Electronic Supplementary Information

Mixing induced thixotropy of a two-component system of alkylurea organogelators having different alkyl chains

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Materials and Methods

SH 245 (decamethylcyclopentasiloxane) was purchased from Dow Corning Toray Co., Ltd.

SEM images were recorded with a SU-8000 scanning electron microscope (Hitachi High-Technologies Corporation) at 1.0 kV; the SEM sample (xerogel of alkylurea organogel) was vacuum dried and placed on a conductive tape on the SEM sample stage. Pt, as a conductive material, was used as a coating on the sample (Pt coating is 10-nm thick).

Measurements of transmittance in the visible region of the toluene organogel in a quartz crystal cell with a light path length of 10 mm were performed with a measurement system consisting of spectrometer HR4000 (Ocean Optics, Inc.), UV-VIS-NIR light source DH-200-BAL (Mikropack GmbH), and variable attenuator FVA-UV (Ocean Optics, Inc.) controlled by PC software OPwave (Ocean Photonics). The measurement system was constructed by Ocean Photonics. The organogel was examined using a Leica DM2500 (Leica Microsystems) polarized optical microscope under crossed nicols.

Thermal analysis was performed with an EXSTAR6000 differential scanning calorimeter DSC (Seiko Instruments Inc.) using a Ag-made closable sample pan.

Rheological measurements of frequency sweep were performed with an MCR-301 rheometer (Anton Paar Japan K.K.) with a parallel plate (8 mm diameter) at a gap of 0.50 mm and γ of 0.01 % (measurement temperature: 25 °C). Rheological measurements of strain sweep were performed with an MCR-301 rheometer with a parallel plate (8 mm diameter) at a gap of 0.50 mm and constant angular frequqncy 1 rad s^{-1} (measurement temperature: 25 °C). For rheological measurements, the organogel sample was applied onto the parallel plate and sample stage (the overflow gel was swept). The organogel sample for rheological measurements was placed on a parallel plate and a sample stage (the overflow gel was swept). Step-shear measurement was carried out by applying normal strain (strain amplitude 0.01 % and frequency 1 Hz) and large strain (shear rate 3000 s^{-1} for 0.1 s), repeatedly.

X-ray diffraction data were recorded on a D8 Discover X-ray diffractometer (Bruker AXS K.K.) with CuKα at 26 °C (the sample was filled in a quartz glass capillary tube of 1 mm diameter).

Table S1 and Fig. S1

Table S1 Critical gel concentration of alkylurea derivatives

Sample	C18U	C4U	ε [1]
PC	3.0 (OG)	2.0 (CG)	66.14
DMF	4.0 (OG)	S	47.24
Methanol	6.0 (OG)	S	33.0
Ethanol	5.0 (OG)	S	25.3
1-Butanol	4.0 (OG)	S	17.84
DCE	3.0 (OG)	3.0 (CG)	10.42
THF	8.0 (OG)	S	7.52
Ethyl Acetate	4.0 (OG)	S	6.0814
SH 245	0.5 (TG)	S	2.50
Toluene	2.0 (TG)	6.0 (CG)	2.379
n-Octane	0.5 (TG)	S	1.948

1) C. Wohlfarth, CRC Handbook of Chemistry and Physics 85th ed., ed. by D.R. Lide , CRC Press 2004, 6-155~6-177.

PC: propylene carbonate, DMF: *N, N*-dimethylformamide, DCE: 1, 2-dichloroethane, THF: tetrahydrofuran, SH 245: decamethylcyclopentasiloxane.

Key: S: solution at 10 wt%, TG: turbid gel, OG: opaque gel, CG: clear gel.

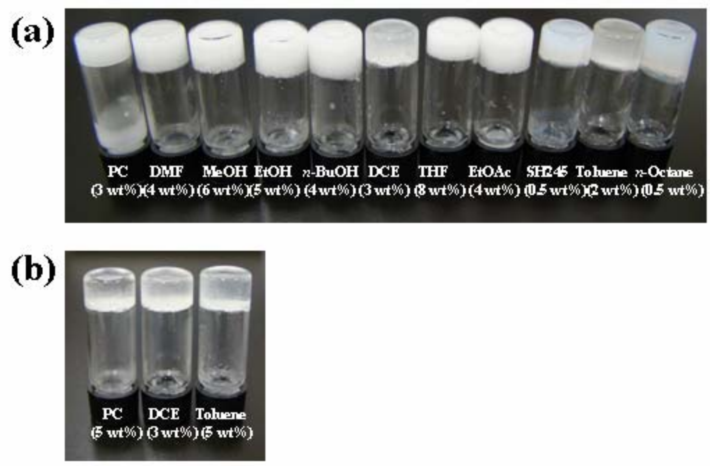

Fig. S1 Photographs of single component organogels; (a) C18U gels, (b) C4U gels.

Tables S2 and S3

Table S2 Transmittance of toluene organogels in visible region

Sample	T% at 400 nm	T% at 500 nm	T% at 600 nm	T% at 700 nm
C18U 2 wt% gel	0.14	0.04	0.03	0.02
C4U 6 wt% gel	0.07	0.03	0.04	0.07
C18U/C4U 2/1* 3 wt% gel	8.5	4.7	3.4	3.8
C18U/C4U 1/1* 3 wt% gel	9.4	7.6	6.5	7.9
C18U/C4U 1/2* 3 wt% gel	4.7	5.3	6.6	9.6
C18U/C4U 1/4* 3 wt% gel	4.5	3.7	5.9	10.2
C18U/C4U 1/10* 3 wt% gel	4.2	1.7	1.2	1.8

* A mixing ratio denoted as w/w.

Table S3 Transition temperatures of toluene organogels obtained by differential scanning calorimetry (DSC) measurements (heating and cooling rate was 2 °C/min)

Sample	$T_{gel\rightarrow sol}$ /°C (ΔH/mJ mg^{-1})	$T_{sol\rightarrow gel}$ /°C (ΔH/mJ mg^{-1})
C18U 3 wt% gel	67 (8.1)	65 (8.5)
C4U 6 wt% gel	64 (16.1)	58 (16.1)
C18U/C4U 1/1 3 wt% gel	41 (4.7)	39, 36* (4.8)
C18U/C4U 1/2 3 wt% gel	56,* 41 (4.2)	46, 37* (4.1)
C18U/C4U 1/4 3 wt% gel	21, 42* (3.8)	33, 29, 20 (3.7)
C18U/C4U 1/10 3 wt% gel	37, 60* (2.0)	40, 31* (2.1)

* Peak temperature

Fig. S2

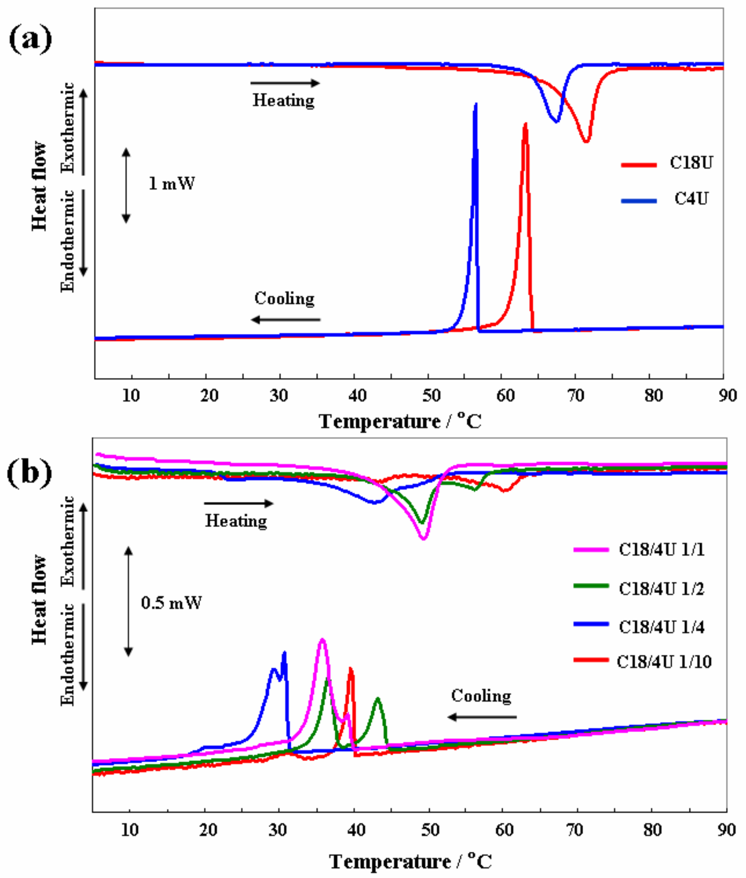

Fig. S2 DSC curves of CnU toluene gels (2 °C/min); (a) CnU (C18U: 2 wt% gel, C4U: 6 wt% gel), (b) mixed CnU 3 wt% toluene gels with mixing ratio denoted as w/w.

Figs. S3 and S4

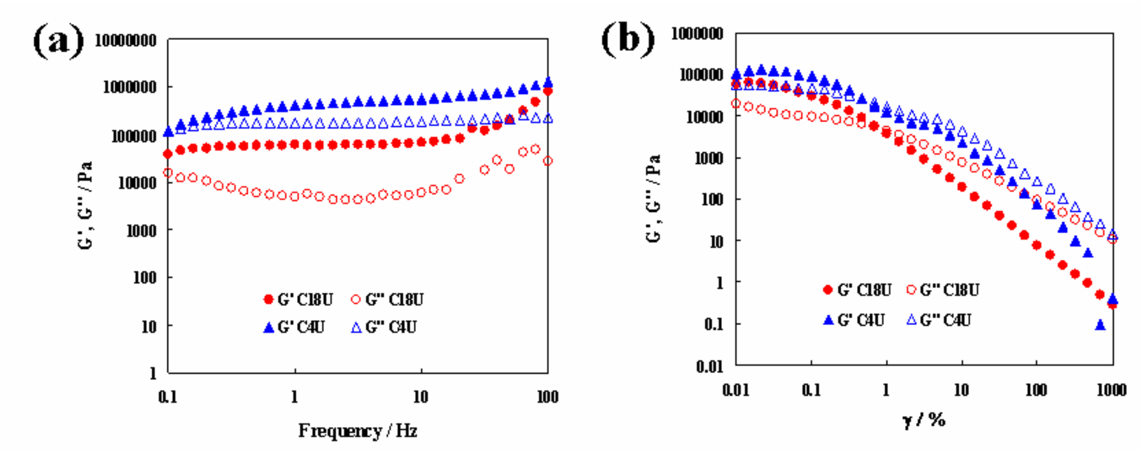

Fig. S3 Dynamic rheological properties of CnU toluene gels; (a) Frequency sweep and (b) strain sweep for C18U 2 wt% gel and C4U 6 wt% gel.

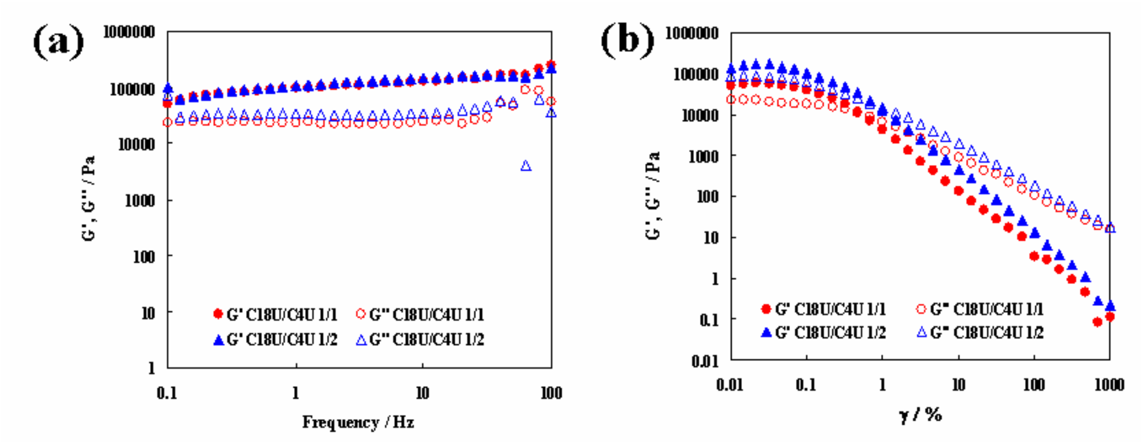

Fig. S4 Dynamic rheological properties of C18U/C4U 3 wt% toluene gels with mixing ratio denoted as w/w; (a) Frequency sweep and (b) strain sweep.

Figs. S5 and S6

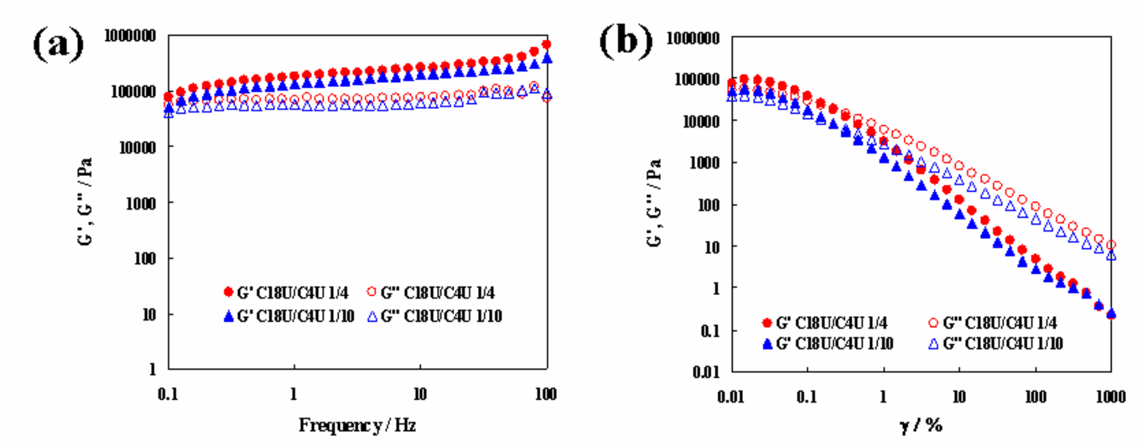

Fig. S5 Dynamic rheological properties of C18U/C4U 3 wt% toluene gels with mixing ratio denoted as w/w; (a) Frequency sweep and (b) strain sweep.

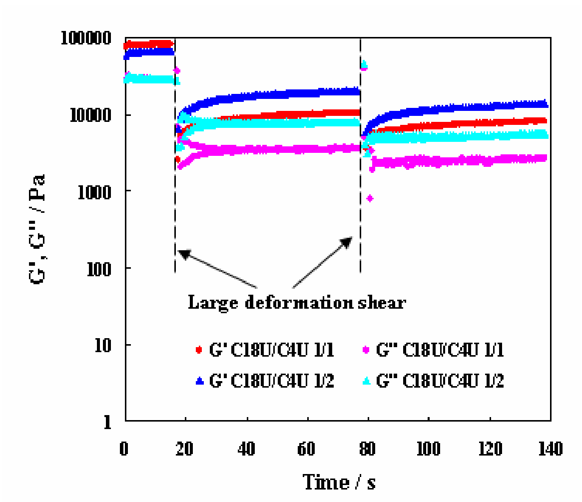

Fig. S6 Periodical step-shear test for thixotropy measurement of three-component alkylurea toluene gels; results of C18U/C4U 3 wt% toluene gels with mixing ratio denoted as w/w.

Figs. S7 and S8

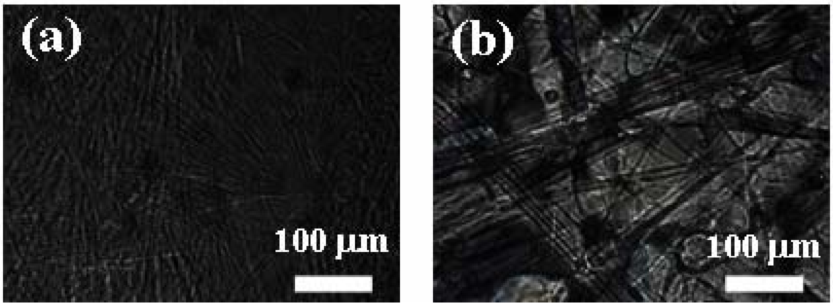

Fig. S7 POM images of CnU toluene gel; (a) C18U 2 wt% toluene gel (tape-like crystals) and (b) C4U 6 wt% toluene gel (sheet-like crystal).

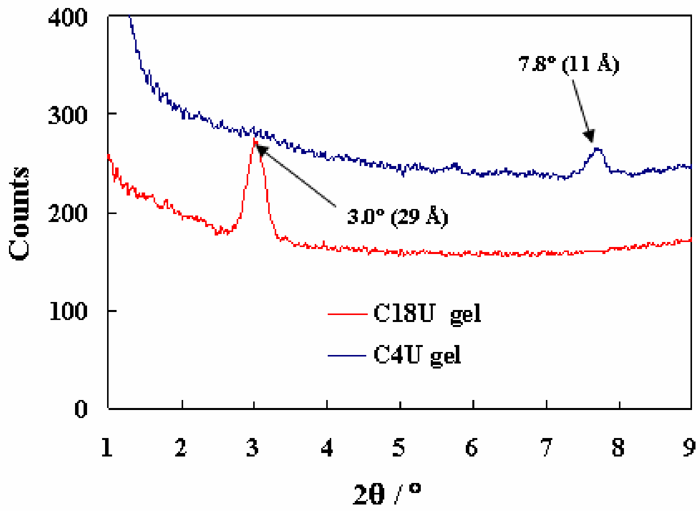

Fig. S8 SAXS data of CnU toluene gels (C18U: 2 wt% gel, C4U: 6 wt% gel).

Figs. S9 and S10

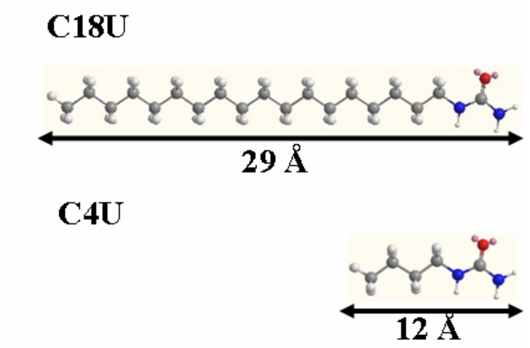

Fig. S9 Contour length of CnUs was obtained from MM2 calculation in ChemDraw. The total length in one molecule is the summation of the contour length of two molecules, two van der Waals radii of $-NH_2$ and two of $-CH_3$.[1,2] The total length in two molecules, assuming hydrogen bonding, is the summation of the contour length of two molecules and two $-CH_3$, subtracting an overlapping length.

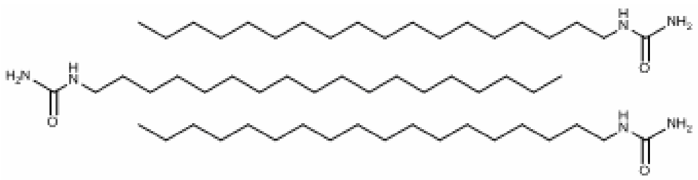

Fig. S10 Schematic illustration of possible interdigitated lamella packing structure of alkylurea.

Acknowledgments

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References

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2 R. Rowland, R. Taylor, *J. Phys. Chem.* 1996, **100**, 7384.