

Physical gelation by amides derived from trans-1, 2-diaminocyclohexane and their tetrasiloxane-based gelators

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Physical gelation by amides derived from *trans*-1,2-diaminocyclohexane and their tetrasiloxane-based gelators

Running Head: Physical gelation by amides derived from *trans*-1,2-diaminocyclohexane

Four compounds were prepared from *trans*-1,2-diaminocyclohexane and were subsequently studied as gelators. These two compounds were chiral *trans*-(1*R*, 2*R*)-1-(2-heptylundecanoylamino)-2-(10-undecenoylamino)cyclohexane and the corresponding racemate. The other two compounds were 1,1,3,3,5,5,7,7-octamethyltetrasiloxane-containing chiral and racemic compounds prepared by a hydrosilylation reaction. Their gelation abilities were evaluated on the basis of the minimum gel concentration, using seven solvents. The thermal stability and transparency of the gels were investigated by UV-vis spectroscopy using three-component mixed solvents of hexadecyl 2-ethylhexanoate, liquid paraffin, and decamethylcyclopentasiloxane (66 combinations). The gel-to-sol phase-transition temperatures were also studied. The viscoelastic behavior of the gels was studied by rheology measurements in the strain sweep mode. Aggregates consisting of three-dimensional networks were studied by transmission electron microscopy. Circular dichroism spectroscopy was performed to verify the existence of helical aggregates in the gel.

Keywords: gelation, gelator, gel, *trans*-1,2-diaminocyclohexane, tetrasiloxane

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INTRODUCTION

K. Almdal et al., proposed that the term “gel” should be limited to systems that fulfill the following phenomenological characteristics: (a) they consist of two or more components, one of which is a liquid, present in a substantial quantity and (b) they are soft, solid, or solid-like materials.¹ According to Almdal’s proposal, they can be divided into three types: chemical, topological, and physical gels. Chemical gels are thermally irreversible and do not show sol–gel transitions, because their three-dimensional networks are built up via covalent bonds. Chemical gels have been widely studied in the field of polymer science,²⁻⁵ whereas topological gels, in which networks are topologically interlocked, have received relatively recent interest.⁶⁻⁹ The latter physical gels are characterized by thermally reversible sol–gel transitions. This feature can be attributed to three-dimensional network structures, which are built up through noncovalent interactions, such as hydrogen bonding, electrostatic interactions, van der Waals forces, and π - π interactions.

It is known that physical gels from synthetic and biological polymers have been studied energetically.¹⁰ On the contrary, low-molecular-weight compounds that can form physical gels are called gelators and have attracted a significant amount of scientific and technological interest. Though early reports regarding gelators are limited,¹¹⁻¹³ research interest increased again during the first half of the 1990s. With advances in the area of supramolecular chemistry, several reports on gelators have been published in recent years.¹⁴⁻²⁶ Gelators are gaining not only academic interest but also interest due to their practical applications. However, the number of gelators used in practical applications remains small. *N*-Lauroyl-L-glutamate- α,γ -bis-*n*-butylamide and 1,3:2,4-dibenzylidene-D-sorbitol are used as ingredients in fragrances and cosmetics, while 12-hydroxystearic acid is used as an edible-oil solidifying agent.

When gels are used to prepare optical materials, the transparency of the formed gels is very important. We have applied gelators to the fabrication of quasi-solid-state dye-sensitized solar cells,^{27,28} in which efficient light transmission is essential. Transparent gels are also needed for cosmetics, which frequently contain colored materials, because the development of a vivid color can be achieved in the transparent gels. In order to produce transparent gels, gelators must have no large absorption in the visible light region and must possess a refractive index close to that of a fluid.²⁹ Reduced light scattering is also important for transparent gels;³⁰ therefore, three-dimensional networks in gels need to be homogeneous and the size should be less than the wavelength of visible light. We focused on flexible and low-refraction oligo(dimethylsiloxane) to achieve transparent gels. The attachment of oligo (dimethylsiloxane) fragments to gelation-driving segments will prevent aggregate growth due to their flexibility and decrease the refractive index owing to their low refractive index.

With these ideas in mind, we prepare diamides with a terminal olefin segment, derived from *trans*-1,2-diaminocyclohexane, and the corresponding tetrasiloxane-based gelators. We compare the gelation abilities on the basis of whether the diamides are chiral or racemic, and whether they are tetrasiloxane-based gelators or not.

EXPERIMENTAL

Instrumentation

Elemental analysis was performed with a Perkin-Elmer 240B analyzer. Infrared spectra were recorded on a Jasco FTIR-7300 spectrometer using KBr plate. The strength of gels was measured with a Sun Science RHEO CR-500DX. UV-vis and CD spectra were recorded on a Jasco V-570UV/VIS/NIR and a Jasco J-600, respectively. Transmission electron microscopy (TEM) was done with a JEOL JEM-SS. Rheology was measured by an Elquest rheologia A300.

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 ethyl acetate, isopropyl myristate, toluene, liquid paraffin, silicone oil (KF-54), decamethylcyclopentasiloxane (D5), and hexadecyl 2-ethylhexanoate. 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.

Synthesis

trans-(1*R*, 2*R*)-(-)-1,2-Diaminocyclohexane and racemic *trans*-1,2-diaminocyclohexane were purchased from Tokyo Chemical Industry Co. Ltd. Karstedt's catalyst solution and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane were supplied by Aldrich and Gelest Inc., respectively.

(*R*, *R*)-g: The hydrogen bromide salt of *trans*-(1*R*, 2*R*)-1-amino-2-(2-heptylundecanoylamino)cyclohexane was prepared by deprotection of *trans*-(1*R*, 2*R*)-1-(Boc-amino)-2-(heptylundecanoylamino)cyclohexane according to the previous paper.³¹ A solution of 13.85 g (30.0 mmol) of HBr salt of *trans*-(1*R*, 2*R*)-1-amino-2-(2-heptylundecanoylamino)cyclohexane and 6.68 g (66.0 mmol) of triethylamine in 300 ml of dry THF was cooled in ice-water bath, and then 6.69 g (33.0 mmol) of 10-undecenoyl chloride was added drop-by-drop. After the mixture was stirred for 3 h at room temperature, 300 ml of water was added to the reaction mixture and a precipitate was filtered off, dried. Recrystallization from a mixture of 650 ml of ethyl acetate and 50 ml of hexane gave 15.47 g (94%) of **(*R*, *R*)-g**. IR (KBr, cm⁻¹): 3283 (νN-H), 1635(νC=O amide I), 1544 (δN-H amide II). Found: C 76.73 H 12.50, N 5.51%. Calcd for C₃₅H₆₆N₂O₂: C 76.86, H 12.16, N 5.12%. ¹H-NMR (400 MHz, CDCl₃, TMS, 25°C): δ = 5.96 (d, 1H, J = 6.80 Hz, NH-CO), 5.89 (d, 1H, J = 7.08 Hz, NH-CO), 5.75-5.85 (ddt, 1H, J = 6.64, 10.16, 16.88, -CH=CH₂), 4.90-5.01 (m, 2H, -CH=CH₂), 3.54-3.70 (m, 2H, -NH-CH(CH₂)-CH(CH₂)-NH-), 2.00-2.12 (m, 6H, -CO-CH₂-CH₂, -CH₂CH=CH₂, cyclohexane-CH₂-), 1.89-1.96 (m, 1H, -CO-CH₂CH₂(CH₂-), 1.72-1.74 (m, 2H, cyclohexane-CH₂-), 1.24-1.37 (br, 44H, alkyl), 0.85-0.89 (m, 6H, -CH₂CH₃).

rac-g: This compound was prepared from HBr salt of racemic *trans*-1-amino-2-(2-

heptylundecanoylamino)cyclohexane³¹ by the similar procedure described in (**R, R**)-**g**. Yield; 90%. IR (KBr, cm⁻¹): 3289 (νN-H) 1644 (νC=O amide I), 1520 (δN-H amide II). Found: C 76.93 H 12.16, N 5.33%. Calcd for C₃₅H₆₆N₂O₂: C 76.86, H 12.16, N 5.12%. ¹H-NMR (400 MHz, CDCl₃, TMS, 25°C): δ = 5.97 (d, 1H, J = 6.72 Hz, NH-CO), 5.90 (d, 1H, J = 7.00 Hz, NH-CO), 5.75-5.85 (ddt, 1H, J = 6.68, 10.26, 16.92, -CH=CH₂), 4.90-5.01 (m, 2H, -CH=CH₂), 3.59-3.69 (m, 2H, -NH-CH(CH₂)-CH(CH₂)-NH-), 2.00-2.12 (m, 6H, -CO-CH₂-CH₂-, -CH₂CH=CH₂, cyclohexane-CH₂-), 1.89-1.96 (m, 1H, -CO-CHCH₂(CH₂-), 1.72-1.74 (m, 2H, cyclohexane-CH₂-), 1.24-1.37 (br, 44H, alkyl), 0.85-0.89 (m, 6H, -CH₂CH₃).

(**R, R**)-**g/Si**: To a solution of 1.59 g (2.91 mmol) of (**R, R**)-**g** in 40 ml of dry toluene, 0.41 g (1.45 mmol) of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane and ca. 40 μl of Karstedt's catalyst solution were added and refluxed for 5 days under an argon atmosphere. After confirming the disappearance of terminal olefin (910 cm⁻¹) by IR, the mixture was evaporated 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 1.07 g (54%) of (**R, R**)-**g/Si**. IR (KBr, cm⁻¹): 3281 (νN-H), 1635 (νC=O amide I), 1544 (δN-H amide II), 1261 (νSi-C), 1092, 1022 (νSi-O-Si). Found: C 68.38, H 11.95, N 4.29%. Calcd for C₇₈H₁₅₈N₄O₇Si₄: C 68.06, H 11.57, N 4.07%. ¹H-NMR (400 MHz, CDCl₃, TMS, 25°C): δ = 5.95 (d, 2H, J = 3.68 Hz, NH-CO), 5.89 (d, 2H, J = 4.20 Hz, NH-CO), 3.59-3.67 (br, 4H, -NH-CH(CH₂)-CH(CH₂)-NH-), 2.02-2.12 (m, 8H, -CO-CH₂-CH₂, cyclohexane-CH₂-), 1.89-1.96 (m, 2H, -CO-CHCH₂(CH₂-), 1.72-1.74 (m, 4H, cyclohexane-CH₂-), 1.24-1.60 (br, ~100H, alkyl), 0.85-0.89 (m, 12H, -CH₂CH₃).

rac-g/Si: This compound was prepared from **rac-g** by the similar procedure described in

(R, R)-g/Si. Yield; 55%. IR (KBr, cm^{-1}): 3281 ($\nu\text{N-H}$), 1636 ($\nu\text{C=O}$ amide I), 1543 ($\delta\text{N-H}$ amide II), 1258 ($\nu\text{Si-C}$), 1085, 1040 ($\nu\text{Si-O-Si}$). Found: C 66.70, H 12.70, N 3.80%. Calcd for $\text{C}_{78}\text{H}_{158}\text{N}_4\text{O}_7\text{Si}_4$: C 68.06, H 11.57, N 4.07%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , TMS, 25°C): δ = 5.97 (d, 2H, J = 3.68 Hz, NH-CO), 5.90 (d, 2H, J = 4.20 Hz, NH-CO), 3.58-3.59 (br, 4H, -NH- $\underline{\text{C}}\text{H}(\text{CH}_2)$ - $\underline{\text{C}}\text{H}(\text{CH}_2)$ -NH-), 1.98-2.06 (m, 8H, -CO- $\underline{\text{C}}\text{H}_2$ -CH₂, cyclohexane- $\underline{\text{C}}\text{H}_2$ -), 1.85-1.89 (m, 2H, -CO- $\underline{\text{C}}\text{HCH}_2(\text{CH}_2)$ -), 1.66-1.68 (m, 4H, cyclohexane- $\underline{\text{C}}\text{H}_2$ -), 1.18-1.52 (br. $\sim 100\text{H}$, alkyl), 0.79-0.83 (m, 12H, -CH₂ $\underline{\text{C}}\text{H}_3$).

RESULTS AND DISCUSSION

Gelation abilities

Four diamides based on *trans*-1,2-diaminocyclohexane were prepared as gelators (Scheme 1). The chiral *trans*-(1*R*, 2*R*)-1-(2-heptylundecanoylamino)2-(10-undecenoylamino)cyclohexane was abbreviated as **(R, R)-g**. The corresponding racemate, which was prepared from racemic *trans*-1,2-diaminocyclohexane, was abbreviated as **rac-g**. Terminal olefin segments in **(R, R)-g** and **rac-g** were incorporated in a hydrosilylation reaction. The hydrosilylation reactions of the terminal olefins in **(R, R)-g** and **rac-g** with 1,1,3,3,5,5,7,7-octamethyltetrasiloxane gave **(R, R)-g/Si** and **rac-g/Si**, respectively. Not only do **(R, R)-g** and **rac-g** act as gelators themselves, but they also play important roles as gelation-driving segments in **(R, R)-g/Si** and **rac-g/Si**.

The present study mainly includes two objects; one is the development of gelators forming semi-permanent stable gels and the other is the development of gelators forming transparent gels. In general, gels composed of low-molecular-weight gelators are metastable and crystallize after standing. In industrial applications of gelators, crystallization involves the breakdown of gels and is a critical disadvantage. Moreover, it

is hardly necessary to say that the transparency of formed gels is essential for optical materials. In this study, we focused on flexible oligo(dimethylsiloxane), with the expectation that oligo(dimethylsiloxane)-containing compounds do not separate as crystals from a solution or transform into huge aggregates because of their flexibility. This is the reason why 1,1,3,3,5,5,7,7-octamethyltetrasiloxane was connected to **(R, R)-g** and *rac-g*.

Gelation tests were carried out using an upside-down test-tube method. The gelation was considered successful when, upon inversion, there was no fluid running down the walls of the tube. The results of the gelation tests with 7 solvents are summarized in Table 1. It is clear that **(R, R)-g** is the best gelator, as it could gel all 7 solvents at concentrations less than ~1 wt%. The compound *rac-g* was able to gel isopropyl myristate, hexadecyl 2-ethylhexanoate (HDEH), liquid paraffin, silicone oil (KF-54), and decamethylcyclopentasiloxane (D5), but separated as crystals in ethyl acetate. The crystallization of *rac-g* from ethyl acetate may be explained by Wallach's rule;^{32,33} namely, a racemic crystal tends to be denser than its chiral counterpart, and the former is more stable than the latter. The gelation ability of **(R, R)-g/Si** was comparable to that of **(R, R)-g**, but the minimum gel concentrations of **(R, R)-g/Si** were somewhat larger than those of **(R, R)-g**. The high gelation ability of **(R, R)-g/Si** demonstrates that the octamethyltetrasiloxane segment in **(R, R)-g/Si** can neither participate in hydrogen bonding nor interrupt aggregation during physical gelation. On the contrary, *rac-g/Si* failed to gel almost all solvents except for isopropyl myristate and HDEH. The compound *rac-g/Si* formed highly viscous solutions in liquid paraffin and KF-54 instead of gels. The formation of a viscous solution or a partial gel by *rac-g/Si* can be explained by the presumption that the racemic gelation-driving segment will arrest the growth of

aggregates suitable for three-dimensional networks. We concluded that the order of gelation ability is $(R, R)\text{-g} \approx (R, R)\text{-g/Si} > \text{rac-g} \gg \text{rac-g/Si}$.

We then noticed a relationship between the transparency of gels and the refractive indices of solvents. The refractive indices of 7 solvents are shown in parentheses for solvents in Table 1. Needless to say, $(R, R)\text{-g}$, rac-g , $(R, R)\text{-g/Si}$, and rac-g/Si have no large absorption in the visible light region. From the analogy that the refractive indices of the present diamides are in the range of 1.5–1.6, the formation of transparent gels in toluene, liquid paraffin, and KF-54 is reasonable. The refractive index of the obtained compound will correspond to what is expected if the attachment of octamethyltetrasiloxane segment with a low refractive index to gelation-driving segments decreases the refractive index of the compound. However, our strategy, involving the attachment of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane with a low refractive index (1.3) to gelation-driving segments to decrease the refractive index, seems to fail, because $(R, R)\text{-g/Si}$ still formed translucent gels with ethyl acetate and HDEH. Although the successful preparation of isorefractive high-internal-phase emulsion organogels were reported,³⁴ the present idea for the achievement of refractive-index-matched gels by controlling the refractive index of gelators seems to be impractical, because the refractive indices of fluids are spread across a wide range; for instance, 1.329 for methanol compared to 1.737 for diiodomethane. As the next strategy for the achievement of transparent gels, we expected a reduced light scattering effect as a result of the attachment of a 1,1,3,3,5,5,7,7-octamethyltetrasiloxane fragment, which will prevent aggregate growth due to its flexibility. Consequently, the flexibility will result in three-dimensional networks with a size of less than the wavelength of visible light. The transparency of gels of $(R, R)\text{-g}$, rac-g , $(R, R)\text{-g/Si}$, and rac-g/Si was investigated using 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. Forming transparent gels is widely desirable from a practical perspective. We evaluated the transparency of gels by UV-vis spectroscopy. Figure 1a shows photos of aspects of transparent gels of **(R, R)-g** and **(R, R)-g/Si**, a translucent gel of **rac-g**, and a viscous solution of **rac-g/Si** in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3). Their transmittance is shown in Figure 1b. The transmittances at 400 nm of gels of **(R, R)-g/Si**, **(R, R)-g**, **rac-g**, and **rac-g/Si** at a concentration of 10 mg ml⁻¹ were 85, 81, 53, and 21%, respectively. The order of transparency of gels over the total wavelength band is **(R, R)-g/Si** > **(R, R)-g** >> **rac-g** >> **rac-g/Si**. The transparency of the gels is thought to depend on the size of aggregates building up three-dimensional networks responsible for 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. Since the octamethyltetrasiloxane segment in **(R, R)-g/Si** will hinder the growth of aggregates that scatter visible light, **(R, R)-g/Si** can form a transparent gel. The introduction of gelation-driving segments into oligo(dimethylsiloxane)s will be useful for developing gelators to form transparent gels.

The gelation behavior of **(R, R)-g**, **rac-g**, **(R, R)-g/Si**, and **rac-g/Si** was investigated in the mixed solvents (66 combinations, with weight ratios ranging from 10:0:0 to 0:0:10 of HDEH, liquid paraffin, and D5) (Figure 2), where the concentrations were fixed at 10 mg ml⁻¹ (gelator/solvent). It was found that **(R, R)-g**, **rac-g**, and **(R, R)-g/Si** could form gels with all these mixed solvent combinations (Figure 2a, b, c). In particular, **(R, R)-g/Si** could form transparent gels in the high-ratio region of liquid paraffin. Meanwhile, **rac-g/Si** formed highly viscous solutions in the region containing a high ratio of HDEH, gave precipitates in mixed solvents including a large amount of D5, and formed partial gels in

the other regions (Figure 2d). The effect of the octamethyltetrasiloxane segment on the formation of semi-permanent stable gels was unclear in the present study. Since the gels formed with **(R, R)-g** were so stable that they did not change into crystals even after one year, we could not evaluate the contribution of the octamethyltetrasiloxane segment in **(R, R)-g/Si** to the formation of semi-permanent stable gels. It is noteworthy that the significance of polysiloxane, polyether, and polycarbonate segments, with respect to the formation of semi-permanent stable gels, was mentioned in the literature.³⁵

Gel-to-sol phase-transition and gel strength

The phase-transition temperatures of the gels formed in the mixed solvents of HDEH, liquid paraffin, and D5 (66 combinations) were investigated (Figure 3). The concentrations of **(R, R)-g**, **rac-g**, and **(R, R)-g/Si** were fixed at 10 mg ml⁻¹. The greatest thermal stability was observed for gels formed with **(R, R)-g**; their phase-transition temperatures for gel to sol were within 75–94°C in the region containing a high ratio of HDEH and 95–110°C in the region containing a low ratio of HDEH (Figure 3a). The second group of thermally stable gels was formed with **(R, R)-g/Si** (Figure 3b). Regarding **rac-g**, if the content of D5 increased in the mixed solvents, the phase-transition temperatures decreased in the region of 31–49°C and were within 65–80°C in the region containing a low ratio of D5 (Figure 3c). The phase-transition temperatures of **rac-g/Si** were not shown, because **rac-g/Si** formed highly viscous solutions, rather than thermally-weak gels.

The gel strength, which is an important factor in the application of gels, will be evaluated by measuring the elastic storage modulus G' and loss modulus G'' values in the following discussion. However, here, we evaluated gel strengths as the power necessary to sink a cylindrical bar (10 mm in diameter) 4 mm deep in the gels. The gel strengths of

the gels formed in the mixed solvents of HDEH, liquid paraffin, and D5 (66 combinations) are shown in Figure 4, where the concentrations of compounds were fixed at 10 mg ml⁻¹. The greatest gel strength was observed for gels formed with **(R, R)-g** (Figure 4a); in particular, hard gels having strengths of more than 100 g cm⁻² were formed around three corners, in which the mixed solvents included a large amount of one component. The gel strengths of gels formed with **(R, R)-g/Si** were in the region of 51 to 100 g cm⁻² (Figure 4b). Weak gels with strengths of less than 60 g cm⁻² were formed with *rac-g* (Figure 4c). Considering that the order of gel strength is **(R, R)-g** > **(R, R)-g/Si** > *rac-g*, their strengths seem to be parallel to the gel-to-sol phase-transition temperatures.

Rheology

The viscoelastic behavior of the gels was studied by rheology measurements in strain sweep mode and frequency sweep mode (Figures S1, S2, S3, and S4). The solvent used for the rheology measurements was a mixture of HDEH, liquid paraffin, and D5 (vol. ratio 4:3:3), and the concentrations were fixed at 20 mg ml⁻¹. Regarding this aspect of gels, we already mentioned that **(R, R)-g** and **(R, R)-g/Si** formed transparent gels, *rac-g* formed a translucent gel, and *rac-g/Si* gave a partial one. From the results in strain sweep mode, the storage elastic moduli (G') of **(R, R)-g** and *rac-g* at a strain of 0.02 were under approximately 8163 and 5002 Pa, respectively. At a strain of 0.07, the loss elastic moduli (G'') of the gels of **(R, R)-g** exceeded the G' and the gels collapsed. On the other hand, the gels formed with *rac-g* collapsed at a strain of 1.0. In frequency sweep mode, the plateau regions were observed in all gels up to 0.3 Hz. A comparison of **(R, R)-g** and *rac-g* in the plateau region of frequency sweep mode indicated that the G_{Ave}' values of **(R, R)-g** were 1.3 times as large as those of *rac-g*. Moreover, though the G'' values of *rac-g* exceeded the G' at 5 Hz, the G' values of **(R, R)-g** were greater than the G'' values, even

at 5 Hz. It is clear that the gel of **(R, R)-g** is harder than that of *rac-g*.

The rheology measurements of **(R, R)-g/Si** and *rac-g/Si* are shown in Figures S3 and S4. The relationship between the viscoelastic behaviors of **(R, R)-g/Si** and *rac-g/Si* was similar to the relationship between those of **(R, R)-g** and *rac-g*. Namely, the G' (5745 Pa, $\gamma = 0.02$) of **(R, R)-g/Si** was greater than that (2036 Pa, $\gamma = 0.02$) of *rac-g/Si*. A comparison of **(R, R)-g/Si** and *rac-g/Si* in the plateau region of frequency sweep mode also indicated that the G_{Ave}' values of **(R, R)-g/Si** were about 7 times as large as those of *rac-g/Si*. It can be said that the gel formed by *rac-g/Si* was the softest in four gelators in this study.

The viscoelastic behavior of *rac-g/Si* in strain sweep mode was different from that of *rac-g* (Figure S2 and S4). The G' and G'' values *rac-g/Si* in the strain sweep mode decreased with increasing strain amplitude, suggesting that the network structures of gels are partially broken due to a large deformation (Figure S4a). The difference of viscoelastic behavior between *rac-g* and *rac-g/Si* was also recognized in the gelation test by an upside-down test-tube method; the gel of *rac-g* did not collapse when the upside-down test tube was tapped lightly; on the contrary, the gel of *rac-g/Si* tumbled down when the tube was tapped lightly. Moreover, the gel strengths of *rac-g* and *rac-g/Si* at 10 mg ml⁻¹ were 38 g cm⁻² and 4.7 g cm⁻², respectively. The 1,1,3,3,5,5,7,7-octamethyltetrasiloxane segment in *rac-g/Si* considerably decreased the gel strength and the G' as compared to in *rac-g*.

TEM observation

The transparency and rheology behavior of the formed gels depended on the chirality of the gelators and the existence of the octamethyltetrasiloxane segment. It is assumed that the properties of gels will be a function of the shape and size of aggregates forming three-dimensional networks. TEM images of loose gels formed with **(R, R)-g**, *rac-g*, **(R, R)-g/Si**, and *rac-g/Si* were obtained (Figure 5). The solvent was a mixture of HDEH, liquid

paraffin, and D5 (vol. ratio 4:3:3), and the concentrations of gelators used to prepare the TEM samples were 2 mg ml^{-1} for **(R, R)-g** and *rac-g* and 1 mg ml^{-1} for **(R, R)-g/Si** and *rac-g/Si*. The image of **(R, R)-g** shows fine thread-like aggregates with nearly homogeneous diameters of approximately 30 nm (Figure 5a), in which a gathering of numerous fibers, juxtaposed and intertwined with the fine thread-like aggregates, was observed. By contrast, the widths of fibers in *rac-g* ranged from approximately 60 nm (Figure 5b), which is larger than the widths of the fibers in **(R, R)-g**. Low-transparency gels of *rac-g* will be formed by the thick aggregates. The image of **(R, R)-g/Si** (Figure 5c) is characterized by fine thread-like aggregates with homogeneous diameters of approximately 20 nm, where no gathering knot was observed. The concentrations for preparing TEM samples were considerably lower than the minimum gel concentrations, so that the images in Figure 5 show the fibers of loose gels before actual gelation. However, the homogeneous fine aggregates without gathering knots will result in high-transparency of gels of **(R, R)-g/Si**; namely, the flexibility of the 1,1,3,3,5,5,7,7-octamethyltetrasiloxane fragment will result in homogeneous three-dimensional networks with less light scattering. The image of *rac-g/Si* was characterized by a gathering of short aggregates and the width of fibers was approximately 50 nm (Figure 5d). The low gelation ability of *rac-g/Si* may be explained by the gathering of short aggregates. The present TEM images demonstrate that the fibers of the racemates are thicker than those of the enantiomers. The octamethyltetrasiloxane segment in *rac-g/Si* probably increases the solvophilic character; consequently, the interaction among the molecules is so weak that they fail to form fibrous aggregates. The poor gelation ability and low gel strength of *rac-g/Si* will be explained by the short aggregates resulting from the weak interaction.

CD spectra

To confirm the helical aggregates of **(R, R)-g** and **(R, R)-g/Si**, which we failed to detect in the TEM images (Figure 2a and 2b), we recorded the CD spectra of the gels. The solvent for CD spectroscopy was a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3), and the concentrations of all the prepared samples were 10 mg ml⁻¹. The spectra of **(R, R)-g** and *rac-g* are shown in Figure 6a and those of **(R, R)-g/Si** and *rac-g/Si* are shown in Figure 6b. The CD spectrum of the loose gel of **(R, R)-g** at 25°C exhibited a markedly strong peak for the amide unit: $[\theta]_{210}$ = approximately 150 mdeg. The intensity of this peak decreased with increasing temperature and disappeared at 50°C; at that time, the loose gel of **(R, R)-g** was transformed into an isotropic solution. The disappearance of the CD signal in the isotropic solution led us to conclude that the strong CD band originates from helical aggregates of **(R, R)-g** and not from the chirality of **(R, R)-g** itself.³⁶ The strong CD band supports the existence of helical aggregates in the gels of **(R, R)-g**. In the case of **(R, R)-g/Si** at 25°C, the spectrum exhibited a strong peak for the amide unit: $[\theta]_{210}$ = approximately 70 mdeg. The intensity of this peak also decreased with increasing temperature and disappeared at 50°C, when the loose gel of **(R, R)-g/Si** was transformed into an isotropic solution. The fact that the $[\theta]_{210}$ of **(R, R)-g/Si** was slightly smaller than that of **(R, R)-g** is explained by the presumption that the octamethyltetrasiloxane segment in **(R, R)-g/Si** partially arrests the growth of helical aggregates.

CONCLUSION

We prepared four gelators based on *trans*-1,2-diaminocyclohexane; the initial two gelators contain structurally different substituents, one being chiral and one racemic. The

others are 1,1,3,3,5,5,7,7-octamethyltetrasiloxane-containing chiral and racemic gelators prepared by hydrosilylation reactions. The results of gelation tests with 7 solvents demonstrated that the order of gelation ability to form stable gels is $(R, R)\text{-g} \approx (R, R)\text{-g/Si} > \text{rac-g} \gg \text{rac-g/Si}$. In particular, $(R, R)\text{-g}$ is the best gelator, gelling all 7 solvents at concentrations less than approximately 1 wt%. The gelation behavior was investigated using three-component mixed solvents of HDEH, liquid paraffin, and D5 (66 combinations). The order of transparency of gels over the total wavelength band was $(R, R)\text{-g/Si} > (R, R)\text{-g} \gg \text{rac-g} \gg \text{rac-g/Si}$. The thermal stabilities of the gels were evaluated on the basis of their phase-transition temperatures. The highest thermal stability was observed for gels formed with $(R, R)\text{-g}$, and the second most thermally stable gels were formed with $(R, R)\text{-g/Si}$. The order of gel strength in the mixed solvents was $(R, R)\text{-g} > (R, R)\text{-g/Si} > \text{rac-g}$, which was consistent with that of the gel-to-sol phase-transition temperatures. The G' values of $(R, R)\text{-g}$ were about ten times as large as those of rac-g . The rheological results for $(R, R)\text{-g/Si}$ and rac-g/Si showed a similar trend in their viscoelastic behavior to the relation between $(R, R)\text{-g}$ and rac-g . A TEM image of $(R, R)\text{-g}$ shows fine thread-like aggregates with nearly homogeneous diameters of approximately 30 nm, in which a gathering knot of numerous fibers was observed. The image of $(R, R)\text{-g/Si}$ is characterized by fine thread-like aggregates with homogeneous diameters of approximately 20 nm without gathering knots. The solvophilic octamethyltetrasiloxane segment in rac-g/Si weakens the interaction among the molecules; consequently, they fail to form fibrous aggregates. The CD spectrum of the loose gel of $(R, R)\text{-g}$ at 25°C exhibited a markedly strong peak for the amide unit, supporting the existence of helical aggregates in the gels of $(R, R)\text{-g}$. The $[\theta]_{210}$ of $(R, R)\text{-g/Si}$ was smaller than that of $(R, R)\text{-g}$, suggesting that the octamethyltetrasiloxane segment in $(R, R)\text{-g/Si}$ slightly arrests

the growth of helical aggregates.

SUPPORTING INFORMATION

Figure S1, Figure S2, Figure S3, and Figure S4

ACKNOWLEDGEMENTS

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1 Almdal, K., Dyre, J., Hvidt, S. & Kramer, O. Towards a phenomenological definition of the term 'gel', *Polym. Gels Networks* **1**, 5-17 (1993).

2 Addad, J. P. C. Physical properties of polymeric gels (Chichester: John Wiley, 1996).

3 Salamone, J. C. Polymeric materials encyclopedia, Vol. 4, 2728-2755 (Boca Raton; Tokyo: CRC Press, 1996).

4 DeRossi, D. Polymer gels: fundamentals and biomedical applications (New York: Plenum Press, 1991).

5 Dickie, R. A., Labana, S. S. & Bauer, R. S. Cross-linked polymers: chemistry, properties, and applications, (Washington, DC: American Chemical Society, 1988).

6 Okumura, Y. & Ito, K. The polyrotaxane gel: A topological gel by figure-of-eight cross-links, *Adv. Mater.* **13**, 485-490 (2001).

7 Li, J., Harada, A. & Kamachi, M. Sol-gel transition during inclusion complex-formation between alpha-cyclodextrin and high-molecular-weight poly(ethylene glycol)s in aqueous-solution, *Polym. J.* **26**, 1019-1026 (1994).

- 8 Watanabe, J., Ooya, T. & Yui, N. Feasibility study of hydrolyzable polyrotaxanes aiming at implantable materials, *J. Artif. Organs* **3**, 136-142 (2002).
- 9 Oku, T., Furusho, Y. & Takata, T. A concept for recyclable cross-linked polymers: Topologically networked polyrotaxane capable of undergoing reversible assembly and disassembly, *Angew. Chem., Int. Ed.* **43**, 966-969 (2004).
- 10 Burchard, W. & Ross-Murphy, S. B. *PHYSICAL NETWORKS Polymers and Gels*, (London and New York: Elsevier Applied Science, 1990).
- 11 Tachibana, T. Mori, T. & Hori, K. Chiral mesophases of 12-hydroxyoctadecanoic acid in jelly and in the solid state. I. A new type of lyotropic mesophase in jelly with organic solvents, *Bull. Chem. Soc. Jpn.* **53**, 1714-1719 (1980).
- 12 Terech, P. & Wade, R. H. The relationship between a dried and native steroid gel, *J. Colloid Interface Sci.* **125**, 542-551 (1988).
- 13 Lin, Y., Kachar, B. & Weiss, R. G. Novel family of gelators of organic fluids and the structure of their gels, *J. Am. Chem. Soc.* **111**, 5542-5551 (1989).
- 14 Terech, P. & Weiss, R. G. Low molecular mass gelators of organic liquids and the properties of their gels. *Chem. Rev.* **97**, 3133-3159 (1997).
- 15 van Esch, J. H. & Feringa, B. L. New functional materials based on self-assembling organogels: From serendipity towards design. *Angew. Chem. Int. Ed.* **39**, 2263-2266 (2000).
- 16 Estroff, L. A. & Hamilton, A. D. Water gelation by small organic molecules. *Chem. Rev.* **104**, 1201-1217 (2004).
- 17 Suzuki, M. & Hanabusa, K. L-Lysine-based low-molecular-weight gelators. *Chem. Soc. Rev.* **38**, 967-975 (2009).
- 18 John, G., Shankar, B. V., Jadhav, S. R. & Vemula, P. K. Biorefinery: A Design Tool for Molecular Gelators. *Langmuir* **26**, 17843-17851 (2010).

- 19 Svobodová, H., Noponen, V., Kolehmainen, E. & Sievänen, E. Recent advances in steroidal supramolecular gels. *RSC Advances* **2**, 4985–5007 (2012).
- 20 Raeburn, J., Cardoso, A. Z. & Adams, D. J. The importance of the self-assembly process to control mechanical properties of low molecular weight hydrogels. *Chem. Soc. Rev.* **42**, 5143-5156 (2013).
- 21 Yu, G., Yan, X., Han C. & Huang, F. Characterization of supramolecular gels. *Chem. Soc. Rev.* **42**, 6697-6722 (2013).
- 22 Segarra-Maset, M. D., Nebot, V. J. Miravet, J. F. & Escuder, B. Control of molecular gelation by chemical stimuli. *Chem. Soc. Rev.* **42**, 7086-7098 (2013).
- 23 Hanabusa, K. Development of low-molecular-weight gelators and polymer-based gelators, *Polym. J.* **46**, 776-782 (2014).
- 24 Babu, S. S., Praveen, V. K. & Ajayaghosh, A. Functional pi-gelators and their applications, *Chem. Rev.* **114**, 1973-2129 (2014).
- 25 Kumar, D. K. & Steed, J. W. Supramolecular gel phase crystallization: orthogonal self-assembly under non-equilibrium conditions, *Chem. Soc. Rev.* **43**, 2080-2088 (2014).
- 26 Lan, Y., Corradini M. G., Weiss, R. G., Raghavanc, S. R. & Rogers, M. A. To gel or not to gel: correlating molecular gelation with solvent parameters, *Chem. Soc. Rev.* **44**, 6035-6058 (2015).
- 27 Kubo, W., Kitamura T., Hanabusa, K., Wada, Y. & Yanagida, S. Quasi-solid-state dye-sensitized solar cells using room temperature molten salts and a low molecular weight gelator, *Chem. Commun.* **4**, 374-375 (2002).
- 28 Kubo, W., Kambe, S., Nakade, S., Kitamura T., Hanabusa, K., Wada, Y. & Yanagida, S. Photocurrent-determining processes in quasi-solid-state dye-sensitized solar cells using ionic gel electrolytes, *J. Phys. Chem. B* **107**, 4374-4381 (2003).
- 29 Qin, L., Duan, P., Xie, F., Zhang, L., Liu, M. A metal ion triggered shrinkable supramolecular hydrogel and controlled release by an amphiphilic peptide dendron, *Chem. Commun.* **49**, 10823-10825 (2013).

- 30 Katsube, S., Kinoshita, M., Amano, K., Sato, T., Katsumoto, Y., Umecky, T., Takamura, T., Kaji, T., Hiramoto, M., Tsurunaga, Y., Nishiyama, K. Solvent-dependent properties and higher-order structures of aryl alcohol + surfactant molecular gels, *Langmuir* **32**, 4352-4360 (2016).
- 31 Nakagawa, H., Fujiki, M., Sato, T., Suzuki, M., Hanabusa, K. Characteristics of gelation by amides based on *trans*-1,2-diaminocyclohexane: The importance of different substituents, *J. Colloid & Interface Sci.* in contribution.
- 32 Wallach, O. *Justus Liebigs Ann. Chem.* **286**, 90-143 (1895).
- 33 Brock, C. P., Schweizer, W. B., Dunitz, J. D. On the validity of Wallach's rule: on the density and stability of racemic crystals compared with their chiral counterparts, *J. Am. Chem. Soc.* **113**, 9811-9820 (1991).
- 34 Zhang, T., Guo, Q. Isorefractive high internal phase organogels for light induced reactions, *Chem. Commun.* **52**, 4561-4564 (2016).
- 35 Hanabusa, K., Suzuki, M. Development of low molecular weight gelators and polymer-based gelators, *Polym. J.* **46**, 776-782 (2014).
- 36 Hanabusa, K., Yamada, M., Kimura, M., Shirai, H. Prominent gelation and chiral aggregation of alkylamides derived from *trans*-1,2-diaminocyclohexane, *Angew. Chem., Int. Ed.* **35**, 1949-1951 (1996).

Figure Captions

Scheme 1 Preparation of **(R, R)-g**, **rac-g**, **(R, R)-g/Si**, and **rac-g/Si**.

Figure 1 Photos of gels (a) and transmittance of gels in UV-visible region (b).

A mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3) was used as a solvent. The concentration was 10 mg ml⁻¹.

Figure 2 Aspects of gels of (a) **(R, R)-g**, (b) *rac-g*, (c) **(R, R)-g/Si**, and (d) *rac-g/Si* in a mixed solvent of HDEH, liquid paraffin, and D5 at concentration of 10 mg ml⁻¹.

Figure 3 Gel-to-sol temperatures in a mixture of HDEH, liquid paraffin, and D5 at 10 mg mL⁻¹; (a) **(R, R)-g**, (b) *rac-g*, and (c) **(R, R)-g/Si**.

Figure 4 Gel strengths of gels prepared from (a) **(R, R)-g**, (b) *rac-g*, and (c) **(R, R)-g/Si**.

A mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3) was used as a solvent. The concentration was 10 mg ml⁻¹.

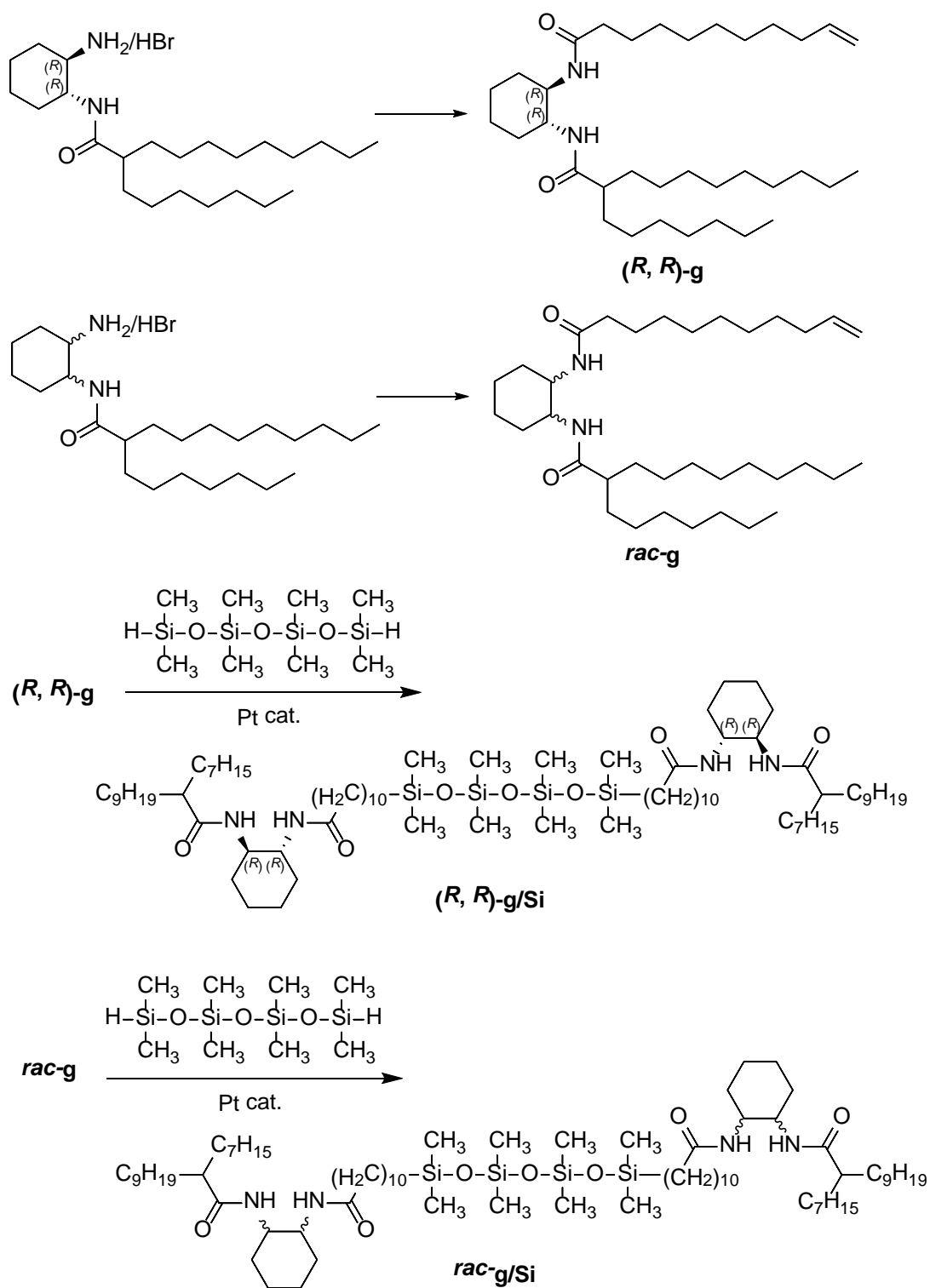
Figure 5 TEM images of gels prepared from (a) **(R, R)-g** (2 mg ml⁻¹), (b) *rac-g* (2 mg ml⁻¹), (c) **(R, R)-g/Si** (1 mg ml⁻¹), and (d) *rac-g/Si* (1 mg ml⁻¹) in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3).

Figure 6 Circular dichroism spectra. (a); **(R, R)-g** and *rac-g*, (b); **(R, R)-g/Si** and *rac-g/Si*. Sol and gel were prepared from chloroform and a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3), respectively. The concentrations were 10 mg ml⁻¹.

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

Solvents (refractive index)	(R, R)-g	rac-g	(R, R)-g/Si	rac-g/Si
Ethyl acetate (1.37)	GTL(8)	P	GTL(10)	P
Isopropyl myristate (1.43)	GTL(4)	GTL(8)	GT(8)	GTL(40)
HDEH (1.45)	GTL(10)	GTL(10)	GTL(10)	GTL(40)
Toluene (1.49)	GT(20)	PG	GT(40)	PG
Liquid paraffin (1.48)	GT(8)	GT(10)	GT(8)	VS
Silicone oil; KF-54 (1.51)	GT(2)	GT(2)	GT(4)	VS
D5 (1.40)	GTL(4)	GTL(10)	GTL(10)	P

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



Scheme 1 Preparation of $(R, R)\text{-g}$, $rac\text{-g}$, $(R, R)\text{-g/Si}$, and $rac\text{-g/Si}$.

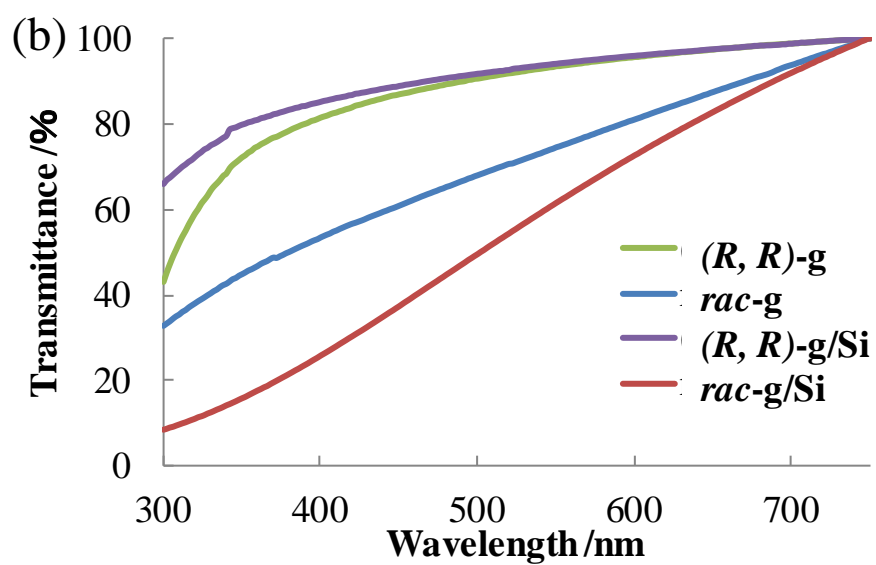
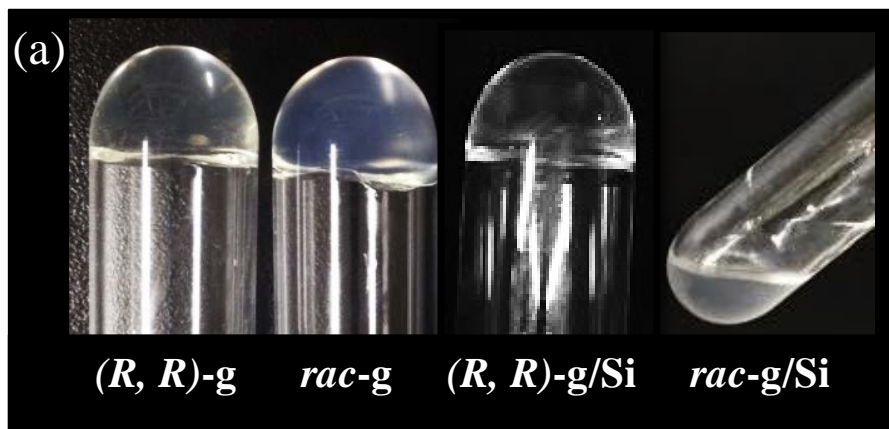


Figure 1 Photos of gels (a) and transmittance of gels in UV-visible region (b).

A mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3) was used as a solvent. The concentration was 10 mg ml^{-1} .

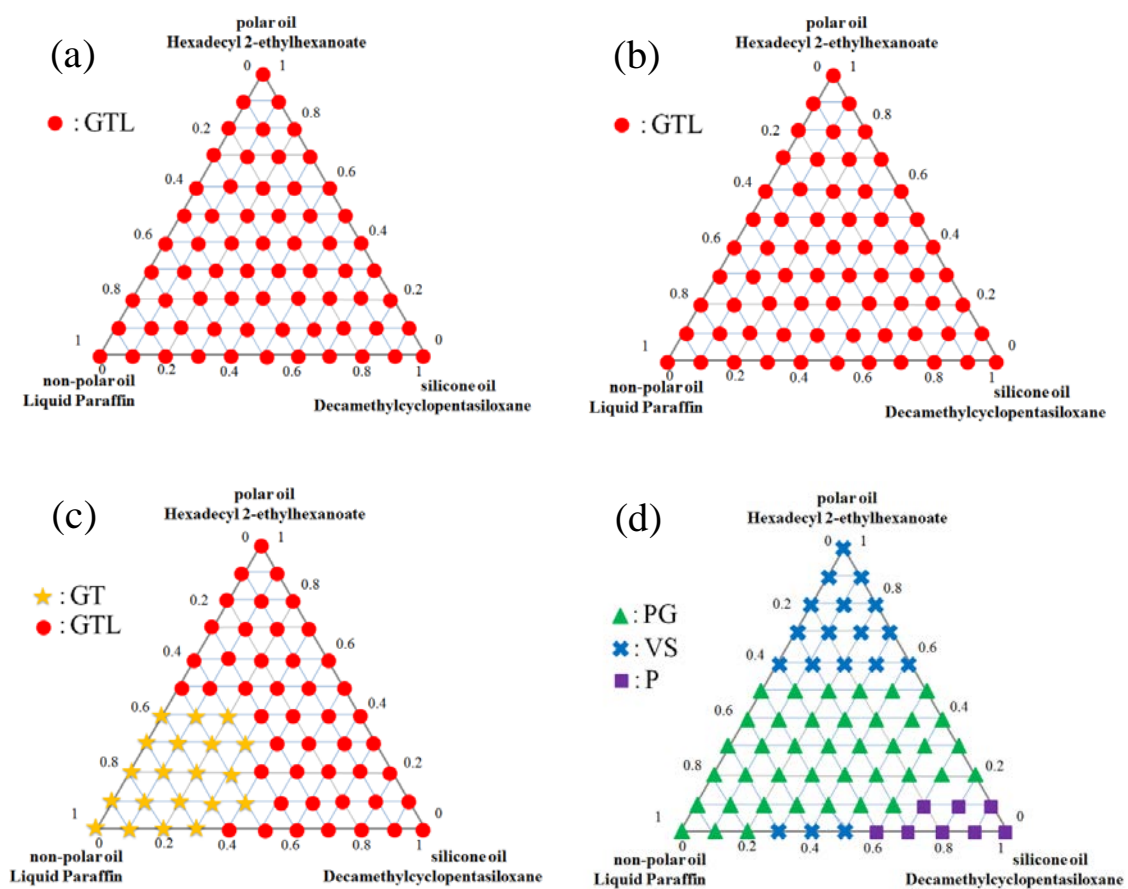


Figure 2 Aspects of gels of (a) (*R, R*)-g, (b) *rac*-g, (c) (*R, R*)-g/Si, and (d) *rac*-g/Si in a mixed solvent of HDEH, liquid paraffin, and D5 at concentration of 10 mg ml^{-1} .

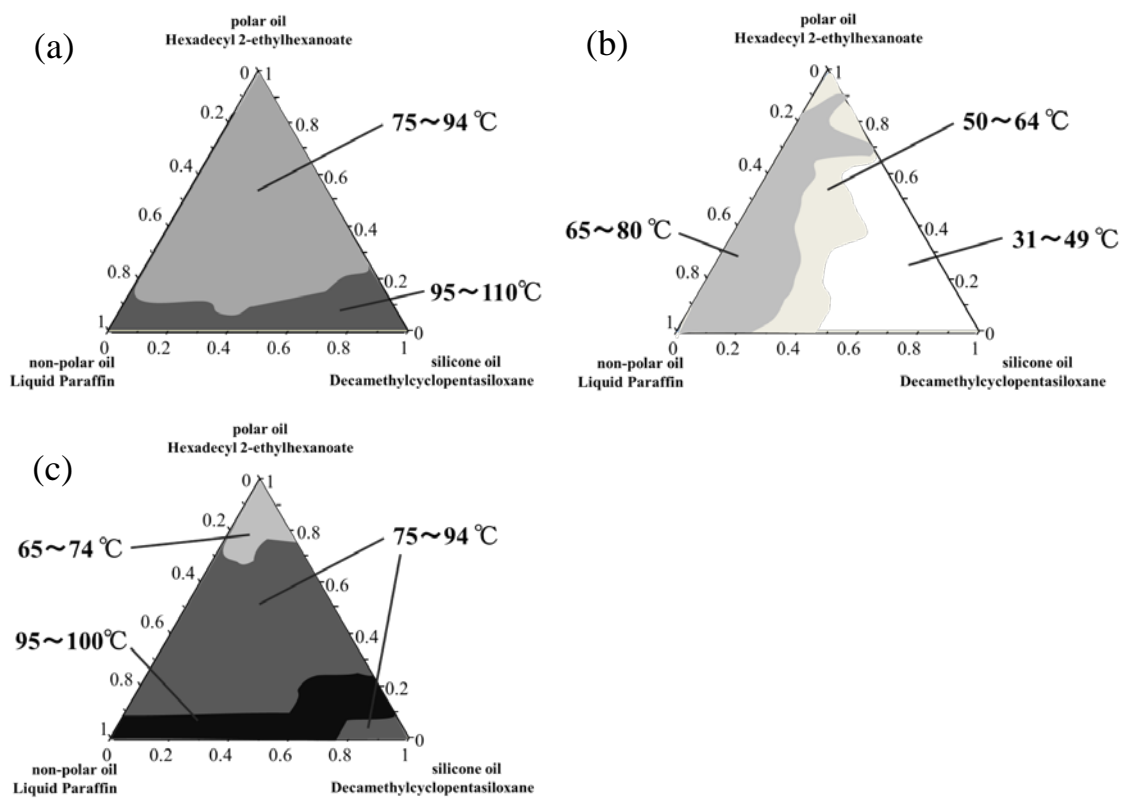


Figure 3 Gel-to-sol temperatures in a mixture of HDEH, liquid paraffin, and D5 at 10 mg mL⁻¹; (a) *(R, R)*-g, (b) *rac*-g, and (c) *(R, R)*-g/Si.

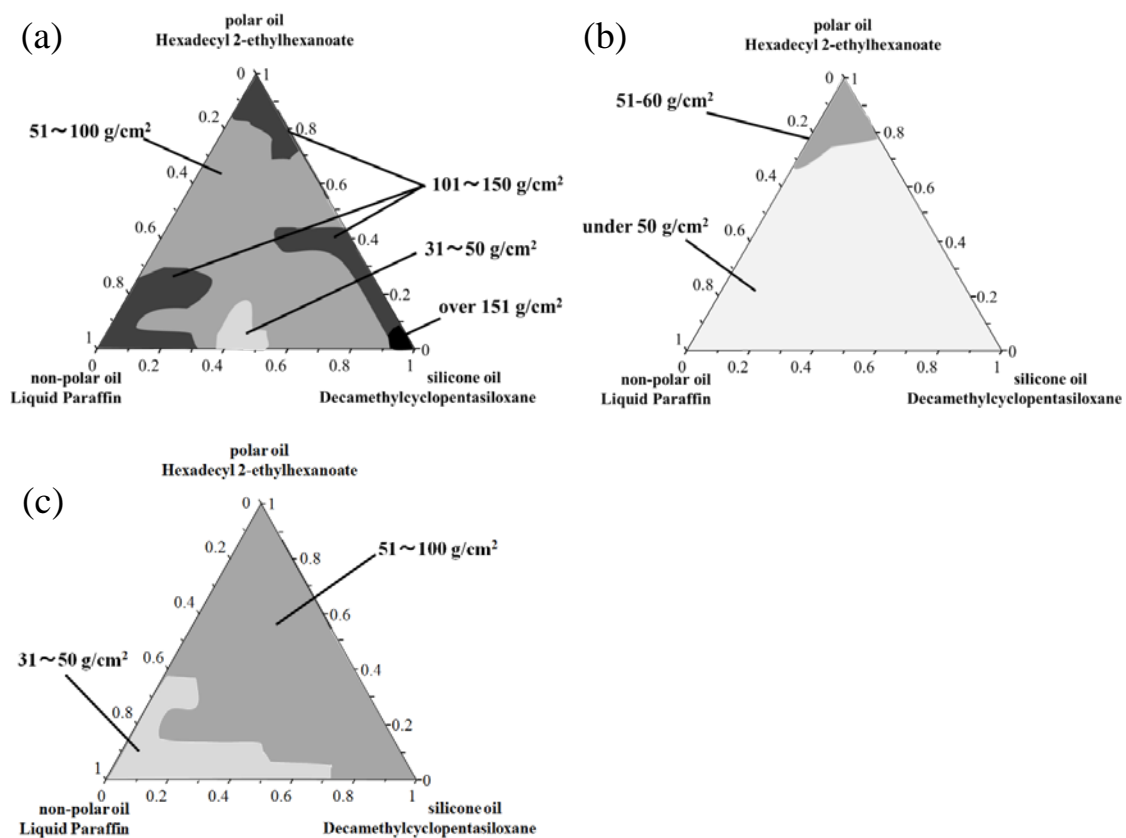


Figure 4 Gel strengths of gels prepared from (a) **(R, R)-g**, (b) **rac-g**, and (c) **(R, R)-g/Si**. A mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3) was used as a solvent. The concentration was 10 mg ml⁻¹.

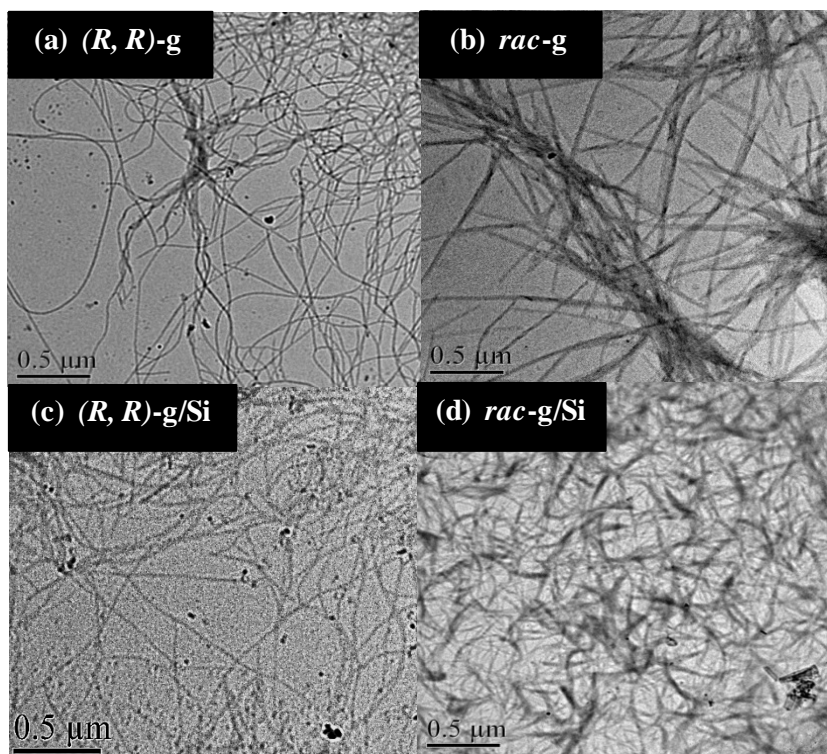


Figure 5 TEM images of gels prepared from (a) **(R, R)-g** (2 mg ml^{-1}), (b) **rac-g** (2 mg ml^{-1}), (c) **(R, R)-g/Si** (1 mg ml^{-1}), and (d) **rac-g/Si** (1 mg ml^{-1}) in a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3).

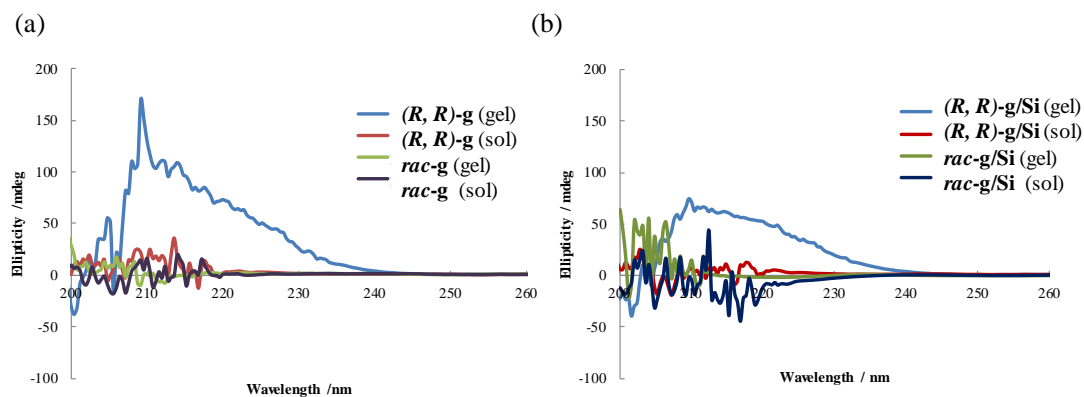
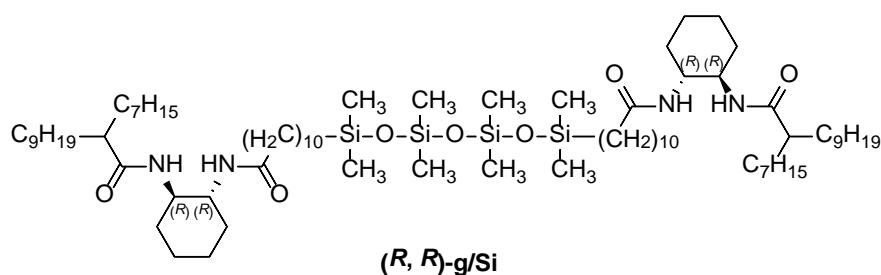


Figure 6 Circular dichroism spectra.

(a); (R,R) -g and rac -g, (b); (R,R) -g/Si and rac -g/Si.

Sol and gel were prepared from chloroform and a mixture of HDEH, liquid paraffin, and D5 (vol. ratio; 4:3:3), respectively. The concentrations were 10 mg ml^{-1} .

Graphical Abstract



The 1,1,3,3,5,5,7,7-octamethyltetrasiloxane-containing gelator, **(R, R)-g/Si**, was synthesized by a hydrosilylation with a gelation-driving segment based on *trans*-(1*R*, 2*R*)-1,2-diaminocyclohexane. Gelation abilities were investigated in the mixed solvents of HDEH, liquid paraffin, and D5. **(R, R)-g/Si** could form stable and transparent gels due to the flexible octamethyltetrasiloxane segment.