

Supporting Information for

Kinetics of 5 α -cholestan-3 β -yl N-(2-naphthyl)carbamate/*n*-alkane organogel formation and its influence on the fibrillar networks

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Experimental Section

Materials. *n*-Octane (Aldrich, 98%), *n*-dodecane (Acros, 99+%), and *n*-dodecane-*d*₂₆ (MSD Isotopes, 98 atom% D) were used as received. 5 α -Cholestan-3 β -yl N-(2-naphthyl) carbamate (**CNC**) was synthesized as described in the literature¹ to yield material of mp 184.1-184.9 °C (lit mp 178 - 180 °C¹). Elemental Analysis: calcd for C₃₈H₅₅NO₂, C 81.82%, H 9.94%, N 2.51%; found, C 81.83%, H 10.38%, N 2.53%. ¹H-NMR: 8.00, 7.80-7.72, 7.46-7.28 (m, 7H, aromatic), 6.72 (s, 1H, NH), 4.80-4.65 (m, 1H, CH), 2.20-0.60 ppm (m, 47H, cholestanyl).

Instrumentation and sample preparation. Samples for gelation studies were prepared by placing known amounts of solvent and **CNC** in 5 mm (i.d.) glass tubes or 0.5 or 0.8 mm pathlength flattened capillaries. The containers with the gel components were flame-sealed and then heated until the gelator completely dissolved. Thereafter, the hot solutions/sols were cooled by different protocols until gelation occurred. They included

submerging the tubes in an ice-water bath (fast cooling), placing the tubes in air at ambient temperature (moderate cooling), or submerging the tubes in a thermostatted bath set at a temperature below T_g (controlled cooling). Qualitatively, gelation was considered successful if no sample flow was observed upon inverting the container at room temperature (i.e., the ‘inverse flow’ method²) after a third heating and cooling cycle. If part of the sample fell, the sample was classified as a partial gel. More detailed determinations of gel formation were provided by rheology measurements (vide infra).

Optical micrographs were recorded on a Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage, a Photometrics CCD camera interfaced to a computer, and an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. The samples, sealed in 0.5mm thickness flatted capillary tubes, were heated to their isotropic phase in a boiling water bath and cooled in an ethylene glycol bath that was equilibrated at a designated temperature. Optical micrographs were recorded after the samples were in the bath for 30 minutes (incubation at $< 30\text{ }^{\circ}\text{C}$) or overnight (incubation at $> 30\text{ }^{\circ}\text{C}$) to ensure that gelation had occurred.

UV spectra were obtained using a Cary 300 BIO UV-vis spectrophotometer.

Fluorescence spectra were recorded on Spex Fluorolog III spectrometer equipped with a VWR-1140 circulating thermostating bath.

X-ray diffraction (XRD) of samples was performed on a Rigaku R-Axis image plate system with Cu $K\alpha$ X-rays ($\lambda = 1.54056\text{ \AA}$) generated by a Rigaku generator operating at 46 kV and 46 mA with the collimator at 0.3 mm. Data processing and analyses were

performed using Materials Data JADE (version 5.0.35) XRD pattern processing software. Samples were sealed in either 1.0 mm (gels, exposures for 10 h) or 0.5 mm (neat powder, exposure for 30 min) glass capillaries (W. Müller, Schönwalde, Germany).

Kinetics of gelation by CD spectroscopy. CNC, dissolved in hot *n*-octane, was transferred to a 1.0 mm thick water-jacketed CD cell that was kept at 90 °C. CD spectra were recorded on a Jasco-700 CD spectrometer immediately after liquid at a predetermined temperature was flowed from a thermostating circulating bath through the jacket of the cell. ‘Zero’ time was defined as when the first spectrum was recorded; the approximate period required for temperature equilibration after sample transfer was less than 30 seconds since a very small amount of sample was used. The shortest period to complete gelation was 10-15 min. The scan rate and other instrumental parameters were set to optimize the signal-to-noise ratio. Infinite time values, when spectra no longer changed perceptibly with time (i. e., gelation was complete), were the average of signals from twenty scans.

Kinetics of gelation by fluorescence spectroscopy. CNC and *n*-octane in a sealed 3 mm pathlength flattened quartz tube or a 0.8 mm pathlength flattened Pyrex tube was heated until all solids dissolved. Then, the tube was placed into a thermostatted cell holder of the fluorimeter and the emission intensity at 375 nm (excitation at 318 nm) was recorded from the front-face as a function of time at a rate of 1 datum per second. In the data treatment, sets of 10 or 100 consecutive points were averaged and fitted to the kinetic models.

Kinetics of gelation by small angle neutron scattering (SANS). Data were obtained on the 30 m SANS beam line at the National Center for Neutron Research of the National Institute of Standards and Technology, Gaithersburg, MD (5 m scattering, $\lambda = 8.09 \text{ \AA}$) using 2 mm pathlength cylindrical quartz cells placed in a thermostatted ($\pm 0.1 \text{ }^\circ\text{C}$) cell holder. Hot samples (with *n*-dodecane-*d*₂₆ as the liquid) were transferred to the thermostatted cells as described above. The delay between the moment of transfer and initial measurements was less than 10 s. In the kinetic runs, intensity data were summed over a *Q* range of 0.008-0.1 \AA^{-1} for 10 s increments with 35 s delays between collections.

Kinetics of gelation by rheological measurements. Rheology data were recorded on a Rheometric Scientific RFS II rheometer equipped with parallel plates (25 mm diameter) on thermostatted ($\pm 0.1 \text{ }^\circ\text{C}$) samples. The gap between the plates (0.3-0.5 mm) did not influence mechanical properties of the samples, as indicated by the elastic modulus (G'), the loss modulus (G''), the ratio between G'' and G' ($\tan \delta$), and the complex viscosity (η^*). Dynamic rheology experiments were performed between 0.01 and 100 rad/s at a constant strain (1%) that is well within the linear regime of deformation. Hot solutions of CNC in *n*-dodecane were transferred onto the lower plate that was at 40 $^\circ\text{C}$ when the desired temperature was higher than 20 $^\circ\text{C}$ or at 20 $^\circ\text{C}$ higher than the desired temperature when the desired temperature was below 20 $^\circ\text{C}$. The plate was cooled quickly (ca. 30 s) to the desired temperature after the plate gap was adjusted to the desired separation. Recording of data commenced immediately thereafter. To minimize

evaporation of the solvent, a plastic cover with a liner soaked with *n*-dodecane was placed over the apparatus when measurements were made at 35 or 40 °C.

Multiple waveform rheology is a technique that applies a compound waveform on the sample, as described in equation 1.³ γ , the total applied strain, is the sum of the Fourier series described by each individual strain. ω_i , the applied frequencies, are harmonics (integer multiples) of a fundamental frequency. In our experiment, the fundamental frequency is 1 rad/s and the harmonic frequencies are 5, 10, 50, and 100 rad/s. Since the strain for each frequency is 0.2%, their sum γ , 1%, is well within the linear regime of deformation.

$$\gamma = \sum_{i=1}^m \gamma_i \sin(\omega_i t) \quad (1)$$

Supporting Table 1. Gelation procedures and appearances of CNC/*n*-alkane samples.^a

[CNC], wt %	Liquid	Gelation protocol ^b	Stability period ^c	Phase notations	T _g (°C)
0.80	<i>n</i> -dodecane	Slow	-	Precipitate	-
0.80	<i>n</i> -dodecane	Fast	-	Precipitate	-
1.1	<i>n</i> -dodecane	Slow	> 5 days	Translucent, strong gel ^d	38.5-58.1
1.1	<i>n</i> -dodecane	Moderate	~1-2 days	Translucent, weak gel ^{d,e}	53.0-53.5
1.1	<i>n</i> -dodecane	Fast	< 1 day	Translucent, weak gel ^{d,e}	42.3-51.5
0.89	<i>n</i> -octane	Slow	> 1 week	Translucent, strong gel	47.4-49.8
0.89	<i>n</i> -octane	Moderate	~ 2 days	Translucent, weak gel	41.0-49.7
0.89	<i>n</i> -octane	Fast	-	Partial gel	-
1.0	<i>n</i> -octane	Slow	> 6 months	Translucent, strong gel ^d	51.8-56.7
1.0	<i>n</i> -octane	Moderate	~1-2 days	Translucent, weak gel ^d	40.5-56.2
1.0	<i>n</i> -octane	Fast	<1 day	Translucent, weak gel ^d	52.0-52.2
1.5	<i>n</i> -octane	Slow	> 1 week	Translucent, strong gel	63.2
1.5	<i>n</i> -octane	Moderate	~ 2 days	Translucent, weak gel	62.1-63.5
1.5	<i>n</i> -octane	Fast	< 1 day	Translucent, weak gel	62.5-64.2
1.9	<i>n</i> -octane	Slow	> 1 week	Translucent, strong gel	69.5
1.9	<i>n</i> -octane	Moderate	~ 2 days	Translucent, strong gel	69.0-69.5

1.9	<i>n</i> -octane	Fast	< 1 day	Translucent, weak gel	72.1-73.0
3.0	<i>n</i> -octane	Slow	> 1 week	Opaque, strong gel	70.2-81.4
3.0	<i>n</i> -octane	Moderate	~ 2 days	Opaque, strong gel	79.5
3.0	<i>n</i> -octane	Fast	< 1 day	Translucent, strong gel	80.1-80.4

^a A 1 wt % concentration corresponds to ca. 1.3×10^{-2} mol/L. ^b Fast gelation—sol immersed in an ice-water bath; moderate—sol cooled in air; slow—sol cooled in a water bath at 40 °C. ^c Period before macroscopic phase separation at ambient temperature in a sealed container. ^d Weak gel—flow upon mild agitation (shaking by hand); strong gel—no flow induced by mild agitation. ^e Thixotropic; a stronger gel reformed after agitation.

Supporting Table 2. Summary of *K* and *n* values from analyses of kinetic experiments on gelation of 1.0 wt % CNC in *n*-alkane samples incubated at different temperatures.

Method	Liquid	Temp (°C)	<i>n</i> ^a	<i>K</i> (s ⁻¹) ^b	<i>R</i> ² ^c
CD	<i>n</i> -Octane	40.0	0.97±0.02 (303nm)	$(5.99 \pm 0.06) \times 10^{-4}$	0.93
	<i>n</i> -Octane	40.0	1.01±0.02 (337nm)	$(5.19 \pm 0.09) \times 10^{-4}$	0.95
	<i>n</i> -Octane	40.0	0.91±0.04 (303nm)	$(3.59 \pm 0.06) \times 10^{-4}$	0.99
	<i>n</i> -Octane	40.0	0.96±0.02 (337nm)	$(3.56 \pm 0.05) \times 10^{-4}$	0.99
	<i>n</i> -Octane	35.0	1.00±0.02 (302nm)	$(1.11 \pm 0.04) \times 10^{-3}$	0.98
	<i>n</i> -Octane	35.0	1.28±0.03 (336nm)	$(1.14 \pm 0.07) \times 10^{-3}$	0.95
	<i>n</i> -Octane	35.0	0.91±0.02 (302nm)	$(1.79 \pm 0.02) \times 10^{-3}$	0.97
	<i>n</i> -Octane	35.0	1.23±0.05 (336nm)	$(1.44 \pm 0.09) \times 10^{-3}$	0.95
	<i>n</i> -Octane	30.0	1.18±0.04 (344nm) ^d	$(9.94 \pm 0.10) \times 10^{-3}$	0.99
	<i>n</i> -Octane	25.0	0.98±0.05 (344nm) ^d	$(2.61 \pm 0.07) \times 10^{-3}$	0.99
	<i>n</i> -Octane	20.2	1.02±0.02 (344nm) ^d	$(2.25 \pm 0.06) \times 10^{-2}$	0.99
	<i>n</i> -Octane	1.4	1.22±0.04 (344nm) ^d	$(1.34 \pm 0.06) \times 10^{-2}$	0.99
	<i>n</i> -Octane	12.1	1.19±0.05 (344nm) ^d	$(1.78 \pm 0.04) \times 10^{-2}$	0.98
	<i>n</i> -Octane	8.7	0.96±0.02 (344nm) ^d	$(3.45 \pm 0.07) \times 10^{-2}$	0.99
	<i>n</i> -Octane	5.4	1.06±0.03 (344nm) ^d	$(2.26 \pm 0.09) \times 10^{-2}$	0.99
SANS	<i>n</i> -Dodecane- <i>d</i> ₂₆	40.0	1.09±0.02	$(8.79 \pm 0.06) \times 10^{-5}$	0.99
	<i>n</i> -Dodecane- <i>d</i> ₂₆	40.0	1.15±0.02	$(7.90 \pm 0.04) \times 10^{-5}$	1.00
Rheology	<i>n</i> -Dodecane	0.0 ^e	1.25±0.02	$(9.78 \pm 0.12) \times 10^{-3}$	1.00
	<i>n</i> -Dodecane	5.0 ^e	1.29±0.02	$(1.65 \pm 0.07) \times 10^{-2}$	0.99
	<i>n</i> -Dodecane	10.0 ^e	1.28±0.04	$(4.73 \pm 0.09) \times 10^{-3}$	1.00
	<i>n</i> -Dodecane	15.0 ^e	1.21±0.04	$(9.48 \pm 0.14) \times 10^{-3}$	0.99
	<i>n</i> -Dodecane	35.0 ^e	1.01±0.02	$(4.03 \pm 0.09) \times 10^{-3}$	0.99
	<i>n</i> -Dodecane	40.0 ^e	1.26±0.03	$(8.79 \pm 0.07) \times 10^{-4}$	1.00
	<i>n</i> -Dodecane	35.0 ^f	1.00±0.02 (1 rad/s)	$(4.87 \pm 0.09) \times 10^{-4}$	1.00
	<i>n</i> -Dodecane	35.0 ^f	1.03±0.03 (5 rad/s)	$(4.80 \pm 0.07) \times 10^{-4}$	1.00

	<i>n</i> -Dodecane	35.0 ^f	1.09±0.05 (10 rad/s)	$(4.76±0.10) \times 10^{-4}$	1.00
	<i>n</i> -Dodecane	35.0 ^f	1.14±0.02 (50 rad/s)	$(4.15±0.06) \times 10^{-4}$	1.00
	<i>n</i> -Dodecane	35.0 ^f	1.16±0.05 (100 rad/s)	$(3.98±0.04) \times 10^{-4}$	1.00
	<i>n</i> -Dodecane	40.0 ^f	1.04±0.05 (1 rad/s)	$(9.63±0.11) \times 10^{-4}$	0.99
	<i>n</i> -Dodecane	40.0 ^f	1.05±0.02 (5 rad/s)	$(1.07±0.06) \times 10^{-3}$	1.00
	<i>n</i> -Dodecane	40.0 ^f	1.00±0.02 (10 rad/s)	$(1.06±0.06) \times 10^{-3}$	1.00
	<i>n</i> -Dodecane	40.0 ^f	1.11±0.03 (50 rad/s)	$(9.94±0.09) \times 10^{-4}$	1.00
	<i>n</i> -Dodecane	40.0 ^f	1.11±0.03 (100 rad/s)	$(9.58±0.07) \times 10^{-4}$	1.00
Fluorescence ^g	<i>n</i> -Octane	1.1	1.08±0.02	$(1.92±0.14) \times 10^{-3}$	1.00
	<i>n</i> -Octane	3.9	1.11±0.02	$(2.82±0.09) \times 10^{-3}$	1.00
	<i>n</i> -Octane	9.4	0.97±0.02	$(2.69±0.07) \times 10^{-3}$	1.00
	<i>n</i> -Octane	13.9	1.20±0.03	$(3.83±0.09) \times 10^{-3}$	1.00
	<i>n</i> -Octane	22.5	1.28±0.02	$(3.62±0.06) \times 10^{-3}$	1.00
	<i>n</i> -Octane	23.8	0.98±0.02	$(1.78±0.06) \times 10^{-3}$	1.00
	<i>n</i> -Octane	32.0	0.99±0.02	$(5.02±0.12) \times 10^{-4}$	0.99
	<i>n</i> -Octane	39.2	1.16±0.02	$(1.69±0.07) \times 10^{-4}$	1.00

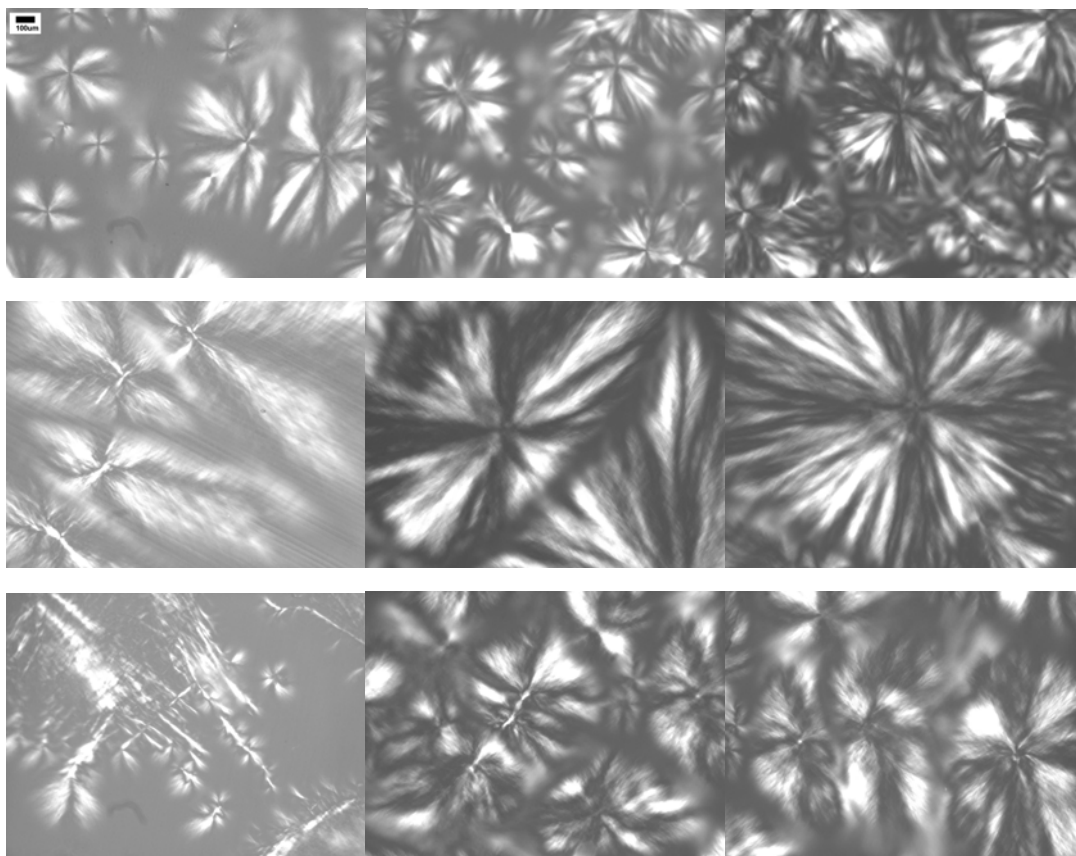
^a From linear Avrami fit. ^b From single exponential decay Avrami fit. ^c Square of correlation coefficient based on a linear fit. ^d Average of intensities between 343 and 347 nm. ^e Time-sweep experiments. ^f Multiple wave-form experiments. ^g λ_{ex} 318nm, λ_{em} 375 nm.

Supporting Table 3. Concentration and temperature dependence of Avrami parameters from fluorescence experiments on samples in *n*-octane^a

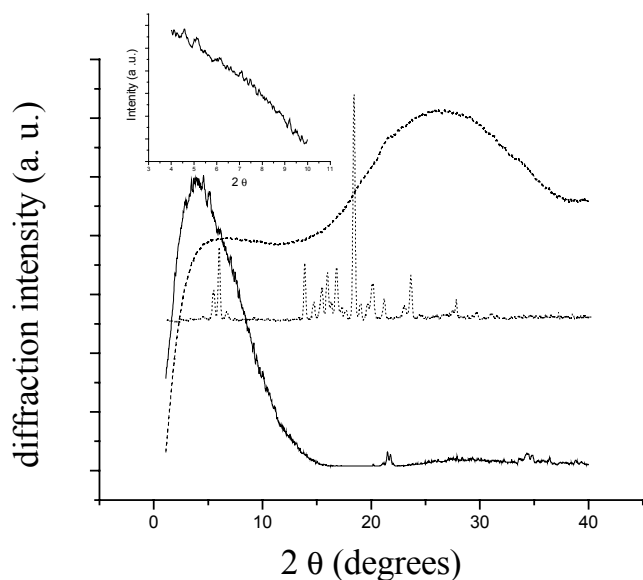
Temp (°C)	[CNC] (wt %)	<i>n</i>	<i>K</i> (s ⁻¹)	<i>R</i> ² ^b
14.5	0.89	1.19±0.02	$(8.75±0.09) \times 10^{-3}$	0.98
14.5	1.0	1.18±0.02	$(3.83±0.09) \times 10^{-3}$	1.00
14.5	1.5	0.97±0.03	$(1.89±0.10) \times 10^{-2}$	0.99
14.5	1.9	0.98±0.06	$(3.30±0.19) \times 10^{-2}$	0.99
32.2	0.89	0.98±0.02	$(7.02±0.06) \times 10^{-4}$	0.99
32.2	1.0	0.99±0.05	$(6.67±0.07) \times 10^{-4}$	0.99
32.2	1.5	0.96±0.04	$(9.43±0.09) \times 10^{-3}$	1.00
32.2	1.9	0.98±0.04	$(1.24±0.05) \times 10^{-2}$	0.99
32.2	2.5	1.12±0.02	$(3.01±0.11) \times 10^{-2}$	0.99

32.2	3.0	1.07±0.02	$(1.93±0.09)×10^{-2}$	0.99
36.3	0.89	1.35±0.04	$(2.27±0.08)×10^{-4}$	0.99
36.3	1.5	1.14±0.02	$(9.01±0.12)×10^{-3}$	0.99
36.3	1.9	1.00±0.02	$(1.20±0.07)×10^{-2}$	0.99

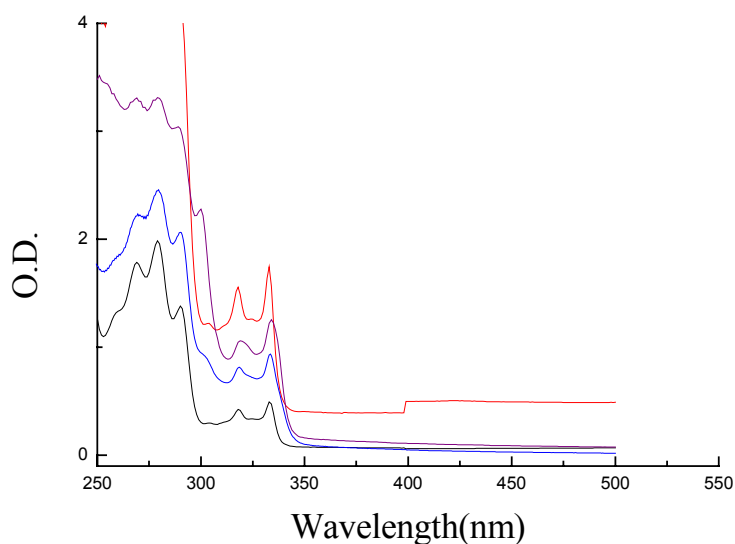
^a λ_{ex} 318nm, λ_{em} 375nm, front-face geometry; ^b Square of correlation coefficient based on a linear fit.



Supporting Figure 1. Optical micrographs of **CNC/*n*-octane** organogels. From left to right: 0.89, 1.46 and 1.94 wt % **CNC**; from top to bottom: incubated at 14.5, 32.2 and 36.3 °C after cooling from well above T_g . The scale bar, 100μm, applies to all micrographs.

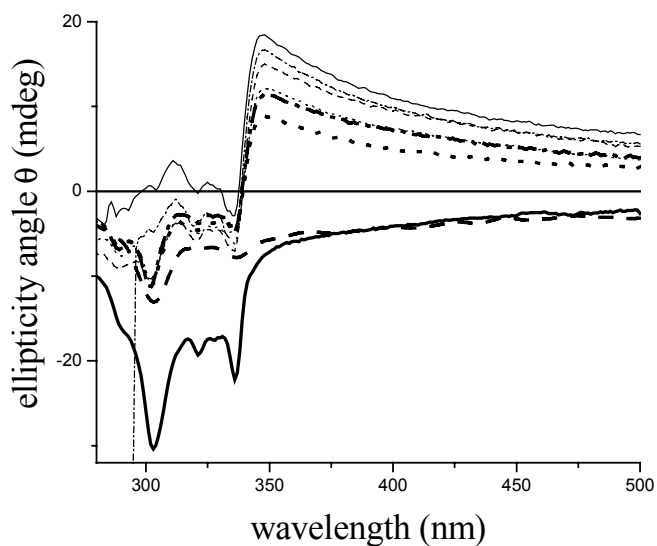


Supporting Figure 2. XRD patterns of a 3.0 wt % **CNC**/*n*-octane gel (incubation at 0 °C after heating above T_g , ----), gel diffraction with an empirical subtraction of the diffraction by neat octane (—), and the diffraction of neat solid **CNC** (····). The inset is an amplification of peaks from the gel in the low angle region.

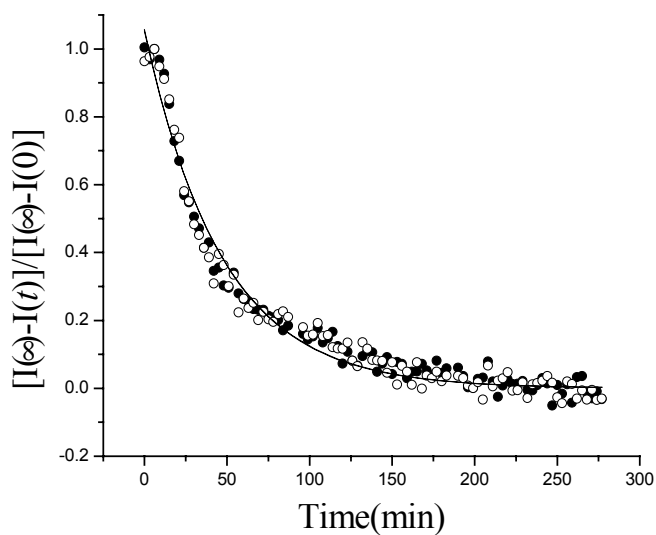


Supporting Figure 3. UV-vis spectra of **CNC**/*n*-octane organogels and solutions: 0.02 wt % solution (red, 5 cm pathlength); 0.19 wt % solution (black, 1 cm pathlength); 1.0 wt % gel formed at 40 °C (purple, 1 mm pathlength) and 1.0 wt % gel formed at 0 °C (blue, 1 mm pathlength). Gelated samples were incubated at the temperatures noted after being

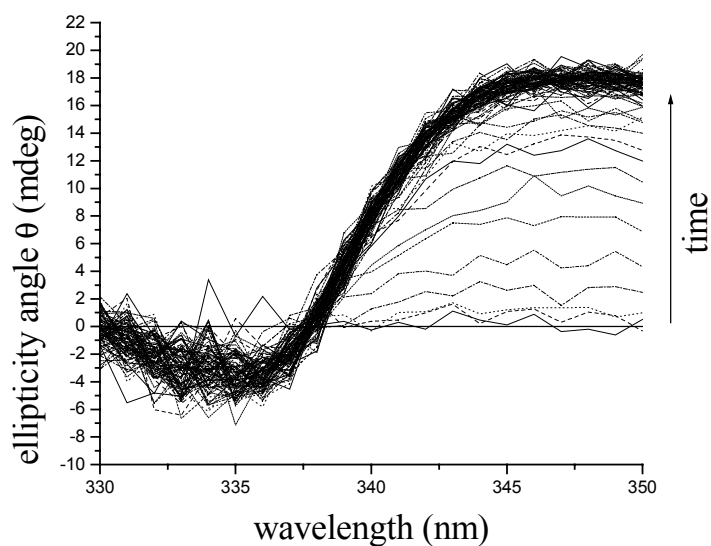
cooled from well above T_g .



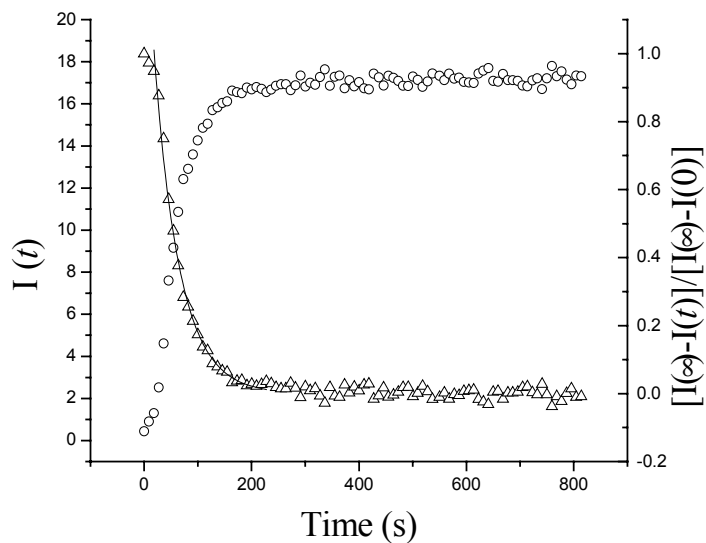
Supporting Figure 4. CD spectra of 1.0 wt % CNC/*n*-octane gels formed upon incubation at 5.4 (—), 8.7 (----), 12.1 (····), 20.2 (-·-·-), 25.0 (—•—), 30.0 (····), 35.0 (—×—) and 40.0 °C (—) after being cooled from well above T_g .



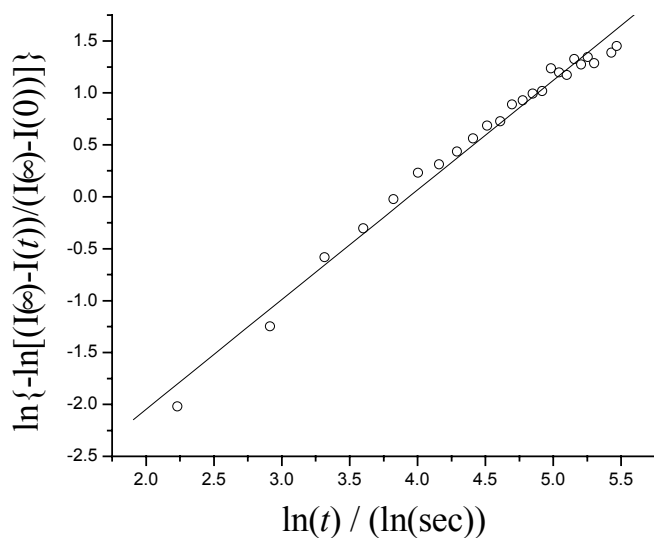
Supporting Figure 5. CD spectral intensities from bands at 303 (●; $Y = 1.05e^{(-x/46.48)}$, $R^2 = 0.98$) and 336 nm (○; $Y = 1.05e^{(-x/46.88)}$, $R^2 = 0.98$) of a 1.0 wt % CNC/*n*-octane sample incubated at 40 °C (after being heated above T_g). The two lines representing the best fits to the exponential form of the Avrami equation (see parentheses) are nearly superimposed.



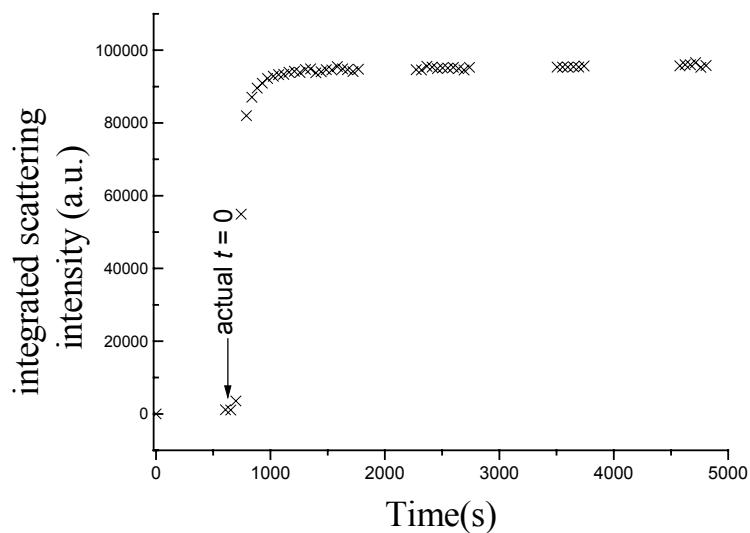
Supporting Figure 6. CD spectra associated with gelation of a 1.0 wt % CNC/*n*-octane sample incubated at 5.4 °C after being cooled from well above T_g . The time period covered is from 0 to 814 seconds.



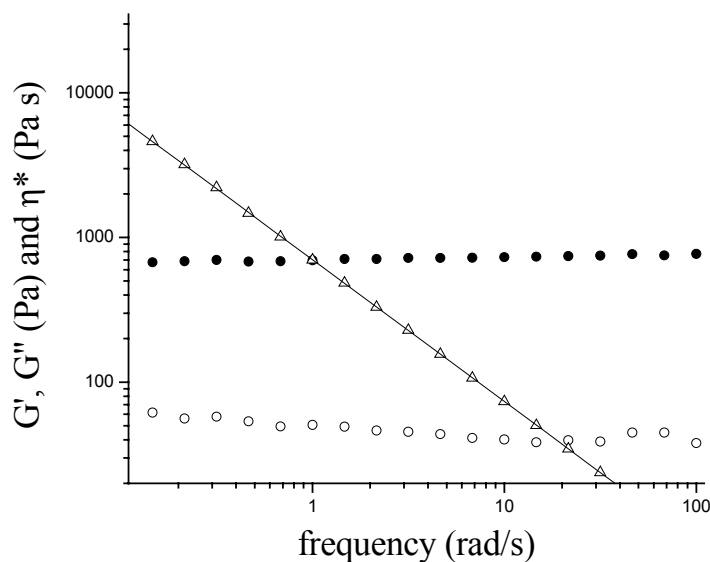
Supporting Figure 7. Plots of $I(t)$ from CD experiments (o, average of intensities between 343 and 347nm) and $[I(\infty) - I(t)]/[I(\infty) - I(0)]$ (Δ) versus time for a 1.0 wt % CNC/*n*-octane gel formation at 5.4 °C after being cooled from well above T_g . The line is the best fit of the data points to a single exponential function: $Y = 1.48e^{(-x/47.4)}$, $R^2 = 0.99$.



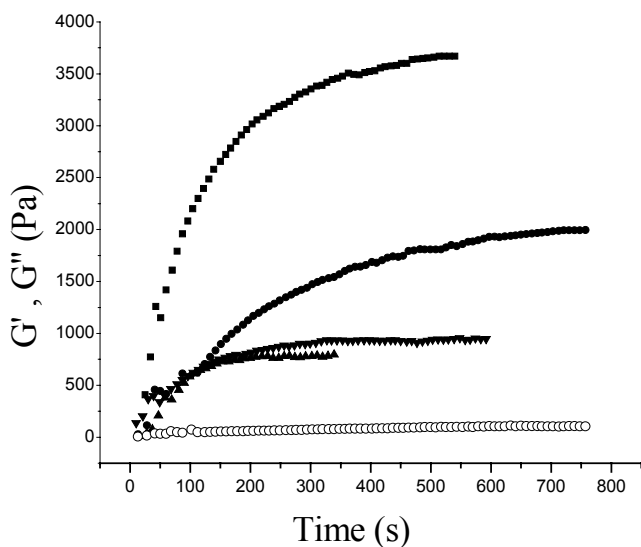
Supporting Figure 8. Plot of data from CD experiments for formation of a 1.0 wt % CNC/*n*-octane gel at 5.4 °C (after being cooled from well above T_g) according the log-log form of the Avrami equation. The slope = 1.06 ($R^2 = 0.99$).



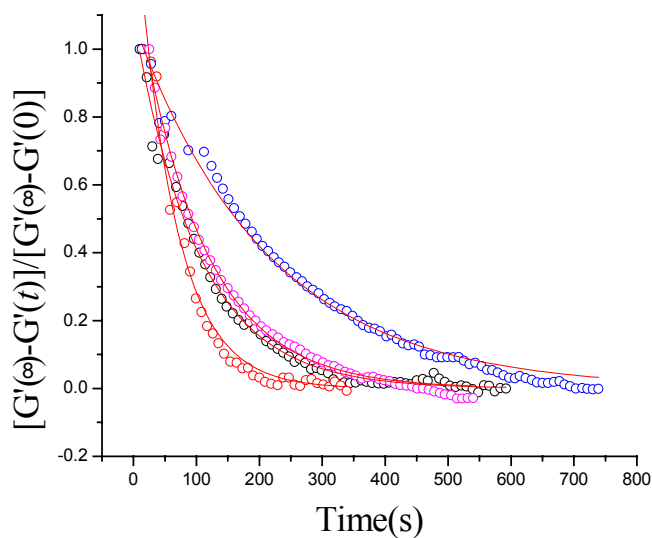
Supporting Figure 9. Time dependence of SANS intensities integrated over a 0.008-0.1 \AA^{-1} q range for a 3.0wt % CNC/*n*-dodecane- d_{26} sample incubated at 40 °C after being cooled from well above T_g .



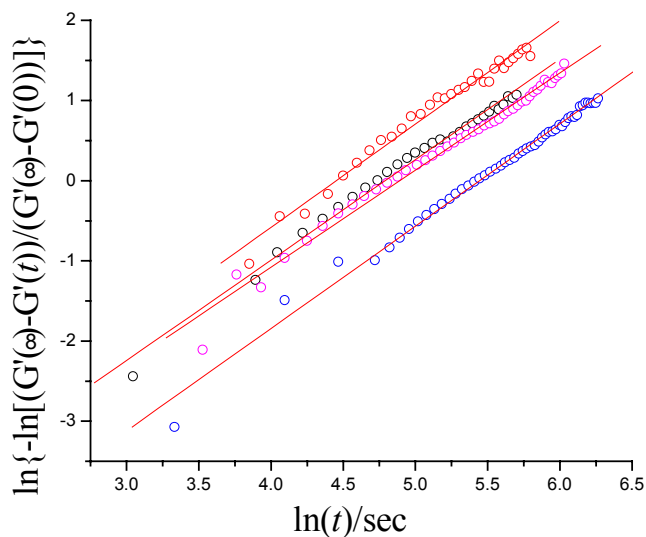
Supporting Figure 10. Dynamic rheological behavior at 25.0 °C of a 1.0 wt % CNC/*n*-dodecane gel prepared at 40.0 °C (1 % strain): G' (●), G'' (○); η^* (Δ), slope = -1.



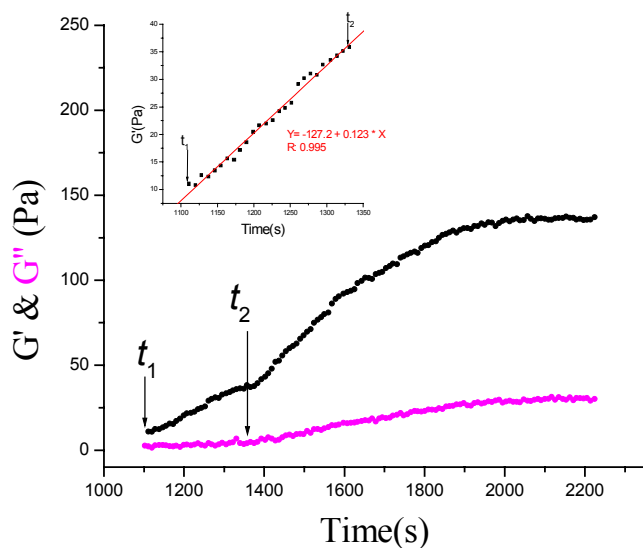
Supporting Figure 11. Plots of G' and G'' versus time for a 1.0 wt % CNC/*n*-dodecane sample that was incubated at 0 (G' , ▼), 5 (G' , ▲), 10 (G' ●, G'' ○), and 15 °C (G' , ■) after being cooled from well above T_g ; 10 rad/s, 1% strain. Mechanical properties were measured at each equilibrated temperature.



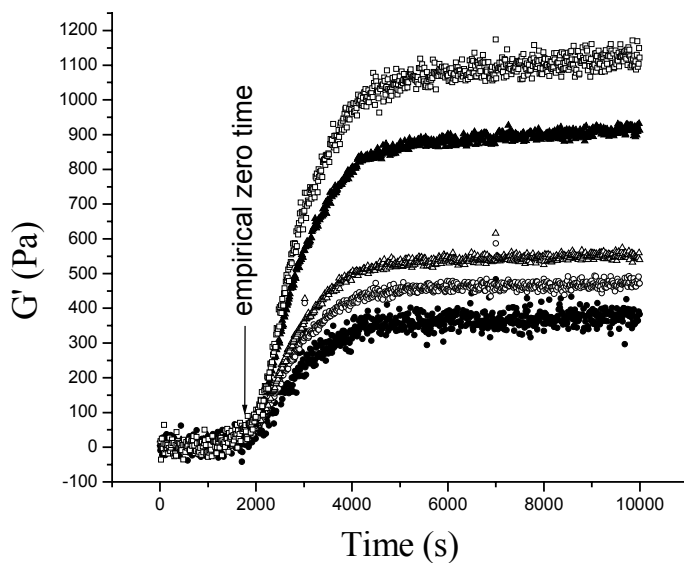
Supporting Figure 12. Plots of $[G'(\infty) - G'(t)]/[G'(\infty) - G'(0)]$ for a 1.0 wt % CNC in *n*-dodecane sample versus time and their single-exponential decay fits to the Avrami equation (solid lines) from kinetic rheology data at 0, 5, 10 and 15 °C after the sample was cooled from well above T_g . Data Fits: $Y = 1.09e^{-x/102.3}$, $R^2 = 0.99$ at 0 °C (\circ); $Y = 1.47e^{-x/60.7}$, $R^2 = 0.99$ at 5 °C (\circ); $Y = 1.21e^{-x/211.5}$, $R^2 = 0.99$ at 10 °C (\circ); $Y = 1.08e^{-x/105.5}$, $R^2 = 0.99$ at 15 °C (\circ).



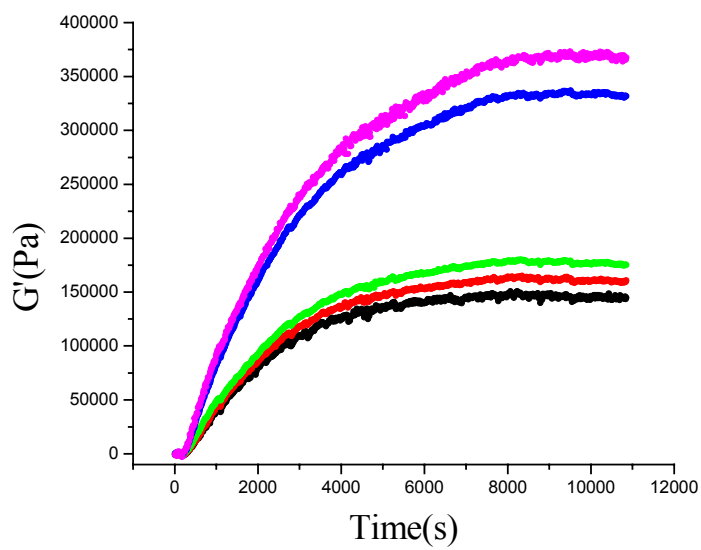
Supporting Figure 13. Linear Avrami fits of G' from kinetic rheology data for a 1.0 wt % CNC in *n*-dodecane sample incubated at 0, 5, 10 and 15 °C after being cooled from well above T_g . Data Fits: slope = 1.21 ($R^2 = 1.00$) at 0 °C (\circ); slope = 1.29 ($R^2 = 0.99$) at 5 °C (\circ); slope = 1.28 ($R^2 = 0.99$) at 10 °C (\circ); slope = 1.21 ($R^2 = 0.99$) at 15 °C (\circ).



Supporting Figure 14. Dynamic mechanical (G' (●) and G'' (●)) changes with time of a 1.0 wt % CNC/*n*-dodecane sample while incubated at 35.0 °C (10 rad/s, 1% strain) after being cooled from well above T_g . The inset is G' versus time during the $t_1 - t_2$ period and the best linear fit to these data; slope = 0.08 ($R^2 = 1.00$).



Supporting Figure 15. Multiple waveform dynamic mechanical plots for a 1.0 wt % CNC/*n*-dodecane sample incubated at 40 °C after being cooled from well above T_g : 1 (●), 5 (○), 10 (Δ), 50 (▲), and 100 rad/s (□).



Supporting Figure 16. Multiple waveform dynamic mechanical spectra of a 1.0 wt % CNC/*n*-dodecane sample incubated at 35 °C after being cooled from well above T_g . 1Hz (black); 5Hz (red), 10Hz (green); 50Hz (blue); 100Hz (purple).

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