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How does A Tiny Terminal Alkynyl End Group Drive Fully Hydrophilic Homopolymers to Self-Assemble into Multicompartment Vesicles and Flower-Like Complex Particles?

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1. Synthesis of ATRP initiators

Propargyl 2-bromoisobutyrate (**I_1**), propargyl 2-bromo-2-methylpropionamide (**I_2**), and benzyl 2-bromoisobutyrate (**I_5**) were synthesized according to the references, respectively.[S1-S3] The characterization data were listed as following. For **I_1**: ^{1}H NMR ($CDCl_3$, δ, ppm): 4.78 (2H, −C***H_2***−O−); 2.53 (1H, C***H***≡C−); 1.96 (6H, −CO−C(C***H_3***)$_2$−). ^{13}C NMR ($CDCl_3$, δ, ppm): 171.12 (−***C***O−C(CH_3)$_2$−); 77.36 (CH≡***C***−); 75.36 (***C***H≡C−); 54.92 (−***C***H_2−O−); 53.36 (−CO−***C***(CH_3)$_2$−); 30.65 (−CO−C(***C***H_3)$_2$−). FTIR (KBr) 3404 cm^{-1} (ν, ≡C−H); 2120 cm^{-1} (ν, C≡C); 1734 cm^{-1} (ν,−COO−); 541 cm^{-1}(ν, C−Br). For **I_2**: ^{1}H NMR ($CDCl_3$, δ, ppm): 7.25-6.72 (1H, −CH_2−N***H***−); 4.05 (2H,−C***H_2***−NH−); 2.27 (1H, C***H***≡C−); 1.96 (6H, −CO−C(C***H_3***)$_2$−). ^{13}C NMR ($CDCl_3$, δ, ppm): 171.87 (−***C***O−C(CH_3)$_2$−); 76.73 (CH≡***C***−); 72.12 (***C***H≡C−); 61.73 (−CO−***C***(CH_3)$_2$−); 32.60 (−CO−C(***C***H_3)$_2$−); 30.23 (−***C***H_2−NH−). FTIR (KBr) 3401 cm^{-1} (ν, ≡C−H); 2123 cm^{-1} (ν, C≡C); 535 cm^{-1}(ν, C−Br). For **I_5**: ^{1}H NMR ($CDCl_3$, δ, ppm): 7.75-7.25 (5H, Ph(***H***)−); 5.22 (2H, Ph−C***H_2***−O−); 2.20-1.74 (6H, −CO−C(C***H_3***)$_2$−). ^{13}C NMR ($CDCl_3$, δ, ppm): 171.48 (−***C***O−C(CH_3)$_2$−); 135.66, 128.60, 127.9 (Ph−); 65.37 (Ph−***C***H_2−); 55.81 (−CO−***C***(CH_3)$_2$−); 30.80 (−CO−C(***C***H_3)$_2$−). FTIR (KBr): 3233.6 cm^{-1} (ν, Ph（C−H）); 2927 cm^{-1} (ν,−CH_2−); 1734 cm^{-1} (ν,−COO−); 1496.57 cm^{-1} (ν, Ph(C=C)); 596 cm^{-1}(ν, C−Br).

Dipropargyl 2-bromo-2-methylpropionamide (**I_3**) was synthesized by the amidation reaction of Dipropargylamine and 2-Bromo-2-methylpropionyl bromide. Dipropargylamine (744 mg, 8 mmol), 4-dimethylaminopyridine (244 mg, 2 mmol), pyridine (759 mg, 9.6 mmol) was dissolved in dried CH_2Cl_2 (20 ml). After cooling to 0 ^{o}C, 2-bromo-2-methylpropionyl bromide (2.2 g, 9.6 mmol) was added dropwise to the solution. The mixture was then stirred at room temperature for 24 h. After completion of strring, deionized water (100 mL) was added in the mixture. The organic solution was washed with deionized water three times. After the organic solution was dried with anhydrous sodium sulfate, the CH_2Cl_2 was removed by rotary evaporator. The crude product was purified by column chromatography (silica gel size: 70-100 μm，column diameter: 7 cm，column length: 30 cm) using petroleum ether/ethyl acetate (V/V=1/1) as elute, yielding dipropargyl-2-Bromo-2-methylpropionyl bromo amide was yellow liquid. Yields: 66.4%. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.20-4.02 (4H, (CH≡C−C***H_2***)$_2$−N−); 2.35-2.25 (2H, (C***H***≡C−CH_2)$_2$−N−); 2.05-1.95 (6H, −CO−C(C***H_3***)$_2$−). ^{13}C NMR ($CDCl_3$, δ, ppm):

169.36 (−***C***O−C$(CH_3)_2$−); 77.87 ((***C***H≡C−CH_2)$_2$−N−); 72.88 ((CH≡***C***−CH_2)$_2$−N−); 56.24 (−CO−***C***$(CH_3)_2$−); 35.70-38.41 ((CH≡C−***C***H_2)$_2$−N−); 32.47 (−CO−C(***C***H_3)$_2$−). FTIR (KBr): 3211 cm^{-1} (ν, ≡C−H); 2112 cm^{-1} (ν, C≡C); 519 cm^{-1} (ν, C−Br). Electrospray ionization mass spectrometry ($CDCl_3$, m/z): calcd for $C_{10}H_{12}ONBr$: 241.01; found for [M-H]$^+$: 241.13. Elemental analysis (%): calcd for $C_{10}H_{12}ONBr$: C 49.587, H 4.959, N 5.785; found: C 45.256, H 4.526, N 5.368.

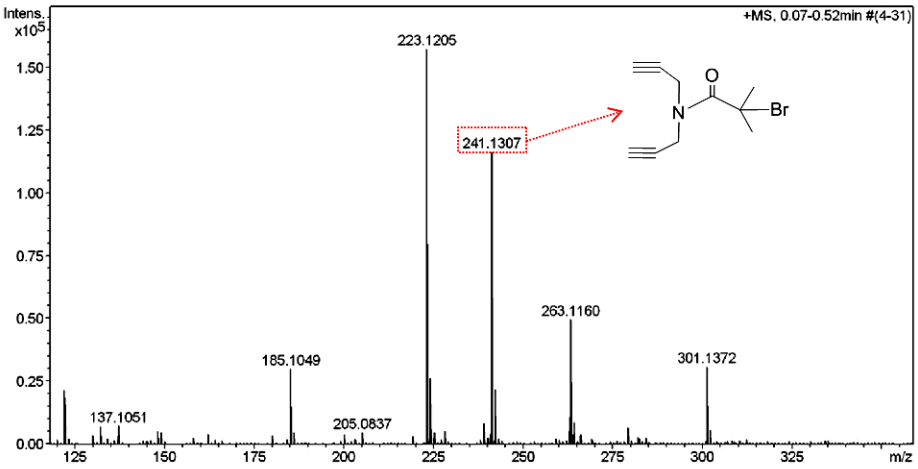


Figure S1 Electrospray ionization mass spectrum of **I_3**.

The $(M-H)^+$ peak was found at m/z = 241.13, which is consistent with the calculated value m/z =241.01.

2. Synthesis of linear homopolymers

*Synthesis of homopolymers **1-3***. The typical procedure was as follows. A Schlenk tube was added with NIPAM (2.83 g, 25 mmol), Me_6TERN (115 mg, 0.5 mmol), CuBr (121 mg, 0.5 mmol), **I_1** (103 mg, 0.5 mmol) and dry DMF (5 ml) under nitrogen. The mixture was then stirred for 5 min and subjected to three freeze-vacuum-thaw cycles, and then the tube was immersed into an oil bath at 60 °C to perform polymerization. After 24 h, the mixture was diluted with THF and passed though a neutral alumina column. The solid was dissolved in distilled water and dialyzed (molecular weight cut off: 3500) for 5 d. Homopolymer **1** was obtained by lyophilization. Yields: 45.1%. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.50-7.04 (−N***H***−CH$(CH_3)_2$−); 4.63 (2H, HC≡C−C***H_2***−); 3.86 (−NH−C***H***$(CH_3)_2$); 1.97 (−C***H***(CO)−CH_2−); 1.45 (−CH(CO)−C***H_2***−); 1.25-0.81 (−NH−CH (C***H_3***)$_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 175.24 (−***C***O−NH−); 165.04 (HC≡C−CH_2−***C***OO−); 43.09 (−NH−***C***H$(CH_3)_2$); 37.06 (−CH(CO)−***C***H_2−); 23.69 (−NH−CH(***C***H_3)$_2$). FTIR (KBr): 3411 cm^{-1} (ν, ≡C−H); 3301 cm^{-1} (ν, N−H); 2124 cm^{-1}

(ν, C≡C); 1710 cm^{-1} (ν, −COO−); 531 cm^{-1} (ν, C−Br). Homopolymers including **2** and **3** were synthesized with the similar procedure except for the ratio of NIPAM to $\mathbf{I_1}$. Their polymerization results were shown in Table S1.

*Synthesis of homopolymers **4**.* The synthesis and purification procedures were similar with homopolymer **1** except that $\mathbf{I_2}$ was used instead of $\mathbf{I_1}$. Yields: 53.1%. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.75-6.89 (−N***H***−CH$(CH_3)_2$); 5.56 (2H, HC≡C−C***H*****$_2$**−); 3.87 (−NH−C***H***$(CH_3)_2$−); 2.18 (***H***C≡C−CH_2−); 1.97 (−C***H***(CO)−CH_2−); 1.46 (−CH(CO)−C***H*****$_2$**−); 1.05 (−NH−CH(C***H*****$_3$**$)_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 174.78 (−***C***O−NH−CH$(CH_3)_2$); 165.04 (CH≡C−CH_2−NH−***C***O−); 82.78 (CH≡***C***−CH_2−); 73.49 (***C***H≡C−CH_2−); 43.10 (−NH−***C***H$(CH_3)_2$); 38.82 (−CH(CO)−***C***H_2−); 35.72 (−NH−CO−C(***C***$H_3)_2$−); 32.05 (−***C***H(CO)−***C***H_2−); 29.92 (CH≡C−***C***H_2−); 23.63 (−CO−NH−CH(***C***$H_3)_2$). FTIR (KBr): 3511 cm^{-1} (ν, ≡C−H); 3295 cm^{-1} (ν, N−H); 2124 cm^{-1} (ν, C≡C); 1710 cm^{-1} (ν,−CONH−); 527 cm^{-1} (ν, C−Br).

*Synthesis of homopolymer **5**.* The synthesis and purification procedures were similar with homopolymer **1** except that $\mathbf{I_3}$ was used instead of $\mathbf{I_1}$. Yields: 40.4%. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.75-7.10 (−N***H***−CH$(CH_3)_2$); 4.08 (4H, (CH≡C−C***H*****$_2$**$)_2$−N−); 3.94 (2H, −CH(CO)−C***H*****$_2$**−Br); 3.92-3.75 (−NH−C***H***$(CH_3)_2$); 2.16 (2H, (C***H***≡C−$CH_2$$)_2$−N−); 2.18-1.75 (−C***H***(CO)−CH_2−); 1.75-1.22 (−CH(CO)−C***H*****$_2$**−); 1.25-0.75 (−NH−CH(C***H*****$_3$**$)_2$); ^{13}C NMR (DMSO-d_6, δ, ppm): 173.16 (−***C***O−NH−CH$(CH_3)_2$); 41.55 (−NH−***C***H$(CH_3)_2$); 36.45 (−CH(CO)−***C***H_2−); 33.90 (−CH(CO) −***C***H_2−Br); 30.47 (−***C***H(CO)−CH_2−); 22.55 (−NH−CH(***C***$H_3)_2$); 20.94 (=N−CO−C(***C***$H_3)_2$−). FTIR (KBr): 3211 cm^{-1} (ν, ≡C−H); 3308 cm^{-1} (ν, N−H); 2112 cm^{-1} (ν, C≡C); 1646 cm^{-1} (ν,−CONH−); 520 cm^{-1} (ν, C−Br).

*Synthesis of homopolymer **7**.* The synthesis and purification procedures were similar with homopolymer **1** except that $\mathbf{I_4}$ was used instead of $\mathbf{I_1}$. Yields: 55.1%. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.35 (−CO−N***H***−CH$(CH_3)_2$); 4.03 (CH_3−C***H*****$_2$**−O−); 3.85 (−NH−C***H***$(CH_3)_2$); 1.99 (−C***H***(CO)−CH_2−); 1.41 (−CH(CO)−C***H*****$_2$**−); 1.17 (−COO−C(C***H*****$_3$**$)_2$−); 1.06 (−NH−CH(C***H*****$_3$**$)_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 173.86 (−***C***O−NH−CH$(CH_3)_2$); 164.03 (CH_3−CH_2−***C***OO−); 42.10 (−NH−***C***H$(CH_3)_2$); 36.19 (−CH(CO)−***C***H_2−); 30.88 (−***C***H(CO)−CH_2−); 25.12 (CH_3−***C***H_2−COO−); 24.54 (***C***H_3−CH_2−COO−); 22.74 (−NH−CH(***C***$H_3)_2$). FTIR (KBr): 3490 cm^{-1}(ν, ≡C−H); 3295 cm^{-1} (ν, N−H); 1698 cm^{-1} (ν,−

COO−); 530 cm^{-1} (ν, C−Br).

*Synthesis of homopolymer **8***. The synthesis and purification procedures were similar with homopolymer **1** except that $\mathbf{I_5}$ was used instead of $\mathbf{I_1}$. Yields: 49.1%. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.36 (5H, Ph(***H***)); 7.65-6.959 (−CO−N***H***−CH$(CH_3)_2$); 5.03(Ph−C***H₂***−O−); 3.84 (−NH−C***H***$(CH_3)_2$); 1.98 (−C***H***(CO)−CH_2−); 1.43 (−CH(CO)−C***H₂***−); 1.05 (−NH−CH(C***H₃***$)_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 173.88 (−***C***O−NH−CH$(CH_3)_2$); 164.13 (Ph−CH_2−***C***OO−); 132.40-125.18 (Ph(***C***)); 66. 37 (Ph−***C***H_2−COO−); 42.18 (−NH−***C***H$(CH_3)_2$); 35. 91 (−CH(CO)−***C***H_2−); 22.80 (−NH−CH(***C***$H_3)_2$). FTIR (KBr): 2933 cm^{-1} (ν,−CH_2−); 1709 cm^{-1} (ν,−COO−); 1497 cm^{-1} (ν, Ph(C=C)); 531 cm^{-1} (ν, C−Br).

*Synthesis of homopolymer **9***. A mixture of $\mathbf{I_1}$ (103 mg, 0.5 mmol), $OEGMA_{475}$ (2.85 g, 6 mmol) and PMDETA (86 mg, 0.5 mmol) in 5 ml H_2O/methanol (1:1, v/v) was bubbled with nitrogen gas for 15 min at 0 °C, CuBr (14 mg, 0.1 mmol) and $CuCl_2$ (54 mg, 0.4 mmol) was then added. The solution was bubbled with nitrogen gas for 30 min at 0 °C and sealed under N_2 atmosphere. The polymerization was conducted at 0 °C for 4 h. It was terminated by exposing to air and diluting with THF. After passing through a neutral alumina column and evaporating most of solvent, the residues were precitated and dried in a vacuum 3 d. Homopolymer **9** was obtained. Yields: 45.1%. ^{1}H NMR (DMSO-d_6, δ, ppm): 4.22 (2H, HC≡C−C***H₂***−); 4.02 (−COO−C***H₂***−CH_2−); 3.59 (−COO−CH_2−C***H₂***−O−); 3.51 (−CH_2−C***H₂***−O−); 3.44 (6H, −COO−C(C***H₃***$)_2$−); 3.32 (−O−C***H₃***); 1.75 (−C***H₂***−C(CH_3)−); 0.98-0.79 (−CH_2−C(C***H₃***)−). ^{13}C NMR (DMSO-d_6, δ, ppm): 177.76 (−***C***OO−CH_2−CH_2−O−); 72.56 (−COO−CH_2−***C***H_2−O−); 71.18 (−O−***C***H_2−CH_2−O−); 69.75 (−COO−***C***H_2−CH_2−O−); 65.34 (−***C***H_2−C(CH_3)−); 59.14 (−O−***C***H_3); 45.32 (−CH_2−C(***C***H_3)−); 17.56 (−COO−C(***C***$H_3)_2$−). FTIR (KBr): 3298 cm^{-1} (ν, ≡C−H); 2870 cm^{-1} (ν, C−O); 1730 cm^{-1} (ν,−COO−); 524 cm^{-1} (ν, C−Br).

*Synthesis of homopolymer **10***. The synthesis and purification procedures were similar with homopolymer **9** except that $\mathbf{I_2}$ was used instead of $\mathbf{I_1}$. Yields: 52.1%. ^{1}H NMR (DMSO-d_6, δ, ppm): 4.24 (2H, HC≡C−C***H₂***−); 4.02 (−COO−C***H₂***−CH_2−); 3.61 (−COO−CH_2−C***H₂***−O−); 3.51 (−CH_2−C***H₂***−O−); 3.44 (−COO−C(C***H₃***$)_2$−); 3.31(−O−C***H₃***); 1.75 (−C***H₂***−C(CH_3)−); 0.95-0.79 (−CH_2−C(C***H₃***)−). ^{13}C NMR (DMSO-d_6, δ, ppm): 177.86 (−***C***OO−CH_2−CH_2−O−); 72.58 (−COO−CH_2−***C***H_2−O−); 71.19 (−O−***C***H_2−CH_2−O−); 69.85 (−COO−***C***H_2−CH_2−O−); 65.44 (−***C***H_2−C(CH_3)−);

59.35 (−O−***C***H_3); 46.02 (−CH_2−C(***C***H_3)−). FTIR (KBr): 3231 cm^{-1} (*ν*, ≡C−H); 2865 cm^{-1} (*ν*, C−O); 1728 cm^{-1} (*ν*,−NHCO−); 530 cm^{-1} (*ν*, C−Br).

*Synthesis of homopolymer **11***. The synthesis and purification procedures were similar with homopolymer **9** except that $\mathbf{I_3}$ was used instead of $\mathbf{I_1}$. Yields: 69.1%. ^{1}H NMR (DMSO-d_6, *δ*, ppm): 5.75 (−C***H₂***C(CH_3)−Br); 4.21 ((HC≡C)$_2$−C***H₂***−NH−); 4.02 (−COO−C***H₂***−CH_2−O−); 3.74 (−COO−CH_2−C***H₂***−O−); 3.51 (−CH_2−C***H₂***−O−); 3.42 (−COO−C(C***H₃***)$_2$−); 3.24 (−O−C***H₃***); 2.32 ((***H***C≡C−CH_2)$_2$−NH−); 2.25-1.4 (−C***H₂***−C(CH_3)−); 1.2-0.6 (−CH_2−C(C***H₃***)−). ^{13}C NMR (DMSO-d_6, *δ*, ppm): 177.09 (−***C***OO−CH_2−CH_2−O−); 71.41 (−COO−CH_2−***C***H_2−O−); 69.78 (−O−***C***H_2−CH_2−O−); 67.84 (−COO−***C***H_2−CH_2−O−); 63.92 (−***C***H_2−C(CH_3)−); 58.12 (−O−***C***H_3); 44.21 (−CH_2−C(***C***H_3)−); 16.40 (−COO−C(***C***H_3)$_2$−). FTIR (KBr): 3229 cm^{-1} (*ν*, ≡C−H); 2871 cm^{-1} (*ν*, C−O); 1728 cm^{-1} (*ν*,−NHCO−); 517 cm^{-1} (*ν*, C−Br).

3. Synthesis of long chain hyperbranched homopolymer

*Synthesis of **5'***. To obtain **6**, **5'** was first synthesized by the azidation of **5**. The typical procedure was as follows. **5** (250 mg, 0.037 mmol), NaN_3 (24 mg, 0.37 mmol) was mixed with DMF (2 ml). The mixture was stirred at 50 °C for 48 h. After cooling to room temperature, the mixture was dialyzed (molecular weight cut off: 3500) for 3 d. Homopolymer **5'** was obtained by lyophilization. ^{1}H NMR (DMSO-d_6, *δ*, ppm): 7.75-7.10 (−N***H***−CH(CH_3)$_2$−); 4.08 (4H, (CH≡C−C***H₂***)$_2$−N−); 3.92-3.75 (−NH−C***H***(CH_3)$_2$); 3.85 (2H, −CH(CO)−C***H₂***−N_3); 2.21 (2H, (C***H***≡C−CH_2)$_2$−N−); 2.18-1.75 (−C***H***−CH_2−); 2.14 ((C***H***≡C—CH_2)$_2$—N—); 1.75-1.22 (−CH(CO)−C***H₂***−); 1.25-0.75 (−NH−CH(C***H₃***)$_2$). ^{13}C NMR (DMSO-d_6, *δ*, ppm) 173.10 (−***C***O−NH−); 41.50 (−NH−***C***H(CH_3)$_2$−); 36.20 (−***C***H(CO)−CH_2−); 22.24 (−NH−CH(***C***H_3)$_2$). FTIR (KBr): 3211 cm^{-1} (*ν*, ≡C−H); 3308 cm^{-1} (*ν*, N−H); 2112 cm^{-1} (*ν*, C≡C); 1646 cm^{-1} (*ν*,−CO−NH−).

*Synthesis of LCHBH **6***. **5'** (188 mg, 0.029 mmol), CuBr (6.26 mg, 0.043 mmol), PMDETA (7.6 mg, 0.043 mmol), and DMF (1.5 ml) was added into a Schlenk tube. The mixture was then stirred for 5 min and subjected to three freeze-vacuum-thaw cycles, and then the tube was immersed into an oil bath at 100 °C. After 24h, the mixture was diluted with THF and passed though a neutral alumina column. The solid was dissolved in distilled water and dialyzed (molecular weight cut off: 8000~14000) for 5 days.

Homopolymer **6** was obtained by lyophilization. Yields: 65.5%. ^{1}H NMR (DMSO-d_6, δ, ppm): 7.96 (methine proton in 1,2,3-triazole ring); 7.22 (—N***H***—CH$(CH_3)_2$—); 5.35 (—C***H*****$_2$**—, protons in 1,2,3-triazole ring); 3.84 (—NH—C***H***$(CH_3)_2$); 2.14 ((C***H***≡C—$CH_2)_2$—N—); 1.98 (—C***H***(CO)—CH_2—); 1.46 (—CH(CO)—C***H*****$_2$**—); 1.05 (—NH—CH(C***H*****$_3$**$)_2$). ^{13}C NMR (DMSO-d_6, δ, ppm): 173.41 (−***C***O−NH−CH$(CH_3)_2$); 132.1, 127.06 (***C***=***C***, carbons in the 1,2,3-triazole ring); 41.65 (−NH−***C***H$(CH_3)_2$); 36.49 (−CH(CO)−***C***H_2−); 31.50 (−***C***H_2−, carbon attached to 1,2,3-the triazole ring); 28.98 (−***C***H(CO)−CH_2−); 22.48 (−NH−CH(***C***$H_3)_2$). FTIR (KBr): 3308 cm^{-1} (ν, N—H); 3211 cm^{-1}(ν, ≡C—H); 2112 cm^{-1} (ν, C≡C); 1646 cm^{-1} (ν,—NHCO—).

4. Characterization of homopolymers

Table S1. Molecular structure parameters of homopolymers

Code	*Sample*	M_w[a] (*kDa*)	M_n[a] (*kDa*)	M_w/M_n[a]	DP_n[b]	*HPO/HPI* [c] *(wt%)*
1	PIB-PNIPAM-Br	5.8	4.2	1.22	36	2.16
2	PIB-PNIPAM-Br	7.2	5.3	1.35	45	1.74
3	PIB-PNIPAM-Br	12.2	9.9	1.27	85	1.03
4	PMPA-PNIPAM-Br	5.8	4.5	1.29	38	1.40
5	DiPMPA-PNIPAM-Br	5.3	4.1	1.27	34	2.26
6	DiPMPA$_m$-HBPNIPAM-N_3	44.3	42.6	1.04	11	—
7	EIB-PNIPAM-Br	7.5	5.4	1.38	47	1.54
8	BIB-PNIPAM-Br	7.8	6.8	1.14	59	2.27
9	PIB-POEGMA$_{475}$-Br	9.5	6.7	1.43	14	1.31
10	PMPA-POEGMA$_{475}$-Br	9.5	8.5	1.13	18	0.87
11	DiPMPA-POEGMA$_{475}$-Br	15.1	10.7	1.40	22	0.54

[a] Molecular weight and molecular weight distributions determined by SEC/MALLS, [d] Degree of polymerization determined by M_n, [c] The weight fraction of the hydrophobic end group in the whole hydrophilic homopolymer.

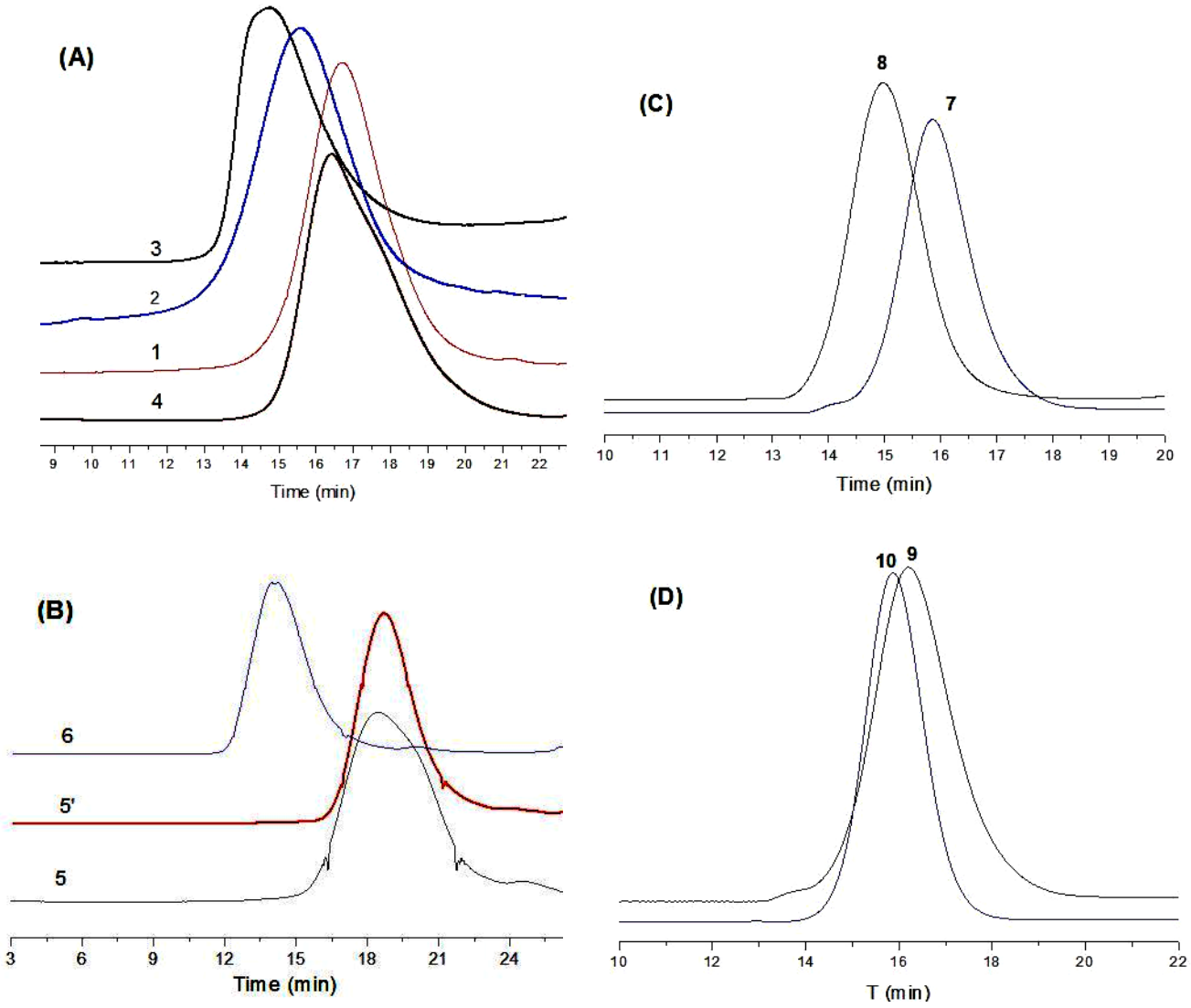


Figure S2 SEC/MALLS curves of homopolymers. (A) homopolymers **1-4 (**in DMF**)**; (B) homopolymers **5**, **5'** and **6 (**in DMF**)**; (C) homopolymers **7** and **8 (**in DMF**)**; (D) homopolymers **9-11 (**in THF**)**.

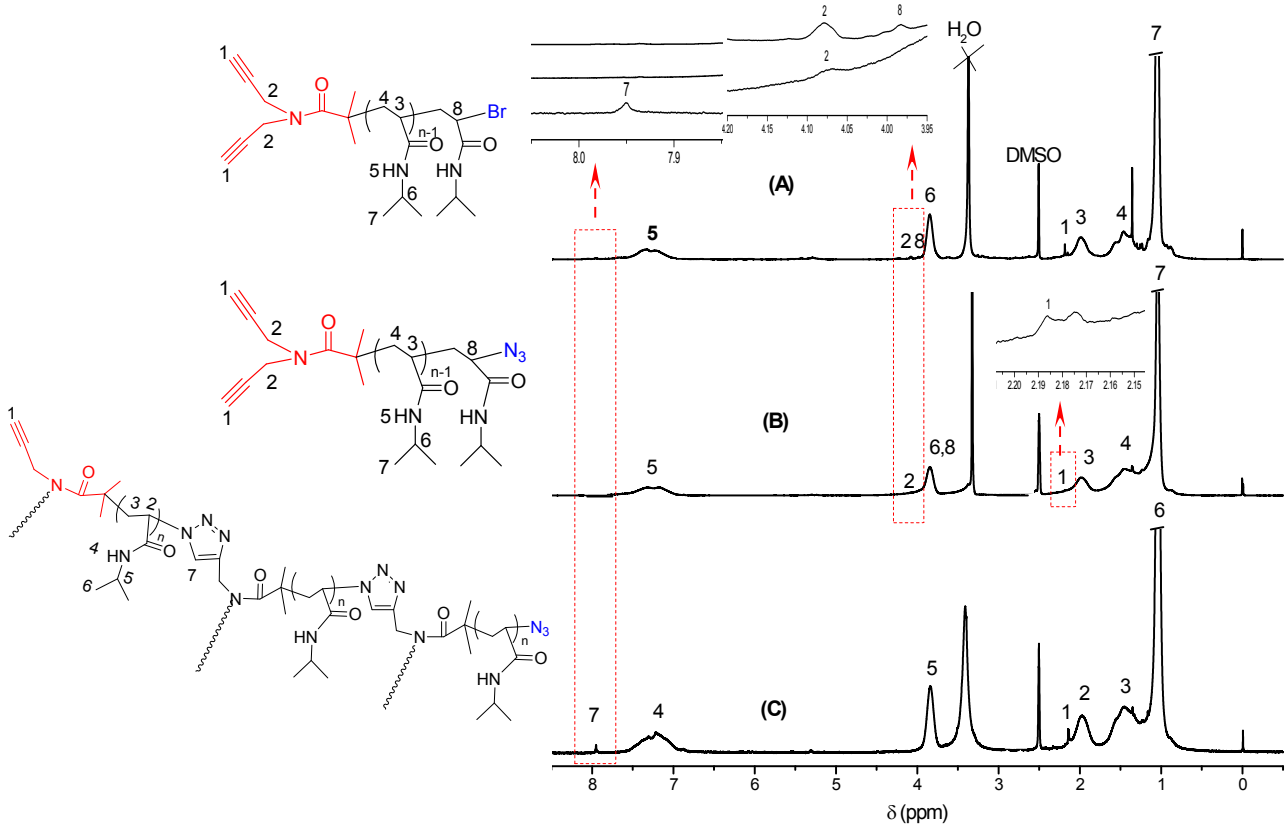


Figure S3 ^{1}H NMR spectra of homopolymers **5** (A), **5'** (B) and **6** (C) in DMSO-d_6.

5. Self-assembly of homopolymers

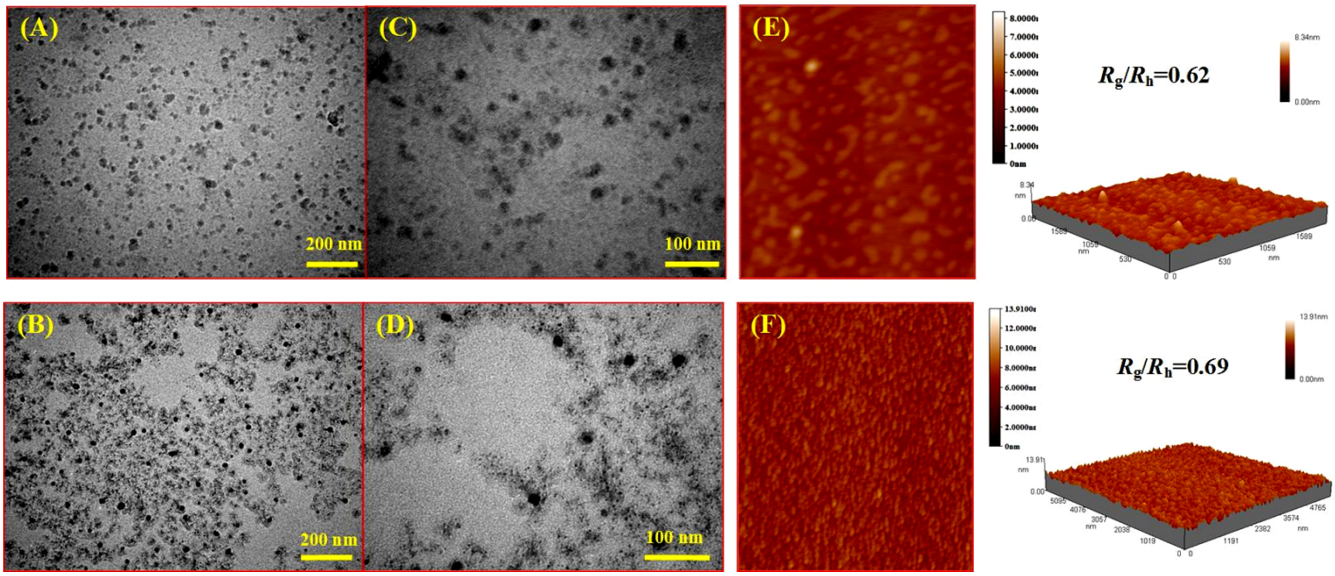
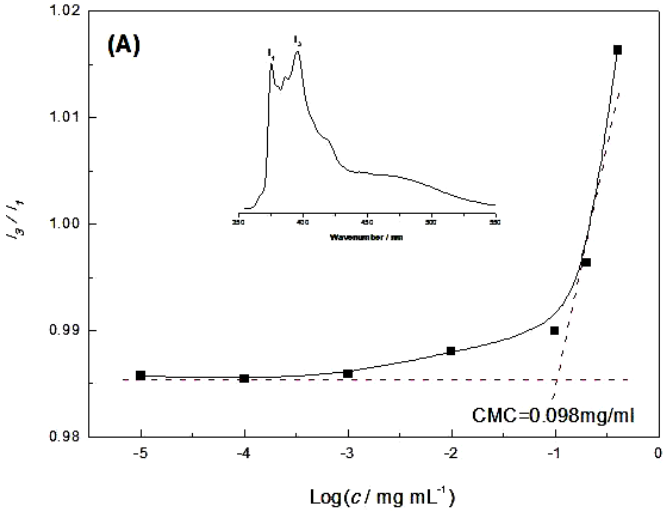
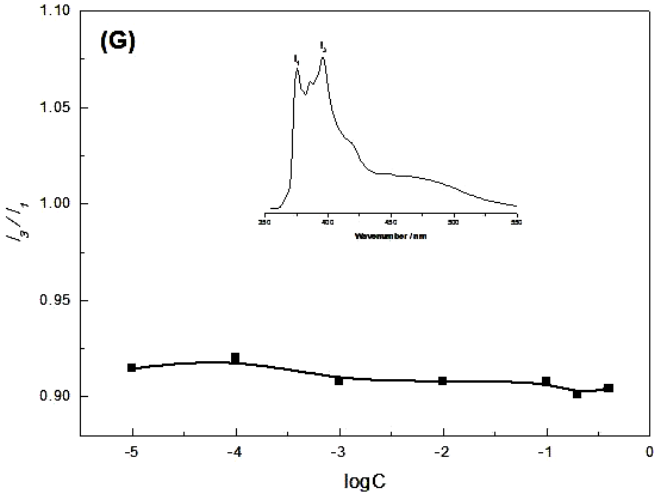
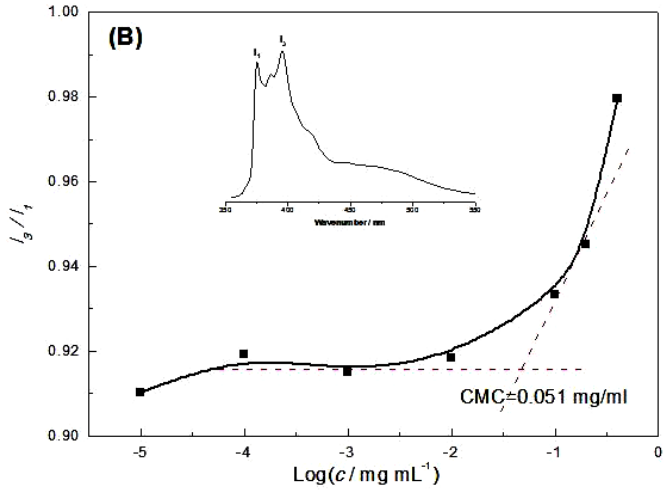
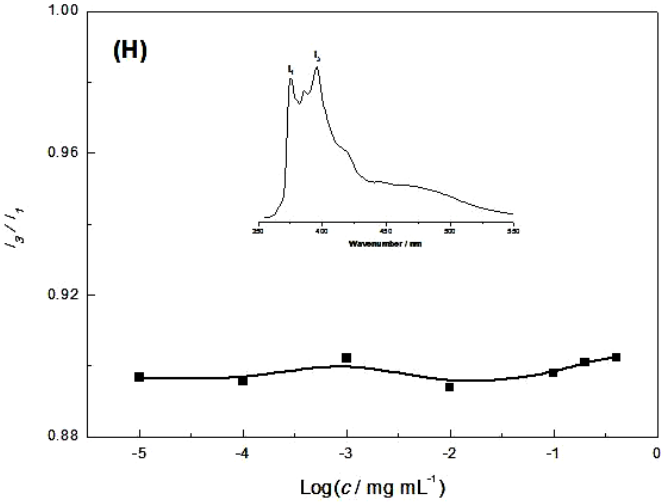


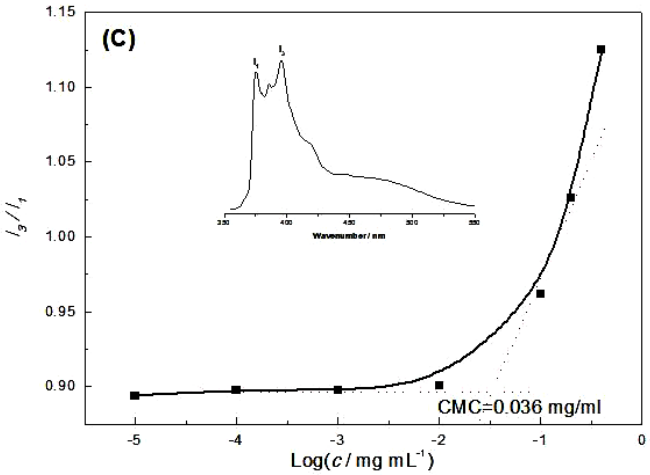
Figure S4 TEM and AFM images of homopolymers **4** and **5** (A-B for TEM and E-F for AFM) aqueous solutions with a concentration of 0.2 mg/mL at 20 °C; (C-D) Typical magnification images of A-B.

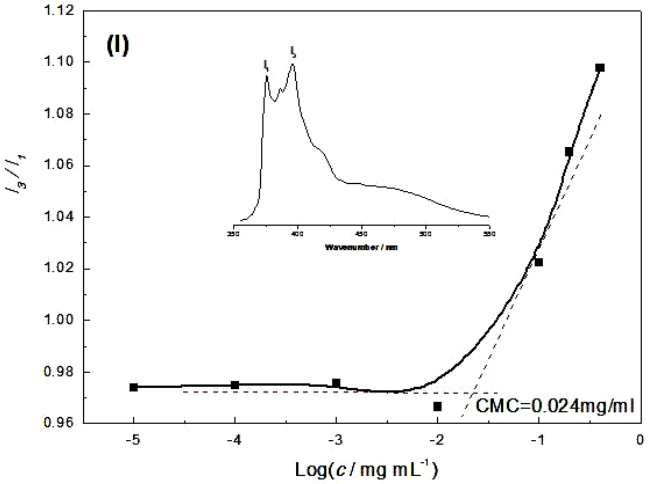

(A)
CMC=0.098mg/ml
Log(c / mg mL-1)


(G)
logC


(B)
CMC=0.051 mg/ml
Log(c / mg mL-1)


(H)
Log(c / mg mL-1)


(C)
CMC=0.036 mg/ml
Log(c / mg mL-1)


(I)
CMC=0.024mg/ml
Log(c / mg mL-1)

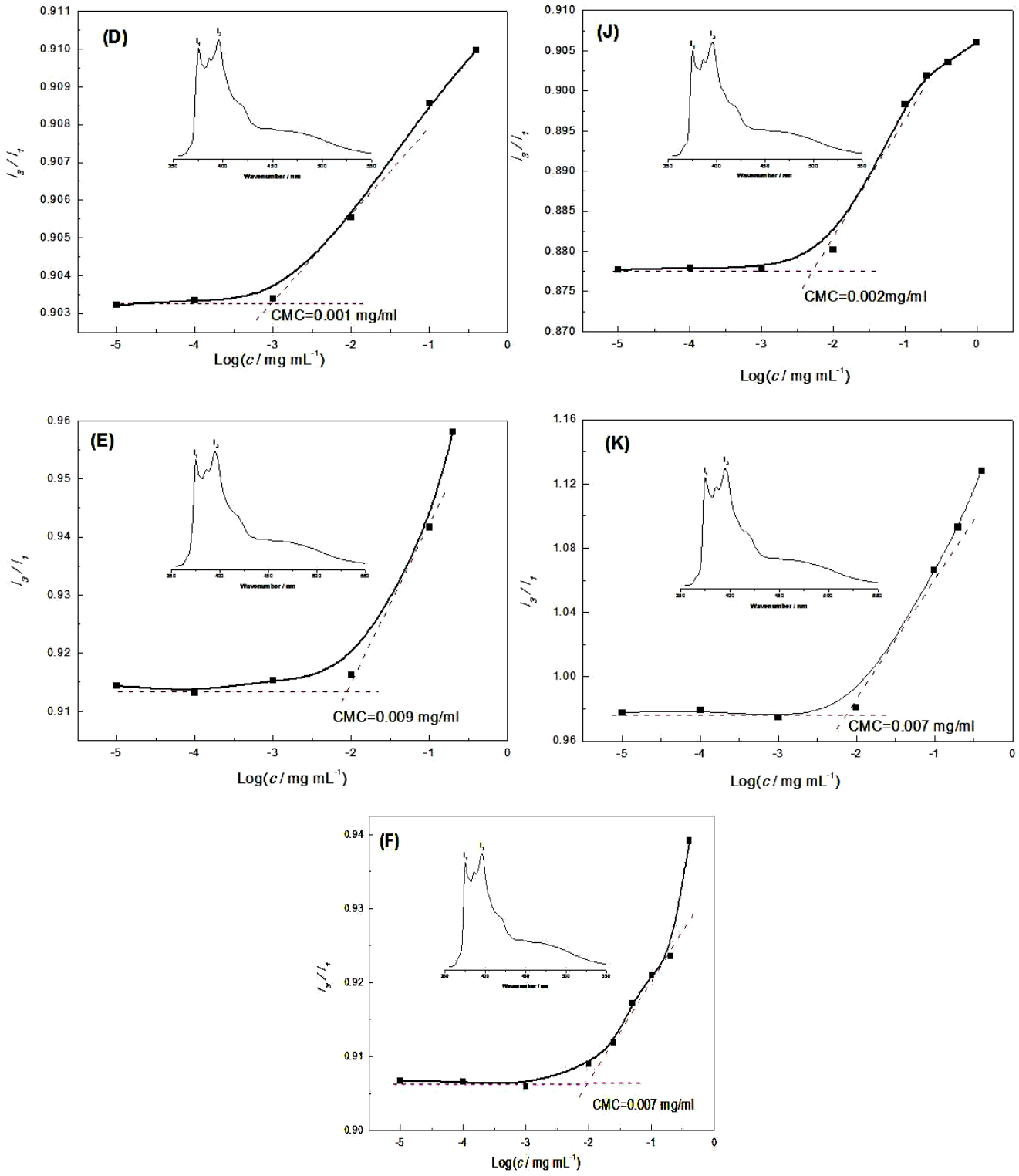


Figure S5 Relationship between the fluorescence intensity ratio (I_3/I_1) and homopolymer concentration in aqueous solution (Inset: fluorescence emission spectrum of pyrene). A-K represent homopolymers **1-11**.

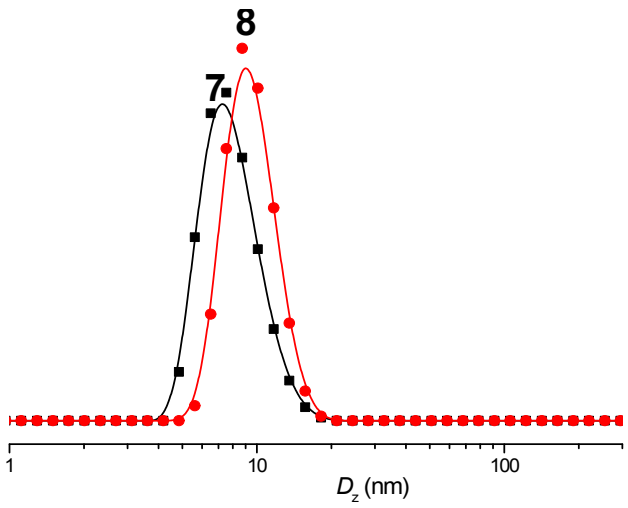


Figure S6 Typical intensity-averaged diameter distributions of the homopolymers **7** and **8** (A and B) aqueous solutions with a concentration of 0.2 mg/mL at 20 °C

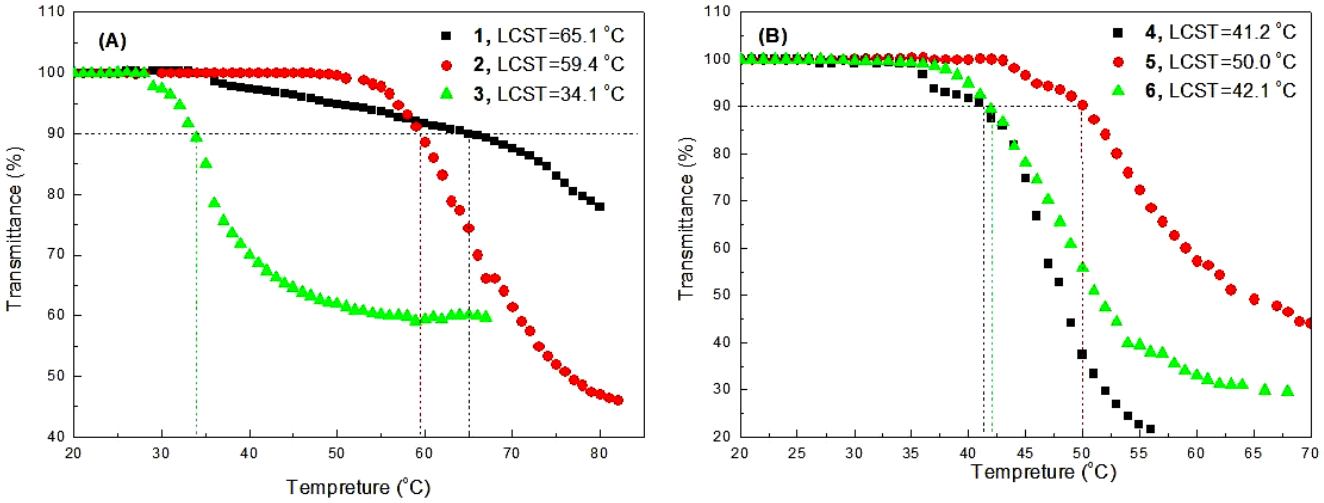


Figure S7 Variation in the transmittance at 550 nm of the homopolymer aqueous solution (A: **1**-**3**; B: **4**-**6**) with a concentration of 0.2 mg/mL as a function of temperature.

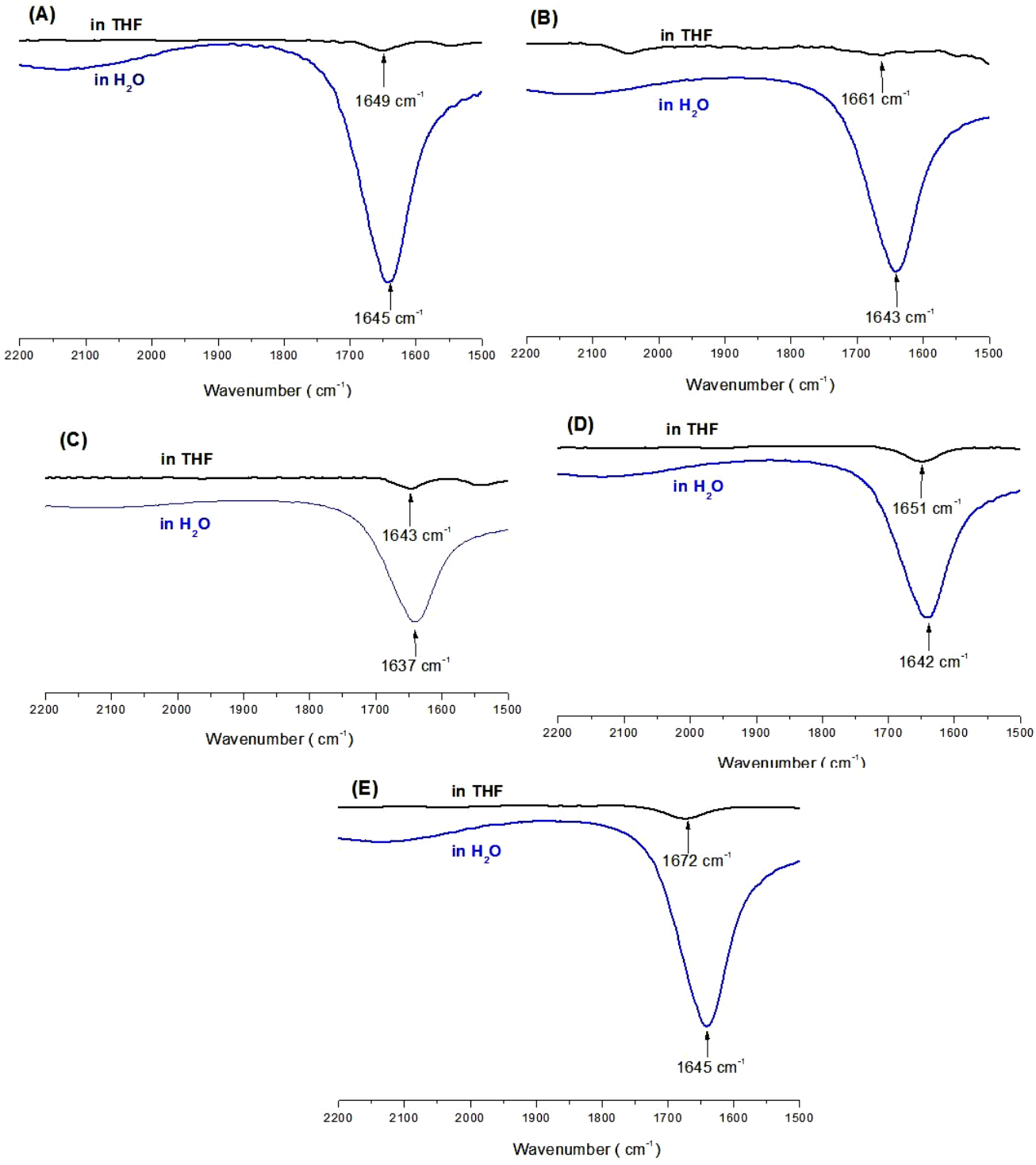
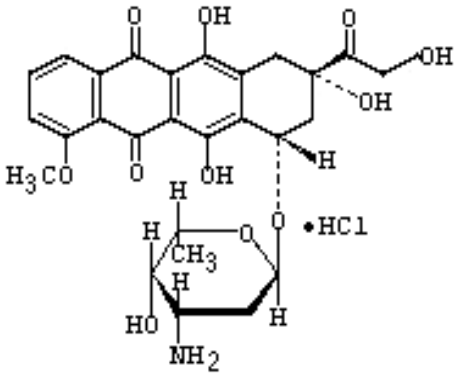


Figure S8. FTIR-ATR spectra of homopolymers **1**, **3**-**6** (A-E) solution in THF and their self-assemblies in H_2O with a concentration of 0.2 mg/mL at 20 ^oC



Scheme S1 Chemical structure of doxorubicin hydrochloride

6. References

[S1] Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558-3561.
[S2] Song, J.; Lee, E.; Cho, B. K. *J. Polym. Sci.: Part A: Polym. Chem.* **2013**, *51*, 446-456.
[S3] Hovestad, N. J.; Koten, G. V.; Bon, S. A. F.; Haddleton, D. M. *Macromolecules* **2000**, *33*, 4048-4052.