Electronic Supplementary Information

Improved mechanical properties of Alkylamide Organogels via a Mixing Enhancement Effect

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Materials and Methods

Stearamide (C18Am, 90%), hexadecanamide (C16Am, 95%) and octanamide (C8Am, 98%) were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. SH 245 (decamethylcyclopentasiloxane) was purchased from Dow Corning Toray Co., Ltd. All solvents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

The gelation tests were performed using the vial inversion method. A crystal of alkylamide was placed in a vial with a solvent at a specific concentration (wt%) and capped. The vial was heated in a dry bath at 100 °C until the alkylamide crystal was dissolved. The alkylamide solution was then left for 1 h at room temperature, and gelation was determined by visual observation after inversion of the vial.

Thixotropic behaviour was evaluated using the vial inversion method. The alkylamide organogel in the vial was shaken and collapsed using a vortex genie (Scientific Industries, Inc). The obtained sol was then left for a set time at room temperature, and the recovery of the gel state from the sol state was determined by visual observation after inversion of the vial.

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

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

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

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

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 placed in a glass capillary tube of 1 mm diameter).

Table S1

Table S1. Critical gel concentrations of alkylamide derivatives.

Sample	C18Am	C16Am	C8Am	ε 1□)
PC	2 (TG)	2 (TG)	3 (CG)	66.14
DMF	2 (TG)	2 (TG)	S	47.24
Methanol	3 (TG)	7 (TG)	S	33.0
Ethanol	3 (OG)	6 (OG)	S	25.3
1-Butanol	3 (OG)	6 (OG)	S	17.84
DCE	2 (TG)	3 (TG)	4 (CG)	10.42
THF	4 (TG)	5 (TG)	S	7.52
Ethyl Acetate	2 (TG)	8 (TG)	3 (TG)	6.0814
SH 245	3 (TG)	2 (TG)	3 (CG)	2.50
Toluene	3 (TG)	6 (TG)	3 (CG)	2.379
n-Octane	2 (TG)	3 (TG)	3 (CG)	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.
SH 245: decamethylcyclopentasiloxane.
Key: S: solution at 10 wt%, TG: turbid gel, OG: opaque gel, CG: clear gel.

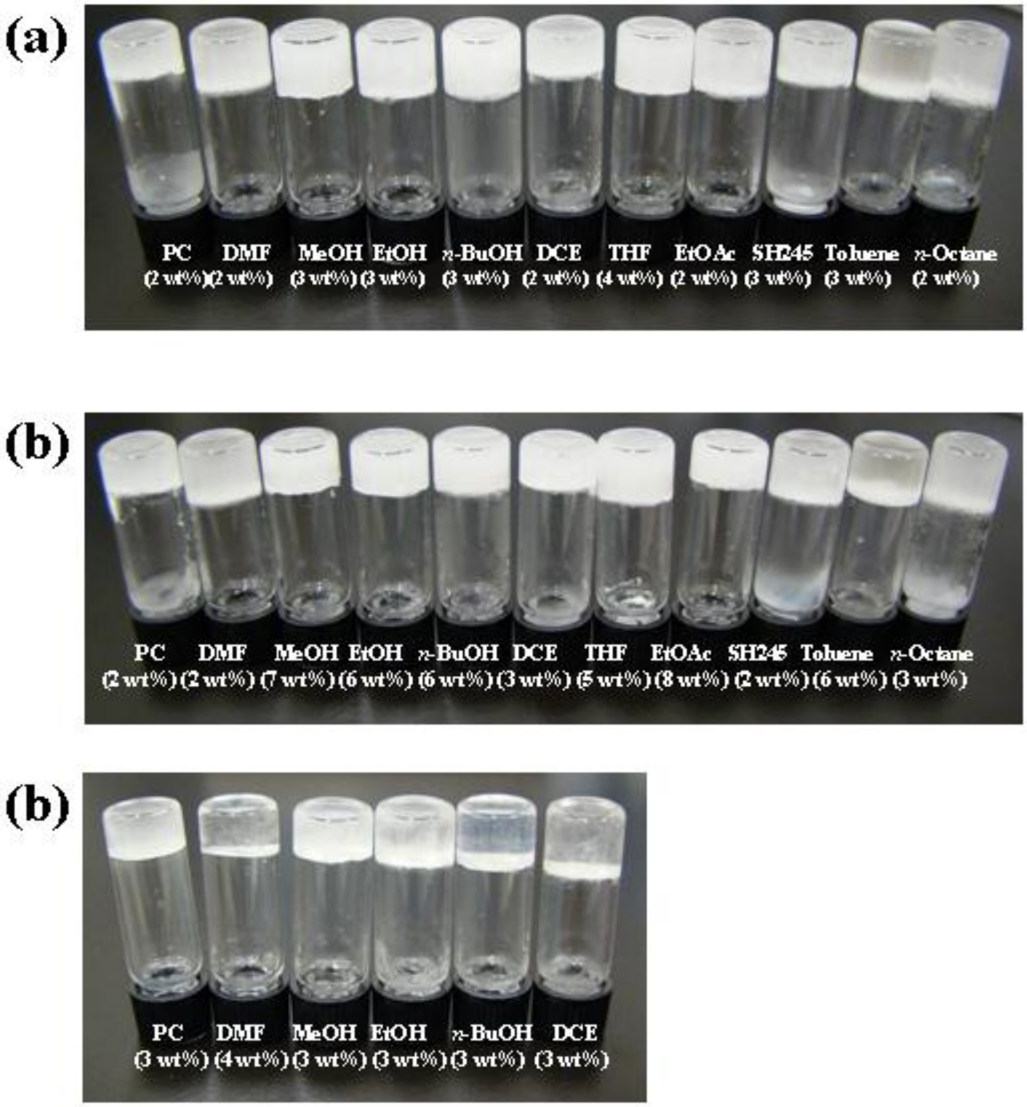

Fig. S1

Fig. S1 Photographs of single-component organogels: (a) C18Am gels, (b) C18Am gels, (c) C8Am gels.

Tables S2 and S3

Table S2 Transmittance of toluene organogels in the visible region.

Sample	T% at 400 nm	T% at 500 nm	T% at 600 nm	T% at 700 nm
C18Am 3 wt% gel	0.15	0.00	0.02	0.01
C16Am 6 wt% gel	0.12	0.03	0.00	0.02
C8Am 3 wt% gel	1.1	2.8	3.8	5.6
C18Am/C16Am/C8Am 1/1/2* 4 wt% gel	0.18	0.15	0.24	0.34
C18Am/C16Am/C8Am 1/1/4* 4 wt% gel	0.79	6.3	24.2	45.2
C18Am/C16Am/C8Am 1/1/10* 4 wt% gel	1.2	11.6	29.9	48.9

* A mixing ratio denoted as w/w/w.

Table S3 Transition temperatures of toluene organogels obtained from DSC measurements (heating and cooling rate: 2 °C/min).

Sample	$T_{gel\rightarrow sol}$ /°C (ΔH/mJ mg^{-1})	$T_{sol\rightarrow gel}$ /°C (ΔH/mJ mg^{-1})
C18Am 3wt% gel	56 (30.7)	67 (30.5)
C16Am 6 wt% gel	61 (53.2)	68 (51.9)
C8Am 3 wt% gel	46 (13.9)	49 (13.7)
C18Am/C16Am/C8Am 1/1/2 4 wt% gel	25 (12.1)	31 (12.0)
C18Am/C16Am/C8Am 1/1/4 4 wt% gel	27 (13.7)	34 (14.5)
C18Am/C16Am/C8Am 1/1/10 4 wt% gel	14, 43* (5.1)	28 (4.6)

* Bimodal peak (peak temperatures).

Fig. S2

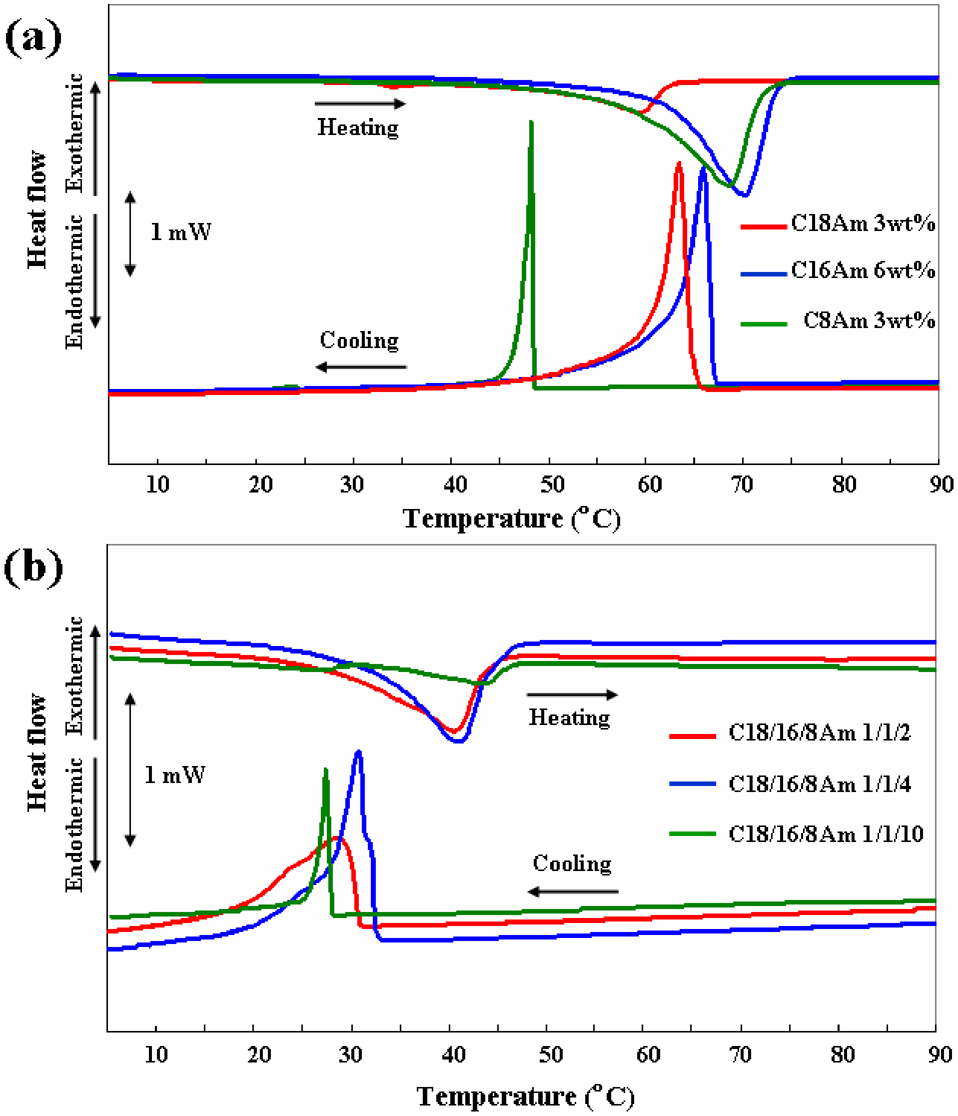

Fig. S2 DSC curves for CnAm toluene gels (2 °C/min): (a) CnAm amd (b) mixed CnAm toluene gels.

Figs. S3 and S4

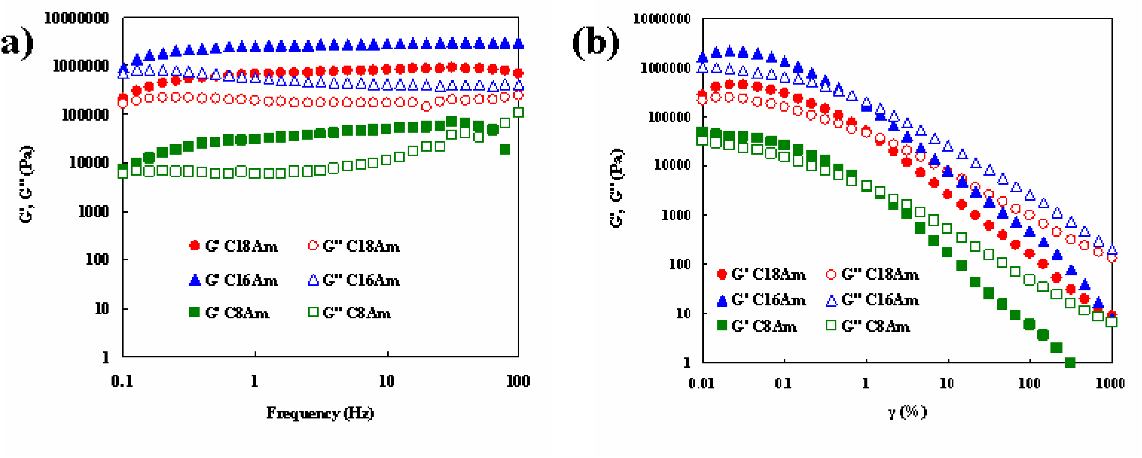

Fig. S3 Dynamic rheological properties of CnAm toluene gels: (a) Frequency sweep and (b) strain sweep for the C18Am (3 wt%), C16Am (6wt%) and C8Am toluene gels.

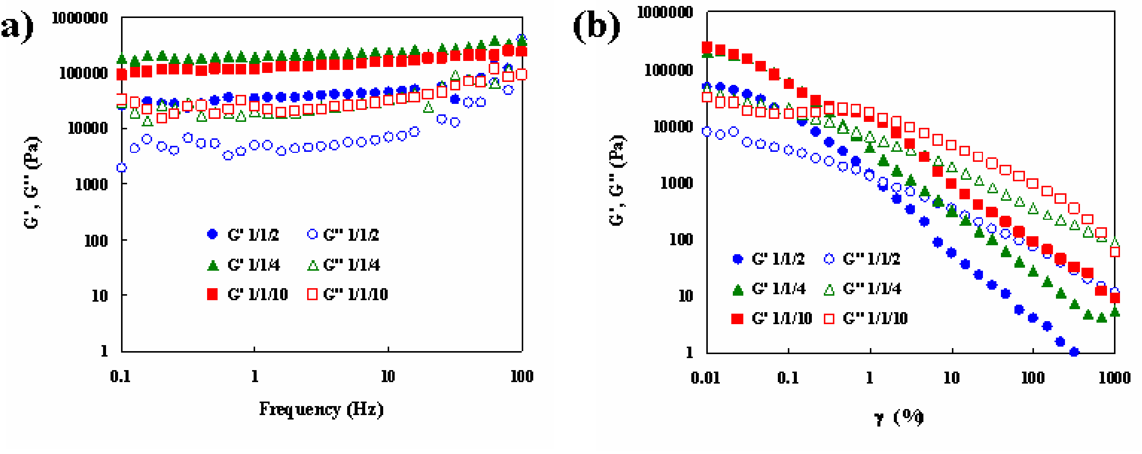

Fig. S4 Dynamic rheological properties of C18Am/C16Am/C8Am (4 wt%) toluene gels with mixing ratios denoted as w/w/w: (a) Frequency sweep and (b) strain sweep.

Figs. S5 and S6

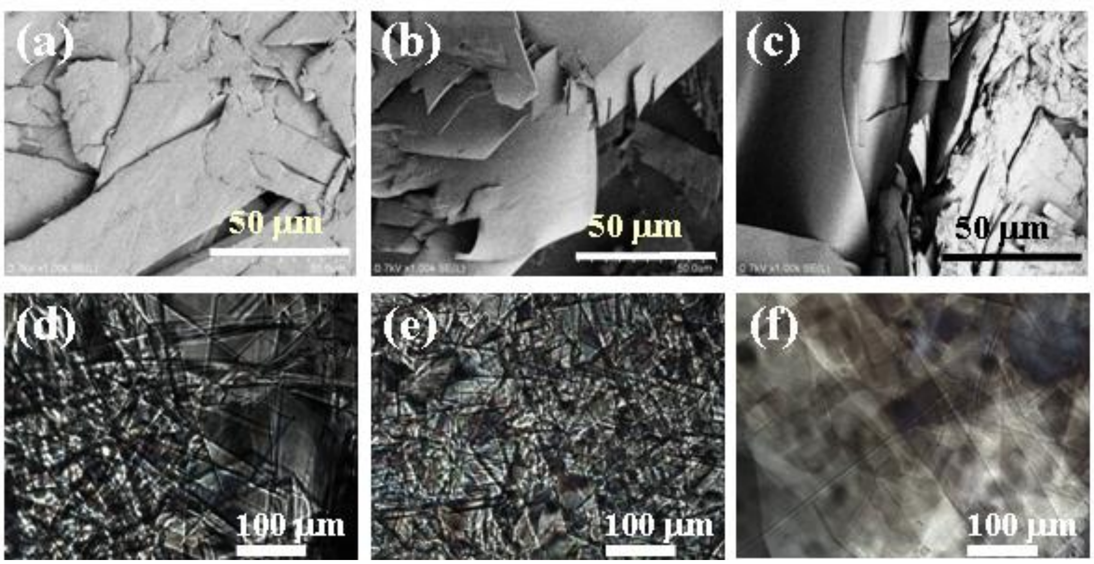

Fig. S5 SEM images of CnAm xerogels (a–c) and POM images of CnAm toluene gels (d–f): (a) C18Am, (b) C16Am, (c) C8Am, (d) 3 wt% C18Am toluene gel, (e) 6 wt% C16Am toluene gel and (f) 3 wt% C8Am toluene gel.

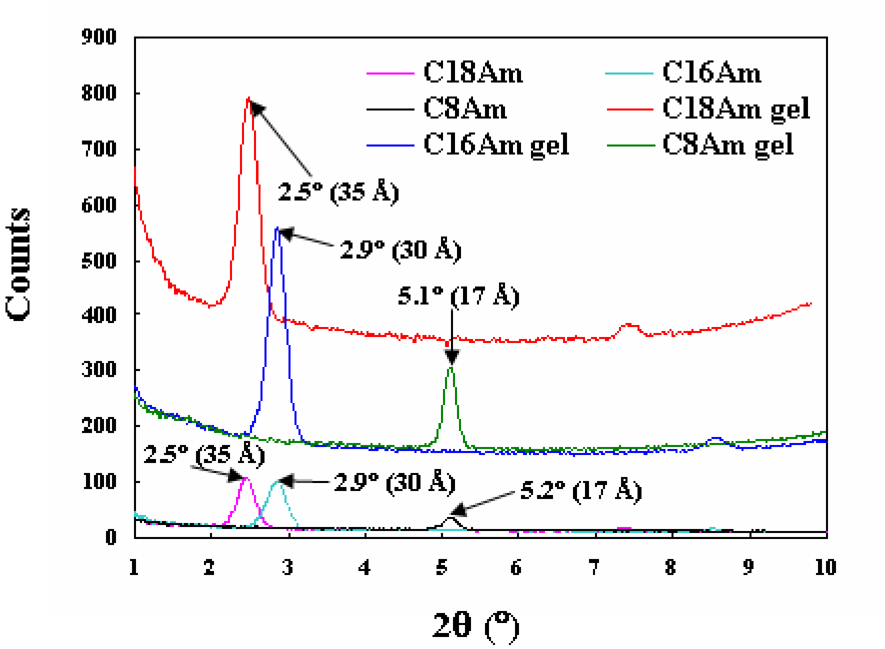

Fig. S6 XRD data for crystals of reagent grade CnAms and 3 wt% CnAm toluene gels.

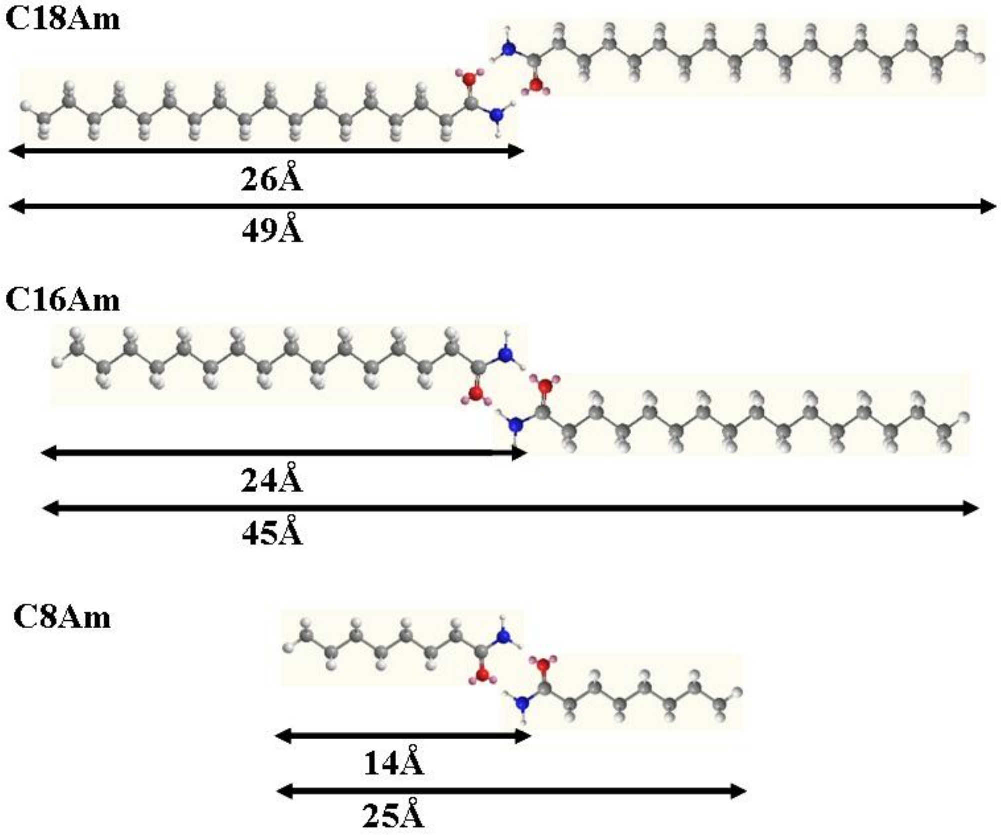

Fig. S7

Fig. S7 Possible bilayer structures of CnAms. Contour length of CnAms was obtained from MM2 calculations of the chemical structures of CnAms using ChemDraw. The total length of one molecule is the sum of the contour length of two molecules, two $-NH_2$ van der Waals radii and two $-CH_3$ van der Waals radii.[1,2] Assuming hydrogen bonding, the total length of two molecules is the sum of the contour length of two molecules and two $-CH_3$ minus any overlapping length.

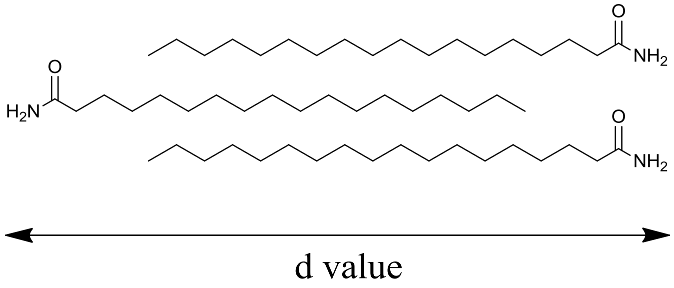

Fig S8. Schematic illustration of possible interdigitated lamella packing structure of alkylamide for longer d value.

Acknowledgments

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References

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