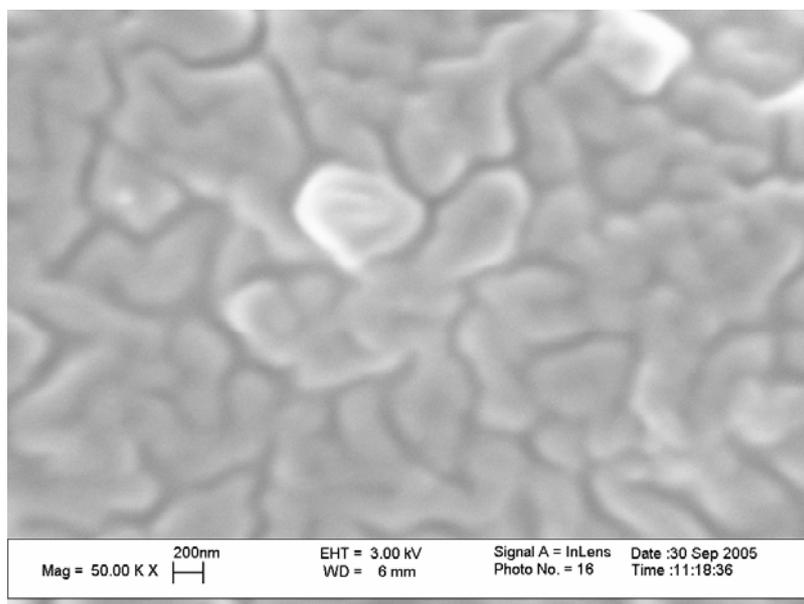


Supplementary Material (ESI) for Chemical Communications
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Supplementary Information

Field Emission Gun Scanning Electron Microscopy of the Insoluble Crosslinked Material

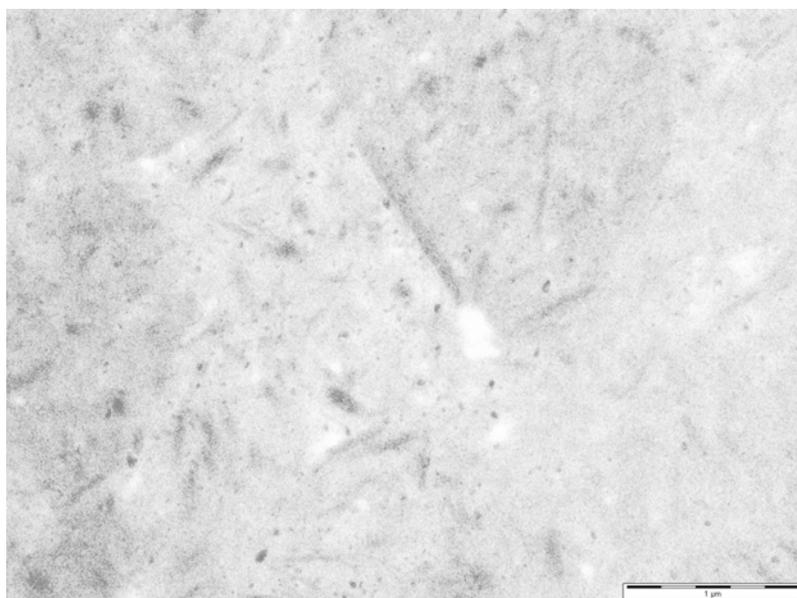
The dried crosslinked material was investigated by FEGSEM. Extended sausage-like objects with diameters of 100-200 nm were observed using this method. This could be a consequence of fibre-fibre crosslinking. It is unclear whether these objects contain internal structuring or whether the observed morphology is an artefact of the drying process.



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Transmission Electron Microscopy of the Insoluble Crosslinked Material

The gel was placed in LR White and polymerised overnight at 50°C, and then sectioned at around 70 nm. The micrographs were taken at 120 kV and contrast enhanced. Dark fibrillar objects can be observed on the TEM image (widths ca. 20-50 nm, lengths 100-1000 nm). These may be associated with the crosslinked self-assembled gelator molecules or could possibly be artefacts of the imaging process. Further work to image the morphologies of these robust crosslinked materials in more detail is currently in progress.



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Materials and Methodology

Solvents and reagents were used as supplied. Silica column chromatography was carried out using silica gel provided by Fluorochem Ltd. (35-70 μ). Thin layer chromatography was performed on commercially available Merck aluminium backed silica plates. Analytical gel permeation chromatographs were recorded using a Waters instrument incorporating Shodex columns (KF-8025 and KF-803 in series), eluted with THF. Proton and carbon NMR spectra were recorded on a Jeol (^1H 400 MHz, ^{13}C 100 MHz) instrument. Chemical shifts (δ) are quoted in parts per million, referenced to residual solvent. Coupling constant values (J) are given in Hz. Positive ion electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer. Positive ion Fast Atom Bombardment (FAB) high resolution mass spectra were recorded on a Fisons Instruments Autospec mass spectrometer. MALDI-TOF mass spectrometry was performed at the Central Science Laboratories in York. The observed isotope distributions were consistent with data calculated from isotopic abundances. Melting points were measured on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. Optical rotation was measured as α_D on a JASCO DIP-370 digital polarimeter. Infra-red spectra were recorded using an ATI Mattson Research Series 1 FTIR spectrometer.

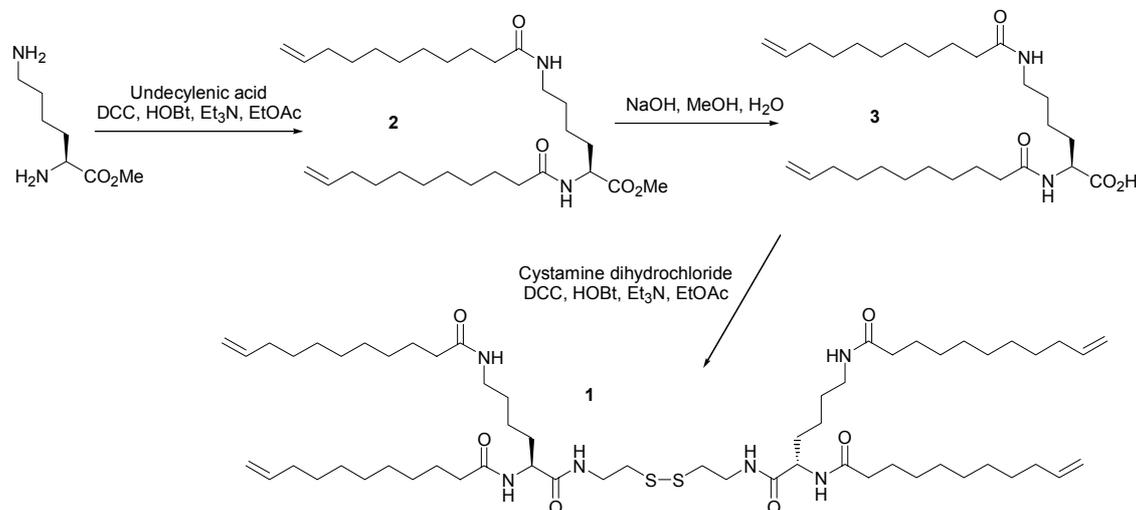
Characterisation of Gels

Gelation was tested by solubilisation of a weighed amount of dendritic gelator in a measured volume of selected pure solvent. The mixture was sonicated at ambient temperature for 30 min before heating and cooling produced a gel. The gel sample was left to stand overnight. Gelation was considered to have occurred when a homogenous ‘solid-like’ material was obtained that exhibited no gravitational flow. The thermally reversible gel-sol transition temperature (T_{gel}) was determined using a tube inversion methodology – the gel-sol transition temperature represents the point at which the stress exerted by the gel exceeds its yield strength, and a single drop of solvent begins to run from the immobilised gel. All gel samples were prepared with a total volume of 1 mL in tubes with a diameter of 10 mm – this ensures that the stress generated by the gel on tube inversion is approximately constant in each case.

Scanning electron micrographs were recorded using a Jeol JSM-6330F instrument. Gel samples were applied to stainless steel stubs and allowed to dry. Prior to examination, the gels were coated with a thin layer of gold/Pt (60:40). Au/Pt deposition was performed using a Denton vacuum LLC.

Transmission electron micrographs were recorded on a Jeol 1200 EX instrument. The gel was placed in LR White and polymerised overnight at 50°C, and then sectioned at around 70 nm. The micrographs were taken at 120 kV and contrast enhanced.

Synthetic Scheme



Compound 2

L-Lysine methyl ester dihydrochloride (7.00 g, 30 mmol) was suspended in EtOAc (40 ml). Et₃N (8.86 ml, 63 mmol) was added followed by undecylenic acid (12.75 ml, 63 mmol). The mixture was stirred under N₂ for 3 min before being cooled to 0°C. HOBT (8.53 g, 63 mmol) and DCC (13.02 g, 63 mmol) were then added simultaneously as a mixture of solids. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. The precipitate was removed by filtration and discarded. The filtrate was washed with an aqueous saturated solution of sodium hydrogen carbonate, aqueous sodium hydrogen sulfate (8 g in 50 ml), then washed again with aqueous sodium hydrogen carbonate and finally water. The solution was dried over magnesium sulfate then rotary evaporated to produce a white solid. This crude product was purified by silica column chromatography (EtOAc:hexane, 7:3) to give a white solid with a yield of 12.00 g (81 %). *R*_f 0.38 (EtOAc:hexane, 7:3, CeMo stain); GPC *R*_t 27.2 min (0.7 mlmin⁻¹); m.p. 71-72°C; α_D²⁹³ + 4.8 (c = 1.0, CHCl₃), - 8.1 (c = 1.0, MeOH); δ_H (270 MHz, CDCl₃) 6.19 (1H, d, *J* = 8, CONH), 5.84-5.72 (2H, m, CH=CH₂), 5.72-5.70 (1H, m, CONH), 5.00-4.90 (4H, m, CH=CH₂), 4.58-4.56 (1H, m, COCHR), 3.73 (3H, s, CO₂CH₃), 3.25-

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3.21 (2H, m, $\text{CH}_2\text{CH}_2\text{NH}$), 2.17 (2H, t, $J = 8$, NHCOCH_2), 2.10 (2H, t, $J = 8$, NHCOCH_2), 2.01 (4H, q, $J = 8$, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.80-1.20, (30H, m, CH_2), δ_{C} (67.9 MHz, CDCl_3) 173.5 (CO_2Me), 173.2, 173.1 (CONH), 139.1 ($\text{CH}=\text{CH}_2 \times 2$), 114.1 ($\text{CH}=\text{CH}_2 \times 2$), 52.3 (COCHRNH), 51.6 (CO_2CH_3), 38.7 ($\text{CH}_2\text{CH}_2\text{NH}$), 36.8, 36.5, 33.7, 32.0, 29.3, 29.0, 28.9, 25.8, 25.6, 22.3 (all CH_2); ν_{max} (KBr disc) 3329m (NH), 3079m, 2912m, 2848m (CH_3 , CH_2), 1748s (C=O), 1638s (C=O), 1556s (CONH), 1468m, 1172s, 995m, 913m; m/z (ES+) $\text{C}_{29}\text{H}_{52}\text{N}_2\text{O}_4$ [M] requires 492, found 515 (100%, $[\text{M}+\text{Na}]^+$).

Compound 3

Compound 2 (8.00 g, 16.30 mmol) was dissolved in MeOH (50 ml). The solution was cooled to 0°C, then aqueous sodium hydroxide solution (48.9 ml, 1 M, 48.9 mmol) was added. The reaction was stirred under N_2 for 24 h. The solvent was removed by rotary evaporation, water added (50 ml), then the mixture was acidified to pH 3 with aqueous sodium hydrogen sulfate. The product was extracted with EtOAc, washed with water and brine, dried over magnesium sulfate and rotary evaporated to dryness to yield a white solid (7.00 g, 89 %). R_f 0.10 (EtOAc:hexane, 7:3, CeMo stain); GPC R_t 27.8 min (0.7 mlmin^{-1}); m.p. 90-92°C, $\alpha_{\text{D}}^{293} + 6.2$ (c = 1.0, CHCl_3), - 0.7 (c = 1.0, MeOH); δ_{H} (270 MHz, CDCl_3) 6.80 (1H, d, $J = 7$, CONH), 5.87-5.86 (1H, m, CONH), 5.82-5.78 (2H, m, $\text{CH}=\text{CH}_2$), 5.01-4.90 (4H, m, $\text{CH}=\text{CH}_2$), 4.54-4.50 (1H, m, COCHR), 3.36-3.32 (1H, m, $\text{CH}_2\text{CH}_2\text{NH}$), 3.24-3.19 (1H, m, $\text{CH}_2\text{CH}_2\text{NH}$), 2.30-2.22 (4H, m, NHCOCH_2), 2.01 (4H, q, $J = 5.5$, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.90-1.20, (30H, m, CH_2); δ_{C} (67.9 MHz, CDCl_3) 174.7 (CO_2H), 174.6, 174.3 (CONH), 139.3 ($\text{CH}=\text{CH}_2 \times 2$), 114.3 ($\text{CH}=\text{CH}_2 \times 2$), 52.3 (COCHRNH), 38.9 ($\text{CH}_2\text{CH}_2\text{NH}$), 36.8, 36.5, 33.9, 31.3, 29.5, 29.4, 29.2, 29.0, 25.9, 25.8, 22.1 (all CH_2); ν_{max} (KBr disc) 3310m (NH), 3080m, 2919m, 2849m (CH_3 , CH_2), 1714s (CO_2H), 1643s (CONH), 1556s (CONH), 1466m, 996m, 913m; m/z (ES+) $\text{C}_{28}\text{H}_{50}\text{N}_2\text{O}_4$ [M] requires 478; found 501 (100%, $[\text{M}+\text{Na}]^+$); (ES-) found 477 (100%, $[\text{M}-\text{H}]^-$); HR-FABMS $\text{C}_{28}\text{H}_{51}\text{N}_2\text{O}_4$ requires 479.3849, found 479.3849.

Gelator 1

Cystamine dihydrochloride (0.22 g, 1 mmol) was suspended in DCM (10 ml). Et₃N (2.1 ml, 2.1 mmol) was added followed by compound **3** (1.00 g, 2.1 mmol). The reaction mixture was stirred under N₂ for 3 min before being cooled to 0°C. DCC (0.43 g, 2.1 mmol) and HOBt (0.28 g, 2.1 mmol) were added simultaneously as a mixture of solids. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. The precipitate was removed via filtration. The filtrate was washed with an aqueous saturated solution of sodium hydrogen carbonate, aqueous sodium hydrogen sulfate (8 g in 50 ml), then washed again with aqueous sodium hydrogen carbonate and finally water and brine. The solution was dried over sodium sulfate then rotary evaporated to produce a pale yellow solid. This solid was purified by silica chromatography (MeOH:DCM, 10:90) to yield the product as a white solid (0.50 g, 46 %). *R_f* 0.35 (CH₂Cl₂:MeOH 90:10, CeMo stain); GPC *R_t* 26.2 min (0.7 mlmin⁻¹); m.p. 159-161°C; $\alpha_D^{293} - 8.7$ (*c* = 1.0, CHCl₃); δ_H (270 MHz, CDCl₃) 7.62-7.58 (2H, m, CONH), 7.04-7.01 (2H, m, CONH), 6.45-6.35 (2H, m, CONH), 5.87-5.72 (4H, m, CH=CH₂), 5.01-4.91 (8H, m, CH=CH₂), 4.58-4.50 (2H, m, COCHR), 3.66-3.63 (2H, m, CH₂CH₂NH), 3.48-3.46 (2H, m, CH₂CH₂NH), 3.24-3.20 (4H, m, SCH₂CH₂NH), 2.80-2.78 (4H, m, SCH₂CH₂NH), 2.46-2.15 (8H, m, NHCOCH₂), 2.04-1.98 (8H, m, CH₂CH=CH₂), 1.60-1.27 (60H, m, CH₂); δ_C (67.9 MHz, CDCl₃) 174.0 (CONH x 2), 173.9 (CONH x 2), 172.8 (CONH x 2), 139.2 (CH=CH₂ x 4), 114.2 (CH=CH₂ x 4), 52.7 (COCHRNH x 2), 39.2 (CH₂NH x 2), 38.6 (CH₂NH x 2), 38.1 (CH₂S x 2), 36.8, 36.6, 33.9, 32.0, 29.5, 29.2, 29.0, 26.1, 25.9 (all CH₂), ν_{max} (KBr disc) 3303m (NH), 3076m, 2927m, 2850m (CH₃, CH₂), 1633s (C=O), 1543s (CONH), 993m, 910m; *m/z* (ES+) C₆₀H₁₀₈N₆O₆S₂ [M] requires 1072.3; found 1095.7 (100%, [M+Na]⁺).