Supporting Information

The Influence of Monomer Ionization and Hydrolysis on the Radical Polymerization Kinetics of 2-(Dimethylamino)ethyl Methacrylate in Aqueous Solution

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Topics

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Ionization

Degree of Ionization of DMAEMA and MAA versus pH

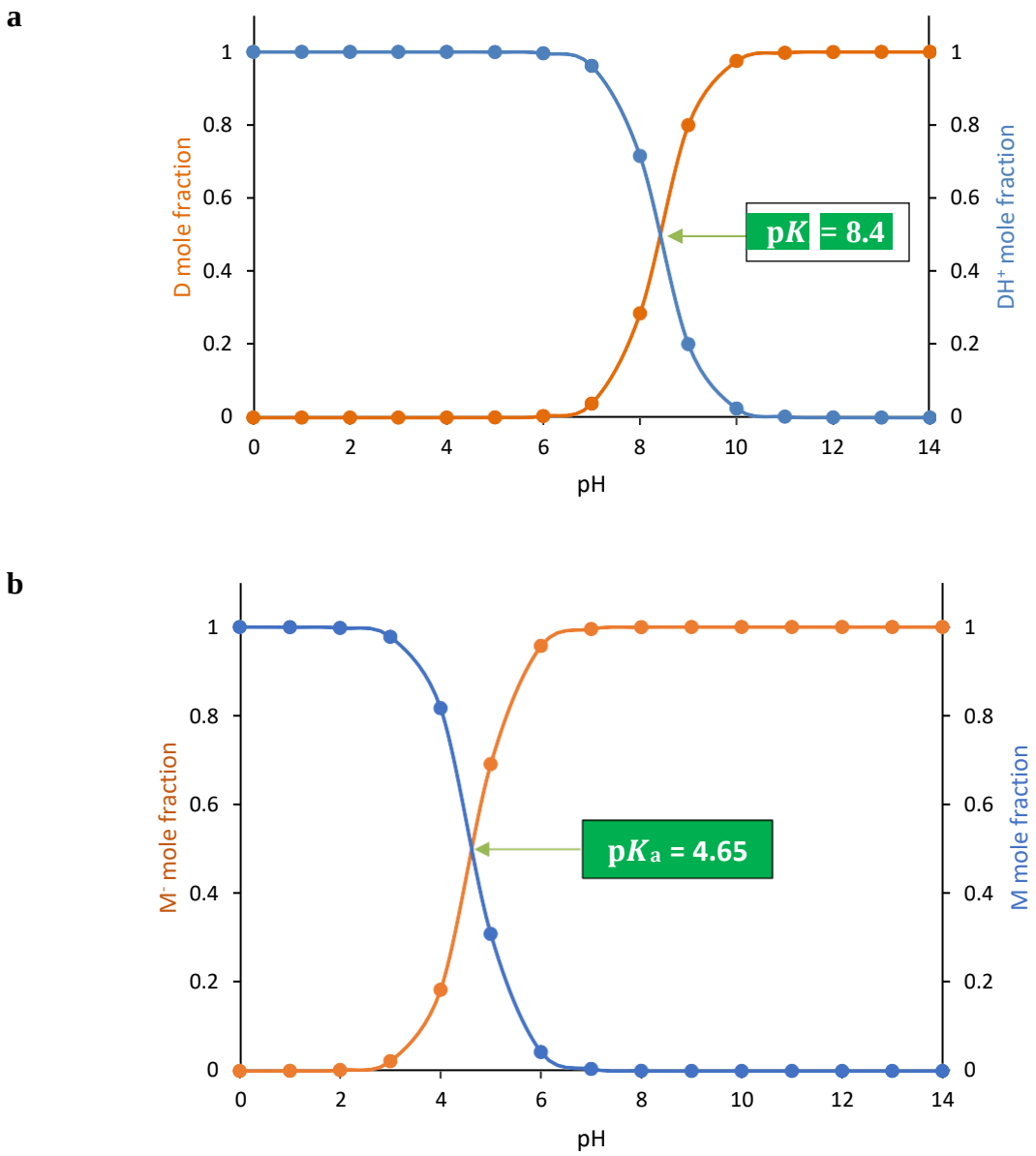

Figure S1. (a) D and DH^+ mole fractions as a function of pH, calculated using a DMAEMA p$K_a$value of 8.4.[1] **(b)** Ionized (M^-) and non-ionized (M) mole fractions for MAA as a function of pH, calculated using a pK_a of 4.65.[2-4]

Hydrolysis

^{1}H-NMR Spectra and Peak Assignments of MAA and DMAE

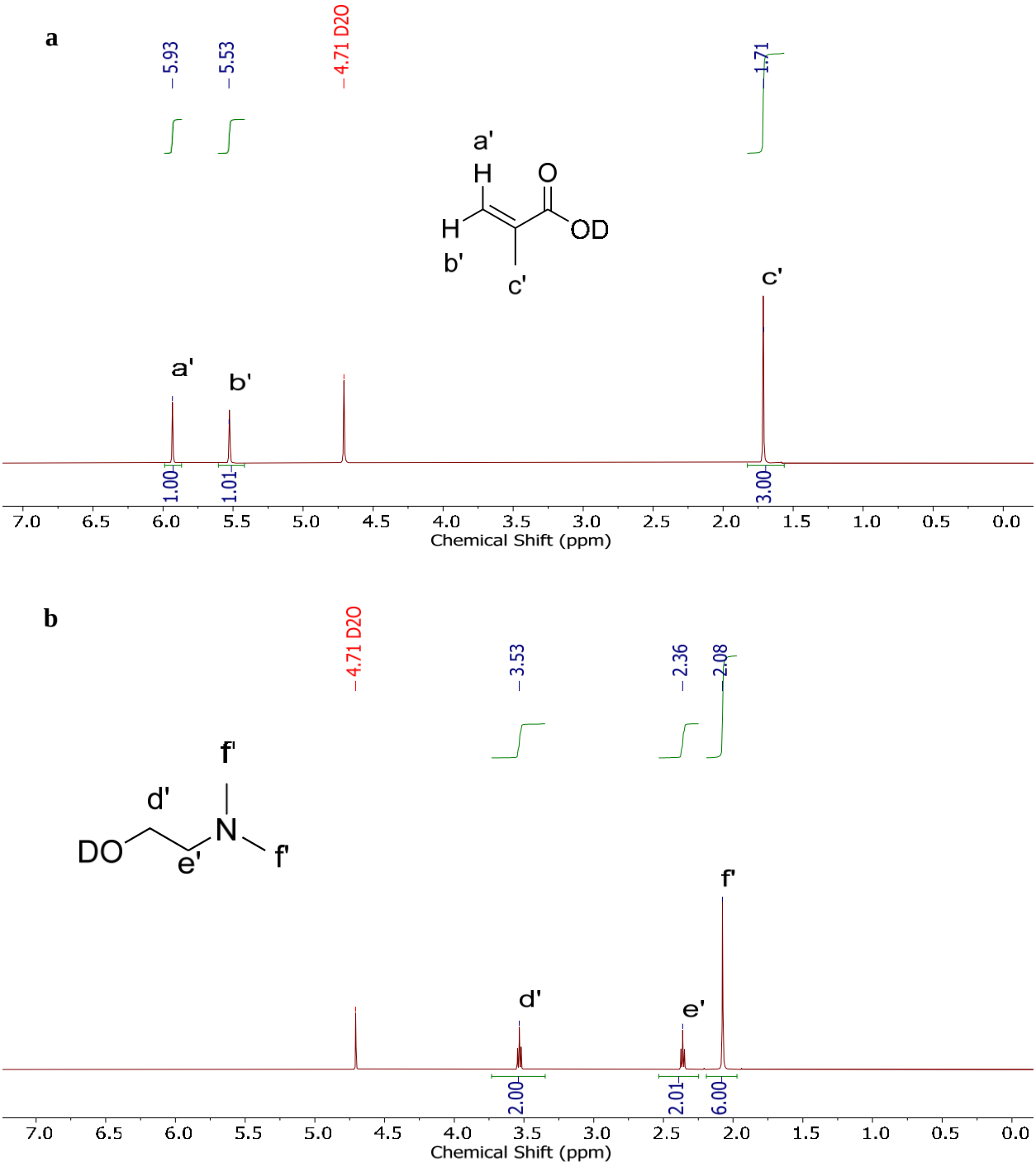

Figure S2. ^{1}H NMR (500 MHz) spectra of: **(a)** MAA in D_2O, with MAA signals at 5.71 ppm (s, 1H, CH=C (cis, a')), 5.38 ppm (s, 1H, CH=C (trans, b')) and 1.92 ppm (s, 3H, CH_3-C (c')). **(b)** DMAE in D_2O with DMAE signals at 3.89 ppm (t, 2H, CH_2-O (d')), 3.11 ppm (t, 2H, CH_2-N (e')) and 2.77 ppm (s, 6H, $(CH_3)_2$-N (f')).[1,5]

Monitoring of DMAEMA Hydrolysis with ^{1}H-NMR Stacked Plot

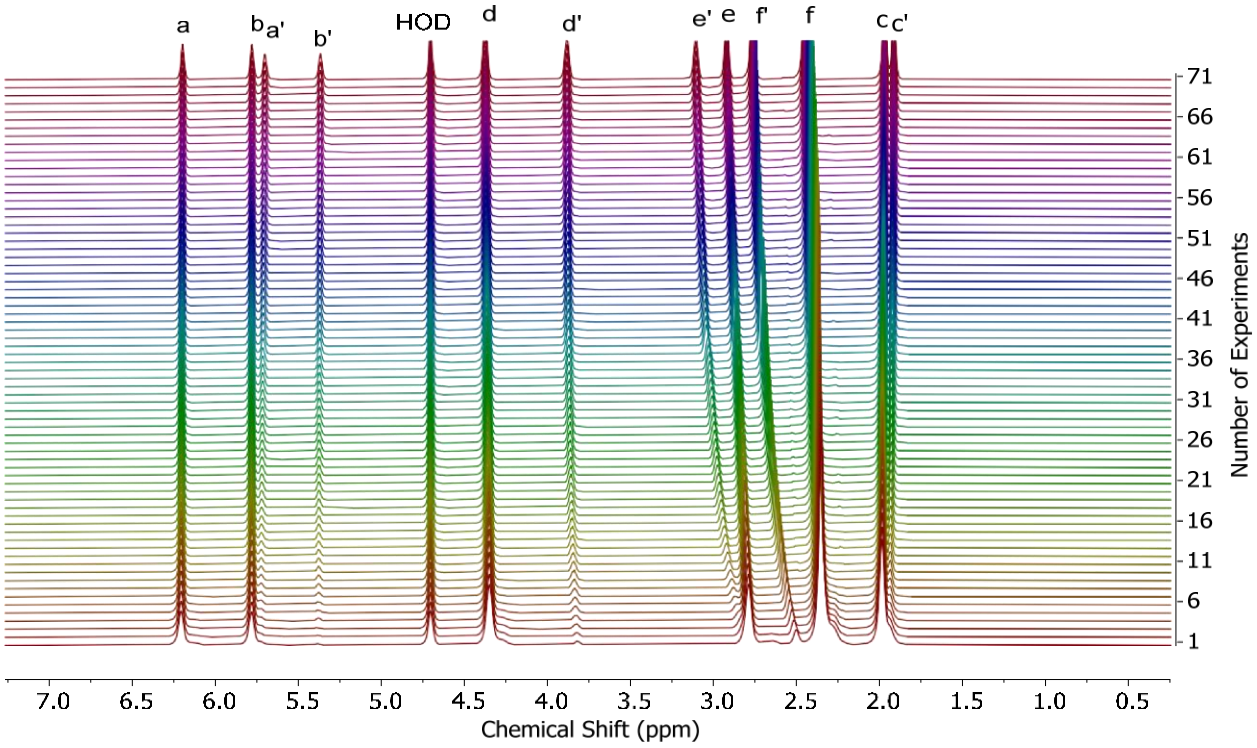

Figure S3. ^{1}H NMR stacked plot (500 MHz) following DMAEMA hydrolysis in D_2O at 40 °C and pH of 10.1. Spectra were acquired every 80 s (1.33 min).

DMAEMA Hydrolysis Rate Coefficients

Table S1. Hydrolysis rate coefficients (k_{obs}) of DMAEMA estimated from various ^{1}H NMR peaks a-f (see Figure 1) at pH 10.1.

Temperature (°C)	**Peak**	$\boldsymbol{k_{obs}}$**× 10^{-4} (s^{-1})**
40	a	0.83
	b	-
	c	-
	d	0.83
	e	-
	f	-
50	a	2.2
	b	2.1
	c	-
	d	2.1
	e	-
	f	2.1
60	a	4.9
	b	4.8
	c	4.8
	d	-
	e	-
	f	-
70	a	9.9
	b	9.7
	c	9.6
	d	-
	e	-
	f	10.0

Variation of pH with Ternary DMAEMA-MAA-DMAE Mixtures

To understand the influence of degradation products (MAA and DMAE) on solution pH, equimolar amounts of MAA and DMAE with DMAEMA in H_2O were prepared and analyzed in the absence of reaction at room temperature. The measurements were conducted using an Orion™ ROSS Ultra™ Refillable pH/ATC Triode™ Combination Electrode, consisting of a glass electrode and reference electrode contained in a single probe and calibrated with buffer solutions of pH 1.68, 4.01, 7.00, 10.01 and 12.46. The electrode was dipped into the solutions and held until a stable pH measurement was achieved, with the probe rinsed with deionized water and soaked in the storage solution when not in use.

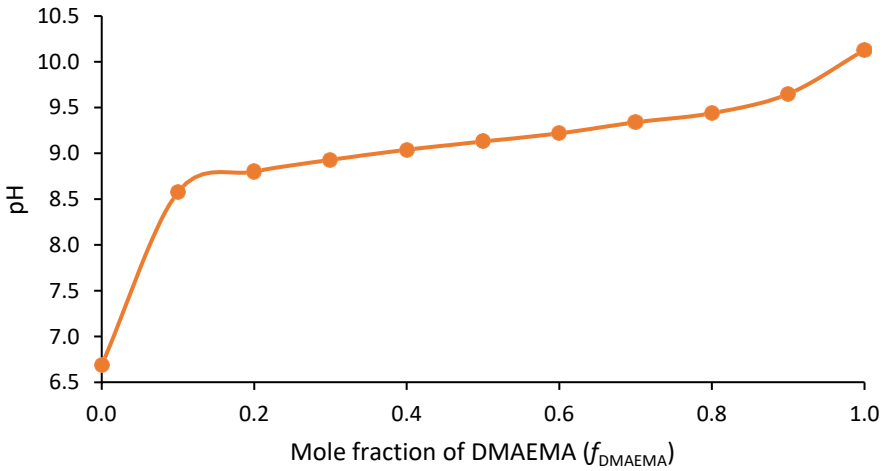

Figure S4. The variation of solution pH with composition of ternary DMAEMA-MAA-DMAE mixtures in H_2O at room temperature, adding MAA and DMAE in equimolar quantities while keeping total content at 10 wt%, where mole fraction of DMAEMA (f_{DMAEMA}) is given by $f_{DMAEMA} = \frac{\text{mol DMÆEMÆ}}{\text{mol DMÆEMÆ + mol MÆÆ + mol DMÆE}}$

Best Fit Arrhenius Parameters of DMAEMA Hydrolysis

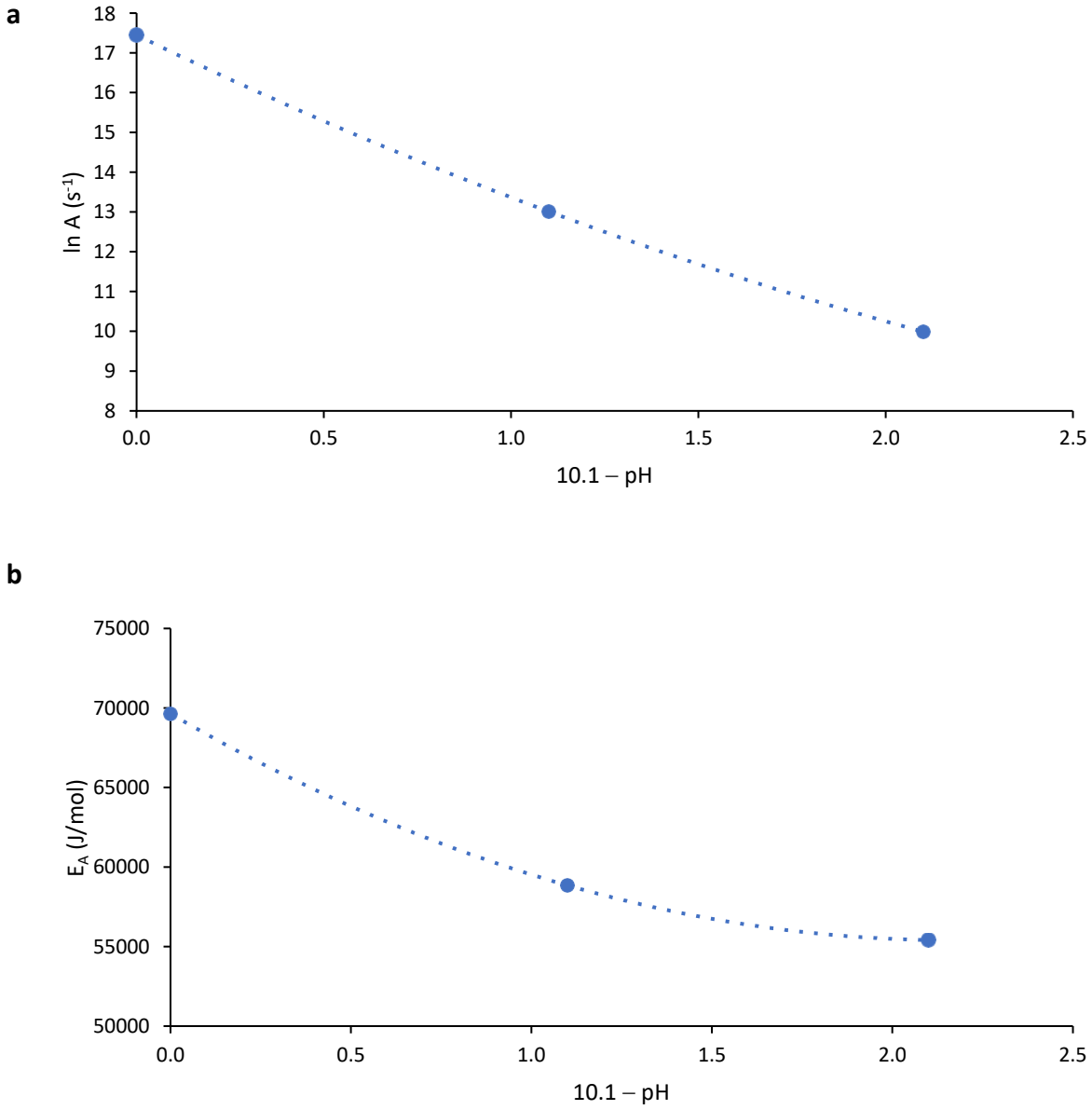

Figure S5. Best fit Arrhenius parameters **(a)** ln A and **(b)** E_A values (points, see Table 2) determined for DMAEMA hydrolysis, plotted as a function of (10.1 – pH). Lines show quadratic fits summarized by Eq. 7-9.

Free Radical Polymerization

Poly(DMAEMA) ^{1}H-NMR Spectra in Acidic Water

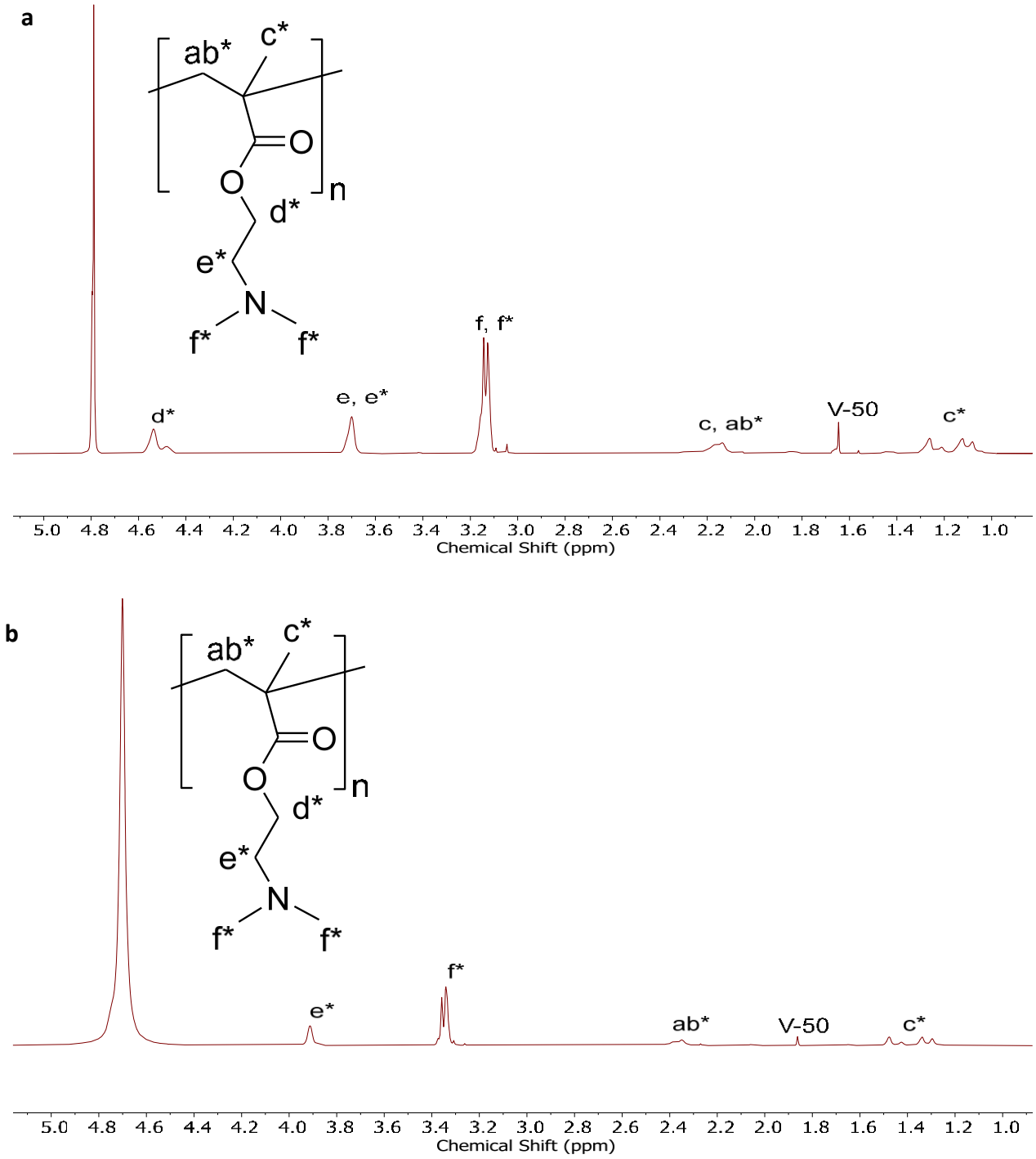

Figure S6. ^{1}H NMR (700 MHz) spectra of poly(DMAEMA) after aqueous polymerization of 5 wt% DMAEMA with 0.4 wt% V-50 to full conversion in D_2O at 60 °C for 1 h at: **(a)** pH = 1.0 and **(b)** pH = 4.0

Calculations of DMAEMA Hydrolysis and Copolymerization Rates

The copolymerization calculation procedures for polymerizations conducted under conditions at which hydrolysis also occurs are given below (A.I. = integration area):

$$C_{\mathrm{DMAEMA_{initial}}} = C_{\mathrm{DMAEMA}}|_t + C_{\mathrm{DMAE}}|_t + C_{\mathrm{P-D}}|_t$$

$$C_{\mathrm{DMAEMA_{initial}}} = (A.I.)_{\mathrm{DMAEMA}}|_{t=0} + \frac{(A.I.)_{\mathrm{DMAE}}|_{t=0}}{2} + C_{\mathrm{P-D}}|_{t=0}$$

$$C_{\mathrm{DMAE}}|_t = C_{\mathrm{MAA}}|_t + C_{\mathrm{P-MAA}}|_t$$

$$C_{\mathrm{DMAE}}|_t = \frac{(A.I.)_{\mathrm{DMAE}}|_t}{2}$$

$$Mole\ fraction\ of\ MAA\ in\ copolymer = \frac{C_{\mathrm{P-MAA}}|_t}{C_{\mathrm{P-MAA}}|_t + C_{\mathrm{P-D}}|_t}$$

$$Mole\ fraction\ of\ DMAEMA\ in\ copolymer = \frac{C_{\mathrm{P-D}}|_t}{C_{\mathrm{P-MAA}}|_t + C_{\mathrm{P-D}}|_t}$$

$$Fraction\ of\ DMAEMA\ lost\ to\ hydrolysis = \frac{C_{\mathrm{DMAE}}|_t}{C_{\mathrm{DMAEMA_{initial}}}}$$

$$Fraction\ of\ DMAEMA\ converted\ to\ copolymer = \frac{C_{\mathrm{P-D}}|_t}{C_{\mathrm{DMAEMA_{initial}}}}$$

$$Fraction\ of\ unreacted\ DMAEMA = 1 - Fraction\ of\ DMAEMA\ lost\ to\ hydrolysis - Fraction\ of\ DMAEMA\ converted\ to\ copolymer$$

$$Effective\ DMAEMA\ conversion = \frac{Fraction\ of\ DMAEMA\ converted\ to\ copolymer}{1 - Fraction\ of\ DMAEMA\ lost\ to\ hydrolysis}$$

$$MAA\ conversion = \frac{C_{\mathrm{P-MAA}}|_t}{C_{\mathrm{DMAE}}|_t}$$

$$Degree\ of\ hydrolysis = \frac{C_{\mathrm{DMAE}}|_t}{C_{\mathrm{DMAEMA_{initial}}}} \times 100$$

where C = concentration, $P - D$ = DMAEMA units in copolymer, $P - MAA$ = MAA units in copolymer

Plots of Polymerization Behaviour at Various pH, Temperature, and Initiator Levels

60 °C, 0.4 wt% V-50, pH 8.0 – 10.1

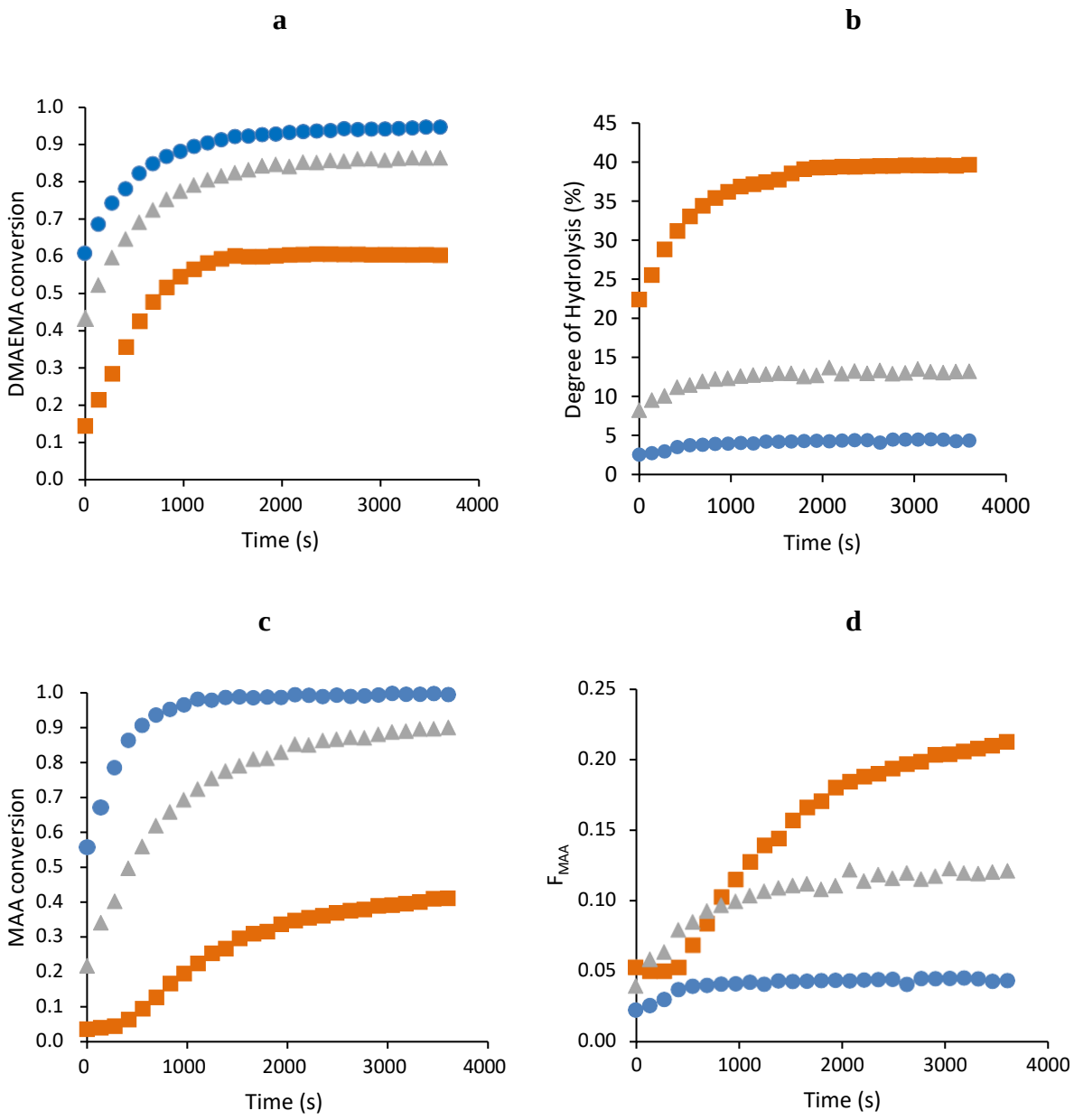

Figure S7. Polymerization of DMAEMA in water at 60 °C with initial $w_{DMAEMA,0}$ = 0.05 and $w_{V\text{-}50}$ = 0.004 to form poly(DMAEMA-co-MAA) at pH 10.1 (orange squares), pH 9.0 (gray triangles) and pH 8.0 (blue circles): **(a)** Fractional conversion profiles of DMAEMA incorporated into polymer; **(b)** Degree of DMAEMA hydrolysis during polymerization; **(c)** Fractional MAA conversion profiles; **(d)** Mole fraction of MAA in the copolymer.

50 °C, 0.1 wt% V-50, pH 8.0 – 10.1

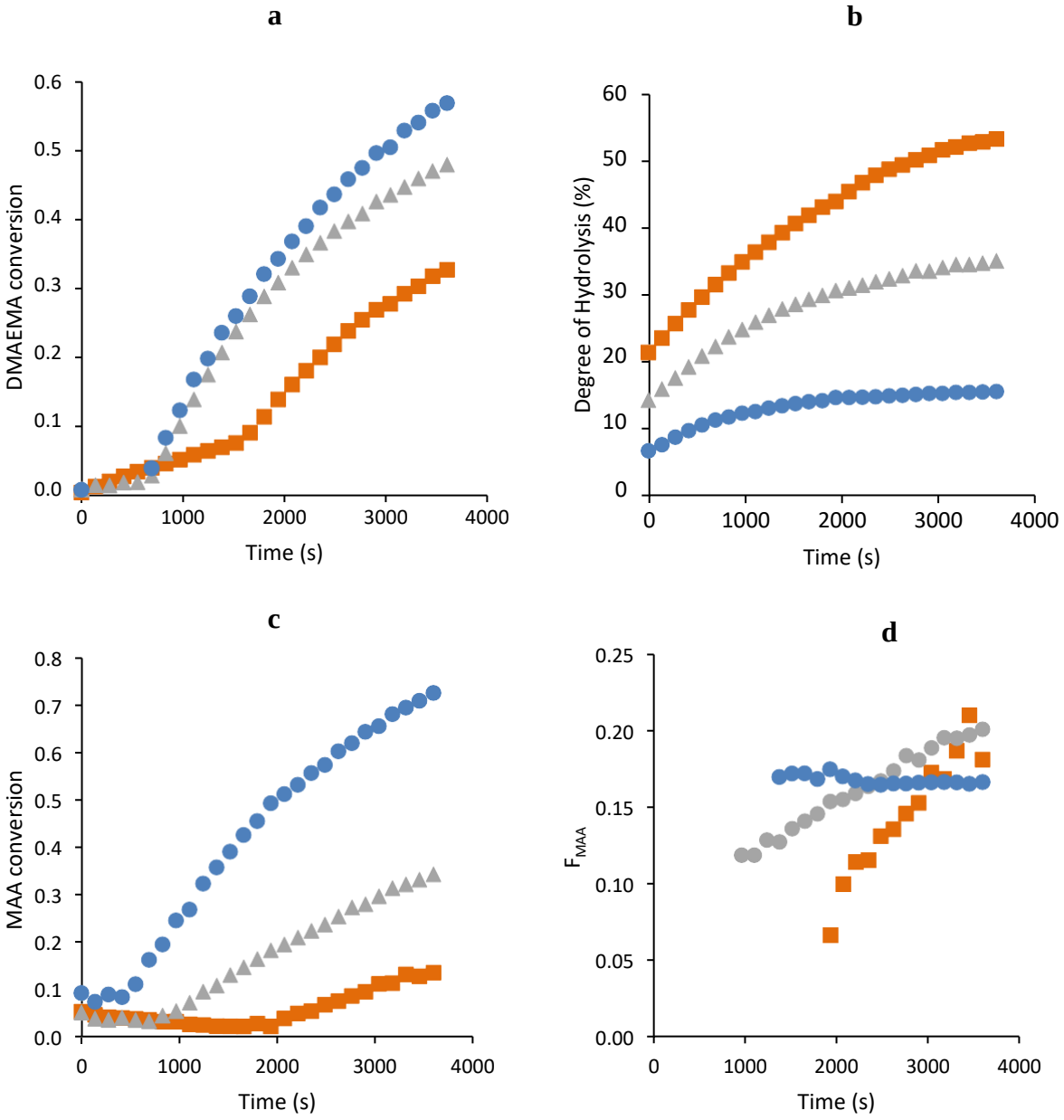

Figure S8. Polymerization of DMAEMA in water at 50 °C with initial $w_{DMAEMA,0}$ = 0.05 and w_{V-50} = 0.001 to form poly(DMAEMA-co-MAA) at pH 10.1 (orange squares), pH 9.0 (gray triangles) and pH 8.0 (blue circles): **(a)** Fractional conversion profiles of DMAEMA incorporated into polymer; **(b)** Degree of DMAEMA hydrolysis during polymerization; **(c)** Fractional MAA conversion profiles; **(d)** Mole fraction of MAA in the copolymer.

50 °C, 0.4 wt% V-50, pH 8.0 – 10.1

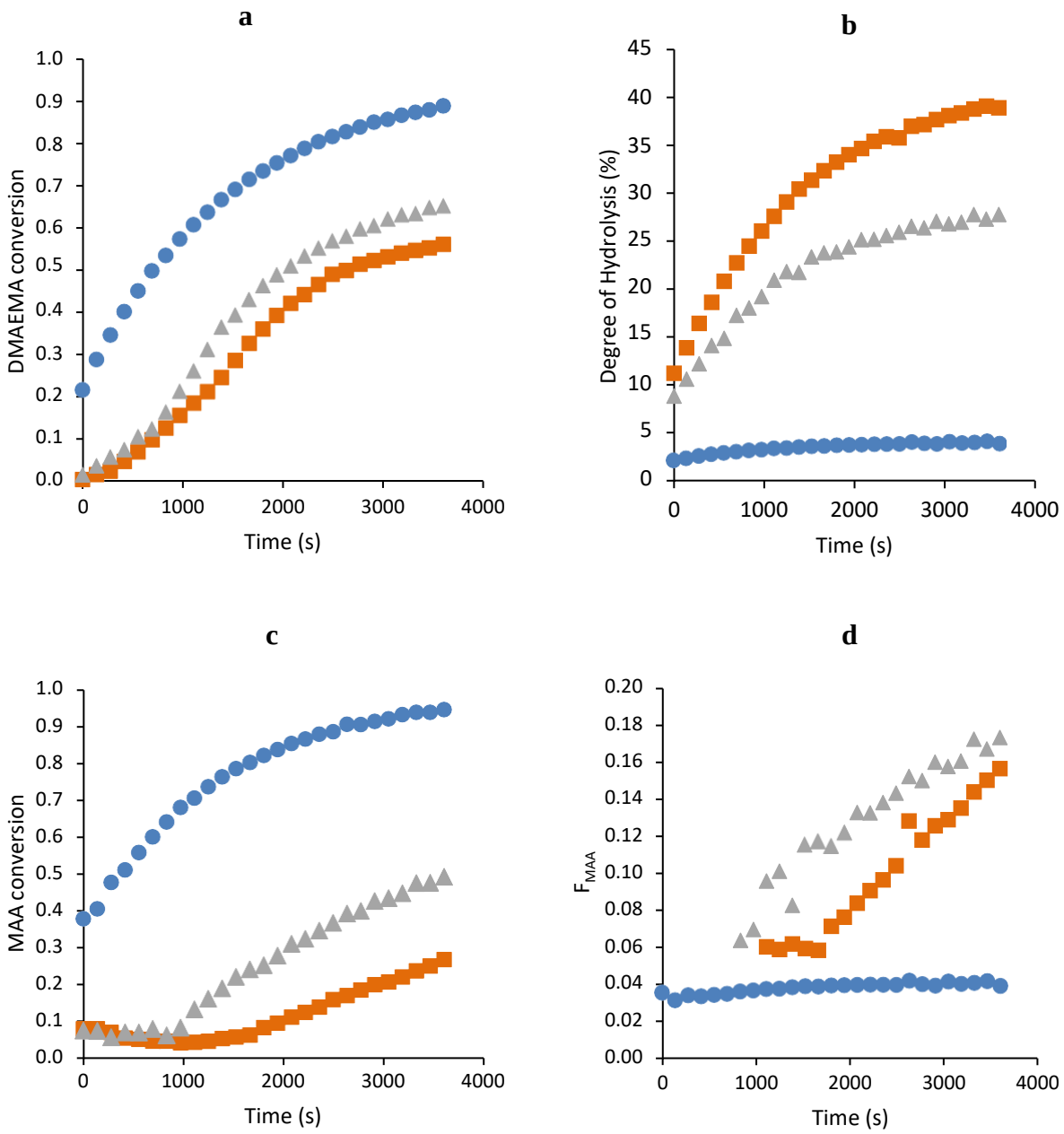

Figure S9. Polymerization of DMAEMA in water at 50 °C with initial $w_{DMAEMA,0}$ = 0.05 and w_{V-50} = 0.004 to form poly(DMAEMA-co-MAA) at pH 10.1 (orange squares), pH 9.0 (gray triangles) and pH 8.0 (blue circles): **(a)** Fractional conversion profiles of DMAEMA incorporated into polymer; **(b)** Degree of DMAEMA hydrolysis during polymerization; **(c)** Fractional MAA conversion profiles; **(d)** Mole fraction of MAA in the copolymer.

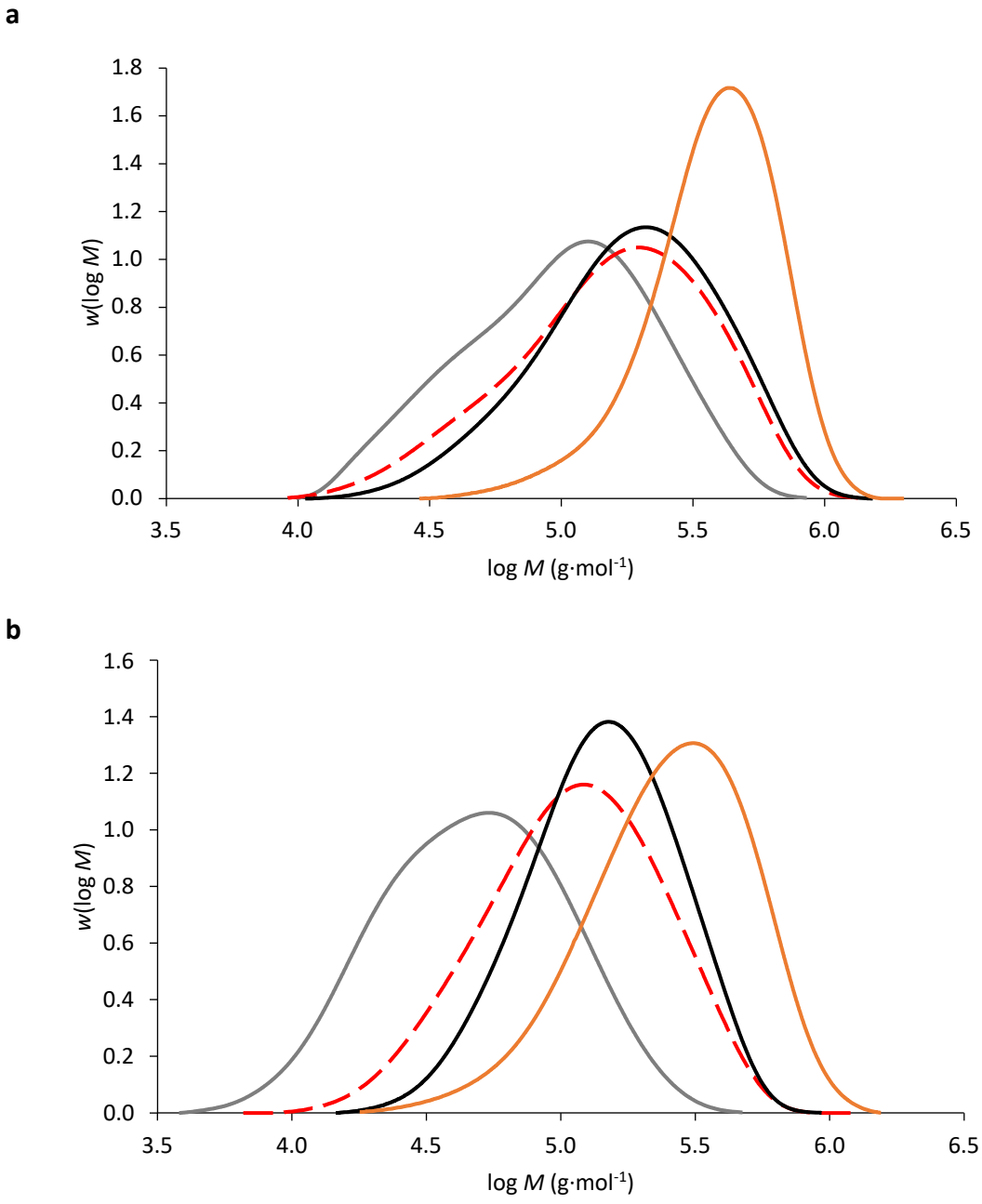

Figure S10. Molar mass distributions of poly(DMAEMA-co-MAA) formed from DMAEMA by radical polymerization in aqueous solutions: $w_{DMAEMA,0}$ = 0.05 (60 °C, w_{V-50} = 0.004 (gray); 60 °C, w_{V-50} = 0.001 (red dashes); 50 °C, w_{V-50} = 0.004 (black); 50 °C, w_{V-50} = 0.001 (orange)) at **(a)** pH = 8.0 **(b)** pH = 10.1

References

1. P. van de Wetering, N. J. Zuidam, M. J. Van Steenbergen, O. A. G. J. Van Der Houwen, W. J. M. Underberg and W. E. Hennink, *Macromolecules,* 1998, **31**, 8063–8068.

2. S. Beuermann, M. Buback, P. Hesse and I. Lacík, *Macromolecules* 2006, **39**, 184–193.

3. I. Lacík, L. Učňová, S. Kukučková, M. Buback, P. Hesse and S. Beuermann, *Macromolecules,* 2009, **42**, 7753–7761.

4. H. Kattner, P. Drawe and M. Buback, *Macromolecules,* 2017, **50**, 1386–1393.

5. P. Zheng, X. Su, C. Fei, X. Shi, H. Yin and Y. Feng, *J. Polym. Sci. B: Polym. Phys*., 2018, **56**, 914–923.