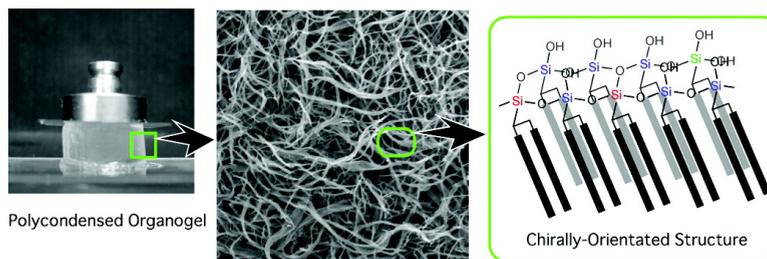


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# Polycondensation and Stabilization of Chirally Ordered Molecular Organogels Derived from Alkoxysilyl Group-Containing L-Glutamide Lipid<sup>†</sup>

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A lipophilic L-glutamide-derived lipid with a triethoxysilyl headgroup (Si-lipid) was newly synthesized as a self-assembling organogelator to stabilize the chirally ordered state of the aggregates. The Si-lipid formed nanofibrous network structures in various organic solvents such as benzene, cyclohexane, and dimethylformamide and entrapped them to form gels. The gels were transformed to sols by heat, and this gel-to-sol transition was thermally reversible. Polycondensation of the triethoxysilyl groups was carried out by acid-catalyzed hydrolysis and condensation in a benzene gel and confirmed by <sup>29</sup>Si CP/MAS NMR and FT-IR measurements. After polycondensation, a gel state was maintained, and the thermal and mechanical stabilities of the aggregates increased markedly. Interestingly, polycondensation in chloroform and acetonitrile induced gelation, whereas no gelation was observed before polycondensation. Xerogel, which was prepared by freeze drying organogels, had fibrous network structures similar to those of the original gels. A strong CD signal was observed around the amide bonds in a cyclohexane gel at 20 °C, indicating that the gel contained chirally oriented structures based on intermolecular hydrogen bonds. An enhanced CD signal was observed even after polycondensation of the ethoxysilyl group of Si-lipid (poly(Si-lipid)) and was maintained at 70 °C, which is above the temperature of the gel-to-sol phase transition of the original gel. These results indicate that the formation of siloxane network structure among the fibrous aggregates stabilizes the chiral orientation of lipid aggregates.

## Introduction

Self-assembled organogels<sup>1</sup> have been recognized as promising materials for bottom-up nanofabrication tools in various fields such as medical, biological, environmental, and industrial sciences. The most successful examples are inorganic<sup>2</sup> and organic<sup>3</sup> nanomaterials with unique shapes prepared using nanofibrillar structures as templates. Creative techniques for nanofabrication using various template materials have been reported for not only self-assembled organo-

gels but also various organic compounds such as synthetic polymers,<sup>4</sup> carbon nanotubes,<sup>5</sup> and biomaterials.<sup>6</sup> In addition, possible improvements in the thermal and mechanical stabilization of self-assembled organogels have been investigated. Self-assembled organogels differ from polymer network gels in that the low-molecular-weight molecules form network structures through aggregation by extensive intermolecular interactions such as hydrogen bonding, van der Waals forces, and  $\pi$ - $\pi$  interactions.<sup>1</sup> Feringa et al.<sup>7</sup> and Hamilton et al.<sup>8</sup> reported that the morphologies of fibrous aggregates were maintained after photoinduced polymerization by UV-light irradiation of the methacrylate-group-attached organogel-forming molecules. The polymerized organogel formations had improved thermal stability. It is possible to use a sorbyl group<sup>9</sup> or diacetylenyl group<sup>10</sup> as a photoinitiated polymerizable group without any photoinduced radical initiator. Shinkai et al. reported that alkoxysilyl-group-attached porphyrin derivatives formed organogels with and without copper ions and their thermal

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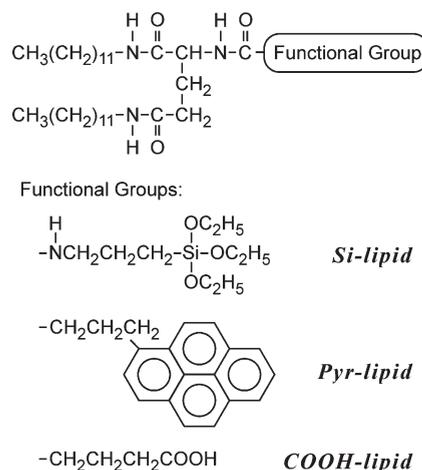
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and mechanical stabilities were improved by the polycondensation of alkoxyethyl groups.<sup>11</sup> The addition of cross-linking compounds to reactive organogels also obtains a robust organogel. A hybrid system of glucosamine-based organogels and diisocyanate cross-linker was reported by Shinkai et al.<sup>12</sup> Host–guest interaction is useful for increasing the thermal stability of organogels. Jung et al. reported that the stabilization of the crown-ether-based organogel was achieved in the presence of a bipyridinium-based ion as a guest molecule.<sup>13</sup> Other examples were presented in a review article.<sup>14</sup> Chiral orientation is important for the formation of fibrillar aggregates in self-assembled organogels. Therefore, circular dichroism (CD) spectroscopy is useful for evaluating the orientational structure of the aggregates. In general, a remarkable decrease in the strength of the CD signal is observed above the gel-to-sol phase-transition temperature because of the disorientation of organogelators. Ishii et al. reported that an enhanced CD spectrum was obtained from the organogel produced from Zn(II) porphyrin-appended cholesterol derivatives with the addition of [60]fullerene (0.5 equiv).<sup>15</sup> The Zn(II) porphyrin moiety was forced to orient chirally in the gel state by interaction with [60]fullerene, and the CD pattern indicated that the porphyrin moiety oriented in an anticlockwise direction. In this case, the thermal stability of the organogel with enhanced CD was increased using the Zn(II) porphyrin–[60]fullerene interaction. Sol–gel transcription has been widely used to create inorganic nanomaterials using organic material as a template. Various inorganic materials with unique shapes<sup>16</sup> have been reported to date. Kawano et al. reported that the enhanced CD spectrum was stabilized with a sugar-appended porphyrin derivative by sol–gel transcription.<sup>17</sup> The CD spectrum of silica-coated porphyrin arrays after sol–gel transcription was similar to that of the original organogel.

We have reported L-glutamide derivatives (Scheme 1) with various functional groups<sup>18–23</sup> as chemical tools for creating self-assembling amphiphiles and lipophilic organogelators. The versatility of L-glutamide derivatives is emphasized by the formation of chirally ordered structures in their aggregates and their supramolecular functions being determined by the

**Scheme 1. Chemical Structures of L-Glutamide-Derived Lipids with Various Functional Headgroups**



selection of hydroxy carbonyl<sup>18</sup> (COOH-lipid in Scheme 1), isoquinoyl,<sup>19</sup> pyrenyl<sup>20</sup> (Pyr-lipid in Scheme 1), azophenyl,<sup>21</sup> spiropyranyl,<sup>22</sup> and porphyrinyl<sup>23</sup> groups as functional headgroups. In any case, enhanced CD spectra were observed around the absorption band of chromophore groups. These induced CD spectra are due to the chiral orientation of attached functional groups based on highly oriented aggregation through intermolecular hydrogen bonding among the L-glutamide moieties. In this letter, we demonstrate the stabilization of chirally oriented structures of glutamide-derived lipids among fibrous aggregates by the polymerization of the lipid molecules. We thus design a new L-glutamide-derived lipid (Si-lipid) in which a triethoxysilyl group is introduced to the head of the lipid via a urea bond. The chemical structure of Si-lipid is given in Scheme 1. The thermal and mechanical stabilities of Si-lipid organogels before and after polycondensation are also discussed.

## Experimental Section

**Synthesis of a Dialkylated L-Glutamide-Derived Lipid with a Triethoxysilyl Headgroup (Si-Lipid).** L-Glutamic acid and palladium/carbon were purchased from Katayama Chemical Industries Co. Ltd. (Osaka, Japan). Diethyl phosphorocyanidate (DEPC) and benzyloxy carbonyl chloride (Z-Cl) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). *n*-Dodecyl amine and triethylamine were obtained from Kanto Chemical Co. Inc. and Nacalai Tesque, Inc., respectively. 3-(Triethoxysilyl)propyl isocyanate was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Tetrahydrofuran was distilled before use, and all other solvents were used as received. The Si-lipid was synthesized as shown in Figure S1. The chemical structure was identified by Fourier transform infrared (FT-IR), <sup>1</sup>H nuclear magnetic resonance (NMR), and elemental analysis. FT-IR spectra were recorded on a Jasco FT/IR-4000 spectrometer (Jasco Corporation, Japan). <sup>1</sup>H NMR spectra were recorded on a Jeol JNM-EX400 spectrometer (Jeol Ltd., Japan) using tetramethylsilane as an internal standard. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and b = broad. *N*<sup>1</sup>,*N*<sup>5</sup>-Didodecyl-L-glutamide was synthesized according to our previous report.<sup>18</sup> *N*<sup>1</sup>,*N*<sup>5</sup>-didodecyl-L-glutamide (1.0 g, 2.1 mmol) was dissolved in dry THF (200 mL), and the solution was cooled to 5 °C. 3-(Triethoxysilyl)propyl isocyanate (2.7 mL, 10.4 mmol) was added to the solution, and the mixture was stirred for 1 h at 5 °C. After being stirred for 12 h at room temperature, the solution was concentrated in vacuo, and 200

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mL of acetonitrile was added to the residue to give a white solid powder: yield 1.39 g (92%); mp 138.5–139 °C. IR spectrum (KBr): 3326  $\text{cm}^{-1}$  ( $\nu\text{N-H}$ ), 2920  $\text{cm}^{-1}$  ( $\nu\text{C-H}$ ), 2850  $\text{cm}^{-1}$  ( $\nu\text{C-H}$ ), 1635  $\text{cm}^{-1}$  ( $\nu\text{C=O}$  amide), 1533  $\text{cm}^{-1}$  ( $\delta\text{N-H}$  (amide and urea)), 1104  $\text{cm}^{-1}$  ( $\delta\text{Si-O}$ ), 1080  $\text{cm}^{-1}$  ( $\delta\text{Si-O}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C, Figure S2 in Supporting Information):  $\delta$  0.60–0.64 (t, 2H,  $\text{CH}_2\text{Si}$ ), 0.86–0.90 (m, 6H,  $\text{CH}_3$  (dodecyl group)), 1.28 (m, 44H,  $\text{CH}_2$  (dodecyl group) and  $\text{CH}_3$  (ethoxy group)), 1.49–1.50 (m, 4H,  $\text{CH}_2\text{CH}_2\text{NH}_2$  (dodecyl group)), 1.56–1.64 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Si}$ ), 1.66–2.07 (m, 2H,  $\text{CH}_2\text{C}^*$ ), 2.26–2.42 (m, 2H,  $\text{CH}_2\text{CH}_2\text{C}^*$ ), 3.13–3.24 (m, 6H,  $\text{CH}_2\text{NH}$  (dodecyl group) and  $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$ ), 3.79–3.84 (m, 6H,  $\text{SiOCH}_2$ ), 4.22–4.28 (t, 1H,  $\text{C}^*\text{H}$ ). Anal. Calcd for  $\text{C}_{39}\text{H}_{80}\text{N}_4\text{O}_6\text{Si}$ : C, 64.2; H, 11.6; N, 7.68. Found: C, 64.0; H, 10.9; N, 7.67.

**Measurements.** Scanning electron microscope (SEM) images of the xerogels were recorded on a Jeol JCM-5700 (Jeol Ltd., Japan). The xerogels were prepared from organogels using freeze drying, and osmium was coated onto the xerogels using a plasma coater (osmium plasma coater OPC60N, Filgen Inc., Japan). Transmission electron microscope (TEM) images were recorded using a Jeol JEM-2000FX (Jeol Ltd., Japan). The samples were spotted onto polyvinyl formal-coated copper grids. After the sample excess was removed with tissue paper and the grids were air dried, they were stained with 2 wt % aqueous ammonium molybdate. CD spectra were recorded on a Jasco J-725 spectrometer (Jasco Corporation, Japan), and the temperature was controlled with a Peltier thermostatted cell holder.  $^{29}\text{Si}$  NMR spectra were recorded on a Varian Unity<sup>Inova</sup> AS400 spectrometer (Varian, Inc.) with a solid probe for cross polarization/magic angle (CP/MAS) NMR at a spin rate of 4000–4500 Hz. Mechanical properties were evaluated by a conventional mechanical compression method with Fudoh rheometer NRM-2010J-CW (Fudoh Kogyo. Co., Ltd., Japan). The specific surface area was measured with a NOVA2200e (Quantachrome Instruments), and the Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption isotherm of nitrogen using the BET equation.

## Results and Discussion

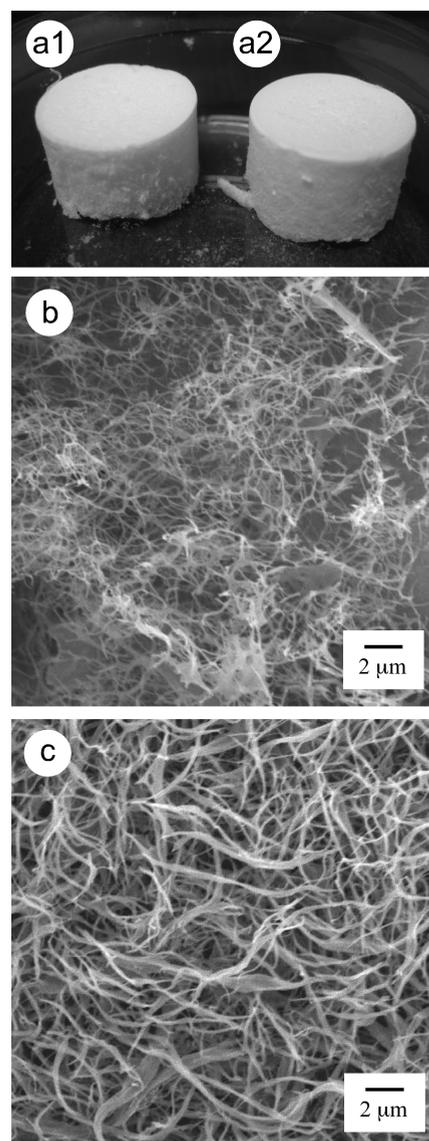
**Organogel Formation from Si-Lipid.** We have reported that lipophilic L-glutamide derivatives can form self-assembled network structures in various organic solvents.<sup>24</sup> The driving force for the lipid aggregation is mainly intermolecular hydrogen bonding as a result of the plural amide bonds around the glutamide moieties. (As shown in Figure S3, FT-IR spectra have a characteristic absorption peak for Si-lipid carbonyl groups at 1656  $\text{cm}^{-1}$  in chloroform (sol state). The peak shifts to 1629  $\text{cm}^{-1}$  in benzene (gel state), which is attributed to the amide bond forming a parallel  $\beta$ -sheet-like structure.<sup>25</sup>) A headgroup of the lipid can be modified by substitution with various functional groups. In this study, a triethoxysilyl group was selected and introduced to the head through a urea bond.

Si-lipid was dissolved in organic solvents at 70 °C and then cooled to 10 °C to form a gel. The gelation properties were evaluated at 20 °C using the inversion fluid method, and the results are summarized in Table 1. The Si-lipid formed organogels over a wide range of organic solvents such as *n*-hexane, benzene, cyclohexane, and dimethylformamide. SEM observations of the cross section of freeze-dried benzene gels indicate that the organogels have fibrous network

**Table 1. Gelation Properties of Si–Lipid in Organic Solvents before and after Condensation<sup>a</sup>**

solvent	before condensation	after condensation
<i>n</i> -hexane	G	I
toluene	G	G <sub>T</sub>
benzene	G	G <sub>T</sub>
cyclohexane	G	G <sub>T</sub>
anisole	G	G <sub>T</sub>
chloroform	S	G
ethyl acetate	G <sub>T</sub>	I
1-butanol	S	S
acetone	G <sub>T</sub>	G <sub>T</sub>
ethanol	S	I
acetonitrile	I	G <sub>T</sub>
methanol	G <sub>T</sub>	I
DMF	G	G <sub>T</sub>

<sup>a</sup>G, gel; G<sub>T</sub>, turbid gel; S, solution; I, precipitate (insoluble).



**Figure 1.** Photograph and SEM images of xerogels from Si-lipid benzene gels (10 mM) before (a1 and b) and after (a2 and c) condensation.

structures (Figure 1b,c). The diameters of fibrous aggregates are several tens to several hundred nanometers. According to TEM observations (Figure S4 in the Supporting Information), the minimum diameter was approximately 10 nm,

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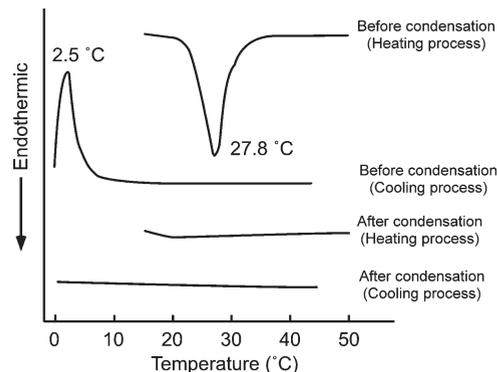
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which was 4 times that of the Si-lipid molecule (2.85 nm; the molecular length of the Si-lipid was estimated using HyperChem version 5.1 with molecular mechanics). These results indicate that the fibrous aggregates produced from the Si-lipid are based on multilayer structures and pile up to form cross-linking points in the network structure.

**Polycondensation of Organogels.** The gel state was broken mechanically into a sol state by a vortex mixer. In the sol state, it was confirmed by TEM and CD measurements that the fibrous aggregates and typical enhanced CD signal (CD spectra was measured in cyclohexane) were still maintained. A typical enhanced CD signal of the chirally oriented Si-lipid was observed in cyclohexane. These indicate that the 3D network structure is readily broken but the chirally oriented structures are maintained in the fragmented fibrous aggregates. When this fragmented gel was aged at 20 °C, a gel state was recovered without additives after 3 days. A similar spontaneous restoring phenomenon of organogels is known as thixotropy.<sup>26</sup>

TFA (0.125 equiv added to the ethoxysilyl group) and water (approximately 6 equiv added to the ethoxysilyl group) were added to the fragmented gel (10 mM), and then the mixture was shaken with a vortex mixer. When the resultant mixture was kept at 20 °C, the gel state was recovered from the fragmented gel in 1 day. This indicates that polycondensation among the ethoxysilyl groups promotes gelation. The detailed mechanism will be discussed later with the results of <sup>29</sup>Si CP/MAS NMR, CD, SEM, and DSC.

To evaluate the thermal stability of the gel after polycondensation, as the inversion fluid test, DSC measurements were applied to the Si-lipid benzene gel before and after polycondensation. According to an inversion fluid test, the polycondensed Si-lipid (poly(Si-lipid)) was stable even at 80 °C, whereas the Si-lipid benzene gel broke up at 32 °C. Typical photographs of benzene gels at 10, 35, and 80 °C before (Si-lipid) and after (poly(Si-lipid)) condensation are shown in Figure S5. DSC thermograms provide strong support for the thermal stability of the poly(Si-lipid) benzene gel. As shown in Figure 2, endothermic (27.8 °C) and exothermic (2.5 °C) peaks were observed in the Si-lipid benzene gel in the heating and cooling processes, respectively. These peaks are due to a gel-to-sol phase transition usually observed in self-assembled organogels produced from L-glutamide derivatives.<sup>27</sup> These peaks completely disappeared for the poly(Si-lipid) benzene gel. TFA, which works as an acid catalyst for condensation reactions of ethoxysilyl groups, is a strong acid and can disturb the intermolecular hydrogen bonding, which is a main driving force for self-assembly. If twice the amount (0.25 equiv added to the ethoxysilyl group) of TFA was added to the benzene gel and the gel was aged at 20 °C for 1 day, then the gel state was observed after condensation but the thermal stability was reduced (the gel-breaking temperature was 68 °C). In contrast, if one-fifth the amount (0.025 equiv added to the ethoxysilyl group) of TFA was used, then a gel state was not recovered even after 3 days. Similar results were obtained for anisole, cyclohexane, toluene, and acetone. It seems that the thermal stability of organogels in these organic solvents is enhanced with the use of an appropriate



**Figure 2.** DSC thermograms of Si-lipid benzene gels (40 mM) before and after condensation in the heating and cooling processes.

amount of TFA for the condensation of ethoxysilyl groups. We have reported that the organogels produced from glutamide-derived lipids exhibit a self-restoring property and the restoration is accelerated by covalently accumulating several organogelators onto a core compound such as cyclophosphazene.<sup>26</sup> In the case of Si-lipid, it is conceivable that the thermal stability is due to intermolecular condensation reactions. Direct evidence of the condensation was obtained spectroscopically as follows. (1) FT-IR spectra had characteristic bands of Si–O–R (1104 and 1080  $\text{cm}^{-1}$ ) and Si–O–Si (1106 and 1039  $\text{cm}^{-1}$ ) structures before and after the condensation reaction, respectively (Figure S6 in Supporting Information). (2) <sup>29</sup>Si NMR is the most powerful technique for estimating the chemical structure of alkoxy-silyl groups after condensation. In the <sup>29</sup>Si CP/MAS NMR spectra of freeze-dried benzene gels (Figure S7), only one strong signal at –46.4 ppm was detected before the condensation reactions; this signal was assigned to the Si species with a triethoxysilyl group (R–Si(OEt)<sub>3</sub>, M). It disappeared after the condensation reaction, and three new signals appeared at –49, –58, and –67 ppm, which were assigned to a monocondensed structure (R–Si(OSi)(OH)<sub>2</sub>, P1), a dicondensed structure (R–Si(OSi)<sub>2</sub>(OH), P2), and a tricondensed structure (R–Si(OSi)<sub>3</sub>, P3), respectively.<sup>28,29</sup> Because the Si signal of the hydrolyzed trihydroxysilyl group (R–Si(OH)<sub>3</sub>) appears at –38 ppm,<sup>28</sup> it is conceivable that the condensation reactions mostly occurred among Si-lipid aggregates. The P1 and P3 structures act as a terminal group and a cross-linking point, respectively. The peak ratio of the three Si species is related to the degree of polymerization and chemical cross-linking of poly(Si-lipid). The peak ratio for poly(Si-lipid) obtained with 0.125 equiv of TFA (15.9:64.0:20.1 P1/P2/P3) is very close to that obtained with 0.25 equiv of TFA (16.6:61.3:22.1 P1/P2/P3). Therefore, the lower thermal stability of the poly(Si-lipid) benzene gel obtained with 0.25 equiv of TFA can be explained by the hindrance of intermolecular hydrogen bonding by TFA. The P1 component increased and the P3 component decreased in the poly(Si-lipid) benzene gel obtained with 0.025 equiv of TFA (25.5:60.2:14.3 P1/P2/P3). This indicates that the degree of polymerization as well as the number of cross-linking points decreased in the poly(Si-lipid) obtained with less TFA. These results are consistent with the gelation properties of Si-lipid after polycondensation. It is clear that the diameters of fibrous aggregates increased after polycondensation

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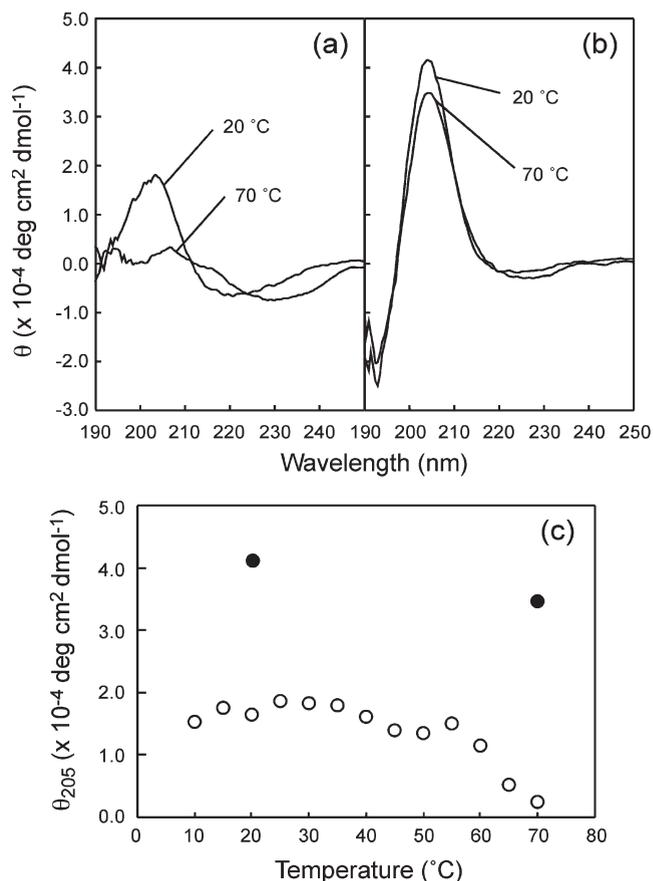
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(Figure 1c). This is probably due to chemical cross-linking between fibrous aggregates during polycondensation reactions in the gel state. In other words, siloxane network structures certainly formed among the fibrous network structures. In addition, the resulting organogels possess silanol groups that can be used for further modification with silane coupling reagents. Interestingly, gelation by polycondensation was observed in chloroform and acetonitrile, whereas no gelation was observed before polycondensation. However, Si-lipid lost its gelation ability after condensation in *n*-hexane, ethyl acetate, ethanol, and methanol, and polycondensed lipids precipitated in the respective solvents (Table 1). It can be seen that the solubility of Si-lipid changed after polycondensation.

**Mechanical Compression Strength of Organogels.** The mechanical strengths of self-assembled organogels are generally less than those of general polymer network gels. Therefore, the mechanical compression strengths of the benzene gels were evaluated. The breaking load of the 10 mM benzene gel was  $11.5 \text{ g cm}^{-2}$  before polycondensation, and it increased to  $20.8 \text{ g cm}^{-2}$  afterwards. As expected, the mechanical strength of the original benzene gel increased with the concentration of Si-lipid ( $21.0 \text{ g cm}^{-2}$  at 20 mM). Surprisingly, the strength of the poly(Si-lipid) benzene gel increased to  $70.2 \text{ g cm}^{-2}$  at 20 mM. As a result of the detailed study, the mechanical compression strength of the poly(Si-lipid) gel markedly increased at an Si-lipid concentration of around 15 mM (Figure S8 in Supporting Information). According to the  $^{29}\text{Si}$  CP/MAS NMR studies, there was less P3 ( $\text{R-Si(OSi)}_3$ ) and more P1 ( $\text{R-Si(OSi)(OH)}_2$ ) the 20 mM polycondensed gel (20.4:62.0:17.6 P1/P2/P3) than there was in the 10 mM gel (15.9:64.0:20.1 P1/P2/P3) in terms of relative amounts. Therefore, although the total amount of the P3 species was much greater in the 20 mM than in the 10 mM polycondensed gel, a remarkable increase in the fraction of the P3 species was not observed. The mechanism for the remarkable increase in strength of around 15 mM is not clear, but it is probably related to the siloxane network structures among the fibrous aggregates.

**Enhanced Circular Dichroism Based on a Highly Oriented Structure.** To evaluate the chiral orientation of Si-lipid aggregates, cyclohexane was used as an organic medium instead of benzene because it has less absorbance around the absorption band of the amide bond. TFA (0.125 equiv added to the ethoxysilyl group) and water (6 equiv added to the ethoxysilyl group) were added to a 0.1 mM cyclohexane solution and mixed well, and then the mixture was incubated for 1 day. CD spectra were recorded before and after condensation. Figure 3 shows CD spectra at 20 and 70 °C (a) before and (b) after polycondensation. A distinct enhancement of the CD intensity was observed around the absorption band of the amide bonds at 20 °C before polycondensation. This is a typical feature of L-glutamide derivatives in organic<sup>21,26</sup> and aqueous<sup>30</sup> solutions, and similar CD enhancements are seen in other organogels<sup>31</sup>/hydrogels<sup>32</sup> having an asymmetric carbon



**Figure 3.** CD spectra of Si-lipid cyclohexane gels (0.1 mM) (a) before and (b) after polycondensation. (c) Temperature dependencies of  $\theta$  values at 205 nm of Si-lipid benzene gels before (○) and after (●) condensation.

atom in the gelator molecule. This feature can be explained by chiral stacking among the chromophore groups. Because positive CD signals appeared at 200 and 205 nm in the cyclohexane gel, it was considered that amide bonds formed two types of stacking structures in the aggregates. Interestingly, the CD signal at 205 nm increased with the disappearance of the CD signal at 200 nm after polycondensation ( $1.65 \times 10^4 \text{ deg cm}^2 \text{ dmol}^{-1}$  to  $4.11 \times 10^4 \text{ deg cm}^2 \text{ dmol}^{-1}$  at 20 °C and 205 nm). This is unusual because the polymerization of lipid aggregates often disturbs the molecular orientation owing to both the decrease in lateral diffusion and the molecular stacking distance becoming unsuitable.<sup>30</sup> Furthermore, the CD signal in the poly(Si-lipid) cyclohexane gel was almost maintained at 70 °C. These results indicate that the polycondensation of ethoxysilyl groups among the fibrous aggregates promoted lipid aggregates to have a more suitable formation for chiral orientation.

## Conclusions

The ethoxysilyl-group-attached L-glutamide-derived lipid (Si-lipid) was newly synthesized as a low-molecular-weight organogelator, and acid-catalyzed polycondensation (hydrolysis and condensation) was performed for the gel state. The gelation efficiency of Si-lipid increased in benzene with the formation of siloxane network structures. The thermal and mechanical stabilities improved with the polycondensation of the triethoxysilyl groups. Furthermore, an enhanced CD signal due to the chiral orientation of Si-lipid was maintained

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for the polycondensed gels even at 70 °C, which corresponds to the temperature for the dispersion state. This is the first confirmed example of the stabilization of the chiral orientation of low-molecular-weight organogels by the polymerization of organogelators. The resulting organogels have a relatively large mesh structure in their skeletons (the BET specific surface area of xerogel from poly(Si-lipid) benzene gel was determined to be 1990 m<sup>2</sup> g<sup>-1</sup>), which provides the possibility for the development of new matrix materials<sup>16,33</sup> for devices such as sensors, electrodes, and catalysts. Silanol groups among the fibrous aggregates could be modified for the functionalization of network structures.

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**Supporting Information Available:** Synthesis route of Si-lipid. <sup>1</sup>H NMR spectrum of Si-lipid. FT-IR spectra of xerogels from benzene gels before (Si-lipid) and after (poly(Si-lipid)) the condensation reaction. TEM image of Si-lipid-benzene gel. Photographs of benzene gels before (Si-lipid) and after (poly(Si-lipid)) polycondensation. IR spectra of Si-lipid in benzene (gel state) and in chloroform (sol state). <sup>29</sup>Si NMR of freeze-dried gels. Mechanical stability of benzene gels before (Si-lipid) and after (poly(Si-lipid)) polycondensation. This material is available free of charge via the Internet at <http://pubs.acs.org>.