

A Mechanistic Study of the Hydrolysis of Poly[N,N-(Dimethylamino)ethyl Acrylates] as
Charge-Shifting Polycations

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Supporting Information

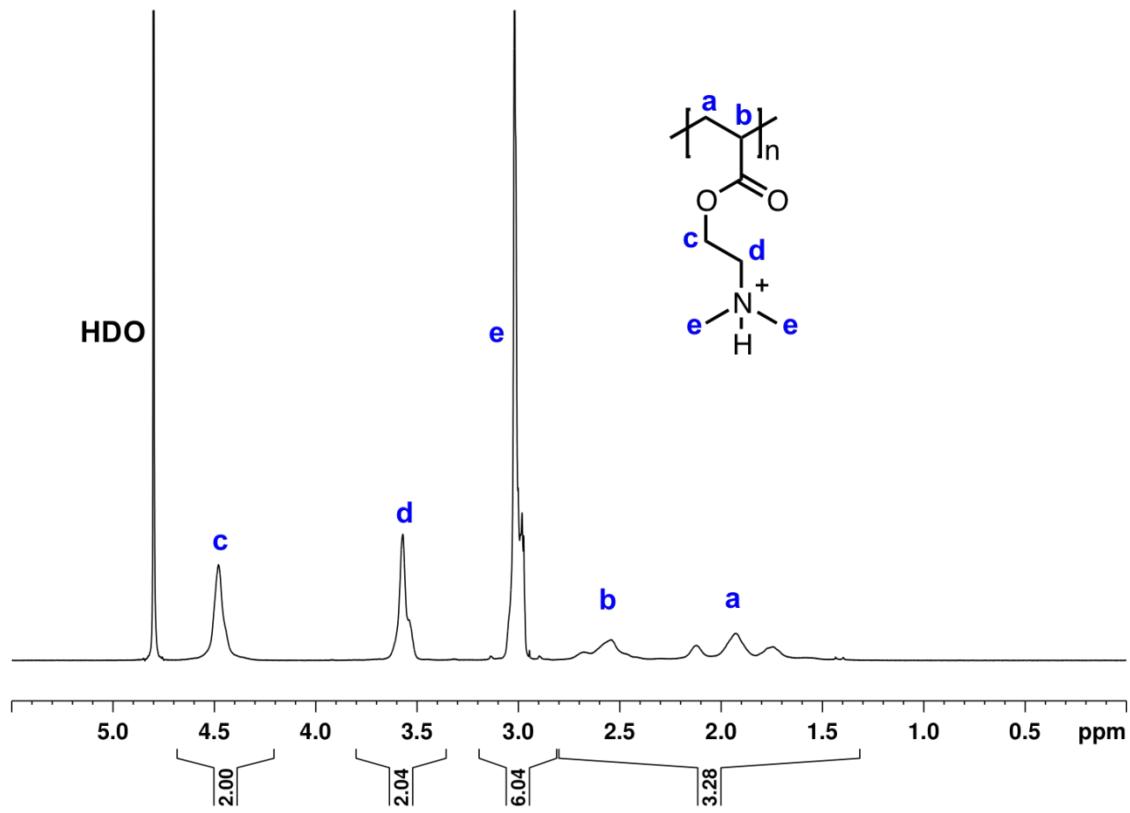


Figure S1. ¹H NMR spectrum of PDMAEA in D₂O (pH 3-4) recorded at 600 MHz.

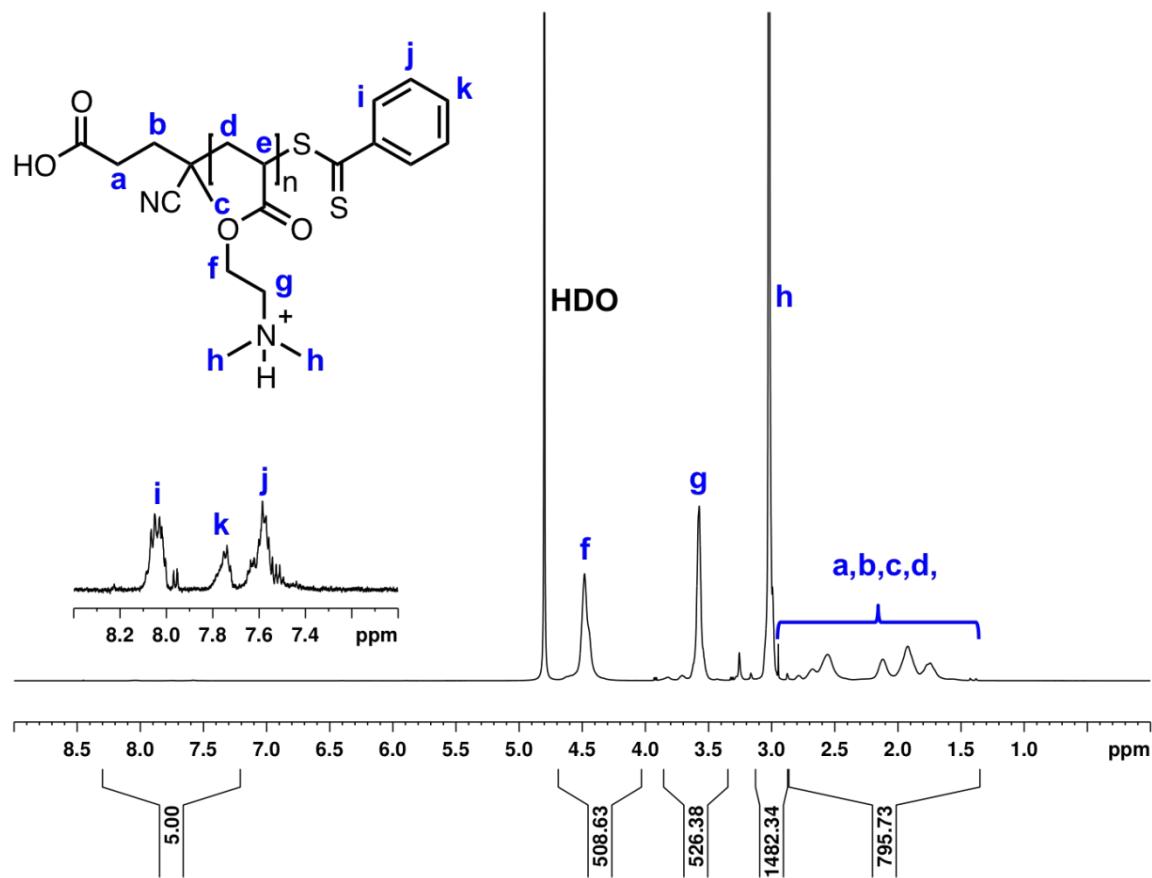
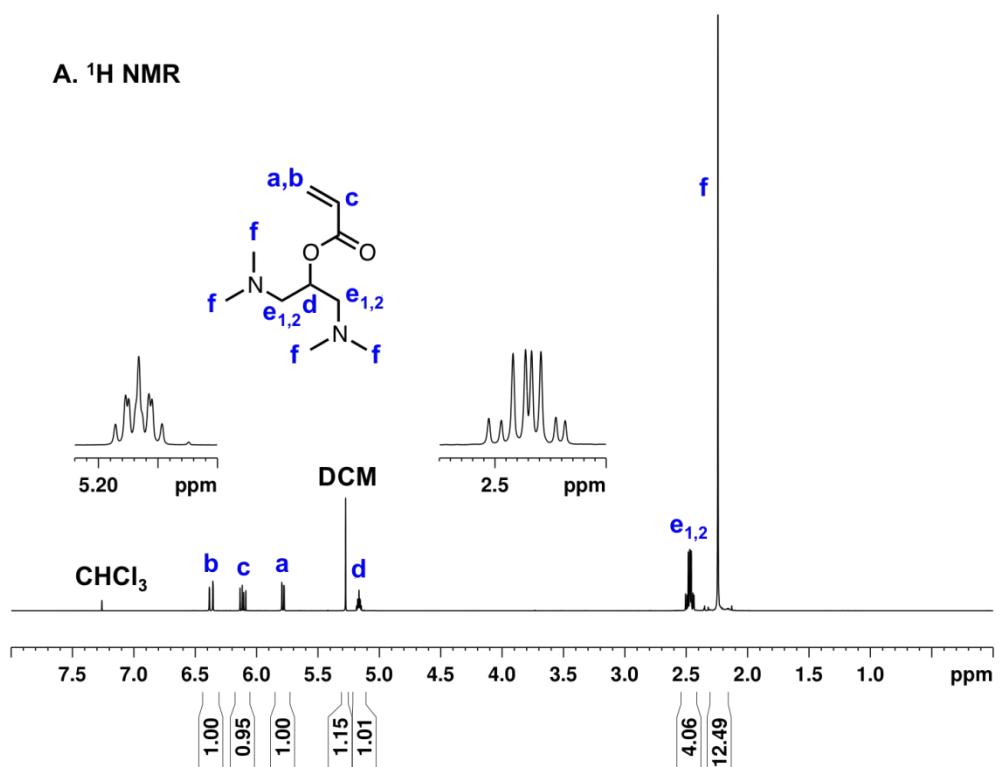


Figure S2. ¹H NMR spectrum of PDMAEA by RAFT polymerization in D_2O (pH 3-4) recorded at 500 MHz with 512 scans. End group analysis of dithiobenzoate group showed DP of approximately 254.

A. ^1H NMR



B. ^{13}C NMR

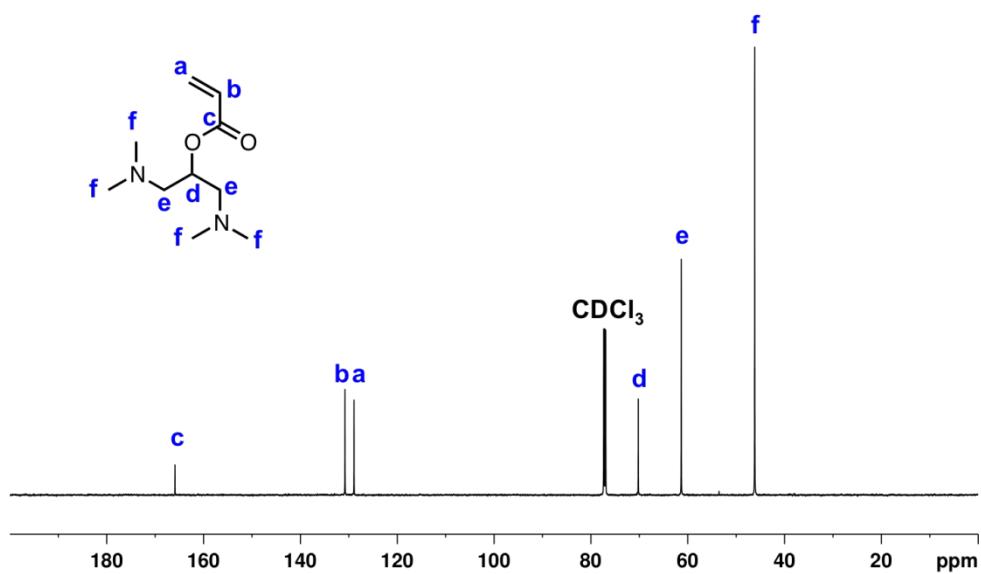


Figure S3. ^1H (A) and ^{13}C (B) NMR spectra of BDMAPA in CDCl_3 recorded at 600 MHz. The protons at position e are diastereotopic, which leads to two distinct signals, each a doublet of doublets.

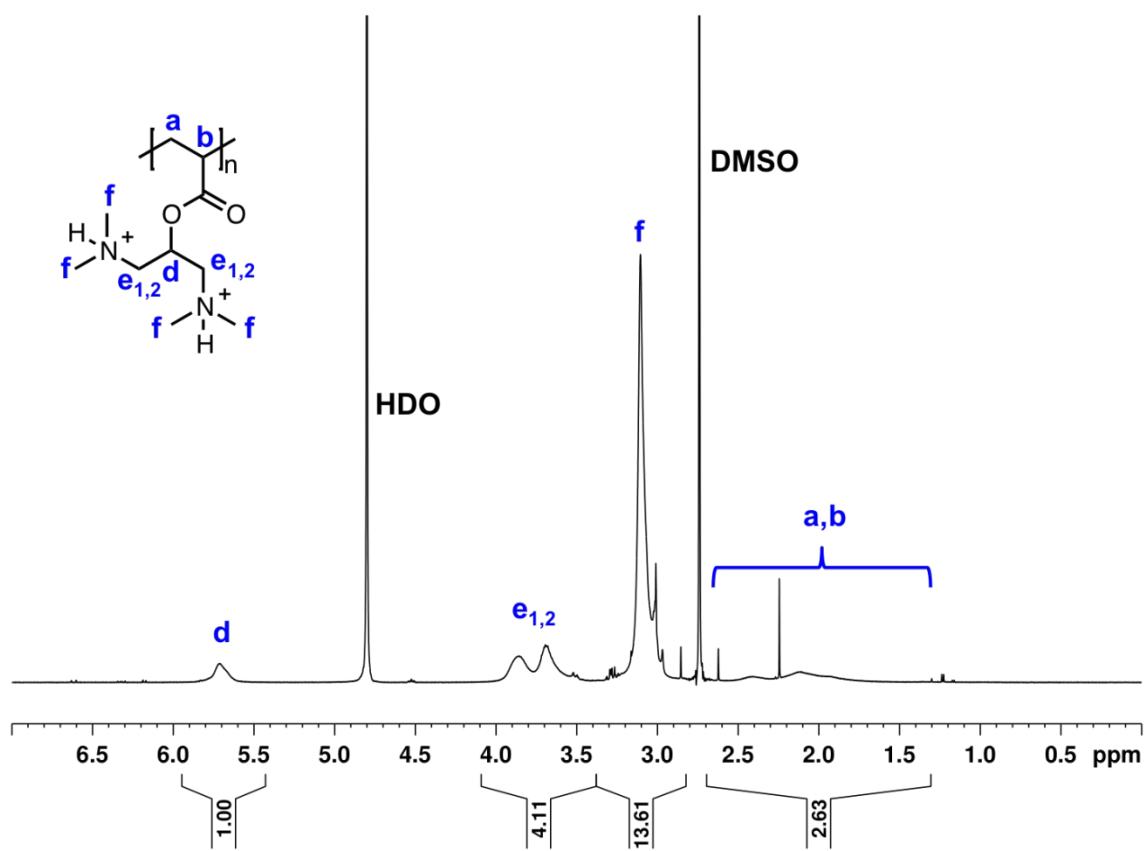
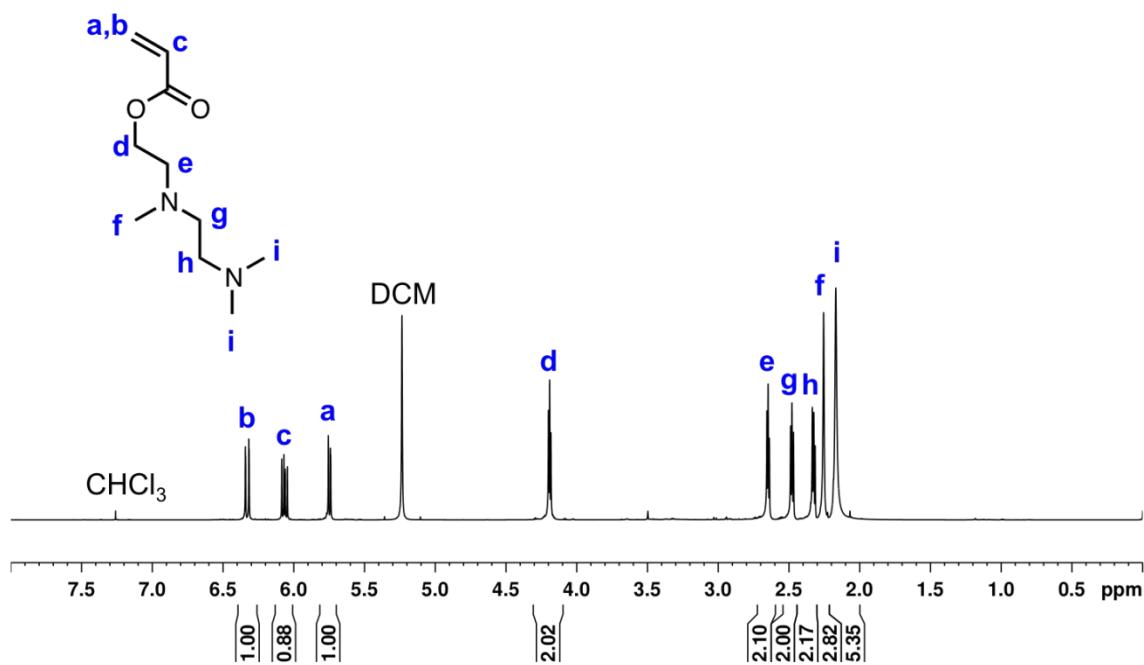


Figure S4. ^1H NMR spectrum of PBDMAPA in D_2O (pH 3-4) recorded at 600 MHz

A. ^1H NMR



B. ^{13}C NMR

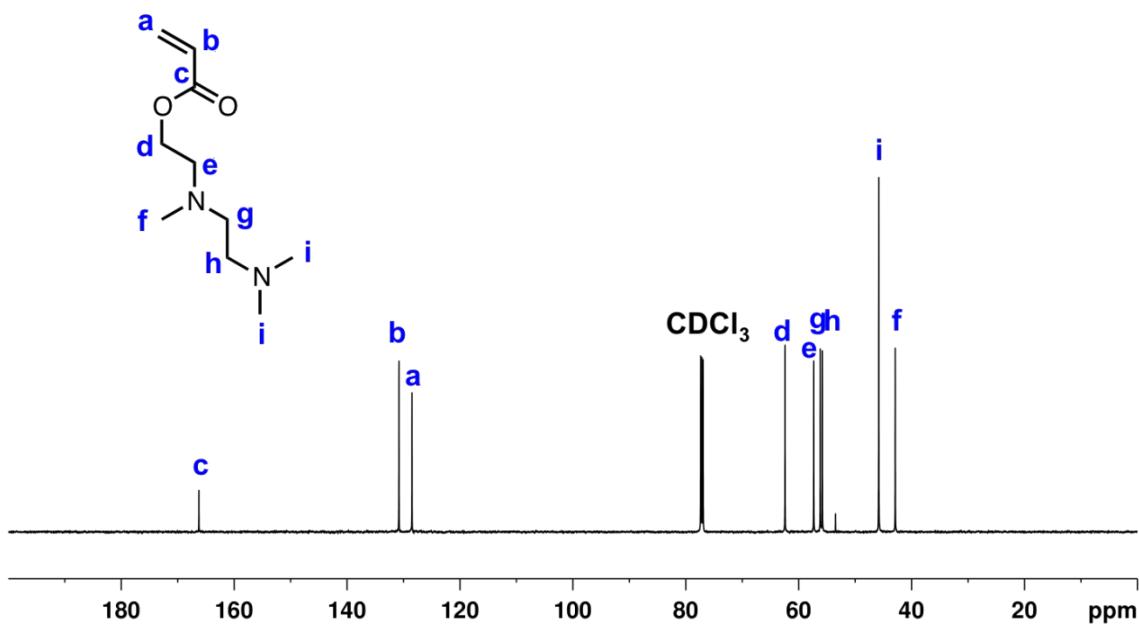


Figure S5. ^1H (A) and ^{13}C (B) NMR spectra of DEMEA in CDCl_3 recorded at 600 MHz.

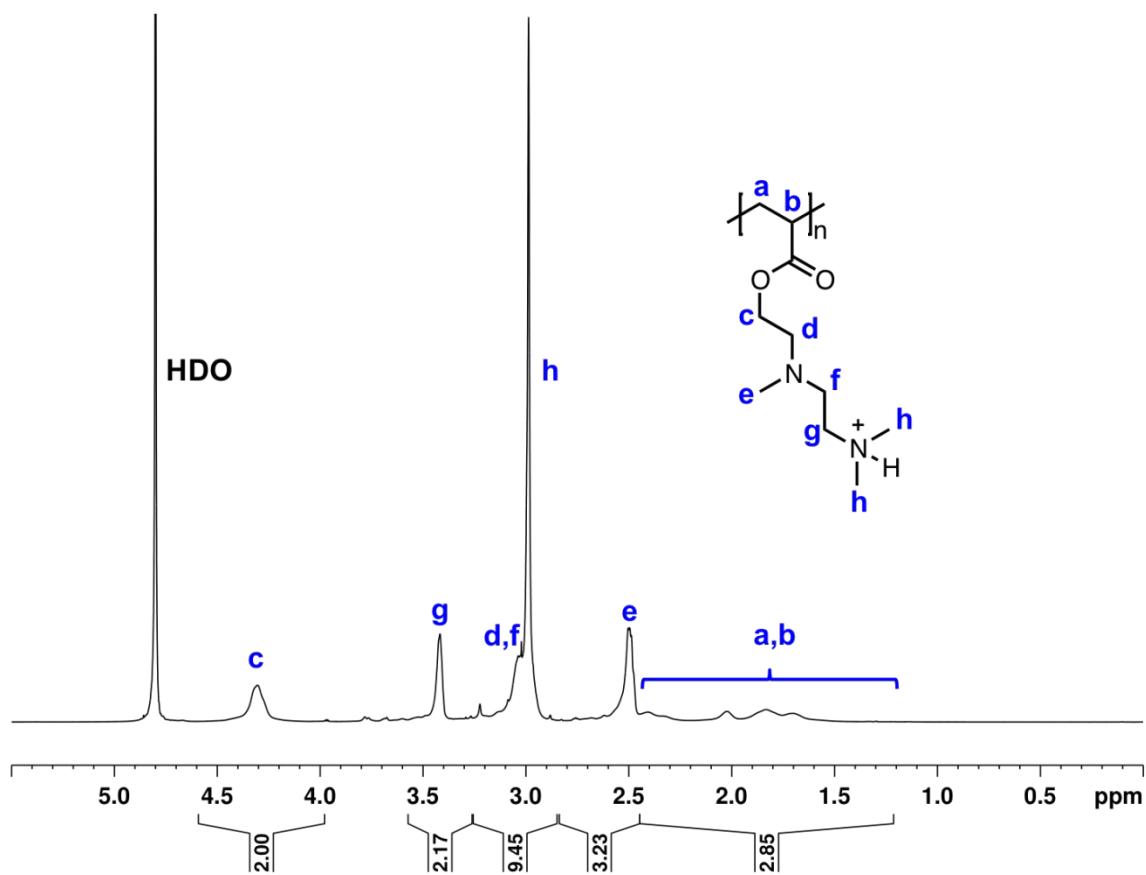


Figure S6. ^1H NMR spectrum of PDEMEA in D_2O (pH 3-4) recorded at 700 MHz.

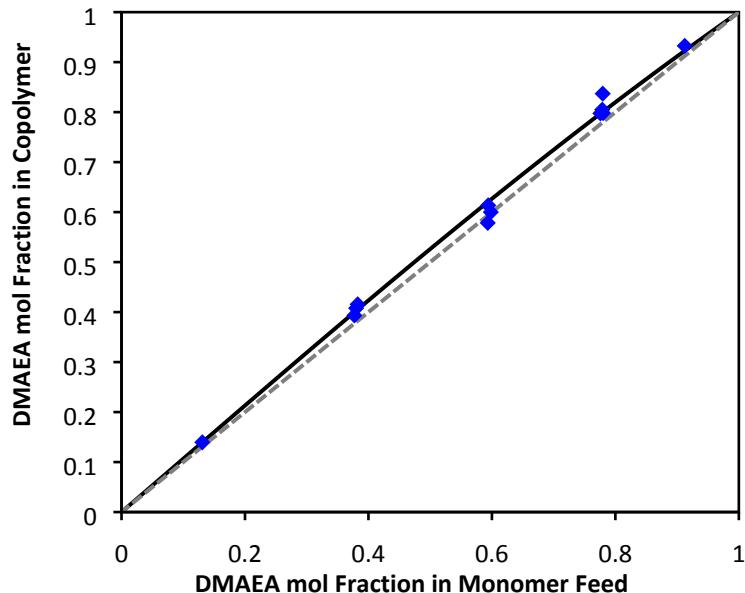


Figure S7. Instantaneous copolymer composition plot showing experimental data points (blue diamonds) from various DMAEA/HEA feed ratios. The solid black line shows the best fit of the copolymer equation to the experimental data obtained using the least squares method with the Solver tool in Microsoft Excel. Reactivity ratios were estimated to be $r_1 = 1.2$ (DMAEA) and $r_2 = 0.9$ (HEA).

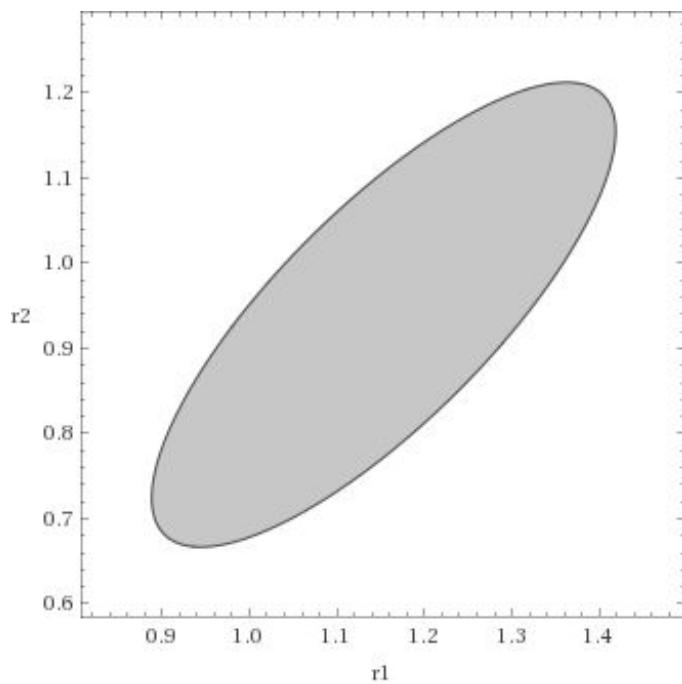


Figure S8. Joint 95% confidence region for reactivity ratios obtained for DMAEA (r_1)/HEA (r_2) (1.2/0.9). The contour was determined using a method described by Smith et al. Error! Bookmark not defined.

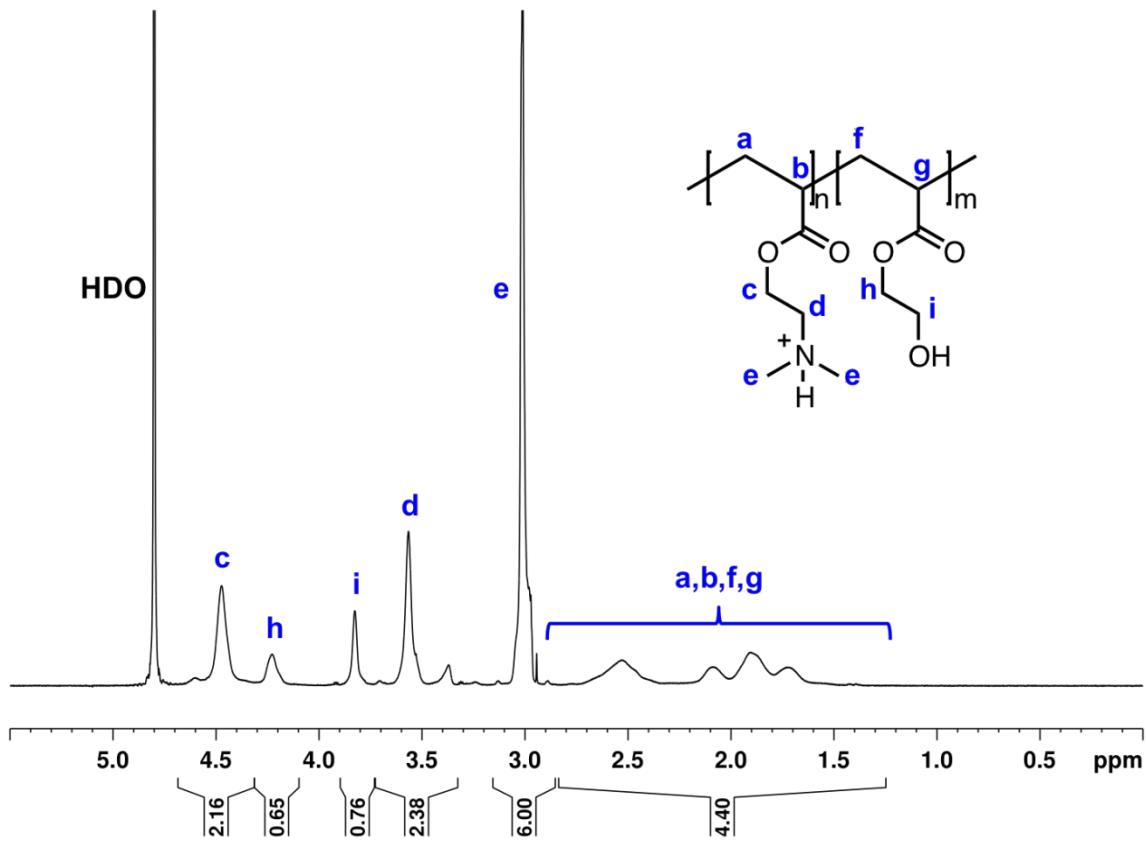


Figure S9. ^1H NMR spectrum of PDH₇₇ in D_2O (pH 3-4) recorded at 600 MHz.

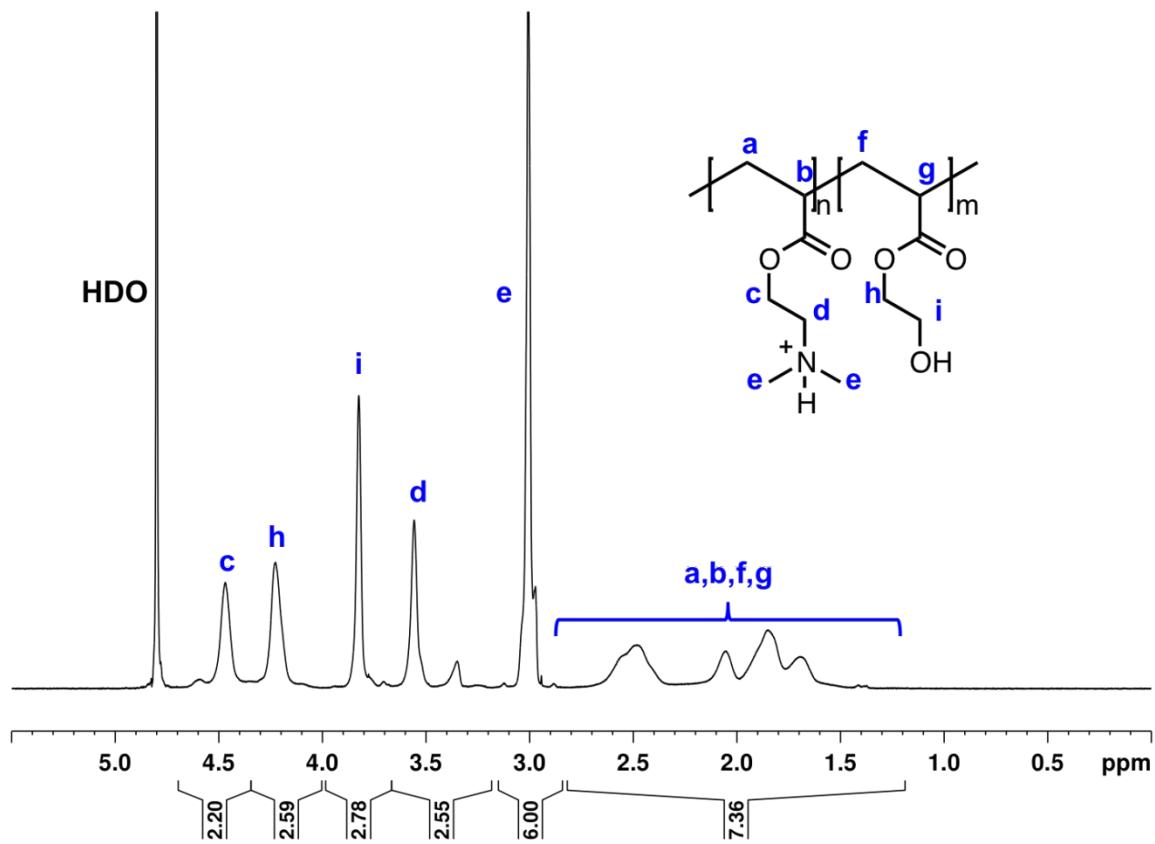


Figure S10. ¹H NMR spectrum of PDH₄₆ in D₂O (pH 3-4) recorded at 600 MHz.

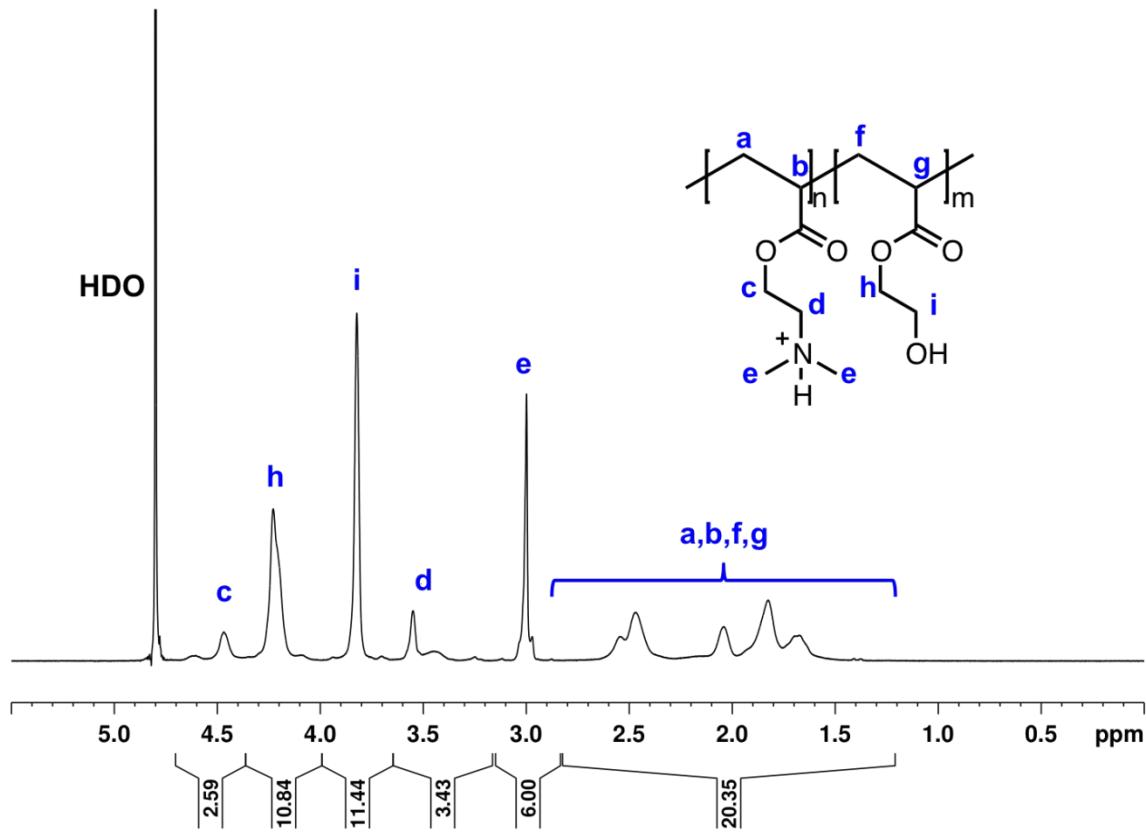


Figure S11. ^1H NMR spectrum of PDH_{19} in D_2O (pH 3-4) recorded at 600 MHz.

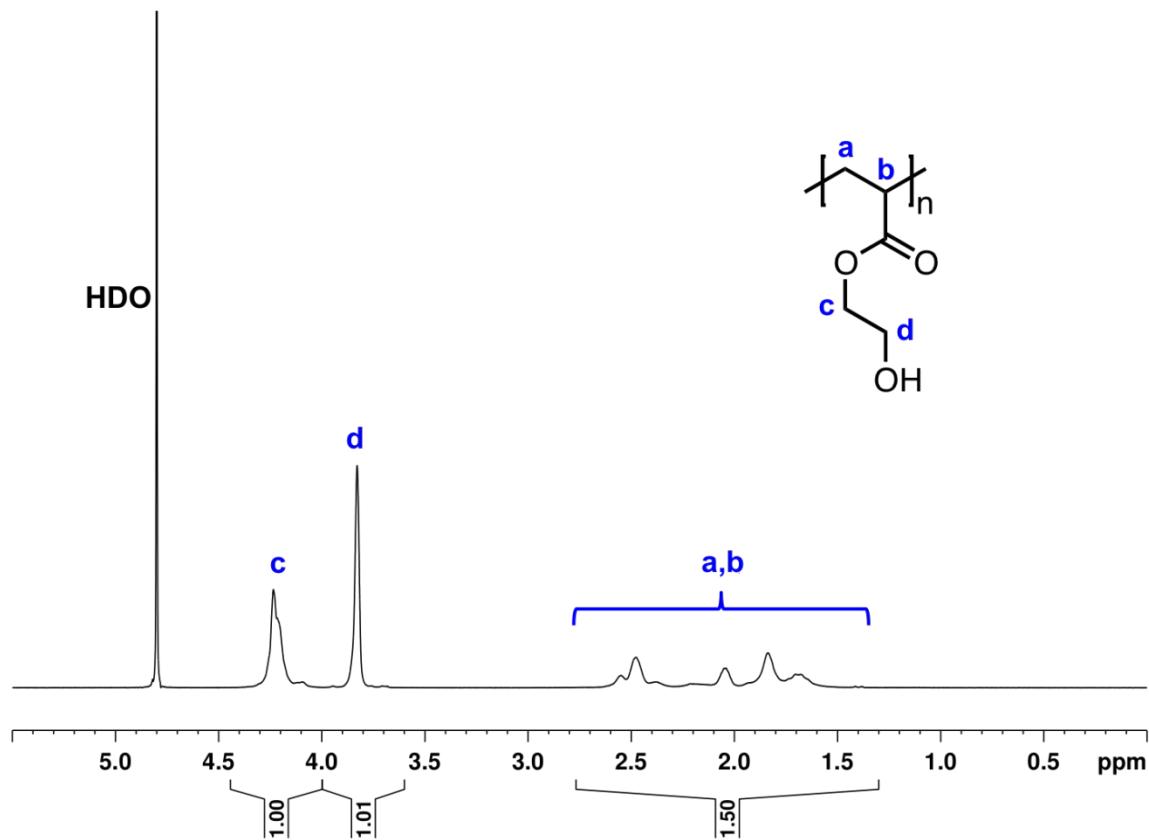


Figure S12. ^1H NMR spectrum of PHEA in D_2O recorded at 600 MHz.

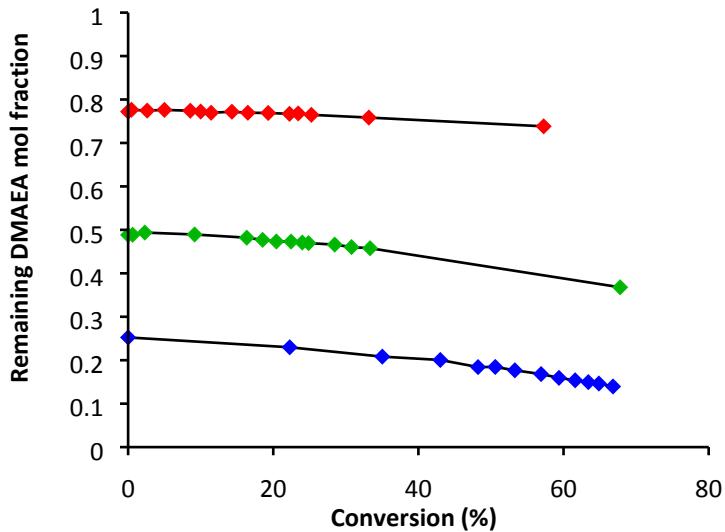


Figure S13 Remaining mol fraction of DMAEA relative to AA throughout copolymerizations at 55 °C in DMSO-*d*6 as a function of total monomer conversion.

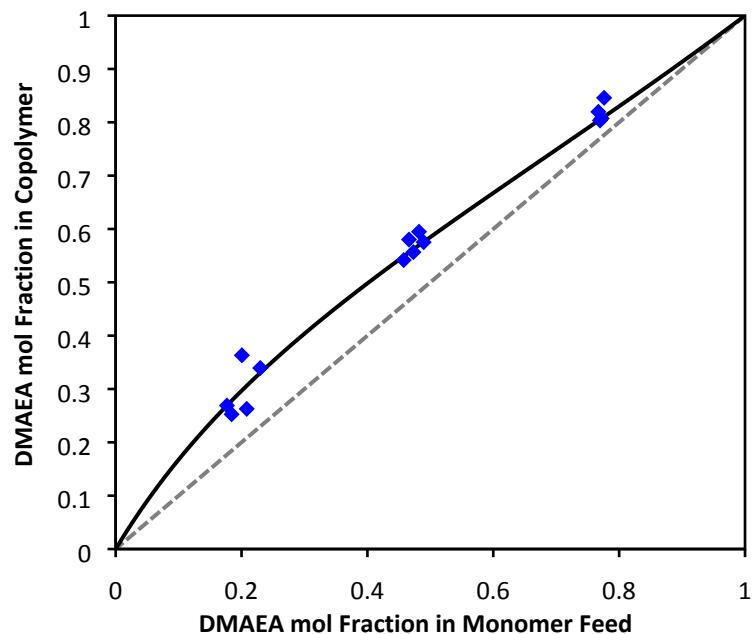


Figure S14. Instantaneous copolymer composition plot showing experimental data points (blue diamonds) from various DMAEA/AA feed ratios. The solid black line shows the best fit of the copolymer equation to the experimental data obtained using the least squares method with the Solver tool in Microsoft Excel. Reactivity ratios were estimated to be $r_1 = 1.1$ (DMAEA) and $r_2 = 0.5$ (AA).

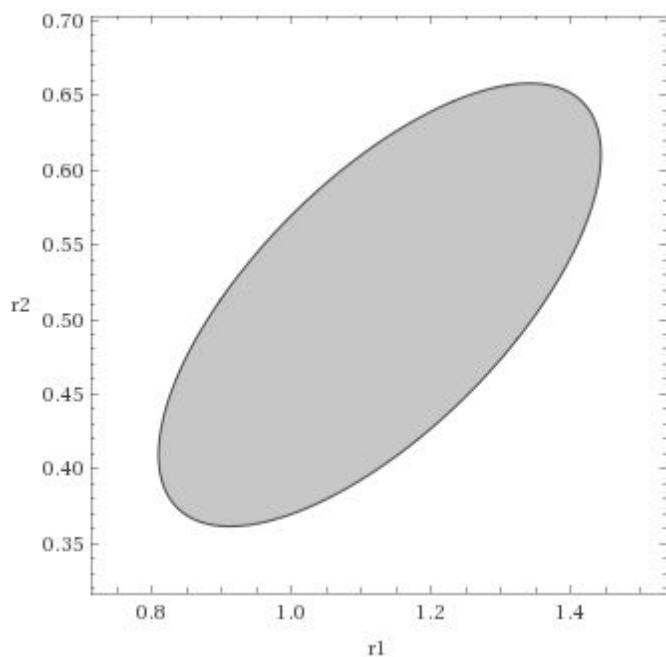


Figure S15 Joint 95% confidence region for reactivity ratios obtained for DMAEA (r_1)/AA (r_2) (1.1/0.5). The contour was determined using a method described by Smith et al.¹

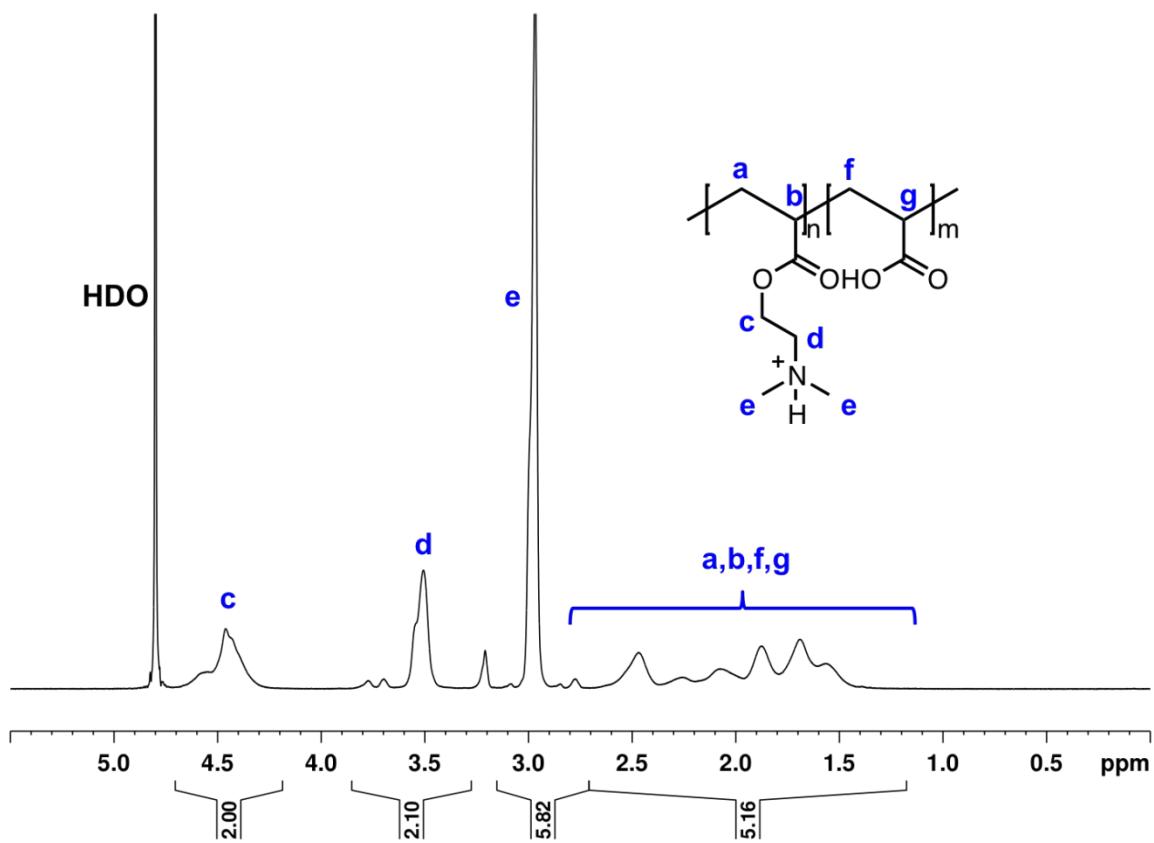


Figure S16. ^1H NMR spectrum of PDA₅₈ in D_2O (pH 3-4) recorded at 600 MHz.

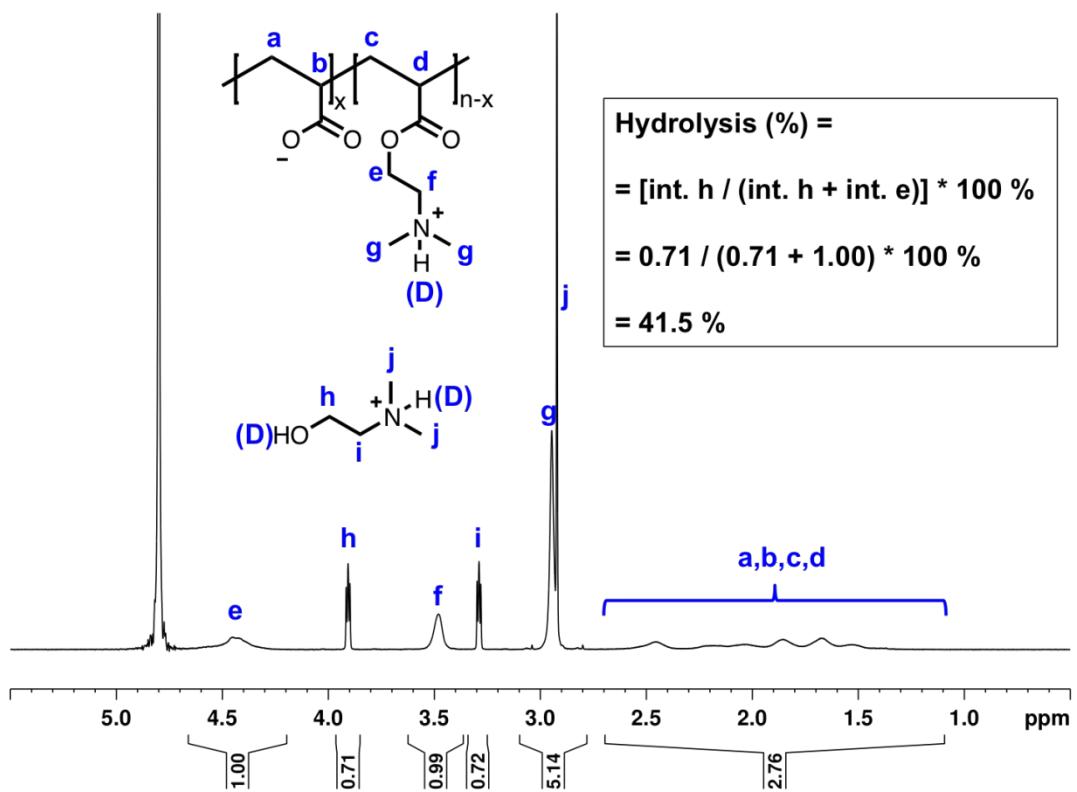


Figure S17. A representative ^1H NMR spectrum of PDMAEA hydrolysis at pH 7 with a sample calculation showing percent hydrolysis.

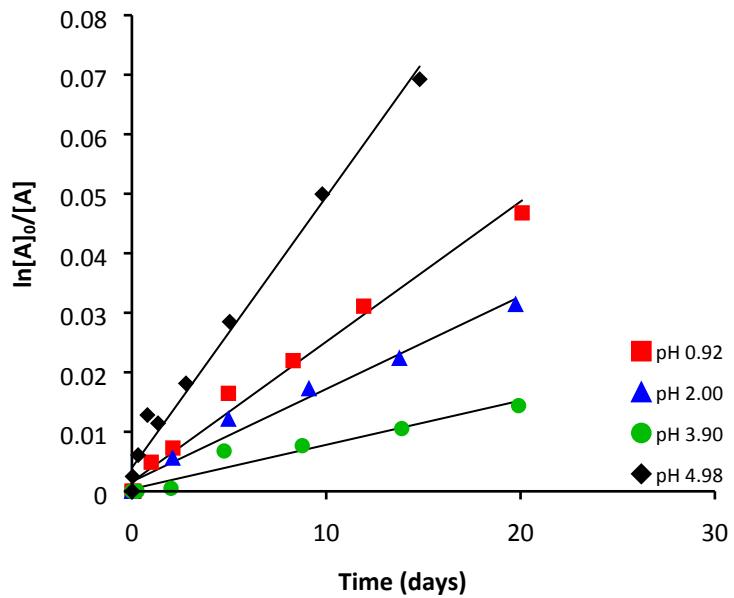


Figure S18. Pseudo-first order kinetic plot of the initial rates of PDMAEA hydrolysis at pH 0.92, 2.00, 3.90, and 4.98 at 22 °C. The y-axis shows the natural log of the ratio of initial ester concentration ($[A]_0$) to the concentration of ester at time t ($[A]$).

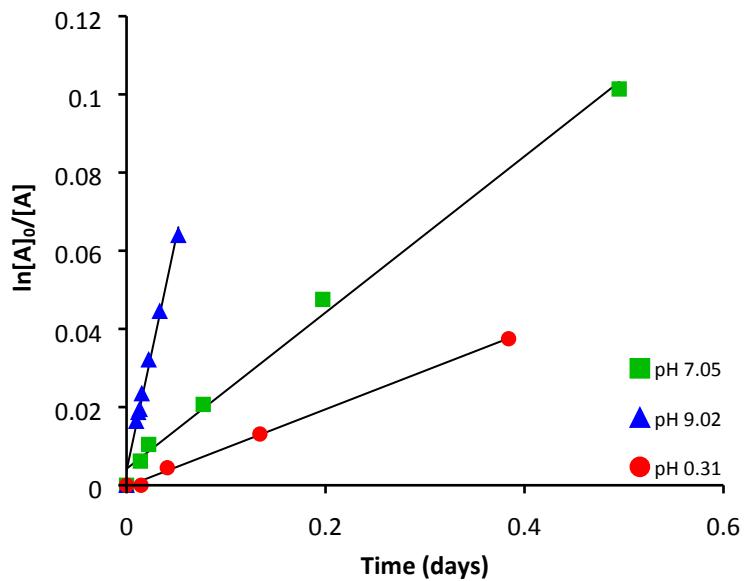


Figure S19. Pseudo-first order kinetic plots of PDMAEA hydrolysis at pH 7.05, 9.02 and 0.31 at 22 °C. The y-axis shows the natural log of the ratio of initial ester concentration ($[A]_0$) to the concentration of ester after hydrolysis with time ($[A]$).

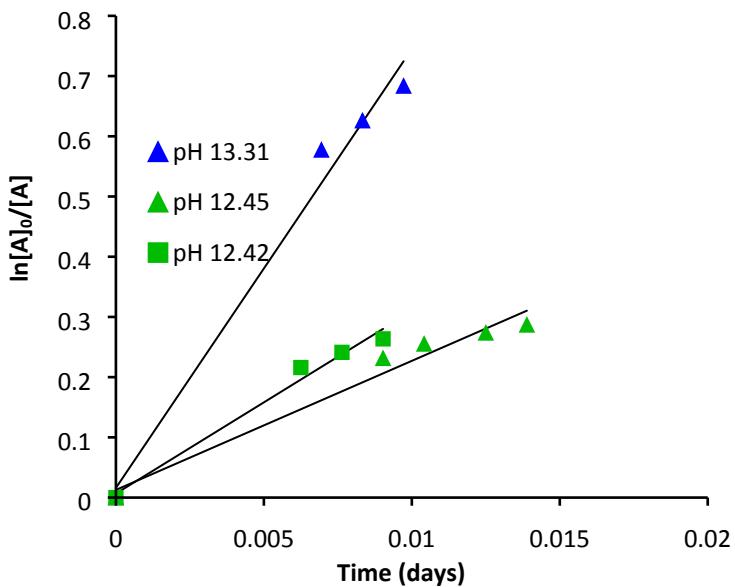


Figure S20. Pseudo-first order kinetic plots of PDMAEA hydrolysis at pH 13.31, 12.45 and 12.42 at 22 °C. The y-axis shows the natural log of the ratio of initial ester concentration ($[A]_0$) to the concentration of ester after hydrolysis with time ($[A]$).

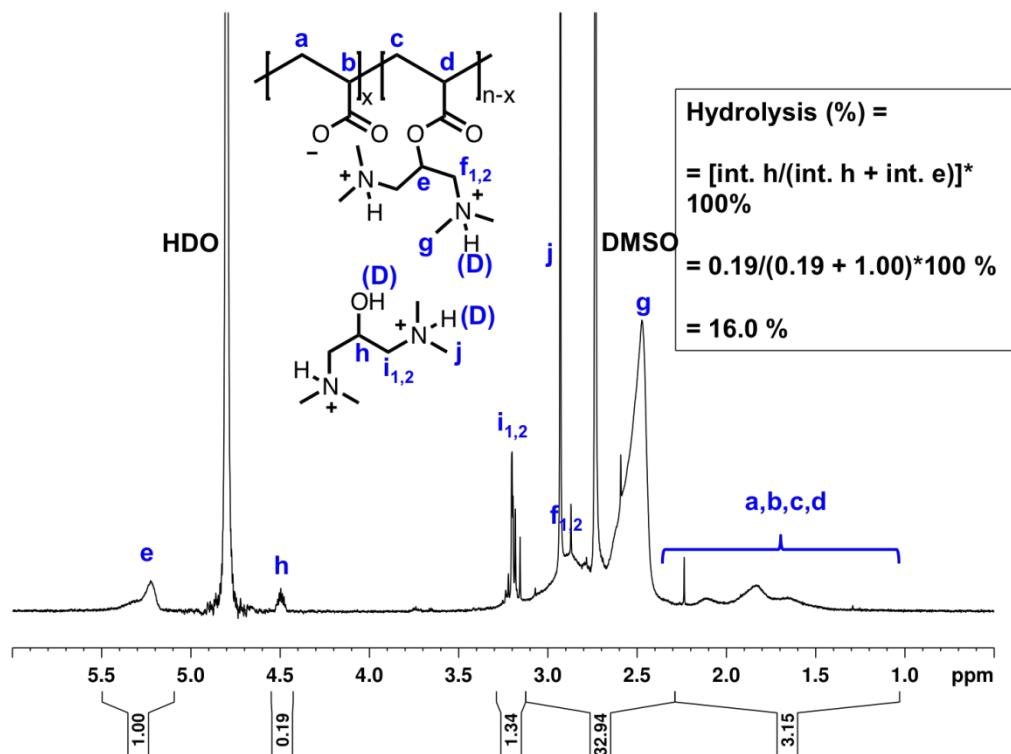


Figure S21. A representative ^1H NMR spectrum of PBDMAPA hydrolysis at pH 7 with a sample calculation showing percent hydrolysis.

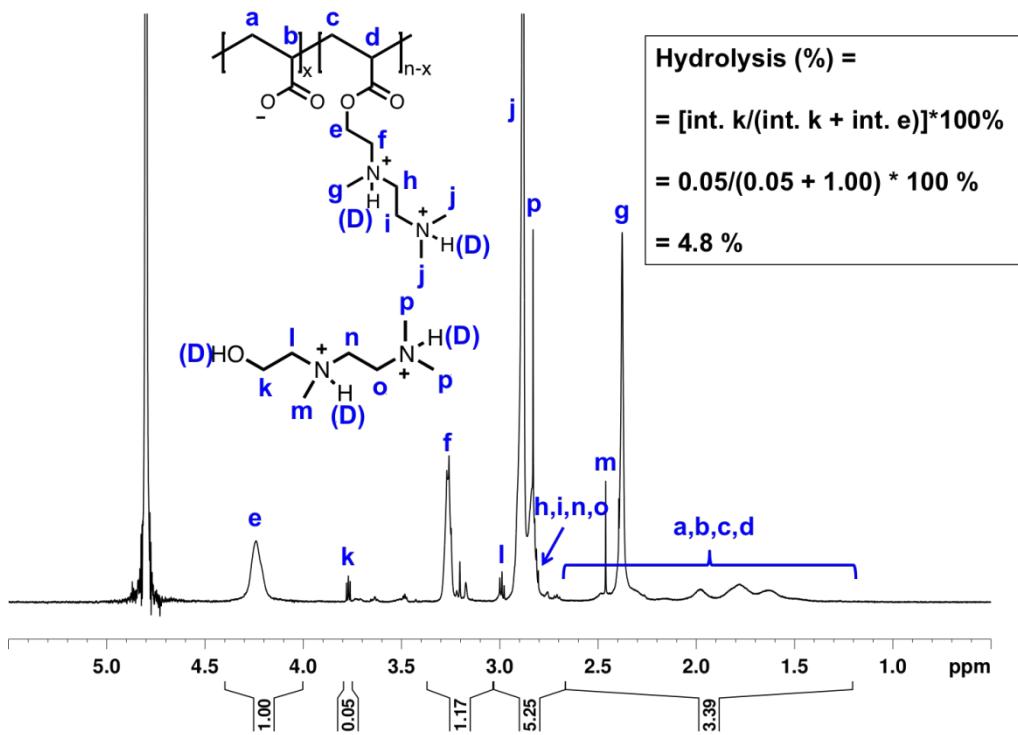


Figure S22. A representative ^1H NMR spectrum of PDEMEA hydrolysis at pH 7 with a sample calculation showing percent hydrolysis.

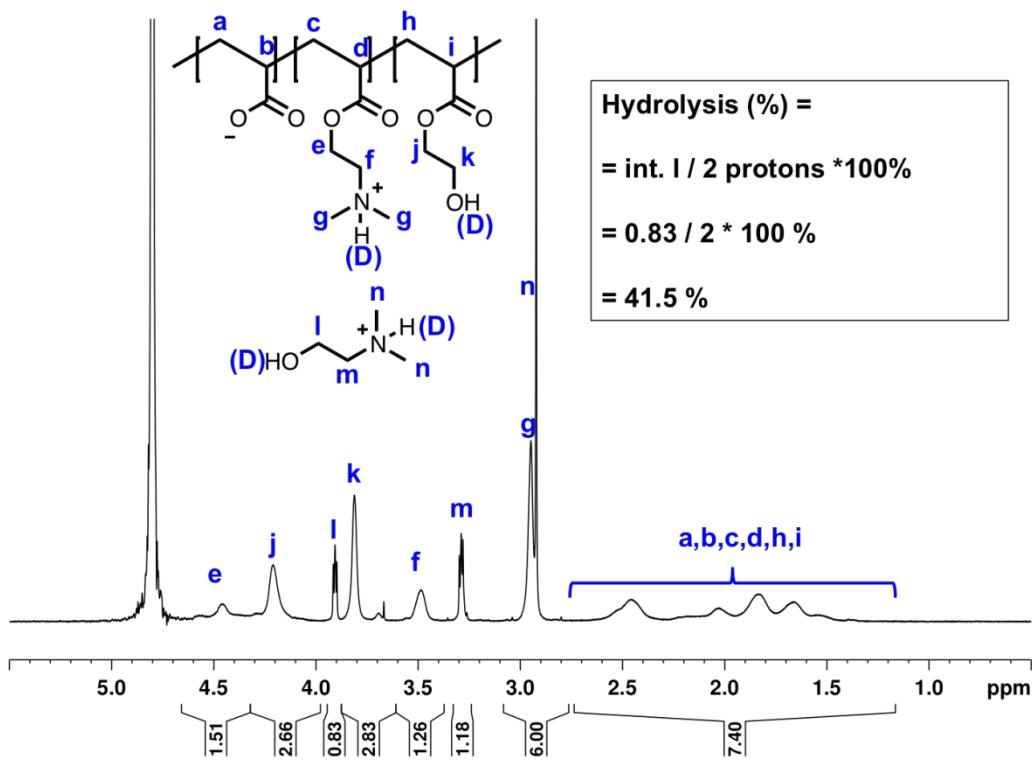


Figure S23. A representative ^1H NMR spectrum of PDH₅₀ hydrolysis at pH 7 with a sample calculation showing percent hydrolysis. The HEA esters remain largely intact as there is little change in peaks **j** and **k** and only a tiny ethylene glycol peak (<1 %) (sharp singlet at 3.65 ppm).

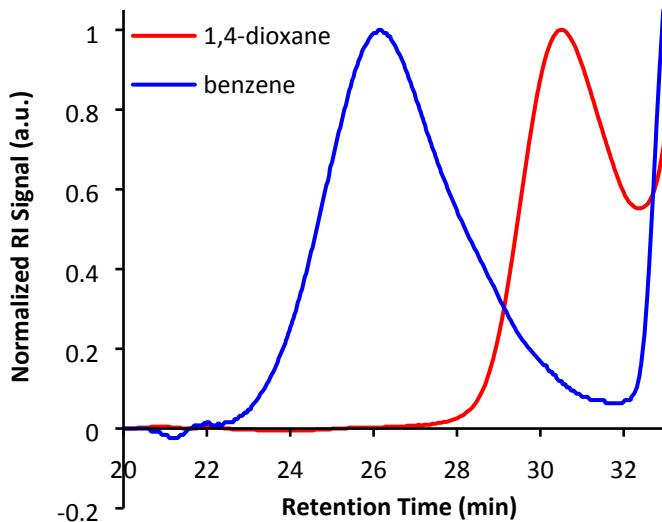


Figure S24. GPC traces of PBDMAPA prepared by conventional free radical polymerization in 1,4-dioxane and by photopolymerization at 0 °C in benzene. The polymers have Mn values of approximately 2800 g/mol ($M_p = 2900$ g/mol) and 9100 g/mol, respectively. Mn for the PBDMAPA polymerized in 1,4-dioxane is given as an estimate as the peak overlaps with the solvent peak after ~ 32 min. GPC traces similar to the one obtained for PBDMAPA made in 1,4-dioxane were seen for polymerization in acetonitrile, DMSO, and toluene.

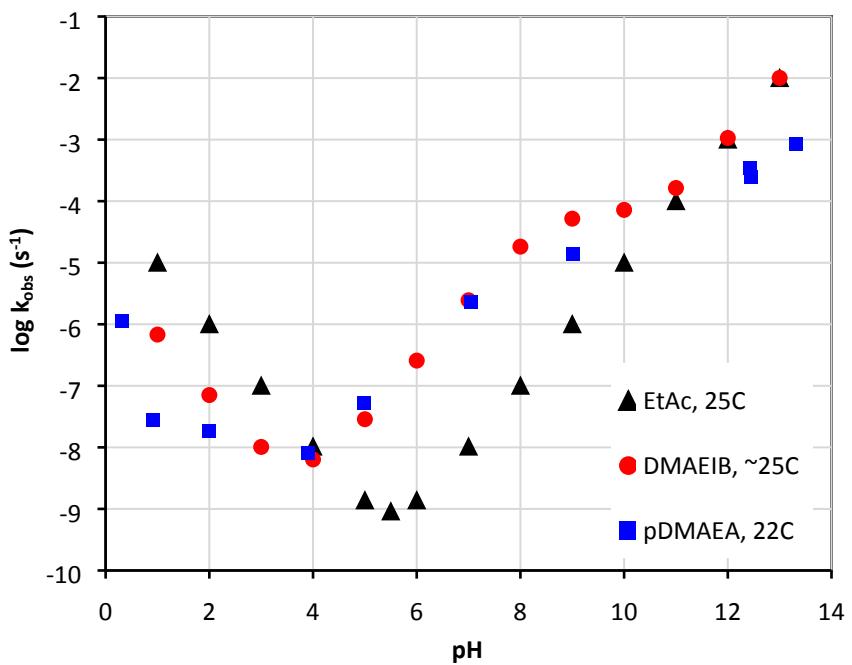


Figure S25. Log k_{obs} vs. pH for hydrolysis of ethyl acetate,^{2,3,4} N,N-dimethylaminoethyl isobutyrate (DMAEIB),⁵ and PDMAEA at ~22-25 °C. van de Wetering et al found that the k_{obs} for DMAEIB hydrolysis decreased ~2.5-fold with a 10 °C decrease in T, so their k values determined at 37 °C were divided by 2.5 to generate the ~25 °C-curve shown in this figure.

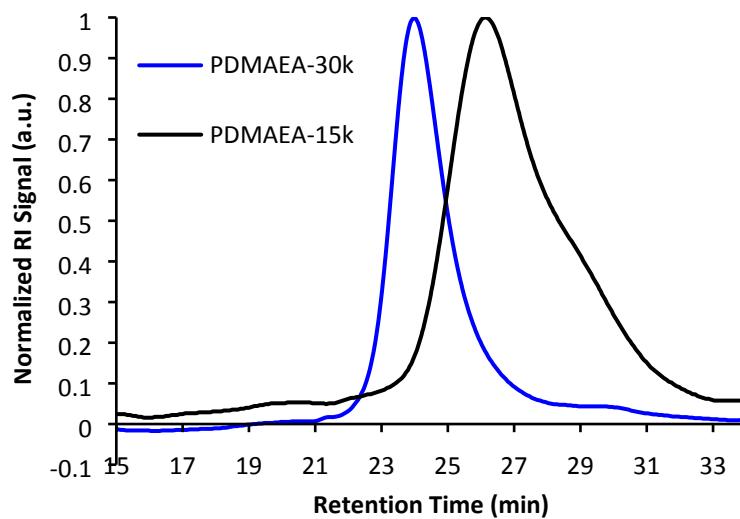


Figure S26. GPC traces of PDMAEA prepared by conventional free radical polymerization and PDMAEA-30k prepared by RAFT polymerization.

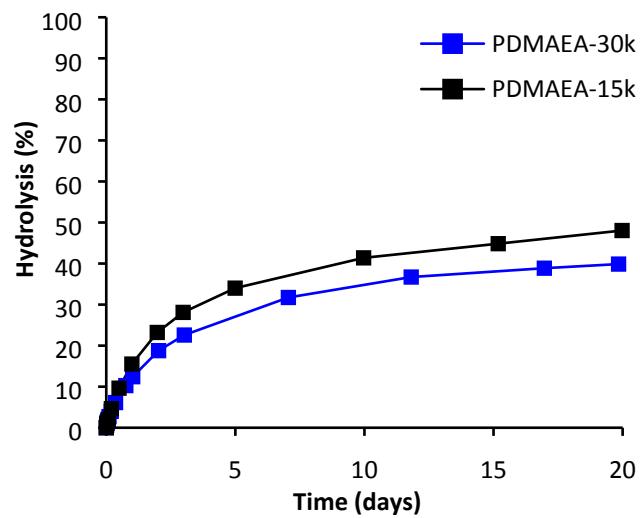


Figure S27. Hydrolysis of PDMAEA-15k by conventional free radical polymerization and PDMAEA-30k by RAFT polymerization at pH 7, room temperature (22 °C).

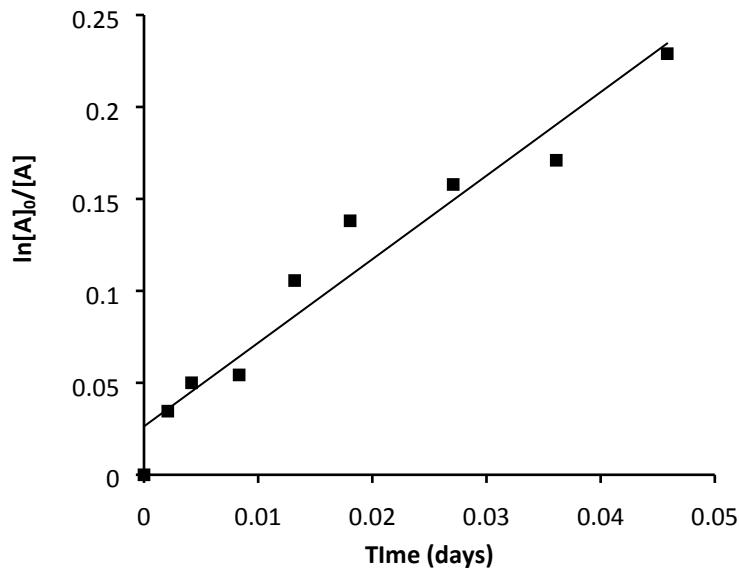


Figure S28. Pseudo-first order kinetic plot of PBDMAPA hydrolysis at pH 7 at 22 °C. The y-axis shows the natural log of the ratio of initial ester concentration ($[A]_0$) to the concentration of ester after hydrolysis with time ($[A]$).

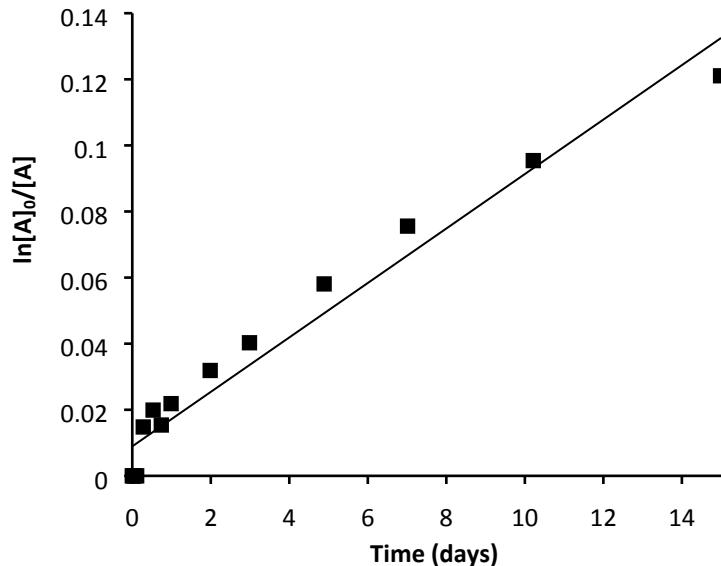


Figure S29. Pseudo-first order kinetic plot of PDEMEA hydrolysis at pH 7 at 22 °C. The y-axis shows the natural log of the ratio of initial ester concentration ($[A]_0$) to the concentration of ester after hydrolysis with time ($[A]$).

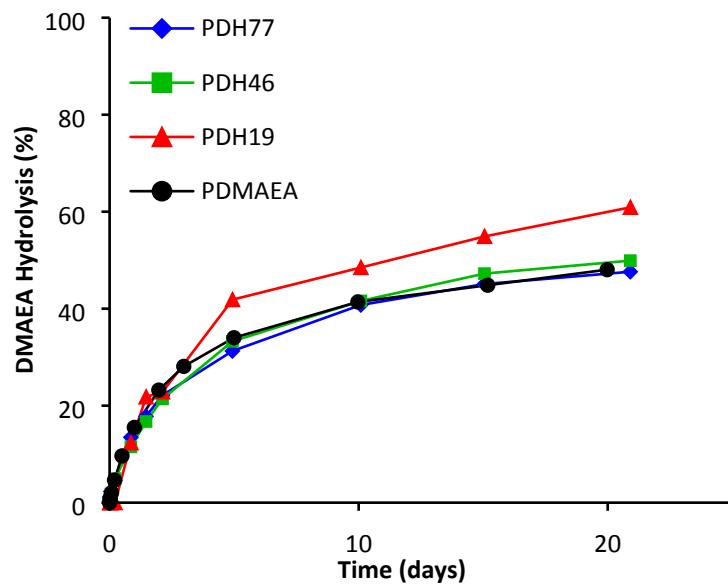


Figure S30. Hydrolysis of DMAEA within PDH copolymers and PDMAEA at pH 7. PHEA showed less than 1 % ester hydrolysis after about 20 days at pH 7 as monitored by appearance of small-molecule ethylene glycol.

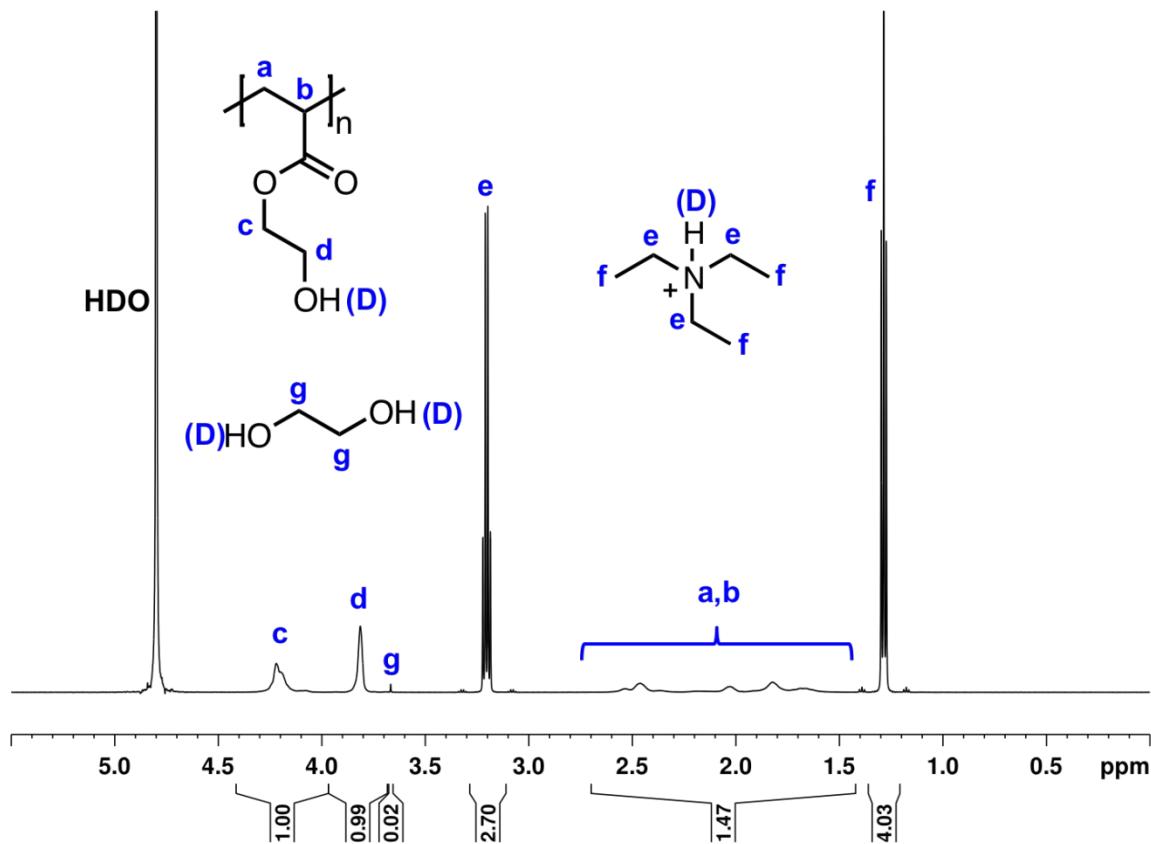


Figure S31. ^1H NMR spectrum of PHEA with ~ 1 mol eq. of triethylamine (TEA) added to model the tertiary amino group of DMAEA that is not covalently bound to the ester. After 20 days in 100 mM phosphate buffer pH 7.03 at room temperature, less than 1 % of ethylene glycol (g) was measured.

References

- ¹ Smith, L. H.; McCarty, P. L., Kitanidis, P. K. Spreadsheet Method for Evaluation of Biochemical Reaction Rate Coefficients and Their Uncertainties by Weighted Nonlinear Least-Squares Analysis of the Integrated Monod Equation. *Applied and Environmental Microbiology* **1998**, 64(6), 2044–2050.
- ² Hilal, S. H. Estimation of Hydrolysis Rate Constants of Carboxylic Acid Ester and Phosphate Ester Compounds in Aqueous Systems from Molecular Structure by SPARC. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-06/105 (NTIS PB2007-100142), **2006**.
- ³ Drossman, H.; Johnson, H.; Mill, T. Structure Activity Relationships for Environmental Processes 1: Hydrolysis of Esters and Carbamates. *Chemosphere* **1988**, 17, 1509-1530.
- ⁴ Taft, R. W. Linear Free Energy Relationships from Rates of Esterification and Hydrolysis of Aliphatic and Ortho-Substituted Benzoate Esters. *J. Am. Chem. Soc.* **1952**, 74, 2729-2732.

⁵ van de Wetering, P.; Zuidam, N. J.; van Steenbergen, M. J.; van der Houwen, O. A. G. J.; Underberg, W. J. M.; Hennink, W. E. A Mechanistic Study of the Hydrolytic Stability of Poly(2-(dimethylamino)ethyl methacrylate). *Macromolecules* **1998**, *31*, 8063–8068.