Electronic Supplementary Information (ESI) for

Nanobowls with controlled openings and interior holes driven by the synergy of hydrogen bonding and π-π interaction

Hui Sun[†], Danqing Liu[†] and Jianzhong Du[*,†,‡]

[†]Department of Polymeric Materials, School of Materials Science and Engineering, Tongji University, 4800 Caoan Road, Shanghai 201804, China. E-mail: jzdu@tongji.edu.cn; Fax: +86-21-6958 0239; Tel: +86-21-6958 0239

[‡]Department of Orthopedics, Shanghai Tenth People's Hospital, Tongji University School of Medicine, Shanghai 200072, China

1. Materials

Glycidyl methacrylate (GMA, 97%), *p*-aminoazobenzene (98%), bismuth(III) chloride (99%), 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (CPAD, 97%) and 2,2'-azobis(2-methylpropionitrile) (AIBN) were purchased from Aladdin. AIBN was recrystallized from methanol and stored at -25 ^{o}C. $CDCl_3$, D_2O and DMSO-d_6 was purchased from J&K Scientific Ltd. Solvents were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

2. Characterization

2.1 GPC

The molecular weights and polydispersities of homopolymers 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^{-1} at 40 °C.

2.2 ^{1}H NMR

^{1}H NMR spectra were recorded using a Bruker AV 400 MHz spectrometer at room temperature with $CDCl_3$ or DMSO-d_6 as the solvents.

2.3 DLS and Zeta potential

The hydrodynamic diameter and polydispersity of the homopolymer complex micelles (HCMs) and nanobowls were determined by ZETASIZER Nano series instrument (Malvern Instruments ZS 90) at a fixed scattering angle of 90°. Data processing was carried out using cumulant analysis of the experimental correlation function and calculated from the computed diffusion coefficients using the Stokes−Einstein equation. Zeta potential studies of HCMs and nanobowls were conducted at 25 °C

using the same instrument.[1] Each reported measurement was conducted for three runs.

2.4 TEM

The aqueous solutions of nanobowls (8.0 μL, 31 μg mL^{-1}) were dropped onto a copper grid and dried at ambient temperature. The samples were viewed after dryness without staining. Images were recorded on a JEOL JEM-2100F instrument at 200 kV equipped with a Gatan 894 Ultrascan 1k CCD camera.

2.5 SEM

SEM was utilized to observe the morphologies of nanobowls. To obtain SEM images, a drop of solution was spread on a silicon wafer and left until dryness. It was coated with gold and viewed by a FEI Quanta 200 FEG electron microscopy operated at 10 kV. The images were recorded by a digital camera.

2.6 UV–vis spectroscopy

The UV–vis spectra of the homopolymers and the corresponding assemblies were acquired using a UV759S UV–vis spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.). All the samples were analyzed using quartz cuvettes. When conducting UV-vis analysis, THF and water are used as background, respectively. The spectra were used without correction.

2.7 Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra of homopolymers and the corresponding freeze-dried HCMs and nanobowls powder were obtained using a thermo Bruker EQUINOXSS/HYPERION2000 spectrometer.

2.8 Differential scanning calorimeter (DSC)

The T_g of $PHAzoMA_{29}$ was measured by DSC using a DSC Q100 (TA Instruments). In the DSC measurement, the freshly extruded sample was kept for 3 min at -80 °C and heated at the rate of 10 °C min^{-1} to 150 °C.

3. Experimental Section

3.1 Synthesis of the monomer 2-hydroxy-3-((4-(phenyldiazenyl)phenyl)amino)propyl methacrylate (HAzoMA)

GMA (4.260 g, 30.00 mmol), *p*-aminoazobenzene (5.913 g, 30.00 mmol) and CH_2Cl_2 (100 mL) were added to a round bottom flask (250 mL). After all the ingredients were dissolved, $BiCl_3$ (0.315 g, 1.00 mmol) was added as catalyst. Then the mixture was stirred at room temperature for 48 h and monitored by TLC. The suspension was filtered to remove the inorganic salts. The filtrate was washed with saturated $NaHCO_3$ (100 mL × 3) and deionized water (100 mL × 3). After dried over anhydrous Na_2SO_4, the organic phase was evaporated by rotary evaporator to remove CH_2Cl_2. The crude product was purified by column chromatography (*n*-hexane/EtOAc = 3/1 (v:v)) to yield 8.342 g of red-brown solid. Yield: ~ 82%.

3.2 Synthesis of PHAzoMA homopolymers

The homopolymer PHAzoMA was synthesized via RAFT polymerization according to the following procedures. CPAD (41.8 mg, 0.150 mmol; 13.9 mg, 0.050 mmol; 7.00 mg, 0.025 mmol; 3.50 mg, 0.013 mmol; 1.80 mg, 0.007 mmol), HAzoMA (0.508 g, 1.50 mmol), and dioxane (1.00 mL) were added to a round bottom flask. Then oxygen was removed by filling with argon into the flask for 30 minutes. AIBN (0.15-fold of the molar amount of CPAD added) was rapidly added in the flask with bubbling for additional 5 minutes. Then the flask sealed with argon was placed in an oil bath at 70 °C. After 24 h,

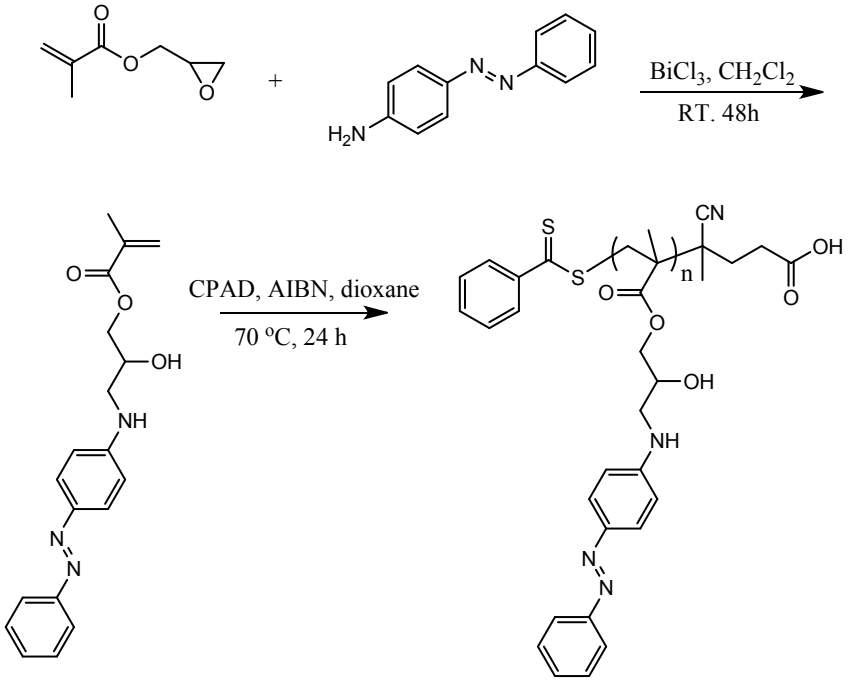
the reaction was terminated by cooling down to room temperature and exposing to the air. The mixture was evaporated under vacuum, then dissolved in dichloromethane and precipitated in diethyl ether for 3 times. After filtration, the filter residue was dried under vacuum for 24 h, yielding a red-brown solid.

3.3 Preparation of nanobowls

The PHAzoMA homopolymers were dissolved in THF with a concentration of 0.5 mg mL^{-1}, followed by adding deionized water (water/THF = 2:1 (v/v)) into the solution dropwise under stirring. The temperature is 25 ^{o}C. The THF was removed by dialyzing against deionized water for 2 days. After dialysis, the nanobowls were characterized by DLS, SEM and TEM.

4. Schemes and Figures

Scheme S1. Synthesis of PHAzoMA homopolymer via RAFT polymerization.



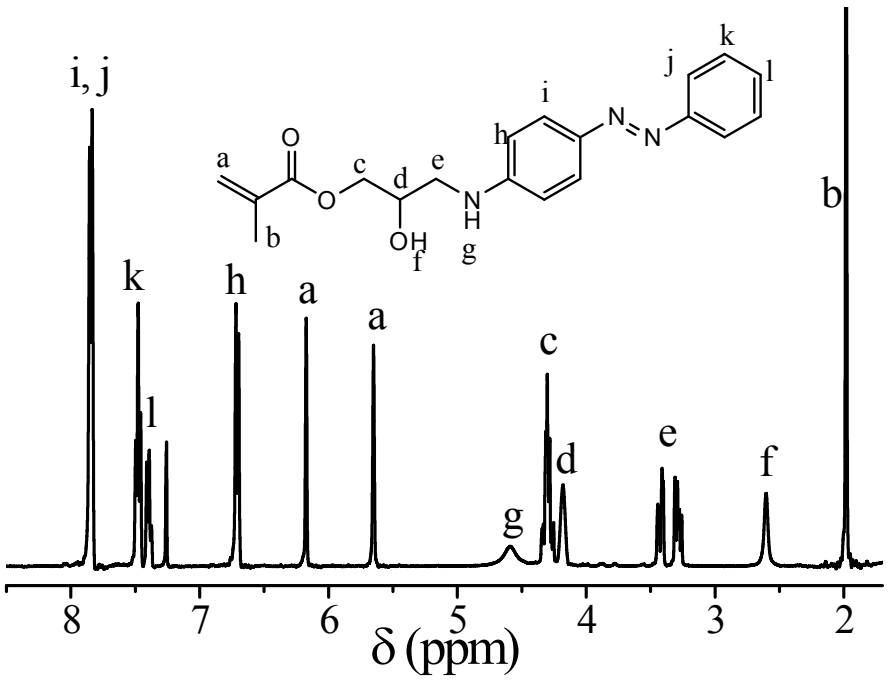


Fig. S1. ^{1}H NMR spectrum of HAzoMA monomer in $CDCl_3$.

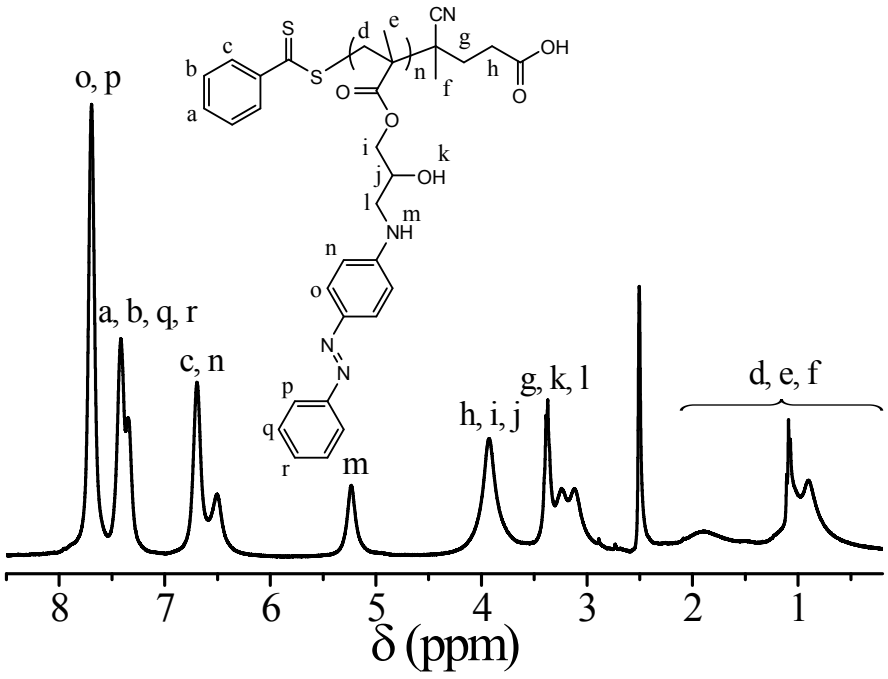


Fig. S2. ^{1}H NMR spectrum of PHAzoMA$_{10}$ in DMSO-d_6.

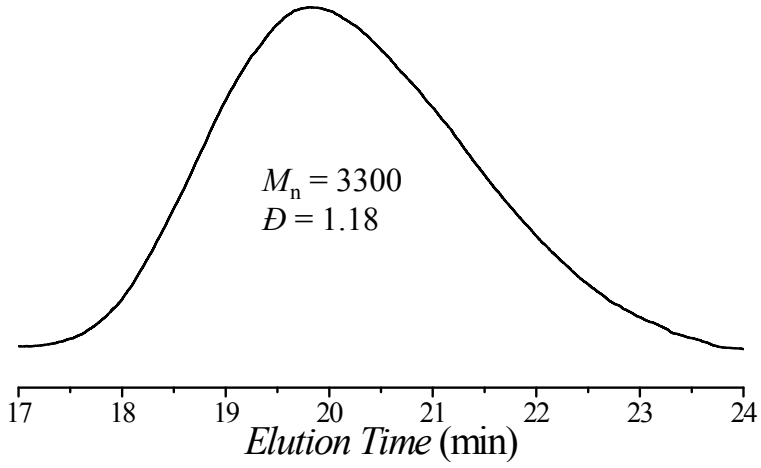


Fig. S3. DMF GPC trace of PHAzoMA$_{10}$ homopolymer.

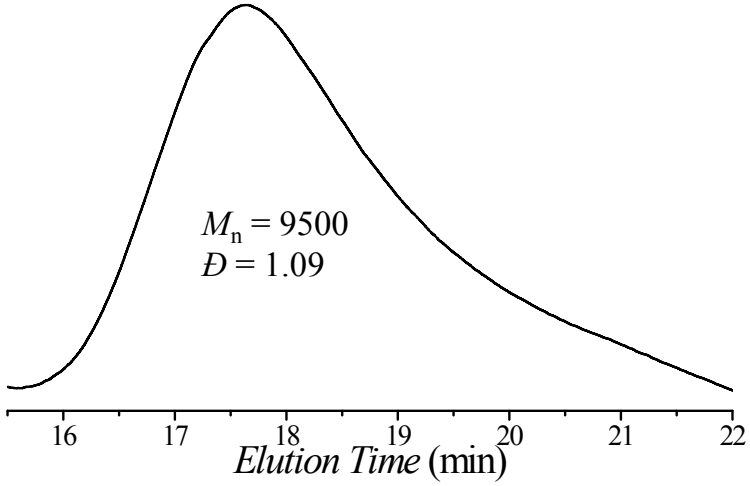


Fig. S4. DMF GPC trace of $PHAzoMA_{29}$ homopolymer.

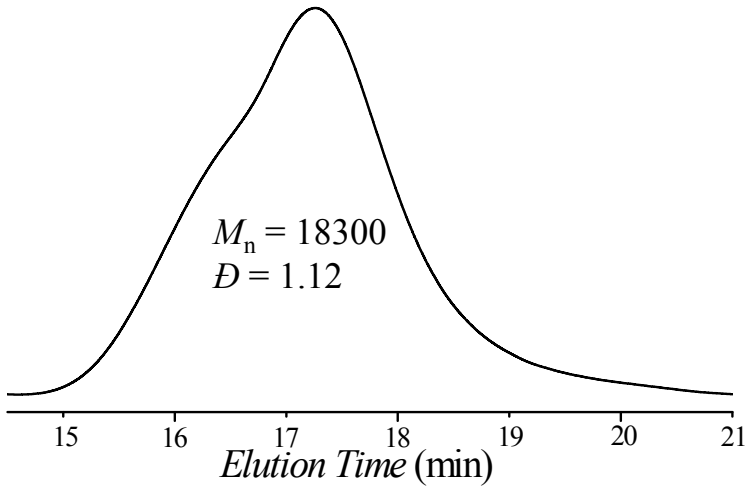


Fig. S5. DMF GPC trace of $PHAzoMA_{59}$ homopolymer.

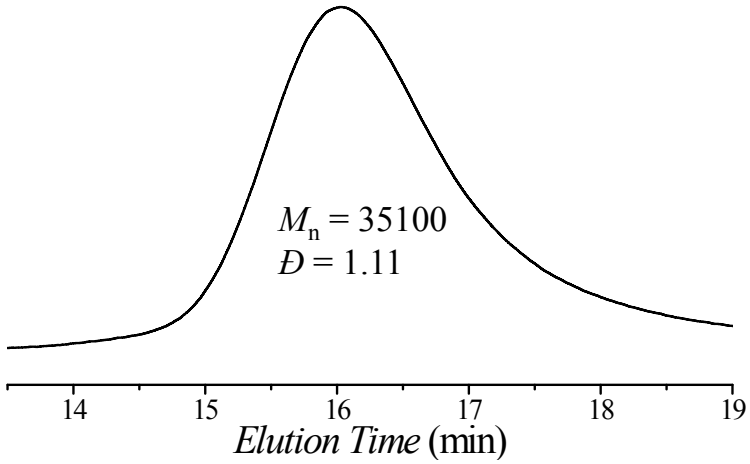


Fig. S6. DMF GPC trace of $PHAzoMA_{116}$ homopolymer.

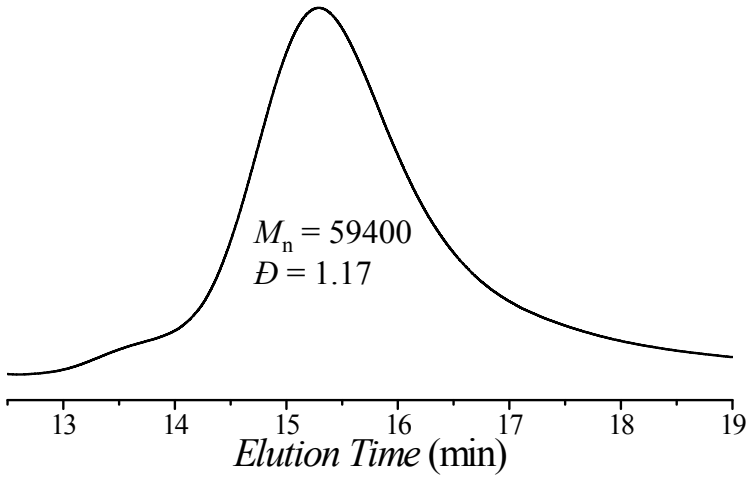


Fig. S7. DMF GPC trace of $PHAzoMA_{226}$ homopolymer.

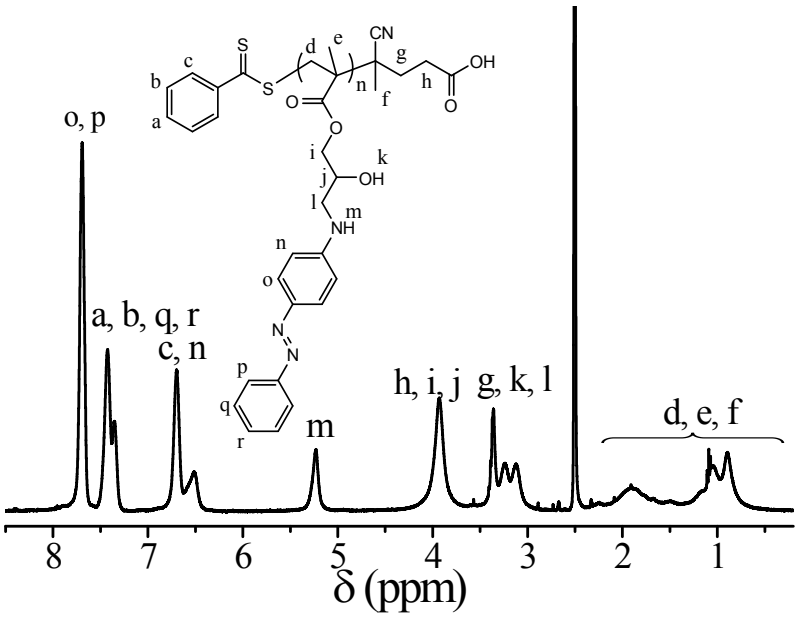


Fig. S8. NMR spectra of nanobowls from $PHAzoMA_{59}$ in DMSO-d_6 after dialysis and washed with D_2O for three times.

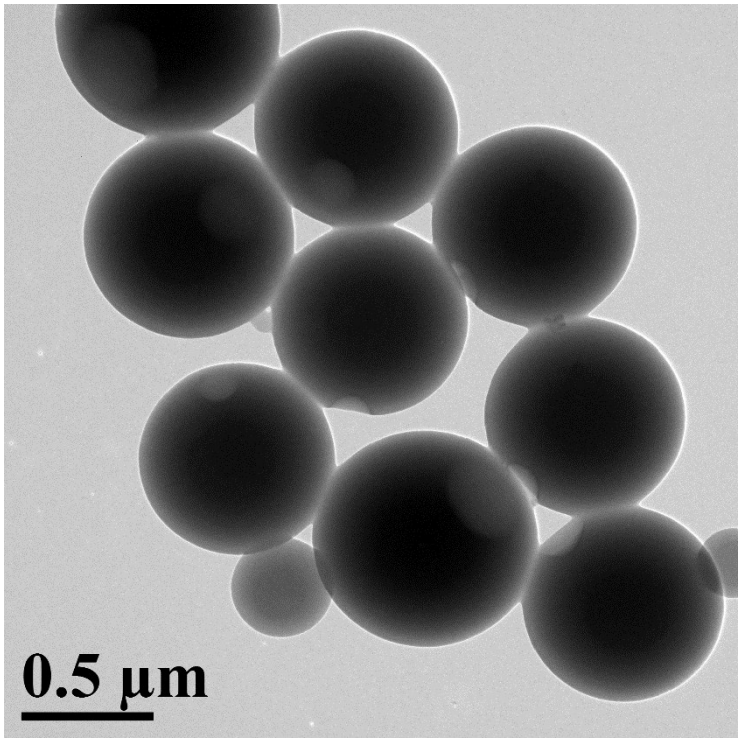


Fig. S9. TEM image of nanobowls from $PHAzoMA_{29}$ after ultrasonic treatment for 5 min.

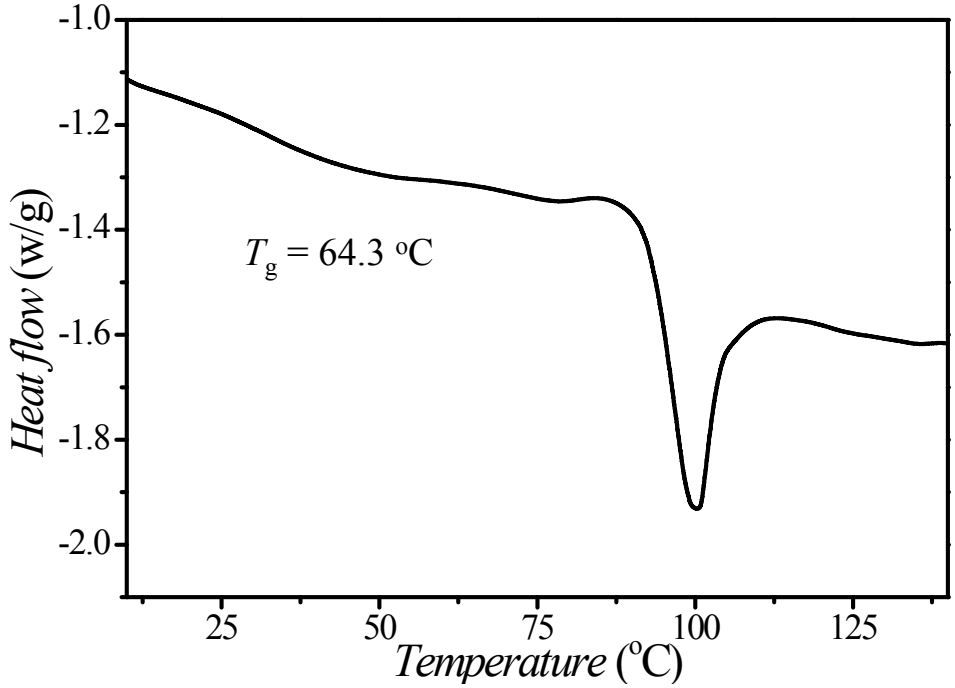


Fig. S10. DSC of $PHAzoMA_{29}$, giving a T_g of 64.3 °C.

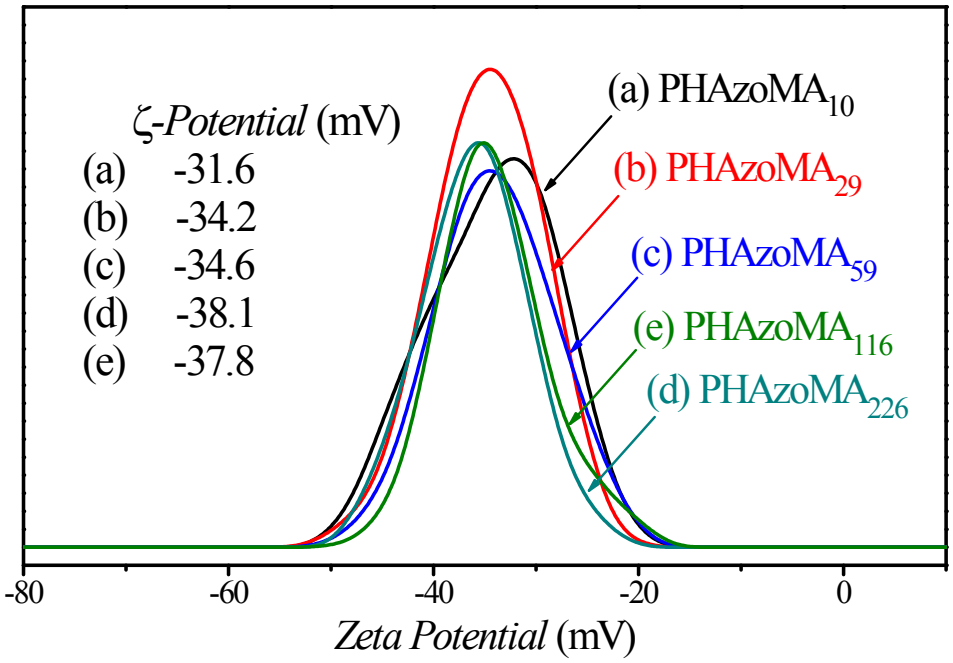


Fig. S11. Zeta potentials of HCMs (a) and nanobowls; (b-e) self-assembled from PHAzoMA homopolymers with different DPs.

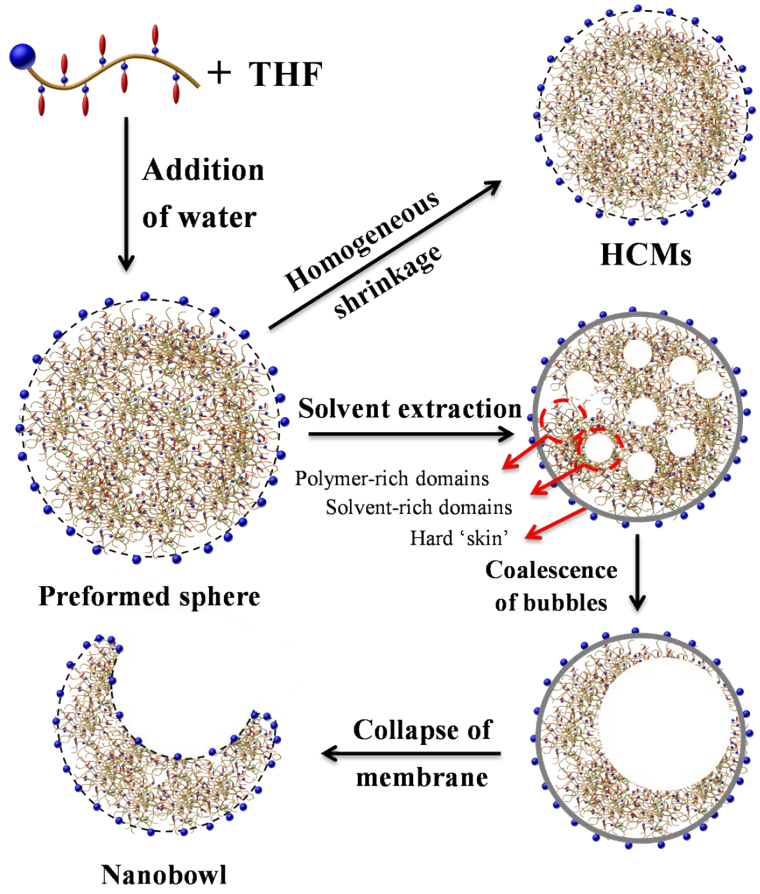


Fig. S12. Formation mechanism of nanobowls.

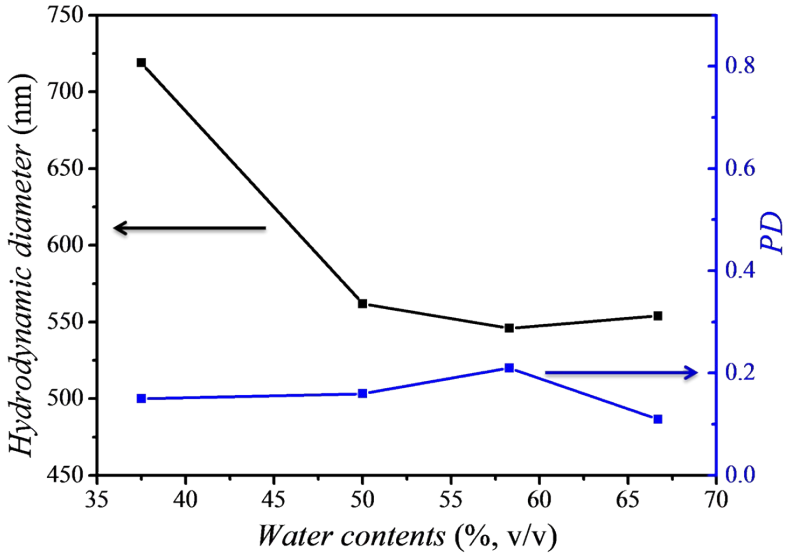


Fig. S13. DLS results of nanostructures at different water contents during self-assembly of $PHAzoMA_{226}$. The viscosity and refractive index of the mixed solvent (water/THF) was corrected by Lorentz-Lorenz equation for calculating the hydrodynamic diameter using Stokes−Einstein equation.[2]

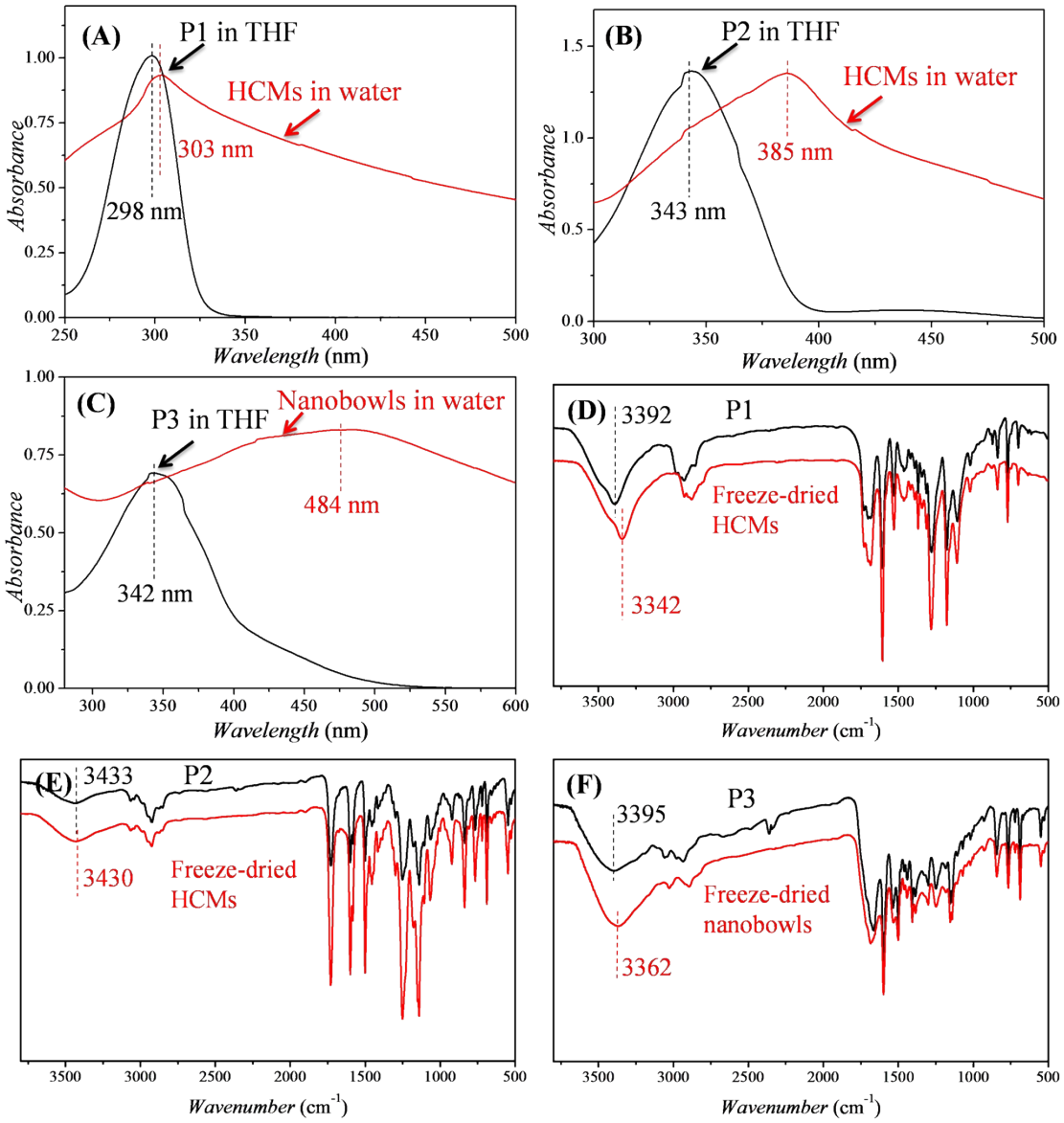


Fig. S14. UV-vis and FTIR spectra of P1, P2 and P3 homopolymers and the corresponding assemblies. (A), (B) and (C) UV-vis spectra of P1, P2 and P3 in THF and the corresponding HCMs (P1 and P2) and nanobowls (P3) in water; (D), (E) and (F) FTIR spectra of P1, P2 and P3 homopolymers (prior to self-assembly) and the corresponding freeze-dried powders of HCMs (P1 and P2) and nanobowls (P3).

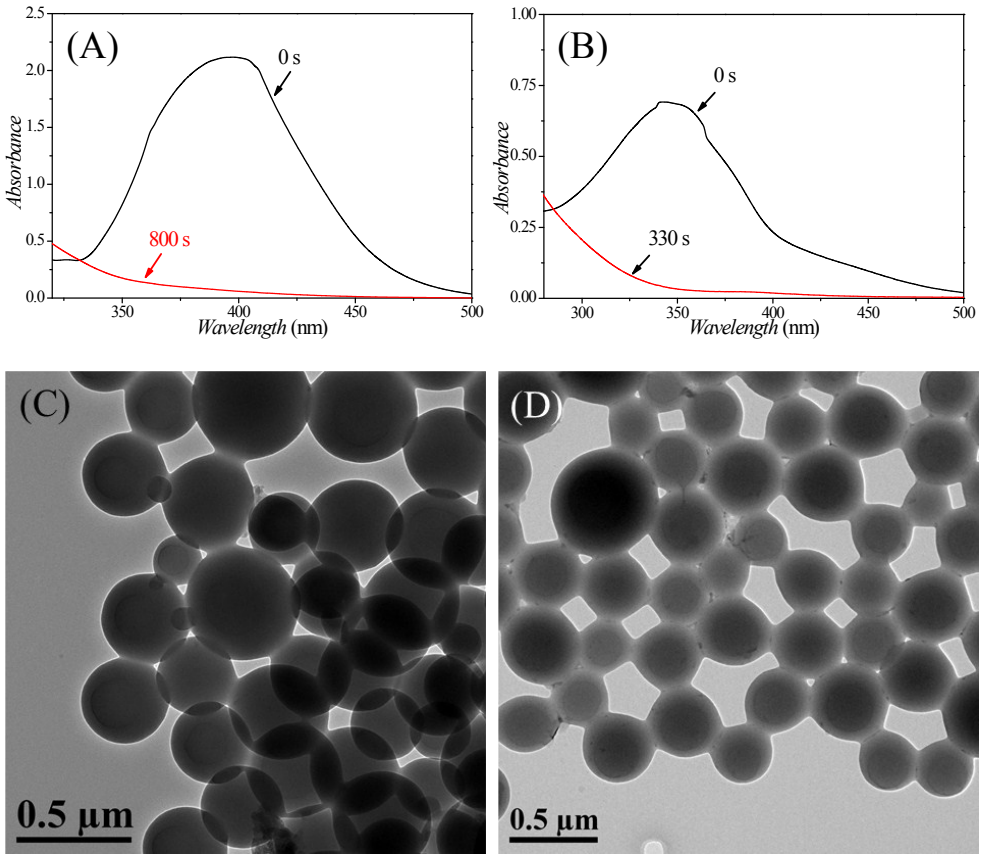


Fig. S15. (A) and (B) UV-vis spectra of $PHAzoMA_{29}$ and P3 before and after UV irradiation in THF, repectively; (B) and (D) TEM images of HCMs from $PHAzoMA_{29}$ and P3 after UV irradiation.

5. References

1. Y. Q. Zhu, L. Liu and J. Z. Du, *Macromolecules*, 2013, **46**, 194-203.
2. T. M. Aminabhavi, *J. Chem. Eng. Data*, 1984, **29**, 54-55.