Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Comprehensive Study of the Reversible Addition-Fragmentation Chain Transfer Polymerization and Co-polymerization of 2-Methacryloyloxyethyl phosphorylcholine

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Supplementary Material (ESI) for Polymer Chemistry

Block Copolymerization of 2-Methacryloyloxyethyl Phosphorylcholine:

Self-Chain Extension of 2-Methacryloyloxyethyl Phosphorylcholine:

MPC based macro-CTAs were first polymerized with different CTP/ACVA ratios (typically CTP/ACVA=2:1) and the polymerization was stopped at 60% conversion by quenching in liquid nitrogen and exposure to air. The resulting polymers were precipitated in acetone and then washed with 12.5 vol% methanol in acetone to remove any traces of monomer. Subsequently, the prepared macro-CTA with additional MPC monomer and ACVA were dissolved in different volume of method to conduct the self-chain extension experiments. In a typical protocol, p(MPC) (0.30 g, 0.032 mmol, M_n = 9.3 x 10^3 g/mol, M_w/M_n=1.07), MPC (0.30 g, 1.0 mmol) and ACVA(0.0020 g, 0.0070 mmol) were dissolved in 2.0 mL methanol. After degassing via four freeze-thaw cycles, the flask was placed in a preheated oil bath for 18 hours at 60 ^oC. At the end of polymerization process, the polymer was recovered by precipitating in acetone. p(MPC-*b*-MPC) molecular weight M_n was found to be around 1.7 x 10^4 g/mol and the polydispersity index M_w/M_n was shown by GPC as 1.2.

Table S1. Evolution of molecular weight of MPC homopolymer was measured by Gel Permeation Chromatography

Code	Reaction Time (min)	Conv.% (NMR)	M_n (Theory) g/mol ($x10^4$)	M_n (GPC) g/mol ($x10^4$)	M_w/M_n (GPC)
S1.1	120	10	0.21	0.42	1.06
S1.2	165	25	0.49	0.59	1.08
S1.3	210	41	0.79	0.79	1.03
S1.4	300	67	1.28	1.11	1.04
S1.5	405	80	1.52	1.26	1.04
S1.6	540	91	1.72	1.27	1.08
S1.7	660	92	1.74	1.29	1.08
S1.8	1320	-	-	1.39	1.09

Table S2: Effect of CTP/ACVA ratio on synthesis of poly(MPC) macroCTA and consequent effect of monomer concentration on self chain extension of MPC

Code	Macro-CTA (Trail 1)				Self-Chain Extension (Trail 2)			
	[CTP]/ [ACVA]	Conv. %	M_n g/mol	M_w/M_n	[Monomer]	Conv. %	M_n g/mol (10^4)	M_w/M_n
S2.1	1.0	83	$1.07x10^4$	1.11	0.20 M	N/A	1.94	1.44
S2.2(a)	2.0	65	$9.40x10^3$	1.09	0.20 M	95	1.45	1.29
S2.2(b)	2.0	65	$9.40x10^3$	1.09	0.50 M	99	1.67	1.21
S2.3	5.0	63	$9.30x10^3$	1.07	0.50 M	98	1.67	1.16

Table S3. Molecular weights and molecular weight distribution of di-block copolymers of MPC:

Code	Di-block Copolymers of MPC	M_n (Theory) g/mol ($x10^4$)	M_n (GPC) g/mol ($x10^4$)	M_w/M_n (GPC)
S3.1	Poly(MPC_{54}-*b*-$LAEMA_{64}$)	4.5	4.6	1.17
S3.2	Poly(MPC_{54}-*b*-$GAEMA_{55}$)	3.6	3.3	1.26
S3.3	Poly(MPC_{54}-*b*- $GAMA_{78}$)	3.61	4.0	1.11
S3.4	Poly(MPC_{54}-*b*-$AEMA_{54}$)	2.7	2.5	1.31

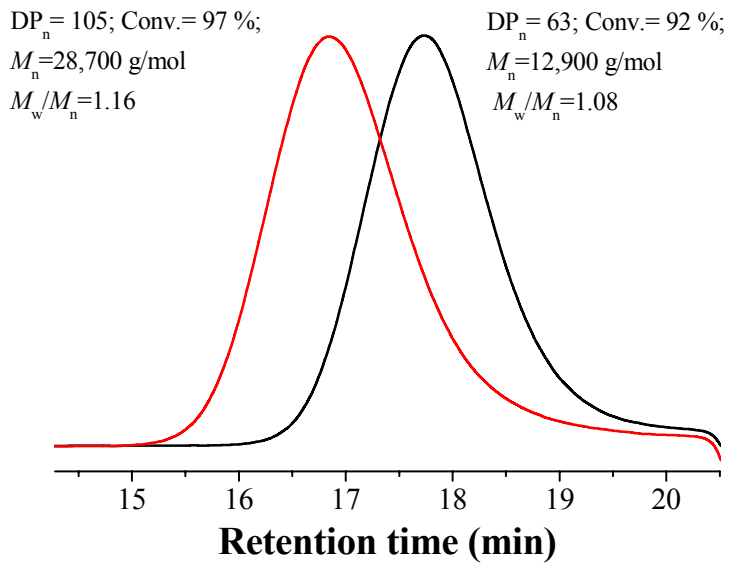

Figure S1. GPC traces of MPC homopolymers of low as well as high molecular weights with controlled molecular weights

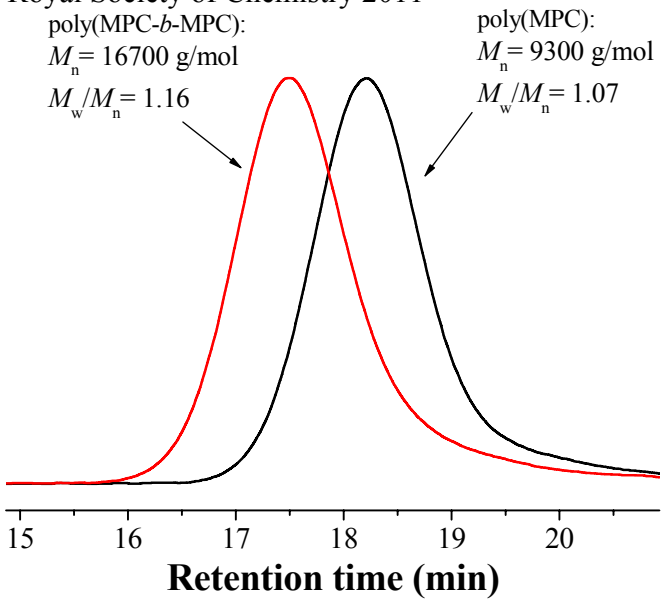

Figure S2 GPC traces of p(MPC) macroCTA and self chain extension reaction with a CTP/ACVA = 5 .0 at 60 °C in methanol.

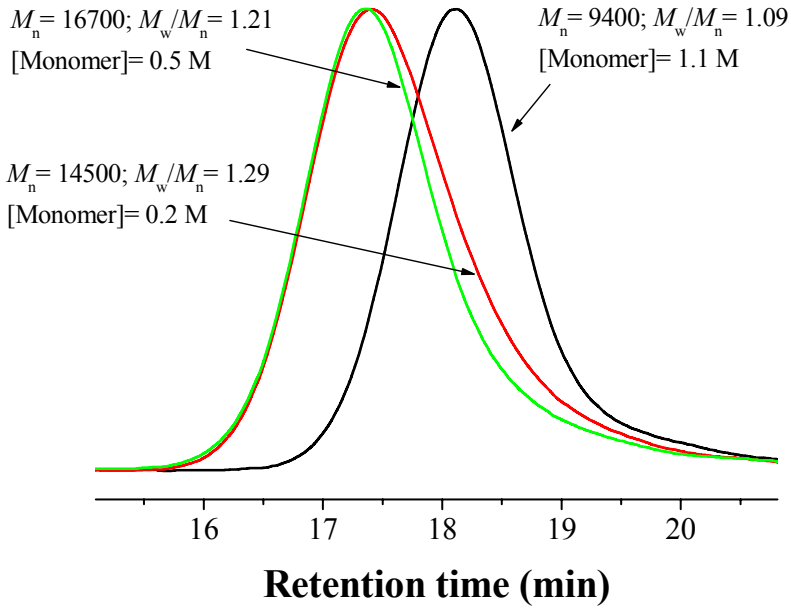

Figure S3. GPC traces showing the effect of monomer concentration on self chain extension of MPC).

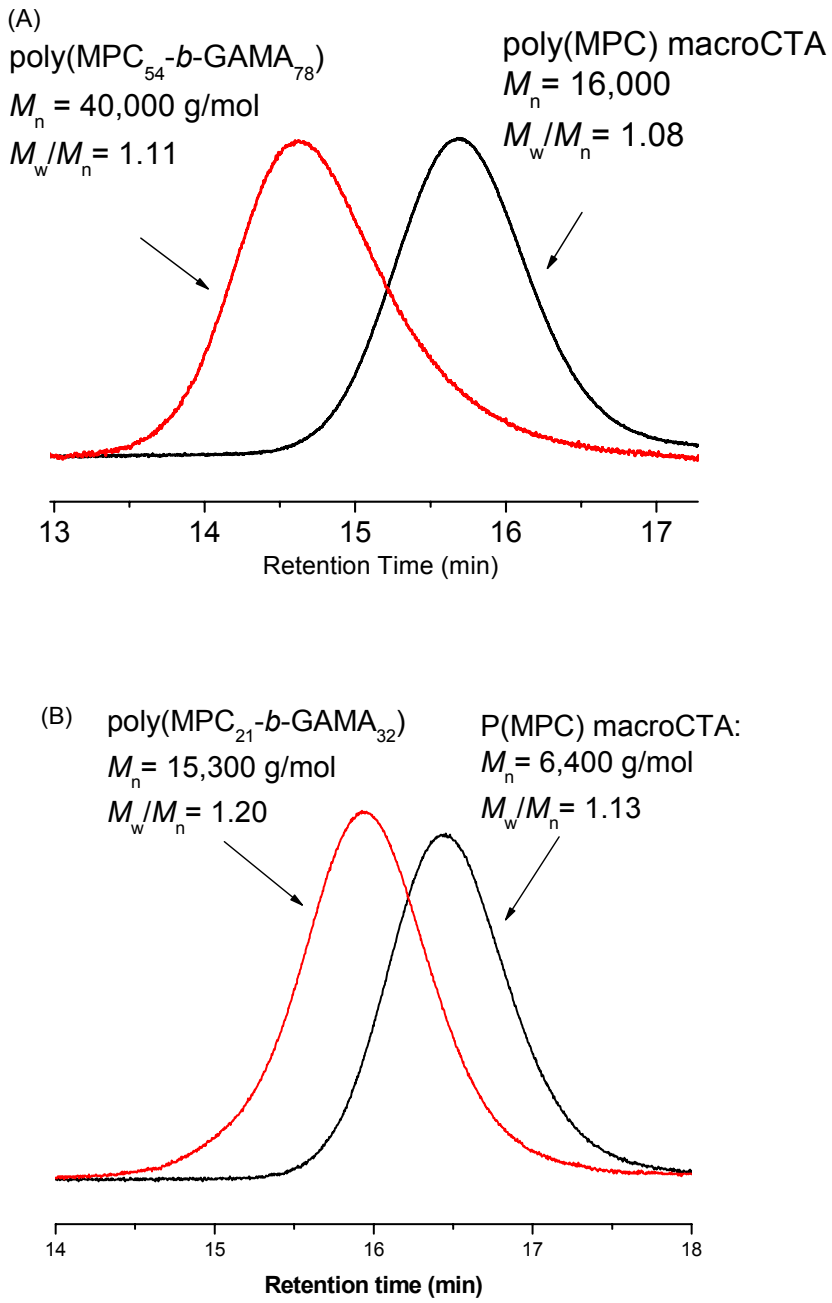

Figure S4: Diblock copolymerization of GAMA with MPC using sequential monomer addition, forming (A) p(MPC_{54}-*b*-$GAMA_{78}$) and (B) p(MPC_{21}-*b*-$GAMA_{32}$)

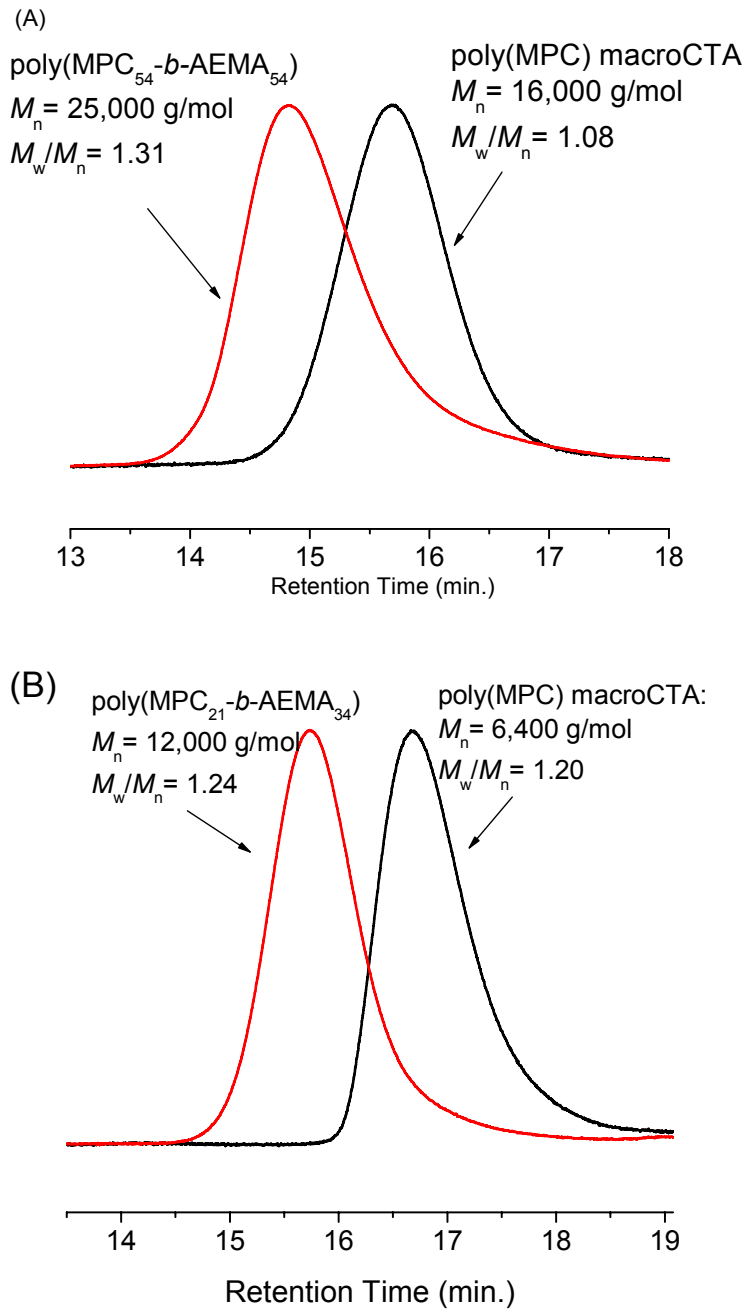

Figure S5: Diblock copolymerization of AEMA with MPC using sequential monomer addition, forming (A) p(MPC_{54}-*b*-$AEMA_{54}$) (B) p(MPC_{21}-*b*-$AEMA_{34}$)

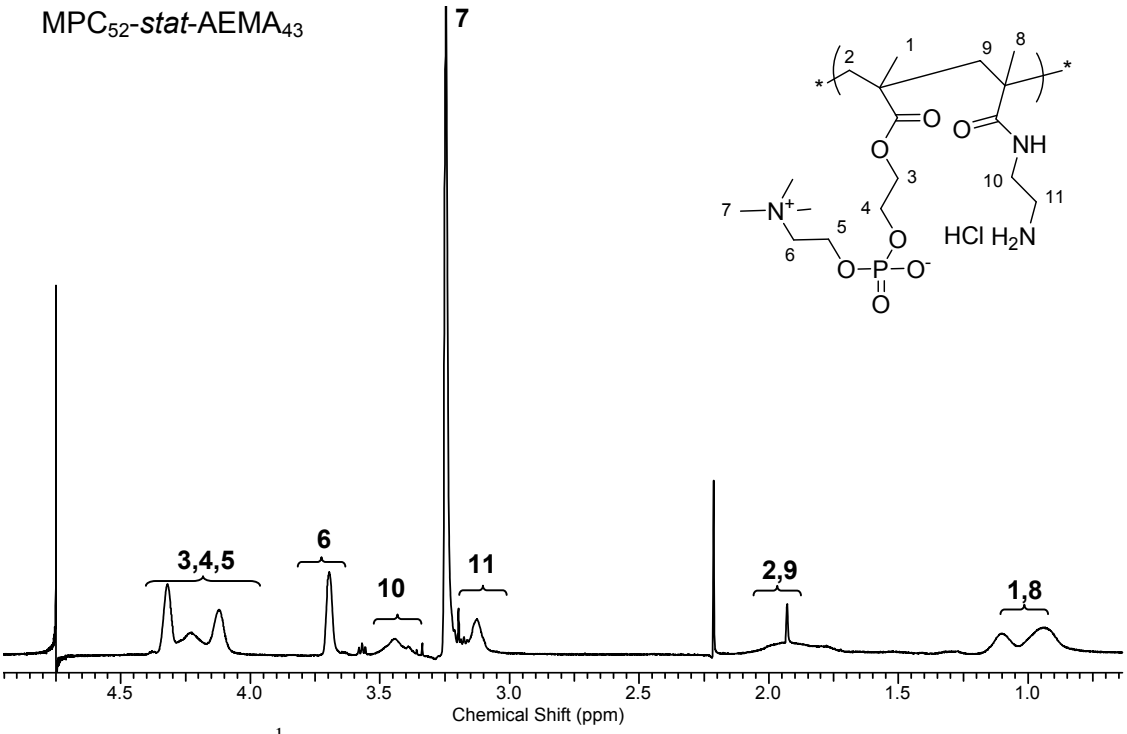

Figure S6: Assigned ^{1}H NMR spectra for poly(MPC$_{52}$-*stat*-AEMA$_{43}$)

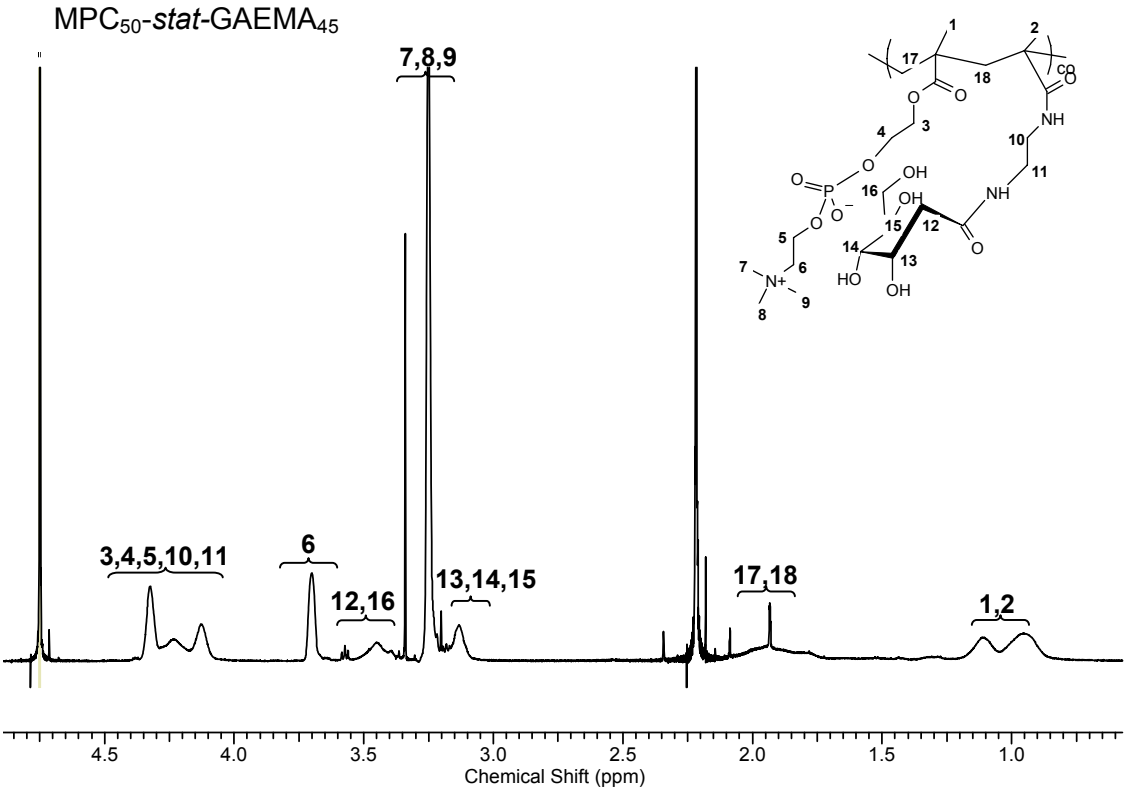

Figure S7: Assigned ^{1}H NMR spectra for poly(MPC$_{65}$-*stat*-GAEMA$_{50}$)