SUPPLEMENTARY INFORMATION

Contents

Synthesis and characterization	
Circular Dichroism spectroscopic measurements	
AFM analysis	
Single- particle tracking analysis	
Vial inversion test	
Rheology	
Single Molecule Force Microscopy analysis	
Semi-flexible network theory	
References and Notes:	

Synthesis and characterisation

Dichloromethane and chloroform were distilled over CaCl₂. Tetrahydrofuran, diethyl ether and toluene were distilled over sodium in the presence of benzophenone. Monomers **1–3** were prepared following described procedures^{S1}. All the other chemicals were used as received from the suppliers. ¹H NMR spectra (yielding only broad signals for the polymers) were recorded on Bruker AC-300 MHz instruments operating at 300 MHz. FT-infrared spectra of the pure compounds were recorded on a ThermoMattson IR300 spectrometer equipped with a Harrick ATR unit. Solution IR spectroscopy was carried out in sealed KBr cuvette (1 mm) on a Bruker Tensor 27 spectrometer operated with Opus software. Solutions of monomers and polymers were prepared in chloroform, tetrahydrofuran or toluene at a concentration of approximately 30 mM.

Synthesis

The synthesis of polymers P1-P3 is shown in Scheme S1. The experimental procedures are given below.



Scheme S1. Preparation of the target polymers P1-P3.

Synthesis of polymer P1. A solution of Ni(ClO₄)₂.H₂O (0.147 mol/L, 10 µL) in toluene/methanol (7:3) was added to a solution of **1** (40 mg, 15 mmol) in freshly distilled toluene (3 mL). The reaction mixture was vigorously stirred under air in a sealed flask for two hours. The solvent was evaporated and the crude polymer was redissolved in CHCl₃ (3 mL), precipitated in diethyl ether (10 mL) and collected by centrifugation (3500 rpm, 7 min). This procedure was repeated two times and the polymer was dried under vacuum to yield P1 (29.2 mg, 10.9 mmol, 73%) as a yellow-brown glassy solid. ¹H NMR (CDCl₃, 300 MHz): 3.74–3.36 (br m, 13H); 1.60 (br s, 6H); FT-IR (cm⁻¹, ATR): 3263 (N–H); 2927, 2880 (C–H); 1740 (C=O); 1656 (C=O amide I); 1531 (N–H amide II); 1214 (C–O ester); 1108 (C–O ethers) $[\alpha]_D^{20}$: +75 (*c* 0.03; CH₂Cl₂); $M_n = 478$ kDa, $M_w = 716$ kDa.

Synthesis of polymer P2. The procedure as described for P1 was used with the exception that tetrahydrofuran was used to redissolve the polymer during the precipitation process. The reaction was carried out with two different monomer: Ni^{2+} ratios:

P2a: Using **2** (40 mg, 12.6 mmol) Ni(ClO₄)₂.H₂O solution (0.126 mol L⁻¹, 10 μL), in toluene (2 mL). Purification of the crude mixture yielded **P2a** (33.7 mg, 10.7 mmol, 85%) as a deep yellow glassy solid. ¹H NMR (CDCl₃, 300 MHz): 3.68–3.34 (b rm, 17H); 1.58 (br s, 6H); FT-IR (cm⁻¹, ATR): 3260 (N–H); 2917, 2875 (C–H); 1740 (C=O); 1657 (C=O amide I); 1530 (N–H amide II); 1210 (C–O ester); 1105 (C–O ethers) $[\alpha]_D^{20}$: +105 (*c* 0.03; CH₂Cl₂); M_n = 830 kDa, M_w = 1327 kDa.

P2b: Using **2** (41 mg, 12.9 mmol), Ni(ClO₄)₂.H₂O solution (1.29 mmol/L, 10 μL), in toluene (2 mL). Purification of the crude mixture yielded **P2b** (32.0 mg, 10.1 mmol, 78%) as a pale yellow glassy solid. ¹H NMR (CDCl₃, 300 MHz): 3.68–3.34 (br m, 17H); 1.58 (br s, 6H); FT-IR (cm⁻¹, ATR): 3260 (N–H); 2917, 2875 (C–H); 1740 (C=O); 1657 (C=O amide I); 1530 (N–H amide II); 1210 (C–O ester); 1105 (C–O ethers); $M_n = 2306$ kDa, $M_w = 3458$ kDa.

Synthesis of polymer P3. The procedure as described for P2 was used. The reaction was carried out with two different monomer: Ni^{2+} ratios:

P3a. Using **3** (50.1 mg, 13.8 mmol), Ni(ClO₄)₂.H₂O solution (0.138 mol/L, 10 μL), in toluene (2.5 mL). Purification of the crude mixture yielded **P3a** (45.2 mg, 12.5 mmol, 90%) as a deep yellow glassy solid. ¹H NMR (CDCl₃, 300 MHz): 3.71–3.35 (br m, 21H); 1.63 (br s, 6H); FT-IR (cm⁻¹, ATR): 3261 (N–H); 2917, 2879 (C–H); 1740 (C=O); 1656 (C=O amide I); 1529 (N–H amide II); 1213 (C–O ester); 1109 (C–O ethers) $[\alpha]_D^{20}$: +175 (*c* 0.01; CH₂Cl₂); $[\alpha]_D^{20}$: +169 (*c* 0.03; H₂O); *M*_n = 249 kDa, *M*_w = 323 kDa.

P3b. Using **3** (56.3 mg, 15.6 mmol), Ni(ClO₄)₂.H₂O solution (1.56 mmol/L, 10 μL), in toluene (2.8 mL). Purification of the crude mixture yielded *P3b* (43.9 mg, 12.2 mmol, 78%) as a pale yellow glassy solid. ¹H NMR (CDCl₃, 300 MHz): 3.71–3.35 (brm, 14H); 1.63 (brs, 6H); FT-IR (cm⁻¹, ATR): 3260 (N–H); 2917, 2875 (C–H); 1740 (C=O); 1657 (C=O amide I); 1530 (N–H amide II); 1210 (C–O ester); 1105 (C–O ethers); $M_n = 1589$ kDa, $M_w = 2702$ kDa.

Circular dichroism measurements

Polymers **P1–P3** were subjected to CD spectroscopic analysis in dichloromethane (**P1–P3**; Fig. S1) and in water (shown **P2b**; Fig.S2). The spectra in both solvents are very similar.



Figure S1 | CD spectra of P1–P3 recorded in DCM (20 °C, 1 mg mL⁻¹).



Figure S2 | CD spectra of **P2b** (1 mg mL⁻¹) in water at 4 °C (solution) and 40 °C (gel)



Temperature dependent CD spectra were recorded in water (Figs. S2 and S3). In a stability experiment, a spectrum was recorded at every temperature after cooling the sample to 5 °C and subsequently heating it to the desired temperature. The CD signal recovers completely at intermediate temperatures. Even at the gel transition temperature, no changes in the helical structure of the polymer are visible. At T = 72 °C the CD signal decreases abruptly and a cooling cycle of the sample the sample did not result in recovery of the signal, indicating permanent damage to the helical structure. After reaching 74 °C, the sample was cooled to 5 °C and kept for three days before measuring again, but the CD signal did not recover.

AFM Analysis

AFM experiments were performed using a dimension 3100 or Multimode microscope operated with nanoscope III or nanoscope IV control units (Digital Instruments) and using NT-MDT NSG10 tips. To visualise single polymer chains, solutions of **P1–P3** ($\approx 10^{-6}$ M in CHCl₃) were spin-coated (1600 RPM) onto freshly cleaved Muscovite Mica, which was subsequently used to determine the contour length (l_c) of isolated polymers chains. **P2b** hydrogels were deposited by direct contact with freshly cleaved HOPG or Muscivite Mica or were generated in situ on the Mica substrate. All images were recorded with the AFM operating in Tapping ModeTM in air at room temperature, with a resolution of 1024 × 1024 pixels, using moderate scan rates (1–1.5 lines/sec). Commercial tapping-mode golden-coated silicon tips (NT-MDT) were used with a typical resonance frequency around 300 kHz. Polymer chain lengths were evaluated using NeuronJ plugin (v1.4.1 by E. Meijering) run on ImmageJ (v1.431) software^{S2}. The polymer chains heights and widths were measured using the Nanoscope software (v6.14r1) from Digital Instruments. Raw pictures were compensated for drift using the Nanoscope software (v6.14r1); no other processing was applied on the data used for the analysis.



Figure S4 | Representative AFM micrograph of individual polymer chains spin-coated from dilute $CHCl_3$ solutions onto mica: (a) **P1**; (b) **P2a**; (c) **P2b**; (d) **P3a** and (e) **P3b**. For all images, the scale bar is 1 μ m and the vertical scale is 2 nm.



Figure S5 | AFM images of **P2b** obtained from samples of different polymer concentration: (a) 0.13 mg mL⁻¹ (scale bar: 400 nm, height range 0.9–8.5 nm), (b) 0.25 mg mL⁻¹ (scale bar: 400 nm, height range 3.3–11.4 nm), (c) 0.50 mg mL⁻¹ (scale bar: 1.0 μ m, height range 1.2–6.4 nm), (d) 0.75 mg mL⁻¹ (scale bar: 1.0 μ m, height range -3.0–4.7 nm), (e) 1.0 mg mL⁻¹ (scale bar: 1.0 μ m, height scale 0.7–7.0 nm), (f) 3.0 mg mL⁻¹ (scale bar: 400 nm, height scale 0.2–0.2 nm). (g) CryoSEM image of **P2b** (*c* = 1.0 mg mL⁻¹, scale bar 1 μ m).

Bundle dimensions from AFM measurements. To measure bundle dimensions as a function of concentration, gels prepared at concentrations ranging from 0.13–3.0 mg mL⁻¹ were transferred to mica substrates and subjected to AFM microscopy. Analysis of the images yielded distributions of bundle heights and bundle widths. The height profiles in samples prepared from a simple gel transfer showed strong variations with the position in the sample and was found to be very unreliable, mostly because the porous nature of the gel results in a poorly defined baseline. More reliable data was obtained from the width profiles. The bundle widths of the measurements at different concentrations are statistically not significantly different. The method for testing is described below.

The distributions of the bundle widths at all concentrations are strongly nonparametric, excluding simple ANOVA tests. The skewedness of the data, together with the presence of two independent factors, concentration and AFM tip dimensions (each concentration was measured with a different

AFM tip), led us to develop a tailored statistical analysis for this specific case. For this purpose, the data was log transformed. The used analysis models the log width W_{ij} of the j^{th} measured fibre at concentration *i* as:

$$W_{ij} = \mu_{ij} + Z_{ij} + U_{ij}.$$
 (S1)

Here, μ_{ij} is the average log width in concentration series *i*, Z_i represents the variation in AFM Stip diameter, assumed to have a normal distribution with variance s_0^2 , and U_{ij} is random noise added to all samples, also normally distributed and independent of other parameters. To test the hypothesis $\mu_1 = ... = \mu_6$, we conducted a likelihood-ratio test. In the limit where tip variance is zero (i.e. $Z_i = 0$), the test is equivalent to the classical ANOVA F-test. As indicated by the supplier of the AFM tips, variation in tip diameters is not small compared to the objects under investigation and, hence, we should consider the case $s_0 > 0$.

To estimate s_0 , the tip specifications supplied by the manufacturer were used.^{S3} The tip was modelled as a hemisphere with average tip radius R = 6 nm, log normal distributed with a probability of 97.5% that R < 10 nm. When the bundles are modelled as a simple block function with height *h*, the bundle widths w_{AFM} as measured by the AFM tip will be:

$$w_{\text{AFM}} = 2\sqrt{2hR} - h^2 \qquad h < 2R$$

$$w_{\text{AFM}} = 2R \qquad h \ge 2R$$
(S2)

We used a simulation to determine the effect of the variation in *R* on the model variable *Z*. For this we used the fibre heights as experimentally determined (Fig. 2c in the manuscript): *h* is normally distributed with mean 1.2 and s.d. 0.19 nm. The simulation provided the standard deviation $s_0 = 0.14$, leading to T = 7, where *T* is twice the log-likelihood ratio statistic. General theory suggests that *T* should have a $\chi^2(5)$ distribution, which was confirmed by simulation. The likelihood-ratio test therefore yields a *p*-value of 0.2 for the null hypothesis, which confirms that the bundle diameters in all measured concentrations are not significantly different (within the 95% probability range). Additional variations in experimental conditions (which are likely to be present) will further increase the observed *p*-value.



Figure S6 | Boxplots of statistical analyses of the AFM data: peak widths (left) and peak heights (right) of **P2b** at concentrations ranging from $0.13 - 3.0 \text{ mg mL}^{-1}$.

Single particle tracking analysis

Particle tracking studies were carried out on a Nanosight LM10 instrument equipped with an Electron Multiplication Charge Coupled Device (EMCCD) camera mounted on an optical microscopic system to track light scattered by particles that are present in a focused (80 µm) beam generated by a single mode laser diode with a 40 mW red laser illumination (640 nm). The cold polymer solutions containing platinum nanoparticles (average diameter 186 nm, concentration 10^6 particles mL⁻¹) were injected in a sample chamber of 0.5 mL size from which a volume of $120 \times 80 \times 20$ microns was visualized under the microscope. The Brownian motion of the nanoparticles was tracked at 30 frames/s. NTA 2.3 software was used to evaluate the mean squared displacements of each visible particle (calibration 166 nm/ pixel). Averaging over multiple particles (n > 50) yielded an average diffusion coefficient



Figure S7 | Tracking analysis. The average apparent diffusion coefficient of the particles as a function of concentration of **P2b** at T = 22 °C. The diffusion coefficient strongly scales to the gel concentration, which suggests that the gels at higher concentrations have more bundles (smaller pores) rather than thicker bundles. The latter restricted particle displacement to a much smaller extent.

Vial inversion test



Figure S8 | Room temperature gel inversion test of **P2b** at c = 2.0 - 0.031 mg mL⁻¹ (or 0.2 - 0.003 wt-%). Gels at concentrations as low as c = 0.063 mg mL⁻¹ pass the vial inversion test.

Rheology

Instrumental. Rheological measurements were performed using a TA Instruments Ares G2 rheometer in a ≈ 20 mL Couette configuration with temperature control using a peltier element. Samples were prepared by mixing the appropriate amount of polymer in demi water (20 mL) and regular vortexing the mixture over time (at least 24 hours) until a homogeneous solution was obtained. Solutions of **P2b** were prepared in refrigerated (4 °C) conditions to avoid early gel formation. The measurements in the linear response regime were conducted at 4% strain at different frequencies between 0.5 and 5 Hz. The data depicted in the manuscript was recorded at 1 Hz. Temperature scans were recorded at a heating or cooling rate of 2 °C min⁻¹. The measurements in the nonlinear regime were taken at constant temperature (15 minutes equilibrated) and at different frequencies (0.5–5 Hz). Again, the data in the manuscript was recorded at 1 Hz.

Strain and Frequency sweeps. Figures S7 and S8 show a strain and frequency sweep of P2b (1 mg mL⁻¹) at T = 5 °C (solution) and T = 50 °C (gel). The moduli are constant for strains up to 10%. We typically measured our gels at 4% strain, to make sure that also in the solution regime of the experiment, reliable data is obtained. Displayed data in Figure S9 has been recorded at an angular frequency $\omega = 6.3$ rad s⁻¹ (or f = 1 Hz). The frequency sweep in the linear regime (Figure S10) was recorded at 4% strain. The moduli G' and G'' scale with the frequency in the cold solution, showing a power law behaviour ($\propto \omega^{0.6}$) and are nearly constant over five decades in the gel.



Figure S9 | Strain sweeps of **P2b** (1 mg mL⁻¹) at T = 5 °C (solution) and T = 50 °C (gel) at f = 1 Hz.



Figure S11 | Moduli G' and G'' of **P2b** ($c = 1 \text{ mg} \text{ mL}^{-1}$) as a function of temperature, measured to 65 °C.



Figure S13 | Storage modulus of **P2b** ($c = 1 \text{ mg mL}^{-1}$) as a function of temperature for 6 sequential heating and cooling runs. The transition temperature remains unaffected.



Figure S10 | Frequency sweeps of **P2b** (1 mg mL⁻¹) at T = 5 °C (solution) and T = 50 °C (gel) at $\gamma = 4\%$.



Figure S12 | Gelation temperatures of **P2b** as a function of concentration *c* determined as the onset of the increase in *G'* and the crossover of *G'* and *G''*. For the former, a relative constant gelation temperature is observed. The large error in the experimental data at $c = 0.05 \text{ mg mL}^{-1}$ prevented a reliable value at this low concentration. The steeper increase in transition temperature when determined as the crossover temperature is the result of the stronger dependence of the absolute values of *G''* on *c* than *G'* on *c*.

Gel temperature. The gel temperature has been defined as the onset of the step in G' at the LCST. Alternatively, one can decide to use the crossover temperature where G' = G''. We find that the latter shows a much stronger concentration dependence, since the absolute values of G' and G'' respond differently to different concentrations. In addition, the crossover definition also depends on the frequency that is applied, whereas the onset temperature (or G' in general) is much less sensitive to different frequencies. The transition temperatures using both definitions are shown in Figure S12 (f = 1Hz).

Single Molecule Force Spectroscopy Analysis

Single Molecule Force Spectroscopy measurements were conducted on a JPK Nanowizard 1 AFM running software version 3.4.18 using Olympus Biolever BL-AC40TS-C2 cantilevers with a resonance frequency of 100–130 kHz in air and \approx 30 kHz in water. The cantilevers were cleaned with concentrated sulfuric acid, neutralized with MilliQ water, washed with ethanol, dried and finally put in an ozone cleaner for at least half an hour. The temperature of the sample was controlled with a peltier element mounted underneath the glass sample holder. To minimize the chance of probing multiple polymers simultaneously, samples were prepared by spin-coating (3000 rpm) dilute polymer solutions $(\approx 3 \text{ mM})$ in dichloromethane on a freshly cleaved muscovite mica surface. Subsequently, these samples were rinsed with MilliQ water to remove any non-adsorbed polymer. The resulting polymer density and morphology were then analysed using tapping mode AFM in air. The force spectroscopy measurements were performed in MilliO water. The polymers were attached to the AFM tip by nonspecific adsorption. The tip was lowered with a speed of 2 μ m s⁻¹ until it made contact with the sample, pressed onto the sample with a force of a few nN for one second and retracted from the surface with a speed of 2 μ m/s. Due to the low polymer density on the surface, a polymer was adsorbed to the AFM tip in less than 1% of the approach-retract cycles. This low interaction frequency also indicates that the chance of adsorbing multiple polymers to the tip simultaneously is extremely low. Curves that showed artefacts such as large nonspecific adhesion or multiple rupture events resulting from the simultaneous pulling of several molecules or multipoint attachment of one polymer were discarded using a custom Matlab program and JPK data processing Version 3.4.18. These programs were also used to fit the statistical polymer models to the selected force-distance curves.

Analysis of the selected force–distance curves revealed a large variation in the contour length. This can be easily explained by the relatively high polydispersity of the sample. Furthermore, the polymers adsorb to both the tip and the surface at random positions along the polymer chain. To obtain the persistence length, the force–distance curves were fitted to the Extensible Worm Like Chain (EWLC) model using least squares fitting. All parameters were fitted for each individual force–distance curve. The distribution of the persistence length l_p for **P2b** at different temperatures is shown in Figure S14, indicating a broad distribution. Temperature sweeps from 10 to 60 °C with steps of 10 °C showed that this effect persisted at al temperatures. The average l_p value is plotted versus temperature and fitted to $e^{\beta T}$ with an exponent β of 0.041 (see Figure 3D in the manuscript).

The absolute values of the $l_{p,0}$ are low in comparison to other materials based on polyisocyanopeptides. This is attributed to solvent effects. Water, the solvent used to carry out the SMFS measurements of **P2b**, is believed to weaken the hydrogen bonds that cause the high stiffness of the polymers. As the temperature increases and water is slowly forced out of the polymer by hydrophobic effects of the ethyleneglycol tails, the core stiffens further. Measurements were also carried out a nonprotic solvent, such as 1,1,2-trichloroethane. A temperature sweep shows a persistence length $l_{p,0}$ of 34 nm with a negligible temperature dependence. Measurements in dioxane, a hydrogen bond acceptor but not a donor, shows $l_{p,0}$ values around 12 nm that are also constant with temperature.



Figure S14 | Persistence length distribution of **P2b** at temperatures ranging from 10 to 60°C.

Semi-flexible network theory

Previously published theories on rheology of semi-flexible networks, based on the Extensible Wormlike Chain model were used for this work^{S4,S5}. The plateau modulus G_0 and the critical stress σ_c of a gel composed of bundles of *N* polymer chain are dependent on the persistence length of the bundle $l_{p,B}$ and the contour length, or the length between crosslinks l_c when this is smaller than the contour length:

$$G_0 = 6\chi \frac{c}{N} k_{\rm B} T \frac{l_{\rm p,B}^2}{l_{\rm c}^3}$$
(1)

and

$$\sigma_{\rm c} = \chi \frac{c}{N} k_{\rm B} T \frac{l_{\rm p,B}}{l_{\rm c}^2} \tag{2}$$

Here, *c* is the concentration, $k_{\rm B}$ is the Boltzmann's constant, *T* is the absolute temperature and χ is composed of (molecular) constants. The related bundle density ρ (in length per volume) can also be used:

$$\rho = \chi \frac{c}{N} = \frac{l_{\rm M} N_{\rm A}}{M} \frac{c}{N}$$
(S3)

in which $l_{\rm M}$ is the length per monomer unit projected along the polymer backbone ($l_{\rm M} = 0.25$ nm), M is the molecular weight of a monomer (for P2: M = 0.316 kg mol⁻¹) and $N_{\rm A}$ is Avogadro's number. When bundling is independent on the concentration as holds for our materials (see manuscript), the pore size can be estimated by calculating the mesh size ξ :

$$\xi = \frac{1}{\sqrt{\rho}} \tag{S4}$$

In a semi-flexible network with relatively flexible bundles, the ξ ($\xi \propto c^{-0.5}$) should roughly correspond to l_c . This, we also observed experimentally ($l_c \propto c^{-0.4}$) and can be rationalized by considering that other contributions that affect (i.e., decrease) ξ , but not l_c , will be entanglements of bundles. If entanglement have a significant impact, l_c is expected to be much larger than ξ , which is experimentally not found (**P2b**, $c = 1 \text{ mg mL}^{-1}$, T = 30 °C: $\xi = 140 \text{ and } l_c = 110 \text{ nm}$), vide supra.

Eqs S5 and S6 combine Eqs. 1 and 2 with S3:

$$G_0 = \frac{6 l_{\rm M}}{M} \frac{c}{N} RT \frac{l_{\rm p,B}^2}{l_{\rm c}^3}$$
(S5)

and

$$\sigma_{\rm c} = \frac{l_{\rm M}}{M} \frac{c}{N} RT \frac{l_{\rm p,B}}{l_{\rm c}^2} \tag{S6}$$

We observed an exponential increase with temperature in the (narrow) experimental temperature window and we insert a phenomenological correction for that in Eqs. S7 and S8 in which β (K⁻¹) is a constant. This temperature contribution to G_0 and σ_c directly results from the stiffening of the individual polymer chains which is included in $l_{p,B}$ (*vide supra*). Since G_0 scales with l_p^2 the exponent also includes a prefactor 2 yielding: $e^{2\beta T}$. In contrast, σ_c scales linear with l_p , resulting in the exponent $e^{\beta T}$.

$$G_{0} = \frac{6 l_{\rm M}}{M} \frac{c}{N} \frac{l_{\rm p,B}^{2}}{l_{\rm c}^{2}} RT e^{2\beta T}$$
(S7)

and

$$\sigma_{\rm c} = \frac{l_{\rm M}}{M} \frac{c}{N} \frac{l_{\rm p,B}}{l_{\rm c}^2} RT e^{\beta T}$$
(S8)

Taking together Eqs S7 and S8, one can calculate $l_{p,B}$ and l_c from the experimentally obtained G_0 and σ_c :

$$l_{\rm p,B} = \frac{1}{36} \frac{l_{\rm M}}{M} \frac{c}{N} \frac{G_0^2}{\sigma_{\rm c}^2} RT e^{-\beta T}$$
(S9)

and

$$l_{\rm c} = 6 \ l_{\rm p,B} \frac{\sigma_{\rm c}}{G_0} e^{\beta T} \tag{S10}$$

The only unknown quantity in Eqs. S9 and S10 is the bundle number N. This was estimated by AFM experiments (N = 6.9), but this can also be calculated using the SMFS measurements. We determined in the manuscript that for the low bundle numbers, the material is in the tight bundle regime, which gives a square N dependency:

$$l_{\rm p,B} = l_{\rm p,0} N^2 \tag{S11}$$

The temperature dependence of $l_{p,0}$ is identical to that of $l_{p,B}$ (exponential with the same constant β), which tells us that the stiffening of the gel is directly related to the stiffening of the individual polymers (and also that *N* does not vary with temperature as would be expected for the gel). Obviously, the temperature dependence of the gel is quadratic, as G_0 scales with l_p^2 . Taking together Eqs. S9 and S10 with S11, we obtain two equations with only two unknown quantities: *N* and l_c :

SUPPLEMENTARY INFORMATION RESEARCH

$$G_0 = \frac{6 l_{\rm M}}{M} N^3 \frac{c}{l_{\rm c}^3} RT l_{\rm p,0}^2 e^{2\beta T}$$
(S12)

and

$$\sigma_{\rm c} = \frac{l_{\rm M}}{M} N \frac{c}{l_{\rm c}^2} RT l_{\rm p,0} e^{\beta T}$$
(S13)

Both have been calculated for different temperatures and concentrations and give very consistent results: N = 9.1 (close to 6.9 estimated by AFM) and $l_c = 110$ nm (at c = 1 mg mL⁻¹), close to the mesh size ($\xi = 140$ nm at this concentration). Reduced versions of Eqs. S12 and S13, highlighting the different design parameters for efficient gel formation are shown in the manuscript:

$$G_0(T) \propto N^3 \frac{c}{l_c^3} RT l_{p,0}^2(T)$$
 (3)

$$\sigma_{\rm c}(T) \propto N \frac{c}{l_{\rm c}^2} RT l_{\rm p,0}(T) \tag{4}$$

The predictions of Figure 4 are made with the assumption that the mesh size and the length between crosslinks are very close: $\xi \approx l_c$, which results, together with Eq. S4 in:

$$G_0 \approx \frac{6 \, l_{\rm M}}{M} N^3 \frac{c}{\xi^3} RT l_{\rm p,0}^2 e^{2\beta T} \approx \frac{6 \, l_{\rm M}}{M} N^3 \sqrt{\rho^3} cRT l_{\rm p,0}^2 e^{2\beta T}$$
(S14)

and

$$\sigma_{\rm c} \approx \frac{l_{\rm M}}{M} N \frac{c}{\xi^2} RT l_{\rm p,0} e^{\beta T} \approx \frac{l_{\rm M}}{M} N \rho c RT l_{\rm p,0} e^{\beta T}$$
(S15)

together with Eq. S3, this leads to:

$$G_0 \approx 6 \left(\frac{N_{\rm A} l_{\rm M}}{M}\right)^{\frac{5}{2}} \sqrt{N^3 c^5} k_{\rm B} T l_{\rm p,0}^2 e^{2\beta T}$$
 (S16)

and

$$\sigma_{\rm c} \approx \left(\frac{N_{\rm A} l_{\rm M}}{M}\right)^2 c^2 k_{\rm B} T \, l_{\rm p,0} e^{\beta T} \tag{S17}$$

which have been used to plot Figure 4. Equations S16 and S17 show that G_0 is dependent on N, c and $l_{p,0}$, whereas σ_c only scales with c and $l_{p,0}$. In the reduced form, analogous to Eqs. 3 and 4, one can write:

$$G_0(T) \propto \sqrt{N^3 c^5} k_{\rm B} T l_{\rm p,0}^2(T)$$
 (S18)

and

$$\sigma_{\rm c}(T) \propto c^2 k_{\rm B} T l_{\rm p,0}(T) \tag{S19}$$

Note that Eqs. S18 and S19 contain the assumption that no cross-over from the tight to the loose bundle regime is expected, also at higher bundle numbers. If, as has been observed for actin filaments, this would be the case, the dependence of G_0 and σ_c on N will change significantly, however, not their dependence on c and $l_{p,0}$. In the loose bundle limit, in which

$$l_{\rm p,B} = l_{\rm p,0} N \tag{S20}$$

Eqs. S18 and S19 change to:

$$G_0(T) \propto \sqrt{N^{-1}c^5} k_{\rm B} T l_{\rm p,0}^2(T)$$
 (S21)

and

$$\sigma_{\rm c}(T) \propto N^{-1} c^2 k_{\rm B} T l_{\rm p,0}(T) \tag{S22}$$

which shows that in this regime the bundling is no longer effective to increase either the gel modulus or its critical stress.

References and Notes:

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