Supporting Information for:

Synthesis of Polyampholytic Diblock Copolymers via RAFT Aqueous Solution Polymerization

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Scheme S1. Alternative wholly aqueous one-pot synthesis of PMAA-PMETAC diblock copolymers via (i) RAFT aqueous solution polymerization of methacrylic acid (MAA) at pH 2, targeting 20% w/w solids using ACVA initiator at 70 °C for 3 h followed by (ii) RAFT aqueous solution polymerization of [2-methacryloyloxy)ethyl]trimethylammonium chloride (METAC) at pH 3.



Scheme S2. Alternative wholly aqueous one-pot synthesis of PMEMA-PMEMA diblock copolymers via (i) RAFT aqueous solution polymerization of methacrylic acid (MAA) at pH 2, targeting 20% w/w solids using ACVA initiator at 70 °C for 3 h followed by (ii) RAFT aqueous solution polymerization of (2-(N-morpholino)ethyl methacrylate) (MEMA) at pH 8.5.



Table S1. Summary of the characterization data obtained for four PMAA-PMETAC and three PMAA-PMEMA diblock copolymers prepared according to Schemes S1 and S2. ¹H NMR spectroscopy was used to calculate the final comonomer conversion for each block. Following a suitable methylation protocol (which was preceded by forced hydrolysis for PMETAC-based copolymers), THF GPC analysis was used to determine the molecular weight of the first block and the diblock copolymer. Isoelectric points (IEP) were determined by aqueous electrophoresis studies (see Figures S2 and S3).

Target diblock copolymer composition	GPC analysis of PMAA precursor		¹ H NMR	GPC analysis of diblock copolymer		¹ H NMR	
	M _n (g mol⁻¹)	M _w /M _n	(%)	M _n (g mol⁻¹)	M _w /M _n	(%)	IEP
PMAA ₆₀ -PMETAC ₁₂₀	5 800	1.27	98	17 800	1.34	95	No IEP
PMAA ₆₀ -PMETAC ₆₀	6 000	1.26	>99	12 400	1.60	97	pH 7.1
PMAA ₆₀ -PMETAC ₃₀	5 900	1.28	98	9 900	1.51	98	pH 5.3
PMAA ₆₀ -PMETAC ₁₅	6 000	1.31	>99	7 900	1.36	96	pH 4.2
PMAA ₆₀ -PMEMA ₁₂₀	6 800	1.29	>99	31 600	1.37	96	pH 6.0
PMAA ₆₀ -PMEMA ₆₀	6 900	1.27	>99	15 600	1.28	99	pH 5.7
PMAA ₆₀ -PMEMA ₃₀	6 800	1.28	>99	11 000	1.22	89	pH 5.1

PMETAC₆₀ CPDB, ACVA, 105 min

0



PMETAC₆₀

Figure S1. Aqueous GPC curves (refractive index detector, PEO calibration standards, Agilent AquaGel OH-30 and OH-40 columns, 0.50 M acetic acid and 0.30 M NaH₂PO₄ at pH 2) comparing the synthesis of PMETAC homopolymer using (i) a CPDB RAFT agent and ACVA initiator at 70 °C for 105 min versus (ii) a CECPA RAFT agent using the VA-044 initiator at 44 °C for 5 h. CECPA clearly provides much better control over the polymerization, because it produces a significantly lower dispersity.



Figure S2. (a) ¹H NMR spectra recorded for a PMEMA₆₀ precursor (lower green spectrum) and the same homopolymer after being subjected to exhaustive methylation using a ten-fold excess of trimethylsilyldiazomethane (upper blue spectrum). No significant spectral changes are observed, indicating that no change in this homopolymer occurs under such conditions. (b) THF GPC curves recorded for the same PMEMA homopolymer before (green dashed trace) and after (blue solid trace) exposure to the same exhaustive methylation conditions, indicating minimal change in the molecular weight distribution.

Figure S3. Zeta potential vs. pH curves constructed for (a) PMAA₆₀-PMEMA₁₂₀, (b) PMAA₆₀-PMEMA₆₀, and (c) PMAA₆₀-PMEMA₃₀ in the presence of 1 mM KCl background salt. The shaded regions indicate colloidal instability, with the mid-point of these regions corresponding to the isoelectric point (IEP) in each case.



Figure S4. Zeta potential vs. pH curves constructed for (a) $PMAA_{60}$ -PMETAC₁₂₀, (b) $PMAA_{60}$ -PMETAC₆₀, (c) $PMAA_{60}$ -PMETAC₃₀, and (d $PMAA_{60}$ -PMETAC₁₅ in the presence of 1 mM KCl background salt. The shaded regions indicate colloidal instability, with the mid-point of these regions corresponding to the isoelectric point (IEP) in each case.

