Supporting Information for:

Metal-Free, Atom Transfer Radical Polymerization

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General Reagent Information

All polymerizations were carried out under an argon atmosphere. Anhydrous *N,N*-Dimethylacetamide was purchased from Sigma-Aldrich and used as received. Methyl methacrylate, benzyl methacrylate, methyl acrylate, and styrene were purchased from Sigma-Aldrich and passed through a plug of basic alumina before use. Methylene blue, Eosin Y, ethyl α-bromophenylacetate, ethyl α-bromoisobutyrate, 10-methyl phenothiazine, phenothiazine, RuPhos, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, 4,4'-dinonyl-2,2'-dipyridyl, *fac*-[Ir(ppy)$_3$], and anhydrous chlorobenzene were purchased from Sigma-Aldrich and used as received. CuBr was purchased from Sigma-Aldrich and purified by washing with acetic acid, followed by ethanol and ether. The resulting CuBr was kept under an argon atmosphere. RuPhos Precatalyst was purchased from Strem Chemicals Inc.

General Analytical Information

Nuclear magnetic resonance spectra were recorded on a Varian 400 MHz, a Varian 500 MHz, or a Varian 600 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. Gel permeation chromatography (GPC) was performed on a Waters 2695 separation module with a Waters 2414 refractive index detector eluting with 0.25 wt% triethylamine/chloroform and a Waters Alliance HPLC System, 2695 separation module with combined Wyatt DAWN HELEOS-II light scattering/Wyatt Optilab rEX refractive index detectors. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards or from light scattering. Reported molecular weights (M_n) were calculated using ^{1}H NMR by comparing the integration of the ethyl protons on the initiating chain end to the polymer side chain peaks unless otherwise noted. Mass spectrometry was performed on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem instrument.

Light Source

LED strips (380 nm) were bought from elemental led (see www.elementalled.com) and used as shown below (Figure S1). Note: 380 nm LED strips are no longer sold by elemental led, but may be bought from LEDlightinghut.com. Reactions were placed next to the 380 nm lights under vigorous stirring while cooling with compressed air. The light intensity was measured to be 0.65 μW/cm^2.

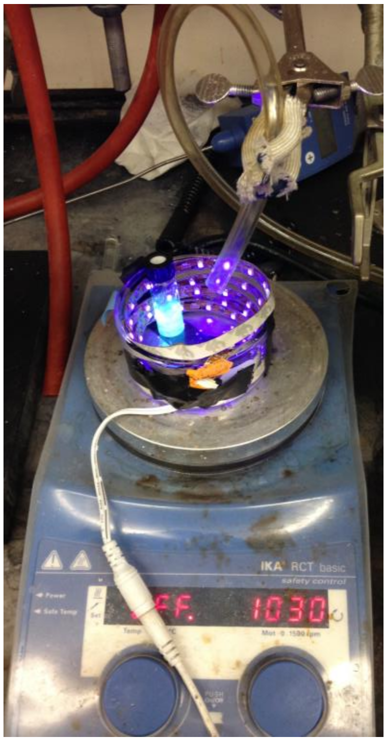
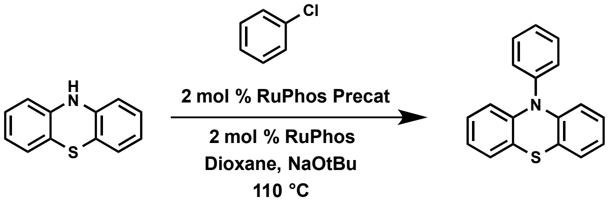


Figure S1. Representative configuration comprising reaction vial surrounded by 380 nm LEDs with a tube blowing compressed air for cooling.

Synthesis of 10-phenylphenothiazine (PTH):



The following procedure was adopted from Maiti et al.[1] To a vial armed with a magnetic stir bar was added NaOtBu (134 mg, 1.4 mmol), phenothiazine (199 mg, 1 mmol), RuPhos Precat (14 mg, 0.02 mmol, 2 mol %), and RuPhos (8 mg, 0.02 mmol, 2 mol %). The vial was evacuated and backfilled 3x with argon before adding dry Dioxane (1 mL). Lastly, anhydrous chlorobenzene (143 μL, 1.4 mmol) was added. The vial was then placed in an oil bath at 110 °C with stirring for 5 h. The vial was then cooled to room temperature, diluted with CH_2Cl_2, washed with water, brine, dried with Mg_2SO_4, and purified using column chromatography (5 % EtOAc/Hexanes). The product was dried under reduced pressure to yield 267 mg of a white solid (97 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.60 (t, *J* = 8 Hz, 2H), 7.49 (t, *J* = 8 Hz, 1H), 7.40 (d, J = 7 Hz, 2H), 7.02 (d, J =

8 Hz, 2H), 6.86-6.79 (m, 4 H), 6.20 (d, J = 8 Hz, 2 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ: 144.5, 141.2, 131.1, 130.9, 128.4, 127.0, 126.9, 122.7, 120.4, 116.3 ppm. HRMS $C_{18}H_{13}NS$ Found 275.0753, Calc'd 275.0769.

Determination of excited state reduction potential:

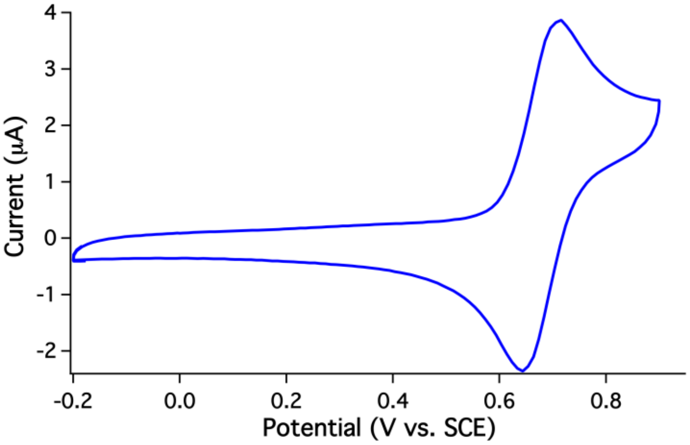


Figure S2. Cyclic voltammetry of 10-phenylphenothiazine to determine excited state reduction potential

Cyclic voltammetry was carried out on a VMP Multichannel Potentiostat with EC lab software. Cyclic voltammetry was conducted using 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte in acetonitrile at 25 °C with a standard calomel reference electrode (E^{ox} = +0.68 V vs. SCE).

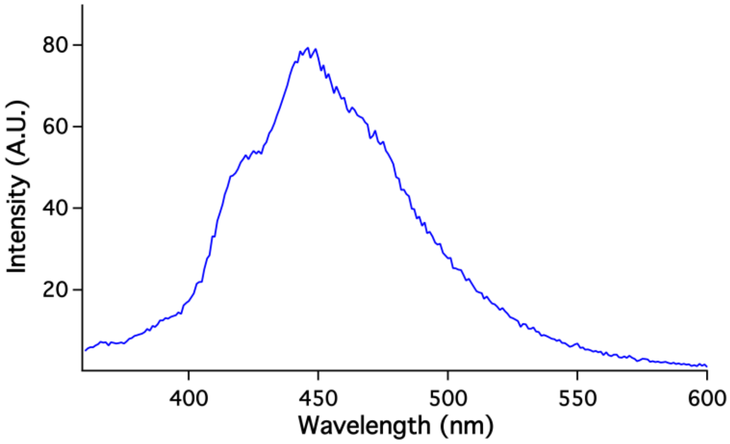


Figure S3. Fluorescence spectrum of **PTH** in *N,N*-dimethylacetamide (0.17 mM)

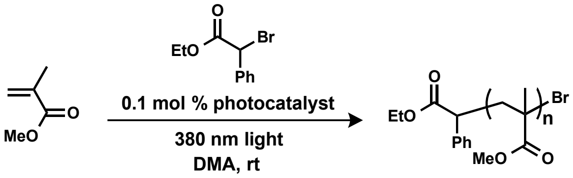
A Varian Cary Eclipse Fluorescence Spectrophotometer was used to measure fluorescence. Photoluminescence max was estimated to be 445 nm (see Figure S3).

Using photoluminescence maximum and E^{ox}, the excited state reduction potential was estimated for **PTH** ($E_{1/2}(PTH^{+\cdot}/PTH^*) = -2.1$ V) according to the following equations:

$$E_{1/2}(PTH^{+\cdot}/PTH^*) = E^{ox} - E_{0,0}$$

$$\text{where } E_{0,0} = hc / \lambda_{max} = 1240 \text{ nm} / \lambda_{max}.$$

General Procedure for Table 1:

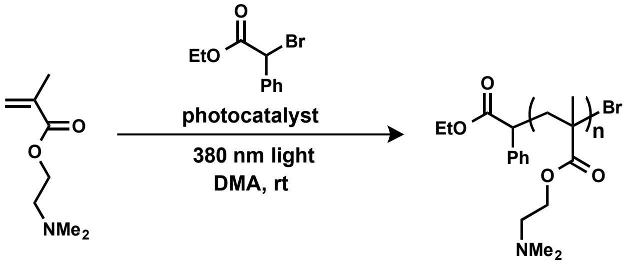


A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl methacrylate (401 µL, 3.75 mmol), photocatalyst (0.1 mol %) and *N,N*-dimethylacetamide (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (0.0188 - 0.075 mmol) was injected via syringe. The reaction was vigorously stirred in front of 380 nm LEDs or 50 W compact fluorescent bulbs while cooling with compressed air to maintain ambient temperature. The reaction was allowed to proceed to ca. 50 % conversion of MMA as monitored by ^{1}H NMR. An aliquot was taken and analyzed using ^{1}H NMR to give the molecular weight (M_n) and GPC to give the molecular weight distribution (M_w/M_n) of the polymer.

Procedure for Figure 2:

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl methacrylate (762 µL, 4.5 mmol), **PTH** (1.2 mg, 0.1 mol %) and *N,N*-dimethylacetamide (1.2 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon, and brought into a glove box containing a nitrogen atmosphere. It was then covered with aluminum foil, and ethyl α-bromophenylacetate (6.9 µL, 0.0396 mmol) was injected via syringe. After 1 h of stirring in the dark, an aliquot was taken. The reaction was then vigorously stirred in front of 380 nm LEDs while cooling with a portable fan to maintain ambient temperature. After 0.5 h and 1 h stirring under light, aliquots were taken from the reaction mixture and, at 1 h, the reaction was immediately wrapped in aluminum foil. This process was repeated multiple times (see Figure 2). Conversion was monitored by ^{1}H NMR. The molecular weight was calculated using ^{1}H NMR. GPC was used to obtain the molecular weight distribution (M_w/M_n) of the polymer.

General Procedure for Table S1:



Entry	Photocatalyst	conversion	M_n (exp) [g/mol]	M_w / M_n
1[b]	Ir(ppy)$_3$	50%	9,400	3.69
2	PTH	73%	8,800	1.11
3	PTH	33%	5,100	1.26

[a] Reaction conditions: DMAEMA (1 equiv.), photocatalyst (0.001 equiv.), **1** (0.01 equiv), DMA (2.7 M of DMAEMA) at room temperature with irradiation from 380 nm LEDs for 0.5-2 h (M_n = number average molecular weight; M_w = weight average molecular weight). M_n and M_w / M_n determined using size exclusion chromatography (SEC) or ^{1}H NMR; [b] used 0.00005 equiv. Ir(ppy)$_3$ (0.005 mol % relative to monomer)

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with 2-(dimethylamino)ethyl methacrylate (634 µL, 3.75 mmol), photocatalyst (0.1 mol % **PTH** or 0.005 mol % Ir(ppy)$_3$) and *N,N*-dimethylacetamide (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (10.3 µL, 0.059 mmol) was injected via syringe. The reaction was vigorously stirred in front of 380 nm LEDs and conversion monitored by ^{1}H NMR. An aliquot was taken and analyzed using ^{1}H NMR to give the molecular weight (M_n) and GPC to give the molecular weight distribution (M_w/M_n) of the polymer.

Procedure for Figure 3:

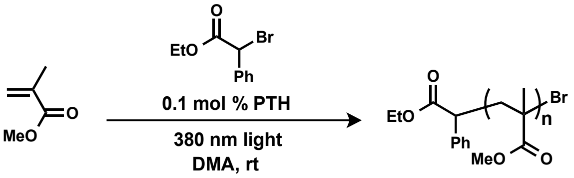


Figure 3a: Poly(methyl methacrylate) by metal-free ATRP: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl methacrylate (401 μL, 3.75 mmol), **PTH** (1 mg, 0.1 mol %) and *N,N*-dimethylacetamide (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (13.1 μL, 0.075 mmol) was injected via syringe. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction was stirred in front of the light for 7.5 h (25 % conv.) and then put into the dark by wrapping it in aluminum foil. A syringe wrapped in aluminum foil was used to transfer the reaction mixture in the dark into a stirring solution of hexanes (15 mL, also wrapped in aluminum foil). The solution was put into a freezer (ca. -40 °C) for 1 h. The white precipitate was decanted, and re-dissolved in dichloromethane before precipitating again into hexanes to yield 24 mg of a white powder. M_n = 1,400 g/mol, M_w/M_n = 1.08.

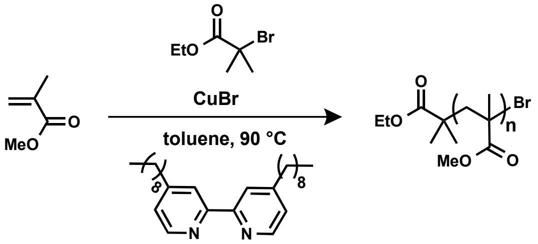


Figure 3b: Poly(methyl methacrylate) by traditional Cu-catlyzed ATRP: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl methacrylate (401 μL, 3.75 mmol), **CuBr** (5.4 mg, 0.0375 mmol), 4,4'-dinonyl-2,2'-dipyridyl (30.7 mg, 0.075 mmol), and toluene (400 μL, 50 vol %). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromoisobutyrate (11 μL, 0.075 mmol) was injected via syringe. The reaction was stirred in a 90 °C oil bath for 2 h (38 % conv.), cooled to room

temperature, diluted with dichloromethane, and filtered through an alumina plug before precipitating into 20 mL of hexanes. The precipitate was filtered, and redissolved in dichloromethane before re-precipitating into hexanes to obtain 5 mg of a white powder. M_n = 1,100 g/mol, M_w/M_n = 1.20.

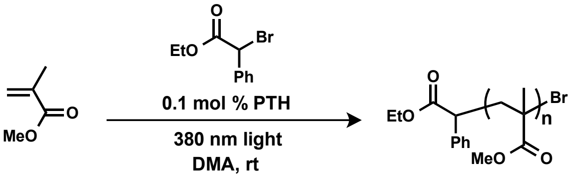
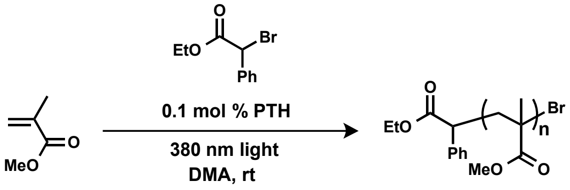


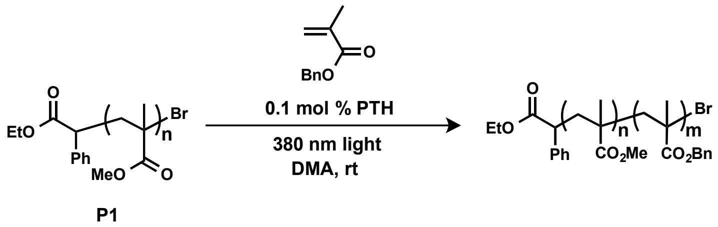
Figure 3c: Poly(methyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a rubber septum was charged with methyl methacrylate (2.4 mL, 22.5 mmol), **PTH** (6.2 mg, 0.1 mol %) and *N,N*-dimethylacetamide (6 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (39 µL, 0.225 mmol) was injected via syringe. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction was stirred in front of the light for 2.5 h (14 % conv.) and then put into the dark by wrapping it in aluminum foil. A syringe wrapped in aluminum foil was used to transfer the reaction mixture in the dark into a stirring solution of hexanes (50 mL, also wrapped in aluminum foil). The white precipitate was decanted, and re-dissolved in dichloromethane before precipitating again into hexanes to yield 197 mg of a white powder. M_n = 2,600 g/mol, M_w/M_n = 1.33.

Procedure for Figure 4:

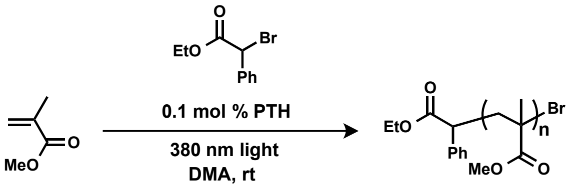


P1

Poly(methyl methacrylate) (P1) A vial equipped with a magnetic stir bar and fitted with a rubber septum was charged with methyl methacrylate (2.4 mL, 22.5 mmol), **PTH** (6.2 mg, 0.1 mol %) and *N,N*-dimethylacetamide (6 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (39 µL, 0.225 mmol) was injected via syringe. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction was stirred in front of the light for 5.5 h (36 % conv.) under a positive pressure of Argon and then put into the dark by wrapping it in aluminum foil. A syringe wrapped in aluminum foil was used to transfer the reaction mixture in the dark into a stirring solution of hexanes (80 mL, also wrapped in aluminum foil). The precipitate was decanted, and re-dissolved in dichloromethane before precipitating again into hexanes to yield 677 mg of a white powder. M_n = 5,100 g/mol, M_w/M_n = 1.12.

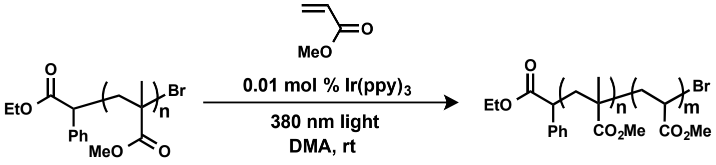


Poly(methyl methacrylate)-*b*-(benzyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl methacrylate (630 µL, 3.72 mmol), **PTH** (1 mg, 0.1 mol %) and *N,N*-dimethylacetamide (500 µL). In another flask, 500 µL of *N,N*-dimethylacetamide was added to the poly(methyl methacrylate) macroinitiator (**P1**, 83.5 mg, 0.0164 mmol). Both reaction mixtures were degassed with three freeze-pump-thaw cycles. Using a syringe, the monomer and catalyst were then transferred to the flask containing macroinitiator. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. After 5 h (61 % conv.) the reaction was stopped by opening to air and precipitated into methanol (20 mL). The precipitate was filtered and redissolved in CH_2Cl_2 before reprecipitating into methanol. The product was analyzed by ^{1}H NMR and GPC. (yield: 189 mg of a white powder) M_n = 25,900 g/mol (determined by GPC), M_w/M_n = 1.31.



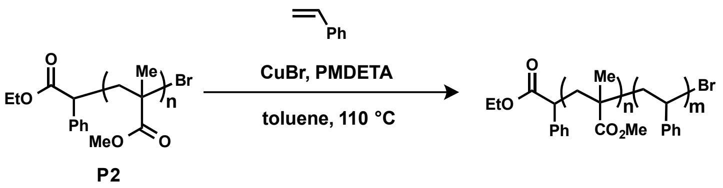
P2

Poly(methyl methacrylate) (P2) A vial equipped with a magnetic stir bar and fitted with a rubber septum was charged with methyl methacrylate (2.4 mL, 22.5 mmol), **PTH** (6.2 mg, 0.1 mol %) and *N,N*-dimethylacetamide (6 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (39 µL, 0.225 mmol) was injected via syringe. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction was stirred in front of the light for 5 h (25 % conv.) and then put into the dark by wrapping it in aluminum foil. A syringe wrapped in aluminum foil was used to transfer the reaction mixture in the dark into a stirring solution of hexanes (50 mL, also wrapped in aluminum foil). The white precipitate was decanted, and re-dissolved in dichloromethane before precipitating again into hexanes to yield 655 mg of a white powder. M_n = 3,600 g/mol, M_w/M_n = 1.19.



P2

Poly(methyl methacrylate)-*b*-(methyl acrylate) A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl acrylate (511 µL, 5.67 mmol), *fac*-Ir(ppy)$_3$ (0.37 mg, 0.01 mol %) and *N,N*-dimethylacetamide (600 µL). In another flask, 500 µL of *N,N*-dimethylacetamide was added to the poly(methyl methacrylate) macroinitiator (**P2**, 30.7 mg, 0.0122 mmol). Both reaction mixtures were degassed with three freeze-pump-thaw cycles. Using a syringe, the monomer and catalyst were then transferred to the flask containing macroinitiator. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. After 4 h (45 % conv.) the reaction was stopped by opening to air and precipitated into MeOH (20 mL). A yellow oil crashed out, and the solution was placed into a freezer (ca. -20 °C) for 1 h. The methanol was then decanted off and the residual solvent was removed under reduced pressure. This process was repeated once to yield 47 mg of a yellow oil. M_n =20,200 g/mol, M_w/M_n = 1.24.



Poly(methyl methacrylate)-*b*-(styrene) A vial equipped with a magnetic stir bar and fitted with a Teflon screw cap septum was charged with Styrene (290 μL, 2.52 mmol), poly(methyl methacrylate) macroinitiator (**P2**, 46 mg, 0.0131 mmol), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (5.5 μL, 0.0262 mmol), and toluene (290 μL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and frozen before adding CuBr (1.9 mg, 0.0131 mmol). After adding CuBr, the vial was evacuated-backfilled with Argon 2 times. The mixture was thawed, and placed into an oil bath heated to 110 °C for 4.5 h (17 % conv.). The reaction was cooled, opened to air, diluted with dichloromethane, and filtered through alumina before precipitating into hexanes. The precipitate was filtered, redissolved in dichloromethane, and re-precipitated into hexanes to yield 10 mg of a white powder. NMR M_n = 11,100 g/mol, GPC M_n = 4,800 g/mol, M_w/M_n = 1.06.

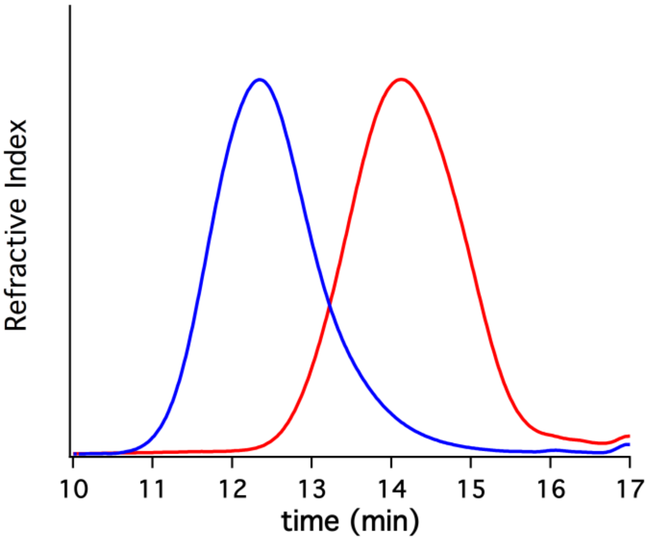
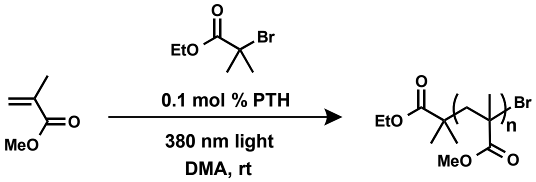
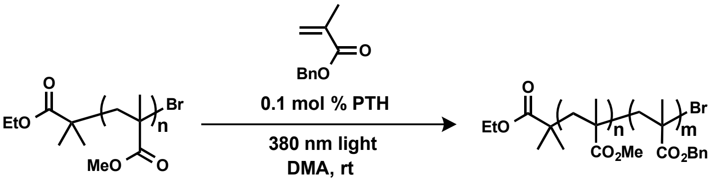


Figure S4: Block copolymerization SEC traces with PMMA (red trace, starting homopolymer) blocked with PBnMA (blue trace, block copolymer), using ethyl α-bromoisobutyrate as initiator.

Procedure for Figure S4:



Poly(methyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a rubber septum was charged with methyl methacrylate (2.4 mL, 22.5 mmol), **PTH** (6.2 mg, 0.1 mol %) and *N,N*-dimethylacetamide (6 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromoisobutyrate (33 µL, 0.225 mmol) was injected via syringe. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction was stirred in front of the light for 5 h (19 % conv.) and then put into the dark by wrapping it in aluminum foil. A syringe wrapped in aluminum foil was used to transfer the reaction mixture in the dark into a stirring solution of hexanes (50 mL, also wrapped in aluminum foil). The white precipitate was decanted, and re-dissolved in dichloromethane before precipitating again into hexanes to yield 273 mg of a white powder. M_n = 5,300 g/mol, M_w/M_n = 1.30.



Poly(methyl methacrylate)-*b*-(benzyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl methacrylate (461 µL, 2.62 mmol), **PTH** (0.7 mg, 0.1 mol %) and *N,N*-dimethylacetamide (350 µL). In another flask, 350 µL of *N,N*-dimethylacetamide was added to the poly(methyl methacrylate) macroinitiator (57.6 mg, 0.0115 mmol). Both reaction mixtures were degassed with three freeze-pump-thaw cycles. Using a syringe, the monomer and catalyst were then transferred to the flask containing macroinitiator. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. After 6 h (62 % conv.) the reaction was stopped by opening to air and precipitated into methanol (20 mL). The precipitate was filtered and redissolved in CH_2Cl_2 before reprecipitating into methanol. The product was analyzed by ^{1}H NMR and GPC. (yield: 163 mg of a white powder) M_n = 27,900 g/mol, M_w/M_n = 1.28.

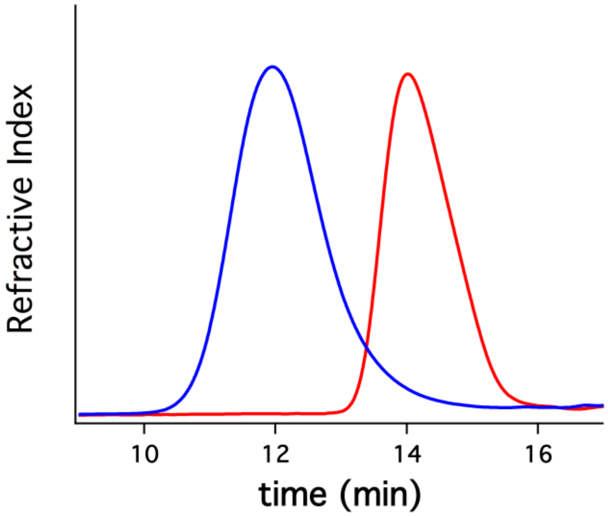
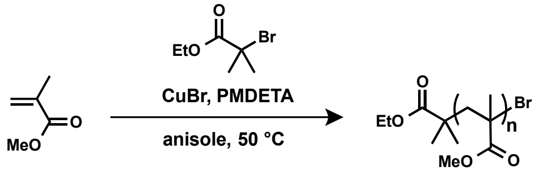
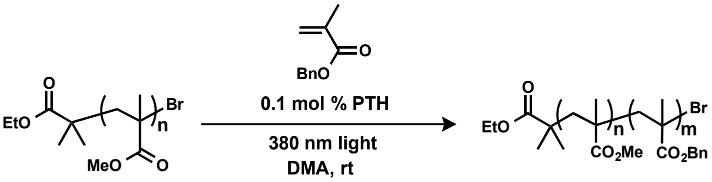


Figure S5: Block copolymerization SEC traces with PMMA (red trace, starting homopolymer) synthesized with traditional ATRP conditions and chain extending with BnMA (blue trace, block copolymer), using metal-free photomediated ATRP conditions.

Procedure for Figure S5:



Poly(methyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl methacrylate (2.4 mL, 22.5 mmol), **CuBr** (16.1 mg, 0.113 mmol), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (47 µL, 0.225 mmol), and anisole (2.4 mL, 50 vol %). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and degassed ethyl α-bromoisobutyrate (33 µL, 0.225 mmol) was injected via syringe. The reaction was stirred in a 50 °C oil bath for 2.5 h (27 % conv.), cooled to room temperature, diluted with dichloromethane, and filtered through an alumina plug before precipitating into 100 mL of hexanes. The precipitate was filtered, and redissolved in dichloromethane before re-precipitating into hexanes to obtain 363 mg of a white powder. M_n = 3,000 g/mol, M_w/M_n = 1.13.



Poly(methyl methacrylate)-b-(benzyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl methacrylate (590 µL, 3.48 mmol), **PTH** (1 mg, 0.1 mol %) and *N,N*-dimethylacetamide (500 µL). In another flask, 500 µL of *N,N*-dimethylacetamide was added to the poly(methyl methacrylate) macroinitiator (46 mg, 0.0153 mmol). Both reaction mixtures were degassed with three freeze-pump-thaw cycles. Using a syringe, the monomer and catalyst were then transferred to the flask containing macroinitiator. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. After 4 h (57 % conv.) the reaction was stopped by opening to air and precipitated into methanol (20 mL). The precipitate was filtered and redissolved in CH_2Cl_2 before reprecipitating into methanol. The product was analyzed by ^{1}H NMR and GPC. (yield: 230 mg of a white powder) GPC M_n = 34,500 g/mol, M_w/M_n = 1.33.

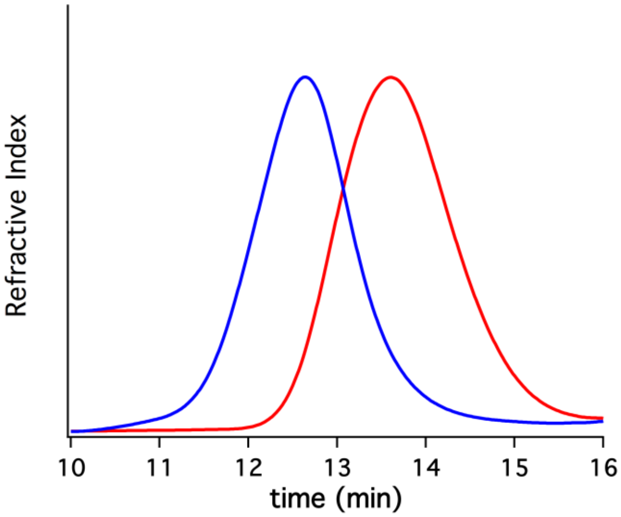
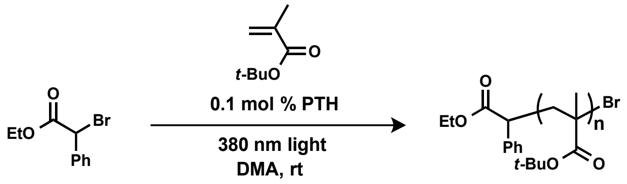
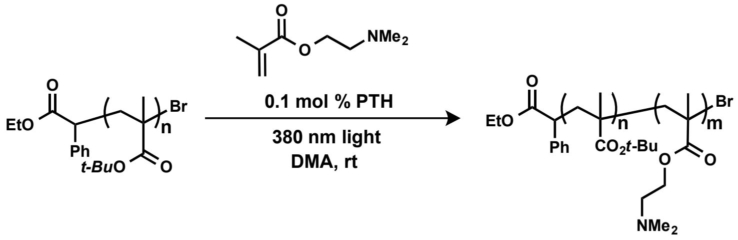


Figure S6: SEC traces with P*t*-BuMA (red trace, starting homopolymer) synthesized using metal-free ATRP conditions and chain extending with DMAEMA (blue trace, block copolymer), using metal-free photomediated ATRP conditions.

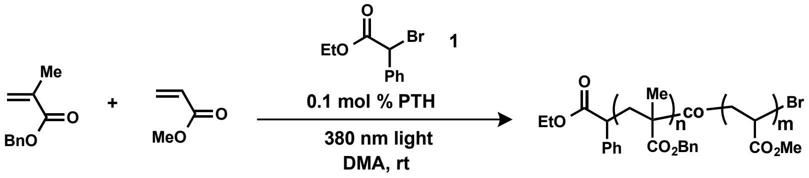


Poly(*t*-butyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a rubber septum was charged with *t*-butyl methacrylate (5 mL, 30.8 mmol), **PTH** (8.5 mg, 0.1 mol %) and dimethylacetamide (8.2 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (38 µL, 0.218 mmol) was injected via syringe. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction was stirred in front of the light for 6 h (41 % conv.) and then put into the dark by wrapping it in aluminum foil. A syringe wrapped in aluminum foil was used to transfer the reaction mixture in the dark into a stirring solution of methanol:water (9:1) (250 mL, also wrapped in aluminum foil). The white precipitate was decanted, and re-dissolved in dichloromethane before precipitating again into methanol:water (9:1) to yield 1.7 g of a white powder. M_n = 8,900 g/mol, M_w/M_n = 1.24.



Poly(*t*-butyl methacrylate)-*b*-(dimethylaminoethyl methacrylate) A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with dimethylaminoethyl methacrylate (1.76 mL, 10.45 mmol), **PTH** (2.9 mg, 0.1 mol %) and N,N-dimethylacetamide (1 mL). In another flask, 4.6 mL of N,N-dimethylacetamide was added to the poly(*t*-butyl methacrylate) macroinitiator (1.45 g, 0.164 mmol). Both reaction mixtures were degassed with three freeze-pump-thaw cycles. Using a syringe, the monomer and catalyst were then transferred to the flask containing macroinitiator. The reaction was stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. After 30 min (36 % conv.) the reaction was stopped by opening to air and precipitated into cold hexanes (200 mL). A white oil crashed out, the hexanes was then decanted off and the oil was redissolved in dichloromethane before precipitating into cold hexanes again. Yield: 800 mg of a white oil. M_n =22,500 g/mol, M_w/M_n = 1.30.

Table S2: Methacrylate/Acrylate Copolymerizations



Entry	BnMA:MA [mol %]	% MA incorp [mol %]	Time	conversion	M_n (exp) [g/mol]	M_n (theo) [g/mol]	M_w / M_n
1	**90:10**	**6**	**6 h**	**71 % BnMA** **49 % MA**	**15,300**	**13,800**	**1.28**
2	**50:50**	**32**	**4.5 h**	**69 % BnMA** **36 % MA**	**12,800**	**11,600**	**1.25**
3	**10:90**	**82**	**3 h**	**86 % BnMA** **47 % MA**	**12,100**	**10,800**	**1.45**

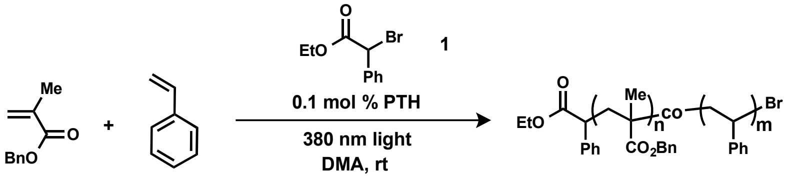
[a] Reaction conditions: BnMA + MA (1 equiv.), photocatalyst (0.001 equiv.), **1** (0.0047-0.008 equiv), DMA at room temperature with irradiation from 380 nm LEDs for 3-6 h (M_n = number average

molecular weight; M_w = weight average molecular weight). M_n and M_w / M_n determined using size exclusion chromatography (SEC) or ^{1}H NMR. % MA incorporation determined using ^{1}H NMR.

General Procedure for Table S2:

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl methacrylate and methyl acrylate (combined 3.75 mmol), **PTH** (1 mg, 0.1 mol %) and *N,N*-dimethylacetamide (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (0.0178 - 0.0315 mmol) was injected via syringe. The reaction was vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. An aliquot was taken and analyzed using ^{1}H NMR to give the conversion. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymer were determined by SEC and ^{1}H NMR.

Table S3: Methacrylate/Styrene Copolymerizations



Entry	BnMA:Styrene [mol %]	% Styrene incorp [mol %]	Time	conversion	M_n (exp) [g/mol]	M_n (theo) [g/mol]	M_w / M_n
1	99:1	3	5 h	68 % BnMA 85 % Styrene	9,800	13,600	1.39
2	95:5	11	5 h	34 % BnMA 88 % Styrene	5,900	7,100	1.41
3	90:10	19	7 h	45 % BnMA 78 % Styrene	15,200	9,400	1.65

[a] Reaction conditions: BnMA + Styrene (1 equiv.), photocatalyst (0.001 equiv.), **1** (0.00847-0.00877 equiv), DMA at room temperature with irradiation from 380 nm LEDs for 5-7 h (M_n = number average molecular weight; M_w = weight average molecular weight). M_n and M_w / M_n determined using size exclusion chromatography (SEC). % Styrene incorporation determined using ^{1}H NMR.

General Procedure for Table S3:

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl methacrylate and styrene (combined 3.75 mmol), **PTH** (1 mg, 0.1 mol %) and *N,N*-dimethylacetamide (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and ethyl α-bromophenylacetate (0.0318 - 0.0329 mmol) was injected via syringe. The reaction was vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. An aliquot was taken and analyzed using ^{1}H NMR to give the conversion. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymer were determined by SEC.