears at ca. 6.8 ppm, the N^ε-H of these oxalyl amide derivatives have some interactions, probably intramolecular hydrogen bonding between N^ε-H and C=O of the oxalyl group due to no concentration effect of the chemical shift. Further information was obtained from the FT-IR spectra. In CHCl₃, the absorption bands arising from the non-interacted amide groups appeared at 3450 cm⁻¹ and 1682 cm⁻¹, characteristic of the N-H stretching vibration (νN^ε-H) and amide I (νC=O), respectively. In addition, the absorption band arising from the amide (νN^α-H) undergoing intramolecular hydrogen bonding was observed at 3387 cm⁻¹, which supported the ¹H-NMR results. In CCl₄ gel, the absorption bands appeared at 3321 cm⁻¹ and 3268 cm⁻¹ (νN-H) and 1661 cm⁻¹ and 1640 cm⁻¹ (νC=O), indicating that both amide groups interact with each other through intermolecular hydrogen bonding, therefore, leading to their self-assembling into nanofibers.

The main characteristic of organogels is their thermo-reversible gel-to-sol transition. However, we found that the cyclohexane gels

formed by **4**, **6**, or **7** had good thermal stabilities. The MGC values for the cyclohexane gels of **3** and **5** hardly changed up to 50 °C, and then sharply increased. Very interestingly, the MGC values for **4**, **6**, and **7** do not depend on temperature up to 70 °C. Compared with **3-5** at 70°C, the MGC values decrease with the increasing alkyl chain length in the ester group due to enhancement of the van der Waals interaction. In contrast, **6** and **7**, possessing the branched alkyl esters, have a superior thermal stability to the linear alkyl ester derivatives **3-5**; especially **7** can gel cyclohexane even at 70 °C at 0.7 wt%. These results may be explained by solubilities of these gelators in cyclohexane. **6** and **7** are difficult to be dissolved in cyclohexane compared with **3-5**. In addition, the dissolution of **4** in cyclohexane needs higher temperature than **3** and **5**. This fact indicates that **6** and **7** possessing the branched alkyl esters as well as **4** have stronger intermolecular interactions than **3** and **5**, which leads to the high thermal stabilities of their cyclohexane gels.

In summary, we revealed the easy and effective synthesis of new gemini organogelators linked by an oxalyl amide and their organogelation abilities. These compounds function as good organogelators that can gel many organic solvents. **3-7** form thermally stable cyclohexane gels; especially **6** and **7** possessing the branched alkyl ester groups have superior thermal stabilities. Considering the cheap availability of the branched alcohols (2-ethyl-1-hexanol and 3,3,5-trimethyl-1-hexanol) and their organogelation properties, **6** and **7** are excellent organogelators. Detailed studies of the role of the ester groups on organogelation are now in progress.

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