

## Electronic Supplementary Information

# Onset of Mixing-Induced Thixotropy in Hydrogels by Mixing Two Homologues of Low-Molecular-Weight Hydrogelators

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## Materials and Methods

All reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K.).

The gelation tests were performed using the vial inversion method using vial with rubber seal (mighty vial; Maruemu corporation). A white crystal of CnNG was placed in a vial with water at a specific concentration (wt%) and capped. The vial was heated in a dry bath at 100 °C until the CnNG crystal was dissolved. The CnNG aqueous 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 prepared hydrogel in the vial was shaken and mechanically 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.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on an AVANCE 500 (500 MHz, Bruker BioSpin K.K.) spectrometers. Elemental analysis was performed with a MICRO CODER JM10 (J-SCIENCE LAB CO., Ltd.). LC-MS was performed with a Waters 3100 single quadrupole LCMS system (ESI, Nihon Waters K. K.).

SEM images were recorded with a SU-8000 scanning electron microscope (Hitachi High-Technologies Corporation) at 1.0 kV; the SEM sample (xerogel made from hydrogel) was freeze-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 with a JFC-1600 auto fine coater (JEOL Ltd., Pt coating is 10-nm thick).

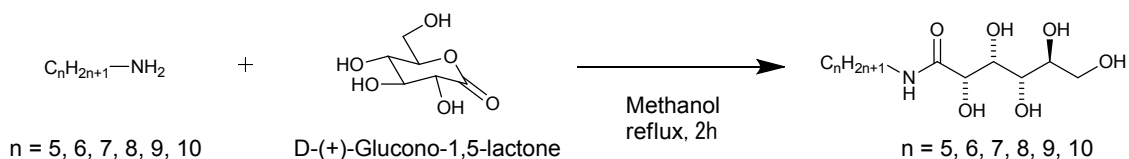
Thermal analysis was performed with an EXSTAR6000 differential scanning calorimeter DSC (Seiko Instruments Inc.) using a Ag-made closable sample pan. Transition temperatures of hydrogels ( $T_{\text{gel} \rightarrow \text{sol}}$  and  $T_{\text{sol} \rightarrow \text{gel}}$ ) were determined as extrapolated onset temperatures from the DSC curves.

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  $\gamma$  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 frequency 1 rad s<sup>-1</sup> (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<sup>-1</sup> for 0.1 s), repeatedly.

XRD data were recorded on a D8 Discover X-ray diffractometer (Bruker AXS K.K.) with CuK $\alpha$  at 26 °C (the sample was filled in a quartz glass capillary tube of 2 mm diameter).

## General procedure for the synthesis of C<sub>n</sub>NGs



C<sub>n</sub>NGs were synthesized using a procedure reported previously.<sup>1,2</sup> Under N<sub>2</sub> atmosphere, a mixture of the appropriate alkylamine and D-(+)-glucono-1,5-lactone were refluxed in methanol for 2 h. The white product, which precipitated out of the cooled mixture, was recrystallized in methanol to yield C<sub>n</sub>NG as a white crystal.

C5NG: Following the general procedure [with D-(+)-glucono-1,5-lactone (3.00 g, 16.50 mmol) and pentylamine (1.54 g, 17.33 mmol) in methanol (10 ml)], C5NG was obtained in 31.7% yield (1.39 g, white crystals). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 7.61 (t, 1H, *J* = 5.8 Hz), 5.37 (d, 1H, *J* = 5.0 Hz), 4.56 (d, 1H, *J* = 5.0 Hz), 4.49 (d, 1H, *J* = 5.0 Hz), 4.41 (d, 1H, *J* = 7.3 Hz), 4.36 (t, 1H, *J* = 5.7 Hz), 3.98 (t, 1H, *J* = 4.3 Hz), 3.90 (m, 1H), 3.58 (m, 1H), 3.47 (s (br), 2H), 3.36 (m, 1H), 3.07 (m, 2H), 1.43 (m, 2H), 1.23 (m, 4H), 0.86 (t, 3H, *J* = 6.8 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 173.10, 74.49, 73.31, 72.38, 71.04, 64.26, 39.09, 29.66, 29.41, 22.70, 14.75. LC-MS: *m/z* calcd for C<sub>11</sub>H<sub>23</sub>NO<sub>6</sub>: 265.15; Found: 264.2 [M-H]<sup>+</sup>. Elemental anal. calcd for C<sub>11</sub>H<sub>23</sub>NO<sub>6</sub>: C, 49.80; H, 8.74; N, 5.28; Found: C, 49.76; H, 8.61; N, 5.26.

C6NG: Following the general procedure [with D-(+)-glucono-1,5-lactone (2.00 g, 11.00 mmol) and hexylamine (1.19 g, 11.55 mmol) in methanol (10 ml)], C6NG was prepared in 54.7 % yield (1.68 g, white crystals). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 7.61 (t, 1H, *J* = 5.8 Hz), 5.36 (d, 1H, *J* = 4.7 Hz), 4.56 (d, 1H, *J* = 4.4 Hz), 4.49 (d, 1H, *J* = 4.4 Hz), 4.41 (d, 1H, *J* = 6.9 Hz), 4.36 (t, 1H, *J* = 5.0 Hz), 3.98 (t, 1H, *J* = 3.9 Hz), 3.90 (m, 1H), 3.57 (m, 1H), 3.47 (s (br), 2H), 3.35 (m, 1H), 3.07 (m, 2H), 1.40 (m, 2H), 1.26 (m, 6H), 0.86 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 173.10, 74.48, 73.31, 72.39, 71.05, 64.26, 39.14, 31.88, 29.97, 26.88, 22.90, 14.75. LC-MS: *m/z* calcd for C<sub>12</sub>H<sub>25</sub>NO<sub>6</sub>: 279.17; Found: 278.2 [M-H]<sup>+</sup>. Elemental anal. calcd for C<sub>12</sub>H<sub>25</sub>NO<sub>6</sub>: C, 51.60; H, 9.02; N, 5.01; Found: C, 51.21; H, 8.89; N, 5.00.

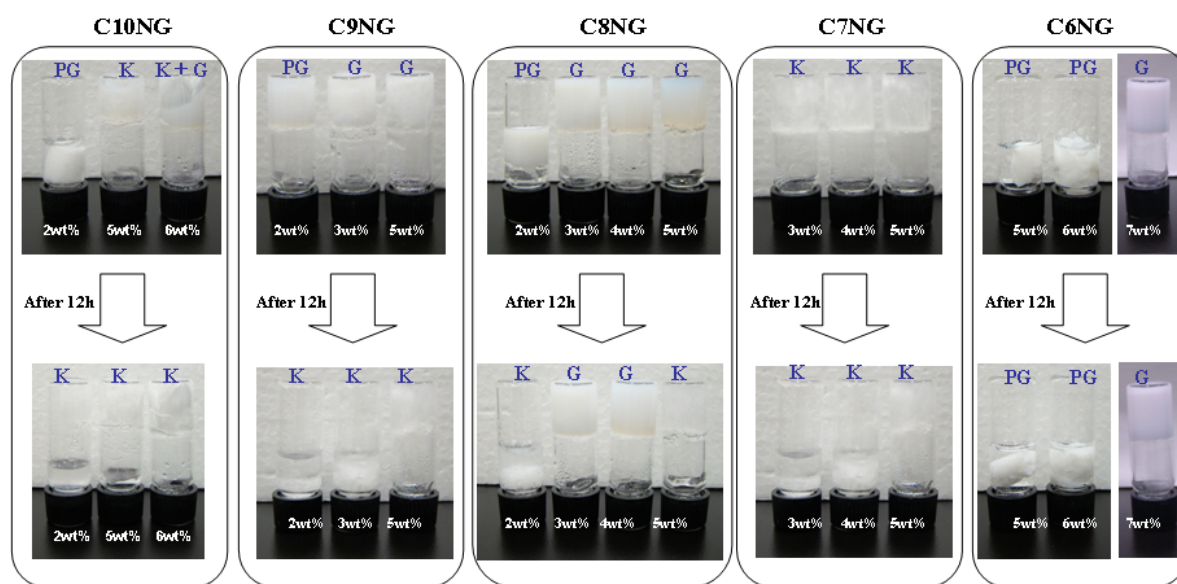
C7NG: Following the general procedure [with D-(+)-glucono-1,5-lactone (3.00 g, 16.50 mmol) and heptylamine (2.04 g, 17.33 mmol) in methanol (15 ml)], C7NG was prepared in 77.1 % yield (3.73 g, white crystals). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 7.61 (t, 1H, *J* = 5.8 Hz), 5.36 (d, 1H, *J* = 5.0 Hz), 4.55 (d, 1H, *J* = 4.7 Hz), 4.48 (d, 1H, *J* = 5.4 Hz), 4.40 (d, 1H, *J* = 7.3 Hz), 4.35 (t, 1H, *J* = 5.7 Hz), 3.97 (t, 1H, *J* = 4.3 Hz), 3.90 (m, 1H), 3.60 (m, 1H), 3.47 (s (br), 2H), 3.38 (m, 1H), 3.08 (m, 2H), 1.41 (m, 2H), 1.26 (m, 8H), 0.87 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 173.08, 74.48, 73.31, 72.39, 71.04, 64.26, 39.13, 32.11, 30.01, 29.30, 27.18, 22.91, 14.79. LC-MS: m/z calcd for C<sub>13</sub>H<sub>27</sub>NO<sub>6</sub>: 293.18; Found: 292.2 [M-H]<sup>+</sup>. Elemental anal. calcd for C<sub>13</sub>H<sub>27</sub>NO<sub>6</sub>: C, 53.23; H, 9.28; N, 4.77; Found: C, 53.36; H, 9.21; N, 4.78.

C8NG: Following the general procedure [with D-(+)-glucono-1,5-lactone (2.00 g, 11.00 mmol) and octylamine (1.52 g, 11.55 mmol) in methanol (10 ml)], C8NG was prepared in 90.2 % yield (3.05 g, white crystals). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 7.61 (t, 1H, *J* = 5.8 Hz), 5.36 (d, 1H, *J* = 5.0 Hz), 4.55 (d, 1H, *J* = 5.0 Hz), 4.48 (d, 1H, *J* = 5.4 Hz), 4.41 (d, 1H, *J* = 6.9 Hz), 4.35 (d, 1H, *J* = 5.7 Hz), 3.98 (t, 1H, *J* = 4.3 Hz), 3.89 (m, 1H), 3.59 (m, 1H), 3.47 (s (br), 2H), 3.35 (m, 1H), 3.07 (m, 2H), 1.45 (m, 2H), 1.25 (m, 10H), 0.86 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 173.08, 74.49, 73.31, 72.39, 71.04, 64.26, 39.14, 32.13, 30.01, 29.62, 29.52, 27.24, 22.95, 14.78. LC-MS: m/z calcd for C<sub>14</sub>H<sub>29</sub>NO<sub>6</sub>: 307.20; Found: 306.2 [M-H]<sup>+</sup>. Elemental anal. calcd for C<sub>14</sub>H<sub>29</sub>NO<sub>6</sub>: C, 54.70; H, 9.51; N, 4.56; Found: C, 54.61; H, 9.51; N, 4.55.

C9NG: Following the general procedure [with D-(+)-glucono-1,5-lactone (3.00 g, 16.50 mmol) and nonylamine (2.53 g, 17.33 mmol) in methanol (20 ml)], C9NG was prepared in 90.4 % yield (4.79 g, white crystals). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 7.61 (t, 1H, *J* = 5.8 Hz), 5.36 (d, 1H, *J* = 4.7 Hz), 4.55 (d, 1H, *J* = 4.4 Hz), 4.48 (d, 1H, *J* = 4.7 Hz), 4.40 (d, 1H, *J* = 6.9 Hz), 4.35 (t, 1H, *J* = 5.5 Hz), 3.97 (d, 1H, *J* = 3.9 Hz), 3.90 (m, 1H), 3.58 (m, 1H), 3.49 (s (br), 2H), 3.37 (m, 2H), 3.07 (m, 2H), 1.40 (m, 2H), 1.26 (m, 12H), 0.86 (t, 3H, *J* = 6.8 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 172.67, 74.08, 72.91, 71.99, 70.64, 63.87, 38.73, 31.76, 29.62, 29.44, 29.27, 29.14, 26.84, 22.55, 14.39. LC-MS: calcd for m/z C<sub>15</sub>H<sub>31</sub>NO<sub>6</sub>: 321.22; Found: 320.2 [M-H]<sup>+</sup>. Elemental anal. calcd for C<sub>15</sub>H<sub>31</sub>NO<sub>6</sub>: C, 56.05; H, 9.72; N, 4.36; Found: C, 55.90; H, 9.78; N, 4.37.

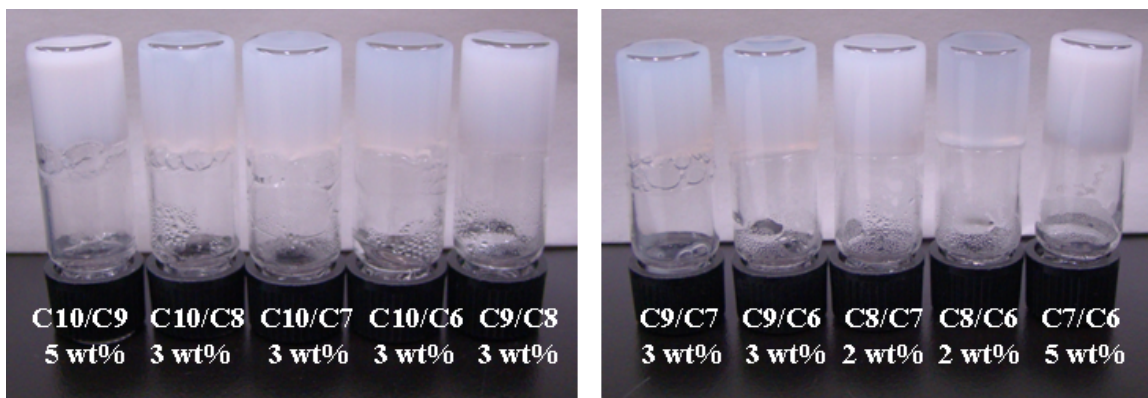
C10NG: Following the general procedure [with D-(+)-glucono-1,5-lactone (2.00 g, 11.00 mmol) and decylamine (1.85 g, 11.55 mmol) in methanol (10 ml)], C10NG was prepared in 37.1 % yield (1.37 g, white crystals). <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 7.61 (t, 1H, *J* = 6.0 Hz), 5.36 (d, 1H, *J* = 4.4 Hz), 4.55 (d, 1H, *J* = 4.4 Hz), 4.48 (d, 1H, *J* = 4.1 Hz), 4.40 (d, 1H, *J* = 6.9 Hz), 4.35 (d, 1H, *J* = 5.5 Hz), 3.98 (s (br), 1H), 3.90 (s (br), 1H), 3.58 (s (br), 1H), 3.47 (s (br), 2H), 3.34 (m, 1H), 3.07 (m, 2H), 1.42 (m, 2H), 1.25 (m, 14H), 0.86 (t, 3H, *J* = 6.8 Hz). <sup>13</sup>C-NMR (125 MHz, DMSO-d<sub>6</sub>, TMS, δ, ppm): 173.08, 74.49, 73.31, 72.39, 71.03, 64.26, 39.14, 32.17, 30.02, 29.90, 29.87, 29.68, 29.57, 27.25, 22.96, 14.79. LC-MS: *m/z* calcd for C<sub>16</sub>H<sub>33</sub>NO<sub>6</sub>: 335.23; Found: 334.3 [M-H]<sup>+</sup>. Elemental anal. calcd for C<sub>16</sub>H<sub>33</sub>NO<sub>6</sub>: C, 57.29; H, 9.92; N, 4.18; Found: C, 57.34; H, 9.94; N, 4.21.

**Fig. S1**

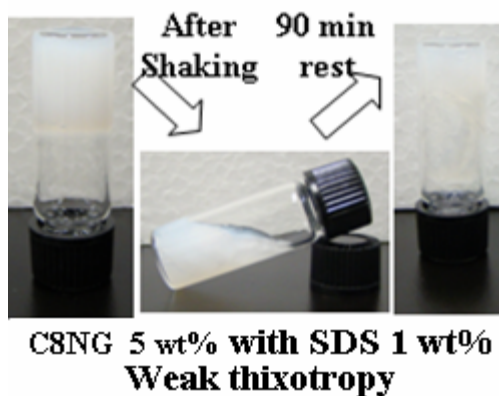


**Fig. S1** Photographs of C<sub>n</sub>NG hydrogels taken after initial cooling to rt and then again after a 12 h period of rest. Key. PG: partial gel, G: gel, K: crystal, K+G: gel with partially crystallized part.

**Figs. S2 and S3**

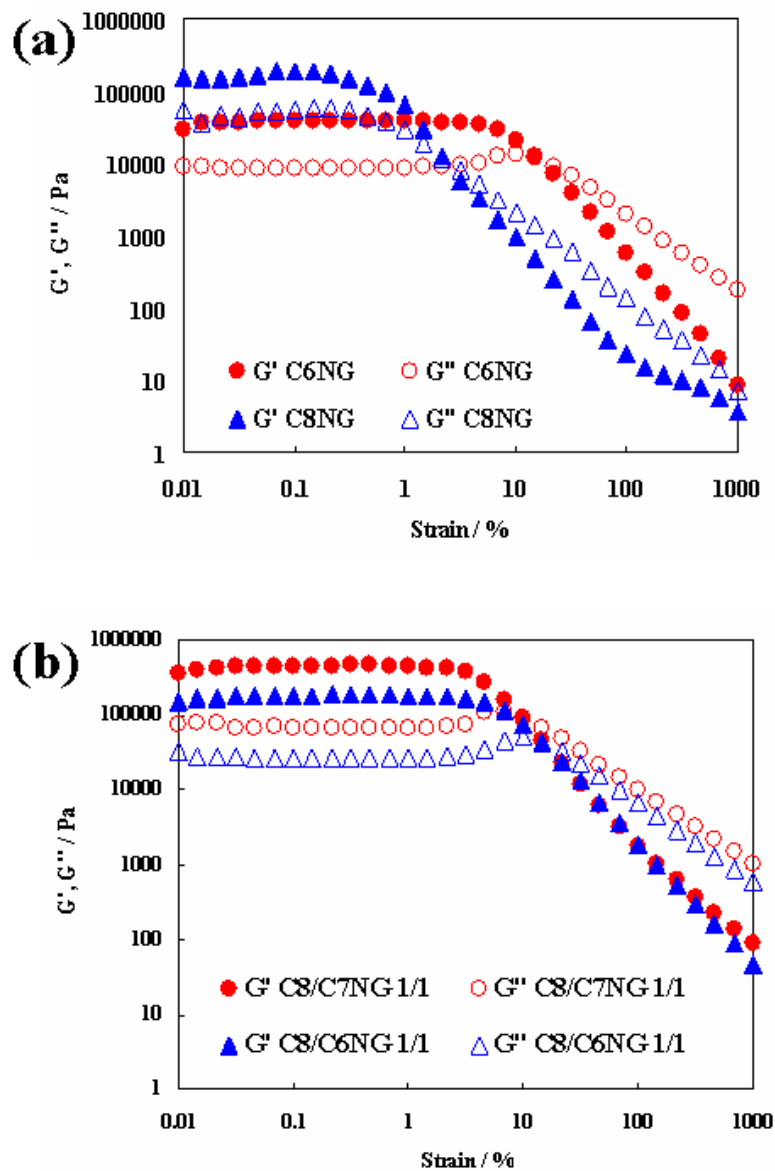


**Fig. S2** Photographs of two-component CnNG hydrogels with 1/1 (w/w) mixing ratio after the gelation test. “Cn” denotes CnNG..



**Fig. S3** Thixotropic behaviour of C8NG (5 wt%)/sodium dodecyl sulfate (SDS, 1 wt%) hydrogel..

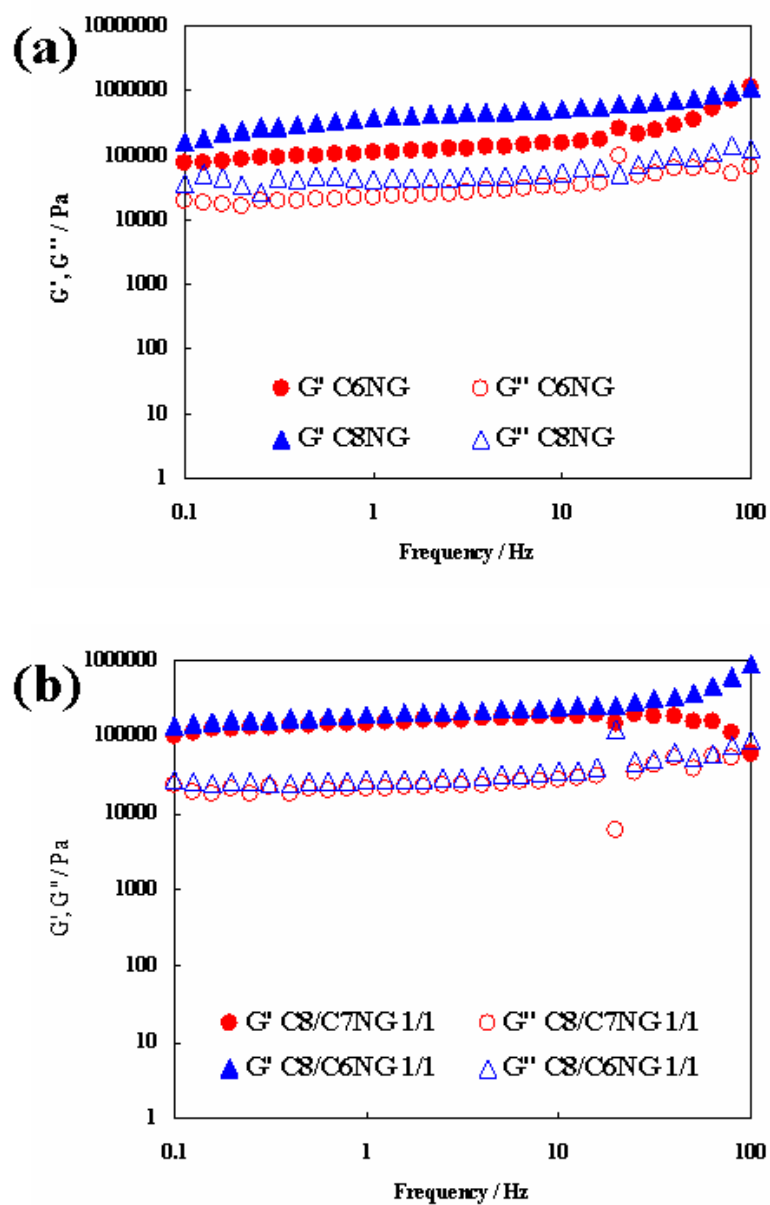
Fig. S4



**Fig. S4** Strain sweep of one- and two-component CnNG hydrogels. (a) one-component hydrogels, C8NG (3 wt%) and C6NG (7 wt%); (b) two-component hydrogels, C8NG/C7NG (mixing ratio, 1/1 (w/w), 5 wt%) and C8NG/C6NG (mixing ratio, 1/1 (w/w), 5 wt%).



Fig. S5



**Fig. S5** Frequency sweep of one- and two-component CnNG hydrogels. (a) single hydrogels, C8NG (3 wt%) and C6NG (7 wt%); (b) mixed hydrogels, C8NG/C7NG (mixing ratio, 1/1 (w/w), 5 wt%) and C8NG/C6NG (mixing ratio, 1/1 (w/w), 5 wt%).

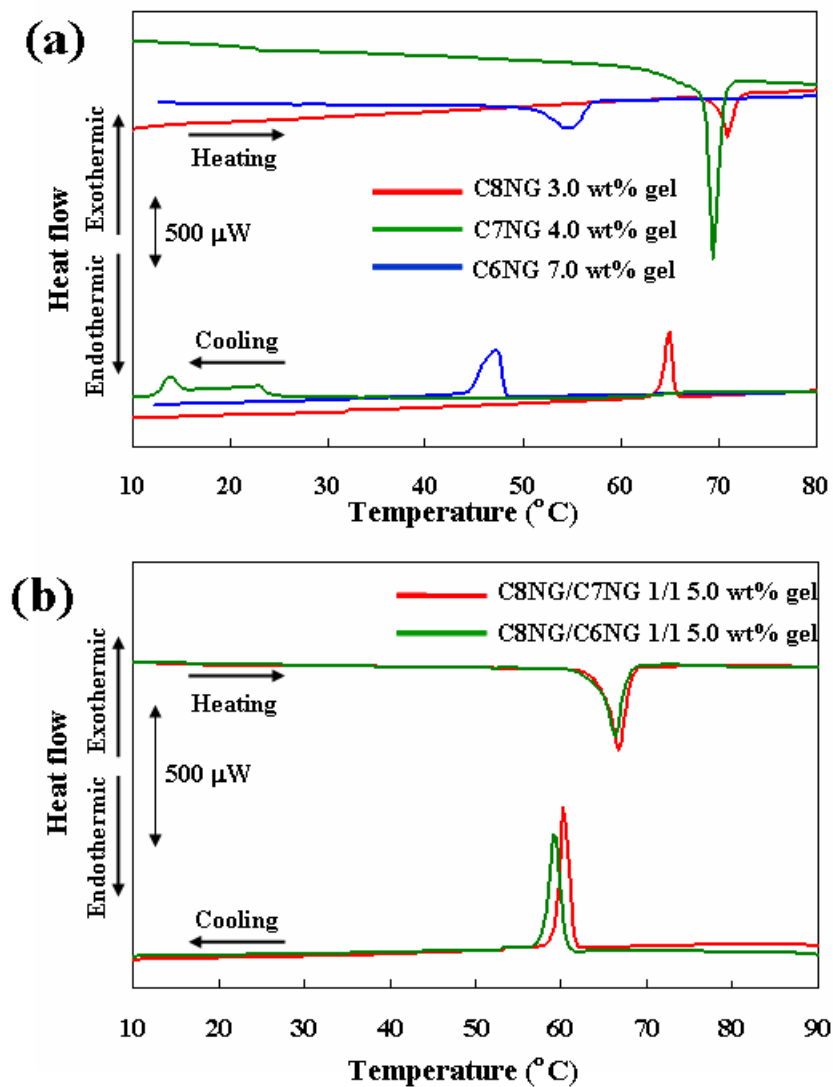
## Table S1

**Table S1** Transition temperatures of select one- and two-component hydrogels obtained from DSC measurements (heating and cooling rates of 2 °C/min)

Sample	$T_{\text{gel} \rightarrow \text{sol}} / ^\circ\text{C}$ ( $\Delta H/\text{mJ mg}^{-1}$ )	$T_{\text{sol} \rightarrow \text{gel}} / ^\circ\text{C}$ ( $\Delta H/\text{mJ mg}^{-1}$ )
C6NG 7 wt% hydrogel	52 (4.40)	50 (3.65)
C7NG solid (crystal like gel) obtained from 3 wt% solution after gel test	69 (9.11)	14, 23* (4.19)
C8NG 3 wt% hydrogel	69 (2.01)	67 (2.20)
C8NG/C6NG 1/1 (w/w) 5 wt% hydrogel	64 (3.64)	62 (3.56)
C8NG/C7NG 1/1 (w/w) 5 wt% hydrogel	63 (3.67)	63 (3.45)

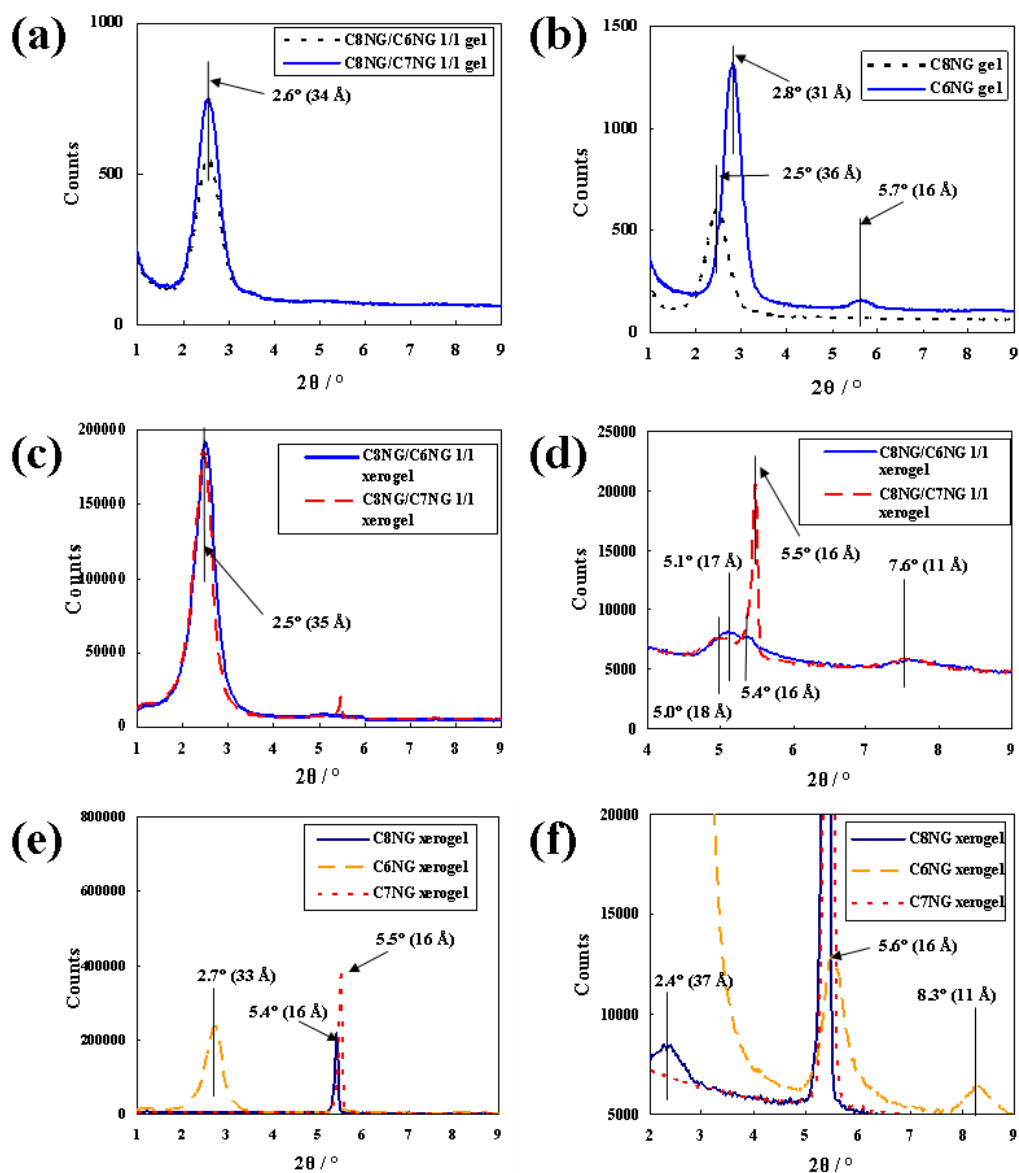
\*peak temperatures of bimodal peak.

Fig. S6



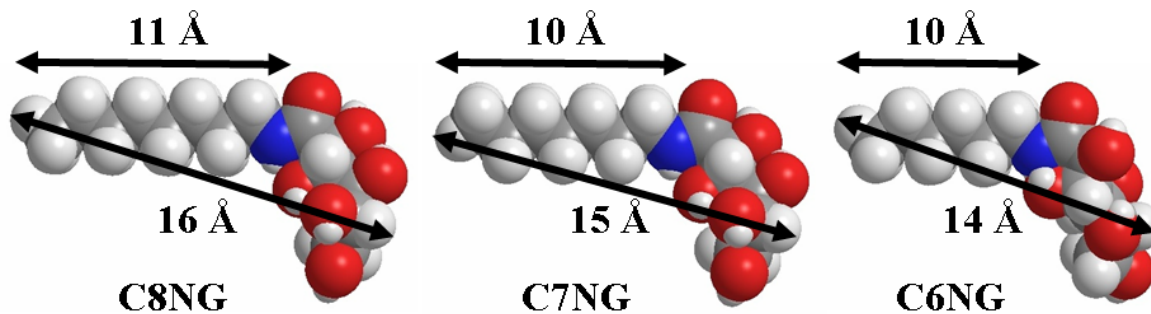
**Fig. S6** DSC curves of CnNG hydrogels (2 °C/min); (a) CnNG hydrogels (C8NG: 3.0 wt% gel, C7NG: 4.0 wt% gel and C6NG: 7.0 wt% gel), (b) mixed C8NG/CnNG 5.0 wt% hydrogels with mixing ratio denoted as w/w (C8NG/C7NG 1/1 5.0 wt% gel and C8NG/C6NG 1/1 5.0 wt% gel).

Fig. S7



**Fig. S7** XRD data of hydrogels and xerogels. (a) two-component hydrogels: C8NG/C7NG (mixing ratio, 1/1 (w/w), 5.0 wt%) and C8NG/C6NG (mixing ratio, 1/1 (w/w), 5.0 wt%); (b) one-component hydrogels, C8NG (3.0 wt%) and C6NG (7.0 wt%); (c and d) xerogels obtained from two-component hydrogels, C8NG/C7NG (mixing ratio, 1/1 (w/w), 5.0 wt%) and C8NG/C6NG (mixing ratio, 1/1 (w/w), 5.0 wt%) and (e and f) xerogels obtained from one-component hydrogels, C8NG (3.0wt%), C7NG (3.0wt%) and C6NG (7.0wt%).

**Fig. S8**



**Fig. S8** MM2 (Chemdraw) optimized structures of C<sub>n</sub>NGs (n = 6, 7 and 8). The contour length and the length of the alkyl chain are shown for each molecule.

### Acknowledgements

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