

Supporting Information

Fast RAFT Aqueous Polymerization in a Continuous Tubular Reactor: Consecutive Synthesis of Double Hydrophilic Block Copolymer

Zhen Li, Weijie Chen, Lifen Zhang,* Zhenping Cheng* and Xiulin Zhu

5 Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

*Corresponding authors. E-mail: chengzhenping@suda.edu.cn (Z. P. Cheng) or 10 zhanglifan@suda.edu.cn (L. F. Zhang), Fax: 86-512-65882787

Table S1 Polymerization of SPMA

Entry	τ (min)	ν_1 (mL/min)	ν_M (mL/min)	ν_I (mL/min)	Con. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	3.0	4.810	4.210	0.600	5.2	1300	7900	1.15
2	5.0	2.886	2.526	0.360	25.7	6300	10500	1.16
3	7.0	2.061	1.804	0.257	45.2	11100	13100	1.16
4	9.0	1.603	1.403	0.200	58.0	14300	15900	1.14
5	11.0	1.312	1.148	0.164	68.8	16900	17800	1.15
6	13.0	1.110	0.972	0.138	74.2	18300	18500	1.14
7	15.0	0.962	0.842	0.120	79.2	19500	19000	1.14
8	18.0	0.802	0.702	0.100	85.6	21100	20400	1.16
9	21.0	0.687	0.601	0.086	92.3	22700	22100	1.16
10	40.0	0.361	0.316	0.045	>99	24400	22700	1.15

Polymerization conditions: $[SPMA]_0/[CTBCOOH]_0/[AIBI]_0 = 100/1/0.2$, $m(SPMA) = 7.28$ g, $V_{water} = 24$ mL, L (tube length) = 6 m, V_t (tube volume) = 14.43 mL, $\nu_1 = \nu_M + \nu_I$, τ (retention time) = V_t/ν_1 , 15 temperature = 70 °C.

Table S2 Polymerization of the 2nd block PEGMA

Entry	1 st block PSPMA			2 nd block PPEGMA					
	Con. (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n	L (m)	τ (min)	Con. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1a	>99	23900	1.13	2	5.8	3.2	23900	23500	1.14
2a	>99	22800	1.18	3	8.8	27.2	29600	25400	1.24
3a	>99	22900	1.17	5	14.6	59.5	37800	27300	1.25
4a	>99	23500	1.16	7	20.4	74.7	42400	28100	1.24
5a	>99	21300	1.17	15	43.8	96.9	45500	29000	1.26
1b	>99	22100	1.16	3	8.8	6.3	23700	23000	1.2
2b	>99	21600	1.16	6	17.5	24.4	26200	24400	1.18
3b	>99	22300	1.15	13	37.9	49.3	31000	26000	1.21
4b	>99	22800	1.19	15	43.8	62.2	33700	27700	1.21
5b	>99	21600	1.16	21	61.3	75.0	34700	28400	1.22

Polymerization conditions: 1st block PSPMA, $[SPMA]_0/[CTBCOOH]_0/[AIBI]_0 = 100/1/0.2$, m (SPMA) = 7.28 g, $V_{water} = 24$ mL, $v_1 = 0.361$ mL/min, retention time = 40 min; 2nd block PPEGMA, entries 1a ~ 5a, $[PEGMA]_0/[macro-CTA]_0/[AIBI]_0 = 50/1/0.1$, entries 1b ~ 5b, $[PEGMA]_0/[macro-5 CTA]_0/[AIBI]_0 = 50/1/0$, $V_{PEGMA} = 7.05$ mL, $v_2 = 0.463$ mL/min, $v = v_1 + v_2 = 0.824$ mL/min, τ (retention time) = V_t (tube volume)/ v , L represents lengths of the tube and the tube inner diameter (ID) = 1.75 mm, temperature = 70 °C.

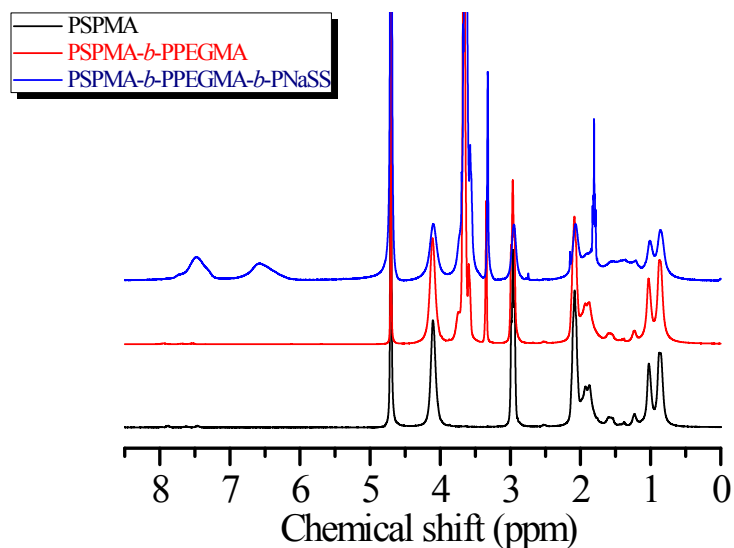


Fig. S1. ¹H NMR spectrum (300MHz, D₂O) of PSPMA, PSPMA-*b*-PPEGMA obtained in a continuous tubular reactor and PSPMA-*b*-PPEGMA-*b*-PNaSS triblock copolymer after chain extension in ampoules. Chain extension polymerization conditions: [NaSS]₀/[PSPMA₁₀₁-*b*-5 PPEGMA₂₄]₀/[AIBI]₀ = 1000/1/0.2, m (NaSS) = 0.31 g, V_{water} = 3.5 mL, t = 50 min, temperature = 70 °C.