Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

A Dual Initiator Approach for Oxygen Tolerant RAFT Polymerization

Nicholas G. Taylor, Marcus H. Reis, Travis P. Varner, Johann L. Rapp, Alexis Sarabia, Frank A. Leibfarth*

[1]*Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599*
*Correspondence to: frankl@email.unc.edu

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1.0 Material and methods

1.1 Reagents

Azobisisobutyronitrile (AIBN), cyclohexyl methacrylate, *N*-acyloylmorpholine, 2-ethylhexyl acrylate, *n*-butyl acrylate, *N*-(isobutoxymethyl)acrylamide, styrene, *tert*-butylstyrene, cyanomethyl dodecyl trithiocarbonate (CMDT), 2-cyano-2-propyl benzodithioate (CPDB), 1,2-dichlorobenzene, 1,4-dioxane, and *N*,*N*-dimethylformamide were purchased from Sigma Aldrich (USA). Propyl acetate was purchased from TCI. V-70 azo initiator was purchased from Wako Chemicals (USA). *tert*-butyl acrylate was purchased from Fisher Scientific. Dibenzyl trithiocarbonate (DBTTC), and 2-(butylthiocarbonothioylthio)propanoic acid (BTTCP) were purchased from Boron Molecular. All monomers were passed through an alumina column to remove inhibitor prior to use.

1.2 Analysis

Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker model DRX 400 MHz spectrometer with a solvent resonance as the internal standard (^{1}H NMR: $CHCl_3$ at 7.26 ppm).

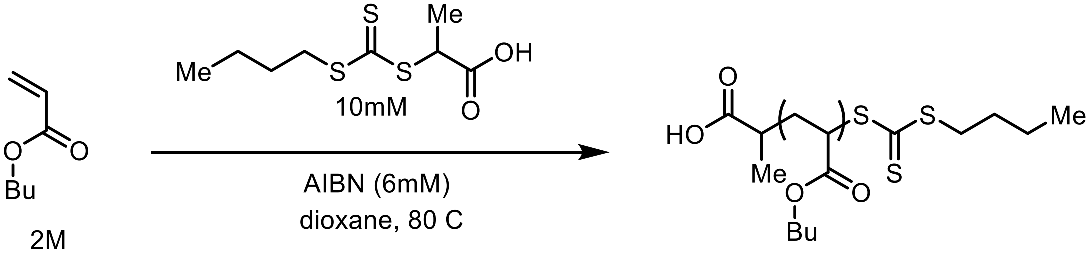
GPC was performed on a Tosoh EcoSEC Elite GPC system equipped with a TSKgel Super HM-M (17392) column maintained at 40 °C with an RI detector and a Tosoh Biosciences Multi-Angle Laser Light Scattering Lens3 Detector. Tetrahydrofuran was used as the mobile phase at a flow rate of 0.5 mL/min. Molecular weight and dispersity data are reported either by multi-angle light scattering using dn/dc values determined from 100% mass recovery, or by RI relative to polystyrene standards.

Reaction monitoring by *in situ* infrared spectroscopy was carried out using a MettlerToledo ReactIR™ 15 instrument with a SiComp™ silicon tip probe, liquid N_2 MCT detector, and the iCIR software 4.3. A dioxane reference spectrum was automatically subtracted. The disappearance of the *n*-butyl acrylate alkene stretch at 1650 cm^{-1} was monitored for all kinetics experiments. Fifty scans were averaged together to produce an IR spectrum time point every fifteen seconds.

Oxygen concentration was monitored using a Hamilton OxyFerm FDA Arc 120 oxygen probe. The probe was calibrated using a two-point calibration of oxygen in ambient conditions (21 % pO_2) and hypoxic conditions (0 % pO_2) performed at room temperature. Scans were acquired every three seconds of each polymerization.

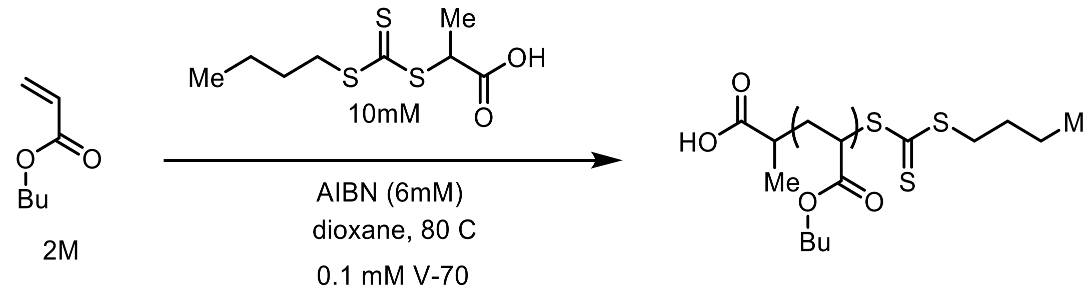
2.0 General Remarks for Batch Polymerization Kinetics Performed in a Three Neck Flask

All reactions were run on a 16 mmol scale in a three neck 10 mL round bottom flask with a magnetic stir bar at 600 rpm. One of the side necks was fitted with septa. The central neck was fitted with a Hamilton OxyFerm FDA Arc 120 oxygen probe. Finally, the SiComp™ silicon tip probe was fitted into the third neck with a greased ground glass joint adaptor (see attached image below).



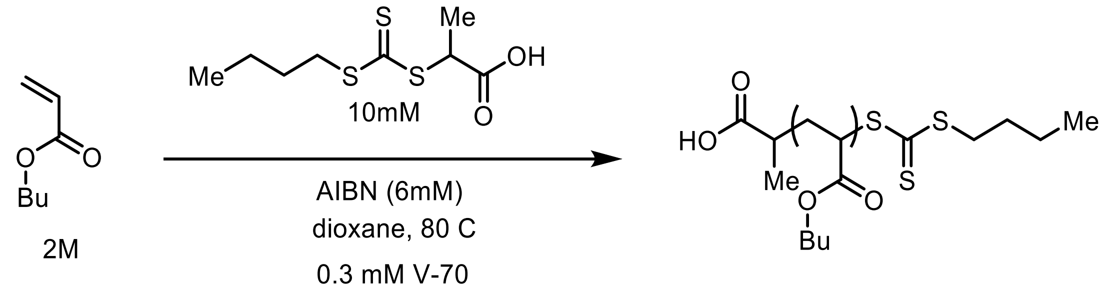
2.1 Batch Reaction Set-Up for IR and O_2 Analysis of Polymerization with 6 mM AIBN

A three neck 10 mL round bottom flask equipped with a magnetic stir bar, a Hamilton OxyFerm FDA Arc 120 oxygen probe, and the SiComp™ silicon tip probe (*vide supra*) was prepared. To this reaction flask was added 19.1 mg of 2-(butylthiocarbonothioylthio)propanoic acid (0.08 mmol), 5.60 mL of dioxane, and 2.30 mL of *n*-butyl acrylate (16 mmol). The solution was then heated to 80° C using an oil bath. After ensuring complete heating, the recording of IR spectra and O_2 data was started, immediately followed by the addition of 0.1 mL of 480 mM AIBN in dioxane to the reaction vessel. When the signal from the monomeric alkene had stopped decreasing in intensity, an aliquot of the reaction was taken and placed over butylated hydroxytoluene to quench.



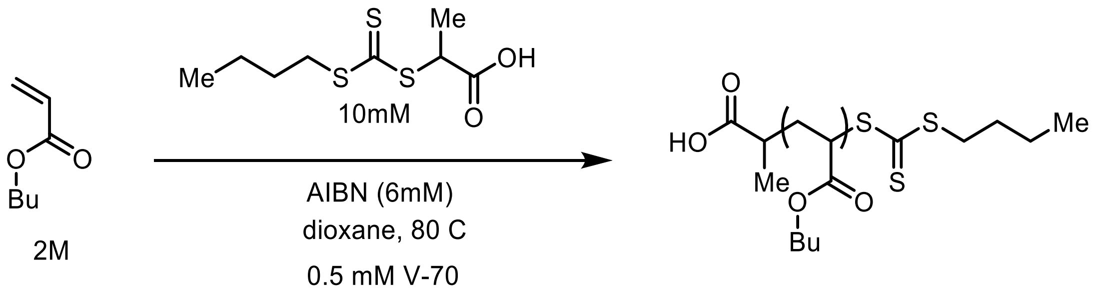
2.2 Batch Reaction Set-Up for IR and O_2 Analysis of Polymerization with 6 mM AIBN and 0.1 mM V-70

A three neck 10 mL round bottom flask equipped with a magnetic stir bar, a Hamilton OxyFerm FDA Arc 120 oxygen probe, and the SiComp™ silicon tip probe (*vide supra*) was prepared. To this reaction flask was added 19.1 mg of 2-(butylthiocarbonothioylthio)propanoic acid (0.08 mmol), 5.47 mL of dioxane, and 2.30 mL of *n*-butyl acrylate (16 mmol). The solution was then heated to 80° C using an oil bath. After ensuring complete heating, the recording of IR spectra and O_2 data was started, immediately followed by the simultaneous addition of 0.1 mL of 480 mM AIBN in dioxane and 0.13 mL of 6 mM V-70 in dioxane to the reaction vessel. When the signal from the monomeric alkene had stopped decreasing in intensity, an aliquot of the reaction was taken and placed over butylated hydroxytoluene to quench.



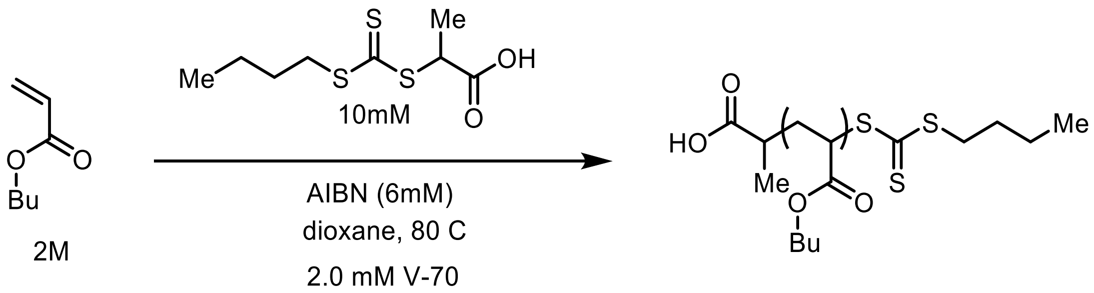
2.3 Batch Reaction Set-Up for IR and O_2 Analysis of Polymerization with 6 mM AIBN and 0.3 mM V-70

A three neck 10 mL round bottom flask equipped with a magnetic stir bar, a Hamilton OxyFerm FDA Arc 120 oxygen probe, and the SiComp™ silicon tip probe (*vide supra*) was prepared. To this reaction flask was added 19.1 mg of 2-(butylthiocarbonothioylthio)propanoic acid (0.08 mmol), 5.47 mL of dioxane, and 2.30 mL of *n*-butyl acrylate (16 mmol). The solution was then heated to 80° C using an oil bath. After ensuring complete heating, the recording of IR spectra and O_2 data was started, immediately followed by the simultaneous addition of 0.1 mL of 480 mM AIBN in dioxane and 0.13 mL of 18.4 mM V-70 in dioxane to the reaction vessel. When the signal from the monomeric alkene had stopped decreasing in intensity, an aliquot of the reaction was taken and placed over butylated hydroxytoluene to quench.



2.4 Batch Reaction Set-Up for IR and O_2 Analysis of Polymerization with 6 mM AIBN and 0.5 mM V-70

A three neck 10 mL round bottom flask equipped with a magnetic stir bar, a Hamilton OxyFerm FDA Arc 120 oxygen probe, and the SiComp™ silicon tip probe (*vide supra*) was prepared. To this reaction flask was added 19.1 mg of 2-(butylthiocarbonothioylthio)propanoic acid (0.08 mmol), 5.47 mL of dioxane, and 2.30 mL of *n*-butyl acrylate (16 mmol). The solution was then heated to 80° C using an oil bath. After ensuring complete heating, the recording of IR spectra and O_2 data was started, immediately followed by the simultaneous addition of 0.1 mL of 480 mM AIBN in dioxane and 0.13 mL of 30.8 mM V-70 in dioxane to the reaction vessel. When the signal from the monomeric alkene had stopped decreasing in intensity, an aliquot of the reaction was taken and placed over butylated hydroxytoluene to quench.

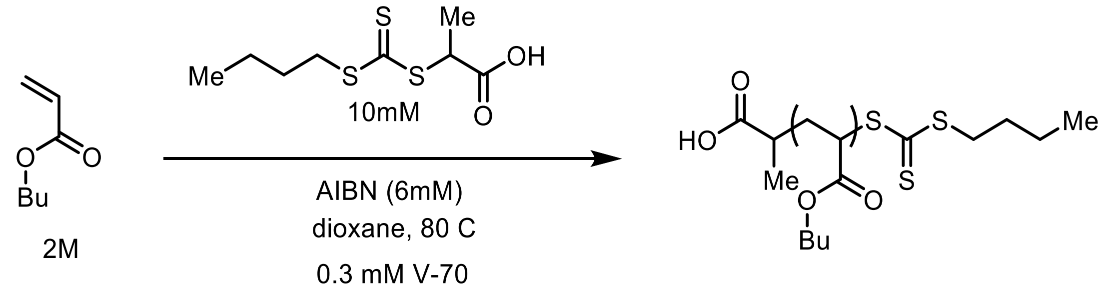


2.5 Batch Reaction Set-Up for IR and O_2 Analysis of Polymerization with 6 mM AIBN and 2.0 mM V-70

A three neck 10 mL round bottom flask equipped with a magnetic stir bar, a Hamilton OxyFerm FDA Arc 120 oxygen probe, and the SiComp™ silicon tip probe (*vide supra*) was prepared. To this reaction flask was added 19.1 mg of 2-(butylthiocarbonothioylthio)propanoic acid (0.08 mmol), 5.47 mL of dioxane, and 2.30 mL of *n*-butyl acrylate (16 mmol). The solution was then heated to 80° C using an oil bath. After ensuring complete heating, the recording of IR spectra and O_2 data was started, immediately followed by the simultaneous addition of 0.1 mL of 480 mM AIBN in dioxane and 0.13 mL of 123 mM V-70 in dioxane to the reaction vessel. When the signal from the monomeric alkene had stopped decreasing in intensity, an aliquot of the reaction was taken and placed over butylated hydroxytoluene to quench.

2.6 General Remarks for Batch Polymerization Kinetic Studies Performed in Vials

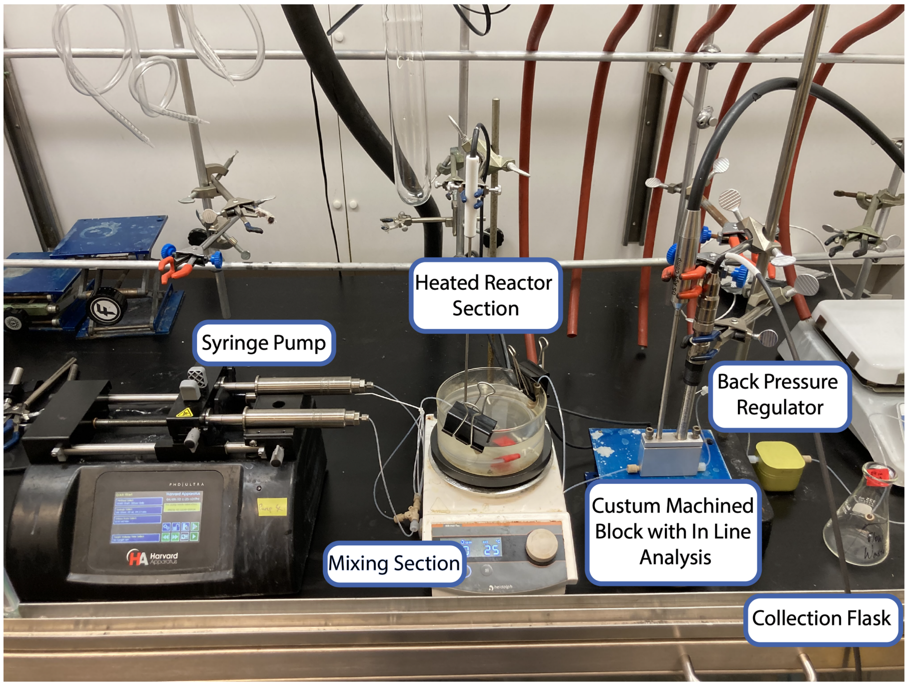
All reactions were performed in 1-dram, 2-dram, or 20 mL vials containing a magnetic stir bar at 300 rpm unless stated otherwise. Polymerizations were either capped or uncapped (open-to-air). The surface area of each reaction vessel was estimated using a radius caliper.

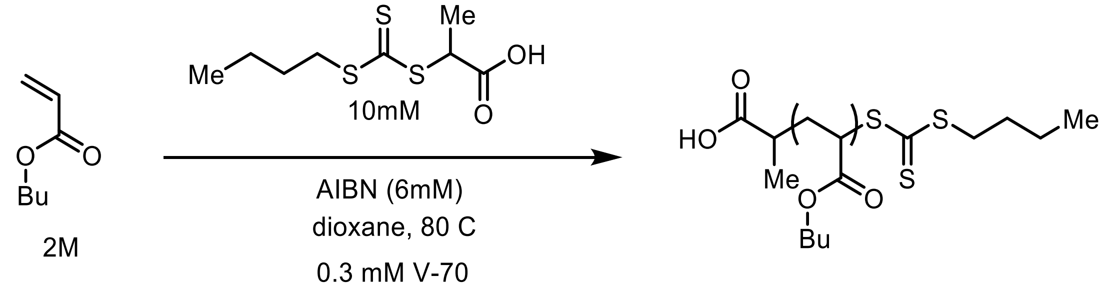


2.7 Batch Reaction Set-Up for Evaluating Polymerization Surface-To-Volume Ratios (SA:V) open to air and Obtaining Kinetics Under Optimized Alpha Values

To a 40 mL vial was added 2 mg V-70 (0.006 mmol), 18 mg of AIBN (0.11 mmol) 37 mg of 2-(butylthiocarbonothioylthio)propanoic acid (0.08 mmol), 5.2 mL *n*-butyl acrylate (36 mmol), and 12.8 mL of dioxane. Different volumes of the resulting yellow solution were aliquoted to separate 2-dram vials (estimated polymerization surface area of 2.5 cm^2) to understand the effect of SA:V. Polymerizations were conducted for 30 minutes open-to-air at 80° C using an aluminum pi block. In a separate experiment, identical volumes were aliquoted into 2-dram vials for the collection of distinct time points to elucidate polymerization kinetics without continuous disruption of the air-liquid interface.

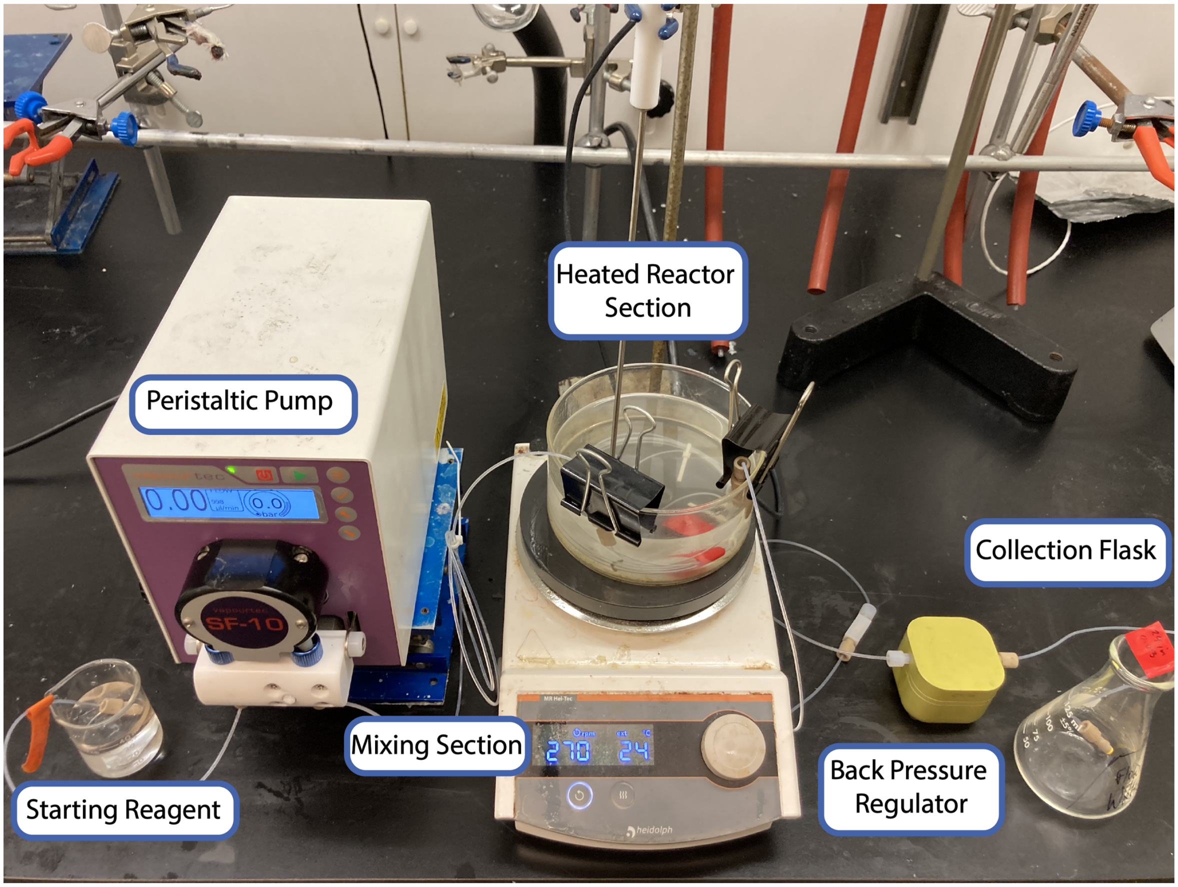
2.7 General Remarks for Kinetic Study Performed in Continuous Flow:





One vial of 20.0 mL of 1,4-dioxane and 40.0 mg (6 mM) of AIBN, and another vial of 94.6 mg of 2-(butylthiocarbonothioylthio)propanoic acid (BTTCP), 11.52 mL of *n*-butyl acrylate, and 8.48 mL of 1,4-dioxane were prepared. A second set of experiments were conducted with an addition of 3.7 mg (0.3 mM) of V-70 azo-initiator. The solutions were withdrawn into 20 mL stainless steel syringes, and any excess gassed was purged from the syringe. The Mettler Toledo React IR probe were calibrated and inserted into the custom machined flow cell. The syringes were loaded into the Ph.D Ultra syringe pump and began flowing at a constant flow rate (equivalent of a 1-minute retention time) until steady state was reached. Once steady state was reached the flow rate was decreased exponentially which resulted in a linear increase of residence times starting from 1 min to 30 min. After a residence time of 30 min was reached, the flow rate was held constant for at least 30 more minutes and then a sample was collected for monomer conversion and molecular weight determination. A LabVIEW code was written which programmed the syringe pump to exponentially decrease the flow rate over a given time, which resulted in a linear increase of the residence time. This decay of flow rate was based off an approach laid out by Moore and coworkers.[1]

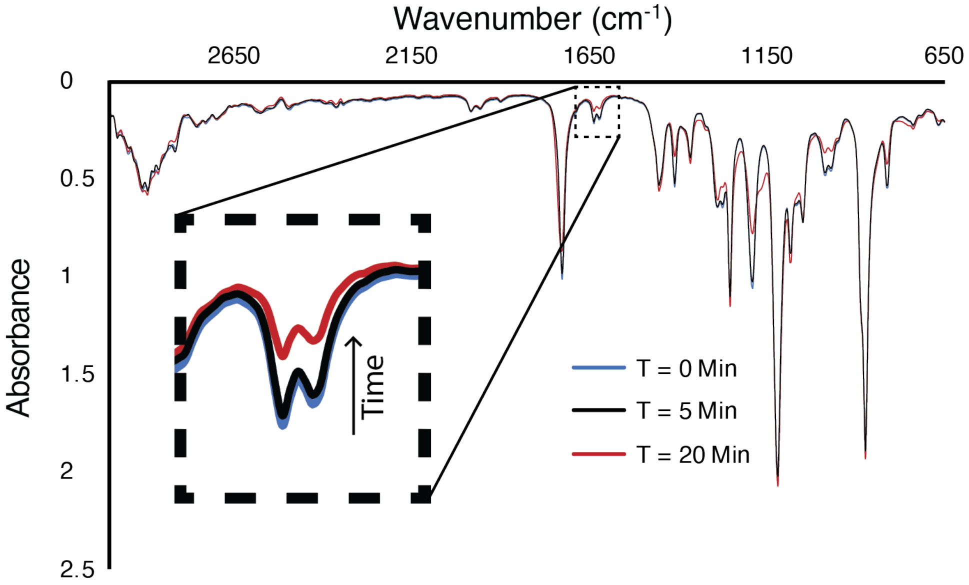
2.8 Experimental Set Up for Monomer Scope Studies Performed in Continuous Flow:



A small amount of solvent (varied per monomer sample) was used to flown through the reactor and used prime the flow set up. All starting materials (as outlined in table 2 within the main text) were mixed into a scintillation vial, and attached to the input port of the Vapourtec SF-10 peristaltic pump. The starting materials were pumped through the set up at a constant flow rate which corresponded to the reaction times outlined in table 2. These flow rates can be calculated by dividing the volume of the tubing in the heated section by the reaction time. The solution was pumped through the set up for a total of three times the reaction time before a sample was collected, ensuring homogenous mixing and the removal of any unwanted material left behind from previous runs which can lead to uneven polymerization conditions. This procedure was used for all monomer classes except for the styrenics which were run in dichlorobenzene, which is incompatible with the lining of the peristaltic pumps used. The styrenic polymerizations were run the Ph.D Ultra syringe pumps and with the exact same set up as outlined above.

2.9 IR Data Analysis

The *n*-butyl acrylate alkene stretch signal and time point data provided by the ReactIR™ 15 iCIR software was exported to Excel for further analysis. The magnitude of the alkene stretch at 1650 cm^{-1} present in the first acquired IR spectrum data point was considered to be 2.0 M, the initial monomer concentration. The monomer concentration present immediately prior to quenching was found through the following protocol. After an aliquot was quenched (*vide supra*) with butylated hydroxytoluene, an NMR sample was prepared with 0.1 mL of the quenched reaction solution and 0.5 mL of $CDCl_3$. The unique proton signals from poly(*n*-butyl acrylate) allowed this to serve as an internal standard, against which the vinyl protons of *n*-butyl acrylate were integrated to calculate conversion. Knowing the % conversion allowed for the calculation of the monomer concentration present immediately prior to quenching. In this report, we defined the inhibition periods having $\ln(M_o/M_t)$ values less than 0.05 for both batch and continuous flow experiments as observed from *in situ* infrared spectroscopy kinetic studies.



2.10 O_2 Data Analysis

The dissolved oxygen signal and time point data provided by the Hamilton ArcAir software was exported to Excel for further analysis.

2.11 Method for Simulating Radical Concentrations

Simulated radical concentrations were estimated from the decomposition rate (k_d) of AIBN and V-70 radical initiators. The Arrhenius equation was used: $k_d = Ae^{\frac{-E_a}{RT}}$, where A is the pre-exponential factor, E_a is the activation energy, R is the Universal gas constant, and T is the temperature. Pre-exponential factor were estimated from frequency factors obtained by Wako for V-70 (27.01). Activation energies for V-70 were also obtained by Wako (94.3 kJ/mol). 80 °C was used as the temperature for each calculation. From these calculations, the k_d for V-70 was estimated to be 6.0×10^{-3} s^{-1}, respectively. A reported k_d of 1.32×10^{-4} s^{-1} under identical conditions was used for AIBN.[2]

The thermal decompositions of each azo initiator were assumed first-order, which allowed for the estimation of radical initiator concentrations at a given time using the equation: $[A] = [A]_0 e^{-k_d t}$, where [A] represents the concentration of an azo initiator. From the calculation of [A], radical concentration, [R], could be estimated using the following equation: $[R] = 2([A]_0 - [A])$. Simulations calculating the radical concentrations of a dual initiating system required the summation of radicals generated from the decomposition calculations of both V-70 and AIBN.

2.12 Method for Calculating Theoretical Molecular Weight (Theo. M_n)

Theoretical molecular weights were determined using the equation[3]:

$$Theo.\ M_n = \frac{[M]_0 p M_M}{[CTA]_0 + 2f[I]_0(1 - e^{-k_d t})\left(1 - \frac{f_c}{2}\right)} + M_{CTA}$$

Where $[M]_0$, $[CTA]_0$, $[I]_0$ are the initial concentrations of monomer, chain transfer agent, and initiator, respectively. M_M and M_{CTA} are the molecular weights of monomer and chain transfer agent, respectively. Monomer conversion (p) was determined by ^{1}H NMR analysis. Radical efficiency (f) was assumed to 0.5. Decomposition rate (k_d) was estimated from the above simulated method (2.11). A coupling factor (f_c) of 0 was used to assume 100% termination by disproportionation.

3.0 Supplementary Tables – Batch RAFT Polymerizations Performed in a Vials

Table S1. Determination of how SA:V affects *n*-butyl acrylate polymerizations in capped reaction vessels.

SA:V[a] (cm^{-1})	Conv. (%)[b]	Theoretical M_n (kg/mol)	Exp. M_n[c] (kg/mol)	*Đ*
0.8	86	19.8	13.9	1.14
1.0	85	19.6	15.5	1.09
1.2	81	18.7	13.3	1.15
1.4	76	17.5	11.6	1.09
1.6	58	13.4	13.4	1.22
1.8	46	10.7	8.0	1.10
2.0	33	7.8	5.2	1.09

Conditions: [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, [V-70] = 300 uM, 80 °C, stirring, capped vials. [a]Interfacial surface area estimated by measuring the base of the vial. [b]Monomer conversion as determined from ^1H NMR using a 1,4-bis(trimethylsilyl)benzene internal standard. [c]Molecular weight and dispersity calculated using MALS on a THF GPC.

Table S2. Effect of stirring speed on open-to-air RAFT polymerizations

Stirring Speed (rpm)	**SA:V[a] (cm^{-1})**	**Conv. (%)[b]**	**Theo. M_n (kg/mol)**	**Exp. M_n[c] (kg/mol)**	**$Đ$**	**Notes**
None	0.60	80	18.5	15.0	1.15	-
100	0.60	80	18.5	14.8	1.17	-
300	0.60	77	17.8	16.2	1.08	-
400	0.60	85	19.5	15.5	1.14	-
600	0.60	53	12.3	13.0	1.05	Disruption of interface
800	0.60	39	9.1	8.2	1.03	Disruption of interface
1000	0.60	5	1.4	Not observed	Not observed	Disruption of interface

Conditions: [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, [V-70] = 300 uM, 80 °C, open-to-air, 2-dram vial. [a]Interfacial surface area estimated by measuring the base of the vial. [b]Monomer conversion as determined from ^{1}H NMR using a 1,4-bis(trimethylsilyl)benzene internal standard. [c]Molecular weight and dispersity calculated using MALS on a THF GPC.

Table S3. Validation of SA:V = 0.60 by polymerizing in different sized vials.

Reactor	**SA:V[a] (cm^{-1})**	**Conv. (%)[b]**	**Theo. M_n (kg/mol)**	**Exp. M_n[c] (kg/mol)**	**Đ**
1-dram (4 mL) vial Open-to-air	0.6	80	18.5	15.0	1.04
2-dram (8 mL) vial Open-to-air	0.6	79	18.2	15.7	1.12
2-dram (8 mL) vial Open-to-air	2	5	NA	Not observed	Not observed
20 mL vial Open-to-air	0.6	75	17.3	14.6	1.14
20 mL vial Open-to-air	2	2	NA	Not observed	Not observed

Conditions: [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, [V-70] = 300 uM, 80 °C, stirring. [a]Interfacial surface area estimated by measuring the base of the vial. [b]Monomer conversion as determined from ^{1}H NMR using a 1,4-bis(trimethylsilyl)benzene internal standard. [c]Molecular weight and dispersity calculated using MALS on a THF GPC.

Table S4. Kinetic chain length experiments of open-to-air polymerizations of *n*-butyl acrylate

Monomer Concentration	**Conv.[a] (%)**	**Exp. M_n[b] (kg/mol)**	**$Đ$**
2 M	93	47.2	1.96
4 M	95	76.4	1.67 (bimodal)

Conditions: Uncapped 2-dram vial, stirring, SA:V value of 0.60. [*n*-butyl acrylate] = 2 M or 4 M, [AIBN] = 6 mM, [V-70] = 300 uM, 80 °C, stirring. [a]Monomer conversion as determined from ^{1}H NMR using a 1,4-bis(trimethylsilyl)benzene internal standard. [b]Molecular weight and dispersity calculated using MALS on a THF GPC.

Table S5. Open-to-air RAFT polymerizations under different reaction conditions in batch.

Monomer	**Reaction Conditions**	**Conv.[a] (%)**	**Theo. M_n (kg/mol)**	**Exp. M_n[b] (kg/mol)**	***Đ***
n-butyl acrylate[c]	Degassed [AIBN] = 6 mM	86	19.8	16.9	1.13
	[V-70] = 0.3 mM, [AIBN] = 6 mM	78	18.0	15.6	1.08
	[V-70] = 6 mM	58	13.4	11.6	1.07
	[V-70] = 1 mM	55	12.8	7.7	1.02
N-acryloyl morpholine[d]	Degassed [AIBN] = 6 mM	80	10.3	13.6	1.13
	[V-70] = 0.3 mM, [AIBN] = 6 mM	75	9.6	10.1	1.09
	[V-70] = 6 mM	73	9.4	10.4	1.23
	[V-70] = 1 mM	59	7.6	8.7	1.02
styrene[e]	Degassed [ABCN] = 6 mM	44	13.3	12.8	1.33
	[V-70] = 0.3 mM, [ABCN] = 6 mM	36	10.9	11.9	1.12
	[V-70] = 6 mM	27	8.3	3.5	1.09
	[V-70] = 1 mM	27	8.3	3.4	1.07
	No initiator	9	2.9	1.5	1.05
cyclohexyl methacrylate[f]	Degassed [AIBN] = 6 mM	62	14.1	13.6	1.27
	[V-70] = 0.3 mM, [AIBN] = 6 mM	49	11.4	13.3	1.26
	[V-70] = 6 mM	25	5.8	4.5	1.21
	[V-70] = 1 mM	2	0.7	1.5	1.38

Conditions: Uncapped 2-dram vial, stirring, SA:V value of 0.60. [a]Conversion calculated from ^{1}H NMR relative to a 1,4-bis(trimethylsilyl)benzene internal standard. [b]All polymer molecular weights were calculated using multi-angle light scattering. [c]BTTCP used as CTA in dioxane solvent at 80 °C with a monomer:CTA ratio of 200:1, ran for 30 minutes. [d]CMDT used as CTA in DMF solvent at 80 °C with a monomer:CTA ratio of 100:1, ran for 15 minutes. [e]DBTTC used as CTA in dichlorobenzene solvent at 100 °C with a monomer:CTA ratio of 300:1, ran for 2 hours. [f]CPDB used as CTA in toluene solvent and reaction vessel capped at 100 °C with a monomer:CTA ratio of 200:1, ran for 20 minutes.

Table S6. Open-to-air RAFT polymerizations with single component high-temperature azo initiators in batch.

Monomer	**Azo Initiator**	**Conv.**[a] **(%)**	**Theo. M_n (kg/mol)**	**Exp. M_n**[b] **(kg/mol)**	**Đ**
n-butyl acrylate[c]	6 mM AIBN	56	13.0	10.7	1.20
N-acryloyl morpholine[d]	6 mM AIBN	78	10.0	11.3	1.09
styrene[e]	6 mM ABCN	42	12.7	11.1	1.18
cyclohexyl methacrylate[f]	6 mM AIBN	36	8.5	10.0	1.36

Conditions: Uncapped 2 dram vial, stirring, SA:V value of 0.60. [a]Conversion calculated from ^{1}H NMR relative to a 1,4-bis(trimethylsilyl)benzene internal standard. [b]All polymer molecular weights were calculated using multi-angle light scattering, except poly(methacrylates) which were analyzed by the RI of the THF GPC. [c]BTTCP used as CTA in dioxane solvent at 80 ºC with a monomer:CTA ratio of 200:1, ran for 30 minutes. [d]CMDT used as CTA in DMF solvent at 80 ºC with a monomer:CTA ratio of 100:1, ran for 15 minutes. [e]DBTTC used as CTA in dichlorobenzene solvent at 100 ºC with a monomer:CTA ratio of 300:1, ran for 2 hours. [f]CPDB used as CTA in toluene solvent and reaction vessel capped at 100 ºC with a monomer:CTA ratio of 200:1, ran for 20 minutes.

3.1 Supplementary Tables – RAFT Polymerizations Performed in a Continuous Flow

Table S7. RAFT polymerizations using only V-70 (6 mM) as an initiator under different reaction conditions in continuous-flow.

Monomer	Conv. (%)[a]	Target M_n (kg/mol)	Exp. M_n[b] (kg/mol)	Đ
n-butyl acrylate[c]	42	9.8	9.7	1.03
tert-butyl acrylate[c]	49	11.3	12.1	1.01
2-ethylhexyl acrylate[c]	49	16.3	12.0	1.09
N-acryloyl morpholine[d]	71	9.6	10.0	1.08
N-(isobutoxymethyl)acrylamide[d]	29	4.5	7.8	1.06
styrene[e]	15	4.8	7.3	1.21
tert-butylstyrene[e]	33	10.3	15.0	1.29
cyclohexyl methacrylate[f]	14	3.3	3.8	1.27
isobornyl methacrylate[f]	12	3.5	6.8	1.26

Conditions: Uncapped 2 dram vial, stirring, SA:V value of 0.60. [a]Conversion calculated from ^{1}H NMR relative to a 1,4-bis(trimethylsilyl)benzene internal standard. [b]All polymer molecular weights were calculated using multi-angle light scattering, except poly(methacrylates) which were analyzed by the RI of the THF GPC. [c]BTTCP used as CTA in dioxane solvent at 80 ºC with a monomer:CTA ratio of 200:1, ran for 30 minutes. [d]CMDT used as CTA in DMF solvent at 80 ºC with a monomer:CTA ratio of 100:1, ran for 15 minutes. [e]DBTTC used as CTA in dichlorobenzene solvent at 100 ºC with a monomer:CTA ratio of 300:1, ran for 2 hours. [f]CPDB used as CTA in toluene solvent and reaction vessel capped at 100 ºC with a monomer:CTA ratio of 200:1, ran for 20 minutes.

4.0 Supplementary Figures – RAFT Polymerizations Performed in a Sealed Three Neck Round Bottom

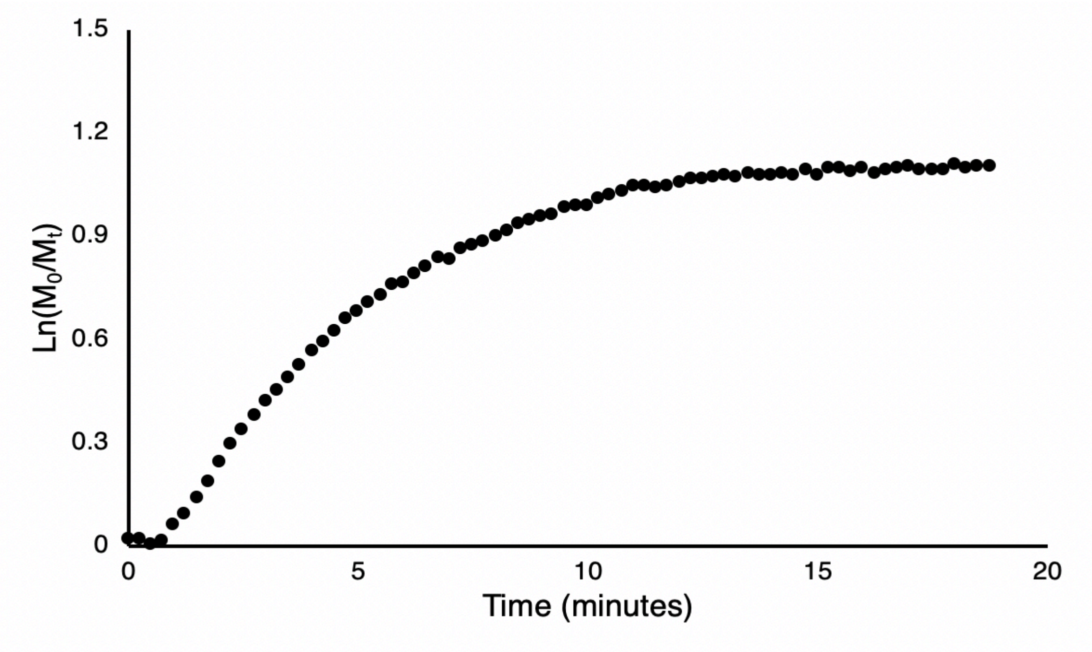


Figure S1. Monitoring of monomer conversion of a non-degassed polymerization with [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, and [V-70] = 6 mM as the sole initiator in dioxane solvent at 80 °C while stirring at 600 rpm. Monomer conversion was monitored using *in situ* infrared spectroscopy in a sealed three neck round bottom setup that is described on page 3.

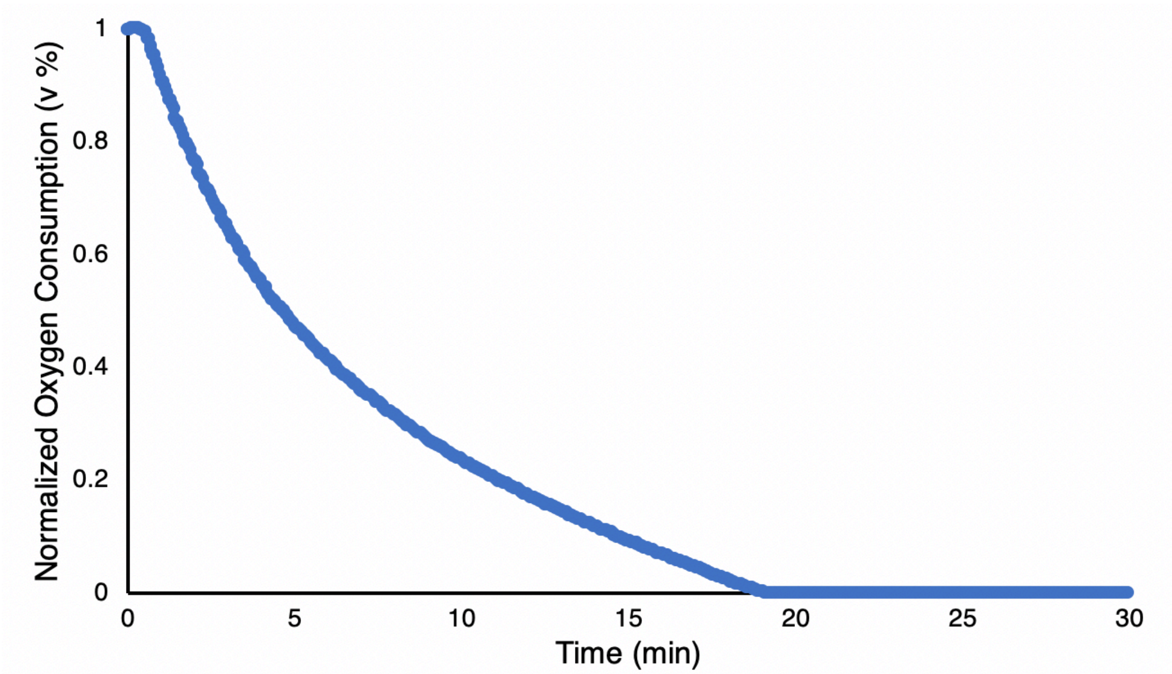


Figure S2. Monitoring of oxygen consumption of a non-degassed polymerization with [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, and [AIBN] = 6 mM as the sole initiator in dioxane solvent at 80 °C while stirring at 600 rpm. Oxygen concentration was monitored *in situ* using a Hamilton OxyFerm FDA Arc 120 oxygen probe in a sealed three neck round bottom setup that is described on page 3.

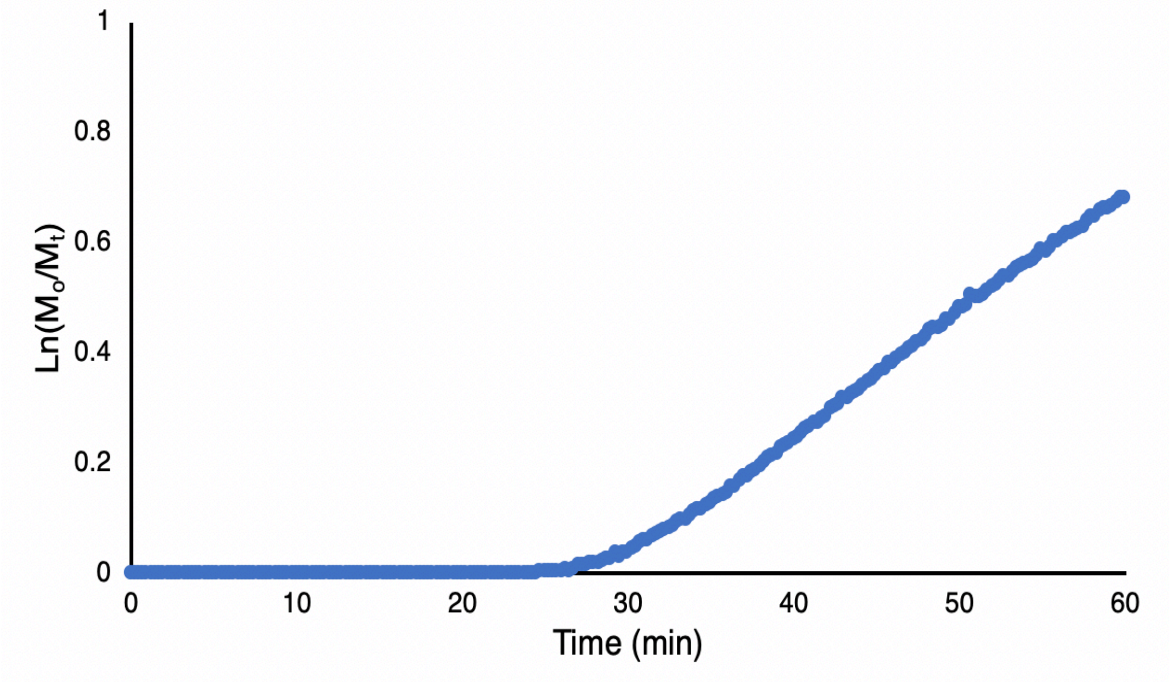


Figure S3. Monitoring of monomer conversion of a non-degassed polymerization with [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, and [AIBN] = 6 mM as the sole initiator in dioxane solvent at 80 °C while stirring at 600 rpm. Monomer conversion was monitored using *in situ* infrared spectroscopy in a sealed three neck round bottom setup that is described on page 3.

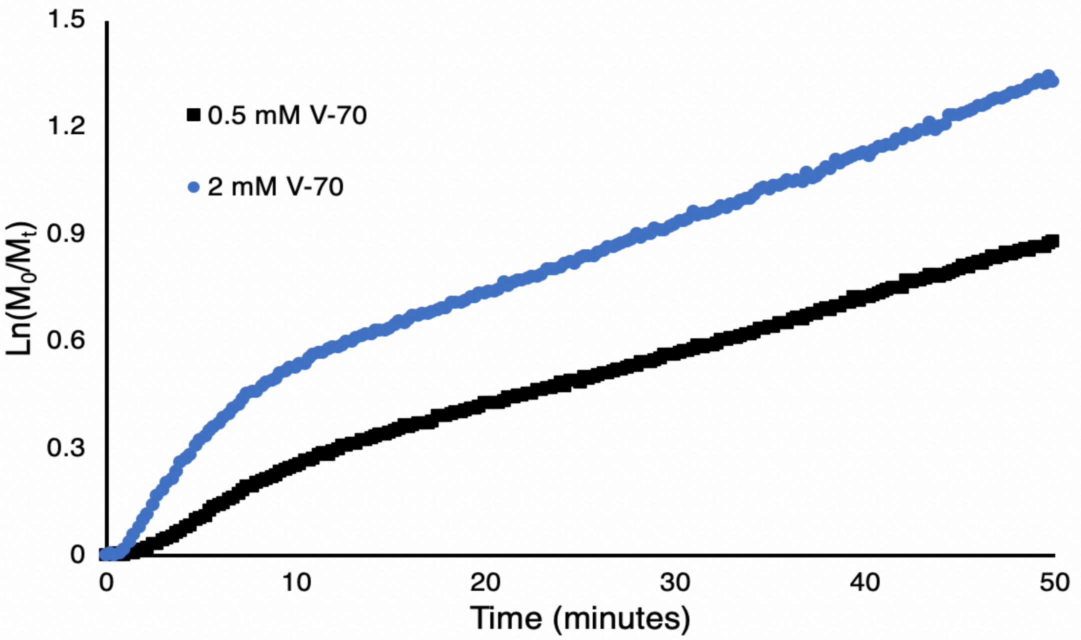


Figure S4. Monitoring of monomer conversion of non-degassed RAFT polymerizations with [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, and [V-70] = 2 mM or 0.5 mM in dioxane solvent at 80 °C while stirring at 600 rpm. Monomer conversion was monitored using in-situ infrared spectroscopy in a sealed three neck round bottom setup that is described on page 3.

4.1 Supplementary Figures – Batch RAFT Polymerizations Performed in Vials

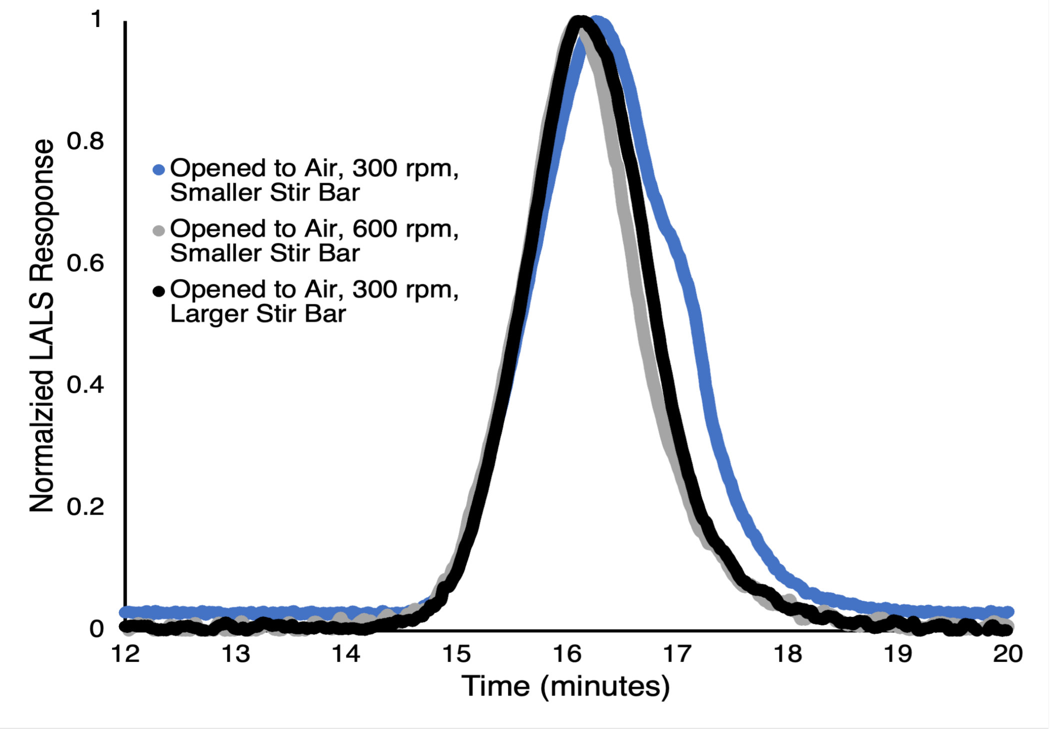


Figure S5. Comparison of GPC chromatograms taken from non-degassed, open-to-air RAFT polymerizations of [*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM on a 12 mL scale (20 mL vial) in dioxane solvent at 80 °C. Polymerizations were performed open-to-air under different stirring conditions. Either the stirring speed was altered (300 or 600 rpm), or the size of the stir bar was altered ([Small] = cylinder, length of 13 mm, diameter of 3 mm, [Large] = oval, length of 15 mm, diameter of 6 mm) to probe the effect of solution mixing on the appearance of the low molecular weight shoulder. Each polymerization was derived from identical stock solutions, performed with a SA:V value of 0.60.

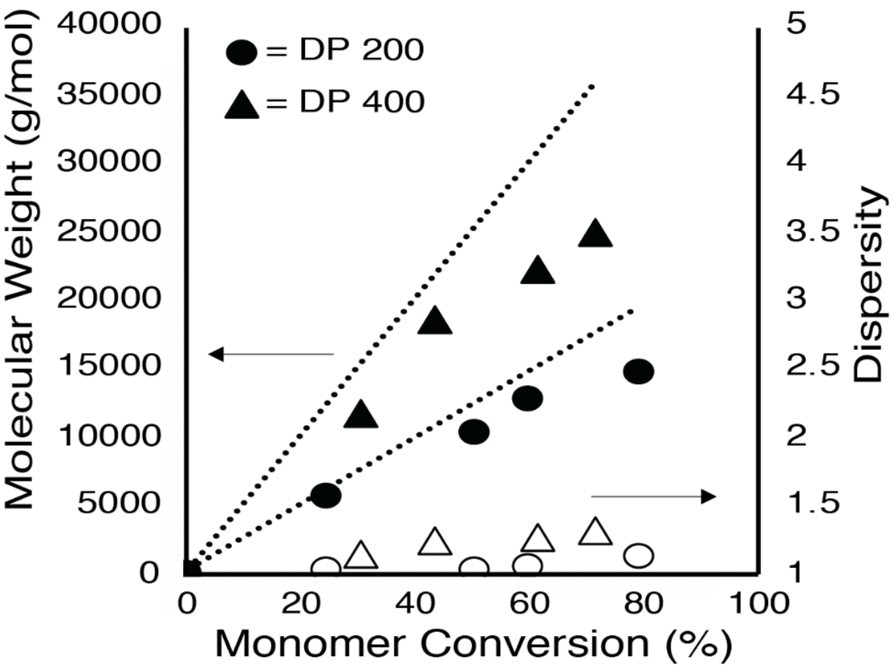


Figure S6. Monitoring of polymer molecular weight during non-degassed, open-to-air RAFT polymerizations of *n*-butyl acrylate in 2-dram vials. The concentration of *n*-butyl acrylate was altered (2 M [circle] or 4 M [triangle]), and [BTTCP] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM were held constant with dioxane used as solvent. Polymerizations were run at 80 °C for a total of 30 minutes with a SA:V value of 0.60 and stirred at 300 rpm. Conversion was calculated from ^{1}H NMR relative to a 1,4-bis(trimethylsilyl)benzene internal standard and polymer molecular weights were calculated using multi-angle light scattering. Each data point represents a separate polymerization run in-parallel to account for the disruption of the polymerization surface while removing aliquots for ^{1}H NMR analysis. The black dotted line represents theoretical molecular weight targeted for each degree of polymerization at the observed monomer conversion.

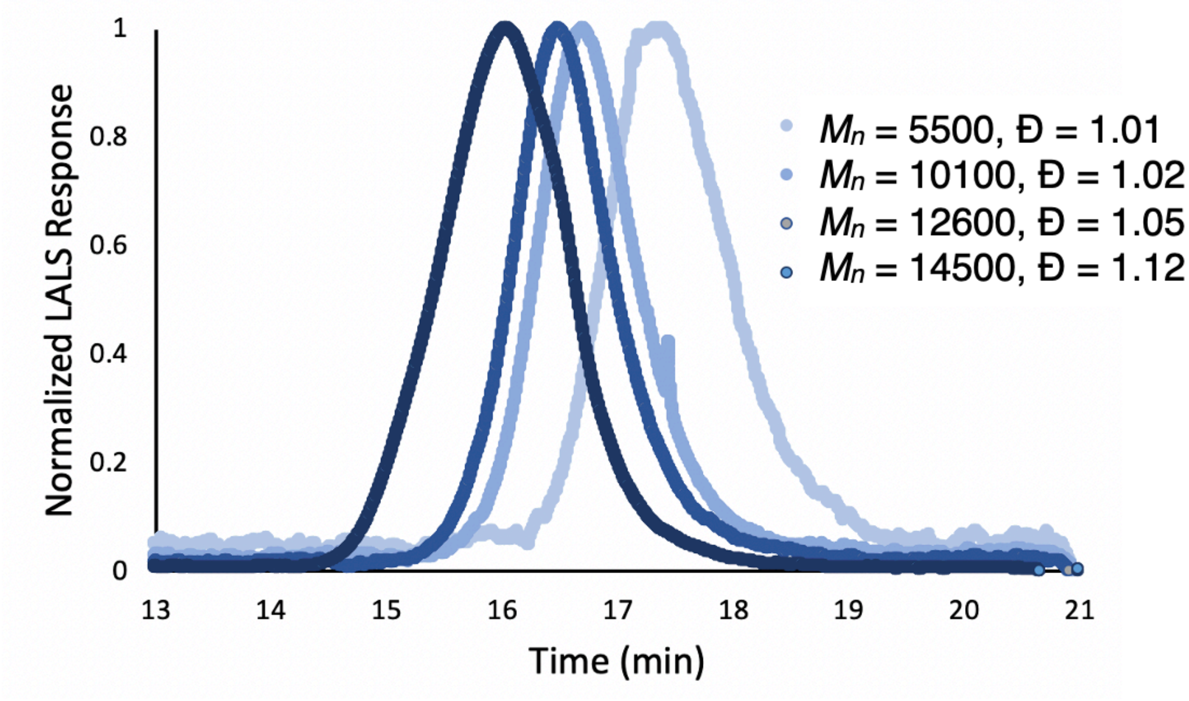


Figure S7. A comparison of GPC chromatograms acquired at different times during the non-degassed, open-to-air RAFT polymerization of *n*-butyl acrylate targeting a DP of 200 in 2-dram vials. Each polymerization was run in-parallel under identical conditions ([*n*-butyl acrylate] = 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM with dioxane used as solvent) to account for the disruption of the polymerization surface while removing aliquots for GPC analysis. Polymerizations were run at 80 °C for a total of 30 minutes with a SA:V value of 0.60 and stirred at 300 rpm.

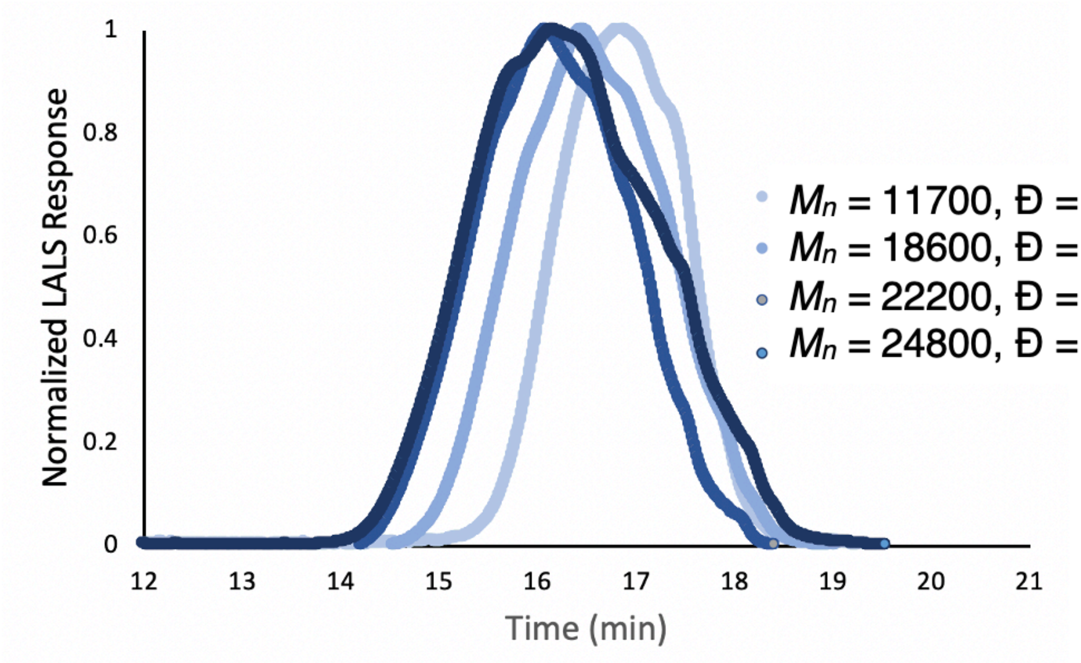


Figure S8. A comparison of GPC chromatograms acquired at different times during the non-degassed, open-to-air RAFT polymerization of *n*-butyl acrylate targeting a DP of 400 in 2-dram vials. Polymerizations were run in parallel under identical conditions ([*n*-butyl acrylate] = 4 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM with dioxane used as solvent) to account for the disruption of the polymerization surface while removing aliquots for GPC analysis. Polymerizations were run at 80 °C for a total of 30 minutes with a SA:V value of 0.60 and stirred at 300 rpm.

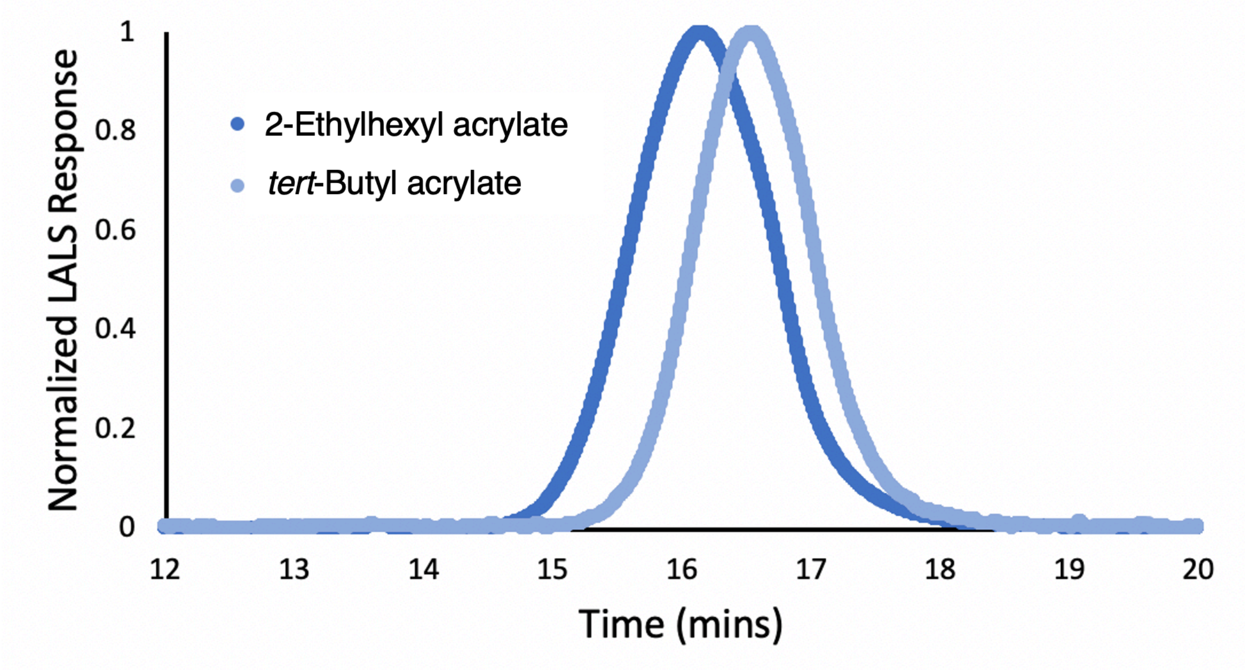


Figure S9. Representative GPC chromatograms of non-degassed, open-to-air RAFT polymerizations of *tert*-butyl acrylate and 2-ethylhexyl acrylate ran in 2-dram vials. Polymerizations were run under identical conditions ([Monomer]= 2 M, [BTTCP] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM with dioxane used as solvent). Polymerizations were subjected to 80 °C for a total of 30 minutes with a SA:V value of 0.60 and stirred at 300 rpm.

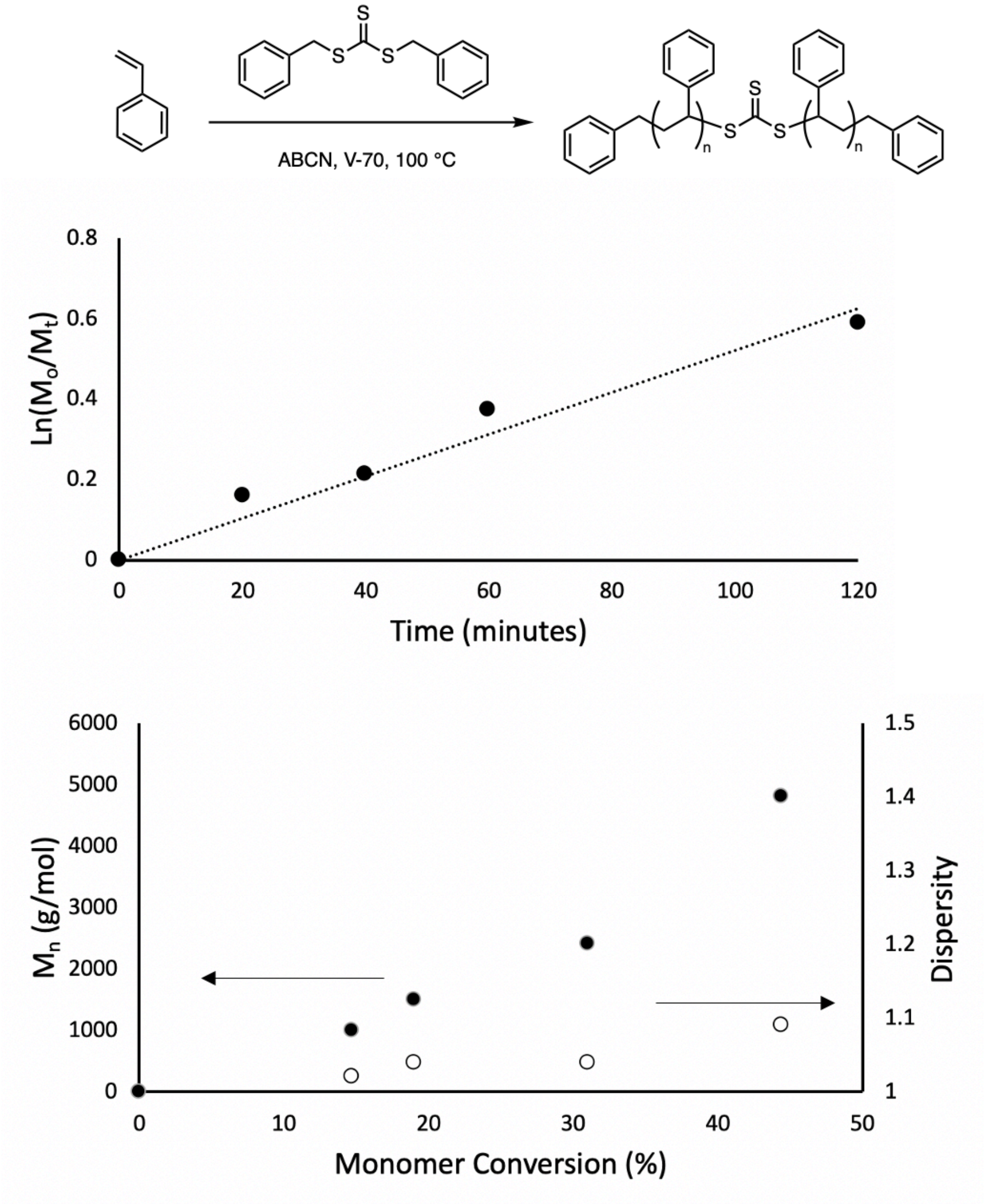


Figure S10A. Polymerization kinetics of degassed RAFT polymerizations of styrene monomer in a capped 2-dram vial. Polymerizations had [styrene] = 3 M, [DBTTC] = 10 mM, [ABCN] = 6 mM, and [V-70] = 0.3 mM all dissolved in dichlorobenzene solvent, and were initially degassed with N_2 before subjected to 100 °C for a total of 2 hours. A 1,4-bis(trimethylsilyl)benzene internal standard was also added to the polymerization to track monomer conversion using ^{1}H NMR.

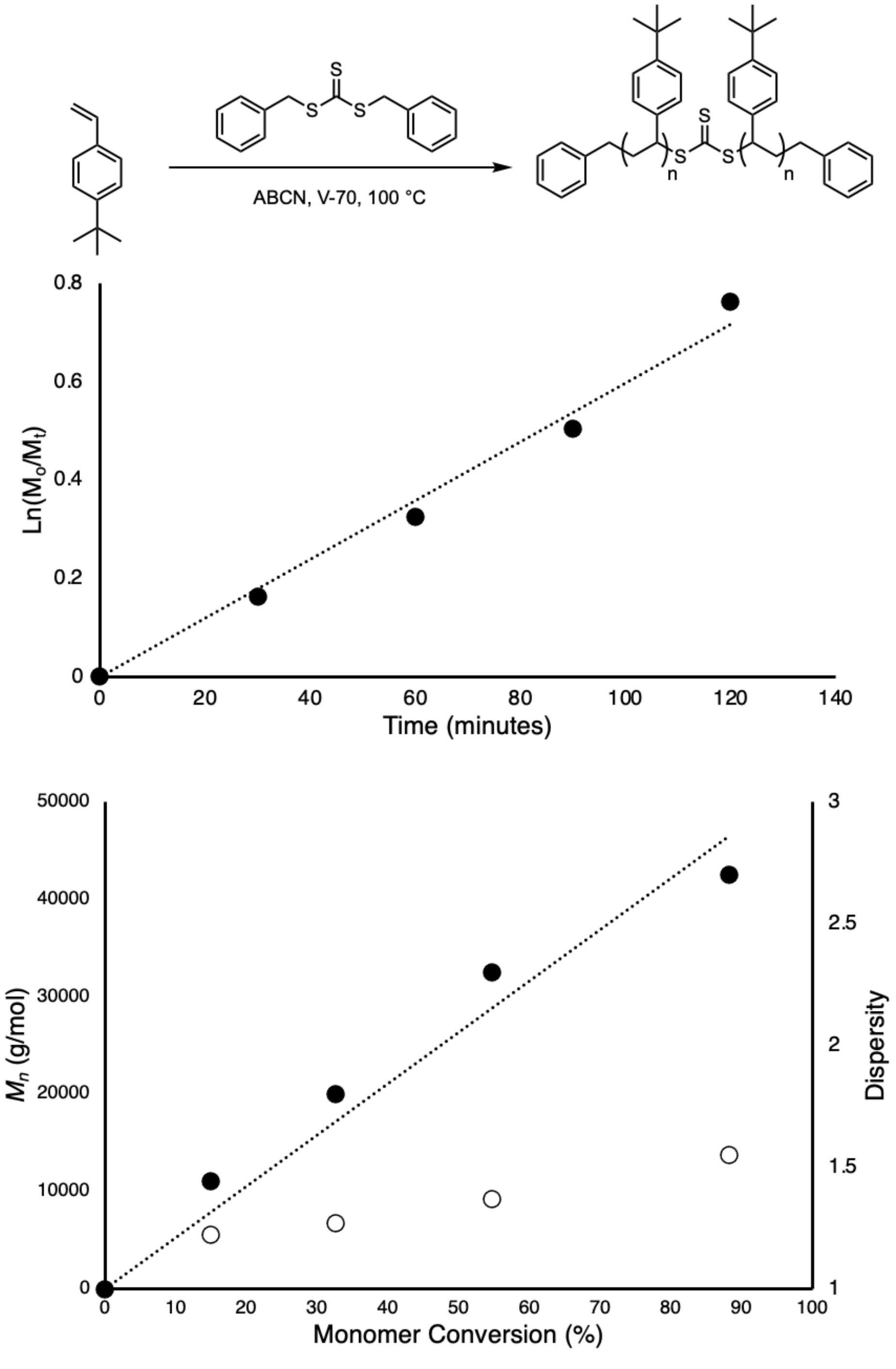


Figure S10B. Polymerization kinetics of degassed RAFT polymerizations of *tert*-butyl styrene monomer in a capped 2-dram vial. Polymerizations had [*tert*-butyl styrene] = 3 M, [DBTTC] = 10 mM, [ABCN] = 6 mM, and [V-70] = 0.3 mM all dissolved in dichlorobenzene solvent, and were initially degassed with N_2 before subjected to 100 °C for a total of 2 hours. A 1,4-bis(trimethylsilyl)benzene internal standard was also added to the polymerization to track monomer conversion using ^{1}H NMR.

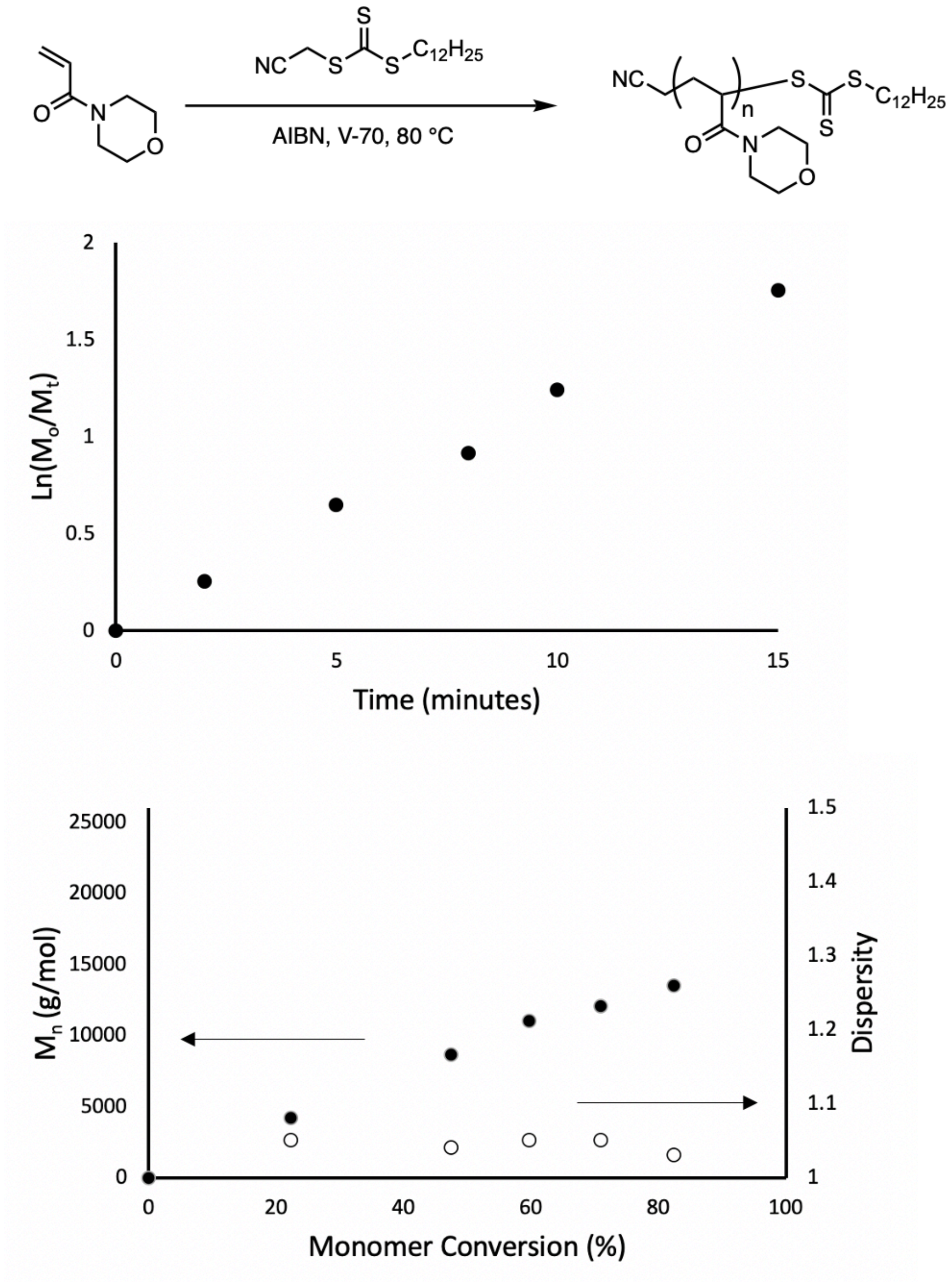


Figure S10C. Polymerization kinetics of degassed RAFT polymerizations of *N*-acryloylmorpholine monomer in a capped 2-dram vial. Polymerizations had [*N*-acryloylmorpholine] = 1 M, [CMDT] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM all dissolved in DMF solvent, and were initially degassed with N_2 before subjected to 80 °C for a total of 15 minutes. A 1,4-bis(trimethylsilyl)benzene internal standard was also added to the polymerization to track monomer conversion using ^{1}H NMR.

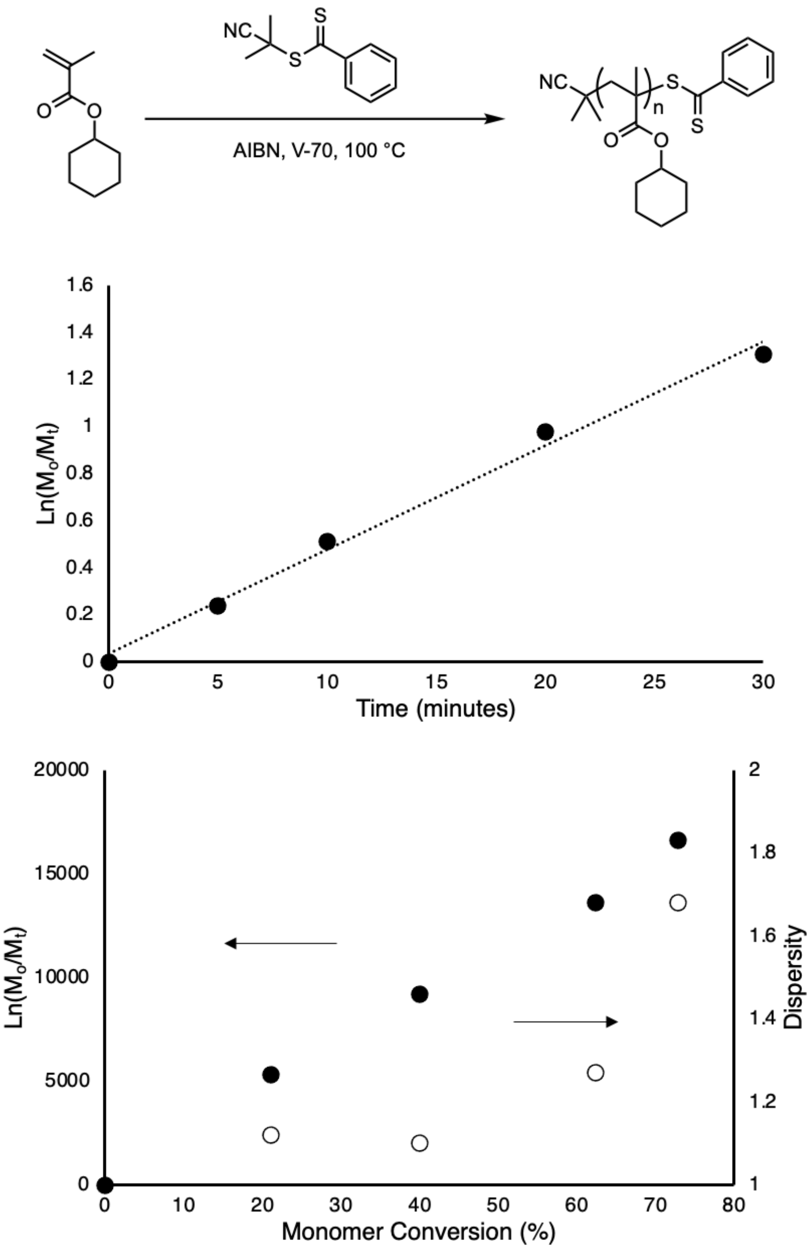


Figure S10D. Polymerization kinetics of degassed RAFT polymerizations of cyclohexyl methacrylate monomer in a capped 2-dram vial. Polymerizations had [cyclohexyl methacrylate] = 2 M, [CPDB] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM all dissolved in toluene solvent, and were initially degassed with N_2 before subjected to 100 °C for a total 20 minutes. A 1,4-bis(trimethylsilyl)benzene internal standard was also added to the polymerization to track monomer conversion using ^{1}H NMR.

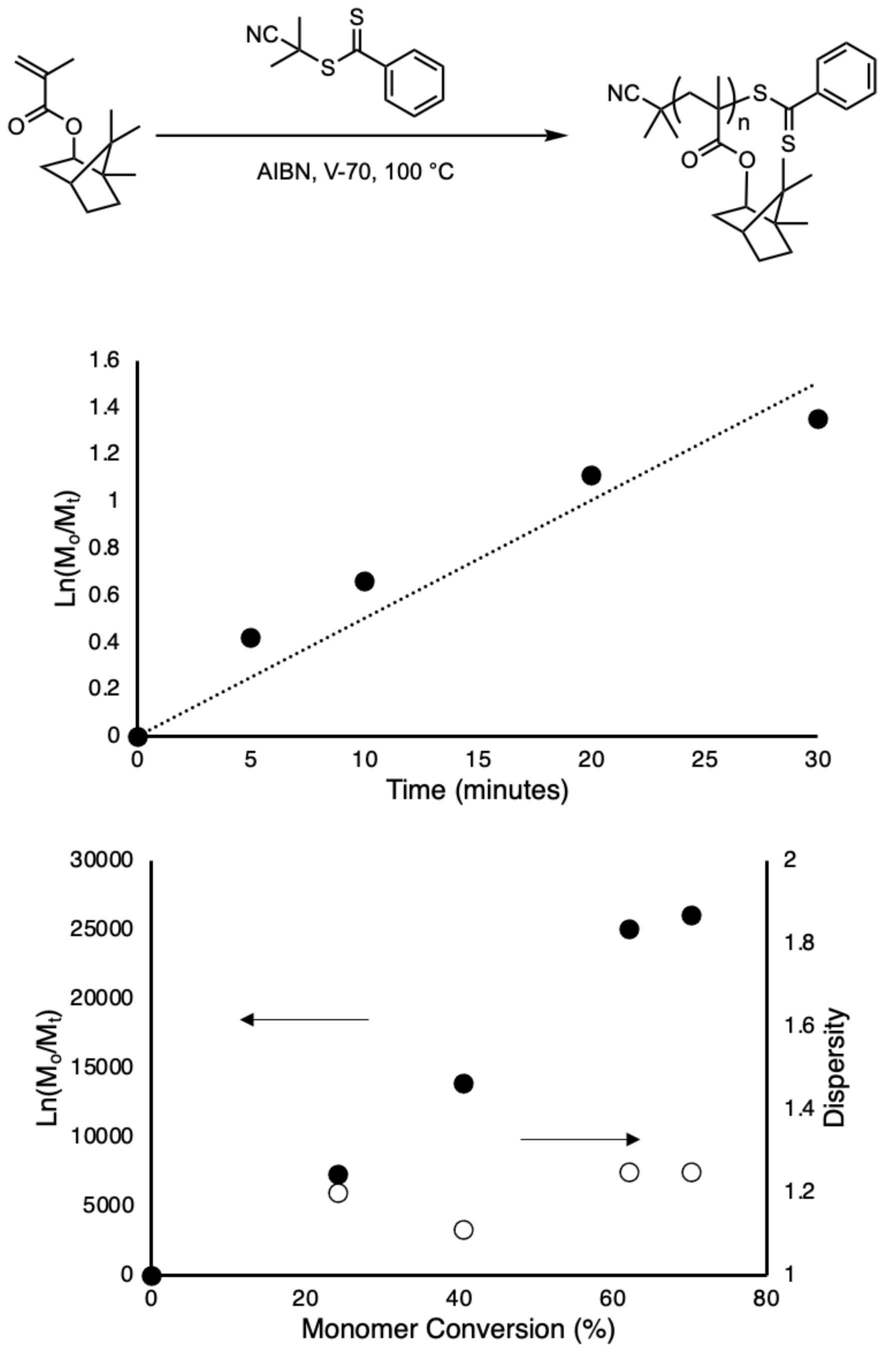


Figure S10E. Polymerization kinetics of degassed RAFT polymerizations of cyclohexyl methacrylate monomer in a capped 2-dram vial. Polymerizations had [isobornyl methacrylate] = 2 M, [CPDB] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM all dissolved in propyl acetate solvent, and were initially degassed with N_2 before subjected to 80 °C for a total of 1 hour. A 1,4-bis(trimethylsilyl)benzene internal standard was also added to the polymerization to track monomer conversion using ^{1}H NMR.

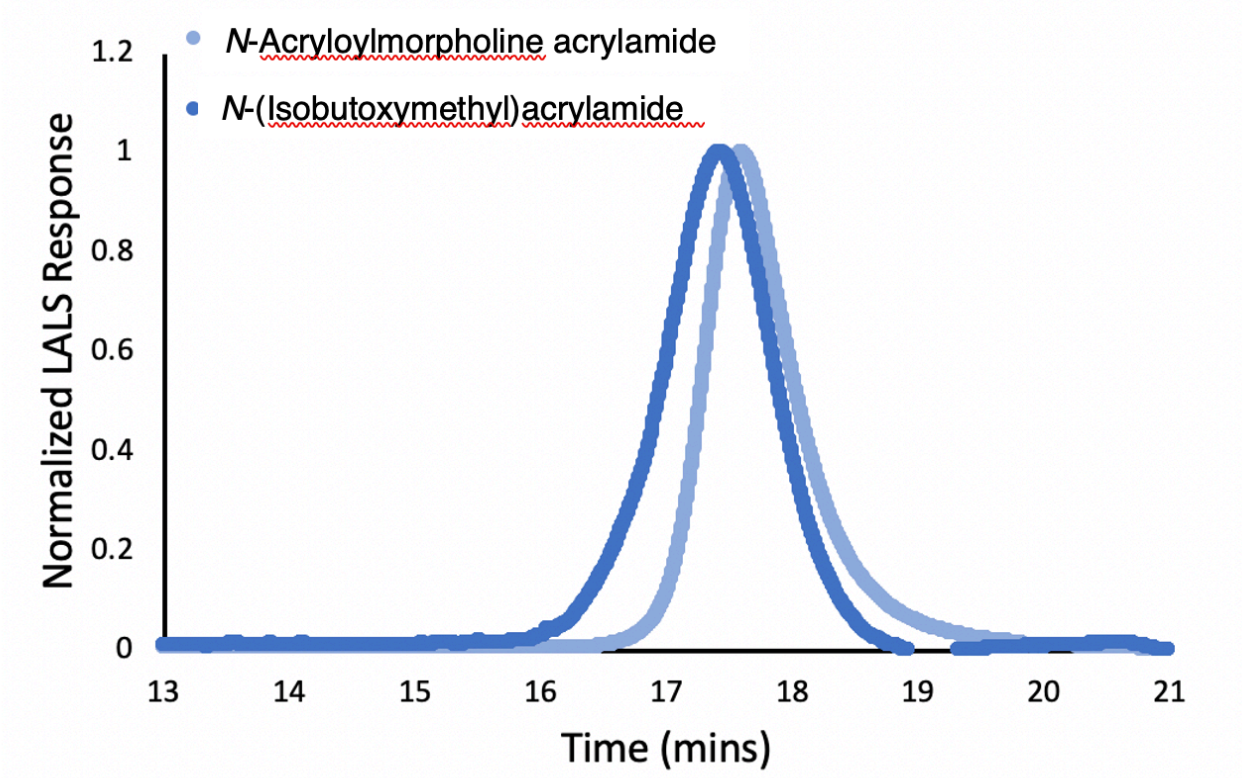


Figure S11. Representative GPC chromatograms of non-degassed, open-to-air RAFT polymerizations of *N*-acryloylmorpholine acrylamide and *N*-(isobutoxymethyl)acrylamide ran in 2-dram vials. Polymerizations were run under identical conditions ([Monomer] = 1 M, [CMDT] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM with DMF used as solvent). Polymerizations were subjected to 80 °C for a total of 15 minutes with a SA:V value of 0.60 and stirred at 300 rpm.

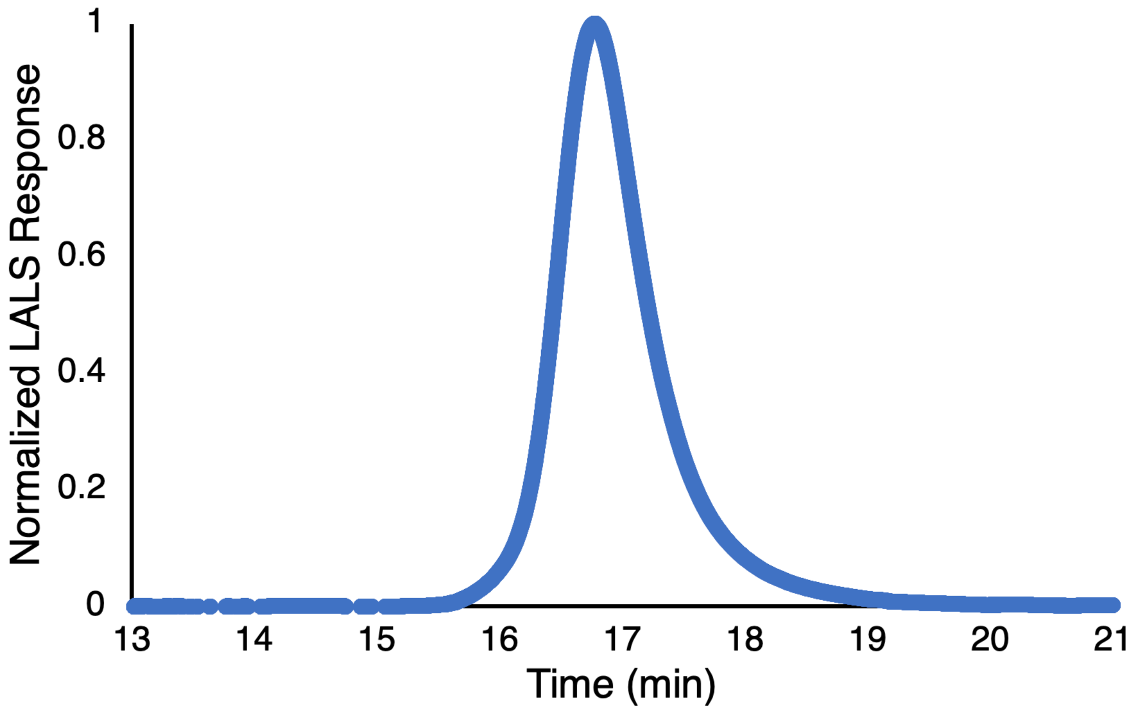


Figure S12. Representative GPC chromatograms of non-degassed, open-to-air RAFT polymerizations of *N*-acryloylmorpholine acrylamide targeting a DP of 200 in a 2-dram vial. Polymerizations had [*N*-acryoylmorpholine] = 2 M, [CMDT] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM with DMF used as solvent. Polymerizations were subjected to 80 °C for a total of 15 minutes with a SA:V value of 0.60 and stirred at 300 rpm.

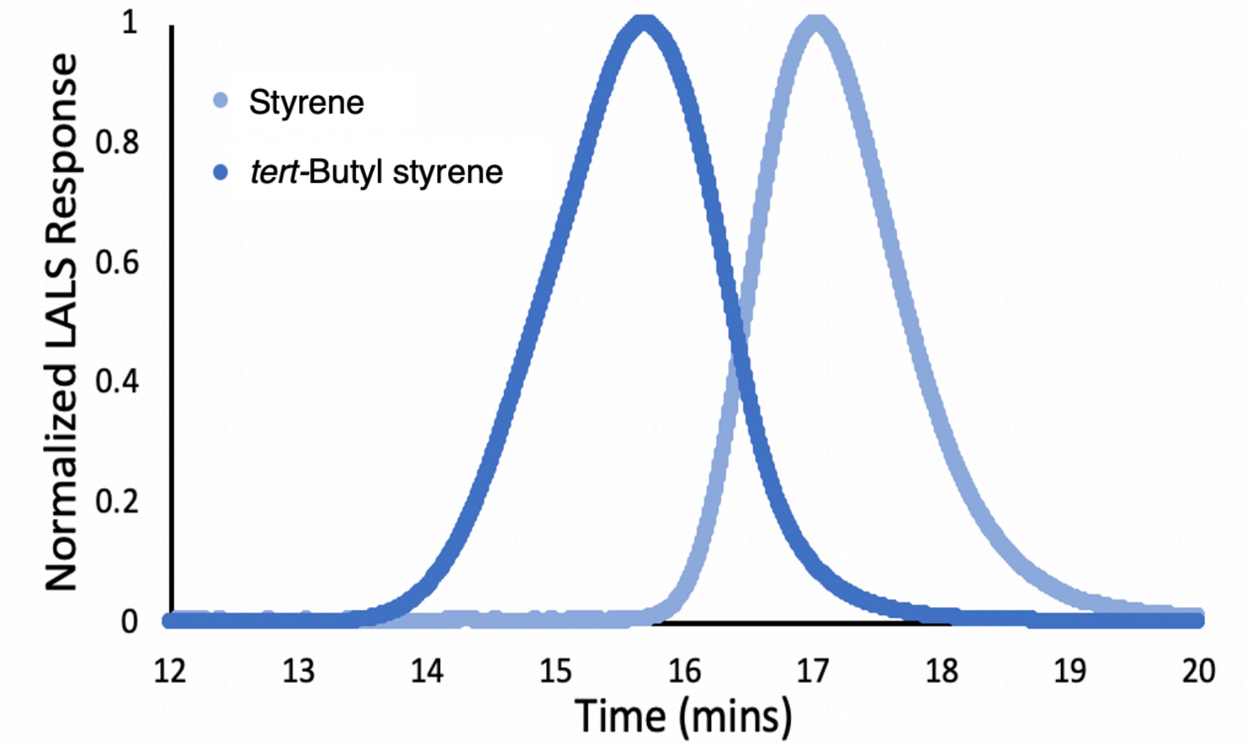


Figure S13. Representative GPC chromatograms of non-degassed, open-to-air RAFT polymerizations of styrene and *tert*-butyl styrene ran in 2-dram vials. Polymerizations were run under identical conditions ([Monomer] = 3 M, [DBTTC] = 10 mM, [ABCN] = 6 mM, and [V-70] = 0.3 mM with dichlorobenzene used as solvent). Polymerizations were subjected to 100 °C for a total of 2 hours with a SA:V value of 0.60 and stirred at 300 rpm.

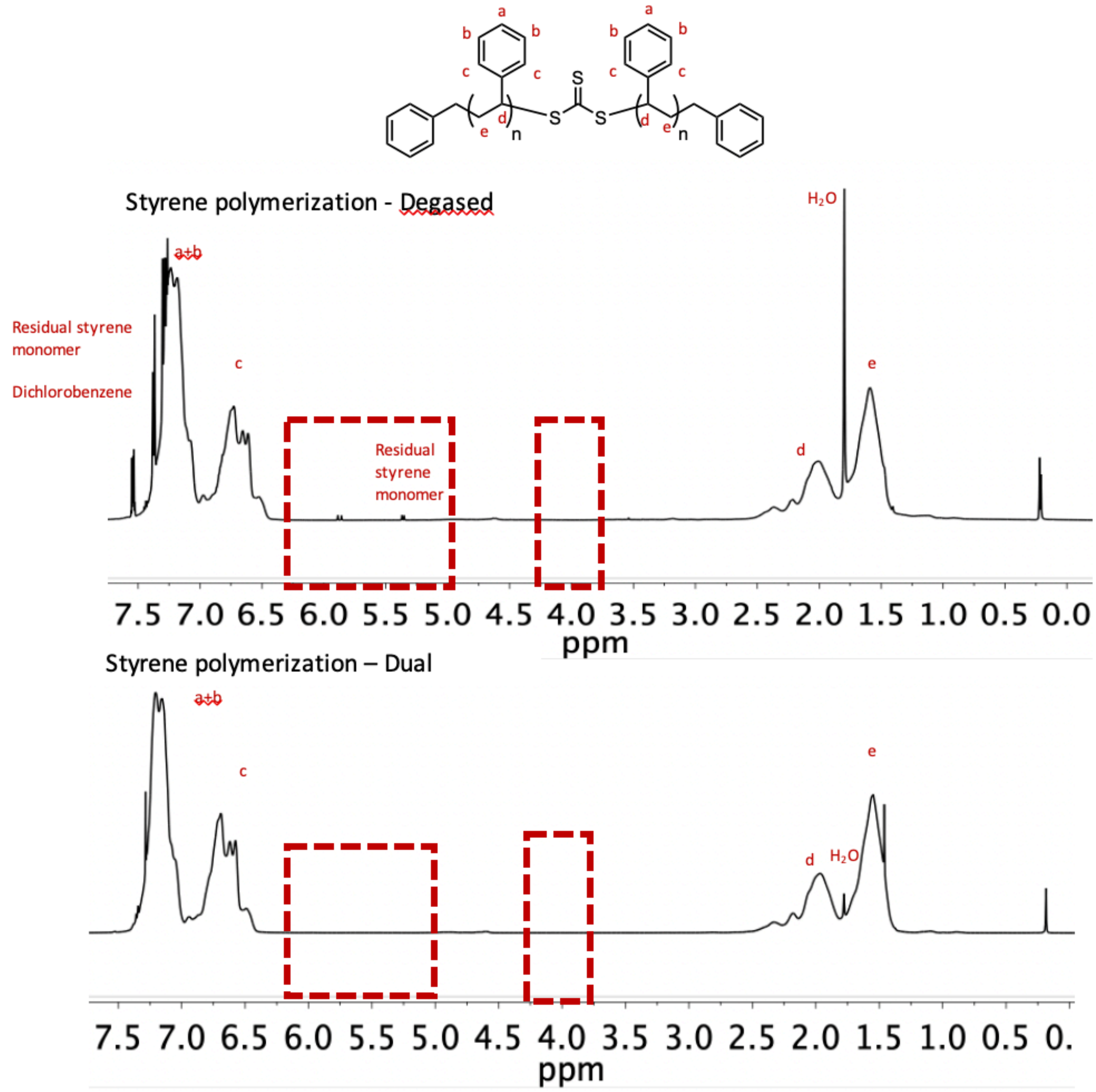


Figure S14. Comparison of ^{1}H NMRs of polystyrene prepared from the dual initiator approach and from solution degassing. Dashed box indicates previously published ppm range to expect poly(styrene peroxide).[4–6]

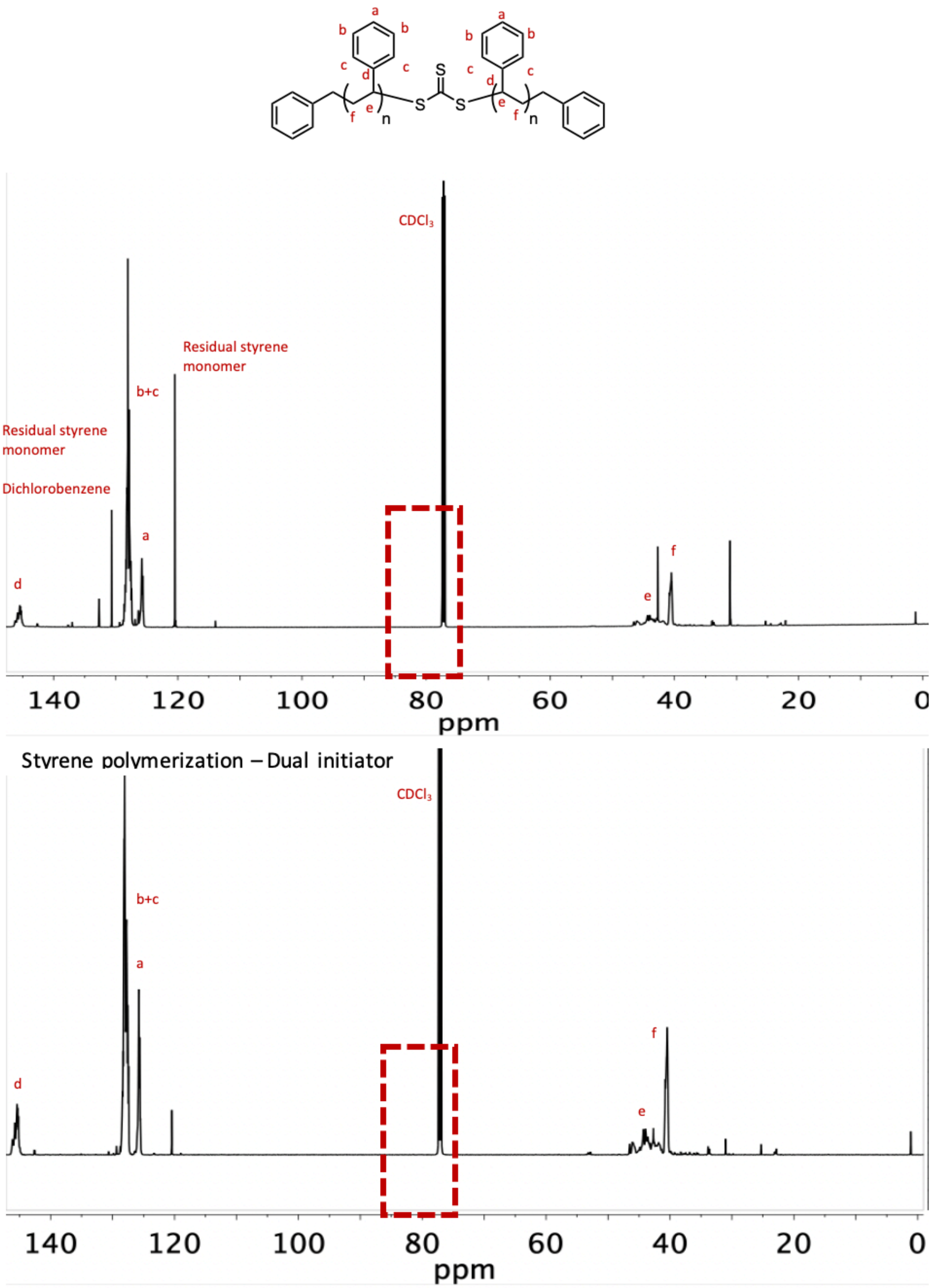


Figure S15. Comparison of ^{13}C NMRs of polystyrene prepared from the dual initiator approach and from solution degassing. Dashed box indicates previously published ppm range to expect poly(styrene peroxide).[4]

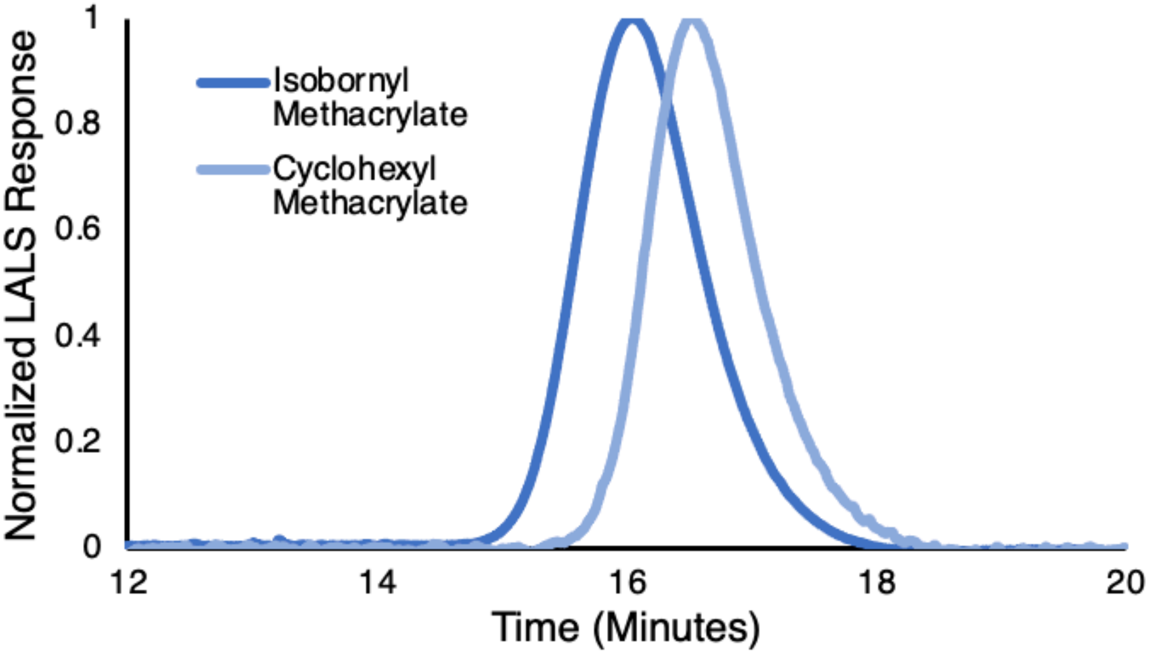


Figure S16. Representative GPC chromatogram of a non-degassed RAFT polymerization of cyclohexyl methacrylate and isobornyl methacrylate in a capped 2-dram vial. Polymerizations had [monomer] = 2 M, [CPDB] = 10 mM, [AIBN] = 6 mM, and [V-70] = 0.3 mM with toluene used as solvent. Capped polymerizations were subjected to 100 °C for a total of 20 minutes with a SA:V value of 0.60 and stirred at 300 rpm.

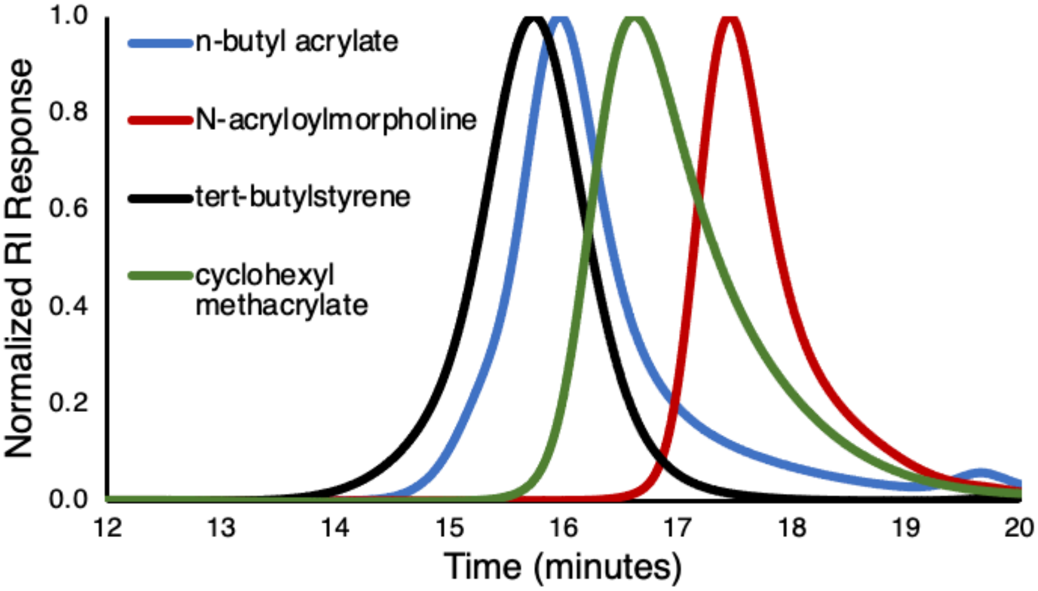


Figure S17. Representative GPC chromatograms degassed RAFT polymerizations of different monomer classes. Conditions: [AIBN] = 6 mM, [V-70] = 300 uM, uncapped 2-dram vial, 300 rpm stirring, SA:V value of 0.60. All polymer molecular weights were calculated using multi-angle light scattering. [a]Conversion calculated from ^{1}H NMR relative to an internal standard. [b]2-(butylthiocarbonothioylthio) propanoic acid (BTTCP) used as the CTA in a monomer:CTA molar ratio of 200:1 in dioxane at 80 ºC and ran for 30 minutes. [c]Cyanomethyl dodecyl trithiocarbonate (CMDT) used as the CTA in a monomer:CTA molar ratio of 100:1 in DMF at 80 ºC and ran for 15 minutes. [d]Dibenzyl trithiocarbonate (DBTTC) used as the CTA in a monomer:CTA molar ratio of 300:1 in dichlorobenzene with 6 mM ABCN used in place of AIBN at 100 ºC and ran for 2 hours. [e]2-cyano-2-propyl benzodithioate (CPDB) used as the CTA in a monomer:CTA molar ratio of 200:1 in toluene and reaction vessel capped at 100 ºC and ran for 20 minutes.

4.1 Supplementary Figures – RAFT Polymerizations Performed in Continuous Flow

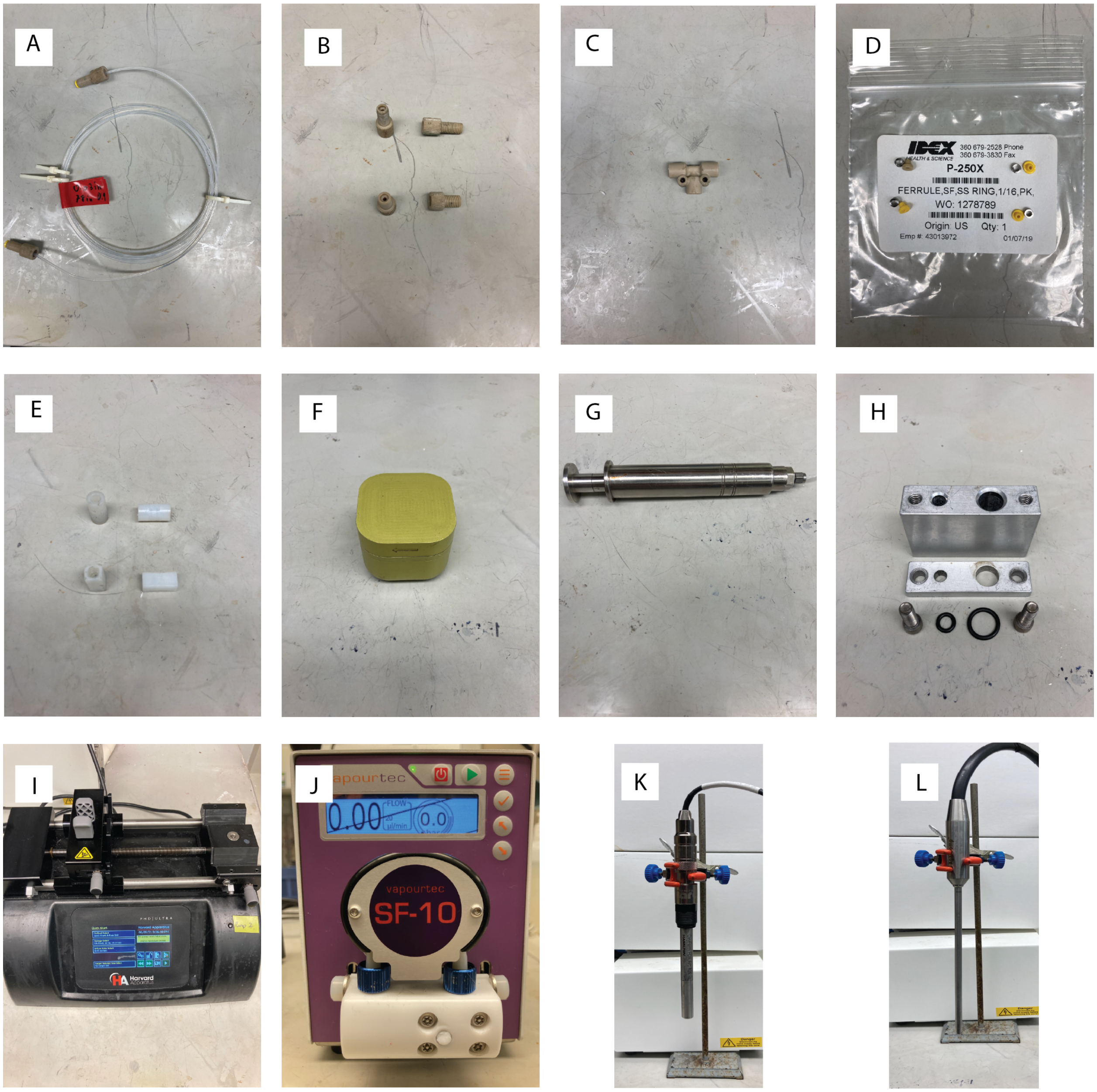


Figure S18: **A.** 77.7 in. of 0.03 in. interior diameter tubing (900 µL reactor volume) **B.** PEEK super-flangeless nut **C.** Static mixing Tee T-Mix **D.** Yellow super-flangeless ferrule with corresponding stainless steel ferrule ring – sold separately – larger sizes need for 0.063 and 0.093 in. tubing **E.** Low Pressure ETFE Unions **F.** Back Pressure Regulator **G.** 20 mL stainless steel syringe **H.** Custom machined aluminum flow cell for in line analysis **I.** Ph.D Ultra syringe pump **J.** Vapourtec SF-10 peristaltic pump **K.** Hamilton OxyFerm FDA Arc 120 oxygen probe **L.** Mettler Toledo React IR

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(5) Kishore, K. Spectral and Thermal Data on Polystyrene Peroxide. *J. Chem. Eng. Data* **1980**, *25* (1), 92–94.
(6) Jayanthi, S.; Kishore, K. Oxidative Copolymerization: Microstructure Analysis of the Terpolymer of Styrene, Methyl Methacrylate, and Oxygen. *Macromolecules* **1993**, *26* (8), 1985–1989.