Supporting information

Morphological transitions of cationic PISA particles by salt, triflate ions

and temperature; comparison of three polycations

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Characterization

1H NMR Spectroscopy

The NMR spectra were collected with Bruker Avance III 500 and 400 MHz spectrometers at 25 °C. The conversions of cationic monomers and DAAM were measured in D_2O and DMSO-d6 solvents. All the purified polycations and copolymers were recorded in D_2O and methanol-d4 respectively.

Size Exclusion Chromatography

The size exclusion chromatography (SEC) of the reaction aliquots and purified polycation m-CTAs were conducted with the set up equipped with Waters 515 HPLC pump, Biotech DEGASi GPC degasser, Waters 2410 differential refractometer and Waters 2487 Dual λ absorbance detector. Water/acetonitrile (60/40) with 0.1% triflouroacetic acid mixture as an eluent and column set Ultrahyhdrogel 120, 250 and 2000 were used to collect the eluograms. Poly(ethylene oxide) standards were used for calibration.

Transmittance

For the transmittance measurements, JASCO V-750 UV-Vis spectrometer equipped with a JASCO CTU-100 water jacketed Peltier thermostat system was used. All the transmittance curves were collected at 600 nm wavelength using 1°C min⁻¹ cooling or heating rates. The aqueous solutions consist of 1mg ml⁻¹ of polymer concentration and X mM LiOTf salt were stabilized 10 minutes at starting temperatures prior to measurements.

Dynamic light scattering (DLS) and electrophoresis

DLS and electrophoresis measurements were conducted using Malvern instruments ZetaSizer Nano-ZS equipped with a 4mW He-Ne laser operating at 633 nm. The size distributions of the particles from 0.1 wt. %

dilute dispersions were collected with back scattering at 173°. The hydrodynamic diameters were averaged from three consecutive measurements.

Transmission Electron Microscopy (TEM)

TEM imaging of the particles was performed with JEOL JEM-1400 transmission electron microscope (Jeol Ltd., Tokyo, Japan) fitted with an Orius SC1000B bottom mounted CCD-camera (Gatan Inc., USA) operating at 80-120 kV. A carbon coated Copper grids were glow discharged prior to use. The dilute dispersions (3-5 μ L) were placed on the freshly prepared grids. Then an anionic stain, 0.7 μ L uranyl acetate (3 wt. %), was added to the sample drop prior to blotting the excess sample. The diameters of the particles were measured manually using image analysis software Flji ImageJ.¹

¹H NMR spectra of polycation macro-CTAs



Figure S1. ¹H NMR spectra of polycation macro-CTAs in D₂O. (A) PMOTAC. (B) PAMPTMAC and (C)) PVBTMAC.

RAFT dispersion polymerization of DAAM



Figure S2. ¹H NMR spectra of block copolymers in methnol-D4.

Table S1. The dispersions obtained from salt series at constant solids content 15 w/w % and [DAAM]:[CTA]:[I] = 500:1:0.3.

entry	dispersion	NaCl (M)	^a ionic ratio [NaCl]/[C _p]	DAAM conversion (%)	^b M _{n (theo)} (g/mol)	size _(DLS) (d.nm)	PDI _(DLS)	morphology _(тем)
1		0	0	99.7	89 656	67	0.129	spheres
2		0.10	2	99.4	89 402	76	0.049	spheres
3		0.20	4	99.5	89 487	78	0.036	spheres
4	V ₂₄ -D ₅₀₀	0.39	8	99.9	89 825	86	0.016	spheres
5		0.59	12	99.5	89 487	102	0.009	spheres
6		0.78	16	99.1	89 149	151	0.009	cloudberry-like
7		0.98	20	99.5	89 487	410	0.114	vesicle

8		1.18	24	99.2	89 233	394	0.134	vesicle
9		0	0	98.4	94156.24	77	0.146	spheres
10		0.19	2	98.2	93987.02	72	0.046	spheres
11		0.38	4	98.2	93987.02	77	0.041	spheres
12	V -D	0.57	6	-	-	80	0.011	spheres
13	V 50 D 500	0.76	8	97.6	93479.36	87	0.010	spheres
14		1.14	12	97.9	93733.19	113	0.006	cloudberry-like
15		1.52	16	94.9	91194.89	162	0.027	raspberry-like
16		1.90	20	95.1	91364.11	184	0.053	raspberry-like
17		0	0	99.6	97071.56	160	0.213	spheres
18		0.22	2	98.8	96394.68	89	0.028	spheres
19		0.44	4	99.3	96817.73	112	0.070	spheres
20	V - D	0.66	6	98.3	95971.63	100	0.043	spheres
21	V 61 ⁻ D 500	0.88	8	99.7	97156.17	109	0.061	spheres
22		1.32	12	99.1	96648.51	125	0.016	cloudberry-like
23		1.76	16	98.6	96225.46	183	0.053	raspberry-like
24		2.20	20	98.9	96479.29	184	0.020	raspberry-like
25		0	0	99.9	89925.39	84	0.040	spheres
26		0.10	2	99.9	89925.39	106	0.023	spheres
27		0.20	4	99.9	89925.39	105	0.016	spheres
28	MD	0.40	8	99.9	89925.39	116	0.034	spheres
29	10124 0 500	0.60	12	99.9	89925.39	130	0.018	spheres
30		0.80	16	99.9	89925.39	175	0.018	cloudberry-like
31		1.00	20	99.9	89925.39	248	0.018	raspberry-like
32		1.20	24	99.9	89925.39	229	0.027	raspberry-like
33		0	0	99.4	90402.34	135	0.025	spheres
34		0.12	2	99.8	90740.78	127	0.013	spheres
35		0.23	4	99.8	90740.78	134	0.023	spheres
36	ΔΠ	0.46	8	99.9	90825.39	158	0.016	spheres
37	A ₂₉ -D ₅₀₀	0.69	12	99.8	90740.78	173	0.018	spheres
38		0.92	16	99.9	90825.39	203	0.008	raspberry-like
39		1.15	20	99.8	90740.78	376	0.111	raspberry-like
40		1.39	24	99.8	90740.78	455	0.135	raspberry-like

^a ionic ratio= [salt] per [polycation repeating unit].

^b Theoretical M_n was calculated from the equation $M_n = \frac{[M]}{[CTA]} \times Conv.\% \times M_{monomer} + M_{CTA}$.

TEM images of particles from the salt series



Figure S3. TEM images of the particles of V_{24} - D_{500} dispersions with various ionic strength at 15 w/w %. Image e is enlarged to show the cloudberry structures.



Figure S4. TEM images of the particles of V_{50} - D_{500} dispersions with various ionic strengths at 15 w/w %.



Figure S5. TEM images of the particles of V_{61} - D_{500} dispersions with various ionic strengths at 15 w/w %. e) is enlarged to show clear raspberry structures.



Figure S6. TEM images of the particles of M_{24} - D_{500} dispersions with various ionic strengths at 15 w/w %.



Figure S7. TEM images of the particles of A_{29} - D_{500} dispersions with various ionic strengths at 15 w/w %. c and d have also been enlarged.



Figure S8. Average diameters of the particles measured from TEM images (NaCl series) using ImageJ.

Table S2. The dispersions obtained wit	h constant solids content 20 w/w	% and [DAAM]:[CTA]:[I] = 500:1:0.3.
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entry	dispersion	NaCl (M)	^a ionic ratio [NaCl]/[C _p]	DAAM conversion (%)	^b M _{n (theo)} (g/mol)	size _(DLS) (d.nm)	PDI _(DLS)	morphology _(тем)
41	V - D	0.42	6	97	87300	122	0.010	cloudberry-like
42	V ₂₄ -D ₅₀₀	0.84	12	98	88200	560	0.197	worms, lamella,

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								vesicles
43	V ₅₀ -D ₅₀₀	0.81	6	98	93800	220	0.090	cloudberry-like
44		1.61	12	97	92900	192	0.040	cloudberry-like
45	M ₂₄ -D ₅₀₀	0.43	6	99.9	89925.39	203	0.026	cloudberry-like
46		0.85	12	99.7	89756.17	262	0.018	raspberry-like
47	A ₂₉ -D ₅₀₀	0.49	6	99.6	89671.56	492	0.126	raspberry-like
48		0.98	12	99	89163.9	579	0.116	raspberry-like

^a ionic ratio= [salt] per [polycation repeating unit].

^b Theoretical M_n was calculated from the equation $M_n = \frac{[M]}{[CTA]} \times Conv.\% \times M_{monomer} + M_{CTA}$.

Table S3. The dispersion polymerization of DAAM in aqueous triflate solutions with constant target DP500.

		Solids		DAAM			
Entry	dispersion		LiOTf (M)	[LiOTf]/[C _p]	Conversion	M _{n (theo)}	
		(~~/~~/~)			(%)		
1		15	0.05	1	99.8	89740.78	
2		15	0.24	5	80.6	73495.66	
3	V_{24} - D_{500}	17	0.05	1	99.8	89740.78	
4		20	0.07	1	99.9	89825.39	
5		20	0.14	2	99.5	89486.95	
6		20	0.21	3	99.7	89656.17	
7	V50-D500	15	0.09	1	99.9	89825.39	
8	- 30 - 300	20	0.13	1	99.7	89656.17	
9	Vc1-Droo	15	0.11	1	99.4	89402.34	
10	01 2 300	20	0.15	1	99.8	89740.78	
11	Mad-Droo	15	0.05	1	99.6	89571.56	
12	24 - 500	20	0.07	1	99.4	89402.34	
13	App-Drop	15	0.06	1	99.6	89571.56	
14	29 2 500	20	0.08	1	99.5	89486.95	

TEM images of the particles obtained from the triflate series



Figure S9. TEM images of the particles from A_{29} - D_{500} (a) and M_{24} - D_{500} (b), and (c) size distributions of the dispersions obtained with different stabilizers at 15 w/w %. All the diluted samples were prepared from hot reaction dispersions.



Figure S10. TEM images of the particles from V_{24} - D_{500} at 17 w/w %. From hot (left) and cooled dispersion (right).



Figure S11. TEM images of the particles from hot dispersions V_{50} - D_{500} (top) and V_{61} - D_{500} (bottom) obtained at 20 w/w %.

Reference

1 C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 2012, **9**, 671-675.