Supporting Information

Tailoring polymer dispersity by mixing ATRP initiators

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Experimental

Materials

All chemicals were obtained from Sigma Aldrich. Methyl acrylate was purified by passing through a column of basic alumina before being used. Other chemicals were used as received. Tris-(2-(dimethylamino)ethyl)amine (Me_6Tren) was prepared following literature procedures and vacuum distilled before use.[1] The UV lamp (Type III, 36W, λmax = 360 nm) was purchased from Youmaxx.

Instrumentation

^{1}H NMR spectra were measured in $CDCl_3$ (99.8 %, ReseaChem) on a Bruker Avance-300 spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane and are referenced to residual solvent proton signals. To obtain monomer conversion for poly(methyl acrylate) (PMA) synthesis, the monomer vinyl proton peaks were integrated against combined monomer and polymer ester signals. It is noted that the error in monomer conversion calculations was <2% as determined via reproducing the same experiment three times as well as by measuring the same NMR sample multiple times utilizing different number of scans. Additionally, in the cases where slow initiation is observed, a slight deviation between the actual and the calculated theoretical molecular weight may be observed due to incomplete initiator consumption.

SEC traces were obtained from Shimadzu equipment comprising a CBM-20A system controller, an LC-20AD pump (flow rate at 1 mL min-1), a SIL-20A automatic injector, a 10.0 μm bead-size guard column (50 × 7.5 mm), followed by three KF-805L columns (300 × 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), an SPD-20A ultraviolet detector, and an RID-20A differential refractive index detector. The columns' temperature was maintained at 40 °C using a CTO-20A oven. N,N-dimethylacetamide (HPLC grade, Acros) with 0.03% w/v LiBr was used as eluent. Molecular weights were determined according to calibration with commercial narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 5000 to 1.5 × 10^6 g mol^{-1} (Agilent technology). Before injection, all samples were passed through 0.45 μm filters.

General Procedure

Synthesis of PMA utilizing photo-ATRP

A stock solution of $CuBr_2$ (1.49 mg) and Me_6Tren (10.71 µL) was prepared in DMSO (3 mL). From this stock solution, 1 mL of $CuBr_2$ (0.496 mg, 0.01 equiv.) and Me_6Tren (3.57 µL, 0.06 equiv.) were transferred along with an additional 1 mL of DMSO to a glass vial. Methyl acrylate (MA, 2 mL, 100 equiv.) and (EBP, 28.84 µL, 1 equiv.) were subsequently added and the vial was sealed with a septum, following by deoxygenation by bubbling with nitrogen for 10 minutes. Polymerization was conducted under a UV lamp and stirred at 200 rpm. Samples were taken periodically under a nitrogen blanket for ^1H NMR analysis and passed through a short column of basic alumina to remove dissolved copper salts prior to SEC analysis. Same procedure was followed for other photo-ATRP polymerizations.

Chain extension of PMA by photo-ATRP

A stock solution of $CuBr_2$ (1.49 mg) and Me_6Tren (10.71 µL) was prepared in DMSO (3 mL). From this stock solution, 1 mL of $CuBr_2$ (0.496 mg, 0.01 equiv.) and Me_6Tren (3.57 µL, 0.06 equiv.) were transferred along with an additional 1 mL of DMSO to a glass vial. Methyl acrylate (MA, 2 mL, 100 equiv.) and (EBP, 5.77 µL, 0.2 equiv. and ECP, 22.64 µL, 0.8 equiv.) were subsequently added and the vial was sealed with a septum, following by deoxygenation by bubbling with nitrogen for 10 minutes. Polymerization was conducted under a UV lamp and stirred at 200 rpm. After 2 hours of polymerization, the vial was removed from the UV lamp. The polymers were diluted into ethyl acetate and passed through neutral alumina column. The obtained polymer solution was dialyzed against acetone for 1 day. After dialysis the polymer was dried under vacuum to remove any excess of solvent. The obtained polymer, was used as a macro-initiator and the same procedure as described above was followed to obtain PMA-b-PMA.

Synthesis of PMA utilizing Cu(0)-RDRP

A stock solution of $CuBr_2$ (1.49 mg) and Me_6Tren (32.13 µL) was prepared in DMSO (3 mL). From this stock solution, 1 mL of $CuBr_2$ (0.496 mg, 0.01 equiv.) and Me_6Tren (10.71 µL, 0.18 equiv.)) were transferred along with an additional 1 mL of DMSO to a glass vial. Methyl acrylate (MA, 2 mL, 100 equiv.) and (EBP, 21.7 µL, 1 equiv.) were subsequently added. A stirring bar wrapped around with 5 cm of copper wire was added into the vial without touching the solution. The vial was then sealed with a septum, following by deoxygenation by bubbling with nitrogen for 10 minutes. After deoxygenation, the stirring bar/copper wire was immersed into the polymerization solution to start the polymerization. Polymerization was conducted at ambient conditions and stirred at 200 rpm. Samples were taken periodically under a nitrogen blanket for ^1H NMR analysis and passed through a short column of basic alumina to remove dissolved copper salts prior to SEC analysis.

In-situ chain extension of PMA utilizing Cu(0)-RDRP, yielding P(MA-*b*-MA)

A stock solution of $CuBr_2$ (1.49 mg) and Me_6Tren (32.13 µL) was prepared in DMSO (3 mL). From this stock solution, 1 mL of $CuBr_2$ (0.496 mg, 0.01 equiv.) and Me_6Tren (10.71 µL, 0.18 equiv.)) were transferred along with an additional 1 mL of DMSO to a glass vial. Methyl acrylate (MA, 2 mL, 100 equiv.) and (EBP, 11.54 µL, 0.4 equiv. and ECP, 16.98 µL, 0.6 equiv.) were subsequently added. A stirring bar wrapped around with 5 cm of copper wire was added into the vial without touching with the solution. The vial was sealed with a septum, following by deoxygenation by bubbling with nitrogen for 10 minutes. After deoxygenation, the stirring bar/copper wire was immersed into the polymerization solution to start the polymerization. Polymerization was conducted at ambient conditions and stirred at 200 rpm. After the polymerization has reached almost quantitative conversion (95%), a degassed solution of methyl acrylate (4 mL, 200 equiv.) and DMSO (4 mL), was injected into the polymerization mixture. After 2 hours, the polymerization was

stopped by exposing to air. Samples were taken periodically under a nitrogen blanket for ^{1}H NMR analysis and passed through a short column of basic alumina to remove dissolved copper salts prior to SEC analysis.

Table S1: ^{1}H NMR and SEC analysis of PMA synthesized with various ratios of EBP and ECP, via photo-ATRP (aligned by M_p value).

[MA]:[EBP]:[ECP]:[$CuBr_2$]:[Me_6Tren]	Entry	Time (min)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
100:0:1:0.01:0.06	1	120	74	6600	16000	**1.71**
100:0.05:0.95:0.01:0.06	2	40	27	2500	17200	**1.51**
100:0.2:0.8:0.01:0.06	3	80	62	5500	18000	**1.35**
300:1:0:0.01:0.06	4	115	88	22900	24200	**1.13**

Table S2: ^{1}H NMR and SEC analysis of PMA synthesized with various ratios of EBP and ECP via photo-ATRP (aligned by M_n value).

[MA]:[EBP]:[ECP]:[$CuBr_2$]:[Me_6Tren]	Entry	Time (min)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
100:0:1:0.01:0.06	1	180	92	8100	17400	**1.76**
100:0.05:0.95:0.01:0.06	2	40	27	2500	17200	**1.51**
100:0.2:0.8:0.01:0.06	3	35	47	4200	16300	**1.33**
300:1:0:0.01:0.06	4	55	52	13600	17200	**1.09**

Table S3: ^{1}H NMR and SEC analysis of kinetic of PMA synthesized with EBP via photo-ATRP.

[MA]:[EBP]:[ECP]:[$CuBr_2$]: [Me_6Tren]	Entry	Time (min)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
300:1:0:0.01:0.06	1	10	10	2800	4500	**1.23**
	2	25	21	5600	7700	**1.17**
	3	40	37	9700	12600	**1.12**
	4	55	52	13600	17200	**1.09**
	5	70	61	15900	19700	**1.08**
	6	85	70	18300	21800	**1.08**
	7	100	76	19800	23500	**1.08**
	8	115	80	20800	25200	**1.08**
	9	180	90	23500	28300	**1.08**

Table S4: ^{1}H NMR and SEC analysis of kinetic of PMA synthesized with EBP: ECP in a ration 60: 40 via photo-ATRP.

[MA]:[EBP]:[ECP]:[$CuBr_2$]: [Me_6Tren]	Entry	Time (min)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
100:0.6:0.4:0.01:0.06	1	10	10	1100	4900	**1.33**
	2	25	29	2700	7800	**1.29**
	3	40	44	4000	10700	**1.23**
	4	55	56	5100	13100	**1.21**
	5	70	65	5800	14500	**1.21**
	6	85	72	6400	15100	**1.22**
	7	100	78	7000	16100	**1.23**
	8	115	83	7400	16600	**1.23**
	9	180	94	8300	16700	**1.27**

Table S5: ^{1}H NMR and SEC analysis of kinetic of PMA synthesized with ECP via photo-ATRP.

[MA]:[EBP]:[ECP]:[$CuBr_2$]: [Me_6Tren]	Entry	Time (h)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	Đ
100:0:1:0.01:0.06	1	0.5	1	-	-	-
	2	1	5	-	-	-
	3	1.5	16	1000	14400	**1.55**
	4	2	39	3500	14800	**1.67**
	5	2.5	58	5100	15800	**1.66**
	6	3	71	6300	15800	**1.69**
	7	3.5	78	6900	16200	**1.66**
	8	4	84	7400	15800	**1.69**
	9	10	98	8600	16000	**1.70**

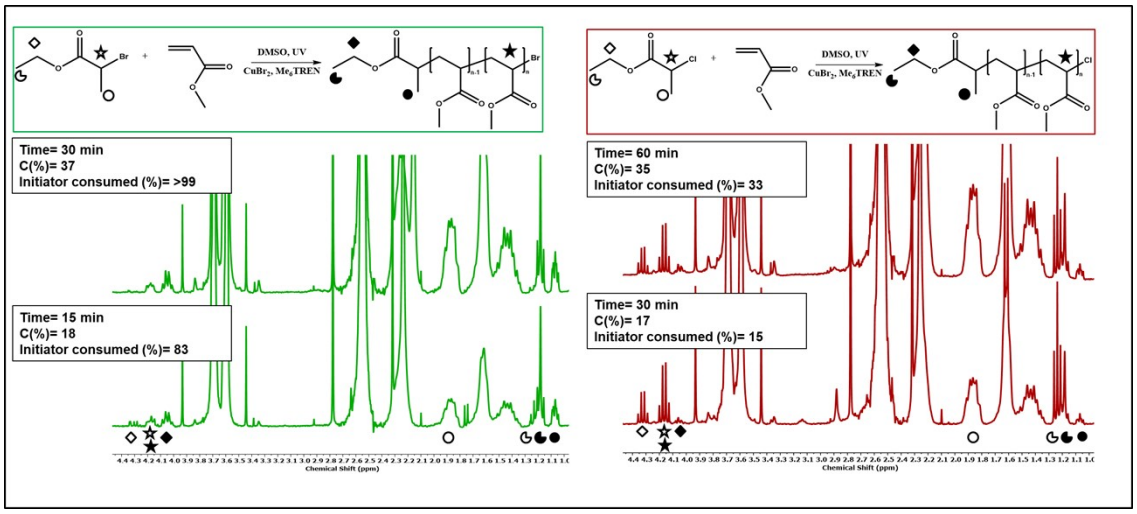

Figure S1: ^{1}H NMR-spectra showing initiator consumption during the polymerization using EBP (left/green) and ECP (right/red) as initiator**.**

Table S6: ^{1}H NMR and SEC analysis of kinetic of PMA-*b*-PMA synthesized with mixture of EBP: ECP via photo-ATRP.

Block	[MA]:[EBP]:[ECP]:[$CuBr_2$]:[Me_6Tren]	Entry	Time (h)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
B1	100:0.2:0.8:0.01:0.06	1	2	86	7600	19000	**1.49**
B2	300:0.2:0.8:0.01:0.06	2	2	77	27400	72500	**1.49**
B1	100:0.05:0.95:0.01:0.06	3	2	77	6800	20000	**1.70**
B2	300:0.05:0.95:0.01:0.06	4	2	60	22300	64000	**1.77**

Table S7: ^{1}H NMR and SEC analysis of PMA synthesized with various ratios of EBP and ECP, via Cu(0)-RDRP (aligned by M_p value).

[MA]:[EBP]:[ECP]:[$CuBr_2$]:[Me_6Tren]	Entry	Time (min)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
100:0:1:0.01:0.06	1	120	67	6000	16700	**1.67**
100:0.2:0.8:0.01:0.06	2	90	62	5500	17600	**1.52**
100:0.4:0.6:0.01:0.06	3	90	78	6900	19400	**1.40**
300:1:0:0.01:0.06	4	80	90	23400	27200	**1.12**

Table S8: ^{1}H NMR and SEC analysis of PMA macro-initiator, synthesized with a mixture of EBP: ECP, in situ chain extension synthesized with MA, via Cu(0)-RDRP.

Block	[MA]:[EBP]:[ECP]:[$CuBr_2$]: [Me_6Tren]	Entry	Time (h)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
B1	100:0.6:0.4:0.01:0.18	1	2.5	95	8400	13200	**1.22**
B2	DP200	2	2	86	23600	25600	**1.20**

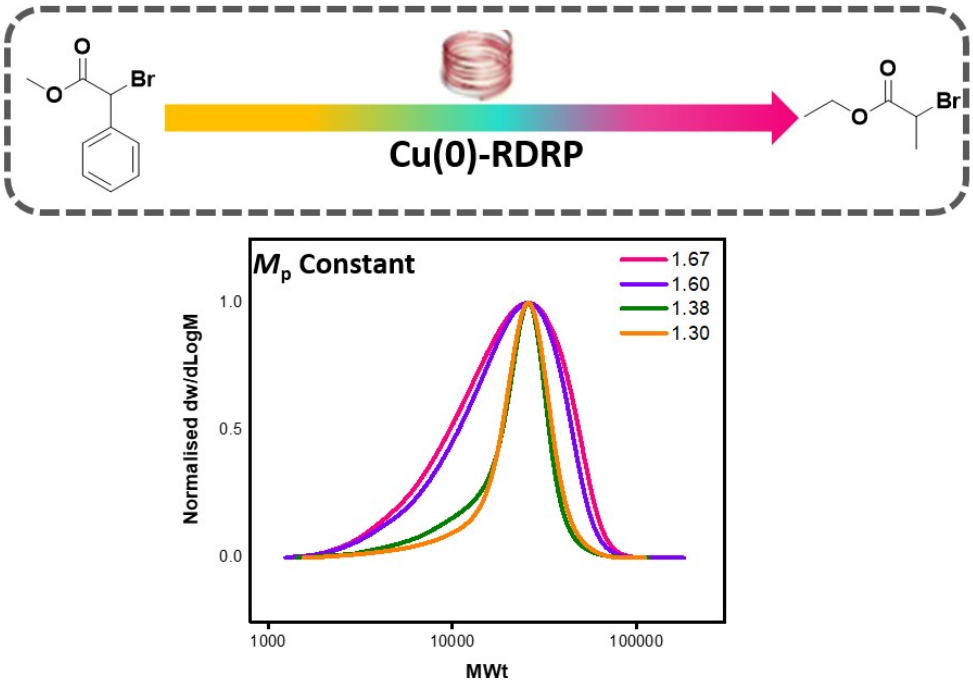

Figure S2: SEC analysis of PMMA synthesized via Cu(0)-RDRP, illustrating the variation in dispersity as MBPA and EBP are mixed in different ratios (aligned by M_p value).

Table S9: ^{1}H NMR and SEC analysis of PMMA synthesized with various ratios of MBPA and EBP, via Cu(0)-RDRP (aligned by M_p value).

[MA]:[MPBA]:[EBP]:[$CuBr_2$]:[Me_6Tren]	Entry	Time (h)	Conversion (%)	$M_{n\ (Theo.)}$	$M_{n\ (SEC)}$	$Đ$
300:1:0:0.01:0.06	1	1	10	3200	18600	**1.30**
50:0.8:0.2:0.01:0.06	2	11	90	4800	16200	**1.38**
50:0.2:0.8:0.01:0.06	3	11	85	4500	13800	**1.60**
50:1:0:0.01:0.06	4	11	82	4300	13600	**1.67**

References:

[1] Ciampolini, M.; Nardi, N., *Inorg. Chem*. **1966**, 5 (1), 41-44