

Synthesis and physical gelation induced by self-assembly of well-defined poly(arylene ether sulfone)s with various numbers of arms

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Supporting Information

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1 Experimental

1.1 Materials

All chemicals were purchased from Sigma-Aldrich. Aniline, 1,4-phenylenediamine, 1,2,4,5-benzenetetramine tetrahydrochloride, 4-fluoro-3-trifluoromethylbenzoyl chloride, 4,4'-difluorodiphenyl sulfone, 18-crown-6 were used without further purification. Triethylamine (TEA), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and benzene were distilled under reduced pressure before use. 1,3,5-Benzenetriamine was prepared according to the literature procedure.¹

1.2 Characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Fourier Transform AC 400 (400 MHz) spectrometer. Chemical shift of NMR was reported in part per million (ppm) using residual proton resonance of solvent as internal reference. Gel permeation chromatography (GPC) traces were obtained with Viscotek T60A equipped with a refractive index (RI) detector and packing column (PLgel 10 μm

MIXED-B) using THF as an eluent at 35 °C. Matrix-assisted laser absorption ionization time-of-flight (MALDI-TOF) mass spectroscopy study was performed on a Voyager-DE-STR using reflector mode for operation. Ionization was performed with a 337 nm pulsed N₂ laser, and samples were prepared with dithranol or 2,5-dihydroxybenzoic acid (DHB) as a matrix. Differential scanning calorimetry (DSC) study was performed on a TA Q100 differential scanning calorimeter. Glass transition temperatures (T_g) of the synthesized compounds were obtained with the DSC instrument at a heating rate of 5 °C min⁻¹ in N₂ (2nd scan). Reduced viscosity measurements were carried out using a Schott micro-Ubbelohde viscometer (type No. 53710, Capillary No. M1). The solutions for the measurement were prepared at least 1 day before the measurement by dissolving the polymer in pure solvent. Before usage, the solution was filtered through a 0.45 μm filter. The relative viscosity (η_{rel}) was calculated by measuring the flow time of pure solvent and the solution in a temperature-controlled bath. Then it was converted to the reduced viscosity (η_{rd}) following the relationship $\eta_{rd} = (\eta_{rel} - 1) C^{-1}$ where C is the concentration of the solution. FT-IR spectra were obtained with a Bruker EQUINOX-55 spectrometer. Field-emission scanning electron microscopy (FE-SEM) study was conducted using a Nova 230 FE-SEM. Samples prepared on silicon wafers were sputtered with gold and investigated. Field-emission transmission electron microscopy (FE-TEM) study was performed on a Tecnai G2 F30 FE-TEM (300 kV). Specimens were prepared by stamping formvar/carbon-coated copper grid on the top of the diluted gel and investigated without staining. Powder X-ray diffraction (XRD) pattern was obtained on a Rigaku D/MAX III diffractometer with sampling width of 0.01 ° and sampling rate of 0.5 °/min, using CuK_α (λ = 0.1541 nm) as a light source.

1.3 Synthesis

4-Fluoro-3-trifluoromethylbenzamidobenzene (1-arm initiator, 1A). Aniline (0.27 ml, 3.00 mmol) and TEA (0.42 ml, 3.00 mmol) in NMP (10 mL) were stirred in one-neck round bottomed flask. 4-Fluoro-3-trifluoromethylbenzoylchloride (0.46 ml, 3.00 mmol) was dissolved in NMP (5 mL) and slowly added to the flask at room temperature. After 24 h, the reaction mixture was poured into distilled

water. The solid was filtered off and dried *in vacuo* at 60 °C for overnight. The solid was purified by recrystallization from toluene to yield white needle-like crystals (0.636 g, 74.9%). mp 161 °C. ESI-MASS: 284.08 for $[M+H]^+$ (Calcd: 284.23). δ_H (400 MHz; DMSO- d_6 ; Me₄Si) 10.44 (1H, s, NH), 8.34 (2H, m, Ar), 7.75 (2H, d, $J = 8.7$ Hz, Ar), 7.67 (1H, t, $J = 9.7$ Hz, Ar), 7.36 (2H, t, $J = 7.9$ Hz, Ar), 7.12 (1H, t, $J = 7.4$ Hz, Ar). δ_C (100 MHz; DMSO- d_6 ; Me₄Si) 163.01, 160.6 (dd, $J_1 = 256.9$ Hz, $J_2 = 2.1$ Hz), 138.71, 135.01 (d, $J = 9.7$ Hz), 131.71 (d, $J = 3.6$ Hz), 128.63, 126.92 (br), 124.02, 122.37 (q, $J = 270.7$ Hz), 120.54, 117.46 (d, $J = 20.9$ Hz), 116.56 (dq, $J_1 = 32.5$ Hz, $J_2 = 12.8$ Hz). Anal. Calcd for C₁₄H₉F₄NO: C, 59.37; H, 3.20; F, 26.83; N, 4.95; O, 5.65. Found: C, 60.01; H, 3.29; N, 4.95.

1,4-Bis(4-fluoro-3-trifluoromethylbenzamido)benzene (2-arm initiator, 2A). 2A was synthesized from 1,4-phenylenediamine using the same protocol for 1A. The product was purified by recrystallization from a mixture of methanol and toluene to yield white needle-like crystals. mp 279-280 °C. ESI-MASS: 487.07 for $[M-H]^-$ (Calcd: 487.07). δ_H (400 MHz; DMSO- d_6 ; Me₄Si) 10.48 (2H, s, NH), 8.34 (4H, m, Ar), 7.75 (4H, s, Ar), 7.70 (2H, t, $J = 9.6$ Hz, Ar). δ_C (100 MHz; DMSO- d_6 ; Me₄Si) 162.83, 160.55 (d, $J = 256.6$ Hz), 135.02 (d, $J = 9.7$ Hz), 134.81, 131.70 (d, $J = 3.5$ Hz), 126.88 (br), 122.38 (q, $J = 270.5$ Hz), 120.84, 117.52 (d, $J = 20.8$ Hz), 116.76 (dq, $J_1 = 32.4$ Hz, $J_2 = 13.0$ Hz). Anal. Calcd for C₂₂H₁₂F₈N₂O₂: C, 54.11; H, 2.48; F, 31.12; N, 5.74; O, 6.55. Found: C, 54.75; H, 2.48; N, 5.78.

1,3,5-Tris(4-fluoro-3-trifluoromethylbenzamido)benzene (3-arm initiator, 3A). 3A was synthesized from 1,3,5-benzenetriamine using the same protocol for 1A. The product was purified by recrystallization from a mixture of methanol and toluene to yield reddish brown solid. mp 262 °C. MALDI-TOF-MS: 694.24 for $[M+H]^+$ (Calcd: 694.10). δ_H (400 MHz; DMSO- d_6 ; Me₄Si) 10.60 (3H, s, NH), 8.38 (6H, m, Ar), 8.11 (3H, s, Ar), 7.66 (3H, t, $J = 9.6$ Hz, Ar). δ_C (100 MHz; DMSO- d_6 ; Me₄Si) 163.22, 160.72 (d, $J = 258.8$ Hz), 139.11, 135.21 (d, $J = 9.7$ Hz), 131.65 (d, $J = 3.4$ Hz), 127.07 (br), 122.43 (q, $J = 270.5$ Hz), 117.45 (d, $J = 20.8$ Hz), 116.58 (dq, $J_1 = 32.4$ Hz, $J_2 = 12.6$ Hz). Anal. Calcd for C₃₀H₁₅F₁₂N₃O₃: C, 51.96; H, 2.18; F, 32.88; N, 6.06; O, 6.92. Found: C, 52.30; H, 2.23; N, 6.72.

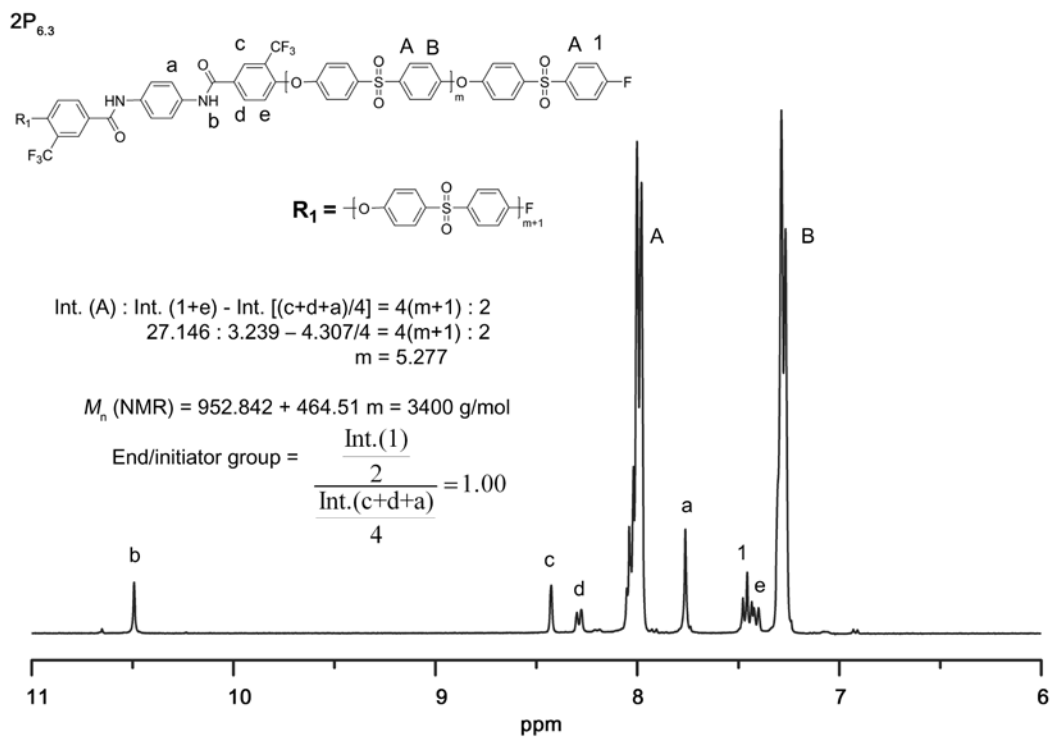
1,2,4,5-Tetrakis(4-fluoro-3-trifluoromethylbenzamido)benzene (4-arm initiator, 4A). 4A was

synthesized from 1,2,4,5-benzenetetramine tetrahydrochloride using the similar protocol for **1A**, and also the procedure was reported.² The reaction mixture was heated to 80 °C and stirred for 24 h. After work-up procedures, the product was purified by recrystallization from a mixture of *N,N*-dimethylformamide (DMF) and toluene to yield yellowish white solid. MALDI-TOF-MS: 897.48 for [M-H]⁻ (Calcd: 897.10). δ_{H} (400 MHz; DMSO-*d*₆; Me₄Si) 10.33 (4H, s, NH), 8.33 (8H, m, Ar), 8.02 (4H, s, Ar), 7.67 (4H, t, *J* = 9.5 Hz, Ar). δ_{C} (100 MHz; DMSO-*d*₆; Me₄Si) 163.34, 160.63 (d, *J* = 257.0 Hz), 135.16 (d, *J* = 9.5 Hz), 131.35 (d, *J* = 3.1 Hz), 128.82, 127.08 (br), 123.07, 122.29 (q, *J* = 270.3 Hz), 117.52 (d, *J* = 20.7 Hz), 116.43 (dq, *J*₁ = 32.8 Hz, *J*₂ = 12.9 Hz). Anal. Calcd for C₃₈H₁₈F₁₆N₄O₄: C, 50.79; H, 2.02; F, 33.83; N, 6.24; O, 7.12. Found: C, 50.87; H, 2.01; N, 6.23.

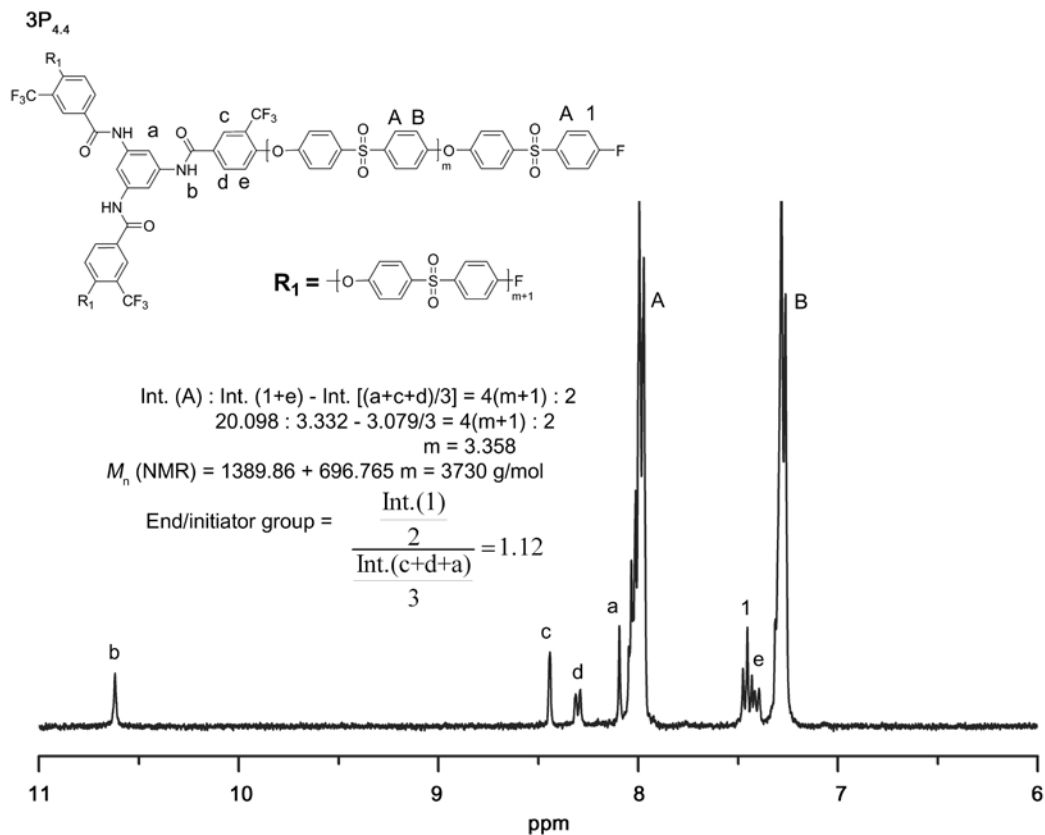
4-Fluoro-4'-hydroxydiphenyl sulfone potassium salt (1). 4-Fluoro-4'-hydroxydiphenyl sulfone potassium salt was prepared according to the literature procedure.² To a mixture of 4,4'-difluorodiphenyl sulfone (12.9 g, 50.7 mmol) and DMSO (35 mL) was added slowly with stirring aqueous solution (15 mL) of potassium hydroxide (11.3 g, 201 mmol). Then the solution was heated to 40 °C and stirred for 10 h under N₂. The reaction mixture was cooled to room temperature and then poured into water. Unreacted 4,4'-difluorodiphenyl sulfone was removed by filtration and the solution was acidified with concentrated hydrochloric acid to precipitate a white powder. This solid, 4-fluoro-4'-hydroxydiphenyl sulfone, was filtered off and dried. Then it was dissolved in methanol, and potassium hydroxide (0.99 eq to 4-fluoro-4'-hydroxydiphenyl sulfone) was added. The mixture was stirred at room temperature until it became homogeneous. After evaporation of methanol, plate-like product was filtered and dried *in vacuo* at 60 °C for overnight. The solid was purified by recrystallization from a mixture of methanol and toluene to yield white needle-like crystals (4.30 g, 53.6%). mp of acidified product: 156 °C. ESI-MS of acidified product: 275.02 for [M+Na]⁺ (Calcd: 275.02). δ_{H} (400 MHz; DMSO-*d*₆; Me₄Si) 7.78 (2H, m, Ar), 7.31 (2H, t, *J* = 8.9 Hz, Ar), 7.20 (2H, d, *J* = 7.2 Hz, Ar), 6.00 (2H, d, *J* = 7.1 Hz, Ar). δ_{C} (100 MHz; DMSO-*d*₆; Me₄Si) 177.10, 163.37 (d, *J* = 248.0 Hz), 142.26 (d, *J* = 3.0 Hz), 129.64, 128.60 (d, *J* = 9.2 Hz), 119.43, 116.03 (d, *J* = 22.2 Hz), 112.77. Anal. Calcd for C₁₂H₈FKO₃S: C, 49.64; H, 2.78; F, 6.54; K, 13.47; O, 16.53; S, 11.04. Found: C, 47.86; H, 3.48; S, 10.84.

Polymerization. Polymerization was conducted in a 50 mL three-necked round bottomed flask equipped with a nitrogen inlet, a Dean-Stark trap, and a reflux condenser. The flask was charged with 4-fluoro-4'-hydroxydiphenyl sulfone potassium salt (**1**), initiator (**1A-4A**), 18-crown-6 (1 eq to the monomer), DMSO (5 wt% to monomer contents), and benzene. The reaction mixture was heated to 80 °C and the water was removed azeotropically with benzene through Dean-stark trap for 2 h. Then, the temperature was raised to 100 °C and the mixture was allowed to polymerize. The conversion of the monomer was investigated by measuring crude ¹H NMR of the polymerization mixture which was carefully extracted via syringe under dry argon atmosphere at a certain time interval. After the polymerization was complete, the mixture was poured into an excess of methanol containing acetic acid and stirred. The precipitated polymer was collected by filtration, and washed with distilled water and methanol. The polymer was dried *in vacuo* at 60 °C for overnight.

(a)



(b)



(c)

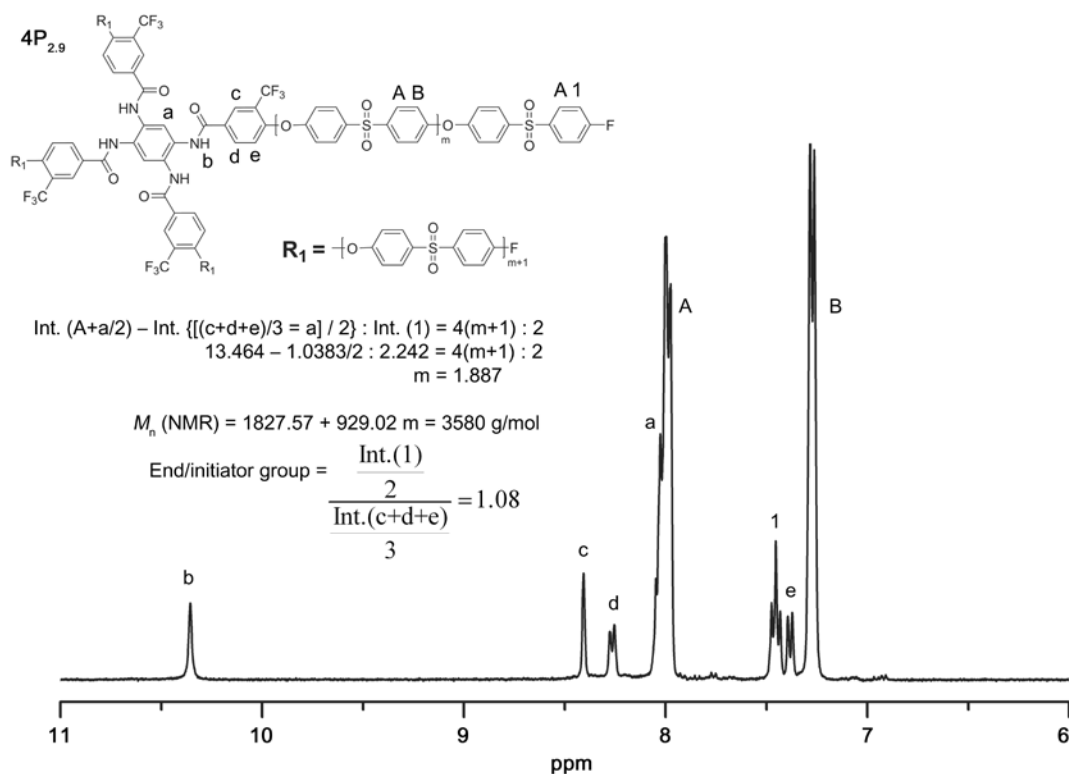


Fig. S1 ^1H NMR spectra of (a) $2P_{6.3}$, (c) $3P_{4.4}$, and (c) $4P_{2.9}$ ($\text{DMSO-}d_6$, 400 MHz).

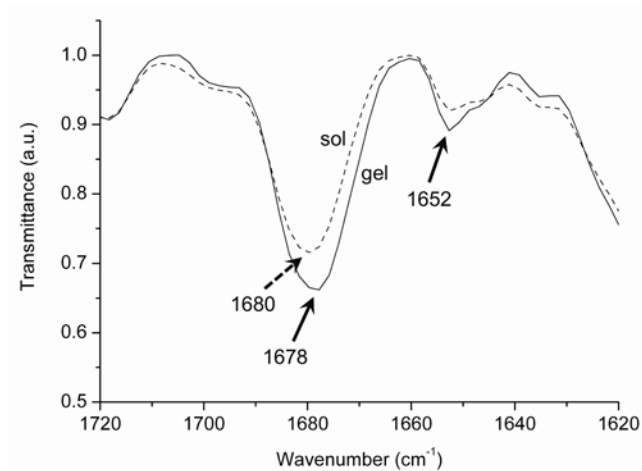


Fig. S2 FT-IR spectra of the sol (dashed line) and gel (solid line) state of $3P_{5.3}$ (10 g L^{-1} , THF).

References

1. M. J. Jeong, J. H. Park, C. J. Lee and J. Y. Chang, *Org. Lett.*, 2006, **8**, 2221-2224.
2. J. Park, M. Moon, M. Seo, H. Choi and S. Y. Kim, *Macromolecules*, 2010, **43**, 8304-8313.