Supplemental Information

Synthesis of Star Polymers using Organocatalyzed Atom Transfer Radical Polymerization Through a Core-first Approach

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Materials

Visible-light photoreactor:

All polymerizations were carried out using the same photoreactor system as previously reported.[1] All materials to build the light source were purchased from Creative Lighting Solutions.

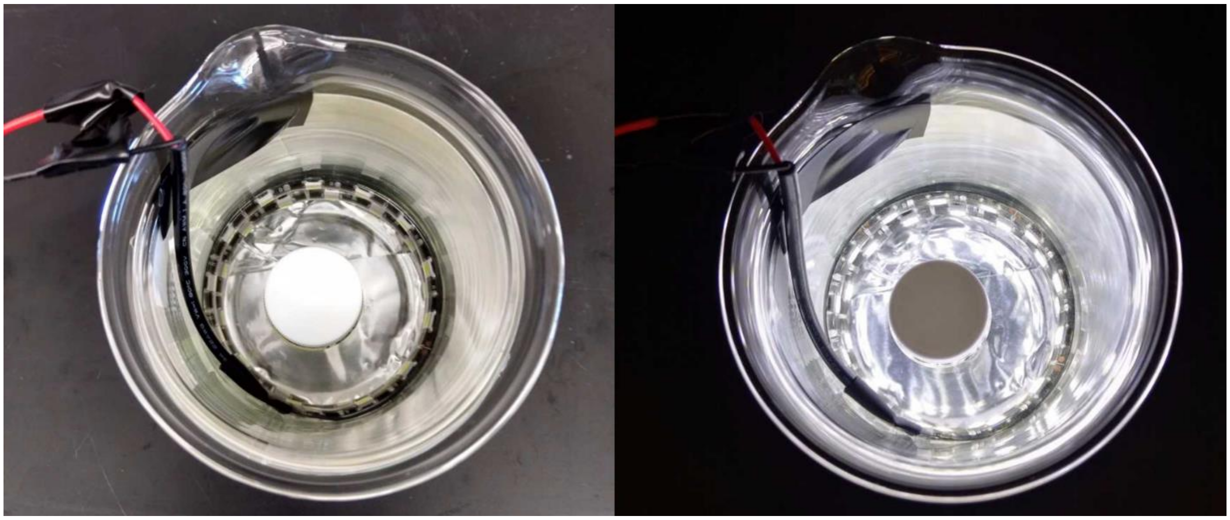
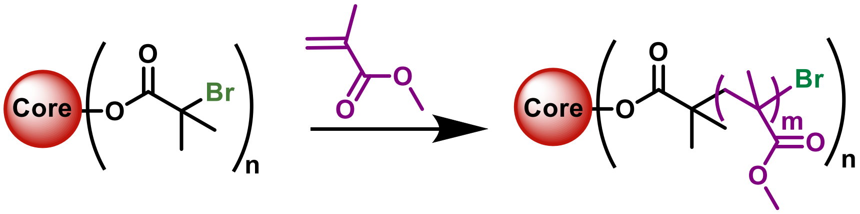


Figure S1: LED beaker photoreactors shown off (left) and on (right).

Polymerization Procedures

General star polymer synthesis using core-first approach:



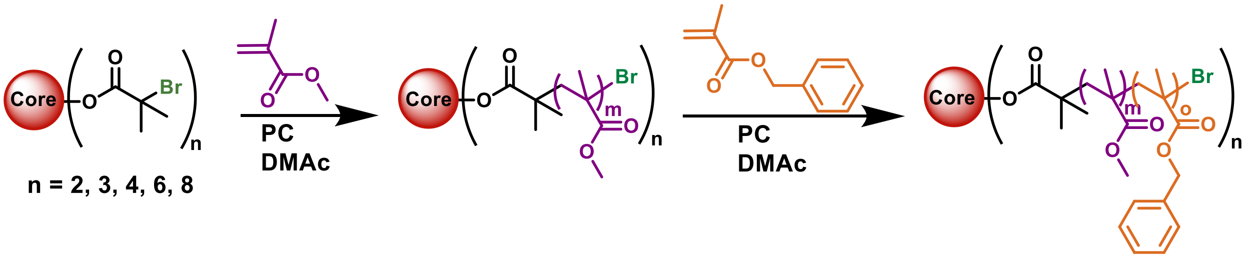
Scheme S1: Reaction scheme for synthesis of poly(methyl methacrylate) star polymers using cores with *n* number of initiating sites, where n is 2, 3, 4, 6, or 8.

Using the difunctional initiator as an example for a typical polymerization using the core-first approach, the stoichiometry was determined as follows for a targeted degree of polymerization of 50 for each arm: [MMA]:[MfI]:[PC] is [1000]:[10]:[1]. To set up polymerization, a 20 mL scintillation vial with a polypropylene lined cap was charged with a small stir bar and 33.8 mg (9.39×10^{-5} mol) of multifunctional ATRP initiator, then brought into a glovebox with nitrogen atmosphere. Then 5.74 mg (9.39×10^{-6} mol) PC from a stock solution was added, followed by 1 mL (9.39×10^{-3} mol) of methyl methacrylate (MMA). At that time, the vial was capped and placed in a photoreactor and irradiated by white LEDs. Once the reactions exhibited increased viscosity an additional 1 mL of DMAc was added, typically in the 3rd hour. Aliquots were taken for kinetic analysis by quenching approximately 0.075 mL of reaction mixture into 0.7 mL of deuterated chloroform containing 250 ppm of butylated hydroxytoluene as radical inhibitor. For each aliquot collected, 0.5 mL of the quenched aliquot was used for ^{1}H NMR analysis. Conversion was determined through relative integration of the methyl ester monomer peak at 3.46 ppm to the methyl ester polymer peak at 3.32 ppm. The remaining 2 mL of quenched aliquot was dried under ambient conditions for a minimum of 24 hours, fully dissolved in THF and analyzed by GPC for molecular weight and dispersity analysis. Full details of stoichiometric amounts for each star type can be seen below (Table SX).

Table S1: Stoichiometry used for O-ATRP of methyl methacrylate targeting a degree of polymerization of 50 for each arm for telechelic polymer and stars containing 3, 4, 6, and 8 arms.

# arms	[MMA]:[RBr$_n$]:[PC]	MMA (mL)	RBR$_n$ (mg)	PC (mg)
2	[1000]:[10]:[1]	1	33.8	5.74
3	[1500]:[10]:[1]	1	36.4	3.84
4	[2000]:[10]:[1]	1	34.4	2.88
6	[3000]:[10]:[1]	1	35.9	1.90
8	[6000]:[10]:[1]	1	36.7	1.44

Chain extension experiments:



Scheme S2: Reaction scheme for synthesis of multifunctional macroinitiator containing *n* number of arms, followed by chain extension using benzyl methacrylate (BzMA).

General Procedure for Macroinitiator Synthesis: Star polymer macroinitiator synthesis was carried out by setting up a standard polymerization experiment targeting a degree of polymerization of 50 for each arm. After all reaction components were loading into a scintillation vial the reaction was irradiated by white LEDs. To ensure chain-end group fidelity, polymerization was stopped at 1.5 hours, targeting conversions between 30% and 40%. At that time the reactions were brought out of the glovebox, where an aliquot was taken for ^{1}H NMR analysis to determine monomer conversion and the remaining reaction was quenched by exposure to air and rapid precipitation into cold methanol, followed by isolation via gravity filtration through a fine filter frit. The resulting white powder was dried overnight under vacuum at 50 ^{o}C. See Table S1 for full results of polymerization and stoichiometric details.

Table S2: Overview of results of PMMA star polymer macroinitiator synthesis using O-ATRP.[a]

# arms	[MMA]:[RBr$_n$]:[PC]	Conv. (%)[b]	M_n (kDa)[c]	$Đ$ (M_w/ M_n)[c]	Yield (%)[d]
2	[1000]:[10]:[1]	37	8.6	1.17	26
3	[1500]:[10]:[1]	38	10.9	1.27	41
4	[2000]:[10]:[1]	43	12.9	1.42	59
6	[3000]:[10]:[1]	43	19.1	1.25	64
8	[6000]:[10]:[1]	42	21.2	1.36	56

[a]Experimental conditions are using 1:1 of MMA:DMAc, using a constant 1 mL of MMA for each reaction. Irradated by white LEDs. [b]Determined by ^{1}H NMR. [c]Determined by GPC. [d]Determined by mass recovered after polymer purification.

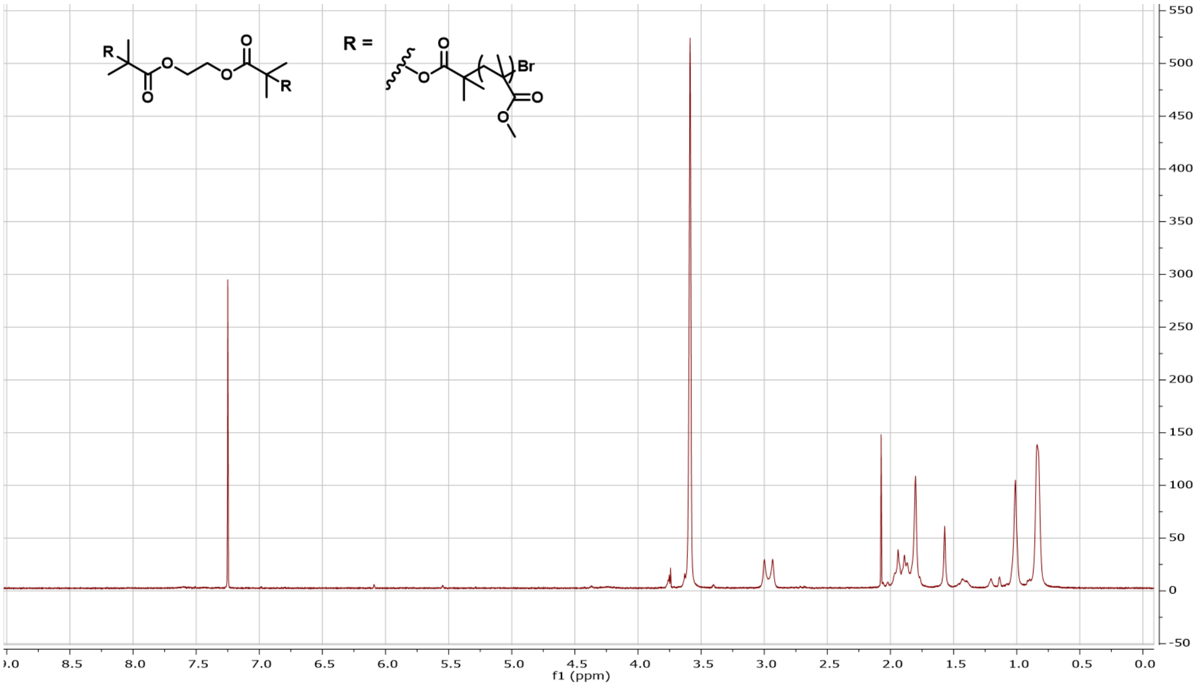


Figure S2: ^{1}H NMR spectra of 2-arm telechelic polymer macroinitiator.

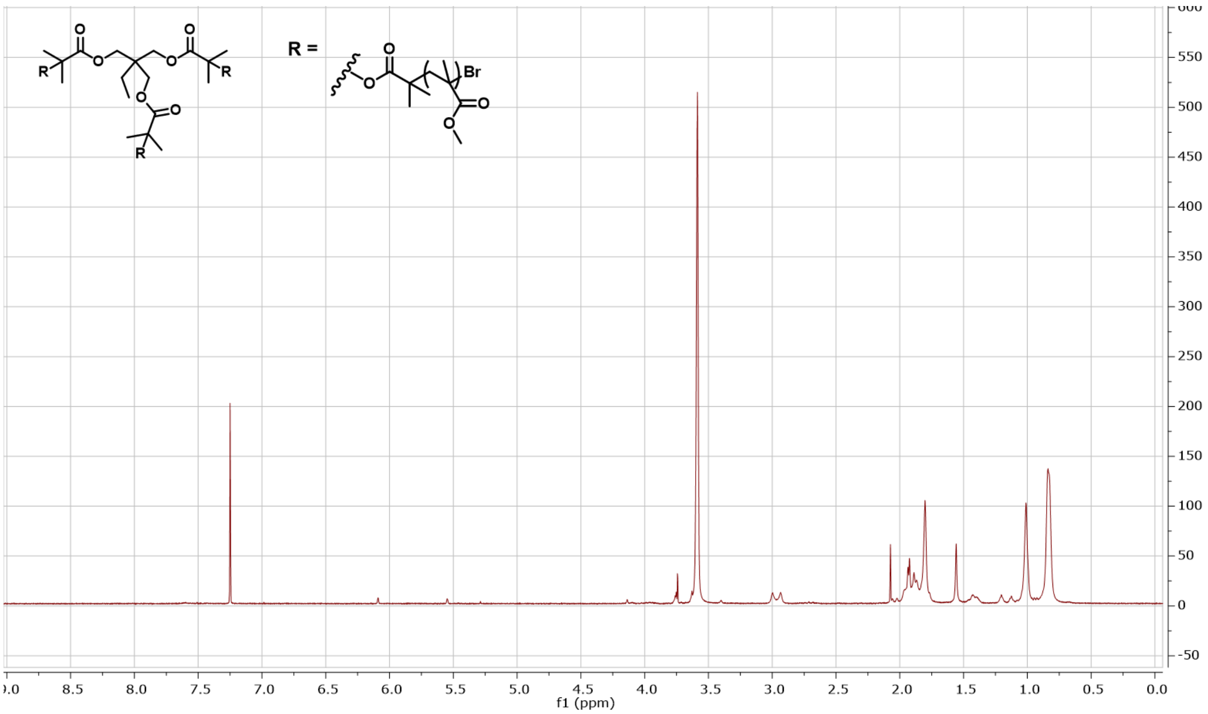


Figure S3: ^{1}H NMR spectra of 3-arm star polymer macroinitiator.

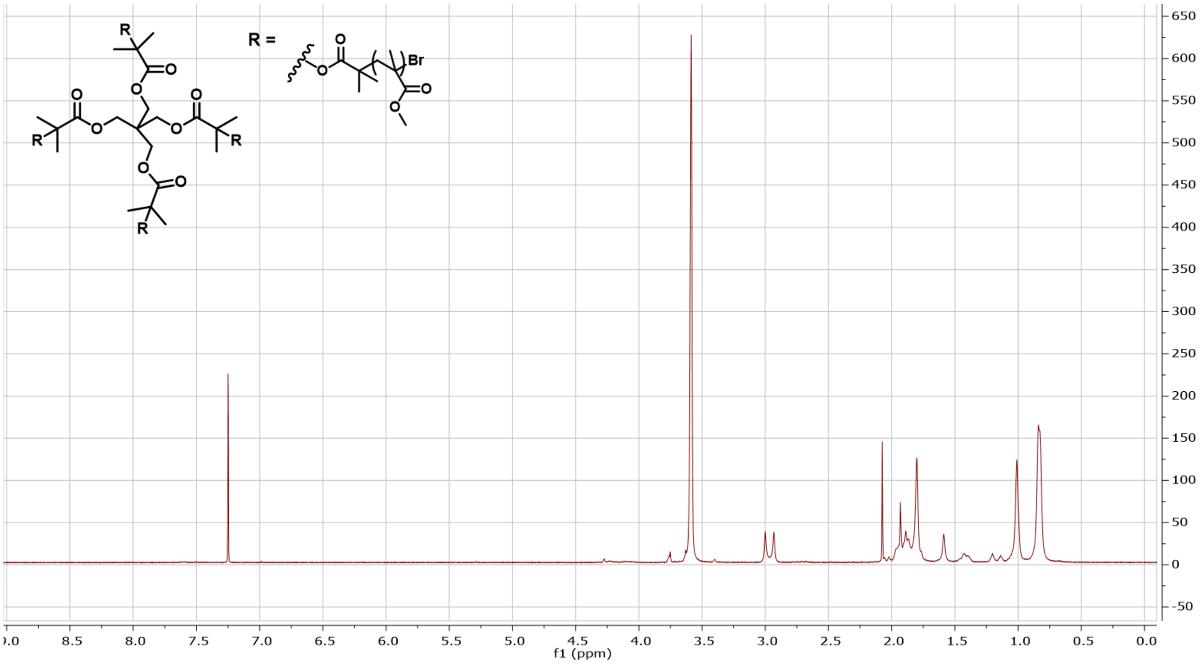


Figure S4: ^{1}H NMR spectra of 4-arm star polymer macroinitiator.

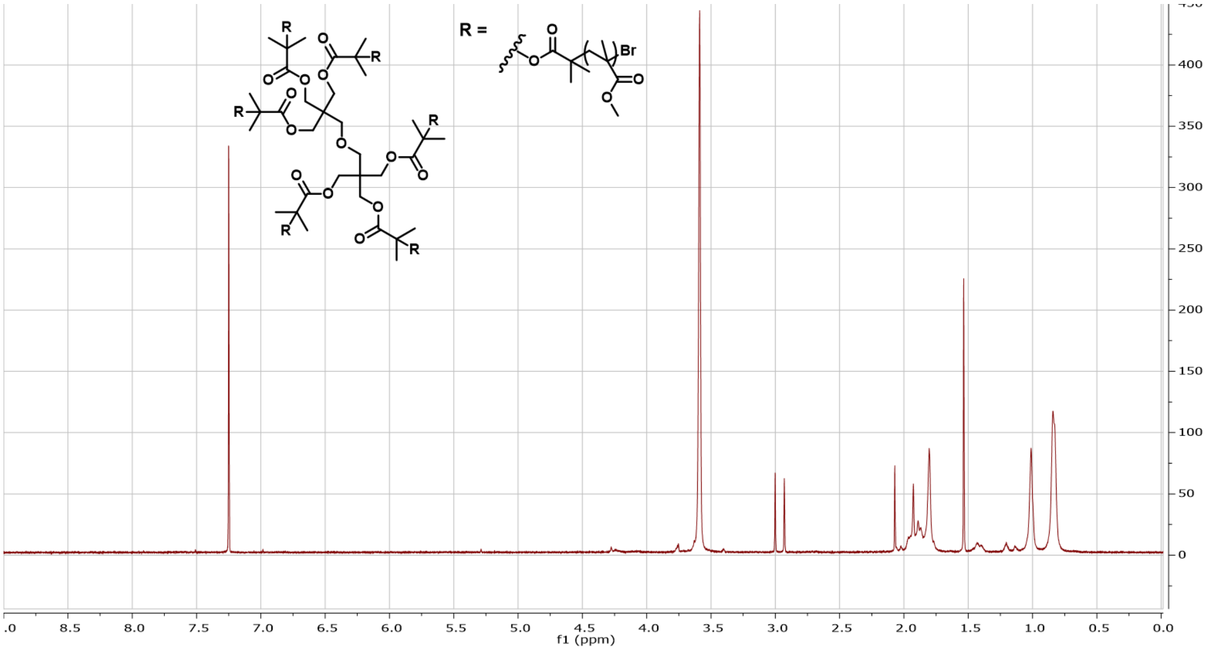


Figure S5: ^{1}H NMR spectra of 6-arm star polymer macroinitiator.

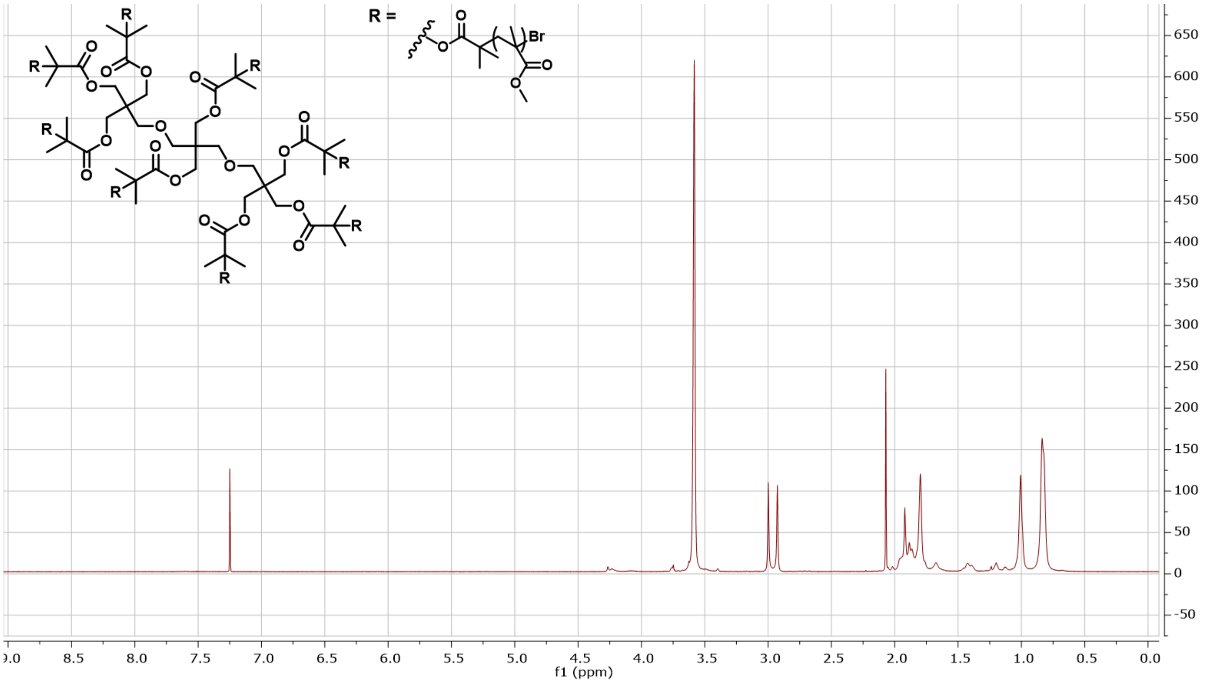


Figure S6: ^{1}H NMR spectra of 8-arm star polymer macroinitiator.

General Procedure for Chain-Extension: 50 mg of purified macroinitiator was loaded into a 20 mL scintillation vial with a small stir bar, then brought into a nitrogen atmosphere glovebox. Then, DMAc was added to the vial, the vial was capped and allowed to stir until all macroinitiator was dissolved, or approximately 1 hour. At that time, a stock solution containing PC **1** was added, followed by benzyl methacrylate (BzMA), targeting an additional 100 monomer units for each star polymer arm. All reactions used a total reaction volume of 2 mL, combined from BzMA and DMAc, and a ratio of [10]:[1] of [RBr_n]:[**1**]. After all components were loaded into the vial, the vial was capped and irradiated by white LEDs for 8 hours. Then, the reactions were brought out of the glovebox, quenched with methanol, isolated via gravity filtration through a fine filter frit, and dried at 50 ºC for 48 hours. The polymer was then weighed and analyzed via ^{1}H NMR and GPC. See Table S2 for full results and stoichiometric details.

Table S3: Results of PMMA block copolymer star polymer synthesis using O-ATRP.[a]

# arms	[BzMA]:[RBr_n]: [PC]	BzMA (mL)	DMAc (mL)	Yield (%)[b]	$M_{n\text{ theo}}$ (kDa)[c]	M_n (kDa)[d]	$Đ$ (M_w/ M_n)[d]	I^* (%)[e]
2	[2000]:[10]:[1]	0.20	1.80	72	31.3	40.2	1.41	128
3	[3000]:[10]:[1]	0.23	1.77	50	31.8	68.7	1.27	46
4	[4000]:[10]:[1]	0.26	1.74	83	69.2	62.7	1.42	111
6	[6000]:[10]:[1]	0.27	1.73	91	113.9	81.3	1.71	140
8	[8000]:[10]:[1]	0.32	1.68	94	151.9	107	1.86	143

[a]Experimental conditions are using 50 mg of macroinitiator (RBr_n) and a constant total reaction volume of 2 mL. Irradiated by white LEDs. [b]Determined gravimetrically. [c]Calculated by $(Conv \times [Mon]/[Init.] \times Mw_{Mon})/1000$. [d]Determined by GPC. [e]Calculated by $(Theo. M_n/Calc. M_n) \times 100$.

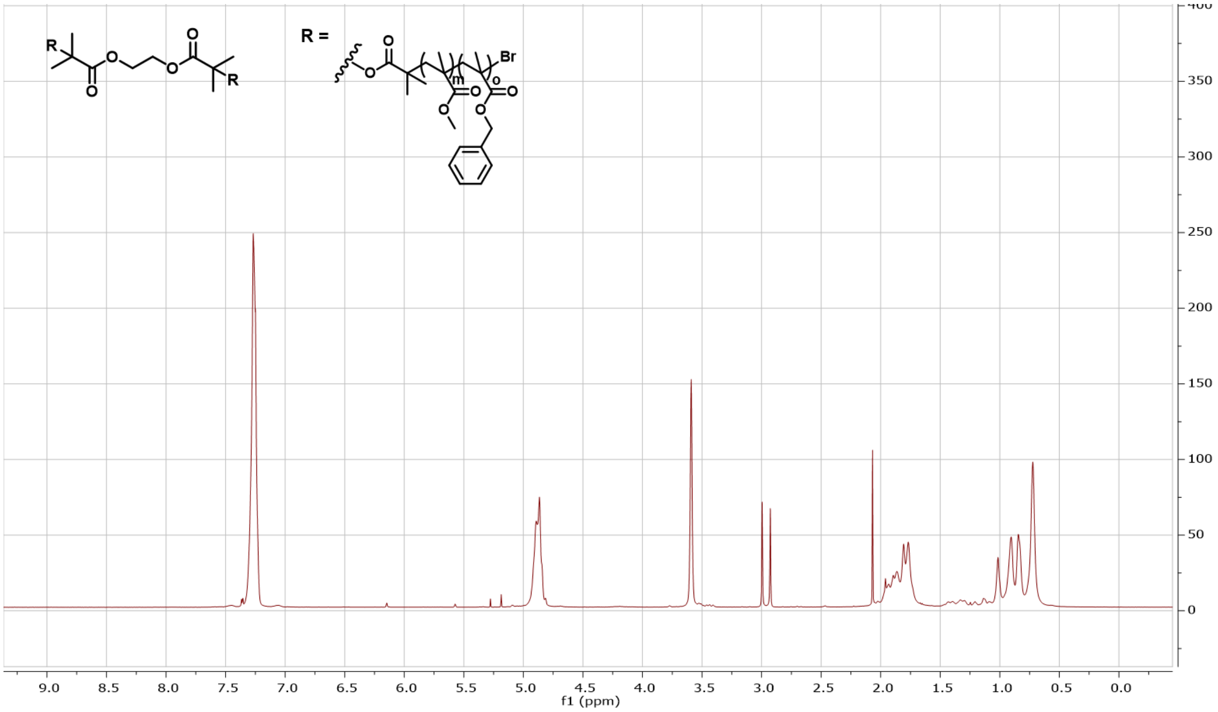


Figure S7: ^{1}H NMR spectra of telechelic 2-arm (MMA-BzMA) diblock polymer.

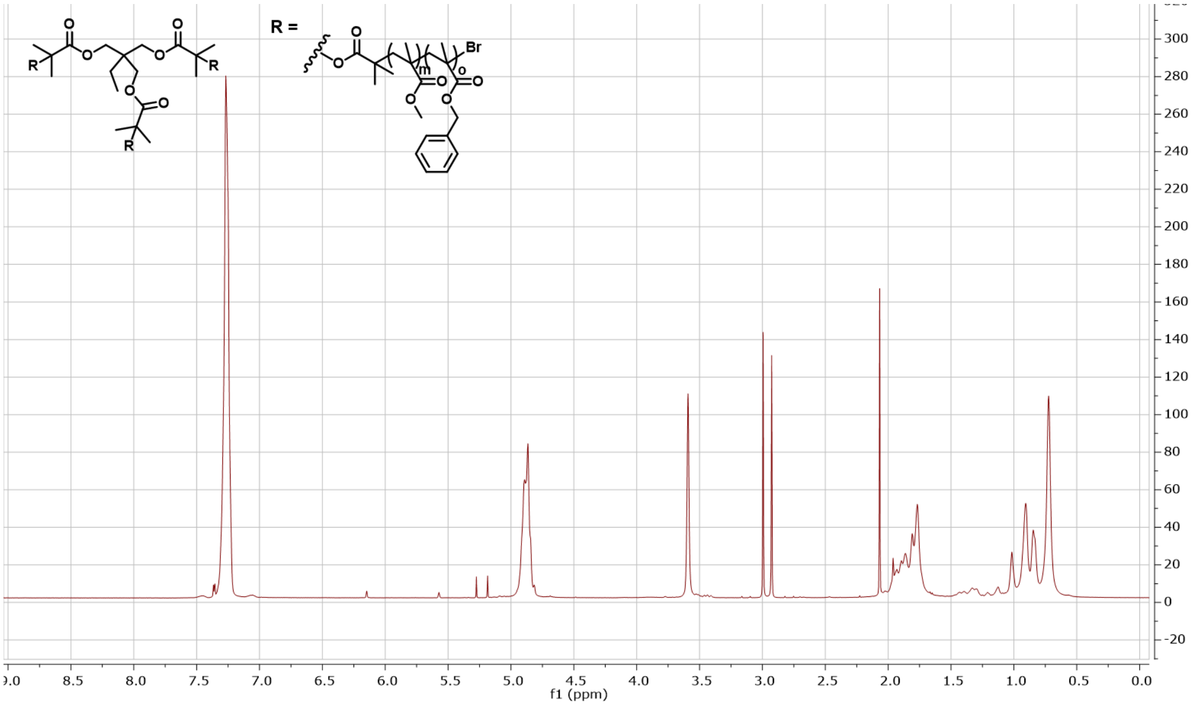


Figure S8: ^{1}H NMR spectra of 3-arm (MMA-BzMA) diblock star polymer.

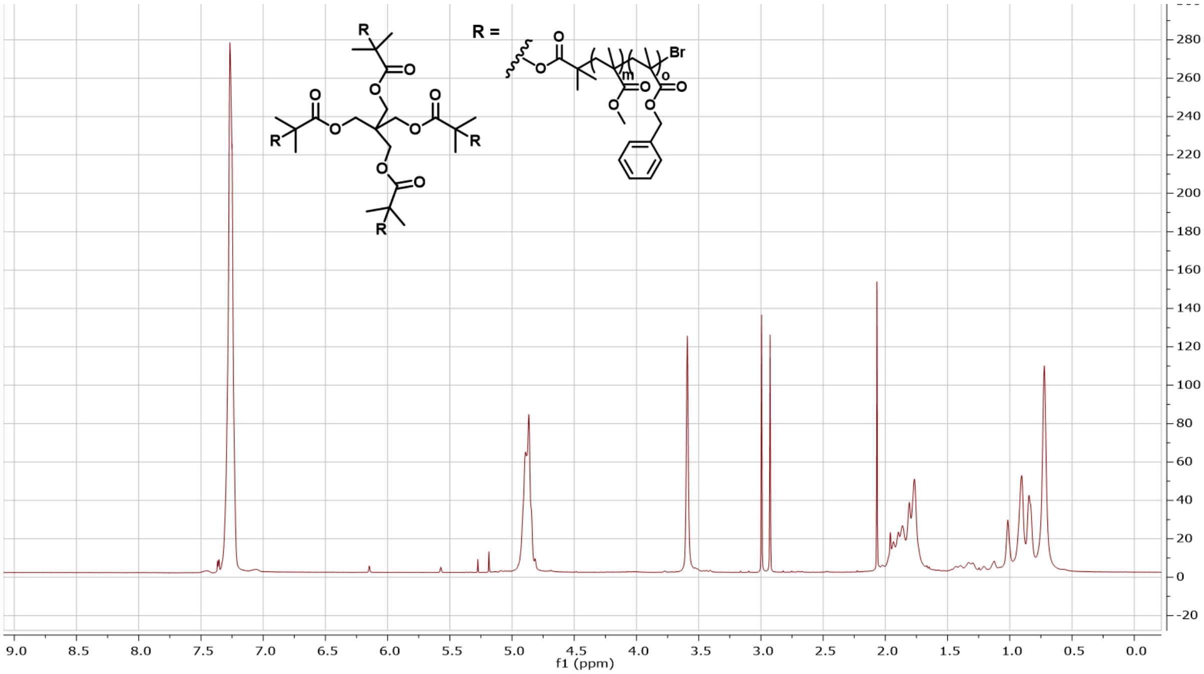


Figure S9: ^{1}H NMR spectra of 4-arm (MMA-BzMA) diblock star polymer.

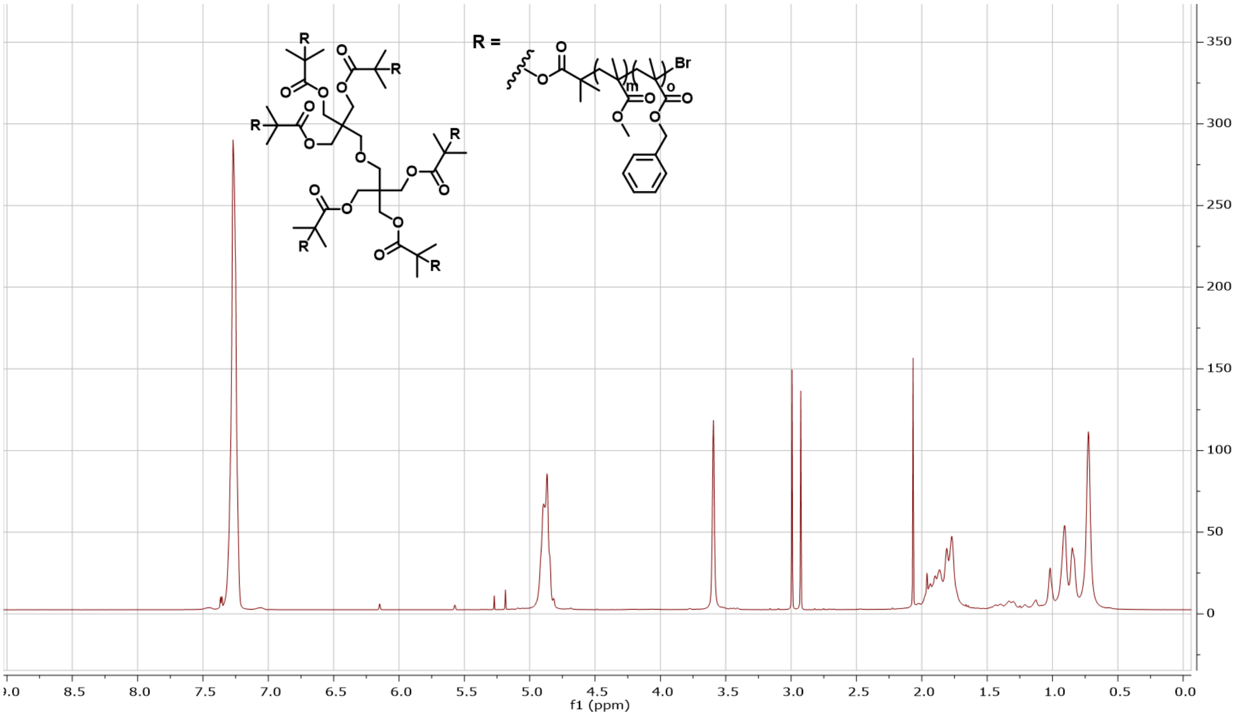


Figure S10: ^{1}H NMR spectra of 6-arm (MMA-BzMA) diblock star polymer.

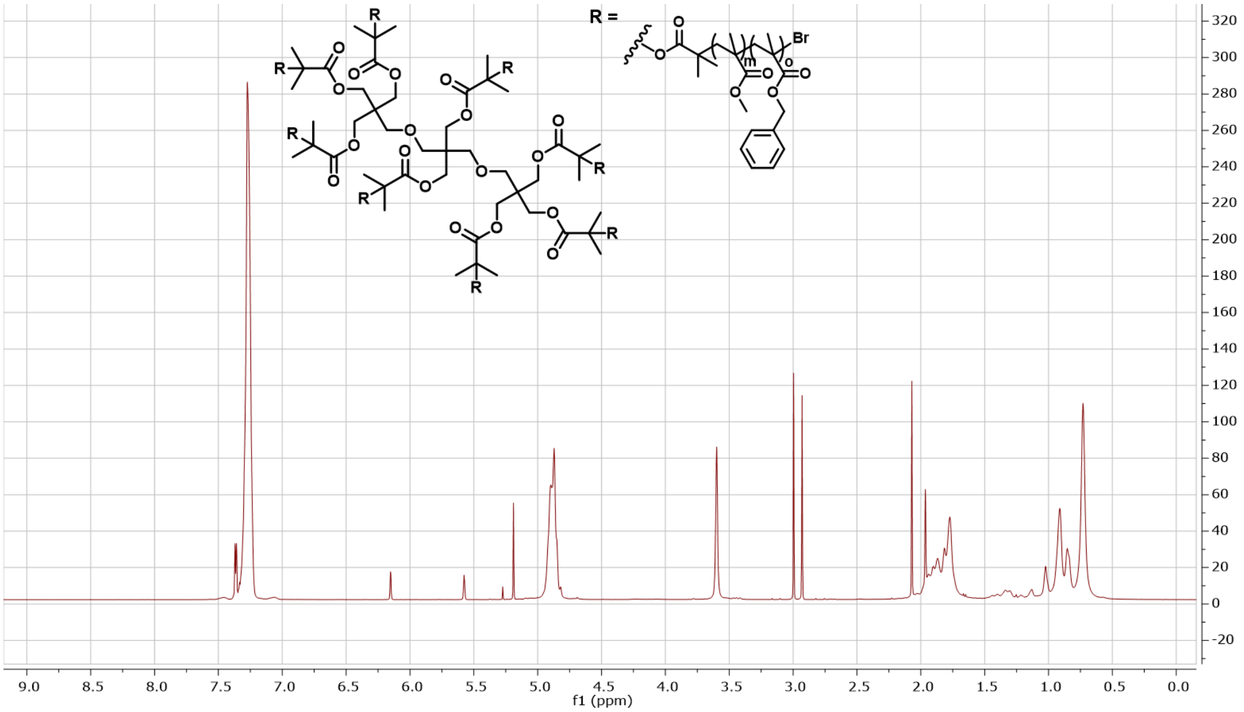


Figure S11: ^{1}H NMR spectra of 8-arm (MMA-BzMA) diblock star polymer.

Additional Results of Polymerization

Effect of reaction concentrations:

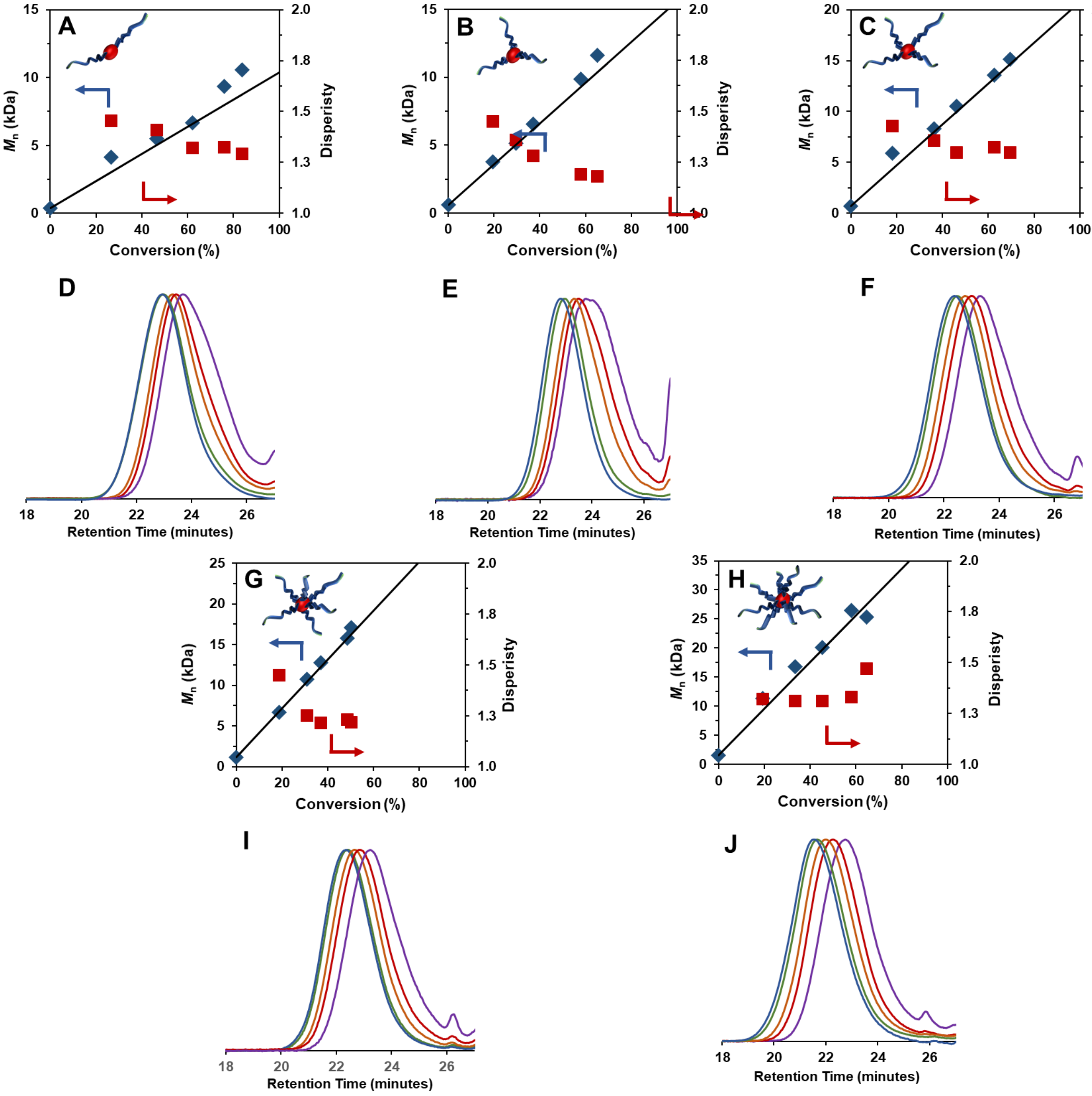


Figure S12: Plots of M_n (blue diamonds), dispersity (red squares) and theoretical M_n (black line) versus conversion for (A) linear polymer and (B) 3-arm, (C) 4-arm, (G) 6-arm, and (H) 8-arm star polymers with corresponding GPC traces shown. Conditions for polymerization are targeting 50 repeat units of MMA, [10]:[1] of [RBr_n]:[**1**], and 1 equivalents of DMAc to MMA by volume, using 1.0 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

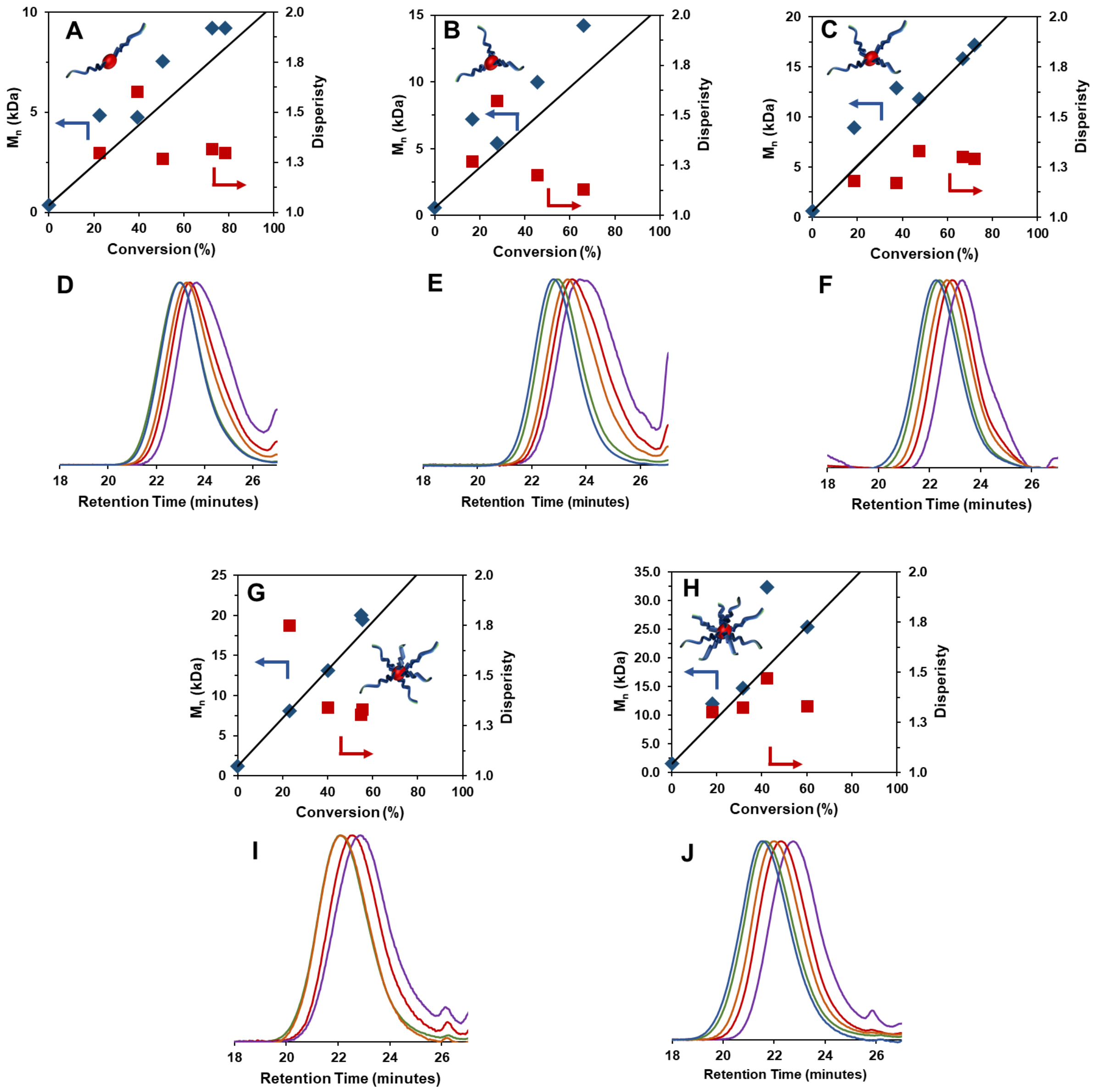


Figure S13: Plots of M_n (blue diamonds), dispersity (red squares) and theoretical M_n (black line) versus conversion for (A) linear polymer and (B) 3-arm, (C) 4-arm, (G) 6-arm, and (H) 8-arm star polymers with corresponding GPC traces shown. Conditions for polymerization are targeting 50 repeat units of MMA, [10]:[1] of [RBr$_n$]:[**1**], and 2 equivalents of DMAc to MMA by volume, using 0.67 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

PC loading studies:

<u>2-arm star:</u>

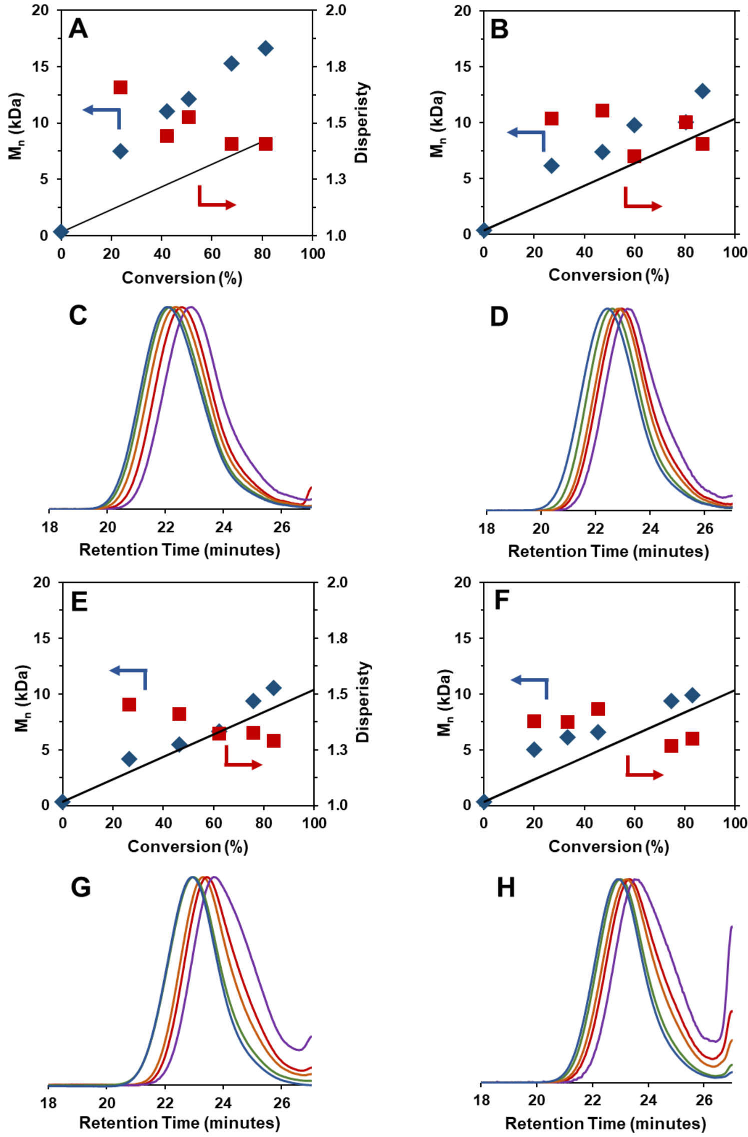


Figure S14: Plots of M_n (blue diamonds), dispersity (red squares) and theoretical M_n (black line) versus conversion for 2-arm linear polymer, using [1000]:[10] of [MMA]:[RBr_2] and (A) [10]:[0.1], (B) [10]:[0.2], (C) [10]:[1], and (D) [10]:[2] of [RBr_2]:[**1**] with corresponding GPC traces using 1:1 of MMA:DMAc by volume and 1.0 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

3-arm star:

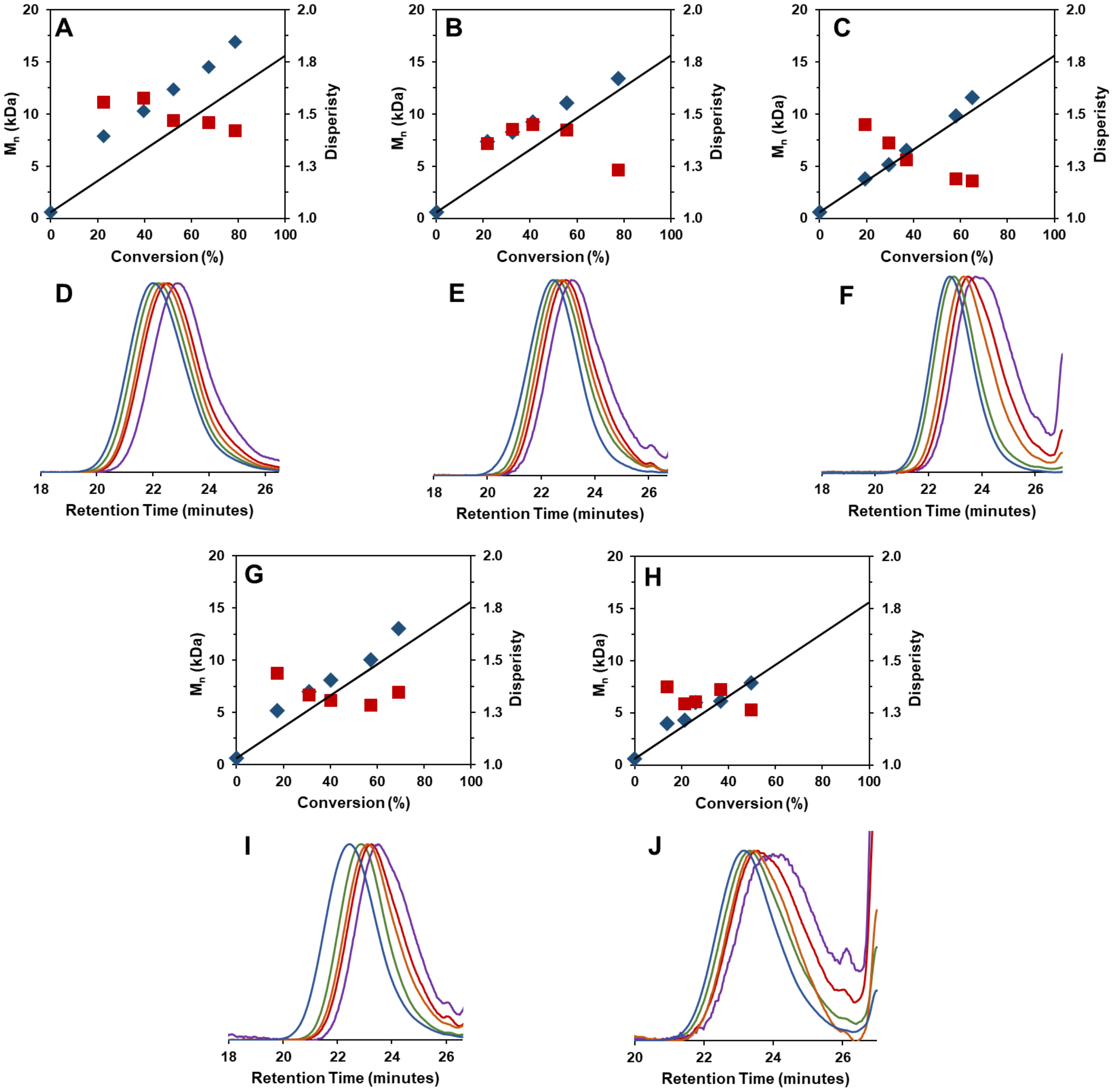


Figure S15: Plots of M_n (blue diamonds), dispersity (red squares) and theoretical M_n (black line) versus conversion for 3-arm star polymer using [1500]:[10] of [MMA]:[RBr_3] and (A) [10]:[0.15], (B) [10]:[0.3], (C) [10]:[1], (G) [10]:[1.5], and (H) [10]:[3] of [RBr_3]:[**1**] with corresponding GPC traces 1:1 of MMA:DMAc by volume and 1.0 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

4-arm star:

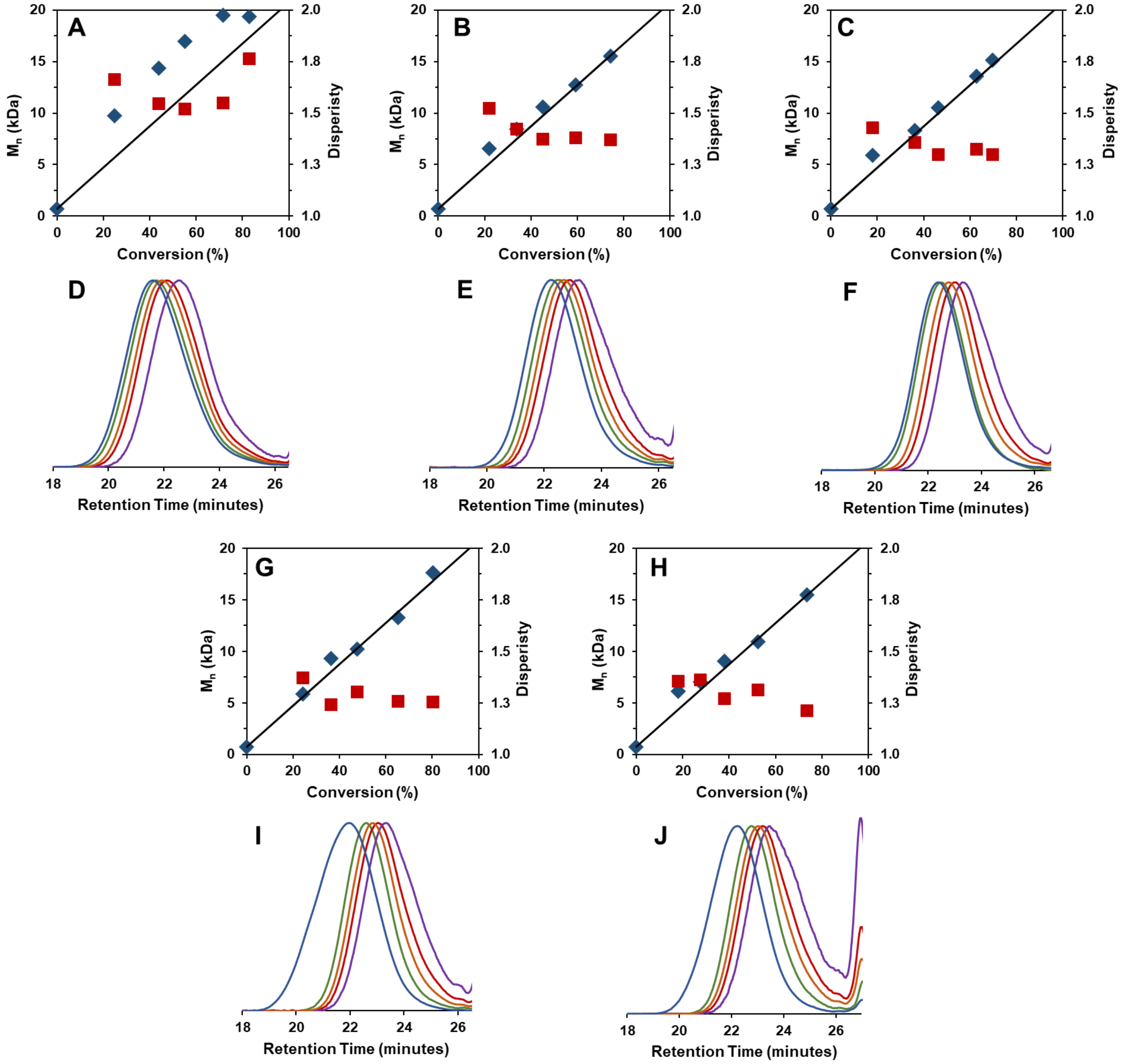


Figure S16: Plots of M_n (blue diamonds), dispersity (red squares) and theoretical M_n (black line) versus conversion for 4-arm star polymer, using [2000]:[10] of [MMA]:[RBr_4] and (A) [10]:[0.15], (B) [10]:[0.3], (C) [10]:[1], (G) [10]:[1.5], and (H) [10]:[3] of [RBr_4]:[**1**] with corresponding GPC traces 1:1 of MMA:DMAc by volume and 1.0 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

<u>6-arm star:</u>

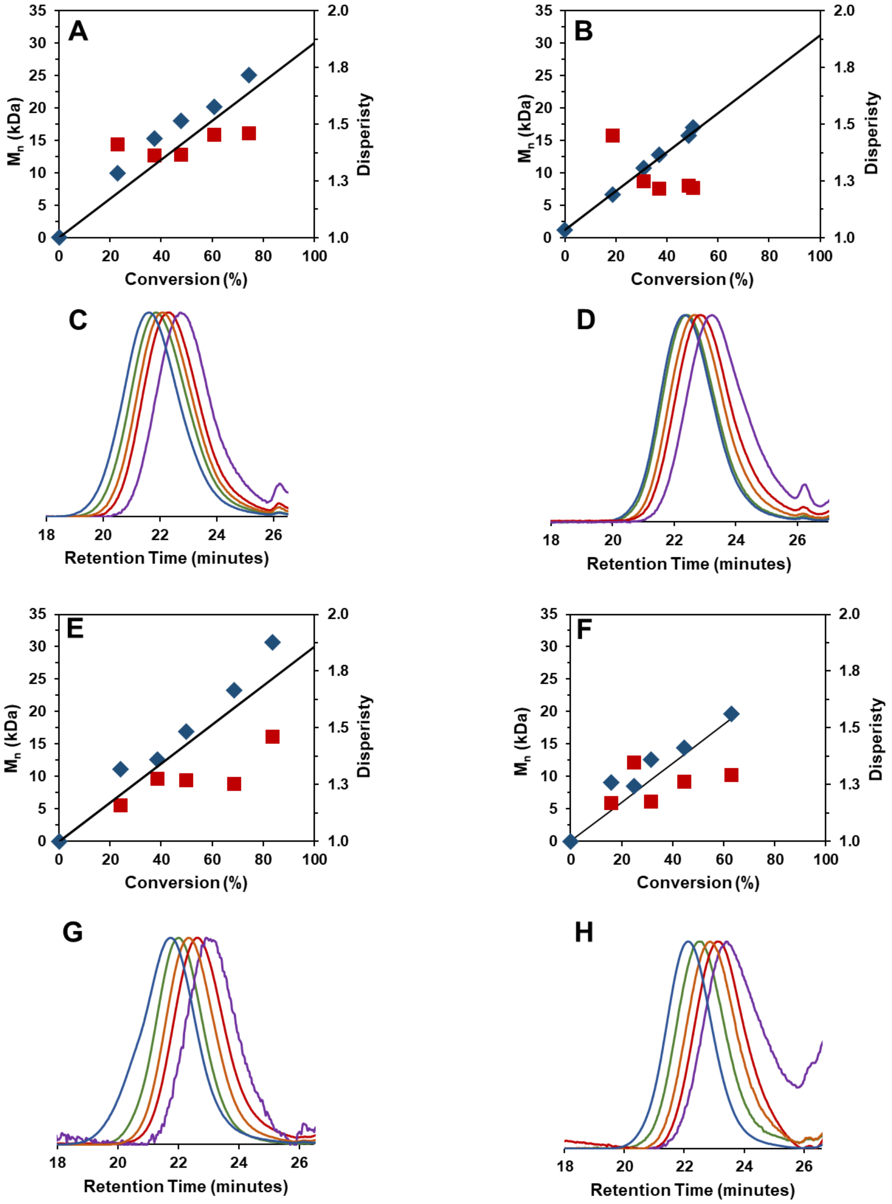


Figure S17: Plots of M_{n} (blue diamonds), dispersity (red squares) and theoretical M_{n} (black line) versus conversion for 6-arm star polymer, using [3000]:[10] of [MMA]:[RBr$_6$] and (A) [10]:[0.6], (B) [10]:[1], (C) [10]:[3], and (D) [10]:[6] of [RBr$_6$]:[**1**] with corresponding GPC traces using 1:1 of MMA:DMAc by volume and 1.0 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

8-arm star:

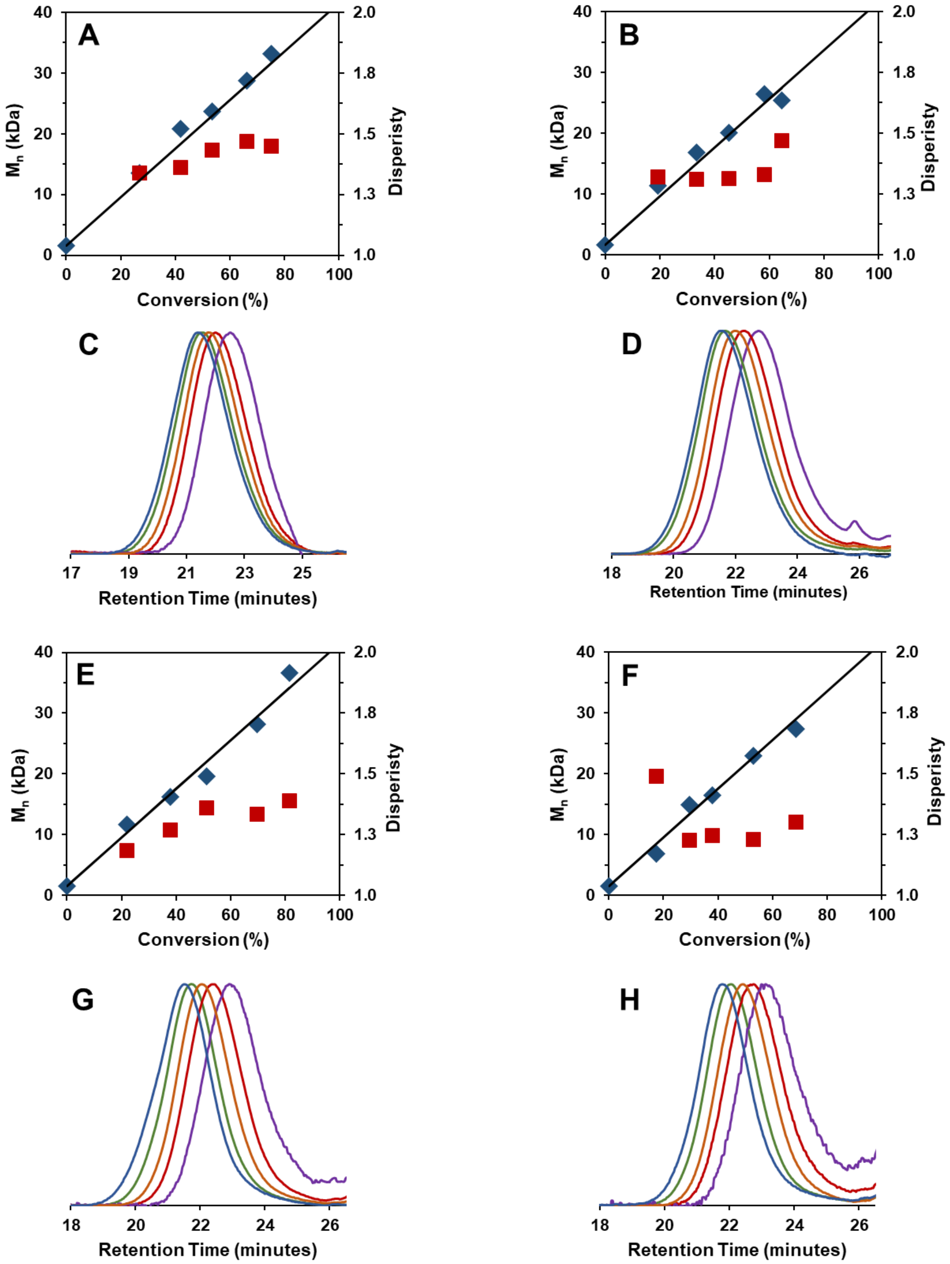


Figure S18: Plots of M_n (blue diamonds), dispersity (red squares) and theoretical M_n (black line) versus conversion for 8-arm star polymer using [4000]:[10] of [MMA]:[RBr_8] and (A) [10]:[0.8], (B) [10]:[1], (C) [10]:[4], and (D) [10]:[8] of [RBr_8]:[**1**] with corresponding GPC traces using 1:1 of MMA:DMAc by volume and 1.0 mL of MMA. An additional 1.0 mL of DMAc was added at 3 hours. Polymerizations are irradiated by white LEDs.

Photocatalyst Loading Summary Table

Table S4: Overview of results of PMMA star polymer synthesis after 8 hours using O-ATRP.[a]

# arms	[MMA]:[RBr$_n$]:[PC]	Conv. (%)[b]	$M_{n\ (actual)}$ (kDa)[b]	$Đ$ (M_w/ M_n)[b]	I^* (%)[b]
2	[1000]:[10]:[2]	83	9.8	1.30	88
	[1000]:[10]:[1]	84	8.8	1.29	83
	[1000]:[10]:[0.2]	87	12.8	1.40	71
	[1000]:[10]:[0.1]	81	16.7	1.41	51
3	[1500]:[10]:[3]	50	7.9	1.26	103
	[1500]:[10]:[1.5]	69	13.0	1.35	84
	[1500]:[10]:[1]	65	11.6	1.18	89
	[1500]:[10]:[0.3]	78	13.4	1.23	91
	[1500]:[10]:[0.15]	79	16.9	1.42	73
4	[2000]:[10]:[4]	74	15.5	1.21	100
	[2000]:[10]:[2]	80	17.6	1.25	95
	[2000]:[10]:[1]	70	15.1	1.30	97
	[2000]:[10]:[0.4]	74	15.5	1.37	100
	[2000]:[10]:[0.2]	83	19.4	1.76	90
6	[3000]:[10]:[6]	63	19.7	1.29	96
	[3000]:[10]:[3]	84	30.7	1.46	82
	[3000]:[10]:[1]	50	17.1	1.22	95
	[3000]:[10]:[0.6]	74	25.1	1.46	89
8	[4000]:[10]:[8]	69	27.3	1.30	106
	[4000]:[10]:[4]	82	36.6	1.39	93
	[4000]:[10]:[1]	60	25.4	1.33	101
	[4000]:[10]:[0.8]	75	33.1	1.45	96

[a] All experiments employ a targeted degree of polymerization of 50 for each arm, using 1 equivalent of DMAc to MMA by volume, with 2 mL of reaction volume total. [b] See footnote for Table S2 for full details.

References

1. M. D. Ryan, R. M. Pearson, T. A. French, G. M. Miyake, *Macromolecules,* 2017, **50,** 4616-4622.