Electronic Supplementary Material (ESI) for Polymer Chemistry

Elementary Supplementary Information

Synthesis of Multi-Block Copolymer Stars Using a Simple Iterative Cu(0)-Mediated Radical Polymerization Technique

Cyrille Boyer, Aurelia Derveaux, Per B. Zetterlund and Michael R. Whittaker

Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia.

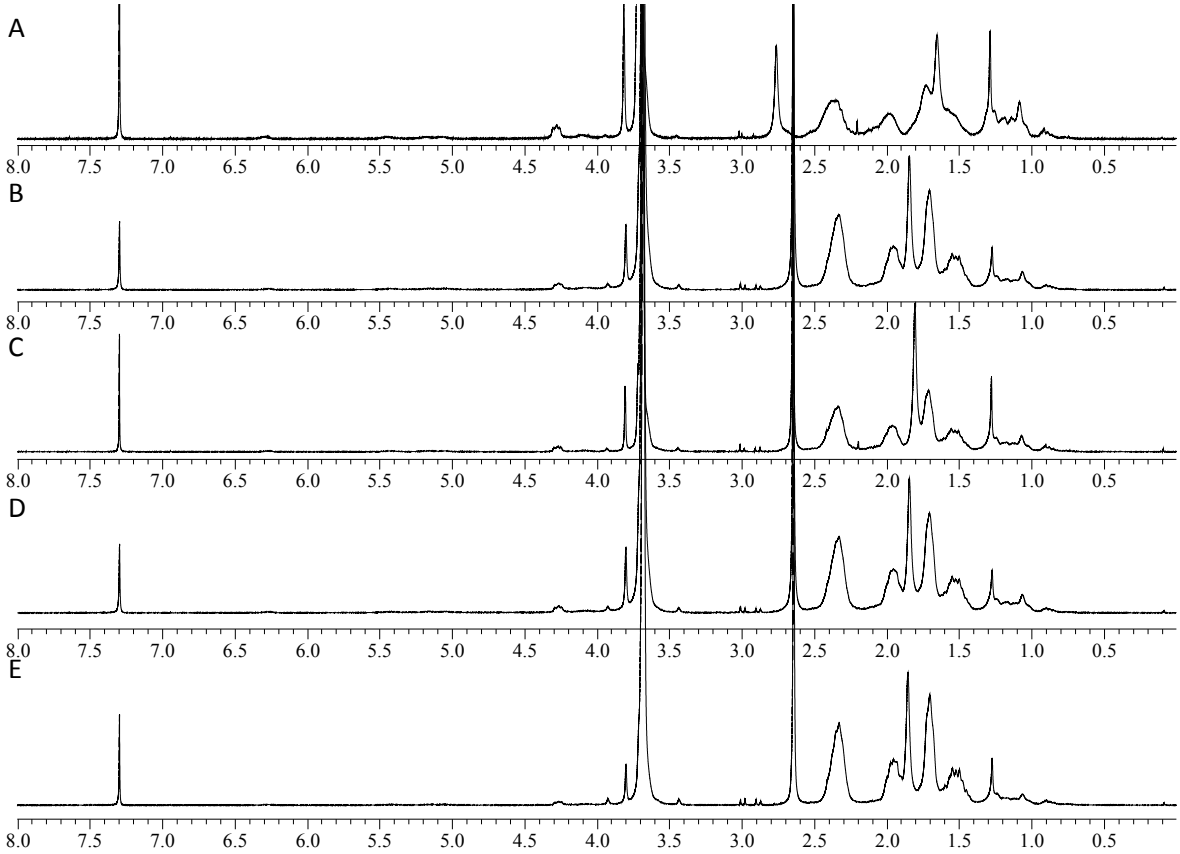

Figure S1. ^{1}H NMR spectra (A) of poly(MA); (B) poly(PMA-*b*-PMA); (C) Poly(PMA-*b*-PMA-*b*-PMA); (D) Poly(PMA-*b*-PMA-*b*-PMA-*b*-PMA); (E) Poly(PMA-*b*-PMA-*b*-PMA-*b*-PMA-*b*-PMA) multi-block copolymers (Star 1 of Table S1).

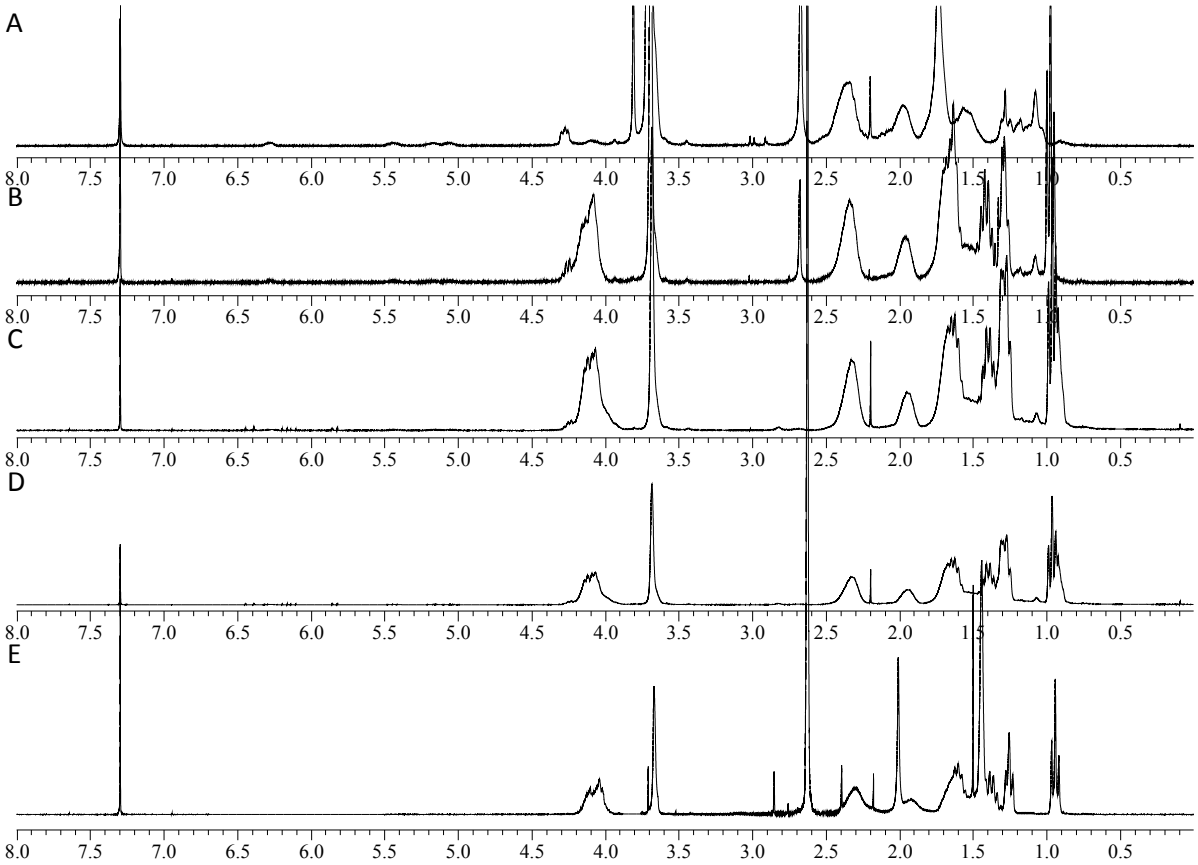

Figure S2. ^{1}H NMR spectra (A) of poly(MA); (B) poly(PMA-*b*-PBA); (C) poly(PMA-*b*-PBA-*b*-PEA); (D) poly(PMA-*b*-PBA-*b*-PEA-*b*-PEHA); (E) poly(PMA-*b*-PBA-*b*-PEA-*b*-PEHA-*b*-P*t*BA) multi-block copolymers (Star 2 of Table S1).

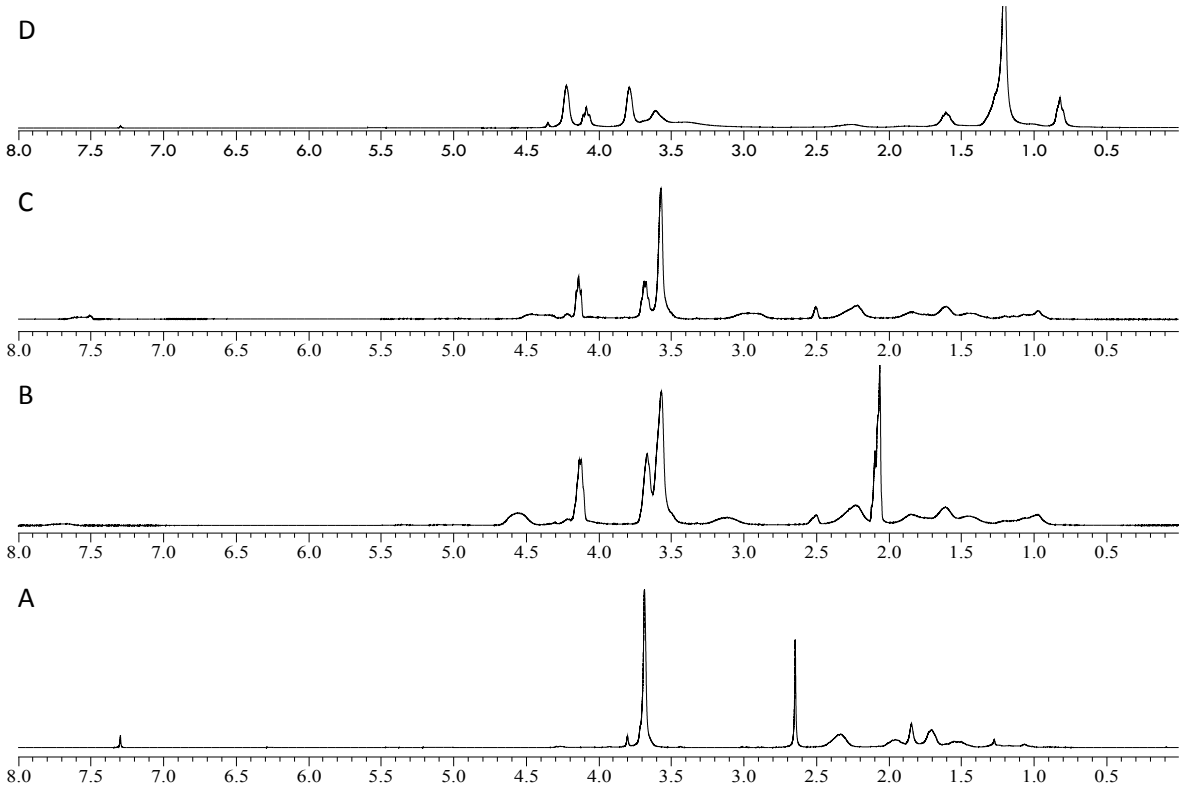

Figure S3. ^{1}H NMR spectra (A) of poly(MA); (B) poly(PMA-*b*-PHEA); (C) Poly(PMA-*b*-PHEA-*b*-PDMEA); (D) Poly(PMA-*b*-PHEA-*b*-PDMEA-*b*-PDA) multi-block copolymers (Star 3 of Table S1).

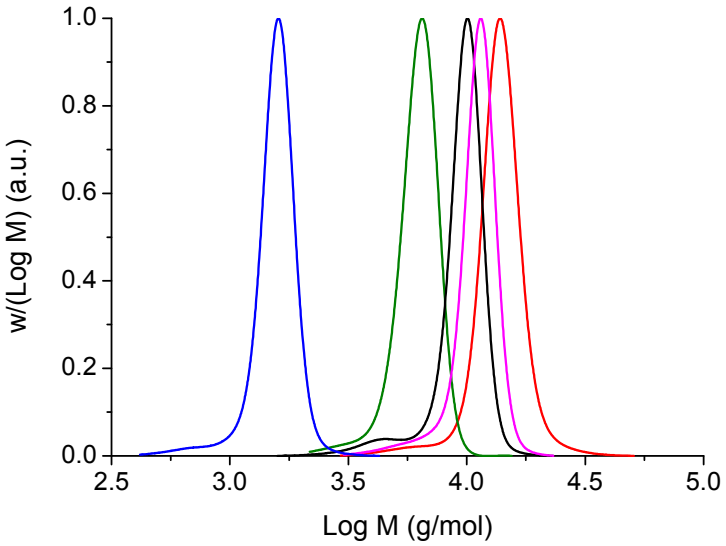

Figure S4. Molecular weight distributions for poly(PMA-*b*-P*n*BA-*b*-PEA-*b*-PEHA-*b*-P*t*BA) multi-block star copolymers obtained via iterative Cu(0)-mediated polymerization (approximate molecular weight of each block = 500 g/mol, degree of polymerization ≈ 4-5).

Note: THF used as mobile phase.

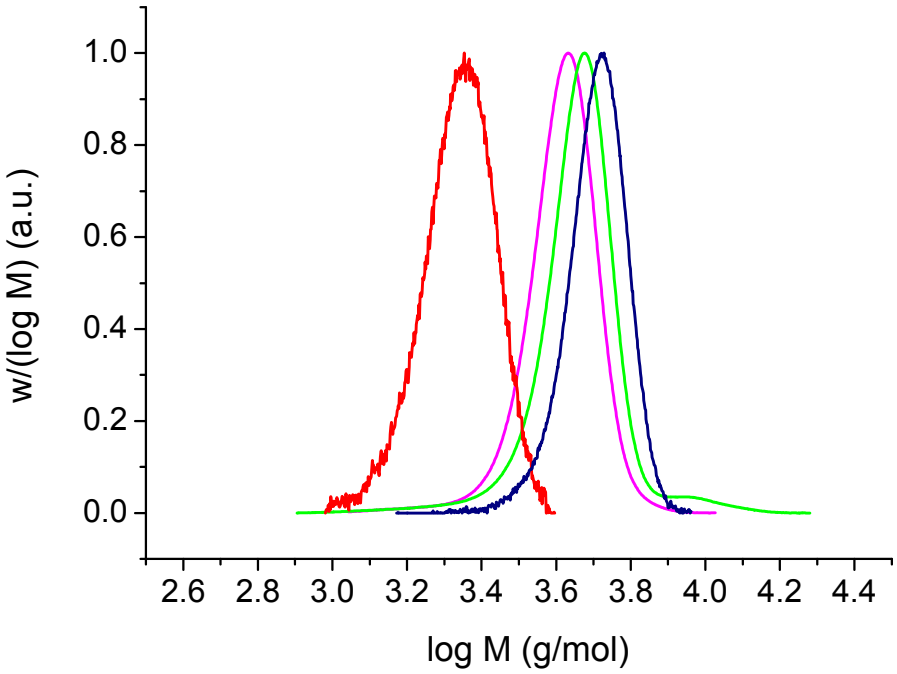

Figure S5. Molecular weight distributions for Poly(PMA-*b*-PHEA-*b*-PDMEA-*b*-PDA multi-block star copolymers obtained via iterative Cu(0)-mediated polymerization (approximate molecular weight of each block = 500 g/mol, degree of polymerization ≈ 4-5). Note: DMAc used as mobile phase.

Table S1. Molecular weight data pertaining to the syntheses of multi-block star copolymers obtained via iterative Cu(0)-mediated polymerization.

Star	Cycles	Block Copolymer Composition	Time (days)	Monomer Conversion (%)	$M_{n,th}$	$M_{n,(GPC)}$	$M_{n,(NMR)}$	PDI
Star 1	1	Poly(PMA)	1	>99	3500	1100	3000	1.04
	2	Poly(PMA-*b*-PMA)	2	99	6000	2400	4800	1.07
	3	Poly(PMA-*b*-PMA-*b*-PMA)	3	99	8500	5800	7800	1.05
	4	Poly(PMA-*b*-PMA-*b*-PMA-*b*-PMA)	4	98	11000	7800	1000	1.05
	5	Poly(PMA-*b*-PMA-*b*-PMA-*b*-PMA-*b*-PMA)	5	97	13500	9500	13200	1.06
Star 2	1	Poly(PMA)	1	>99	3500	1200	3800	1.05
	2	Poly(PMA-*b*-PHEA)	2	>99	6000	5400	4800	107
	3	Poly(PMA-*b*-PHEA-*b*-PDMEA)	3	>95	8500	6300	7786	1.02
	4	Poly(PMA-*b*-PHEA-*b*-PDMEA-*b*-PDA)	4	>90	11000	7000	10539	1.04
Star 3	1	Poly(PMA)	1	>99	3500	1200	3800	1.04
	2	Poly(PMA-*b*-PBA)	2	>99	6000	6400	5800	1.05
	3	Poly(PMA-*b*-PBA-*b*-PEA)	3	>99	8500	9700	8400	1.05
	4	Poly(PMA-*b*-PBA-*b*-PEA-*b*-PEHA)	4	>99	11000	12800	10500	1.04

5	Poly(PMA-*b*-PBA-*b*-PEA-*b*-PEHA-*b*-P*t*BA)	**5**	>98	13500	14500	15000	1.05