Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Synthesis of AB_n-type colloidal molecules by polymerization-induced particle-assembly (PIPA)

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1. Experimental Section

1.1 Materials

N,N-dimethylaminoethyl methacrylate (DMA, 99%, TCI), benzyl methacrylate (BzMA, 98%, TCI) 2-hydroxypropyl methacrylate (HPMA, 97%, TCI), and diactone acrylamide (DAAm, 98%, TCI) 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 ℃. 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. 4-(4-Cyanopentanoic acid) dithiobenzoate (CPADB) was synthesized accordingly.[1]

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.

1.3 Syntheses of $PDMA_{70}$-*b*-$PBzMA_y$.

A series of $PDMA_{70}$-*b*-$PBzMA_y$ 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 14.42%.

1.4 Kinetic study of aqueous dispersion RAFT polymerization of HPMA.

$PDMA_{70}$-*b*-$PBzMA_{96}$ seed dispersion (6.00 mL, 14.42 wt% solids concentration, dialyzing against water to remove ethanol), HCl (6 mol/L, 0.90 mL, adjusting the solution pH = 2.0), ACVA (9.79 μmol, 2.74 mg) and HPMA (4.90 mmol, 706 mg) were dissolved in water in a 50 mL Schlenk tube. The mixture (16.34 ml, ca. 10 wt% solids concentration) was bubbled with argon for 25 min, and stirred in a 70 °C oil bath. Periodically, the mixture was sampled by approximate 1 mL for SEC, ^{1}H NMR characterization.

1.5 Syntheses of $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PHPMA_z$ Colloidal Molecules.

A series of $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PHPMA_z$ colloidal molecules were prepared via RAFT polymerization of HPMA at 5 wt% solids concentration in water. $PDMA_{70}$-*b*-$PBzMA_{96}$ seed aqueous dispersion (2.00 mL, 14.42 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 (1.64 mmol, 235.0 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. 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.

1.6 Synthesis of PBzMA and PHPMA homopolymers.

PBzMA and PHPMA homopolymers were prepared via RAFT solution polymerization. BzMA (10.0 mmol, 1.76 g) and HPMA (12.0 mmol, 1.73 g) were dissolved in THF (4.97 mL) and C_2H_5OH (6.29 mL) in 50 mL Schlenk tube, respectively. After feeding AIBN (8.00 μmol, 1.31 mg) as the initiator and CPADB (0.02 mmol, 5.59 mg) as the RAFT agent, the mixture was bubbled with argon for 25 min, then stirred at 70 °C for 24 h. After quenching the reaction in ice water, the mixture was dialyzed against THF and C_2H_5OH to remove residual monomers. The corresponding flat membranes were obtained after evaporation of the solvents.

1.7 Syntheses of $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PDAAm_z$ Colloidal Molecules.

$PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PDAAm_z$ colloidal molecules were prepared via RAFT polymerization of HPMA at 5 wt% solids concentration in water. $PDMA_{70}$-*b*-$PBzMA_{96}$ seed aqueous dispersion (2.00 mL, 14.42 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. The polymerizations were quenched at desired monomer conversion. After quenching the polymerization in ice water, the dispersion was dialyzed against ethanol to remove residual monomers.

2. Characterization

2.1 ^{1}H NMR: All the ^{1}H NMR spectra were recorded on 400 MHz JEOL JNM-EA 400 spectrometer using DMSO-d6 or $CDCl_3$ as the solvent.

2.2 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 weights (M_n) and dispersities ($Đ$) 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.

2.3 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.

2.4 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.

2.5 Cryo-TEM: The samples were prepared by FEI Vitrobot Mark IV instrument. TEM images were acquired on FEI Tecnai Spirit at 120 kV.

2.6 Zeta potential measurement: The measurements were performed on Marven Zetasizer Nano ZS90 laser light scattering spectrometer. The dispersions were diluted at 1.0 mg/mL for Zeta potential measurements.

3. Molecular characterizations of polymer

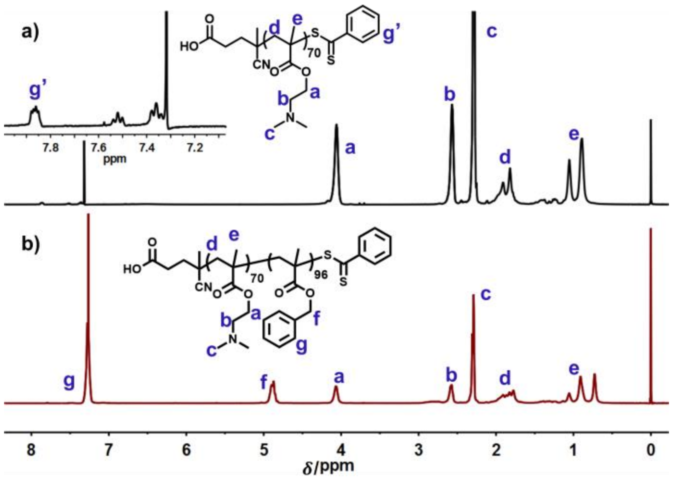


Fig. S1 ^{1}H NMR spectra of: a) PDMA$_{70}$ macro-CTA, b) PDMA$_{70}$-*b*-PBzMA$_{96}$ diblock copolymer in CDCl$_3$ at 25 °C. DPs of PDMA macro-CTA and PBzMA were calculated via comparing the integral area (I_i) ratio of peak a, f and g', as

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

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

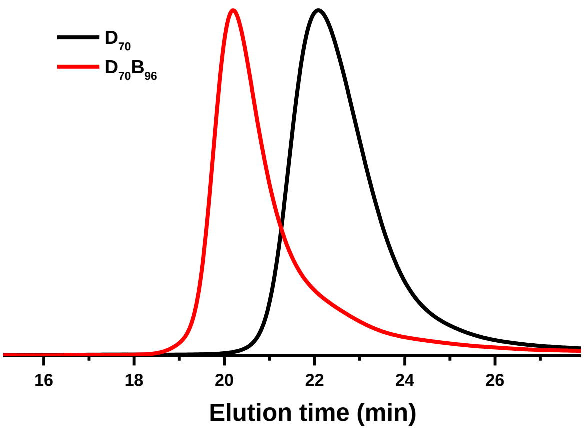


Fig. S2 SEC traces of PDMA$_{70}$ and PDMA$_{70}$-*b*-PBzMA$_{96}$ diblock copolymers. (THF as eluent)

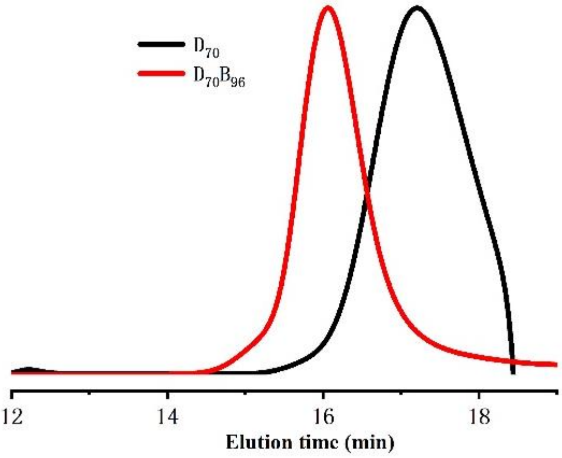


Fig. S3 SEC traces of $PDMA_{70}$ and $PDMA_{70}$-*b*-$PBzMA_{96}$ diblock polymers. (DMF as eluent)

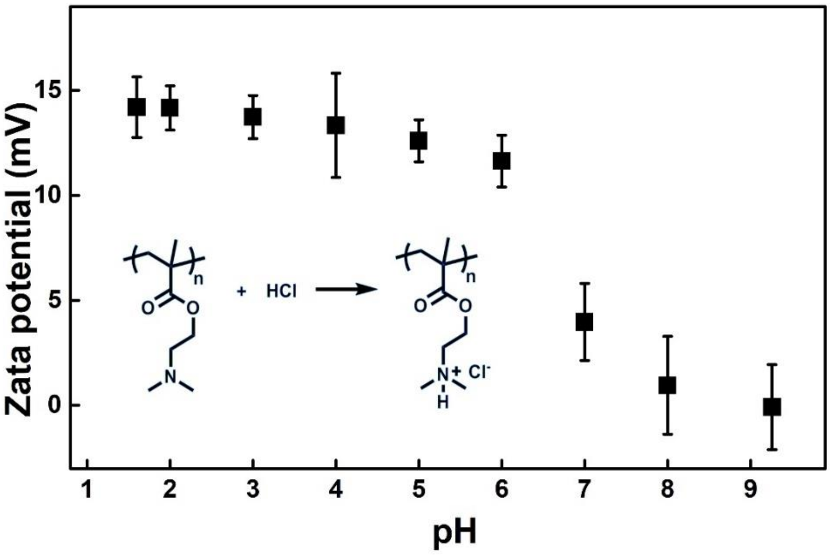


Fig. S4 Zeta potential of $PDMA_{70}$-*b*-$PBzMA_{96}$ seed depending on pH in 0.01 wt% aqueous dispersion with 10 mM NaCl as background. The insert shows the protonation of PDMA. The pH was adjusted to pH 2 for the protonation of PDMA chains, which provide sufficient electrostatic repulsion for cluster stabilizing. Without the addition of HCl, the polymerization tends to produce large clusters and precipitates. [2, 3]

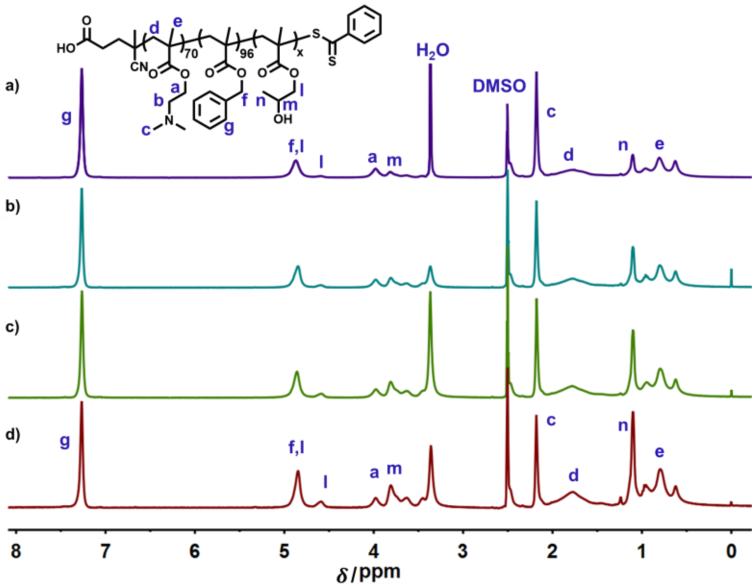


Fig. S5 ^{1}H NMR spectra in DMSO-d_6 at 25 °C: a) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{20}$, b) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{46}$, c) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{70}$, and d) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{109}$. DP of PHPMA was calculated via comparing the integral area (I_i) ratio of peak f, l, and g, as

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

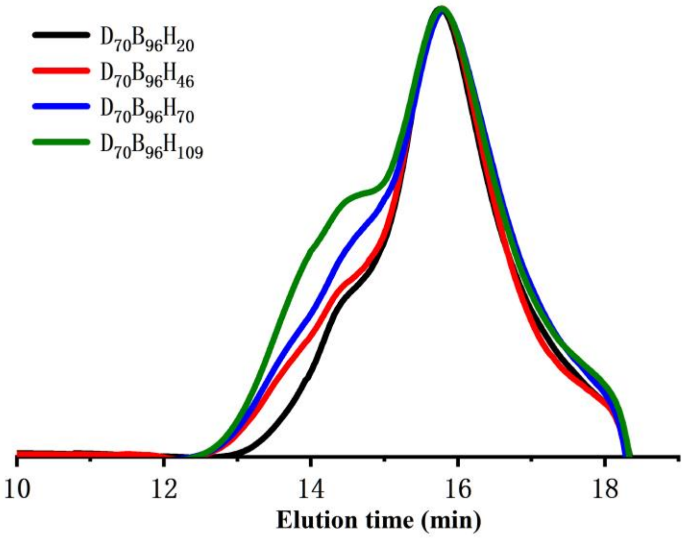


Fig. S6 SEC traces of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_z$ triblock terpolymers. (DMF as eluent) High polydispersity is attributed to the relatively low block efficiency and the crosslinking of the growing PHPMA chains due to a small amount of dimethacrylate impurity within the HPMA monomer.

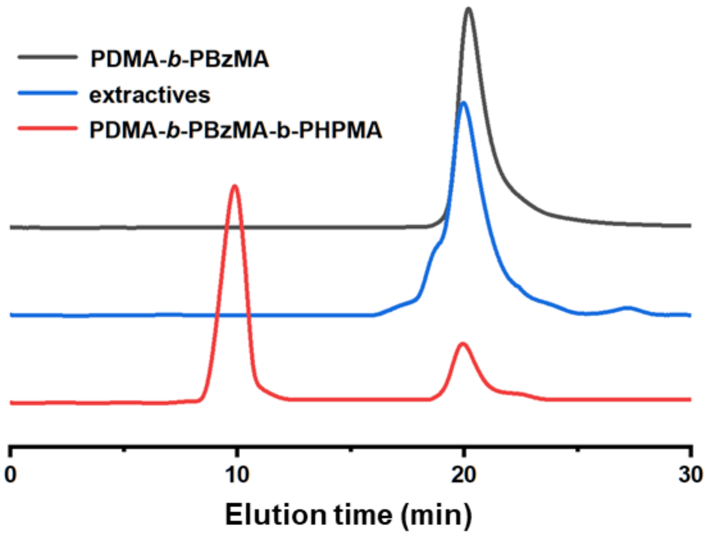


Fig. S7 the SEC traces of red) PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$, blue) extractives from PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$ using THF, black) PDMA$_{70}$-*b*-PBzMA$_{96}$ macro-CTA. (using THF as eluent)

Unreacted PDMA-*b*-PBzMA macro-CTA was observed from the SEC characterization using THF as eluent. Since the PDMA-*b*-PBzMA-*b*-PHPMA (especially with partial crosslinking) has poor solubility in THF, the SEC traces give a peak with elution time less than 10 min, and also a peak of unreacted PDMA-*b*-PBzMA with elution time same to PDMA$_{70}$-b-PBzMA$_{96}$ seed. By extracting experiments, we determined the ratio of the diblock PDMA$_{70}$-b-PBzMA$_{96}$ in PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$ samples. The PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$ samples ($Đ$ = 1.70, 128 mg) are dispersed in THF and stirred for 1 h. The suspensions were filtered through a PTFE filter (pore size = 0.45 µm) and the insoluble polymer was collected. This process was repeated three times, and the filtrates were combined and evaporated to give 16 mg extractives, majorly PDMA$_{70}$-*b*-PBzMA$_{96}$ diblock copolymer. The weight ratio of PDMA$_{70}$-*b*-PBzMA$_{96}$ in PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$ samples is 12.5%, and the molar ratio of unreacted PDMA$_{70}$-*b*-PBzMA$_{96}$ is 33%. Therefore, the blocking efficiency of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$ samples is 67%. The relatively low blocking efficiency is cause by the b collapse of the polymer chains and the CTA embedded in hydrophobic PBzMA cores.

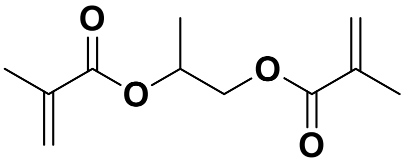


Figure S8. Structure of the 'dimethacrylate impurity' (1,2-bismetharyloyl propane) in HPMA.

Table S1. Molecular weight and morphologies of the samples

No.	Sample [a]	solid content (wt%)	Time (h)	Conv. (%)[b]	SEC [c]		DLS		V_H/V_B [d]	morphology
					M_n (kDa)	Đ	D_h (nm)	PDI		
1	$D_{70}B_{96}$	15	12	96	22.7	1.11	31	0.0	0	sphere
2	$D_{70}B_{321}$	15	12	94	43.6	1.07	56	0.0	0	sphere
3	$D_{70}B_{96}H_{20}$	5	1.5	40	34.2	1.49	35	0.0	0.34	sphere
4	$D_{70}B_{96}H_{46}$	5	1.5	46	44.7	1.52	42	0.27	0.79	sphere/AB_2
5	$D_{70}B_{96}H_{70}$	5	1.5	35	50.2	1.59	52	0.04	1.20	AB_2
6	$D_{70}B_{96}H_{109}$	5	1.5	55	51.3	1.68	56	0.26	1.87	AB_2/AB_3/AB_4
7	$D_{70}B_{96}H_{167}$	10	2	81*	54.7	1.82	66	0.06	2.87	AB_3/AB_4/cluster
8	$D_{70}B_{96}H_{194}$	10	4	92*	55.8	1.87	68	0.08	3.33	AB_3/AB_4/cluster
9	$D_{70}B_{96}H_{319}$	5	1.5	46	65.9	1.70	92	0.27	5.48	AB_3/AB_4/AB_5/AB_6
10	$D_{70}B_{321}H_{169}$	5	2	79	46.8	1.55	-	-	0.89	chain

[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, $Đ = M_w/M_n$.

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

$$V_H/V_B = \frac{\psi m_{\mathrm{H}}/d_{\mathrm{H}}}{m_{\mathrm{B}}/d_{\mathrm{B}}} = \psi \frac{M_{\mathrm{H}} d_{\mathrm{B}}}{M_{\mathrm{B}} d_{\mathrm{H}}}$$

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, as defined by equation,

$$\psi = \frac{V_{\mathrm{H,solvated}}}{V_{\mathrm{H,polymer}}}$$

Where $V_{\mathrm{H,solvated}}$ is the volume of solvated PHPMA block in water, $V_{\mathrm{H,polymer}}$ is the volume of pure PHPMA block. Since the PHPMA block is easily swollen in water, $V_{\mathrm{H,\,solvated}}$ is larger than $V_{\mathrm{H,\,polymer}}$. Therefore, ψ is always larger than 1. ψ is calculated by the equation.

$$\psi = \frac{V_{\mathrm{H,solvated}}}{V_{\mathrm{B}}} \frac{M_{\mathrm{B}} d_{\mathrm{H}}}{M_{\mathrm{H}} d_{\mathrm{B}}}$$

$V_{\mathrm{H,solvated}}$ and V_B of AB_2 CM are estimated from the cryo-TEM images, using cylindrical and spherical model, respectively. The size is determined by statistical analysis of 241 sample particles using ImageJ. ψ is calculated as 2.0, which is consistent with the previous report. [4]

3. Kinetic study of RAFT aqueous dispersion polymerization of HPMA

Table S2. Kinetic studies of RAFT aqueous dispersion polymerizations of HPMA.

Time (h)	Conversion (%) [a]	SEC [b]		DLS	
		M_n (kDa)	$Đ$	D_h (nm)	PDI
0	0	22.7	1.11	31	0.06
0.25	7.2	24.9	1.15	39	0.05
0.5	16.5	29.8	1.46	46	0.07
0.75	38.1	51.5	1.64	57	0.07
1	48.5	53.8	1.73	60	0.08
1.25	68.0	54.7	1.74	63	0.03
1.5	71.1	54.8	1.73	65	0.03
2	78.3	54.7	1.82	66	0.06
2.5	82.5	55.4	1.79	68	0.08
3	84.5	55.7	1.83	68	0.08
4	90.7	55.8	1.87	68	0.08
5	91.8	55.8	1.87	68	0.08

[a] Detected by ^{1}H NMR. [b] DMF as eluent.

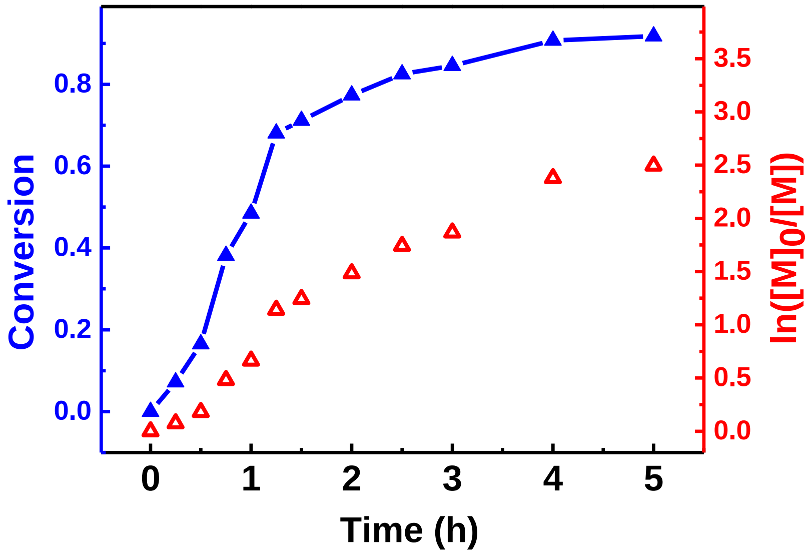


Fig. S9 Conversion-time and ln([M]$_0$/[M])-time plots for the polymerization of HPMA in water at 70 ˚C. (Solids content = 10 wt%. [ACVA]/[PDMA$_{70}$-PBzMA$_{96}$]/[HPMA] = 0.4/1/200.

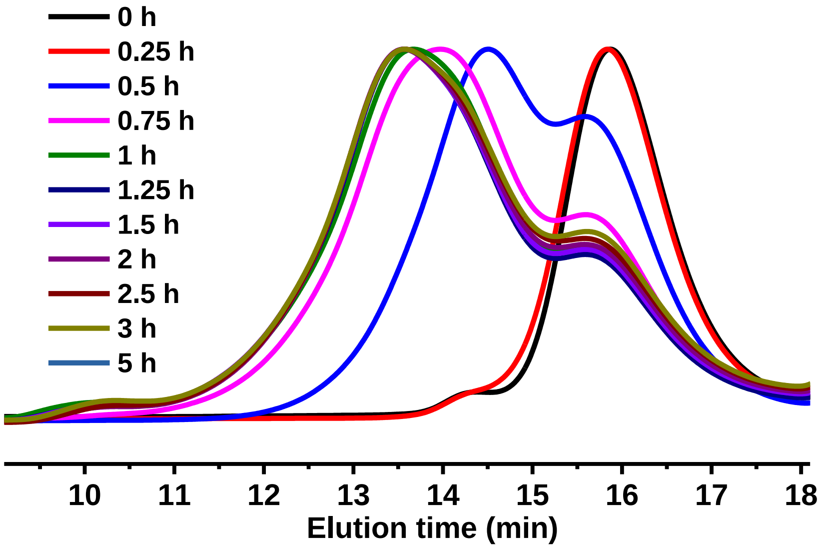


Fig. S10 SEC traces of PDMA$_{70}$-*b*-PBzMA$_{96}$ and PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_Z$ triblock terpolymers extracted during the aqueous dispersion polymerization of HPMA in water at 70 ˚C. (Solids content = 10 wt%. [ACVA]/[PDMA$_{70}$-PBzMA$_{96}$]/[HPMA] = 0.4/1/200.

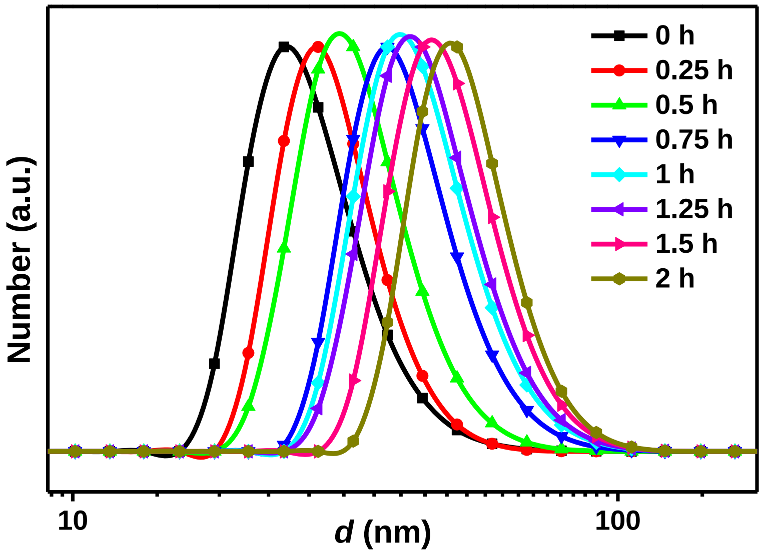


Fig. S11. DLS profiles of the dispersion extracted during the kinetic experiment. (70 ˚C, Solids content = 10 wt%. [ACVA]/[PDMA$_{70}$-PBzMA$_{96}$]/[HPMA] = 0.4/1/200.)

4. Supplemented morphological studies of colloidal molecules

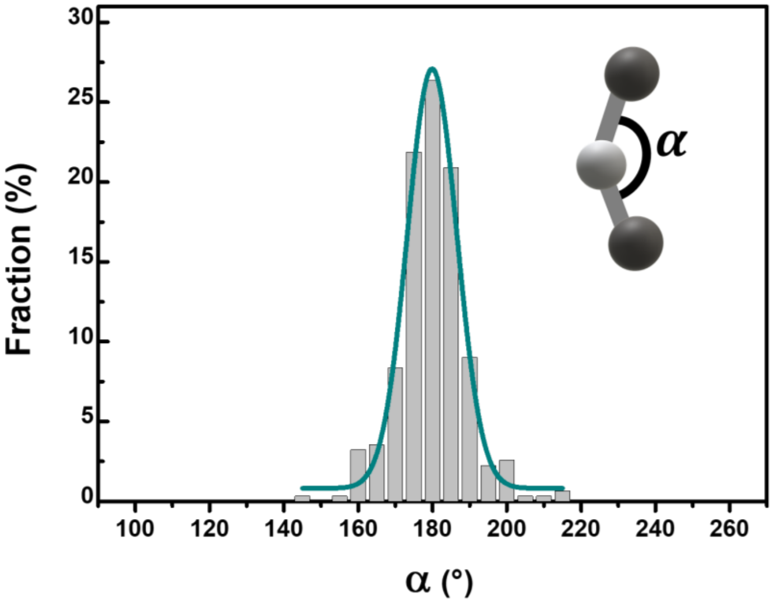


Fig. S12. The distribution of "bonding angle" (α) of AB_2-type CMs. By Statistic analysis of 340 particles from cryo-TEM images.

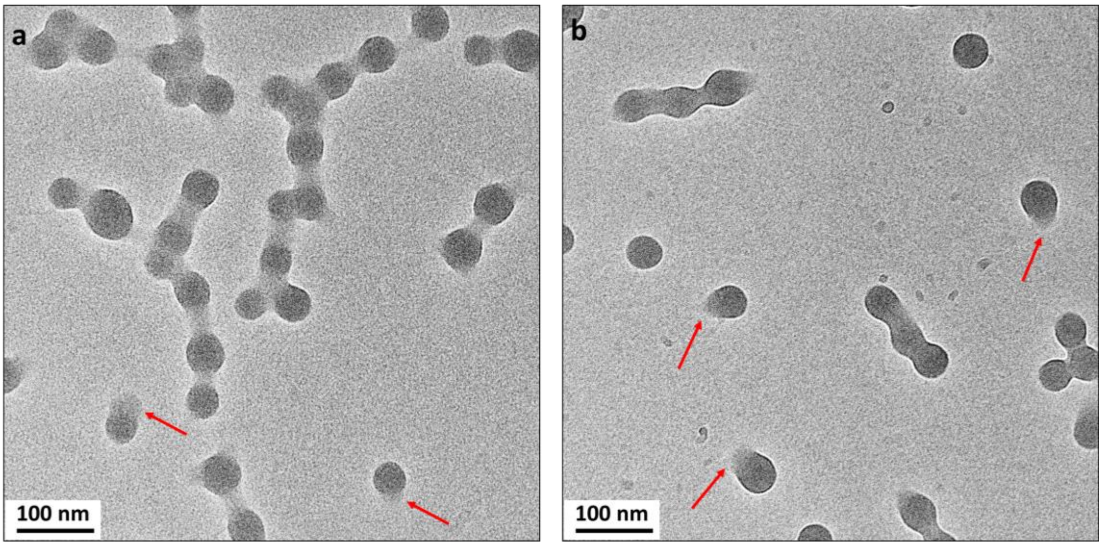


Fig. S13 Cryo-TEM images of typical Janus intermediates (red arrow) in $PDMA_{70}$-*b*-$PBzMA_{321}$-*b*-$PHPMA_{169}$.

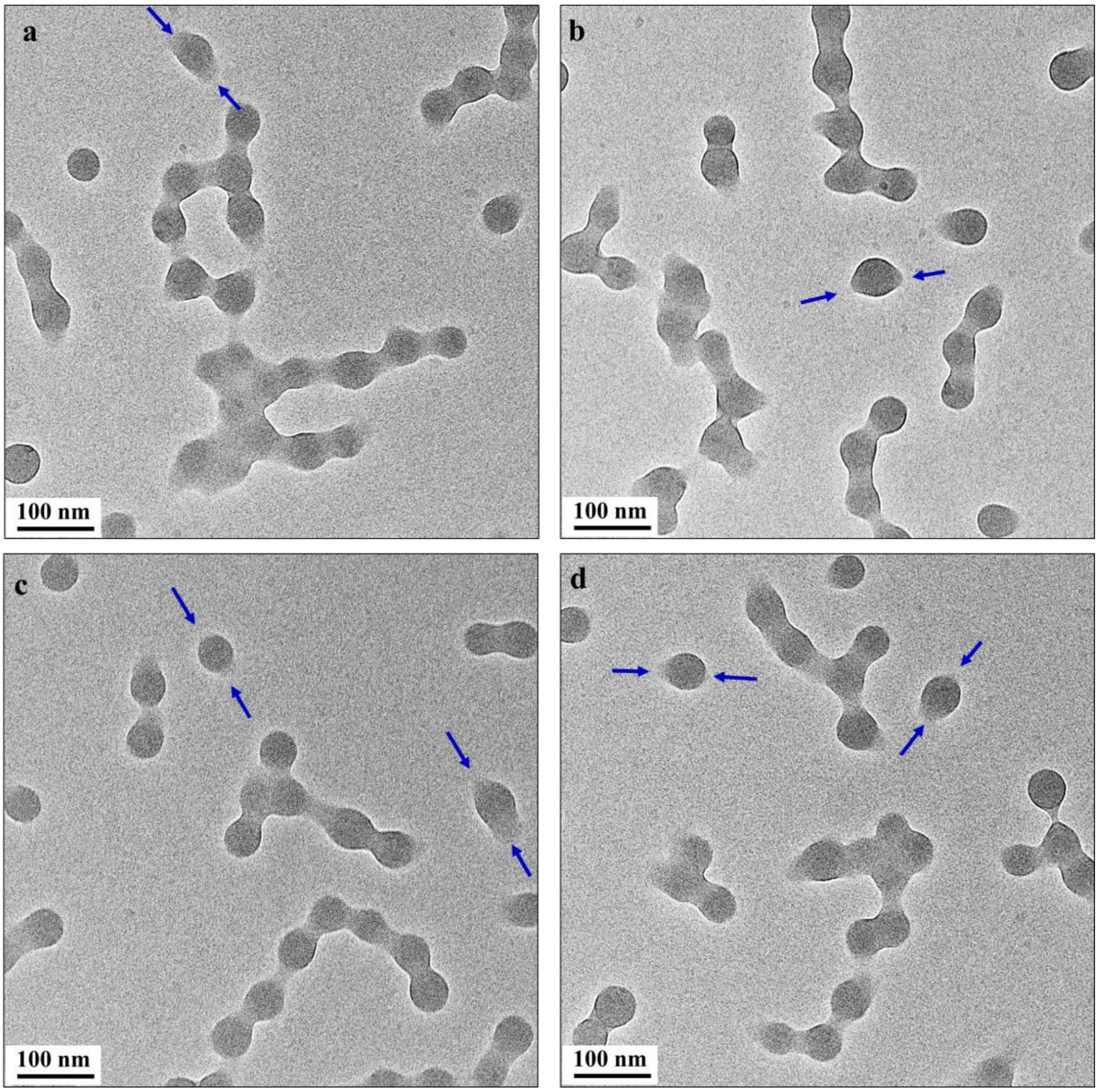


Fig. S14 Cryo-TEM images of typical "hamburger" intermediates (blue arrow) in PDMA$_{70}$-*b*-PBzMA$_{321}$-*b*-PHPMA$_{169}$.

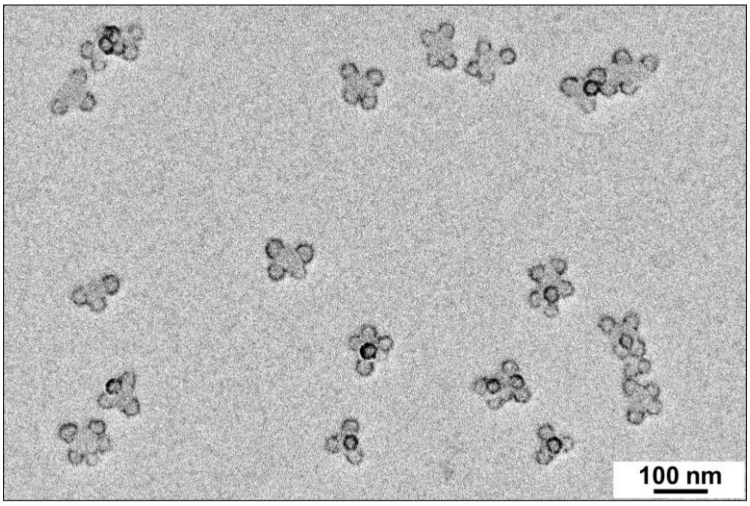


Fig. S15 TEM image of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{319}$ CMs.

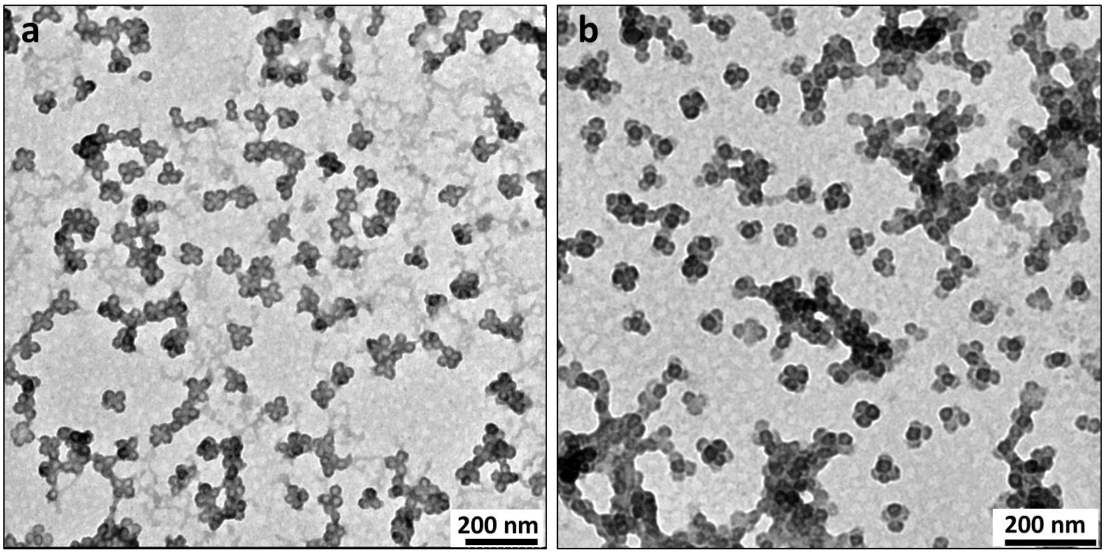


Fig. S16 TEM images of CMs obtained at high monomer conversion. (10 wt% solid content) a) 2h, 78.3% monomer conversion, M_n=54.7 kDa, $Đ$=1.82, b) 4 h, 90.7% monomer conversion, M_n=55.8 kDa, $Đ$=1.87. The large clusters are obtained due to the association of large hydrophobic PHPMA domains, and possibly the intercluster crosslinking as the monomer conversion increases.

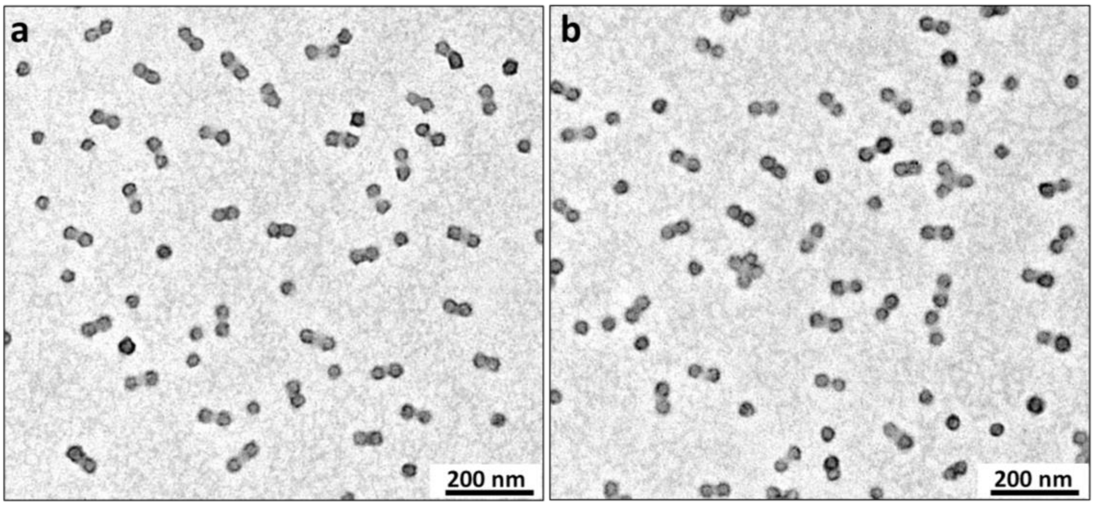


Fig. S17 TEM images of CMs with/without the addition of monomers. a) $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PHPMA_{70}$, monomer removed by dialysis against pure water, b) $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PHPMA_{70}$, with addition of 5 wt% monomer. The impact of remaining monomers on the formations of CMs are studied by comparing CM with/without monomers. The TEM characterization shows unreacted monomer has no significant influence over the morphology.

6. Calculation of surface and interfacial tension

The surface and interfacial tensions of PBzMA and PHPMA was calculated based on Owens–Wendt–Rabel–Kaelble method[5 6]:

$$\gamma_s = \gamma_{sl} + \gamma_l cos\theta \qquad (1)$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \qquad (2)$$

Where γ_{sl}, γ_s, and γ_l: solid/liquid, solid/gas, and liquid/gas interface tensions. θ: the contact angle. γ^d: the dispersive component of the surface tension, γ^p: the polar component. These two components are related as $\gamma = \gamma^d + \gamma^p$.

We synthesized PBzMA (M_n = 90.4 kDa, $Đ$ = 1.20) and PHPMA (M_n = 113.2 kDa, $Đ$ = 1.39). By taking contact angle values for two liquids of widely different properties on various surfaces and calculating γ^d, γ^p, and γ. The properties of the liquids at 20°C are given below Table S3. The surface tensions of polymer PBzMA and PHPMA, as summarized in Table S4.

Table S3. Dispersion and polar contributions to liquid surface tension of water and diiodomethane (T = 20 °C)

Surface	Components of surface tension (mN·m^{-1})		
	γ^d	γ^p	γ
H_2O	29.1	43.7	72.8
CH_2I_2	49.5	1.3	50.8

Table S4. Dispersion and polar contributions to surface tension of various solids

Surface	contact angle(°)		Components of surface tension (mN·m^{-1})		
	Water	diiodomethane	γ^d	γ^p	γ
PBzMA	72.2±3.4	15.1±1.1	46.7±1.9	2.6±0.1	49.3±2.0
PHPMA	56.8±1.1	35.4±1.4	35.5±1.0	13.4±0.4	48.9±1.1

Then we calculated the surface tension at homopolymer-water interface, as summarized in Table S5. γ_{BW}: the interfacial tension of PBzMA-water interface. γ_{HW}: the interfacial tension of PHPMA-water interface. γ_{BH}: the interfacial tension of PBzMA-PHPMA interface, calculated by equation 2[5].

Table S5. The interfacial tensions of various phase for PDMA-*b*-PBzMA-*b*-PHPMA triblock terpolymer in water (PDMA as stabilizer).

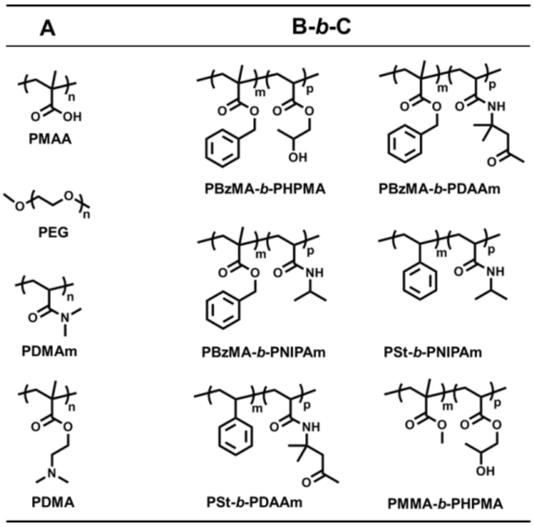
γ_{BW} (mN·m^{-1})	γ_{HW} (mN·m^{-1})	γ_{BH} (mN·m^{-1})
27.1 ± 2.5	9.0 ± 1.6	5.0 ± 3.1

7. The study of additional monomer and the discussion of suitable ABC triblock terpolymer for the synthesis CMs by seeded polymerization.

Polymerization-induced particle-assembly (PIPA) strategy is an extension of PISA for the rational design and mass production of BCP nanoparticles with structural hierarchies. For ABC linear triblock terpolymer with A as the stabilizer, the design of ABC triblock terpolymer requires; 1) strong phase separation between B and C blocks, 2) monomer C suitable for PISA. And the morphology of HNPs is tuned by the interfacial tension, and V_C/V_B of ABC triblock terpolymer.

Based on these requirements, PIPA could be applied to vast different triblock systems, in either water, or organic solvents. In this work, we focus on the aqueous dispersion polymerization. The block A should be steric stabilizer in water, and there are a lot of choice of block A, e.g. poly methacrylic acid (PMAA), polyethylene glycol (PEG), poly(*N,N*-dimethylacrylamide) (PDMA), poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA). The monomer C should be suitable for aqueous PISA, which could be found in related literature; R. O'Reilly and coworkers have summarized and predicted monomers for aqueous PISA.[7] Besides, the phase separation between block B and block C is required. Therefore, a few possible ABC triblock terpolymers are summarized in table S6.

Table S6. Possible ABC triblock terpolymer for aqueous polymerization-induced colloid-assembly.



PNIPAm, poly(*N*-isopropylacrylamide), PSt, polystyrene, PMMA, polymethyl methylacrylate.

As an example, we have studied the aqueous seeded polymerization of diacetone acrylamide (DAAm), using $PDMA_{70}$-*b*-$PBzMA_{96}$ spheres as seeds. The triblock terpolymer was studied by ^1H NMR and SEC (Fig. S19 and S20). $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PDAAm_{95}$ ($Đ$ =1.38) self-assembled into a mixture of AB_2 and AB_4 CMs, with PDAAm as attractive domains (Fig S21). As the DP of PDAAm increased, $PDMA_{70}$-*b*-

PBzMA$_{96}$-*b*-PDAAm$_{114}$ ($Đ$ =1.52) produced majorly AB$_4$ CMs (Fig. S22). We have demonstrated that PIPA could be readily applied to another triblock terpolymer systems for the synthesis of CMs.

PIPA strategy is promising for the synthesis of functional HNPs. We would take efforts to study more ABC triblock terpolymers in future work.

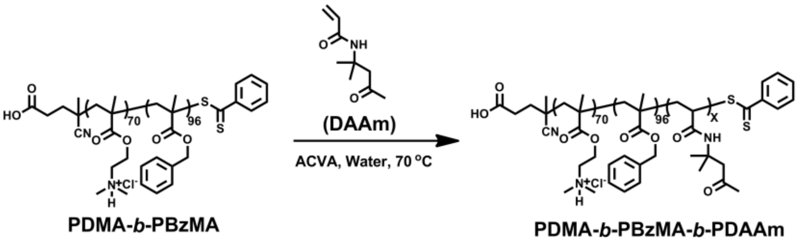


Fig. S18 Aqueous dispersion polymerization of DAAm, using PDMA-*b*-PBzMA as seeds.

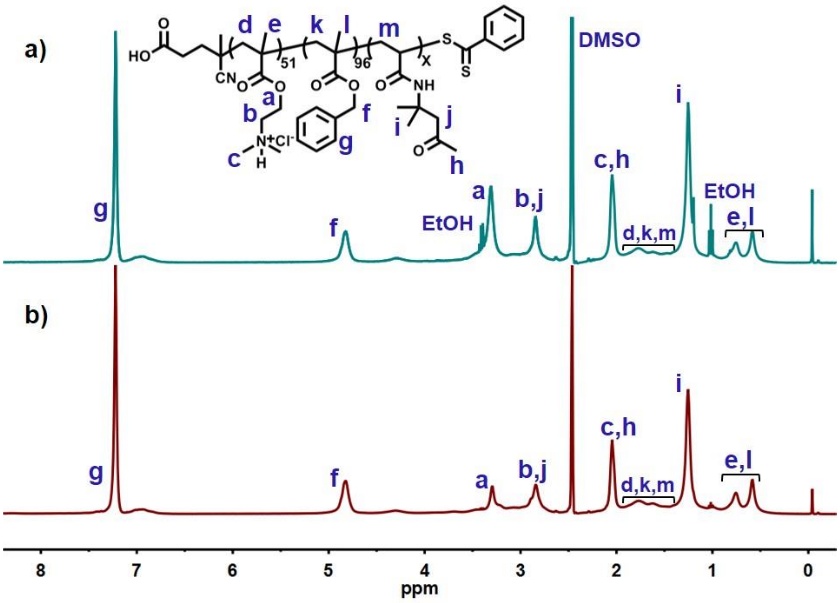


Fig. S19 ^{1}H NMR spectra in DMSO-d_6 at 25 ^{o}C. Red, PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{95}$, green, PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PHPMA$_{114}$

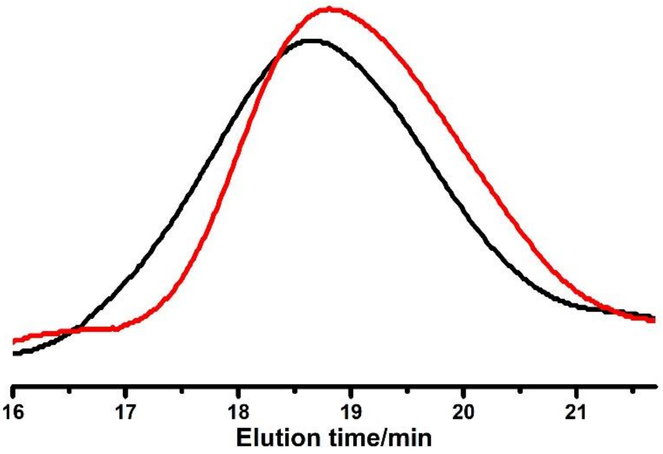


Fig. S20 SEC traces of PDMA-*b*-PBzMA-*b*-PDAAm triblock terpolymers. (THF as eluent) Red, PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PDAAm$_{96}$, M_n=27.6 kDa, $Đ$=1.38. Black, PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PDAAm$_{114}$, M_n = 32.3 kDa, $Đ$ = 1.52.

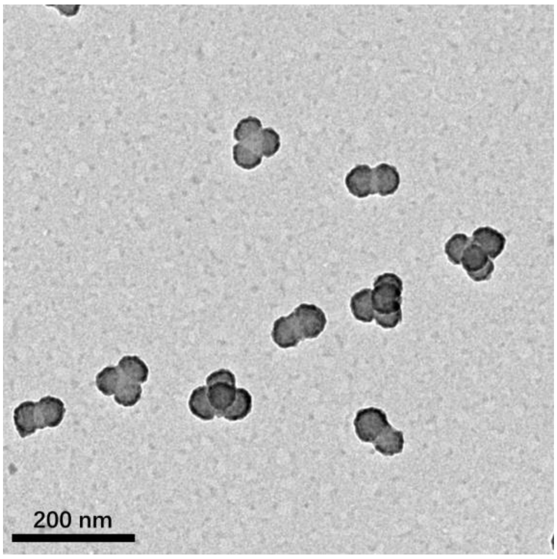


Fig. S21 TEM image of PDMA$_{70}$-*b*-PBzMA$_{96}$-*b*-PDAAm$_{95}$ CMs.

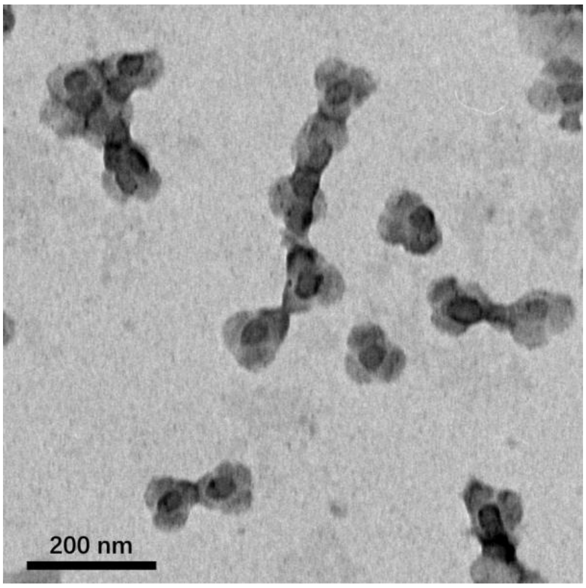


Fig. S22 TEM image of $PDMA_{70}$-*b*-$PBzMA_{96}$-*b*-$PDAAm_{114}$ CMs.

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