

Electronic Supplementary Information

Changes in Viscosity Behavior from a Normal Organogelator to a Heat-Induced Gelator for a Long-chain Amidoamine Derivative

Clara Morita, Hiroki Sugimoto, Keisuke Matsue, Takeshi Kondo, Yoshiro Imura and Takeshi Kawai*

Department of Industrial Chemistry, Tokyo University of Science
1-3, Kagurazaka, Shinjuku, Tokyo, 162-8601, Japan
kawai@ci.kagu.tus.ac.jp

Materials

All chemicals were reagent grade and obtained from Aldrich or Kanto chemicals. Commercially available reagents and solvent were used without further purification, except methyl acrylate (Kanto chemicals), which was purified by distillation under reduced pressure in a nitrogen atmosphere, and octadecylamine, which was recrystallized two times from hexane.

Synthesis of C18AA ¹⁾

An amount of methyl acrylate 10.22 g (0.12 mol) was added to 2.0 g (7.12 mmol) of octadecylamine in 15 mL of methanol. The solution was stirred at 40 °C for 3 days and then the solvents and excess methyl acrylate were removed from solution by rotary evaporation. 3-[(2-methoxycarbonyl-ethyl)-octadecyl-amino]-propionic acid methyl ester (C18ME) was obtained as a viscous liquid. Yield: 95 %.

¹H-NMR (CDCl₃): δ 0.88 (t, 3H, CH₂CH₃), 1.25 (br, 28H, CH₂), 1.42 (br, 4H, CH₂CH₃, CH₂CH₂CH₂N), 2.37 (t, 4H, CH₂CH₂CO), 2.43 (t, 2H, CH₂N), 2.76(t, 4H, NCH₂CH₂CO), 3.66 (s, 6H, OCH₃). HRMS: calcd for C18ME (M+Na⁺) 464.37, found 464.38.

C18ME (3.2 g) and ethylenediamine 17.8 g (0.30mol) were dissolved in 15 mL of methanol and the mixture was stirred for 1 week at room temperature. Upon removal of the solvent and ethylenediamine by evaporation and freeze-drying, C18AA was obtained as a light yellow solid. The crude solid was recrystallized from a mixed solvent of toluene and methanol. Yield: 90 %.

¹H-NMR (CDCl₃): δ 0.88 (t, 3H, CH₃), 1.25 (br, 28H, CH₂), 1.45 (br, 4H, CH₂CH₃, CH₂CH₂CH₂N), 2.36 (t, 4H, CH₂CH₂O), 2.42 (t, 2H, CH₂N), 2.73 (t, 4H, NCH₂CH₂CO), 2.82 (t, 4H, CH₂NH₂), 3.29 (q, 4H, NHCH₂). HRMS: calcd for C18AA (M+H⁺) 498.47, found 498.48.

NMR spectra were recorded in CDCl₃ on a Bruker 400 Ultrashield spectrometer operating at 400 MHz.

- 1) (a) Y. Imura, K. Matsue, H. Sugimoto, R. Ito, T. Kondo, T. Kawai, *Chemistry Letter* **2009**, 38, 778 – 789
(b) T. Kawai, R. Ito, T. Kondo, Gold 2006, New Industrial Applications for Gold, University of Limerick, Abstract p113 (2006)

Characterization of toluene gels

XRD measurements were performed using a Ultima IV (Rigaku Co. Japan) diffractometer. Samples were prepared by freeze-drying a 2-wt% C18AA/toluene gel.

FT-IR measurements were carried out with a Nicolet 6700 FT-IR spectrophotometer equipped with a MCT detector with a resolution of 4 cm^{-1} . In the FT-IR measurements, a demountable liquid cell with a ZnSe window was employed for the toluene- d_8 gel and CDCl_3 solution. Observed bands at 3445, 2927, 2855, 1658, 1518 and 1467 cm^{-1} in CDCl_3 solution of C18AA are assigned to the amide A, antisymmetric and symmetric CH_2 stretching, amide I and II, and CH_2 scissoring bands, respectively.²⁾ These bands appeared at 3330, 2918, 2849, 1644, 1543 and 1473 and 1463 cm^{-1} in the spectrum of the toluene gel. Since the amide A, and amide I and II bands for non hydrogen-bond (free) states are expected to be observed at ~ 3430 , ~ 1650 and $\sim 1510\text{ cm}^{-1}$, respectively,³⁻⁵⁾ the appearance at lower frequencies for amide A and amide I, and the higher frequency of amide II in the gel spectrum, indicates that the amide groups are linked through hydrogen bonding to adjacent amide groups. Thus, the network of the self-assembled C18AA aggregates is mainly formed through hydrogen-bonding interactions, as shown in Figure S3 (B).

It is well known that the CH_2 stretching and scissoring frequencies of surfactants provide sensitive monitors of the conformational disorder and the lateral packing of chains, respectively.³⁻⁶⁾ The values of 2918 and 2849 cm^{-1} for the antisymmetric and symmetric CH_2 stretching modes in the toluene gel are characteristic of an all-trans methylene chain, while those of 2927 and 2855 cm^{-1} in the CHCl_3 solution are characteristic of melting of the methylene chain. The appearance of the CH_2 scissoring bands at 1473 and 1463 cm^{-1} as a doublet in the gel indicates orthorhombic packing of the hydrocarbon chains,⁶⁾ as illustrated in Figure S3 (C). As mentioned in the SAXS result, C18AA aggregates have an interdigitated structure. The hydrocarbon chains shown in blue and red in Figure S3 (C) are present in the bottom layer, while the green chain is in the upper layer.

2) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, 34,821 – 836.

3) M. Suzuki, T. Sato, A. Kurose, H. Shirai, K. Hanabusa, *Tetrahedron Letters* **2005**, 46, 2741 – 2745

4) M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai, K. Hanabusa, *Langmuir* **2003**, 19, 8622 – 8624.

5) T. Kawai, J. Umemura, T. Takenaka, M. Gotoh, J. Sunamoto, *Langmuir* **1988**, 4, 449 – 452.

6) R. G. Snyder, *J. Chem. Phys.* **1979**, 71, 3229 – 3235.

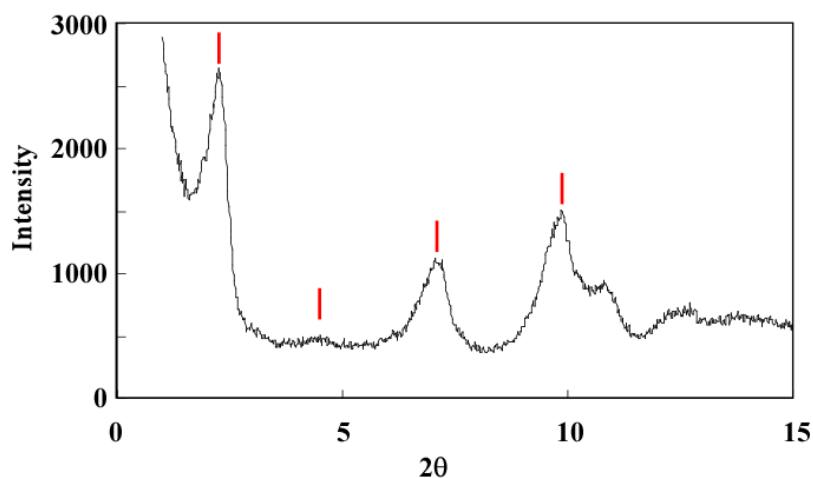


Fig. S1. X-ray diffraction pattern of C18AA toluene gel.

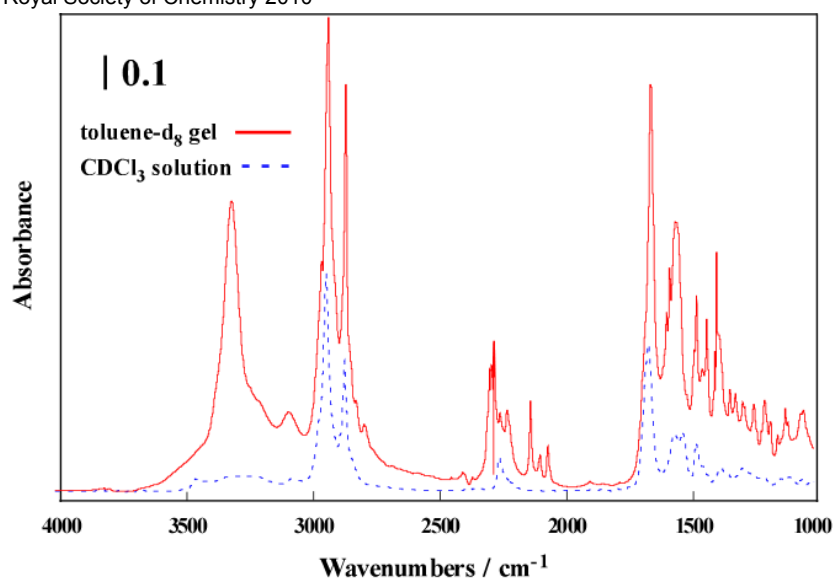


Fig. S2. FT-IR spectra of toluene-d₈ gel and CDCl₃ solution of C18AA.

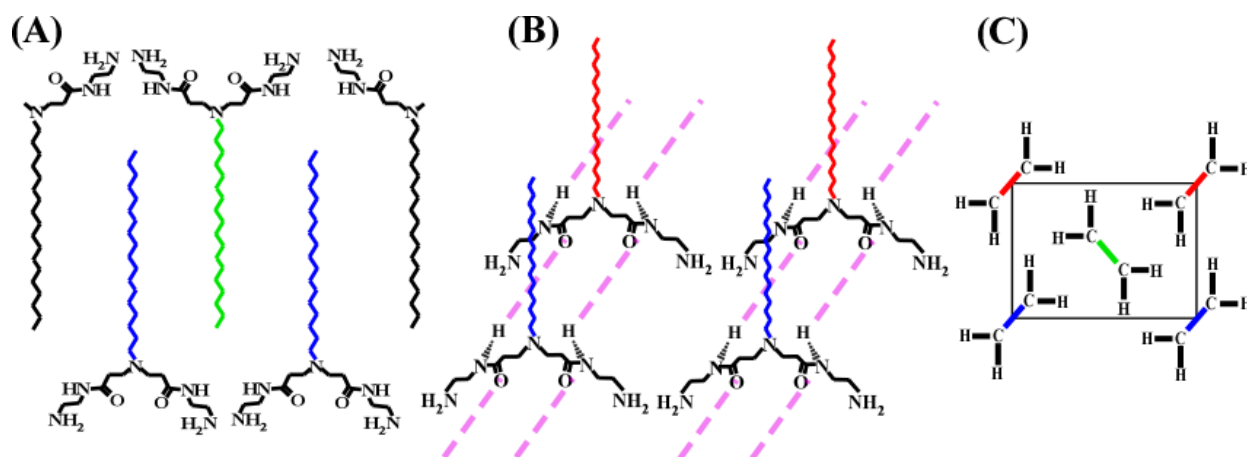


Fig. S3. Schematic illustration of lamellar structure of C18AA in the organogel.

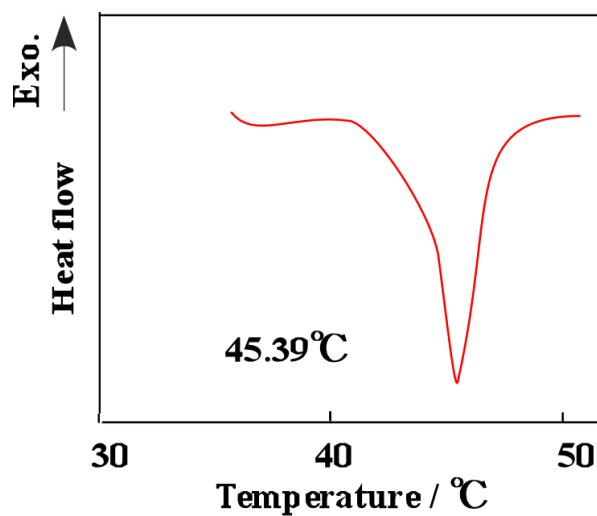


Fig. S4. DSC thermogram for the 5 wt%-C18AA toluene gel.

Thermoresponsive behavior

Dynamic rheological experiments were performed on a Thermo, MARS rheometer. A cone-plate with a diameter of 35 mm and an angle of 1° was employed. Measurements of storage (G') and loss (G'') moduli to give the complex viscosity η^* were performed as a function of temperature from 10 – 70 °C at a constant frequency of 1 Hz. The experimentals were carried out in the linear viscoelastic regime of the samples, which was determined by the dynamic stress sweep experiments. The rate of temperature increase was controlled at 3 °C /min. The complex viscosity η^* was obtained from the storage (G') and loss (G'') moduli as $\eta^* = [(G'^2 + G''^2)/(2\pi f)^2]^{1/2}$, where f is the frequency of oscillation. The sol-gel transition temperature was evaluated from the crossover point of G' and G'' plots against temperature.

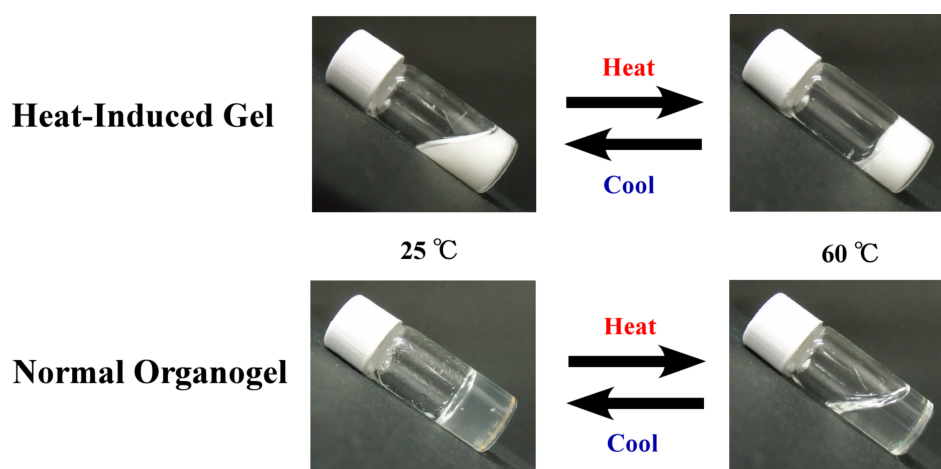


Fig. S5. Photographs of the heat-induced gel and normal organogel at 25 °C and 60 °C.

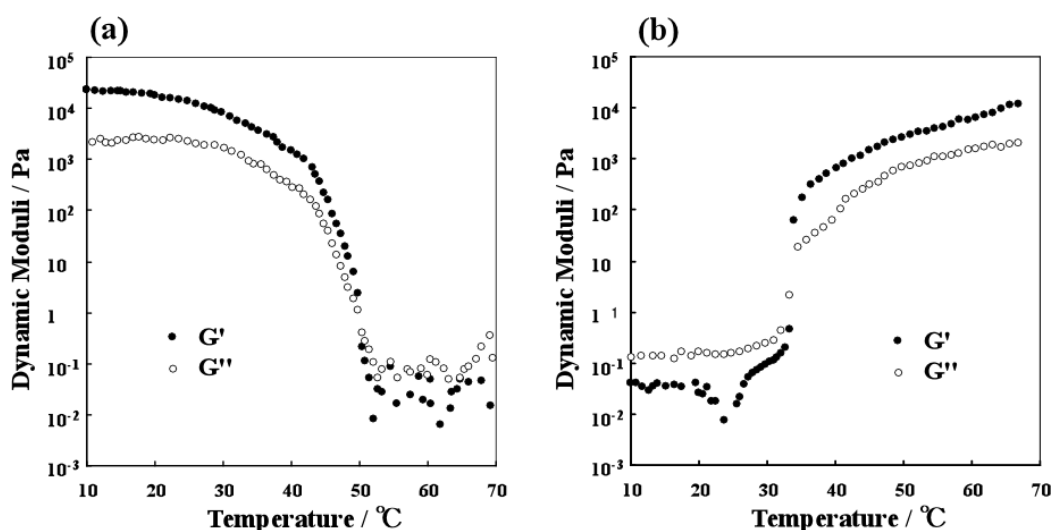


Fig. S6. Temperature dependence of the dynamic moduli of (a) 1.2 wt%-C18AA/toluene (toluene gel) and (b) 1.1 wt%-C18AA/toluene/0.1 M LiCl (heat-induced gel).

Fluorescence microscopic image of heat-induced gel

In order to investigate differences in the molecular assembly of C18AA between the sol and gel states, we obtained optical microscopic images of the opaque water phase for [C18AA]=1.2 wt% at 25 °C and 40 °C, which were in the sol and gel states, respectively.

It is well known that a viscosity increase is usually induced by phase inversion of the emulsion. However, in this system phase inversion did not occur on heating as shown by the identification of an O/W structure in fluorescence microscopic images of the emulsions obtained using the water-soluble dye rhodamine 6G.

7) J. Allouche, E. Tyrode, V. Sadtler, L. Choplin, J.-L. Salager, Langmuir 2004, 20, 2134-2140

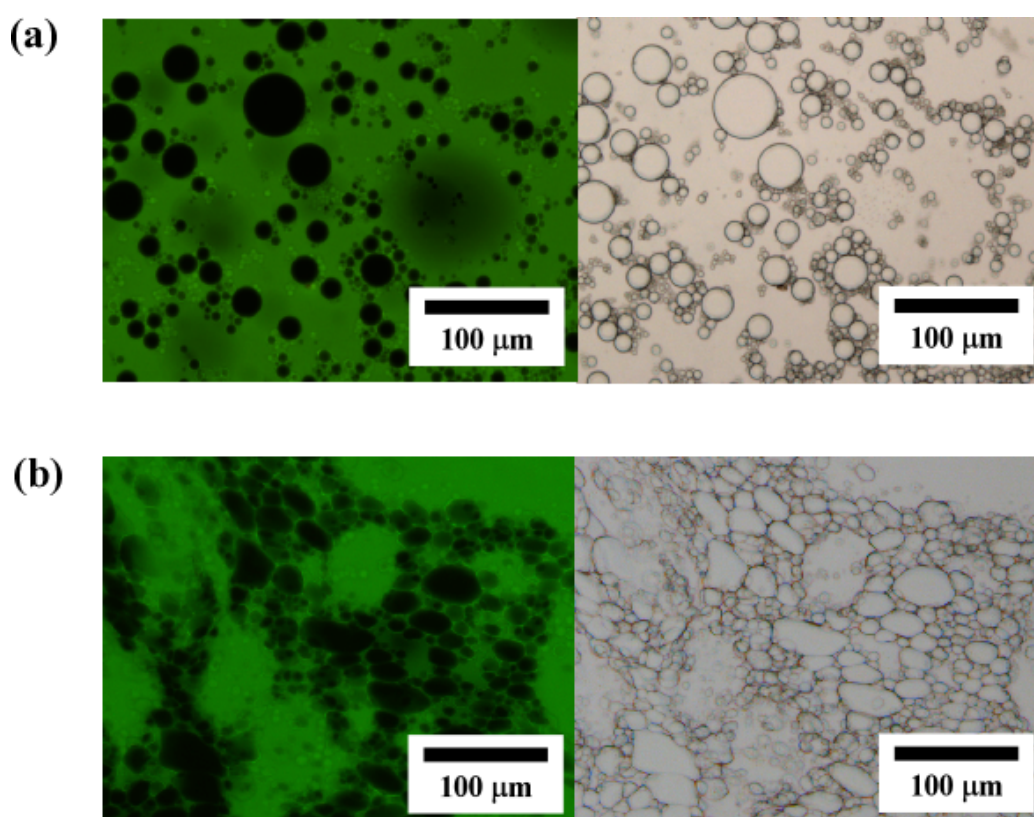


Fig. S7. Fluorescence microscopic images (left) and differential interference contrast microscopic images (right) of 1.2 wt%-C18AA/toluene/0.1 M LiCl at (a) 25 °C (sol state) and (b) 40 °C (gel state).

Distribution coefficient of C18AA in O/W emulsion

To determine the distribution of C18AA among the water, toluene and water/toluene interface in the heat-induced gel (i.e. toluene/0.1 M LiCl aq. emulsion), the solubility of C18AA in the water and toluene phases was measured by the weight method.

An emulsion was prepared in the proportions 0.5 wt%-C18AA/toluene (100 mL)/0.1 M LiCl (4 mL), in which the total amount of C18AA was 0.6 g. After undergoing creaming at a given temperature, the O/W emulsions were observed to separate into a clear water phase in the bottom layer, an excess transparent toluene phase in the upper layer and a opaque emulsion phase in the middle layer (Figure S7 (a)). The water and toluene phases were withdrawn by pipette to measure the solubility of C18AA. The water and toluene were then removed by freeze-drying in a vacuum. The C18AA and LiCl remaining were determined by measuring the residual weight. Here, we assume that the C18AA concentration in the toluene phase in the emulsion oil droplets is equal to that in the excess toluene phase, and that LiCl is insoluble in the toluene phase.

On the basis of the described weight method, we obtain the distribution coefficients for C18AA in the water phase (ϕ_W) and oil (toluene) phase (ϕ_O). The coefficient at the O/W interface (ϕ_i) can then be obtained from $\phi_W + \phi_i + \phi_O = 100\%$.

The distribution coefficient in the water phase ϕ_W was increased on heating in any systems, while ϕ_W in the system containing LiCl was bigger than that in the system with water.

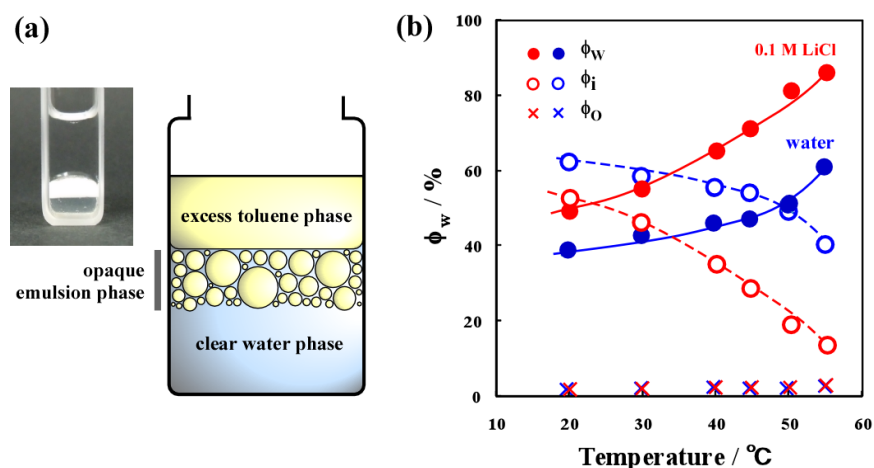


Fig. S8. (a) Images of C18AA/toluene/0.1 M LiCl aq. emulsion with creaming and (b) temperature dependence of distribution coefficient of C18AA in toluene/0.1 M LiCl (red) and in toluene/water (blue).

Dynamic light scattering measurements of C18AA aqueous solutions

Dynamic light scattering (DLS) measurements were carried out with a spectrometer Zetasizer Nano ZS (Malvern) with Peltier based temperature control. A He-Ne laser with output power of 4 mW at 633 nm was used as the light source. DLS measurements were performed at a scattering angle of 173° . The autocorrelation function of scattering data was analyzed via the NNLS method and the distribution of the hydrodynamic radius, R_h , of C18AA aggregation was obtained. The samples were introduced into the 10mm glass cell without no filtration to avoid loss of giant aggregates of C18AA.

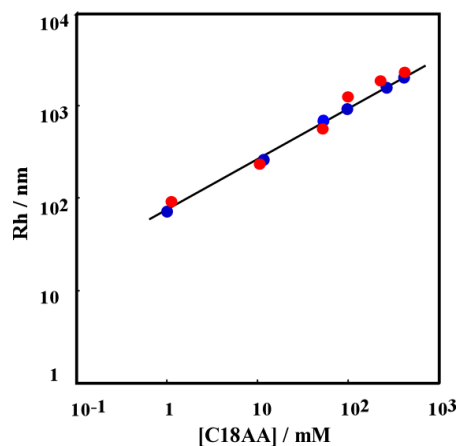


Fig. S9. Variation of hydrodynamic radius (R_h) as a function of the [C18AA] in the 0.1 M LiCl aq. (red) and the water (blue).