Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Chirality Dependent Inverse-Melting and Re-entrant Gelation in α-Cyclodextrin/1-Phenylethylamine Mixtures

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Supporting Figures, Tables and Equations

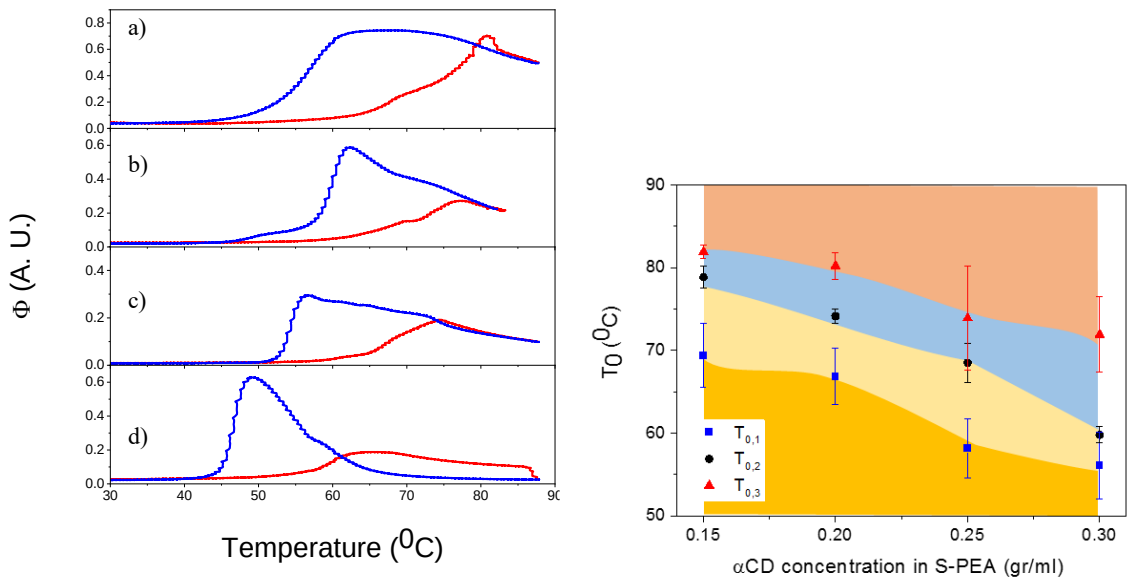


Figure S1: Transmittance results of **αCD/S-PEA** mixtures having different concentrations of **αCD**. **Left:** Transmittance as a function of the temperature (heat-and-cool cycle, 0.13 °C/min) of **a)** 0.15gr/ml, **b)** 0.2 gr/ml, **c)** 0.25 gr/ml and **d)** 0.3 gr/ml mixtures. **Right:** Sigmoid midpoints T_0 and ΔT (as error bars) for each sample at a heating and cooling rate of 0.13°C/min. Yellow and light yellow: cold gel phases, blue: liquid phase, light red: hot gel phase.

Equation S1:

$$\Phi(T) = \mathrm{p} + \Phi_0 \left[\frac{b}{1 + e^{\frac{(T - T_{0,1})}{\Delta T_1}}} + \frac{1 - b}{1 + e^{\frac{(T - T_{0,2})}{\Delta T_2}}} \right]$$

where Φ_0 and p are the initial and final values in the fitting regime, respectively, $T_{0,1}$ and $T_{0,2}$ are the two sigmoid midpoints, ΔT_1 and ΔT_2 are the width of the decay region for $T_{0,1}$ and $T_{0,2}$ respectively, and b is the relative part of each sigmoid function.

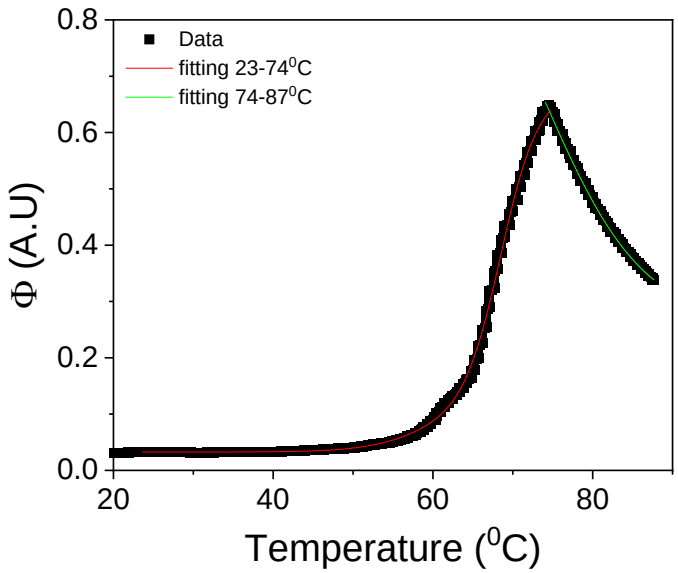


Figure S2: Transmittance results of **αCD/S-PEA** 0.25 gr/ml: data points (black), cold gel melting fitting curve (equation S1, red) and hot gel formation fitting curve (equation 4, green).

Table S1: Transmittance fitting parameters of **αCD/S-PEA** 0.25 gr/ml:

Temperature region	Equation	Parameter	Fitting value	error
23^0-74^{0}C	Equation S1	Φ_0	0.03	0.003
		y	0.646	0.003
		b	0.10	0.02
		$T_{0,1}$	58	1
		$T_{0,2}$	68	1
		ΔT_1	-3.9	0.4
		ΔT_2	-2.4	0.4
74^{0}C-87^{0}C	Equation 4	Φ_0	1.06	0.06
		y	0.26	0.01
		$T_{0,3}$	74	1
		ΔT_3	6.2	0.4

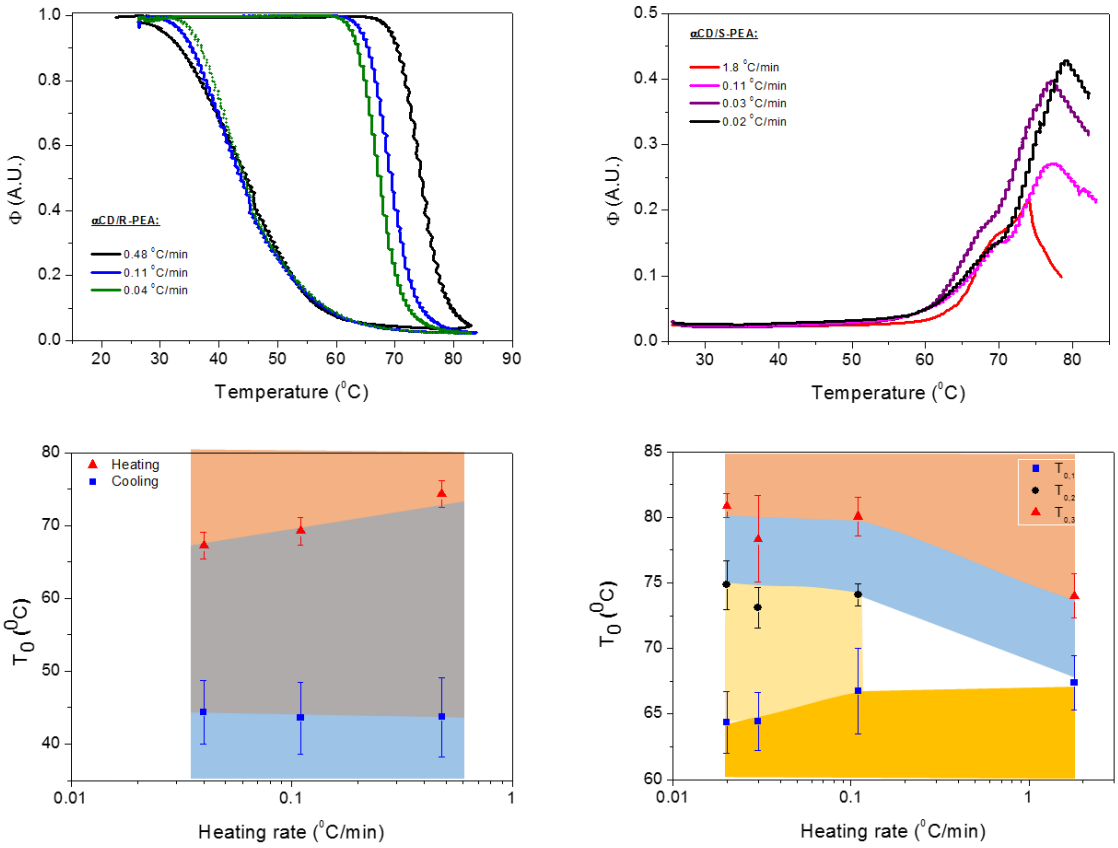


Figure S3: Transmittance results of **αCD/PEA** mixtures measured at different heating rates: a) transmittance of **αCD/R-PEA** as a function of the temperature (0.25 gr/ml), b) Sigmoid midpoints T0 and ΔT (as error bars) for each sample, c) transmittance of **αCD/S-PEA** as a function of the temperature (0.2 gr/ml), d) Sigmoid midpoints T_0 and ΔT (as error bars) for each sample. Yellow and light yellow: cold gel phases, blue: liquid phase, light red: hot gel phases, grey: hysteresis, and white: uncharacterized conditions.

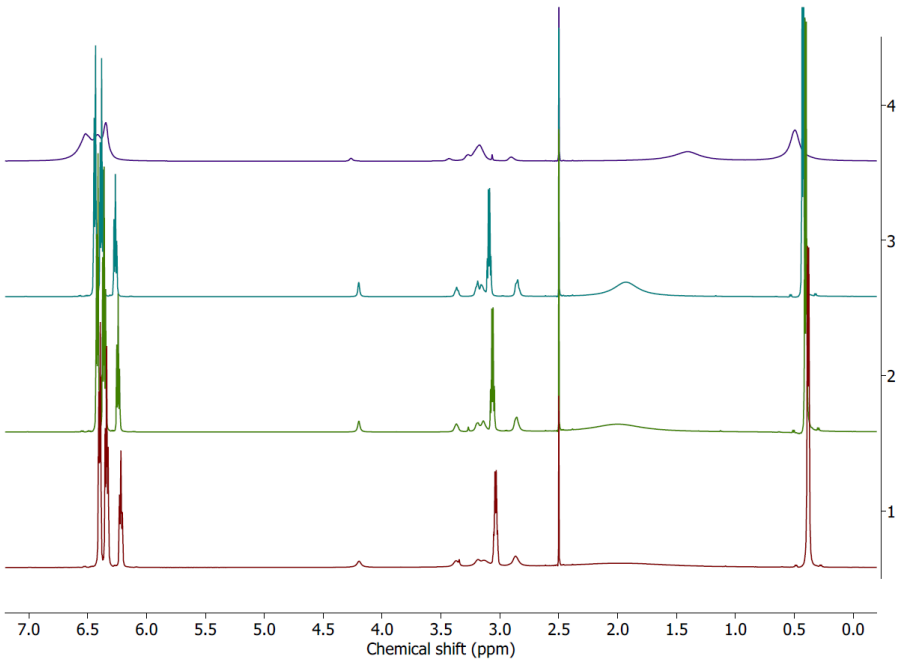


Figure S4: ^{1}H-NMR spectra of **αCD/R-PEA** at 27°C (1), 42°C (2), 57°C (3) and 82°C (4). Chemical shifts (ppm, DMSO-d_6 capillary): 0.4 (PEA-CH_3), 1.3-4 (protic hydrogen atoms), 2.5 (DMSO), 2.9 (αCD H_2,H_4), 3.0 (PEA-CH), 3.1-3.4 (αCD –H_3,H_5,H_6), 4.2 (αCD-H_1), 6.2-6.4 (PEA-aromatic hydrogen atoms).

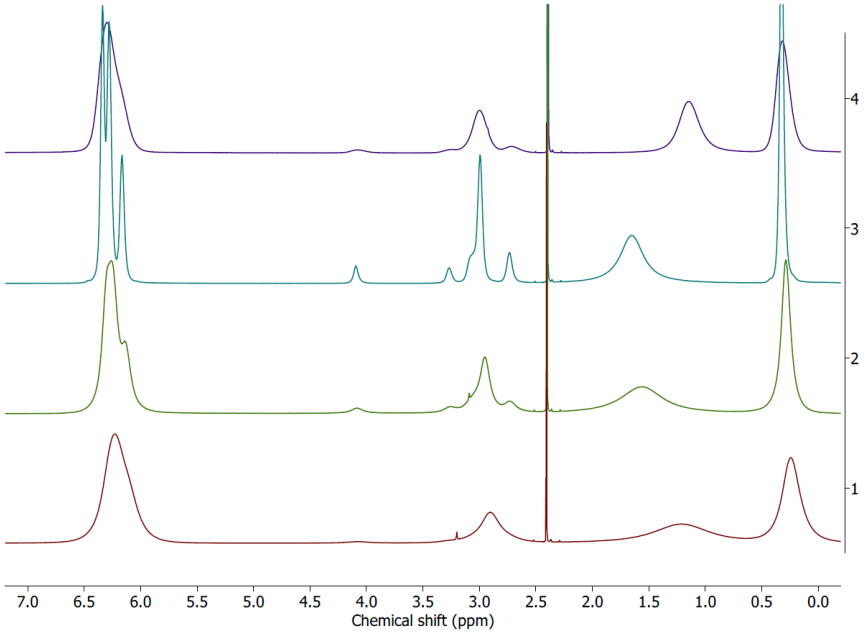


Figure S5: ^{1}H-NMR spectra of **αCD/S-PEA** at 27°C (1), 44°C (2), 57°C (3) and 73°C (4).

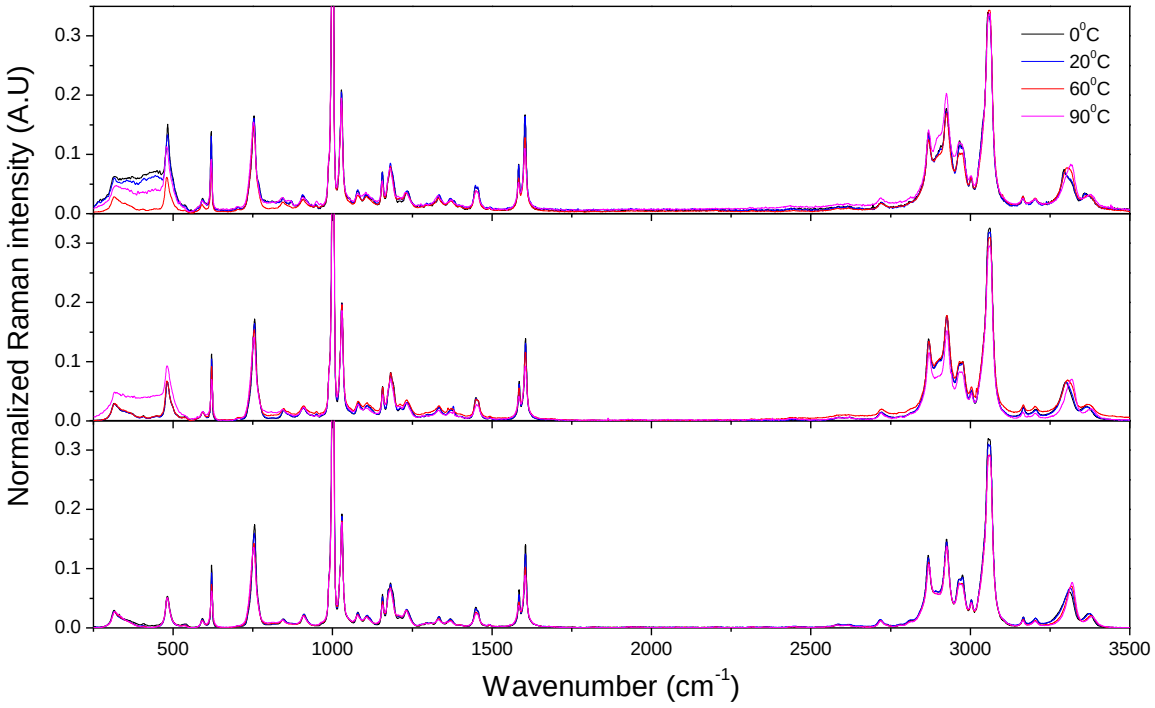


Figure S6: Raman spectra of **PEA** (bottom), **αCD/R-PEA** (middle) and **αCD/S-PEA** (top) at different temperatures: 0°C, 20°C, 60°C and 90°C.

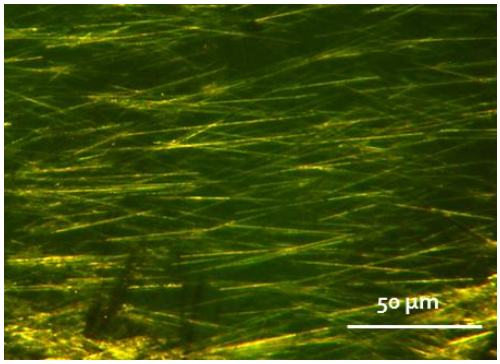
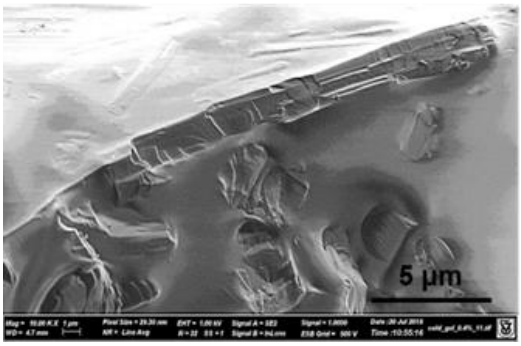
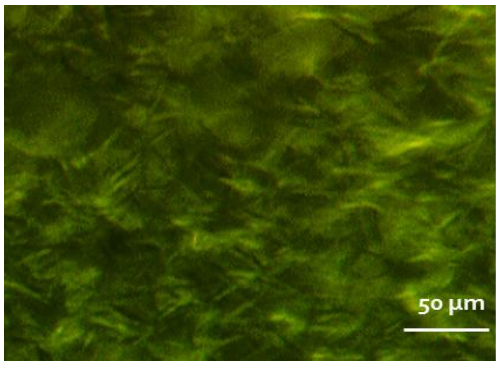
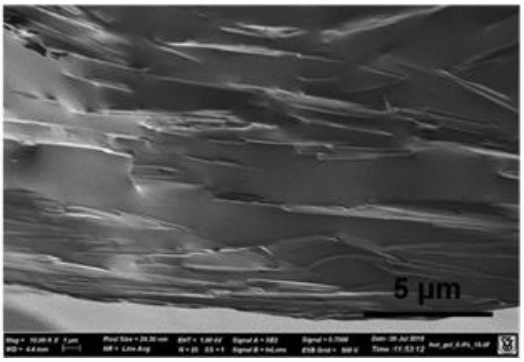
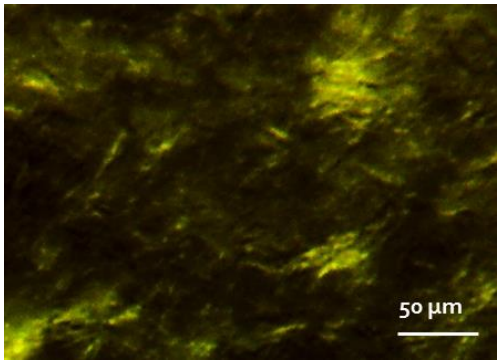
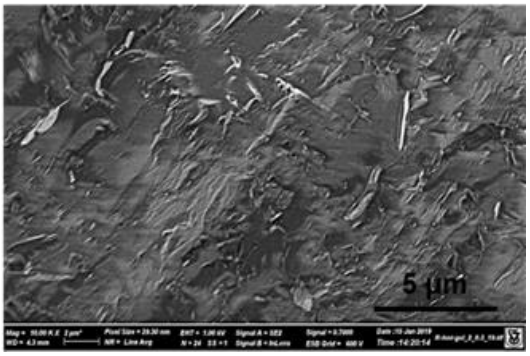
	Light microscopy	*Cryo-SEM*
αCD/S-PEA cold gel		
αCD/S-PEA hot gel		
αCD/R-PEA hot gel		

Figure S7: : Light microscopy images (left) and cryo-SEM pictures (right) of **αCD/S-PEA** "cold gel"(top), **αCD/S-PEA** "hot gel" (middle) and **αCD/R-PEA** "hot gel" (bottom).

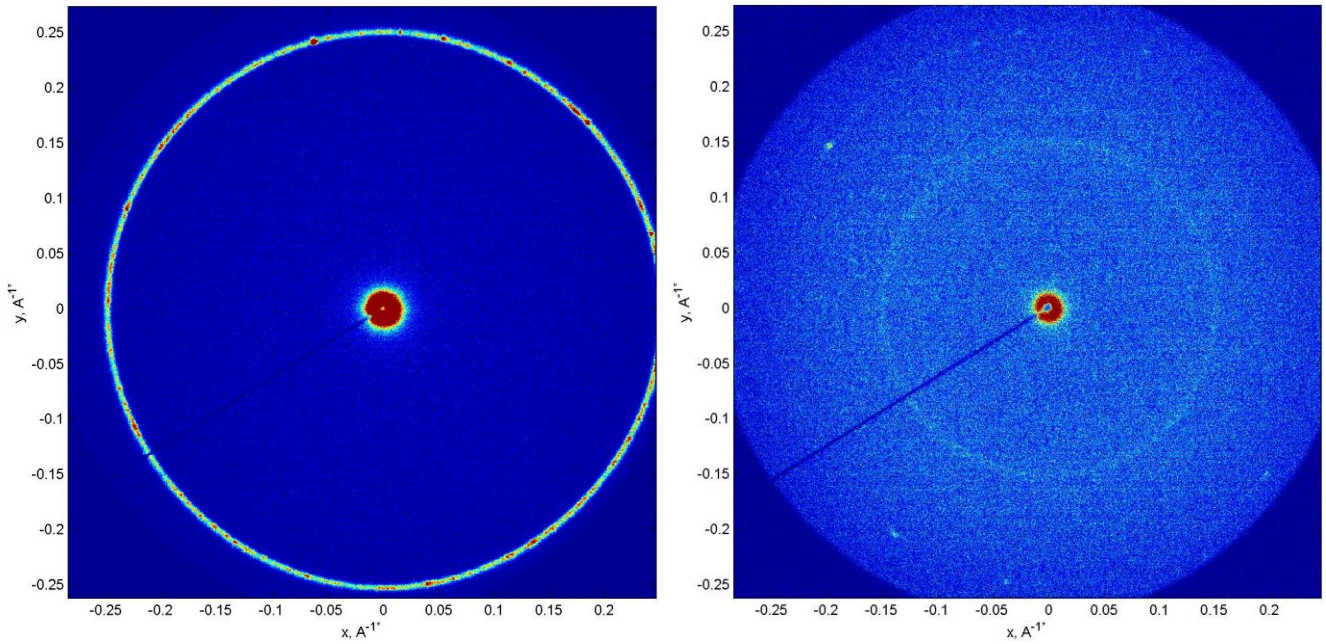


Figure S8: SAXS pattern of **αCD/S-PEA** hot gel (left) and **αCD/R-PEA** hot gel (right) in capillary 90°C.

Equation S2:

$$I(h, A, a) = \frac{A}{h^4} + a$$

where, A is constants reflected particle Surface area, concentration factors, contrast between particle and solvent; a – background.

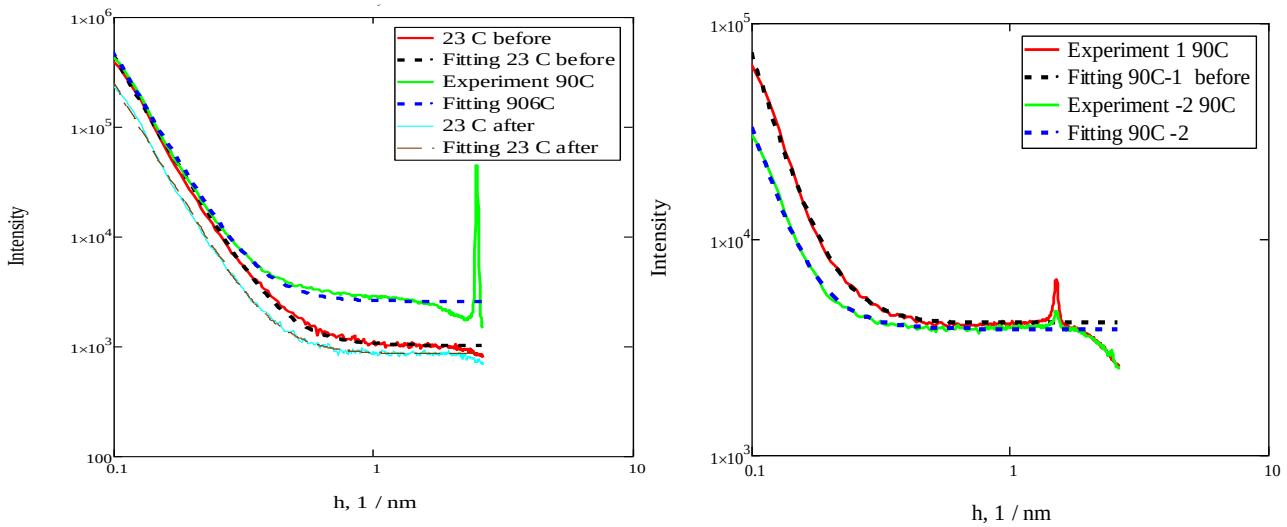


Figure S9: Experimental and fitting equation S2 for **αCD/S-PEA** (left) and **αCD/R-PEA** (right) SAXS (Log – Log scales).

Table S2: SAXS fitting parameters

Parameter	αCD/S-PEA cold gel	αCD/S-PEA hot gel	αCD/R-PEA hot gel
a	1036 ± 145	2580 ± 140	3970 ± 122
A	31 ± 9	47 ± 2	5 ± 2

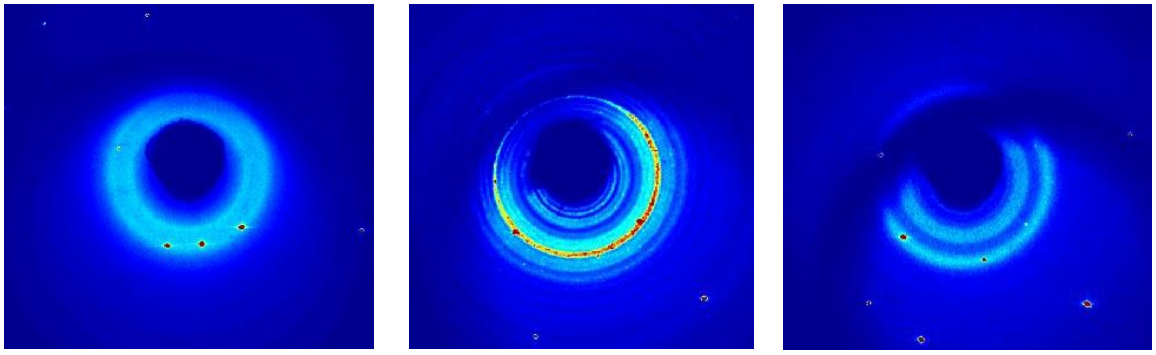


Figure S10: WAXS pattern of **αCD/R-PEA** hot gel (left) and **αCD/S-PEA** cold and hot gels (middle and right).