

Physical Gelation of Polar Aprotic Solvents Induced by Hydrogen Bonding Modulation of Polymeric Molecules

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Supporting Information

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1. Synthesis and characterization of PAA

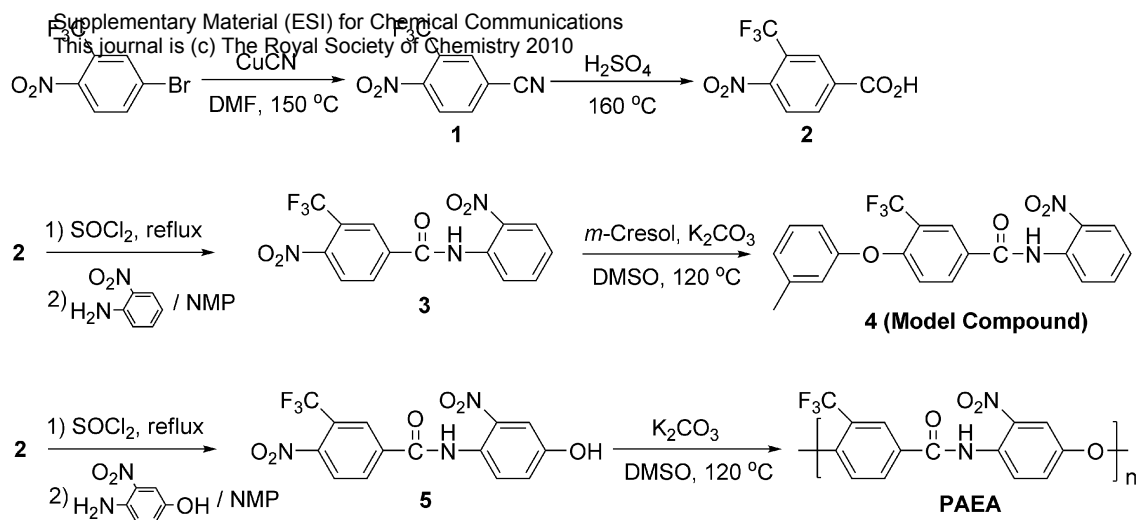
General measurement

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Fourier Transform AC400 spectrometer. Chemical shifts are expressed in parts per million (ppm) using residual solvent protons as references. All DOSY experiments were performed at 298 K on a Bruker Avance 800 spectrometer equipped with a Bruker 5mm micro-imaging PFG probe and a gradient amplifier, which provides a z-direction gradient strength of up to 50 G/cm. The temperature was maintained constant within ± 0.1 °C by means of the BVT-2000 unit. DOSY experiments were performed using the bipolar pulse longitudinal eddy current delay pulse sequence (BPPLED). The spoil gradients were also applied at the diffusion period and the eddy current delay. Typically, a value of 4.4 ~ 5.6 ms was used for the gradient duration (δ), 50-150 ms for the diffusion time (Δ), and the gradient strength (g) was varied from 1.7 G/cm to 32 G/cm in 32 steps. Each parameter was chosen to obtain ~95% signal attenuation for the slowest diffusion species at the last step experiment. The pulse repetition delay (including acquisition time) between each scan was larger than 3 s. Data acquisition and analysis were performed using the Bruker TopSpin software (version 2.1). The DOSY processing program as implemented in the TopSpin was used to calculate the diffusion coefficients and to create two-dimensional spectra with NMR chemical shifts along one dimension and the calculated diffusion coefficients along the other. Glass transition temperature of the synthesized polymer was obtained by differential scanning calorimetry (DSC) using TA-Q100 at a heating rate of 10 °C/min in N_2 . Thermogravimetric analysis (TGA) measurements were performed with TA-Q500 at a heating rate of 20 °C/min in N_2 . Molecular weight and molecular weight distribution of the polymer was measured by means of gel permeation chromatography (GPC; Viscotek T60A, column; PLgel 10 μm MIXED-B). The GPC measurements were carried out with THF as eluent at a rate of 1 mL/min at 35 °C and the GPC result was calibrated with polystyrene standards. Infrared (FT-IR) spectra were obtained with a Bruker EQUINOX-55 spectrometer using KBr pellet. Powder X-ray Diffraction (XRD) pattern was obtained on a Rigaku D/MAX III diffractometer with sampling width of 0.01 °, using $\text{Cu}_{K\alpha}$ ($\lambda = 0.154\text{nm}$) as a light source. Field-emission Scanning Electron Microscopy (FE-SEM) study was performed on a Philips XL30S FE-SEM. Samples prepared on silicon wafer were

sputtered with gold and investigated by SEM. Transmission Electron Microscopy (TEM) study was conducted using an EM 912 OMEGA electron microscope with the beam voltage of 120 keV. Samples were prepared by stamping carbon-coated TEM grid on the top of the **PAEA** gel and investigated without staining. Flow behavior measurements were carried out using an Advanced Rheological Expansion System (ARES, Viscometrics) fluid rheometer. The flow measurements were performed by spreading gel on parallel plate (60 mm), using a smooth plate-and-plate geometry (1 mm gap) according to each frequency sweep and step strain sweep mode. Polarized optical micrographs were obtained using a Nikon ME600 inspection microscope attached with a DXM1200F digital camera. The pKa value of samples were calculated using ACD/Chemsketch software from the structure of the molecule and also were collected on a Sirius GLpKa instrument with a D-PAS spectrometer controlled from a computer using Refinement Pro software (V.2.2., Sirius Analytical Instruments td., UK). Samples were initially dissolved in pure DMSO to form a 10 mM solution and three measurements were made at 25 °C by UV. A multi-wavelength UV spectrum was measured while the sample was titrated. The titration media was ionic-strength adjusted (ISA) with 0.15 M KCl (aq). The measurement was carried out from pH 1.8 to 12.2 as a triple titration.

Materials

The chemicals were purchased from Aldrich or Fluorochem and used as received. The synthetic procedures of 4-nitro-3-trifluoromethylbenzotrile (**1**), 4-nitro-3-trifluoromethylbenzoic acid (**2**), and 4-nitro-3-trifluoromethyl-*N*-(4-hydroxyphenyl)benzamide (**5'**) were reported elsewhere.¹ Synthetic scheme of the model compound, the monomer, and the polymer is shown in SS1.



SS1. Synthesis of model compound **4** and **PAEA** containing *o*-nitroanilide moiety

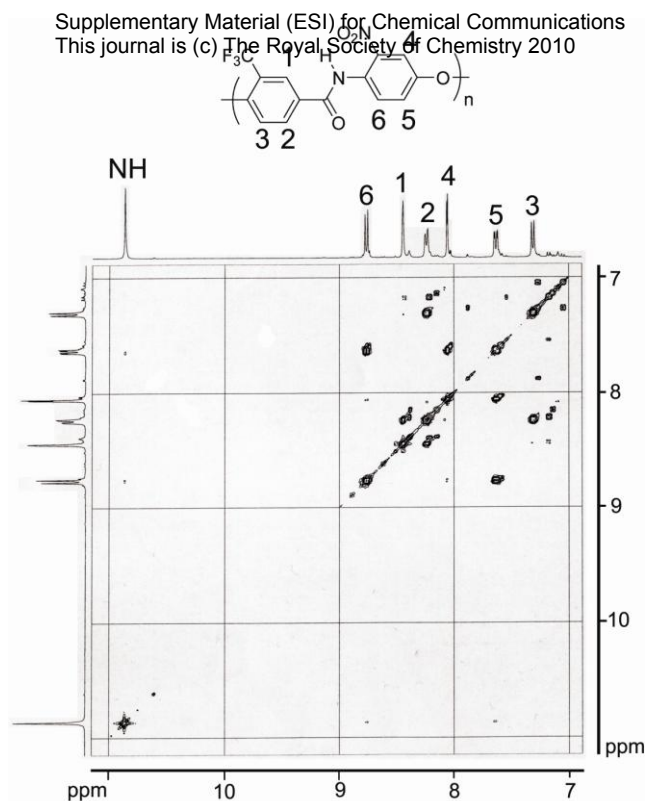
4-Nitro-3-trifluoromethyl-N-(2-nitrophenyl)benzamide (3). **2** (1.5 g, 6.38 mmol) and thionyl chloride (11 mL) were placed in a round bottomed flask. The reaction mixture was refluxed for 6 h in nitrogen atmosphere. The yellowish reaction mixture was cooled to room temperature and the residual thionyl chloride was removed under reduced pressure. The reaction mixture was diluted with anhydrous *N*-methylpyrrolidone (NMP, 7.5 mL), and added dropwise to a solution of *o*-nitroaniline (0.88 g, 6.38 mmol) in anhydrous NMP (7.5 mL) under nitrogen atmosphere at 5 °C. The reaction mixture was stirred overnight at room temperature, and then poured into water, filtered and dried in a vacuum oven at 100 °C. Further purification was accomplished by column chromatography (ethyl acetate/hexane = 1/4) to give a yellow solid (1.97 g, 87% yield). m. p. 142 °C. MS [M – H][–] : m/e 354.04 (Calcd: 355.23). ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C) : δ [ppm] = 11.43 (s, 1H, CONH), 8.49 (s, 1H, ArH), 8.46 (dd, 1H, *J*₁ = 8.4 Hz, *J*₂ = 1.7 Hz, ArH), 8.37 (d, 1H, *J* = 8.3 Hz, ArH), 8.04 (dd, 1H, *J*₁ = 8.2 Hz, *J*₂ = 1.4 Hz, ArH), 7.80 (m, 1H, ArH), 7.71 (dd, 1H, *J*₁ = 8.1 Hz, *J*₂ = 1.4 Hz, ArH), 7.50 (m, 1H, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C) : 162.57, 149.00, 143.57, 137.45, 134.03, 133.88, 130.35, 127.24 (q, ³*J*_{C-F} = 5 Hz), 126.68, 126.61, 126.09, 125.038, 121.79 (q, ¹*J*_{C-F} = 272 Hz), 121.66 (q, ²*J*_{C-F} = 34 Hz). Anal. Calcd for C₁₄H₈F₃N₃O₅: C, 47.34; H, 2.27; F, 16.04; N, 11.83; O, 22.52. Found: C, 48.82; H, 2.22; N, 10.25.

4-(3-methylphenoxy)-3-trifluoromethyl-N-(2-nitrophenyl)benzamide (4). A mixture of **3** (0.25 g, 0.70 mmol), *m*-cresol (0.076 g, 0.70 mmol), potassium carbonate (0.165 g, 1.20 mmol) in anhydrous dimethyl sulfoxide (DMSO, 1.1 mL) and benzene (1.1 mL, for azeotropic distillation of water) was stirred at 90 °C for 4 h under nitrogen atmosphere. The temperature was then raised to 120 °C, and stirring was continued for an additional 4 h. The reaction mixture was cooled to room temperature, poured into water, filtered and dried in vacuum to give a yellow solid (0.28 g, 96% yield). m. p. 55 °C. MS [M – H][–]: m/e 370.04 (Calcd: 371.04). ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C): δ [ppm] = 10.86 (s, 1H, CONH), 8.36 (d, 1H, *J* = 2.1 Hz, ArH), 8.19 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 4 Hz, ArH), 8.00 (dd, 1H, *J*₁ = 8.4 Hz, *J*₂ = 1.4 Hz, ArH), 7.76 (m, 1H, ArH), 7.70 (dd, 1H, *J*₁ = 8 Hz, *J*₂ = 1.5 Hz, ArH), 7.44 (m, 1H, ArH), 7.36 (m, 1H, ArH), 7.10 (m, 2H, ArH), 7.00 (s, 1H, ArH), 6.96 (dd, 1H, *J*₁ = 7.9 Hz, *J*₂ = 2.5 Hz, ArH), 2.33 (s, 3H, ArCH₃); ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C): 163.51, 158.05, 154.76, 143.39, 140.46, 134.26, 133.94, 131.04, 130.19, 127.71, 126.92 (q, ³*J*_{C-F} = 5 Hz), 126.35, 125.99, 124.96, 123.13 (q, ¹*J*_{C-F} = 271 Hz), 120.25, 119.98 (q, ²*J*_{C-F} = 31 Hz), 118.40, 116.81, 20.80. Anal. Calcd for C₂₁H₁₅F₃N₂O₄: C, 60.58; H, 3.63; F, 13.69; N, 6.73; O, 15.37. Found: C, 60.65; H, 3.71; N, 5.86.

4-nitro-3-trifluoromethyl-N-(4-hydroxy-2-nitrophenyl)benzamide (5). The procedure described above for compound **3** was repeated with 4-amino-3-nitrophenol (3.28 g, 21.27 mmol) to give **5** (6.71 g, 85% yield). m. p. 184 °C. MALDI-TOF-MS [M – H][–]: m/e 415.01 (Calcd: 416.35). ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C): δ [ppm] = 10.85 (s, 1H, CONH), 10.41 (s, 1H, OH), 8.46 (s, 1H, ArH), 8.43 (d, 1H, *J* = 8.4 Hz, ArH), 8.32 (d, 1H, *J* = 8.4 Hz, ArH), 7.48 (d, 1H, *J* = 8.8 Hz, ArH), 7.38 (d, 1H, *J* = 2.7 Hz, ArH), 7.17 (dd, 1H, *J*₁ = 8.8 Hz, *J*₂ = 2.9 Hz, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆, 25 °C): 162.57, 155.83, 148.96, 144.62, 137.79, 133.74, 128.82, 127.18 (q, ³*J*_{C-F} = 5 Hz), 126.07, 121.89 (q, ¹*J*_{C-F} = 272 Hz), 121.63, 121.76 (q, ²*J*_{C-F} = 34 Hz), 121.03, 110.98. Anal. Calcd for C₁₄H₈F₃N₃O₆: C, 45.30; H, 2.17; F, 15.35; N, 11.32; O, 25.86. Found: C, 45.44; H, 2.06; N, 9.89.

Synthesis of poly(aryl ether amide) (PAEA-1). A mixture of **5** (2 g, 5.39 mmol), potassium carbonate (1.27 g, 9.16 mmol), anhydrous DMSO (8.0 mL), and benzene (8.0 mL, for the azeotropic distillation of water) was mechanically stirred at 90 °C for 4 h under a nitrogen atmosphere. The temperature was then raised to 120 °C, and stirring was continued for an additional 10 h. The reaction mixture was cooled to room temperature and precipitated into water acidified by acetic acid (0.5 mL). The polymer was collected by filtration and washed several times with water and methanol. Further purification was carried out by dissolving the polymer in tetrahydrofuran (THF), and then reprecipitating it into a methanol/water mixture. The obtained polymer was dried in a vacuum oven at 100 °C (1.57 g, 90% yield). ¹H NMR (400 MHz, THF-*d*₈, 25 °C) : δ [ppm] = 10.87 (s, 1H, CONH), 8.77 (d, 1H, *J* = 9.2 Hz, ArH), 8.44 (s, 1H, ArH), 8.24 (d, 1H, *J* = 8.7 Hz, ArH), 8.06 (d, 1H, *J* = 2.8 Hz, ArH), 7.64 (dd, 1H, *J*₁ = 9.1 Hz, *J*₂ = 2.8 Hz, ArH), 7.31 (d, 1H, *J* = 8.7 Hz, ArH); ¹³C NMR (100 MHz, THF-*d*₈, 25 °C) : 164.01, 158.74, 151.78, 140.50, 134.00, 132.09, 130.56, 128.23 (q, ³*J*_{C-F} = 5 Hz), 127.72, 126.32, 124.05 (q, ¹*J*_{C-F} = 271 Hz), 121.94 (q, ²*J*_{C-F} = 32 Hz), 119.64, 117.76.

Using the same protocol, **PAEA-2** and **PAEA-3** were synthesized at 15% (w/v) and 10% (w/v) of the monomer concentrations in DMSO.

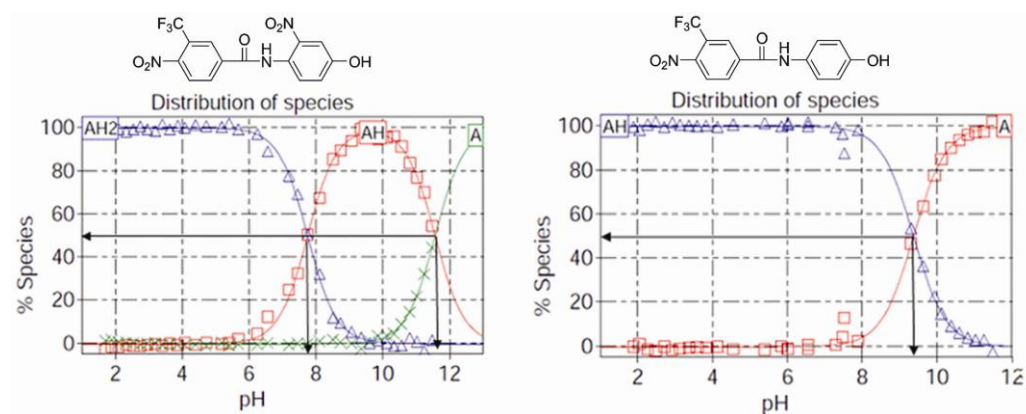


SF1. 2D ¹H-¹H COSY spectrum of PAEA-1.

ST1. The pKa values of 5 and 5' (pKa of hydroxyl/amide group)

	Method	5	5'
pKa	ACD/Labs	7.76/11.06	9.77/12.35
	GLpKa ^a	7.72±0.07 11.60±0.06	9.39±0.05

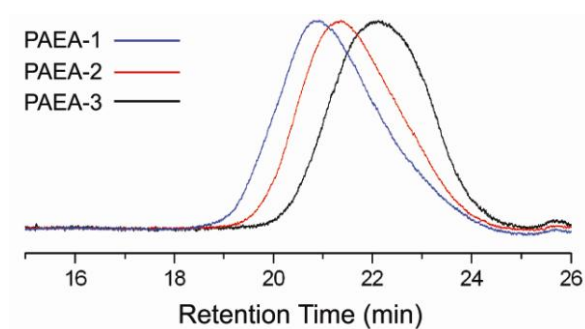
^aThe measurement was carried out from pH 1.8 to 12.2.



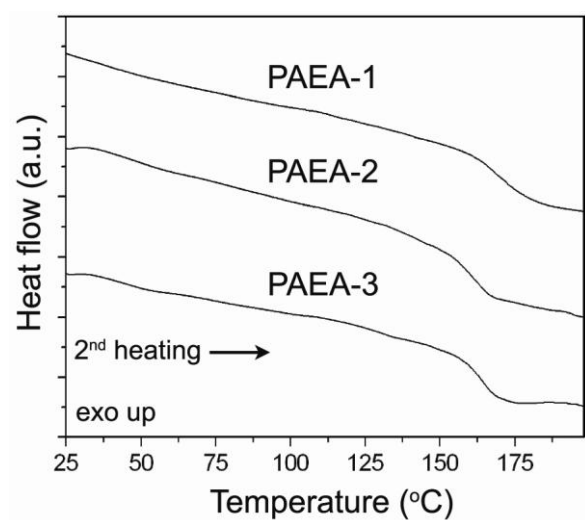
SF2. Titration curve of 5 and 5' from GLpKa.

Entry	M_n^a	PDI ^a	T_g^b (°C)	T_{d5}^c (°C)
PAEA-1	11,400	2.03	162	358
PAEA-2	9,100	1.74	156	363
PAEA-3	6,500	1.52	157	350

^aDetermined by GPC using THF as eluent with polystyrene standard. ^bMeasured by DSC with the heating rate of 20 °C/min under N₂. ^c5 % weight loss temperature measured by TGA with the heating rate of 20 °C/min under N₂.

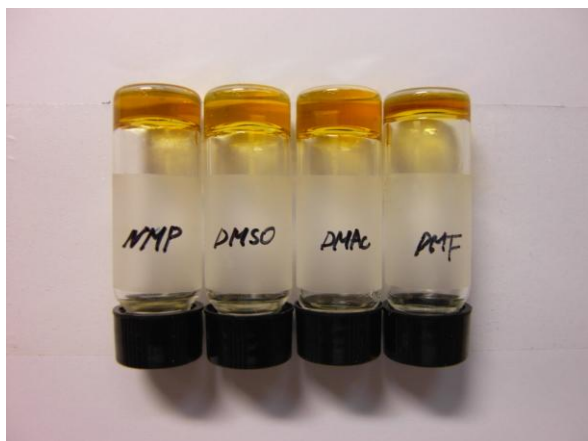


SF3. THF-GPC profiles of **PAEAs**.



SF4. DSC profiles of **PAEAs**.

2. Gelation of PAEA in polar aprotic solvents

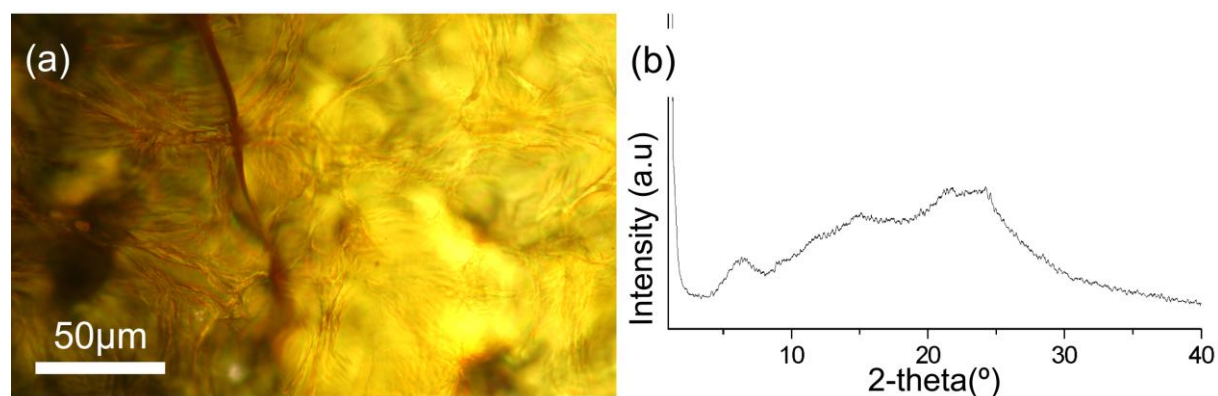


SF5. Gels of **PAEA-1** formed in polar aprotic solvents.

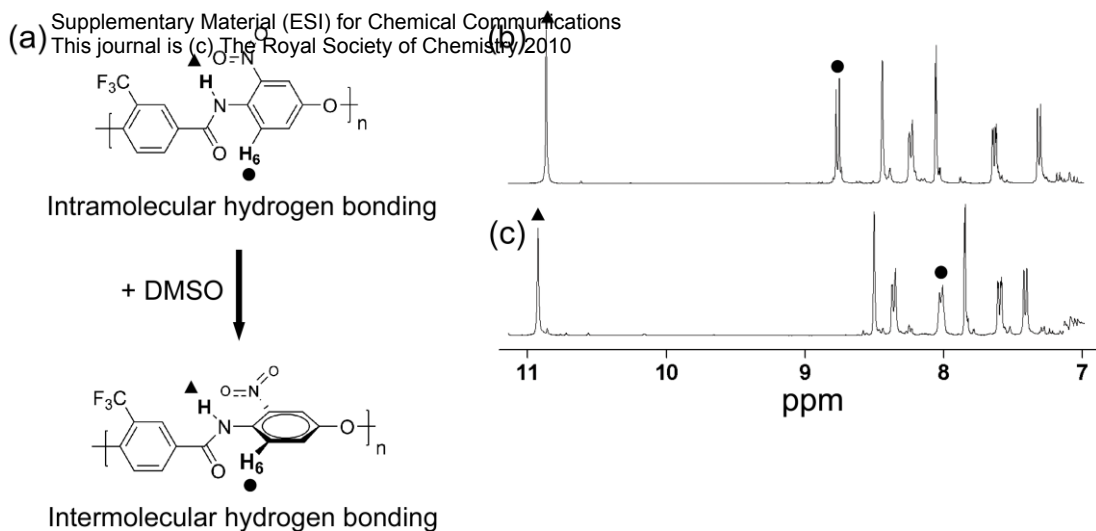
ST3. Gel-to-sol transition temperature of **PAEA** DMF gels.

gel→sol ^a	PAEA-1 (1 wt%)	PAEA-1 (2 wt%)	PAEA-1 (3 wt%)	PAEA-2 (3 wt%)	PAEA-3 (3 wt%)
Temperature (°C)	61	63	70	68	63

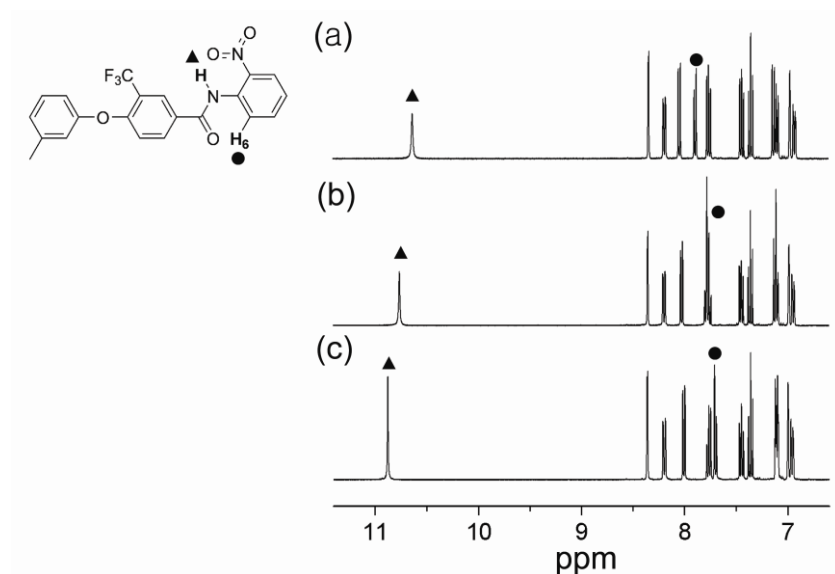
^a Gel-to-sol transition temperatures were measured by vial inverting method.



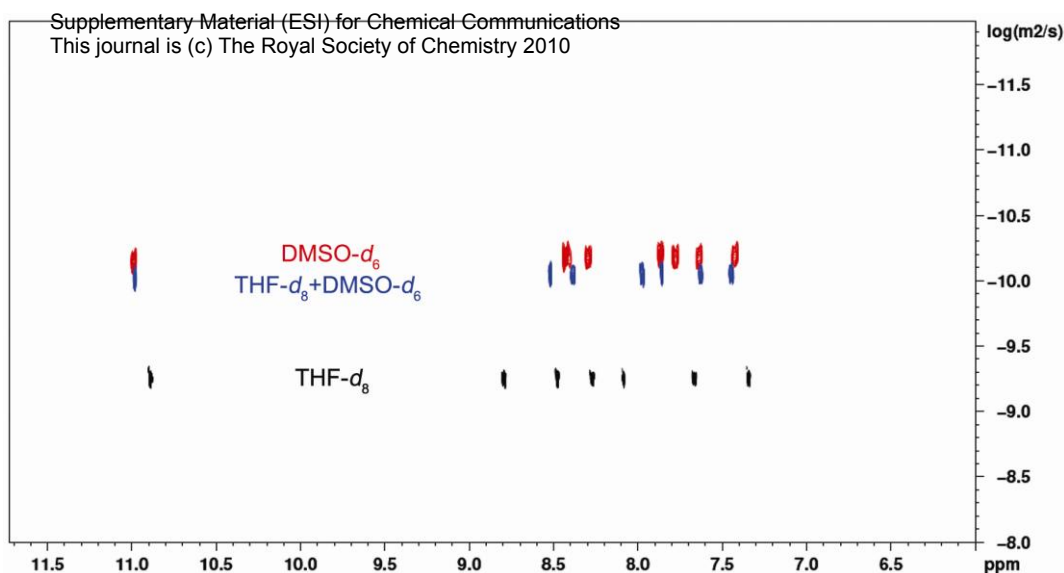
SF6. Self-assembled fibrillar network of **PAEA-1** in DMF gel. (a) OM image. (b) powder XRD pattern of **PAEA-1** from DMF xerogel.



SF7. (a) Conformational change of **PAEA-1** in THF upon addition of DMSO. (b) Solvent-dependent ^1H NMR spectra of **PAEA-1** (400 MHz) in THF- d_8 (c) ^1H NMR spectra of **PAEA-1** in THF- d_8 with few drops of DMSO- d_6 .



SF8. Temperature-dependent ^1H NMR spectra of model compound **4** (DMSO- d_6 , 400 MHz) at (a) 80 °C; (b) 50 °C; (c) 25 °C.

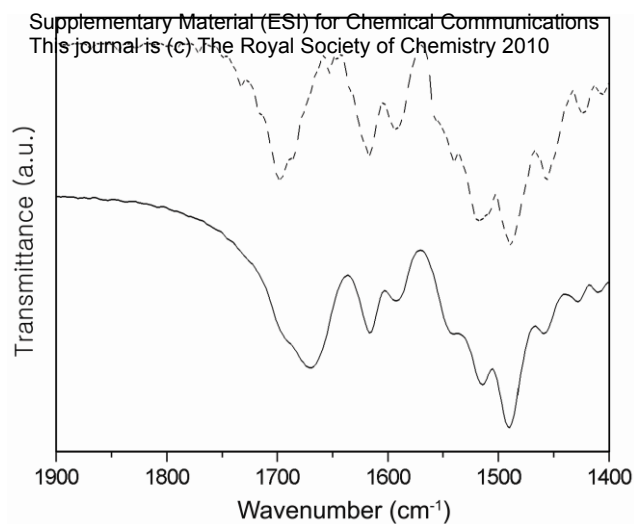


SF9. 2D ¹H DOSY spectrum of **PAEA-2** in different solvents.

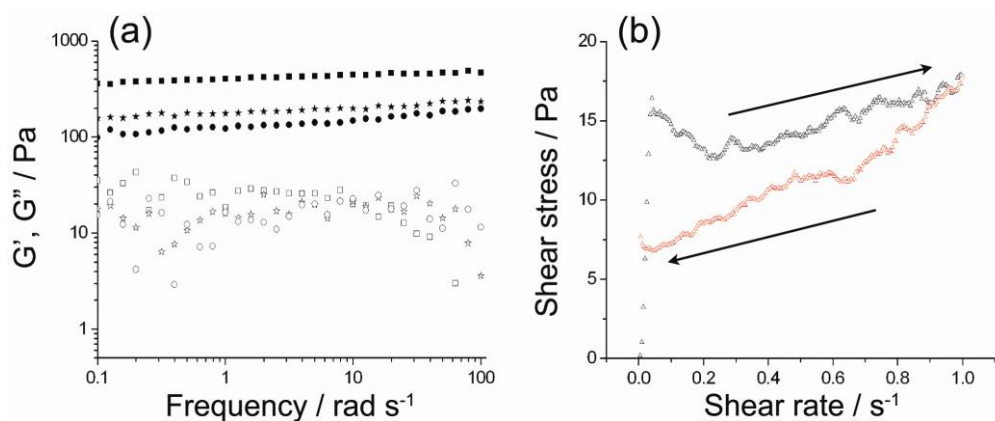
ST4. Diffusion coefficient and relative hydrodynamic radii of **PAEA-2** in different solvents

<i>a</i>	η (cP) ^{<i>b</i>}	D ($\times 10^{-10}$ m ² /s) ^{<i>c</i>}	$R/R_{\text{THF-}d_8}$ ^{<i>d</i>}
THF- <i>d</i> ₈	0.46	5.363	1
THF- <i>d</i> ₈ :DMSO- <i>d</i> ₆ (5:2)	0.69	0.942	3.80
DMSO- <i>d</i> ₆	1.99	0.676	1.83

^{*a*}Attenuated spectra were obtained from 3 wt% samples at 298 K. ^{*b*}The viscosity values of THF and DMSO were used for THF-*d*₈ and DMSO-*d*₆, and the viscosity of mixtures was estimated using the Refutas equation.² ^{*c*}Diffusion coefficients from the ¹H DOSY plots. ^{*d*}Relative hydrodynamic radii was calculated from the Stokes- Einstein equation. ($R \propto 1/\eta D$)



SF10. FT-IR spectral change of the **PAEA-1** prepared from different solutions. (C=O stretching vibration region (amide I, 1650 - 1710 cm^{-1})). dashed line: dried from the THF solution of **PAEA-1**; solid line: dried from the DMF solution of **PAEA-1**.



SF11. (a) Frequency sweep of **PAEA** gels in DMF (20 mg/ml) from 0.1 to 100 rad s^{-1} at 25 °C; Square: gel of **PAEA-1**; Star: **PAEA-2**; Circle: **PAEA-3**; filled: G' (storage modulus); hollow: G'' (loss modulus). (b) Thixotropic loop test of **PAEA-1**. Shear rate was linearly varied during 100 s.

References

- (a) H. S. Lee, S. Y. Kim, *Macromol. Rapid Commun.* 2002, **23**, 665-671; (b) H. Choi, I. S. Chung, K. Hong, C. E. Park, S. Y. Kim, *Polymer* 2008, **49**, 2644-2649.
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