Supporting Information

for

Expanding the Polymerization Potential of Itaconic Acid Through Methacrylate Functionalization

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S1 Experimental Methods

S1.1. Materials and Reagents

All materials purchased were reagent grade. Azobisisobutyronitrile (AIBN, Millipore Sigma, ≥98.0%) was recrystallized from methanol and dried in vacuum before being used. Methyl methacrylate (MMA, ≥99.0%, Millipore Sigma) and styrene (≥99.0%, Millipore Sigma) were passed through a column of basic alumina mixed with 5 wt% calcium hydride to remove inhibitors before being used in polymerization. 2-cyano-2-propyl benzodithioate (≥97.0%, RAFT agent) was purchased from Sigma Aldrich. BlocBuilder™ (≥99.0%, alkoxyamine for NMP) was obtained from Arkema. 1-heptanol (≥99.9%, Oleris) was also purchased from Arkema. Bis(pinacolato)diboron (B_2Pin_2, ≥99.0%) was purchased from Chem Impex. Itaconic acid (IA, ≥99.0%), benzyl alcohol (≥99.0%), butylated hydroxytoluene (BHT, ≥99.0%), *para*-toluene sulfonic acid monohydrate (pTSOH·H_2O, ≥99.0%), benzyl alcohol (≥99.0%), anhydrous magnesium sulfate ($MgSO_4$, ≥97.0%), copper (I) chloride (CuCl, ≥99.0%), sodium tert-butoxide (NaOtBu, ≥97.0%), sodium perborate tetrahydrate ($NaBO_3·4H_2O$, ≥96.0%), methacryloyl chloride (≥97.0%), triethylamine (≥99.5%), ethyl α-bromoisobutyrate (EbiB, ≥98%), copper (I) bromide (CuBr, ≥99%), N,N,N′,N″,N″- pentamethyldiethylenetriamine (PMDETA, ≥99%), anhydrous tetrahydrofuran (THF, ≥99.9%), deuterated chloroform ($CDCl_3$, ≥99.0%), silica gel 60 (230-400 Mesh ASTM) and celite were all purchased from Millipore Sigma. Bis[(2-diphenylphosphino)phenyl] ether (DPEPhos, ≥98.0%), tetrahydrofuran (THF, HPLC grade), methanol (≥99.8%), ethyl acetate (≥99.0%), hexanes (≥99.0%), dichloromethane (≥99.8%), toluene (≥99.0%), and 1,4-dioxane (≥99.0%) were all purchased from Fisher Scientific.

S1.2. ^{1}H NMR Spectroscopy

^{1}H NMR spectra were obtained using a Bruker AVIIIHD 500 MHz Spectrometer using an average of 16 scans in deuterated chloroform ($CDCl_3$) at room temperature.

S1.3. Gel Permeation Chromatography

Samples for gel permeation chromatography were run on two independent instruments.

The molecular weight and dispersity of samples collected during polymerization reactions were analyzed using a GPC (Waters Breeze) calibrated with narrow molecular weight p(MMA) standards. HPLC grade THF at a flowrate of 0.3mL/min was used as the mobile phase for detection

by a differential refractive index detector (RI 2414). The instrument was equipped with three Waters Styragel HR columns that were heated to 40°C during the analysis. The Mark-Houwink-Sakurada equation was not applied for the analysis of these samples, and the resulting molecular weight and dispersity data is therefore relative to the calibration from the p(MMA) standards. The p(MMA) standards obtained from Varian ranged from 2 710 g/mol to 1 677 000 g/mol.

For final polymers, the samples were first dried under reduced pressure at 70°C overnight to remove any moisture. The following day, solutions of the samples were prepared in HPLC grade THF in concentrations of approximately 2 mg/mL, and these solutions were then allowed to fully dissolve overnight. The samples were then filtered through 2 μm filters and added to an Agilent 1260 Infinity II multidetector suite system equipped with refractive index and multi-angle light scattering detector. Calibration of the system was completed using Varian narrow p(MMA) standards (2 710 g/mol to 1 677 000 g/mol). This system had two Polypore separation columns set at 40°C and a flowrate of 0.3 mL/min with HPLC grade THF as the eluent. Determination of absolute molecular weight and *dn/dc* by light scattering using the Agilent software assumed all the injected sample mass eluted from the column and was contained within the integration peak of the sample.

S1.4. Differential Scanning Calorimetry

The glass transition temperatures for the sets of polymers were determined by differential scanning calorimetry using a TA Instruments Discovery 2500 under a nitrogen atmosphere, following a heat/cool/heat cycle. The samples were equilibrated at -90°C for 5 minutes before being heated to 20°C at a rate of 2°C/min, held at 20°C for 5 minutes, and cooled back to -90°C at a rate of 2°C/min. They were then once again held at -90°C for 5 minutes and then heated a final time to 20°C at 2°C/min. The glass transition temperature was taken from the second heating cycle using the glass/step transition analysis tool in the TA Instruments Universal Analysis 2000 software where the inflection point is reported as the glass transition temperature.

S1.5. Thermal Gravimetric Analysis

The thermal stability of the synthesized polymers was evaluated using a TA Instruments Discovery 5500 instrument under a nitrogen flowrate of 25 mL/min. Samples were loaded onto platinum sample pans, and heated from 25 to 700°C at a rate of 10°C/min. The onset temperature

at a weight loss of 10% is reported, obtained from using the weight loss at temperature tool in the TA Instruments TRIOS software.

S1.6. Rheology

Prior to rheological assessment, the samples were dried under vacuum for 48 hours at 40°C. An Anton Paar MCR 302 instrument was used for rheology and viscosity tests, equipped with a 25 mm parallel plate sample mount. Samples were added to the parallel plate apparatus using a spatula, except for MbH1 which was first hot-pressed into a disk shape due to being more rigid. Frequency sweep tests were performed at a strain of 0.1%, and the samples were allowed to equilibrate at the testing temperature for 10 minutes before being run.

S1.7. Thin Film Preparation

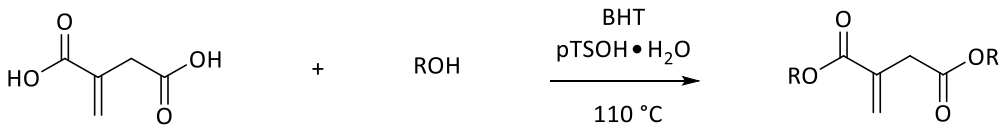
Approximately 0.2 g of diblock polymer samples were dissolved in approximately 0.2g THF and then applied using a glass pipette onto a glass microscope plate. The samples were then added to an oven at 120°C and ambient pressure for 3 hours, after which reduced pressure was applied. The oven was then turned off and allowed to cool to room temperature overnight.

S1.8. Small Angle X-Ray Scattering

SAXS patterns were obtained on a SAXSpoint 2.0 (Anton Paar) instrument using a Cu Kα radiation source with an Eiger R 1M horizontal detector. The detector was set at 557 mm, with the radiation source giving a wavelength of 1.54 Å. The thin film samples were laid onto 10 mm ×10 mm sample holders obtained from Anton Paar. The samples were exposed to X-rays for 20 minutes per frame, for a total of three frames per sample. The SAXS patterns were corrected and given as a function of the scattering vector ($q=(4\pi/\lambda)sin\theta$, with 2θ being the scattering angle in degrees (°) and q in nm^{-1}).

S1.9. Synthesis of Monomer

An overview of the first synthesis step is shown in Schematic S1.



Schematic S1. Functionalization of itaconic acid via dehydration.

Step 1. Itaconic acid (23.74 g, 182.5 mmol, 1 eq.) was added to a 250 mL three-necked round bottom flask containing a magnetic Teflon stir bar along with *para*-toluene sulfonic acid monohydrate (pTSOH·H_2O) (2.37 g, 10 wt% of itaconic acid) and butylated hydroxytoluene (BHT) (237 mg, 1wt% of itaconic acid). 1-heptanol (52.85 mL, 374.1 mmol, 2.05 eq.) was subsequently added and the flask was heated at 110°C under strong nitrogen bubbling for 2.5 hours via an oil bath, while connected to a Dean-Stark apparatus. The mixture was then cooled to room temperature and diluted with 400 mL of ethyl acetate in a separatory funnel. This organic fraction was first washed with 400 mL of saturated $NaHCO_3$ solution then 400 mL of brine, before being dried with $MgSO_4$, and filtered. Excess solvent was removed by rotary evaporation to obtain diheptyl itaconate (55.49 g, 170.0 mmol) as a colourless oil with 93% yield. Figures S1 and S2 give the ^{1}H NMR spectra of the diheptyl and dibenzyl products, respectively, that resulted from Step 1.

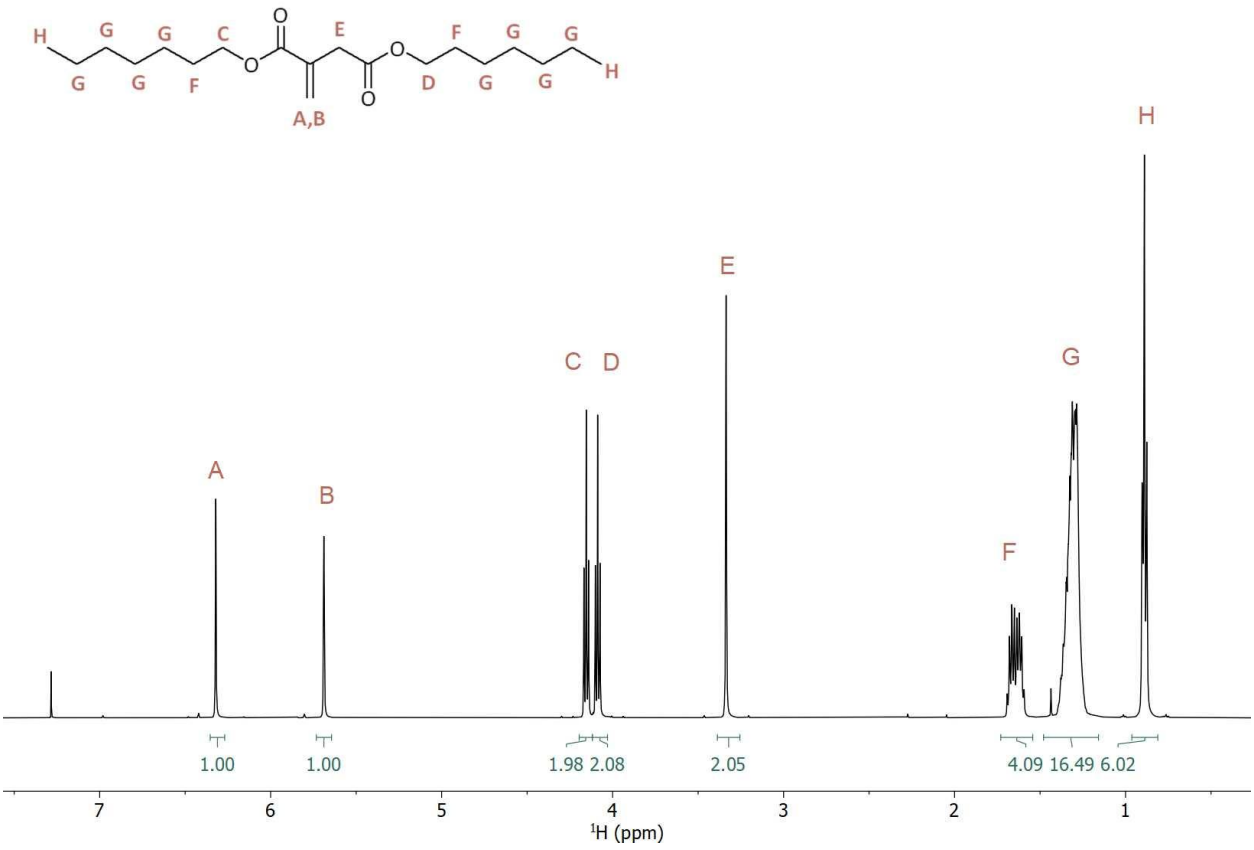


Figure S1. ^{1}H NMR of diheptyl itaconate: δ 6.32 (A) (s, 1H), 5.69 (B) (s, 1H), 4.15 (C) (t, 2H), 4.09 (D) (t, 2H), 3.34 (E) (s, 2H), 1.65 (F) (m, 4H), 1.31 (G) (m, 16H), 0.89 (H) (t, 6H).

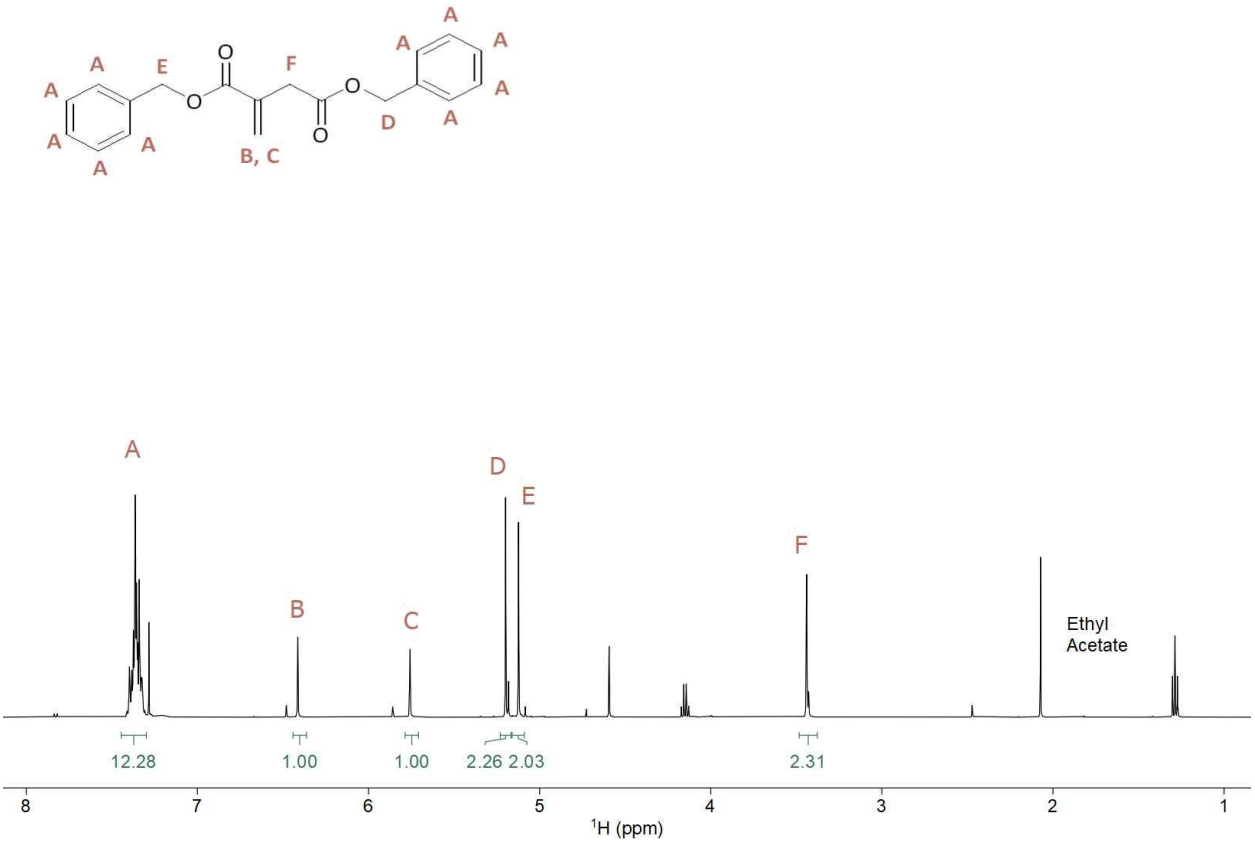
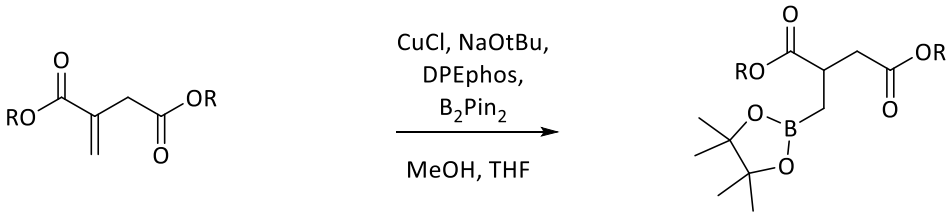


Figure S2. ^{1}H NMR of dibenzyl itaconate: δ 7.36 (A) (m, 10H), 6.41 (B) (s, 1H), 5.76 (C) (s, 1H), 3.43 (F) (d, 2H).

An overview of the second synthesis step is shown in Schematic S2.



Schematic S2. Boration of the itaconic acid derivative.

Step 2. A 250 mL round bottom flask containing a magnetic Teflon stir bar was first flame dried and then purged with nitrogen for 10 minutes. Then, copper chloride (178.2 mg, 1.8 mmol, 0.06 eq.), sodium tert-butoxide (518.9 mg, 5.4 mmol, 0.18 eq.), bis[(2-diphenylphosphino)phenyl] ether (1.050 g, 1.8 mmol, 0.06 eq.) and lastly anhydrous tetrahydrofuran (60mL) were added and

stirred for 30 minutes under nitrogen. Bis(pinacolato)diboron (8.380 g, 33 mmol, 1.1 eq.) was added with the remaining anhydrous tetrahydrofuran (30 mL) and stirred for 10 minutes. Previously synthesized diheptyl itaconate (9.794 g, 30 mmol, 1 eq.) was added with methanol (4.87 mL, 120 mmol, 4 eq.) and left under nitrogen overnight.[1] The mixture was passed through a bed of celite the following day, and the solvent removed by rotary evaporation to yield a pale blue oil containing the excess bis(pinacolato)diboron. The product was used without further purification. Figures S3 and S4 give the ^{1}H NMR spectra of the diheptyl and dibenzyl products, respectively, that resulted from Step 2. Unreacted bis(pinacolato)diboron remains in the solution at this point, resulting in the lack of stoichiometric integration values in the NMR.

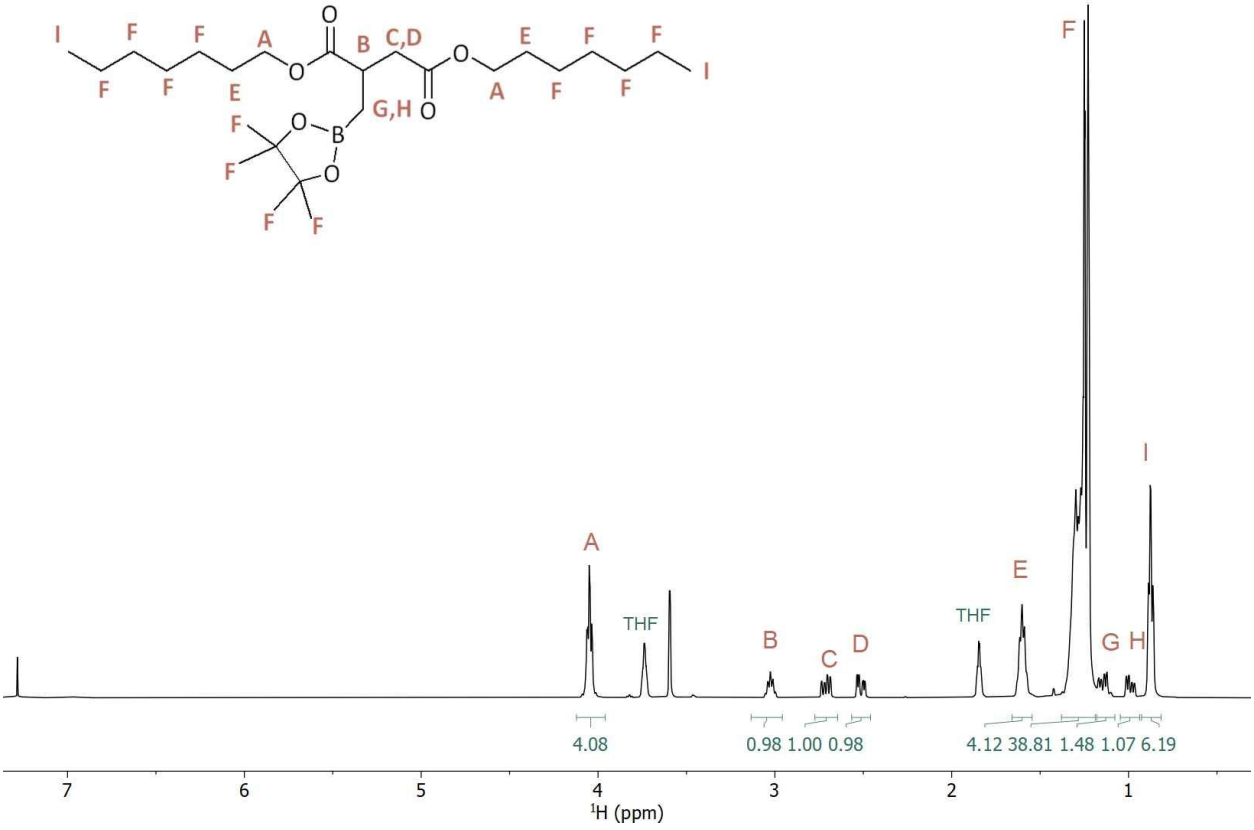


Figure S3. ^{1}H NMR of borated diheptyl itaconate: δ 4.05 (A) (td, 4H), 3.02 (B) (m, 1H), 2.71 (C) (dd, 1H), 2.51 (D) (dd, 1H), 1.61 (E) (q, 4H), 1.24 (F) (m, 16H), 1.15 (G) (dd, 1H), 0.99 (H) (dd, 1H), 0.88 (I) (td, 6H).

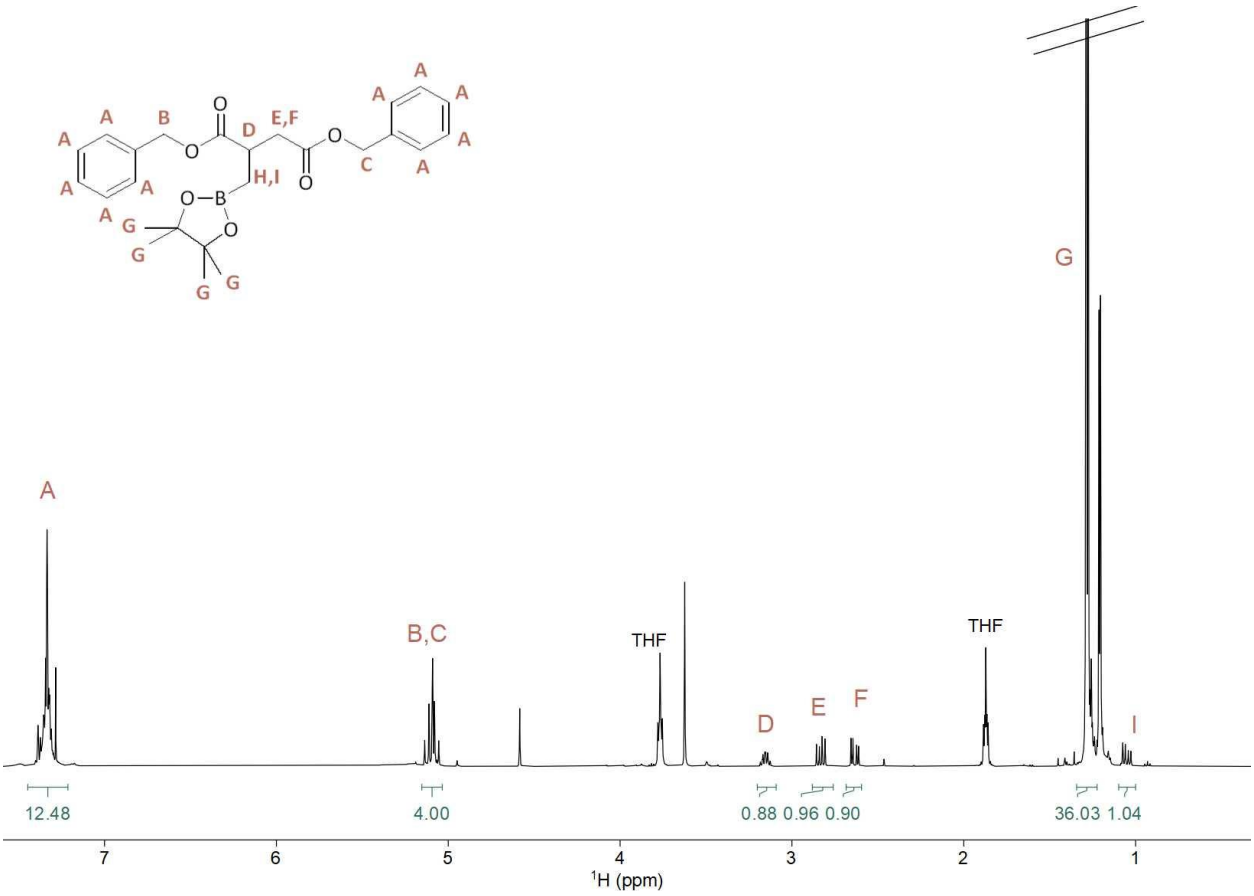
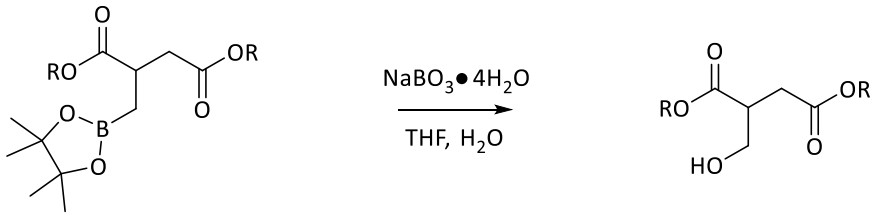


Figure S4. ^{1}H NMR of borated dibenzyl itaconate: δ 7.34 (A) (m, 10H), 5.09 (B, C) (m, 4H), 3.16 (D) (m, 1H), 2.83 (E) (dd, 1H), 2.63 (F) (dd 1H), 1.28 (G) (m, 12H), 1.05 (I) (dd, 1H).

An overview of the third synthesis step is shown in Schematic S3.



Schematic S3. Oxidation of borated adduct.

Step 3. The product from Step 2 (15 mmol, 1 eq.) was dissolved in tetrahydrofuran (60 mL) and reverse osmosis water (60 mL) in a 250 mL round bottom flask, to which was added sodium perborate tetrahydrate (6.924 g, 45 mmol, 3 eq.). The mixture was then stirred for 1.5 hours. The reaction was quenched by the addition of 90 mL reverse osmosis water and washed with 120 mL of brine, then extracted with 180 mL of ethyl acetate. Two more extractions of the aqueous phase

were completed using 120 mL of ethyl acetate. The combined organic fractions were washed with 150 mL of brine, before being dried with $MgSO_4$, filtered, and the excess solvent removed by rotary evaporation to obtain a yellow-green oil. Purification by column chromatography at 70:30 hexanes:ethyl acetate was monitored by thin layer chromatography to isolate a colourless oil as the product (3.3 g, 9.58 mmol) in a 63.9 % yield across both Step 2 and Step 3. Figures S5 and S6 give the ^{1}H NMR spectra of the diheptyl and dibenzyl products, respectively, that resulted from Step 3.

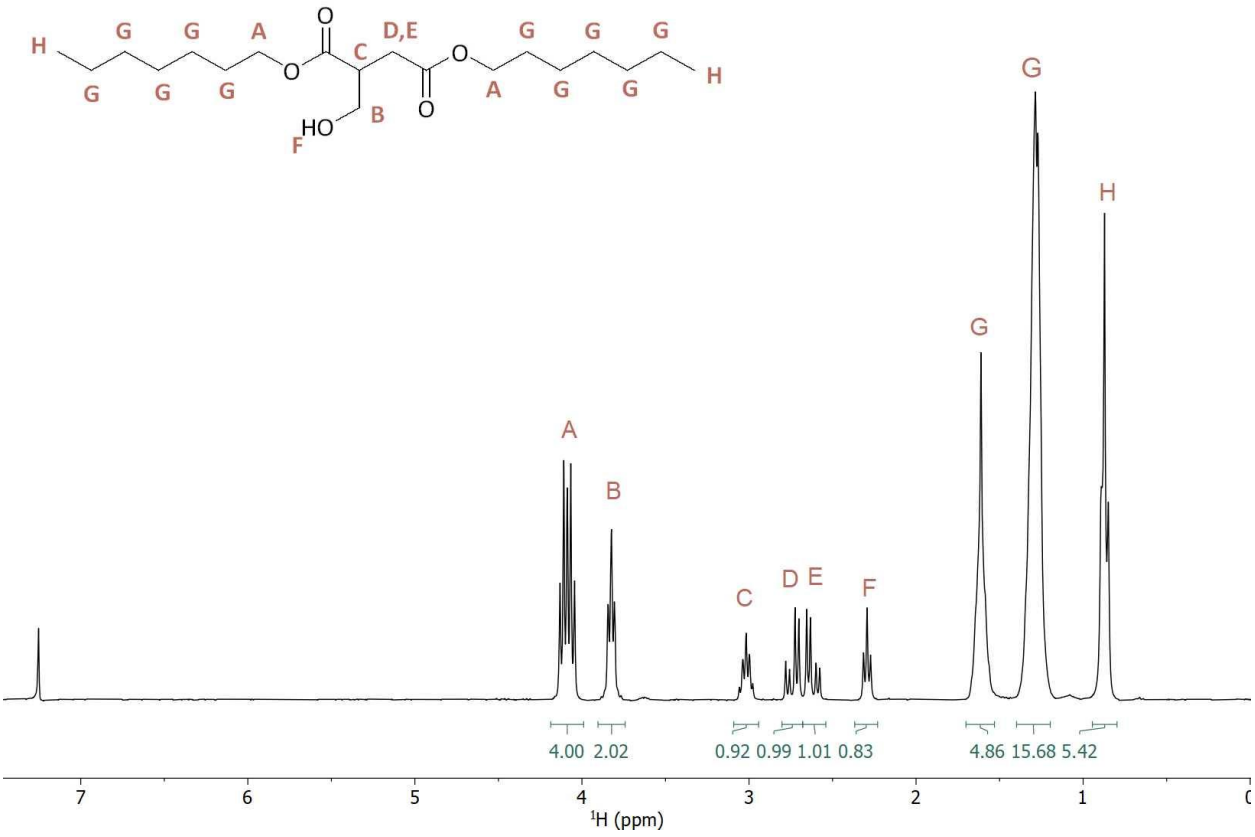


Figure S5. ^{1}H NMR of oxidized diheptyl itaconate: δ 4.09 (A) (dt, 4H), 3.82 (B) (t, 2H), 3.02 (C) (p, 1H), 2.72 (D) (dd, 1H), 2.62 (E) (dd, 1H), 2.29 (F) (t, 1H), 1.20-1.72 (G) (m, 20H), 0.88 (H) (m, 6H).

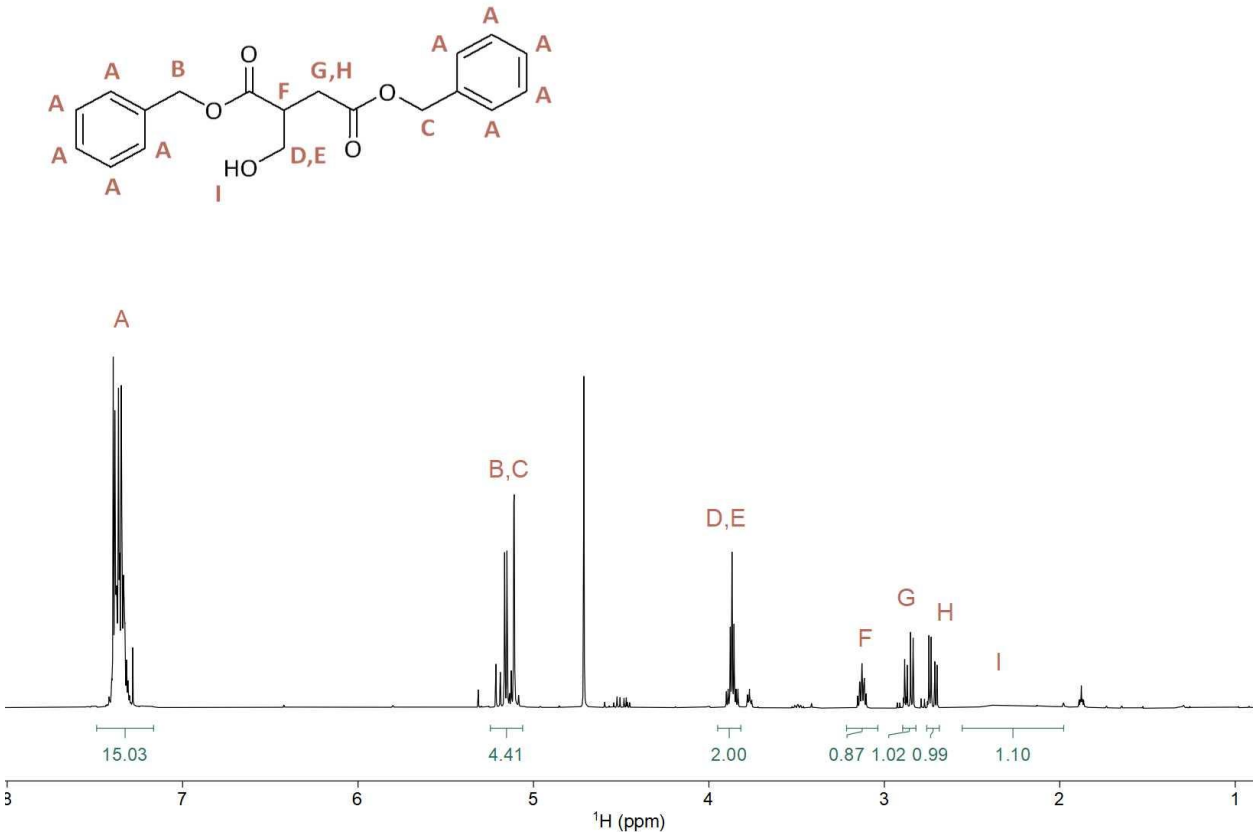
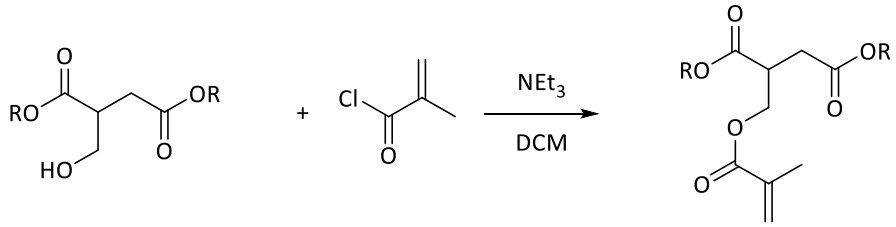


Figure S6. ^{1}H NMR of oxidized dibenzyl itaconate: δ 7.36 (A) (m 10H), 5.15 (B, C) (m 4H), 3.86 (D, E) (h, 2H), 3.13 (F) (tt, 1H), 2.86 (G) (dd, 1H), 2.72 (H) (dd, 1H), 1.98-2.58 (I) (br, 1H).

An overview of the fourth synthesis step is shown in Schematic S4.



Schematic S4. Methacrylation of oxidized itaconate.

Step 4. 370 mL of dichloromethane were added to a flame-dried 1000 mL reactor containing a magnetic stir bar, which was then cooled in an ice bath. The product from Step 3 (17.47 g, 50.7 mmol, 1 eq.) was then dissolved into the solvent, and triethylamine was added (13.5 mL, 96.3 mmol, 1.9 eq.). Methacryloyl chloride (5.95 mL, 60.8 mmol, 1.2 eq.) was added dropwise, and the mixture was allowed to warm to room temperature while being stirred overnight. The reaction was

quenched the following day by the addition of 150 mL of saturated $NaHCO_3$ solution. The resulting aqueous phase was extracted twice with 150 mL of dichloromethane each time, and the combined organic phase was washed with 150 mL of brine before being dried with anhydrous $MgSO_4$ and filtered. Evaporation of excess solvent by rotary evaporation produced a peach hued oil that was purified by column chromatography using hexanes: ethyl acetate at 70:30, with the product being the first component to elute from the column. The product was a colourless oil with a yield of 76.2% (15.94 g, 38.6 mmol). Figures S7 and S8 give the ^{1}H NMR spectra of the purified diheptyl and dibenzyl monomers, respectively, that resulted from Step 4.

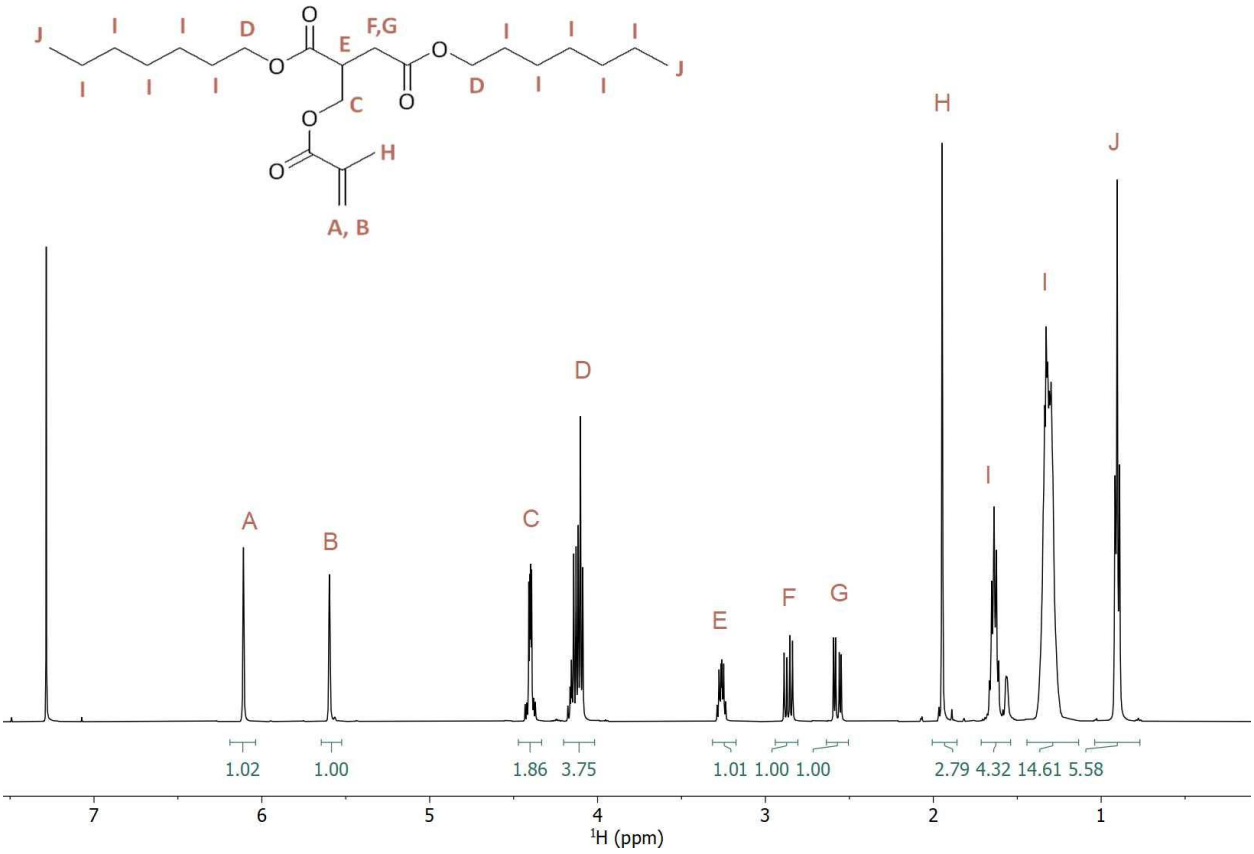


Figure S7. ^{1}H NMR of diheptyl itaconyl methacrylate: δ 6.11(A) (s, 1H), 5.6 (B) (s, 1H), 4.40 (C) (m, 2H), 4.12 (D) (dt, 4H), 3.26 (E) (dq, 1H), 2.86 (F) (dd, 1H), 2.57 (G) (dd, 1H), 1.95 (H) (s, 3H), 1.20-1.72 (I) (m, 20H), 0.91 (J) (td, 6H).

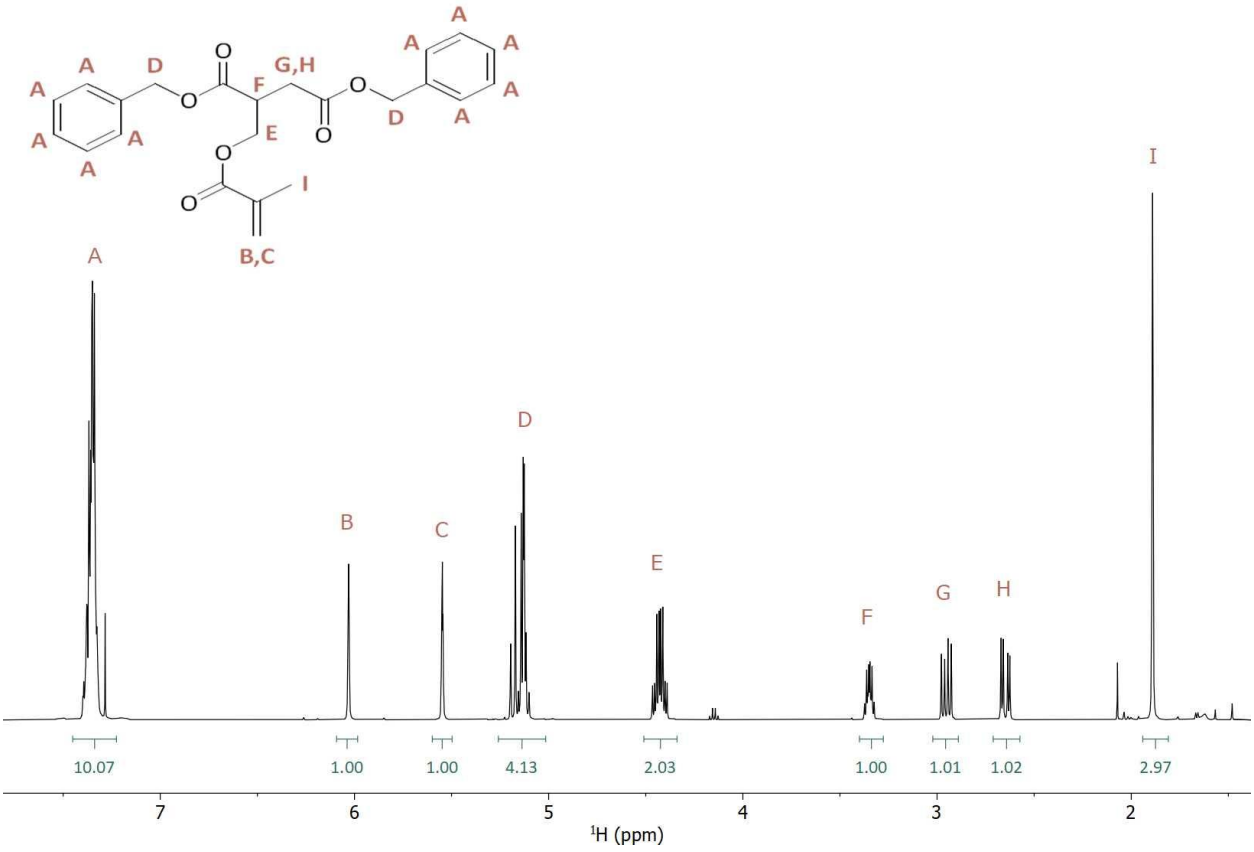
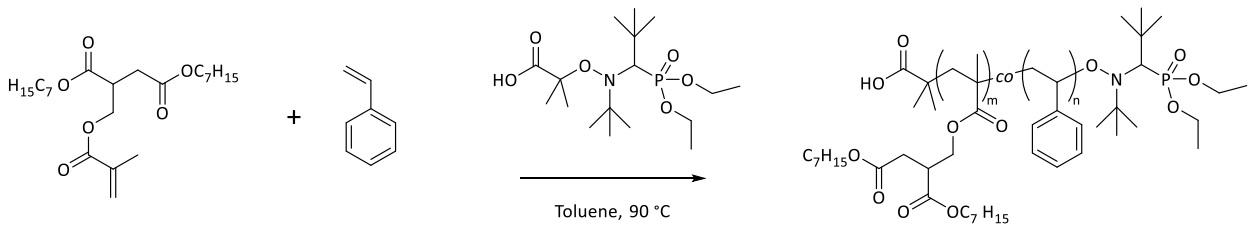


Figure S8. ^{1}H NMR of dibenzyl itaconyl methacrylate: δ 7.36 (A) (m, 10H), 6.03 (B) (s, 1H), 5.55 (C) (s, 1H), 5.15 (D) (m, 4H), 4.43 (E) (qd, 2H), 3.35 (F) (m, 1H), 2.95 (G) (dd, 1H), 2.65 (H) (dd, 1H), 1.89 (I) (s, 3H).

S1.10. Nitroxide Mediated Polymerization of DHIAMA

An overview of the polymerization is given in Schematic S5.

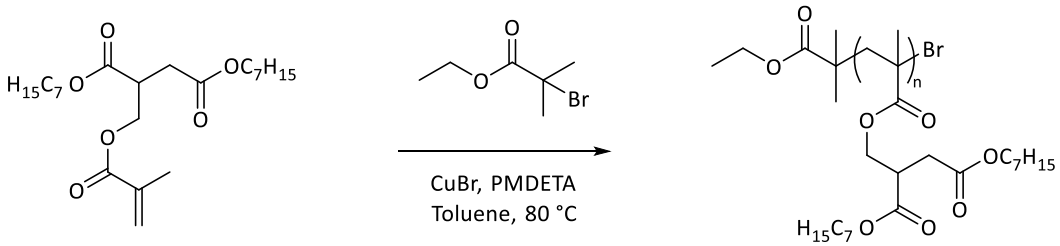


Schematic S5. Polymerization conditions via nitroxide mediated polymerization.

BlocBuilder was used as the nitroxide initiator and radical source during the nitroxide mediated polymerization of DHIAMA. Due to its methacrylic structure, styrene was used as a co-monomer in small amounts ~ 10 mol% with DHIAMA to impart control over the nitroxide mediated polymerization.[2] For the synthesis of the polymer, DHIAMA (1.466 g, 3.55 mmol), styrene (41 mg, 0.39 mmol), and BlocBuilder (23 mg, 0.06 mmol) were dissolved in an equivalent mass of toluene (1.76 mL) in a 10 mL three-neck round-bottom flask containing a magnetic stir bar, and fitted to a reflux condenser. Nitrogen gas was purged through the solution for 30 minutes before the flask was placed in an oil bath preheated to 90°C for 6 hours. Samples for ^{1}H NMR and GPC were taken periodically for kinetic analysis. The reaction was stopped by removing the flask from the oil bath and allowing the solution to cool to room temperature before being precipitated three times with methanol from THF. The resulting viscous liquid was dried overnight under reduced pressure at 40°C.

S1.11. Atom Transfer Radical Polymerization of DHIAMA

An overview of the polymerization is given in Schematic S6.



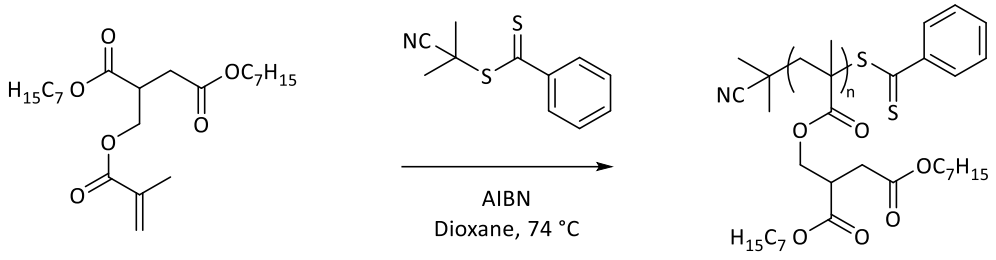
Schematic S6. Polymerization conditions via atom transfer radical polymerization.

A standard method of ATRP was employed to synthesize a homopolymer of DHIAMA. The target degree of polymerization, representing the number of repeat monomer units, was set to 50, with the degree of polymerization:ligand:catalyst:initiator ratio set to 50:1:0.5:1. For the reaction, half the toluene (total toluene volume of 1.15 mL) was added to a 10 mL three-necked-flask with copper I bromide (catalyst, 4 mg, 0.027 mmol) and PMDETA (ligand, 9.6 mg, 0.055 mmol). This mixture was stirred under nitrogen for 15 minutes. The DHIAMA (monomer, 1.15 g, 2.78 mmol), remaining toluene (final solution 50wt% monomer and solvent), and EBiB (initiator, 10.8 mg, 0.055 mmol) were then added to the reactor, and the mixture was left to purge for an additional 15 minutes. The flask was then submerged halfway into an oil bath preheated to 80°C, marking the start of the polymerization. Samples for GPC and NMR were taken throughout for kinetic analysis.

After 70 minutes the reaction was stopped by removing the reactor from the oil bath, with the polymer being precipitated 3 times by methanol from THF.

S1.12. Reversible Addition-Fragmentation Chain Transfer Polymerization of DHIAMA

An overview of the polymerization is given in Schematic S7.



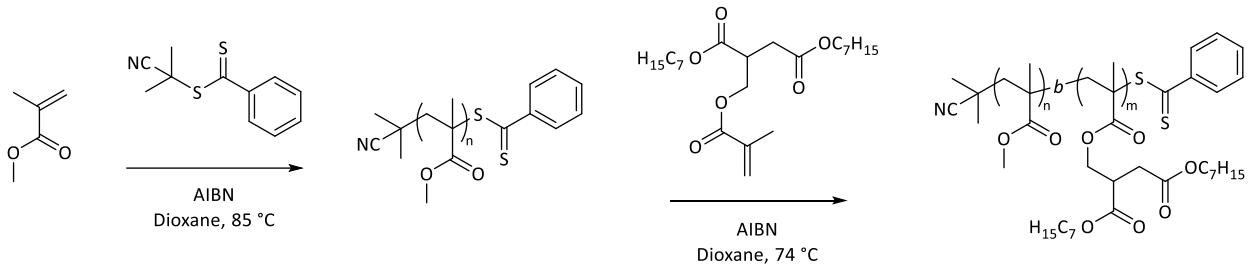
Schematic S7. Polymerization conditions via reversible addition-fragmentation chain transfer.

Reversible addition-fragmentation chain transfer (RAFT) polymerization was selected for the synthesis of the homopolymer series, as its ability to produce polymers with narrow molecular weight distributions and active chain ends would be useful for designing more complex architectures (e.g., block copolymers). Further, having high control over the degree of polymerization and maintaining a low dispersity make it favorable for producing samples where the molecular weight dependance of properties can be studied.

Reaction conditions were constant for the homopolymer series, except for reaction run time. As an example for H3, the reaction setup began with the addition of DHIAMA (1 g, 2.42 mmol), the chain transfer agent 2-cyano-2-propyl benzodithioate (11.19 mg, 0.051 mmol), the initiator AIBN (1.66 mg, 0.010 mmol) and the solvent, dioxane (2 mL, to reach a volumetric solution ratio of 1:2 for monomer: solvent), to a 10 mL three-necked-flask. A magnetic stir bar was added to the flask, and the mixture was stirred under nitrogen purge for 30 minutes before being added to a preheated oil bath at 72°C, marking the start of the reaction. Samples for GPC and NMR were taken throughout to allow for kinetic analysis, and the reaction was terminated by removing the flask from the oil bath and cooling the mixture. Polymers were obtained by being precipitated three times using methanol and THF.

S1.13. Block Copolymer Synthesis

An overview of the two-step polymerization is given in Schematic A8.

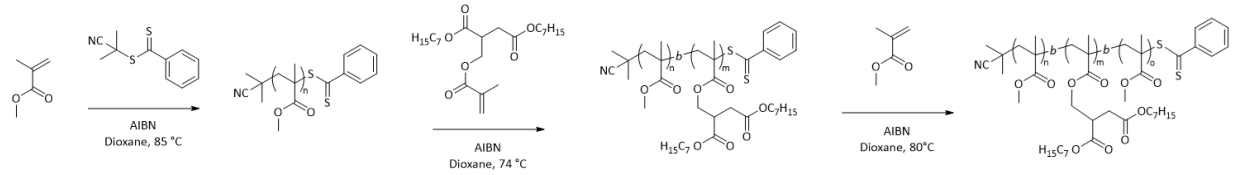


Schematic S8. Two-step polymerization conditions of diblock copolymers via reversible addition-fragmentation chain transfer.

Preparation of the macro-RAFT CTA agent was completed following the method outlined in Section S1.12 above, using methyl methacrylate (MMA) as the monomer, a volumetric solution ratio of 1:1 monomer:dioxane and a temperature of 85°C. Following three precipitation cycles, the macro-RAFT agent was dried in a fume hood for 24 hours and then under reduced pressure at 40°C for 24 hours to remove any remaining solvent. Chain extensions of the macro-RAFT agent again followed the procedure outlined above. As an example, for MbH1: p(MMA) macro-RAFT agent (800 mg, 0.080 mmol), AIBN (3.94 mg, 0.024 mmol), DHIAMA (840 mg, 2.04 mmol) and dioxane (3 mL, to reach an approximate polymer/monomer: solvent ratio of 2:1) were added to a 10mL three-necked-flask. The mixture was stirred under nitrogen purge for 30 minutes before being added to a preheated oil bath at 74°C to initiate polymerization. The reaction was halted by cooling the mixture, and the polymer precipitated three times from THF using methanol.

S1.14. Triblock Copolymer Synthesis

To confirm the chain end fidelity of the synthesized itaconyl methacrylate polymers, a chain extension of MbH3 was conducted. An overview is given in Schematic S9 below.



Schematic S9. Three-step polymerization conditions of triblock copolymer via reversible addition-fragmentation chain transfer.

The preparation of the macro-RAFT CTA was completed following the method outlined in Section S1.13 above, to give p(MMA-b-DHIAMA). Following three precipitation cycles, this macro-RAFT agent was dried in a fume hood for 24 hours and then under reduced pressure at 40°C for 24 hours to remove any remaining solvent. For this extension: the MbH3 p(MMA-b-DHIAMA) macro-RAFT agent (0.6 g, 0.0037 mmol), AIBN (0.17 mg, 0.001 mmol), MMA (79 mg, 0.0008 mmol) and dioxane (3 mL, to give a solution viscosity that could be stirred with the stir bar) were added to a 10mL three-necked-flask. The mixture was stirred under nitrogen purge for 30 minutes before being added to a preheated oil bath at 80°C to initiate polymerization. The reaction became viscous and was halted after 210 minutes by cooling the mixture, with the polymer being precipitated three times from THF using methanol.

S2. Homopolymers

S2.1. Light Scattering vs. Refractive Index Gel Permeation Chromatography Data

Gel permeation chromatography data obtained from a refractive index (RI) detector is presented alongside the light scattering (LS) detector data, for comparison. It can be seen the RI detector gives lower molecular weights, and higher dispersity values, but still follows the trends indicated by the LS detector.

Table S1. Refractive Index, and Light-Scattering Gel Permeation Chromatography Data for the p(DHIAMA) Series

Polymer	M_n, RI Detector [g mol^{-1}]	M_n, LS Detector [g mol^{-1}]	$Đ$, RI Detector	$Đ$, LS Detector
H1	8,600	-	1.07	-
H2	11,300	15,700	1.14	1.07
H3	20,900	28,700	1.16	1.07
H4	20,200	37,000	1.11	1.07
H5	19,100	39,000	1.19	1.05
H6	32,100	64,900	1.27	1.12
H7	34,500	93,900	1.23	1.09
H8	57,900	148,900	1.19	1.13
H9	72,200	198,200	1.80	1.60

Table S2. Refractive Index, and Light-Scattering Gel Permeation Chromatography Data for the p(DBIAMA) Series

Polymer	M_n, RI Detector [g mol^{-1}]	M_n, LS Detector [g mol^{-1}]	$Đ$, RI Detector	$Đ$, LS Detector
B1	6,300	15,400	1.27	1.15
B2	8,300	22,400	1.22	1.16
B3	13,600	30,700	1.18	1.11
B4	13,000	45,900	1.31	1.14
B5	26,800	88,000	1.22	1.13
B6	33,600	105,200	1.37	1.27
B7	66,400	136,000	1.62	1.40

S2.2. Nuclear Magnetic Resonance

An example NMR spectrum of p(DHIAMA) is given in Figure S9 and for p(DBIAMA) in Figure S10.

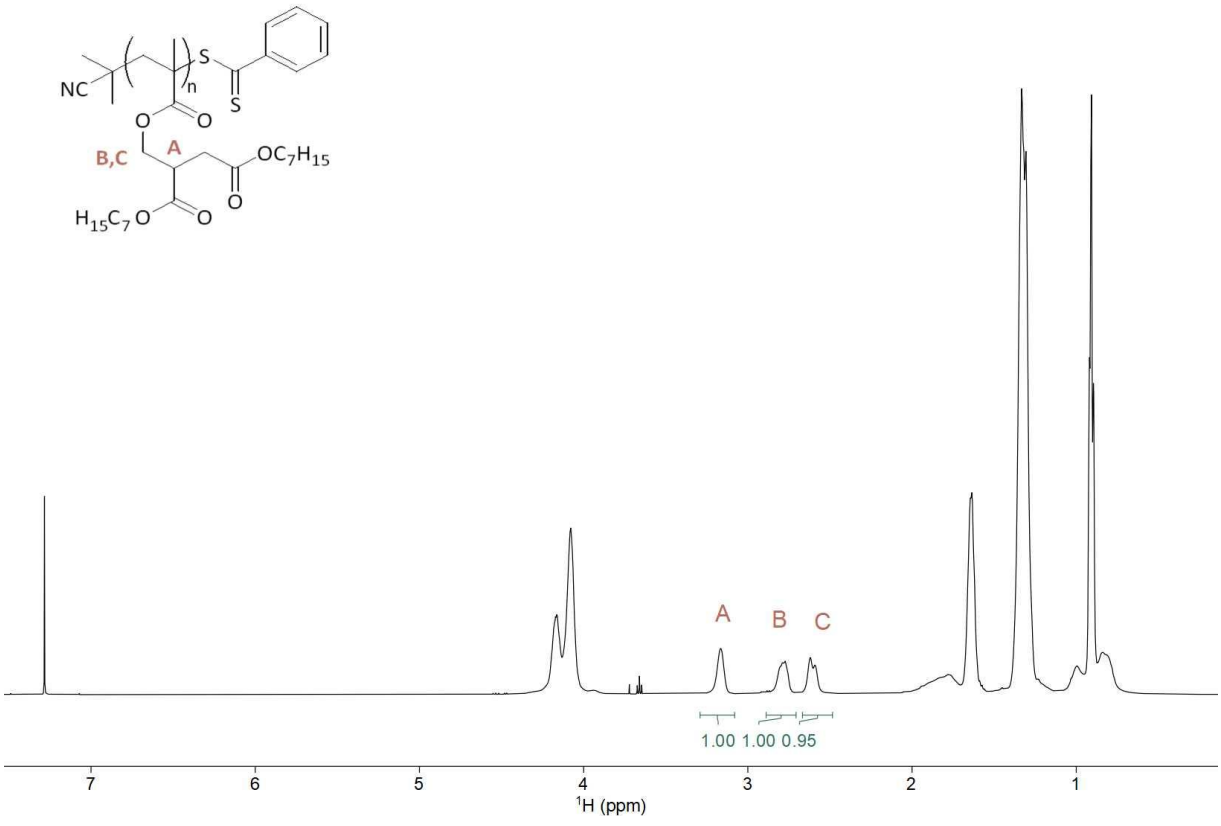


Figure S9. ^{1}H NMR of p(DHIAMA): δ 3.07-3.25 (A) (br, 1H), 2.71-2.89 (B) (br, 1H), 2.48-2.67 (C) (br, 1H).

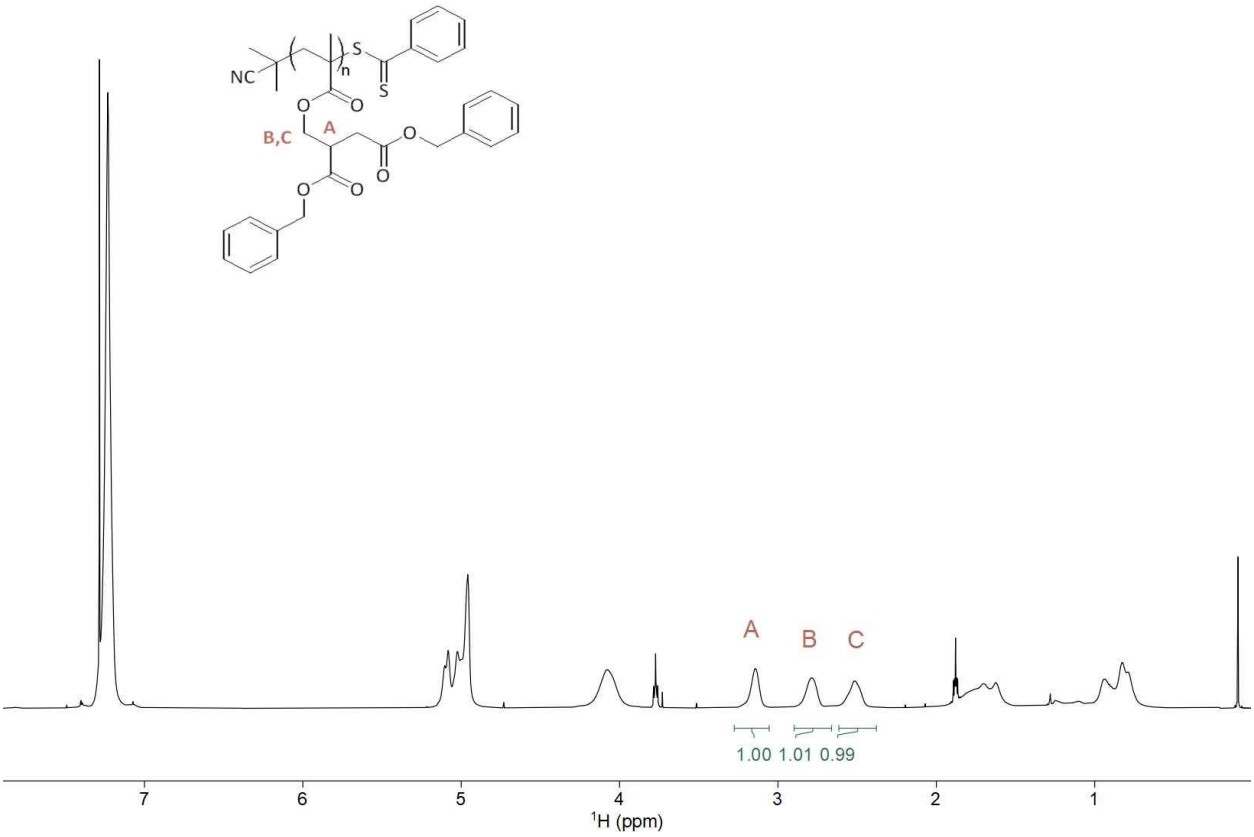


Figure S10. ^{1}H NMR of p(DBIAMA): δ 3.07-3.25 (A) (br, 1H), 2.71-2.89 (B) (br, 1H), 2.48-2.67 (C) (br, 1H), (trace impurities at 1.85 and 3.76 from THF).

S2.3. p(DBIAMA) Reaction Kinetics

Polymerization kinetics of p(DBIAMA) following the procedure outlined in Section S1.12 are shown in Figures S11 and S12.

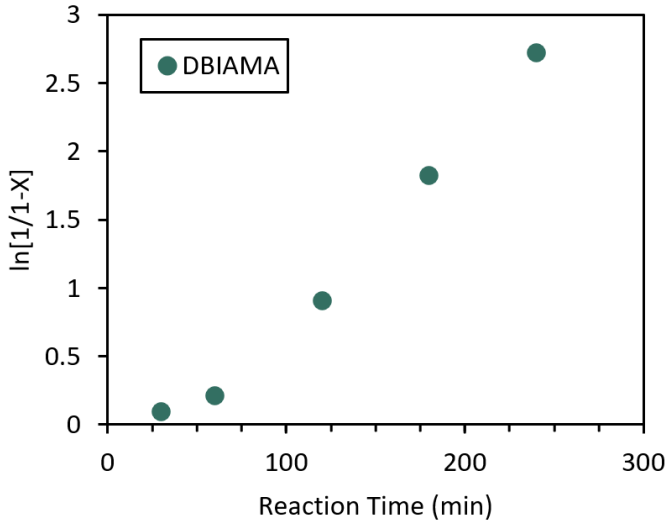


Figure S11. Pseudo-first order monomer conversion with time for a standard polymerization of dibenzyl itaconyl methacrylate (DBIAMA) using RAFT at 74°C. Monomer conversion was determined from the integration of monomer peaks in NMR samples.

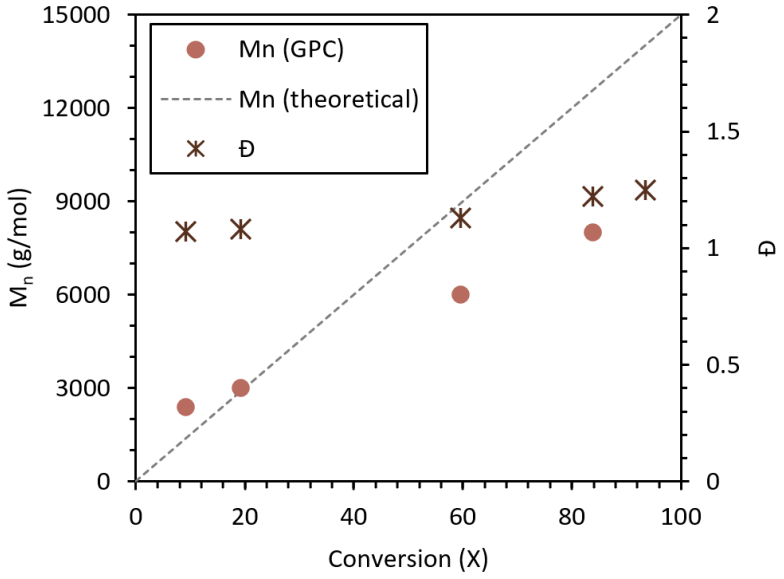


Figure S12. Number average molecular weight M_n and dispersity $Đ$ of the growing polymer during the polymerization of DBIAMA by RAFT. Molecular weight and $Đ$ values were determined from GPC samples analyzed by an RI detector as described in Section S1.3.

S2.4. p(DHIAMA) Viscosity Sweep

Viscosity sweeps conducted on the p(DHIAMA) series are shown in Figure S13, with the zero-shear plateau modulus plotted against the number average molecular weight in Figure S14.

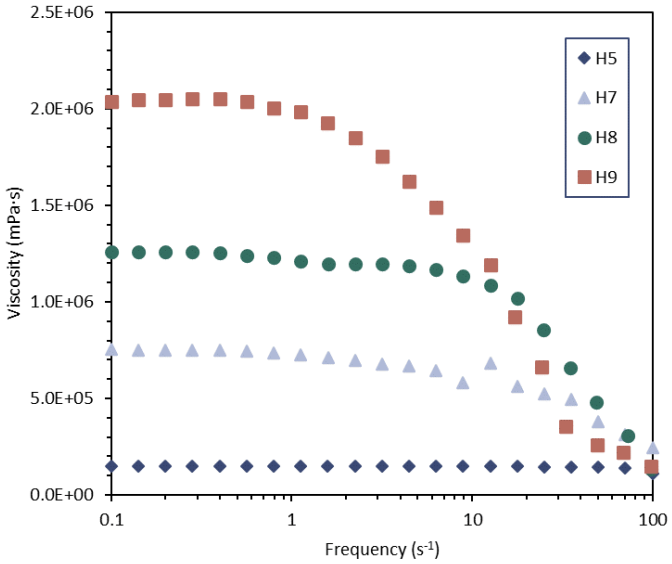


Figure S13. Example viscosity curves of p(DHIAMA) homopolymers from which zero-shear viscosity values were obtained from the plateau at low frequencies.

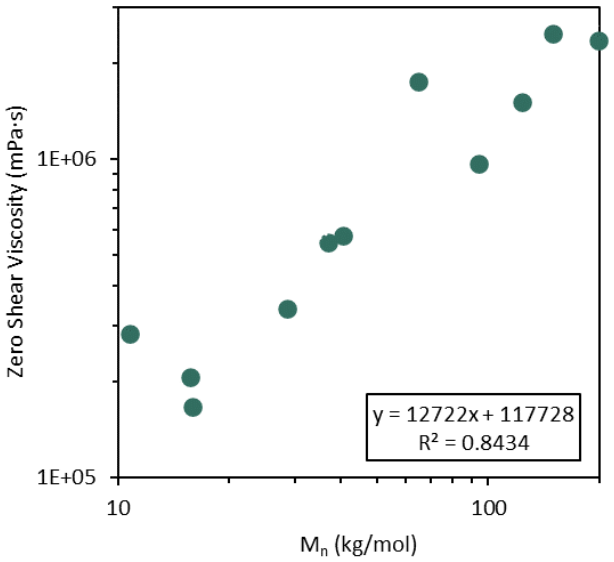


Figure S14. Zero-shear viscosities as function of molecular weight under the tested homopolymers gave a reasonable linear fit (R^2=0.8434). The molecular weight of entanglement was not in the synthesized range.

S2.5. Flory- Fox Model Fit

Figures S15 and S16 contrast the experimental glass transition temperature and molecular weight data with the Flory-Fox model as described by Equation (1) (see main body) for p(DHIAMA) and p(DBIAMA), respectively.

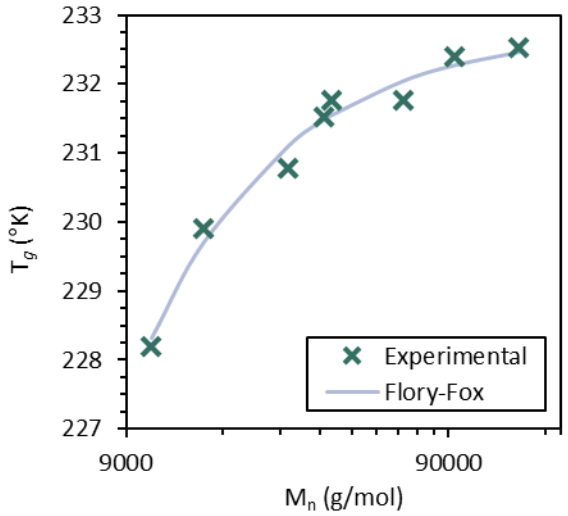


Figure S15. Experimental data and Flory-Fox fit for the p(DHIAMA) homopolymer series.

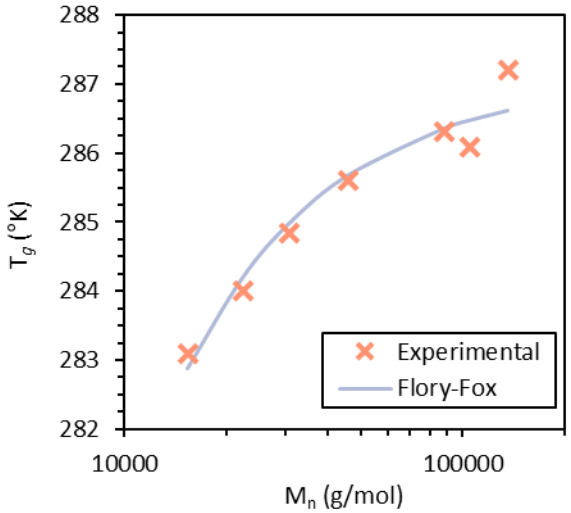


Figure S16. Experimental data and Flory-Fox fit for the p(DBIAMA) homopolymer series.

S3. Block Copolymers

S3.1. Solubility Parameter Calculation p(DHIAMA)

The Hoftyzer-Van Krevelen method was used to estimate the solubility parameter of DHIAMA (δ_{DHIAMA}) using the group contribution method.[3] In this approach, the solubility parameter is given by Equation (S1):

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{S1}$$

where:

$$\delta_d = \frac{\sum F_{di}}{V}; group\ contribution\ from\ dispersion\ forces \tag{S2}$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V}; group\ contribution\ from\ polar\ forces \tag{S3}$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V}}; group\ contribution\ from\ hydrogen\ bonding \tag{S4}$$

The parameters of the relevant functional groups in DHIAMA can be found in literature and are provided in Table S1.

Table S3. Structural group solubility parameter contributions.[3]

Structural Group	F_d ($J^{0.5}cm^{1.5}mol^{-1}$)	F_p ($J^{0.5}cm^{1.5}mol^{-1}$)	E_h ($J\ mol^{-1}$)
$-CH_3$	420	0	0
$-CH_2-$	270	0	0
>CH-	80	0	0
$=CH_2$	400	0	0
=C<	70	0	0
-COO-	390	490	7000

A pycnometer was used to find the density of p(DHIAMA) as $\rho = 1.05\ g/cm^3$, leading to a molar volume of $V_{p(DHIAMA)}$ as 392.8 cm^3/mol. Thus, the solubility parameter was estimated to be $\delta_{DHIAMA} = 18.8\ (J/cm^3)^{0.5}$.

S3.2. Flory-Huggins Interaction Parameter Calculation

The interaction parameter of p(DHIAMA) and p(MMA) systems can be calculated using the Flory-Huggins method by:

$$\chi = \frac{\bar{V}}{RT}(\delta_{DHIAMA} - \delta_{MMA})^2 \quad \text{(S5)}$$

with the average molar volume given by Equation (S6).

$$\bar{V} = \sqrt{V_{DHIAMA} V_{MMA}} \quad \text{(S6)}$$

where R is the universal gas constant and T is the absolute temperature.

From literature, the molar volume of p(MMA) is 86.5 cm^3/mol and δ_{MMA} = 23.5 $(J/cm^3)^{0.5}$.[4]

Their interaction parameter can then be estimated as χ = 1.627 at 25°C. To expect phase separation in the polymer, the (χN) value must exceed 10.5, where N is the total degree of polymerization. Using this, the block copolymers were designed such that the degree of polymerization for the target composition would be expected to result in microphase separation, as shown in Table S2.

Table S4. χN values of the targeted p(MMA-*b*-DHIAMA) block copolymers.

Copolymer	M_n p(MMA), GPC	M_n p(DHIAMA), target	N_{total}, expected	(χN)
MbH1	10,000	10,500	125	200
MbH2	10,000	24,000	158	250
MbH3	10,000	85,000	306	500
MbH4	10,000	118,000	386	630
MbH5	32,300	137,000	655	1 100

With the χN values falling over an order of magnitude above 10.5, it is estimated the diblock polymers will exhibit phase separation if synthesized as designed.

S3.3. Block Copolymer Reaction Kinetics

Example reaction kinetics using the methods outlined in Section S1.13 for the synthesis of a diblock copolymer are given in Figures S17 through S20.

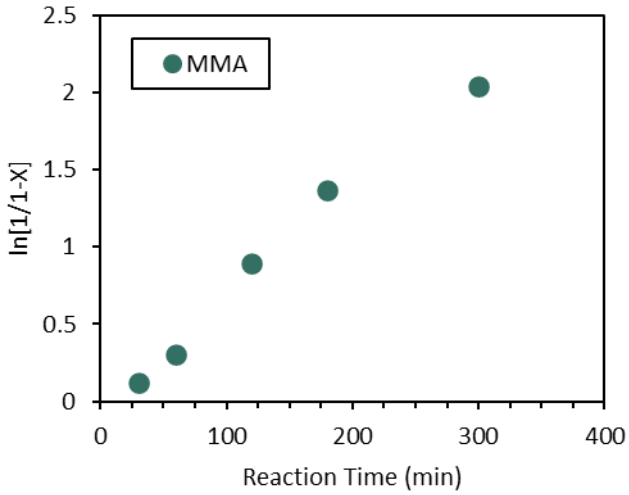


Figure S17. Pseudo first-order conversion of MMA during polymerization by RAFT to form the macro-RAFT agent.

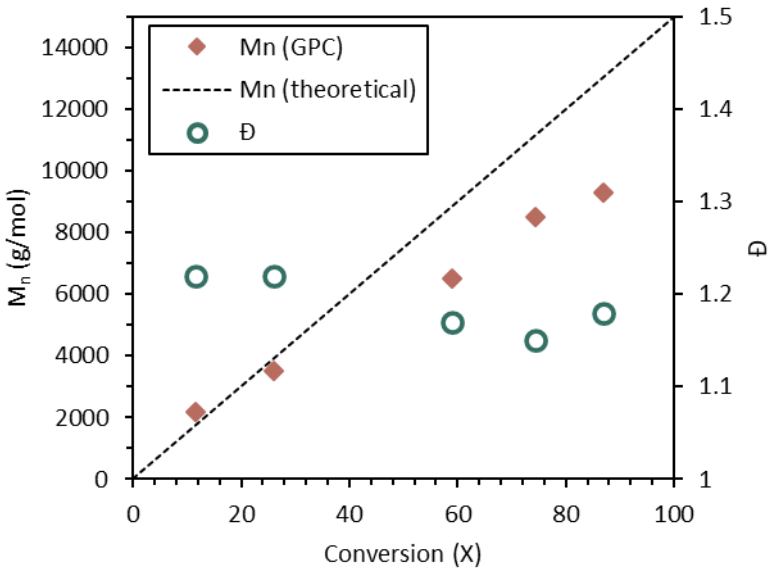


Figure S18. Number average molecular weight and dispersity values during the polymerization of MMA to generate the macro-RAFT agent.

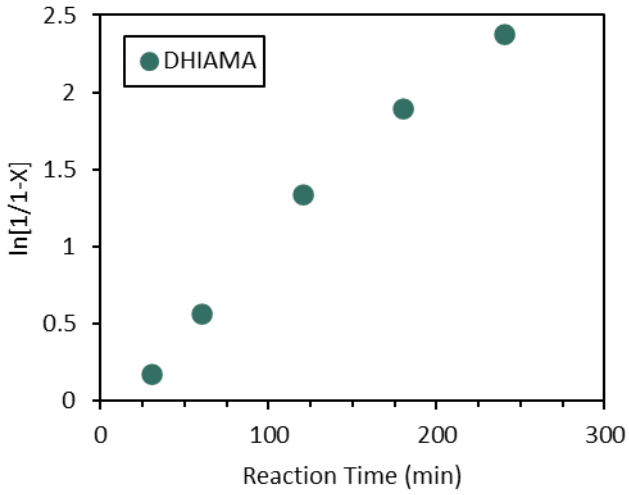


Figure S19. Pseudo first-order conversion of DHIAMA during the chain extension of the p(MMA) macro-RAFT agent to give a diblock copolymer.

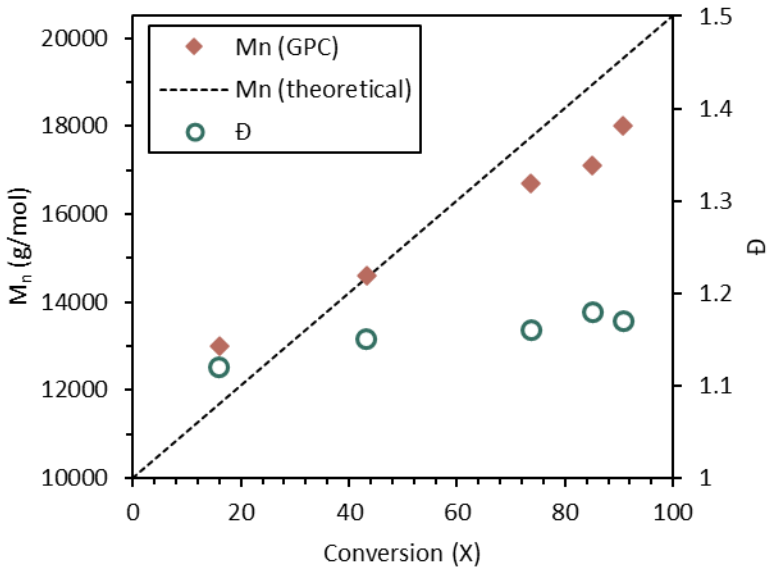


Figure S20. Number average molecular weight and dispersity of the growing polymer during the chain extension reaction to produce p(MMA-*b*-DHIAMA), with the starting M_n of the macro-RAFT agent being 10 000 g/mol.

S3.4. Nuclear Magnetic Resonance

An example of an NMR spectrum of a diblock copolymer is given in Figure S21.

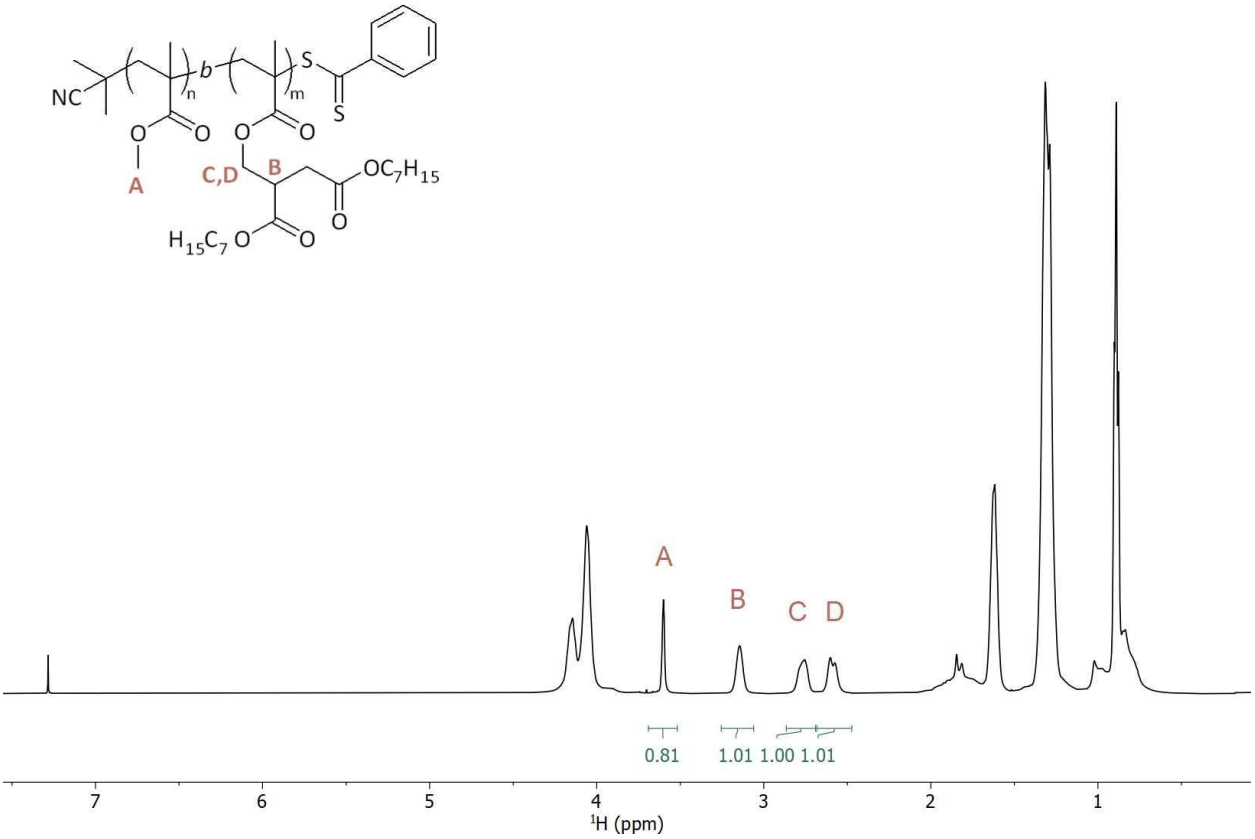


Figure S21. ^{1}H NMR of p(MMA-*b*-DHIAMA): δ 3.50-3.65 (A) (3H, p(MMA)), 3.07-3.25 (B) (1H, p(DHIAMA)), 2.71-2.89 (C) (1H, p(DHIAMA)), 2.48-2.67 (D) (1H, p(DHIAMA)).

S3.5. Copolymer Composition Calculation

The composition of the diblock copolymers was determined using the ^{1}H NMR spectrum of the dried samples. The integration values found from the chemical shifts were used in Equation (S7) to determine the composition:

$$F_i = \frac{\left(\int_{\text{range start}}^{\text{range end}} \left(\frac{1}{\text{Number of Hydrogens}}\right)\right)_i}{\sum_1^{N\ components} \int_{\text{range start}}^{\text{range end}} \left(\frac{1}{\text{Number of Hydrogens}}\right)} \quad \text{(S7)}$$

S3.6. Differential Scanning Calorimetry

The results of DSC performed on the diblock copolymers, following the method outlined in Section S1.4, are given in Figure S22.

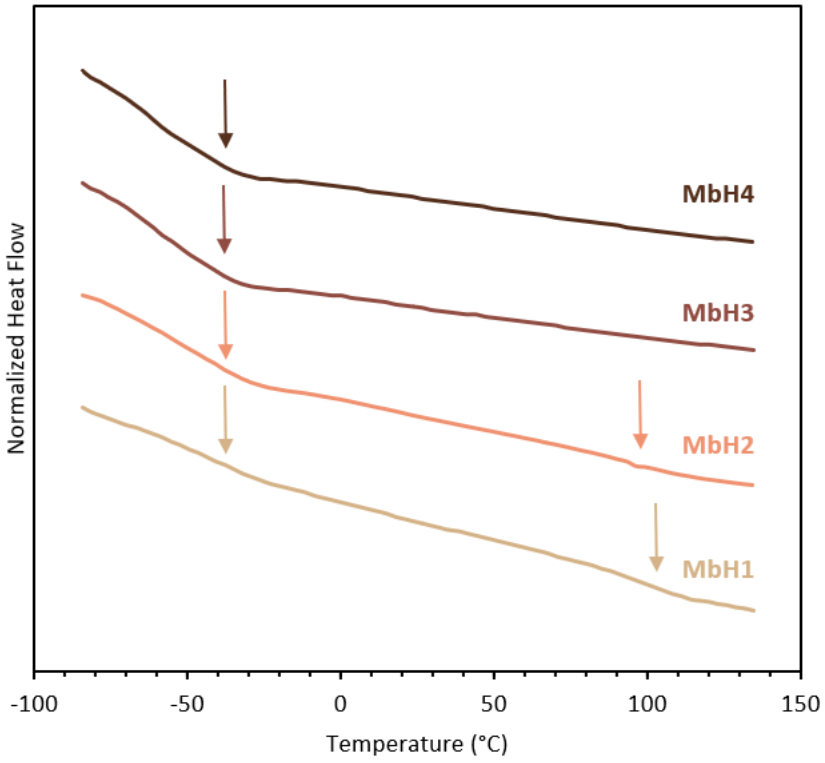


Figure S22. Differential scanning calorimetry scans of the p(MMA-*b*-DHIAMA) series with discernable glass transition temperatures indicated by arrows.

S3.7. SAXS of MbH5 and H9

The SAXS traces of MbH5 and H9 in Figure S23 show a distinct scattering pattern for MbH5 indicative of a bicontinuous microstructure, while a lack of scattering peaks in H9 confirms its existence as a single phase material.

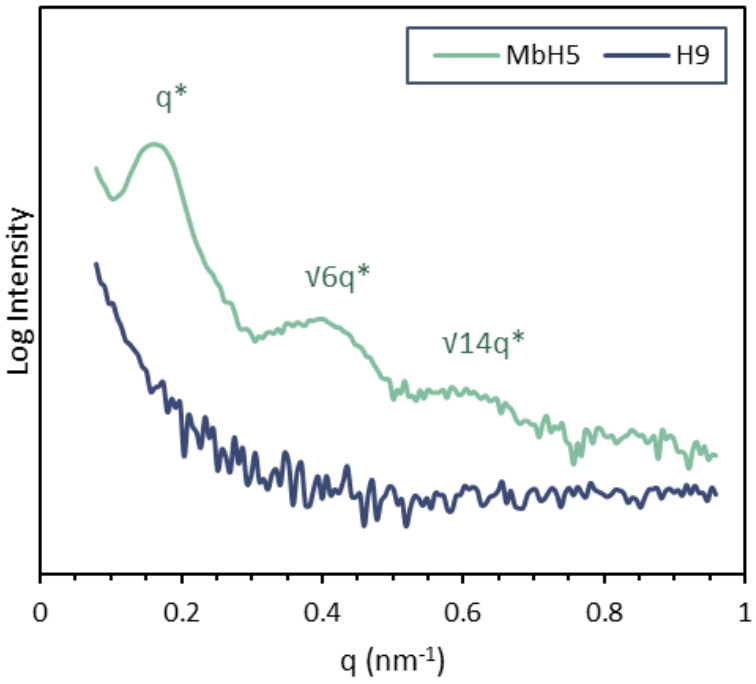


Figure S23. SAXS traces of MbH5 and H9

S3.8. End Group Fidelity Triblock Experiment

Section S1.14 details the reaction conditions used for the triblock synthesis, to confirm the end group fidelity of the polymerized methacrylate itaconates. Table S5 below shows the GPC samples results (RI detector calibrated using p(MMA) standards) from the experiment, and Figure S24 gives the linearized monomer conversion with time for the experiment.

Table S5. Molecular Weight and *Đ* During Triblock Experiment

Time	M_n, GPC	*Đ*
0	52,200	1.29
30	52,300	1.29
60	53,300	1.28
120	50,700	1.33
210	52,100	1.32
Precipitated	57,600	1.28

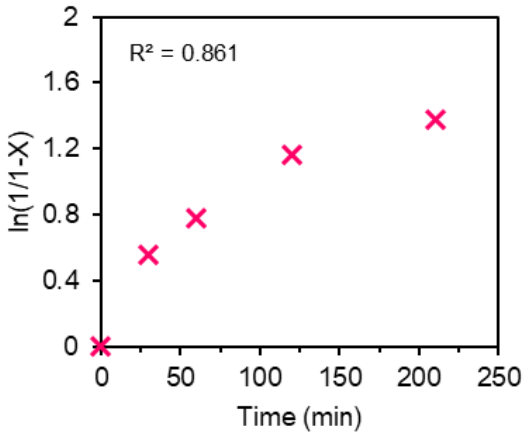


Figure S24. Pseudo first-order conversion of MMA during the chain extension of the p(MMA-b-DHIAMA) macro-RAFT agent to give a triblock copolymer.

The reaction achieved a monomer conversion of 74.7%, and saw a 5,000 g/mol increase onto the p(MMA-b-DHIAMA) macro-RAFT CTA without increasing the *Đ*. The chain end fidelity of the p(MMA-b-DHIAMA) was therefore considered to be high, with the ability to produce p(MMA-b-DHIAMA-b-MMA) triblock copolymers.

References

1 S. Mun, J.-E. Lee and J. Yun, *Organic Letters,* 2006, ***8***, 4887-4889.

2 M. Y. Zaremski, A. V. Plutalova, M. B. Lachinov and V. B. Golubev, *Macromolecules,* 2000, ***33***, 4365-4372.

3 D. W. Krevelen, in *Properties of Polymers,* ed. K. te Nijenhuis, Elsevier, Amsterdam, Fourth Edition, 2009, 7, 189-227.

4 J. C. Arnold, in *Comprehensive Structural Integrity,* ed. I. Milne, R. O. Ritchie and B. Karihaloo, Elsevier, Oxford, Third Edition, 2003, 6, 281-319.