

Electronic Supporting Information for

Regulation of the Nanostructures Self-Assembled from an

Amphiphilic Azobenzene Homopolymer: Influence of Initial

Concentration and Solvent Solubility Parameter

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1. Materials

Methacryloyl chloride (96%), 4-aminoazobenzene (98%), triethylamine (AR), tetrahydrofuran (THF, AR), n-hexane (AR), NaHCO₃ (AR), 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%), 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (CPAD, 97%), DMF (HPLC), anhydrous Na₂SO₄ (AR) and ethyl acetate (AR) were purchased from Aladdin. CDCl₃ was purchased from J&K Scientific Ltd. THF was dried via sodium before use, and AIBN was recrystallized in ethanol before use. The other reagents were used without further purification.

2. Characterizations

2.1 ¹H NMR

The ¹H NMR spectra of the monomer and homopolymer were obtained by using a Bruker AV 400 MHz spectrometer with CDCl₃ as solvent.

2.2 GPC

The molecular weight and molecular weight distribution of the homopolymer were evaluated using a DMF GPC conducted by an Agilent 1260 Infinity GPC analysis system with two Shedex GPC KD series columns with HPLC grade DMF as the eluent at a flow rate of 0.8 mL/min at 50 °C. And poly(ethylene glycol) with different molecular weights were used as standards.

2.3 DSC

The T_g of PAzoMAA was determined by a differential scanning calorimeter (Discovery X3 DSC) with a heating rate of 10 °C min⁻¹.

2.4 DLS

The hydrodynamic diameter and polydispersity of the nanobowls, nanotubes and nanofibers were

determined by Malvern ZETASIZER instrument (Zetasizer Ultra) at scattering angles of 173 and 13°.

And the Zeta potentials of the nano-objects were also obtained.

2.5 UV-vis spectroscopy

The UV-vis spectra of PAzoMAA and bowl-shaped nanoparticles were recorded by a UV759S UV-vis spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.). All the samples were analyzed using quartz cuvettes.

2.6 SEM

To obtain SEM image, a drop of solution of the bowl-shaped nanoparticles was dropped onto a silicon wafer and dried at ambient temperature. Then gold nanoparticles were coated on the surface of the samples and it was viewed by a FEI Quanta 200 FEG electron microscope operated at 10 kV.

2.7 TEM

The aqueous solutions of the nano-objects (8.5 μ L) were dropped onto the carbon film supported by copper grid and dried at ambient temperature. The images were recorded on a JEOL JEM-2100F instrument at 200 kV equipped with a Gatan 894 Ultrascan 1k CCD camera.

3. Experimental Section

3.1 Synthesis of 4-(phenyldiazenyl)phenyl methacrylamide (AzoMAA) monomer

Triethylamine (2.024 g, 20.00 mmol) and 4-aminoazobenzene (2.955 g, 15.00 mmol) were dissolved in 50 mL of anhydrous tetrahydrofuran in a round bottom flask. The mixture was immersed in an ice-water bath. Methacryloyl chloride (1.350 g, 15.00 mmol) was diluted in 20 mL of anhydrous tetrahydrofuran and dropped into the flask in 30 min. Then the solution was stirred at room temperature for 24 h. Then

the dispersion was filtered and dried under vacuum. The filtrate was dissolved in ethyl acetate and washed with saturated NaHCO_3 and water for 3 times, respectively. The organic layer was dried via anhydrous Na_2SO_4 and dried under vacuum after filtration. The obtained crude product was purified by column chromatography (ethyl acetate/n-hexane = 1/3 (v/v)) to give pure AzoMAA (yield: 88%).

3.2 Synthesis of PAzoMAA

The homopolymer PAzoMAA was synthesized via RAFT polymerization according to the following procedures. CPAD (41.8 mg, 0.150 mmol), AzoMAA (1.039 g, 3.90 mmol), and THF (2.00 mL) were added to a 5 mL round bottom flask. Then oxygen was removed by bubbling with argon for 30 minutes. AIBN (3.70 mg, 0.0225 mmol) was rapidly added into the flask and bubbled with argon for another 5 minutes. Then the flask was placed in an oil bath at 70 °C. After 24 h, the reaction was terminated by cooling down to room temperature. The solvent was removed by evaporating under vacuum to give a red-brown solid for further characterization.

3.3 Self-assembly of PAzoMAA by solvent switch method

The PAzoMAA was dissolved in DMF (5 mL) with a concentration of 0.05 to 1.0 mg mL^{-1} , respectively, followed by adding deionized water (water/DMF = 2:1 (v/v)) into the solution dropwise with a speed of 5 mL hour^{-1} under stirring (250 rpm). DMF was removed by dialyzing against deionized water for 2 days to afford aqueous solutions of compound micelles and bowl-shaped nanoparticles with different opening sizes.

3.4 Self-assembly of PAzoMAA by solvothermal method

The PAzoMAA was dissolved in ethanol, isopropanol and butanol with a concentration of 0.5 mg mL^{-1} , respectively. Then the solution was heated to 75 °C for 4 h and cooled to room temperature naturally.

Nanotubes, twisted nanofibers and nanofibers solutions were obtained for further characterizations.

3.5 UV-induced *trans-cis* isomerization of PAzoMAA and bowl-shaped nanoparticles

The DMF solution of PAzoMAA and aqueous solution of bowl-shaped nanoparticles were exposed to UV light (365 nm, 8000 mW cm⁻²) for different time and then UV-vis spectrometer was used to monitor the *trans-cis* isomerization of azobenzene pendants.

3.6 Solubility parameters (δ) of the solvents

The solubility parameters of ethanol, isopropanol and butanol are 26.3, 23.5 and 23.3 J^{1/2} cm^{-3/2}, respectively.

3.7 Calculation of the molecular length of PAzoMAA

The degree of polymerization of PAzoMAA is 26. Therefore, there are 31 C–C bonds, 2 C–S bonds and 1 benzene group in the main chain of PAzoMAA. Considering that the length of C–C bond, C–S bond are 0.154 and 0.186 nm and the diameter of benzene is 0.58 nm, respectively. Besides, the angle of C–C bond is 109°, so the length of the molecular chain (l) of PAzoMAA is:

$$l = 0.154 \times \sin(109^\circ/2) \times 31 + 0.186 \times \sin(109^\circ/2) \times 2 + 0.58 \approx 4.8 \text{ nm}$$

4. Scheme and Figures

Scheme S1. Synthesis of PAzoMAA.

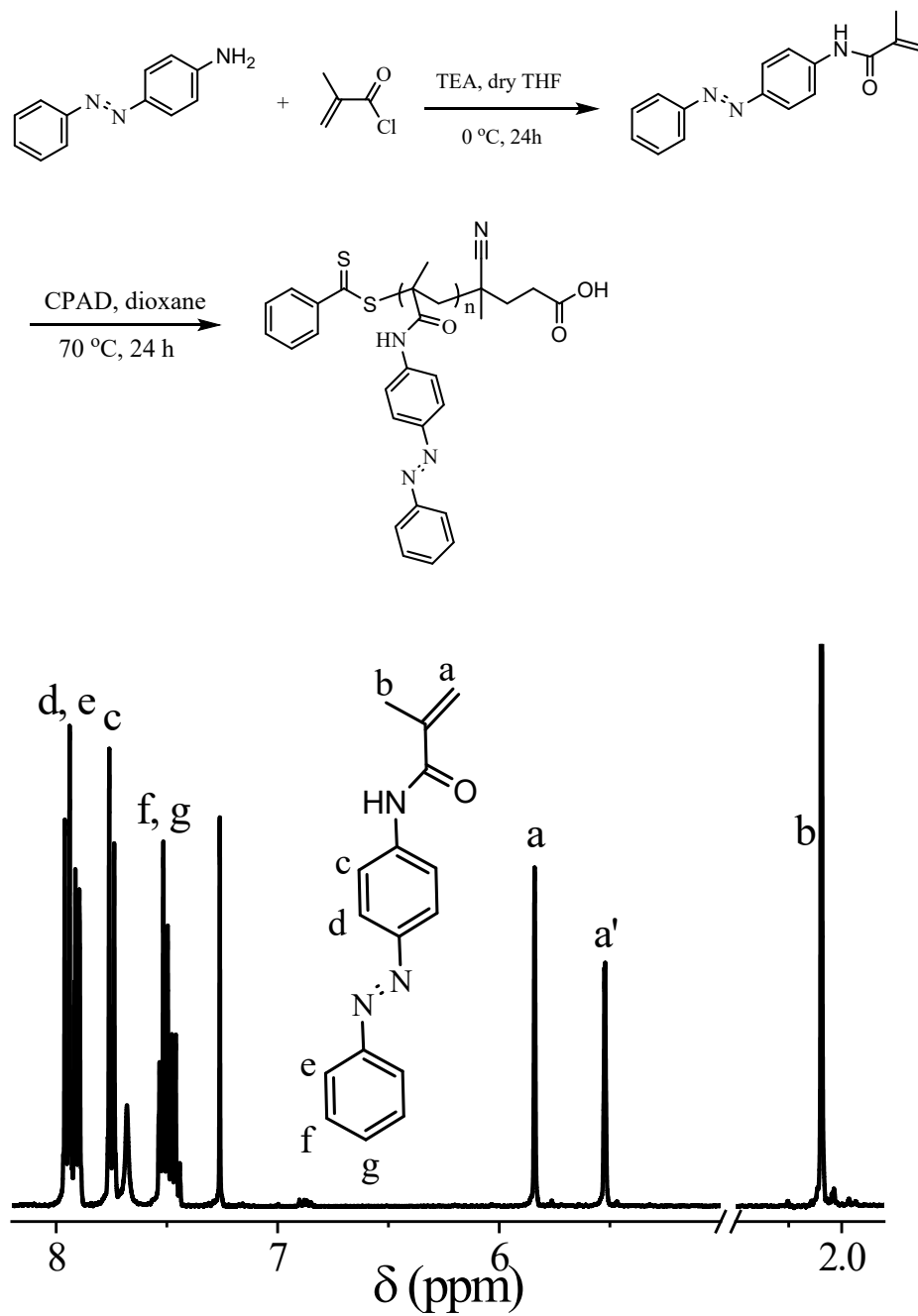


Fig. S1. NMR spectrum of AzoMAA.

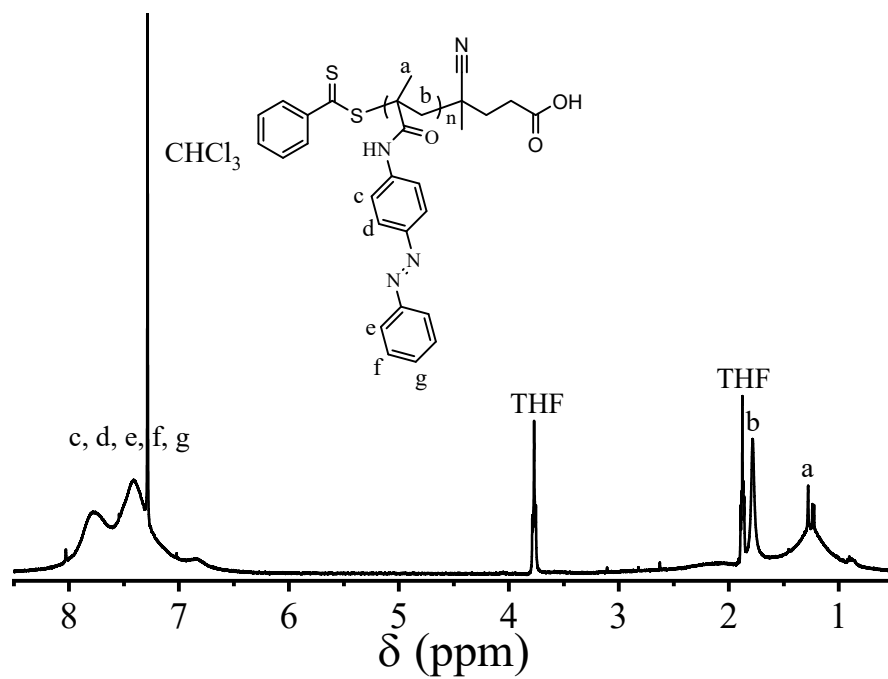


Fig. S2. NMR spectrum of PAzoMAA.

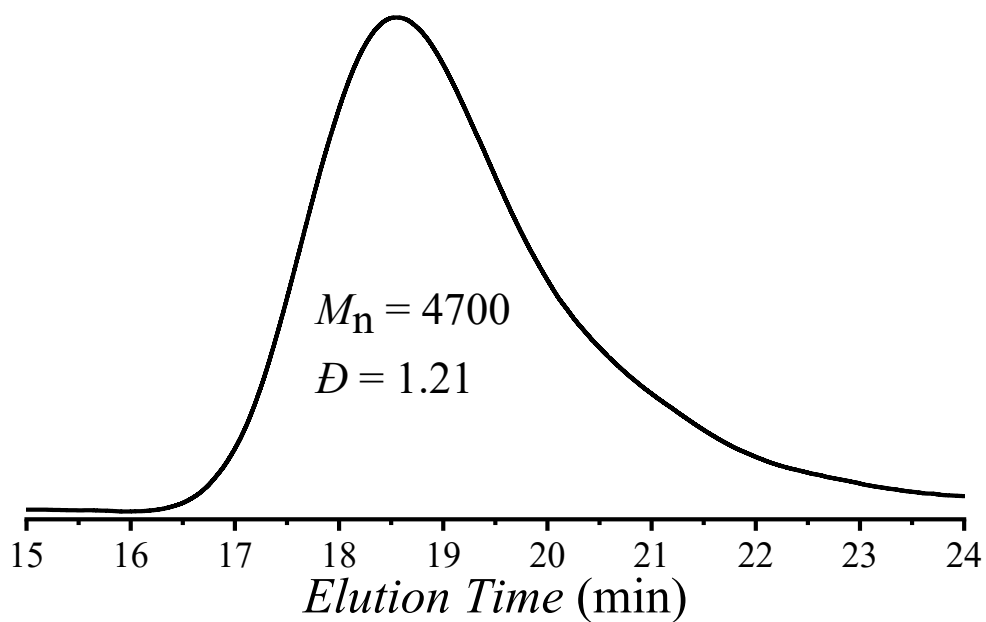


Fig. S3. DMF GPC trace of PAzoMAA.

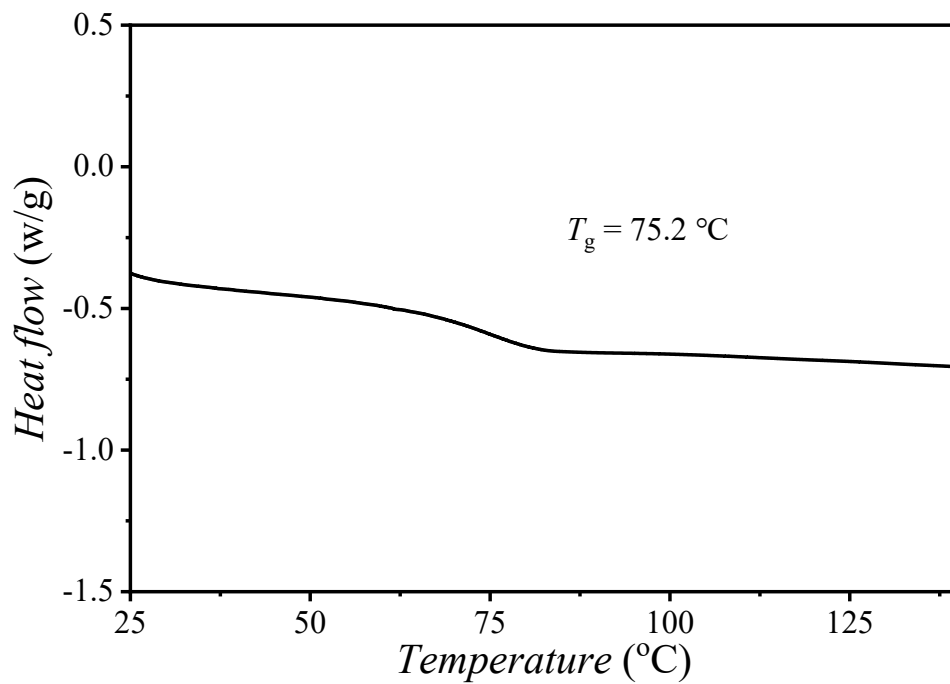


Fig. S4. DSC curve of PAzoMAA.

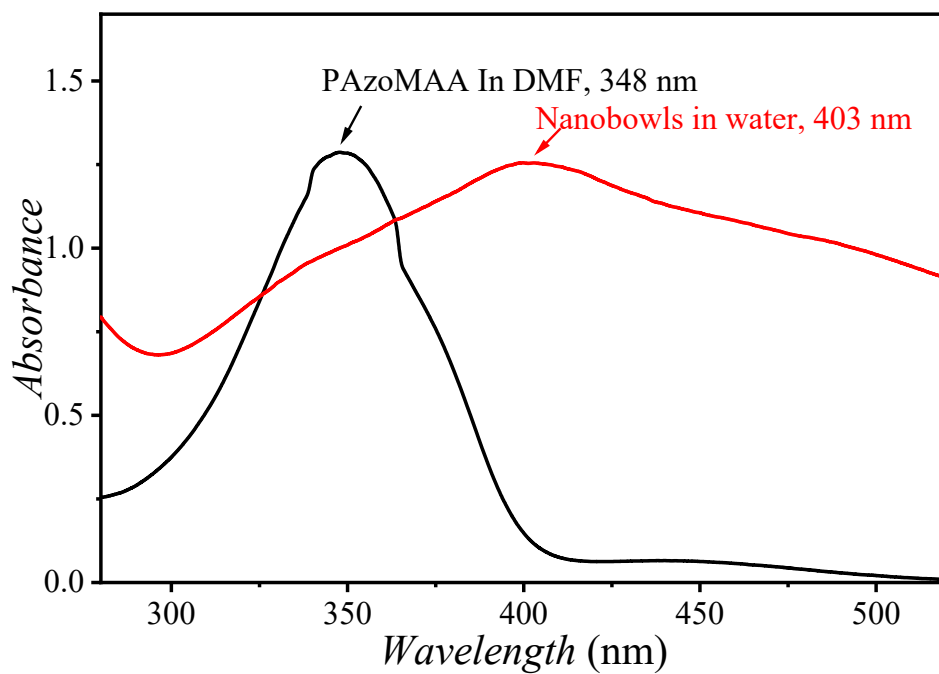


Fig. S5. UV-vis spectrum of PAzoMAA in DMF and bowl-shaped nanoparticles in water.

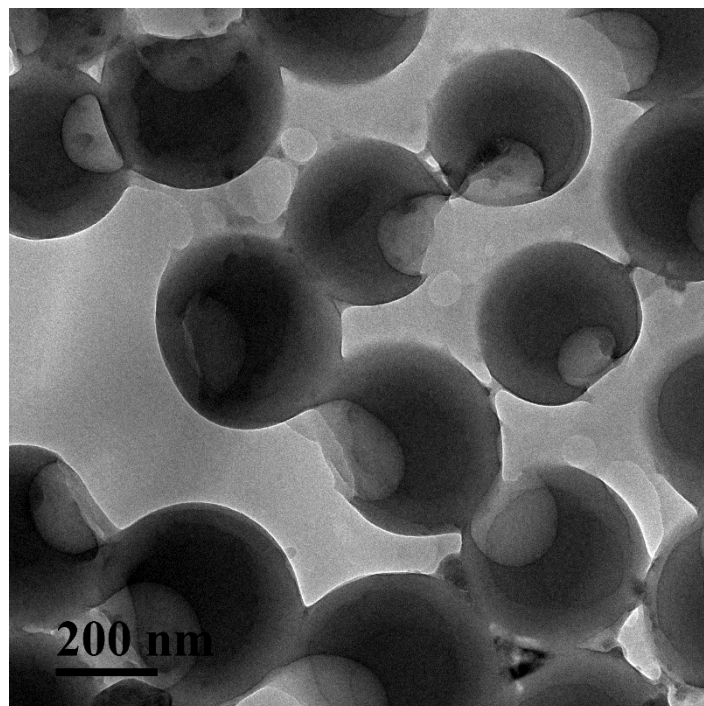


Fig. S6. TEM image of bowl-shaped nanoparticles prepared with a concentration of 0.4 mg mL^{-1} and water drop rate of 2 mL hour^{-1} .

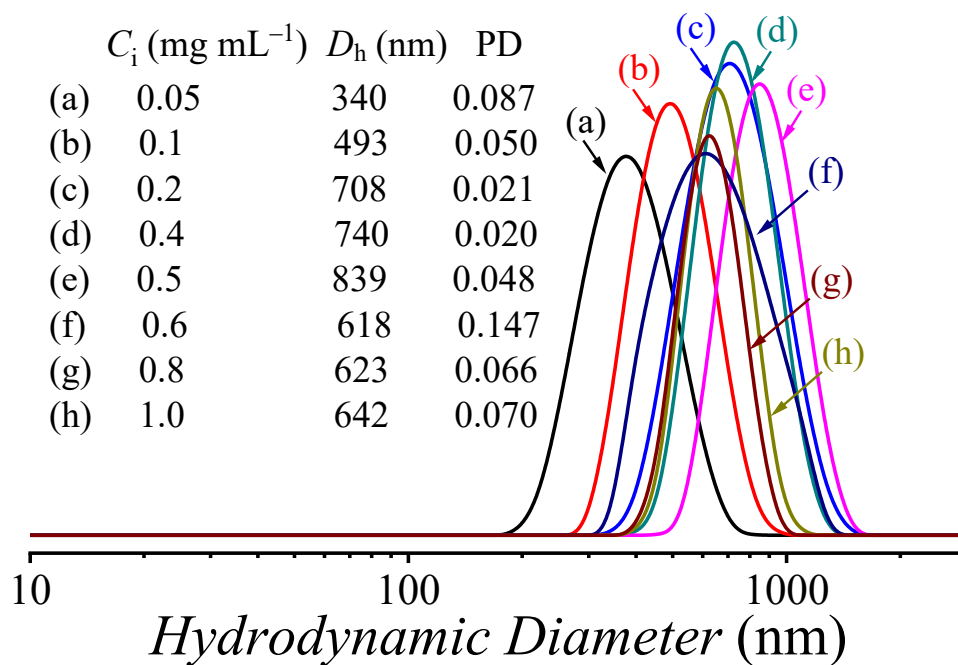


Fig. S7. DLS results of compound micelles and bowl-shaped nanoparticles self-assembled at different initial polymer concentrations.

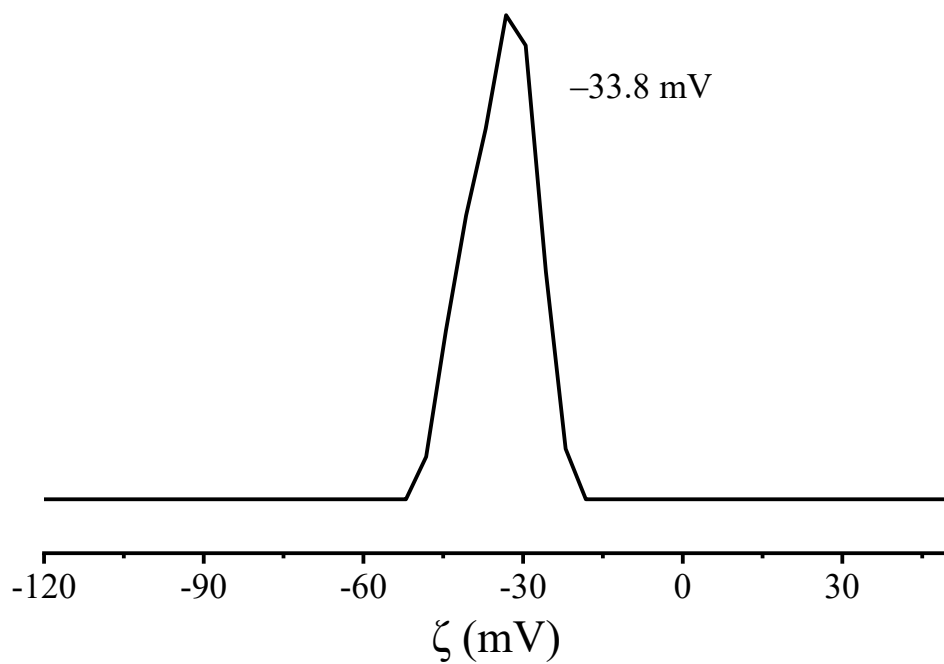


Fig. S8. Zeta potential of bowl-shaped nanoparticles self-assembled at concentration of 0.6 mg mL^{-1} .

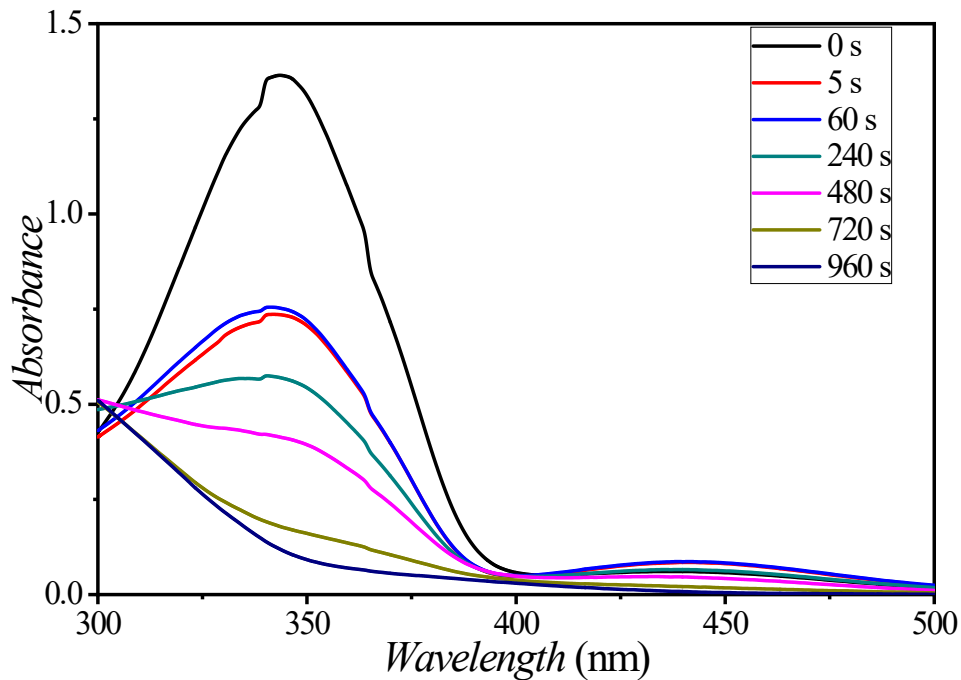


Fig. S9. UV-vis spectra of PAzoMAA in DMF upon exposure to UV irradiation for different time.

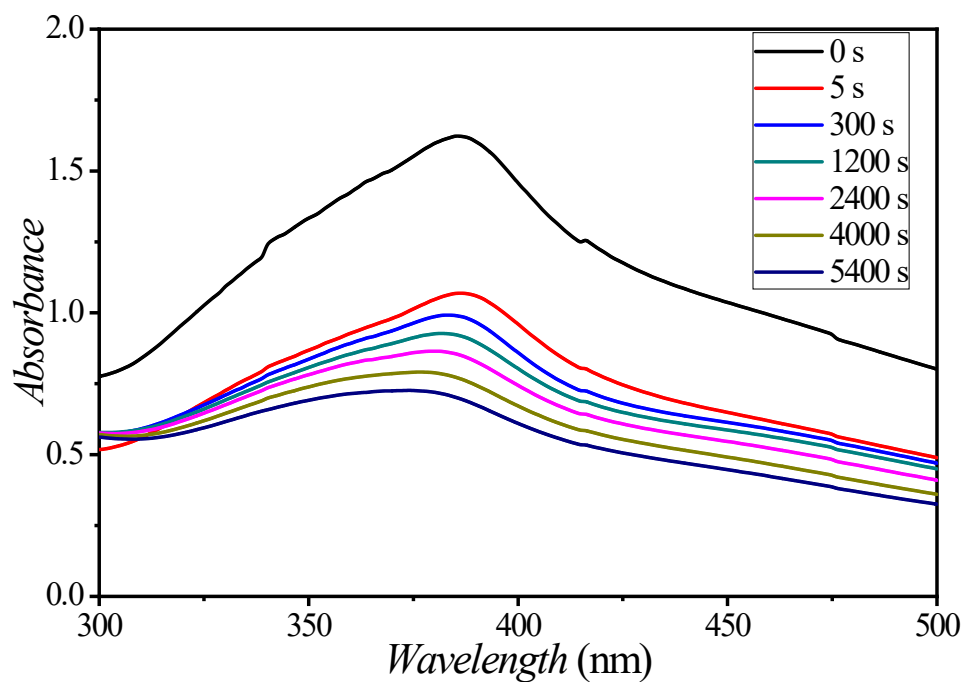


Fig. S10. UV-vis spectra of bowl-shaped nanoparticles obtained at initial concentration of 0.6 mg mL^{-1} in water upon exposure to UV irradiation for different time.

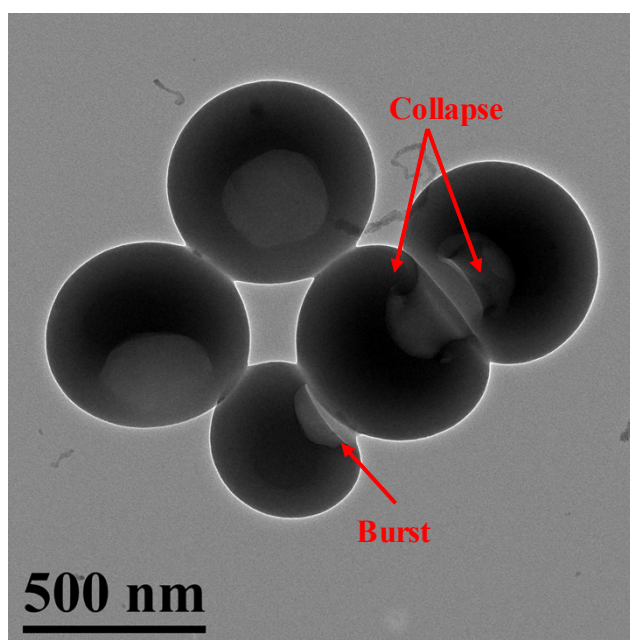


Fig. S11. TEM image bowl-shaped nanoparticles self-assembled with a polymer concentration of 0.55 mg mL^{-1} .

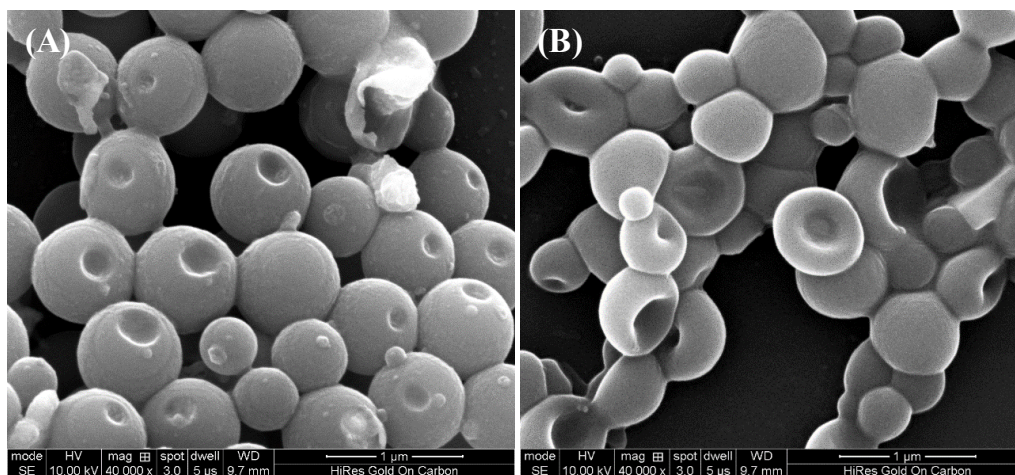


Fig. S12. SEM images bowl-shaped nanoparticles self-assembled with initial concentrations of (A) 0.4 mg mL^{-1} and (B) 0.6 mg mL^{-1} .

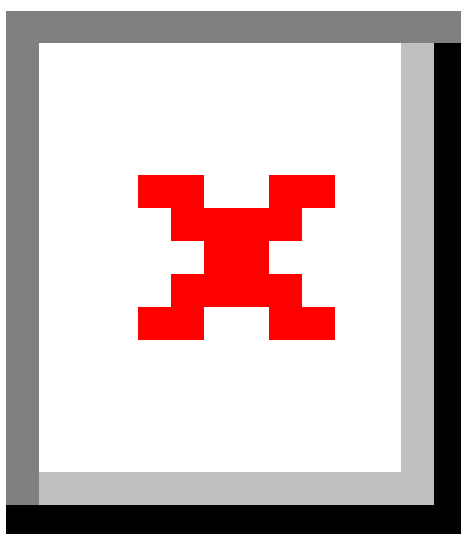


Fig. S13. Enlarged TEM images of (A) nanotube, (B) twisted nanowires and (C) nanowires.

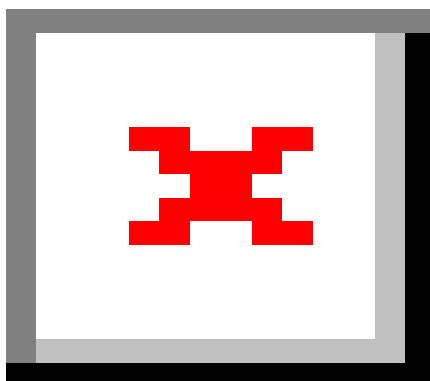


Fig. S14. Zeta potential of nanotube self-assembled in ethanol at 75 °C.

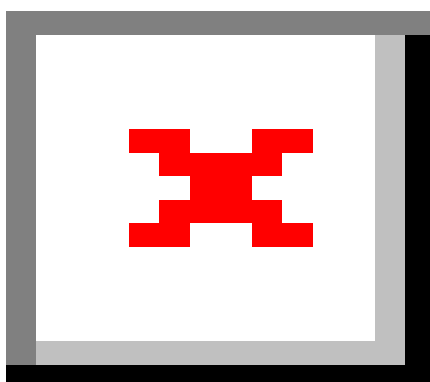


Fig. S15. Zeta potential of twisted nanofibers self-assembled in isopropanol at 75 °C.

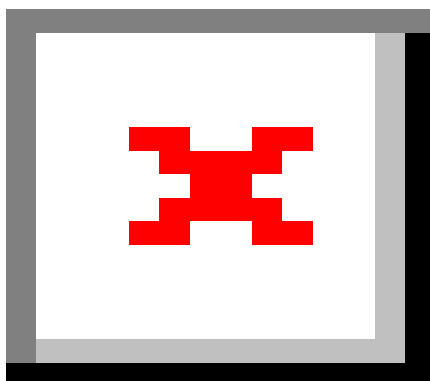


Fig. S16. Zeta potential of nanofibers self-assembled in butanol at 75 °C.

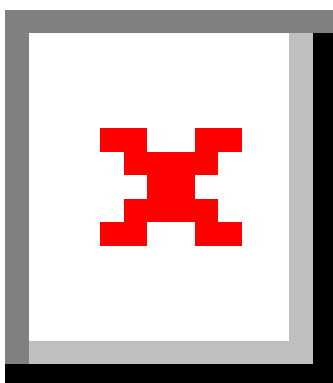


Fig. S17. TEM image of compound micelles self-assembled in butanol at 100 °C.

Table S1. Calculation of the solubility parameter (δ) of PAzoMAA.¹

Groups	$\sum E_i$ (J/mol) ^a	$\sum V_i$ (cm ³ /mol) ^b
1 -CH ₃	4710	33.5
1 -CH ₂ -	4940	16.1
1 >C<	1470	-19.2
1 -CO-	17370	10.8
1 -NH-	8370	4.5
1 Phenyl	31940	71.4
1 Phenylene	31940	52.4
1 -N=N-	4190	-
	$E_{\text{coh}} = 104930^c$	$V = 169.5^d$

^aThe cohesive energy of different groups, ^bVolume of different groups, ^cTotal cohesive energy of PAzoMAA and ^dTotal volume of PAzoMAA.

$$\delta = \left(\frac{E_{\text{coh}}}{V} \right)^{1/2} = \left(\frac{104930}{169.5} \right)^{1/2} = 24.9 J^{1/2} \text{ cm}^{-3/2}$$

5. References

- (1) D. W. VAN KREVELEN and K. TE NIJENHUIS. *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*; Fourth, completely revised edition; Elsevier: **2009**, Chapter 7, p.189-225.