Supporting Information for

Synthesis of multicompartment nanoparticles of ABC miktoarm star polymers by seeded RAFT dispersion polymerization

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Experimental

1 Materials

The monomers of N,N-dimethylacrylamide (DMA, 99%, Alfa), butyl methacrylate (BMA, 98%, Tianjin Chemical Company, China), and styrene (St, >98%, Tianjin Chemical Company, China) were passed through a short alkaline aluminum oxide column to remove inhibitors before Cumyl dithiobenzoate (CDB), use. S-1-dodecyl-S'-(α, α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDMAT) and 3-butynyl previously.¹⁻³ 2-bromoisobutyrate reported were synthesized as 2,2'-Azobis(2-methylpropionitrile) (AIBN, >99%, Tianjin Chemical Company, China) was recrystallized from ethanol and stored at -20 °C prior to use. Epichlorohydrin (ECH, 99%), 3-butyn-1-ol (97%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 99%), copper(I) bromide (CuBr, 98%), copper(I) chloride (CuCl, 99%), sodium azide (NaN₃, 99%) and 2-bromo-2-methylpropionyl bromide (98%) were purchased from Aldrich and used as received. Uranyl acetate was used as negative stain was from Aladdin. Toluene and tetrahydrofuran (THF) were purified by refluxing over sodium before use. Triethylamine (TEA), dichloromethane (CH₂Cl₂) and N,N-dimethylformamide (DMF) were purified by distillation under reduced pressure over CaH₂ before utilization. Deionized water was used

in the present study.

2 Characterization

¹H NMR spectra were collected at room temperature on a Bruker Avance III 400 MHz NMR spectrometer using CDCl₃ as the solvent. Gel permeation chromatography (GPC) analysis was conducted on a waters 600E GPC system equipped with three TSK-GEL columns and a 2414 refractive index detector, in which polystyrene standards with narrow distribution were used as calibration and THF containing 2% of triethylamine was acted as the eluent at a flow rate of 0.6 mL min⁻¹ at 40 °C. DSC analysis was performed on a Mettler-Toledo DSC1 differential scanning calorimeter under the nitrogen atmosphere. About 3-5 mg of the polymer was encapsulated in an aluminum pans and then was heated from 0 to 150 $\,^{\circ}$ at a heating/cooling rate of 10 $\,^{\circ}$ min⁻¹. Transmission electron microscopy (TEM) images were recorded on a Tecnai G² F20 electron microscope at 200 kV. For TEM sample preparation, a small drop of diluted colloid dispersion was placed onto the carbon-coated copper grid and dried at room temperature. This process was repeated for three times. To improve the quality of TEM images, the nanoparticles were stained by uranyl acetate (UA, 1%) solution at some cases. All there samples were air-dried at room temperature before observation. Dynamic light scattering (DLS) was performed on a NanoBrook Omni (Brookhaven) laser light scattering spectrometer with He-Ne laser at the wavelength of 633 nm at 90° angle, in which the hydrodynamic diameter (D_h) of the polymer nanoparticles was determined by intensity following the CONTIN method. The conductivities of emulsions were measured using the identical Digital Conductivity Meter (Dapu Instruments Corp., Shanghai). Interfacial tension was measured by a Dataphysics OCA20 via drop shape analysis using the pendent drop method. A drop of polymer nanoparticles aqueous solution (0.10 wt%) was slowly formed in n-hexane via a needle. The shape of the droplet, which formed at the needle tip, was captured by a CCD camera. The interfacial tension can be solved from the Laplace-Young equation and hydrostatic calculations.

3 Synthesis of PDMA-TTC-N₃

PDMA containing functional moieties of trithiocarbonate (TTC) and azido group,

PDMA-TTC-N₃, was synthesized by solution RAFT polymerization and five post-functionalization steps including (1) synthesis of PDMA by RAFT polymerization of DMA in toluene using CDB as chain transfer agent (CTA), (2) synthesis of sulfhydryl terminated PDMA (PDMA-SH) through hydrazinolysis of the RAFT terminal, (3) synthesis of epoxide terminated PDMA (PDMA-epoxy), (4) synthesis of PDMA containing functional moieties of hydroxyl and azido group (PDMA-OH-N₃) and (5) synthesis of PDMA-TTC-N₃ by esterification reaction of the hydroxyl group in PDMA-OH-N₃ with the carboxyl group in DDMAT.

PDMA was synthesized by solution RAFT polymerization. Herein, a typical RAFT polymerization using CDB as chain transfer agent (CTA) under [DMA]₀:[CDB]₀:[AIBN]₀ = 300:2.5:1 with the monomer concentration of 50 *wt*% was introduced. Typically, DMA (10.0 g, 0.101 mol), CDB (0.229 g, 0.841 mmol), AIBN (0.055 g, 0.336 mmol), the internal standard of 1, 3, 5-trioxane (0.909 g, 0.010 mol) and toluene (10.0 g) were added into a 50 ml Schlenk flask with a magnetic bar. The mixture solution was initially deoxygenated at 0 °C, and then the polymerization was performed at 60 °C for 12 h. The polymerization was quenched by rapid cooling upon immersion of the flask in iced water. The monomer conversion at 83.2% was determined by ¹H NMR analysis by comparing the integral areas of the monomer protons of C=C-*H* at δ = 5.67 ppm with those of the 1,3,5-trioxane internal standard at δ = 5.10 ppm. The synthesized PDMA was precipitated into excess cold diethyl ether three times, and then dried under vacuum at room temperature overnight to afford the pink powder of the dithiobenzoate terminated PDMA₁₀₀.

PDMA-SH was synthesized by hydrazinolysis of the RAFT terminal. Typically, in a round-bottom flask with a magnetic bar, the dithiobenzoate terminated PDMA₁₀₀ (8.0 g) was dissolved in ethanol (500 ml) under magnetic stirring, and then hydrazine (3.0 ml, 80 wt%) was added dropwise into the solution. The hydrazinolysis reaction started immediately as indicated by the rapid fading of the pink color of the solution. After stirring for 2 h at room temperature under nitrogen atmosphere, the solution was concentrated and precipitated in excess cold diethyl ether. The PDMA₁₀₀-SH was dried under vacuum at room temperature overnight for the next use. Figure S1 shows the ¹H NMR spectra of PDMA₁₀₀ and PDMA₁₀₀-SH.



Figure S1. The detailed ¹H NMR spectra of PDMA₁₀₀ and PDMA₁₀₀-SH demonstrating the complete removal of the dithiobenzoate terminal by hydrazinolysis.

PDMA-epoxy was synthesized as follows: Briefly, PDMA₁₀₀-SH (7.5 g, 0.745 mmol) was dissolved into 100 mL anhydrous CH₂Cl₂, to which NaH (89.4 mg, 3.726 mmol) was added. The mixture was stirred at room temperature for about 4 h before epichlorohydrin (0.3 mL, 3.726 mmol) being added. After stirring at room temperature for another 24 h, the mixture was filtered and the filtrate was concentrated and then precipitated into cold diethyl ether. The product was dried under vacuum at room temperature. The FT-IR spectra PDMA-epoxy are shown in Figure S2.



Figure S2. FT-IR spectra of PDMA₁₀₀-OH-N₃ (bottom) and PDMA₁₀₀-epoxide (top).

PDMA-OH-N₃ was prepared by the ring-opening reaction of PDMA-epoxy with NaN₃. Typically, PDMA₁₀₀-epoxy (7.0 g, 0.692 mmol), NaN₃ (0.450 g, 6.917 mmol), NH₄Cl (0.370 g, 6.917 mmol) and DMF (50 mL) were added into a 250 ml round-bottled flask, and the mixture was stirred at 50 °C for 48 h, and then filtration to remove the insoluble salts. After removing the solvent on a rotary evaporator, the obtained solid was dissolved in 10 ml CH₂Cl₂, followed by precipitation into cold diethyl ether, filtered and dried under vacuum overnight, PDMA₁₀₀-OH-N₃ was obtained as a white powder. The FTIR spectra PDMA-OH-N₃ are shown in Figure S2.

PDMA-TTC-N₃ was synthesized by esterification reaction of the hydroxyl group in PDMA-OH-N₃ with the carboxyl group in DDMAT. Briefly, DDMAT (0.467 g, 1.280 mmol) and CH₂Cl₂ (20.0 mL) were added into a 100 ml flask, and then (COCl)₂ (0.541 mL, 6.396 mmol) dissolved in CH₂Cl₂ (10.0 mL) was subsequently added dropwise over 10 min under nitrogen atmosphere. The mixture was stirred under a nitrogen atmosphere at 25 °C for 2 h. The solvent and excess (COCl)₂ were removed by rotary evaporation. PDMA₁₀₀-OH-N₃ (6.5 g, 0.640 mmol) in CH₂Cl₂ (40.0 mL) was added into the flask and the reaction was carried out at 25 °C for 24 h with magnetic stirring under a nitrogen atmosphere. The solution was concentrated and then precipitated into cold diethyl ether. The product was collected and dried in a vacuum oven at room temperature. ¹H NMR and GPC were used to characterize the molecular structure and the molecular weight of PDMA₁₀₀-TTC-N₃ with $M_{n,NMR} = 10.6$ kg/mol, $M_{n, GPC} = 10.2$ kg/mol and D = 1.12.





Figure S3. ¹H NMR spectra (A), GPC traces (B) and FT-IR spectra (C) of PDMA₁₀₀, PDMA₁₀₀-SH, PDMA₁₀₀-epoxide, PDMA₁₀₀-OH-N₃ and PDMA₁₀₀-TTC-N₃.

The ¹H NMR spectra, GPC traces and FT-IR spectra of PDMA₁₀₀-TTC-N₃ and its precursors are shown in Figure S3.

4 Synthesis of *α*-alkynyl-PBMA (PBMA-C≡CH)

PBMA-C≡CH was synthesized by ATRP polymerization of BMA using 3-butynyl 2-bromoisobutyrate as initiator and CuCl/PMDETA as catalyst, respectively. In a typical run, 3-butynyl 2-bromoisobutyrate (0.154 g, 0.703 mmol), BMA (20.0 g, 0.141 mol), CuCl (34.8 mg, 0.352 mmol), PMDETA (60.9 mg, 0.352 mmol) and acetone (20 mL) were added

into a 100 ml Schlenk flask. After three freeze-pump-thaw cycles, the reaction mixture was placed into a 50 °C thermostatic oil bath. ¹H NMR indicated 50.2% monomer conversion in 10 h. The reaction mixture was quenched by liquid nitrogen and diluted with CH₂Cl₂, and then passed through a column of alkaline aluminum oxide to remove copper salts. After being concentrated by rotary evaporation, the residue was precipitated into cold methanol to obtain the PBMA₁₀₀-C=CH with $M_{n, NMR} = 15.2 \text{ kg/mol}$, $M_{n, GPC} = 19.2 \text{ kg/mol}$, and D = 1.06. The ¹H NMR spectrum of PBMA₁₀₀-C=CH and GPC trace of PBMA₁₀₀-C=CH are shown in Figure S4.



Figure S4. (A) ¹H NMR spectrum of PBMA₁₀₀-C=CH in CDCl₃; (B) GPC trace of PBMA₁₀₀-C=CH.

5 Synthesis of DB diblock copolymer

DB diblock copolymer was synthesized by click reaction of PDMA-TTC-N₃ and PBMA₁₀₀-C=CH. Briefly, PDMA₁₀₀-TTC-N₃ (2.0 g, 0.190 mmol of azide moieties), PBMA₁₀₀-C=CH (3.3 g, 0.228 mmol of alkynyl moieties), CuBr (32.8 mg, 0.228 mmol), PMDETA (47.7 μ L, 0.228 mmol) and diethylamine (16.7 mg, 0.228 mmol) were dissolved into 50 mL THF. The mixture was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 48 h. After passing through a column of neutral aluminum oxide to remove copper salts, the solution was concentrated and precipitated into *n*-hexane and water successively to remove the unreacted PBMA and PDMA. After purification, ¹H NMR and GPC (Figure S5) were used to characterize the molecular structure and the molecular

weight of $D_{100}B_{100}$ with $M_{n,NMR} = 26.7$ kg/mol, $M_{n, GPC} = 28.2$ kg/mol and D = 1.07.



Figure S5. (A) ¹H NMR spectrum of $D_{100}B_{100}$ in CDCl₃; (B) FT-IR spectrum of PDMA₁₀₀-TTC-N₃ (bottom) and $D_{100}B_{100}$ (top). The azide peak (2106 cm⁻¹) disappears and a new C=O peak (1731 cm⁻¹) appears after the Cu(I)-catalyzed click reaction, which confirms the formation of $D_{100}B_{100}$.

6 Preparation of DB micelles

The DB micelles were prepared by dispersed DB in the 80/20 ethanol/water at 10 *wt*% concentration of DB with the help of ultrasonic. Typically, into a 25 mL Schlenk tube with a magnetic bar, the $D_{100}B_{100}$ diblock copolymer (0.80 g, 0.032 mmol) and the ethanol/water mixture (7.2 g, 80/20 by weight) were added, and then the mixture was dispersed by an ultrasonic bath (SC-40, Sonicor, Copiaque, NY) for 30 min to form $D_{100}B_{100}$ micelles with 10 *wt*% concentration. Figures S6 and S7 show the D_h of DB nanoparticles by DLS and the TEM images of the DB nanoparticles.



Figure S6. D_h of DB nanoparticles (0.10 *wt*%) with different DP of B (PBMA) in 80/20 ethanol/water mixture at 15 °C.



Figure S7. SEM images of the DB micelles with different DP of B blocks.

7 Synthesis of μ -DBS nanoparticles

The μ -DBS nanoparticles were synthesized by seeded RAFT dispersion polymerization of styrene in the 80/20 ethanol/water at 10 *wt*% concentration. Herein, a typical synthesis of μ -D₁₀₀B₁₀₀S₉₀ nanoparticles under [St]₀:[D₁₀₀B₁₀₀]₀:[AIBN]₀ = 300:3:1 is introduced. Into a 25 mL Schlenk tube with a magnetic bar, the prepared dispersion of the D₁₀₀B₁₀₀ micelles (8.0 g, 10 *wt*%, 0.032 mmol) was added. Then, the monomer of St (0.334 g, 3.20 mmol) was added, and the mixture was vigorous stirred for 30 min. Subsequently, AIBN (1.8 mg, 0.011 mmol) dissolved in the 80/20 ethanol/water mixture (2.82 g) was added. After nitrogen purging for 20 min, the Schlenk tube was immersed into preheated oil bath at 70 °C with vigorous stirring. After 24 h, polymerization was quenched by immersing the flask in iced water, and the colloidal dispersion of μ -D₁₀₀B₁₀₀S₉₀ nanoparticles was obtained. The 89.6% monomer conversion was identified by ¹H NMR analysis. The colloidal dispersion was dialyzed against ethanol to remove the residual styrene monomer (cutoff 50000 Da) and dialyzed against water to make aqueous dispersion of μ -D₁₀₀B₁₀₀S₉₀ nanoparticles for the next use.

8 Synthesis of the reference D₁₀₀S₂₀₀ nanoparticles via PISA

To synthesize the reference $D_{100}S_{200}$ nanoparticles, AIBN (1.15 mg, 0.007 mmol), the dithiobenzoate terminated PDMA₁₀₀ (0.215 g, 0.020 mmol), styrene (0.6 g, 5.75 mmol) in the 80/20 ethanol/water mixture (6.43 g) were mixed in a 20 ml round-bottom flask equipped with a Teflon stirring bar. The mixture was degassed by three freeze-pump-thaw cycles. Subsequently, the reaction vessel was submerged into a preheated, stirring oil bath

maintained at 70 °C. After 24 hours, the reaction was quenched by immediately placing the flask into ice water and opening it to air. The colloidal dispersion of $D_{100}S_{200}$ nanoparticles was obtained. The 69.8% monomer conversion was identified by ¹H NMR analysis. Polymer characterization: $M_{n, NMR} = 16.7$ kg/mol, $M_{n, GPC} = 18.2$ kg/mol, D = 1.07.



Scheme S1. Synthesis of $D_{100}S_{200}$ nanoparticles.



Figure S8. TEM image of the reference $D_{100}S_{200}$ nanoparticles.

Scheme S1 shows the synthesis of the $D_{100}S_{200}$ nanoparticles via PISA and Figure S8 shows the TEM iamges of $D_{100}S_{200}$ nanoparticles.

9 Characterization of μ -DBS nanoparticles

Entry	Sample	M _n /kDa			- Dd
		$M_{n,th}^{a}$	$M_{n,NMR}^{b}$	$M_{n,GPC}^{c}$	- <i>D</i> -
1	PDMA ₅₀ -TTC-N ₃	5.6	5.7	5.5	1.17
2	PDMA ₁₀₀ -TTC-N ₃	10.5	10.6	10.2	1.12
3	PDMA ₁₅₀ -TTC-N ₃	15.5	15.8	14.8	1.12
4	PBMA ₅₀ -C≡CH	7.3	8.4	12.8	1.05
5	PBMA ₁₀₀ -C≡CH	14.4	15.2	19.2	1.06
6	PBMA ₁₅₀ -C≡CH	21.5	22.5	27.3	1.05
7	$D_{50}B_{100}$	20.0	21.8	24.6	1.07
8	$D_{100}B_{50}$	17.8	20.1	21.5	1.09
9	$D_{100}B_{100}$	24.9	26.7	28.2	1.07
10	$D_{100}B_{150}$	32.0	34.5	37.4	1.05
11	μ -D ₅₀ B ₁₀₀ S ₂₅₀	46.0	56.9	62.6	1.59
12	μ -D ₁₀₀ B ₁₀₀ S ₉₀	34.3	39.7	42.3	1.57
13	μ -D ₁₀₀ B ₁₀₀ S ₂₂₀	47.8	46.5	64.2	1.35
14	μ -D ₁₀₀ B ₁₀₀ S ₃₄₀	60.3	59.1	75.6	1.48
15	μ -D ₁₀₀ B ₅₀ S ₂₅₀	43.8	58.4	69.7	1.44
16	μ -D ₁₀₀ B ₁₅₀ S ₂₂₀	54.9	64.5	72.4	1.56
17	$D_{100}S_{200}$	32.0	33.4	36.4	1.07

Table S1. Summary of the molecular weights of PDMA-TTC-N₃, PBMA₁₀₀-C≡CH, DB and μ -DBS.

^{*a*} Theoretical molecular weight determined by monomer conversion. ^{*b*} The molecular weight determined by GPC in THF with calibrated PS standards. ^{*c*} The molecular weight determined by ¹H NMR analysis.

^d $D = M_w/M_n$ determined by GPC analysis.

$$M_{n, th} = \frac{[\text{monomer}]_0 \times M_{\text{monomer}}}{[\text{RAFT}]_0} \times conversion + M_{RAFT} \quad (eq. S1)$$



Figure S9. ¹H NMR spectra of PDMA₁₀₀-TTC-N₃, PBMA₁₀₀-C=CH, D₁₀₀B₁₀₀ and μ -D₁₀₀B₁₀₀S₉₀.



Figure S10. GPC traces of PDMA₁₀₀-TTC-N₃, PBMA₁₀₀-C=CH, $D_{100}B_{100}$ and μ -D₁₀₀B₁₀₀S₉₀.



Figure S11. DSC thermograms of PBMA₁₀₀-C=CH, PS₁₀₀-TTC, PDMA₁₀₀-TTC-N₃, $D_{100}B_{100}$ and μ -D₁₀₀B₁₀₀S₉₀ under nitrogen at a heating rate of 10 °C/min in the range of 0 to 150 °C.



Figure S12. ¹H NMR spectrum of μ -D₁₀₀B₁₀₀S₉₀ nanoparticles dispersed in D₂O, in which the hydrophilic PS and PBMA blocks are almost undetectable.



Figure S13. TEM images of μ -DBS nanoparticles stained with uranyl acetate.

Entry	Sample	Interfacial and Surface Tension ^a (mN m ⁻¹)			
Entry		<i>n</i> -hexane/water ^b	air/water ^c		
1	μ -D ₅₀ B ₁₀₀ S ₂₅₀	28.44	67.46		
2	μ -D ₅₀ B ₁₀₀ S ₂₅₀	17.21 ^{<i>d</i>}	67.46		
3	μ -D ₁₀₀ B ₁₀₀ S ₉₀	24.02	66.13		
4	μ -D ₁₀₀ B ₁₀₀ S ₂₂₀	23.68	66.60		
5	μ -D ₁₀₀ B ₁₀₀ S ₃₄₀	24.01	67.05		
6	μ -D ₁₀₀ B ₅₀ S ₂₅₀	28.03	66.87		
7	μ -D ₁₀₀ B ₁₅₀ S ₂₂₀	20.43	66.79		

Table S2. The effects of different arm lengths of μ -DBS miktoarm star polymer on interfacial and surface tension.

^a The interfacial and surface tensions in the presence of 0.10 wt% aqueous solution of μ -DBS nanoparticles at 15 °C by the pendant drop method at pH 7. ^{*b*} *n*-hexane was used as the organic phase in the interfacial tension measurement.

^c Surface intension was measured in the air/water interphase.

^d PhMe was used as the organic phase in the interfacial tension measurement.



Figure S14. Typical pendant drop (digitized image) of emulsion containing μ -D₁₀₀B₁₀₀S₉₀ nanoparticles immersed in *n*-hexane at 15 °C.



Figure S15. $D_{\rm h}$ of 0.10 *wt*% nanoparticles of (A) μ -D₁₀₀B₅₀S₂₅₀, μ -D₁₀₀B₁₀₀S₂₂₀, μ -D₁₀₀B₁₅₀S₂₂₀ and (B) μ -D₁₀₀B₁₀₀S₉₀, μ -D₁₀₀B₁₀₀S₂₂₀, μ -D₁₀₀B₁₀₀S₃₄₀ in the 80/20 ethanol/water mixture.



Figure S16. (A) D_h of μ -D₅₀B₁₀₀S₂₅₀ and μ -D₁₀₀B₁₀₀S₂₂₀ nanoparticles with 0.10 *wt*% aqueous solution, and (B) the average nanoparticle diameter *D* measured by TEM and D_h by DLS of μ -D₅₀B₁₀₀S₂₅₀ and μ -D₁₀₀B₁₀₀S₂₂₀ nanoparticles and the interfacial tension (IFT) in *n*-hexane/water.



The particle size decreases with the DP of B

The particle size increases with the DP of S



The particle size increases with the DP of D



Figure S17. TEM images of the μ -DBS nanoparticles with different DP of D, B and S.



The particle size decreases with the DP of B

The particle size increases with the DP of S



The particle size increases with the DP of D



Figure S18. SEM images of the μ -DBS nanoparticles with different DP of D, B and S.

References

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