

Development of New D,L-Methionine-based Gelators

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Abstract: D,L-Methionine was chosen as a starting material for the preparation of a new gelator *N*-10-undecenoyl-D,L-methionylaminooctadecane (DL-Met-R₁₈). Three oligo (dimethylsiloxane)-containing gelators, DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅, were also prepared from DL-Met-R₁₈ by hydrosilylation reactions. Their gelation abilities were evaluated on the basis of the minimum gel concentration using nine solvents. Compound DL-Met-R₁₈ was able to gelate liquid paraffin and silicone oil, but it crystallized in most solvents. However, DL-Met-R₁₈/Si₇₋₈ resulted to be the best gelator, gelling eight solvents at low concentrations. The results of gelation tests demonstrated that the ability to form stable gels decreases in the following order: DL-Met-R₁₈/Si₇₋₈ \approx DL-Met-R₁₈/Si₁₄₋₁₅ > DL-Met-R₁₈/Si₃ \gg DL-Met-R₁₈. The aspects and thermal stabilities of the gels were investigated using three-component mixtures of solvents composed of hexadecyl 2-ethylhexanoate, liquid paraffin, and decamethylcyclopentasiloxane (66 combinations). DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅ could form gels with all these mixed solvent combinations; particularly, DL-Met-R₁₈/Si₇₋₈ gave rise to transparent or translucent gels. FT-IR spectra suggested that the formation of hydrogen bonds between the NH and C=O groups of the amides is one of driving forces involved in the gelation process. Aggregates comprising three-dimensional networks were studied by transmission electron microscopy. Moreover, the viscoelastic behavior of the gels was investigated by rheology measurements.

Key words: gel, gelator, gelation, methionine, hydrogen bonding, cosmetic, siloxane

1 INTRODUCTION

In recent years, low-molecular-weight gelators have become a research hotspot because very small amounts of such compounds can often immobilize large volumes of solvent. Gelators are also characterized by thermally reversible sol-gel transitions, which can be attributed to three-dimensional network structures built up through noncovalent interactions such as hydrogen bonding, van der Waals interactions, and π - π interactions. As the gel formed by a low-molecular-weight gelator is often a supramolecular gel, numerous reports on gelators have provided advances in supramolecular chemistry¹⁻²¹. Recent research on gelators has focused on their application in fields such as drug delivery and drug release in biomaterials²²⁻²⁸, scaffold materials for cells in tissue engineering^{29, 30}, sensors³¹⁻³⁵, templates for the synthesis of inorganic nanostructures³⁶⁻⁴⁰, auxiliary agents for producing organic electronics⁴¹⁻⁴³, electrolytes that prevent liquid leakage⁴⁴, detectors for explosives⁴⁵⁻⁴⁸, and agents for gel-emulsions^{49, 50}. Another reason for the increasing interest in gelators lies in their potential industrial applications. Cur-

rently, the practical applications of gelators are limited to a few examples; 12-hydroxystearic acid⁵¹ has been practically used as a gelator for cooking oil, and (1,3:2,4)-dibenzylidene sorbitol⁵² and the α,γ -bis-*n*-butylamide of *N*-lauroyl-L-glutamic acid are ingredients in fragrances and cosmetics. As other examples, aromatic diureas are used as ingredients for the preparation of greases, and aluminum 2-ethylhexanoate is used as a thickener for ink. Despite the considerable amount of recent papers about gelators, the number of gelators that have found practical use is extremely small. This is mainly owing to their large manufacturing cost. Given that the starting materials of the aforementioned gelators for their practical use are cheap ricinoleic acid, D-sorbitol, L-glutamic acid, diisocyanate, and 2-ethylhexanoic acid, it is essential to select cheap available compounds as starting materials for developing new gelators. In terms of the low cost, it is noted that amino acid-containing gelators were prepared by ring-opening reaction of glucono δ -lactone recently⁵³. Although many gelators based on amino acids have been studied^{1, 2, 6, 7}, gelators derived from methionine have never been reported

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so far because the good crystallinity of the derivatives hinders their gelation.

In the present paper, we focused on D,L-methionine, which has been widely used as growth-promoting feed additive for domestic animals and is one of the cheap mass-produced goods available. In contrast to most amino acids, which are selectively produced by microbial fermentation in the chiral L-form⁵⁴⁾, D,L-methionine is produced by Strecker amino acid synthesis. Since D-methionine is converted to L-methionine *in vivo*^{55, 56)}, there is no difference nutritionally between both chiral forms. Therefore the cheap racemic D,L-methionine is provided as a nutritional fortification substance in feed additives. In this study, we would like to report the first gelator derived from D,L-methionine and the preparation of oligo(dimethylsiloxane)-containing gelators. We present their gelation behavior toward three-component mixtures of solvents composed of hexadecyl 2-ethylhexanoate (HDEH), liquid paraffin, and decamethylcyclopentasiloxane (D5), which are frequently found in cosmetic.

2 EXPERIMENTAL PROCEDURES

2.1 Instrumentation

Elemental analysis was performed with a Perkin-Elmer 240B analyzer. Infrared spectra were recorded on a Jasco FTIR-7300 spectrometer using KBr plate for solids and KBr sealed cell with a spacer having a width of 0.5 mm for gels and solutions. ¹H NMR spectra were performed on a Bruker AVANCE 400 spectrometer. Transmission electron microscopy (TEM) was done with a JOEL IEM-2010 electron microscope. Rheology and gel strength were measured by an Elquest rheologia A300 and a Sun Science RHEO CR-500DX, respectively.

2.2 Reagents

D,L-Methionine was purchased from Wako Pure Chemical Industries, Ltd. 10-Undecenoyl chloride was purchased from Tokyo Chemical Industry Co. Ltd. Karstedt's catalyst solution and 1,1,1,3,5,5,5-heptamethylsiloxane were supplied by Aldrich. Hydride terminated poly(dimethylsiloxane)s were purchased from Gelest Inc.

2.3 Gelation test

Gelation test was carried out by an upside-down test tube method. A typical procedure is as follows: A weighed sample and 1 mL of solvent in a septum-capped test tube with internal diameter of 14 mm was heated until the solid dissolved. The resulting solution was cooled at 25°C for 2 h and then the gelation was checked visually. When no fluid ran down the wall of the test tube upon inversion of the test tube, we judged it to be gel. The gelation ability was evaluated by the minimum gel concentration, which is the

concentration of a gelator necessary for gelation at 25°C. The unit is g L⁻¹ (gelator/solvent). The solvents used for gelation test were liquid paraffin, isopropyl myristate (IPM), hexadecyl 2-ethylhexanoate (HDEH), silicone oils (KF-54, KF-56), decamethylcyclopentasiloxane (D5), acetone, ethyl acetate, and toluene. The gel strength of gels was measured and evaluated as the power necessary to sink a cylinder bar (10 mm in diameter) 4 mm deep in the gels.

2.4 Synthesis

DL-Met-R₁₈. A solution of 14.92 g (0.10 mol) of D,L-methionine, 4.00 g (0.10 mol) of NaOH in 50 mL of water was cooled in ice-water bath. Ether (30 mL) was added to the solution and stirred vigorously. 10-Undecenoyl chloride (20.27 g, 0.10 mol) and 50 mL (0.10 mol) of 2 M NaOH were added to the solution under stirring in ice-water bath by 5 portions. After stirring vigorously in ice-water bath for 2 h, the solution was returned to room temperature. The taken aqueous layer was acidified by 4 M of hydrochloric acid, extracted with 100 mL of ethyl acetate. After evaporating the organic layer, the oily product was recrystallized from ligroin. *N*-10-Undecenoyl-D,L-methionine was obtained in a yield of 25.10 g (80%).

N,N'-Diisopropylcarbodiimide (5.05 g, 0.040 mol) was added to a solution of 11.45 g (0.036 mol) of 10-undecenoyl-D,L-methionine in ice-water bath and stirred for 30 min. To the solution 9.70 g (0.036 mol) of *n*-octadecylamine was added and stirred at 35°C overnight. The matter after evaporation was recrystallized from methanol twice. **DL-Met-R₁₈** was obtained in a yield of 18.54 g (91%). FT-IR (KBr): 3287 cm⁻¹ (ν N-H, amide A), 1635 cm⁻¹ (ν C=O, amide I), 1563 cm⁻¹ (δ N-H, amide II), 910 cm⁻¹ (terminal olefin). Found: C 72.21, H 12.37, N 4.84%. Calcd for C₃₄H₆₆N₂O₂S: C 72.03, H 11.73, N 4.94%. ¹H NMR (400 MHz, CDCl₃, TMS, 25°C): δ = 6.35 (t, 1H, -CO-NH-), 6.29 (d, 1H, -CO-NH-), 5.75-5.86 (m, 1H, CH₂=CH-), 4.90-5.02 (m, 2H, CH₂=CH-), 4.54-4.57 (m, 1H, -NH-CH₂-CO-), 3.17-3.29 (m, 2H, -NH-CH₂-), 2.44-2.68 (m, CH₂-CH₂-S-), 2.20 (t, 2H, -CH₂-CO-), 2.11 (s, 3H, -S-CH₃), 1.90-2.07 (m, 4H, -CH₂-CH₂-S-, CH₂=CH-CH₂-), 1.60-1.63 (m, 2H, -CH₂-CH₂-CO-), 1.47-1.51 (m, 2H, -NH-CH₂-CH₂-), 1.25 (s, 38H, -CH₂-), 0.87 (t, 3H, CH₃-octadecyl).

DL-Met-R₁₈/Si₃. Karstedt's catalyst solution (42 μL) was added to a solution of 1.00 g (1.76 mmol) of **DL-Met-R₁₈** in 46 mL of dry THF, and then, 0.43 g (1.94 mmol) of 1,1,1,3,5,5,5-heptamethylsiloxane was added slowly followed by refluxed for 2 days under an argon atmosphere. An additional Karstedt's catalyst solution (42 μL) was poured to the solution and refluxed for 2 days under an argon atmosphere. After confirming the disappearance of terminal olefin (910 cm⁻¹) by IR, the solvent was removed and the resulting matter was dissolved in 40 ml of hot methanol, followed by charcoal treatment. The filtrate

without charcoal was left to stand at room temperature and the precipitate was filtered off. The twice charcoal treatment of methanol solution gave 0.99 g (71%) of **DL-Met-R₁₈/Si₃**. FT-IR (KBr): 3287 cm^{-1} (ν N-H, amide A), 1635 cm^{-1} (ν C=O, amide I), 1563 cm^{-1} (δ N-H, amide II), 1261 cm^{-1} (ν Si-C), 1021 cm^{-1} (ν Si-O-Si). Found: C 63.21, H 11.84, N 3.88%. Calcd for $\text{C}_{40}\text{H}_{86}\text{N}_2\text{O}_4\text{Si}_3$: C 62.38, H 11.24, N 3.55%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS, 25°C): δ = 6.31 (t, 1H, -CO-NH-), 6.26 (d, 1H, -CO-NH-), 4.53-4.58 (m, 1H, -NH-CH₂-CO-), 3.20-3.27 (m, 2H, -NH-CH₂-), 2.43-2.63 (m, 2H, -CH₂-CH₂-S-), 2.20 (t, 2H, -CH₂-CO-), 2.11 (s, 3H, -S-CH₃), 1.90-2.07 (m, 2H, -CH₂-CH₂-S-), 1.62 (m, 4H, -CH₂-CH₂-CO-, -NH-CH₂-CH₂-), 1.49 (m, 2H, -Si-CH₂-), 1.25 (br, 44H, -CH₂-), 0.88 (t, 3H, CH₃-octadecyl).

DL-Met-R₁₈/Si₇₋₈. This compound was prepared from 2.00 g (3.53 mmol) of **DL-Met-R₁₈** and 0.88 g (ca. 1.76 mmol) of hydride terminated poly(dimethylsiloxane) (Mw = 400–500) by the similar procedure described above. Yield; 1.91 g (66%). FT-IR (KBr): 3289 cm^{-1} (ν N-H), 1637 cm^{-1} (ν C=O, amide I), 1260 cm^{-1} (ν Si-C, Si-CH₃), 1091 cm^{-1} (ν Si-O-Si), disappeared 2150 cm^{-1} (ν Si-H), disappeared 910 cm^{-1} (δ CH, CH₂=CH-). Found: C 59.68, H 11.07, N 3.56%. Calcd for $\text{C}_{82}\text{H}_{176}\text{N}_4\text{O}_{10}\text{Si}_7$ (as $n=5$): C 60.09, H 10.82, N: 3.42%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS, 25°C): δ = 6.36-6.51 (m, 2H, -CO-NH-), 6.26 (m, 2H, -CO-NH-), 4.53-4.59 (m, 2H, -CO-CH-NH-), 3.20-3.29 (m, 4H, -NH-CH₂-), 2.44-2.63 (m, 4H, -CH₂-CH₂-S-), 2.20 (t, 4H, -CH₂-CO-), 2.11 (br, 6H, -S-CH₃), 1.94-2.06 (m, 4H, -CH₂-CH₂-S-), 1.60 (br, 8H, -CH₂-CH₂-CO-, -NH-CH₂-CH₂-), 1.50 (t, 4H, -Si-CH₂-), 1.25 (br, 88H, -CH₂-), 0.88 (t, 6H, CH₃-octadecyl), 0.04-0.07 (m, 6($n+2$)H, Si-(CH₃)₂).

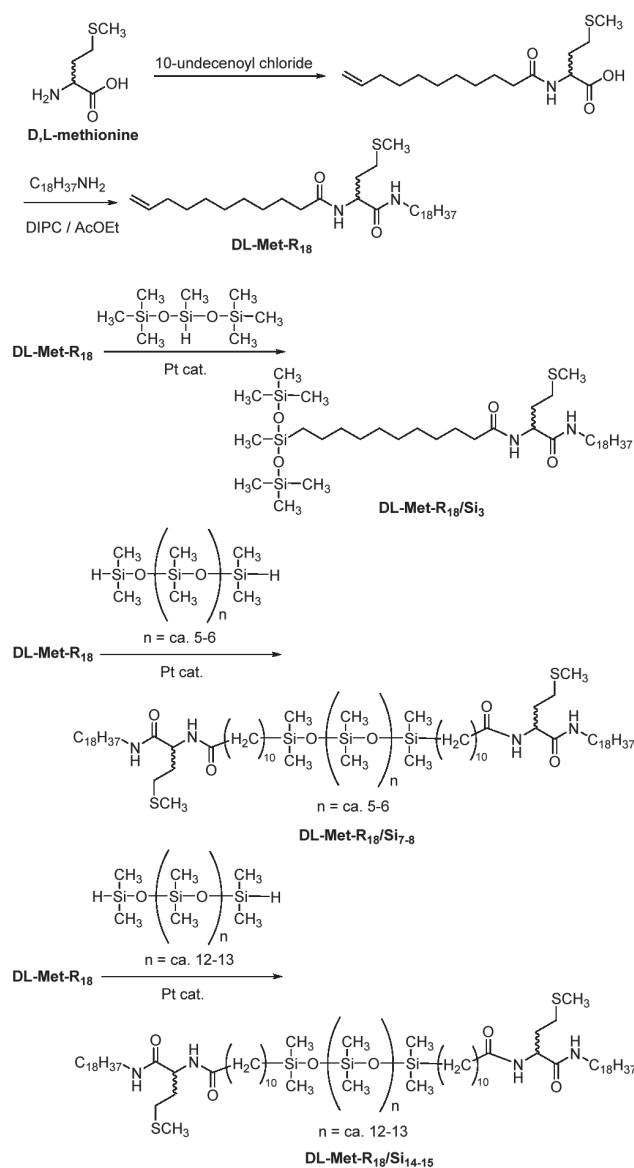
DL-Met-R₁₈/Si₁₄₋₁₅. This compound was prepared from 3.00 g (5.29 mmol) of **DL-Met-R₁₈** and 2.82 g (ca. 2.65 mmol) of hydride terminated poly(dimethylsiloxane) (Mw = 1000–1100) by the similar procedure described above. Yield; 5.14 g (88%). FT-IR (KBr): 3287 cm^{-1} (ν N-H, amide A), 1635 cm^{-1} (ν C=O, amide I), 1563 cm^{-1} (δ N-H, amide II), 1261 cm^{-1} (ν Si-C), 1021 cm^{-1} (ν Si-O-Si). Found: C 53.44, H 10.52, N 2.80%. Calcd for $\text{C}_{97}\text{H}_{221}\text{N}_4\text{O}_{17.5}\text{Si}_{14.5}$ (as $n=12.5$): C 53.43, H 10.08, N 2.60%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS, 25°C): δ = 6.22-6.48 (m, 4H, -CO-NH-), 4.56 (m, 2H, CH₂=CH-), 4.52-4.59 (m, 2H, -CO-CH-NH-), 3.21-3.30 (m, 4H, -NH-CH₂-), 2.44-2.64 (m, 4H, -CH₂-CH₂-S-), 2.20 (t, 4H, -CH₂-CO-), 2.11 (br, 6H, -S-CH₃), 1.93-2.06 (m, 4H, -CH₂-CH₂-S-), 1.59 (br, 8H, CH₂-CH₂-CO-, -NH-CH₂-CH₂-), 1.49 (t, 4H, -Si-CH₂-), 1.25 (br, 88H, -CH₂-), 0.88 (t, 6H, CH₃-octadecyl), 0.06 (m, 6($n+2$)H, Si-(CH₃)₂).

3 RESULTS AND DISCUSSION

3.1 Gelation abilities

As previously mentioned in the introduction, in spite of racemates being generally unsuitable for developing gela-

tors, we selected D,L-methionine as a starting material owing to its low cost and widespread use as growth-promoting feed for domestic animals. To the best of our knowledge, gelators derived from D,L-methionine have never been reported so far. First, we prepared N-10-undecenyl-D,L-methionylaminooctadecane (referred hereafter as **DL-Met-R₁₈**) as a new gelator as well as three siloxane-containing gelators derived from **DL-Met-R₁₈** (Scheme 1), which have been abbreviated as **DL-Met-R₁₈/Si₃**, **DL-Met-R₁₈/Si₇₋₈**, and **DL-Met-R₁₈/Si₁₄₋₁₅**. It should be noticed that the gels formed by racemic compounds are usually unstable and prone to crystallization. To overcome this drawback and ensure the formation of semi-stable gels from D,L-methionine-based gelators, we focused on flexible oligo (di-



Scheme 1 Preparation of **DL-Met-R₁₈**, **DL-Met-R₁₈/Si₃**, **DL-Met-R₁₈/Si₇₋₈**, and **DL-Met-R₁₈/Si₁₄₋₁₅**.

methylsiloxane) fragments with the expectation that they provided the corresponding oligo(dimethylsiloxane)-containing compounds with enough flexibility to prevent their crystallization.

Gelation tests were performed using an upside-down test tube method. The gelation was considered successful when no fluid was observed running down the walls of the tube upon inversion. The results of the gelation tests performed with nine solvents are summarized in Table 1. Compound DL-Met-R₁₈ was able to gelate liquid paraffin and silicone oil (KF-54), whereas it crystallized in HDEH, acetone, and ethyl acetate. However, the opaque gel of liquid paraffin of DL-Met-R₁₈ was so unstable that it precipitated one week later (Fig. 1). The crystallization of DL-Met-R₁₈ from these solvents may be explained by Wallach's rule⁵⁷⁾; namely, a racemic crystal tends to be denser and more stable than its chiral counterpart. It is clear from Table 1 that the connection of siloxane fragments to DL-Met-R₁₈ improved the gelation ability. In particular, DL-Met-R₁₈/Si₇₋₈ could gelate most solvents except for toluene. The gelation ability was found to decrease as follows: DL-Met-R₁₈/Si₇₋₈ > DL-Met-R₁₈/Si₁₄₋₁₅ > DL-Met-R₁₈/Si₃ > DL-Met-R₁₈. The attachment of siloxane fragments to DL-Met-R₁₈ prevents aggregate growth resulting in crystallization due to their flexibility. The relatively low gelation ability of DL-Met-R₁₈/Si₃ may be explained by the lower number of connected DL-Met-R₁₈ parts as gelation-driving segments as compared with DL-Met-R₁₈/Si₇₋₈ and DL-Met-R₁₈/Si₁₄₋₁₅, which have two gelation-driving segments at both ends. Therefore, it seems that the hydrogen bonding and van der Waals interactions between amide bonds and long alkyl chains, respectively, play an important role in the gelation process. It is noteworthy that, since DL-Met-R₁₈/Si₇₋₈ and DL-Met-R₁₈/Si₁₄₋₁₅ are prepared from racemic DL-Met-R₁₈,

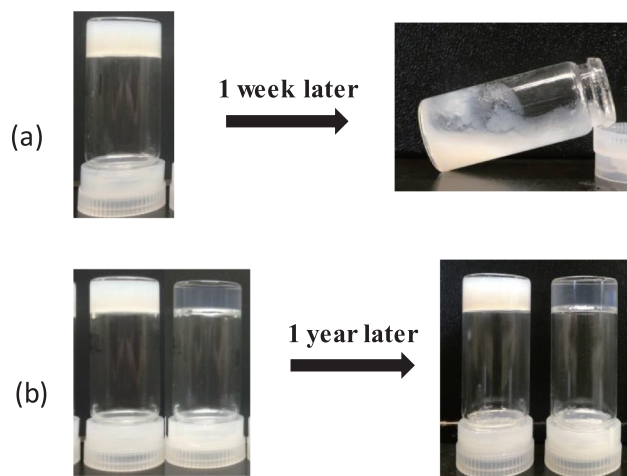


Fig. 1 Photos of gel aspects. (a) Unstable gel formed by DL-Met-R₁₈ in liquid paraffin. (b) Stable gels formed by DL-Met-R₁₈/Si₃ (left) and DL-Met-R₁₈/Si₁₄₋₁₅ (right) in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3).

L-Met-R₁₈ and D-Met-R₁₈ randomly react with the Si-H, i.e., they are composed of a mixture of three chiral compounds (L~L, D~D, and L~D). The existence of three chiral compounds also has an effect in the formation of stable gels. The difference in the gelation ability of DL-Met-R₁₈/Si₇₋₈ and DL-Met-R₁₈/Si₁₄₋₁₅ suggests that the chain length of the oligo(dimethylsiloxane) fragments is relevant. Considering that DL-Met-R₁₈/Si₁₄₋₁₅ is miscible in acetone and ethyl acetate, while the same solvents were gelated by DL-Met-R₁₈/Si₇₋₈, this fortuitous balance of structural features in oligo(dimethylsiloxane)s also predominate the gelation abilities. In contrast to DL-Met-R₁₈, the gels formed by DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅ were

Table 1 Results of gelation test towards ordinary solvents at 25°C.

Solvents	DL-Met-R ₁₈	DL-Met-R ₁₈ /Si ₃	DL-Met-R ₁₈ /Si ₇₋₈	DL-Met-R ₁₈ /Si ₁₄₋₁₅
Liquid paraffin	GO (20)	GTL (40)	GTL (2)	GT (8)
IPM	PG	S	GTL (8)	GTL (40)
HDEH	P	GO (40)	GTL (2)	GTL (20)
KF-54	GO (20)	GT (4)	GTL (20)	GO (10)
KF-56A	PG	PG	GT (4)	GTL (8)
D5	PG	GO (10)	GTL (8)	GO (10)
Acetone	P	P	GO (20)	S
Ethyl acetate	P	S	GTL (40)	S
Toluene	VS	S	S	S

GT: Transparent gel. GTL: Translucent gel. VS: Viscous solution. P: Precipitation. PG: Partial gel. S: Solution. IPM: Isopropyl myristate. HDEH: Hexadecyl 2-ethylhexanoate. KF-54: Poly (methylphenylsiloxane) of 400cS. KF-56A: Poly (methylphenylsiloxane) of 15cS. D5: Decamethylcyclopentasiloxane. The values indicate the minimum gel concentrations at 25°C; the units are g L⁻¹ (gelator/solvent).

very stable and neither separation nor collapse occurred, even after one year of storage (Fig. 1).

We studied the gelation behavior using the following three-component mixed solvents frequently found in cosmetics: HDEA as a polar oil, liquid paraffin as a non-polar oil, and D5 as a silicone oil. The gelation behavior of DL-Met-R₁₈, DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅ was investigated in the mixed solvents (66 combinations, with a weight ratio ranging from 10:0:0 to 0:0:10 of HDEH, liquid paraffin, and D5) (Fig. 2), where the concentrations of DL-Met-R₁₈ and DL-Met-R₁₈/Si₃ were fixed at 40 mg mL⁻¹ and those of DL-Met-R₁₈/Si₇₋₈ and DL-Met-R₁₈/Si₁₄₋₁₅ at 20 mg mL⁻¹ (gelator/solvent). As can be deduced from Fig. 2a, the good crystallinity of DL-Met-R₁₈ prevented it from having any gelation ability against the mixed solvents. On the other hand, DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅ could form gels with all these mixed solvent combinations. Although DL-Met-R₁₈/Si₃ formed opaque gels in a wide region (Fig. 2b), DL-Met-R₁₈/Si₁₄₋₁₅ could form transparent gels in the high ratio of liquid paraffin region (Fig. 2d). Meanwhile, DL-Met-R₁₈/Si₇₋₈ formed translucent gels in all areas (Fig. 2c). The formation of transparent gels is widely desirable from a practical perspective. The transparency of the gels is thought to depend

on the size of the aggregates building up the three-dimensional networks responsible for the physical gelation. When the width of the aggregates is equivalent to the wavelength of visible light, the formed gels will be opaque due to the scattering of visible light. The formation of transparent gels from DL-Met-R₁₈/Si₁₄₋₁₅ is therefore most likely due to the oligo (dimethylsiloxane) fragment hindering the growth of aggregates that scatter visible light. As mentioned above, the gels formed by DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅ are characterized by a high stability (Fig. 1). Therefore, the introduction of oligo (dimethylsiloxane) fragments into gelation-driving segments has proved to be a useful tool for the development of gelators that can form transparent and stable gels.

3.2 Gel strength and gel-to-sol phase-transition temperature

The gel strength, which is an important factor for the development of their applications, was evaluated by measuring the elastic storage modulus G' and loss modulus G'' values, as will be discussed later. However, we also evaluated the gel strength as the power necessary to sink a cylindrical bar (10 mm in diameter) 4 mm deep in the gels. The strength and phase-transition temperature of the gels

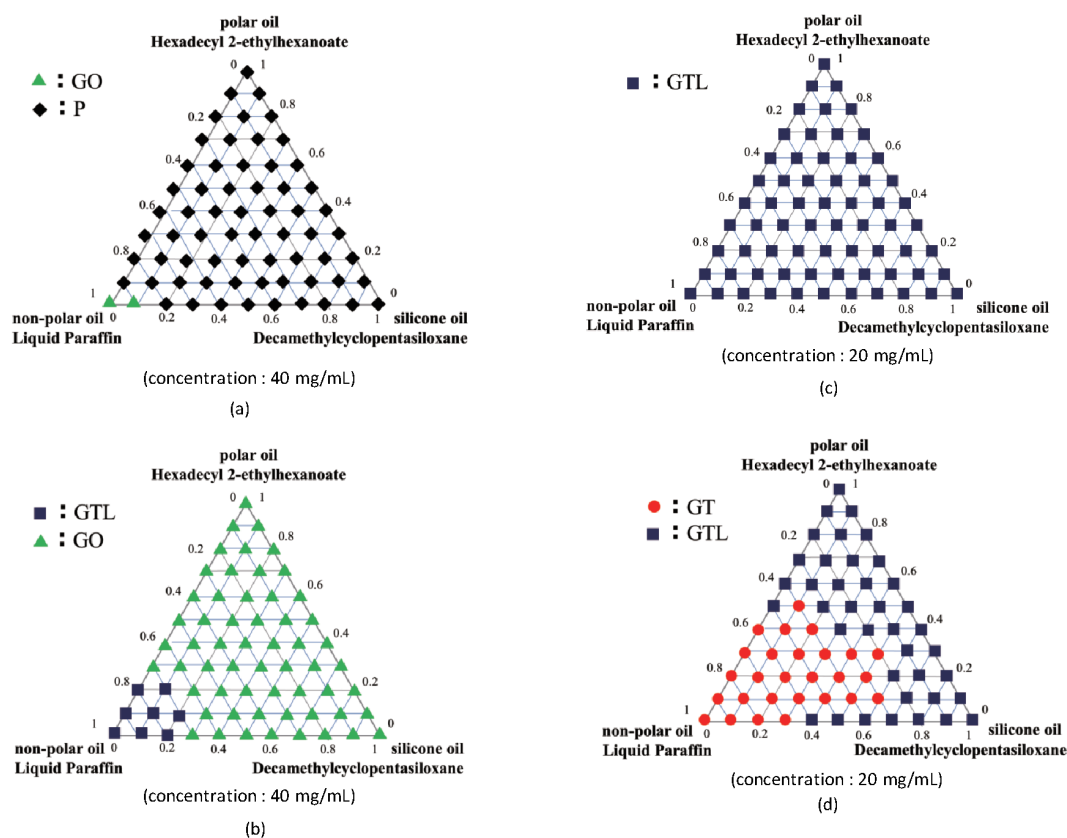


Fig. 2 Aspects of gels of (a) DL-Met-R₁₈, (b) DL-Met-R₁₈/Si₃, (c) DL-Met-R₁₈/Si₇₋₈, (d) DL-Met-R₁₈/Si₁₄₋₁₅ in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3).

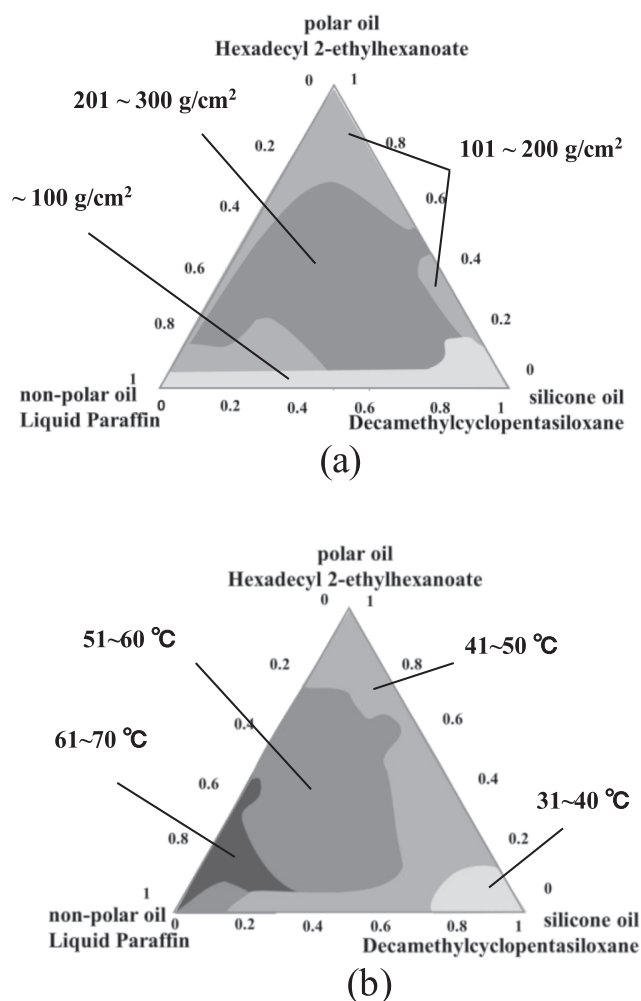


Fig. 3 Gel strengths and gel-to-sol phase transition temperatures of gels prepared by DL-Met-R₁₈/Si₁₄₋₁₅ at 20 mg mL⁻¹ in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3). (a) Gel strengths, (b) Gel-to-sol phase transition temperatures.

formed by DL-Met-R₁₈/Si₁₄₋₁₅ in the mixed solvents of HDEH, liquid paraffin, and D5 are shown in Fig. 3, where the concentrations of DL-Met-R₁₈/Si₁₄₋₁₅ were fixed at 20 mg mL⁻¹. It was found that the gel strength could be controlled in the range of 40–300 g cm⁻² by adjusting the ratio of HDEH, liquid paraffin, and D5 (Fig. 3a). Given that the gel strengths of jelly-like hand cream, skin cream, and lip balm tube are ~15 g cm⁻², ~70 g cm⁻², and ~230 g cm⁻², respectively, the gel strengths observed in Fig. 3a render DL-Met-R₁₈/Si₁₄₋₁₅ potentially useful for cosmetic applications.

The gel-to-sol phase-transition temperatures for the gels formed with DL-Met-R₁₈/Si₁₄₋₁₅ are shown in Fig. 3b. The phase-transition temperatures for gel-to-sol ranged from 61°C to 70°C in the region containing a high ratio of liquid paraffin and from 31°C to 40°C in the region containing a

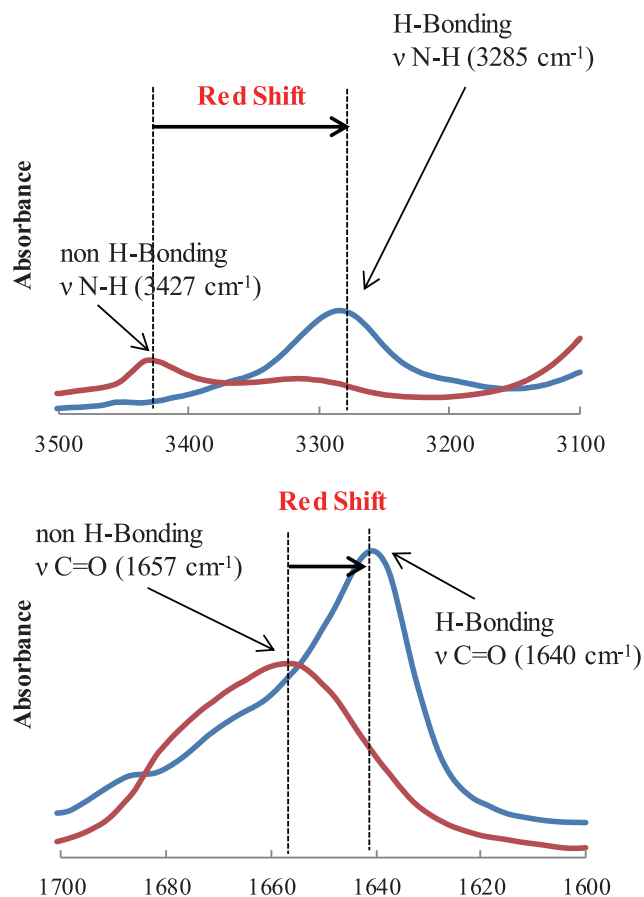


Fig. 4 FT-IR spectra of gel and chloroform solution prepared from DL-Met-R₁₈/Si₁₄₋₁₅ at 20 mg mL⁻¹. Blue line is the gel prepared from a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3). Red line is the chloroform solution.

high ratio of HDEH. As can be extracted from Fig. 3b, the phase-transition temperature can also be controlled by adjusting the ratio of the three solvents. High gel strengths and phase-transition temperatures were observed in the gels of DL-Met-R₁₈/Si₇₋₈ and DL-Met-R₁₈/Si₁₄₋₁₅ compared with those of DL-Met-R₁₈/Si₃, which can be attributed to the presence of two gelation-driving segments at both ends of DL-Met-R₁₈/Si₇₋₈ and DL-Met-R₁₈/Si₁₄₋₁₅.

3.3 FT-IR and TEM

Gelation by amino acid derivatives is primarily driven by hydrogen bonding. FT-IR spectra of the gel and a chloroform solution prepared from DL-Met-R₁₈/Si₁₄₋₁₅ are shown in Fig. 4. The FT-IR spectrum of the gel of ternary mixture solvent of DL-Met-R₁₈/Si₁₄₋₁₅ shows a NH stretching vibration at 3285 cm⁻¹ and amide C=O stretching vibrations at 1640 cm⁻¹. These stretching vibrations are indicative of the formation of hydrogen bonds between the amide NH and C=O groups, leaving almost no unbonded NH or C=O present. In contrast, chloroform could not be gelated with

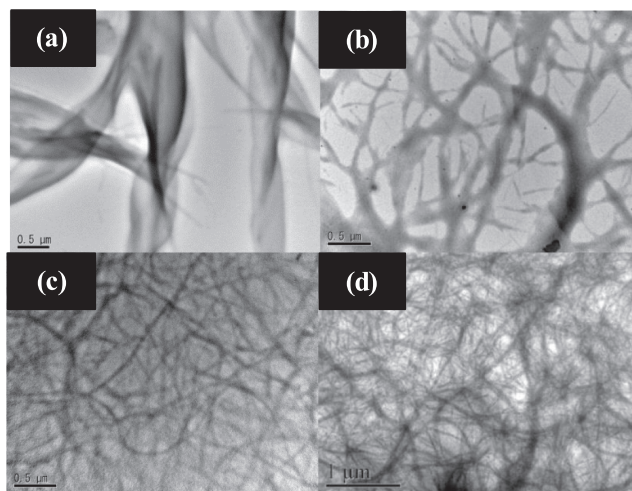


Fig. 5 TEM images of gels prepared from (a) DL-Met-R₁₈ at 1 mg mL⁻¹, (b) DL-Met-R₁₈/Si₃ at 1 mg mL⁻¹, (c) DL-Met-R₁₈/Si_{7.8} at 1 mg mL⁻¹, and (d) DL-Met-R₁₈/Si_{14.15} at 2 mg mL⁻¹ in liquid paraffin.

DL-Met-R₁₈/Si_{14.15} owing to their miscibility, and the following peaks indicative of the presence of unbonded NH and C=O are observed: NH stretching vibrations at 3427 cm⁻¹ and amide C=O stretching vibrations at 1657 cm⁻¹. These results suggest that the formation of hydrogen bonding between the amide NH and C=O groups constitutes a driving force in the gelation process.

We observed that the gelation ability of gelators depended on the existence of the oligo(dimethylsiloxane) fragment. Since the properties of gelators are normally attributed to the shape and size of aggregates forming three-dimensional networks, we decided to subject the gels to TEM measurements. TEM images of loose gels formed in liquid paraffin are shown in Fig. 5. The concentration of DL-Met-R₁₈ used to prepare the TEM sample was 2 mg mL⁻¹, whereas the other samples were prepared at concentrations of 1 mg mL⁻¹. Table 1 includes the aspects of the liquid paraffin gels, which were opaque (DL-Met-R₁₈), translucent (DL-Met-R₁₈/Si₃), translucent (DL-Met-R₁₈/Si_{7.8}), and transparent (DL-Met-R₁₈/Si_{14.15}). The image of DL-Met-R₁₈ shows ribbon-like aggregates with large diameters of approximately 500 nm (Fig. 5a), which would explain the formation of the opaque gel. By contrast, Fig. 5b displays smaller fibers with widths that ranged from 80 to 400 nm in DL-Met-R₁₈/Si₃. The image of DL-Met-R₁₈/Si_{7.8} (Fig. 5c) is characterized by fine thread-like aggregates with homogeneous diameters of ~50 nm. Finally, the image of DL-Met-R₁₈/Si_{14.15} shows very fine thread-like aggregates with nearly homogeneous diameters from 30 to 50 nm (Fig. 5d), in which a gathering of numerous fibers, juxtaposed and intertwined with the fine thread-like aggregates, can be observed. The concentrations for preparing the TEM samples were considerably lower than the

minimum gel concentrations to ensure that the images in Fig. 5 show the fibers of loose gels before actual gelation. However, it can be deduced that the homogeneous fine thread-like aggregates of DL-Met-R₁₈/Si_{14.15} results in highly transparent gels because the flexibility of the slightly longer oligo(dimethylsiloxane) fragments gives rise to homogeneous three-dimensional networks with less light scattering. The large minimum gel concentration of DL-Met-R₁₈/Si₃ in liquid paraffin may be explained by the gathering of short and thick aggregates. Moreover, the poor gelation ability of DL-Met-R₁₈ is most likely due to the short and thick aggregates resulting from the weak interaction.

3.4 Rheology

From the morphology of the aggregates observed in the TEM images, it was deduced that the viscoelastic behavior of gels also depends on the oligo(dimethylsiloxane) fragments. The viscoelastic behavior of the gels was studied by rheology measurements in strain sweep mode and frequency sweep mode (Fig. 6). A mixture of HDEH, liquid paraffin, and D5 (vol. ratio 4:3:3) was used as solvent. Regarding this aspect of gels, we already mentioned that DL-Met-R₁₈/Si₃ formed an opaque gel, and DL-Met-R₁₈/Si_{7.8} and DL-Met-R₁₈/Si_{14.15} formed translucent gels (see Fig. 2).

From the results in strain sweep mode, the storage elastic moduli (G') of all samples up to a strain of 0.02 were in the plateau region. After that, the G' gradually decreased until the loss elastic moduli (G'') of the gels exceeded the G' , and the gels collapsed at a strain of 0.1. In frequency sweep mode at a strain of 0.02, the plateau regions, in which the G' exceeded the G'' , were observed in all gels between 0.01 and 0.3 Hz. Average G' and G'' in the plateau regions of 0.01 to 0.3 Hz, referred to as G'_{Ave} and G''_{Ave} , and loss angle $\tan \delta_{Ave}$ are summarized in Table 2, where the tangent of the phase angle ($\tan \delta_{Ave}$)-the ratio of G''_{Ave} to G'_{Ave} is a useful quantifier of the presence and extent of elasticity in a gel system^{58–60}. The $\tan \delta_{Ave}$ values of less than unity indicate elastic-dominant behavior and values near unity indicate viscous-dominant behavior. The order of $\tan \delta_{Ave}$ was found to be DL-Met-R₁₈/Si_{14.15} < DL-Met-R₁₈/Si₃ ≈ DL-Met-R₁₈/Si_{7.8}. Therefore, the smallest $\tan \delta_{Ave}$ value of DL-Met-R₁₈/Si_{14.15} suggests that this derivative forms the most elastic hard gels, which was verified by measuring the gel strength (see Fig. 3). The hardness of gels seems to depend on the morphology of the three-dimensional networks of aggregates. As mentioned in the TEM images, DL-Met-R₁₈/Si_{14.15} formed very fine thread-like aggregates with nearly homogeneous diameters from 30 to 50 nm, whereas the widths of fibers in DL-Met-R₁₈/Si₃ ranged from 80 to 400 nm, which is larger than those of DL-Met-R₁₈/Si_{14.15}.

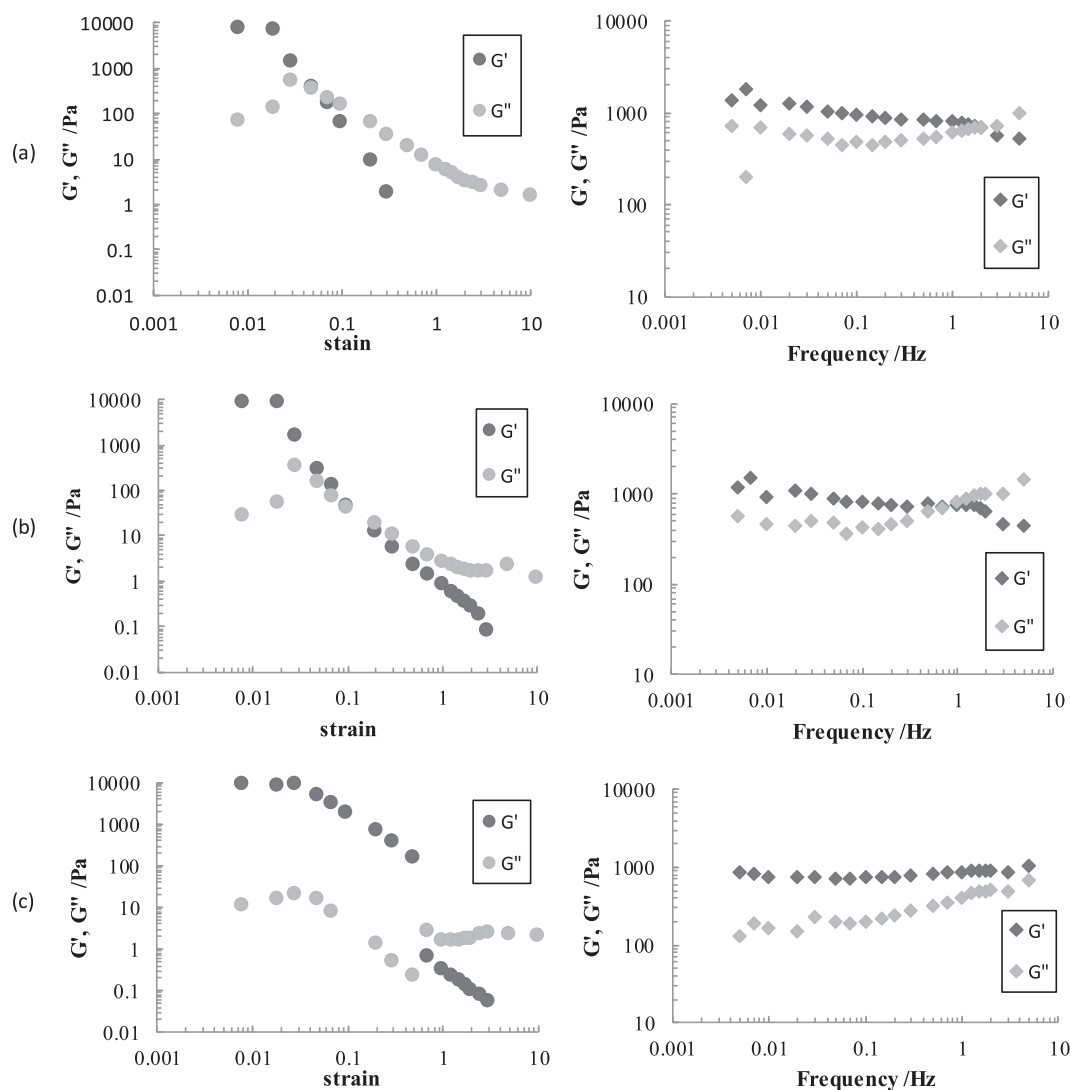


Fig. 6 Rheological measurement in strain sweep mode (left) and frequency sweep mode (right) for the gel prepared from (a) DL-Met-R₁₈/Si₃ at 40 mg mL⁻¹, (b) DL-Met-Si₇₋₈ at 20 mg mL⁻¹, and (c) DL-Met-Si₁₄₋₁₅ at 20 mg mL⁻¹ in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3) at 25°C.

Table 2 G_{Ave}' , G_{Ave}'' , and $\tan \delta_{Ave}$ under a strain of 0.02 at 25°C.

	G_{Ave}' (Pa)	G_{Ave}'' (Pa)	$\tan \delta_{Ave}$
DL-Met-R ₁₈ /Si ₃	1128	507	0.51
DL-Met-R ₁₈ /Si ₇₋₈	960	386	0.52
DL-Met-R ₁₈ /Si ₁₄₋₁₅	763	199	0.28

4 CONCLUSIONS

A gelator (DL-Met-R₁₈) derived from D,L-methionine was developed for the first time. Three oligo(dimethylsiloxane) fragment-containing gelators (DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅) were also prepared from DL-Met-R₁₈ by hydrosilylation reactions. The results of gelation tests performed with nine solvents demonstrated that the gelation ability to form stable gels follows the order DL-

Met-R₁₈/Si₇₋₈ \approx DL-Met-R₁₈/Si₁₄₋₁₅ > DL-Met-R₁₈/Si₃ \gg DL-Met-R₁₈. Compound DL-Met-R₁₈ was able to gelate liquid paraffin and silicone oil, but it crystallized in most solvents. On the contrary, DL-Met-R₁₈/Si₇₋₈ proved to be the best gelator, gelling eight solvents at low concentrations. The connection of flexible oligo(dimethylsiloxane) fragments to DL-Met-R₁₈ overcame the crystallinity issue, leading to the creation of good gelators. The gelation behavior was inves-

tigated using 66 combinations of three-component mixed solvents (HDEH, liquid paraffin, and D5). DL-Met-R₁₈/Si₃, DL-Met-R₁₈/Si₇₋₈, and DL-Met-R₁₈/Si₁₄₋₁₅ formed gels with all these mixed solvent combinations. Of particular interest were the transparent or translucent gels formed by DL-Met-R₁₈/Si₇₋₈. The gel strength and gel-to-sol phase-transition temperature could be controlled by adjusting the ratio of HDEH, liquid paraffin, and D5. The FT-IR spectra suggested that the hydrogen bonding between the amide NH and C=O groups plays an important role in the gelation process. The TEM image of DL-Met-R₁₈/Si₁₄₋₁₅ showed very fine thread-like aggregates with nearly homogeneous diameters from 30 nm to 50 nm, in which a gathering of numerous fibers, juxtaposed and intertwined with the fine thread-like aggregates were observed. The $\tan \delta_{\text{Ave}}$ obtained from rheology measurements indicated that DL-Met-R₁₈/Si₁₄₋₁₅ formed elastic hard gels.

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