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Rational controlled morphological transitions in the self-assembled multi-headed giant surfactants in solution

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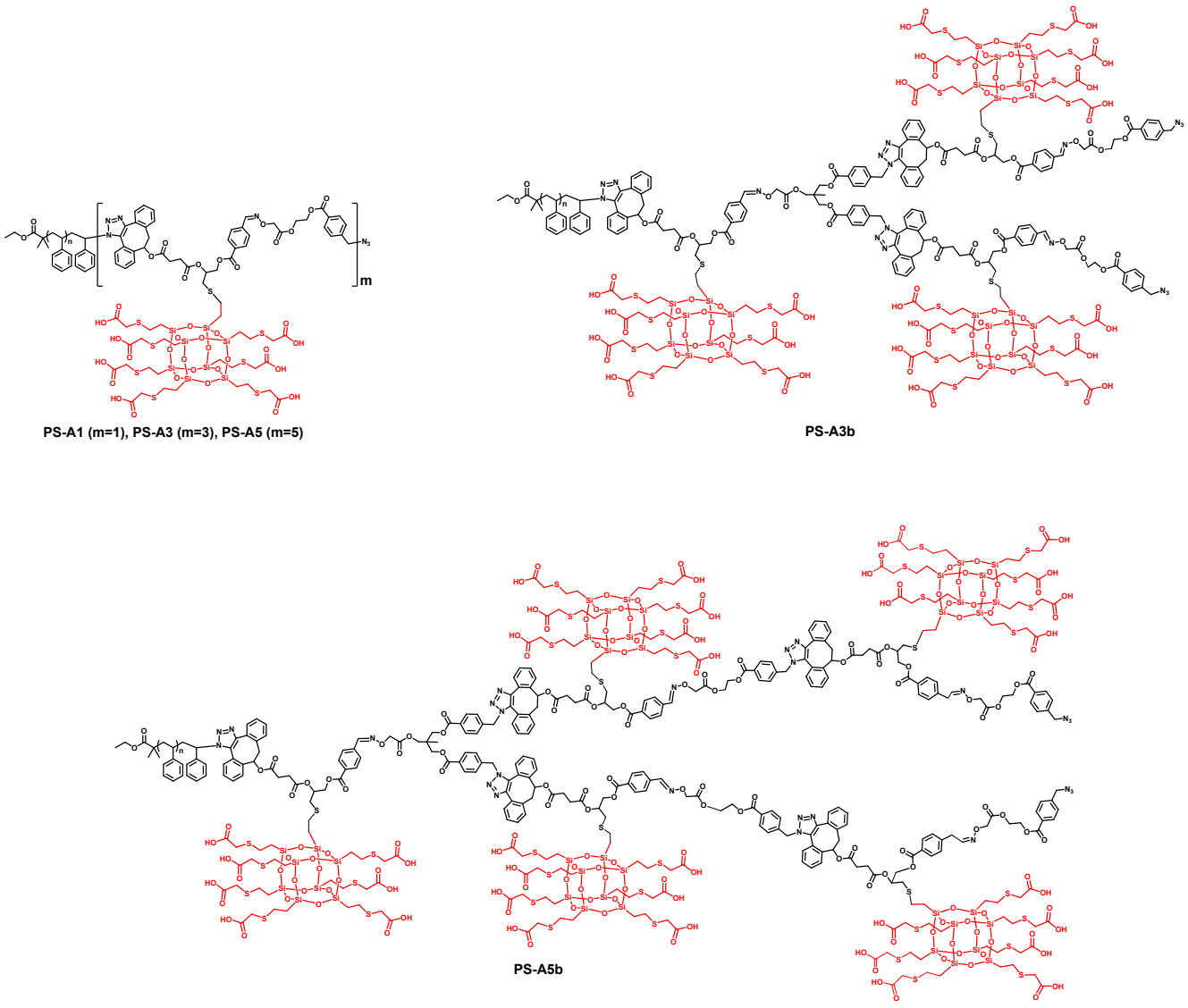
This file includes:

Table S2. Summary of the light scattering results of the concentration of 0.05 mg/mL **PS-A1**, **PS-A3**, **PS-A3b**, **PS-A5** and **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

Table S3. Summary of the light scattering results of the concentration of 0.5 mg/mL **PS-A1**, **PS-A3**, **PS-A3b**, **PS-A5** and **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

Chemical and solvents:

All chemicals and solvents were used as received from Sigma-Aldrich, Acros Organic, or Fisher Scientific. The PS-vinyl POSS precursor were prepared based on our previous report,[21] which together with 2 eq. of thiol ligands mercaptoacetic acid to vinyl group and 0.03 eq. of photoinitiator Irgacure 2959 were dissolve in THF (5 mL). The solution was illuminated under 365 nm UV light (Rayonet RPR-200 photochemical reactor) for 10 min before precipitated into methanol/water 1:5. The products were collected by filtration. ^{1}H-NMR (Varian Mercury, 500M, in $CDCl_3$) spectra of all five samples are included below (Figures S8-12). The representative peaks from APOSS (~3.2 ppm) increased relative to that of PS (~6.3-7.4 ppm), as more hydrophilic APOSS are incorporated. In addition, the major signals of the pairs of topological isomers are almost identical.



Scheme S1. Chemical structures of various giant surfactants in the main text.

Sample preparation:

For a typical sample preparation with the concentration of 0.15 mg/mL, 0.75 mg sample was dissolved in 5.0 mL DMF and sonicate for 30 min. A certain amount of ultrapure water (0.05 μs/cm from a Millipore filtration system, pH 6-7) was added drop by drop into the solution at the rate of 50 μL/hour. Water was stopped to be added until the water content reached 20 v/v%. Water was added drop by drop to another sets of samples until the water content reached 25 v/v% for examination the SLS intensity change.

Static light scattering (SLS) and Dynamic light scattering (DLS): Experiments were both performed on a commercial Brookhaven laser scattering spectrometer that was equipped with a 637 nm laser. For SLS, the angle from 30° to 120° with an interval of 3° was applied. The radius of gyration (R_g) was directly calculated by the Rayleigh-Gans-Debye equation from the software. For DLS, an intensity-intensity BI-9000AT correlator was used to get the correlation function based on the particle movement. The diffusion coefficient D could be obtained by $\Gamma = Dq^2$, which Γ was calculated by CONTIN method. The hydrodynamic radius (R_h) can be calculated according to the Stokes-Einstein equation: $R_h = k_bT/6\pi\eta D$ in which k_b is the Boltzmann constant and η is the viscosity of the solution.

Transmission electron microscopy (TEM): A JEOL JEM-2000 electron microscope operated at 200 kV was used for obtaining the images. The samples were prepared by dropping 10 μL of solution on a copper grid which was coated with a thin carbon film and dried at room temperature for overnight.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR): A THERMO NICOLET Is-50R FTIR SPECTROMETER equipped with an ATR setup which was specific for solution samples was used to investigate the IR spectrum. 100 μL of the samples were dropped onto the ATR window and tested immediately for 36 times. An average IR spectrum was obtained.

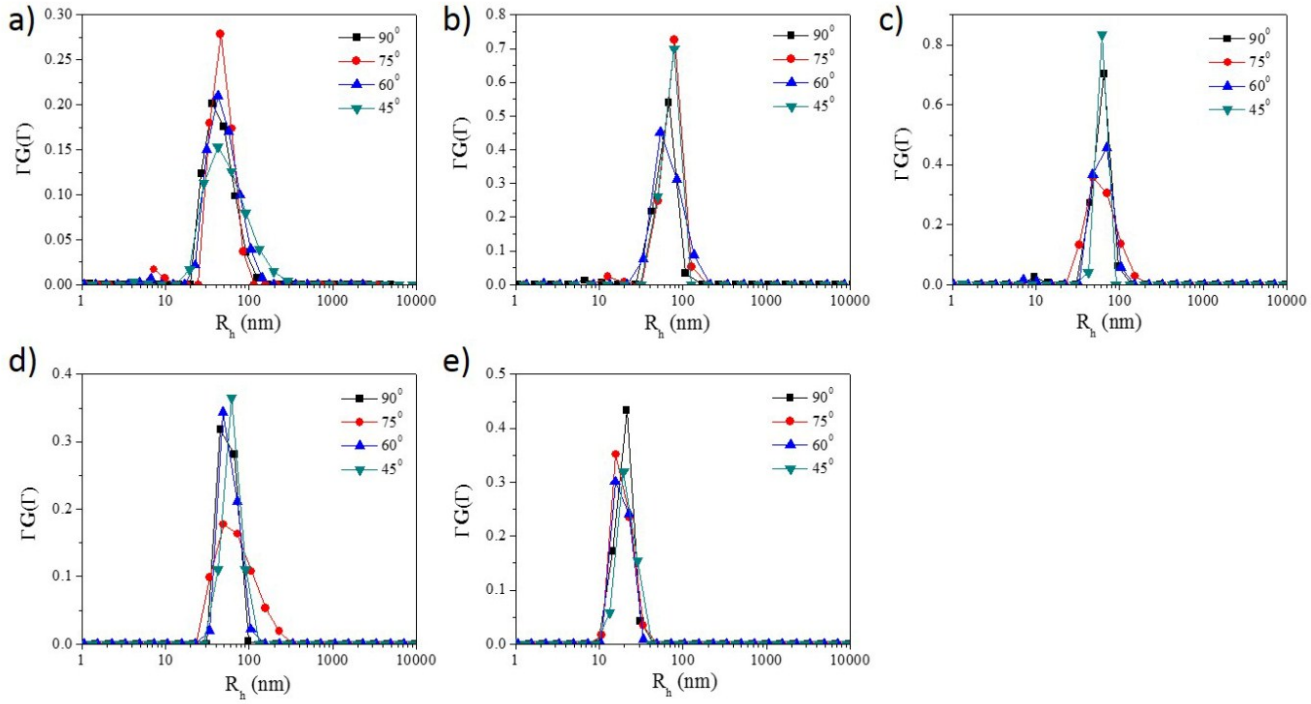


Figure S1. CONTIN analysis of the DLS data of the concentration of 0.15 mg/mL (a) **PS-A1**, (b) **PS-A3**, (c) **PS-A3b**, (d) **PS-A5** and (e) **PS-A5b** in 20 v/v% H2O/DMF solution at different scattering angles.

Table S1. Summary of the light scattering results of the concentration of 0.15 mg/mL **PS-A1**, **PS-A3**, **PS-A3b**, **PS-A5** and **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

	R_h (nm)					R_g [c] (nm)	R_g/R_h	Morphology based on light scattering [d]
	90° [a]	75°	60°	45°	0° [b]			
PS-A1	42	46	46	48	48	46	0.96	Vesicle
PS-A3	53	57	57	61	63	95	1.5	Cylindrical micelle
PS-A3b	57	57	57	62	58	77	1.3	Cylindrical micelle
PS-A5	58	63	58	60	60	87	1.4	Cylindrical micelle
PS-A5b	13	12	13	13	13	9.7	0.75	Spherical micelle

[a] The R_h at 90°, 75°, 60° and 45° are calculated based on CONTIN analysis from DLS correlation function. [b] The R_h at 0° is extrapolated by the R_h at other angles. [c] The R_g is obtained by SLS and calculated directly from the software. [d] The morphology is indicated by: $R_g/R_h \approx 0.77$, spherical micelle; $R_g/R_h \approx 1$, vesicle; $R_g/R_h > 1$, cylindrical micelle.

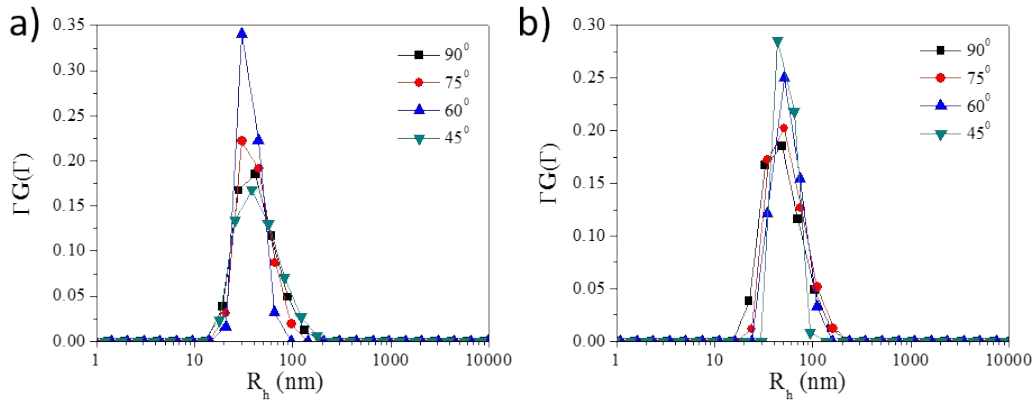


Figure S2. CONTIN analysis of the DLS data of the concentration of 0.05 mg/mL (a) **PS-A1**, (b) **PS-A3** in 20 v/v% H_2O/DMF solution at different scattering angles.

Table S2. Summary of the light scattering results of the concentration of 0.05 mg/mL **PS-A1**, **PS-A3**, **PS-A3b**, **PS-A5** and **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

	R_h (nm)					R_g (nm)	R_g/R_h	Morphology based on light scattering and TEM
	90°	75°	60°	45°	0°			
PS-A1	38	37	37	39	38	61	1.6	Cylindrical micelle
PS-A3	49	51	51	49	50	70	1.4	Cylindrical micelle
PS-A3b	Low Intensity							Spherical micelle
PS-A5	Low Intensity							Spherical micelle
PS-A5b	Low Intensity							Spherical micelle

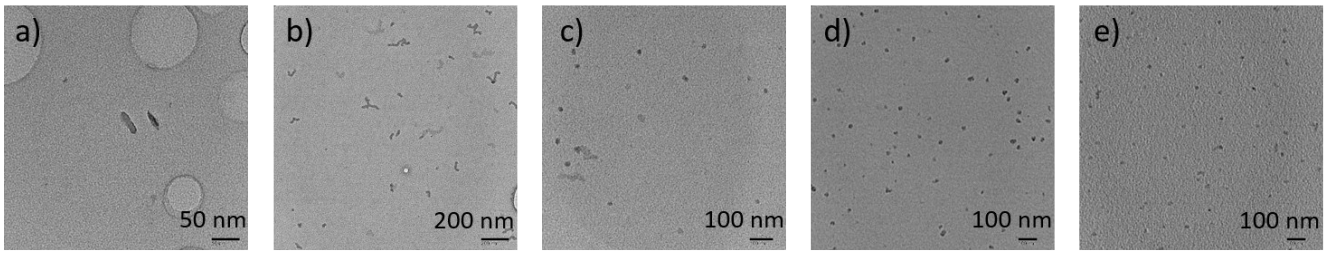


Figure S3. TEM images of the assemblies in the concentration of 0.05 mg/mL (a) **PS-A1**, (b) **PS-A3**, (c) **PS-A3b**, (d) **PS-A5** and (e) **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

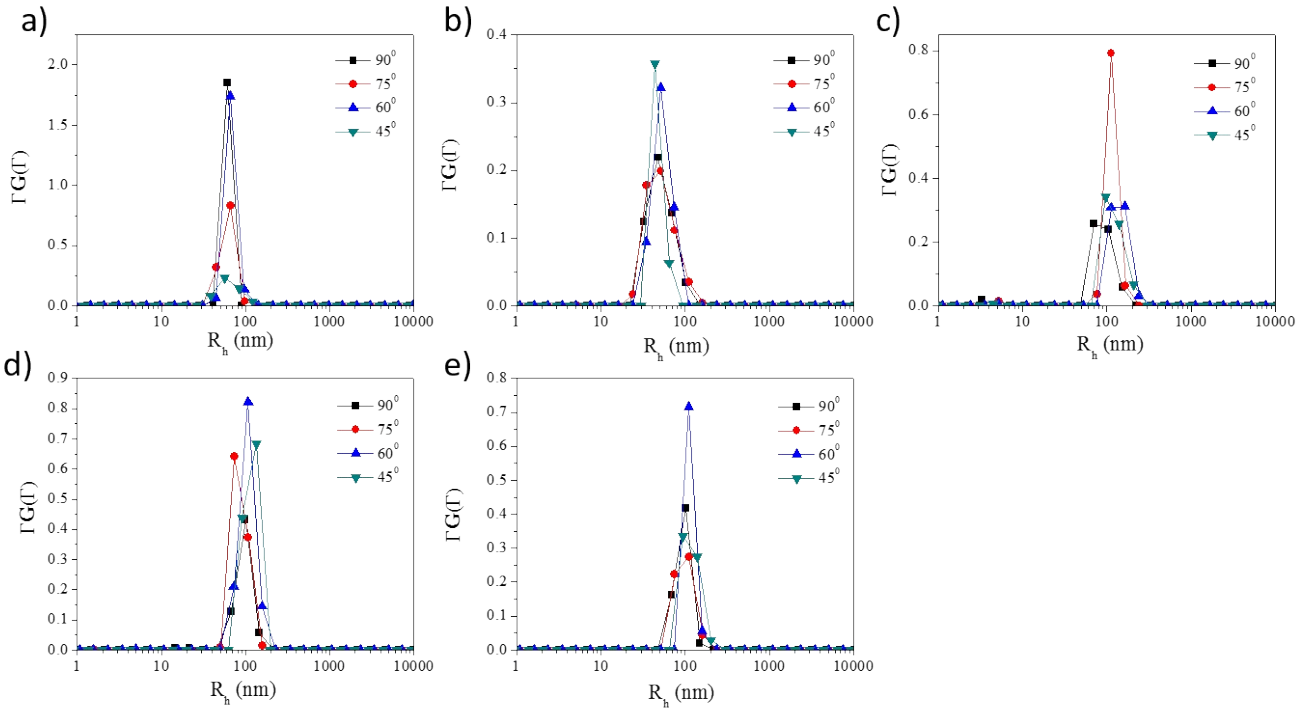


Figure S4. CONTIN analysis of the DLS data of the concentration of 0.5 mg/mL (a) **PS-A1**, (b) **PS-A3**, (c) **PS-A3b**, (d) **PS-A5** and (e) **PS-A5b** in 20 v/v% H_2O/DMF solution at different scattering angles.

Table S3. Summary of the light scattering results of the concentration of 0.5 mg/mL **PS-A1**, **PS-A3**, **PS-A3b**, **PS-A5** and **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

	R_h (nm)					R_g (nm)	R_g/R_h	Morphology based on light scattering results
	90°	75°	60°	45°	0°			
PS-A1	60	62	66	60	63	62	0.98	Vesicle
PS-A3	46	49	51	50	53	53	1.0	Vesicle
PS-A3b	92	114	120	123	130	182	1.4	Cylindrical micelle
PS-A5	89	88	99	106	114	218	1.9	Cylindrical micelle
PS-A5b	86	100	115	107	130	214	1.6	Cylindrical micelle

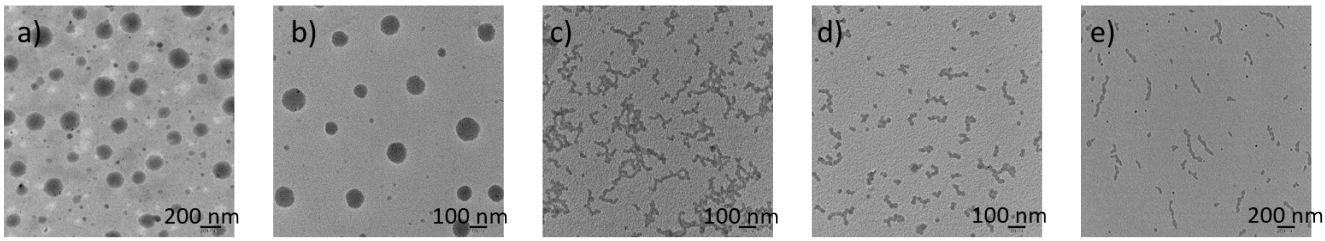


Figure S5. TEM images of the assemblies in the concentration of 0.5 mg/mL (a) **PS-A1**, (b) **PS-A3**, (c) **PS-A3b**, (d) **PS-A5** and (e) **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

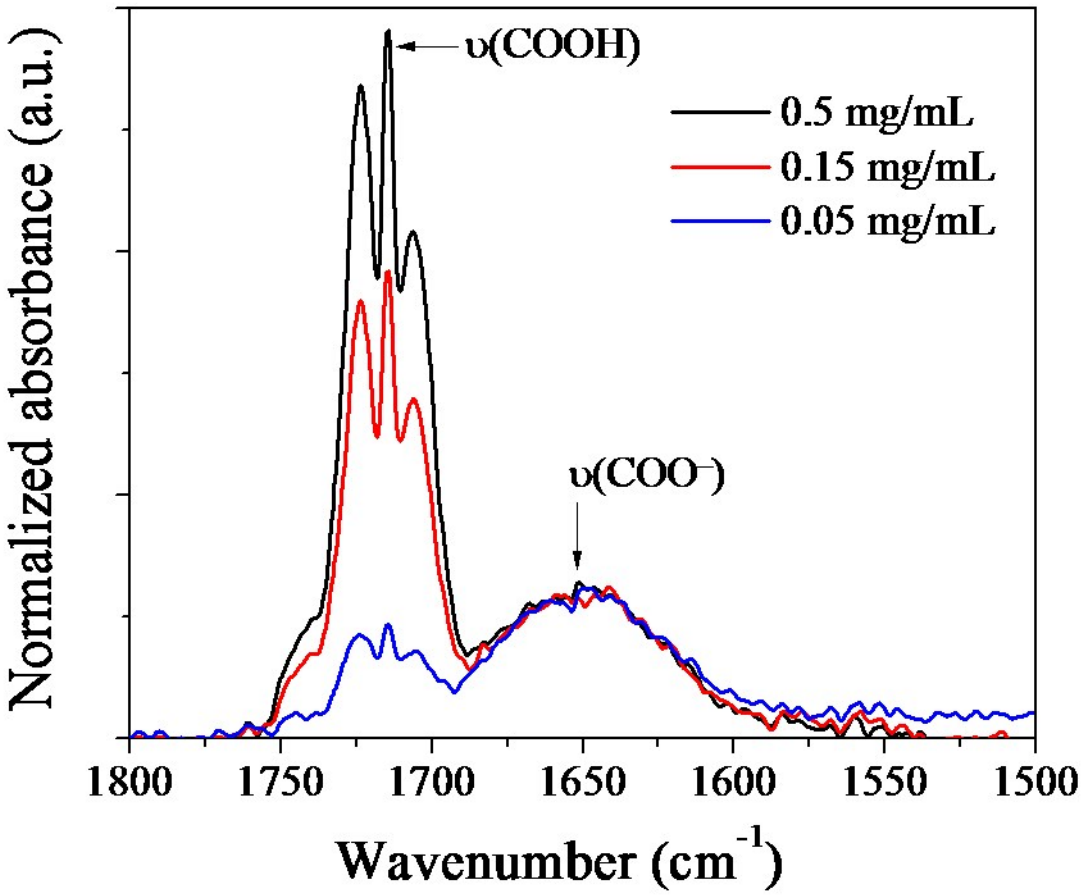


Figure S6. ATR-FTIR spectra of **PS-A1** in 20 v/v% H_2O/DMF mixed solvent with the concentration of 0.05 mg/mL, 0.15 mg/mL and 0.50 mg/mL, respectively.

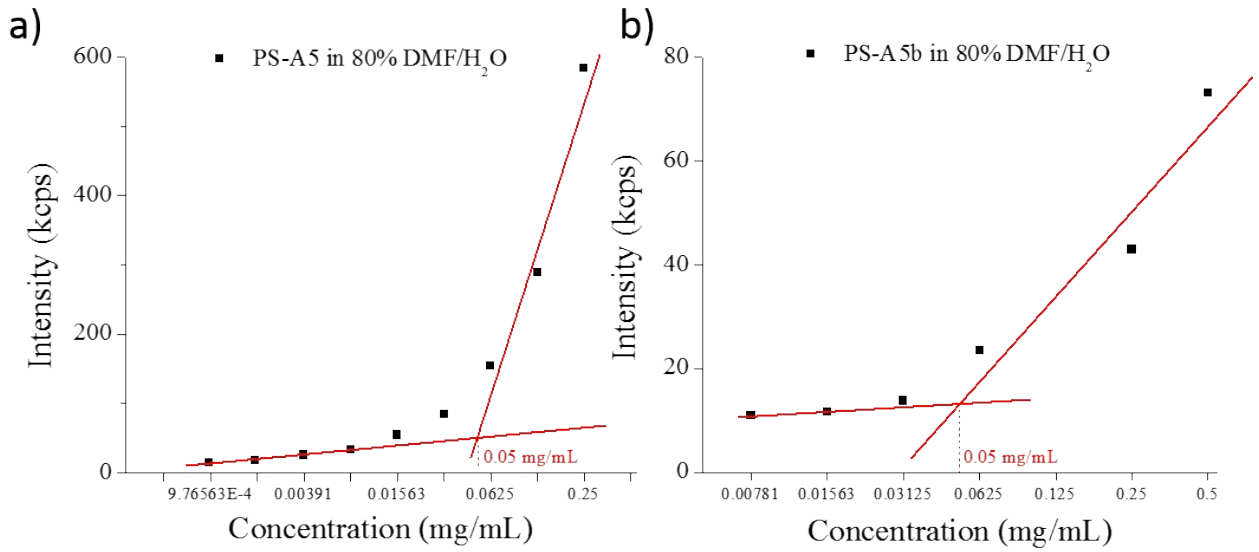


Figure S7. Concentration-dependent scattered intensity of SLS of (a) **PS-A5** and (b) **PS-A5b** in 20 v/v% H_2O/DMF mixed solvent.

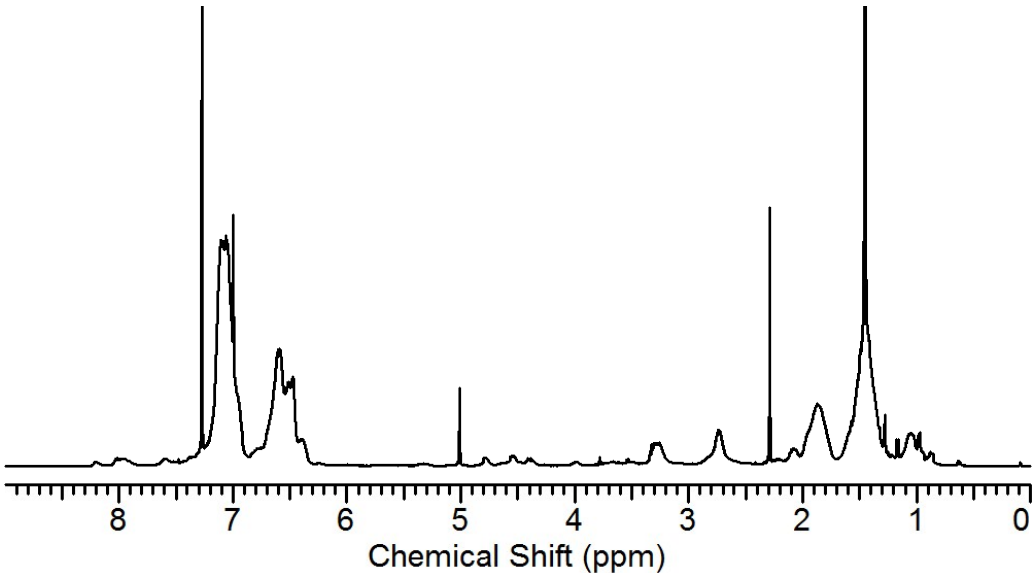


Figure S8. ^{1}H NMR spectrum of **PS-A1**.

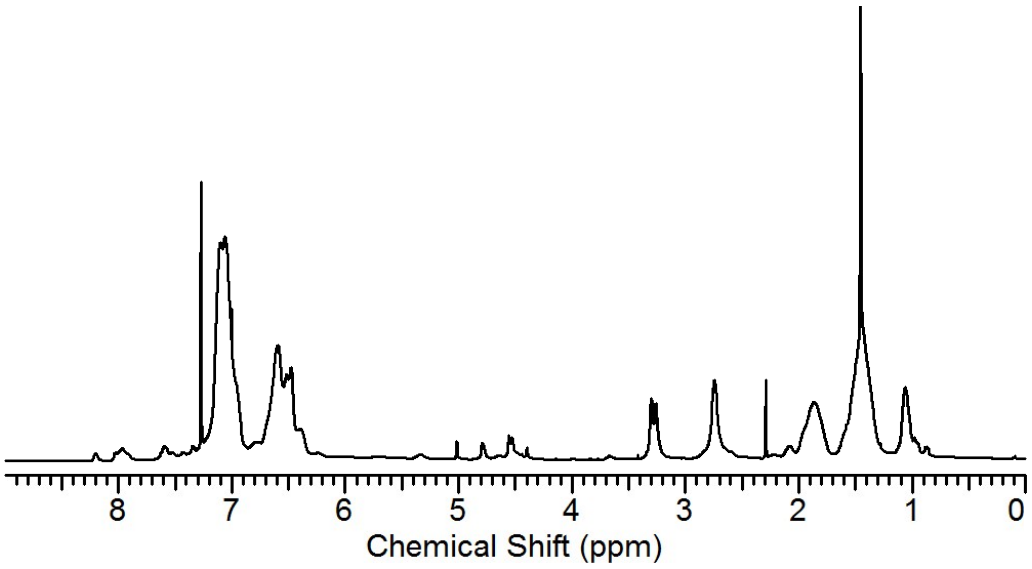


Figure S9. ^{1}H NMR spectrum of **PS-A3**.

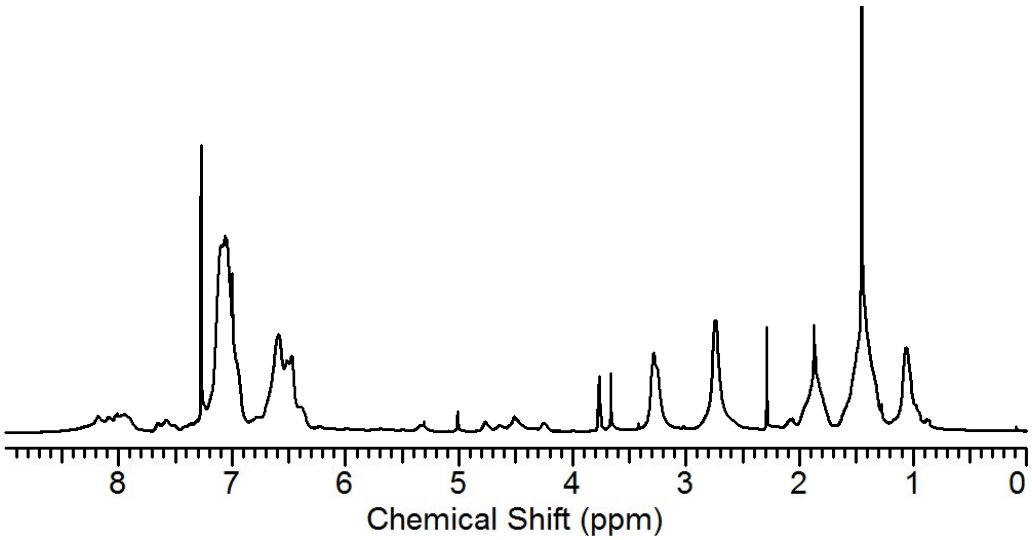


Figure S10. ^{1}H NMR spectrum of **PS-A5**.

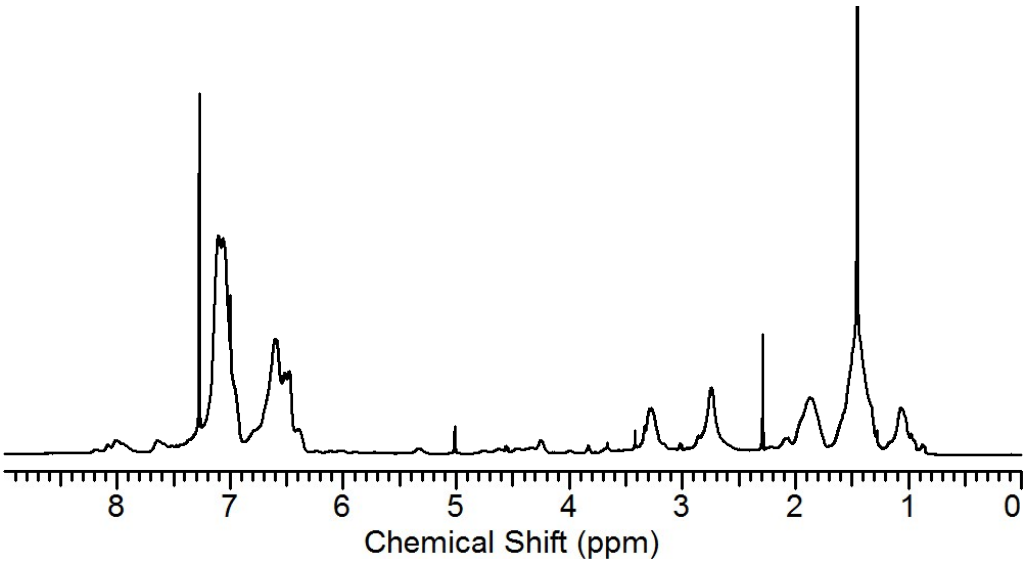


Figure S11. ^{1}H NMR spectrum of **PS-A3b**.

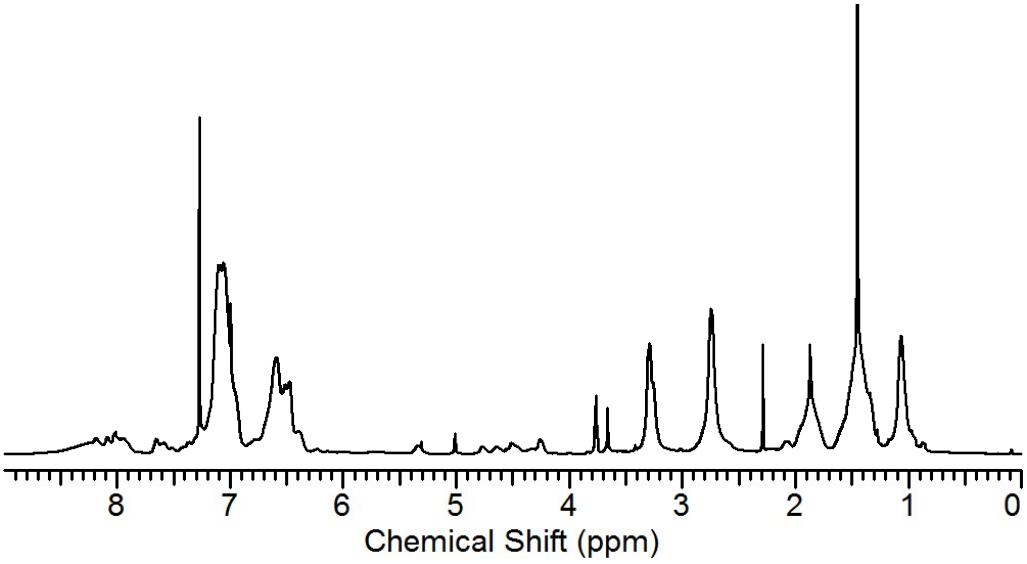


Figure S12. ^{1}H NMR spectrum of **PS-A5b**.