

Supporting Information

Control of particle size in the self-assembly of amphiphilic statistical copolymers

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Summary of monomer properties

Table S1. Summary of monomer properties used to synthesize the series of statistical copolymers

Monomer	Molar mass (g mol ⁻¹)	Ester side-chain length (Number of carbons)	log P^1
MAA	86	-	0.93
DMAEMA	157	-	1.13
MMA	100	1	1.38
EMA	114	2	1.94
BMA	142	4	2.88
HMA	170	6	3.73
EHMA	198	6,2	4.54

Copolymerization kinetic analysis

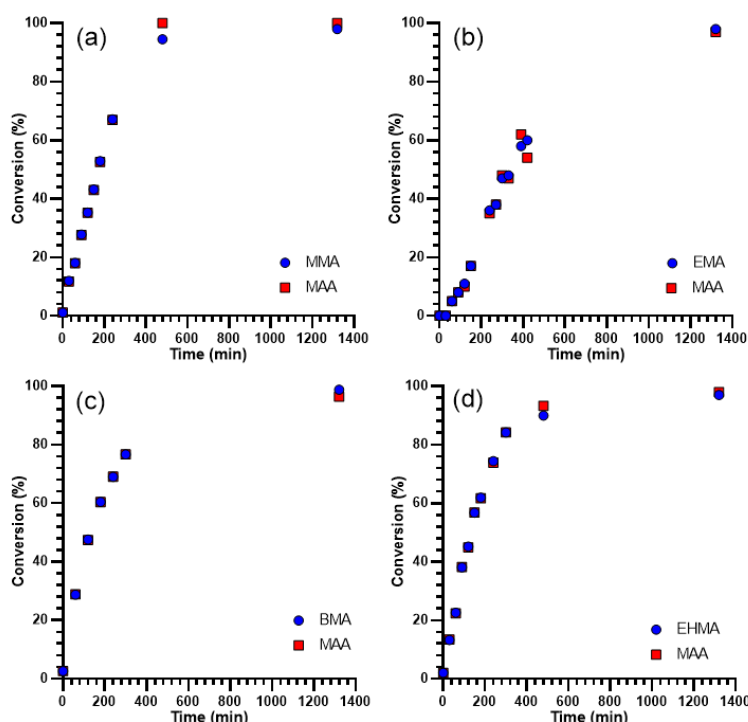


Figure S1. Rate of polymerization (the monomer conversion as determined by ^1H NMR spectroscopy against the time of the reaction) of (a) MMA and MAA monomers, (b) EMA and MAA monomers, (c) BMA and MAA monomers, and (d) EHMA and MAA monomers. The copolymerization of BMA with MAA was performed in 1,4-dioxane at 50% w/w whereas the copolymerization of the other monomer pairs was performed in IPA at 50% w/w. Size of the symbols used for the graphs corresponds to the estimated error range of the measurements.

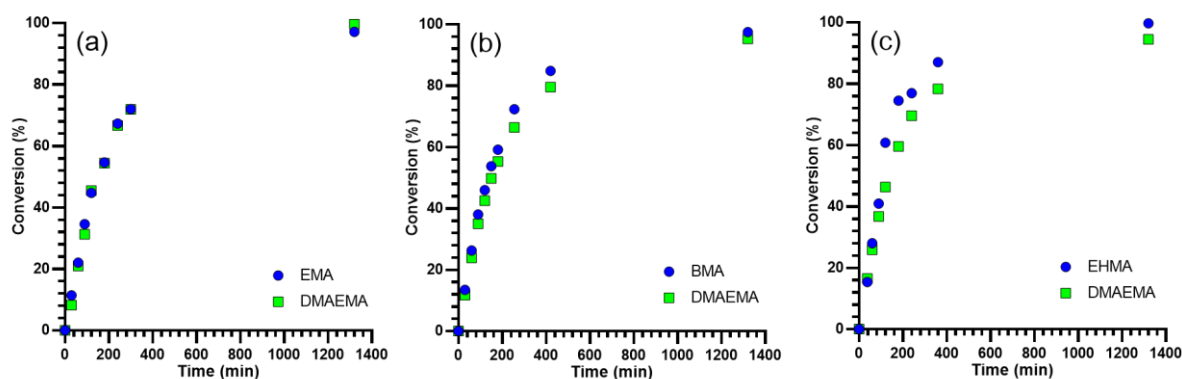


Figure S2. Rate of polymerization (the monomer conversion as determined by ^1H NMR spectroscopy against the time of the reaction) of (a) EMA and DMAEMA monomers, (b) BMA and DMAEMA monomers, (c) EHMA and DMAEMA monomers. The copolymerization was performed in IPA at 50% w/w. Size of the symbols used for the graphs corresponds to the estimated error range of the measurements.

Representative NMR spectra of alkylated copolymers

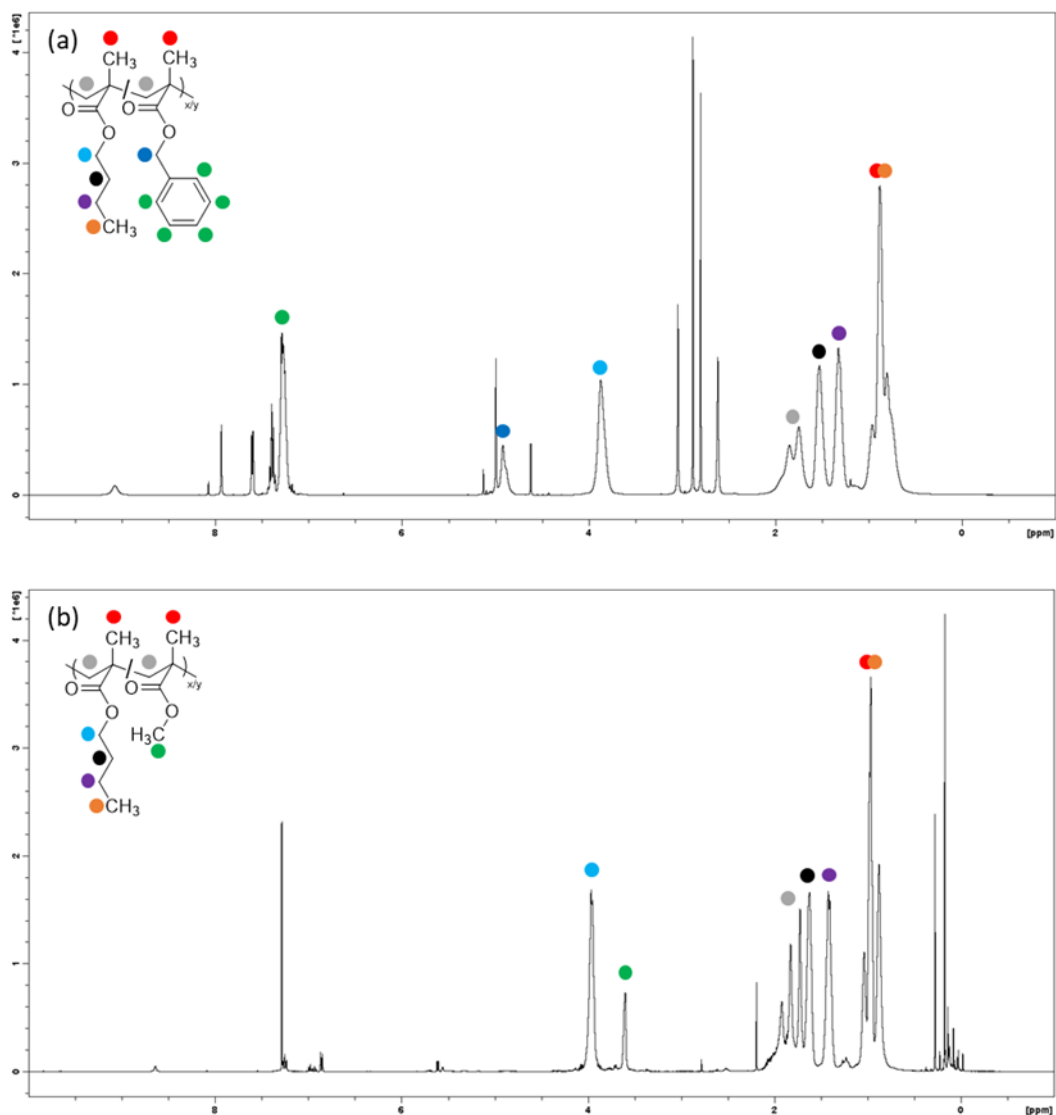


Figure S3. Representative ^1H NMR spectra of the product of two different alkylation techniques where BM₈₀₂₀ is alkylated with either benzyl bromide or trimethylsilyldiazomethane converting MAA to BzMA and MMA, respectively - (a) is the product of benzylation and (b) is the product of methylation. Both samples were run in deuterated chloroform (7.26 ppm).

Representative NMR spectra showing calculation of copolymer composition

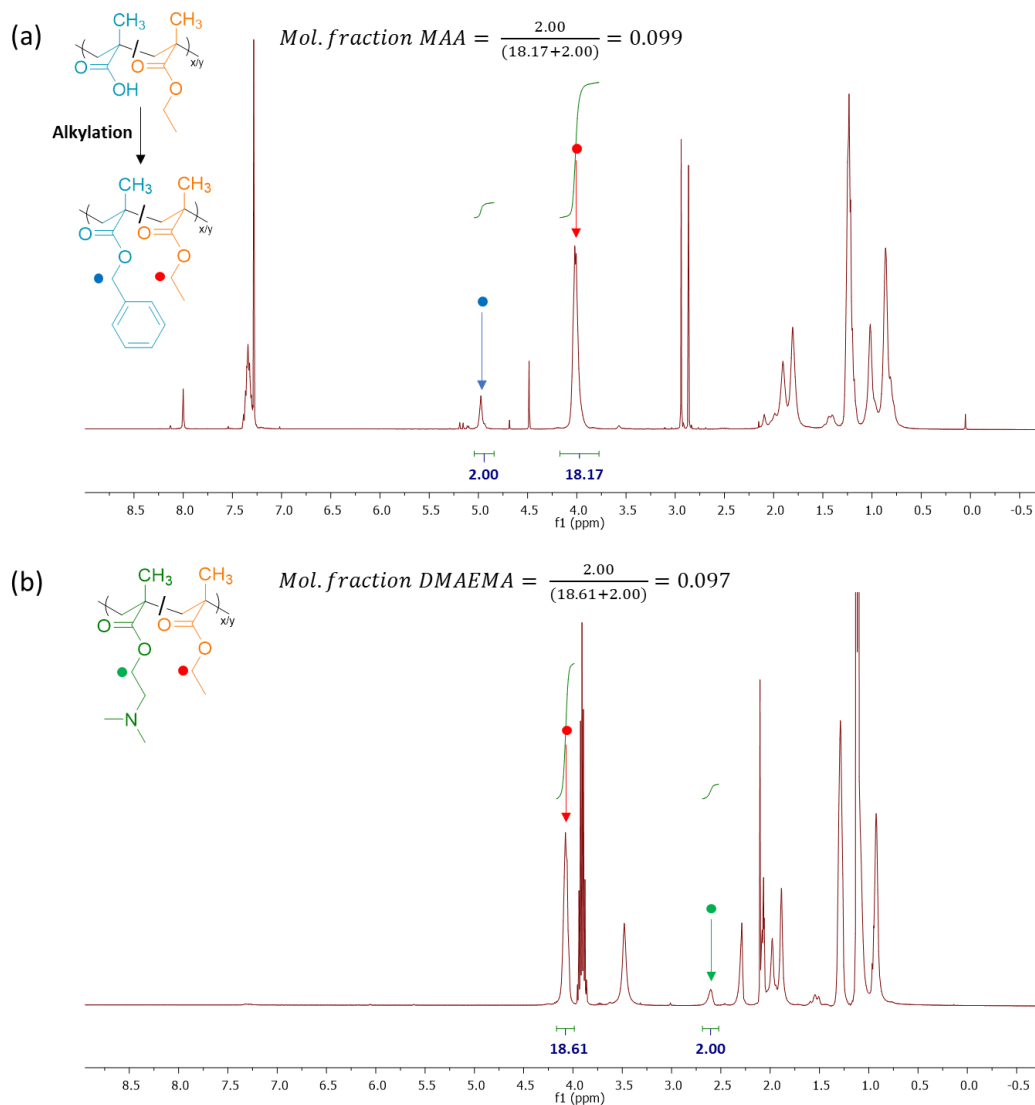


Figure S4. Representative ^1H NMR spectra used to calculate copolymer composition, where (a) is the alkylated version of EM₉₀₁₀ and (b) is ED₉₀₁₀.

Representative GPC chromatograms

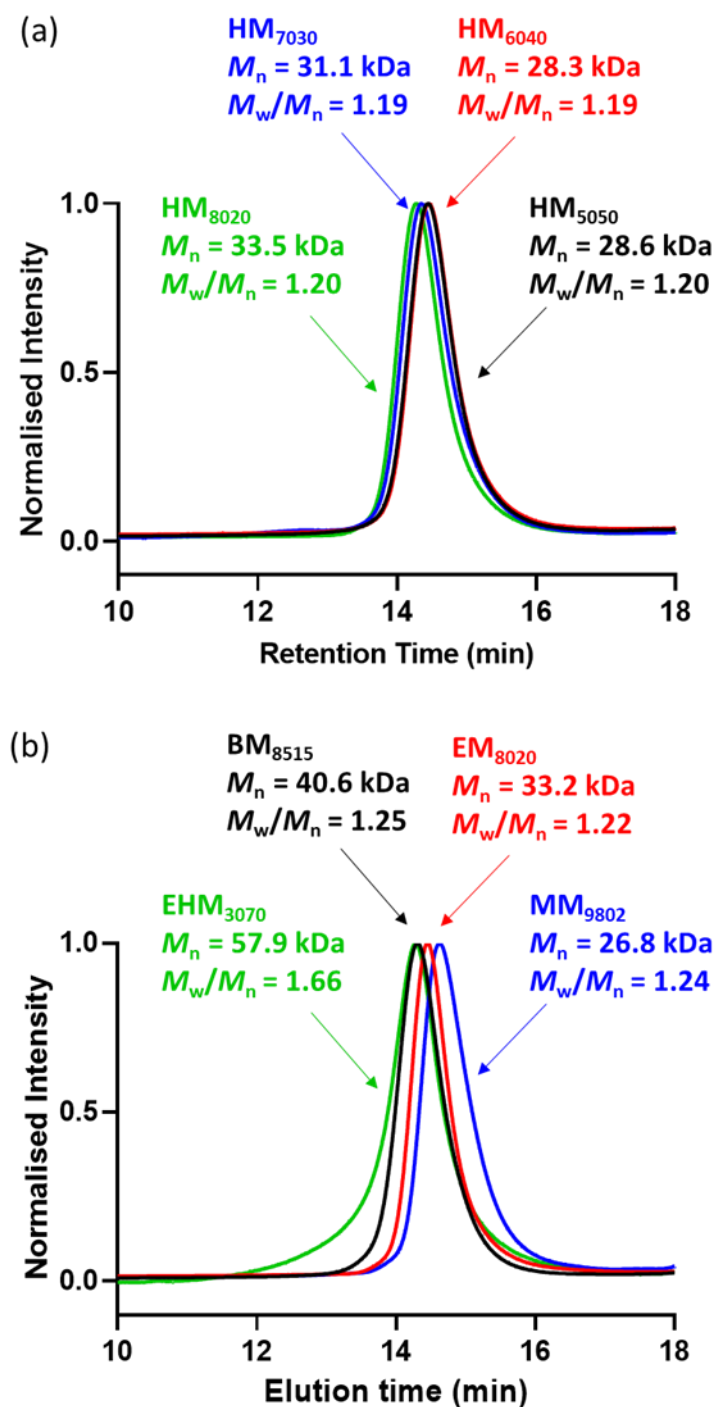


Figure S5. Representative GPC chromatograms of (a) the HM copolymer series and (b) a selection of the statistical copolymers investigated in this work. The molecular weights of the displayed copolymers were determined by GPC using a THF eluent containing 4% v/v acetic acid.

SAXS patterns for aqueous dispersions of the statistical copolymer particles containing MAA

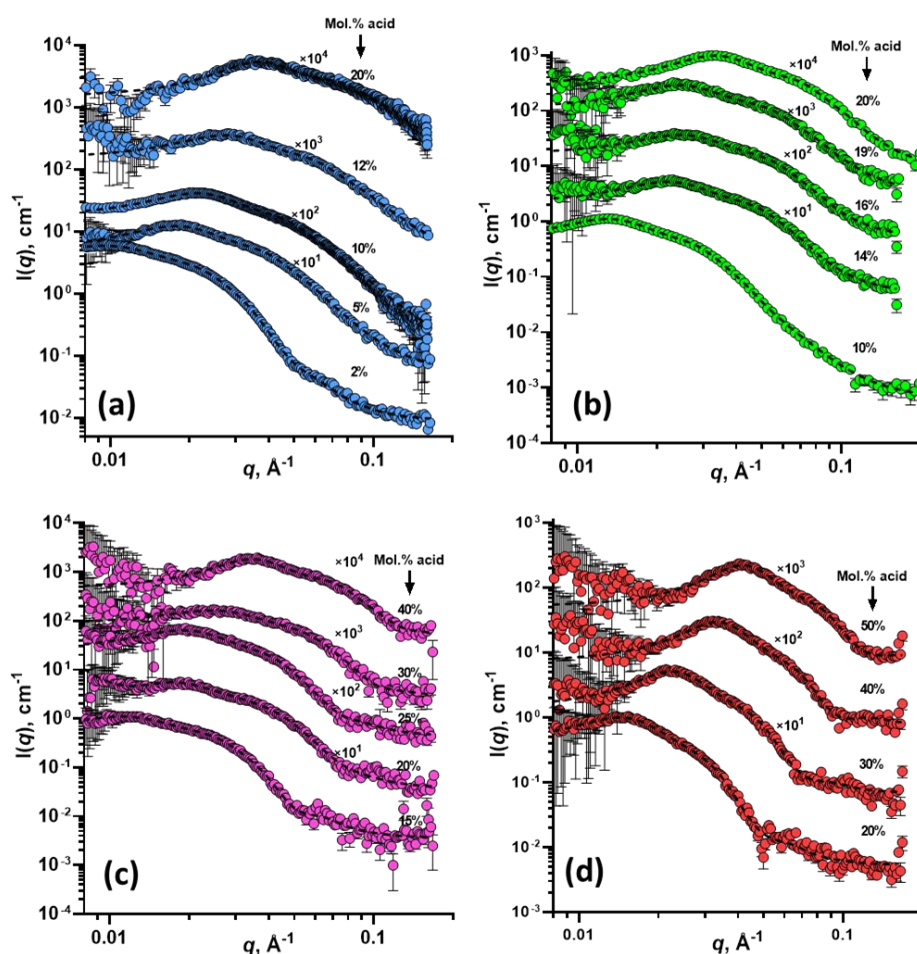


Figure S6. Radially-averaged and corrected SAXS data recorded from 1.0% w/w aqueous dispersions of the statistical copolymer particles formed by ASCs with different molar composition of MAA (symbols) fitted using a refined spherical particle model (dotted lines), where (a) is the MM series (excluding the patterns fit with the spheroid model), (b) is the EM series (excluding the patterns fit with the spheroid model), (c) is the BM series, and (d) is the HM series. Some patterns are shifted upwards by arbitrary factors, indicated on the plots, to avoid overlap. Either a Xenocs Xeuss instrument [(a) and (b)] or a Bruker AXS Nanostar instrument [(c) and (d)] were used to collect the data.

TEM analysis of P(*A-stat*-MAA) dispersions

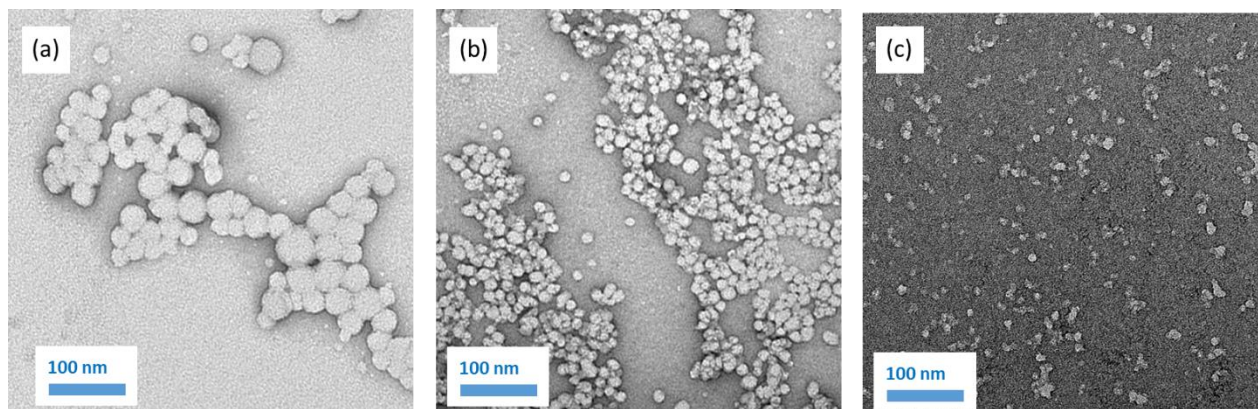


Figure S7. Representative TEM images recorded for P(*A-stat*-MAA) spherical nano-objects formed after dilution to 0.1% w/w with water from an initial 50% w/w copolymer solution in IPA for: (a) BM₉₀₁₀(FRP); (b) BM₈₀₂₀(FRP); and (c) EM₉₀₁₀.

Summary of parameters from model-fitting the SAXS data for aqueous dispersions of the statistical copolymer particles

Table S2. Summary of parameters obtained from model-fitting the SAXS data from 1.0% w/w copolymer dispersions using an intensity equation convoluted with either a Hayter-Penfold structure factor (HP) or a hard-sphere structure factor solved using the Percus-Yevick closure relation (PY): mean particle radius (R), the standard deviation of the mean particle radius (σ_R), half of interparticle correlation distance (R_{HP} or R_{PY}), and the effective volume fraction (f_{HP} or f_{PY}). For each series the rows are presented in order of decreasing mol% acid (the last two digits of the sample code subscript).

Sample	HP				PY			
	R (Å)	σ_R (Å)	R_{HP} (Å)	f_{HP}	R (Å)	σ_R (Å)	R_{PY} (Å)	f_{PY}
MM ₈₀₂₀	12	9	35	0.02	14	10	78	0.17
MM ₈₈₁₂	19	14	48	0.02	21	14	99	0.13
MM ₉₀₁₀	24	20	63	0.02	26	20	126	0.13
MM ₉₅₀₅	40	20	72	0.02	41	20	152	0.13
MM ₉₈₀₂	87	19	127	0.02	87	19	271	0.08
EM ₇₀₃₀	14	8	30	0.02	15	10	69	0.19
EM ₈₀₂₀	20	11	38	0.02	23	12	85	0.17
EM ₈₁₁₉	28	13	52	0.02	30	13	113	0.14
EM ₈₄₁₆	34	11	52	0.02	35	11	109	0.13
EM ₈₆₁₄	39	12	58	0.02	40	13	124	0.14
EM ₉₀₁₀	68	21	95	0.02	71	21	209	0.14
BM ₆₀₄₀	26	6	35	0.02	27	6	84	0.20
BM ₇₀₃₀	35	7	52	0.02	36	8	106	0.11
BM ₇₅₂₅	51	10	65	0.02	53	12	142	0.15
BM ₈₀₂₀	49	11	68	0.02	57	12	155	0.16
BM ₈₅₁₅	78	13	113	0.02	80	14	238	0.11
HM ₅₀₅₀	26	5	39	0.05	27	5	70	0.21
HM ₆₀₄₀	35	6	49	0.05	36	7	86	0.22
HM ₇₀₃₀	48	9	72	0.05	50	10	125	0.20
HM ₈₀₂₀	72	13	113	0.05	76	14	187	0.15
EHM ₃₀₇₀	37	10	47	0.05	26	10	81	0.21
EHM ₄₀₆₀	47	13	50	0.05	43	8	85	0.2
EHM ₅₀₅₀	58	18	57	0.05	48	8	99	0.2
EHM ₆₀₄₀	88	23	108	0.02	64	17	190	0.18
EHM ₇₀₃₀	105	20	-	-	-	-	-	-
ED ₈₅₁₅	26	10	43	0.02	26	10	95	0.16

ED ₉₀₁₀	36	20	69	0.02	36	20	151	0.17
ED ₉₃₀₇	43	21	74	0.02	43	21	176	0.21
ED ₉₅₀₅	53	21	78	0.02	53	21	189	0.23
BD ₆₀₄₀	25	7	32	0.02	25	7	75	0.21
BD ₇₀₃₀	31	3	35	0.02	31	3	81	0.19
BD ₇₅₂₅	34	4	38	0.02	34	4	88	0.20
BD ₈₀₂₀	43	9	49	0.02	43	9	115	0.20
BD ₈₅₁₅	60	31	78	0.02	60	31	178	0.16
EHD ₅₀₅₀	37	5	47	0.05	37	5	82	0.23
EHD ₆₀₄₀	44	3	52	0.05	44	3	96	0.26
EHD ₇₀₃₀	62	2	71	0.05	62	2	131	0.26
BM _{7030(FRP)}	35	13	47	0.05	35	13	77	0.15
BM _{8020(FRP)}	66	16	97	0.04	66	16	176	0.16
BM _{9010(FRP)}	137	33	-	-	137	33	-	-

Representative images of unstable copolymer dispersions

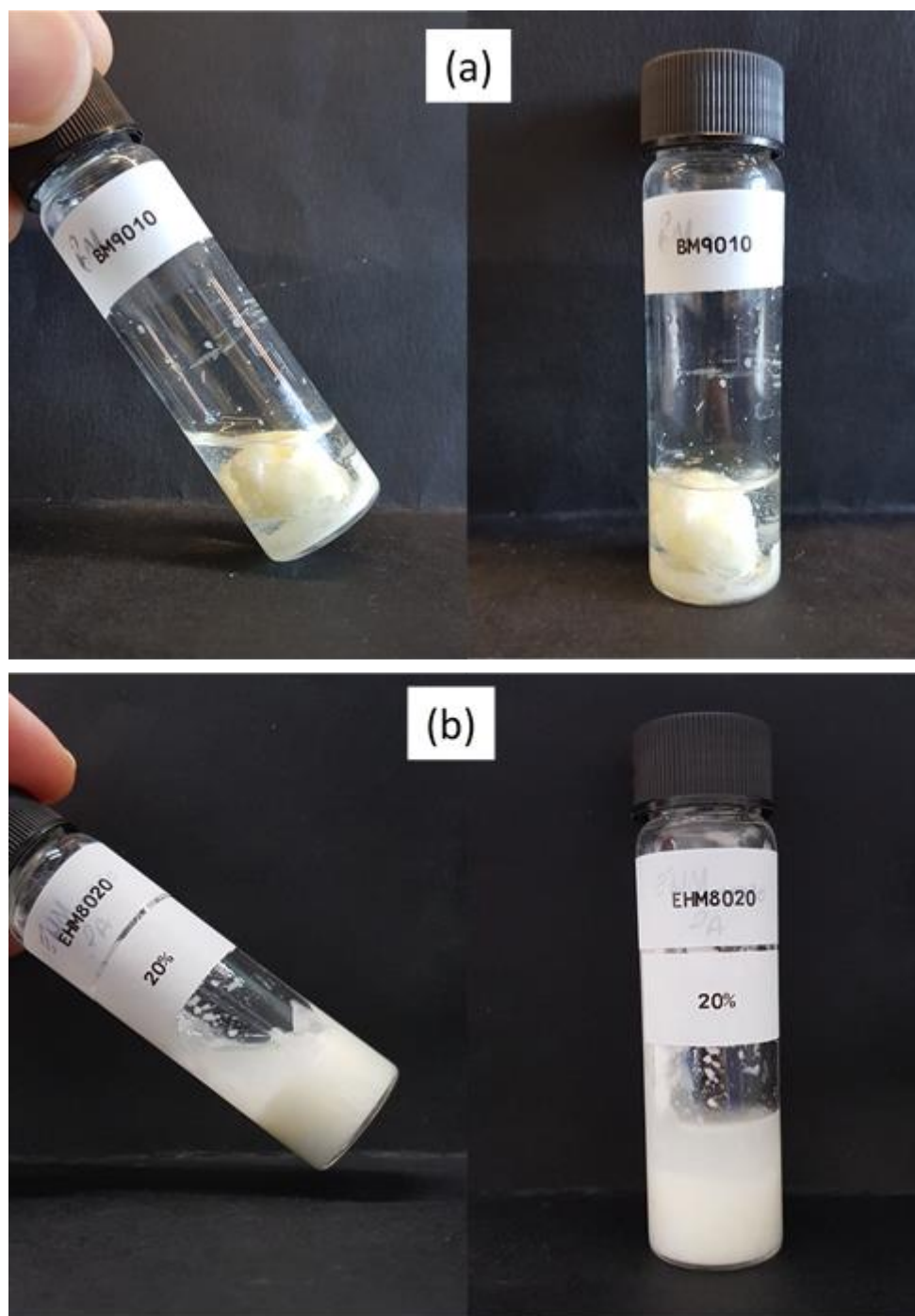


Figure S8. Images of the unstable copolymer compositions that have precipitated during the solvent switch process to form particles in water, where (a) is BM₉₀₁₀ and (b) is EHM₈₀₂₀.

SAXS pattern for dispersions of MM₆₀₄₀ copolymer

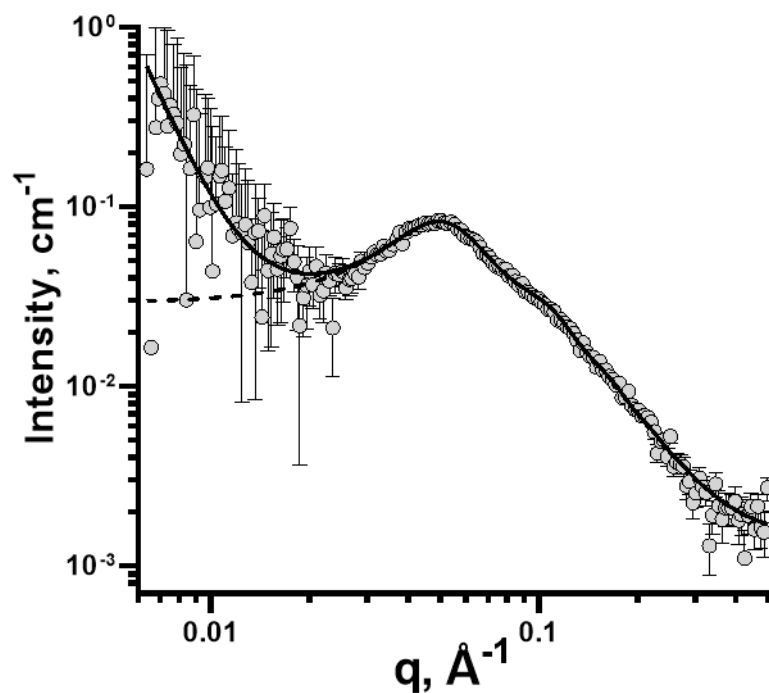


Figure S9. Radially-averaged and corrected SAXS data recorded from a 1.0% w/w aqueous dispersion of MM₆₀₄₀ copolymer particles (symbols) fitted with a spheroid model with an incorporated aspect ratio (dotted line) to extract a particle size. Additionally, a unified parametrization was incorporated in the fitting to account for the upturn at low q -values caused by particle aggregation. A Bruker AXS Nanostar instrument was used for the measurements.

SAXS patterns for aqueous dispersions of the statistical copolymer particles containing DMAEMA

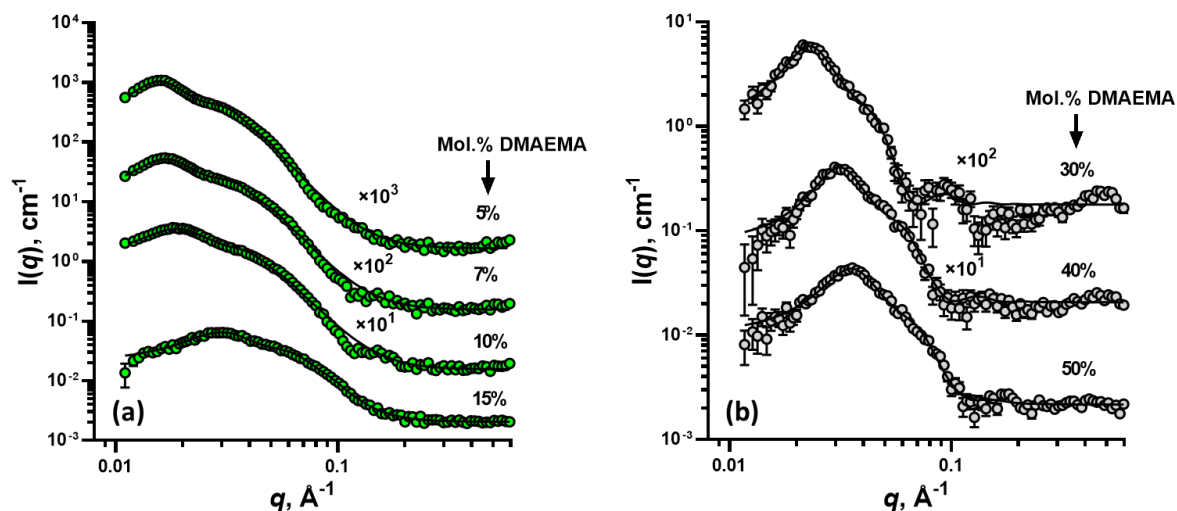


Figure S10. Radially-averaged and corrected SAXS data recorded from 1.0% w/w aqueous dispersions of the statistical copolymer particles (symbols) fitted using a refined spherical particle model (solid lines) comparing the size of the particles formed by ASCs with different molar composition of DMAEMA, where (a) is the ED series, and (b) is the EHM series. Some patterns are shifted upwards by arbitrary factors, indicated on the plots, to avoid overlap. A Xenocs Xeuss instrument were used to collect the data.

Comparison of the particle behavior of the copolymers synthesized by FRP and by RAFT polymerization

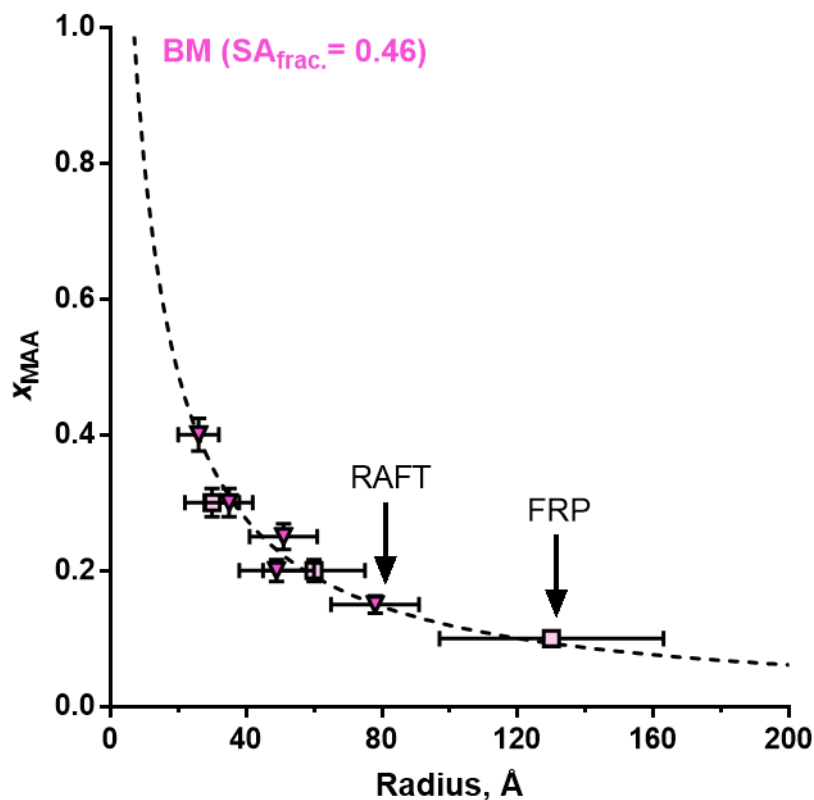


Figure S11. Relationship between the mole fraction of MAA units in the amphiphilic statistical copolymer chains, x_{MAA} , and the corresponding mean particle radius formed by copolymer self-assembly in aqueous solution: experimental data (symbols) fitted by the PSC model (dashed lines) assuming that $k = 1$ (eqs 1-3). This data compares the particle behavior of the copolymers synthesized by FRP (squares) and by RAFT (upside-down triangles).

Summary of the size parameters from model-fitting the SAXS data for aqueous dispersions of the statistical copolymer particles containing MAA

Table S3. Summary of the size parameters obtained by model-fitting the SAXS data from 1.0% w/w anionic copolymer dispersions with the core-shell model (eqs S8-S16) assuming that either $k = 1$ or $k = 0.5$: mean particle radius (R), and the standard deviation of the mean particle radius (σ_R).

Copolymer	$k = 1$		$k = 0.5$	
	R (Å)	σ_R (Å)	R (Å)	σ_R (Å)
MM ₆₀₄₀	13 ^{a,b}	1	13 ^{a,b}	1
MM ₇₀₃₀	13 ^{a,b}	1	13 ^{a,b}	1
MM ₈₀₂₀	12 ^b	9	13 ^b	9
MM ₈₈₁₂	19 ^b	14	20 ^b	14
MM ₉₀₁₀	24	20	25	20
MM ₉₅₀₅	40	20	41	20
MM ₉₈₀₂	87	19	88	1
EM ₆₀₄₀	15 ^{a,b}	1	15 ^{a,b}	1
EM ₇₀₃₀	14 ^b	8	16 ^b	8
EM ₈₀₂₀	20	11	22	11
EM ₈₁₁₉	28	13	30	13
EM ₈₄₁₆	34	11	35	11
EM ₈₆₁₄	39	12	40	12
EM ₉₀₁₀	68	21	70	21
BM ₆₀₄₀	26	6	28	6
BM ₇₀₃₀	35	7	37	7
BM ₇₅₂₅	51	10	53	11
BM ₈₀₂₀	49	11	51	12
BM ₈₅₁₅	78	13	81	13
BM ₉₀₁₀ ^c	-	-	-	-
HM ₅₀₅₀	26	5	29	5
HM ₆₀₄₀	35	6	38	6
HM ₇₀₃₀	48	9	52	10
HM ₈₀₂₀	72	13	77	14

EHM₃₀₇₀	37	10	27	17
EHM₄₀₆₀	47	13	40	8
EHM₅₀₅₀	58	18	48	10
EHM₆₀₄₀	88	23	76	20
EHM₇₀₃₀	105	20	101	21
EHM₈₀₂₀^c	-	-	-	-
BM₇₀₃₀(FRP)	35	13	5	1
BM₈₀₂₀(FRP)	66	16	25	1
BM₉₀₁₀(FRP)	137	33	281	1

^aFitted using a spheroid model for anisotropic particles with an aspect ratio different from unity.

^bAssigned to single-chain nanoparticles, although their N_{agg} is not exactly one. ^cCopolymer compositions did not form stable colloidal dispersions when diluted with water.

Small-angle scattering models

The equations describing the scattering models have been ordered so that a logical description can be achieved with minimal repetition. However, this means that the equations shown are not in the order that they appear in the main manuscript.

The intensity of coherent scattering produced by a particle dispersion is expressed as the product of the particle form factor and the structure factor:

$$I(q) = NS(q) \int_0^\infty \dots \int_0^\infty F(q, r_1, \dots, r_k) \Psi(r_1, \dots, r_k) dr_1 \dots dr_k \quad (\text{S1})$$

where $F(q, r_1, \dots, r_k)$ is the form factor defined by a k number of r parameters corresponding to a certain particle shape, $\Psi(r_1, \dots, r_k)$ is the distribution function of these parameters, N is the particle number density per unit sample volume, and $S(q)$ is the structure factor.

Spheroid model

This model (Figure S12a) assumes a dispersion of homogenous spheroidal particles with an aspect ratio α where the associated scattering length density (SLD) is averaged across the whole particle. The form factor is defined as:

$$F_{\text{sph}}(q, r) = \Delta\xi^2 \cdot \int_0^{\frac{\pi}{2}} A_{\text{sph}}^2(q, r) \sin \beta d\beta \quad (\text{S2})$$

where averaging is performed over all possible particle orientations defined by β (the angle between the axis of the spheroid and the scattering vector). $\Delta\xi$ is the SLD contrast given by $\Delta\xi = \xi_p - \xi_{\text{sol}}$ with ξ_p and ξ_{sol} representing the SLDs of the copolymer particle and the background solvent, respectively. ξ_p in this case corresponds to the averaged scattering length density of the copolymer calculated as:

$$\xi_p = \xi_A \cdot v_A + \xi_B \cdot v_B \quad (\text{S3})$$

where ξ_A and ξ_B are the scattering length densities of *A* and *B* units, and v_A and v_B are the volume fractions of *A* and *B* units, respectively. The spheroidal form factor amplitude is defined as:

$$A_{\text{sph}}(q, r) = \frac{3[\sin(qrE) - qrE \cos(qrE)]}{(qrE)^3} \quad (\text{S4})$$

where r is the spheroid radius (Figure S12a) and E is a term associated with the aspect ratio of the spheroidal particle defined as:

$$E = \sqrt{\sin^2\beta + \alpha^2 \cos^2\beta} \quad (\text{S5})$$

Additionally, assuming that no solvent penetrates into the particle the copolymer aggregation number (N_{agg}) can be calculated from:

$$N_{\text{agg}} = \frac{V}{V_{\text{poly}}} \quad (\text{S6})$$

where $V = \frac{4}{3}\pi r^3 \alpha$ is the copolymer particle volume and V_{poly} is the volume of a single copolymer molecule.

Sphere model

If $\alpha = 1$ then the spheroidal particle is simply a sphere (Figure S12b) and $E = 1$. Therefore, the spheroidal form factor amplitude in eq S2 can be simplified as:

$$A_{\text{sph}}(q, r) = \frac{3[\sin(qr) - qr \cos(qr)]}{(qr)^3} \quad (\text{S7})$$

where r is the radius of the spherical particle. The copolymer aggregation number per particle (N_{agg}) can be calculated from eq. S6 assuming that $V = \frac{4}{3}\pi r^3$.

Core-Shell model

A core-shell model (Figure S12c) was used when the associated ionic shell that surrounds the charged particle (Figure 1b) is highly scattering in regard to the background solvent. In this case the assembly of a particle and an ionic shell can be represented by a core-shell model with the form factor defined as:

$$F_{cs}(q, r) = A_{cs}^2(q, r) \quad (S8)$$

In this case the form factor amplitude containing information about the SLD contrasts of the particle and the ionic shell is defined as:

$$A_{cs}(q, r) = (\xi_p - \xi_{sol})VA_{sph}(q, r) + (\xi_s - \xi_{sol})\Delta VA_{sph}(q, \Delta r) \quad (S9)$$

$$\Delta V = V_{total} - V \quad (S10)$$

$$\Delta r = r_{total} - r \quad (S11)$$

where ξ_s and ξ_p are the SLDs of the ionic shell and particle, respectively. r and $V = \frac{4}{3}\pi r^3$ are the radius and volume of the particle, respectively. r_{total} and $V_{total} = \frac{4}{3}\pi r_{total}^3$ are the radius and volume of the entire core-shell assembly, respectively. ΔV and Δr are the volume and thickness of the shell, respectively. $A_{sph}(q, x)$ is the normalized scattering amplitude of a sphere defined by eq S7. The copolymer aggregation number (N_{agg}) for the core-shell model is calculated according to eq S6.

Approximation of the TEA unit length

The thickness of the ion shell (Δr) is equivalent to the length of a single TEA unit (l_{TEA}) approximated using the following equation:

$$l_{\text{TEA}} = \sqrt[3]{\frac{M_w}{N_A \rho_{\text{TEA}}}} \quad (\text{S12})$$

where, M_w is the molar mass of TEA, N_A is Avogadro's constant, and ρ_{TEA} is the TEA density. l_{TEA} was calculated to be 6 Å and was consequently fixed during the fitting of SAXS and SANS patterns.

SLD of cation shell

The SLD of the cation shell populated by TEA is highly dependent on the volume of water molecules present within the shell. It is assumed that every negatively charged MAA unit on the particle surface associates with a TEA cation. Based on these assumptions the relative volumes of TEA and water within the cation shell can be estimated. First the number of MAA in the particle ($N_{\text{MAA,p}}$) is calculated:

$$N_{\text{MAA,p}} = N_{\text{agg}} DP_{\text{MAA}} \quad (\text{S13})$$

where N_{agg} is the aggregation number and DP_{MAA} is the average number of MAA units in a single polymer chain. Since it is assumed that the number of TEA units ($N_{\text{TEA,s}}$) in the shell is proportional to the MAA units on the surface of the particle, $N_{\text{TEA,s}}$ can be calculated:

$$N_{\text{TEA,s}} = N_{\text{MAA,p}} k \quad (\text{S14})$$

where k is the fraction of the MAA units that locate on the particle surface. In this first instance k is assumed to be 1 (it was later found through extensive SANS analysis that $k = 0.5$ is more realistic). Using $N_{\text{TEA,s}}$ volume of water within the shell (or the hydration of the shell, H) can be calculated:

$$H = [\Delta V - (N_{\text{TEA,s}} V_{\text{TEA}})] \quad (\text{S15})$$

where ΔV is the total volume of the cation shell and V_{TEA} is the volume of a single TEA unit (l_{TEA}^3). The SLD of the cation shell (ξ_s) can then be calculated using the following equation:

$$\xi_s = (H\xi_{\text{sol}}) + [(1 - H)\xi_{\text{TEA}}] \quad (\text{S16})$$

where, ξ_{sol} and ξ_{TEA} are the scattering length densities of the solvent and TEA, respectively, and H is the hydration fraction of the shell. $H = 0$ corresponds to a situation when no solvent is present within the ion shell and $H = 1$ when the shell is fully hydrated, $\xi_s = \xi_{\text{sol}}$. These equations were incorporated into the core-shell model so that both the particle size and the ξ_s were calculated simultaneously during fitting.

Core-Shell-Shell model

A core-shell-shell model (Figure S12d) describes a situation where the comonomer distribution across the particle is assumed to be inhomogeneous and a distinct core and shell is formed (Figure 5a). In addition to this first shell within the particle itself, this model also accounts for the associated ionic (second) shell that surrounds the charged particle. In this case the scattering form factor is defined as:

$$F_{\text{css}}(q, r_c) = A_{\text{css}}^2(q, r_c) \quad (\text{S17})$$

where the form factor amplitude containing information about the SLDs contrast of the core and the both shells is expressed as:

$$\begin{aligned} A_{\text{css}}(q, r_c) = & (\xi_{\text{core}} - \xi_{\text{sol}})V_{\text{core}}A_{\text{sph}}(q, r_c) + (\xi_{\text{s1}} - \xi_{\text{sol}})\Delta V_{\text{s1}}A_{\text{sph}}(q, \Delta r_{\text{s1}}) \\ & + (\xi_{\text{s2}} - \xi_{\text{sol}})\Delta V_{\text{s2}}A_{\text{sph}}(q, \Delta r_{\text{s2}}) \quad (\text{S18}) \end{aligned}$$

$$\Delta V_{\text{s1}} = V - V_{\text{core}} \quad (\text{S19})$$

$$\Delta V_{s2} = V_{\text{total}} - V \quad (\text{S20})$$

$$\Delta r_{s1} = r - r_c \quad (\text{S21})$$

$$\Delta r_{s2} = r_{\text{total}} - r \quad (\text{S22})$$

where ζ_{core} , ζ_{s1} and ζ_{s2} are the SLDs of the particle core, the particle shell and the ionic shell, respectively. The value of ζ_{s2} was calculated following eqs 13-16. r_c and $V_{\text{core}} = \frac{4}{3}\pi r_c^3$ are the radius and volume of the core, respectively. r and $V = \frac{4}{3}\pi r^3$ are the radius and volume of the entire polymer particle, respectively. r_{total} and $V_{\text{total}} = \frac{4}{3}\pi r_{\text{total}}^3$ are the radius and volume of the entire polymer particle plus the ionic shell, respectively. ΔV_{s1} and Δr_{s1} are the volume and thickness of the particle (first) shell, respectively. ΔV_{s2} and Δr_{s2} are the volume and thickness of the ionic (second) shell. $A_{\text{sph}}(q, x)$ is the normalized scattering amplitude of a sphere defined by eq S7.

ζ_{sol} was varied during the contrast variation SANS experiment by using H₂O/D₂O mixtures. The ζ_{sol} for each mixture can be calculated from a linear relationship based upon the scattering length density and volume fraction of each component:

$$\zeta_{\text{sol}} = \zeta_{\text{H}_2\text{O}}\nu_{\text{H}_2\text{O}} + \zeta_{\text{D}_2\text{O}}\nu_{\text{D}_2\text{O}} \quad (\text{S23})$$

Furthermore, the values of ζ_{core} and ζ_{s1} are linked in the model by the copolymer composition to give a consistent redistribution of the hydrophilic and hydrophobic units within the particle. For example, a P(BMA-*stat*-MAA) copolymer composition molar ratio of 80:20 (BMA:MAA) equates to a volume ratio of 0.89:0.11 where it was taken that mass density of the BMA units and MAA units is $\rho_{\text{BMA}} = 1.05 \text{ g cm}^{-3}$ and $\rho_{\text{MAA}} = 1.25 \text{ g cm}^{-3}$, respectively. The obtained values can be used as the volume fraction of BMA (ν_{BMA_p}) and MAA (ν_{MAA_p}) to calculate the total volume of BMA in the particle (V_{BMA_p}):

$$V_{\text{BMA}_p} = v_{\text{BMA}_p} V \quad (\text{S24})$$

The volume fraction of BMA in the core (v_{BMA_c}) can be calculated as:

$$v_{\text{BMA}_c} = \frac{(\xi_{\text{core}} - \xi_{\text{MAA}})}{(\xi_{\text{BMA}} - \xi_{\text{MAA}})} \quad (\text{S25})$$

where ξ_{core} is the model fitting parameter corresponding to the particle core SLD, and ξ_{BMA} and ξ_{MAA} are the SLDs of BMA and MAA, respectively. Thus, v_{BMA_c} can be used to calculate the total volume of BMA in the particle shell:

$$V_{\text{BMA}_{s1}} = V_{\text{BMA}_p} - v_{\text{BMA}_c} V_{\text{core}} \quad (\text{S26})$$

The volume fraction of BMA in the particle shell can then be calculated from:

$$v_{\text{BMA}_{s1}} = \frac{V_{\text{BMA}_{s1}}}{\Delta V_{s1}} \quad (\text{S27})$$

Using $v_{\text{BMA}_{s1}}$, the volume fraction of MAA in the particle shell can be calculated:

$$v_{\text{MAA}_{s1}} = 1 - v_{\text{BMA}_{s1}} \quad (\text{S28})$$

Finally, the SLD of the shell can be calculated to give a value related to the copolymer composition and the fitted ξ_{core} :

$$\xi_{s1} = v_{\text{BMA}_{s1}} \xi_{\text{BMA}} + v_{\text{MAA}_{s1}} \xi_{\text{MAA}} \quad (\text{S29})$$

Approximation of MAA unit length

The thickness of the particle shell (Δr_{s1}) is equivalent to the length of a single MAA unit (l_{MAA}) approximated using the following equation:

$$l_{\text{MAA}} = \sqrt[3]{\frac{M_w}{N_A \rho_{\text{MAA}}}} \quad (\text{S30})$$

where, M_w is the molar mass of MAA, N_A is Avogadro's constant, and ρ_{MAA} is the density of MAA. l_{MAA} was calculated to be 5 Å and was consequently fixed during the fitting of SANS patterns.

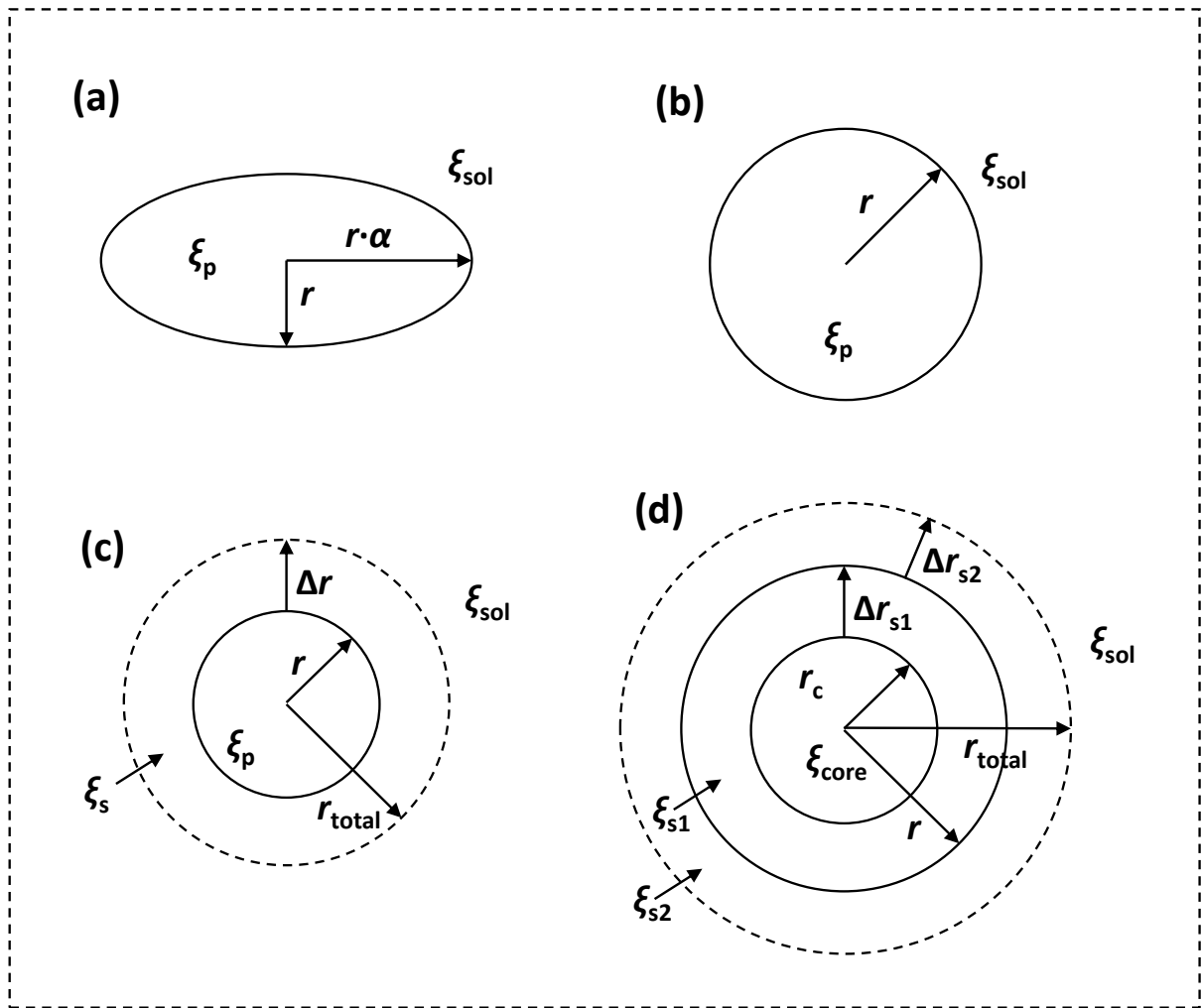


Figure S12. A schematic of structural models used for the scattering pattern analysis: (a) the spheroid model corresponding to a prolate ellipsoid with an aspect ratio $\alpha > 1$, where r is the radius of the particle, ξ_p is the SLD of the particle, and ξ_{sol} is the SLD of the solvent; (b) is a sphere model ($\alpha = 1$); (c) is the core-shell model, where r is the particle radius, r_{total} is the total radius of the particle and ionic shell, Δr is the ionic shell thickness, and ξ_p and ξ_s are the SLDs

of the copolymer particle and the ionic shell, respectively; (d) is the core-shell-shell model, where r_c is the particle core radius, r is the copolymer particle radius, r_{total} is the total radius of the particle and the ionic shell, Δr_{s1} is the copolymer particle shell thickness, Δr_{s2} is the ionic shell thickness, and ζ_{core} , ζ_{s1} , and ζ_{s2} are the SLDs of the particle core, particle shell, and ionic shell, respectively.

Gaussian distribution

The polydispersity of the particle radius, expressed as a Gaussian distribution, is considered for the structural model (eq S1, S34 or S35):

$$\Psi(r) = \frac{1}{\sqrt{2\pi\sigma_R^2}} e^{-\frac{(r-R)^2}{2\sigma_R^2}} \quad (\text{S31})$$

where R is the mean particle radius and σ_R is its standard deviation. For the core-shell-shell particles eq S31 should be rewritten as $\Psi(r_c) = \frac{1}{\sqrt{2\pi\sigma_{R_c}^2}} e^{-\frac{(r_c-R_c)^2}{2\sigma_{R_c}^2}}$, where R_c is the mean particle core radius and σ_{R_c} is its standard deviation.

Normalization by particle number density per unit sample volume

The particle number density per unit sample volume (eq S1, S34 or S35) is expressed as:

$$N = \frac{\phi}{\int_0^\infty V(r)\Psi(r)dr} \quad (\text{S32})$$

where ϕ is the total volume fraction of copolymer particles (excluding the ionic shell) in the sample and $V(r)$ is the *volume* of the copolymer particle.

Hayter-Penfold structure factor

A charged particle Coulomb interaction is usually described by the Hayter-Penfold structure factor:²

$$S(q) = S_{\text{HP}}(q, R_{\text{HP}}, f_{\text{HP}}, M, T, \varepsilon, Q) \quad (\text{S33})$$

where R_{HP} is an interparticle correlation radius (half of the interparticle correlation distance), f_{HP} is an effective volume fraction, M is the ionic strength of the solvent, T is the absolute temperature, ε is the solvent dielectric constant and Q is the particle charge expressed in electrons.

SAXS model with linear background

A plateau in intensity at high q is observed in the majority of the scattering patterns collected (Figures 1a, 2a, S4, S5, and S7). This plateau is caused by fluctuations in scattering length density across the particle. In order to account for these fluctuations a linear fitting parameter (C_1) that is independent of the scattering vector q is incorporated into the intensity equation S1:

$$I(q) = NS(q) \int_0^\infty \dots \int_0^\infty F(q, r_1, \dots, r_k) \Psi(r_1, \dots, r_k) dr_1 \dots dr_k + C_1 \quad (\text{S34})$$

SAXS model with incorporated power law parametrization

An upturn in intensity at low q is observed in the scattering patterns of some dispersions (Figures S4c, S4d, and S7). This deviation from the model is caused by the presence of large aggregates and is commonly fit using a combination of Guinier and power law functions. Since the Guinier region is located at ultra-small scattering angles inaccessible for the performed SAXS experiment, only the power law region is observed in the scattering patterns. Therefore,

in order to account for the presence of large aggregates a power law function is incorporated into the structural model:

$$I(q) = NS(q) \int_0^\infty \dots \int_0^\infty F(q, r_1, \dots, r_k) \Psi(r_1, \dots, r_k) dr_1 \dots dr_k + C_1 + Bq^{-P} \quad (\text{S35})$$

where B is a prefactor that is related to the type of power-law scattering and the regime in which exponent p falls.

Calculation of proportion of MAA located in the particle shell

The SANS analysis demonstrated that there is deviation between the scattering length density of the particle core (ξ_{core}) and the particle surface due to the preferential location of MAA units at the particle-water interface creating a thin shell (ξ_{sl}) (Figure S12d). These scattering length densities extracted from the SANS analysis can be used to calculate the proportion of MAA that locates on the particle surface (in the first shell). Firstly, the volume of MAA in the particle (V_{MAA_p}) is calculated as:

$$V_{\text{MAA}_p} = V - V_{\text{BMA}_p} \quad (\text{S36})$$

where V is the particle volume, and V_{BMA_p} is the volume of BMA in the particle (eq S24).

The volume of MAA in the particle core (V_{MAA_c}) can also be calculated as:

$$V_{\text{MAA}_c} = (1 - v_{\text{BMA}_c})V_{\text{core}} \quad (\text{S37})$$

where v_{BMA_c} is the volume fraction of BMA in the core (eq S25) and V_{core} is the particle core volume. Once both V_{MAA_c} and V_{MAA_p} are known, the proportion of MAA that locates within the particle shell (k) can be calculated:

$$k = 1 - \left(\frac{V_{\text{MAA}_c}}{V_{\text{MAA}_p}} \right) \quad (\text{S38})$$

References

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- (2) Hayter, J. B.; Penfold, J. An Analytic Structure Factor for Macroion Solutions. *Mol. Phys.* **1981**, *42*, 109–118.