

Supplementary Information

¹H-NMR Spectra of Copolymers

PH-PEG-0% ¹H-NMR (600 MHz, D₂O): δ 0.7–0.9 (bm, 14H), 1.15–1.37 (bm, 30H), 1.4–2.5 (bm, 51H), 2.51–2.7 (m, 4H), 3.1–3.3 (bm, 17H), 3.45–3.6 (m, 3H), 3.8–4.3 (bm, 26H).

PH-PEG-10% ¹H-NMR (600 MHz, D₂O): δ 0.7–0.9 (bm, 12H), 0.91–1.15 (m, 5H), 1.16–1.37 (bm, 24H), 1.4–2.5 (bm, 45H), 2.52–2.75 (m, 4H), 3.1–3.35 (bm, 18H), 3.4–3.7 (bm, 32H), 3.85–4.3 (bm, 17H).

PH-PEG-20% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.15 (bm, 21H), 1.17–1.4 (bm, 24H), 1.45–2.5 (bm, 44H), 2.52–2.8 (bm, 4H), 3.05–3.3 (bm, 23H), 3.4–3.75 (bm, 52H), 3.8–4.3 (bm, 25H).

PH-PEG-30% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.13 (bm, 27H), 1.15–1.4 (bm, 25H), 1.5–2.5 (bm, 44H), 2.52–2.8 (m, 4H), 3.1–3.4 (bm, 28H), 3.47–3.7 (bm, 79H), 3.8–4.3 (bm, 28H).

PH-PEG-40% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.15 (bm, 36H), 1.16–1.4 (bm, 30H), 1.15–2.5 (bm, 54H), 2.51–2.75 (m, 4H), 3.17–3.3 (bm, 39H), 3.5–3.7 (bm, 127H), 3.8–4.3 (bm, 40H).

PH-PEG-50% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.16 (bm, 67H), 1.16–1.4 (bm, 44H), 1.5–2.5 (bm, 80H), 2.51–2.7 (m, 4H), 3.1–3.3 (bm, 65H), 3.4–3.73 (bm, 248H), 3.8–4.3 (bm, 62H).

PH-PEG-75% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.14 (bm, 81H), 1.2–2.5 (bm, 94H), 2.51–2.7 (bm, 4H), 3.1–3.3 (bm, 77H), 3.4–3.8 (bm, 346H), 3.9–4.3 (bm, 65H).

PB-PEG-0% ¹H-NMR (600 MHz, D₂O): δ 0.75–0.9 (bm, 13H), 1.2–1.34 (bm, 10H), 1.35–2.5 (bm, 51H), 2.51–2.7 (m, 4H), 3.1–3.25 (bm, 18H), 3.5–3.6 (m, 3H), 3.9–4.3 (bm, 26H).

PB-PEG-10% ¹H-NMR (600 MHz, D₂O): δ 0.7–0.9 (bm, 16H), 0.91–1.15 (bm, 5H), 1.2–2.5 (bm, 66H), 2.51–2.7 (m, 4H), 3.1–3.25 (bm, 22H), 3.48–3.7 (bm, 27H), 3.9–4.3 (bm, 30H).

PB-PEG-20% ¹H-NMR (600 MHz, D₂O): δ 0.78–1.17 (bm, 20H), 1.2–2.5 (bm, 51H), 2.52–2.75 (m, 4H), 3.1–3.3 (bm, 25H), 3.5–3.7 (bm, 45H), 3.9–4.3 (bm, 26H).

PB-PEG-30% ¹H-NMR (600 MHz, D₂O): δ 0.76–1.14 (bm, 22H), 1.2–2.5 (bm, 48H), 2.52–2.75 (m, 4H), 3.1–3.3 (bm, 28H), 3.4–3.7 (bm, 57H), 3.9–4.3 (bm, 26H).

PB-PEG-40% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.15 (bm, 22H), 1.21–2.5 (bm, 42H), 2.51–2.75 (m, 4H), 3.1–3.3 (bm, 31H), 3.42–3.72 (bm, 68H), 3.8–4.3 (bm, 25H).

PB-PEG-50% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.16 (bm, 35H), 1.2–2.5 (bm, 77H), 2.51–2.76 (m, 4H), 3.1–3.3 (bm, 34H), 3.4–3.7 (bm, 146H), 3.8–4.3 (bm, 34H).

PB-PEG-75% ¹H-NMR (600 MHz, D₂O): δ 0.7–1.2 (bm, 74H), 1.2–2.5 (bm, 76H), 2.5–2.73 (m, 4H), 3.1–3.3 (bm, 69H), 3.46–3.75 (bm, 377H), 3.8–4.3 (bm, 58H).

Calculation of Actual mole % of Comonomers from ¹H-NMR

Actual mole contents were calculated through analysis of ¹H-NMR spectra. Using PH-PEG-30% as an example, the integrations of the peaks of interest for mole percentage calculation are positioned at: 4.0 ppm (hexyl acrylate's methylene proton), 3.3 ppm (PEGMA-300's methyl proton), and 3.2 ppm (2-aminoethyl acrylate's methylene proton). The formula for the sum of integrations after content adjustments is as follows:

$$(3.40/2) + (6.46/3) + (5.41/2) = 6.56$$

The mole contents of each comonomer can be found by dividing the adjusted integrations of the comonomer by the sum of adjusted integrations of all three comonomers.

Hexyl acrylate mole content: $[(3.40/2)/6.56] \times 100\% = 26\%$

PEGMA mole content: $[(6.46/3)/6.56] \times 100\% = 33\%$

2-Aminoethyl acrylate mole content: $[(5.41/2)/6.56] \times 100\% = 41\%$

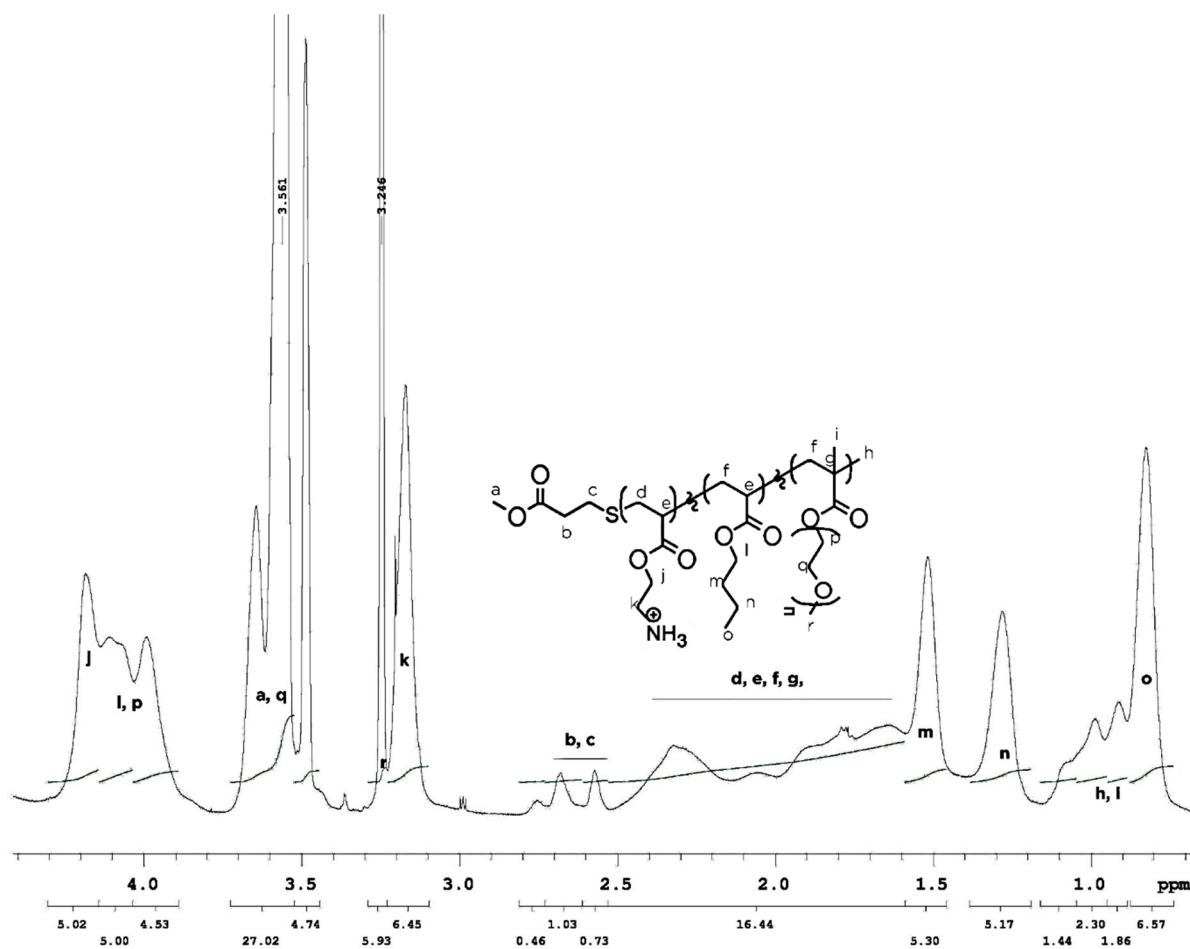


Figure S1. ¹H-NMR of PH-PEG-30% (42% M2, 28% butyl acrylate, 30% PEG).

Table S1. Characterization of copolymers.

Copolymer	Alkyl Side Group	M_w kDa	M_n kDa	PDI	Actual Mol % Hydrophobic Monomer (Butyl or Hexyl Acrylate)	Mol % 2-((<i>Tert</i> -butoxycarbonyl) amino)ethyl Acrylate (Actual)
PB-PEG-0%	Butyl	5.1	4.0	1.28	36.5	63.5
PB-PEG-10%	Butyl	5.6	4.2	1.34	33.3	55.7
PB-PEG-20%	Butyl	5.1	3.8	1.35	31.3	47.9
PB-PEG-30%	Butyl	5.8	4.1	1.41	30.3	43.2
PB-PEG-40%	Butyl	5.9	4.2	1.41	28.7	36.5
PB-PEG-50%	Butyl	6.6	4.5	1.36	22.8	30.8
PB-PEG-75%	Butyl	7.1	4.6	1.54	13.9	14.6
PH-PEG-0%	Hexyl	4.4	3.4	1.28	35	65
PH-PEG-10%	Hexyl	4.6	3.6	1.28	31	52
PH-PEG-20%	Hexyl	5.2	3.8	1.36	31	46
PH-PEG-30%	Hexyl	5.2	3.9	1.34	26	41
PH-PEG-40%	Hexyl	6.7	4.6	1.46	23	33
PH-PEG-50%	Hexyl	7.2	4.6	1.57	18	29
PH-PEG-75%	Hexyl	9.9	6.4	1.59	12	16