Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Customizable nano-sized colloidal tetrahedrons by polymerization-induced particle self-assembly (PIPA)

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Experimental Section

1. Materials

N,N-dimethylaminoethyl methacrylate (DMA, 99%, TCI), benzyl methacrylate (BzMA, 98%, TCI), 2-hydroxypropyl methacrylate (HPMA, 97%, TCI), diactone acrylamide (DAAm, 98%, TCI) and 2-(perfluorobutyl)ethyl methacrylate (FBEMA, J&K, 99%) were purified by passing through a basic alumina oxide column to remove the inhibitors prior to use. 2,2-Azobisisobutyronitrile (AIBN, J&K, 99%) was recrystallized in ethanol and stored at -20 ˚C. 4,4'-Azobis(4-cyanopentanoic acid) (ACVA, J&K, 98%) was used as received. Ruthenium (VIII) oxide (RuO_4) (0.5 wt% aqueous solution) was purchased from J&K. Phosphotungstic acid (PTA) (analytical grade, Beijing Chemical Co.) was dissolved in water for 0.5 % solution. Uranyl acetate (analytical grade, Beijing Chemical Co.) was dissolved in water for 0.2 % solution. 4-(4-Cyanopentanoic acid) dithiobenzoate (CPADB) was synthesized accordingly.[1]

2. Synthesis of PDMA macro-CTA.

PDMA macro-CTA was synthesized via RAFT polymerization. Briefly, PDMA macro-CTA was synthesized by RAFT polymerization of DMA (210.0 mmol, 33.0 g) using CPADB (3.0 mmol, 838.1 mg) as the RAFT agent and AIBN (0.5 mmol, 82.1 mg) as the initiator. The mixture was stirred at 70 ^{o}C for 5 h, concentrated under reduced pressure, and precipitated in diethyl ether. After drying, PDMA macro-CTA was collected. $PDMA_{70}$ macro-CTA (DP = 70, $M_{n,NMR}$ = 11.0 kDa, $M_{n,SEC}$ = 9.3 kDa, $Đ$ = 1.23) was determined by ^{1}H NMR and SEC measurements.

3. Syntheses of PDMA$_{70}$-*b*-PbzMA$_{x}$ spherical colloids.

A series of $PDMA_{70}$-*b*-$PBzMA_x$ were prepared via RAFT polymerization of BzMA in the solution in ethanol (15%). A typical procedure to synthesize $PDMA_{70}$-*b*-$PBzMA_{96}$ was given. AIBN (0.04 mmol, 6.6 mg), $PDMA_{70}$ macro-CTA (0.1 mmol, 1.10 g) and BzMA (10.0 mmol, 1.76 g) were dissolved in ethanol (16.5 mL). The mixture was bubbled with argon for 25 min, then stirred at 70 °C for 12 h. After quenching the polymerization in ice water, the dispersion was dialyzed against ethanol to remove residual monomers. After totally drying by evaporation, solid content of the dispersion was measured 14.4 wt%.

4. Syntheses of PDMA$_{70}$-*b*-PBzMA$_x$-*b*-PHPMA$_y$ CTs.

A series of PDMA$_{70}$-*b*-PBzMA$_x$-*b*-PHPMA$_y$ colloidal molecules were prepared via RAFT polymerization of HPMA at 10 wt% solids concentrations in water. A typical procedure to synthesize PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{258}$ was given. PDMA$_{70}$-*b*-PBzMA$_{96}$ seed aqueous dispersion (2.00 mL, 14.4 wt% solids concentration, dialyzing against water to remove ethanol), HCl (6 mol/L, 0.30 mL, adjusting the solution pH = 2), ACVA (3.26 μmol, 0.91 mg) and HPMA (4.08 mmol, 587.6 mg) were dissolved in water in a 50 mL Schlenk tube. The mixture (ca. 10 wt% solids content) was bubbled with argon for 25 min, then stirred at 70 °C. The polymerizations were quenched at desired monomer conversion. After quenching the polymerization in ice water, the dispersion was dialyzed against water to remove residual monomers. A portion of the dispersions was dried under vacuum for ^{1}H NMR and SEC characterizations.

5. Syntheses of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PDAAm$_{114}$ CTs.

PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PDAAm$_{114}$ CTs were prepared via RAFT polymerization of DAAm at 5 wt% solids concentration in water. PDMA$_{70}$-*b*-PBzMA$_{96}$ seed aqueous dispersion (2.00 mL, 14.4 wt% solids concentration, dialyzing against water to remove ethanol), HCl (6 mol/L, 0.30 mL, adjusting the solution pH = 2), ACVA (3.26 μmol, 0.91 mg) and DAAm (1.64 mmol, 277.1 mg) were dissolved in water in a 25 mL Schlenk tube. The mixture (ca. 5 wt% solids content) was bubbled with argon for 25 min, then stirred at 70 °C. After quenching the polymerization in ice water, the dispersion was dialyzed against ethanol to remove residual monomers. The polymerization of 2HBA, 4HBA, DEGA, and DEGMA are conducted in similar procedures.

6. Syntheses of PDMA$_{82}$-*b*-PTFEMA$_{227}$-*b*-PBzMA$_{1000}$ CTs.

PDMA$_{82}$-*b*-PFBEMA$_{227}$-*b*-PBzMA$_{1000}$ CTs were prepared via RAFT polymerization of BzMA at 5 wt% solids concentrations in ethanol. PDMA$_{82}$-*b*-PFBEMA$_{227}$ seeds ethanol dispersion (1.00 mL, 13.8 wt% solids concentration), AIBN (1.22 μmol, 0.20 mg) and BzMA (1.33 mmol, 234.4

mg) were dissolved in ethanol in a 25 mL Schlenk tube. The mixture (ca. 5 wt% solids content) was bubbled with argon for 25 min, then stirred at 70 °C. The polymerizations were quenched at desired monomer conversion. After quenching the polymerization, the dispersion was dialyzed against ethanol to remove residual monomers.

Characterization

^{1}H Nuclear Magnetic Resonance (^{1}H NMR): All the ^{1}H NMR spectra were recorded on 400 MHz JEOL JNM-EA 400 spectrometer using DMSO-d_6 or $CDCl_3$ as the solvent.

Size-Exclusion Chromatography (SEC): SEC (DMF as eluent) The number average molecular weights (M_n) and polydispersity index ($Đ$) of the polymers were characterized using Shimadzu LC-20AD GPC system equipped with a Shimadzu RID-10A refractive index detector using *N*,*N*-dimethyl formamide (DMF) as the eluent at a flow rate of 1.0 mL/min.

SEC (THF as eluent) The number-average molecular weight (M_n) and dispersity ($Đ$) of the polymers were characterized by a Waters 1515 GPC instrument at 35 °C with THF (containing 2% trimethylamine) as the eluent with a flow rate of 1.0 mL min^{-1}. A series of narrow distribution linear polystyrene was used for SEC calibration.

Dynamic Light Scattering (DLS): DLS measurements were recorded using Malvern Zetasizer Nano ZS90 at 25 °C with a He-Ne laser (633 nm). Scattering light at 90° was detected. The dispersions were diluted at approximately 1 mg/mL for the DLS measurements.

Transmission Electron Microscope (TEM): Morphologies of the samples were observed using Hitachi H-7650B transmission electron microscope at the accelerating voltage of 80 kV. The dispersions were diluted at approximately 0.3 mg/mL. 10 μL of the diluted dispersion was dropped onto a 400-mesh carbon-coated copper grid for ambient drying. The samples onto the copper grid were further stained with PTA solution for 1 min or RuO_4 vapor for 20 min.

Scanning electron microscopy (SEM): SEM images were acquired on a Hitachi SU-8010 field emission scanning electron microscope at with an accelerating voltage of 5 kV.

Atomic force microscopy (AFM)： For AFM, a Bruker Multimode 8 scanning probe microscope was used under tapping mode to collect the height images and phase images of the samples.

Cryo-TEM: The cryo-EM specimens were prepared by FEI Vitrobot Mark IV instrument. For details, the aqueous dispersion (~5 µL) of the clusters was added onto a freshly glow-discharged holey carbon-coated copper grid. The extra liquid was blotted by filter papers and the grid was then plunged into a liquid ethane bath cooled with liquid nitrogen. The specimens were transferred into TEM under liquid nitrogen environment using a cryo holder (Gatan), and observed in a FEI Tecnai F20 electron microscope (200 kV) and at a nominal magnification of 19000X with low-dose imaging strategy. Images were recorded with a 2 K×2 K low scan CCD camera (Gatan).

Negatively-staining TEM analysis: For negative staining specimen preparation, a drop of ~ 3µL clusters sample solution was applied onto the freshly glow-discharged grid coated by continuous carbon film, and incubated for ~1 min. Afterwards, the extra solution was blotted off by filter paper from the grid edge, immediately followed by addition of 2% uranyl acetate stain. After staining for ~1 min, the extra stain solution was blotted by filter paper and air-dried. We collected 51 micrographs on FEI Tecnai Spirit TEM with an accelerating voltage of 120 kV, equipped with a Gatan US4000 (895) CCD. CTF parameters were determined by using the program Ctffind4[2, 3]. 12,518 particles were semi-automatically picked using e2boxer.py of the EMAN2[4], and then applied for 2D classification in Relion 3.0[5]. Particles grouped in good classes were selected for further reconstruction. The initial model was generated by running a "3D initial model" job in Relionn 3.0, and low-pass filtered to 100 Å as the reference for following 3D classification. Finally, 5,909 particles were left for 3D refinement, and we reconstructed the both structures with T and C1 (i.e., no symmetry) symmetry applied.

Electron tomography: During electron tomography experiments, tilt series were collected automatically from −60° to +60° at 2° intervals along the tilt axis by using the FEI tomography software. The defocus was approximately 10 µm and the magnification was set such that each CCD pixel corresponded to 1.08 nm at the specimen level. For image processing, the 2D projection images were aligned with the IMOD software package images and then tomographic reconstructions were calculated by weighted back-projection using the Priism package.

Figures, Tables and Calculations

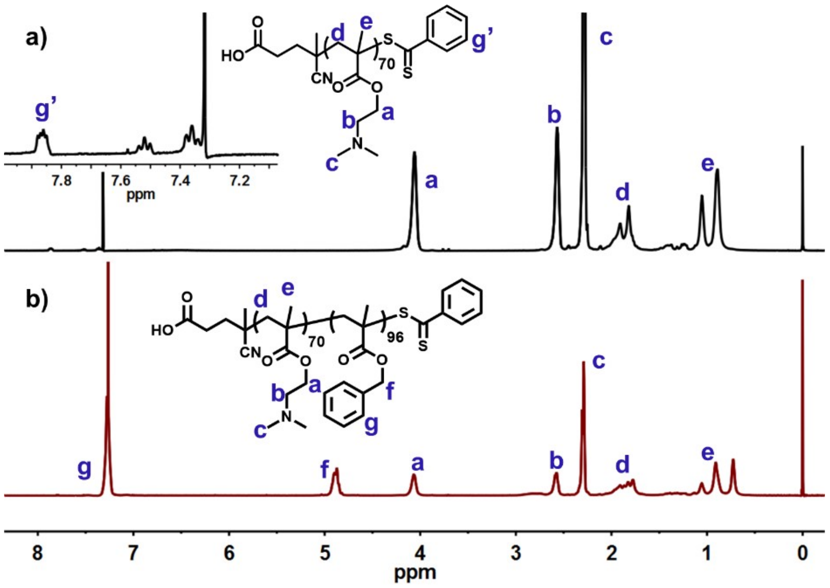

Fig. S1 Representative ^{1}H NMR spectra of: (a) PDMA$_{70}$ macro-CTA; (b) PDMA$_{70}$-*b*-PBzMA$_{96}$ diblock copolymer in CDCl$_3$ at 25 ^{o}C. DPs of PDMA macro-CTA and PBzMA were calculated via comparing the integral area (I_i) ratio of peak a, f and g', as

$$DP_{PDMA} = \frac{I_a}{I_{g'}}$$

$$DP_{PBzMA} = \frac{I_f}{I_a} \times DP_{PDMA}$$

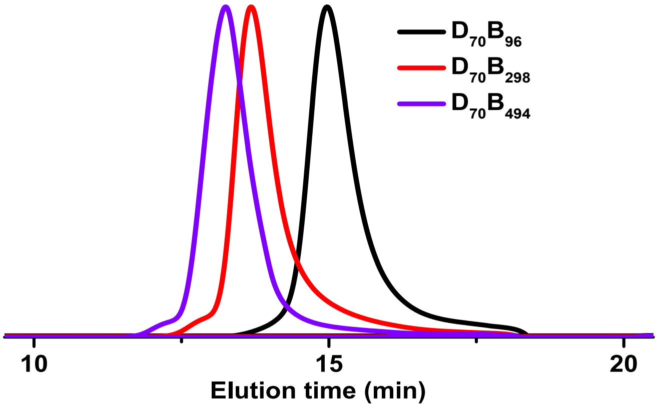

Fig. S2 SEC traces of PDMA$_{70}$-*b*-PBzMA$_x$ diblock copolymers. (DMF as eluent)

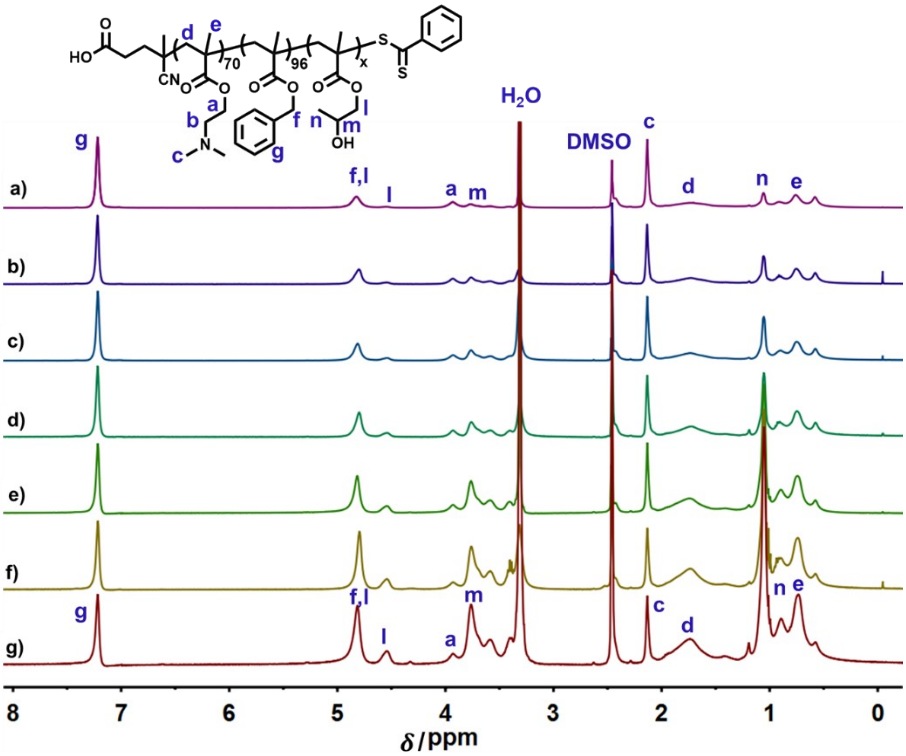

Fig. S3 Representative ^{1}H NMR spectra in DMSO-d_6 at 25 °C: (a) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{20}$; (b) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{46}$; (c) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{70}$;(d) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{109}$; (e) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{258}$; (f) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$; (g) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{456}$. DP of PHPMA was calculated via comparing the integral area (I_i) ratio of peak f, l, and g, as

$$DP_{PHPMA} = \left(\frac{I_f + I_l}{2} - \frac{I_g}{5}\right) / I_g \times DP_{PBzMA} \times 5$$

Table S1. Molecular weight of triblock terpolymer and corresponding morphologies

No.	Sample [a]	Solid content (wt%)	Time (h)	Conv. (%)[b]	SEC [c]		DLS		Morphology
					M_n (kDa)	Đ	D_h (nm)	PDI	
1	$D_{70}B_{96}$	15	12	96	22.7	1.11	31	0.06	sphere
2	$D_{70}B_{298}$	15	12	94	43.6	1.07	56	0.08	sphere
3	$D_{70}B_{494}$	15	12	99	54.8	1.17	71	0.21	sphere
4	$D_{70}B_{96}H_{20}$	5	1.5	40	34.2	1.49	35	0.05	sphere
5	$D_{70}B_{96}H_{46}$	5	1.5	46	44.7	1.52	42	0.27	sphere/AB_2
6	$D_{70}B_{96}H_{70}$	5	1.5	35	50.2	1.59	52	0.04	AB_2
7	$D_{70}B_{96}H_{109}$	5	1.5	55	51.3	1.68	56	0.26	AB_2/AB_3/AB_4
8	$D_{70}B_{96}H_{167}$	10	2	81*	54.7	1.82	66	0.06	AB_4
9	$D_{70}B_{96}H_{194}$	10	4	92*	55.8	1.87	68	0.08	AB_4
10	$D_{70}B_{96}H_{258}$	10	1.5	52	63.8	1.79	74	0.02	AB_4
11	$D_{70}B_{96}H_{319}$	5	1.5	46	65.9	1.70	92	0.27	AB_5/AB_6

12	$D_{70}B_{96}H_{456}$	5	1.5	45	80.1	2.34	100	0.02	AB_6/cluster
13	$D_{70}B_{298}H_{411}$	10	1.5	79	96.8	1.55	132	0.04	AB_4
14	$D_{70}B_{494}H_{690}$	5	1.5	51	142.2	2.52	146	0.04	AB_4

[a] Determined by ^{1}H NMR. Here, D, B and H are short for PDMA, PBzMA and PHPMA block, respectively.

[b] Measured by gravimetric method. * Measured by ^{1}H NMR.

[c] DMF as eluent, $Đ = M_w/M_n$.

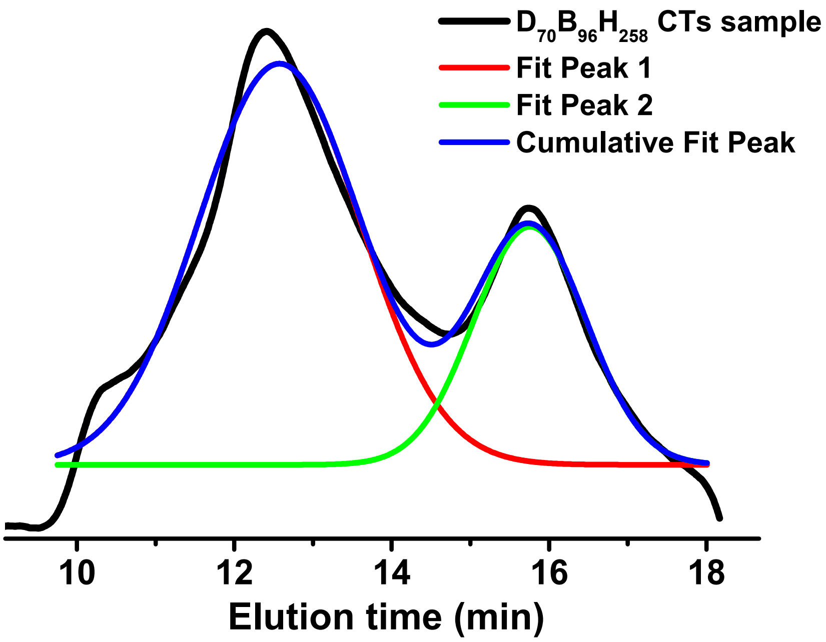

Fig. S4 SEC trace of $PDMA_{70}$-*b*-$PBzMA_{96}$-b-$PHPMA_{258}$, showing the fit peaks of PDMA-b-PBzMA-b-PHPMA triblock terpolymer and PDMA-*b*-PBzMA diblock copolymer. (DMF as eluent) High polydispersity is attributed to the relatively low block efficiency and the crosslinking of the growing PHPMA chains due to a small amount of dimethacrylate impurities within the HPMA monomers. The fit peak 1 represents $PDMA_{70}$-*b*-$PBzMA_{96}$-b-$PHPMA_{258}$ triblock terpolymer and the fit peak 2 is $PDMA_{70}$-*b*-$PBzMA_{96}$ diblock copolymer. The integral area of peak 1 is 2.17, the area of peak 2 is 0.9. Therefore, the block efficiency is 71%, calculating the integral area ratio of peak 1 and peak 2.

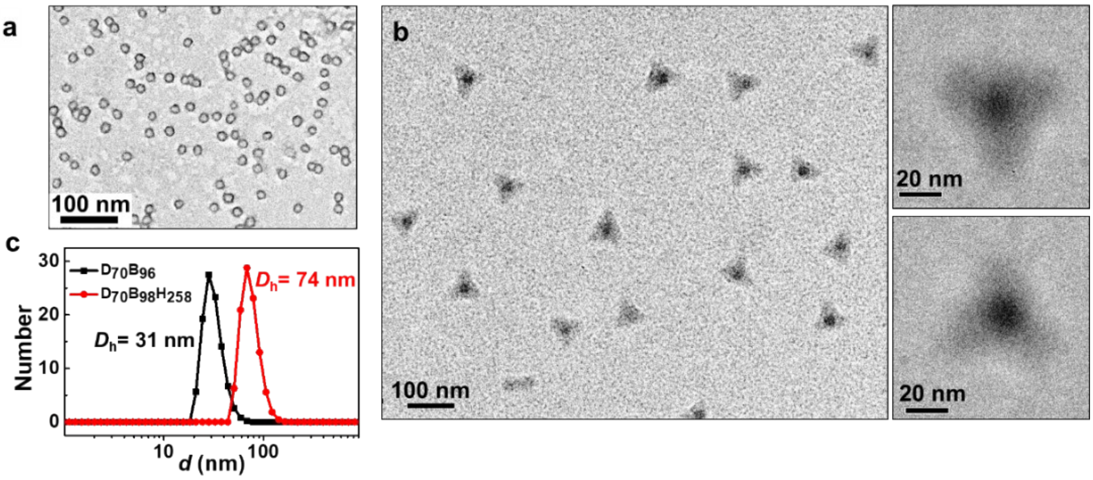

Fig. S5 (a) TEM image of spherical PDMA$_{70}$-*b*-PBzMA$_{96}$ colloids after PTA-staining PDMA corona. (b) TEM images of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{258}$ CTs without staining. (c) DLS profiles of the PDMA$_{70}$-*b*-PBzMA$_{96}$ colloidal spheres (black) and PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{258}$ CTs (red).

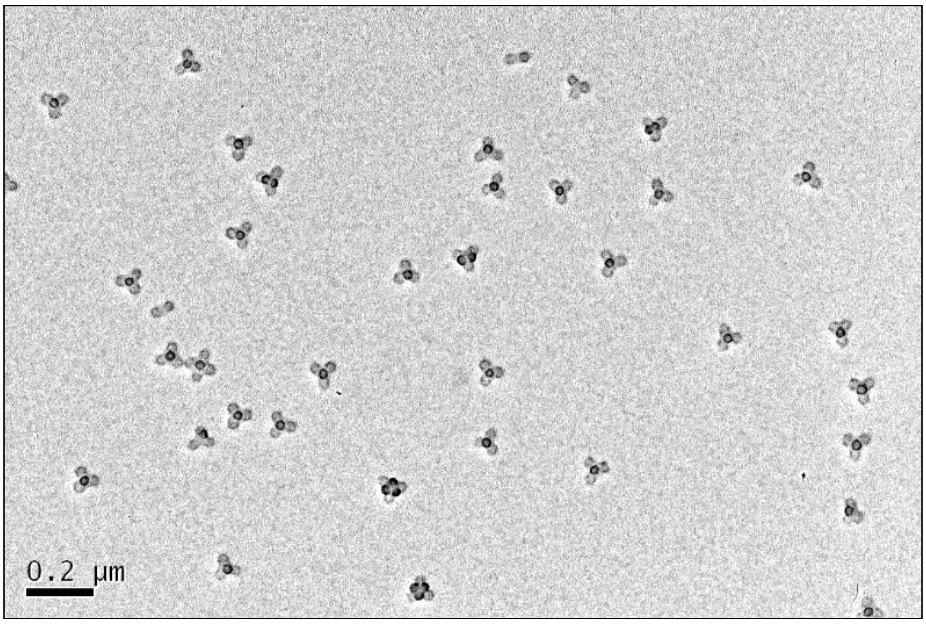

Fig. S6 TEM image of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{258}$ CTs after PTA-staining.

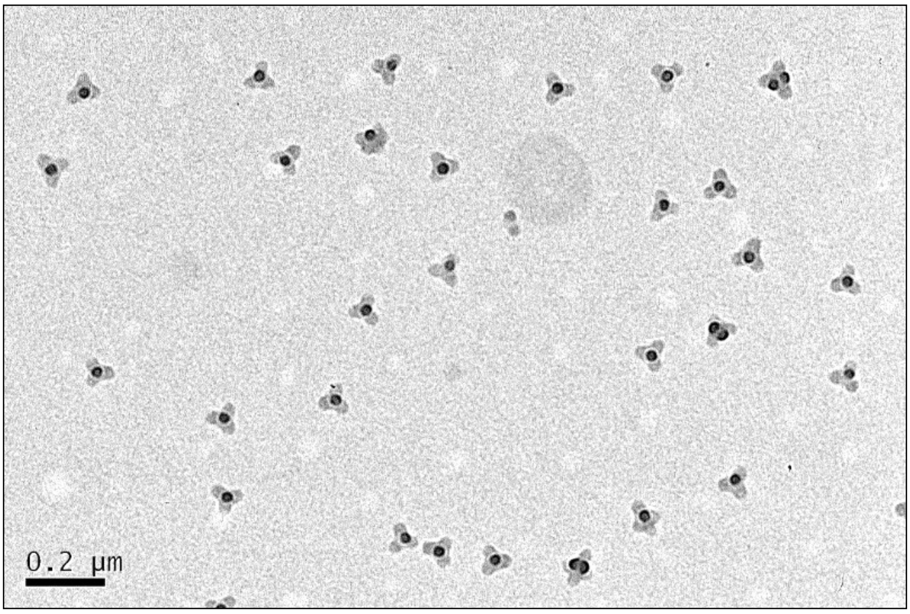

Fig. S7 TEM image of PDMA $_{70}$-*b*-PBzMA $_{96}$-*b*-PHPMA$_{258}$ CTs after RuO$_4$-staining.

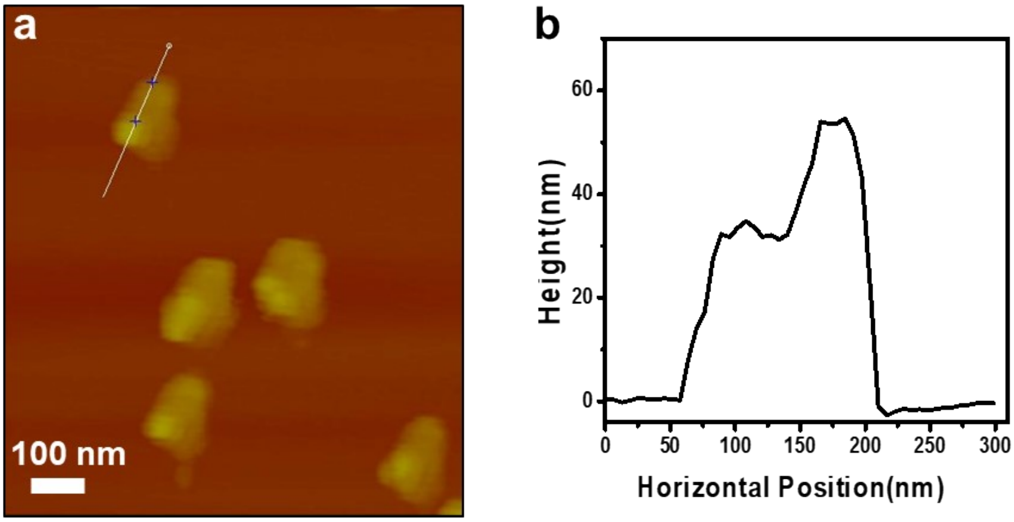

Fig. S8 (a) AFM image of PDMA $_{70}$-*b*-PBzMA $_{96}$-*b*-PHPMA$_{70}$ CTs. (b) Height plot of CTs.

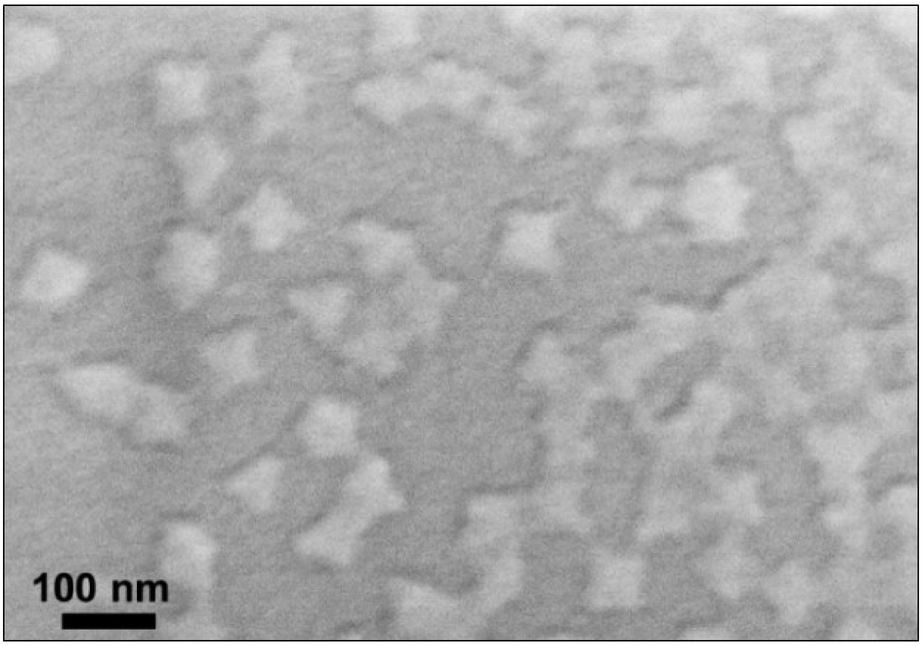

Fig. S9 SEM image of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{258}$ CTs.

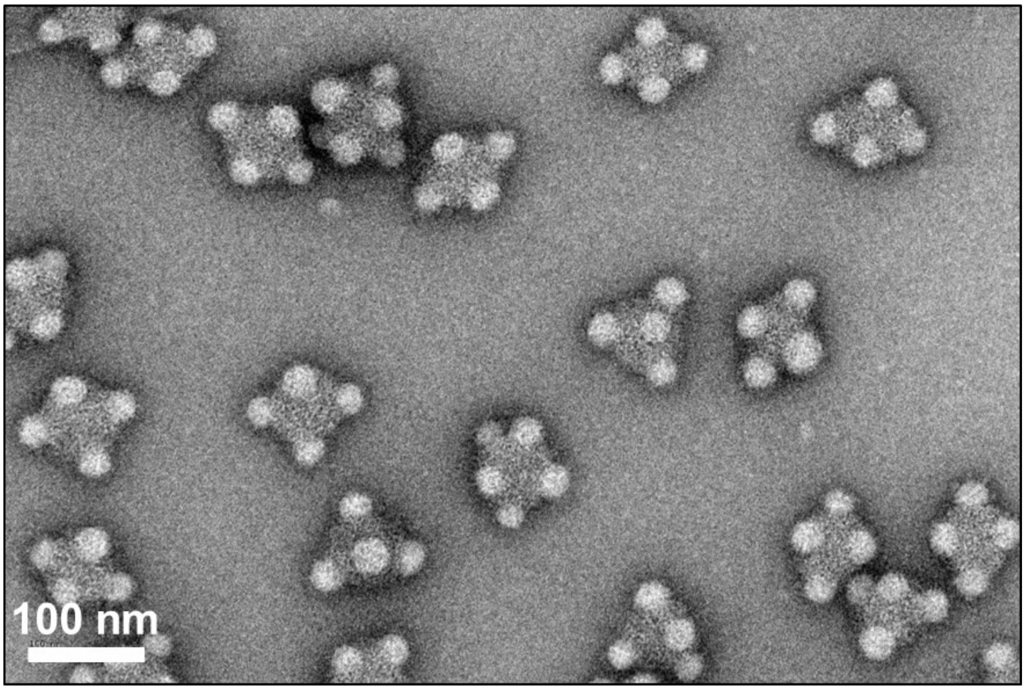

Fig. S10 Representative TEM image of PDMA $_{70}$-*b*-PBzMA $_{96}$-*b*-PHPMA$_{70}$ CTs after uranyl acetate negatively staining.

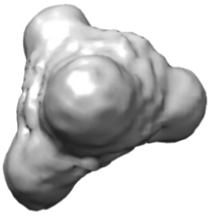

Fig. S11 The 3D reconstruction of tetrahedron without imposing any symmetry.

Table S2. Statistics of cluster structures from varied copolymers. [a]

Composition	R_H/R_B*	% spheres	% AB_2	% AB_3	% AB_4	% AB_5	% AB_6	% AB_7	%	N
$D_{70}B_{96}H_{20}$	0.69	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1
$D_{70}B_{96}H_{46}$	1.03	58.3	37.8	3.6	0.3	0.0	0.0	0.0	0.0	1.5
$D_{70}B_{96}H_{70}$	1.38	3.4	78.5	4.2	13.2	0.3	0.4	0.0	0.0	2.3
$D_{70}B_{96}H_{109}$	1.71	3.2	50.2	15.7	22.9	5.0	3.0	0.0	0.0	2.9
$D_{70}B_{96}H_{167}$	2.17	0.0	16.3	5.7	68.3	5.7	4.0	0.0	0.0	3.8
$D_{70}B_{96}H_{194}$	2.32	0.0	8.0	3.8	74.8	8.3	5.1	0.0	0.0	4.0
$D_{70}B_{96}H_{258}$	2.59	0.0	2.5	2.7	78.3	10.0	5.7	0.3	0.5	4.2
$D_{70}B_{96}H_{319}$	2.95	0.0	1.1	2.1	43.2	19.3	24.8	6.8	2.7	5.0
$D_{70}B_{96}H_{456}$	3.54	0.0	0.0	0.0	19.1	21.8	28.0	13.7	17.4	5.9

[a] By statistic analysis of TEM images over about 350, 421, 735, 440, 320, 341, 819, 216, and 225 cluster samples, respectively.

*Radius ratio of PHPMA and PBzMA CAs (R_H/R_B) is calculated from mean valence number (N) and Volume ratio of PHPMA and PBzMA (V_H/V_B) as,

$$R_H/R_B = \left(N * V_H/V_B\right)^{1/3} = \left(N\psi\frac{M_H d_B}{M_B d_H}\right)^{1/3}$$

Where N is the mean valence calculated from statistics of cluster structures from varied samples, as Table S2 shown. V_H/V_B is calculated from molecular weight, polymer density and swelling coefficient of PHPMA (ψ, ca. 2.0) as previous report.

Volume ratio of PHPMA and PBzMA (V_H/V_B) is calculated from molecular weight, polymer density and swelling coefficient of PHPMA (ψ) as,

$$V_H/V_B = \frac{\psi m_H/d_H}{m_B/d_B} = \psi\frac{M_H d_B}{M_B d_H}$$

Where d_B (1.035 g/cm^3) and d_H (1.027 g/cm^3) are densities of PBzMA and PHPMA. m_H and m_B are weights of PHPMA and PBzMA blocks in a AB_2 CM. M_H and M_B are molecular weights of PHPMA and PBzMA blocks. ψ is swelling coefficient of PHPMA in water, $\psi = 2.0$. [6]

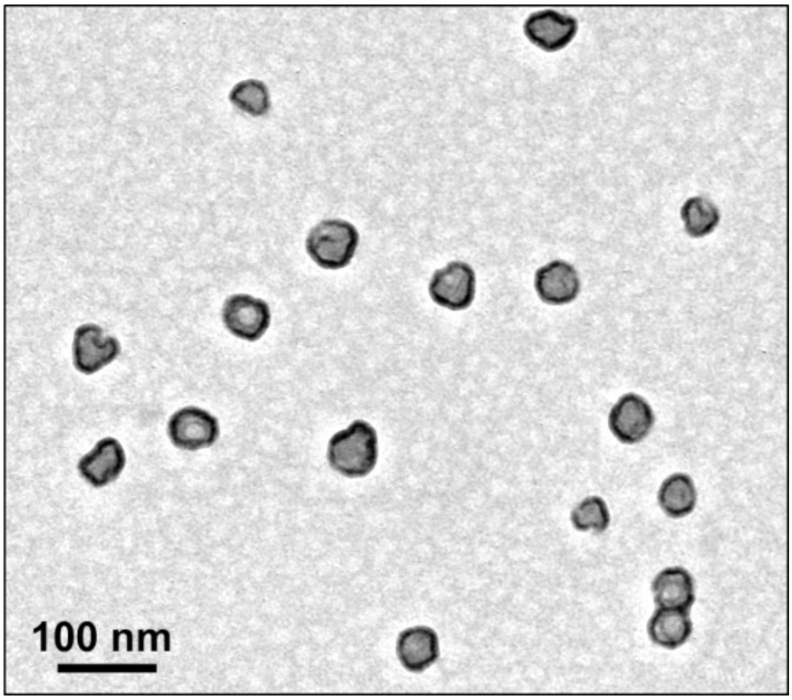

Fig. S12 TEM image of PDMA $_{70}$-*b*-PBzMA$_{298}$ seeds after PTA-staining.

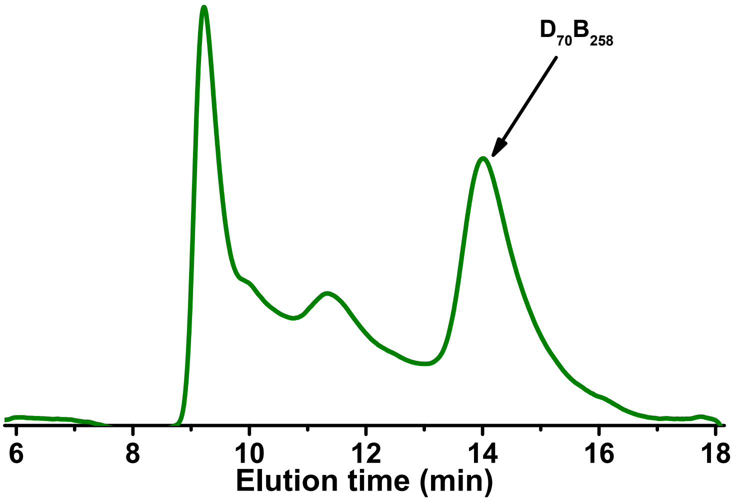

Fig. S13 SEC trace of PDMA$_{70}$-*b*-PBzMA$_{298}$-*b*-PHPMA$_{411}$ triblock terpolymers. (DMF as eluent) High polydispersity is attributed to the relatively low block efficiency and the crosslinking of the growing PHPMA chains due to a small amount of dimethacrylate impurity within the HPMA monomer.

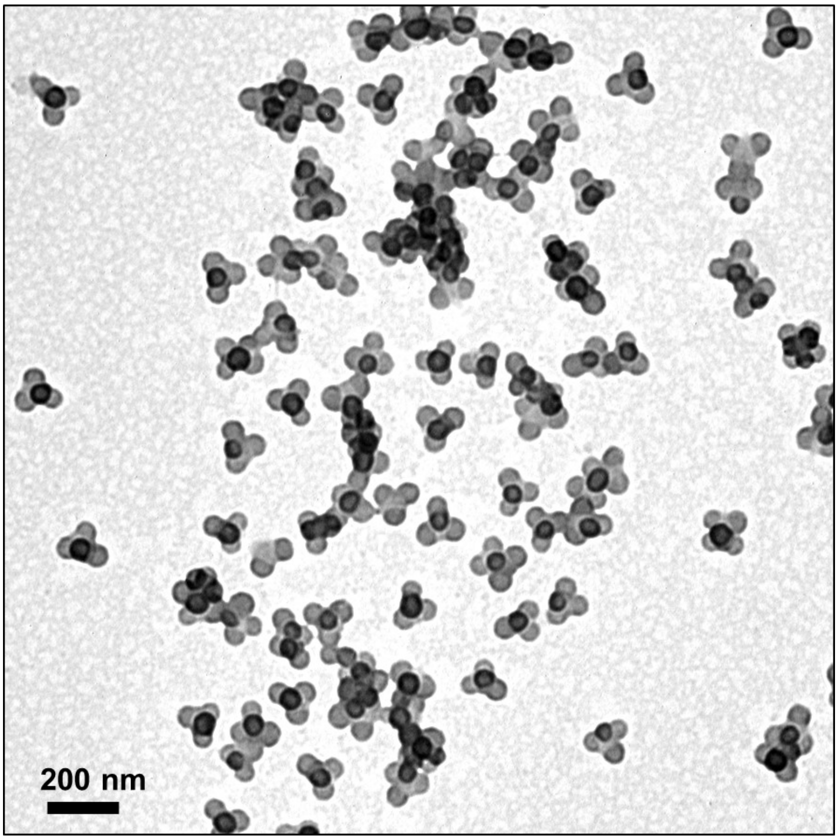

Fig. S14 TEM image of $PDMA_{70}$-*b*-$PBzMA_{298}$-*b*-$PHPMA_{411}$ CTs.

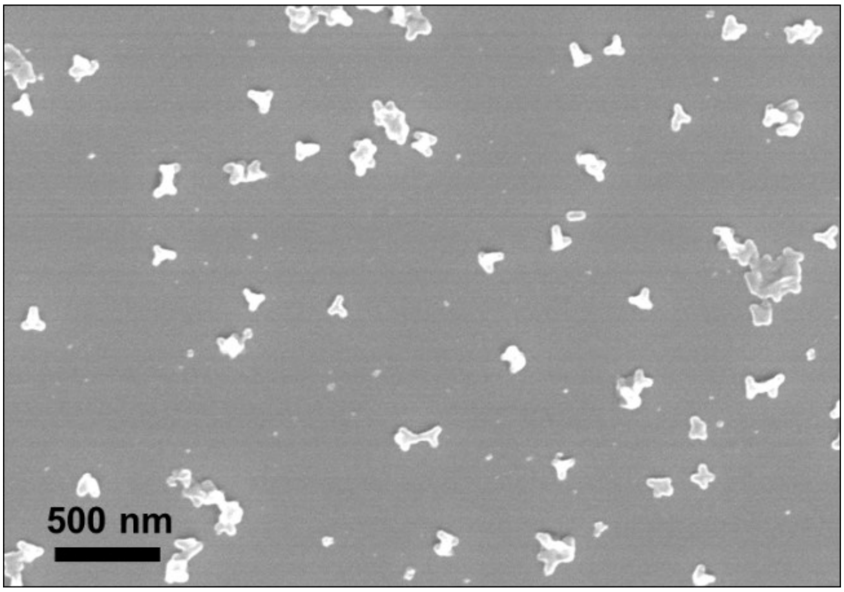

Fig. S15 SEM image of $PDMA_{70}$-*b*-$PBzMA_{298}$-*b*-$PHPMA_{411}$ CTs.

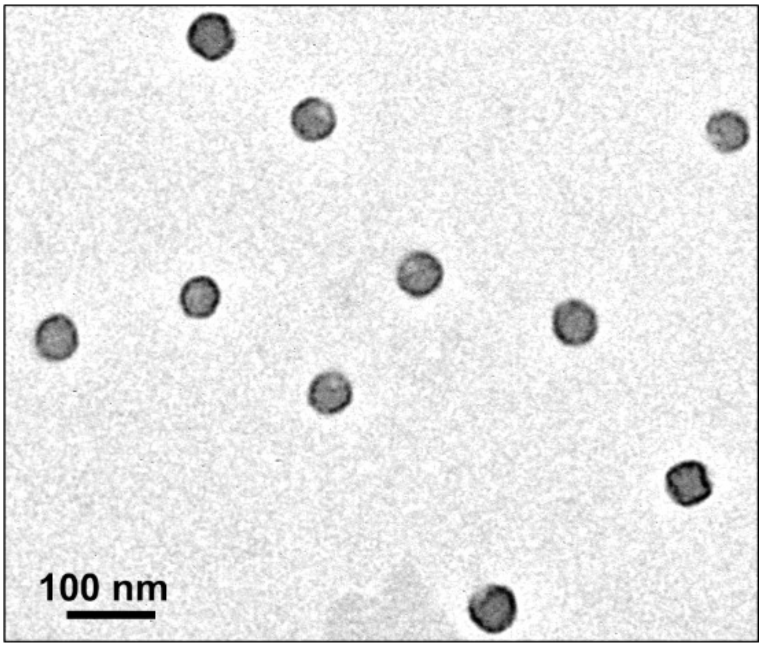

Fig. S16 TEM image of PDMA $_{70}$-*b*-PBzMA$_{494}$ seeds after PTA-staining.

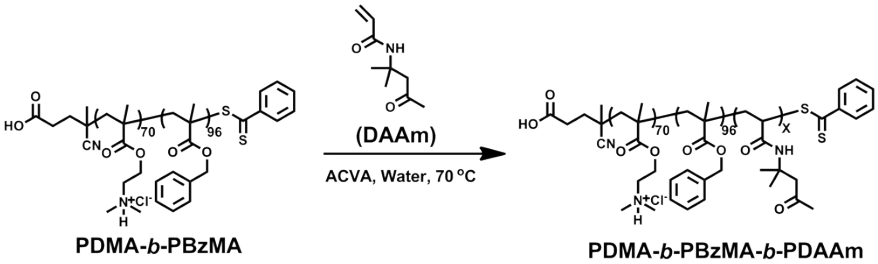

Fig. S17 Aqueous dispersion polymerization of DAAm, using PDMA$_{70}$-*b*-PBzMA$_{96}$ as seeds.

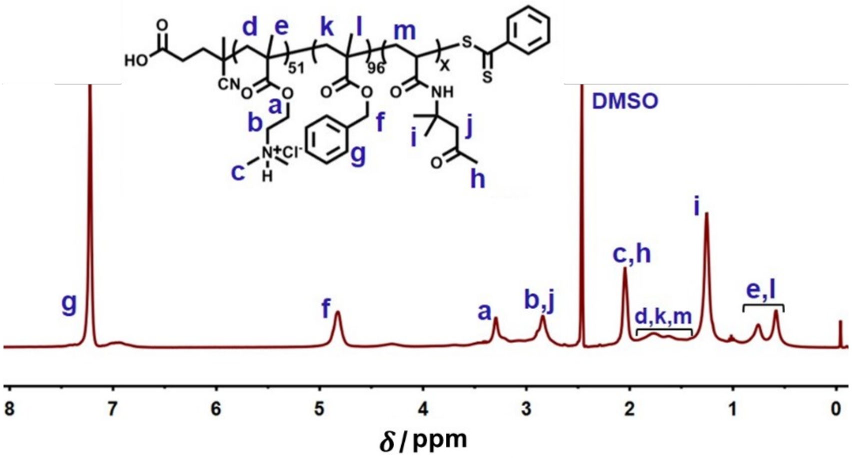

Fig. S18 ^{1}H NMR spectra of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{114}$ in DMSO-*d*$_6$ at 25 ^{o}C.

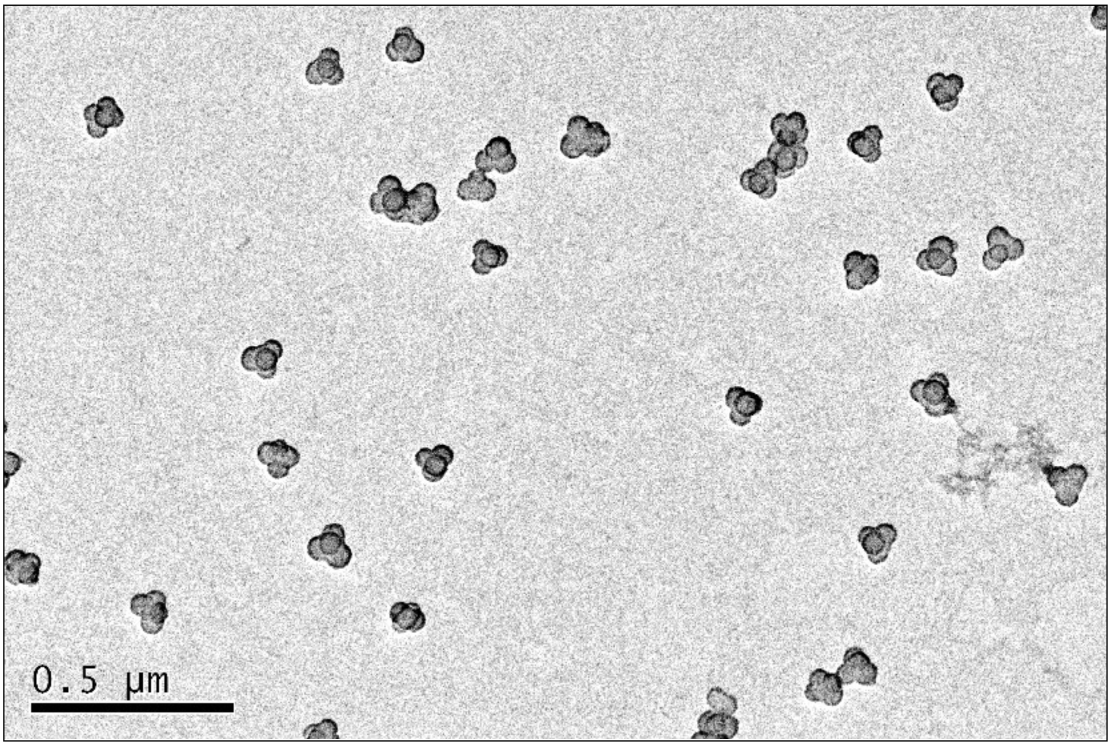

Fig. S19 TEM image of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PDAAm$_{114}$ CMs.

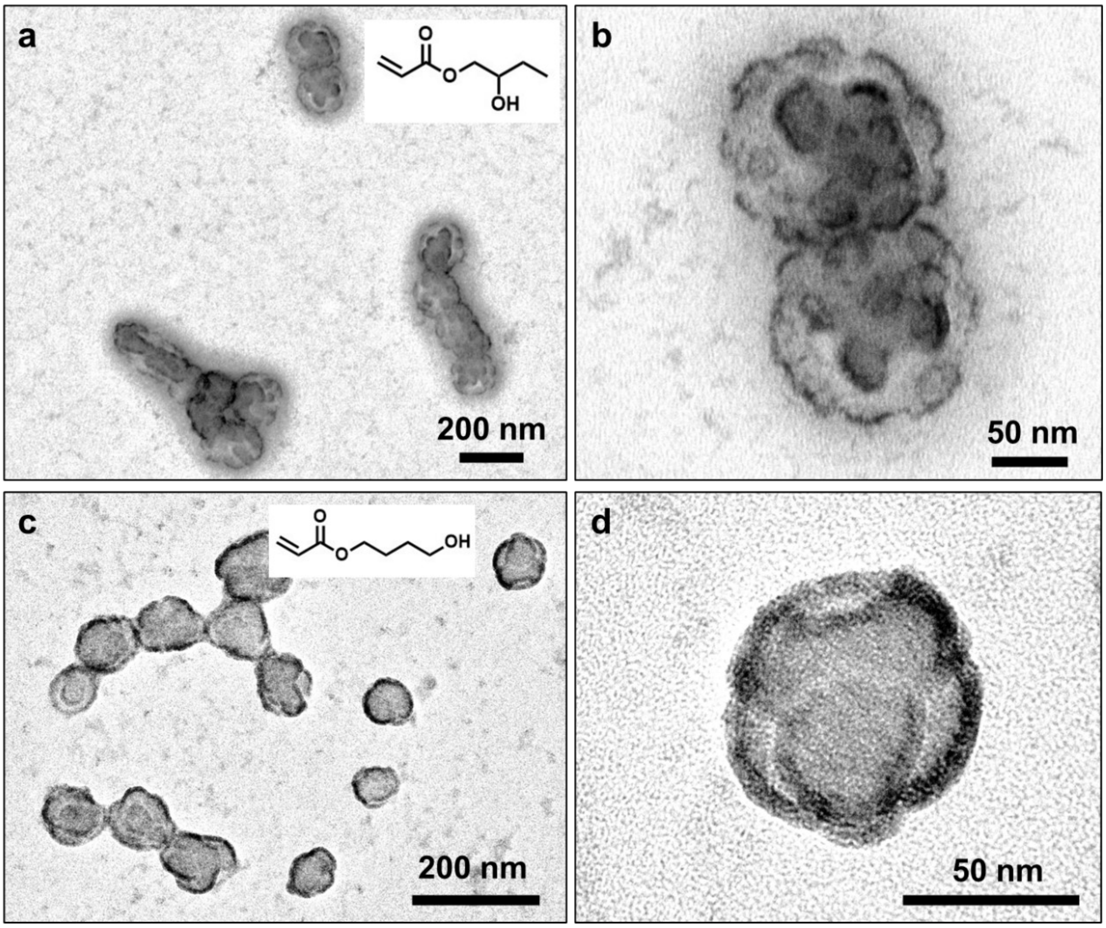

Fig. S20 TEM images of (a, b) PDMA-*b*-PBzMA-*b*-P2HBA and (c, d) PDMA-*b*-PBzMA-*b*-P4HBA football-like MCMs, targeting DP =200.

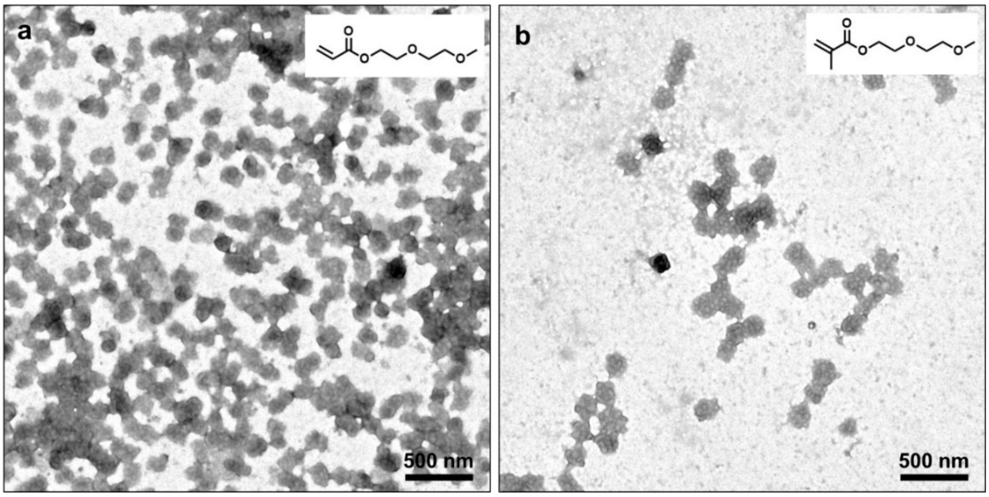

Fig. S21 TEM images of (a) PDMA-*b*-PBzMA-*b*-PDEGA and (b) PDMA-*b*-PBzMA-*b*-PDEGMA MCMs, targeting DP =200.

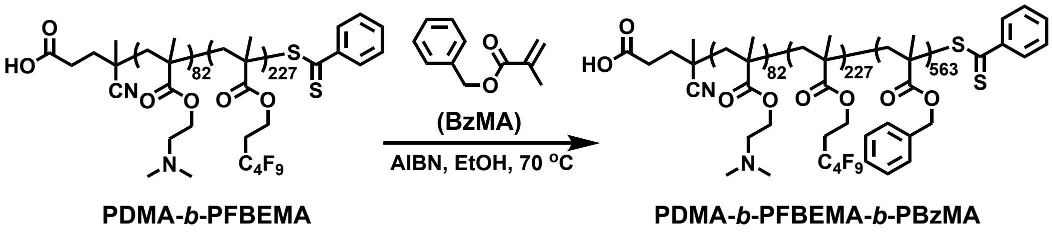

Fig. S22 Aqueous dispersion polymerization of BzMA, using $PDMA_{82}$-*b*-$PFBEMA_{227}$ as seeds.

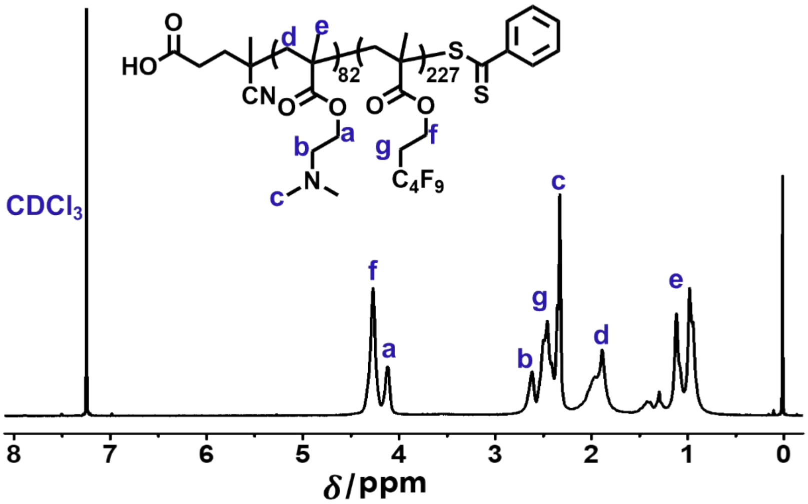

Fig. S23 Representative ^1H NMR spectra of $PDMA_{70}$-*b*-$PFBEMA_{227}$ in $CDCl_3/CF_2ClCFCl_2$ (1/1, v/v).

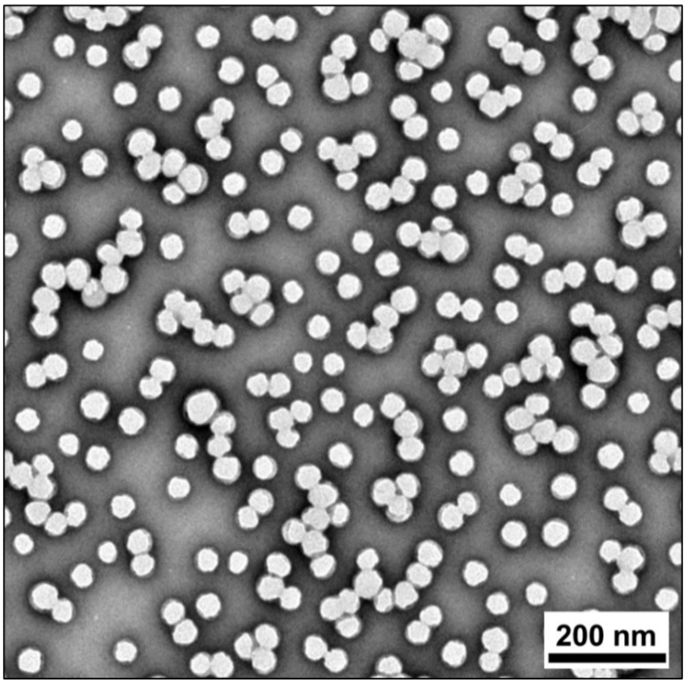

Fig. S24 TEM image of PDMA$_{70}$-*b*-PTFEMA$_{298}$ seeds after PTA-staining.

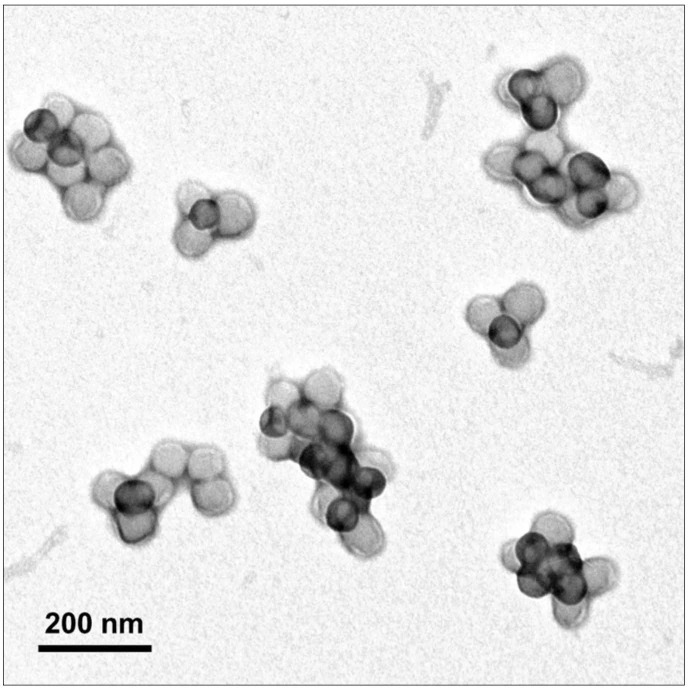

Fig. S25 TEM image of PDMA$_{82}$-*b*-PFBEMA$_{227}$-*b*-PBzMA$_{563}$ after PTA-staining. DP of BzMA judged by monomer conversion.

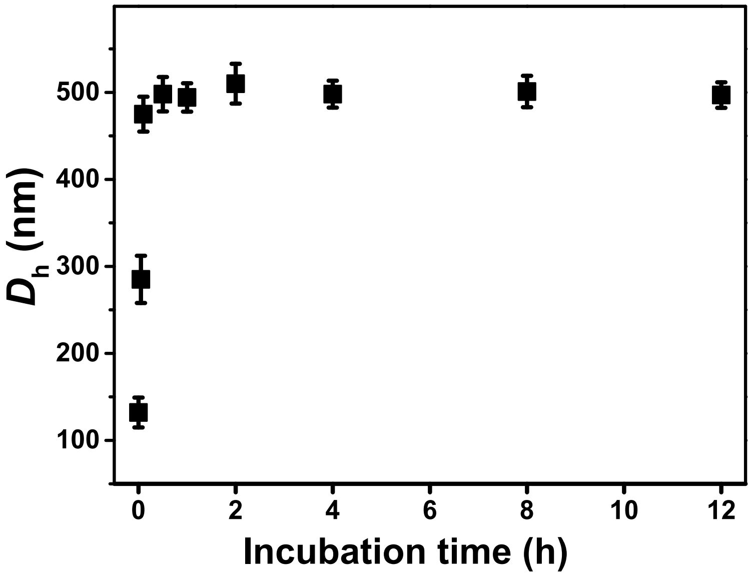

Fig. S26 The D_h of PDMA$_{70}$-b-PBzMA$_{298}$-b-PHPMA$_{411}$ CTs in ethanol/water = 3:2 (C_E = 60%) varies with the incubation time.

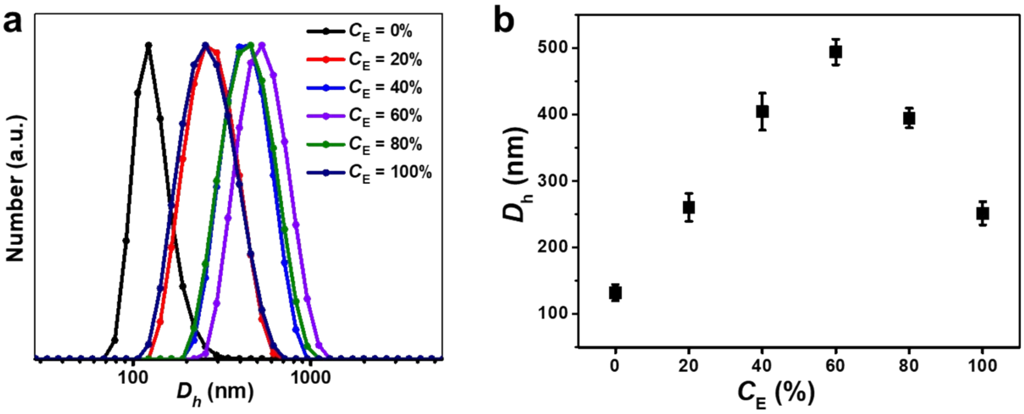

Fig. S27 (a) DLS profiles of the PDMA$_{70}$-b-PBzMA$_{298}$-b-PHPMA$_{411}$ CTs in ethanol/water with different ethanol content. (b) The D_h of PDMA$_{70}$-b-PBzMA$_{298}$-b-PHPMA$_{411}$ assemblies varies with the ethanol content.

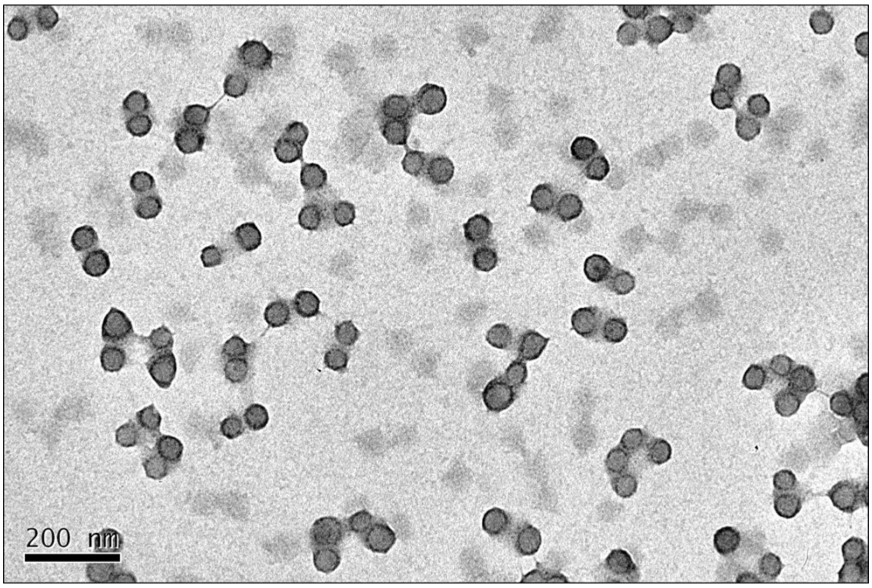

Fig. S28 Representative TEM image of PDMA$_{70}$-*b*-PBzMA$_{298}$-*b*-PHPMA$_{411}$ CTs disassembly into θ-type dimers in ethanol/water = 4:1 (CE = 80%).

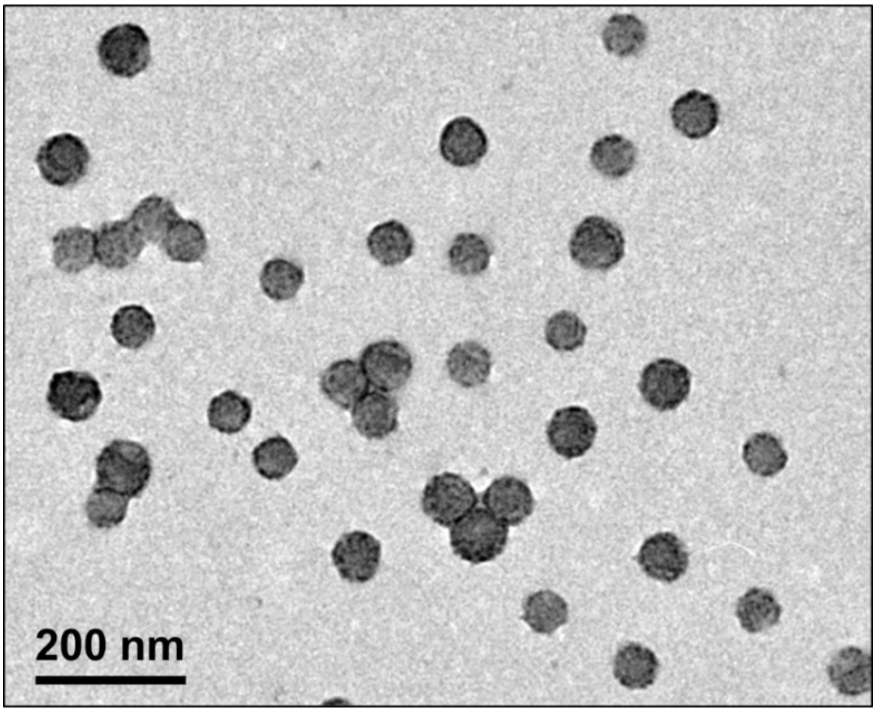

Fig. S29 Representative TEM image of PDMA$_{70}$-*b*-PBzMA$_{298}$-*b*-PHPMA$_{411}$ CTs disassembly into spherical micelles in ethanol (C_E = 100%).

Calculation of solubility parameter values of different solvents

The solubility parameter(δ) values of mixed solvents can be calculated as follows:

$\delta_{mix} = \delta_{\mathrm{E}} C_{\mathrm{E}} + \delta_{\mathrm{w}} C_{\mathrm{w}}$

Here, δ_E, δ_w and C_E, C_w represent the solubility parameter values and volume fractions of ethanol and water, respectively.

In this paper, δ of ethanol and water are 26.3 and 47.9 J/cm^3.[7, 8] The calculated solubility parameters of the solvent mixtures with different ethanol content (C_E) are listed in Table S3.

Table S3. δ-value of mixture solvents with different C_E

Solvent	C_E (%)	*δ*-value (J/cm^3)	Morphology
ethanol/wate	0	47.9	CTs
ethanol/wate	20	43.6	swollen CTs
ethanol/wate	40	39.2	quadrilateral cluster
ethanol/wate	60	34.9	colloidal ladder-like
ethanol/wate	80	30.5	AB_2
ethanol/wate	100	26.3	spheres

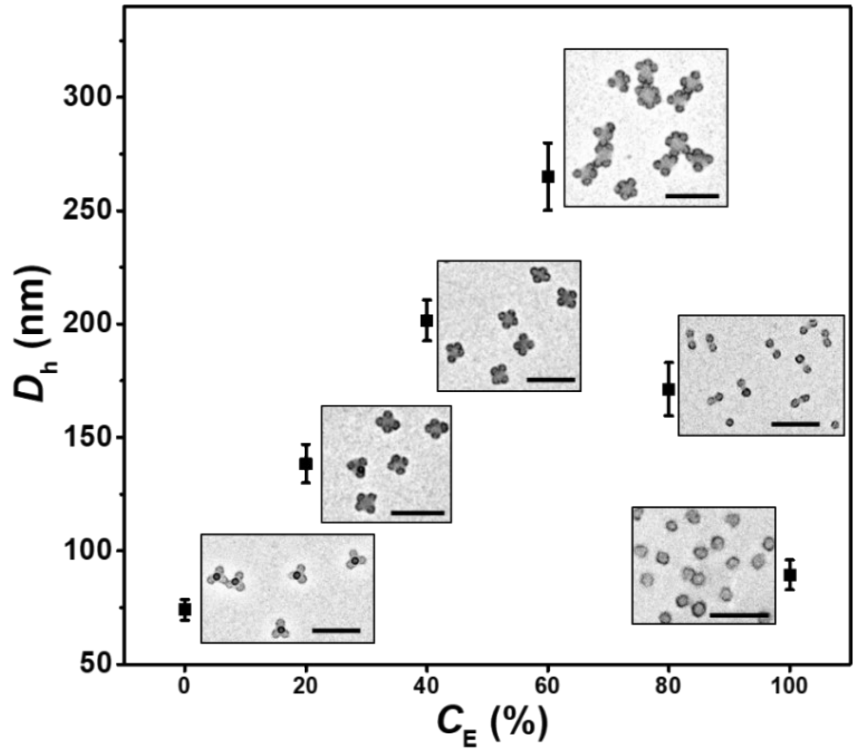

Fig. S30 The D_h of $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PHPMA_{258}$ assemblies varies with the ethanol content, inset is TEM image of the assemblies. Scale bars are 200 nm.

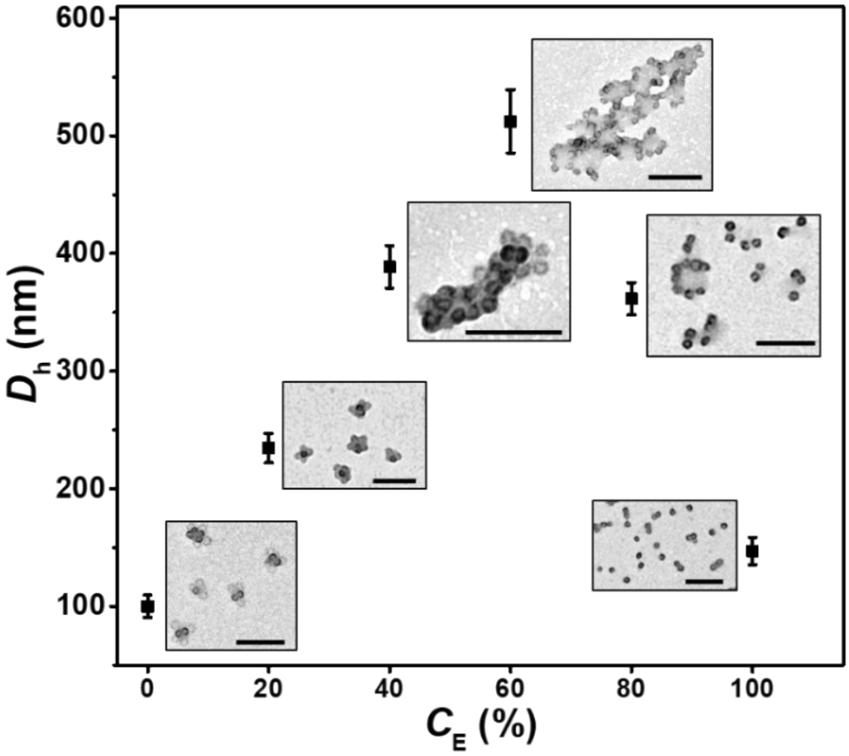

Fig. S31 The D_h of $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PHPMA_{456}$ assemblies varies with the ethanol content, inset is TEM image of the assemblies. Scale bars are 200 nm.

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