Supporting Information for

Using polymeric additives to enhance molecular gelation: Impact of poly(acrylic acid) on pyridine-based gelators

Yash J. Adhia, Tracy H. Schloemer, Maria T. Perez and Anne J. McNeil*

Department of Chemistry and Macromolecular Science and Engineering Program

University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109

Contents: **Page**

I. Materials

Poly(acrylic acid) (PAA), poly(styrene sulfonic acid) (PSS, M_w = 70 kDa) and poly(styrene sodium sulfonate) (PSS-Na, M_w = 500 kDa) were purchased from Scientific Polymers Inc. and used as received unless otherwise noted. Dextran (M_w = 70 kDa) was purchased from Sigma Aldrich. Anhydrous DMSO was purchased from Acros Organics, USA. Ultrapure water was obtained using a Synergy Water purification system, Millipore Inc.. Capillary tubes were purchased from Charles-Supper Company, Inc. Gelator **1** was synthesized as described previously.[1,2] PAA with M_w = 450 kDa was used in this paper, unless otherwise noted.

II. General Experimental

Preparing Stock Solutions in 1/1 DMSO/H_2O (v/v): Accurate and equal volumes of anhydrous DMSO and H_2O were measured with volumetric flasks at room temperature and mixed. Known weights of polymers were dissolved in this solution by stirring them overnight at rt.

Preparing an HCl solution in 1/1 DMSO/H_2O (v/v): Acidified solutions of 1/1 DMSO/H_2O (v/v) were prepared by adding a drop of conc. HCl to 15 mL of 1/1 DMSO/H_2O (v/v), resulting in a solution with pH = 2. Further dilution of the above solution was carried out with 1/1 DMSO/H_2O (v/v) while continuously monitoring the pH (using a pH meter) until the desired pH was obtained. This procedure ensured that the overall volume ratio of DMSO/H_2O did not change significantly during acidification.

Deprotonation of PAA in 1/1 DMSO/H_2O (v/v): For preparing the sodium salt of PAA (PAA-Na), 0.2 wt% PAA solution in 1/1 DMSO/H_2O (v/v) was titrated with a 0.13 N NaOH solution prepared in 1/1 DMSO/H_2O (v/v) until the pH was 9-10 as measured by a pH meter. The titrant was prepared by diluting 0.10 mL of 50% NaOH solution in water to 15 mL using 1/1 DMSO/H_2O (v/v). This procedure ensured that the overall volume ratio of DMSO/H_2O did not change significantly during titration.

General Procedure for Heat/cool-induced Gelation: A 4 mL vial was charged with a known weight of the gelator and 1 mL of 1/1 DMSO/H_2O (v/v) solution. The vial was capped and the mixture was heated until it formed a homogeneous solution. The hot solution was allowed to cool to rt. After 2 h, the stability of the gels was determined by the vial inversion test. If the gels were unstable, the heat-cool cycle was repeated and the vial inversion test was performed after 24 h. For gelation in the presence of polymers, a polymer solution of fixed concentration in 1/1 DMSO/H_2O (v/v) was used.

General Procedure for Measuring the Critical Gel Concentration (cgc): A stable gel was initially formed using the above procedure in a 4 mL vial. Additional 0.1 mL aliquots of the 1/1 DMSO/H_2O (v/v) solution or the polymer solution was added and the heat/cool cycle was performed. This process was continued until the gels were determined to be unstable by the vial inversion test. The cgc is reported for the last stable gel.

Rheological Measurements

Rheological measurements were performed using an AR2000-ex rheometer (TA Instruments) in the controlled stress mode. Oscillatory experiments were performed using 20 mm serrated

parallel plate geometry at a gap of 500 µm. A Peltier temperature control system equipped with water cooling enabled precise control of temperature during the measurements.

Oscillatory rheological experiments were performed by forming gels in the gap between the plates of the rheometer. A serrated plate with a recessed end was used in order to minimize the errors due to slipping of the sample. Gels of **1** were formed in 4 mL vials at the desired concentration. The gel in the vial was heated again until a clear-solution was obtained and approximately 0.3 mL of the hot solution was withdrawn with a pre-heated 1 mL air-tight syringe, and injected onto the peltier base held at 90 ºC. The geometry was immediately lowered to the desired gap of 500 µm and the temperature of the base plate was rapidly cooled to 30 ºC. Water was added to the recessed end of the serrated plate and a physical solvent trap was used to minimize water evaporation. The sample was allowed to equilibrate at this temperature for 30 min and oscillatory experiments were performed.

Frequency sweep measurements were performed under a constant stress of 0.6 Pa from 0.1 to 100 rad/s. A low value of control stress ensured that the rheological measurements were done in the linear viscoelastic regime. The suitability of this value of control stress was previously verified by stress sweep tests. The oscillatory stress sweep measurements were performed under a constant frequency of 6.283 rad/s from 0.06 Pa to 200 Pa.

Viscosity measurements were performed using the 40 mm parallel plate geometry at a constant shear rate of 10 s^{-1}.

Optical Microscopy

Optical microscopy was performed using a Leica DMLB microscope under the transmission mode. The images were captured using a QICAM Fast 1394 Color digital camera mounted on the microscope and processed using the QCapture Pro v6.0 software. Gel samples were drop-cast on a glass slide and immediately imaged under the microscope.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed using a Quanta 200 3D scanning electron microscope in the high vacuum mode. The gel samples were drop-cast on a glass slide and allowed to dry overnight. The samples were sputtered with gold for 60 s prior to imaging. Image processing and measurement of fiber diameters were performed using the QCapture Pro v6.0 software. Fiber diameter distribution for each experimental condition was calculated using approx. 250 fibers from 20 images.

Transmission Electron Microscopy

The gel samples were deposited onto a carbon-coated copper grid and the excess solvent was removed using kimwipes. The sample was then examined under a JEOL 3011 High Resolution Electron microscope operated at 300 kV under high vacuum. The brightfield images were acquired digitally with the AMT Imaging Software v5.4 and subsequently processed using QCapture Pro v6.0 software. Multiple images were taken across each sample and all experimental conditions (without PAA and with PAA) were analyzed with three independently prepared gel samples to ensure reproducibility. The fiber diameter distribution for each experimental condition was calculated using approx. 60 fibers from 10 different images.

Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) analysis of samples was performed on a Bruker D-8 Advance system equipped with a LynxEye detector and parallel beam optics with Cu-Kα X-rays (λ = 1.5406 Å). The samples were loaded onto glass microscope slides. Data processing and analyses were performed using EVA (version 13) pattern processing software.

Solubility Measurements:

The concentration of **1** in the solution was analyzed by Perkin Elmer Lambda 850 UV-Vis spectrometer.

An 8 mL vial was charged with the gelator (~ 10 mg) and 1/1 DMSO/H_2O (v/v) or 0.2 wt% PAA solution in 1/1 DMSO/H_2O (v/v) (~ 6 mL). The heterogeneous mixture was equilibrated for 24 h (without stirring) at each of the temperatures studied (25, 35, 47 and 59 ºC). At each temperature, an aliquot of fixed volume was taken from the solution with a micro-syringe and the syringe was rinsed with 1/1 DMSO/H_2O (v/v) (2 x 200 µL). The aliquot and combined rinses were further diluted with 1/1 DMSO/H_2O (v/v) to achieve a final volume of 2.8 mL. The concentration of the gelator was determined using a calibration curve by calculating the extinction coefficient of the gelator in neat DMSO and in 0.2 wt% PAA solution in DMSO at 304 nm.

At each temperature, 2 different vials were set up and 2 aliquots were taken from each vial, producing a total of 4 samples at each temperature. The concentrations reported are the average of the 4 samples.

To calculate the enthalpy and entropy of dissolution (ΔH_{diss} and ΔS_{diss}, respectively), van't Hoff plots were constructed based on the equation

$$\ln x = -\frac{\Delta H_{diss}}{RT} + \frac{\Delta S_{diss}}{R}$$

where x is the mole fraction solubility of the corresponding compound, R is the gas constant (1.98 cal/mol·K), and T is the temperature in K. ΔH_{diss} was obtained from the slope and ΔS_{diss} was calculated from the intercept. The reported errors for ΔH_{diss} and ΔS_{diss} were obtained from the statistical analysis in Sigmaplot 10. The individual errors reported on each point in the van't Hoff plots were calculated as the relative error as shown below:

$$r.e. = \frac{\Delta x}{x}$$

where Δx is the error associated with the mole fraction solubility.

Induction time measurements:

Two vials were each charged with 2.0 mg of **1**. In vial A, 1.0 mL of 1/1 DMSO/H_2O (v/v) was added, and in vial B, 1.0 mL of a 0.2 wt% PAA solution in 1/1 DMSO/H_2O (v/v) was added (overall [**1**] = 5.2 mM). The vials were sealed with PTFE caps and heated simultaneously to 90 ºC to form a homogeneous solution and allowed to cool to rt. The time required until the first

visual observation of fibers is noted as the induction time. All measurements were repeated 10 times to ensure reproducibility.

Hot-stage Microscopy:

Hot-stage microscopy was performed on a Nikon Eclipse 80i microscope equipped with cross-polarizers and a LTS350 temperature-controlled stage connected to a LNP95 liquid nitrogen based cooling system (Linkam Scientific Instruments, U.K.). The temperature was controlled using a T95-Linksys controller with the Linksys32 temperature control and image capture software. The images were captured digitally using a QICAM Fast 1394 Color digital camera mounted on the microscope.

Linear growth rates were measured by forming gels in 1 mm capillary tubes. A 250 µL syringe was pre-heated to 90 ºC. Gels of **1** at 2.0 mg/mL (0.2 wt%) in 1/1 DMSO/H_2O (v/v) and PAA solutions in 1/1 DMSO/H_2O (v/v) were formed in 4 mL vials. The vial was heated until the solution became homogeneous. A small aliquot of this hot solution was withdrawn using the pre-heated syringe and injected into the capillary. The capillary was flame-sealed and placed on the heating stage of the microscope. The temperature of the stage was ramped at 30 ºC/min to 90 ºC, and the sample was allowed to equilibrate for 2 min at this temperature. At this point, the solution was completely homogeneous. The solution is then cooled at 30 ºC/min to 30 ºC, and the stage was held at this temperature as the gel fibers begin to grow along the axis of the capillary. The images captured in the first 20 s of the fiber growth were used for measuring growth rates.

The subsequent image processing and length measurements were performed using the QCapture Pro v6.0 software.

III. Cgc versus Polymer Structure

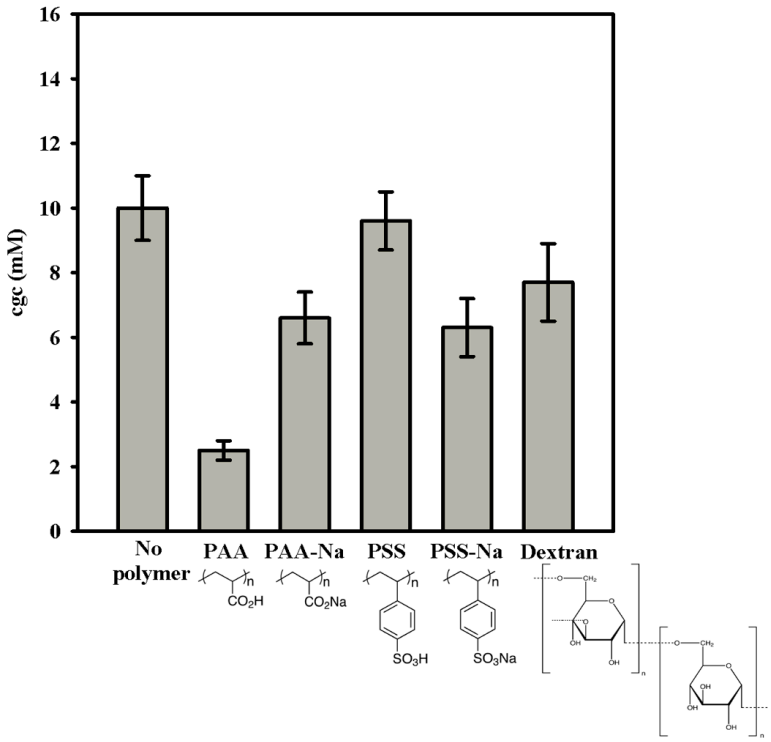

Figure S1. Plot of the cgc of **1** in the presence of different polymers in 1/1 DMSO/H_2O (v/v) ([polymer] = 0.2 wt%)*.

Table S1. Data for Figure S1.

Condition	Cgc (mM)
No polymer	10 ± 1
PAA	2.5 ± 0.3
PAA-Na*	6.6 ± 0.8
PSS	9.6 ± 0.8
PSS-Na	6.3 ± 0.9
Dextran	8 ± 1

* [PAA-Na] = 0.08 wt%. For comparison, the cgc at 0.08 wt% PAA was 2.2 ± 0.1 mM

IV. Poly(acrylic Acid) (PAA)

A. Cgc Data

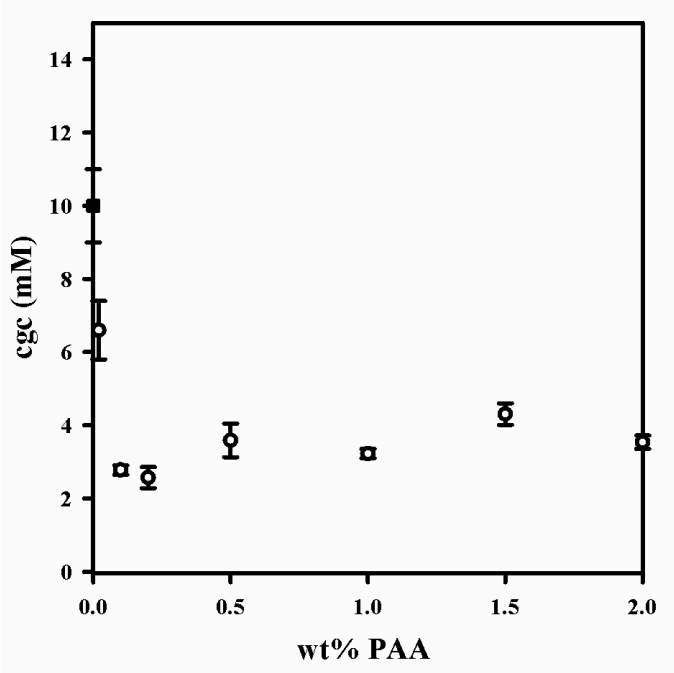

Figure S2. Plot of the cgc of **1** versus wt% PAA in 1/1 DMSO/H_2O (v/v) (■ represents [PAA] = 0 wt%).

Table S2. Data for Figure S2.

wt% PAA	Cgc (mM)
0.0	10 ± 1
0.02	6.7 ± 0.7
0.05	3.0 ± 0.1
0.1	2.8 ± 0.1
0.2	2.5 ± 0.3
0.5	3.6 ± 0.5
1.0	3.2 ± 0.1
1.5	4.3 ± 0.3
2.0	3.5 ± 0.6

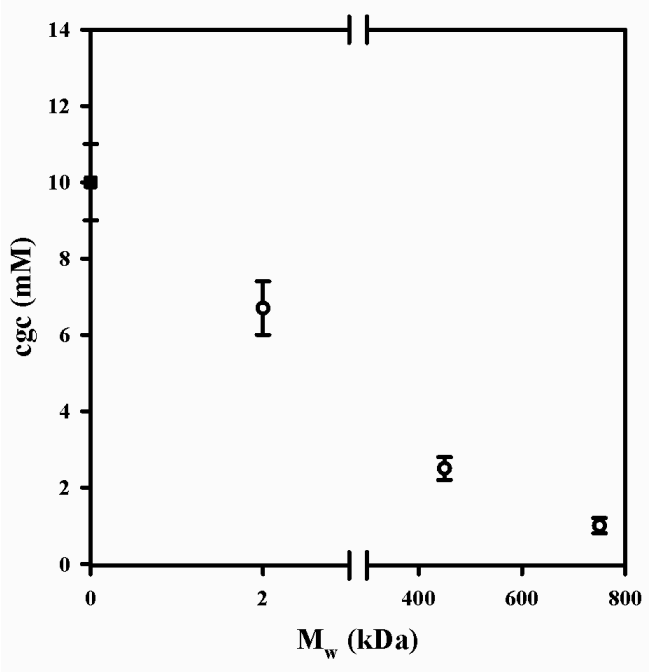

Figure S3. Plot of the cgc of **1** versus molecular weight of PAA in 1/1 DMSO/H_2O ([PAA] = 0.2 wt%, ■ represents [PAA] = 0 wt%).

Table S3. Data for Figure S3.

M_w (kDa)	Cgc (mM)
2	6.7 ± 0.7
450	2.5 ± 0.3
750	1.0 ± 0.2

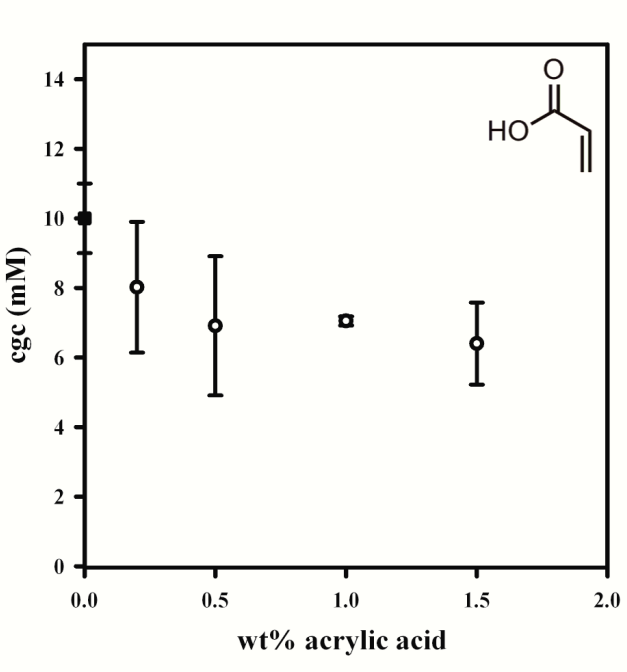

Figure S4. Plot of the cgc of **1** versus wt% acrylic acid in 1/1 DMSO/H_2O (v/v) (■ represents [acrylic acid] = 0 wt%).

Table S4. Data for Figure S4.

Acrylic acid (wt%)	Cgc (mM)
0.2	8 ± 2
0.5	7 ± 2
1.0	7.0 ± 0.1
1.5	6 ± 1

Table S5. Cgc in 1/1 DMSO/H_2O (v/v) acidified using HCl

pH	Cgc (mM)
6.0 (no HCl)	10 ± 1
4.2	8.0 ± 0.7
3.5	5 ± 2
2.5	2.8 ± 0.1

B. Rheology

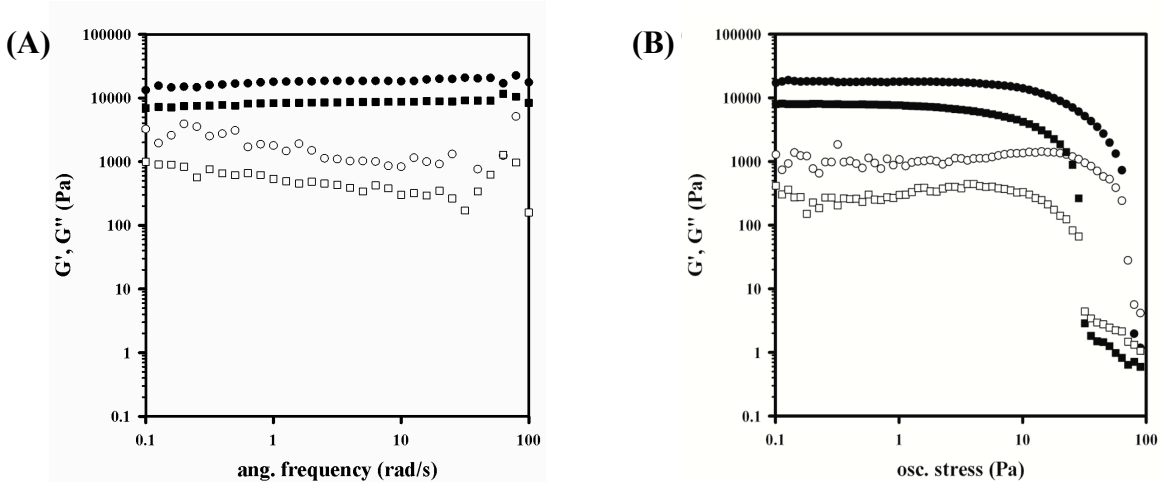

Figure S5. Plots of the elastic (G′, filled symbols) and storage (G″, open symbols) moduli as a function of (A) frequency and (B) stress for gel samples of **1** ([**1**] = 18 mM) without PAA (■,□) and with 0.2 wt% PAA (●,○) in 1/1 DMSO/H_2O (v/v).

Table S6. Data for Figure S5.

Sample	G′ (Pa × 10^3)	G″ (Pa × 10^2)	σ_b (Pa)
1	7 ± 1	8 ± 3	19 ± 8
1 + 0.2 wt% PAA	20 ± 10	20 ± 10	70 ± 50

C. Thermal stability

Thermal stability was measured using the falling ball method.[3] A gel of **1** (29 mM) was formed in a 4 mL vial in 1/1 DMSO/H_2O (v/v) with a known concentration of PAA. The gel was allowed to sit for 12 h and a copper ball (330 mg) was gently placed on top of the gel. The vial was sealed and placed in a stirred oil bath that was slowly heated (typically 2-4 ºC/min). The position of the steel ball was observed while simultaneously monitoring the temperature. The temperature at which the copper ball reached the bottom of the vial was considered as the gel-to-sol transition temperature (T_{gel}).

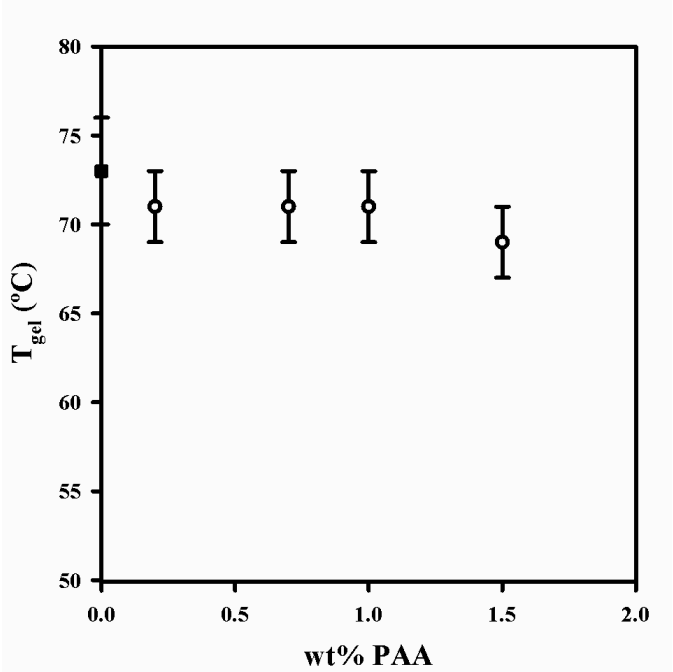

Figure S6. Plot of gel-to-sol transition temperature (T_{gel}) versus wt% poly(acrylic acid) in 1/1 DMSO/H_2O (v/v) (■ represents [PAA] = 0 wt%).

Table S7. Data for Figure S6.

[PAA] (wt%)	T_{gel} (°C)
0.0	73 ± 3
0.2	71 ± 2
0.7	71 ± 2
1.0	71 ± 2
1.5	69 ± 2

D. Unstable Gel Test

Two vials were each charged with 2.0 mg of **1**. In vial A, 1.0 mL of 1/1 DMSO/H_2O (v/v) was added, and in vial B, 1.0 mL of a 0.2 wt% PAA solution in 1/1 DMSO/H_2O (v/v) was added (overall [**1**] = 5.2 mM). The vials were sealed with a PTFE cap and heated until the solution became homogeneous. Both vials were cooled to rt and left undisturbed overnight. Vial A resulted in an unstable gel while vial B resulted in a stable gel. 0.3 mL of a 7.5 wt% PAA solution in 1/1 DMSO/H_2O (v/v) was added to both vials, and the vials were allowed to sit at rt for 58 h. The stability of the gels was subsequently determined using the vial inversion test.

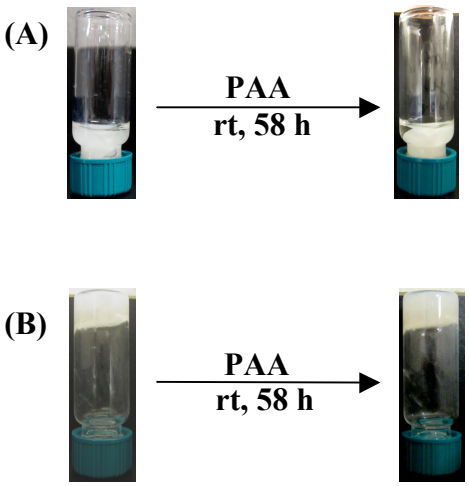

Figure S7. Effect of adding PAA to (A) an unstable gel and (B) a stable gel.

E. Microscopy

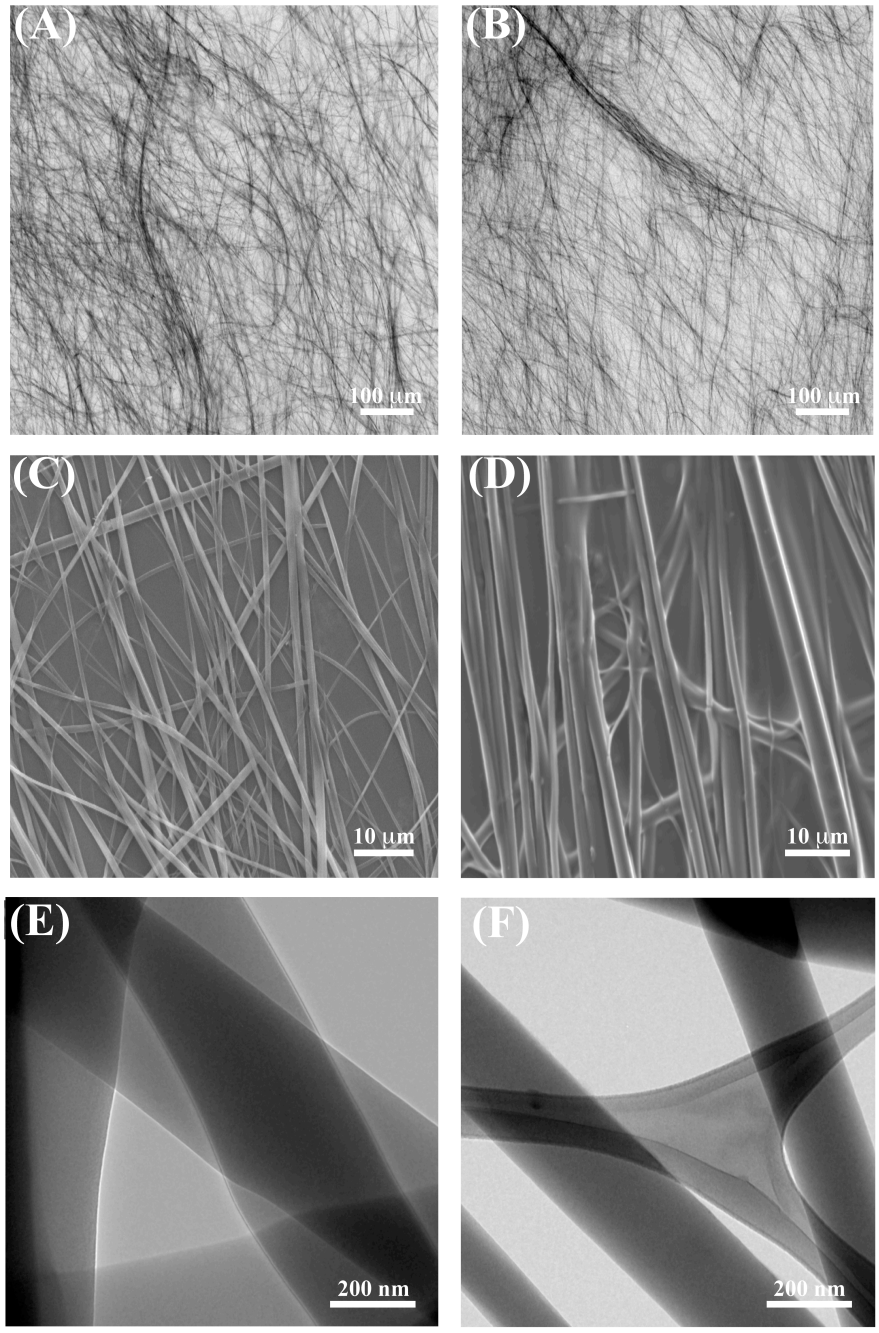

Figure S8. (A, B) Optical microscope, (C, D) scanning electron microscope and (E, F) transmission electron microscope images of gels formed in (A, C, E) 1/1 DMSO/H_2O (v/v) and (B, D, F) 0.2 wt% solution of PAA in 1/1 DMSO/H_2O (v/v) ([**1**] = 2.5 mM).

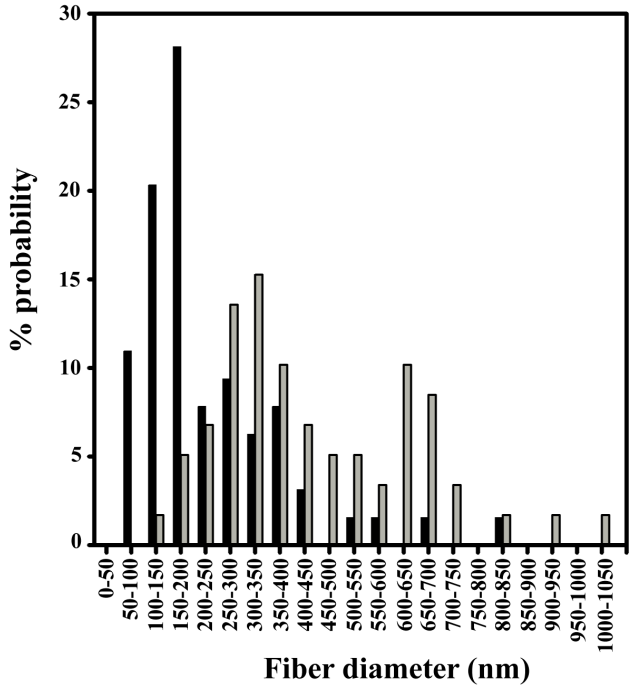

Figure S9. Fiber diameter distribution of gels formed in 1/1 DMSO/H_2O (v/v) (gray) and 0.2 wt% solution of PAA in 1/1 DMSO/H_2O (v/v) (black) as analyzed by transmission electron microscopy.

F. Powder X-ray Diffraction

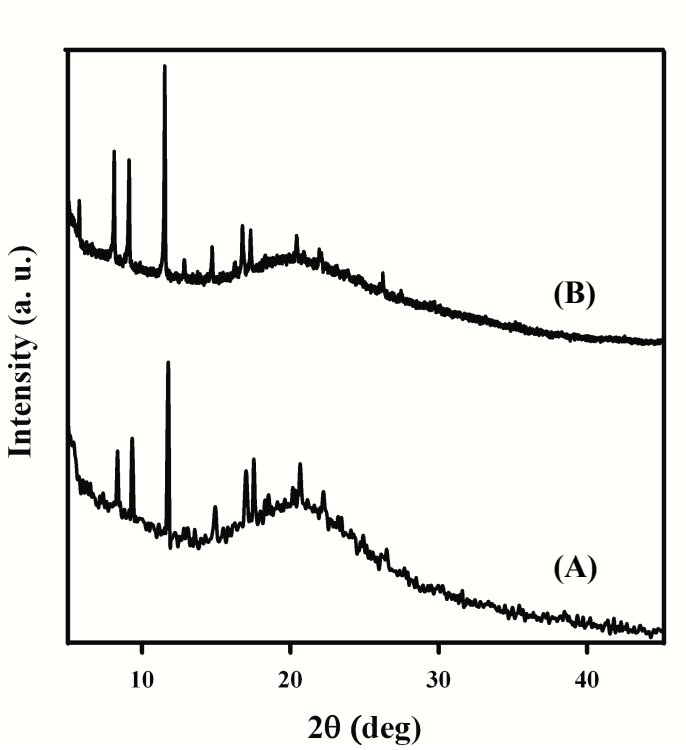

Figure S10. Powder X-ray diffraction pattern of (A) wet gel of **1** (B) wet gel of **1** with PAA formed in 2/1 DMSO/H_2O (v/v). ([**1**] = 26 mM, [PAA] = 1.0 wt%)

G. Solubility Data

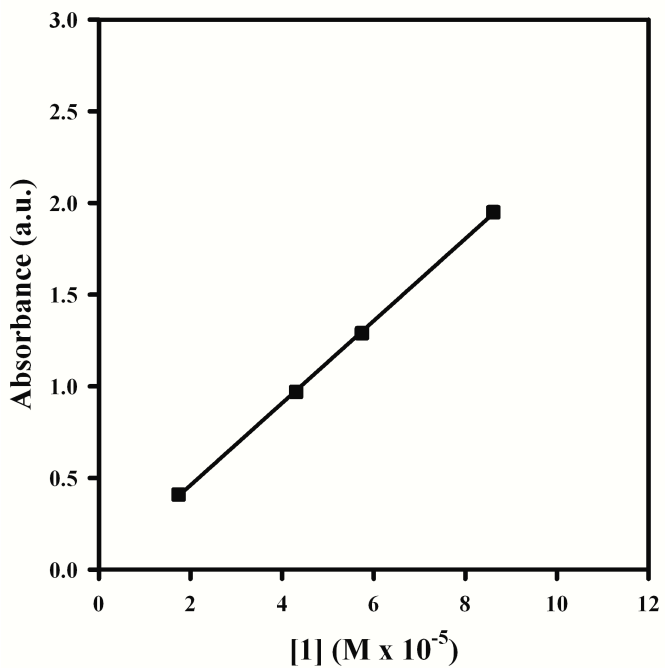

Figure S11. Plot of absorbance versus **[1]** in neat DMSO fitted to y = mx + b, where m = 2.24 × 10^{-1} M^{-1} and b = 1.17 × 10^{-2}.

Table S8. Data for Figure S11.

[1] (M × 10^{-5})	**Absorbance (a.u.)**
1.7	0.41
4.3	0.97
5.7	1.29
8.3	1.95

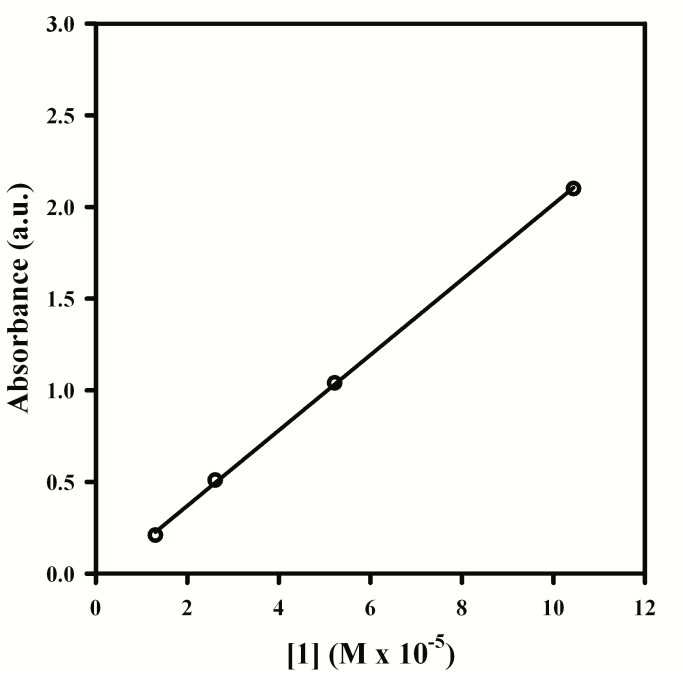

Figure S12. Plot of absorbance versus [**1**] in 0.2 wt% PAA solution in neat DMSO fitted to y = mx + b, where m = 2.05×10^{-1} M^{-1} and b = -4.13×10^{-2}.

Table S9. Data for Figure S12.

[1] (M $\times 10^{-5}$)	**Absorbance (a.u.)**
1.3	0.21
2.6	0.51
5.2	1.04
10.4	2.10

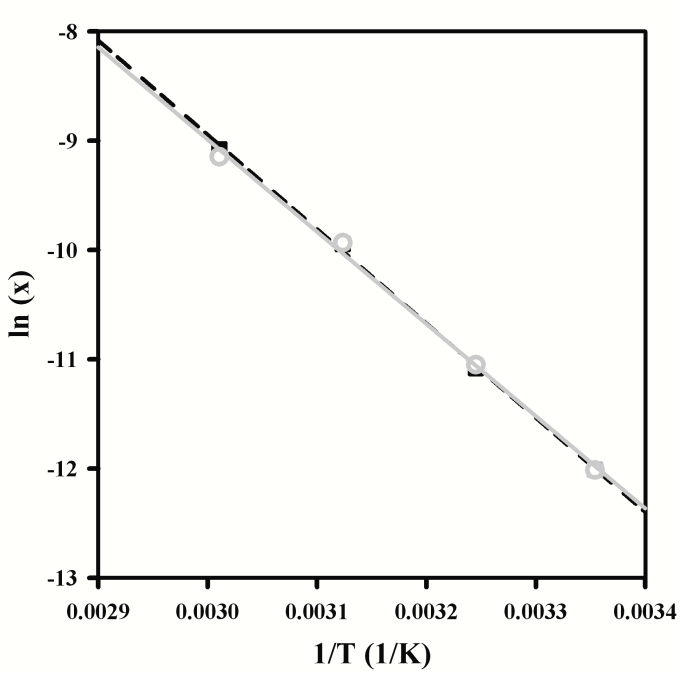

Figure S13. van't Hoff plot of **1** in 1/1 DMSO/H_2O (v/v) (--) and 0.2 wt% PAA solution (--) in 1/1 DMSO/H_2O (v/v) fitted to y = mx + b where m = -8632 K , b = 16.95 (without PAA), and m = -8437 K, b = 16.32 (with 0.2 wt% PAA).

Table S10. Data for Figure S13

1/T ($K^{-1} \times 10^{-3}$)	**ln (x)**	
	Without PAA	**With PAA**
3.01	-9.07 ± 0.03	-9.14 ± 0.02
3.12	-9.95 ± 0.01	-9.93 ± 0.02
3.24	-11.08 ± 0.03	-11.05 ± 0.02
3.35	-12.01 ± 0.03	-12.01 ± 0.05

Table S11. Thermodynamic parameters of **1** as calculated from Figure S13.

Sample	**ΔH_{diss} (kcal/mol)**	**ΔS_{diss} (kcal/mol·K)**
Without PAA	17.1 ± 0.4	0.033 ± 0.001
With PAA	16.3 ± 0.7	0.031 ± 0.002

H. Induction Time Measurements

Table S12. Measurement of induction times of **1** in 1/1 DMSO/H_2O (v/v) and in 0.2 wt% PAA in 1/1 DMSO/H_2O (v/v) ([**1**] = 5.2 mM)**.**

Trial number	**Induction time in 1/1 DMSO/H_2O (v/v)**	
	Without PAA (mm:ss)	**With 0.2 wt% PAA (mm:ss)**
1	4:40	4:40
2	4:03	4:03
3	5:13	3:40
4	4:09	3:42
5	4:21	4:10
6	4:49	4:24
7	4:15	3:45
8	3:55	3:34
9	4:00	4:15
10	4:30	3:25
Average ± std. dev.	4:24 ± 0:24	4:00 ± 0:24

I. Growth Rate Measurements

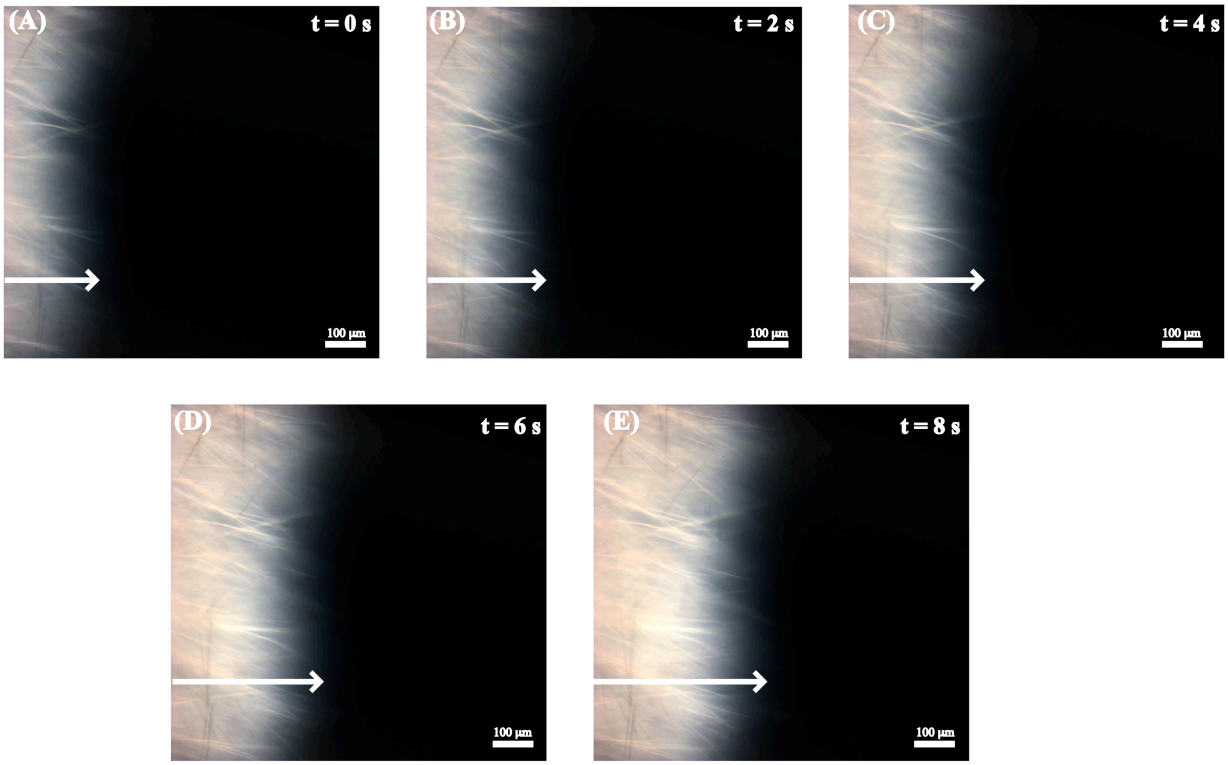

Figure S14. Representative images showing the real-time growth of **1** in a 1 mm capillary tube over time (a) t = 0 s (b) t = 2 s (c) t = 4 s (d) t = 6 s (e) t = 8 s at 30 ºC in 1/1 DMSO/H_2O (v/v) ([**1**] = 5.0 mM).

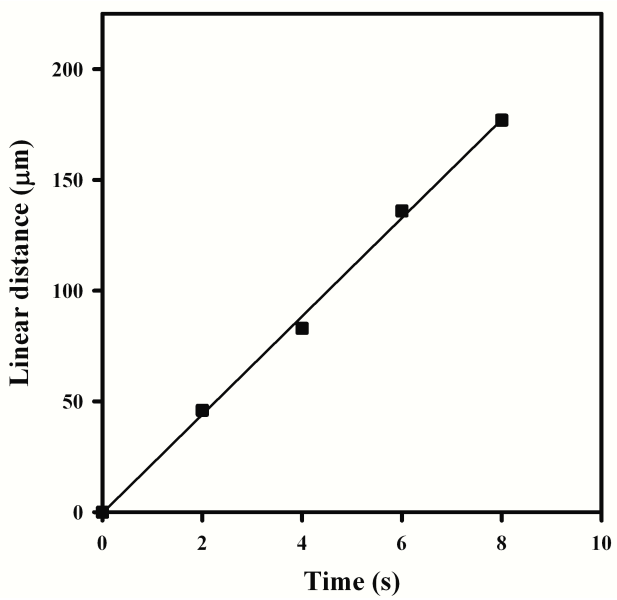

Figure S15. Plot of linear distance versus time fitted to y = mx, where m = 22 μm/s.

Table S13. Data for Figure S15.

Time (s)	Linear distance (μm)
0	0
2	46
4	83
6	136
8	177

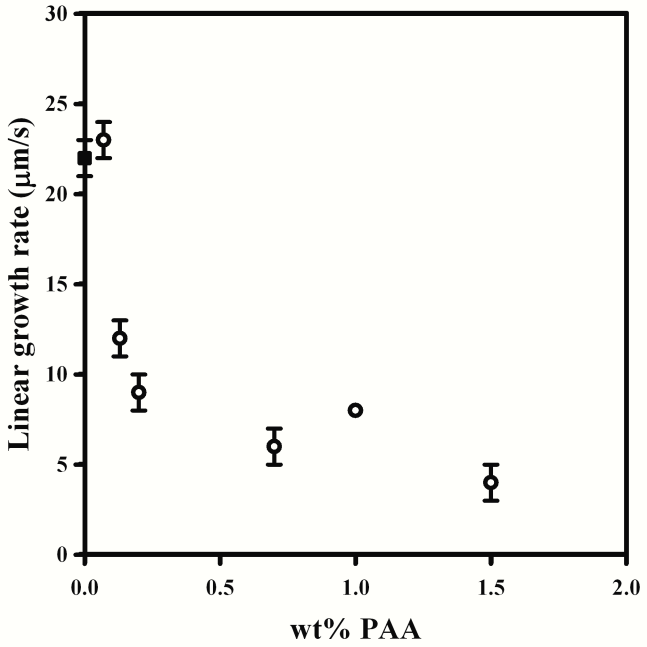

Figure S16. Plot of linear growth rates of **1** versus wt% PAA at 30 ºC in 1/1 DMSO/H_2O (v/v) ([**1**] = 5.0 mM, ■ represents [PAA] = 0 wt%).

Table S14. Data for Figure S16.

wt% PAA	Growth rate (µm/s)
0.0	22 ± 1
0.07	23 ± 1
0.1	12 ± 1
0.2	9 ± 1
0.7	6 ± 1
1.0	8
1.5	4 ± 1

V. Viscosity Measurements

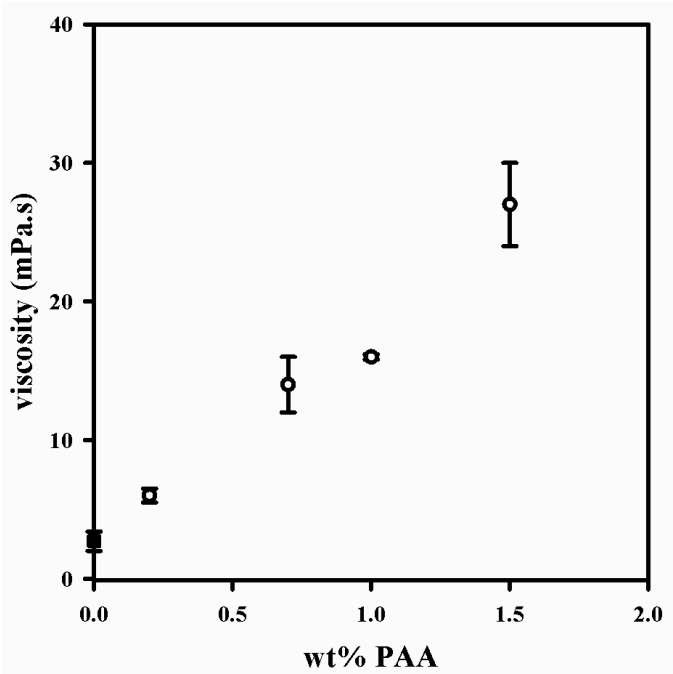

Figure S17. Plot of viscosity versus wt% PAA (■ represents [PAA] = 0 wt%).

Table S15. Data for Figure S17.

wt% PAA	Viscosity (mPa·s)
0.0	2.7 ± 0.7
0.2	6.0 ± 0.5
0.7	14 ± 2
1.0	16.0 ± 0.2
1.5	27 ± 3

VI. References

1. J. Chen and A. J. McNeil, *J. Am. Soc. Chem.,* 2008, **130**, 16496-16497.

2. J. Chen, J. W. Kampf and A. J. McNeil, *Langmuir*, 2010, **26**, 13076-13080.

3. J. van Esch, F. Schoonbeek, M. de Loos, H. Kooijman, A. L. Spek, R. M. Kellogg and B. L. Feringa *Chem. Eur. J.*,1999, **5**, 937-950.