Supplementary Information

Tuning Ligand Concentration in Cu(0)-RDRP: A Simple Approach to Control Polymer Dispersity.

Takanori Shimizu,[±,a,b] Nghia P. Truong,[±,a] Richard Whitfield*[,a] and Athina Anastasaki*[,a]

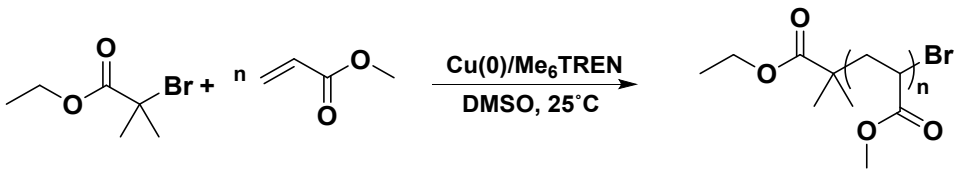
[a]Laboratory of Polymeric Materials, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland.

[b]Science & Innovation Center, Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aoba-ku, Yokohama-shi, Kanagawa 227-8502, Japan.

Contents

Cu(0)-RDRP to Control the Dispersity of PMA

Additional Data



Scheme S1: Schematic representation of poly(methyl acrylate) synthesis.

Understanding Dispersity Control

General Procedures

Kinetic Experiment: [MA]:[EBiB]:[Me_6TREN]=100:1:0.18

In a 5 mL vial, 2 mL of DMSO, 2 mL of MA (22.4 mmol, 100 eq.) and 10.7 µL of Me_6TREN (0.040 mmol, 0.18 eq.) were added. EBiB (32.6 µL, 0.224 mmol, 1 eq.) was transferred into the reaction vessel via microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 10 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, before it was sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was stirred at 200 rpm and reaction proceeded at 25 °C. Samples were periodically taken and analyzed via ^{1}H NMR and SEC.

Kinetic Experiment: [MA]:[EBiB]:[Me_6TREN]=100:1:0.00075

In a 5 mL vial, 2 mL of DMSO, 2 mL of MA (22.4 mmol, 100 eq.) and 0.045 µL of Me_6TREN (0.17 µmol, 0.00075 eq. via a stock solution) were added. EBiB (32.6 µL, 0.224 mmol, 1 eq.) was transferred into the reaction vessel via microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 10 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, before it was sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was stirred at 200 rpm and reaction proceeded at 25 °C. Samples were periodically taken and analyzed via ^{1}H NMR and SEC.

Additional Data

Table S1: ^{1}H NMR and SEC analysis of PMA prepared by Cu(0)-RDRP with various concentrations of ligand.[a]

Entry	[Me_6TREN]/[I]	t_0 DP by NMR[b]	Time (h)	Conversion (%)[b]	$M_{n\,(Theo.)}$ (Da)	$M_{n\,(SEC)}$[c]	$M_{w\,(SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	0.18	96	3	97	8200	12500	13200	12600	1.06
2	0.06	93	3	96	7900	11800	12400	12100	1.05
3	0.02	102	8	77	7000	9400	10000	9800	1.07
4	0.005	100	24	70	6200	8400	9700	9700	1.16
5	0.0025	102	22	64	5800	7500	9800	9900	1.31
6	0.00125	93	22	62	5200	7700	12200	12100	1.58
7[d]	0.0010	80	22	65	4700	6500	10400	10000	1.59
8	0.000625	98	22	48	4300	8900	15700	15000	1.76

[a] All reactions were performed on a 1mL monomer scale with the volume ratio of DMSO to MA maintained at 1:1. [b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC. [d] DP100 was targeted for all entries except in entry 7 where the target DP was adjusted to 80, so to provide an M_p alignment.

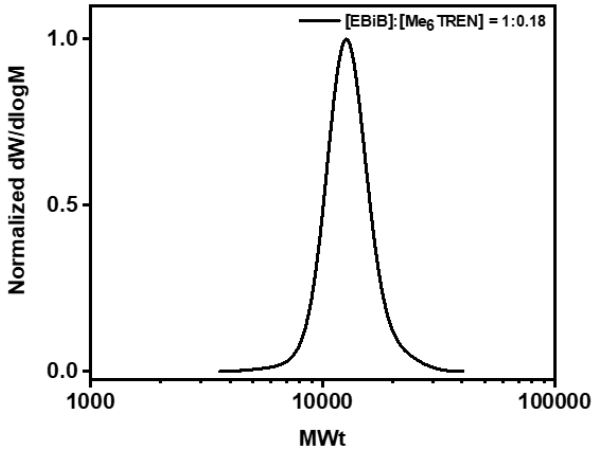


Figure S1: SEC analysis of low dispersity PMA prepared by Cu(0)-RDRP with 0.18 equivalents of ligand w.r.t initiator.

Table S2: Kinetic analysis of PMA prepared by Cu(0)-RDRP with 0.18 equivalents of ligand w.r.t initiator.[a]

[MA]:[EBiB]:[Me_6TREN]	Time (min)	Conversion (%)[b]	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$[c]	$M_{n\ (SEC)}$[c]	$Đ$[c]	*% initiator consumed*[d]
100:1:0.18	0	3	500	-	-	-	42
	4	15	1500	2300	2400	1.06	100
	8	40	3600	5100	5800	1.13	100
	12	57	5100	7100	7700	1.09	100
	16	67	6000	8400	9000	1.08	100
	20	73	6500	9100	9900	1.08	100
	28	78	6900	9900	10700	1.08	100
	36	82	7300	10300	11200	1.09	100

[a] The volume ratio of DMSO to MA was maintained at 1:1 for all entries. The target DP was 100 [b] Conversion was measured by ^{1}H NMR [c] Molecular weight and dispersity values were determined by SEC. [d]Calculated from NMR data shown in Figure S3.

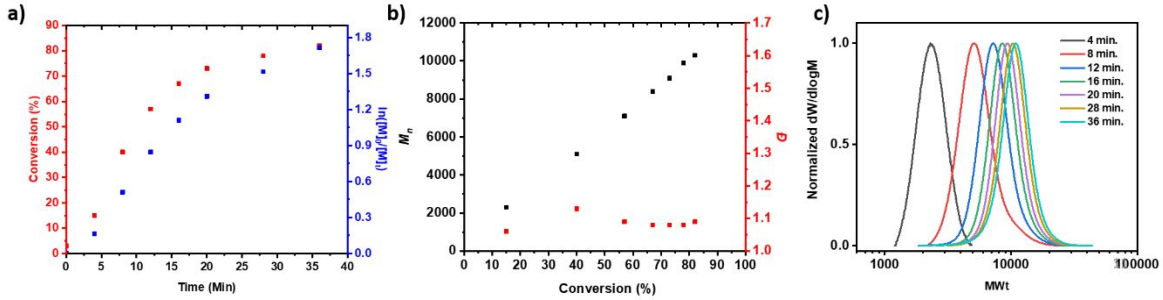


Figure S2: Kinetic data illustrating a) the evolution of conversion with time, b) the evolution of molecular weight and dispersity with reaction conversion and c) SEC data for each data point. Reaction conditions were a ratio of [MA]:[EBiB]:[Me_6TREN] = 100:1:0.18, 10cm of Cu(0) wire and 1:1 volume ratio of monomer to solvent.

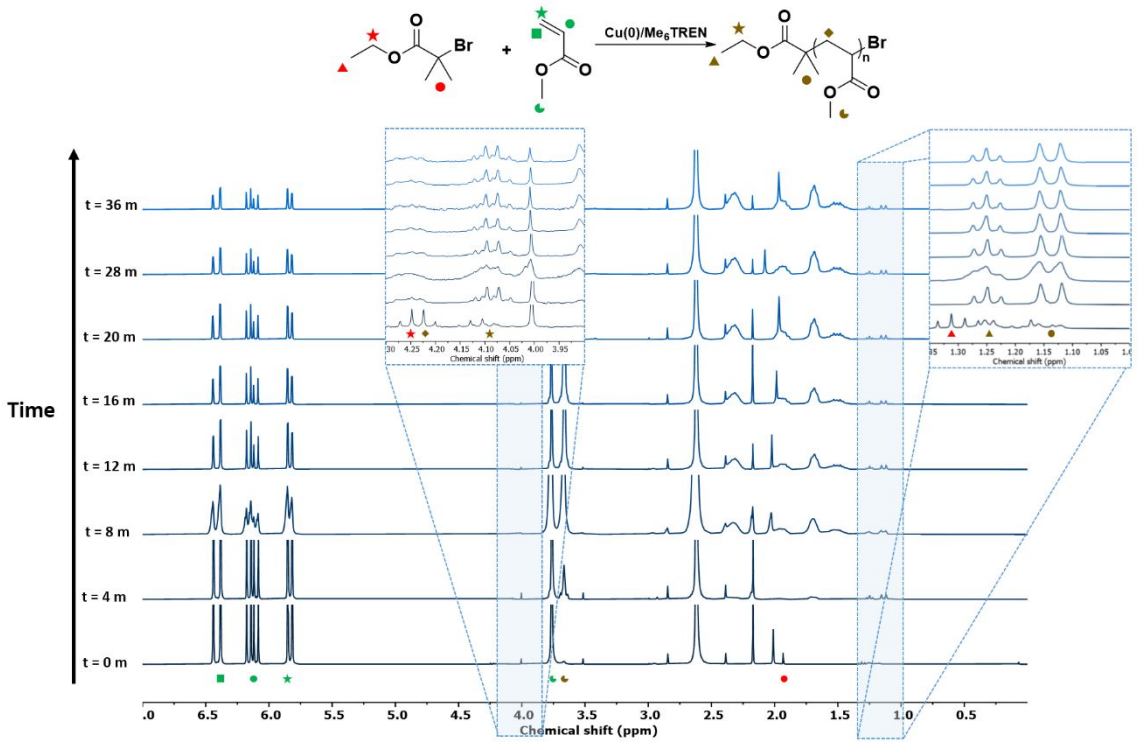


Figure S3: Kinetic ^{1}H NMR data for the synthesis of low dispersity PMA. This corresponds to the kinetic data in Figure S2.

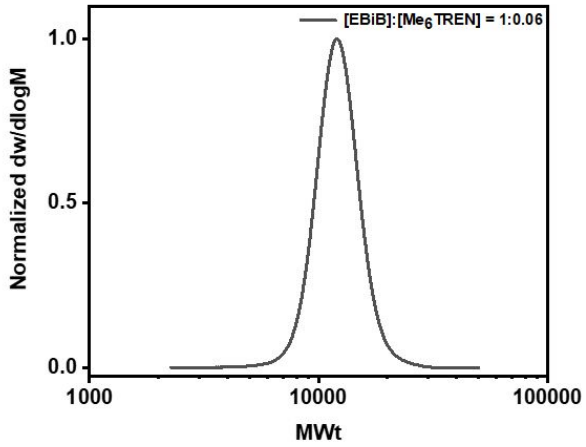


Figure S4: SEC analysis of PMA prepared by Cu(0)-RDRP with 0.06 equivalents of ligand with respect to initiator.

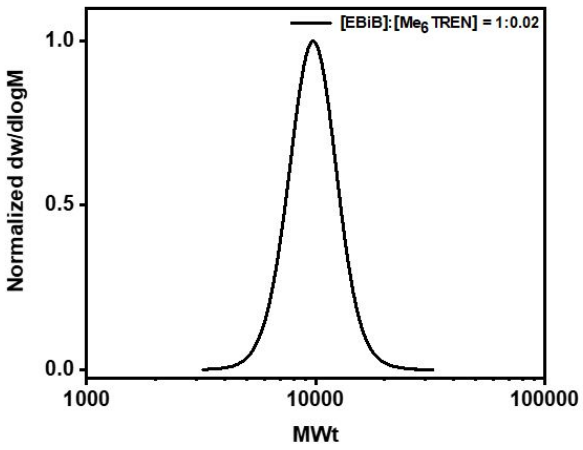


Figure S5: SEC analysis of PMA prepared by Cu(0)-RDRP with 0.02 equivalents of ligand with respect to initiator.

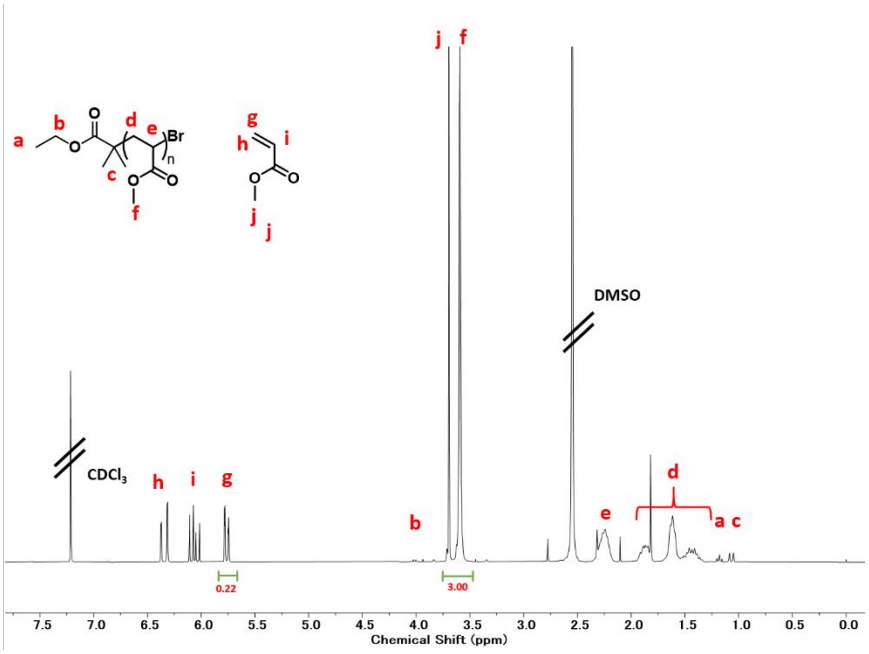


Figure S6: ^{1}H NMR measurement illustrating how the monomer conversion was calculated. This example is for the synthesis of PMA using 0.02 equivalents of ligand with respect to initiator. The calculated conversion was 82%.

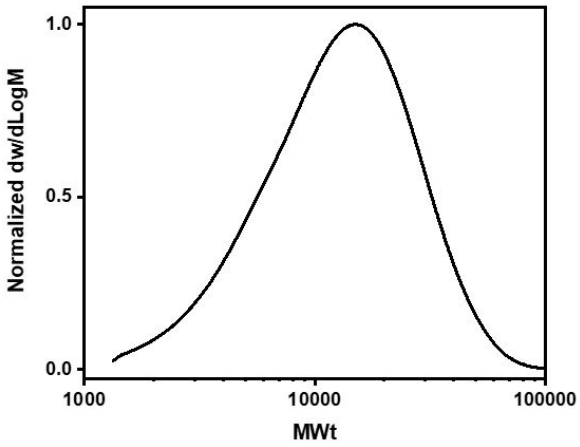


Figure S7: SEC analysis of PMA prepared by Cu(0)-RDRP with [MA]:[EBiB]:[Me_6TREN]=100:1:0.000625. The final M_n was 8900 and the dispersity was 1.76.

Table S3: ^{1}H NMR and SEC analysis illustrating the effect of scaling the preparation of PMA by Cu(0)-RDRP.[a]

Entry	[Me_6TREN]/[I]	Cu(0) wire length	t_0 DP by NMR[b]	Time (h)	Conv. (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	0.00125	5cm	93	24	62	5200	7700	12200	12100	1.58
2	0.00125	10cm	96	24	53	4600	6800	9600	9600	1.40
3	0.00075	10cm	91	24	55	4500	6500	10300	10200	1.58

[a] All reactions were performed with the volume ratio of DMSO to MA maintained at 1:1 and a target DP of 100 [b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC.

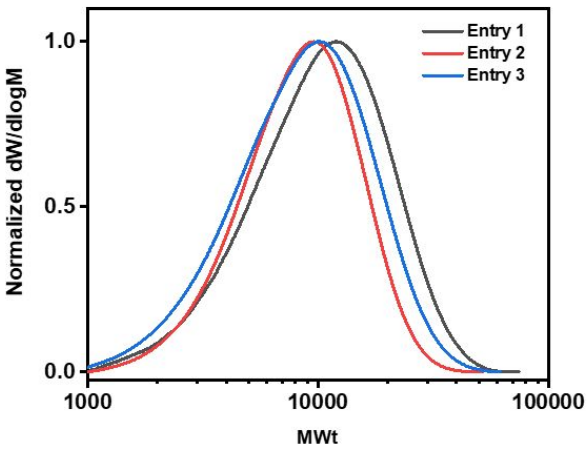


Figure S8: SEC analysis of PMA prepared by Cu(0)-RDRP to illustrate the optimization of scaling from 1 mL to 2 mL of monomer. Black, red and blue traces correspond to entry numbers in Table S3.

Table S4: Kinetic analysis of PMA prepared by Cu(0)-RDRP with 0.18 equivalents of ligand w.r.t initiator.[a]

[MA]:[EBiB]:[Me_6TREN]	Time (h)	Conversion (%)[b]	$M_{n\,(Theo.)}$	$M_{n\,(SEC)}$[c]	$M_{n\,(SEC)}$[c]	$Đ$[c]	% initiator consumed[d]
	2	7	800	6800	10900	1.60	9
	4	14	1300	5800	9500	1.65	25
	6	24	2100	5500	8600	1.65	43
100:1:0.00075	8	33	2800	5200	8400	1.62	74
	10	37	3200	5200	8500	1.62	95
	12	42	3600	5600	8800	1.55	100
	24	61	5100	7100	10800	1.51	100

[a] The volume ratio of DMSO to MA was maintained at 1:1 and 10 cm of Cu(0) wire was utilized. The target DP was 100. [b] Conversion was measured by ^{1}H NMR [c] Molecular weight and dispersity values were determined by SEC. [d]Calculated from NMR data shown in Figure 3.

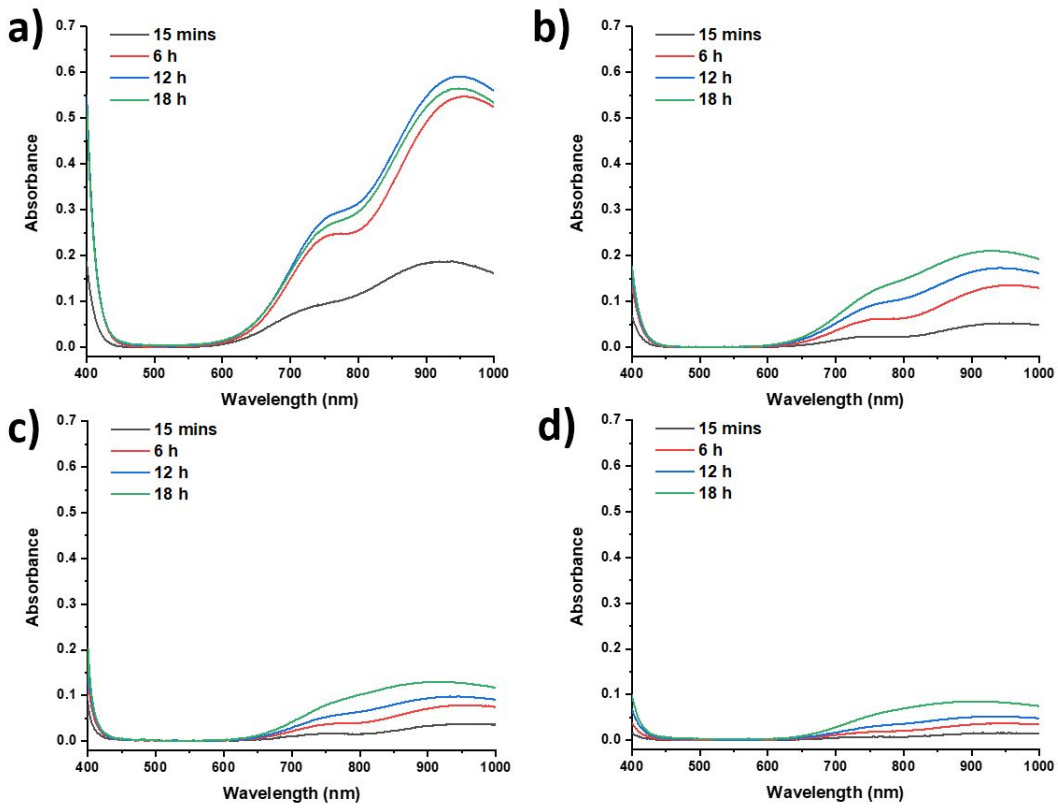


Figure S9: UV-Vis data with various concentrations of ligand at various times. In all experiments reaction concentrations were comparable to those in Figure 1, with a) 0.02 b) 0.005 c) 0.0025 and d) 0.00125 equivalents of Me_6TREN with respect to initiator. All reactions were performed in the absence of monomer.

End-Group Fidelity Analysis

General Procedures

Synthesis of low dispersity PMA: [MA]:[EBiB]:[Me_6TREN]=20:1:0.02

In a 5 mL vial, 1mL of DMSO, MA (1 mL, 11.2 mmol, 20 eq.) and Me_6TREN (3.0 µL, 0.012 mmol, 0.02 eq.) were added. EBiB (81.8 µL, 0.56 mmol, 1 eq.) was transferred into the reaction vessel via microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was allowed to proceed at 25°C, with stirring rate set at 200 rpm. Samples were taken and analysed via ^{1}H NMR and SEC. Once reaction was complete the crude reaction mixture was subsequently diluted in ethyl acetate prior to extraction three times with sodium bromide aqueous solution, thus removing copper salts. Magnesium sulfate was added to the remaining reaction mixture to remove water and then the mixture was filtered. The organic phase was then diluted with acetone (6.0 mL) and then concentrated by blowing with air. This process was repeated a total of three times and the final polymer was isolated by drying in vacuum oven at 25 °C overnight.

Synthesis of high dispersity PMA: [MA]:[EBiB]:[Me_6TREN]=20:1:0.00075

A stock solution of 6.6 µL of Me_6TREN was prepared in 5 mL of DMSO. In a 5 mL vial, 0.1 mL of the stock solution (Me_6TREN 0.112 µL, 0.45 µmol, 0.00075 eq.), 0.9 mL of DMSO and MA (1 mL, 11.2 mmol, 20 eq.) were added. EBiB (81.8 µL, 0.56 mmol, 1 eq.) was transferred into the reaction vessel via microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was allowed to proceed at 25°C, with stirring rate set at 200 rpm. Samples were taken and analysed via ^{1}H NMR and SEC. Once reaction was complete the crude reaction mixture was subsequently diluted in ethyl acetate prior to extraction three times with sodium bromide aqueous solution, thus removing copper salts. Magnesium sulfate was added to the remaining reaction mixture to remove water and then the mixture was filtered. The organic phase was then diluted with acetone (6.0 mL) and then concentrated by blowing with air. This process was repeated a total of three times and the final polymer was isolated by drying in vacuum oven at 25 °C overnight.

Additional Data

Table S5: ^{1}H NMR and SEC analysis of low and high dispersity PMA prepared by Cu(0)-RDRP for MALDI-ToF-MS.[a]

Entry	[Me_6TREN]/[I]	Time (h)	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	0.02	8	93	1800	2300	2500	2500	1.08
2[d]	0.00075	23	62	1300	2000	3000	2500	1.53

[a] All reactions were performed with the volume ratio of DMSO to MA maintained at 1:1 and a target DP of 20 [b] Conversion was measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC. [d] a small amount of the distribution is excluded at low molecular weight so the true dispersity value is larger than 1.53.

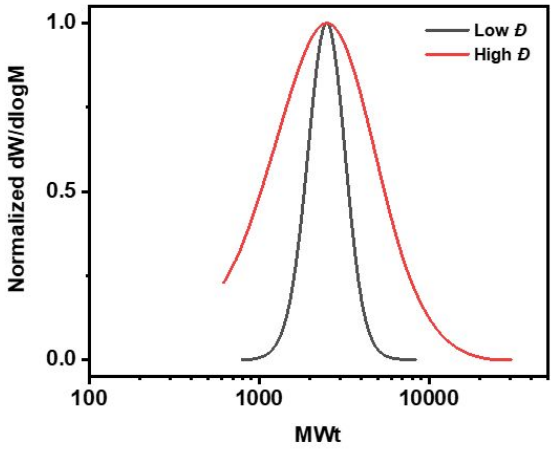


Figure S10: SEC analysis of low and high dispersity PMA prepared by Cu(0)-RDRP for MALDI-ToF-MS.

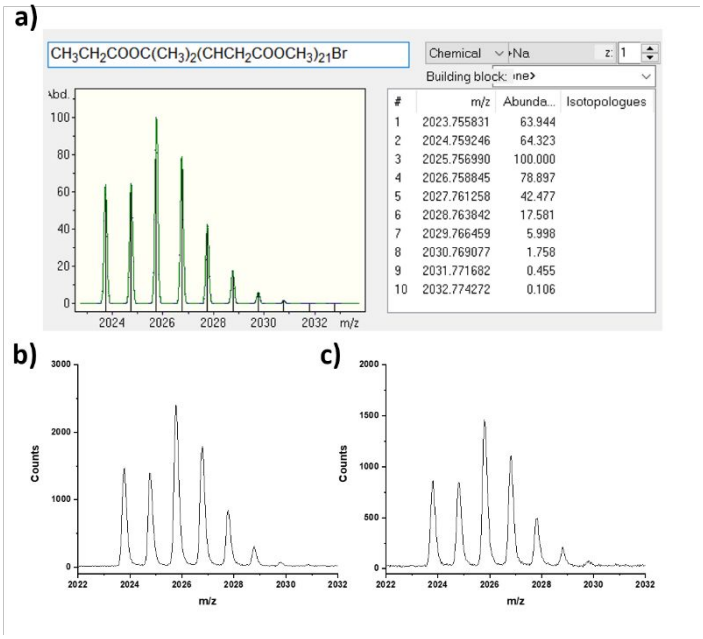


Figure S11: Isotope pattern analysis of PMA used for MALDI-ToF-MS measurements where a) is the simulated isotope pattern and b) and c) show the isotope pattern of low and high dispersity polymers prepared by Cu(0)-RDRP (data corresponding to that presented in Figure 3).

Block Copolymer Synthesis
General Procedures

Synthesis of P(MA-*b*-BA)

PMA macroinitiator was prepared as described in General Procedure 2 of the main manuscript.

A stock solution of 2.53 µL of Me_6TREN was prepared in 1 mL of DMSO. In a 5 mL vial, the PMA macroinitiator (24.1 mg, DP = 51, 5.26 µmol, 1 eq.) was dissolved in 0.5 mL of DMSO. 0.1 mL of the stock solution (Me_6TREN 0.253 µL, 0.947 µmol, 0.18 eq.) and BA (0.3 mL, 2.1 mmol, 400 eq.) were added. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was stirred at 200 rpm to proceed at 25 °C. Samples were taken and analyzed via ^{1}H NMR and SEC.

Synthesis of P(MA-*b*-PEGA)

PMA macroinitiator was prepared as described in general procedure 2 of the main manuscript.

A stock solution of 5.46 µL of Me_6TREN was prepared in 1 mL of DMSO. In a 5 mL vial, the PMA macroinitiator (52 mg, DP = 51, 11.3 µmol, 1 eq.) was dissolved in 0.5 mL of DMSO. 0.1 mL of the stock solution (Me_6TREN 0.546 µL, 2.04 µmol, 0.18 eq.) and $PEGA_{480}$ (0.3 mL, 0.681 mmol, 60 eq.) were added. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was stirred at 200 rpm to proceed at 25 °C. Samples were taken and analyzed via ^{1}H NMR and SEC.

Additional Data

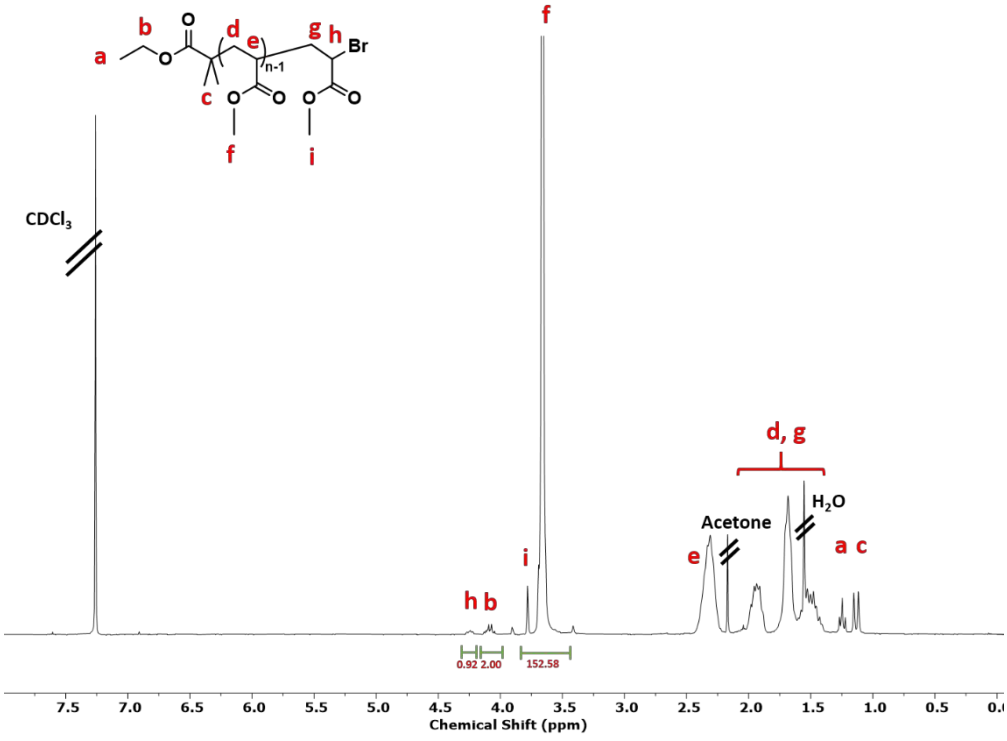
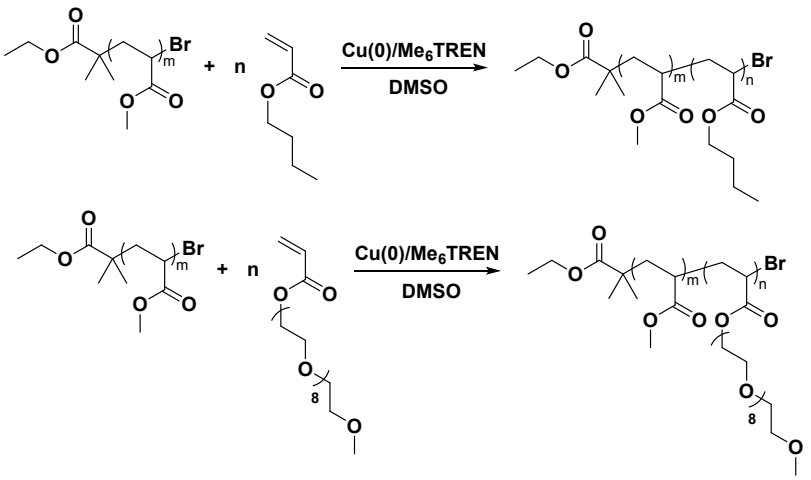


Figure S12: ^{1}H NMR of DP51 PMA macroinitiator (M_n = 4585.64 Da, $Đ$ = 1.55).

Table S6: Chain extension of a high dispersity PMA macroinitiator with various concentrations of ligand via Cu(0)-RDRP.

Entry	[Me_6TREN]/[I]	Time (h)	t_0 DP by NMR[b]	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	-	-	**51**	-	4585.64	6500	10100	9800	1.55
2	**0.18**	3	**105**	98	13400	17000	19700	16600	1.16
3	**0.005**	48	**87**	80	10600	12900	17000	16000	1.31
4	**0.0025**	48	**77**	70	9200	11900	17500	16600	1.47

[a] All chain extension reactions were performed with the volume ratio of DMSO to MA maintained at 2:1 and a target DP of 100. The same 4585 Da macroinitiator was used for all experiments. [b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC.



Scheme S2: Block copolymers prepared using a high dispersity PMA macroinitiator via Cu(0)-RDRP.

Table S7: Block copolymer formation from a high dispersity PMA macroinitiator via Cu(0)-RDRP.

Entry	Polymer	[MA]:[MI]:[Me_6TREN]	Time (h)	t_0 DP by NMR[b]	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	PMA	-	-	51	-	4585.64	6500	10100	9800	1.55
2	P(MA-*b*-BA)	400:1:0.18	3	419	53	33000	29400	35100	32700	1.19
3	P(MA-*b*-PEGA$_{480}$)	60:1 0.18	3	54	99	30500	22400	25900	23300	1.16

[a] All chain extension reactions were performed with the volume ratio of DMSO to MA maintained at 2:1 and a target DP of 100. The 4585 Da macroinitiator was used for all experiments. [b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC.

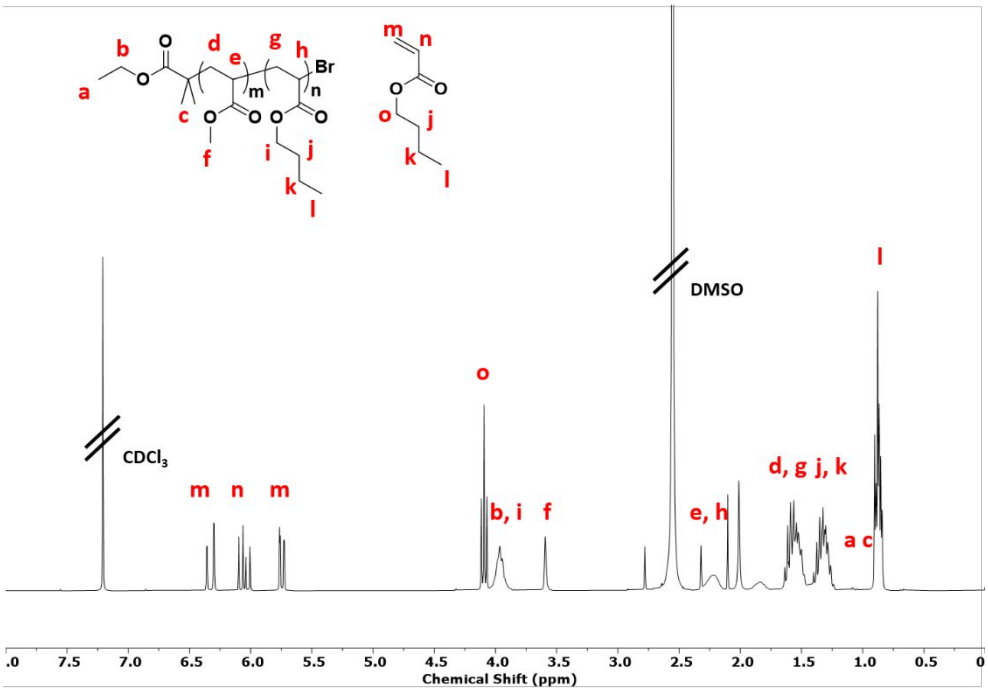


Figure S13: Crude ^{1}H NMR for the synthesis of P(MA-*b*-BA) from a high dispersity PMA macroinitiator. The spectrum illustrates a polymerization conversion of 60%.

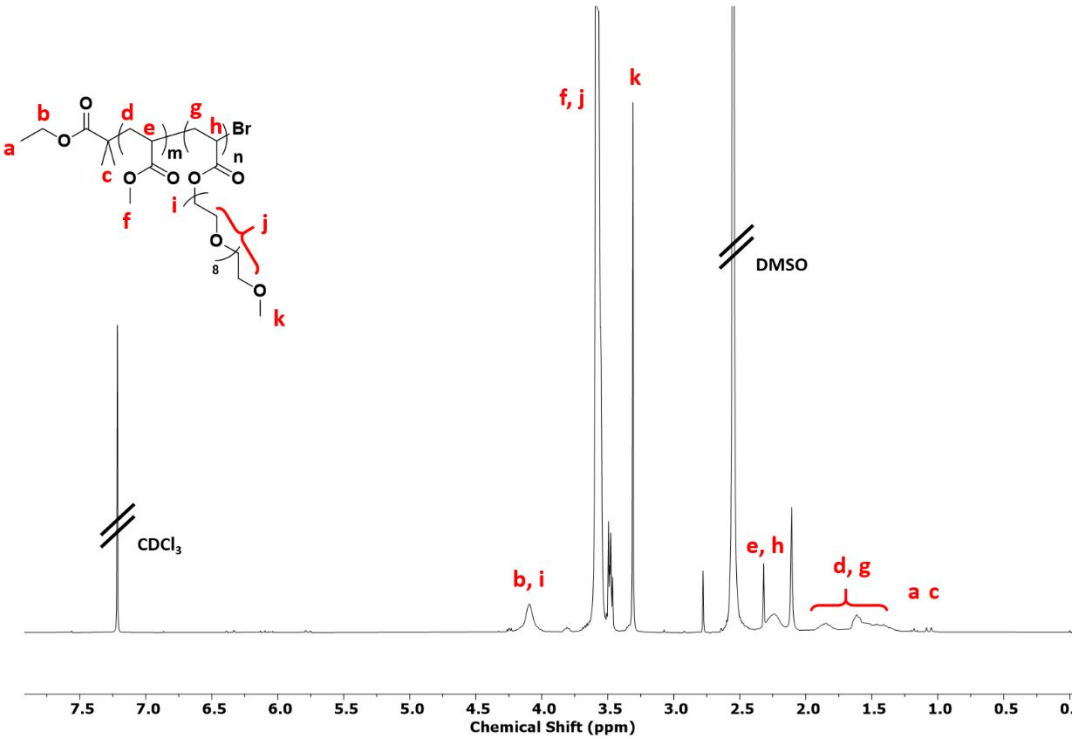


Figure S14: Crude ^{1}H NMR for the synthesis of P(MA-*b*-PEGA) from a high dispersity PMA macroinitiator. The spectrum illustrates a polymerization conversion of 99%.

Expanding the Scope of our method using PMDETA as the ligand

General Procedures

Synthesis of dispersity controlled PMA

A stock solution of 4.7 µL of PMDETA was prepared in 1 mL of DMSO. In a 5 mL vial, 0.1 mL of the stock solution (0.47 µL, 2.2 µmol, 0.02 eq.), 0.9 mL of DMSO and MA (1 mL, 11.2 mmol, 100 eq.) were added. EBiB (16.4 µL, 0.112 mmol, 1 eq.) was transferred into the reaction vessel via microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was stirred at 200 rpm to proceed at 25 °C. Samples were taken and analyzed via ^{1}H NMR and SEC. Subsequent experiments were performed with lower amounts of ligand to increase the dispersity. For example, reactions were performed with 0.005 equivalents of ligand (25 µL of stock solution, 0.55 µmol), 0.0025 equivalents of ligand (12.5 µL of stock solution, 0.275 µmol) and 0.00125 equivalents of ligand (6.25 µL of stock solution, 0.138 µmol) yielding dispersity values of 1.40, 1.72 and 2.04.

One-Pot in situ chain extension to prepare to prepare a medium to low dispersity diblock

As a first step, PMA macroinitiator was synthesized using 0.0050 eq. of PMDETA as given above. In a separate vial, 1.5mL of DMSO, 1.5 mL of MA and 1.22 µL of PMDETA were mixed. The vial was sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. 2 mL of the mixture was transferred into the vial in which polymerization was conducted via a gas tight syringe. Consequently, the components of the reaction mixture were; 2 mL of DMSO, PMA macroinitiator (0.112 mmol, 1 eq.), MA (1mL, 11.2 mmol, 100 eq.) and PMDETA (0.47 µL , 2.2 µmol, 0.02 eq.). The reaction mixture was stirred at 200 rpm at 25 °C. Samples were taken and analyzed via ^{1}H NMR and SEC.

One-Pot Chain in situ chain extension to prepare a high to low dispersity diblock

As a first step, PMA macroinitiator was synthesized using 0.0025 eq. of PMDETA as given above. In a separate vial, 1.5mL of DMSO, 1.5 mL of MA and 1.22 µL of PMDETA were mixed. The vial was sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. 2 mL of the mixture was transferred into the vial in which polymerization was conducted via a gas tight syringe. Consequently, the components of the reaction mixture were; 2 mL of DMSO, PMA macroinitiator (0.112 mmol, 1 eq.), MA (1mL, 11.2 mmol, 100 eq.) and PMDETA (0.47 µL , 2.2 µmol, 0.02 eq.). The reaction mixture was stirred at 200 rpm at 25 °C. Samples were taken and analyzed via ^{1}H NMR and SEC.

Synthesis of dispersity controlled PS

To avoid evaporation of solvent and monomer, test tubes were used as a reaction vessel (ϕ 1.5 cm, 16 cm in length). In a test tube 0.9 mL of toluene, 0.1 mL of acetonitrile, styrene (1 mL, 8.7 mmol, 100 eq.) and PMDETA (6.6 µL, 0.032 mmol, 0.36 eq.) were added. EBP (11.3 µL, 0.087 mmol, 1 eq.) was transferred into the reaction vessel via microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the test tube, sealed with a rubber septum, and deoxygenated by bubbling with nitrogen for 15 minutes. The reaction mixture was stirred at 200 rpm at 60 °C. Samples were taken and analysed via ^{1}H NMR and SEC (final Đ = 1.16). Subsequent experiments were performed with lower amounts of ligand to

increase the dispersity. A stock solution of 11.0 µL of PMDETA was prepared in 1 mL of DMSO. Reactions were performed with 0.06 equivalents of ligand (0.1 mL of stock solution, 5.3 µmol), 0.035 equivalents of ligand (58.3 µL of stock solution, 3.1 µmol) and 0.01 equivalents of ligand (16.7 µL of stock solution, 0.89 µmol) yielding dispersity values of 1.24, 1.32 and 1.52.

Additional Data

Table S8: ^{1}H NMR and SEC analysis of PMA prepared by Cu(0)-RDRP with various concentrations of PMDETA.[a]

Entry	[PMDETA]/[I]	Time (h)	t_0 DP by NMR[b]	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	0.02	7	105	96	8900	10500	12400	11500	1.18
2	0.005	18	99	96	8200	10000	13900	12100	1.40
3	0.0025	18	97	86	7500	9000	15400	12500	1.72
4	0.00125	18	98	83	7200	21500	43600	34400	2.04

[a] All reactions were performed on a 1mL monomer scale with the volume ratio of DMSO to MA maintained at 1:1.[b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC.

Table S9: *In-situ* chain extension of a medium and a high dispersity PMA macroinitiator via Cu(0)-RDRP.

Entry	[PMDETA]/[I]	Time (h)	t_0 DP by NMR[b]	Conversion (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	$Đ$[c]
1	0.00250	26	**99**	90	7900	10800	17800	14700	1.66
2	0.02	6	-	93	15900	22700	27500	24400	1.21
3	0.005	18	**92**	97	7900	10700	14500	12500	1.35
4	0.02	6	**-**	95	16100	21600	24600	22700	1.14

[a] All chain extension reactions were performed in situ with the volume ratio of DMSO to MA maintained at 1:1 and a target DP of 100. [b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC.

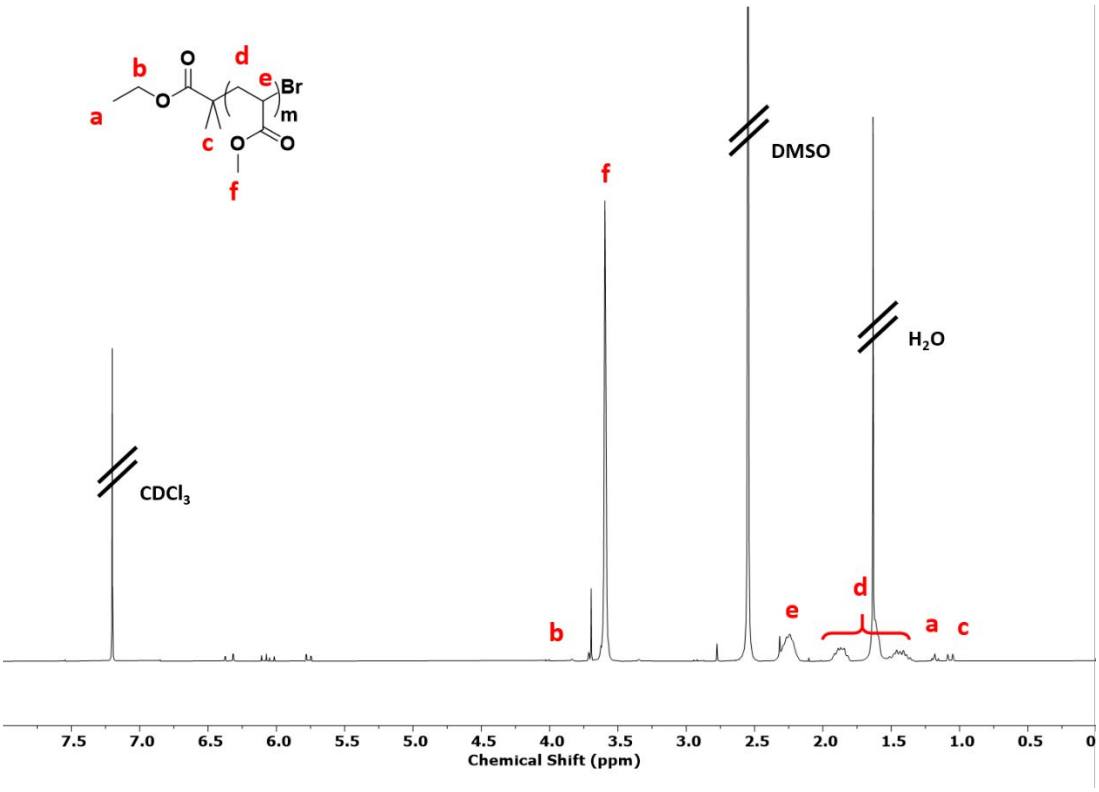


Figure S15: Example ^{1}H NMR spectrum of PMA at high conversions prior to *in-situ* chain extension.

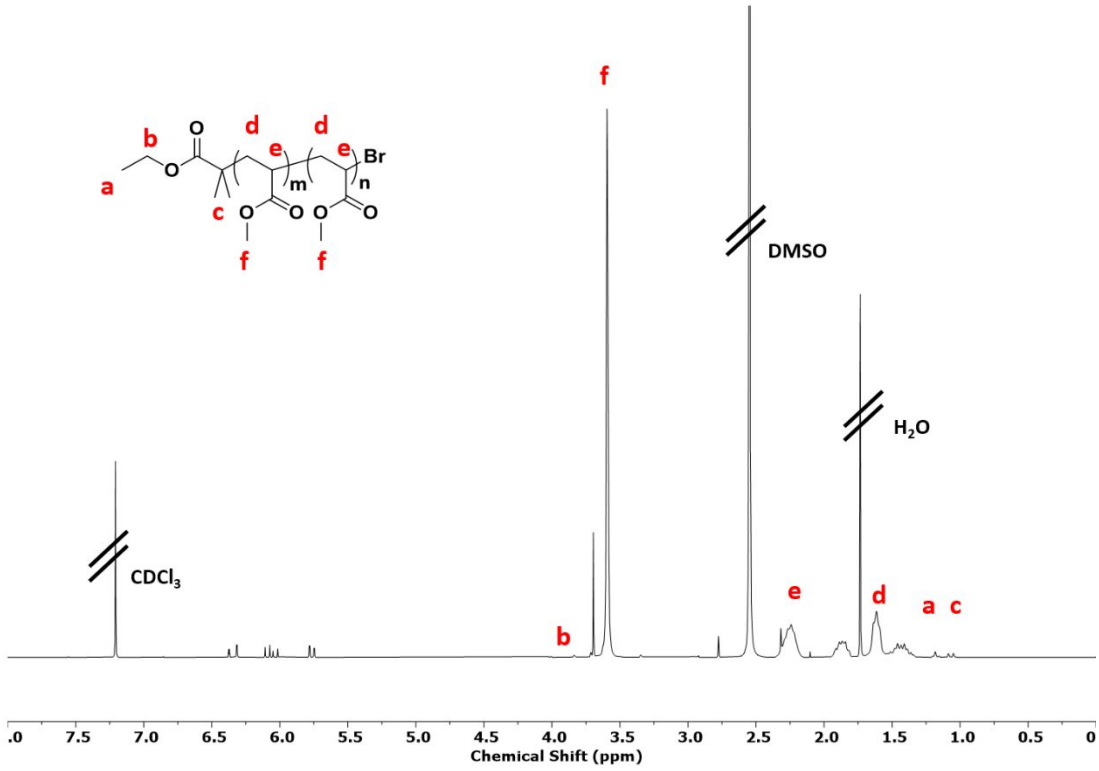


Figure S16: Example ^{1}H NMR spectrum of PMA after *in-situ* chain extension.

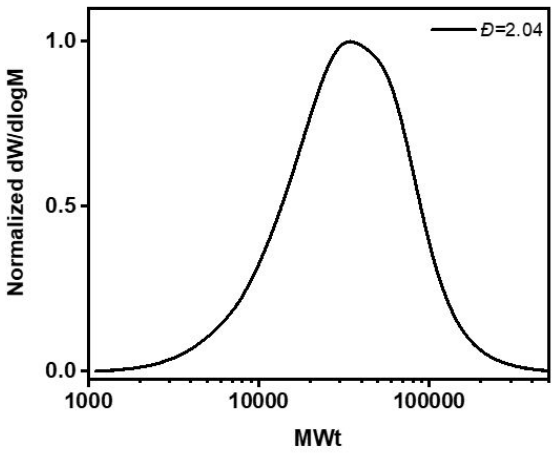
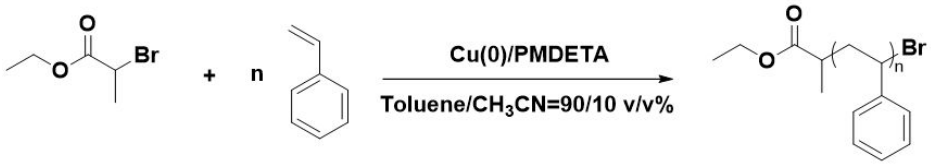


Figure S17: SEC analysis of PMA prepared by Cu(0)-RDRP with [MA]:[EBiB]:[PMDETA]=100:1:0.00125. The final M_n was 21500 and the dispersity was 2.04.



Scheme S3: Schematic representation of polystyrene synthesis.

Table S10: ^{1}H NMR and SEC analysis of PS prepared by Cu(0)-RDRP with various concentrations of PMDETA.[a]

Entry	[PMDETA]/[I]	t_0 DP by NMR[b]	Time (h)	Conv. (%)[b]	$M_{n\ (Theo.)}$ (Da)	$M_{n\ (SEC)}$[c]	$M_{w\ (SEC)}$[c]	$M_{P(SEC)}$[c]	Đ[c]
1	0.36	150	12	29	4700	6000	7000	6400	1.16
2	0.06	150	24	32	5200	5100	6300	6200	1.24
3	0.035	150	42	23	3800	4700	6100	6000	1.32
4[d]	0.01	96	24	27	2900	4300	6500	6500	1.52

[a] All reactions were performed on a 1mL monomer scale with the volume ratio of DMSO to MA maintained at 1:1. [b] Conversion and target DP at time zero were measured by ^{1}H NMR. [c] Molecular weight and dispersity values were determined by SEC. [d] DP150 was targeted for all entries except in entry 4 where the target DP was adjusted to 100, so to provide an M_p alignment.

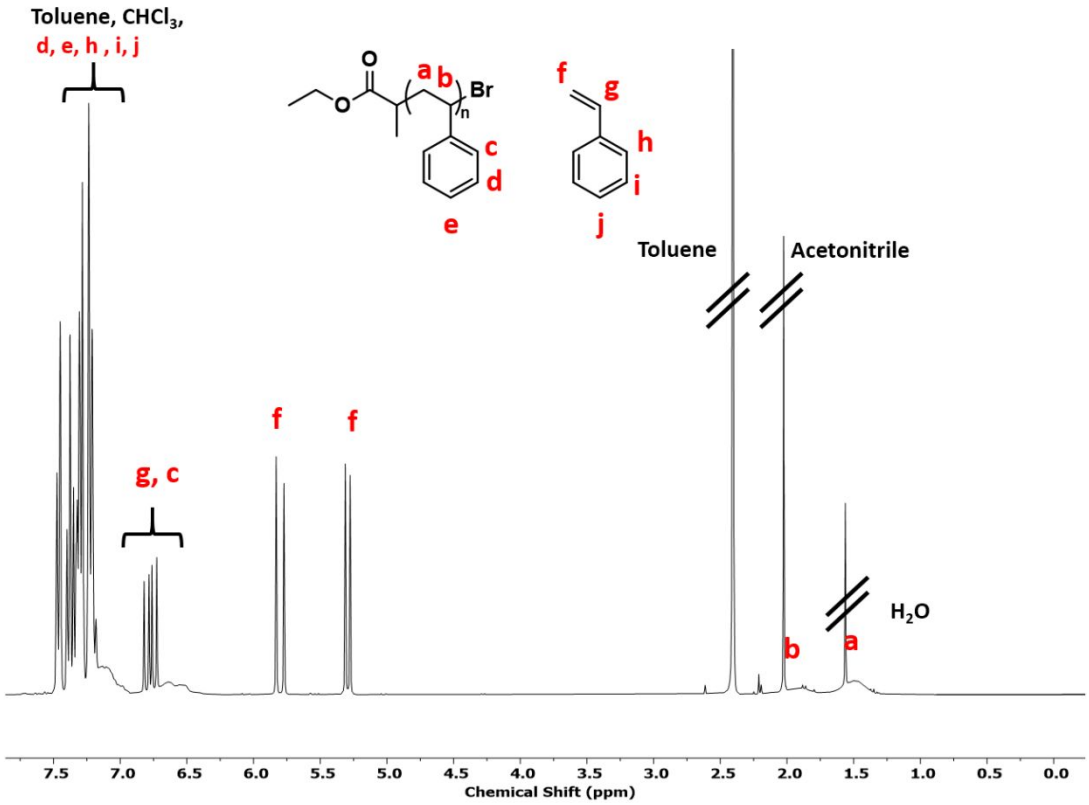


Figure S18: Crude ^{1}H NMR spectrum of PS conversion measurement.