

Star Architecture Promoting Morphological Transitions during Polymerization-Induced Self-Assembly

Materials.

Poly(ethylene glycol) methyl ether (PEG₁₁₃-OH, 5000 g/mol), 2,4,6-trichloro-1,3,5-triazine (TCT, 99%), trifluoroacetic acid (99%), sodium trifluoroacetate (NaTFA, 98%) and diacetone acrylamide (DAAM, 99%) were purchased from Sigma-Aldrich. P-toluenesulfonyl chloride (PTSC, 99%) was purchased from Aladdin Reagent. Dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, 99%) and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50, 97%) were purchased from J&K Scientific. *N,N*-diisopropylethylamine (DIPEA, 98+%) was purchased from Alfa Aesar. 4-Aminopiperidine (97%) was purchased from Acros Organics. Dithranol (98%) was purchased from AK Scientific. Triethylamine (Et₃N, AR) and *N*-hydroxysuccinimide (NHS, AR) were obtained from Sinopharm Chemical Reagent. The materials were used without further purification. The chain transfer agent, 2-(ethylsulfanyllthiocarbonylsulfanyl) propionic acid was synthesized according to a previously reported procedure (*Journal of Polymer Science, Part A: Polymer Chemistry* 2016, 54, 1036–1043).

Characterization and methods.

¹H NMR spectroscopy: ¹H NMR spectra were acquired on a Bruker AV 500 MHz spectrometer in d₆-DMSO (linear and star block copolymers), D₂O (PEG₁₁₃-NH₂) or CDCl₃ (CTAs and macro-CTAs). Chemical shifts were referenced to the corresponding solvent residue. ¹H NMR spectroscopy for PEG-DCT and PEG-(NH₂)₂ was conducted on an Inoz 500 MHz, 2 RF channel instrument at 25 °C in CDCl₃.

Gel permeation chromatography (GPC): A Viscotek TDMax triple-detector GPC system was utilized to quantify the absolute molecular weights and dispersities of the PEG-(PDAAM)₂ star block copolymers. The Viscotek TDMax triple-detector GPC system (Viscotek, Malvern Instruments Ltd., UK) was equipped with a Viscotek GPCmax combination of degasser, pump, and autosampler, a Viscotek GPC column oven, a T6000M column (ID 7.8 mm × 300 mm, particle size 10 μm). Detection was performed on a Viscotek TDA 305 triple-detector array including a refractive index (RI) detector, a viscometer and a light scattering (LS) detector (90° and 7° angles), using *N,N*-dimethylformamide (HPLC grade, containing 20 mM LiBr) as the eluent at a flow rate of 0.7 mL/min. The temperature of the column and detectors was set at 45 °C. OmniSEC 5.12 software was used for the data acquisition and analysis. A Waters GPC system calibrated with a series of ten PMMA standards ($2.5 \times 10^3 - 9.8 \times 10^5$ g/mol) was used to quantify the relative molecular weights and dispersities of PEG-PDAAM linear copolymers

synthesized in this work. The GPC system consisted of a Waters Alliance e2695 system, a Styragel guard column, three Waters Styragel columns (HR3, HR4 and HR5, set at 65 °C) and a 2414 refractive index detector (set at 45 °C). The flow rate of DMF (HPLC, containing 1 mg/ mL LiBr) was set as 0.8 mL/min.

Dynamic light scattering (DLS): A Malvern ZS90 with a He–Ne laser (633 nm, 4 mW) was used for DLS analysis. Diluted nano-object dispersions (0.1% w/v) in glass cuvettes were measured. Z-average diameter (D_h) and polydispersity (PDI) of nano-objects were reported.

Transmission electron microscopy (TEM): A Jeol 200CX TEM (200 kV) was utilized to identify the morphologies of nano-objects. Diluted nano-object dispersions at either 0.1% or 0.2% w/v were used to prepare the TEM samples on carbon-coated copper grids. The TEM samples were dried under vacuum at 40 °C for 12 h after brief drying under ambient conditions. The number-average diameter (D_n) and membrane thickness (δ) of vesicles were determined from around 200 particles for each sample.

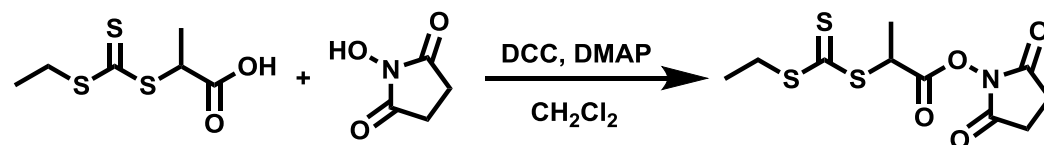
Matrix-assisted laser desorption/ionization-time of flight (MALDI-ToF):

MALDI-ToF mass spectrometry for PEG-OH and PEG-diamine was performed on a Bruker Microflex LRF MALDI-ToF (Billerica, MA) mass spectrometer in reflectron, positive ion mode using an N₂ on-axis laser. Spectra were collected in flexControl (Bruker Daltronics Inc., Billerica, MA) and analyzed using flexAnalysis (Bruker Daltronics Inc., Billerica, MA) and Polymerix Version 3 software (Sierra Analytics, Modesto, CA). The samples were prepared by mixing solutions of dithranol matrix (20.0 mg/mL in dichloromethane), NaI (1.00 mg/mL in 1:1 dichloromethane:acetone), and polymer (2.00 mg/mL in dichloromethane) at a v:v:v ratio of 5:2:2.5 matrix:salt:polymer and 3 μ L were spotted on a stainless steel Bruker MSP 96 target polished steel BC plate and air dried. PEG-diamine samples were prepared by mixing solutions of dithranol matrix (20.0 mg/mL in dichloromethane) and polymer solution (1.0 mg/mL in dichloromethane with 2 drops trifluoroacetic acid) at a v:v ratio of 5:2.5 matrix:polymer and 3 μ L were spotted on a stainless steel Bruker MSP 96 target polished steel BC plate and air dried.

MALDI-ToF mass spectrometry for PEG-(CTA)₂ was performed on a AB SCIEX 5800 using *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. DMF was used as the solvent, and NaTFA was used as the ionic agents.

Atomic force microscopy (AFM): AFM was performed on a Shimadzu SPM-9600 in the phase mode. The nano-object dispersion was diluted to 0.01% w/v and spread on freshly cleaved mica pieces and air-dried.

Synthesis of 2-(ethylsulfanylthiocarbonylsulfanyl) propionic succinimide ester



2-(Ethylsulfanylthiocarbonylsulfanyl) propionic succinimide ester was synthesized by adapting a

reported protocol (*ACS Appl. Mater. Interfaces* 2015, 7, 10132–10145). 2-(Ethylsulfanylthiocarbonylsulfanyl) propionic acid (10.00 g, 47.60 mmol), *N*-hydroxysuccinimide (8.25 g, 71.40 mmol), DMAP (1.16 g, 9.52 mmol) and dry CH₂Cl₂ (100 mL) were added to a 250 mL round-bottom flask. The reaction was placed in an ice bath and was stirred for 30 min. DCC (7.80 g, 61.88 mmol) in CH₂Cl₂ (20 mL) was added dropwise to the reaction. After the reaction was kept at 0 °C for 4 h, it was allowed to gradually warm up to room temperature and left to stir overnight. The reaction mixture was filtered via suction flask to remove the white precipitate. The solvent of the collected filtrate was removed by rotary evaporation to yield a yellow residue which was dissolved in CH₂Cl₂ and then transferred to a separating funnel. The organic layer was washed with water (5×) and dried over anhydrous MgSO₄. After filtration to remove MgSO₄, removal of the solvent by rotary evaporation afforded a yellow crude product which was purified via flash chromatography on SiO₂. Initially, petroleum ether/ethyl acetate (85/15) was used for approximately 5–6 column volumes to elute light yellow impurities and then petroleum ether /ethyl acetate (60/40) was used to elute the yellow product. Removal of the solvent by rotary evaporation provided the product as a viscous yellow oil (7.30 g, 73%). ¹H NMR (Figure S1) δ ppm: 1.36 (t, 3H), 1.75 (d, 3H), 2.83 (s, 4H), 3.38 (t, 2H), 5.14 (q, 1H).

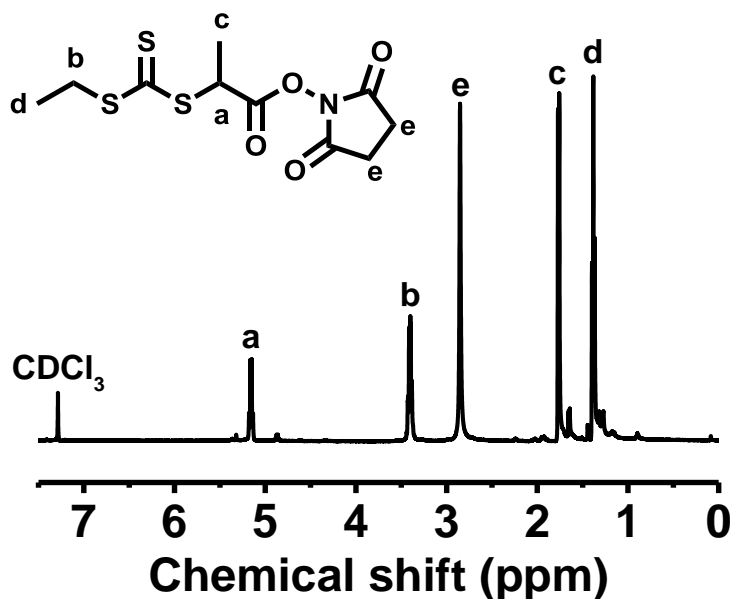
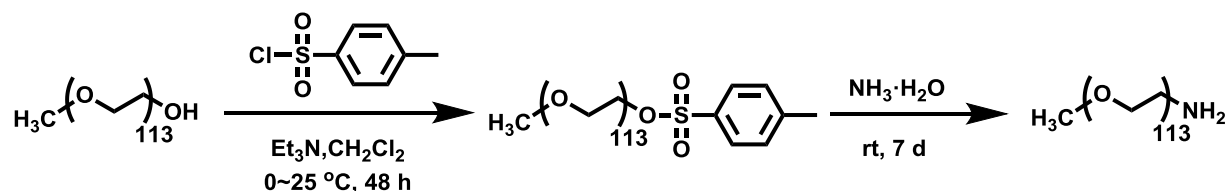


Figure S1. ¹H NMR spectrum of 2-(ethylsulfanylthiocarbonylsulfanyl) propionic succinimide ester in CDCl₃.

Synthesis of PEG-NH₂ from PEG-OH



PEG-NH₂ was prepared by adapting a previously reported protocol (*J. Am. Chem. Soc.* 2014, 136, 1023–1033). PEG₁₁₃-OH (M_n =5000 g/mol, 10.0 g, 2.0 mmol) was dissolved in anhydrous CH₂Cl₂ (30 mL) in a 250 mL round-bottomed flask. The reaction was placed in an ice bath. Triethylamine (1.39 mL, 1.01 g 10.0 mmol) was dropwise added with stirring, followed by the dropwise addition of *p*-toluenesulfonyl chloride (PTSC) (3.81 g, 20.0 mmol) in CH₂Cl₂ (20 mL). The reaction was left to stir for 18 h. The reaction mixture was filtered with suction flask to remove the insoluble white triethylamine hydrochloride salt, followed by precipitation 5× into excess cold diethyl ether. The white PEG-OTs product (7.4 g, 74%) was obtained and dried under vacuum overnight.

PEG-OTs (7.0 g) was added to a 25% aqueous ammonia solution (50 mL) in a 250 mL round-bottomed flask. The reaction was left with stirring for a week at 20 °C. The ammonia was allowed to evaporate in nitrogen atmosphere for 12 h. NaOH (5 M) was dropwise added until the pH reached 13. The product was extracted with CH₂Cl₂ (5×), washed with saturated brines and then dried over anhydrous MgSO₄. The crude product was precipitated 3× into excess cold diethyl ether and dried in nitrogen atmosphere to produce white PEG-NH₂ (5.3 g, 76%).

The final amine end-group functionality was determined to be 97% via ¹H NMR analysis (Figure S2) by comparing the integrated triplet at 2.9 ppm which corresponds to the two methylene protons adjacent to the amine with the integrated multiplet corresponding to the protons on the PEG backbone.

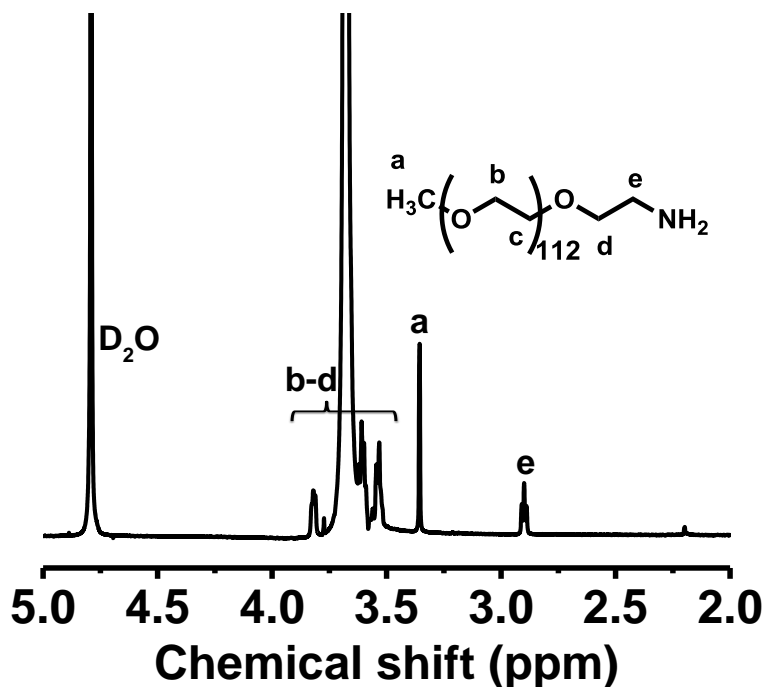
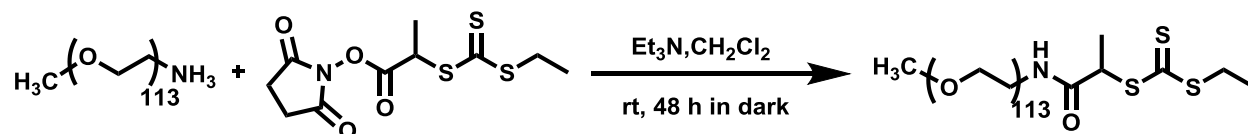


Figure S2. ^1H NMR spectrum of PEG-NH₂ in D₂O.

Synthesis of monofunctional macro-CTA (PEG-CTA) from PEG-NH₂



2-(Ethylsulfanyltiocarbonylsulfanyl) propionic succinimide ester (1.23 g, 4.0 mmol) was dissolved in anhydrous CH₂Cl₂ (5 mL) in a 25 mL round-bottomed flask. PEG-NH₂ (2.0 g, 0.4 mmol) in anhydrous CH₂Cl₂ (10 mL) was dropwise added via a syringe pump. This reaction solution was stirred for 48 h in dark. The reaction mixture was precipitated 5× into excess cold diethyl ether to provide the slightly yellow monofunctional macro-CTA, which was dried under vacuum and was analyzed by ^1H NMR spectroscopy (Figure S3).

The presence of methyl signals at 1.56 and 1.34 ppm confirmed the presence of the terminal trithioester group. Comparison of these integrated multiplet signals with that at 3.0–4.0 ppm corresponding to the protons on the PEG backbone suggested about 92 % trithioester end-group functionality.

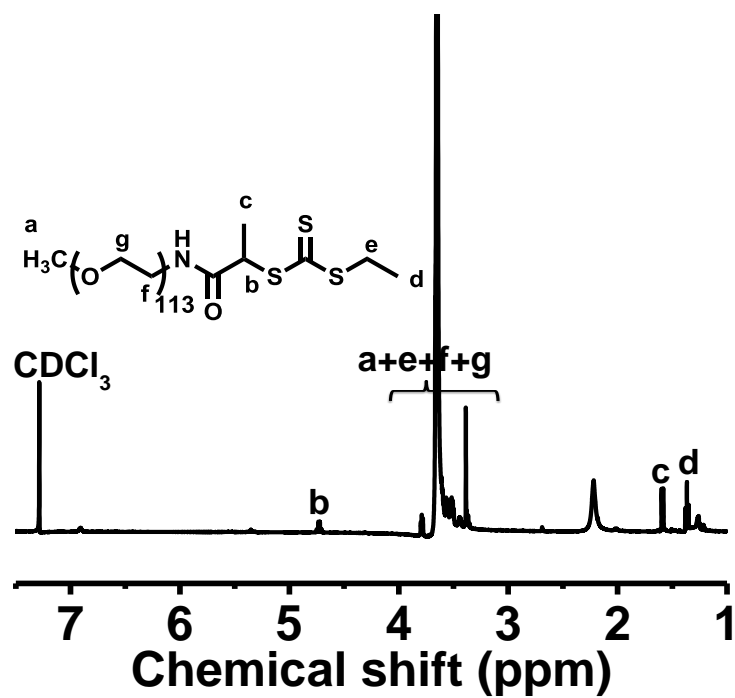


Figure S3. ¹H NMR spectrum of PEG-CTA in CDCl₃.

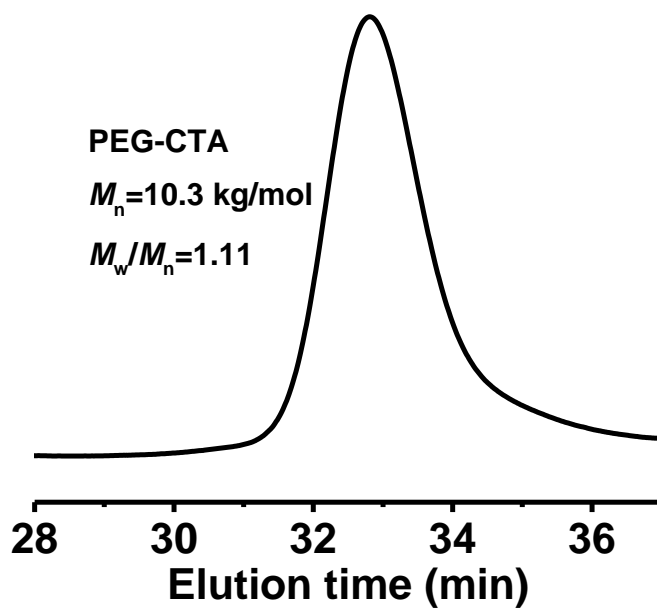
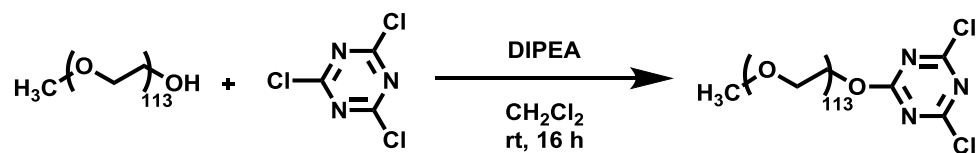


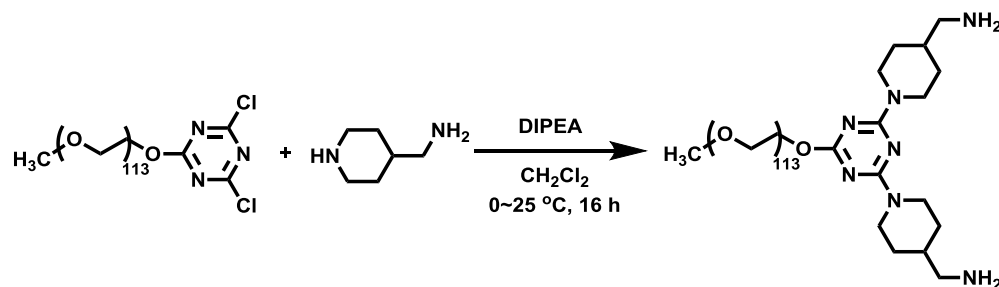
Figure S4. GPC trace of PEG-CTA (RI detector, PMMA standards).

Synthesis of PEG-dichlorotriazine (PEG-DCT) from PEG-OH



PEG₁₁₃-OH (10.0 g, 2.00 mmol), TCT (0.920 g, 5.00 mmol), and DIPEA (0.869 mL, 0.645 g, 5.00 mmol) were added to CH₂Cl₂ (50.0 mL) and left to stir over night. The solution was filtered, precipitated 2× into cold diethyl ether, and vacuum dried yielding PEG-DCT product 8.47 g (82%).

Synthesis of PEG-diamine (PEG-(NH₂)₂) from PEG-DCT



PEG-DCT (7.5 g, 1.50 mmol) was dissolved into CH₂Cl₂ (75 mL). In a separate flask, 4-aminomethylpiperidine (0.718 mL, 684 mg, 6.00 mmol) and DIPEA (1.04 mL, 774 mg, 6.00 mmol) were added to CH₂Cl₂ (75 mL) and cooled to 0 °C. The PEG-DCT solution was then added dropwise via a syringe pump over 8 h to the cooled, stirring solution. After the volume of PEG-DCT solution had been added, the reaction was warmed to room temperature and stirred for a subsequent 8 h. The solution was then filtered, concentrated, precipitated into cold diethyl ether, and vacuum dried yielding PEG-(NH₂)₂ 5.87 g (74%). For characterization of PEG-(NH₂)₂ see Figures S5-7.

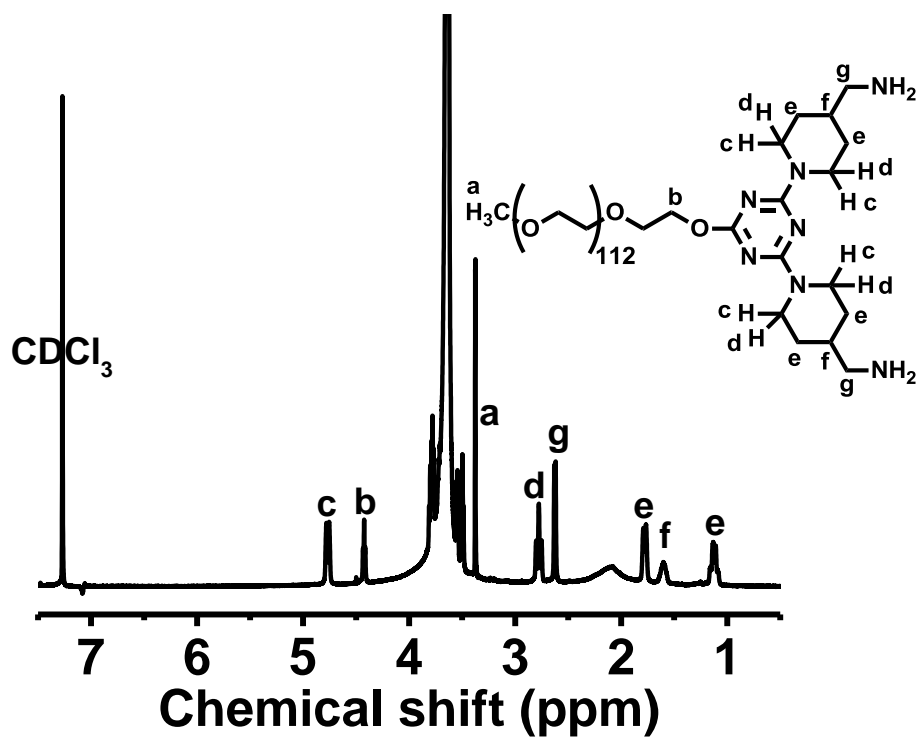


Figure S5. ¹H NMR spectrum of PEG-(NH₂)₂ in CDCl₃.

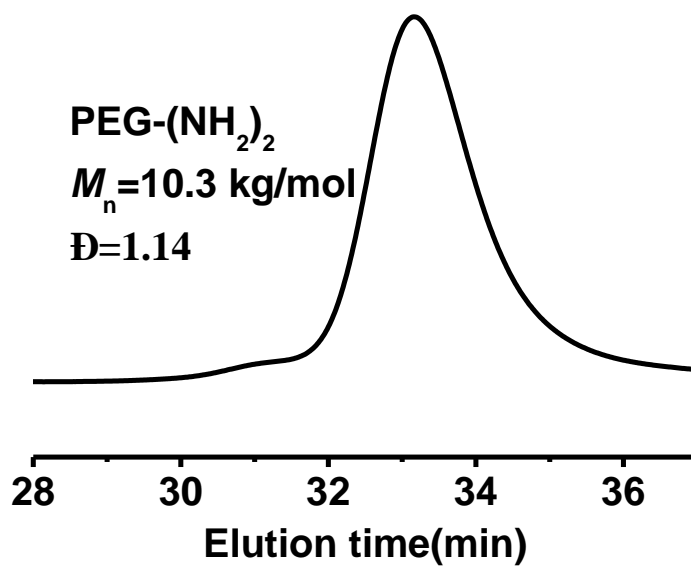


Figure S6. GPC trace (RI detector, PMMA standards) of PEG-(NH₂)₂.

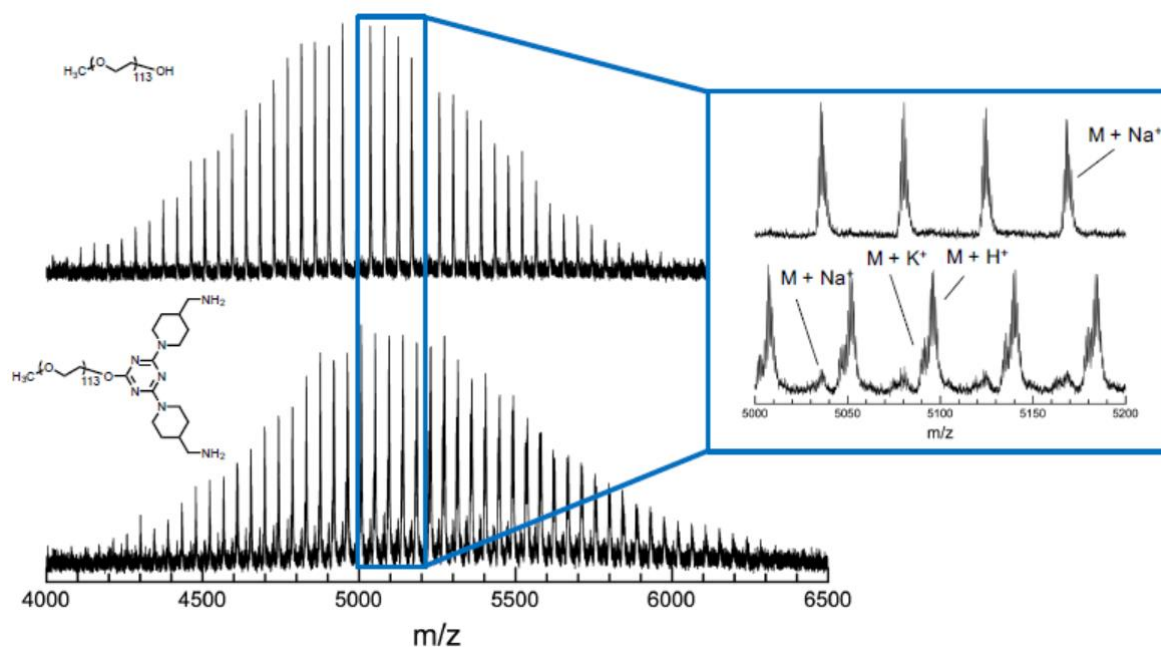
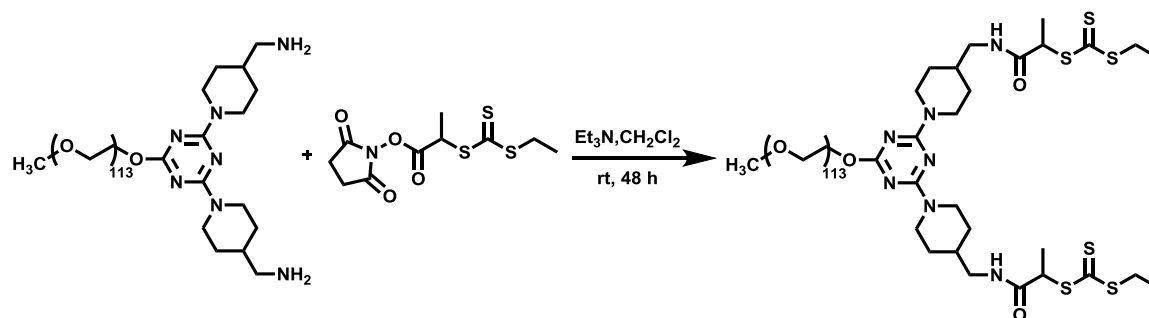


Figure S7. MALDI-ToF spectra and structure analysis for PEG-OH and PEG-(NH₂)₂.

Synthesis of difunctional macro-CTA (PEG-(CTA)₂) from PEG-(NH₂)₂



2-(Ethylsulfanylthiocarbonylsulfanyl) propionic succinimide ester (1.17 g, 3.8 mmol) and trimethylamine (562 μ L, 0.38 g, 3.8 mmol) were dissolved in anhydrous CH₂Cl₂ (4 mL) in a 25 mL round-bottomed flask. PEG-diamine (1.0 g, 0.19 mmol) in anhydrous CH₂Cl₂ (6 mL) was dropwise added via a syringe pump. This reaction solution was stirred for 48 h in dark. The mixture was precipitated 5 \times into excess cold diethyl ether to yield the slightly yellow difunctional macro-CTA (PEG-(CTA)₂), which was dried under vacuum and subjected to analysis by ¹H NMR spectroscopy (Figure S8). The disappearance of the triplet at 2.78 ppm corresponding to the two methylene protons adjacent to the amine indicates the full conversion of original amine. The presence of the methylene signal at 3.13 ppm which corresponds to the two methylene protons adjacent to the amide, methyl signals at 1.57 and 1.36 ppm, methylene signal at 3.37, and methide signal at 5.34 ppm, confirmed the presence of the terminal trithioester group. Comparison of these integrated signals with that at 3.0–4.0 ppm corresponding to the protons on the PEG backbone suggested about 97 % trithioester end-group functionality

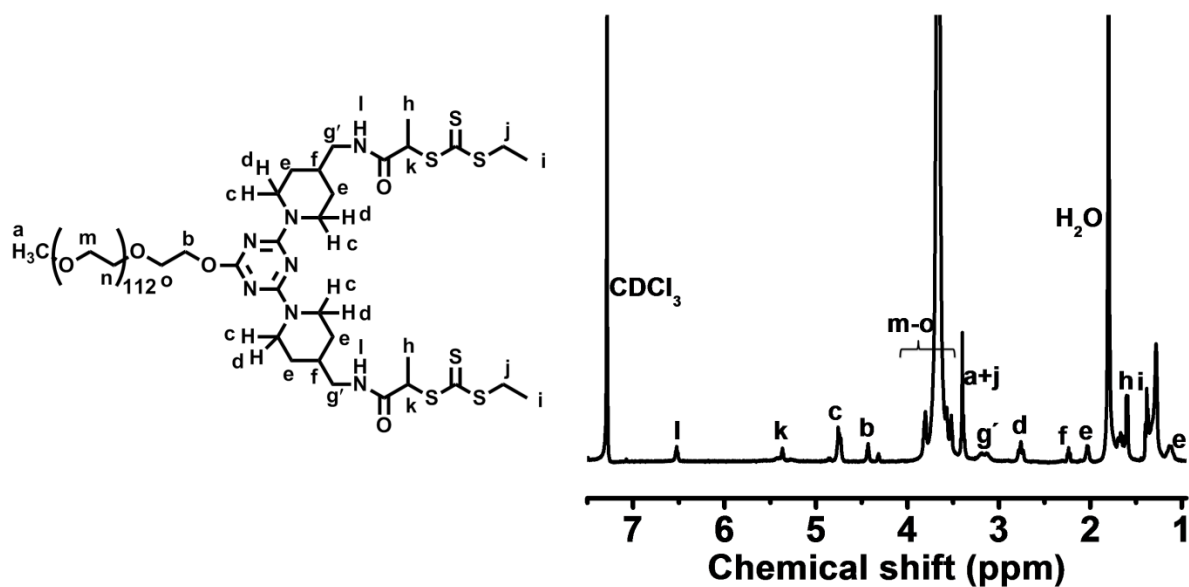


Figure S8. ^1H NMR spectrum of PEG-(CTA) $_2$ with 97% functionality in CDCl_3 .

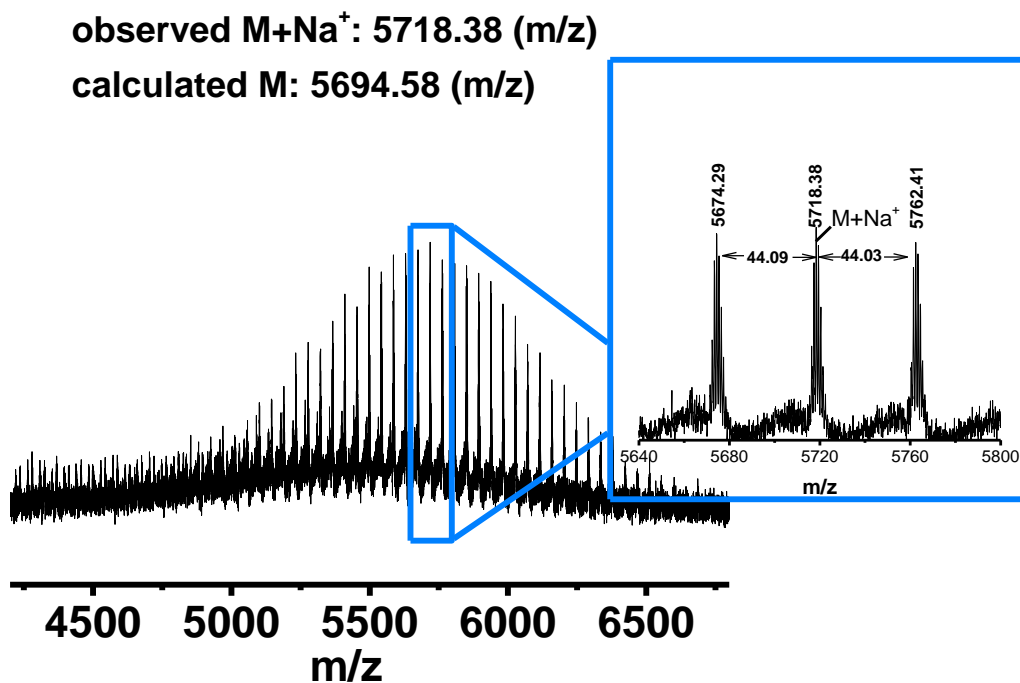


Figure S9. MALDI-ToF spectrum and structure analysis of PEG-(CTA) $_2$ with 97% functionality.

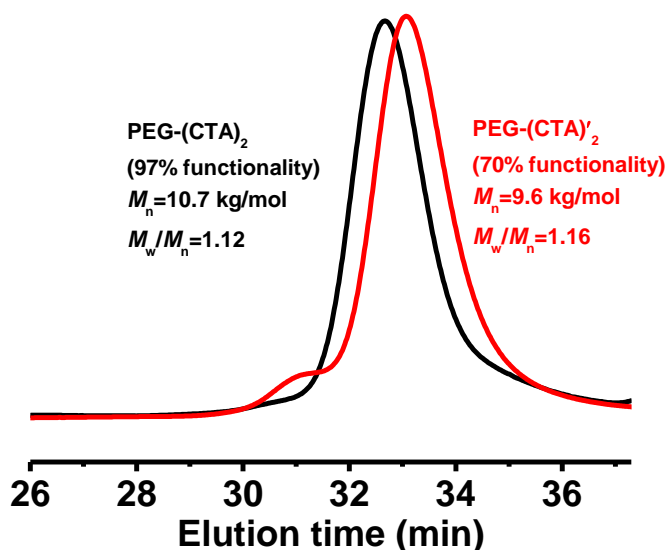


Figure S10. GPC (RI detector, PMMA standards) traces for PEG-(CTA)₂ with 97% functionality (black) and PEG-(CTA')₂ with 70% functionality (red).

RAFT Dispersion Polymerization of DAAM

RAFT dispersion polymerization of DAAM using PEG-CTA or PEG-(CTA)₂ was performed in deionized (DI) water at 70 °C. The synthesis of PEG-(PDAAM₂₀₀)₂ at 15% solids (entry 6, Table S2) was taken as a representative example of RAFT dispersion polymerization of DAAM. PEG-(CTA)₂ (0.023 g, 4.1 μmol) and DAAM (0.277 g, 1.64 mmol) were dissolved in DI water (2 mL). After degassed with nitrogen for 30 min, the mixture was immersed into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed V-50 aqueous solution (100 μL, 0.1332 mg) was injected via a microsyringe. The reaction was then left to continue for 4 h under nitrogen. The final monomer conversion was determined using ¹H NMR by comparing the integral of the proton (s, -CO-NH-, 7.81 ppm) of unreacted DAAM to the integral of proton (s, -CO-NH-, 7.81 ppm) of unreacted DAAM and the protons (-CO-NH-, 6.82-7.23 ppm) of PDAAM.

Supplementary data for RAFT aqueous dispersion polymerization of DAAM using PEG-CTA

Table S1. Characterization data for RAFT aqueous dispersion polymerization of DAAM using PEG-CTA.^a

entry	solids ^b (% w/v)	DP ^c	$M_{n,th}$ ^d (kg/mol)	$M_{n,GPC}$ ^e (kg/mol)	\bar{D} ^e	D_h (nm) (PDI) ^f	morphology ^g
1	15	200	39.0	48.8	1.25	64 (0.02)	spheres
2	15	300	56.0	65.8	1.37	87 (0.03)	spheres
3	15	400	72.9	81.3	1.50	120 (0.06)	spheres
4	15	500	89.8	95.6	1.62	110 (0.02)	spheres
5	15	600	106.7	108.4	1.69	160 (0.06)	spheres
6	20	200	39.0	-	-	99 (0.05)	spheres
7	25	200	39.0	-	-	330 (0.25)	lamellae +vesicles
8	30	200	39.0	-	-	840 (0.21)	vesicles

^aRAFT aqueous dispersion polymerization of DAAM using mono-functional PEG-CTA at 70 °C, [PEG-CTA]/[V-50]=1:0.1. ^bSolids=($W_{macro-CTA}+W_{monomer}$)/ V_{water} . ^cDegree of polymerization of PDAAM. ^dTheoretical molecular weight $M_{n,th}=(M_{monomer} \times DP) \times conversion + M_{PEG-CTA}$. ^eMolecular weight ($M_{n,GPC}$) and dispersity (\bar{D}) determined by GPC (RI detector, PMMA standards). ^fHydrodynamic diameter (D_h) and polydispersity (PDI) measured by DLS. ^gNano-object morphology identified by TEM.

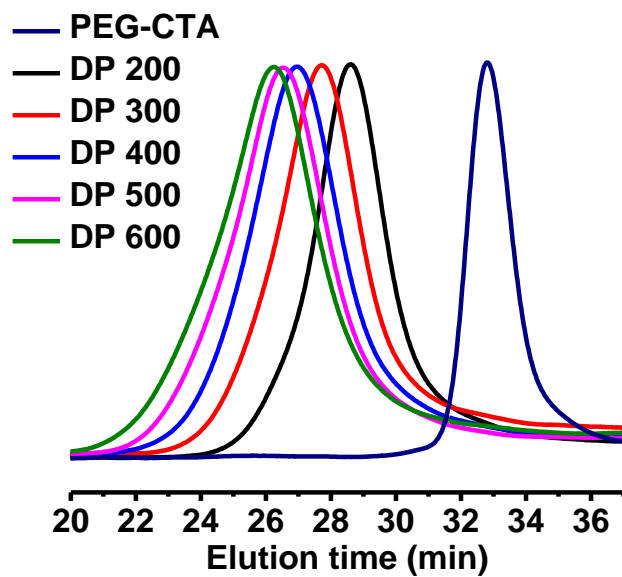


Figure S11. GPC traces for PEG-PDAAM linear block copolymers synthesized at various DPs via RAFT aqueous dispersion polymerization of DAAM at 70 °C ([PEG-CTA]/[V-50]=1/0.1, solids 15%).

Supplementary data for RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂ (97% functionality)

Table S2. Characterization data for RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂.^a

entry	star copolymer	$M_{n,th}^b$ (kg/mol)	$M_{n,GPC}^c$ (kg/mol)	\bar{D}^c	D_h (nm) (PDI) ^d	Morphology ^e
1	PEG-(PDAAM ₆₇) ₂	28.5	36.6	1.23	83 (0.04)	spheres
2	PEG-(PDAAM ₇₀) ₂	29.3	41.3	1.38	610 (0.62)	worms +lamella
3	PEG-(PDAAM ₈₅) ₂	34.4	48.1	1.38	580 (0.24)	lamella
4	PEG-(PDAAM ₁₀₀) ₂	39.5	54.9	1.39	320 (0.24)	lamella
5	PEG-(PDAAM ₁₂₅) ₂	47.9	61.7	1.33	610 (0.11)	lamella +vesicles
6	PEG-(PDAAM ₂₀₀) ₂	73.3	95.3	1.52	410 (0.09)	vesicles

^aRAFT aqueous dispersion polymerization of DAAM using difunctional PEG-(CTA)₂ (97% functionality) at 70 °C, [PEG-(CTA)₂]/[V-50]=1:0.12, solids=15% w/v. ^bTheoretical molecular weight $M_{n,th}=(M_{monomer} \times DP) \times conversion + M_{PEG-(CTA)_2}$. ^cMolecular weight ($M_{n,GPC}$) and dispersity (\bar{D}) determined by GPC with triple detector (entries 1-4) and GPC with RI detector and PMMA standards (entries 5-6). ^dHydrodynamic diameter (D_h) and polydispersity (PDI) measured by DLS. ^eNano-object morphology identified by TEM.

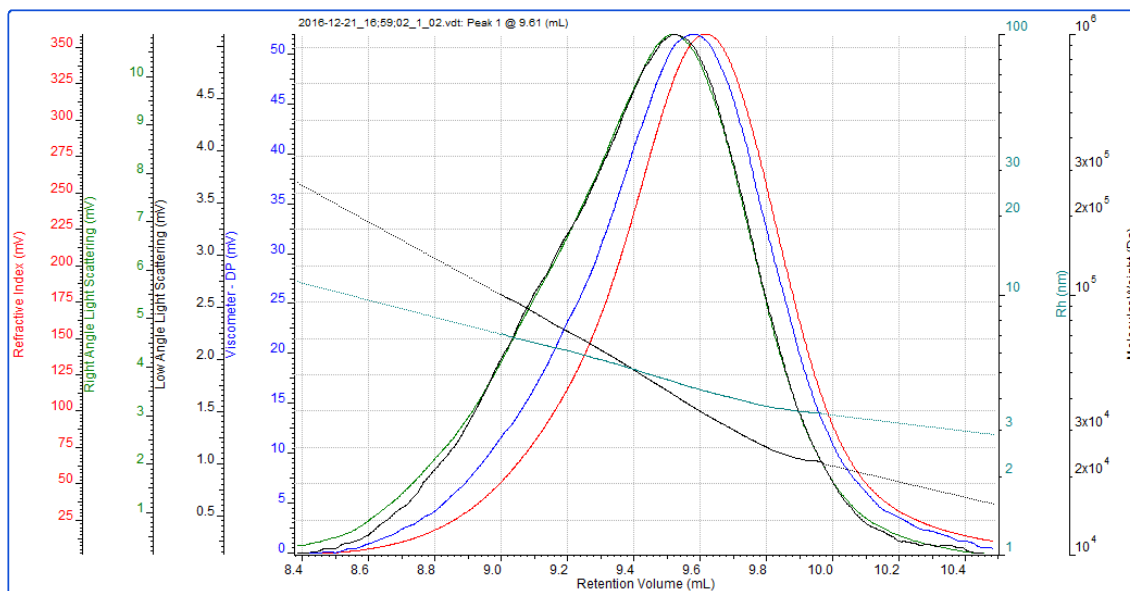


Figure S12. Triple-detector GPC traces for PEG-(PDAAM₆₇)₂ star block copolymer.

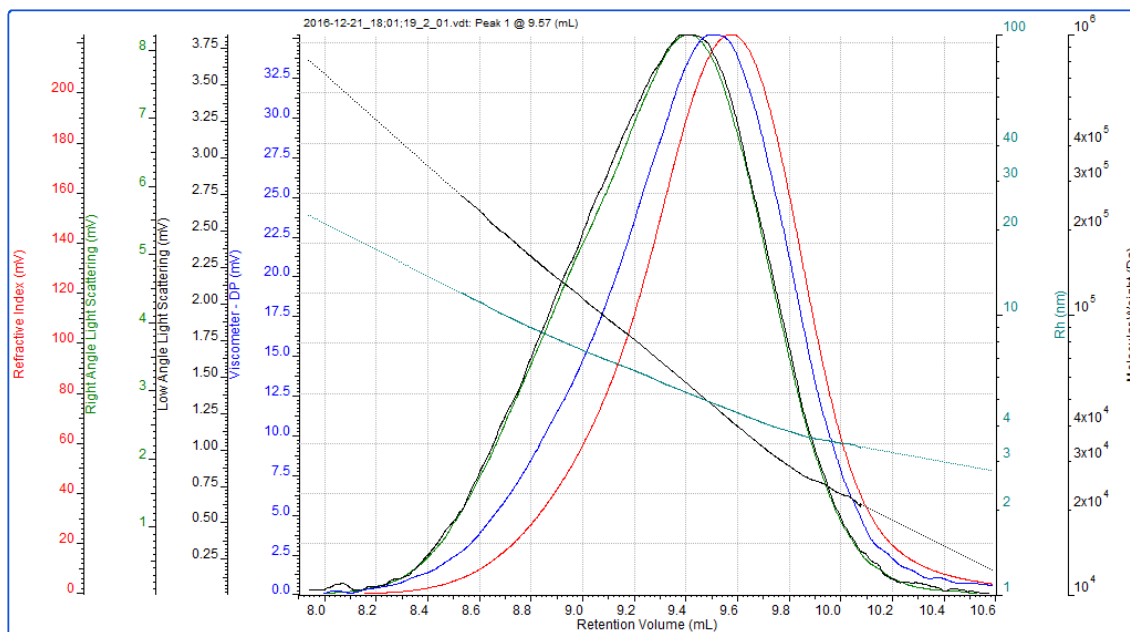


Figure S13. Triple-detector GPC traces for PEG-(PDAAM₇₀)₂ star block copolymer.

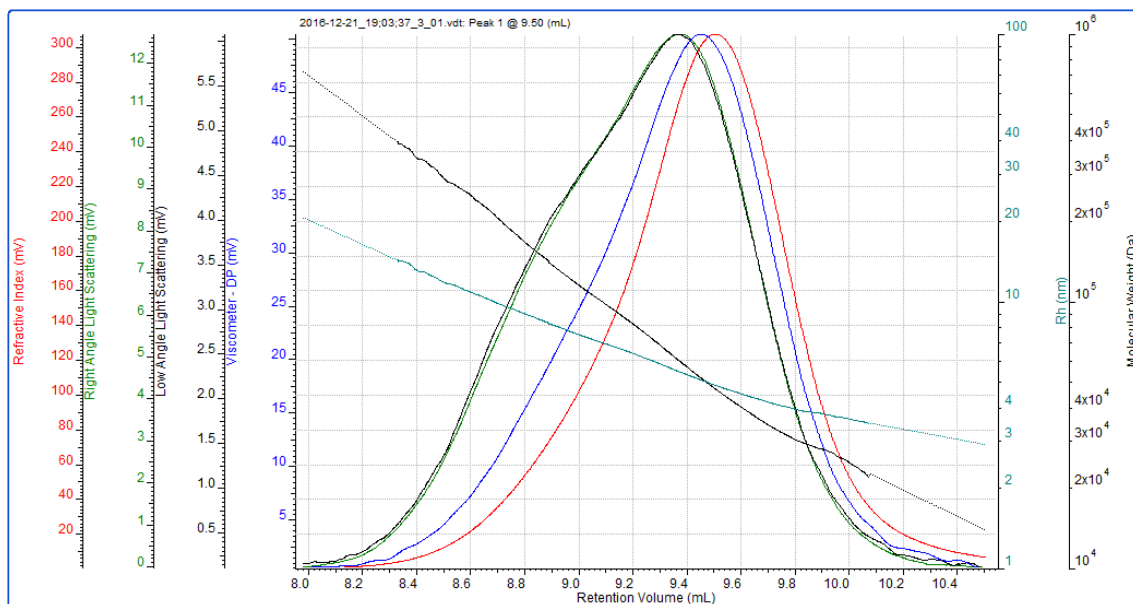


Figure S14. Triple-detector GPC traces for PEG-(PDAAM₈₅)₂ star block copolymer.

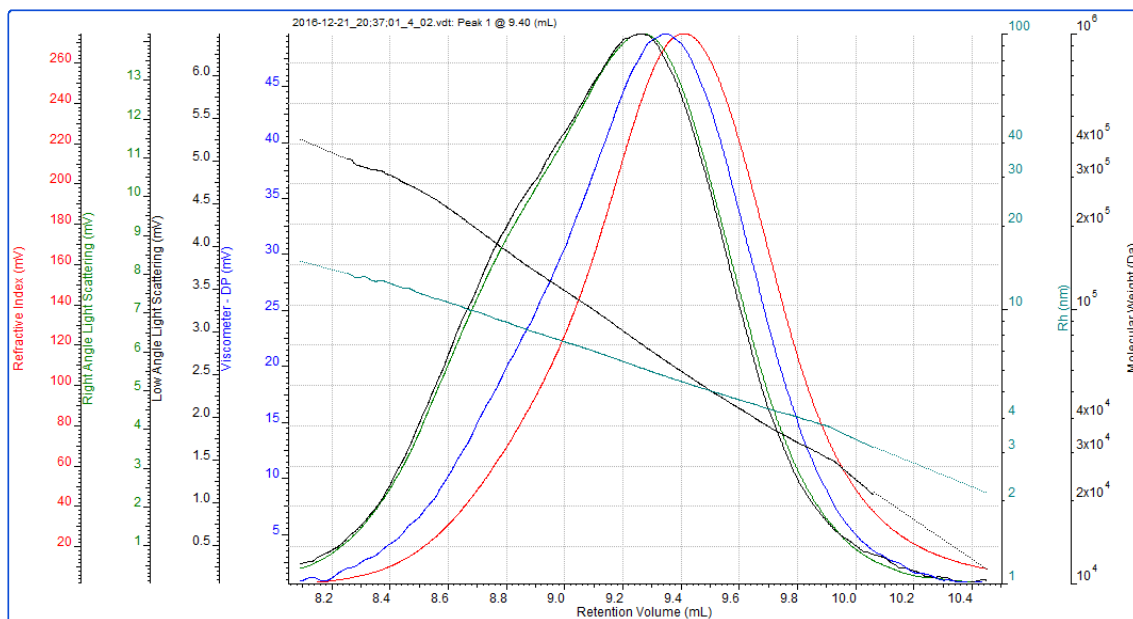


Figure S15. Triple-detector GPC traces for PEG-(PDAAM₁₀₀)₂ star block copolymer.

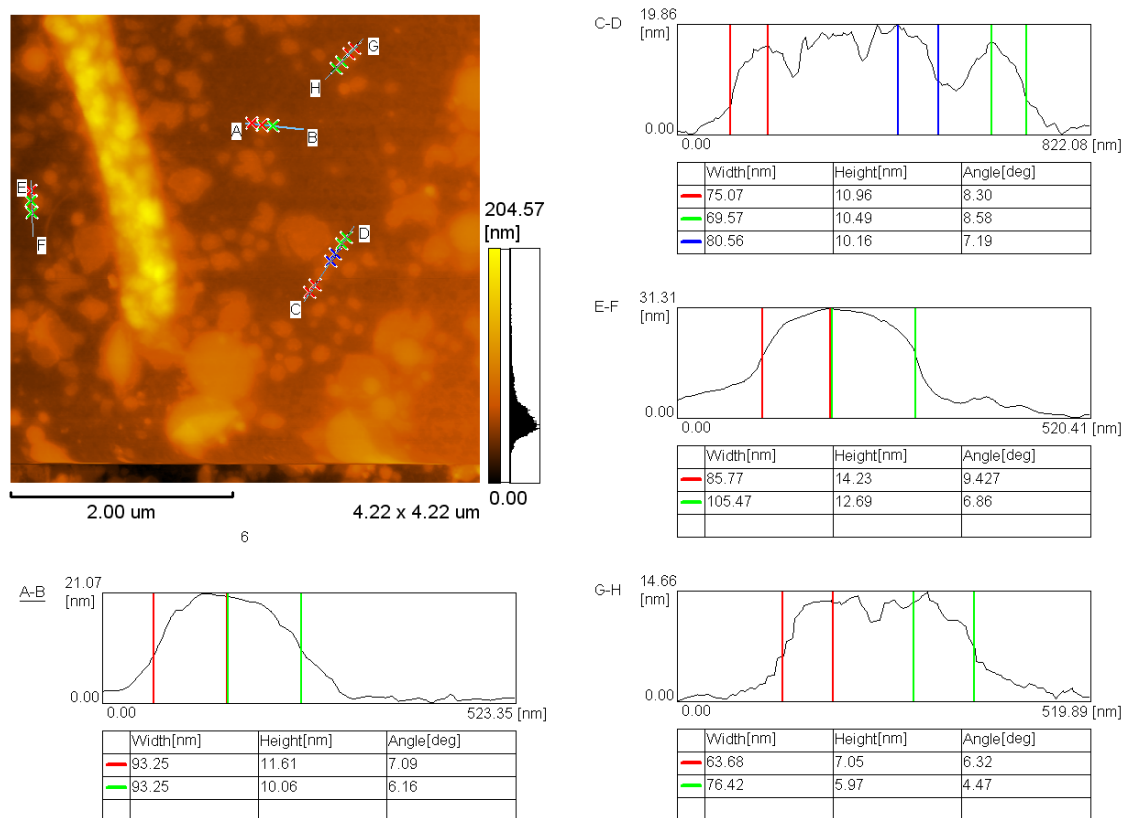


Figure S16. AFM image and analysis of PEG-(PDAAM₁₀₀)₂ star block copolymer nano-objects (entry 4, Table S2).

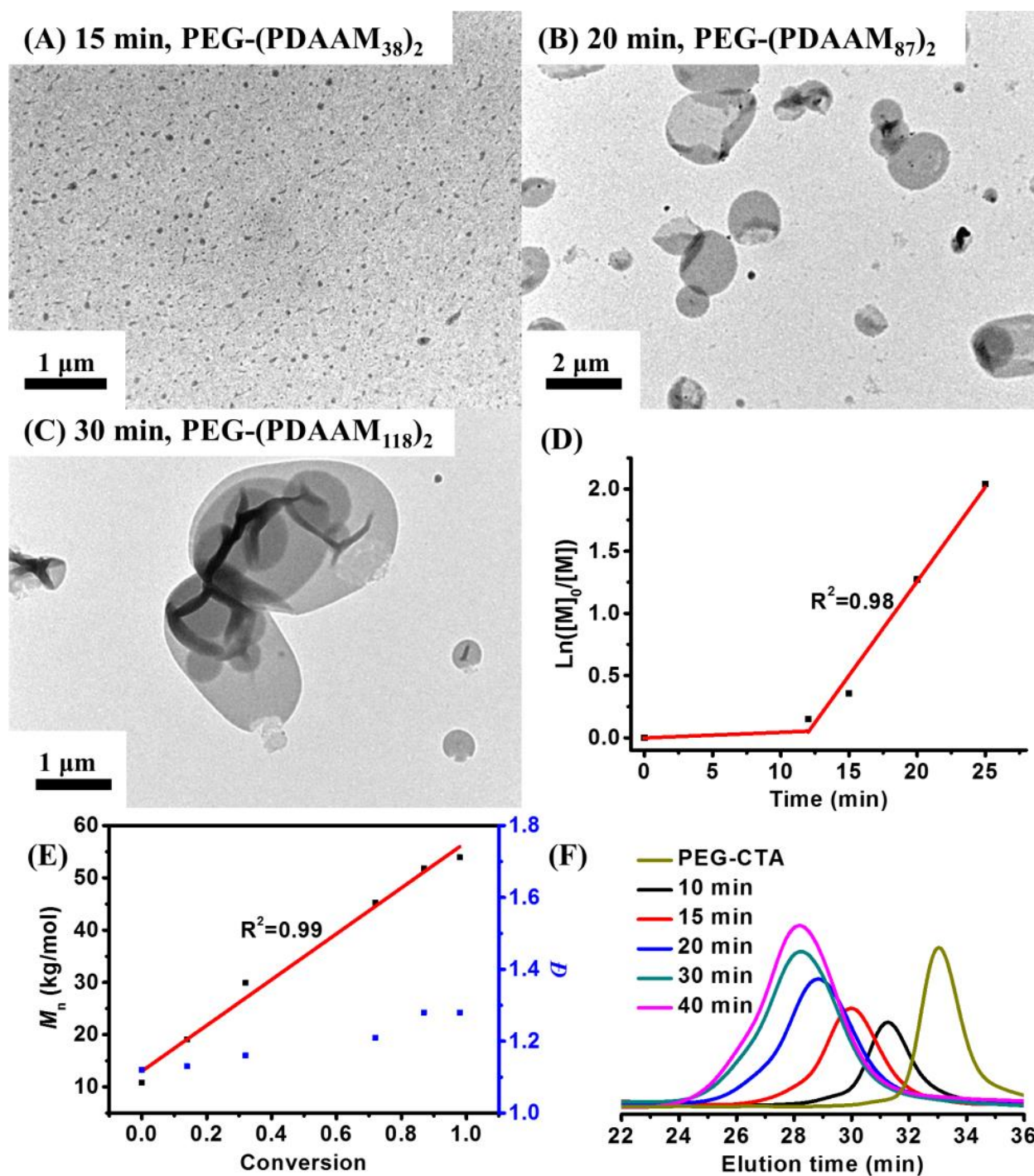


Figure S17. TEM micrographs and polymerization kinetic data during RAFT polymerization of DAAM using PEG-(CTA)₂: [PEG-(CTA)₂]/[DAAM]/[V-50]=1:250:0.12, 70 °C, solids=15% w/v.

Supplementary data for RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)'₂ (70% functionality)

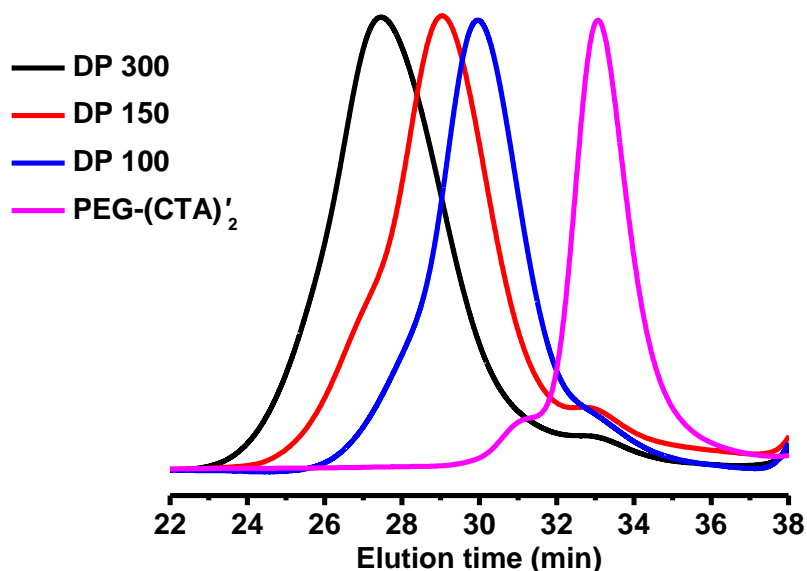


Figure S18. GPC traces (RI detector, PMMA standards) for RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)'₂ (70% functionality) at 70 °C, [PEG-(CTA)₂']/[V-50]=1:0.12 and 15% w/v solids. (The DP of PDAAM was based on the assumption of 100% functionality of PEG-(CTA)'₂ for ease of comparison with the syntheses conducted using PEG-(CTA)₂.)

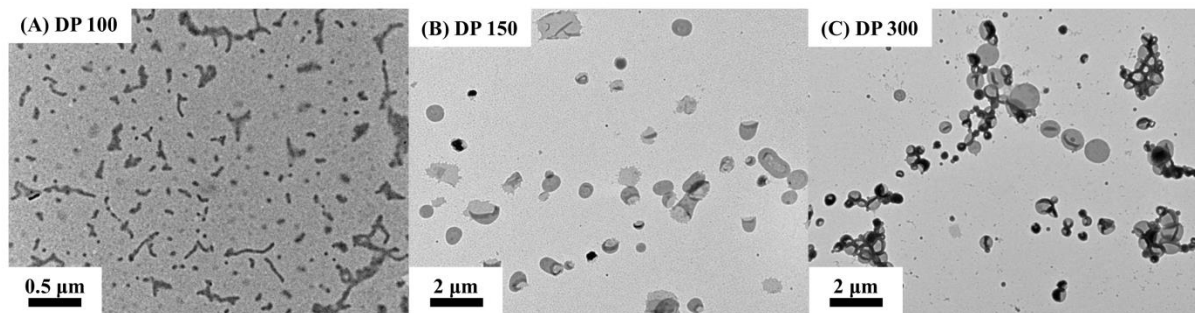


Figure S19. TEM micrographs for nano-objects synthesized via RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)'₂ (70% functionality) at 70 °C, [PEG-(CTA)₂']/[V-50]=1:0.12 and 15% w/v solids. (The DP of PDAAM was based on the assumption of 100% functionality of PEG-(CTA)'₂ for ease of comparison with the syntheses conducted using PEG-(CTA)₂.)

Table S3. Characterization data for RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂' (70% functionality).^a

entry	total DAAM DP ^b	<i>D_h</i> (nm) (PDI) ^c	morphology ^d
1	100	98 (0.04)	spheres+worms
2	150	580 (0.18)	lamellae+vesicles
3	300	360 (0.15)	vesicles

^aRAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂' (70% functionality) at 70 °C, [PEG-(CTA)₂']/[V-50]=1:0.12 and 15% w/v solids. ^bTotal PDAAM DP assuming 100% functionality of PEG-(CTA)₂'. ^cHydrodynamic diameter (*D_h*) and polydispersity (PDI) measured by DLS. ^dNano-object morphology identified by TEM.

Separation of vesicles and spheres in the dispersion synthesized using PEG-(CTA)₂' (70% functionality)

The different morphologies synthesized in RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂' with 70% functionality were separated by centrifugation using a TG1650-WS desktop high speed centrifuge. The dispersion was diluted to 1% w/v and was centrifuged at 8000 r/min for 20 min. After centrifugation, the spheres and inactive PEG remained in the supernate and the vesicles settled to the bottom of the centrifugation tube. The supernate was carefully pipetted out, leaving the vesicle sediment on the bottom. The supernate and sediment were used for characterization by TEM (Figure S19), DLS (Figure S20A) and GPC (Figure S20B).

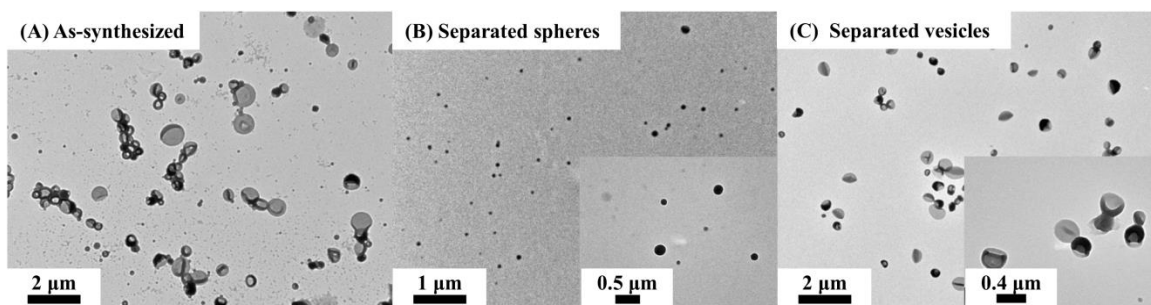


Figure S20. TEM micrographs of (A) as-synthesized nano-objects, (B) spheres in the supernate after centrifugation and (C) vesicles in the sediment after centrifugation for the dispersion prepared via RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂' (70% functionality) at 70 °C, [PEG-(CTA)₂']/[V-50]=1:0.12 and solids=15% w/v targeting PDAAM DP of 300 assuming 100% functionality for PEG-(CTA)₂'.

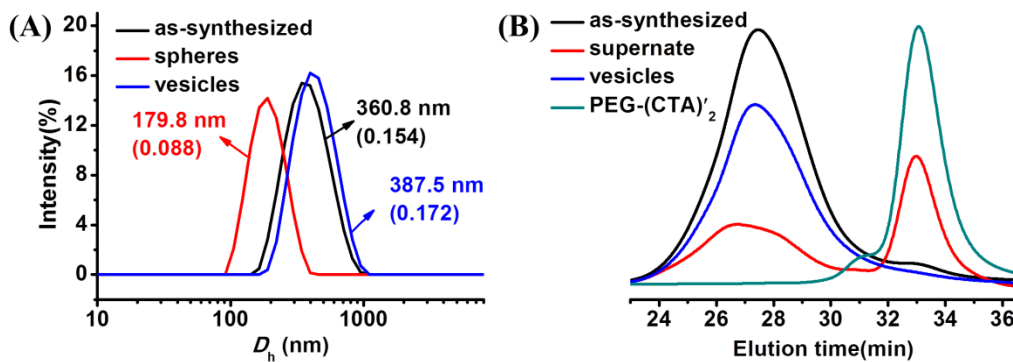


Figure S21. (A) DLS diameter distribution and (B) GPC traces of as-synthesized and separated samples for RAFT aqueous dispersion polymerization of DAAM using PEG-(CTA)₂ (70% functionality) at 70 °C, [PEG-(CTA)₂]/[V-50]=1:0.12 and solids=15% w/v targeting PDAAM DP of 300 assuming 100% functionality for PEG-(CTA)₂.

Supplementary data for RAFT aqueous dispersion polymerization of DAAM using binary mixtures of PEG-CTA and PEG-(CTA)₂

Table S4. Characterization data for RAFT aqueous dispersion polymerization of DAAM using binary mixtures of PEG-CTA and PEG-(CTA)₂.^a

entry	molar fraction of [PEG-(CTA) ₂] ^b	copolymer ^c	<i>D_h</i> (nm) (PDI) ^d	morphology ^e
1	0	P-D ₄₀₀	120 (0.06)	spheres
2	0.25	P-D ₃₂₀ + P-(D ₃₂₀) ₂	130 (0.07)	spheres + small vesicles
3	0.5	P-D ₂₆₆ + P-(D ₂₆₆) ₂	370 (0.09)	vesicles
4	0.75	P-D ₂₂₈ + P-(D ₂₂₈) ₂	400 (0.14)	vesicles
5	1	P-(D ₂₀₀) ₂	410 (0.08)	vesicles

^aRAFT aqueous dispersion polymerization of DAAM using binary mixtures of PEG-CTA and PEG-(CTA)₂ at 70 °C, [PEG-(CTA)₂+PEG-CTA]/[DAAM]/[V-50]=1:400:0.12, solids=15% w/v.

^bMolar fraction of [PEG-(CTA)₂]=[PEG-(CTA)₂]/[PEG-(CTA)₂+PEG-CTA]. ^cMixture of linear and star block copolymers: P represents PEG and D represents PDAAM. The DPs of PDAAM in two copolymers were the theoretical value. ^dHydrodynamic diameter (*D_h*) and polydispersity (PDI) measured by DLS. ^eNano-object morphology identified by TEM.

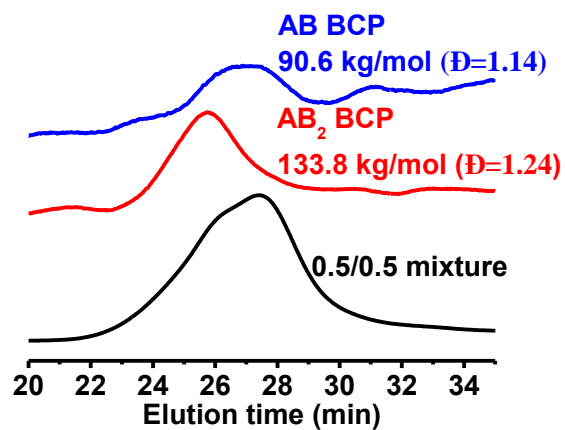


Figure S22. The GPC (DMF, PMMA standards) traces of the AB/AB₂ (0.5/0.5) mixture and the separated AB and AB₂ block copolymers. AB and AB₂ copolymers in the mixture were separated with a preparative GPC (50 mg mixture in 4 mL THF).