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Organogelation by Polymer Organogelators with a L-Lysine Derivative: Formation of a Three-Dimensional Network Consisting of Supramolecular and Conventional Polymers

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Abstract: Polymer compounds consisting of a L-lysine derivative and conventional polymers, such as poly(ethylene glycol), polycarbonate, polyesters, and poly(alkylene), have been synthesized and their organogelation properties examined in various solvents. These polymer compounds function as good organogelators that form organogels in many organic solvents and oils. The organogelation ability is almost independent of the polymer backbone. Observation by field-emission scanning electron microscopy (FE-SEM) demonstrates that the polymer organogelators form a supramolecular polymer with a diameter of several tens of nanometers and create a three-dimensional network in organogels. FT-IR spectroscopic analysis shows that the supramolecular polymer is mainly formed by the self-assembly of L-lysine segments through hydrogen-bonding and van der Waals interactions. Furthermore, the organogels formed by the polymer organogelators have a lower gel–sol temperature and higher gel strength than those of a low-molecular-weight model organogelator.

Keywords: hydrogen bonding · lysine · organogels · polymer organogelators · supramolecular chemistry

Introduction

Supramolecular organogels, which are gels of organic solvents and oils made by low-molecular-weight compounds (hereafter denoted as organogelators), have attracted much interest because of their unique properties and potential applications as new soft materials.[1–8] Indeed, the organogels and organogelators have been used, for example, as organic templates for the fabrication of mesoporous polymer materials[9] and nanoscale designed inorganic materials.[10–13] Furthermore, they have been applied as liquid crystals[14–16] and in photochemistry[17–21] and electrochemistry.[22–24] In addition, gelators have been developed not only as an academic interests but also for industrial fields, such as cosmetics, health care, textiles, foods, and oil technology.[1–8] A supramolecular gel is formed by entrapping solvents into a three-dimensional network created by the entanglement of noncovalently self-assembled nanofibers, so-called supramolecular polymers. Although conventional polymers (macromolecules) have a polymeric unit that the covalent bonds hold together, the monomeric units, supramolecular polymers consist of arrays of the monomer units linked through noncovalent bonds, such as hydrogen-bonding, van der Waals, π-stacking, electrostatic, and coordination interactions (Scheme 1). The supramolecular polymers (or gels) simply and reversibly transfer to monomers by external stimuli, such as temperature, pH value, ionic strength, light, and electricity. The supramolecular polymers or gels are expected to act as new soft materials that are an alternative to conventional polymers. Although many conventional polymers that form hydrogels have been reported[25,26] most vinyl polymers do not form an organogel in organic solvents and oils. One of the reasons for this behavior is that it is difficult for common vinyl polymers to construct a three-dimensional network in organic solvents because these polymers do not have suitable cross-linking points. Although the organogelation using some synthetic polymers, such as polypeptides,[27–30] polyesters,[31] and others,[32–38] has been reported, there are only a limited number of polymer organogelators, and the organogelation abilities are lower relative to low-molecular-weight organogelators. Recently, we proposed a novel strategy for the design of a polymer organogelator

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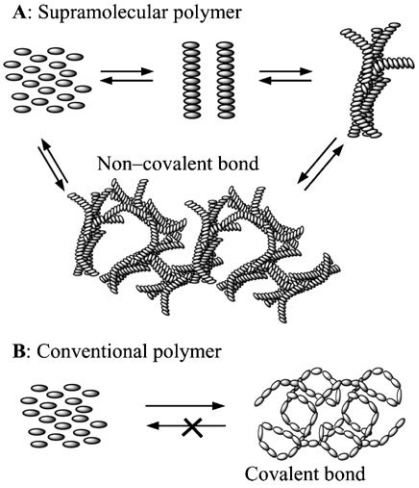


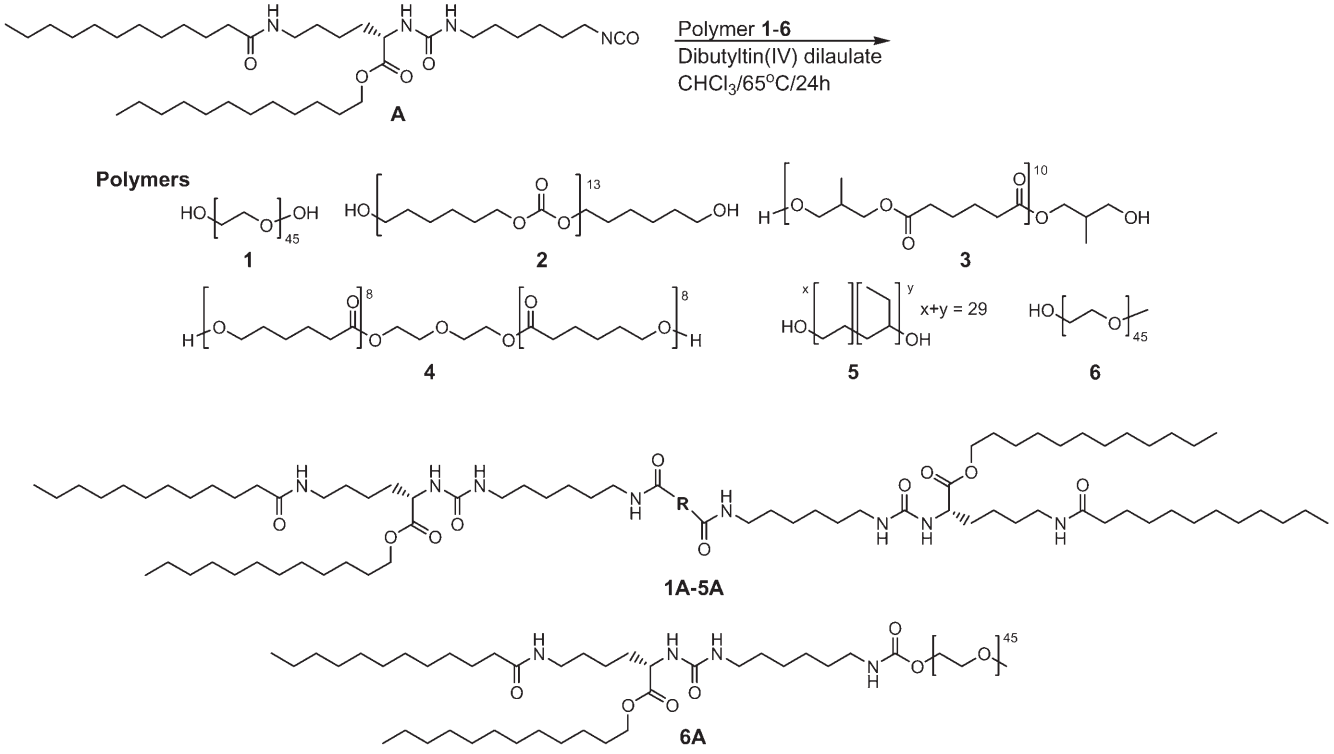
Scheme 1. Formation of supramolecular and conventional polymers.

that is a combination of low-molecular-weight organogelators and conventional polymers.[39–41] The low-molecular-weight gelator introduced into a conventional polymer functions as a gelation-causing segment and forms the supramolecular polymer, thus resulting in the formation of an organogel. Herein, we describe the synthesis of new polymer organogelators that consist of commercially available polycarbonate, polyesters, and poly(ethylene glycol) polymers as the polymer backbone and L-lysine derivatives as the gelator segment and their gelation properties in organic solvents and oils.

Results and Discussion

Synthesis: Polymer organogelators **1A–6A** were prepared from reactive low-molecular-weight gelator **A**, which has an isocyanate group at the terminal position, and diol prepolymers (**1**–**5**) or monool prepoylmer **6** in CH_3Cl in the presence of a tin catalyst (Scheme 2). The reaction period was confirmed by FT-IR spectroscopic analysis (the band of the isocyanate group at 2620 cm^{-1} disappeared). The final products were identified by FT-IR and ^1H NMR spectroscopic analysis, and no OH group remained. Compounds **2A** and **3A** were a semisolid (paste) at room temperature and the other polymer organogelators were obtained as white solids. This is because **2** and **3**, diol-terminated poly(hexamethylene carbonate) and poly(2-methyl-1,3-propylene adipate), are paste and liquid, respectively, whereas the other prepolymers are solid.

Solubility and organogelation properties: The solubility of the prepolymers **1**–**6** was first tested in many organic solvents and oils. Except for **5**, all the prepolymers had almost the same solubility in organic solvents and oils: they were soluble in esters, ketones, cyclic ethers, aromatic solvents, polar solvents, and glycols, but not in oils. In contrast, **5** was soluble in oils, hexane, and cyclohexane and insoluble in gly-



Scheme 2. Synthesis of **1A–6A**.

cols, ethyl acetate, acetone, and dioxane. The long alkyl chain of **5** should be miscible with oils and immiscible with glycols. On the other hand, **A** was soluble in all the solvents listed in Table 1, except for hexane. Interestingly, polymer compounds **1A**–**4A** and **6A** dissolved in many oils, although their prepolymers were insoluble. Polymer **5A** dissolved in glycols and ethyl acetate. This behavior indicates that the solubility of **1A**–**6A** is mainly dominated by that of the L-lysine segment, that is, the solubility of the prepolymers in organic fluids is increased by the introduction of L-lysine segments. In addition, these prepolymers and polymer organogelators were soluble in $CHCl_3$, which was one of the reasons for its use as a solvent in the syntheses.

The results of the organogelation test at 25 °C of **A** and polymer organogelators **1A**–**6A** are also given in Table 1, in which the values denote the real minimum gel concentration (rMGC; units = $g L^{-1}$) necessary for organogelation and those values in parentheses are the apparent MGC (aMGC; units = $g L^{-1}$) normalized by the concentration of the L-lysine segment.[14] As mentioned above, **A** and **1A**–**6A** showed good solubility in $CHCl_3$, and they had absolutely no organogelation ability. The low-molecular-weight organogelator **A** acted as a good low-molecular-weight organogelator that formed an organogel in many solvents, such as alkanes, aromatic solvents, cyclic ethers, polyglycols, and oils. The polymer organogelators **1A**–**5A** formed an organogel in various organic solvents and oils, such as esters, ketones, cyclic ethers, aromatic solvents, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), propylene carbonate, γ-butyrolactone, sulfolane, glycols, polyglycols, mineral oils, and vegetable oils. Polymers **1A**–**5A** had similar organogelation properties regardless of the different polymer backbones, although they showed slightly different organogelation behavior for some solvents, for example, **2A** formed an organogel in alcohols, but not other polymer organogelators, and **2A** and **3A** are not able to gel toluene and chloroben-

Table 1. Solubility[a] and organogelation properties[b] of prepolymers **1**–**6**, low-molecular-weight organogelator **A**, and polymer organogelators **1A**–**6A** at 25 °C.

	1	**2**	**3**	**4**	**5**	**6**	**A**	**1A**	**2A**	**3A**	**4A**	**5A**	**6A**
n-hexane	ins	ins	ins	ins	S	ins	ins	ins	ins	ins	ins	PG	ins
n-dodecane	S	S	ins	S	ins	S	30	30(12)	–	–	40(16)	30(11)	60(15)
c-hexane	ins	ins	ins	ins	S	ins	5	15(6)	10(4)	ins	ins	–	ins
MeOH	ins	ins	ins	ins	ins	ins	P	P	25(10)	P	P	ins	–
EtOH	ins	ins	ins	ins	ins	ins	P	P	35(14)	P	P	ins	–
AcOEt	S	S	S	S	ins	S	P	30(12)	40(16)	–	40(16)	40(14)	–
acetone	S	S	S	S	ins	S	P	30(12)	20(8)	20(8)	30(12)	ins	–
c-hexanone	S	S	S	S	S	S	30	15(6)	40(16)	40(16)	15(6)	–	40(10)
THF	S	S	S	S	S	S	–	PG	40(16)	30(12)	50(20)	40(14)	–
1,4-dioxane	S	S	S	S	ins	S	15	20(8)	15(6)	30(12)	20(8)	–	30(7.5)
$PhCH_3$	S	S	S	S	S	S	15	20(8)	–	–	40(16)	30(11)	–
PhCl	S	S	S	S	S	S	15	10(4)	–	–	40(16)	40(14)	–
$PhNO_2$	S	S	S	S	S	S	15	15(6)	15(6)	15(6)	15(6)	15(5.3)	20(5)
DMF	S	S	S	S	S	S	P	P	60(24)	50(20)	70(28)	ins	60(15)
DMSO	S	S	S	S	S	S	30	15(6)	15(6)	30(12)	20(8)	40(14)	–
$CHCl_3$	S	S	S	S	S	S	–	–	–	–	–	–	–
CH_3CN	ins	ins	ins	ins	ins	ins	P	P	ins	30(12)	20(8)	ins	ins
PC	ins	ins	S	S	ins	ins	15	20(8)	10(4)	30(12)	30(12)	40(14)	25(6.3)
γ-BL	S	S	S	S	S	S	20	20(8)	35(14)	30(12)	30(12)	40(14)	20(5)
sulfolane	S	S	S	S	ins	S	20	20(8)	10(4)	20(8)	10(4)	15(5.3)	40(10)
oleic acid	ins	ins	ins	S	S	ins	7	10(4)	40(16)	15(6)	10(4)	30(11)	30(7.5)
linoleic acid	ins	ins	ins	S	S	ins	15	10(4)	20(8)	30(12)	20(8)	40(14)	30(7.5)
salad oil	ins	ins	ins	ins	S	ins	30	–	35(14)	15(6)	15(6)	15(5.3)	–
silicone oil	ins	ins	ins	ins	ins	ins	–	20(8)	40(16)	40(16)	15(6)	5(1.8)	20(5)
linseed oil	ins	ins	ins	ins	S	ins	15	30(12)	30(12)	30(12)	15(6)	20(7)	–
IPM	ins	ins	ins	ins	S	ins	30	40(16)	40(16)	30(12)	40(16)	15(5.3)	–
triolein	ins	ins	ins	ins	S	ins	15	20(8)	20(8)	15(6)	10(4)	30(11)	–
kerosene	ins	ins	ins	ins	S	ins	10	50(20)	40(16)	10(4)	20(8)	10(3.5)	60(15)
diesel oil	ins	ins	ins	ins	ins	ins	20	70(28)	60(24)	50(20)	40(16)	15(5.3)	60(15)
TEG	S	S	S	S	ins	S	30	20(8)	15(6)	15(6)	5(2)	8(3)	20(5)
PEG 200	S	S	S	S	ins	S	15	20(8)	15(6)	15(6)	10(4)	15(6)	20(5)
PEG 400	S	S	S	S	ins	S	25	20(8)	10(6)	10(4)	10(4)	4(1.4)	20(5)
MePEG 350	S	S	S	S	ins	S	40	20(8)	15(6)	15(6)	5(2)	10(3.5)	20(5)
MePEG 550	S	S	S	S	ins	S	20	20(8)	15(6)	10(4)	4(1.6)	5(1.8)	20(5)
PG 700	S	S	S	S	ins	S	20	20(8)	10(4)	15(6)	10(4)	15(5.5)	20(5)
PPG 1000	S	S	S	S	ins	S	30	20(8)	10(4)	15(6)	10(4)	10(3.5)	20(5)

[a] Solubility test for prepolymers was carried out at 20 $g L^{-1}$. [b] Values denote the real minimum gel concentration (rMGC, $g L^{-1}$) necessary for organogelation and those in parentheses denote apparent MGC (aMGC): aMGC = rMGC × (molecular weight of L-lysine segment)/(molecular weight of polymer organogelators) and aMGC = rMGC for **A**. PC: propylene carbonate, γ-BL: γ-butyrolactone, IPM: isopropyl myristate, TEG: tetraethylene glycol, PEG: poly(ethylene glycol), MePEG: poly(ethylene glycol) monomethyl ether, PPG: poly(propylene glycol); ins: insoluble, S: solution, P: precipitate, PG: partial gel at 50 $g L^{-1}$, –: solution at 50 $g L^{-1}$.

zene, but **1A**, **4A**, and **5A** formed these organogels. In contrast, **6A** showed the lowest organogelation ability of the systems tested, and it did not have the organogelation ability for ethyl acetate, acetone, toluene, chlorobenzene, DMSO, salad oil, linseed oil, IPM, and triolein. Because **6A** has only one L-lysine segment, its lipophilic–lipophobic balance may make it unsuitable.

Very interestingly, the organogelation depended on the properties of the prepolymers and **A** in organic fluids, and a combination of the low-molecular-weight organogelator with conventional prepolymers produced some new functions. For example, in alcohols, **A** precipitates after dissolution by heating, which indicates that **A** undergoes strong intermolecular interactions, and the introduction of **A** into the alcohol-insoluble prepolymers **1**–**6** causes organogelation for **2A**; precipitation for **1A**, **3A**, and **4A**; insolubility for **5A**; and solution for **6A**. The solubility of **1A**–**4A** and **6A** tends to be dominated by **A**, and the insolubility of **5A** is induced by the prepolymer **5**. For **2A**, however, the solubility is affected by **A** and a combination of **2** and **A** provides a suitable lipophilic–lipophobic balance, thus leading to organogelation. Similar behavior is observed in oils and glycols. Such a suitable combination of **A** and prepolymers is observed for many organic fluids, especially, oils and glycols.

Furthermore, the organogelation abilities of the polymer organogelators were improved relative to **A**. Although the real MGC values of **1A**–**5A** were similar to or greater than those of **A**, their apparent MGC values were smaller. Polymers **1A**–**5A** can form an organogel in ethyl acetate, acetone, DMF, and silicone oil, in which **A** cannot gel. The apparent MGC values of **6A** were lower than that of **A**, though the number of solvents with which **6A** can form an organogel is less than that for **A**. In particular, **1A**–**6A** have good organogelation abilities (lower aMGC values) for tetraethylene glycol and polyglycols. As these prepolymers have no organogelation ability for any solvents, the L-lysine segments plays an important role in the organogelation.

Field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM): It is well-known that a low-molecular-weight organogelator creates a three-dimensional network constructed by self-assembled nanofibers of gelator molecules in an organogel.[1–8] We reported that **A** forms self-assembled nanofibers with diameters of several tens of nanometers and three-dimensional network structures.[40] Figure 1 shows the FE-SEM and TEM images of the dried samples prepared from 1,4-dioxane gels based on **1A**–**6A**. The low-magnification FE-SEM images for **1A** and **4A**–**6A** showed the mesostructure in the xerogels, which consisted of microfibers and microsheets. Moreover, the nanoscaled self-assembled nanofibers, which formed with these micrometer-scaled structures and had diameters of several ten of nanometers, were observed by high-magnification FE-SEM studies. The sizes of the nanofibers were independent of the structure of the polymer backbones and were similar to that formed by **A**. Although FE-SEM observations for **2A** and **3A** could not be performed, TEM studies were carried out. These polymer organogelators also created a three-dimensional network formed by entanglement of the supramolecular polymers. FE-SEM observations of dried samples prepared by the same method as that for **1A**–**6A** were carried out to confirm whether the prepolymers form nanostructures in organic solvents. The prepolymers **2** and **3** are semi-solid and liquid, respectively, at room temperature and these nanostructures could not be observed; probably, the interactions between these prepolymers are very weak (or absent). For other prepolymers, the FE-SEM images showed that they never formed a supramolecular polymer in organic solvents (see the Supporting Information). In addition, the polymer organogelators clearly form a microstructure, different from those of the low-molecular-weight organogelators, composed of self-assembled nanofibers. These facts indicate that the L-lysine segments mainly form a supramolecular polymer and that the polymer backbones play an important role in the construction of the microstructures (or organogelation). Therefore, the supramolecular structures are formed by a combination of the supramolecular polymer and the polymer backbone.

FT-IR studies: It is generally well-known that a low-molecular-weight gelator forms a supramolecular polymer (self-assembled nanofiber) in an organogel mainly through hydrogen-bonding and van der Waals interactions, which can be

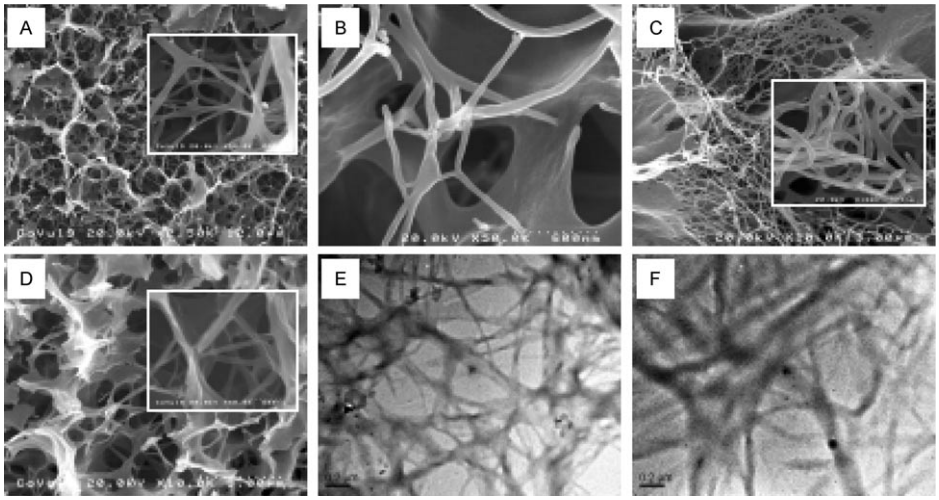


Figure 1. A–D) FE-SEM and E, F) TEM images of dried samples prepared from 1,4-dioxane gels based on **1A**–**6A** at MGC. A: **1A** (20 gL^{-1}); B: **4A** (20 gL^{-1}); C: **5A** (40 gL^{-1}); D: **6A** (30 gL^{-1}); E: **2A** (3 gL^{-1}); F: **3A** (6 gL^{-1}).

analyzed by X-ray studies and NMR, IR, and FT-IR spectroscopy.[1–8] FT-IR spectroscopy is especially sensitive for molecular structural changes and has been used extensively to study organogelation because organogelation can be directly measured in the gel state in addition to in the solid state and solution. In many cases, however, the analysis of the FT-IR spectrum was hampered because of the overlap of some spectra. To analyze the FT-IR spectra in more detail, the FT-IR spectra obtained were resolved by using a curve-fitting program (JASCO FT/IR Plus Series Curve Fitting version 2.00F).

Figure 2 shows the typical FT-IR spectra of **2A**, **4A**, and **5A** in solution with $CHCl_3$ and a CCl_4 gel. The FT-IR spectra demonstrated had broad IR bands corresponding to the polymer organogelators in a solution of $CHCl_3$ and six or seven bands corresponding to the polymer organogelators in the CCl_4 gel (these bands were further resolved into an individual spectrum by using a curve-fitting program): N–H stretching vibration modes (ν(N–H)) of free and hydrogen-bonded urea, urethane, and amide groups; C=O stretching vibration modes (ν(C=O)) of the polymer backbone, the ester moiety in the lysine segment, and free and hydrogen-bonded urethane, amide, and urea groups; the bending vibration modes (δ(N–H)) of free and hydrogen-bonded urethane, amide, and urea groups. In solution with $CHCl_3$, typical IR bands were observed at 3450, around 3350, 1710, 1660, 1560, 1545, and 1520 cm^{-1}, which arose from the non-hydrogen-bonded urea, urethane, and amide groups. In addition, the IR band of the stretching vibration mode of the hydrogen-bonded urethane group was also observed at around 1708 cm^{-1}. It is noteworthy that these polymer organogelators have intermolecular hydrogen-bonding interactions between the urethane groups when in solution with $CHCl_3$. The IR spectra of the polymer organogelators in the CCl_4 gel showed bands at 1684, 1640, 1626, 1568, and 1546 cm^{-1}, which are characteristic of hydrogen-bonded urea, urethane, and amide groups. The IR ν(C=O) bands of the polymer backbones (the carbonate group in **2A** and the ester group in **4A**) and L-lysine segment (ester) appeared at around 1730 cm^{-1} and were independent of their states (i.e., as a gel or in solution); namely, these groups had no intermolecular interactions. On the other hand, the IR spectra in the region of the antisymmetric and symmetric stretching vibrations of C–H showed two bands at 2928 (ν_{as}(C–H)) and 2856 cm^{-1} (ν_s(C–H)) for the CCl_4 gel based on **A**, thus indicating van der Waals interactions between the alkyl groups in the L-lysine derivative. For the CCl_4 gels of the polymer organogelators, two pairs of IR bands appeared at around 2920 (ν_{as}(C–H)), 2848 (ν_s(C–H)), 2930 (ν_{as}(C–H)), and 2857 cm^{-1} (ν_s(C–H)): one band results from the interacting (van der Waals) alkyl groups in the L-lysine segments, the other from the noninteracting alkyl groups in the polymer backbones.

Figure 3 shows the temperature-controlled FT-IR spectra of the DMSO gel based on **3A** and plots of absorbances in the resulting spectra resolved by a curve-fitting program against temperature. In this case, the gel–sol transition temperature T_{gel} of the DMSO gel ([**3A**] = 30 g L^{-1}) is 35 °C. The FT-IR spectra drastically changed over 35 °C, and the gel–sol transition occurred on increasing the temperature (upper in Figure 3); the IR bands arising from hydrogen-bonded urethane, amide, and urea groups decreased and those from the free groups increased. Detailed analysis was performed[41] on the IR spectra resolved by a curve-fitting program. With increasing temperature, the absorbances in each spectrum from the hydrogen-bonded urethane (1680 cm^{-1}), amide (1638 cm^{-1}), and urea (1626 cm^{-1}) groups sharply decreased up to 40 °C, whereas those of the free groups (urethane at 1710 cm^{-1} and amide at 1661 cm^{-1}) increased. In contrast, the IR spectrum of the ester groups only changed slightly: the absorbance decreased minimally up to 35 °C and hardly changed above 35 °C. Such a small change could be induced by exposure to the bulk with supramolecular polymers decomposing into monomers (gel–sol transition). These results indicate that the main driving force for the organogelation, namely, the formation of a supramolecular polymer, is hydrogen bonding and the very weak (or the absence of) interactions within the polymer backbones.

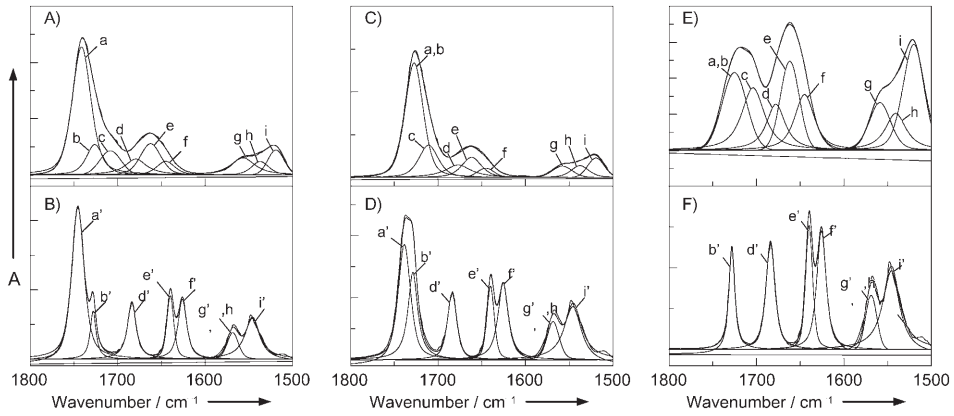


Figure 2. FT-IR spectra of **2A**, **4A**, and **5A** (40 g L^{-1}): A): **2A** in a solution of $CHCl_3$; B): **2A** in a CCl_4 gel; C): **4A** in a solution of $CHCl_3$; D): **2A** in a CCl_4 gel; E): **5A** in a solution of $CHCl_3$; and F): **5A** in a CCl_4 gel. Each spectrum was resolved using a curve-fitting program. a: ν(C=O) (polymer); b: ν(C=O) (ester, lysine); c: ν(C=O) (urethane, free); d: ν(C=O) (urethane, H-bond); e: ν(C=O) (amide **I**, free); f: ν(C=O) (urea, free); g: δ(N–H) (urea, free); h: δ(N–H) (urethane, free, H-bond); i: δ(N–H) (amide **II**, free); a′: ν(C=O) (ester, polymer); b′: ν(C=O) (ester, lysine); d′: ν(C=O) (urethane, H-bond); e′: ν(C=O) (amide **I**, H-bond); f′: ν(C=O) (urea, H-bond); g′, h′: δ(N–H) (urea, urethane, H-bond); i′: δ(N–H) (amide **II**, H-bond).

Thermal stability and gel strength: For these polymer organogelators, although the polymer backbones have hardly any interactions within the organogels, they affect the organogelation properties. The thermal stability and gel strength of the organogels were determined to

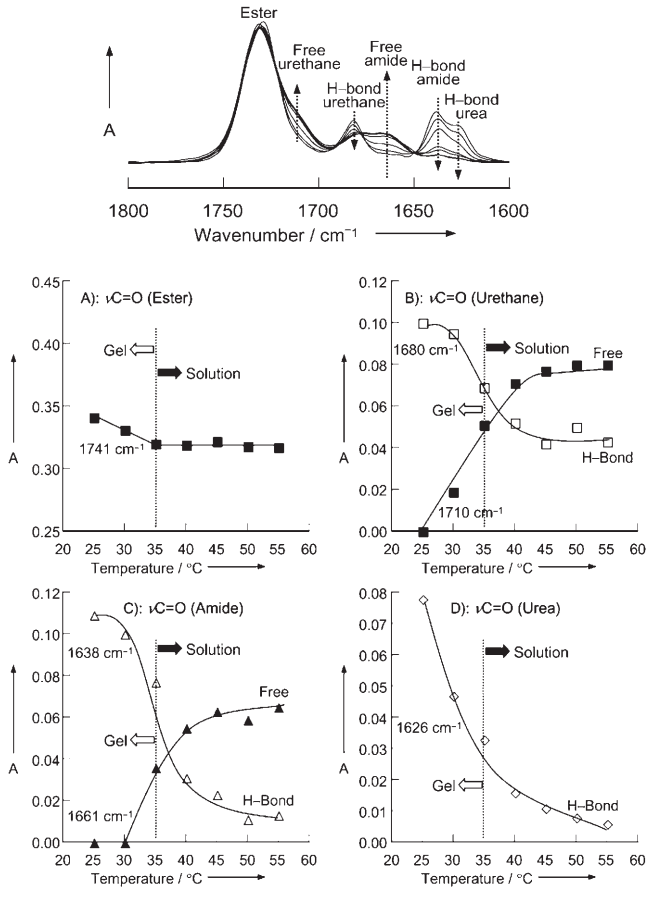


Figure 3. Temperature-controlled FT-IR spectra of **3A** ($30\,g\,L^{-1}$) in DMSO and plots of the absorbances of the spectra (ν(C=O)) resolved by a curve-fitting program against temperature: A) Ester at $1731\,cm^{-1}$; B) free urethane at $1710\,cm^{-1}$ and H-bonded urethane at $1681\,cm^{-1}$; C) free amide at $1664\,cm^{-1}$ and H-bonded urethane at $1638\,cm^{-1}$; D) H-bonded urea at $1626\,cm^{-1}$.

consider the effect of the polymer backbones on organogelation. Table 2 lists the gel-destroyed temperatures (T_{gel}) and gel strengths of the DMSO gels and 1,4-dioxane gels. The DMSO and dioxane gels of **A** have high thermal stabilities and the T_{gel} value is 70 °C at $30\,g\,L^{-1}$. Over 70 °C, however, **A** can not form the gels even at $80\,g\,L^{-1}$. The DMSO and dioxane gels of the polymer organogelators have a slight thermal instability relative to **A**; the dioxane gel of **6A**, in particular, shows a low T_{gel} value. This result indicates that the organogels formed by the polymer organogelators are responsible for the gel–sol transition at the low temperature (low energy). Probably, the large movement of the polymer backbone caused by heating leads to the facile destruction of the gels.

Table 2. T_{gel} values and gel strengths of DMSO gels and 1,4-dioxane gels based on **A** and **1A**–**6A**.[a]

	DMSO gels		1,4-Dioxane gels	
	T_{gel} [°C]	Gel strength [kPa]	T_{gel} [°C]	Gel strength [kPa]
A[b]	70	1.75	70	1.31
1A	60	6.7	60	2.47
2A	60	20.6	50	3.57
3A	50	22.2	60	7.26
4A	60	23.9	50	7.18
5A	50	4.33	–	–
6A	–	–	40	27.3

[a] [L-lysine segment] = $24\,g\,L^{-1}$ at 25 °C. [b] [**A**] = $30\,g\,L^{-1}$.

On the other hand, gel strength, which is an important factor in the wide application of gels, has been evaluated by measuring the elastic storage modulus G' and loss modulus G'' values at different concentrations of gelators.[42] In our study, however, we evaluated gel strength as the power necessary to sink a cylindrical bar (10 mm in diameter) 4 mm deep into the gels.[43] The gel strength of the organogels increased with the increasing concentration of the gelators (see the Supporting Information). This reason is why the polymer organogelators form the more closely packed three-dimensional networks at high concentrations. The gel strength of organogels based on the polymer organogelators is much higher than that of **A** (Table 2). The gel strength, which corresponds to the hardness of the gel, is mainly dominated by the density of the three-dimensional network in the organogels. The three-dimensional network in the organogel of **A** is formed by a supramolecular polymer of **A** molecules, whereas those of the polymer organogelators are composed of supramolecular polymers and polymer backbones. Probably, the polymer backbones help the crosslinking between the supramolecular polymers and play a role in the formation of a closely packed three-dimensional network, which is supported by the fact that the polymer organogelators form an organogel at a lower concentration of the L-amino acid segment than the low-molecular-weight organogelators.

Conclusion

We have shown the organogelation properties of new polymer organogelators composed of commercially available polymers and an L-lysine derivative, and demonstraed the effect of the polymer backbone on the organogelation. The polymer organogelators have good organogelation abilities for many organic solvents and oils. The polymer organogelators construct the mesostructure in the organogels, which consists of microfibers and microsheets. Moreover, the high-magnification FE-SEM observations demonstrate the nanoscaled self-assembled nanofibers with a diameter of several tens of nanometers that are built up of these micrometer-scaled structures. Through detailed FT-IR studies using a curve-fitting program, the supramolecular polymer is found to be mainly formed by the self-assembly of the L-lysine segments through hydrogen bonding of the urea, urethane, and amide groups, and through van der Waals interactions of the alkyl groups in the L-lysine segments, whereas the polymer backbones barely have any interactions. Furthermore, the advantages of the introduction of polymer backbones into a low-molecular-weight organogelator are mainly 1) a high or-

ganogelation ability (low MGC), 2) the formation of more rigid organogels, and 3) a low sol–gel transition temperature (low-energy sol–gel transition).

Experimental Section

Materials: N^{α}-(6-Isocyanatohexylaminocarbonyl)-N^{ε}-lauroyl-L-lysine dodecyl ester was prepared according to a reported procedure.[40] Poly(ethylene glycol) (MW≈2000), poly(hexamethylene carbonate) diol (MW ≈2000), poly(2-methyl-1,3-propylene adipate) diol terminated (MW ≈2000), polycaprolactone diol (MW≈2000), and poly(ethylene-co-1,2-butylene) diol (MW≈2500) were purchased from Aldrich and dried in vacuum at 40 °C for 48 h prior to use. The other chemicals were of the highest commercial grade available and were used without further purification. All the solvents used in the syntheses were purified, dried, or freshly distilled as required.

Synthesis

N^{α}-(6-Isocyanatehexylaminocarbonyl)-N^{ε}-lauroyl-L-lysine dodecyl ester (A): A solution of N^{ε}-lauroyl-L-lysine dodecyl ester (60 mmol) in dry THF (200 mL) was slowly added to a solution of 1,6-hexamethylenediisocyanate (600 mmol) in dry toluene/$CHCl_3$ (500 mL; 1:4) with vigorous stirring. The resulting solution was evaporated to approximately 150 mL and ethyl ether (700 mL) was added with stirring. A white precipitate formed and was filtered, washed with ether, and dried (92%). IR (KBr): $\tilde{\nu}$=3353 (ν(N−H), urea), 3295 (ν(N−H), amide **A**), 2261 (−NCO), 1729 (ν(C=O), ester), 1639 (ν(C=O), amide **I**), 1624 (ν(C=O), urea), 1562 (δ-(N−H), urea), 1549 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, trimethylsilane (TMS)): δ=0.88 (t, J=6.6 Hz, 6H, CH_3), 1.26–1.28 (m, 32H, alkyl), 1.35–1.42 (m, 4H, CH_2CH_3), 1.49–1.65 (m, 10H, $CH_2CH_2CON^{\varepsilon}H$, OCH_2CH_2, CH_2CH_2NCO, $NHCONHCH_2CH_2$, $N^{\varepsilon}HCH_2CH_2$), 1.66–1.88 (m, 2H, $CH_2CHN^{\alpha}H$), 2.16 (t, J=6.8 Hz, 2H, $CH_2CON^{\varepsilon}H$), 3.11–3.27 (m, 4H, $NHCH_2$, $N^{\varepsilon}HCH_2$), 3.29 (t, J=6.6 Hz, 2H, CH_2NCO), 4.11 (t, J=6.6 Hz, 2H, OCH_2), 4.39–4.44 (m, 1H, CH), 4.73 (t, J=5.6 Hz, 1H, NH), 5.22 (d, J=7.8 Hz, 1H, $N^{\varepsilon}H$), 5.74 ppm (t, J=5.6 Hz, 1H, $N^{\alpha}H$); elemental analysis calcd (%) for $C_{38}H_{72}N_4O_5$ (665.00): C 68.63, H 10.91, N 8.43; found: C 68.84, H 10.98, N 8.44.

Typical procedure for the synthesis of the polymer organogelators: Dibutyltin dilaurate (0.2 mmol) was added to a solution of N^{α}-(6-isocyanatohexylaminocarbonyl)-N^{ε}-lauroyl-L-lysine dodecyl ester (20 mmol) and polymer (10 mmol) in $CHCl_3$ (100 mL), and the reaction mixture was heated at 65 °C for 24 h with stirring. The resulting hot solution was filtered and the filtrate evaporated to dryness. The product was purified by reprecipitation of the solution in $CHCl_3$ with diethyl ether.

1A: Yield > 95%; IR(KBr): $\tilde{\nu}$=3357 (ν(N−H), urea), 3325 (ν(N−H), urethane), 3300 (ν(N−H), amide **A**), 1728 (ν(C=O), ester), 1683 (ν(C=O), urethane), 1639 (ν(C=O), amide **I**), 1627 (ν(C=O), urea), 1566 (δ(N−H), urea, urethane), 1546 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ=5.77 (br, 2H), 5.22 (m, 2H), 4.78 (br, 4H), 4.41–4.48 (m, 2H), 4.25–4.32 (m, 4H), 4.06–4.12 (m, 8H), 3.19–3.25 (m, 4H), 3.10–3.15 (m, 8H), 2.15 (t, J=6.8 Hz, 4H), 1.21–1.81 (alkyl), 0.89 ppm (t, J=6.6 Hz, 12H).

2A: Yield > 95%; IR (KBr): $\tilde{\nu}$=3352 (ν(N−H), urea), 3326 (ν(N−H), urethane), 3300 (ν(N−H), amide **A**), 1745 (ν(C=O), carbonate), 1730 (ν-(C=O), ester), 1684 (ν(C=O), urethane), 1640 (ν(C=O), amide **I**), 1626 (ν(C=O), urea), 1567 (δ(N−H), urea, urethane), 1546 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ=5.76 (br, 2H), 5.19 (d, J=7.6 Hz, 2H), 4.75 (br, 4H), 4.41–4.46 (m, 2H), 4.25–4.29 (m, 4H), 4.09–4.13 (m, 8H), 3.21–3.26 (m, 4H), 3.15–3.19 (m, 8H), 2.15 (t, J=6.8 Hz, 4H), 1.21–1.81 (alkyl), 0.88 ppm (t, J=6.6 Hz, 12H).

3A: Yield > 95%; IR (KBr): $\tilde{\nu}$=3354 (ν(N−H), urea), 3327 (ν(N−H), urethane), 3300 (ν(N−H), amide **A**), 1742 (ν(C=O), ester in polymer), 1730 (ν(C=O), ester in L-lysine), 1685 (ν(C=O), urethane), 1640 (ν(C=O), amide **I**), 1626 (ν(C=O), urea), 1567 (δ(N−H), urea, urethane), 1546 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ=5.76 (br, 2H), 5.19 (d, J=7.6 Hz, 2H), 4.75 (br, 4H), 4.41–4.46 (m, 2H), 4.07–4.29 (m, 8H), 3.97–4.05 (m, 26H), 3.22–3.26 (m, 4H), 3.16–3.20 (m, 8H), 2.32–2.36 (m, 26H), 2.13–2.18 (m, 8H), 1.21–1.81 (alkyl), 0.95–0.99 (m, 21H), 0.88 ppm (t, J=6.6 Hz, 12H).

4A: Yield > 95%; IR (KBr): $\tilde{\nu}$=3352 (ν(N−H), urea), 3328 (ν(N−H), urethane), 3299 (ν(N−H), amide **A**), 1740 (ν(C=O), ester in polymer), 1724 (ν(C=O), ester in L-lysine), 1684 (ν(C=O), urethane), 1641 (ν(C=O), amide **I**), 1624 (ν(C=O), urea), 1569 (δ(N−H), urethane), 1561 (δ(N−H), urea), 1544 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ=5.80 (br, 2H), 5.23 (d, J=7.3 Hz, 2H), 4.81 (br, 4H), 4.41–4.44 (m, 2H), 4.04–4.24 (m, polymer), 3.64–3.71 (m, 4H), 3.22–3.26 (m, 4H), 3.17–3.20 (m, 8H), 2.29–2.35 (m, 26H), 2.13–2.18 (m, 4H), 1.21–1.81 (alkyl), 0.88 ppm (t, J=6.6 Hz, 12H).

5A: Yield > 95%; IR (KBr): $\tilde{\nu}$=3352 (ν(N−H), urea), 3326 (ν(N−H), urethane), 3301 (ν(N−H), amide **A**), 1729 (ν(C=O), ester), 1686 (ν(C=O), urethane), 1641 (ν(C=O), amide **I**), 1625 (ν(C=O), urea), 1568 (δ(N−H), urethane, urea), 1544 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ=5.79 (br, 2H), 5.23 (br, 2H), 4.78 (br, 4H), 4.44 (br, 2H), 3.18–3.24 (m, 12H), 2.15 (br, 4H), 1.21–1.81 (alkyl), 0.83–0.88 ppm (br, 30H).

6A: Yield > 95%; IR (KBr): $\tilde{\nu}$=3353 (ν(N−H), urea), 3326 (ν(N−H), urethane), 3300 (ν(N−H), amide **A**), 1730 (ν(C=O), ester), 1686 (ν(C=O), urethane), 1641 (ν(C=O), amide **I**), 1624 (ν(C=O), urea), 1568 (δ(N−H), urethane, urea), 1543 cm^{-1} (δ(N−H), amide **II**); ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C): δ=5.75 (br, 1H), 5.17 (d, J=7.3 Hz, 1H), 4.73 (br, 2H), 4.41–4.46 (m, 1H), 4.09–4.12 (m, 4H), 3.45–3.82 (m, polymer), 3.22–3.26 (m, 2H), 3.13–3.20 (m, 4H), 2.13–2.18 (m, 2H), 1.78 (s, 3H), 1.21–1.70 (alkyl), 0.88 ppm (t, J=6.6 Hz, 6H).

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 ^{1}H NMR spectra were measured on a Bruker AVANCE 400 spectrometer. The transmission electron microscope (TEM) images were obtained by using a JEOL JEM-2010 electron microscope at 200 kV. The FE-SEM observations were carried out using a Hitachi S-5000 field emission scanning electron microscope. The strengths of the organogels were measured using a Sun Rheo Meter CR-500DX (Sun Scientific Co., LTD).

Gelation test: A mixture of a preweighed gelator in solvent (1 mL) in a sealed test tube was heated until a clear solution appeared and then the sample solution stood at 25 °C for 4 h. The formation of an organogel was evaluated by a tube-inversion method.

FE-SEM: Samples were prepared as follows: 1,4-dioxane gels based on **1A** and **4A–6A** at their MGCs (**1A**: 20 $g L^{-1}$; **4A**: 20 $g L^{-1}$; **5A**: 40 $g L^{-1}$; **6A**: 30 $g L^{-1}$) were dried at −60 °C in vacuum for 24 h. The resulting xerogels were shadowed to approximately 10-nm thick with Pt–Pd by sputtering.

Transmission electron microscopy: Samples were prepared as follows: solutions of **2A** (3 $g L^{-1}$) and **3A** (6 $g L^{-1}$) in 1,4-dioxane were dropped onto a collodion- and carbon-coated 400-mesh copper grid and quickly frozen in liquid nitrogen. The grids were then dried under vacuum for 24 h. After negative strain by osmic acid overnight, the grids were dried in vacuum at room temperature 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 resolution of 2 cm^{-1} with 32 scans.

Temperature-controlled FT-IR: 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.

Gel strength: Samples were prepared as follows: a mixture of a preweighed gelator in organic solvent (2 mL) in a sealed sample tube (15 mm in diameter) was heated until a clear solution appeared, and was then stored at 25 °C for 4 h. The gel strength was evaluated as the strength necessary to sink a cylinder bar (10 mm in diameter) 4 mm deep into the gel.

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[43] Herein, the gel strength is not correlated with G' or G'' because when it is obtained by our static measurements it is different from G' and G'' values obtained by the dynamic method; the gel strength corresponds to the gel hardness.

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