Supplementary Information

Reversible Thermal Transition of Polydiacetylene Based on KTTKS Collagen Sequence

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Materials. Chemicals were purchased from Sigma-Aldrich or Fisher (UK) unless stated otherwise.

Synthesis and characterization. Peptide amphiphile C_{25}-KTTKS, 10,12-pentacosadiynoyl-Lys-Thr-Thr-Lys-Ser was prepared by Fmoc solid-phase peptide synthesis on TentaGel S Trt resin (Rapp Polymere) preloaded with Fmoc-Ser(tBu)-OH (0.24 mmol g-1) at a 1.75 mmol scale (7 g of resin) using a stepwise elongation protocol and fivefold excess of each of 9-fluorenylmethoxycarbonyl (Fmoc) protected amino acid derivatives Fmoc-Thr(tBu)-OH and Fmoc-Lys(Boc)-OH (Novabiochem). Fmoc removal was achieved by 20% (v/v) piperidine in dimethylformamide (DMF) for 10 min before each coupling. 2-(7-Aza-1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU) (4.75 equiv) with N,N-diisopropylethylamine (DIEA) (10 equiv) in N-methylpyrrolidone-2 (NMP) were employed for activation of the Fmoc amino acids for 5 min at ambient temperature prior to addition to the Fmoc-deprotected resin. The resin was agitated by a gentle stream of nitrogen for 1 hour, then washed with NMP (25 cm^3) and DMF (50 cm^3), and the deprotection-coupling cycle was repeated until the last amino acid (Lys) was incorporated and the Fmoc-deprotected, then the 10,12-pentacosadiynoic acid was coupled to the N-terminus of the resin-bound peptide under the same conditions as above (5 equiv acid, 4.75 equiv HATU, 10 equiv DIEA in NMP with 5 min pre-activation and 1 h coupling time). After cleavage from the solid support and deprotection, the peptide was purified by RP-HPLC on a Perkin-Elmer System 200 HPLC chromatograph at ambient temperature using a C18 Supelco column (250×22 mm), a linear gradient of 0.01N aq HCl in acetonitrile (Buffer B) in 0.01N aq HCl in water (Buffer A) and a flow rate of 4 cm^3 min^{-1}. The appropriate fractions were pooled and freeze-dried to afford solid peptide. Peptide integrity was confirmed by ESI HRMS (Thermo Scientific LTQ Orbitrap XL): $[M+H]^+$ C_{25}-KTTKS calc. 920.2 Da, obs. 920.6 Da.

Polymerization. Polymerization was carried on a 3.5 mM sample in a quartz cell with a path length of 1 mm using a UV lamp with a distance between sample and source of 22 cm.

UV-VIS spectroscopy. Polymerization and thermochromic behaviour were followed between 200 nm and 800 nm on a Varian Cary 300 Bio UV-visible spectrophotometer

equipped with temperature controller. Spectra were acquired one minute after the desired temperature was reached. Sample was 3.5 mM or 0.035 mM in a quartz cell with a path length of 0.1 mm or 10 mm, respectively.

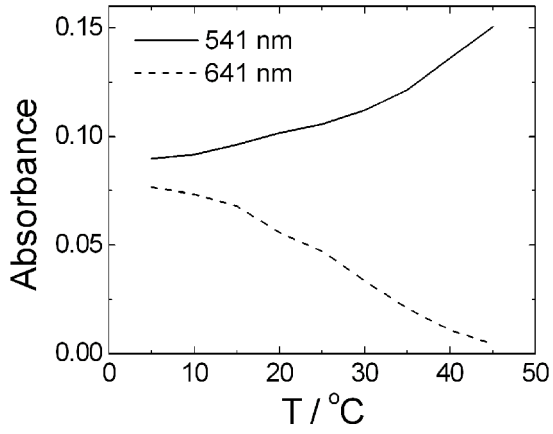

Figure S1. Absorbance of C_{25}-KTTKS polymer at 541 nm (solid line) and 641 nm (dashed line) on increasing temperature.

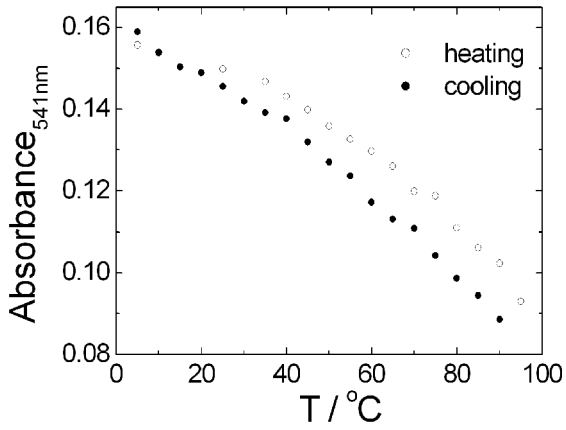

Figure S2. Absorbance at 541 nm *versus* temperature (5 ºC - 95 ºC) of C_{25}-KTTKS polymer in the red phase for heated (A) and cooled (B) samples.

Circular Dichroism (CD). Spectra were measured using a Chirascan™ CD spectrometer equipped with Peltier thermostatted sample holders and CS/JS recirculating chiller. Spectra on a 0.35 mM sample were acquired with samples in quartz cells (pathlength: 1 mm). The wavelength was from 280 to 180 nm. Final spectra were obtained after subtracting contribution from solvent and converting the signal to units of deg cm^2 $dmol^{-1}$. A UV-visible (180 nm - 680 nm) CD spectrum did not show any significant signal in the polydiacetylene region.

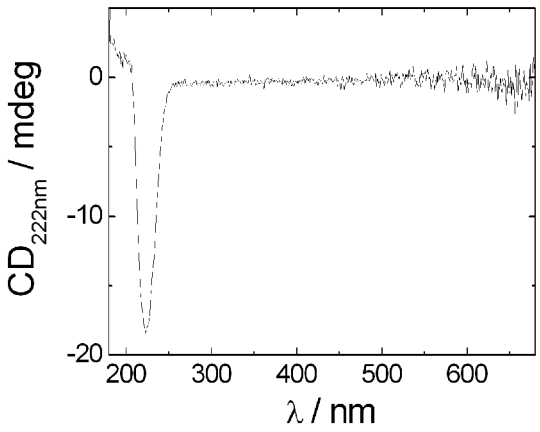

Figure S3. UV-visible (180 nm - 680 nm) CD spectrum of C_{25}-KTTKS polymer.

Fourier transform infrared (FTIR). Spectra of dried film were recorded using a Nexus-FTIR spectrometer equipped with a DTGS detector. All spectra were scanned 128 times over the range of 4000-950 cm^{-1}.

Transmission electron Microscopy (TEM). TEM experiments were performed using a Philips CM20 transmission electron microscope operated at 200 kV. Droplets of the 3.5 mM solution were placed on Cu grids coated with a carbon film (Agar Scientific, UK), stained with uranyl acetate (1 wt%) and dried.

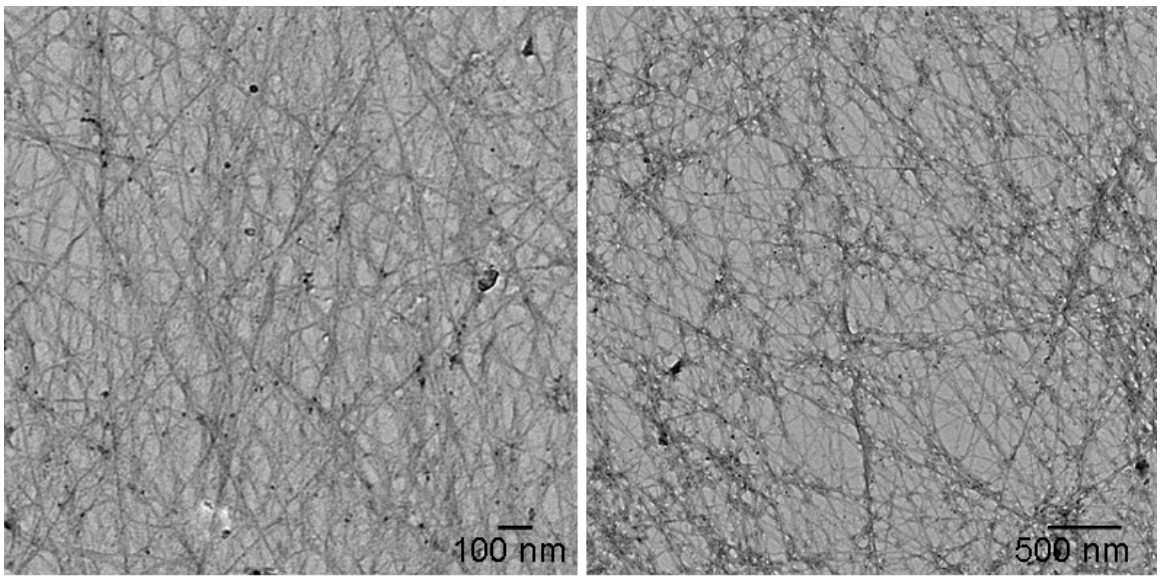

Figure S4. TEM images of C_{25}-KTTKS in the purple phase, at two magnifications.

Small-angle X-ray scattering (SAXS). The measurements were performed on a Bruker Nanostar diffractometer using CuKα radiation from a Incoatec microfocus source. The beam was collimated by a three slit system. Peptide amphiphile (3.5 mM solution) was mounted in a glass capillary (1mm diameter). The sample-detector distance was 67 cm, and a Vantec-2000 photon counting detector was used to collect the SAXS patterns.

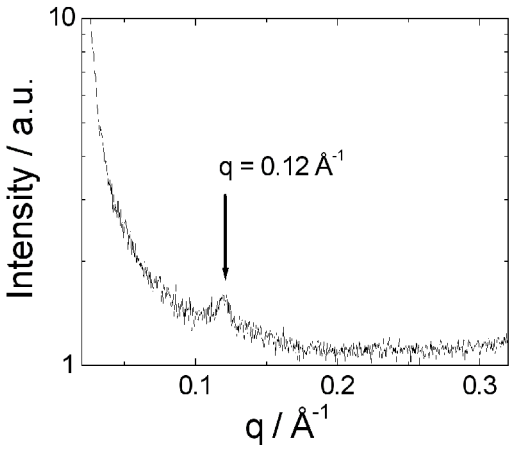

Figure S5. One-dimensional SAXS profile showing Bragg peak position for C_{25}-KTTKS at 3.5 mM in H_2O (arrowed peak position $q^* = 0.12$ Å^{-1}, corresponding domain spacing $d = 52$ Å).