Supporting Information

For

"Organocatalyzed Atom Transfer Radical Polymerization Catalyzed by Core Modified *N*-aryl Phenoxazines Performed under Air"

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Contents

Materials and Methods

Purchased Chemicals and Experimental Equipment

Photocatalyst Synthesis

    Buchwald Coupling: Phenoxazine was purchased from Beantown Chemical and used as received. Phenazine was purchased from Sigma Aldrich and used as received. 2-bromonaphthylene and 1-bromonaphthylene were purchased from VWR. Bis(dibenzylideneacetone) palladium(0) and 1.0 M solution of tri-*tert*-butylphosphine in toluene were purchased from Sigma Aldrich and used as received. Dicyclohexylphosphino-2,6-diisopropoxybiphenyl (RuPhos) and chloro-(2-dicyclohexylphosphino-2,6-diisopropoxy-1,1-biphenyl) [2-(2-aminoethyl)phenyl] palladium(II) - methyl-t-butyl ether adduct (RuPhos precatalyst) were purchased from Sigma Aldrich and used as received. Sodium tert-butoxide was purchased from Sigma Aldrich and used as received. Dioxane and toluene were purified using an mBraun MB-SPS-800 solvent purification system and kept under nitrogen atmosphere.

    Bromination: N-Bromosuccinimide was purchased from VWR and used as received.

    Suzuki Coupling: Tetrakis(triphenyl phosphine) palladium (0) was purchased from Sigma Aldrich. Potassium carbonate was purchased from VWR. The boronic acid coupling partners were purchased from the following vendors and used as received:

4-biphenylboronic acid: TCI America

2-naphthylboronic acid: Sigma Aldrich

pyrene-1-boronic acid: Alfa Aesar

4-(trifluoromethyl)phenylboronic acid: Sigma Aldrich

4-methoxyphenylboronic acid: Sigma Aldrich

4-(diphenylamino)phenylboronic acid: TCI America

Polymer Synthesis

    Methyl methacrylate (MMA), *N,N*-dimethyl acetamide (DMAc), and diethyl 2-bromo-2-methyl malonate (DBMM) were purchased from Sigma Aldrich. Benzyl methacrylate (BnMA) was purchased from TCI. For chemical preparation and storage, please see the following section on page four of the supporting information titled "Chemical Preparation and Storage". The caps used for the 1 dram and 1.5 dram vials are assembled screw caps with hole with PTFE/silicone septum from Sigma Aldrich (product number: SU860078). Similarly, the caps used for the 0.5 dram vials are assembled screw caps with hole with PTFE/silicone septum from Sigma Aldrich (product number: 27262 Supelco).

Light Source Materials

    Light Source: Double-density white-light LEDs were purchased from Creative Lighting Solutions (item no. CL-FRS1210-5M-12V-WH) and used in both of the photoreactors described herein. The emission profile of the light source is shown in Figure S4.

    Connectors: solderless power connectors (Creative Lighting Solutions, product code: CL-FRS1210-2WPWER) are directly connected to the LED strips by cutting the plastic covering the

first LED on the strip and pulling it back to reveal the copper soldering pads which are inserted into the power connector. The other end of the power connector is connected to a male JST connector (creative lighting solutions, product code: CL-JSTCONNECTOR-10PK).

Chemical Preparation and Storage

Polymerizations conducted under air:

Chemical Preparation: Methyl methacrylate was purified by passing it through a plug of aluminum oxide (activated, basic, Brockman grade I, 58 angstrom, purchased from Thermo Fisher Scientific) to remove the inhibitor. The initiator, DBMM, was dried over calcium hydride and distilled, but stored in air. DMAc was used as received (no SureSeal on the bottle so that it was stored under air).

Chemical Storage: Methyl methacrylate and DBMM were stored in a freezer at -25ºC.

Polymerizations conducted under nitrogen:

Chemical Preparation: Methyl methacrylate and DBMM were purified by drying over calcium hydride overnight followed by distillation under reduced pressure. Anhydrous DMAc stored under argon was purchased from VWR and brought into a nitrogen-filled glovebox.

Chemical Storage: Methyl methacrylate and DBMM were stored in the freezer of a nitrogen-filled glovebox. DMAc was stored on the shelf of a nitrogen-filled glovebox.

Instrumentation

Nuclear magnetic resonance spectra were recorded on a Bruker 400 MHz NMR Spectrometer to analyze polymerization conversion and precipitated polymer. 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. Analysis of polymer molecular weights was performed via gel permeation chromatography (GPC) coupled with multi-angle light scattering (MALS), using an Agilent HPLC fitted with one guard column, three PLgel 5 μm MIXED-C gel permeation columns, a Wyatt Technology TrEX differential refractometer, and a Wyatt Technology miniDAWN TREOS light scattering detector, using tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min. The dn/dc value used for PMMA was 0.084 and all other polymers were analyzed using a known concentration (2.00 mg/mL) assuming 100% mass recovery. MALDI-TOF analysis was performed on a Bruker Microflex LRF equipped with a nitrogen laser operating at 337 nm.

Procedures

Synthesis of Photocatalysts (PCs)

Syntheses of PCs **1–6** were performed using previously reported procedures.[1,2]

Polymerization Procedures

The polymerization reactions described herein were carried out in two types of photoreactor setups to accommodate for reaction vial size and allow for rapid screening of reaction conditions. The photoreactor used for larger vials (anything above 0.5 dram) was a beaker and the photoreactor used for 0.5 dram vials was a 3D-printed part, both of which are described in the following sections along with the polymerization procedures used for each. The same white-light LEDs were used to construct both photoreactors, the emission profile of which is shown in Figure S4.

### Polymerization Procedure 1.0: Data for Table 1 (except controls)

A 20 mL scintillation vial was charged with 5.3 mg of PC **1** (8.6×10^{-6} mol, 1.0 equiv.) to which a stir bar, 0.92 mL of DMAc (1:1 v/v of DMAc: MMA), and 0.92 mL of the monomer, MMA, (8.6×10^{-3} mol, 1000 equiv.) were added. Then, 16.4 µL of the initiator, DBMM, (8.60×10^{-5} mol, 10.0 equiv.) was delivered using a Hamilton syringe. A 24/40 septum cap was placed upside down over the vial and wrapped with electrical tape (see Figures S1 and S2). The reaction vial was then placed in the dark while a white-light LED beaker (Figure S3) was turned on. The reaction vial was then introduced to the white-light LED beaker at which point the polymerization was considered to start (t = 0 for kinetic plots). Two cooling fans and compressed air were used to keep the reaction vials at room temperature.

The same general procedure described above was also performed using vials of the following sizes: 0.5 dram (1.85 mL, 0 mL of air headspace), 1 dram (3.70 mL, 1.86 mL of air headspace), 1.5 dram (5.55 mL, 3.71 mL of air headspace), and 2 dram (7.39 mL, 5.55 mL of air headspace). The caps for the vials were varied to fit each corresponding vial and allow for aliquots to be removed without introducing additional air. As such, the following caps were used for each vial:

20 mL scintillation vial: 24/40 septum stopper upside down, wrapped with electrical tape
2 dram vial: 14/20 septum stopper upside down, wrapped with electrical tape
1.5 dram, 1 dram, and 0.5 dram: PP caps with PTFE/Silicone centers (see materials section for more details), wrapped with electrical tape
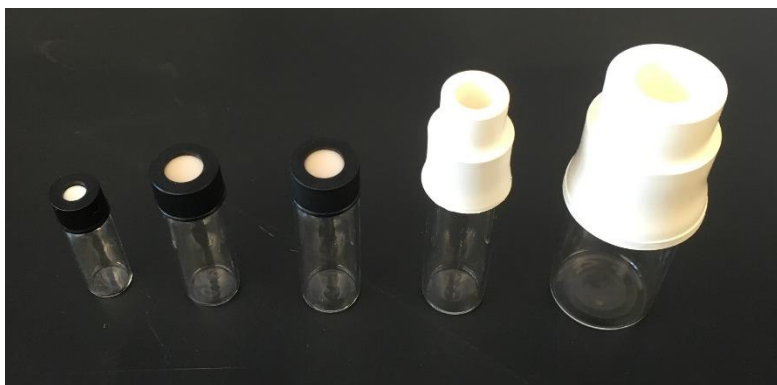
Figure S1. Reaction vials used to study the effect the amount of headspace of air on the polymerization of MMA via O-ATRP.
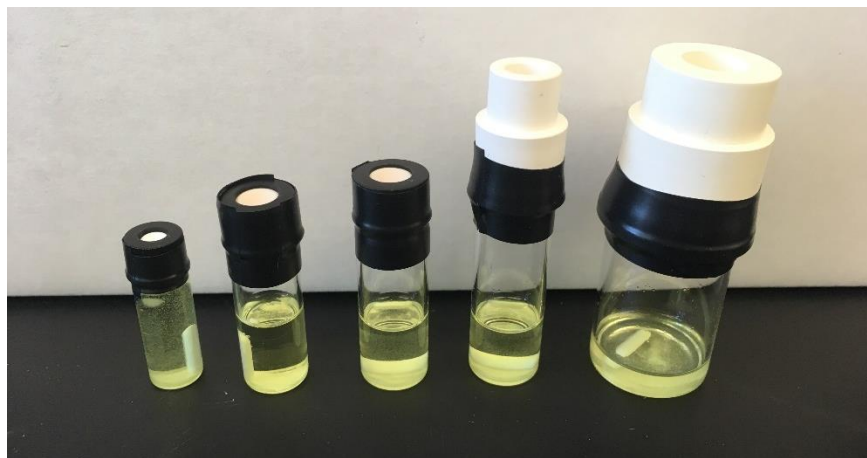
Figure S2. Prepared reaction vials used to study the effect the amount of headspace of air on the polymerization of MMA via O-ATRP.
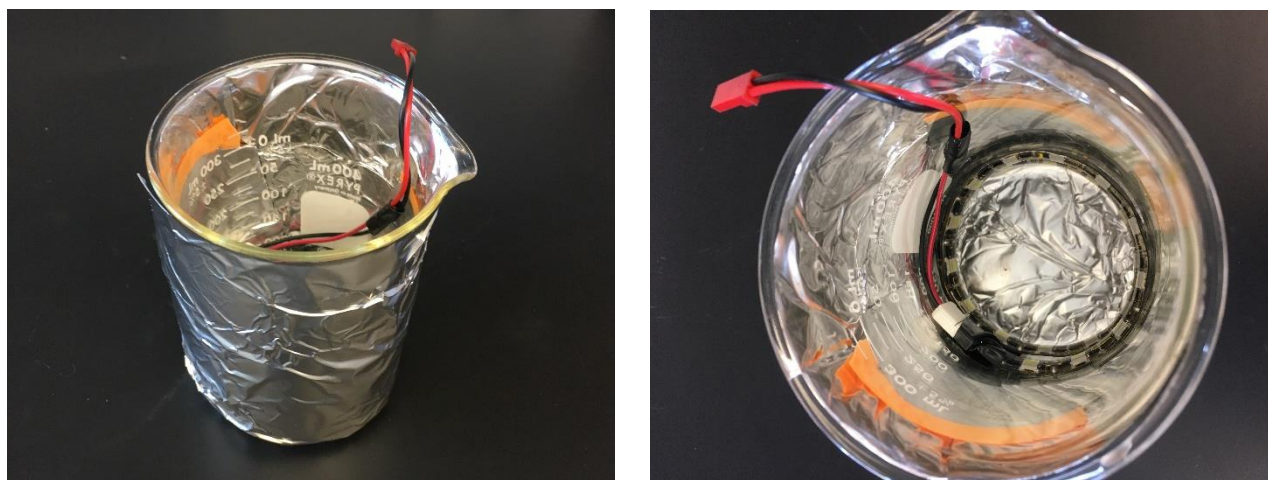
Figure S3. White-light LED beaker used as the light source for Polymerization Procedure 1.0 (see above). The beaker was prepared by wrapping a 400 mL beaker in aluminum foil (see left). Inside the beaker a 16-inch strip of white-light LEDs (27 lights) from Creative Lighting Solutions (item no. CL-FRS1210-5M-12V-WH) was wrapped along the inside. The end of the LED strip was connected to one end of a solderless power connector (Creative Lighting Solutions, product code: CL-FRS1210-2WPWER), the other end of which is connected to a male JST connector (Creative Lighting Solutions, product code: CL-JSTCONNECTOR-10PK). The power connector is wrapped in a piece of electrical tape to keep it firmly closed and to cover the first LED of the strip (26 available LEDs).
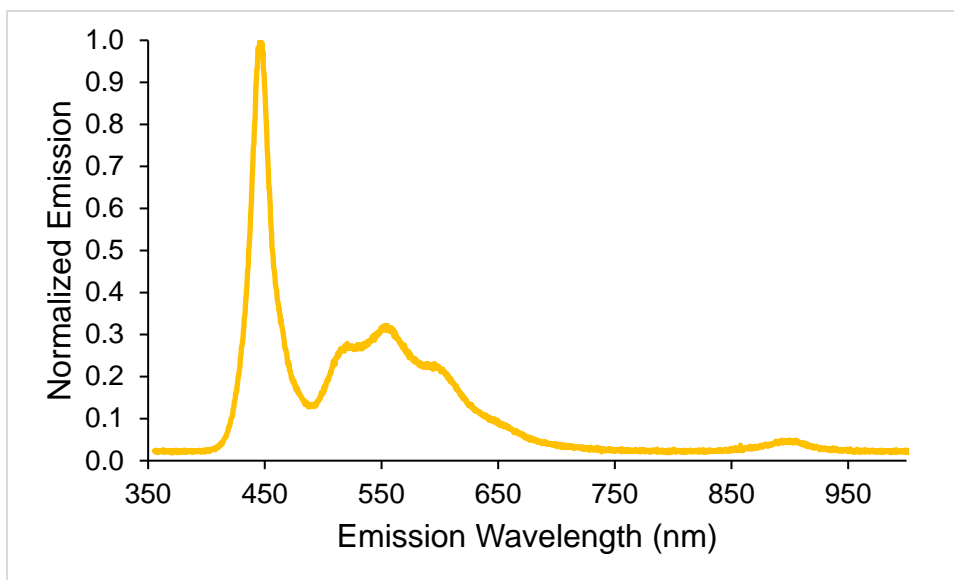
Figure S4. Plot of the normalized emission of the white-light LEDs used to construct the two photoreactor setups described herein.

Procedure for PMMA Macroinitiator Synthesis (Figure 4)

To scale up the polymerization while maintaining no headspace in the reaction vial, a 1.50 dram vial was used which required the use of a white-light LED beaker as the photoreactor.

A 1.50 dram vial was equipped with a stir bar and charged with 15.8 mg of PC **1** (25.7×10^{-6} mol, 1 equiv.) to which 2.75 mL of DMAc (1:1 v/v of DMAc:MMA), 2.75 mL of MMA (25.7×10^{-3} mol, 1000 equiv.), and 49.1 µL of DBMM (25.7×10^{-5} mol, 1 equiv.) were added sequentially. The vial was capped with a PTFE/Silicon screw cap, which was then wrapped in parafilm. The vial was allowed to stir in a white-light LED beaker (described above) for 7 hours before an aliquot was removed and quenched with BHT chloroform to determine conversion by NMR (conversion = 77% by NMR, see procedure for polymerization kinetics and polymer analysis below). The polymerization mixture was then loaded into a syringe and slowly added to 450 mL of stirring methanol in a dry ice/acetone bath (approximately -78ºC). After stirring for an hour, the polymer was collected via vacuum filtration and dried in a vacuum oven at 50ºC overnight to yield 1.018 g of polymer (40% yield) with M_n = 8.21 kDa (see Table S3 for more details). This macroinitiator was then used for chain extension and block copolymerization experiments (see procedures below).

Polymerization Procedure 2.0: Data for Table 2 and Figure 2

      A 0.5 dram (1.85 mL) glass vial was charged with 5.3 mg of PC 1 (8.6×10^{-6} mol, 1.0 equiv.) to which a stir bar, 0.92 mL of DMAc (1:1 v/v of DMAc: MMA), and 0.92 mL of the monomer, MMA, (8.6×10^{-3} mol, 1000 equiv.) were added. Then, 16.4 µL of the initiator, DBMM, (8.60×10^{-5} mol, 10.0 equiv.) was delivered using a Hamilton syringe. A PTFE/Silicon septum cap was used to seal the vial and a small piece of electrical tape was wrapped around the edge of the cap. The reaction vial was then placed in the dark while the white-light LEDs on the 3D-printed photoreactor were turned on (Figure S5). The reaction vial was then introduced to the white-light LEDs at which point the polymerization was considered to start (t = 0 for kinetic plots). Two cooling fans and compressed air were used to keep the reaction vials at room temperature (see "temperature control" section below for more details).

      The photoreactor setup used for these polymerizations was 3D-printed using high-impact polystyrene (HIPS) on a flashforge 3D-printer lined with two 16-inch strips of white-light LEDs which exhibit the emission profile shown in Figure S4. The photoreactor setup was constructed to allow for rapid screening of reaction conditions while keeping stirring and light intensity across reaction vials uniform. This is achieved since the photoreactor is designed with slots to hold 0.5 dram vials in place allowing the reactions to stir efficiently without falling over and ensuring that each vial is placed directly next to four LEDs (see Figure S5). Reaction vials were placed in every other slot to keep the temperature of the reactions that of room temperature (see "temperature control" section for more details).
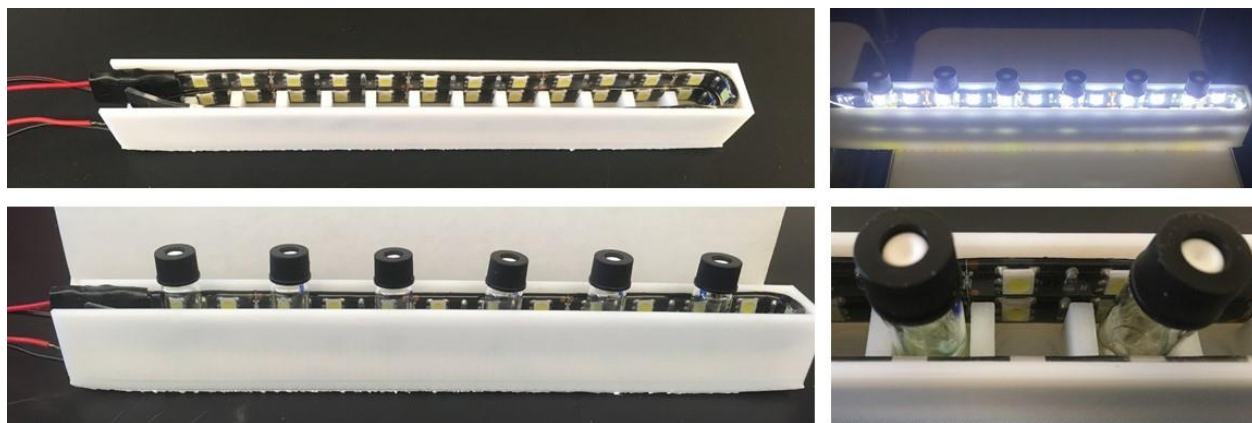
Figure S5. The 3D-printed photoreactor used for polymerizations in 0.5 dram vials is lined with two 16-inch strips of white-light LEDs (top left). The end of each of the white-light LED strips is connected to one end of a solderless power connector (Creative Lighting Solutions, product code: CL-FRS1210-2WPWER), the other end of which is connected to a male JST connector (Creative Lighting Solutions, product code: CL-JSTCONNECTOR-10PK). The power connector is wrapped in a piece of electrical tape to keep it firmly closed and to cover the first LED of the strip. Reaction vials are placed in the holders in every other slot since this configuration was found to be necessary to ensure efficient cooling (bottom left). Reactions running in the photoreactor on a standard stir plate (top right). Each reaction vial is situated directly next to four LEDs (bottom right).

Polymerization Procedure for On/Off Experiment (Figure 3)

The same general procedure as "Polymerization Procedure 2.0" was followed except that in "dark" periods, the reaction flask was wrapped entirely with aluminum foil.

## Polymerization Procedure for Chain Extension from PMMA Macroinitiator (Figure 4)

A 0.5 dram vial was equipped with a stir bar and charged with 2.7 mg of PC **1** (4.4×10^{-6} mol, 1.0 equiv.) and 0.300 g of the PMMA macroinitiator described above (M_n = 8.21 kDa, 3.65×10^{-5}, 8.40 equiv.) which were dissolved in 1.15 mL of DMAc (1.89:1 of DMAc: MMA) using a vortex mixer. Then 0.61 mL of MMA were added (5.7×10^{-3} mol, 1,310 equiv.), the vial was capped with a PTFE/Silicon screw cap, a piece of parafilm was wrapped over the cap, and the vial was introduced to the 3D-printed photoreactor with white-light LEDs for 14 hours. After 14 hours, the reaction mixture as loaded into a syringe and slowly dripped into room temperature methanol to precipitate the polymer. After stirring for an hour, the polymer was collected via vacuum filtration and dried in a vacuum oven at 50°C overnight to yield 0.870 g of polymer (77% conversion by gravimetric analysis). The resulting chain extended PMMA was found to have M_n = 20.6 kDa, $Đ$ = 1.34, and I^* = 89% (See Table S3 for more details). We note that the stoichiometry was odd for this reaction (1310: 8.4: 1 of MMA: macroinitiator: PC) in order to use enough solvent to dissolve the macroinitiator and eliminate vial headspace in the 0.5 dram vial.

Block Copolymerization from PMMA Macroinitiator (Figure 4)

A 0.5 dram vial was equipped with a stir bar and charged with 1.8 mg of PC 1 (2.9×10^{-6} mol, 1.0 equiv.) and 0.200 g of the PMMA macroinitiator described above (M_n = 8.21 kDa, 2.44×10^{-5}, 8.40 equiv.) which were dissolved in 1.27 mL of DMAc (1.5:1 of DMAc: MMA) using a vortex mixer. Then 0.64 mL of BnMA were added (3.7×10^{-3} mol, 1,300 equiv.), the vial was capped with a PTFE/Silicon screw cap, a piece of parafilm was wrapped over the cap, and the vial was introduced to the 3D-printed photoreactor with white-light LEDs for 14.5 hours. After 14.5 hours, an aliquot as taken for analysis by NMR and the rest of the reaction mixture as loaded into a syringe and slowly dripped into room temperature methanol to precipitate the polymer. After stirring for an hour, the polymer was collected via vacuum filtration and dried in a vacuum oven at 50°C overnight to yield 0.632 g of polymer (74% yield). The resulting p(MMA-b-BnMA) copolymer was found to have M_n = 34.3 kDa, $Đ$ = 1.50, and I^* = 86% (see Table S3 for more details).

Temperature Control

A 0.5 dram scintillation vial equipped with a stir bar was charged with 1.00 mL of DMAc and capped with a PTFE/Silicone septum cap. A hole was punctured through the top of the cap with a needle and the probe of a hand-held thermocouple was inserted into the solution of DMAc. The vial was place in the 3D-printed photoreactor with the white-light LEDs turned on. Two small fans and compressed air were used to cool the reaction vial to maintain room temperature. We note that the temperature of our laboratory typically fluctuates between 23ºC and 27ºC throughout the day and we observed that the temperature measured using the hand-held probe does fluctuate in accordance with the fluctuations of the temperature of the room. However, the maximum temperature recorded using the probe was found to be 26.8ºC (Figure S6), allowing us to confirm that no significant heating of the reactions is caused by the photoreactor.
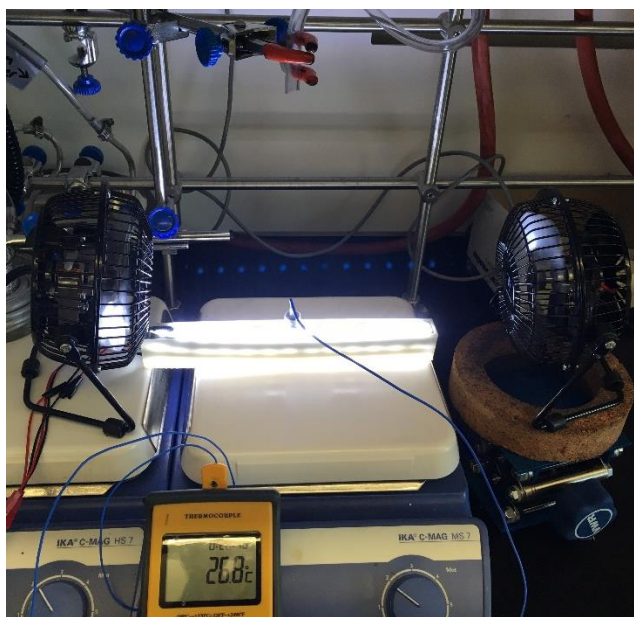
Figure S6. Apparatus used to approximate the temperature of polymerization reactions.

Procedure for Polymerization Kinetics and Polymer Analysis

To evaluate the kinetics and growth of polymer molecular weight as a function of conversion for each reaction, an aliquot of 0.15 to 0.20 mL of reaction mixture was taken using a nitrogen-purged needle and injected into a solution of deuterated chloroform containing the radical inhibitor, butylated hydroxyl toluene (BHT, 250 ppm), at predetermined times after the start of the polymerization (when the reaction mixture was exposed to light). Specifically, the needle of a 1.00 mL syringe is purged with nitrogen by drawing nitrogen from a sacrificial flask three to five times while dispensing in between. On the last iteration, the nitrogen is dispensed from the syringe (plunger is fully depressed) and the needle is used to puncture the septum cap of the reaction flask from which the aliquot is drawn. Finally, after each aliquot is removed, parafilm is immediately used to cover the cap of the reaction vial. Aliquots are taken in this manner to ensure no further introduction of air throughout the polymerization and no accidental injection of nitrogen into the reaction vial during the polymerization. The ^{1}H NMR spectrum of the aliquot is immediately acquired to determine the percent conversion of monomer at that time. After NMR analysis, the sample is dried using compressed air, re-dissolved in HPLC grade, unstabilized tetrahydrofuran and analyzed by GPC.

Procedure for Polymer Analysis by MALDI-TOF

MALDI-TOF spectra were acquired on a Bruker Microflex LRF equipped with a nitrogen laser operating at 337 nm using linear positive ion mode. The PMMA macroinitiator synthesized according to the procedure on page S9 was dissolved in THF to make a 1.0 mg/mL stock solution. Ten microliters of the polymer stock solution was mixed with 10 µL of a solution of dihydroxybenzoic acid, DHB, (matrix) in THF (20.0 mg/mL) to which 1.5 µL of sodium trifluoroacetate was added (cationization agent). The solution was vortexed, centrifuged, and 0.5 µL was withdrawn and dispensed on the target plate. Each polymer sample was analyzed in triplicate. The samples were externally calibrated using a protein mixture (Protein Calibration Standard I, containing Insulin, Ubiquitin I, Cyctochrom C and Myoglobin, Bruker Daltonics Part No. 8206355) for calibration with analytes ranging from 4 kDa to 20 kDa.

Control Experiments

Control experiments were conducted according to "Polymerization Procedure 2.0" except either the initiator (DBMM), light, or the photocatalyst was omitted. For the reaction run in the absence of light, the reaction vial was wrapped in aluminum foil and still placed in the photoreactor on a stir plate. The outcomes of these experiments are described in Table 1 of the main text.

Properties of Photoredox Catalysts

Table S1. Absorption properties of the PCs explored in this work

PC	abs λ_{max} (nm)^a	$\varepsilon_{\lambda max, abs}$ (M^{-1}cm^{-1})^a	Ref.
1	388	26,600	1
2	384	25,900	2
3	363	22,000	2
4	388	21,100	2
5	382	37,700	2
6	379	20,600	2
7	384	25,300	2

^{a}Spectra acquired in DMAc.

Table S2. Redox Properties of the PCs explored in this work

PC	em λ_{max} (nm)	$E_{S1, exp}$ (eV)	$E_{T1, calc}$ (eV)	$E_{1/2}$ (^{2}PC$^{•+}$/^{1}PC) (V vs. SCE)	E^0_{ox} (^{2}PC$^{•+}$/^{1}PC) (V vs. SCE)	$E^{0*}_{S1, exp}$ (^{2}PC$^{•+}$/^{1}PC*) (V vs. SCE)	$E^{0*}_{T1, calc}$ (^{2}PC$^{•+}$/^{3}PC*) (V vs. SCE)	Ref.
1	506	2.45	2.11	0.65	0.42	-1.80	-1.70	1
2	466	2.66	2.13	0.63	0.43	-2.03	-1.70	2
3	532	2.33	2.28	0.52	0.37	-1.81	-1.91	2
4	467	2.65	2.16	0.72	0.58	-1.93	-1.58	2
5	522	2.37	2.18	0.54	0.30	-1.83	-1.88	2
6	564	2.20	2.30	0.66	0.45	-1.54	-1.85	2
7	466	2.66	2.09	0.63	0.40	-2.03	-1.69	2

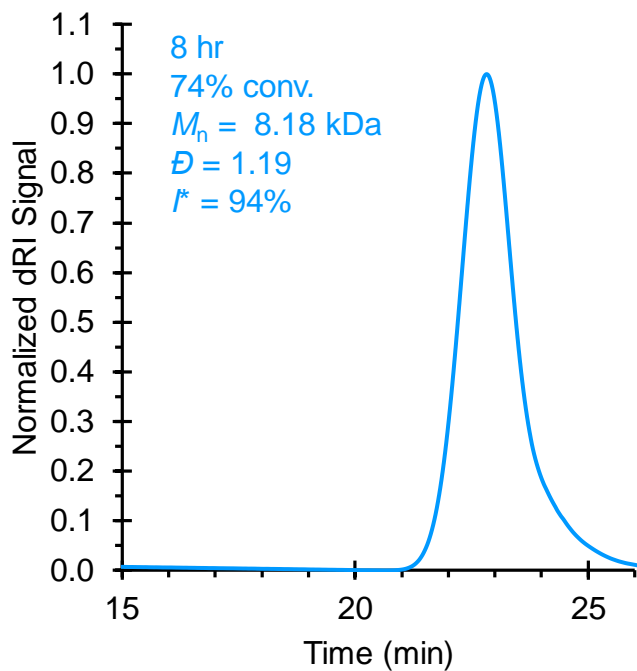# Supplementary Polymerization Data

NMR Spectra of Precipitated Polymers
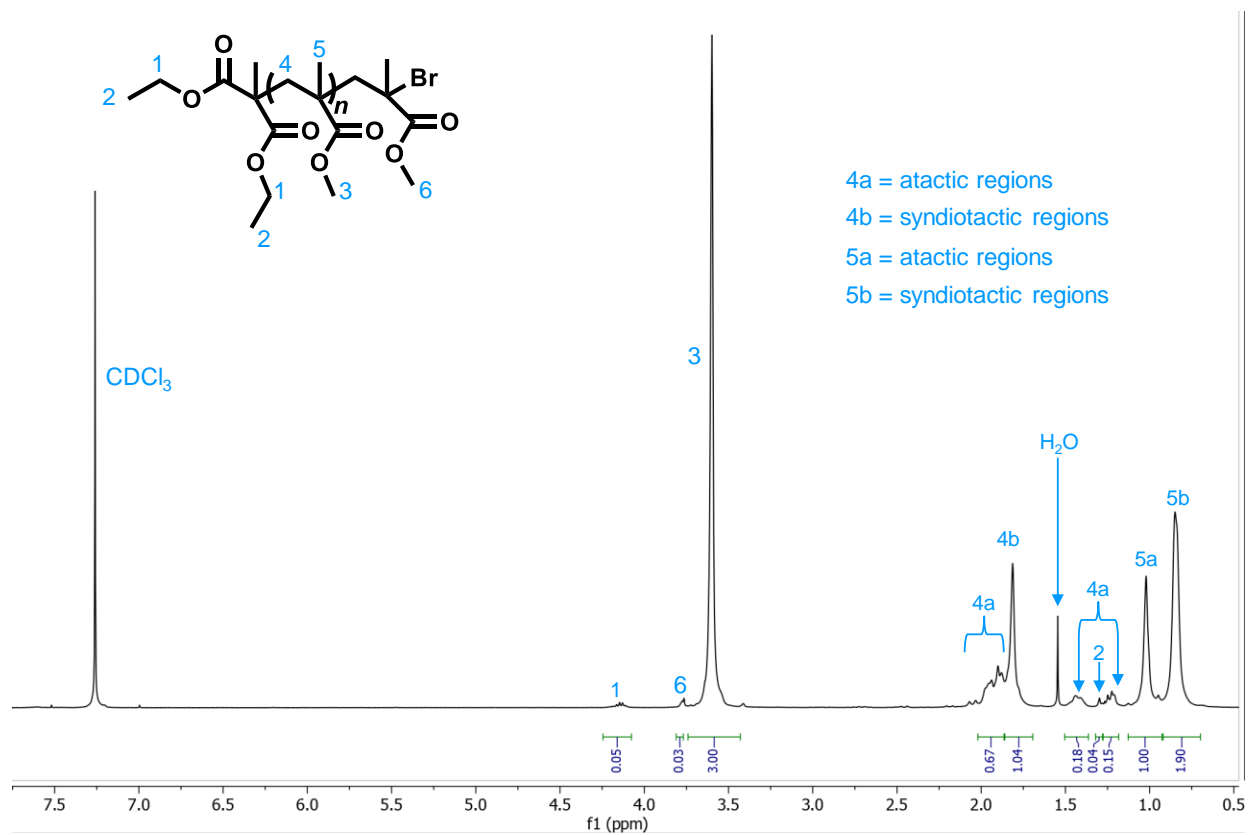
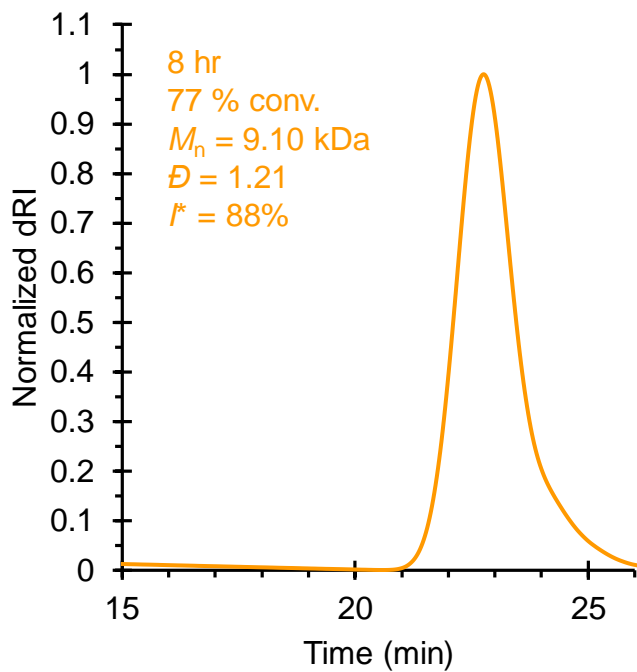**Figure S7.** ^{1}H NMR of PMMA synthesized under nitrogen (CDCl₃, 400 MHz, PMMA DP = 80, $M_{n(NMR)}$ = 8.26 kDa).
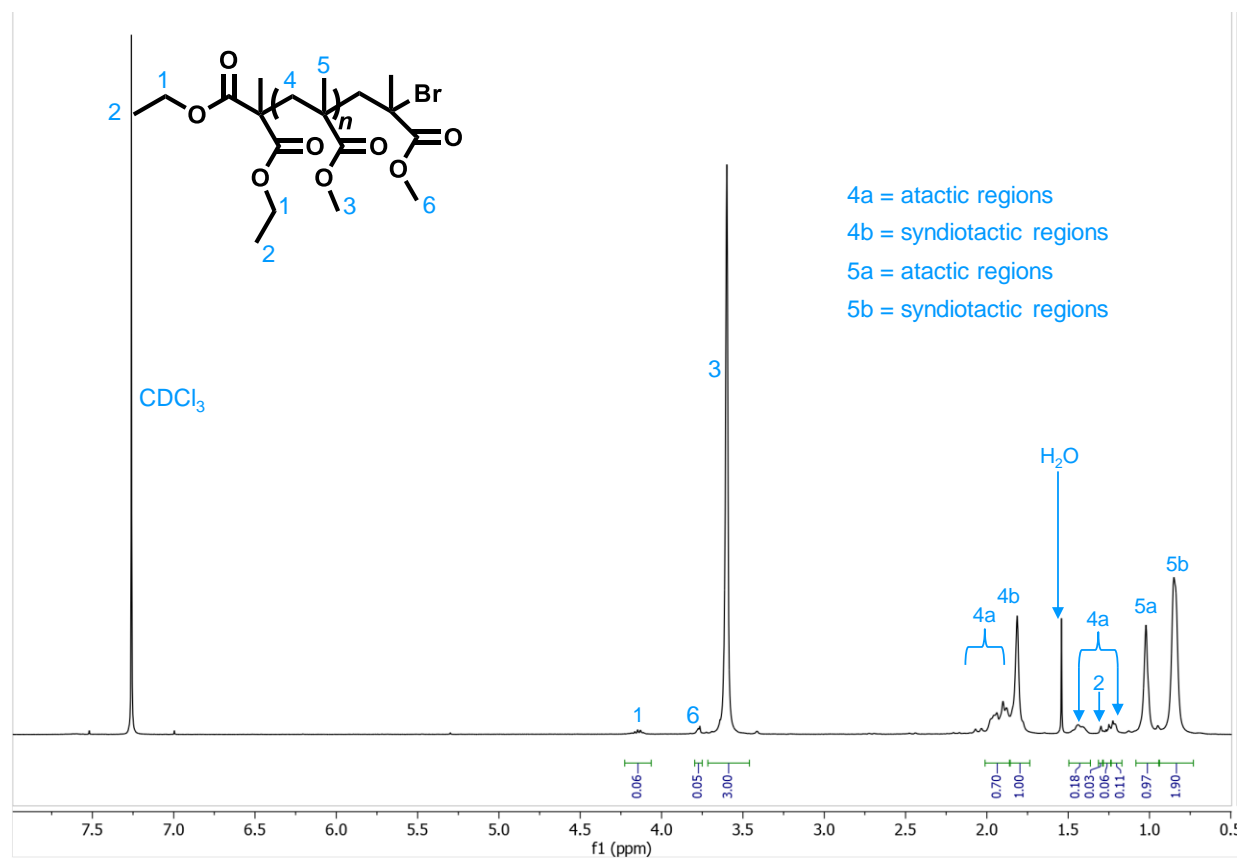
Figure S8. ^{1}H NMR of PMMA synthesized under air (CDCl$_3$, 400 MHz, PMMA DP = 67, $M_{n(NMR)}$ = 6.92 kDa).

8 hr
74% conv.
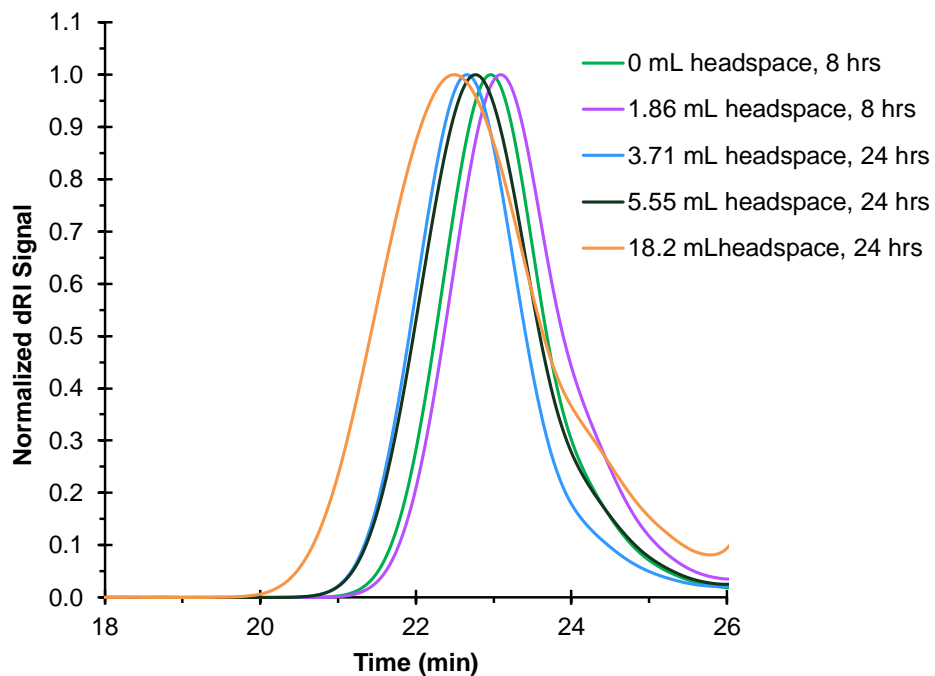M_n = 8.18 kDa
$Đ$ = 1.19
I^* = 94%

Figure S9. GPC trace of PMMA synthesized under nitrogen using PC **1**.
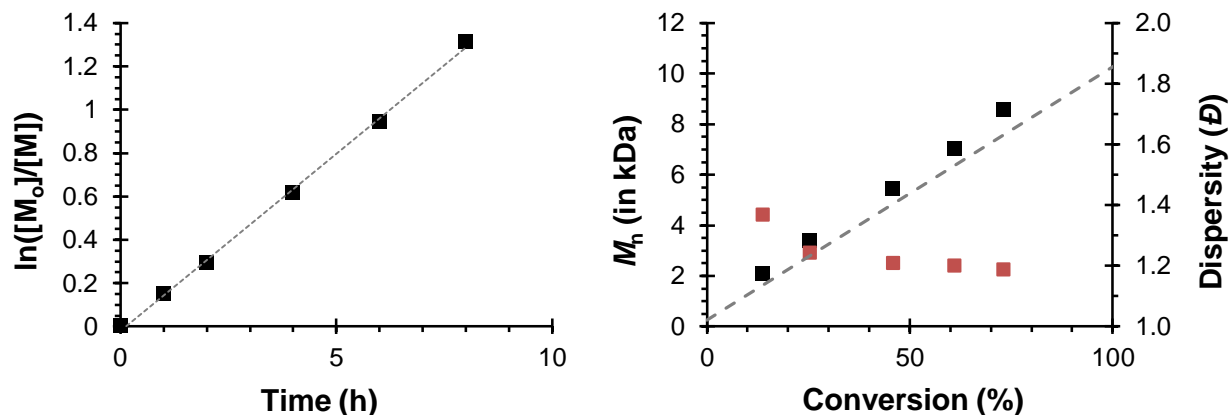
8 hr
77 % conv.
M_n = 9.10 kDa
$Đ$ = 1.21
I^* = 88%

**Figure S10.** GPC trace of PMMA synthesized under air using PC **1**.

Figure S11. GPC traces of PMMA synthesized in vials of different sizes using PC **1**. The corresponding molecular weight and dispersity data are presented in Table 1 of the main text.
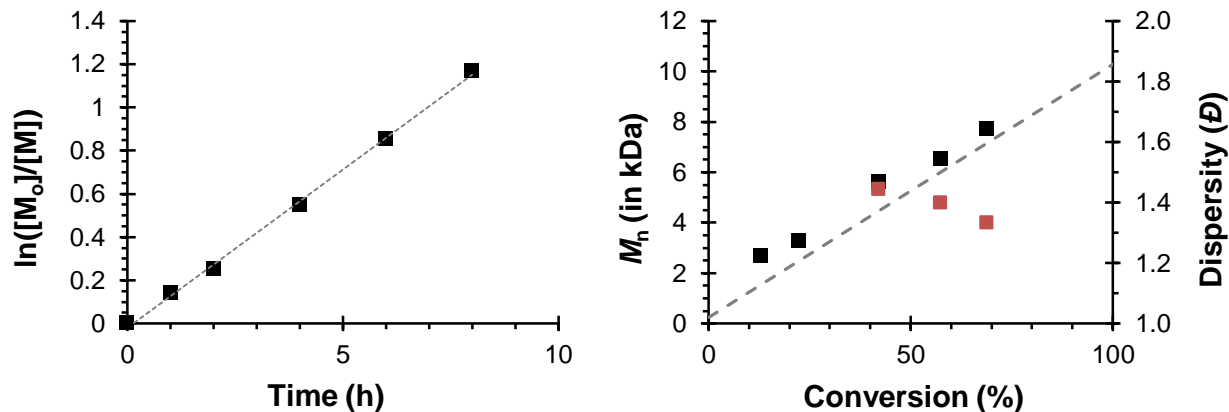
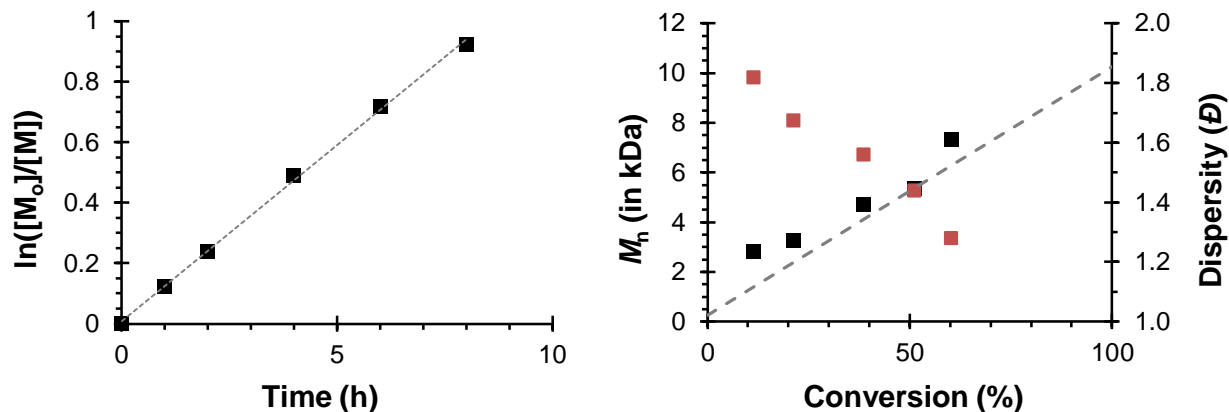# Kinetic Data and Polymer Molecular Weight Growth

Figure S12. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **2** under air. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).
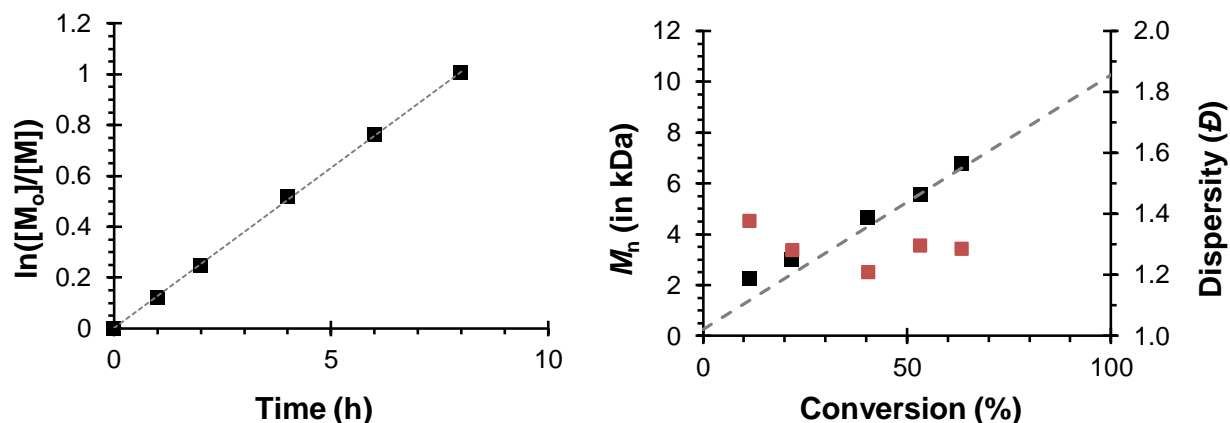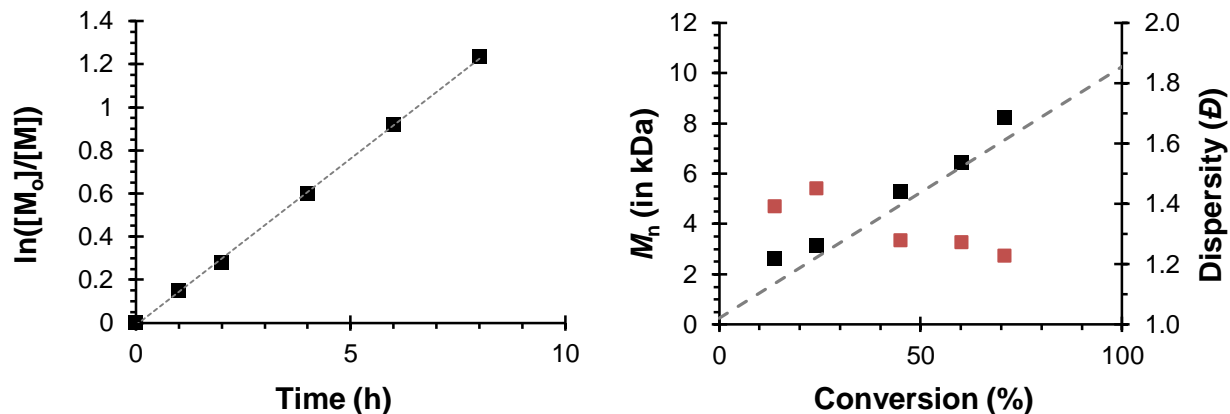

Figure S13. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **2** under nitrogen. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).
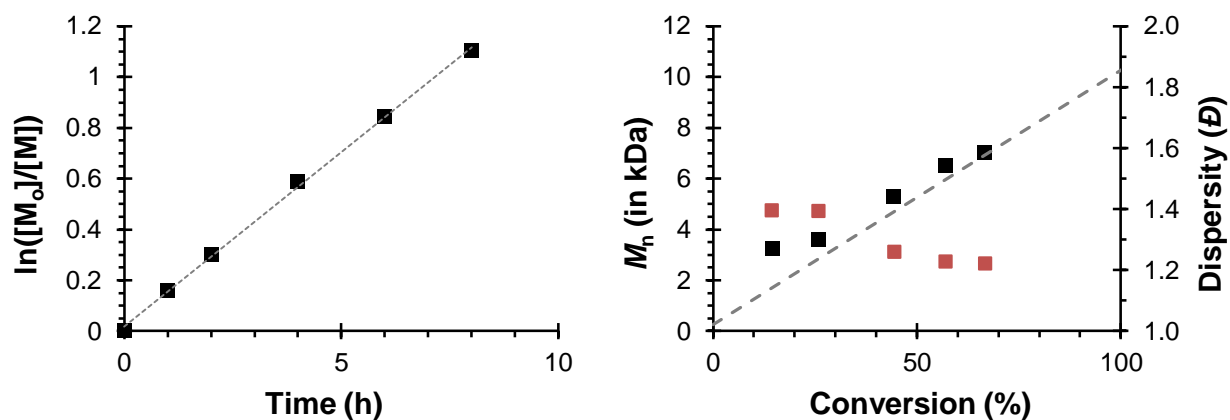
Figure S14. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **3** under air. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis, low conversion values were greater than 2.0).
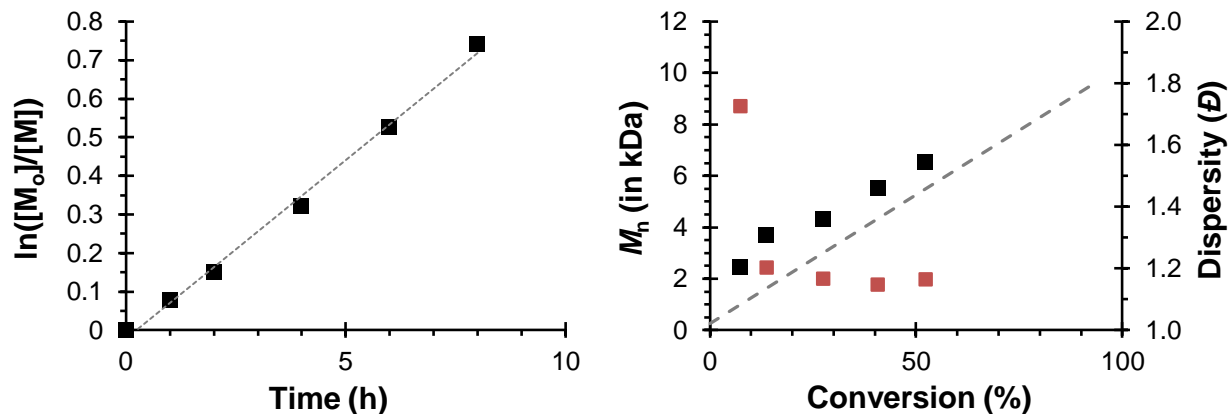

Figure S15. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **3** under nitrogen. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).
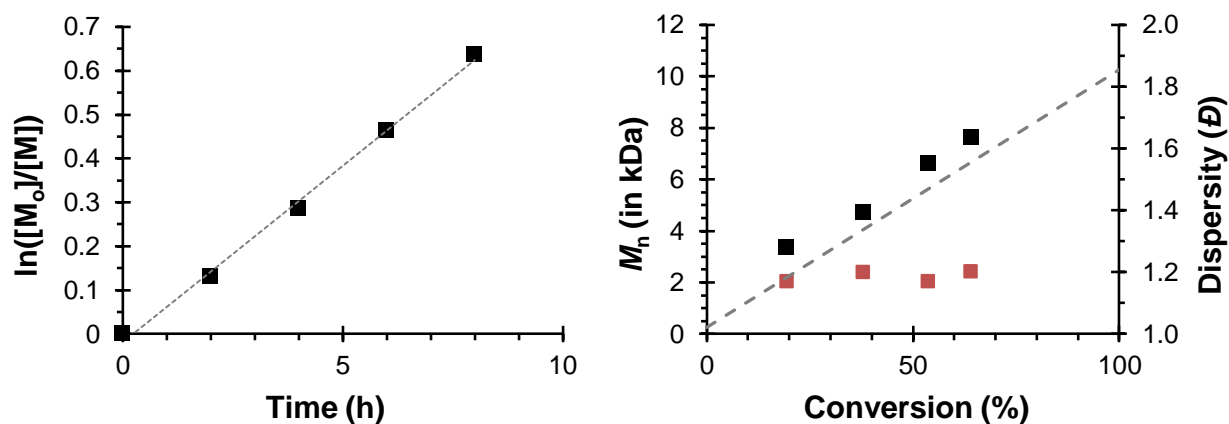
Figure S16. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **4** under air. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).
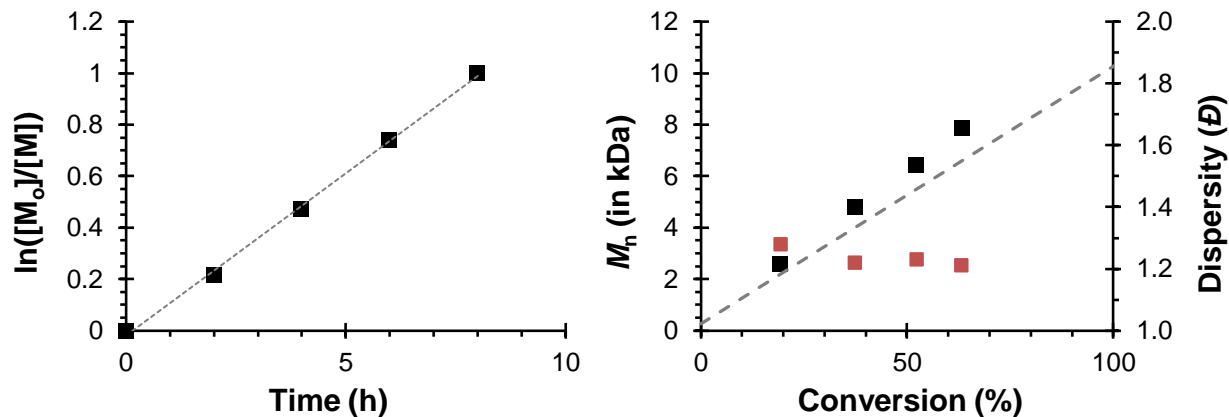

Figure S17. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **4** under nitrogen. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).

Figure S18. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **5** under air. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).
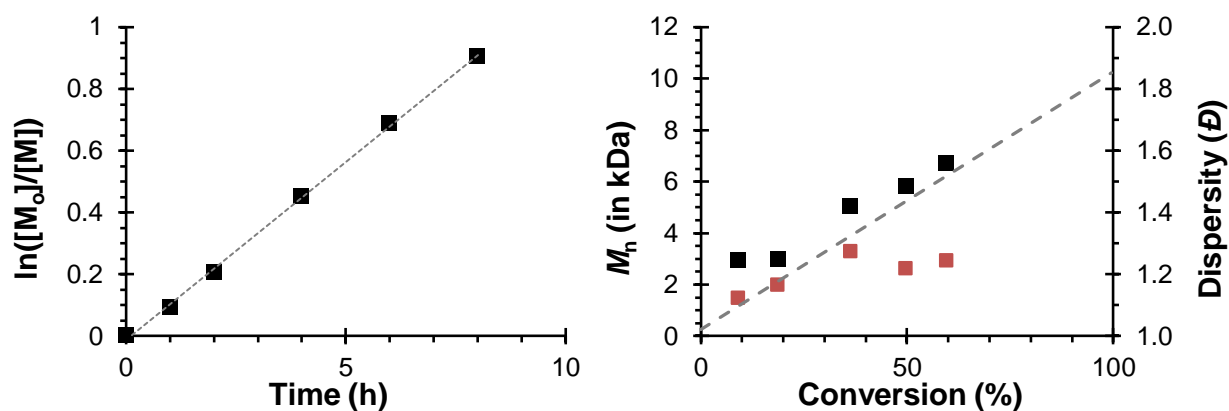

Figure S19. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **5** under nitrogen. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).

Figure S20. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **7** under air. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).
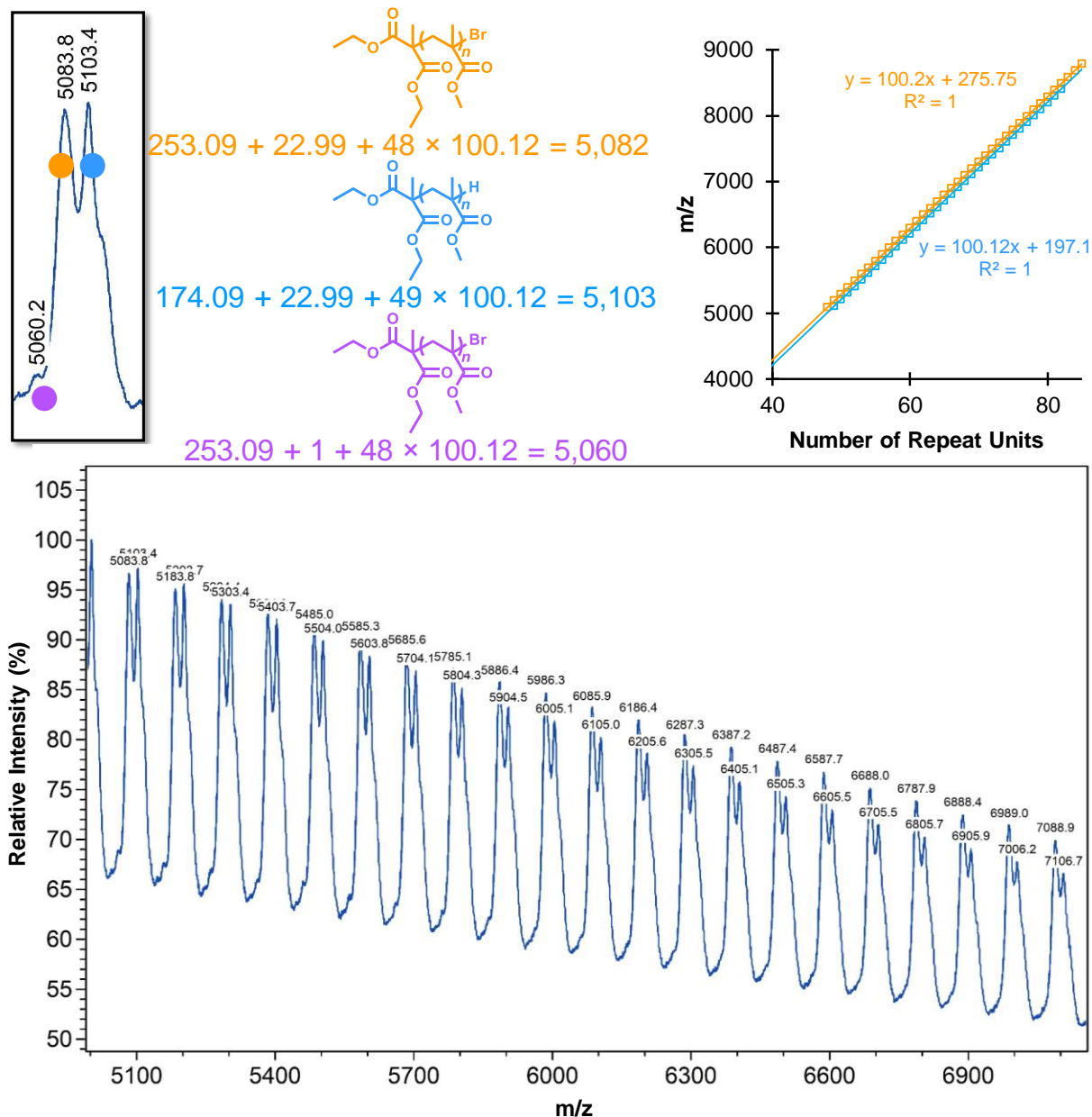

Figure S21. Plot of the natural log of monomer consumption as a function of time (left) for the O-ATRP of MMA mediated by PC **7** under nitrogen. Plot of growth of the experimentally measured number average molecular weight (M_n) as a function of monomer conversion (right graph, black squares) with theoretical values (grey dashed line). Dispersity of the PMMA at each molecular weight are shown (red squares, secondary y-axis).

MALDI-TOF Analysis of Polymer Synthesized under Air

$253.09 + 22.99 + 48 \times 100.12 = 5{,}082$

$174.09 + 22.99 + 49 \times 100.12 = 5{,}103$

$253.09 + 1 + 48 \times 100.12 = 5{,}060$

Figure S22. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) analysis of PMMA synthesized under air (M_n = 8.2 kDa). Two peaks were assigned to polymer chains with alkyl bromide (orange) or hydrogen (blue) terminal groups and the cationization agent, sodium (top left). A third peak was observed corresponding to protonation of alkyl bromide terminated polymer (purple). A plot of the mass-to-charge (m/z) ratio as a function of number of MMA repeat units (MW = 100.12 g/mol) was used to confirm these assignments (top right). However, analysis of the peaks corresponding to protonation (purple) was not performed because only three peaks were resolved.

Additional Chain Extension and Block Copolymerization Data

Table S3. Results for the Chain Extension and Block Copolymerization Performed under Air

Experiment	PC	time (h)	conv. (%)	$M_{n,th}$ (kDa)	M_n (kDa)	M_w (kDa)	$Đ$ (M_w/M_n)	I^* ($M_{n,th}/M_n \times 100$)
PMMA Macroinitiator	1	7	77	8.0	8.2	10.0	1.22	97
Chain Extended PMMA	1	14	77	18.3	20.6	27.6	1.34	89
P(MMA-b-BnMA) Copolymer	1	14.5	94	29.7	34.3	51.3	1.50	86

References

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[2] McCarthy, B. G.; Pearson, R. M.; Lim, C-H.; Sartor, S. M.; Damrauer, N. H.; Miyake, G. M. *J. Am. Chem. Soc.* **2018**, *140*, 5088 –5101.