Supporting information:

Tailoring Polymer Dispersity in Photoinduced Iron-Catalyzed ATRP

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Experimental

Materials

All monomers were purified through basic alumina before being used. Other chemicals were used as received. Methyl α-bromophenylacetate, (MBPA, > 97.0%) and benzyl methacrylate, (BzMA, > 98.0%) were procured from Tokyo Chemical Industries. Anisole (99%) and tetrabutylammonium bromide, (TBABr, ≥ 99%) were obtained from Sigma Aldrich. Iron(III) bromide anhydrous, (FeBr$_3$) was bought from ABCR (abcr GmbH). The blue ECO LED strip light (48 W, λ = 465mm (+/-5nm), 16.4' Spool, 36 SMD 3528 LED's/Foot) was purchased from solid Apollo Led.

Instrumentation

^{1}H nuclear magnetic resonance (NMR) spectra were measured in CDCl$_3$ (99.8 %, ReseaChem) on a Bruker Avance-300 spectrometer. Chemical shifts are given in ppm and are referenced to residual solvent proton signals. To obtain monomer conversion for poly(methyl methacrylate) (PMMA) synthesis, the monomer vinyl proton peaks were integrated against combined monomer and polymer ester signals. In addition, to obtain monomer conversion for poly(benzyl methacrylate) (BzMA) synthesis, the monomer vinyl proton peaks were integrated against combined monomer and polymer –CH$_2$ (adjacent protons to the aromatic ring) signals.

Size-exclusion chromatography (SEC) was measured on 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 was used as eluent (HPLC grade, Acros, with 0.03% w/v LiBr). 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.

MALDI-ToF mass spectrometer (MALDI-ToF-MS) was conducted using a Bruker Daltonics Ultraflex II MALDI-ToF-MS, equipped with a nitrogen laser delivering 10 ns laser pulses at 337 nm with positive ion ToF detection performed using an acceleration voltage of 25 kV. Solutions in tetrahydrofuran of 2,5-dihydroxybenzoic acid (DHB) as the matrix (40 mg. mL^{-1}), sodium trifluoroacetate as the cationization agent (1.0 mg. mL^{-1}) and sample (10 mg. mL^{-1}) were prepared. 10 µL of matrix solution was mixed with 2 µL of cationization agent solution and 10 µL of sample solution, and 0.7 µL of the mixture was applied to the target plate. Spectra were obtained in reflectron mode calibrated with a monomethoxy PEG standard (M_n = 1900).

General Procedures

Procedure 1.1: General procedure for poly(methyl methacrylate) synthesis by photoinduced Iron-catalyzed ATRP.

TBABr (2.05 mg, 0.1 equiv.) and FeBr$_3$ (1.88 mg, 0.1 equiv.) were dissolved in anisole (1mL) in a 6 mL glass vial. This solution is better to be prepared fresh for each experiment. Then, MMA (1mL, 150 equiv.) was introduced, followed by MBPA (10 µL, 1 equiv.). The vial was sealed with a septum and was degassed by bubbling with nitrogen for 5 minutes over ice. Next, the vial was placed under a homemade LED strip blue light box (48 W, λ= 465mm (+/- 5nm)). The stirring rate for all experiments was fixed at 50 rpm. After the desired reaction time the polymerization was stopped by removing the vial from blue light irradiation and opening it to air. It was sampled in order to determine the conversion *via* ^{1}H NMR. The molecular weight and dispersity were calculated by SEC measurements (samples were passed through basic alumina to removed iron prior to SEC analysis). This procedure yielded a polymer with a dispersity of *Đ~* 1.20. The same procedure was followed for all homopolymer syntheses. Nevertheless, the ratio of initiator to catalyst was gradually decreased to increase the dispersity from 1.20 to 1.80. Additionally, changing the targeted DP required an adjustment in the initiator to catalyst ratio to reach a similar dispersity.

Procedure 1.2: Procedure for P(MMA-*b*-BzMA) block copolymerization (High to Low Dispersity) by photoinduced Iron-catalyzed ATRP.

TBABr (0.06 mg, 0.002 equiv.) and FeBr$_3$ (0.0564 mg, 0.002 equiv.) were dissolved in anisole (1mL) in a 6 mL glass vial. This solution is better to be prepared fresh for each experiment. Then, MMA (1mL, 100 equiv.) was introduced, followed by MBPA addition (15 µL, 1 equiv.). The vial was sealed with a septum and was degassed with nitrogen for 5 min over ice. Next, the vial was placed under a homemade LED strip blue light box (48 W, λ = 465mm (+/-5nm)). The stirring rate for all experiments was fixed at 50 rpm. After the desired reaction time, a degassed solution of BzMA (1.76 mL, 100 equiv.), anisole (1 mL), TBABr (3.08 mg, 0.1 equiv.) and FeBr$_3$ (2.8 mg, 0.1 equiv.) was added to the vial with a degassed syringe under nitrogen

atmosphere. After the desired reaction time the polymerization was stopped by removing the vial from blue light irradiation and opening it to air. It was sampled in order to determine the conversion *via* ^{1}H NMR. The molecular weight and dispersity were calculated by SEC measurements (samples were passed through basic alumina to removed iron prior to SEC analysis). The example procedure illustrates the chain extension of high dispersity PMMA (*Đ*~ 1.61) yielding low dispersity P(MMA-*b*-BzMA) block copolymer (*Đ*~1.23). The same procedure was followed for every block copolymer synthesis, with the initiator to catalyst ratio varied depending on the targeted dispersity of each block.
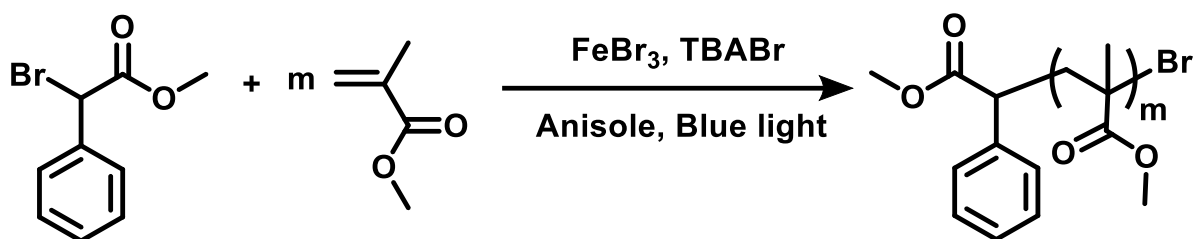

Figure S1: Schematic representation of poly(methyl methacrylate) (PMMA) prepared by photoinduced Iron-catalyzed ATRP.

Figure S2: Experimental setup of poly(methyl methacrylate) (PMMA) polymerization comprising of blue led strips inside a homemade box and a magnetic stirrer (50 rpm).

Table S1: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a low dispersity PMMA (Đ= 1.20) yielding P(MMA-*b*-BzMA) with low dispersity (Đ= 1.26) by photoinduced Fe-catalyzed ATRP.[a]

Entry	Blocks	Monomer	[Monomer]: [FeBr₃]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(Theo.)}$	$M_{P(SEC)}$	$M_{n(SEC)}$	$M_{W(SEC)}$	Đ
1	B1	MMA	150: 0.1: 0.1	4	84	12800	14500	11300	15400	**1.20**
2	B2	BzMA	100: 0.05: 0.05	0.66 (40 min)	66	24400	31000	22000	32100	**1.26**

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr₃:TBABr as the catalyst (target DP=150, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=100, volume ratio of BzMA to anisole 1: 1) and shows the additional ratio of BzMA: FeBr₃: TBABr introduced into the reaction relative to the initial MBPA concentration.[b] Conversion was calculated by ^{1}H NMR.
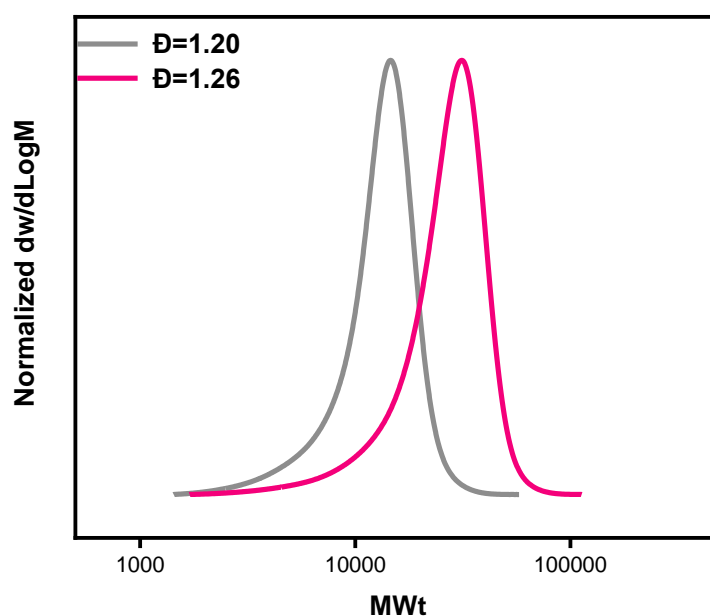

Figure S3: *In situ* chain extension of a low dispersity PMMA (Đ= 1.20) yielding P(MMA-*b*-BzMA) with low dispersity (Đ= 1.26) in the photoinduced Fe-catalyzed ATRP. Polymerization conditions are the following for the first block: [MBPA]: [MMA]: [FeBr₃]: [TBABr] = [1]: [150]: [0.1]: [0.1] and for the second block: [PMMA-Br]: [BzMA]: [FeBr₃]: [TBABr] = 1: [100]: [0.05]: [0.05].

Table S2: ^{1}H NMR and SEC analysis for the polymerization of MMA with [MBPA]: [FeBr$_3$]: [TBABr] of [1]: [0.003]: [0.003] illustrating the catalytic limit of the photoinduced Fe-catalyzed ATRP [a].

Entry	[MBPA]: [MMA]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	M$_{n(Theo.)}$	M$_{P(SEC)}$	M$_{n(SEC)}$	M$_{W(SEC)}$	Đ
1	1:150:0.003:0.003	2.5	54	8300	72600	35500	76300	2.15

[a] Polymerization was performed in anisole with MMA as the monomer, MPBA as the initiator and FeBr$_3$: TBABr as the catalyst. The targeted DP was 150. The volume ratio of anisole to MMA was maintained at 1: 1. [b] Conversion was calculated by ^{1}H NMR.
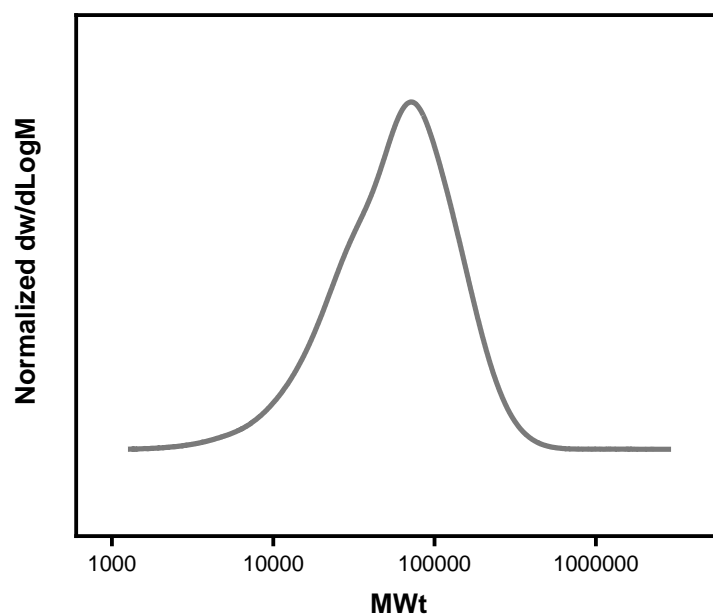

Figure S4: SEC trace for the PMMA synthesized under the following conditions: ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [150]: [0.003]: [0.003]).

Table S3: ^{1}H NMR and SEC analysis for the polymerization of MMA yielding PMMA with constant M_p at ~17500.[a]

Entry	[MBPA]: [MMA]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	M$_{n(Theo.)}$	M$_{P(SEC)}$	M$_{n(SEC)}$	M$_{W(SEC)}$	Đ
1	1: 175:**0.10:0.10**	4	80	14200	17300	13100	15800	**1.19**
2	1: 175:**0.02:0.02**	4	83	14700	17500	12300	17000	**1.35**
3	1: 175:**0.009:0.009**	2	70	12700	17500	11500	17700	**1.53**
4	1: 175:**0.006:0.006**	1	50	8900	17400	10400	20000	**1.80**

[a] all polymerizations were performed in anisole with MMA as the monomer, MPBA as the initiator and FeBr$_3$: TBABr as the catalyst. The targeted DP was 175 and the volume ratio of anisole to MMA was maintained at 1:1 in all entries. [b]Conversion was calculated by ^{1}H NMR.

Table S4: ^{1}H NMR and SEC analysis for the kinetic of PMMA with a targeted dispersity of ~1.40 under the following conditions: ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [150]: [0.015]: [0.015]).[a]

Entry	Time (min)	Conversion[b] (%)	M$_{n(Theo.)}$	M$_{P(SEC)}$	M$_{n(SEC)}$	M$_{W(SEC)}$	Đ
1	20	9	1500	--	--	--	--
2	40	25	4000	6400	4700	6600	1.40
3	60	40	6000	8400	6000	8400	1.42
4	90	58	8900	10700	7500	10700	1.42
5	120	67	10200	12000	8600	12100	1.40
6	180	84	12800	14100	10200	14000	1.38

[a] all polymerizations were performed in anisole with MMA as the monomer, MPBA as the initiator and FeBr$_3$: TBABr as the catalyst. The targeted DP was 150 and the volume ratio of anisole to MMA was maintained at 1:1 in all entries. [b]Conversion was calculated by ^{1}H NMR.
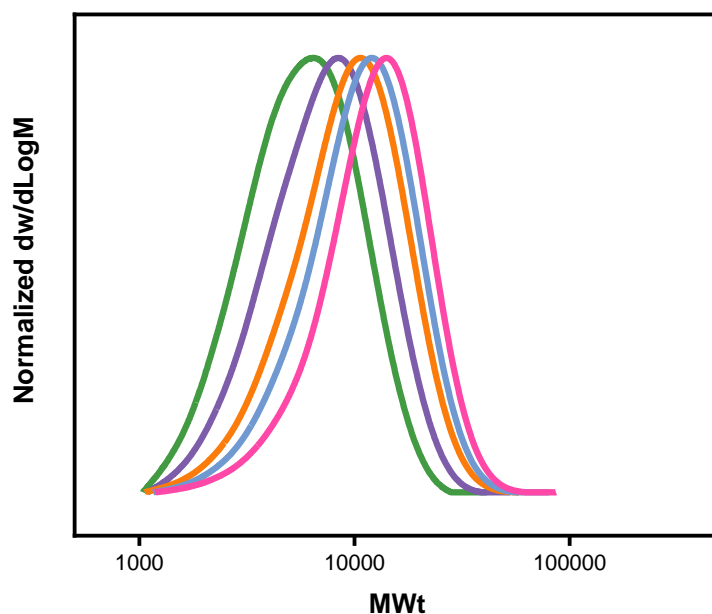

Figure S5: SEC traces for the kinetic of PMMA synthesized under the following conditions: ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [150]: [0.0015]: [0.0015]).
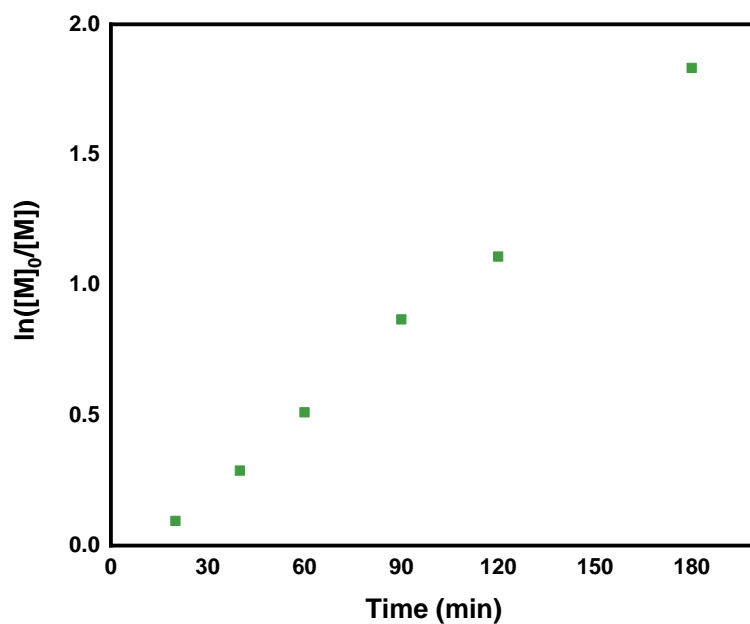
Figure S6: First order kinetic plot of PMMA synthesized under the following conditions: ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [150]: [0.0015]: [0.0015]).
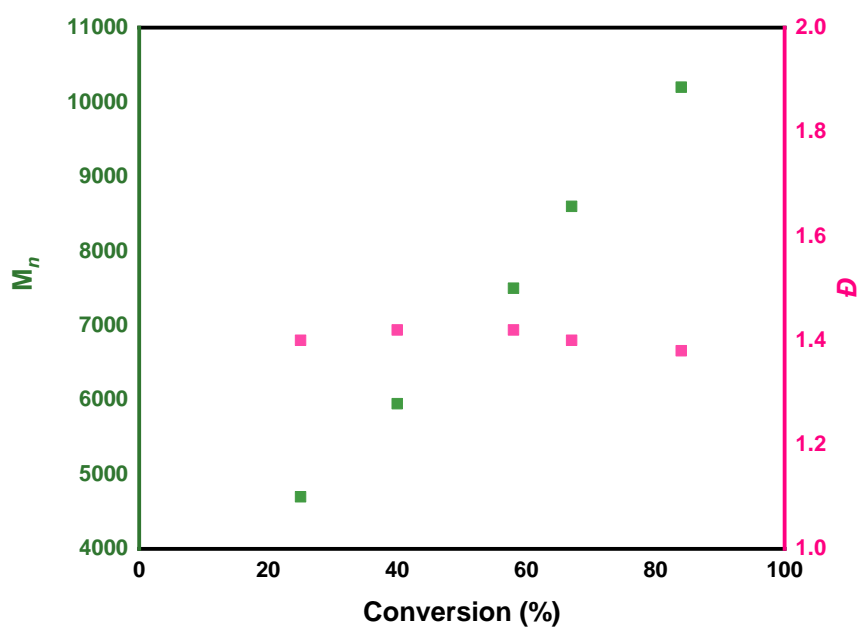

Figure S7: Evolution of M_n and dispersity with conversion of PMMA synthesized under the following conditions: ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [150]: [0.0015]: [0.0015]).

Table S5: ^{1}H NMR and SEC analysis for the polymerization of MMA with low and high catalyst concentrations.[a]

Entry	[MBPA]: [MMA]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(Theo.)}$	$M_{W(SEC)}$	$M_{P(SEC)}$	$M_{n(SEC)}$	Đ
1	1:20:0.0005:0.0005	1.5	84	1900	5400	4300	3500	1.51
2	1:20:0.007:0.007	2	75	1700	2600	2500	2100	1.10

[a] all polymerizations were performed in anisole with MMA as the monomer, MPBA as the initiator and FeBr$_3$: TBABr as the catalyst. The targeted DP was 20 and the volume ratio of anisole to MMA was maintained at 1:1 in all entries. [b]Conversion was calculated by ^{1}H NMR.
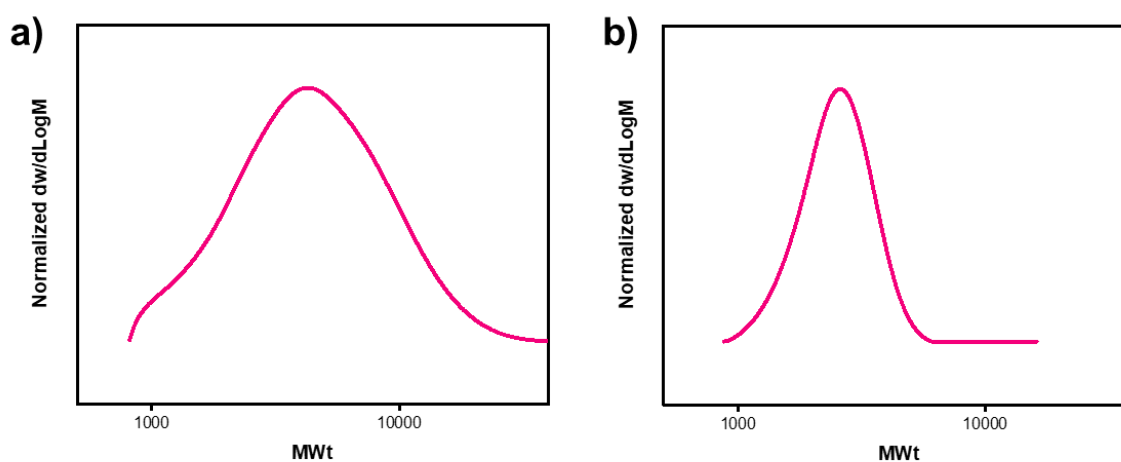

Figure S8: SEC traces for the PMMA synthesized under the following conditions for a) high dispersity Đ~ 1.50 ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [20]: [0.0005]: [0.0005]) and b) low dispersity Đ~ 1.10 ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr]=[1]: [20]: [0.007]: [0.007]).
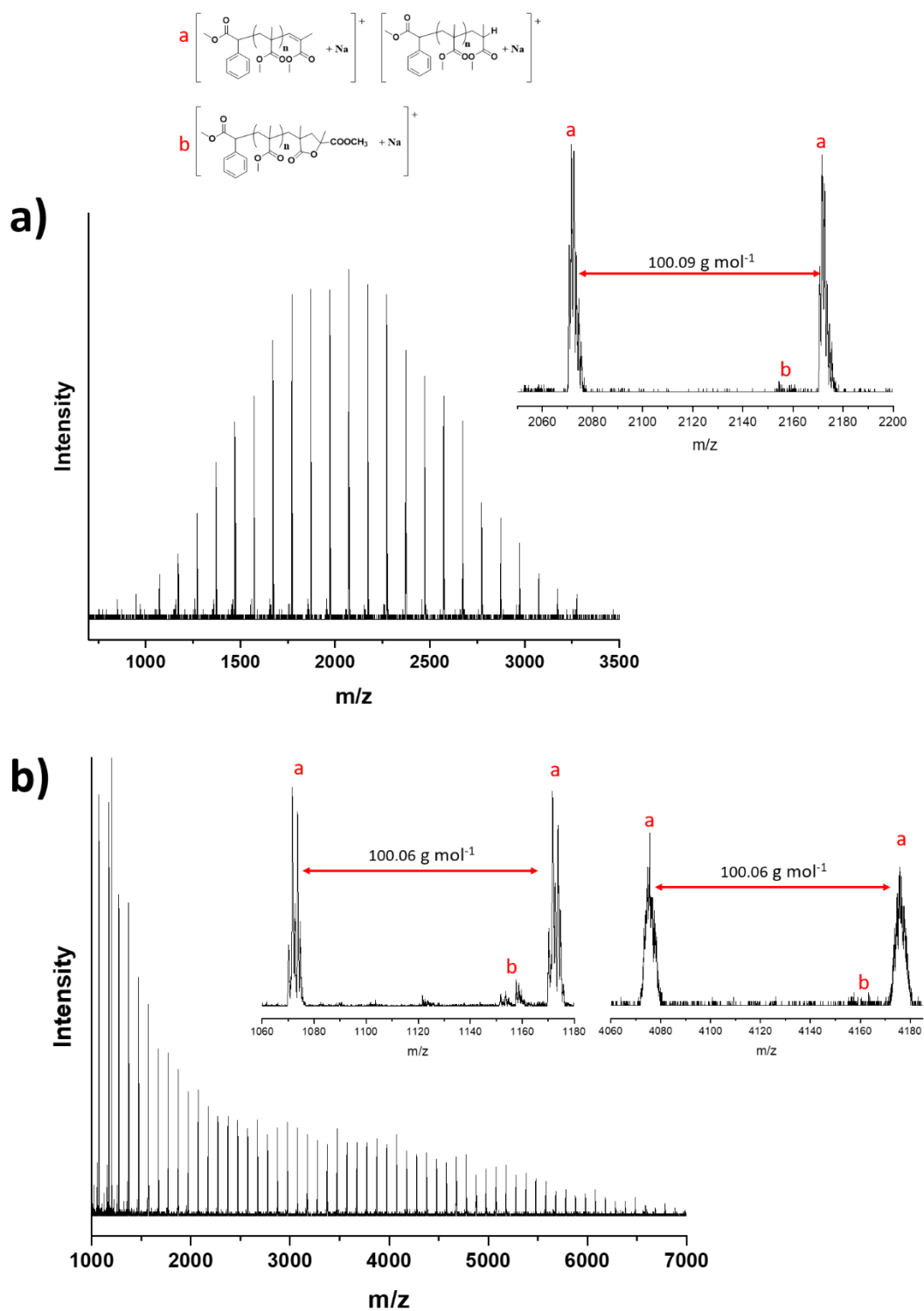
Figure S9: MALDI-TOF-MS analysis of a) low dispersity PMMA (DP= 20) prepared with a ratio of [MBPA]: [FeBr$_3$]: [TBABr] = [1]: [0.007]: [0.007] and b) high dispersity PMMA prepared with a ratio of [MBPA]: [FeBr$_3$]: [TBABr] = [1]: [0.0005]: [0.0005].
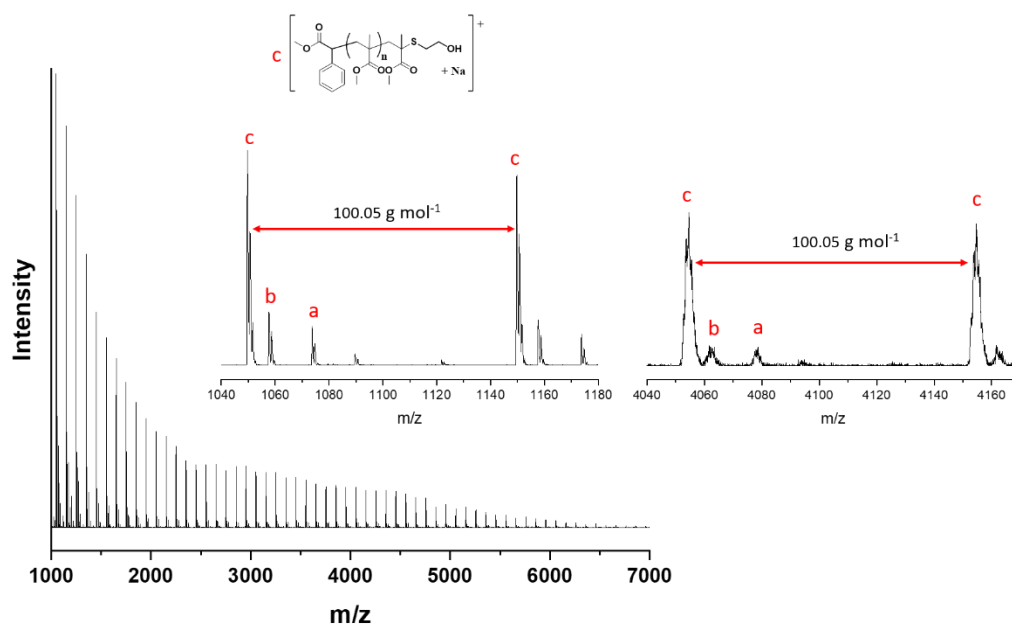
Figure S10: MALDI-TOF-MS analysis of PMMA (DP20, high dispersity PMMA prepared with a ratio of [MBPA]: [FeBr$_3$]: [TBABr] = [1]: [0.0005]: [0.0005]) after end-group modification with 2-mercaptoethanol (2ME). The ratio of [PMMA]:[2ME]:[TEA] was [1]:[40]:[40]. The actually MWt (2050.1) after thio substitution closely matches the predicted MWt (2050.0). Note, that the end group modification was not fully complete which is common for methacrylate polymers (tertiary alkyl halide).

Table S6: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a high dispersity PMMA (*Đ*=1.61) yielding P(MMA-*b*-BzMA) with a dispersity of 1.23 by the photoinduced Fe-catalyzed ATRP.[a]

Entry	Blocks	Monomer	[Monomer]: [FeBr₃]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(Theo.)}$	$M_{P(SEC)}$	$M_{n(SEC)}$	$M_{W(SEC)}$	*Đ*
1	B1	MMA	100: 0.002: 0.002	2.5	92	9400	12000	8200	13600	**1.61**
2	B2	BzMA	100: 0.1: 0.1	1.5	63	20600	17500	16500	20500	1.23

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr₃:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=100, volume ratio of BzMA to anisole 1:0.56) and shows the additional ratio of BzMA: FeBr₃: TBABr introduced into the reaction relative to the initial MBPA concentration. [b] Conversion was calculated by ^{1}H NMR.
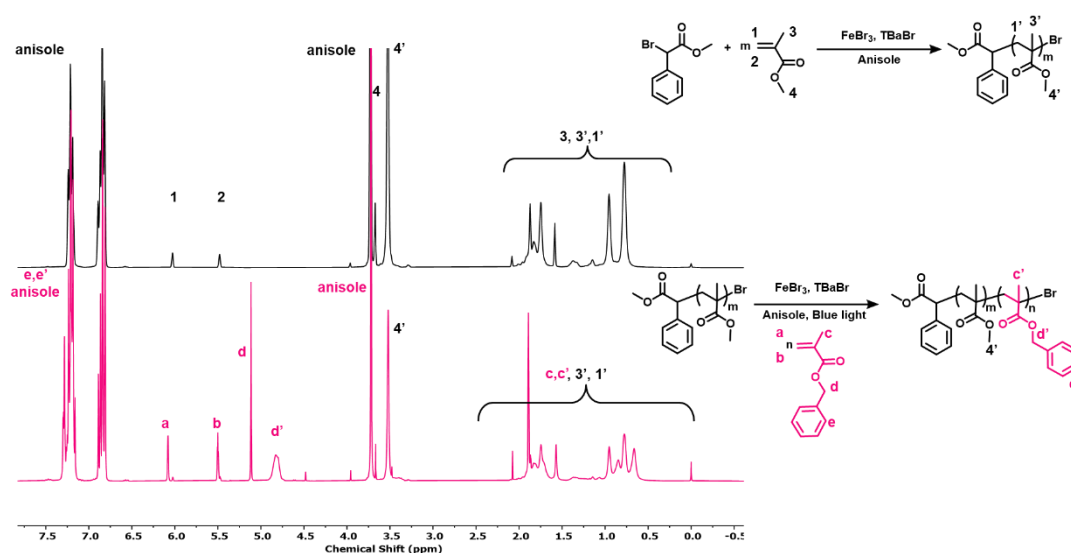

Figure S11: ^{1}H NMR spectra for the *in situ* chain extension of a high-dispersity PMMA (*Đ*= 1.61) yielding P(MMA-b-BzMA) with a final dispersity of 1.23 by photoinduced Fe-catalyzed ATRP.

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Table S7: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a high dispersity PMMA (*Đ*= 1.59) yielding P(MMA-*b*-BzMA) with final dispersity (*Đ*= 1.35) in the photoinduced Fe-catalyzed ATRP. [a]

Entry	Blocks	Monomer	[Monomer]: [FeBr₃]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(Theo.)}$	$M_{P(SEC)}$	$M_{n(SEC)}$	$M_{W(SEC)}$	*Đ*
1	B1	MMA	100: 0.002: 0.002	2.5	94	9600	14000	9500	15800	1.59
2	B2	BzMA	100: 0.07: 0.07	1.5	62	20600	24900	18800	25300	1.35

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr₃:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=100, volume ratio of BzMA to anisole 1:0.56) and shows the additional ratio of BzMA: FeBr₃: TBABr introduced into the reaction relative to the initial MBPA concentration. [b] Conversion was calculated by ^{1}H NMR.
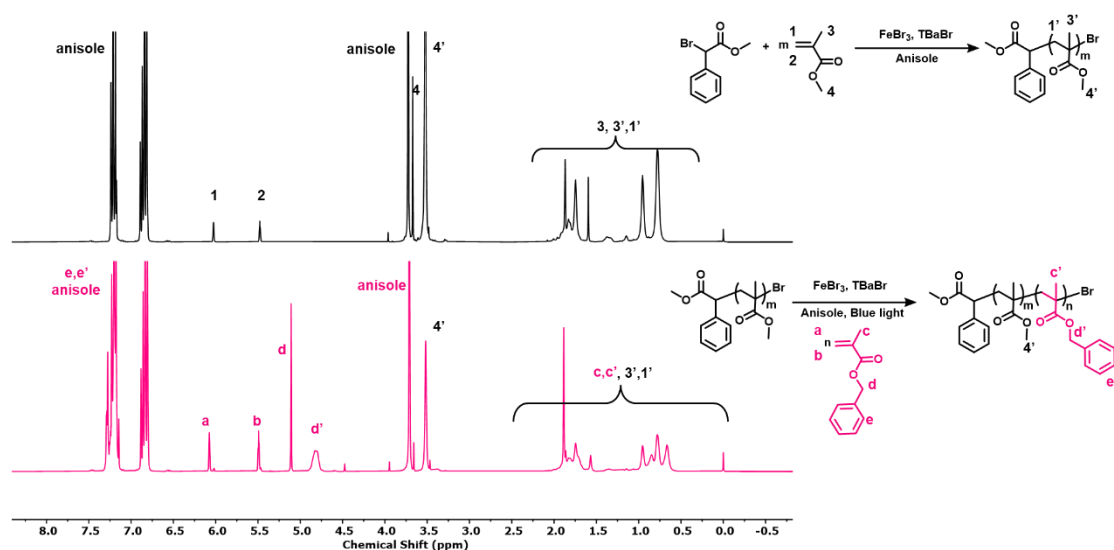

Figure S12: ^{1}H NMR spectra for the *in situ* chain extension of a high dispersity PMMA (*Đ*= 1.59) yielding P(MMA-*b*-BzMA) with final dispersity (*Đ*= 1.35) by photoinduced Fe-catalyzed ATRP .

Table S8: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a high dispersity PMMA (*Đ*= 1.56) yielding P(MMA-*b*-BzMA) with dispersity (*Đ*= 1.44) by the photoinduced Fe-catalyzed ATRP. [a]

Entry	Blocks	Monomer	[Monomer]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(Theo.)}$	$M_{P(SEC)}$	$M_{n(SEC)}$	$M_{W(SEC)}$	*Đ*
1	B1	MMA	100: 0.002: 0.002	2.5	93	9500	14900	10300	16000	1.56
2	B2	BzMA	100: 0.04: 0.04	1	70	21900	31700	21300	30700	1.44

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr$_3$:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=100, volume ratio of BzMA to anisole 1:0.56) and shows the additional ratio of BzMA: FeBr$_3$: TBABr introduced into the reaction relative to the initial MBPA concentration. [b] Conversion was calculated by ^{1}H NMR.
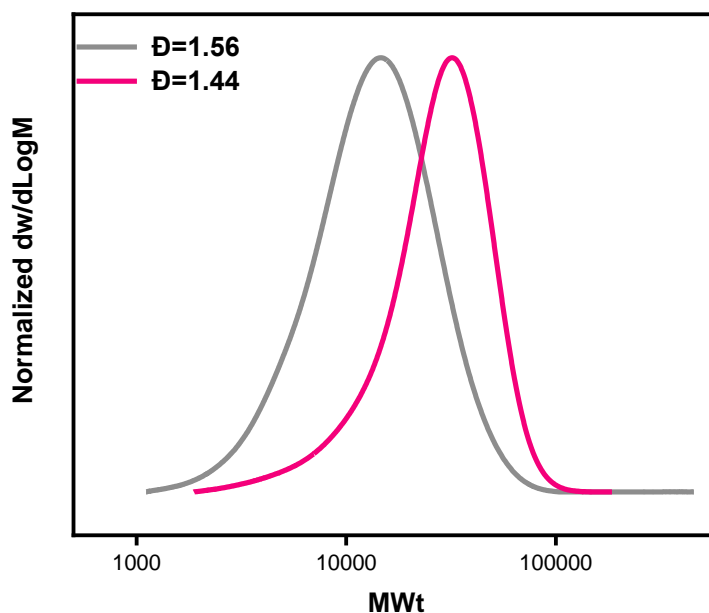

Figure S13: *In situ* chain extension of a high dispersity PMMA (*Đ*= 1.56) yielding P(MMA-*b*-BzMA) with final dispersity (*Đ*= 1.44) by the photoinduced Fe-catalyzed ATRP. Polymerization conditions are the following for the first block: [MBPA]: [MMA]: [FeBr$_3$]: [TBABr] = [1] :[100] :[0.002] :[0.002] and for the second block: [PMMA-Br]: [BzMA]: [FeBr$_3$]: [TBABr] = [1] :[100] :[0.04] :[0.04].

Table S9: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a high dispersity PMMA ($Đ$ = 1.62) yielding P(MMA-*b*-BzMA) with high dispersity ($Đ$= 1.67) in the photoinduced Fe-catalyzed ATRP. [a]

Entry	Blocks	Monomer	[Monomer]: [FeBr₃]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(Theo.)}$	$M_{P(SEC)}$	$M_{n(SEC)}$	$M_{W(SEC)}$	$Đ$
1	B1	MMA	100: 0.002: 0.002	2.5	93	9500	11800	8400	13200	**1.62**
2	B2	BzMA	100: 0.004: 0.004	1.25	68	21400	25300	16800	28200	1.67

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr₃:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=100, volume ratio of BzMA to anisole 1:0.56) and shows the additional ratio of BzMA: FeBr₃: TBABr introduced into the reaction relative to the initial MBPA concentration.[b] Conversion was calculated by ^{1}H NMR.
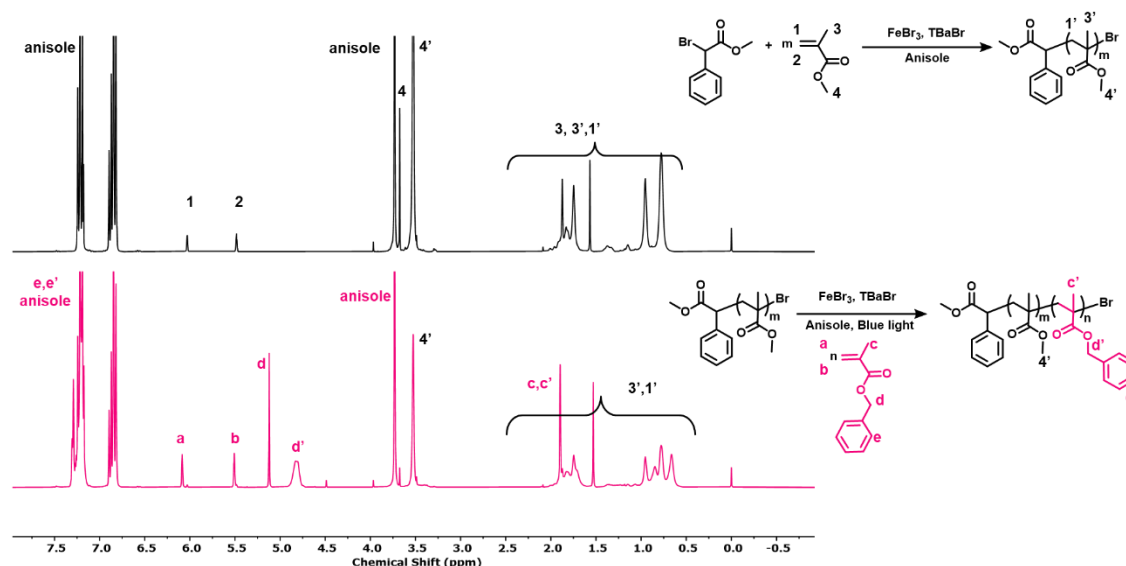

Figure S14: ^{1}H NMR spectra for the *in situ* chain extension of a high dispersity PMMA ($Đ$= 1.62) yielding P(MMA-*b*-BzMA) with high dispersity ($Đ$= 1.67) in the photoinduced Fe-catalyzed ATRP.

Table S10: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a high dispersity PMMA (*Đ*= 1.53) yielding P(MMA-*b*-BzMA) with final dispersity of 2.10, in the absence extra catalyst during the second block addition, for the photoinduced Fe-catalyzed ATRP. [a]

Entry	Blocks	Monomer	[Monomer]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	$M_{n(\text{Theo.})}$	$M_{P(\text{SEC})}$	$M_{n(\text{SEC})}$	$M_{W(\text{SEC})}$	*Đ*
1	B1	MMA	100: 0.002: 0.002	2.5	86	8800	12600	8900	13700	**1.53**
2	B2	BzMA	100: 0: 0	2	73	21700	35900	19600	41400	**2.10**

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr$_3$:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=100, volume ratio of BzMA to anisole 1:0.56) and shows the additional ratio of BzMA: FeBr$_3$: TBABr introduced into the reaction relative to the initial MBPA concentration. [b] Conversion was calculated by ^{1}H NMR.
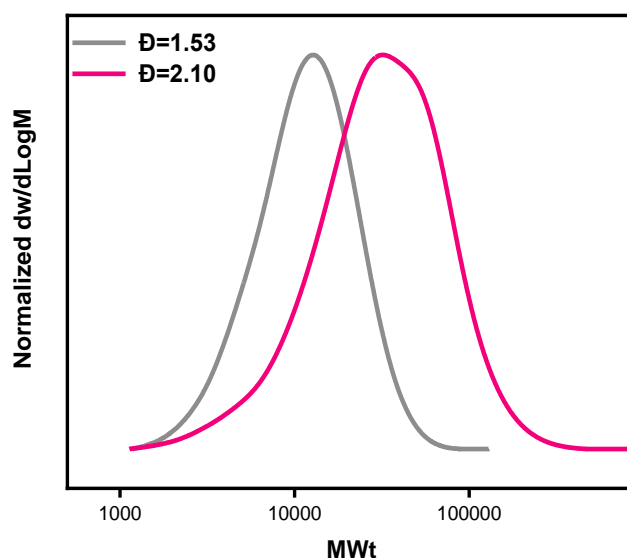

Figure S15: *In situ* chain extension of a high dispersity PMMA (*Đ*= 1.53) yielding P(MMA-*b*-BzMA) with a dispersity of 2.10 by the photoinduced Fe-catalyzed ATRP. Polymerization conditions are the following for the first block: [MBPA]: [MMA]: [FeBr$_3$]: [TBABr] = 1: 100: 0.002: 0.002 and for the second block: [PMMA-Br]: [BzMA]: [FeBr$_3$]: [TBABr] = 1: 100: 0: 0.

Table S11: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a medium dispersity PMMA ($Đ$= 1.41) yielding P(MMA-*b*-BzMA) with low dispersity ($Đ$= 1.23) in the photoinduced Fe-catalyzed ATRP. [a]

Entry	Blocks	Monomer	[Monomer]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	M$_{n(Theo.)}$	M$_{P(SEC)}$	M$_{n(SEC)}$	M$_{W(SEC)}$	$Đ$
1	B1	MMA	100: 0.003: 0.003	3	94	9600	10200	7900	10700	1.41
2	B2	BzMA	113: 0.1: 0.1	1	55	20600	20600	15500	19000	1.23

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr$_3$:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=113, volume ratio of BzMA to anisole 1:0.50) and shows the additional ratio of BzMA: FeBr$_3$: TBABr introduced into the reaction relative to the initial MBPA concentration. [b]Conversion was calculated by ^{1}H NMR.
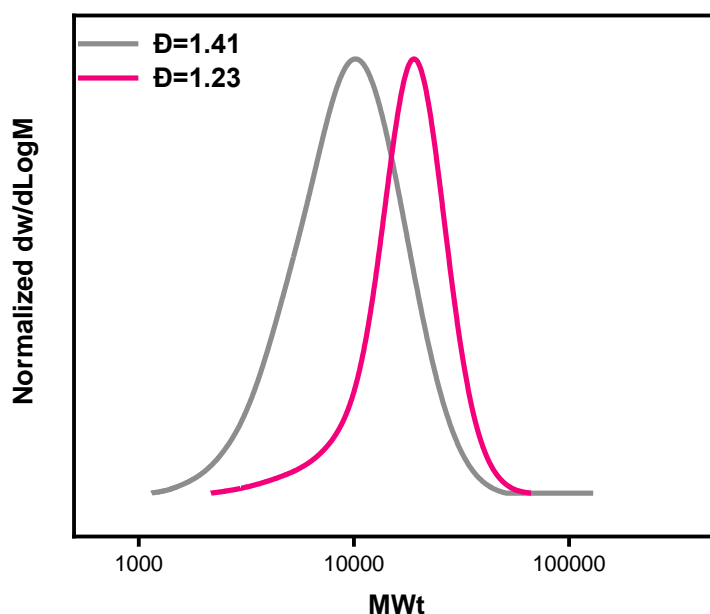

Figure S16: *In situ* chain extension of a medium dispersity PMMA ($Đ$= 1.41) yielding P(MMA-*b*-BzMA) with low dispersity ($Đ$= 1.23) in the photoinduced Fe-catalyzed ATRP. Polymerization conditions are the following for the first block: [MBPA]: [MMA]: [FeBr$_3$]: [TBABr] = 1: 100: 0.003: 0.003 and for the second block: [PMMA-Br]: [BzMA]: [FeBr$_3$]: [TBABr] = 1: 113: 0.1: 0.1.

Table S12: ^{1}H NMR and SEC analysis for the *in situ* chain extension of a medium dispersity PMMA (*Đ*= 1.35) yielding P(MMA-*b*-BzMA) with final low dispersity (*Đ*= 1.25) in the photoinduced Fe-catalyzed ATRP. [a]

Entry	Blocks	Monomer	[Monomer]: [FeBr$_3$]: [TBABr]	Time (h)	Conversion[b] (%)	M$_{n(Theo.)}$	M$_{P(SEC)}$	M$_{n(SEC)}$	M$_{W(SEC)}$	*Đ*
1	B1	MMA	100: 0.004: 0.004	2.4	92	9400	11100	7900	11100	**1.35**
2	B2	BzMA	113: 0.1: 0.1	1	49	19100	20000	15500	19400	**1.25**

[a] Entry 1 shows PMMA prepared in anisole with MBPA as the initiator and FeBr$_3$:TBABr as the catalyst (target DP=100, volume ratio of MMA to anisole 1:1). Entry 2 illustrates the *in situ* chain extension of PMMA with BzMA (target DP=113, volume ratio of BzMA to anisole 1:0.50) and shows the additional ratio of BzMA: FeBr$_3$: TBABr introduced into the reaction relative to the initial MBPA concentration. [b] Conversion was calculated by ^{1}H NMR.
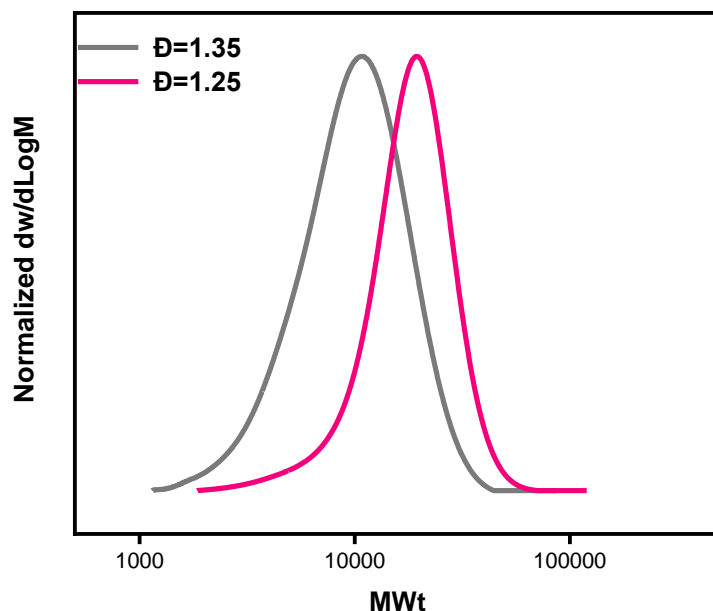

Figure S17: *In situ* chain extension of a medium dispersity PMMA (*Đ*= 1.35) yielding P(MMA-*b*-BzMA) with low dispersity (*Đ*= 1.25) in the photoinduced Fe-catalyzed ATRP. Polymerization conditions are the following for the first blocks: [MBPA]: [MMA]: [FeBr$_3$]: [TBABr] = 1: 100: 0.004: 0.004 and for the second block: [PMMA-Br]: [BzMA]: [FeBr$_3$]: [TBABr] = 1: 113: 0.1: 0.1.

Table S13: ^{1}H NMR analysis showing the lack of temporal control at a high catalyst concentration ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr] = 1: 175: 0.1: 0.1), for the photoinduced Fe-catalyzed ATRP. The "ON" periods were 30 min and the "OFF" periods were 3h. The final dispersity at 60% of conversion was 1.22 with an M_n= 9900.

Entry	ON – OFF	Time (h)	Conversion[a] (%)
1	ON	0 to 0.5	13
2	OFF	0.5 to 3.5	16
3	ON	3.5 to 4	40
4	OFF	4 to 7	42
5	ON	7 to 7.5	60

[a] Conversion was calculated by ^{1}H NMR.

Table S14: ^{1}H NMR analysis showing the perfect temporal control at a low catalyst concentration ([MBPA]: [MMA]: [FeBr$_3$]: [TBABr] = 1: 175: 0.007: 0.007), for the photoinduced Fe-catalyzed ATRP. The "ON" periods were 30 min and the "OFF" periods were 3h. The final dispersity at 41% of conversion was 1.80 with an M_n=10400.

Entry	ON – OFF	Time (h)	Conversion[a] (%)
1	ON	0 to 0.5	23
2	OFF	0.5 to 3.5	23
3	ON	3.5 to 4	36
4	OFF	4 to 7	36
5	ON	7 to 7.5	41

[a] Conversion was calculated by ^{1}H NMR.