Electronic Supplementary Information

ARGET-ATRP Synthesis and Swelling Response of Compositionally Varied Poly(methacrylic acid-*co*-N, N-diethylaminoethyl methacrylate) Polyampholyte Brushes

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Analysis of Parent and Deprotected Brush Thicknesses and Molecular Weights

Compositional information and molecular weight of the chains produced from sacrificial initiator allow the molecular weight of the p(MAA-*co*-DEAEMA) polyampholytes to be determined. This assumes that the chains recovered from solution are appropriate proxies of the brushes and that all tert-butyl groups "protecting" groups are cleaved during conversion of p(tBMA-*co*-DEAEMA) to form the p(MAA-*co*-DEAEMA) polyampholyte brushes.

As shown by Murata and Rühe,[1] when a polymer brush is chemically modified and if assumptions of constant mass density and grafting density are invoked, then ratio of brush heights (before and after chemical modification) equals the ratio of molecular weights of the parent and modified chains comprising the brushes:

$$\frac{H_1}{H_2} = \frac{M_{n,1}}{M_{n,2}} \tag{S1}$$

Recasting this equation for the p(tBMA-*co*-DEAEMA) "parent" and corresponding p(MAA-*co*-DEAEMA) polyampholyte (PA) system, and using the assumption that the conversion from "protected" form to polyampholyte is complete results in

$$\frac{H_1}{H_2} = \frac{M_{n,\,\text{polyampholyte}}}{M_{n,\text{"parent"}}} = \frac{\sum(n_i m_{o,i})}{M_{n,\text{"parent"}}} \tag{S2}$$

where n_i is the number of electrolytic repeating units of type i (i = MAA, DEAEMA) comprising the polyampholyte and $m_{o,i}$ their molar mass. The numbers of repeating units of each type are readily determined from the composition and molecular weight of the parent brush, which is represented by the chains in solution.

*t*BMA:DEAEMA	Mol % DEAEMA[a]	M_n (kDa)[a]	n_{tBMA}	n_{DEAEMA}	$M_{n,\,PA}$ (kDa)[b]
80:20	19	55.8	318	57	37.9
50:50	48	68.4	250	177	54.3
20:80	83	55.3	66	248	51.6

[a] Composition and molecular weight determined from free chains in solution.

[b] Calculated based on numbers of repeating units.

Buffer Recipes and Preparation Procedure

Buffers were prepared following literature procedures using the following acids and salt.[2]

Table S1. Amounts of buffer species and sodium chloride required to make 100 ml of a buffer solution with a concentration of 30 mM and ionic strength of 30 mM at various pH values.

pH	Buffer Species	Mass of Buffer Species (g)	Mass of NaCl (g)
3	Phosphoric Acid	0.294	0.018
5	Acetic Acid	0.180	0.057
7	MOPS free acid[a]	0.627	0.111
8	TAPS[b]	0.729	0.128

[a] 3-(N-morpholino)propanesulfonic acid

[b] N-[Tris(hydroxymethyl)methyl]-3-aminopropanesulfonic acid

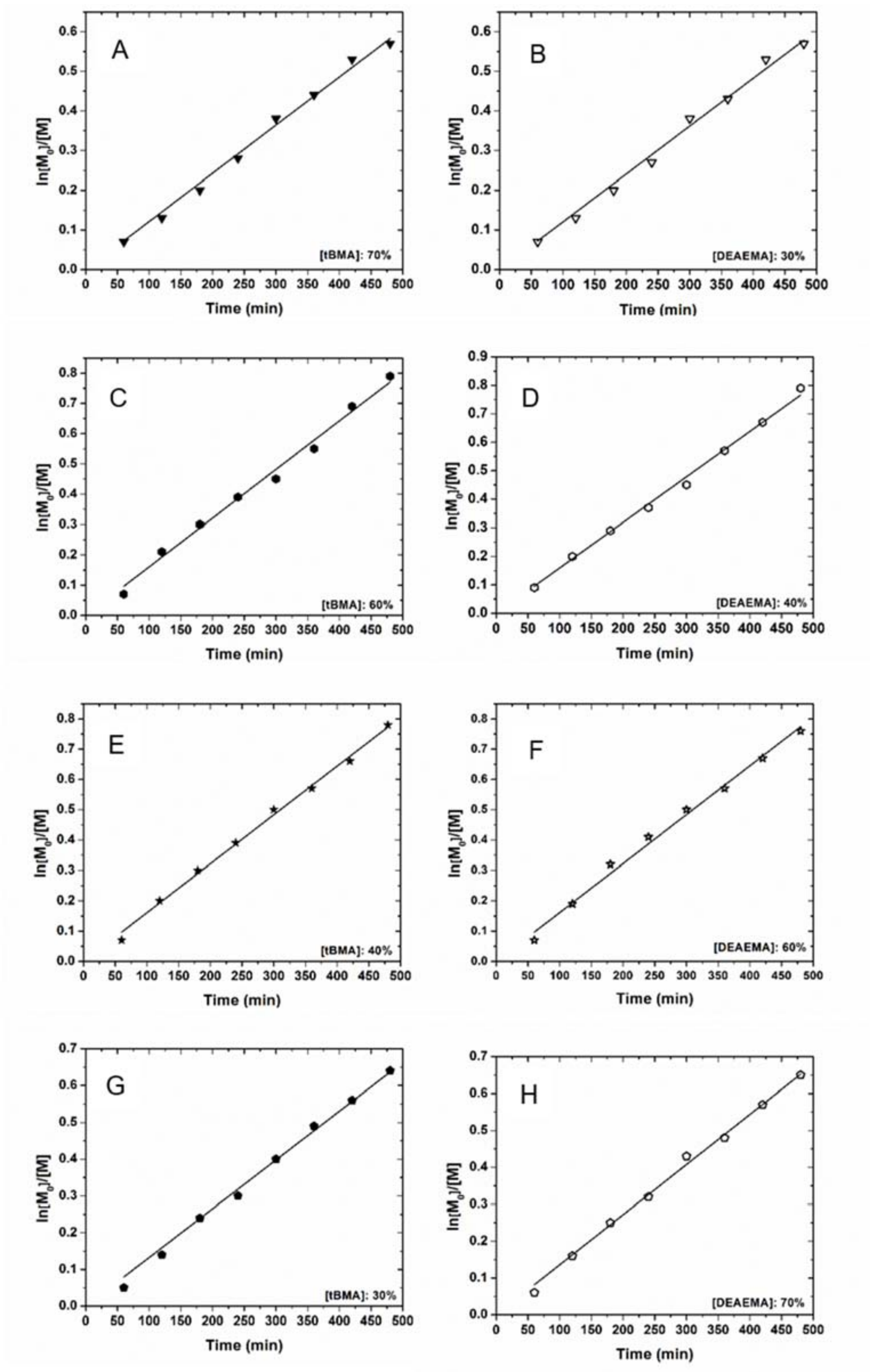


Figure S1. Kinetic plots for ARGET ATRP of P(*t*BMA-*co*-DEAEMA) at various comonomer ratios. The plots for A and B are for a copolymer targeted to be 70% tBMA and 30% DEAEMA; C and D are for a copolymer targeted to be 60% tBMA and 40% DEAEMA; E and F are for a copolymer targeted to be 40% tBMA and 60% DEAEMA; and G and H are for a copolymer targeted to be 30% tBMA and 70% DEAEMA. All reactions were run in anisole at T=35°C for 8 h.

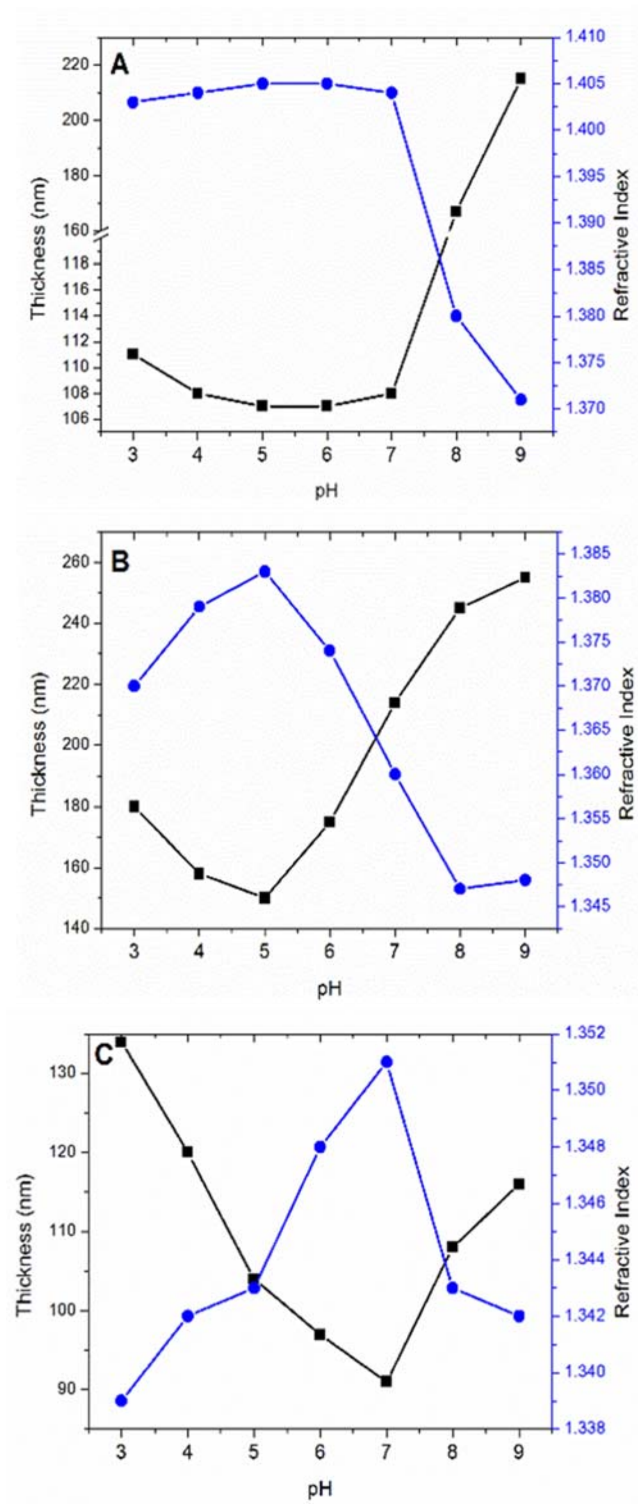
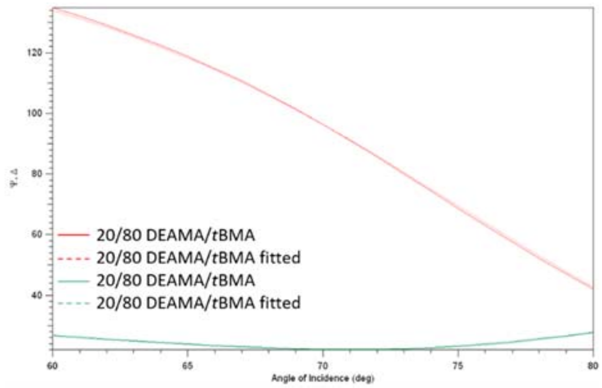
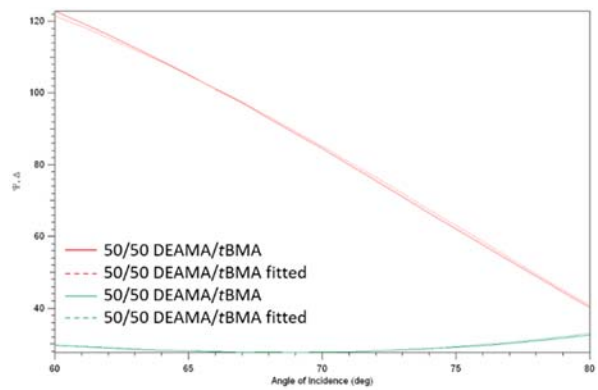


Figure S2. Swelling response of p(DEAEMA-*co*-MAA) brushes as a function of pH. The curves also display the refractive index from the "slab" model used in the analysis of the ellipsometric data.

P(tBMA-*co*-DEAEMA) brush containing 20 mol% DEAEMA
Thickness = 44 nm, $\chi^2 = 1.3 \times 10^{-3}$



P(tBMA-*co*-DEAEMA) brush containing 50 mol % DEAEMA
Thickness = 75 nm, $\chi^2 = 2.5 \times 10^{-3}$



P(tBMA-*co*-DEAEMA) brush containing 80 mol % DEAEMA
Thickness = 39 nm, $\chi^2 = 2.9 \times 10^{-4}$

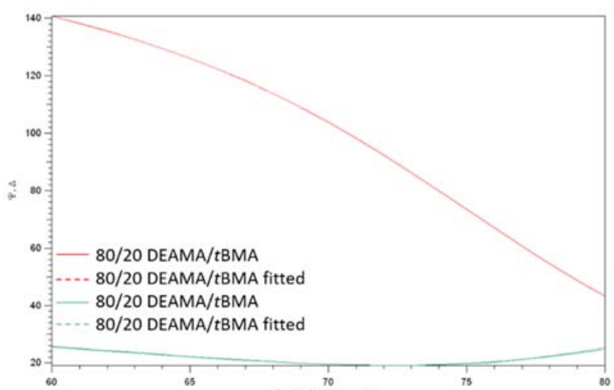
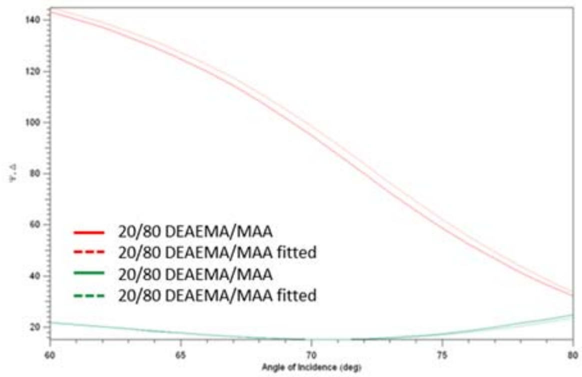
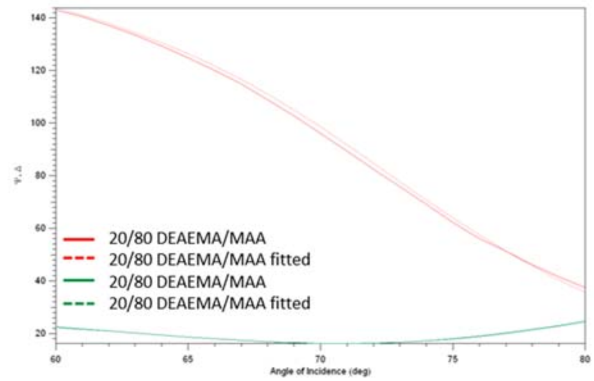


Figure S3. Multiangle ellipsometry data expressed in terms of ellisometric angles (Ψ, Δ) and corresponding best fit models (slab-like model) for P(tBMA-*co*-DEAEMA) brushes. Brush composition, thicknesses and the goodness-of-fit parameter χ^2 are given for each.

Solvated P(MAA-*co*-DEAEMA) brushes containing 20 mol% DEAEMA

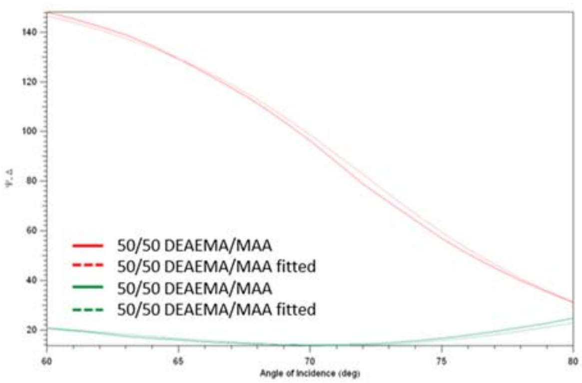
pH = 6: Thickness = 55 nm, $\chi^2 = 4.8 \times 10^{-3}$ pH = 9: Thickness = 66 nm, $\chi^2 = 3.2 \times 10^{-3}$

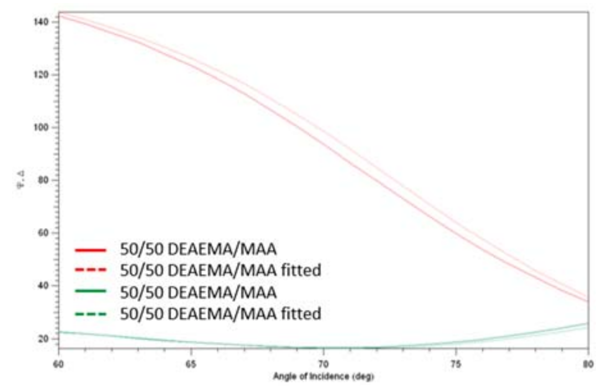




Solvated P(MAA-*co*-DEAEMA) brushes containing 50 mol% DEAEMA

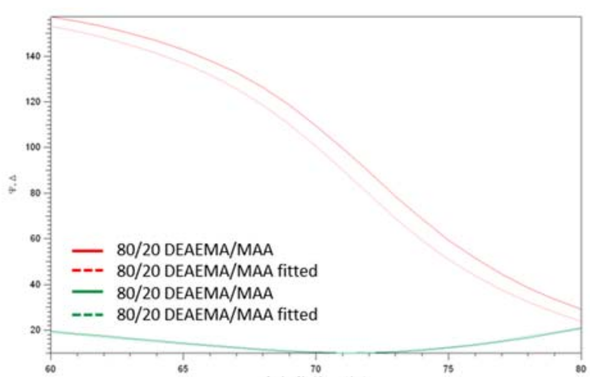
pH = 6: Thickness = 81 nm, $\chi^2 = 1.2 \times 10^{-2}$ pH = 9: Thickness = 107 nm, $\chi^2 = 9.0 \times 10^{-3}$





Solvated P(MAA-*co*-DEAEMA) brushes containing 80 mol% DEAEMA

pH = 6: Thickness = 76 nm, $\chi^2 = 2.3 \times 10^{-2}$ pH = 9: Thickness = 97 nm, $\chi^2 = 3.3 \times 10^{-2}$



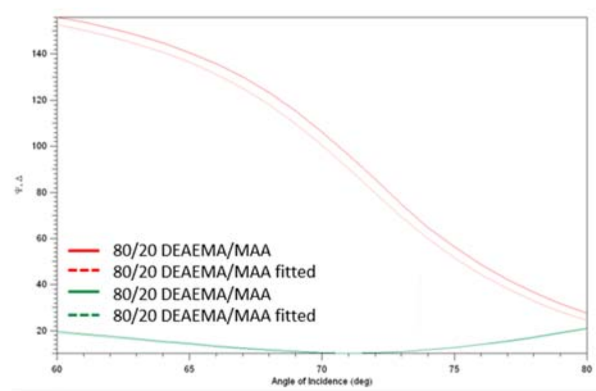


Figure S4. Multiangle ellipsometry data expressed in terms of ellisometric angles (Ψ, Δ) and corresponding best fit models (slab-like model) for solvated P(MAA-*co*-DEAEMA) polyampholyte brushes. Brush composition, thicknesses and the goodness-of-fit parameter χ^2 are given for each, and pH values were chosen to represent collapsed (pH = 6) and swollen (pH = 9) states.

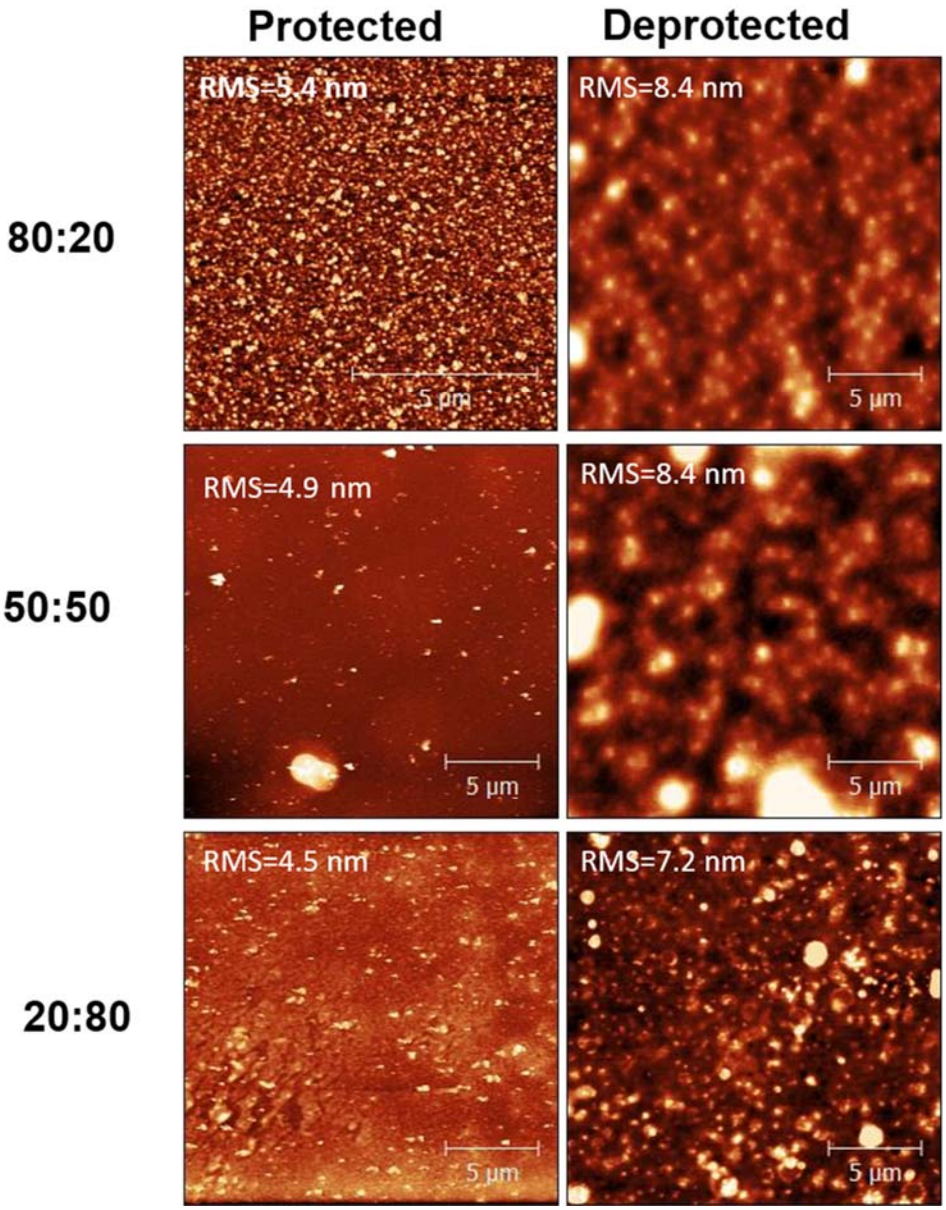


Figure S5. AFM images of p(tBMA-*co*-DEAEMA) brushes ("Protected") and the p(MAA-co-DEAEMA) polyampholyte brushes resulting from deprotection by acid hydrolysis. The compositions, top to bottom, are 80:20, 50:50, and 20:80 [tBMA]:[DEAEMA] (left) and [MAA]:[DEAEMA] (right). RMS roughness values are inset in each image.

References

1. H. Murata, O. Prucker and J. Rühe, Synthesis of Functionalized Polymer Monolayers from Active Ester Brushes, *Macromolecules*, 2007, **40**, 5497–5503.
2. C. Deodhar, E. Soto-Cantu, D. Uhrig, P. Bonnesen, B. S. Lokitz, J. F. Ankner and S. M. Kilbey, Hydration in Weak Polyelectrolyte Brushes, *ACS Macro Lett.*, 2013, **2**, 398–402.