Electronic Supporting Information for

Controlled synthesis and pH-sensitive complexation of poly(methacrylic acid) polyampholytes

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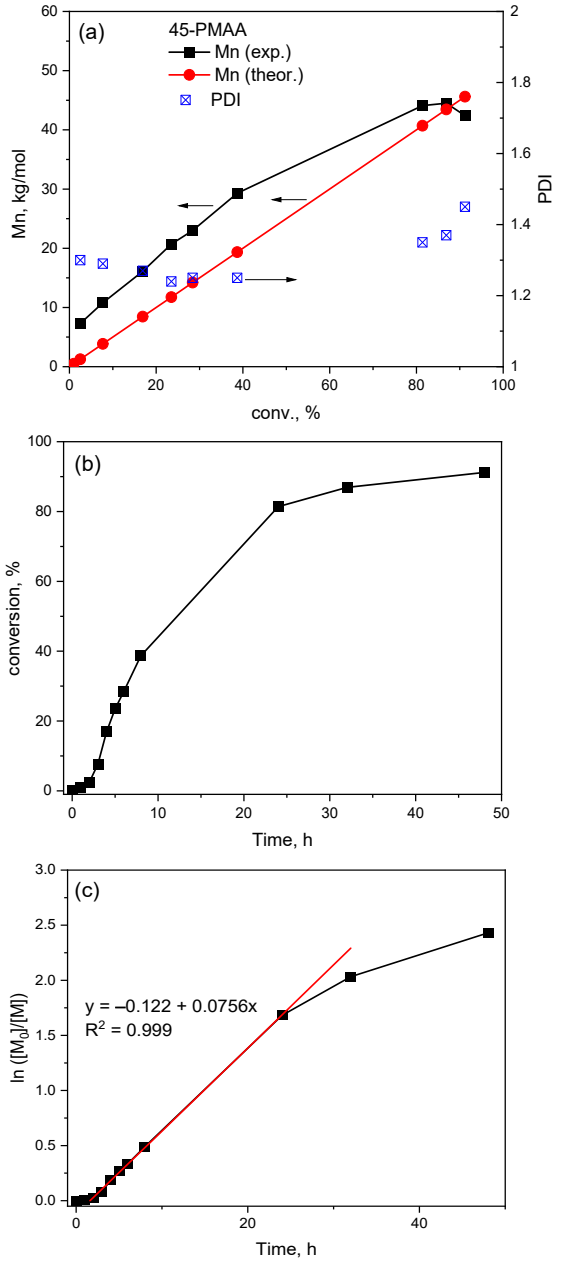

Figure S1. Dependence of M_n and Đ on (a) conversion, (b) monomer consumption, and (c) first-order plot for *t*BMA homopolymerization by RAFT. The linear part of the first-order monomer plot has been fitted for clarity.

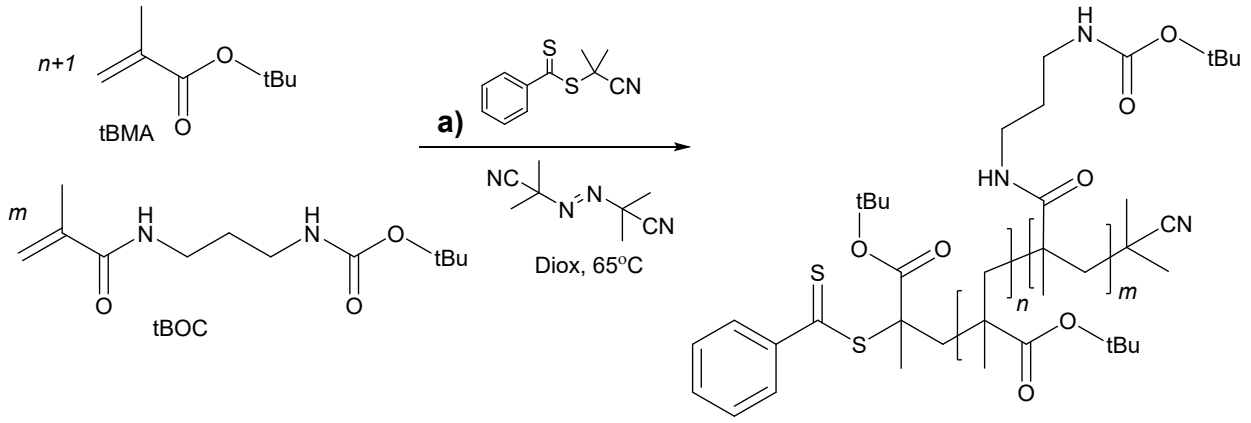

Figure S2. RAFT polymerization of *t*BMA and *t*BOC monomers to obtain poly(methacrylic acid-co-(aminopropyl)-methacrylamide) copolymers (PMAA-NH_2).

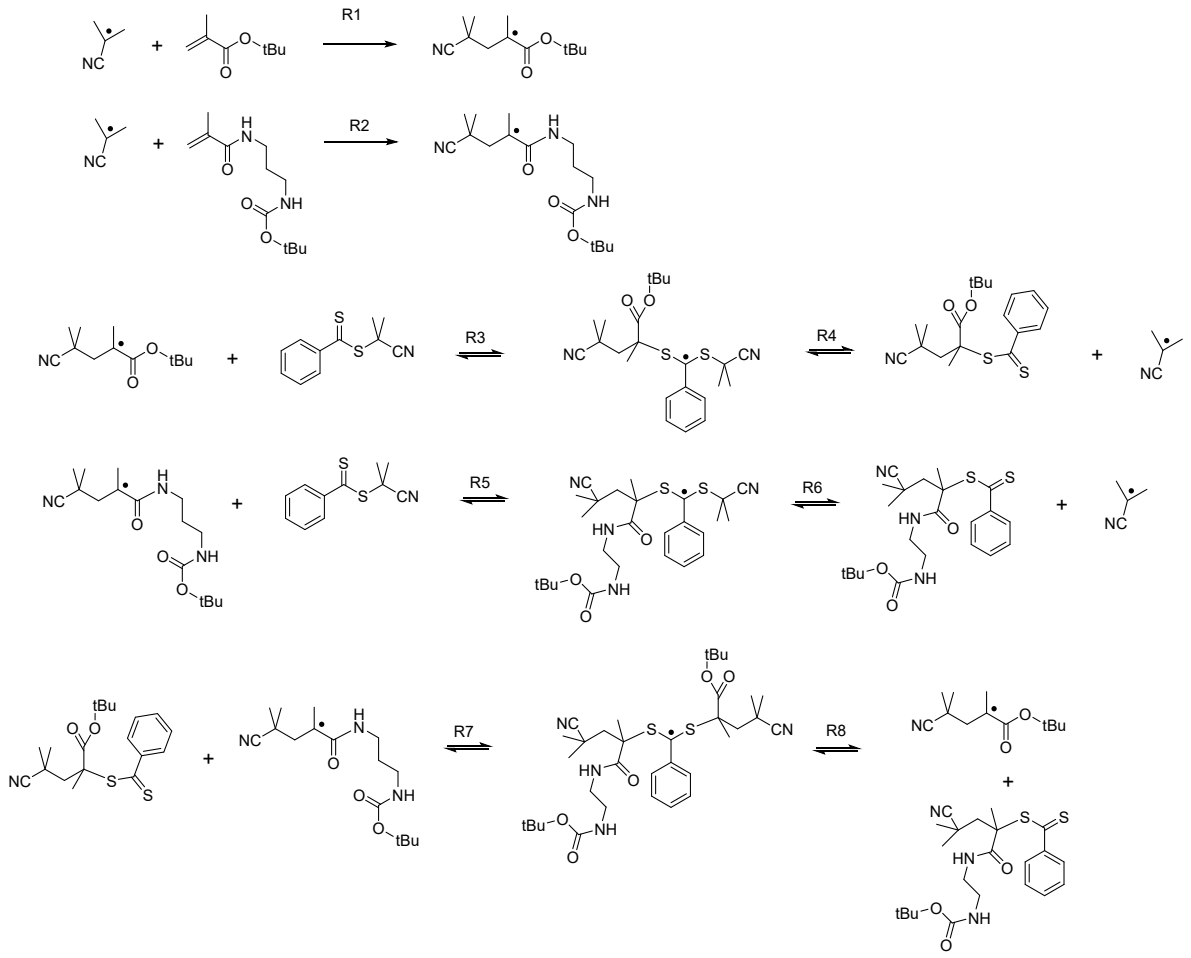

Figure S3. The monomer activities in RAFT polymerization were compared through comparing the energies of the **R1-R8** reactions.

Table S1. Thermodynamic parameters for reactions **R1-R8**.

Reaction	$\Delta_r H_{338}$, kJ/mol	$\Delta_r S_{338}$, J/(mol · K)	$\Delta_r G_{338}$, kJ/mol	Reaction Constant, K_r
1	-23.4	-173.7	35.4	3.4E-06
2	-28.2	-285.3	68.2	2.9E-11
3	21.4	-224.2	97.2	9.5E-16
4	17.6	210.5	-53.6	1.9E+08
5	29.7	-201.0	97.7	8.0E-16
6	4.3	183.3	-57.7	8.2E+08
7	2.0	-233.9	81.1	3.0E-13
8	-7.0	229.9	-84.7	1.2E+13

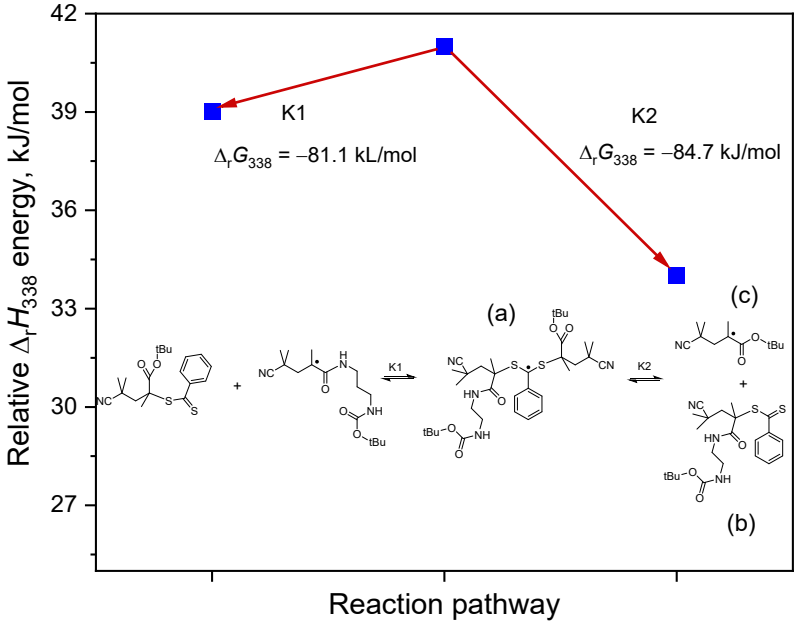

Figure S4. Relative energies ($\Delta_r H_{338}$) and the schematic representation of studied reactions.

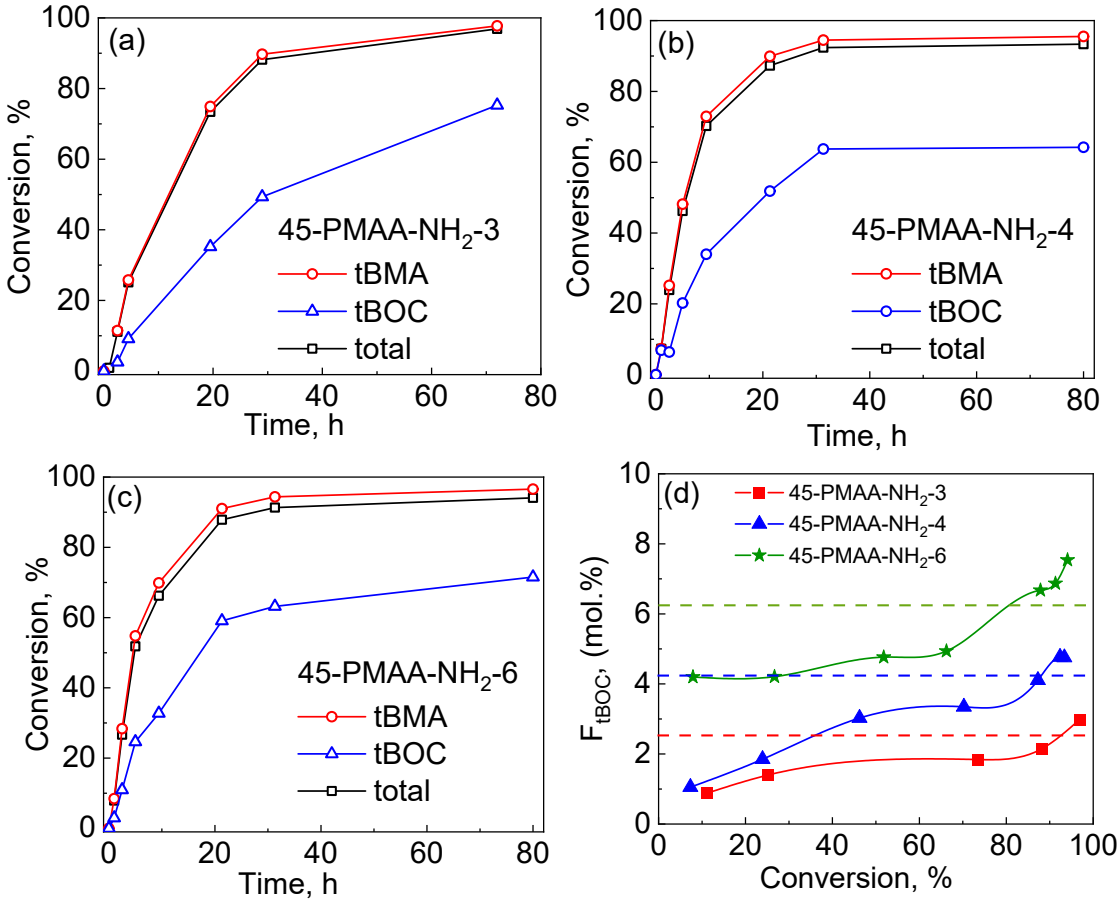

Figure S5. Consumption of *t*BMA and *t*BOC (a-c), and (d) incorporated fraction of *t*BOC (F_{tBOC}) as a function of total monomer conversion for the RAFT-mediated copolymerization of *t*BMA and *t*BOC. Dashed lines in (d) correspond to the final mol.% content of NH_2 groups in copolymers.

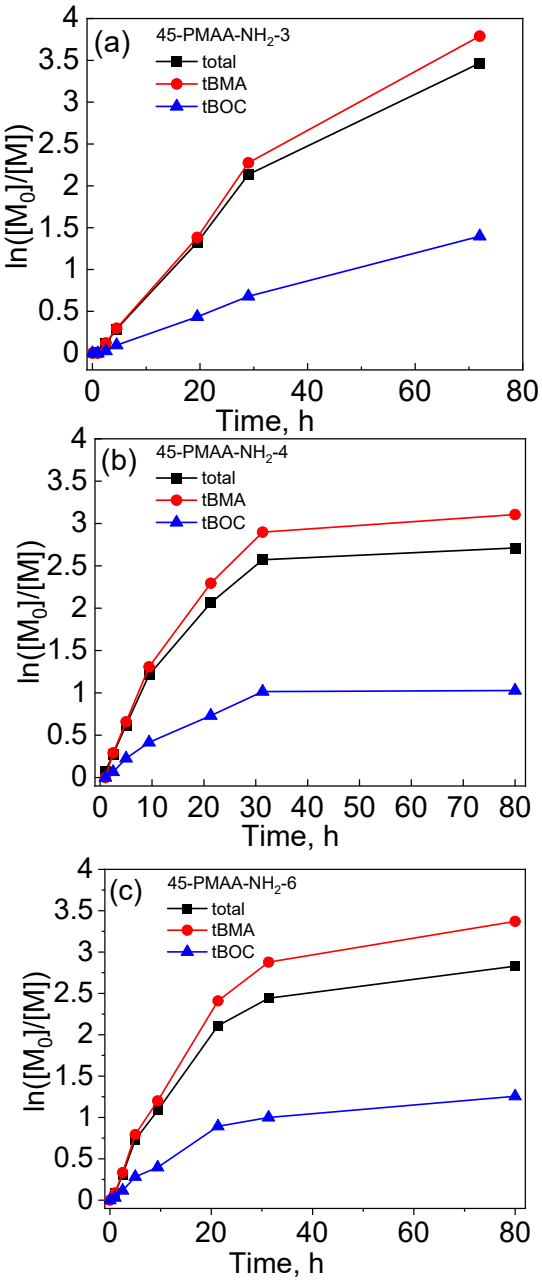

Figure S6. First-order plot for *t*BOC and *t*BMA copolymerization to obtain (a) 45-PMAA-NH_2-3, (b) 45-PMAA-NH_2-4, and (c) 45-PMAA-NH_2-6.

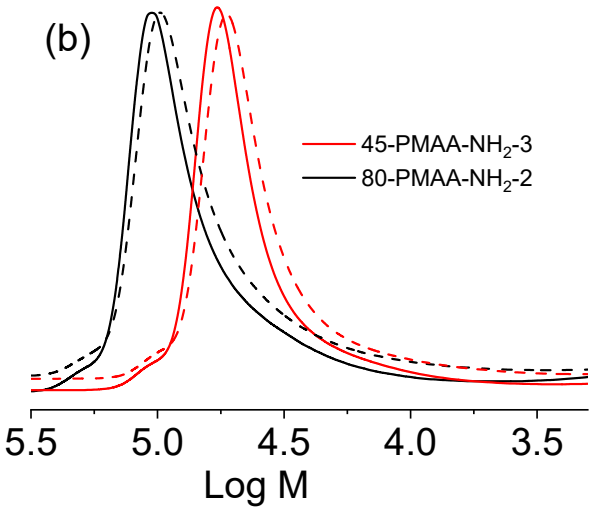

Figure S7. (a) A pphotograph of 45-PMAA-NH_2-6 before (left) and after (right) end-group removal. (b) GPC analysis of 45-PMAA-NH_2-3 and 80-PMAA-NH_2-2 copolymers in THF (0.01 M TBAF) before (solid line) and after (dashed line) end-group removal.

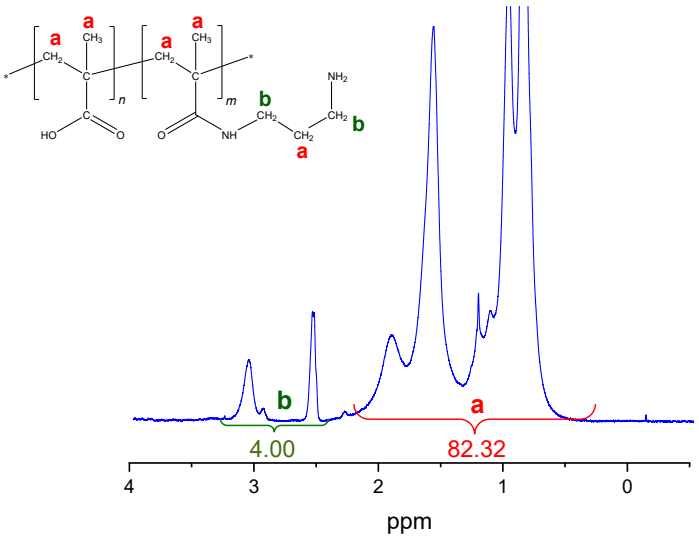

Figure S8. ^{1}H NMR spectrum of 45-PMAA-NH_2-6 (in D_2O+NaOD) after hydrolysis of a tBOC protective group. The content of NH_2-groups was calculated as follows: 100% × [*I*(b)/4]/[*I*(b)/4 + {*I*(a) – 7×*I*(b)/4}/5], where *I*(a) and *I*(b) are the integral intensities of the signals a and b, respectively. Accordingly, the content of NH_2-groups was calculated as follows: 4.00/4/(4.00/4+(82.32-7.00)/5) × 100%.

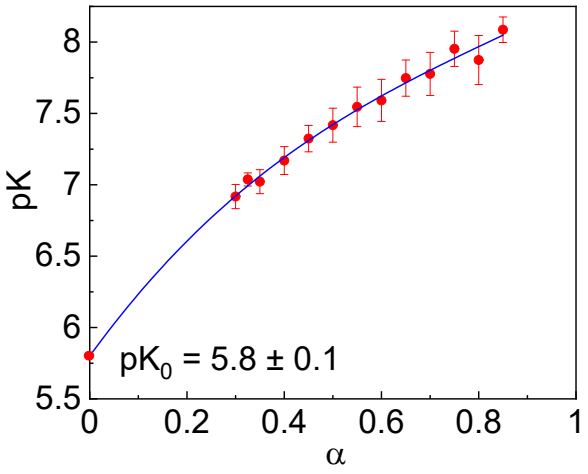

Figure S9. Potentiometric titration of 86 mg mL^{-1} 45-PMAA homopolymer solution with 0.01 M NaOH solution.

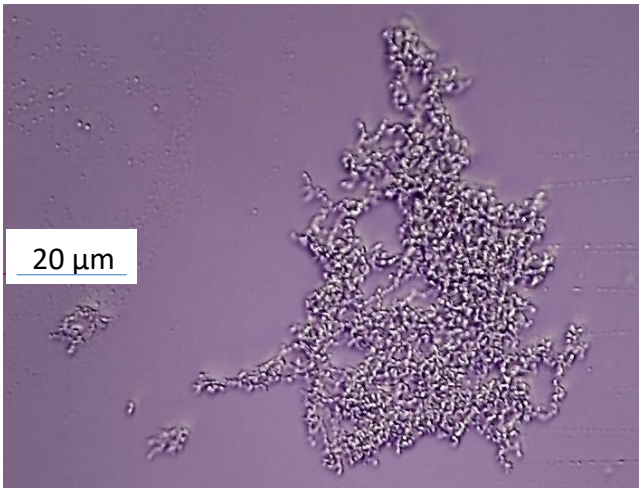

Figure S10. An optical image of the PAC formed from 0.5 mg mL^{-1} 80-PMAA-NH_2-6 solutions in 0.01 M HEPES buffer at pH = 3.4 and 0.20 M NaCl after 2 hours.