Supporting Information

for

pH- and concentration-controlled self-assembly of spherical micelles with cavity, necklaces and cylindrical micelles

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1 Experimental Section

1.1 Materials

Poly (ethylene glycol) methyl ether (MPEG) with a number-average molecular weight of 2000 was purchased from Aldrich and dried in 80 °C vacuum for 24 h. Isophorone diisocyanate (IPDI, 99%), dibutyltin dilaurate (DBTDL, 99%). 2, 2-dimethylolbutyric acid (DMBA, 98%) (Aladdin) was dried in 40°C vacuum for 24h before use. Acetone dried with molecular sieves (4Å) was supplied by Shanghai Chemical Reagent Corporation (Shanghai, China). Sodium tetraborate (pH substances) was supplied by Shanghai Rex Co-perfect Instrument Co., LTD. Potassium phthalate monobasic (pH substances) were obtained from Aladdin. All other reagents were of analytical grade and used as received. The buffer solution A (pH=9.2) was prepared by solving the sodium tetraborate (pH substances) in 250 mL deionized water in the volumetric flask (250 mL). The buffer solution B (pH=4.0) was obtained by solving the sodium tetraborate (pH substances) in 250 mL deionized water in the volumetric flask (250 mL). The other buffer solutions were obtained by diluting solution A and B with deionized water and the values of the pH were determined by laboratory pH meter.

1.2 Measurements

^{1}H-NMR spectra were obtained from a JEOL JNM-ECA300 (300MHz) spectrometer with DMSO-d_6 as the solvent. The FT-IR spectra were recorded on ThermoFisher Nicolet 6700 spectrophotometer in KBr pellets. The molecular weight (Mw, GPC) and the molecular weight distribution (PDI) were measured on a HLC-8320 GPC using monodisperse polystyrene as a standard and THF as the eluent at a flow rate of 1.0 mLmin^{-1} at 40°C. Scan probe microscope (SPM) measurements were made by SHIMADZU SPM-9600 and the samples were dripped to the clean mica sucked on the plate of the spin coater (KW-4A) with the rotate speed at 3000 rpm/min to evaporate the solvents for 30 s before observation. The visualized images of the assemblies were obtained from a HITACHI-H600 Microscope with an accelerating voltage of 75 kV and the sample was stained by 0.2% phosphotungstic acid hydrate

before observation. The size distribution of the aggregates was analyzed by dynamic light scattering (DLS) measurements using a Malvern Zetasizer Nano-ZS.

1.3 Synthesis and characterization of MPEG-b-poly(IPDI-co-DMBA)-EG (MID)

The synthesis of the di-block copolymer was reported as follows (Scheme S1). 2.962g (19.59mmol) DMBA, 4.750g (21.16mmol) IPDI and 0.030g DBTDL were added to a 100ml dried flask with 50ml of anhydrous acetone. The flask was then degassed by nitrogen for 30min. The system was placed at 50°C to react for 12h with stirring under nitrogen atmosphere. After three cycles of heat dissolution and precipitation in anhydrous acetone, the solid-state prepolymer was dissolved in 20ml of tetrahydrofuran (THF). Then, 7.4ml of toluene was added to the solution of THF. The prepolymer as the precipitation could be obtained by the filtration. After another three cycles of dissolution and precipitation from the THF by toluene, the prepolymer (5.452g) was again added to another 100ml dried flask with 50ml of anhydrous acetone, followed by the addition of 3.410g (1.7mmol) of MPEG (Mn=2000) and 0.030g DBTDL. The new system was placed at 50ºC again to react for another 25h after the degasification by nitrogen for 30min. In the end, 6g anhydrous ethanol was added to the system to hold for 2h. The crude products were obtained by precipitation from the above cooled system. Then the obtained crude products were solved in tetrahydrofuran (THF, 20ml). The resultant solution was filtered to remove the precipitation by the addition of toluene (7.4ml). The final filtrate was further dried by rotary evaporation under vacuum. The desired block polymer (yield: 40%) was obtained as a white solid by precipitation from THF (20ml) to toluene (11.2ml) for three times. The di-block polymer was characterized by ^{1}H-NMR spectrum (Figure S1), FT-IR spectrum (Figure S2) and GPC (Figure S3), respectively. The contents of the IPDI and DMBA in MID could be estimated by the ^{1}H-NMR analysis and assured at 6 and 5 (SI 1), respectively. ^{1}H-NMR (300 MHz, DMSO-d_6, δ):[1] 6.80-7.30 (-O(CO)NH-CH-), 5.40-5.80 (-O(CO)NH-CH$_2$-), 2.60-2.85 (-O(CO)NH-CH_2-), 3.10-3.25 (-O(CO)NH-CH-), 3.90-4.2 (-OCH_2-), 3.25-3.45 (-CH_2CH_2O-); FT-IR (KBr):[2] ν =1714.4cm^{-1} (C=O), 1552.4cm^{-1} (NH), 1364.6cm^{-1} (C-N), 1461.8 cm^{-1} (-CH$_2$),

1116.6 cm^{-1} (C-O-C), 948.8 cm^{-1}(C-C), 869.7cm^{-1}(C-C); GPC:calcd: 4013g.mol^{-1} (Mn); found, 6140g.mol^{-1}(Mw) and 1.53 (PDI).
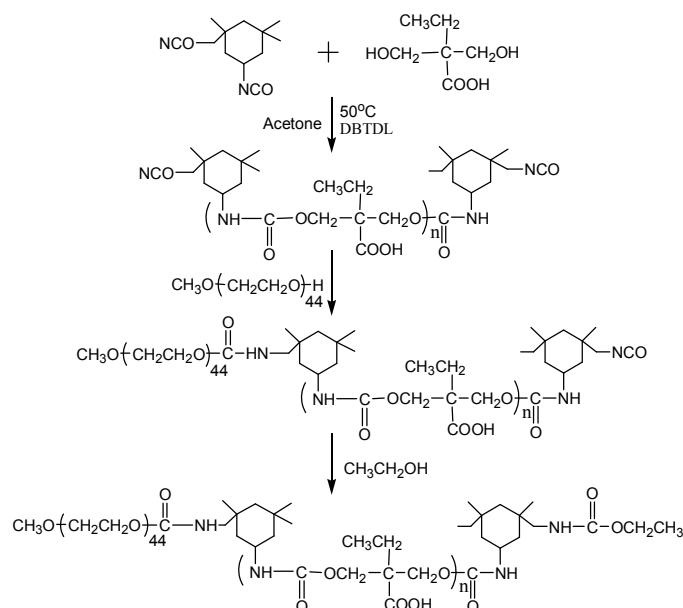
Scheme S1. Synthetic routes of the MID.

1.4 Preparation of polymer micelles

The block copolymer solutions with different polymer concentrations were prepared directly by dissolving the block copolymer in corresponding stoichiometric volumes of the aqueous solutions with pH at 9.2, 8.2, 6.8 and 4.0, respectively. The resultant solutions were vigorously stirred and agitated ultrasonically to promote dissolution, followed by standing 12 h at room temperature prior to use.

1.5 FT-IR experiments for the charateristic of the interactions between the block copolymers in the micelles.

The micellar systems with pH at 8.2, 6.8 and 4.0 were first dried for 24 h at -40 °C vacuum, respectively. Then, the obtained solid samples were charaterized by the FT-IR. Afterwards, these freeze-dried samples were dried by infared rays for 10 min again. The final products were also charaterized by the FT-IR.

2 The contents of the composites in MPEG-b-poly(IPDI-co-DMBA)- EG (MID)

The contents of the composites in the block copolymer (MID) were estimated by the ^{1}H-NMR analysis. The ratio of the IPDI to DMBA was determined by the contrast of the integral values of the peaks at δ=2.8ppm (-CH_2-NH-CO-) and δ=4.05ppm (-OCH_2-C-CH_2O-) as equation (1). The molar weight of the block connected with IPDI

and DMBA could be calculated to be 1728.3 g mol^{-1} by the equations (2), which was corresponding to the molecular weight of the prepolymer (M_n =1748 g mol^{-1}) tested by GPC. The resultant molar weight of the block copolymer estimated by the equations (3) was calculated to be 3728.3 g mol^{-1}. Meanwhile, the molar weight of the block copolymer tested by GPC was 4013 g mol^{-1}. The similar results of the molar weight of the block copolymer (MID) obtained by ^{1}H-NMR and GPC demonstrated the successful synthesis of the diblock copolymer (MID).

The content of MPEG was set at 1 in a single molecule of MID. According to the standard structures of monodisperse MPEG (Mn=2000, PDI=1.07), the molar of the group (-O-CH_2-CH_2-O-) should be fixed at 44 in the MPEG. Then the contents of the IPDI and DMBA in a single molecule of MIDM could be assured at 5 and 4, respectively.

Equation (1)

$$r = 2I_{2.8}/I_{4.05}$$

Equation (2)

$$M_{n, pre} = (222.29r + 148.16)/(r - 1)$$

Equation (3)

$$M_{n, MID} = M_{n, pre} + 2000$$

Where $I_{2.8}$=2.00 and $I_{4.05}$=3.21 were the integral values of the peaks at δ=2.8ppm (-CH_2-NH-CO-) and 4.05ppm (-OCH_2-C-CH_2O-), respectively.

3 Figures

3.1 ^{1}H-NMR for MID
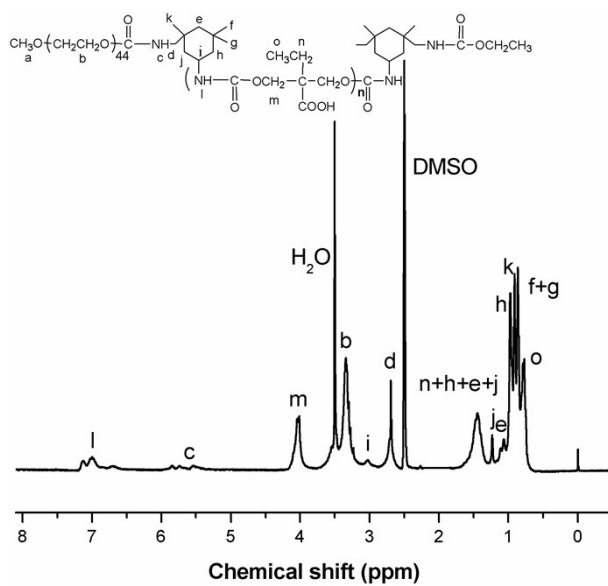
Figure S1. ^{1}H-NMR spectrum of MID in DMSO-d_6.
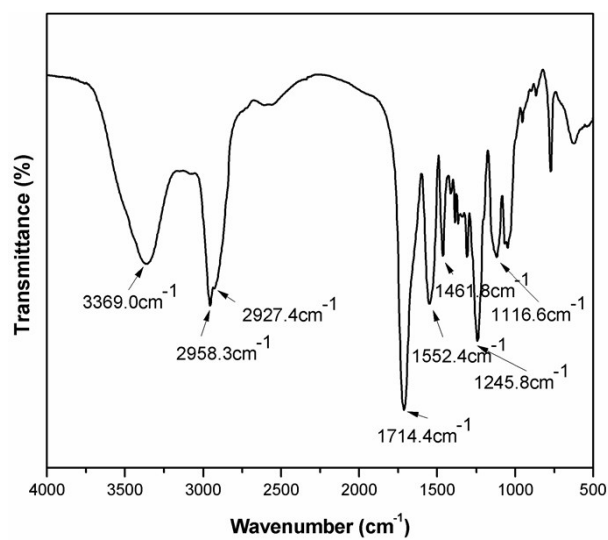
3.2 FT-IR for MID

Figure S2. FT-IR spectrum of MID from 4000cm^{-1} to 500cm^{-1}.

3.3 GPC for the diblock copolymer (MID) and the prepolymer
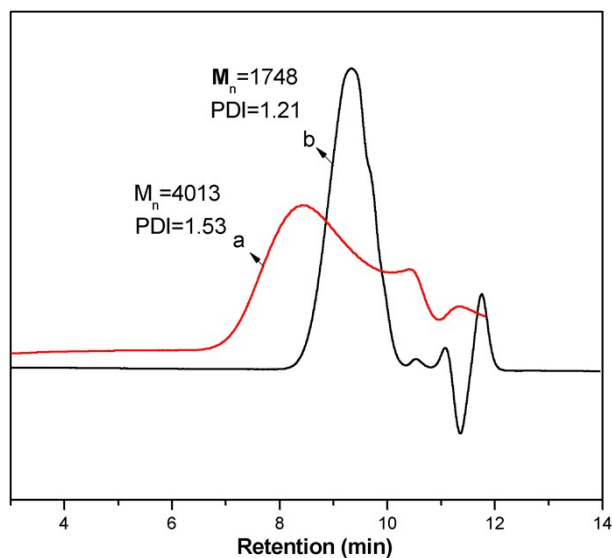
Figure S3. GPC traces of MID (a) and prepolymer (b).

3.4 The DLS results for the MID in aqueous solutions (c=1wt%) with different pH values.

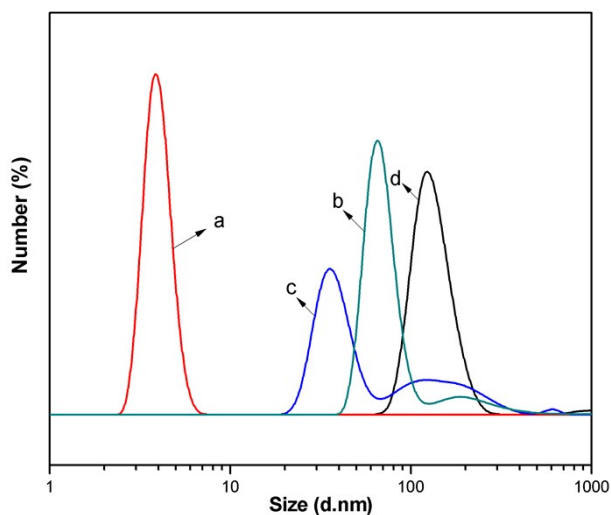Figure S4. The DLS results for the MID in aqueous solutions (c=1wt%) with different pH values: a) pH= 9.2, b) pH= 8.2, c) pH= 6.8, d) pH= 4.0.

3.5 The TEM result for the MID in the system of pH 6.8.
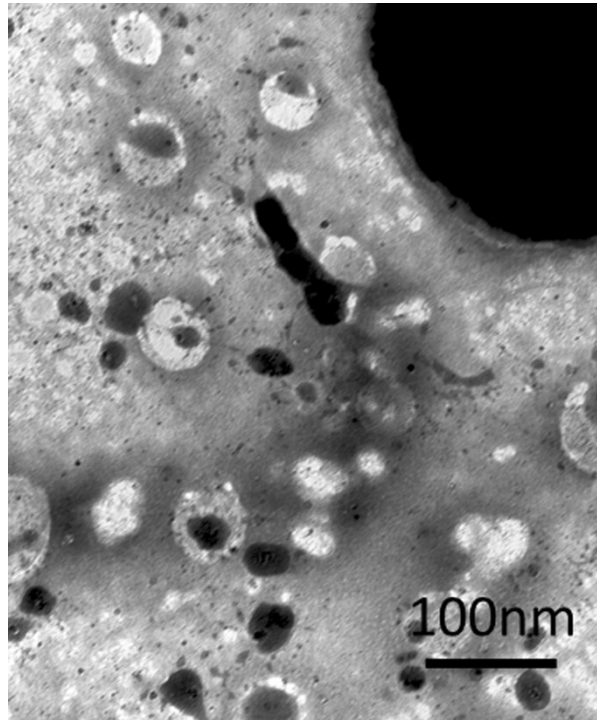
Figure S5. The TEM result for the assembled nanostructures in the system (c=1 wt%) of pH 6.8.

3.6 The SPM results for the nanoparticles assembled by the MID in the aqueous solutions with different pH values.
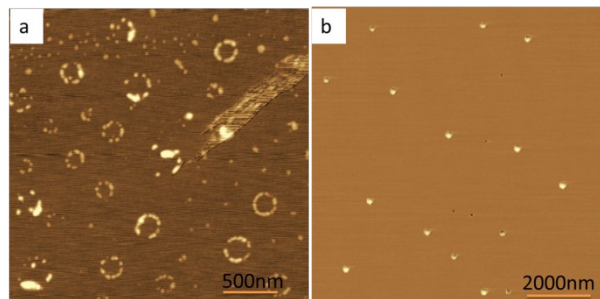
Figure S6. The SPM results for the assembled nanostructures obtained in the aqueous solutions with different pH values: a) pH=6.8; b) pH= 4.0.

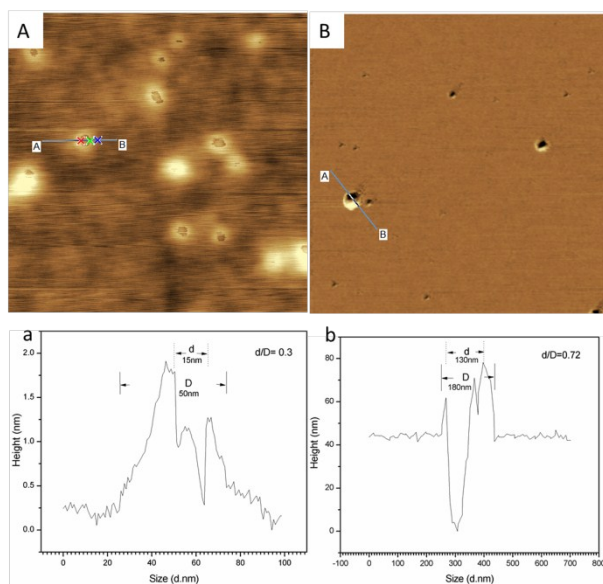## 3.7 The sizes of the assembled nanoparticles in different systems.

Figure S7. The sizes of the assembled nanoparticles obtained in the aqueous solutions with different pH values: a) pH=6.8; b) pH= 4.0.

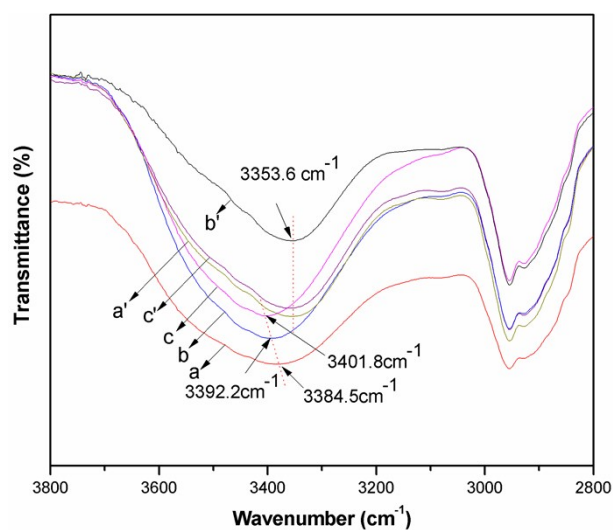## 3.8 FT-IR experiments for the charateristic of the interactions between the block copolymers in the micelles.

Figure S8A The FT-IR for the micellar systems (3800cm^{-1}-2800cm^{-1}): a) pH=8.2, freezed drying, b) pH=6.8, freezed drying, c) b) pH=4.0, freezed drying, a') pH=8.2, infared drying, b') pH=6.8, infared drying, c') pH=4.0, infared drying.
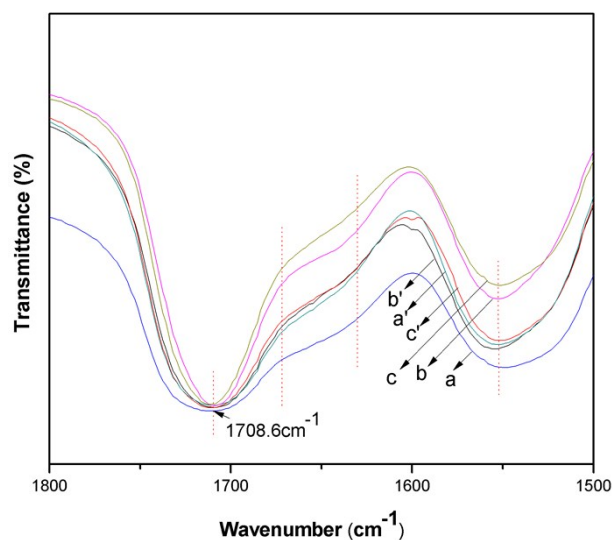
Figure S8B The FT-IR for the micellar systems (1800cm⁻¹-1500cm⁻¹): a) pH=8.2, freezed drying, b) pH=6.8, freezed drying, c) b) pH=4.0, freezed drying, a') pH=8.2, infared drying, b') pH=6.8, infared drying, c') pH=4.0, infared drying.

3.9 The TEM results for the assembled nanostructures obtained in different polymer concentrations in the systems with pH at 6.8.
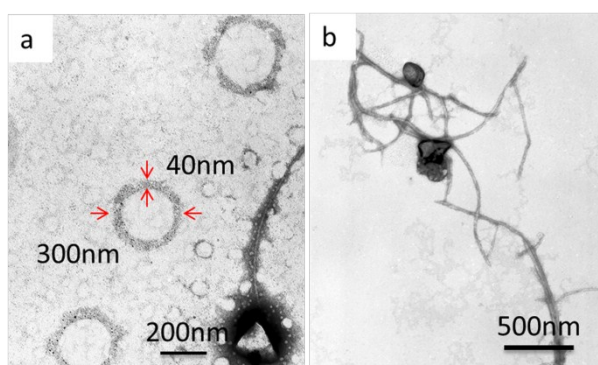

Figure S9. The TEM results for the assembled nanostructures obtained in different polymer concentrations in the systems of pH at 6.8: a) c=1 wt%; b) c=2 wt%.

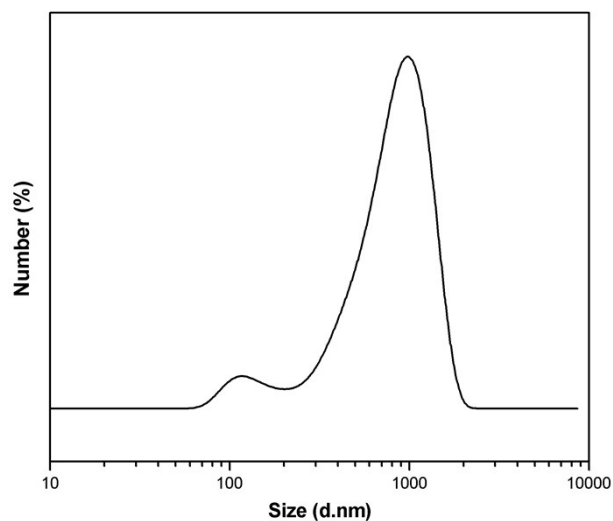**3.10   The DLS result for the MID in aqueous solution (c=2 wt%) at pH 6.8.**

Figure S10. The DLS result for the MID in aqueous solution (c=2 wt%) at pH 6.8.

References

[1] J. B. Tan, B. Wu, J. W. Yang, Y. D. Zhu, Z. H. Zeng, Polymer, 2010, 15, 3394-3401.

[2] R. P. Anji, R. Kumar, E-Journal of Chemistry, 2011, 1, 347-353.