*Supplementary Information For*:

# Pushing the Limits of Mechanoredox RAFT Polymerization Methods

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# 1. General Considerations

### *Materials*

All chemicals were obtained from commercial sources and used as received unless otherwise stated. *Tert*-butyl acrylate (*t*BA), butyl acrylate (BA), ethyl acrylate (EA), and diethylene glycol ethyl ether acrylate (DEGEEA) were purchased from Tokyo Chemical Industry (TCI). Methyl acrylate (MA) was purchased from Acros. Isobornyl acrylate (IBA) was purchased from Sigma-Aldrich. 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) was purchased from Fisher Scientific. All monomers were stabilized by 4-methoxyphenol (MEHQ), which was removed by passing the liquid monomer through basic alumina immediately before use. Diphenyl iodonium hexafluorophosphate (DPIHP) was obtained from TCI. Tetrahedral $BaTiO_3$ nanoparticles (<100 nm size) were purchased from US Research Nanomaterials, Inc.

Acrylate monomers used in glovebox experiments were dried over molecular sieves and degassed via sparging with nitrogen gas for several hours. Anhydrous *N*,*N*-dimethylformamide (DMF) used in glovebox experiments was obtained through a JC Meyer solvent purification system.

Ball milling experiments were performed using a Retsch Mixer Mill (MM 400) in 1.5 mL or 5 mL stainless steel screw-top jars (Retsch Nos. 01.462.0230 & 01.462.0213) with a single 5 mm or 8 mm stainless steel grinding ball (MSE Supplies Nos. BA0402 & BA0403).

### *Characterization*

All $^1$H nuclear magnetic resonance ($^1$H NMR) spectra were obtained on a Bruker AVANCE-500 NMR spectrometer at 25 °C. $^1$H NMR spectra samples were prepared in chloroform-*d* ($CDCl_3$) and referenced to $Me_4Si$ (TMS, $\delta = 0.00$ ppm). All $^1$H NMR spectra were analyzed using MestreNova processing software. Chemical shifts are represented in parts per million (ppm). Integration values of the sidechains from monomers (and their corresponding polymers) were used as internal standards and compared to the decreasing integration values of the vinylic protons (ca. 5.5–6.5 ppm) of each monomer to calculate monomer conversion. See Figure S3 for a graphical example.

Gel permeation chromatography (GPC) data were obtained on an Agilent 1260 HPLC equipped with a Wyatt 8-angle DAWN NEON light-scattering detector, ViscoStar NEON viscometer, and Optilab NEON refractive index detector. GPC samples were analyzed at a flow rate of 1 mL/min in chloroform stabilized with 0.5%-1.0% ethanol through two Agilent PLgel MIXED-C columns at 35 °C. GPC samples were prepared at ca. 10 mg/mL in chloroform and were filtered through 0.2 µm PTFE filters before analysis. The following d*n*/d*c* values (in mL/g) were used, and were measured by the 100% mass recovery method using Wyatt Astra 7.3 software:

**poly(*t*BA)**: 0.024; **poly(*n*BA)**: 0.033; **poly(EA)**: 0.029; **poly(MA)**: 0.039; **poly(2-MEA)**: 0.035; **poly(DEGEEA)**: 0.057; **poly(IBA)**: 0.061 mL/g.

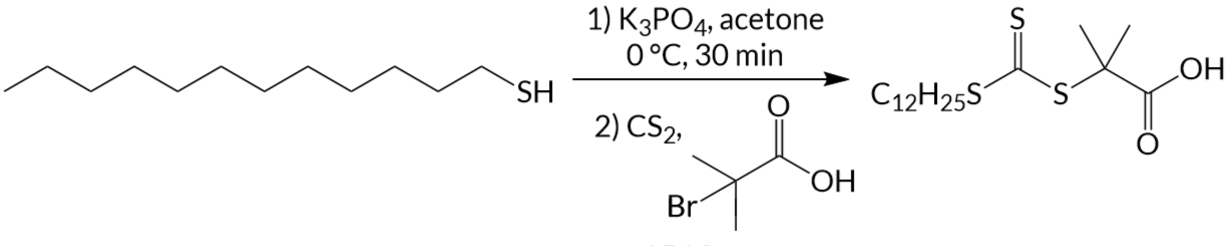
Small angle X-ray scattering (SAXS) was performed using Xeuss 3.0 by Xenocs (Grenoble, France). The system is equipped with a GeniX 3D microfocus X-ray generator with Cu k-alpha (wavelength = 1.5402 Å) as the source. The measurements were made with sample-to-detector distances of 1.80 m, 0.90 m, 0.37 m, and 0.05 m. The 2D images were processed and merged using XSACT 2.10.3 by Xenocs (Grenoble, France). The peak positions were determined by SASView 6.0 using the broad peak model.

Differential scanning calorimetry (DSC) was collected on a TA Instruments Discovery DSC 2500 using a heat-cool-heat cycle ranging from −70 °C to 150 °C. The heating cycles were run at a rate of 10 °C/min and the cooling cycle was run at a rate of 20 °C/min. Glass transition temperatures ($T_g$) were determined from each curve's inflection points using the TRIOS software from TA Instruments.

Diffusion-order spectroscopy (DOSY) was performed on a Bruker AVANCE-500 NMR spectrometer with a Bruker Smartprobe (iProbe) (maximum gradient strength = 56 Gauss/cm at 10 A) at 25 °C. All samples were prepared in $CDCl_3$ and referenced to TMS (δ = 0.00 ppm). The following general parameters were used: 16 scans, D1 = 1 s, "Little Delta" = 2.3 ms. "Big Delta" values are listed in the captions for each DOSY spectrum (**Figures S31–S33**). All spectra were analyzed using TopSpin 4.4.0 and Dynamics Center 2.8.9 from Bruker, using the following parameters for the DOSY plots: F1 display range set manually with a minimum F1 of 1.0E−13 and a maximum F1 of 1.0E−9, number of points in F1 = 32, number of points in F2 = 32768.

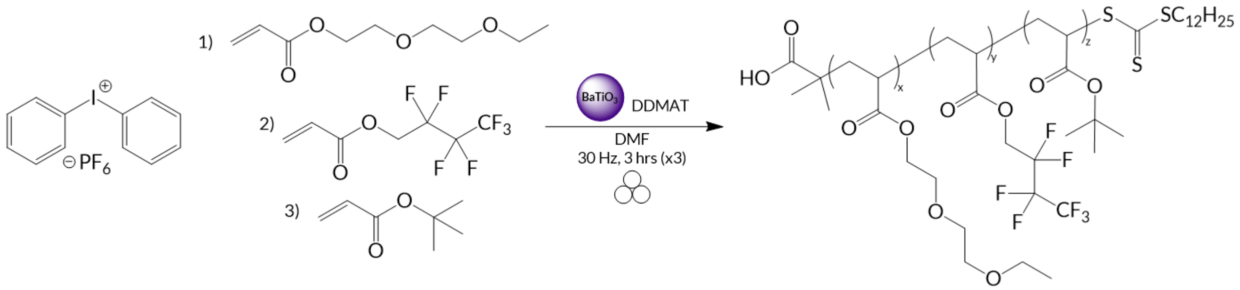
## 2. Synthetic and Experimental Procedures

**Synthesis of 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT)**:



The synthesis of DDMAT was carried out following the procedure from our previous literature.[1] In a 250 mL round bottom flask, a suspension of $K_3PO_4$ (4.2 g, 20 mmol) in acetone (60 mL) was prepared, and 1-dodecanthiol (4.0 g, 20 mmol) was added. The resulting mixture was stirred in an ice bath for 30 minutes. $CS_2$ (3.3 mL, 54 mmol) was then added dropwise over 15 minutes, forming a yellow suspension. Then, 2-bromo-2-methylpropionic acid (3.0 g, 18 mmol) was added into the reaction mixture over 20 minutes while maintaining the internal temperature below 15 °C. The reaction was left stirring overnight, allowing it to return to room temperature. 50 mL of dichloromethane was added, and the reaction was neutralized with 1.0 M aq. HCl (50 mL). The resulting organic layer was washed with water (1×50 mL) and brine (2×50 mL), dried over $Na_2SO_4$, and concentrated through rotary evaporation. Finally, the crude product was recrystallized from hexane to yield yellowish solid DDMAT (2.5 g, 40%). $^1H$ NMR (300 MHz, $CDCl_3$): δ (ppm) 0.90 (t, 3H, *J* = 7.0 Hz), 1.20–1.50 (m, 18H), 1.60–1.85 (m, 8H), 3.25 (t, 2H, *J* = 7.0 Hz), 11.0 (s, 1H). See **Figure S1**.

**Representative procedure for air-free MR-RAFT polymerization of DEGEEA/HFBA/*t*BA as an ABC triblock copolymer:**



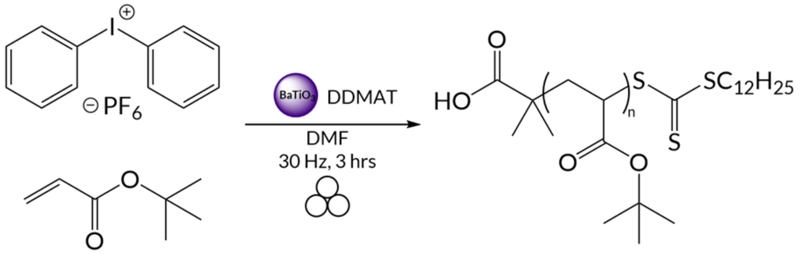
To a 1.5 mL stainless steel milling jar charged with a 5 mm stainless steel milling ball was added $BaTiO_3$ (47.1 mg, 15 wt% of the other reactants), DPIHP (6.8 mg, 0.02 mmol), and DDMAT (6.2 mg, 0.02 mmol), and the jar was transferred to a nitrogen-filled glovebox. Anhydrous DMF (21.7 µL, 6% v/w = volume of DMF relative to the total mass of all other reaction components) was added for liquid-assisted grinding (LAG). DEGEEA (296 µL, 1.6 mmol) was added after passing through a plug of basic alumina to remove its inhibitor. The milling jar was sealed under nitrogen, secured in the ball mill, and shaken at 30 Hz for 3 hours.

To prepare the second block, the sealed jars were brought back into a nitrogen-filled glovebox, and an aliquot was removed for NMR and GPC analysis. The jar was then charged with additional $BaTiO_3$ (62 mg, 15 wt% of the second set of reactants), DPIHP (6.8 mg, 0.020 mmol), and anhydrous DMF (28 µL, 6% v/w = volume of DMF relative to the total mass of the second set of reactants). After passing through a plug of basic alumina, HFBA (290 µL, 1.6 mmol) was added to the jar, which was subsequently sealed under nitrogen, secured in the ball mill, and shaken at 30 Hz for 3 hours.

The third block was added with the same method as the second, adding $BaTiO_3$ (32.7 mg, 15 wt% of the third set of reactants), DPIHP (6.8 mg, 0.020 mmol), anhydrous DMF (15 µL, 6% v/w = volume of DMF relative to the total mass of the third set of reactants), and *t*BA (230 µL, 1.6 mmol) immediately after filtering through a plug of basic alumina, before sealing under nitrogen, securing in the ball mill, and shaking at 30 Hz for 3 hours.

ABA triblock copolymers were prepared in an identical fashion, with the first monomer being used again for the third block.

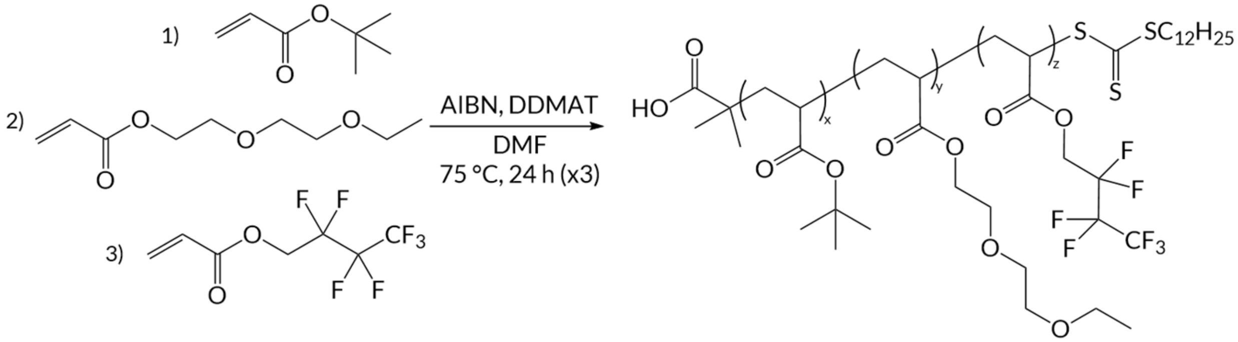
**Representative procedure for air-free MR-RAFT polymerization of *t*BA to achieve an ultra-high molecular weight:**



Stock solutions of DPIHP and DDMAT (10 mg/mL in anhydrous DMF) were prepared and degassed by sparging with nitrogen for >2 hours.

To a 5 mL stainless steel milling jar charged with an 8 mm stainless steel milling ball was added $BaTiO_3$ (0.35 g, 15 wt% of the other reactants), and the jar was transferred to a nitrogen-filled glovebox. 40 µL of the DPIHP stock solution (0.90 µmol, 1.0 eq.) and 35 µL of the DDMAT stock solution (0.90 µmol, 1.0 eq.) were added to the jar. After passing through a plug of basic alumina, *t*BA (2.5 mL, 17 mmol, 18,000 eq.) was added to the jar, which was subsequently sealed under nitrogen, secured in the ball mill, and shaken at 30 Hz for 3 hours. Refer to **Table 3** for $[M_0]/[CTA]$ and the milling time for each UHMW material.

**Solution-state RAFT polymerization procedure using immiscible monomers:**



To an oven-dried 7 mL glass vial was added a stir bar, DDMAT (5.0 mg, 0.01 mmol, 1.0 eq), and AIBN (2.3 mg, 0.01 mmol, 1.0 eq.). The vial was brought into a nitrogen-filled glovebox and 2 mL of anhydrous DMF was added, followed by 1.00 mL of *t*BA (6.8 mmol, 500 eq.) immediately after filtering through a plug of basic alumina to remove the inhibitor. The vial was sealed and the yellow transparent solution stirred (700 rpm) at 75 °C.

After 24 h, an aliquot was removed for $^1H$ NMR and GPC analysis. Additional AIBN (2.3 mg, 0.01 mmol, 1.0 eq.) and DMF (1 mL) were added, followed by 0.25 mL of DEGEEA (1.4 mmol, 100 eq) immediately after filtering through a plug of basic alumina. The vial was sealed and the light-yellow transparent solution was stirred at 75 °C.

After 24 h, another aliquot was removed for $^1$H NMR and GPC analysis. Additional AIBN (2.3 mg, 0.01 mmol, 1.0 eq.) and DMF (1 mL) were added, followed by 0.25 mL of HFBA (1.4 mmol, 100 eq.) immediately after filtering through a plug of basic alumina. Within ca. 10 minutes, the solution became a cloudy white suspension. The vial was again sealed and stirred at 75 °C overnight, after which the final material was analyzed by $^1$H NMR spectroscopy and GPC.

**Table S1**: Experimental details for the synthesis of the triblock copolymers and UHMW polymers reported in the main text. All milling jars and milling media used were made of stainless steel, with a single milling ball used for each reaction, shaking at 30 Hz. For the triblock copolymers, the addition of each block was carried out over 3 hours. The milling time for the UHMW polymers is reported in **Table 3**.

| Polymer Architecture | Main Text Entry | Monomer Sequence | Milling Jar Volume (mL) | Milling Media Diameter (mm) | Total Fill Ratio$^{\dagger}$ |
|---|---|---|---|---|---|
| ABA Triblock | **Table 1**, entry 1 | *t*BA / MA / *t*BA | 5 | 8 | 0.36 |
| | **Table 1**, entry 2 | 2-MEA / HFBA / 2-MEA | 1.5 | 5 | 0.60 |
| | **Table 1**, entry 3 | *t*BA / HFBA / *t*BA | 5 | 8 | 0.22 |
| ABC Triblock | **Table 2**, entry 1 | *t*BA / HFBA / 2-MEA | 1.5 | 5 | 0.31 |
| | **Table 2**, entry 2 | *t*BA / DEGEEA / HFBA | 1.5 | 5 | 0.51 |
| | **Table 2**, entry 3 | DEGEEA / HFBA / *t*BA | 5 | 8 | 0.23 |

| | | | | | |
|---|---|---|---|---|---|
| UHMW Homopolymer | **Table 3**, entry 1 | *t*BA | 5 | 8 | 0.58 |
| | **Table 3**, entry 2 | *n*BA | 5 | 8 | 0.60 |
| | **Table 3**, entry 3 | EA | 5 | 8 | 0.58 |
| | **Table 3**, entry 4 | IBA | 5 | 8 | 0.58 |
| | **Table 3**, entry 5 | MA | 5 | 8 | 0.60 |
| UHMW Diblock Copolymer | **Table 3**, entry 6 | *t*BA / 2-MEA | 5 | 8 | 0.33 |
| | **Table 3**, entry 7 | *t*BA / EA | 5 | 8 | 0.37 |

† We define the total fill ratio as the volume of the jar occupied by the combined reaction components for every block relative to the total volume of the jar (1.5 or 5 mL). For simplicity, we excluded the marginal volumes occupied by the initiator (DPIHP) and chain transfer agent (DDMAT) from our calculations, and only considered the volumes of monomer, DMF, $BaTiO_3$ nanoparticles (vendor density reported as 5.85 g/cm$^3$), and the milling media.

**Table S2**: Experimental details and resulting polymer properties targeting an UHMW poly(MA) on two different scales. Both experiments were performed in 5 mL stainless steel jars with one 8 mm stainless steel ball, shaking at 30 Hz for 6 h.

| **[$M_0$]/[CTA]** | **Fill Ratio** | **Monomer Conversion (%)** | **$M_{w, MALS}$ (MDa) [est. DP]** |
|---|---|---|---|
| 35,000 | 0.60[a] | 68 | 1.4<br>[16,000] |
| | 0.49 | 26 | 0.83<br>[9,700] |

[a] **Table 3**, entry 5.

# 3. $^1$H NMR Spectra

## 3.1 Starting Material

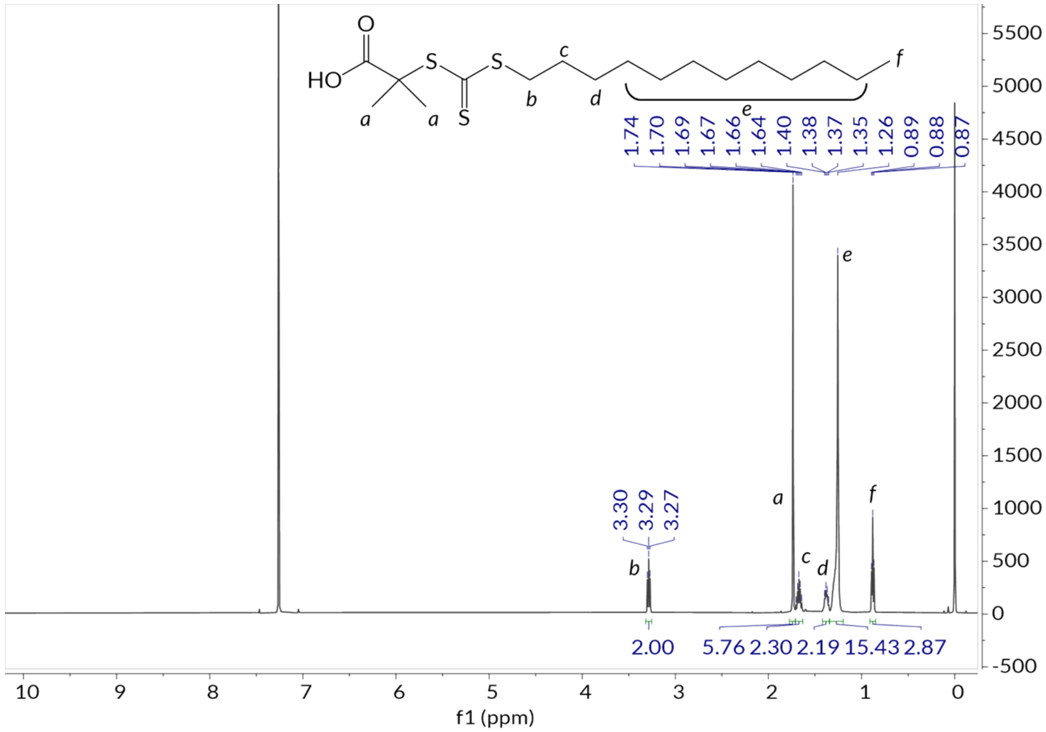


**Figure S1:** $^1$H NMR spectrum of DDMAT, the chain transfer agent. 500 MHz, $CDCl_3$.

## 3.2 ABA Triblock Polyacrylates

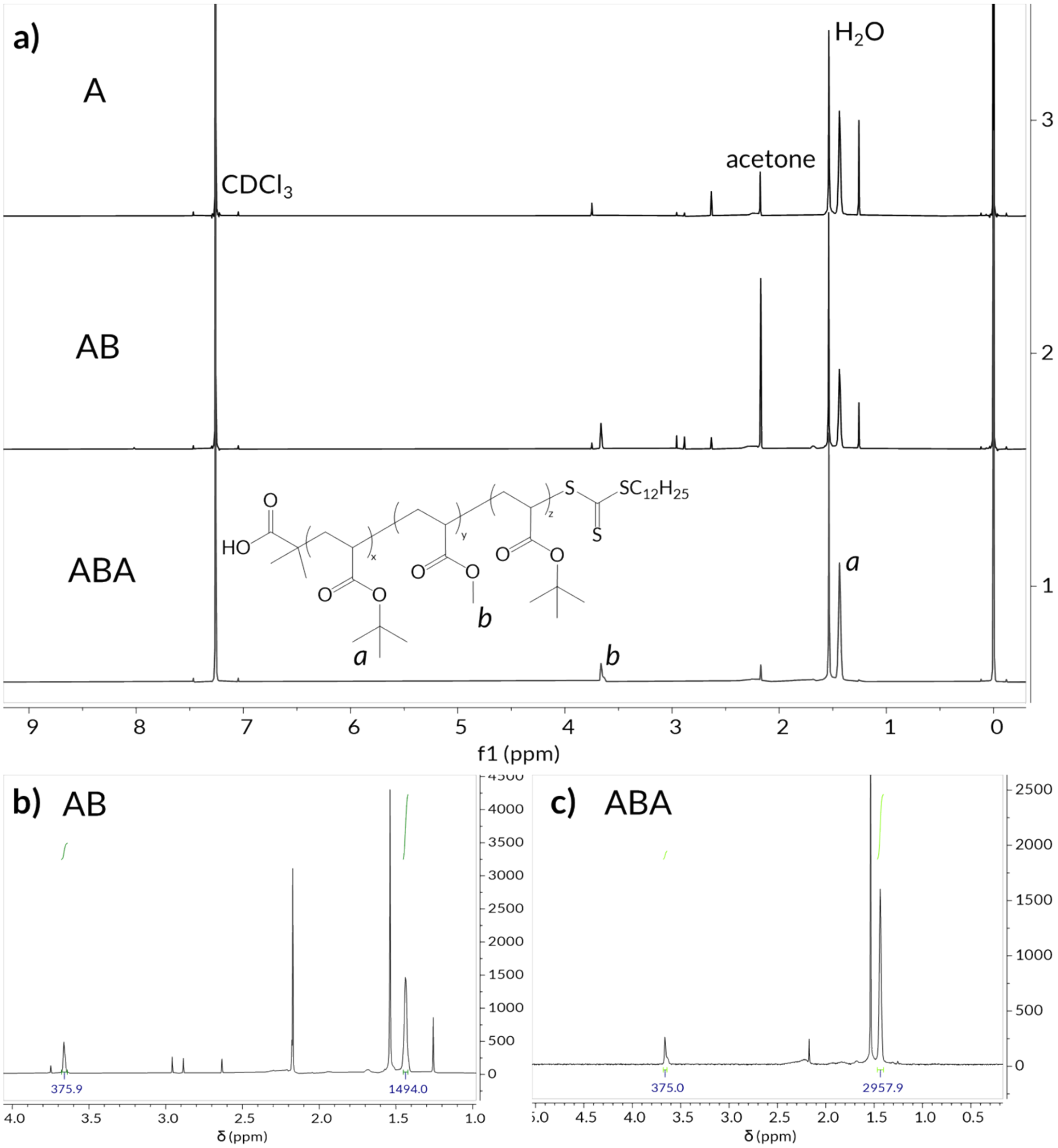


**Figure S2**: **a)** $^1$H NMR spectra of ABA triblock poly(*t*BA-*b*-MA-*b*-*t*BA) (bottom), precursor AB diblock poly(*t*BA-*b*-MA) (middle), and precursor A block poly(*t*BA) (top). **b)** Zoomed-in spectrum of AB diblock intermediate, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **c)** Zoomed-in spectrum of final ABA triblock copolymer, showing the integrations set to calculate B3 DP. 500 MHz, $CDCl_3$ (**Table 1**, entry 1).

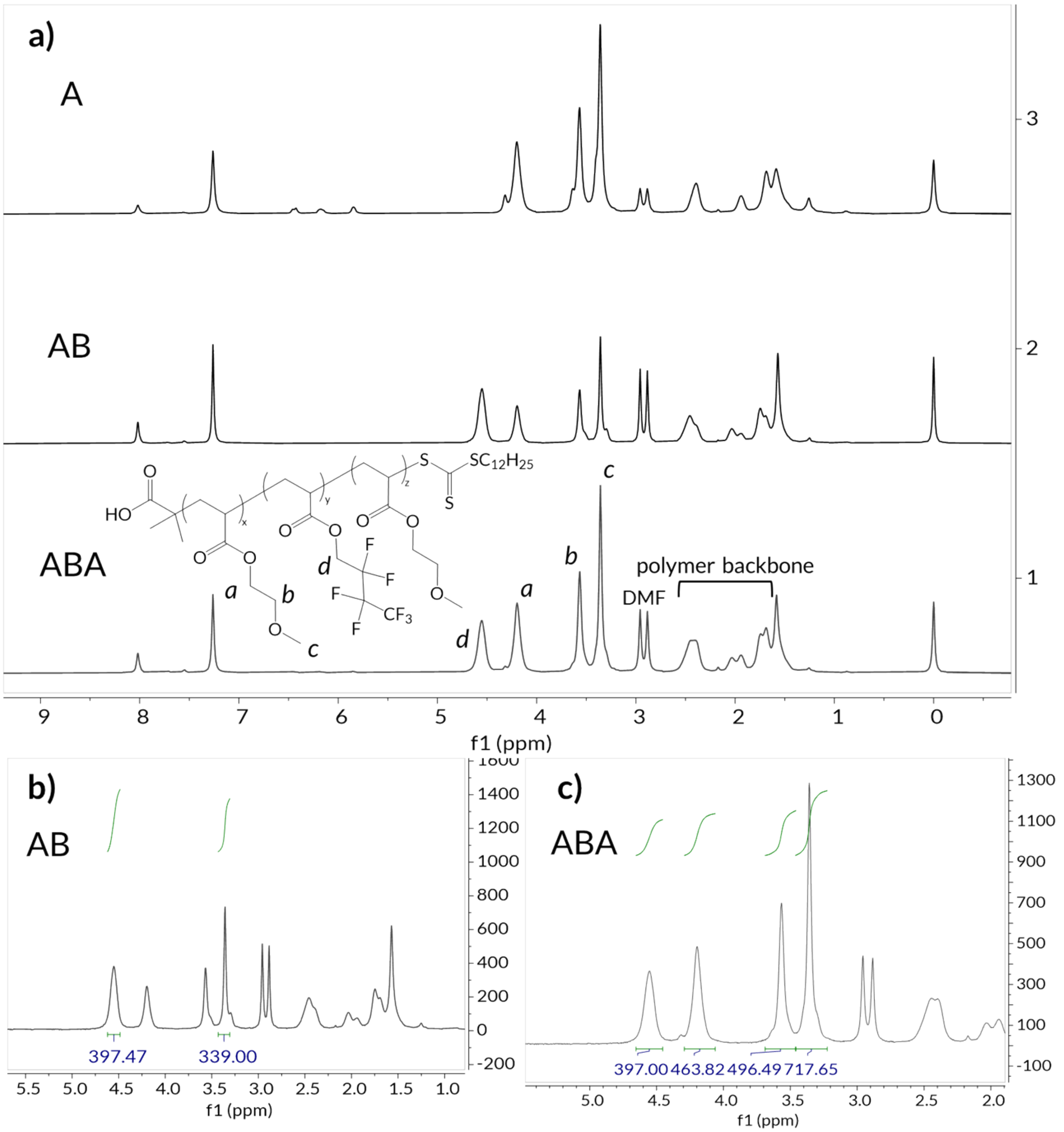


**Figure S3**: **a)** $^1$H NMR spectra of ABA triblock poly(2-MEA-*b*-HFBA-*b*-2-MEA) (bottom), precursor AB diblock poly(2-MEA-*b*-HFBA) (middle), and precursor A block poly(2-MEA). **b)** Zoomed-in spectrum of AB diblock intermediate, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **c)** Zoomed-in spectrum of final ABA triblock copolymer, showing the integrations set to calculate B3 DP. **Equation S3** was used on the integration of each A monomer resonance, and the resulting DPs were averaged. 500 MHz, $CDCl_3$ (**Table 1**, entry 2).

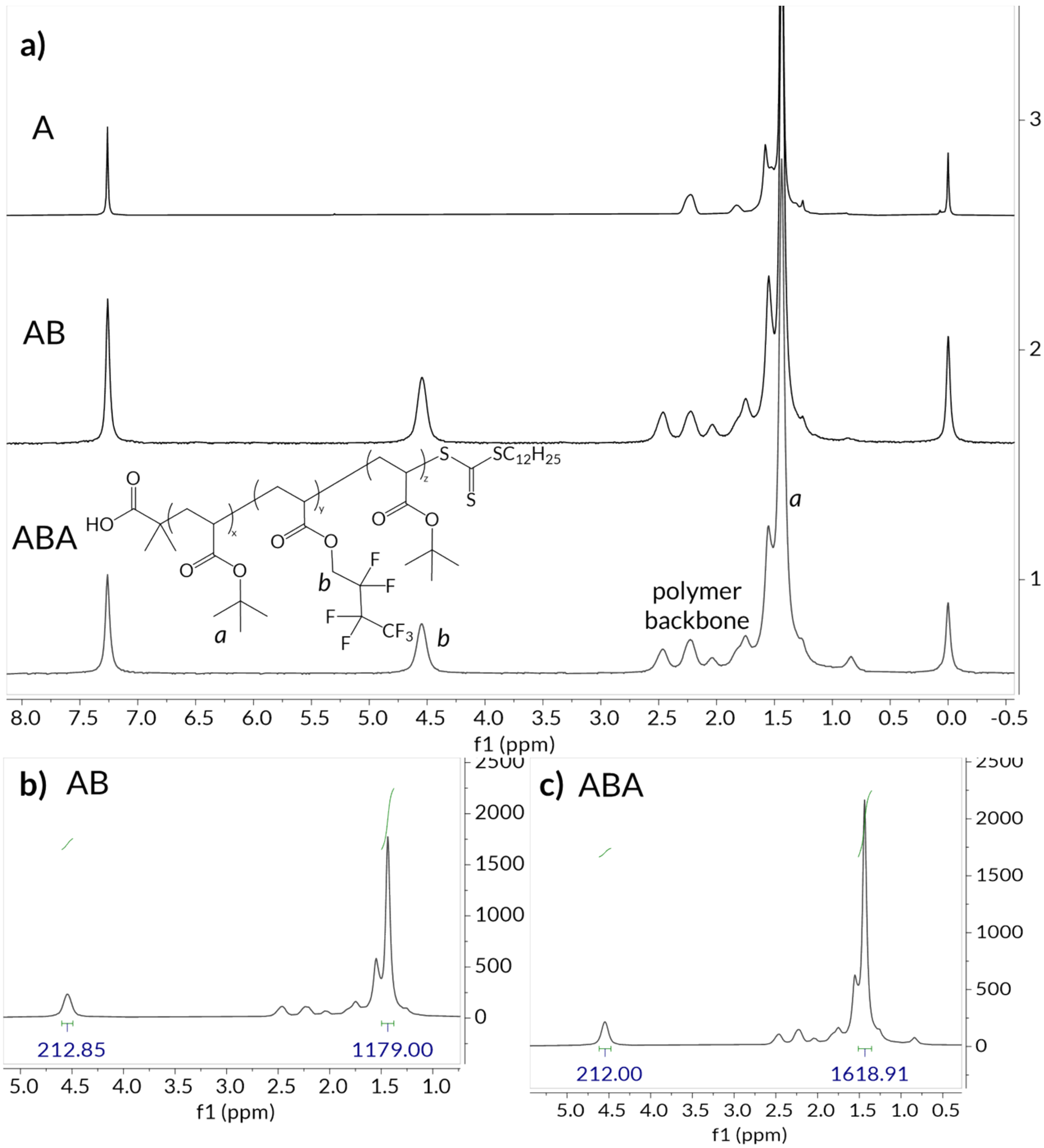


**Figure S4**: **a)** $^1$H NMR spectra of ABA triblock poly(*t*BA-*b*-HFBA-*b*-*t*BA) (bottom), precursor AB diblock poly(*t*BA-*b*-HFBA) (middle), and precursor A block poly(*t*BA). **b)** Zoomed-in spectrum of AB diblock intermediate, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **c)** Zoomed-in spectrum of final ABA triblock copolymer, showing the integrations set to calculate B3 DP. 500 MHz, $CDCl_3$ (**Table 1**, entry 3).

## 3.3 ABC Triblock Polyacrylates

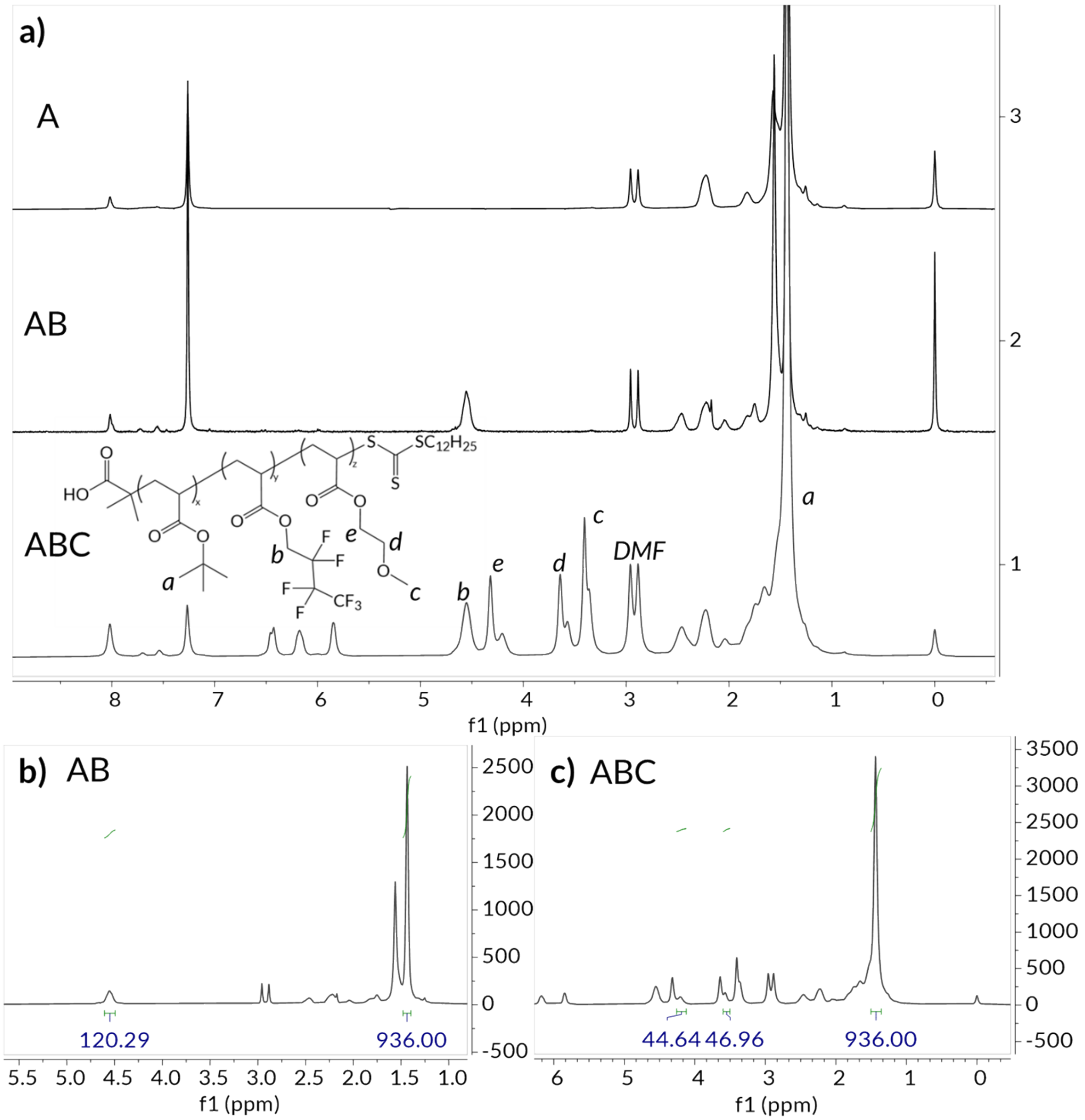


**Figure S5**: **a)** $^1$H NMR spectra of ABC triblock poly(*t*BA-*b*-HFBA-*b*-2-MEA) (bottom), precursor AB diblock poly(*t*BA-*b*-HFBA) (middle), and precursor A block poly(*t*BA). **b)** Zoomed-in spectrum of AB diblock intermediate, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **c)** Zoomed-in spectrum of final ABA triblock copolymer, showing the integrations set to calculate B3 DP. **Equation S3** was used on the average integrations of two C monomer resonances, and the resulting DPs were averaged. 500 MHz, $CDCl_3$ (**Table 2**, entry 1).

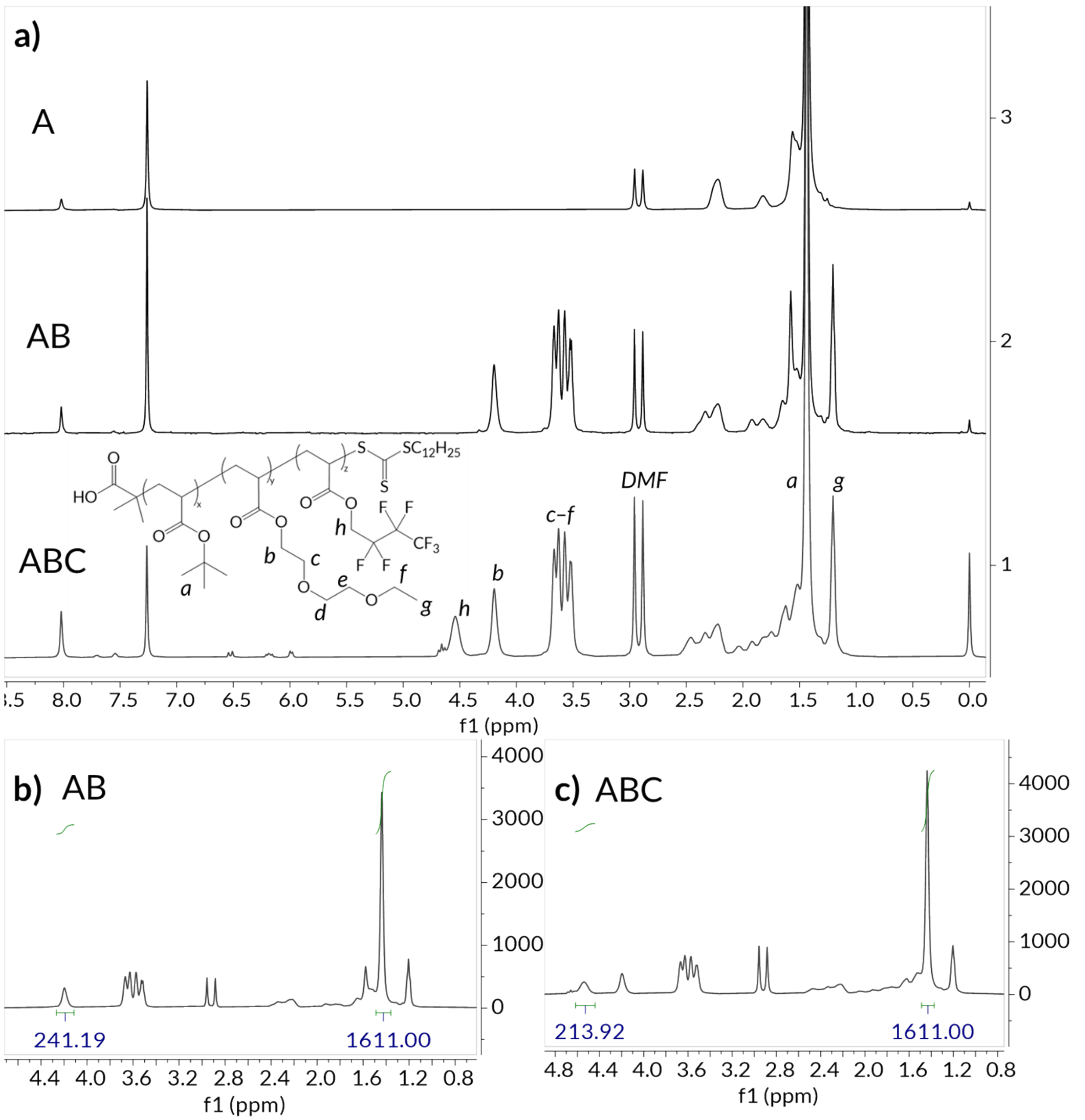


**Figure S6**: **a)** $^1$H NMR spectra of ABC triblock poly(*t*BA-*b*-DEGEEA-*b*-HFBA) (bottom), precursor AB diblock poly(*t*BA-*b*-DEGEEA) (middle), and precursor A block poly(*t*BA). **b)** Zoomed-in spectrum of AB diblock intermediate, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **c)** Zoomed-in spectrum of final ABA triblock copolymer, showing the integrations set to calculate B3 DP. 500 MHz, $CDCl_3$ (**Table 2**, entry 2).

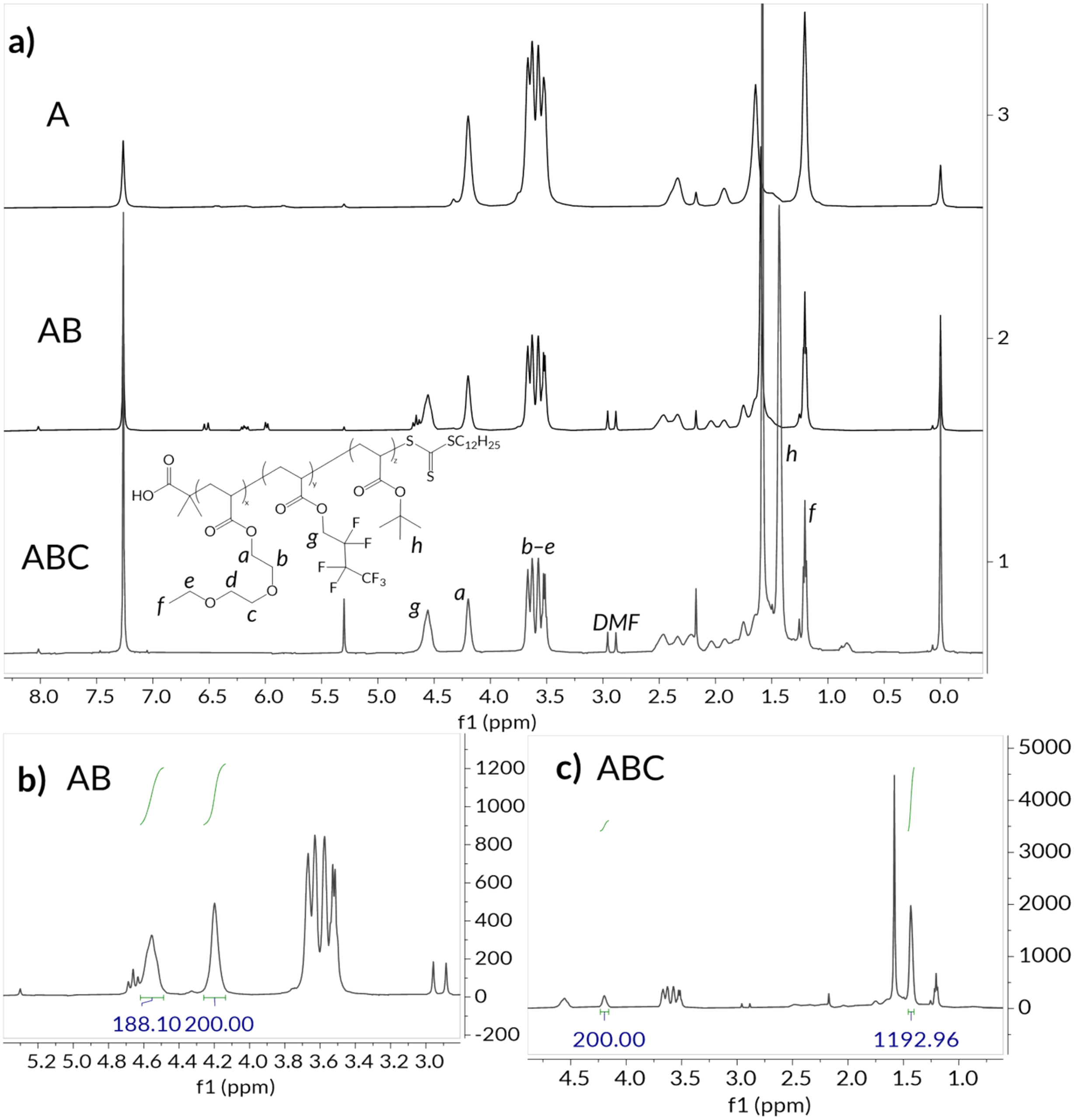


**Figure S7**: **a)** $^1$H NMR spectra of ABC triblock poly(DEGEEA-*b*-HFBA-*b*-*t*BA) (bottom), precursor AB diblock poly(DEGEEA-*b*-HFBA) (middle), and precursor A block poly(DEGEEA). **b)** Zoomed-in spectrum of AB diblock intermediate, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **c)** Zoomed-in spectrum of final ABA triblock copolymer, showing the integrations set to calculate B3 DP. 500 MHz, $CDCl_3$ (**Table 2**, entry 3).

## 3.4 Attempted Solution-State ABC Triblock Copolymer

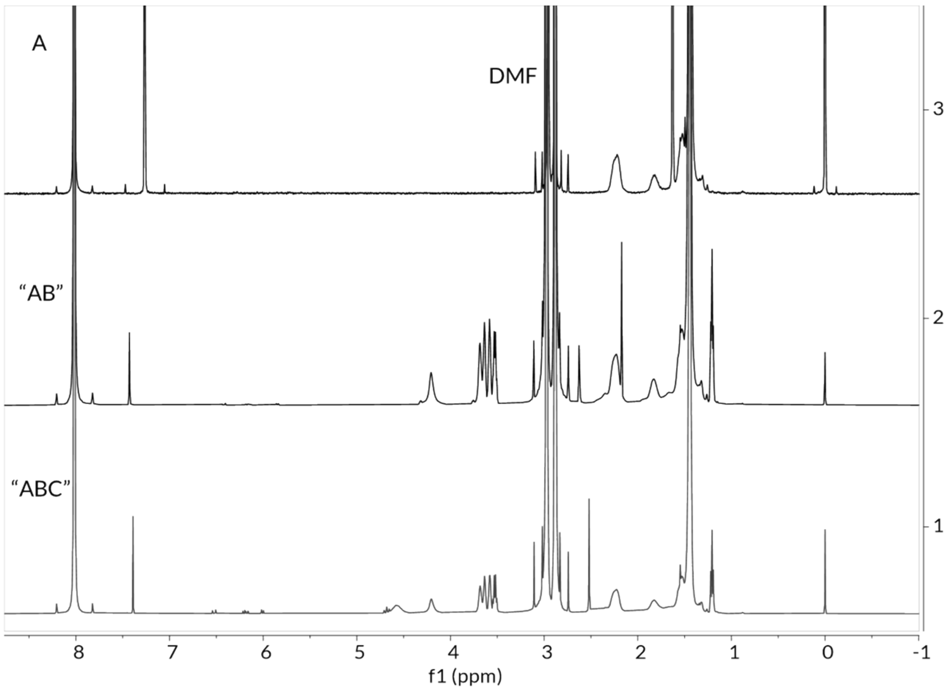


**Figure S8**: $^1$H NMR spectra of aliquots taken from solution-state RAFT polymerization targeting the ABC formulation poly(*t*BA-*b*-DEGEEA-*b*-HFBA) upon stirring for 24 h after the addition of each monomer.

## 3.5 Ultra-High Molecular Weight Polyacrylates

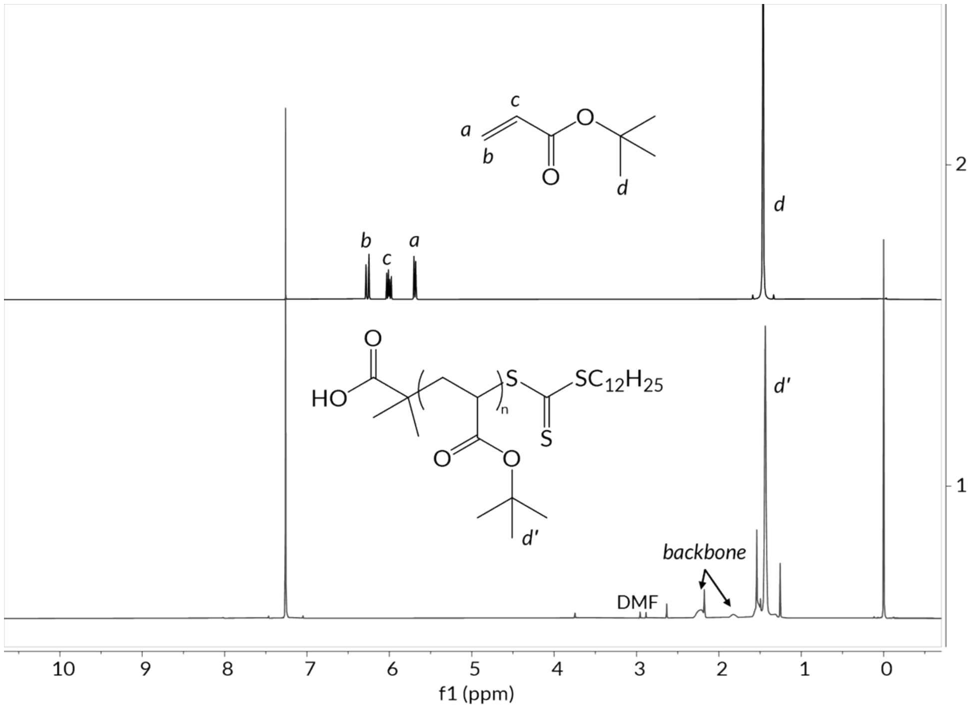


**Figure S9**: $^1$H NMR spectra of UHMW poly(*t*BA) (bottom) and *tert*-butyl acrylate monomer (top). 500 MHz, $CDCl_3$ (**Table 3**, entry 1).

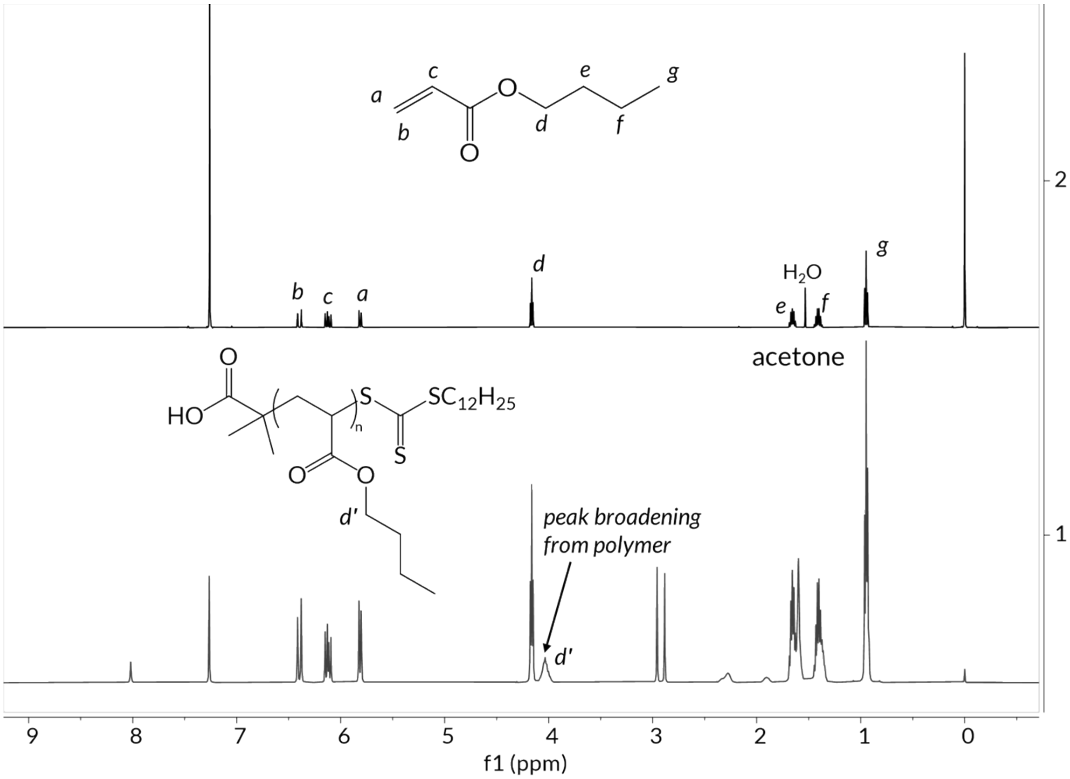


**Figure S10**: $^1$H NMR spectra of UHMW poly(*n*BA) (bottom) and *n*-butyl acrylate monomer (top). 500 MHz, $CDCl_3$ (**Table 3**, entry 2).

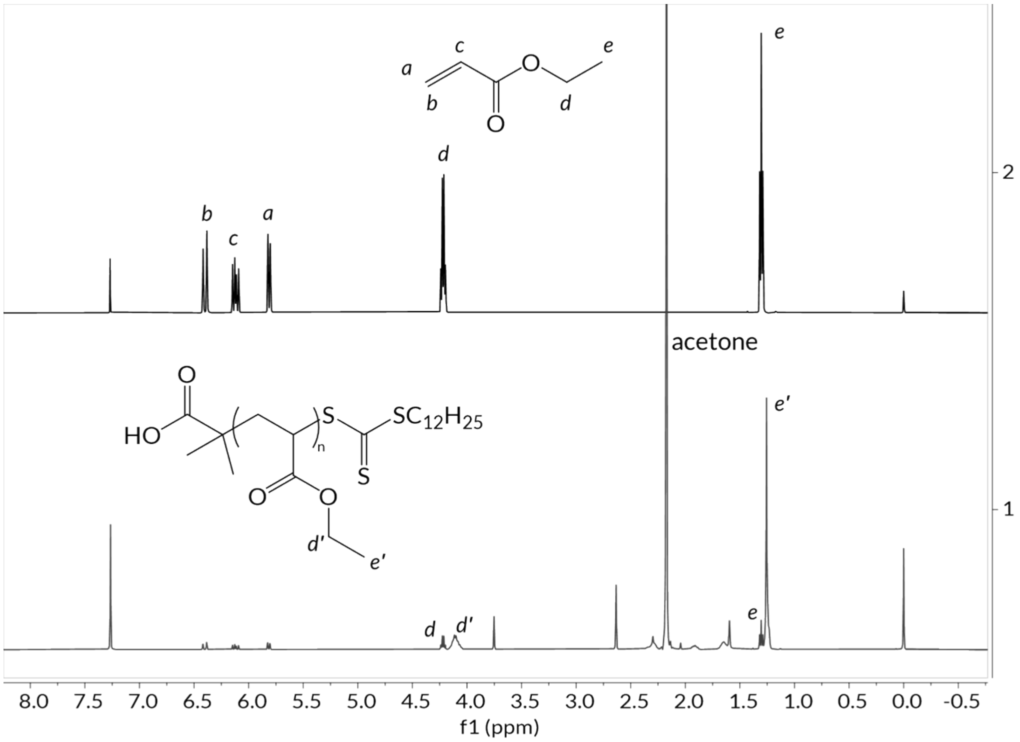


**Figure S11**: $^1$H NMR spectra of UHMW poly(EA) (bottom) and ethyl acrylate monomer (top). 500 MHz, $CDCl_3$ (**Table 3**, entry 3).

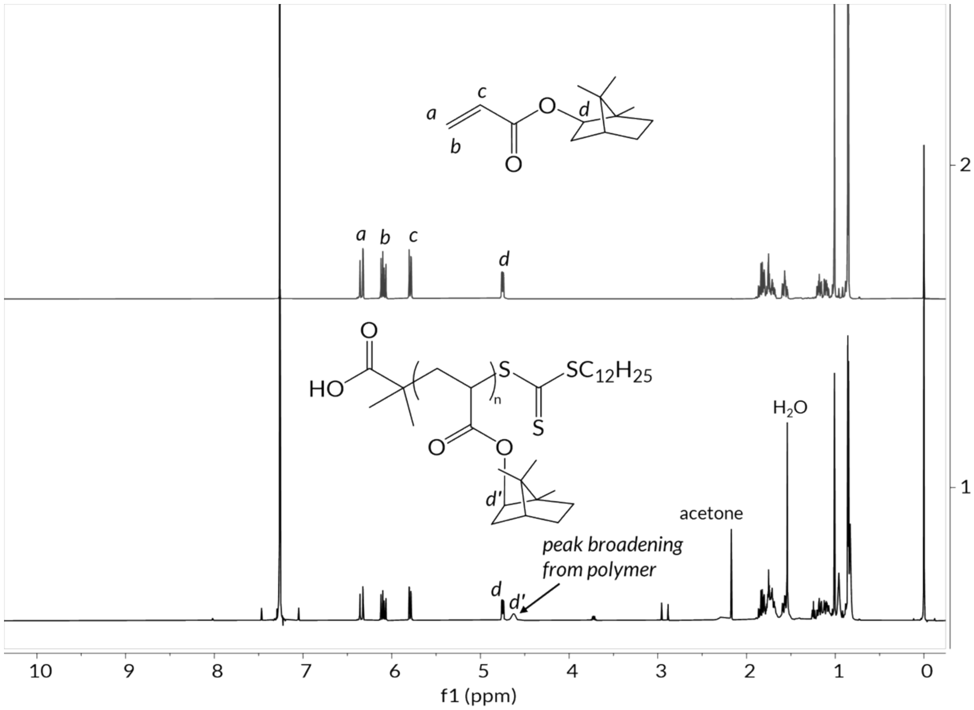


**Figure S12**: $^1$H NMR spectra of UHMW poly(IBA) (bottom) and isobornyl acrylate monomer (top). 500 MHz, $CDCl_3$ (**Table 3**, entry 4).

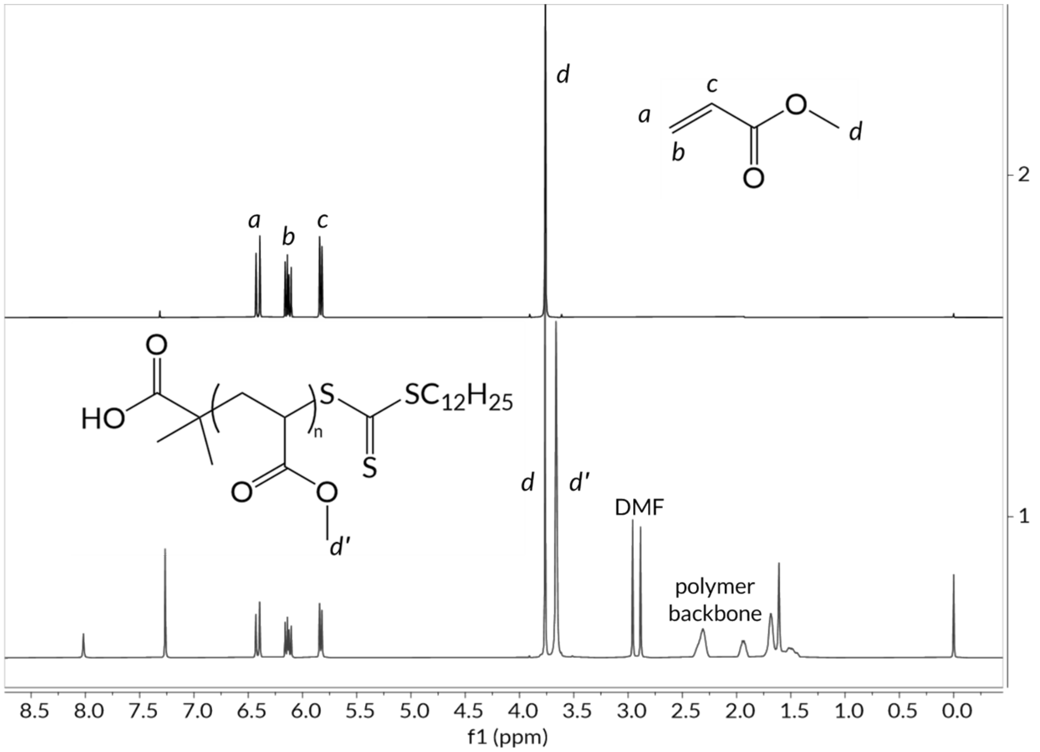


**Figure S13**: $^1$H NMR spectra of UHMW poly(MA) (bottom) and methyl acrylate monomer (top). 500 MHz, $CDCl_3$ (**Table 3**, entry 5).

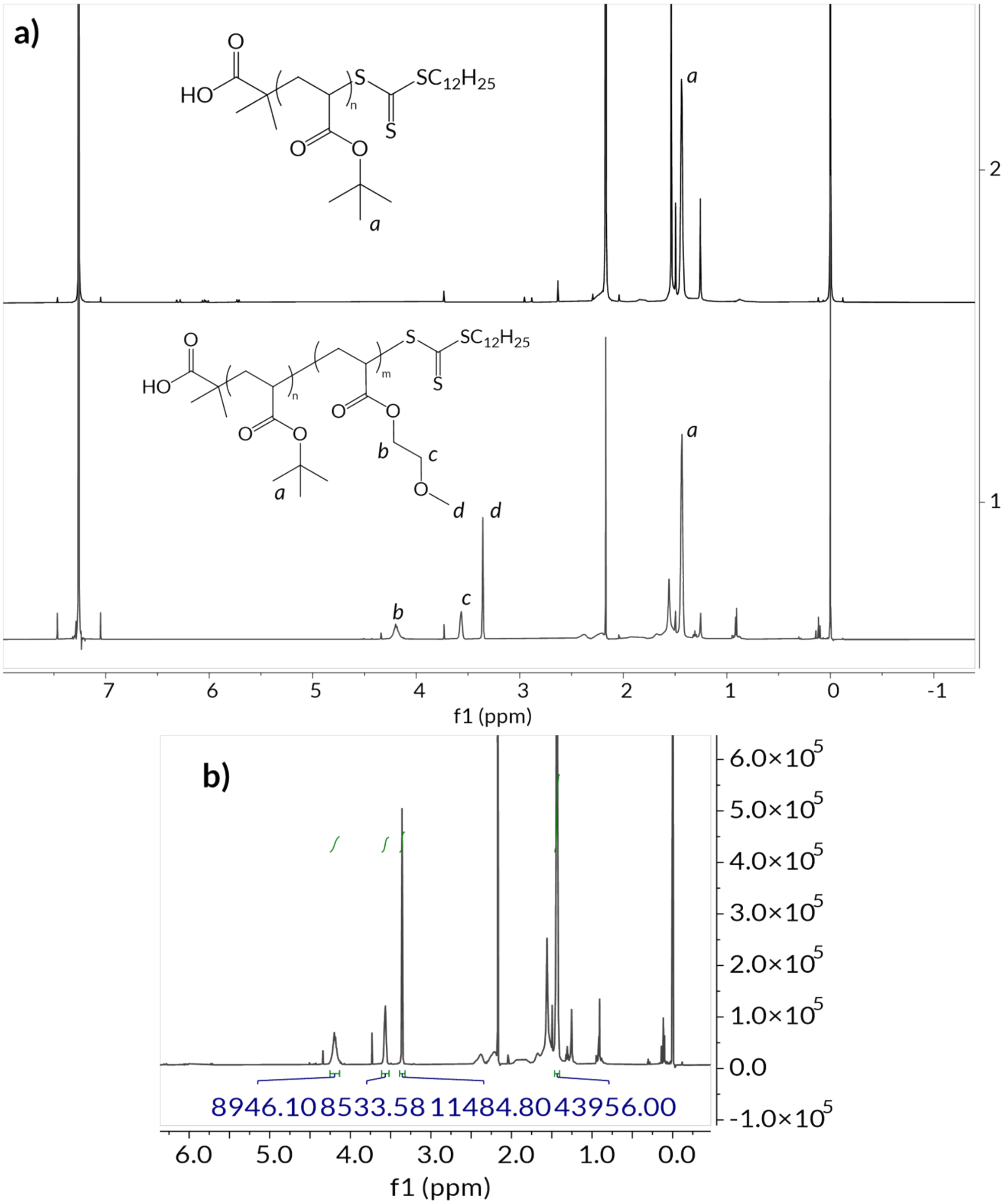


**Figure S14**: **a)** $^1$H NMR spectra of an UHMW poly(*t*BA-*b*-2-MEA) diblock copolymer (bottom) and the poly(*t*BA) precursor block (top). **b)** Zoomed-in spectrum, showing integrations set to calculate B2 DP (see **Equations S1–S4**). **Equation S3** was used on the integration of each B monomer resonance, and the resulting DPs were averaged. 500 MHz, $CDCl_3$ (**Table 3**, entry 6).

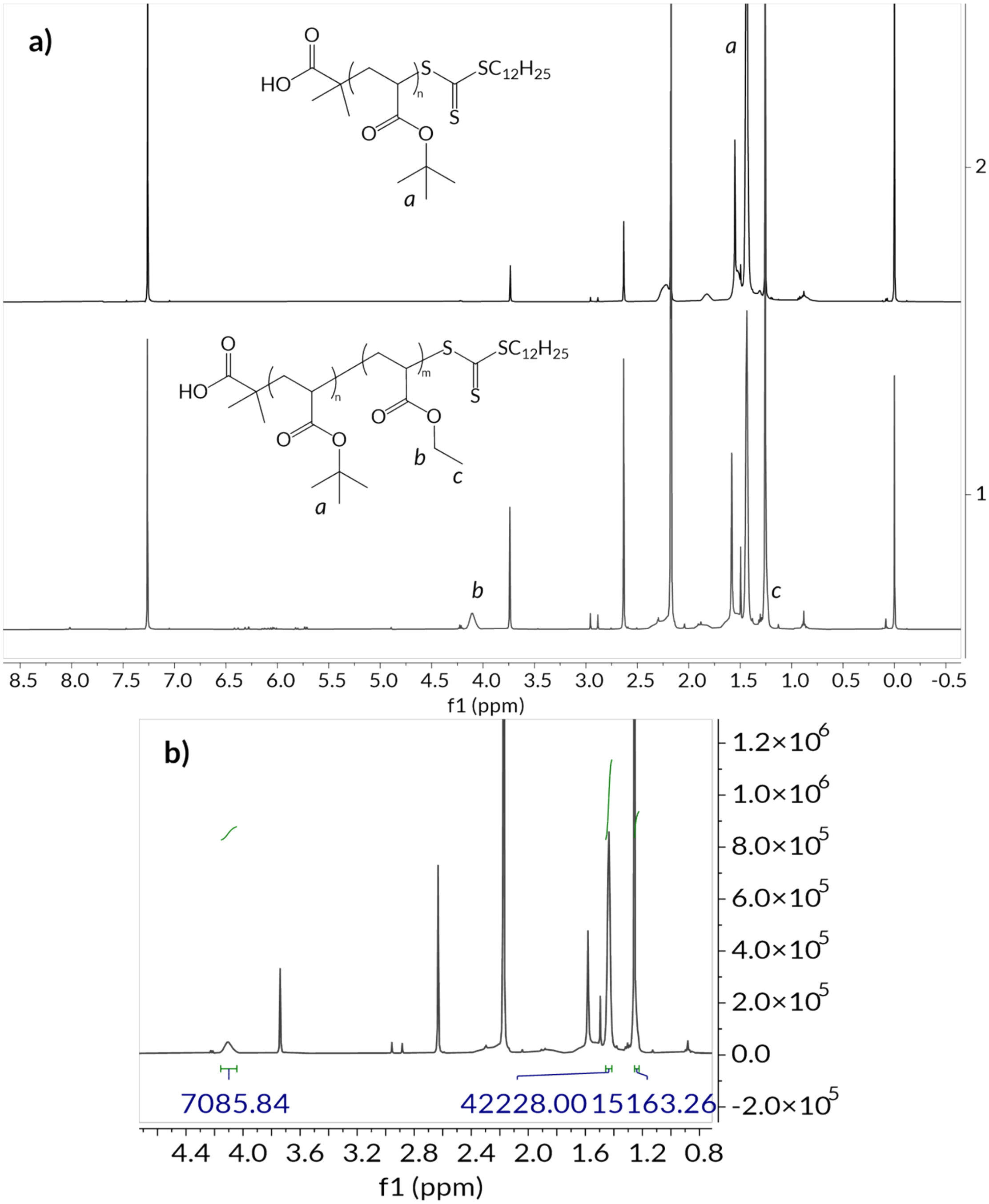


**Figure S15**: **a)** $^1$H NMR spectra of an UHMW poly(*t*BA-*b*-EA) diblock copolymer (bottom) and the poly(*t*BA) precursor block (top). **b)** Zoomed-in spectrum, showing integrations set to calculate B2 DP (see **Equations S1–S4**). 500 MHz, $CDCl_3$ (**Table 3**, entry 7).

# 4. Gel Permeation Chromatography Spectra

## 4.1 ABA Triblock Copolymers

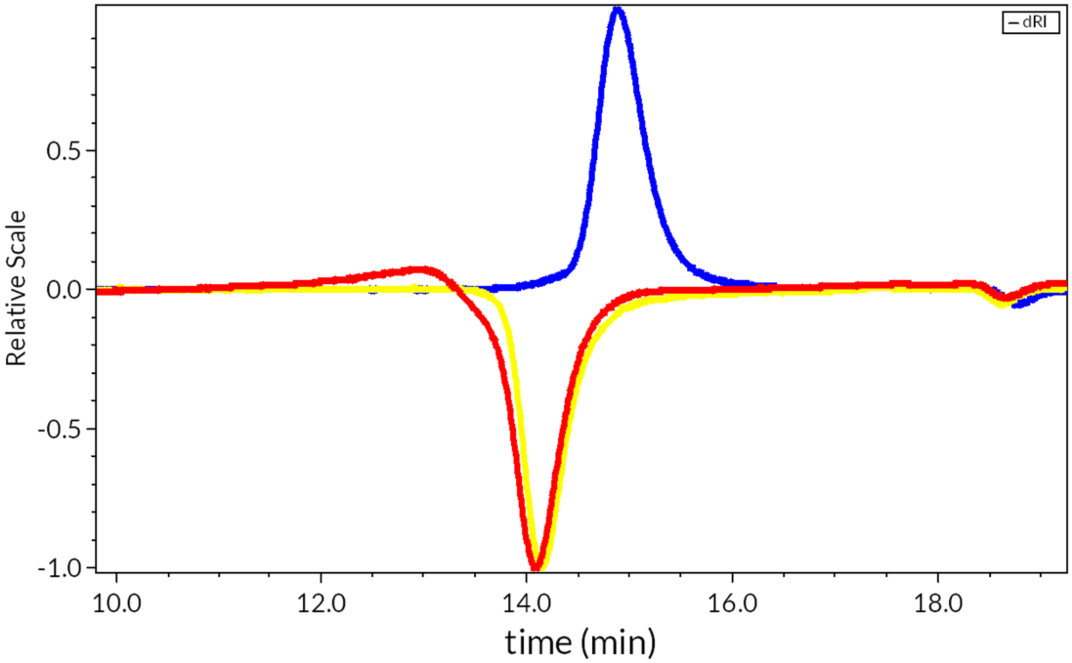


**Figure S16**: GPC traces of ABA poly(2-MEA-*b*-HFBA-*b*-2-MEA) and precursor blocks. Blue = A, Yellow = AB, Red = ABA. (**Table 1**, entry 2).

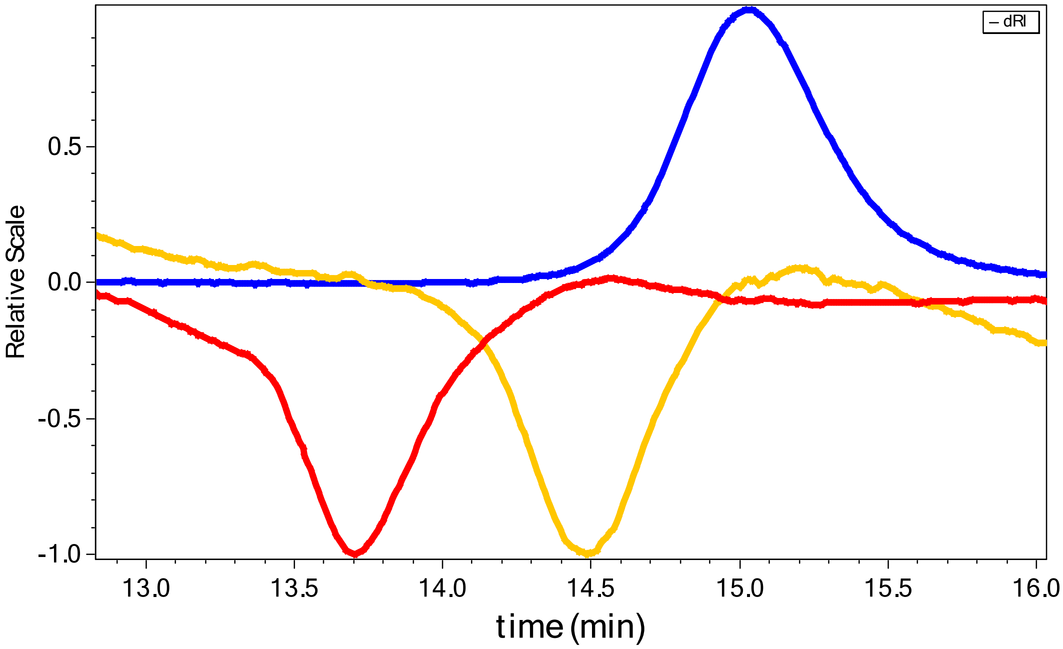


**Figure S17**: GPC traces of ABA poly(*t*BA-*b*-HFBA-*b*-*t*BA) and precursor blocks. Blue = A, Yellow = AB, Red = ABA. (**Table 1**, entry 3).

### 4.2 ABC Triblock Copolymers

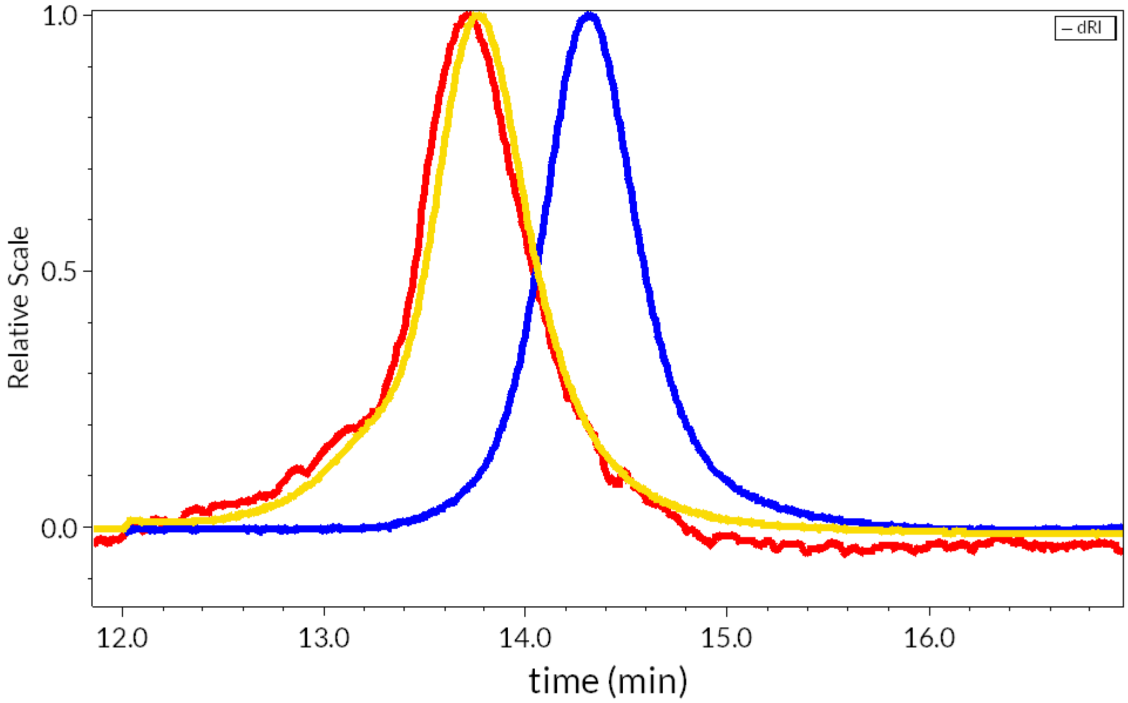


**Figure S18**: GPC traces of ABC poly(*t*BA-*b*-HFBA-*b*-2-MEA) and precursor blocks. Blue = A, Yellow = AB, Red = ABC. (**Table 2**, entry 1).

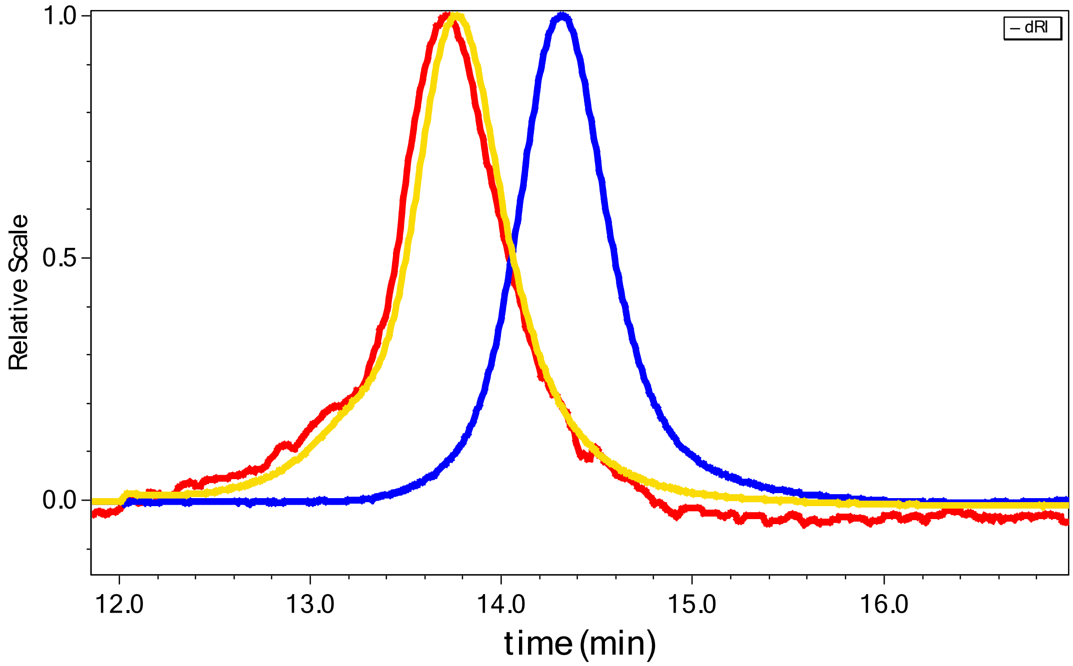


**Figure S19**: GPC traces of ABC poly(*t*BA-*b*-DEGEEA-*b*-HFBA) and precursor blocks. Blue = A, Yellow = AB, Red = ABC. (**Table 2**, entry 2).

### 4.3 Attempted Solution-State ABC Triblock Copolymer

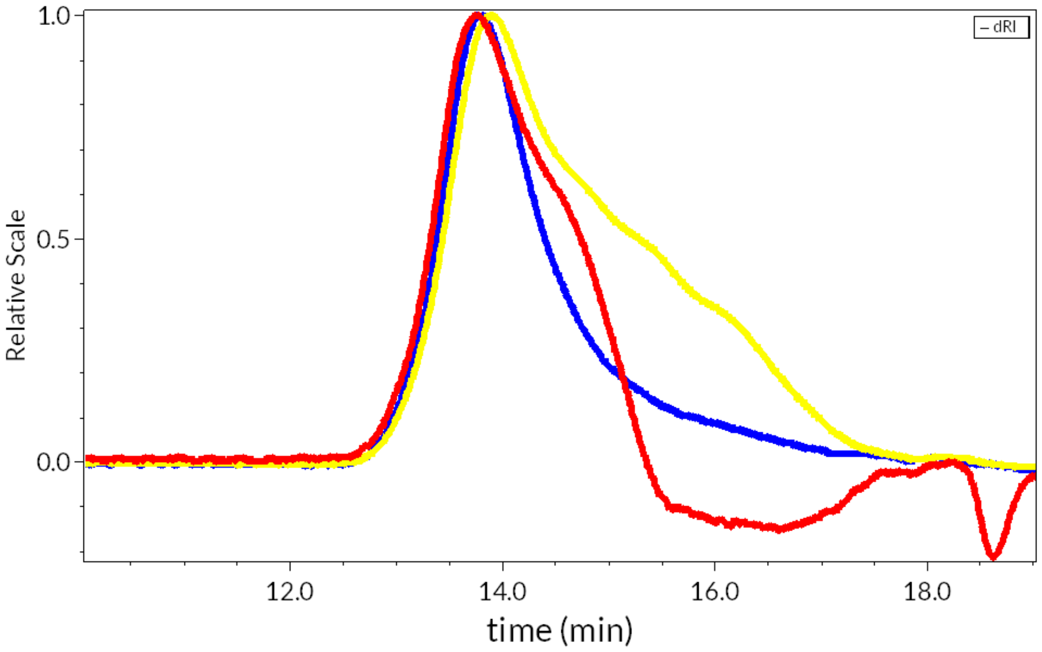


**Figure S20**: GPC traces of aliquots taken from solution-state RAFT polymerization targeting the ABC formulation poly(*t*BA-*b*-DEGEEA-*b*-HFBA) upon stirring for 24 h after the addition of each monomer. Blue = A, Yellow = "AB," Red = "ABC."

### 4.4 UHMW Diblock Copolymers

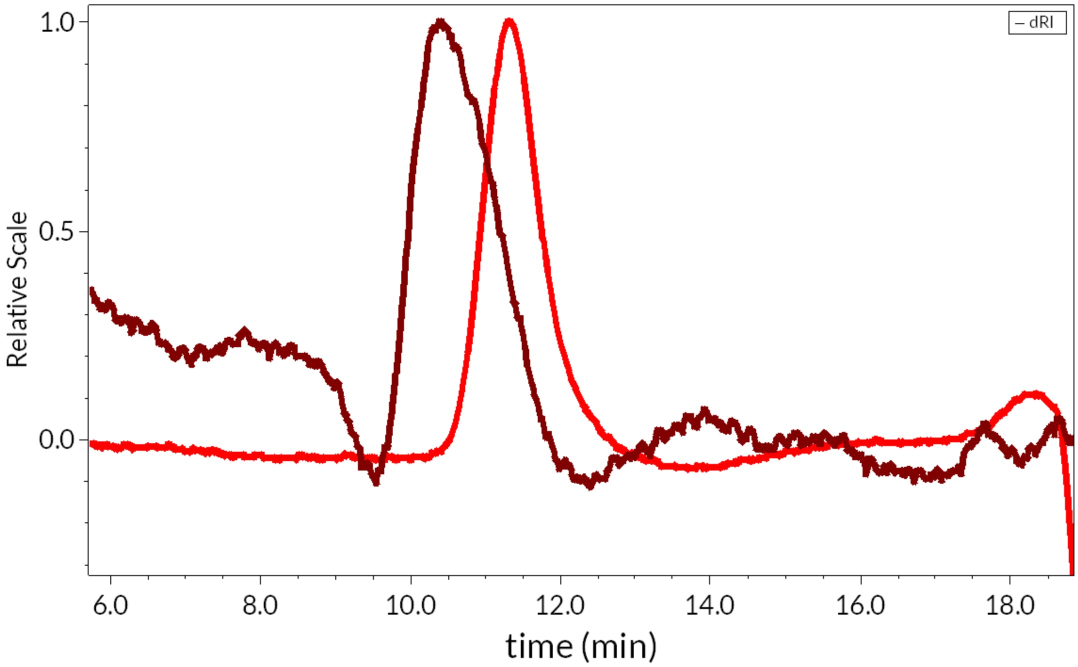


**Figure S21**: GPC traces of UHMW poly(*t*BA-*b*-2-MEA) and precursor poly(*t*BA). Red = A, maroon = AB copolymer. Solubility of the final polymer limited the RI signal (**Table 3**, entry 6). B1 *Đ* < 1.1.

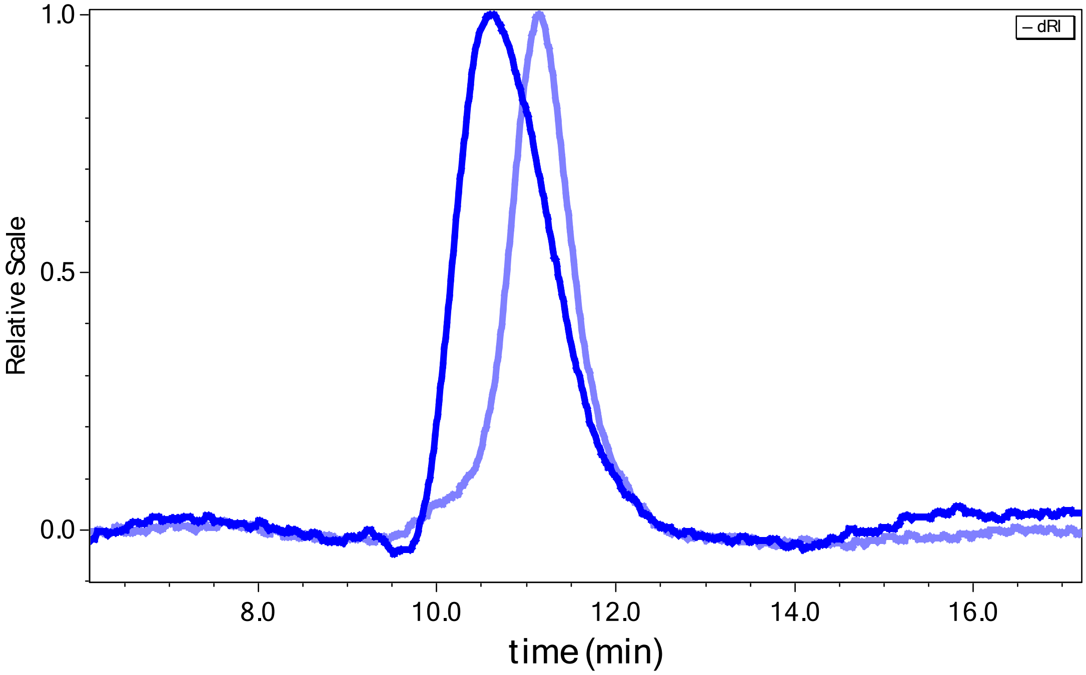


**Figure S22**: GPC traces of UHMW AB poly(*t*BA-*b*-EA) and precursor poly(*t*BA). Light blue = A, dark blue = AB copolymer (**Table 3**, entry 7). B1 *Đ* < 1.1.

### 4.5 Fill Ratio Experiment Targeting UHMW poly(MA)

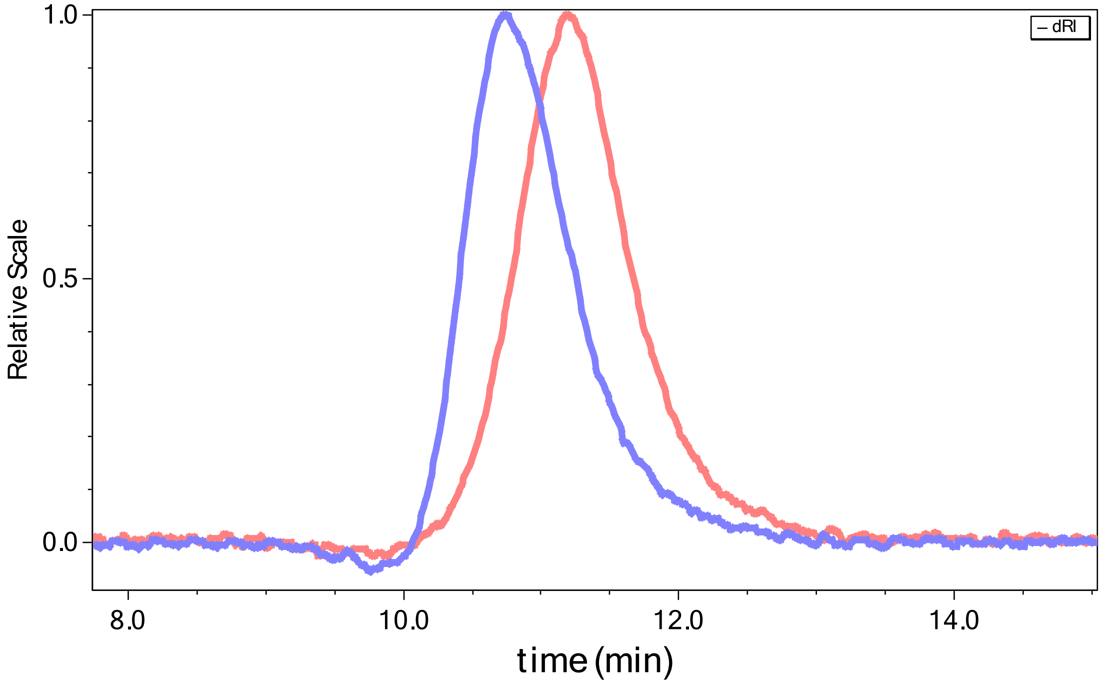


**Figure S23**: GPC traces of poly(MA) prepared in 5 mL stainless steel milling jars on two different scales (see **Table S3**). Blue curve fill ratio = 0.60 (**Table 3**, entry 5), $M_n$ = 1.4 MDa. Pink curve fill ratio = 0.49, $M_n$ = 0.83 MDa.

## 5. Mark–Houwink–Sakurada (MHS) Plots of UHMW Polyacrylates

The following log-log MHS plots were used to assess the linearity of the UHMW homopolymers reported in **Table 3**, based on the slopes, *a*, of the linear regressions: $\ln[\eta] = \ln K + a(\ln M_w)$.

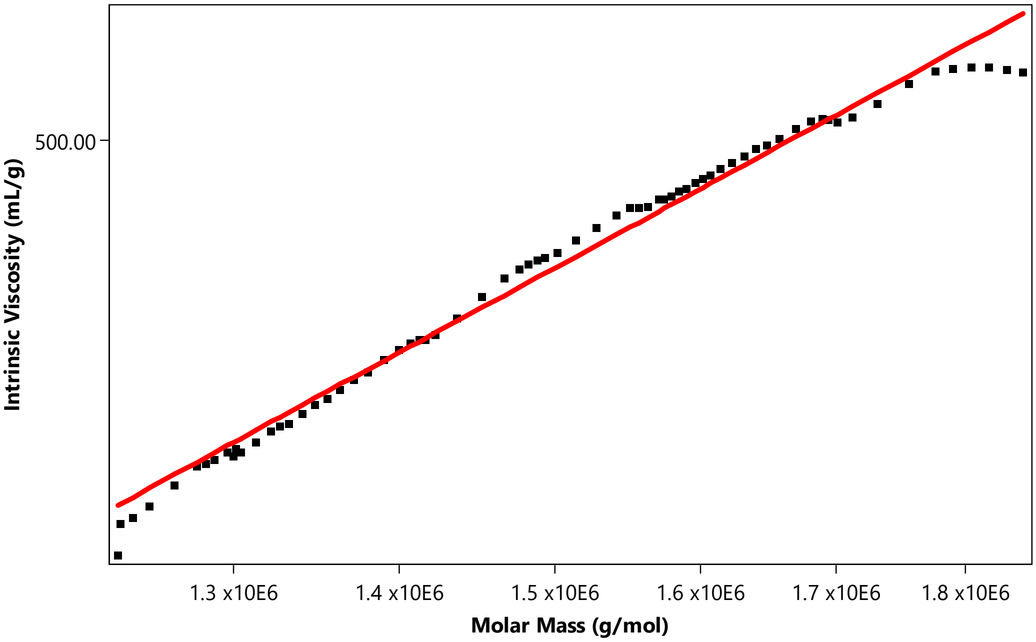


**Figure S24**: MHS plot of UHMW poly(*t*BA). $a = 0.562 \pm 0.011$.

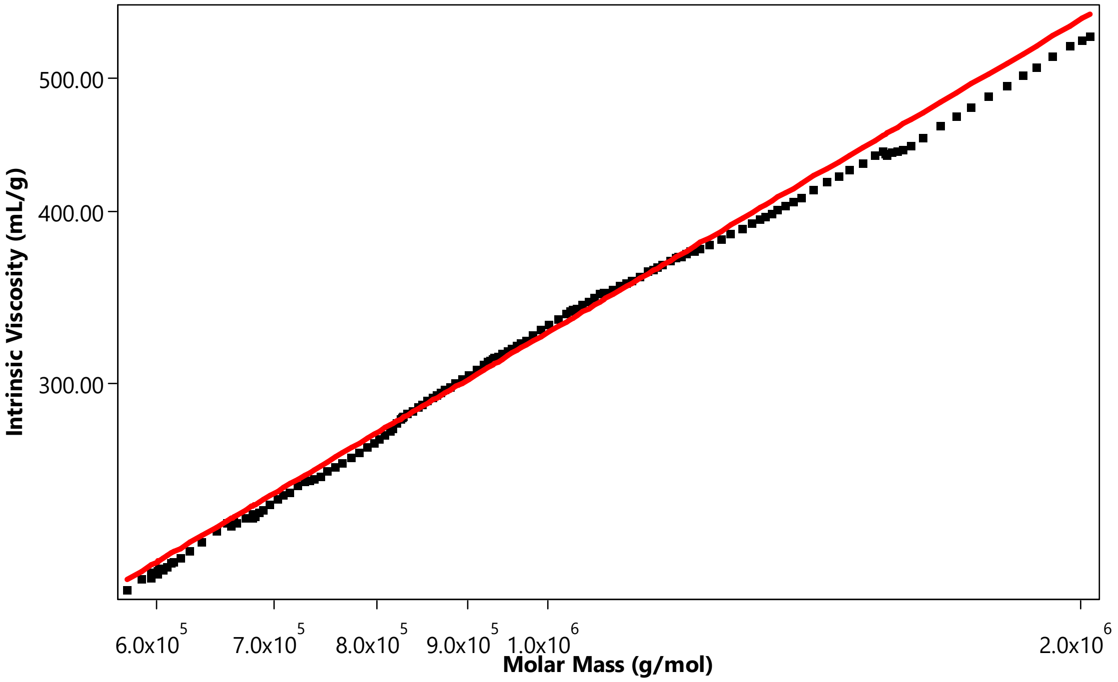


**Figure S25**: MHS plot of UHMW poly(*n*BA). *a* = 0.754 ± 0.003.

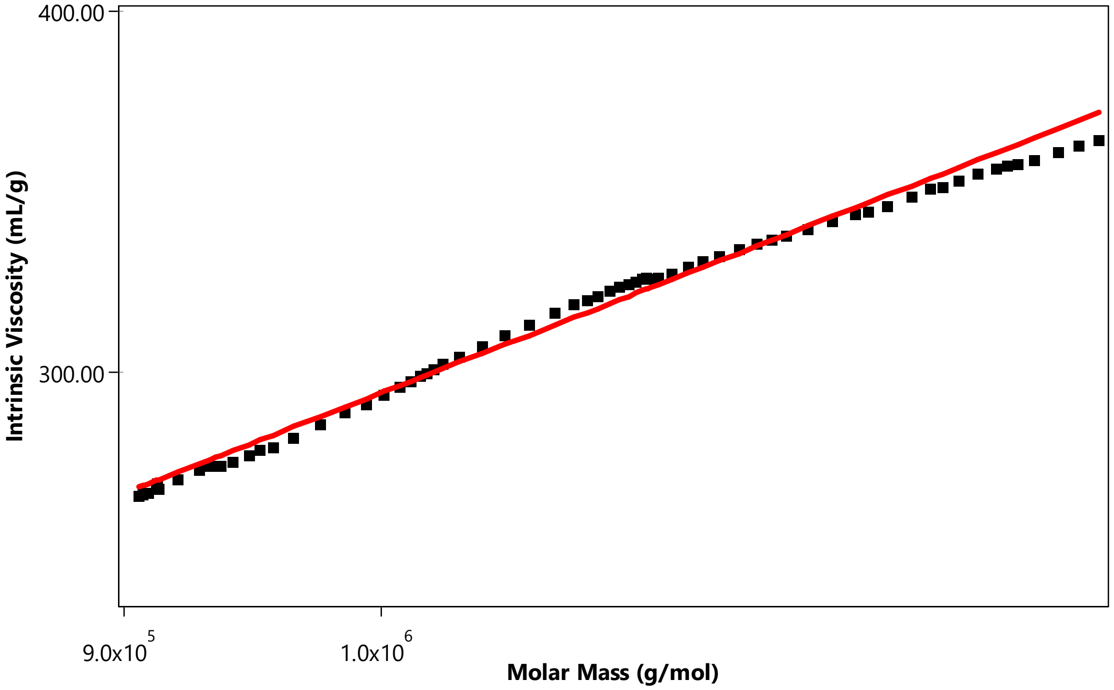


**Figure S26**: MHS plot of UHMW poly(EA). *a* = 0.761 ± 0.010.

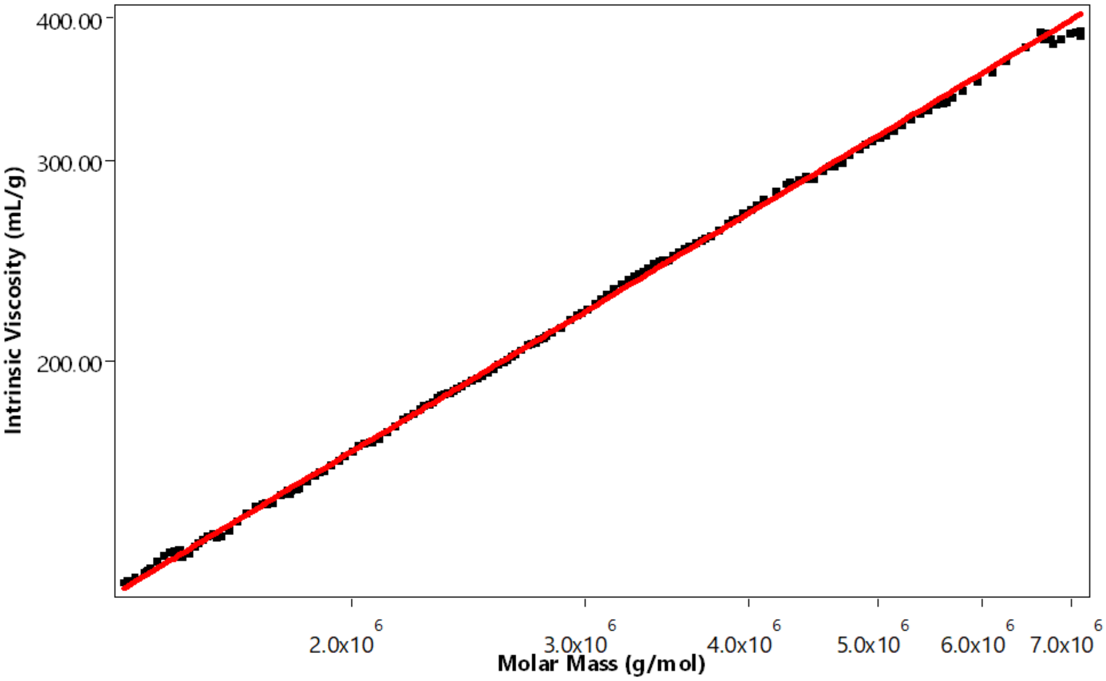


**Figure S27**: MHS plot of UHMW poly(IBA). *a* = 0.697 ± 0.002.

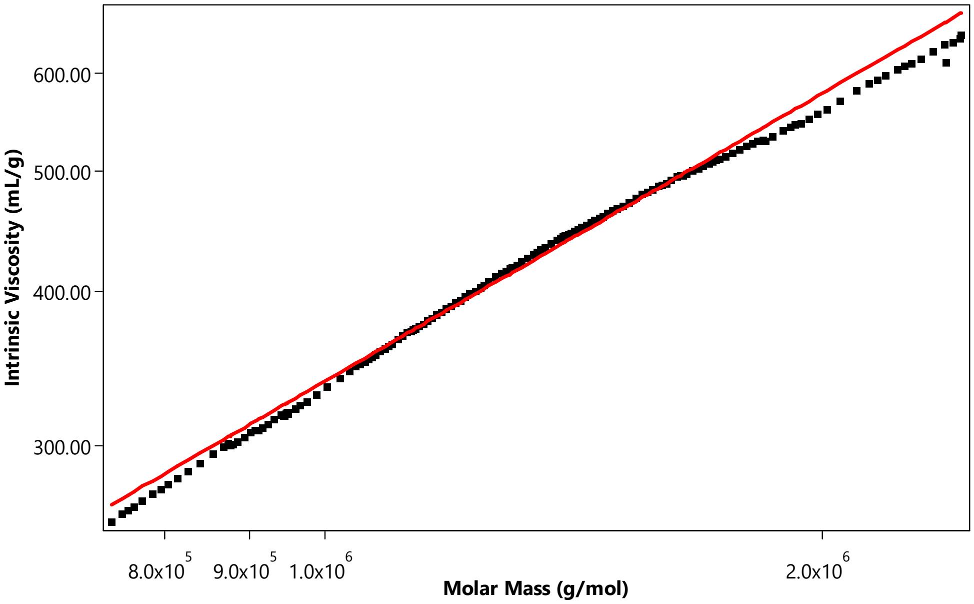


**Figure S28**: MHS plot of UHMW poly(MA). *a* = 0.772 ± 0.005.

## 6. Image

**Figure S29**: Image of UHMW AB poly(*t*BA-*b*-EA) (**Table 3**, entry 6) taken upon opening the milling jar. Approximately 2 g of polymer was capable of supporting the lower part of the 5 mL jar (mass = 253 g).

## 7. Analytical Calculations

The following calculations show the determination of B2 and B3 $M_n$ by $^1$H NMR spectroscopy relative to the known $M_n$ determined by GPC-MALS for a selected ABC triblock copolymer: poly(*t*BA-*b*-DEGEEA-*b*-HFBA) (**Table 2**, entry 2).

The $M_n$ of first block of the polymer was determined by GPC (**Figure S18**) to be 23.33 kDa.

$$23{,}330\ Da - 364.6\ Da = 22{,}965.4\ Da$$

**Equation S1** Determination of monomer molecular weight by subtraction of chain end molar mass (DDMAT = 364.6 Da) from $M_n$ determined by GPC.

$$\frac{22{,}965.4\ Da}{128.17\ Da} = 179\ tBA\ monomers$$

**Equation S2** Determination of B1 DP by dividing polymer $M_n$ by monomer molar mass.

The number of monomers can then be multiplied by the number of protons in the relevant peak (9 in this case) to determine the total integration of 1,611 protons.

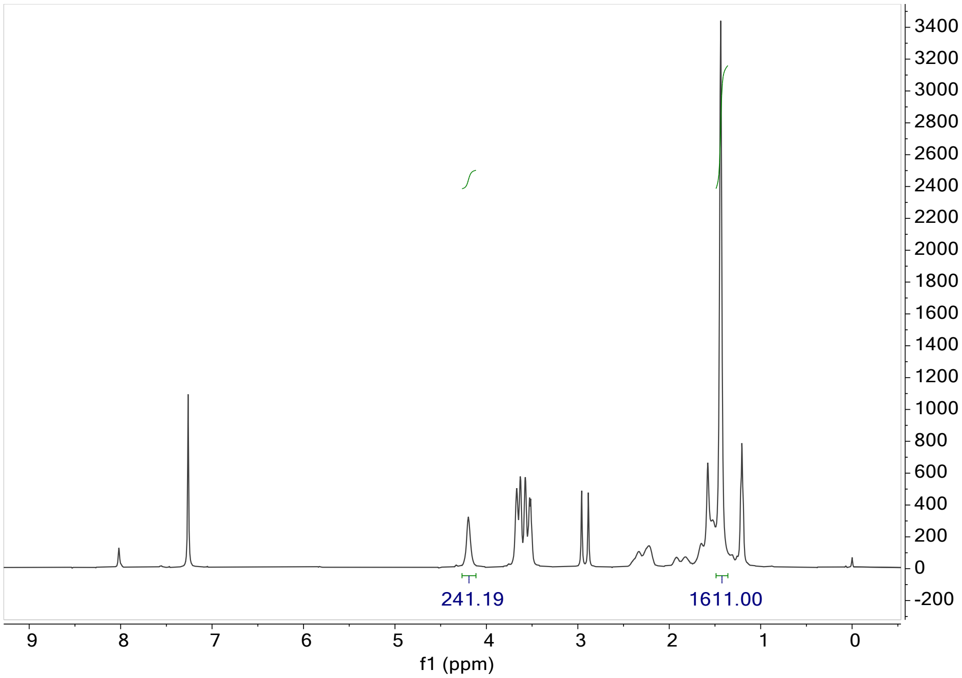


**Figure S30**: $^1$H NMR of AB poly(*t*BA-*b*-DEGEEA), with the integration of the *tert*-butyl signal at 1.4 ppm set based on the calculated DP. The peak at δ 4.2 ppm corresponds to the methylene of DEGEEA closest to the polymer backbone. 500 MHz, $CDCl_3$.

The normalized integration of the B2 peak can be divided by the number of protons (2) in the structure to give the number of monomers in B2:

$$\frac{241.19}{2H} = 121\ monomers$$

**Equation S3**: Dividing the relative integration of the DEGEEA methylene peak at 4.2 ppm by 2 protons to determine the number of monomers in B2.

The number of monomers can by multiplied by the molar mass of the monomer to give the $M_n$ of B2

$$121\ monomers\ \times\ 188.22\ Da = 22{,}774\ Da$$

**Equation S4**: Multiplication of the number of monomers in B2 by the monomer molar mass to yield $M_n$ of the DEGEEA block.

The same process (**Equation S1–S4**) can be repeated to determine $M_n$ for B3, referencing the diagnostic methylene peak of HFBA (δ4.5 ppm) to the *tert*-butyl signal of B1. In cases where a monomer has multiple diagnostic peaks (e.g., 2-MEA), **Equation S3** was applied to the integration of each peak (if well enough resolved) and the resulting DPs were averaged.

For the ABA triblock copolymers, the diagnostic peak of B3 must be integrated based on the DP of B2 to yield the total number of A protons. Then, the known DP of B1 can be subtracted from the combined DP of the A monomer to determine the DP of B3.

## 8. Small-angle X-Ray Scattering (SAXS)

**Table S3**: Tabulated SAXS data (**Figure 4**) for poly(DEGEEA-*b*-HFBA-*b*-*t*BA) (**Figure 3** and **Table 2**, entry 3).

| Peak Positions (1/Å) | Real Space (Å) | Relative Spacing |
|---|---|---|
| 0.0115 | 545.7 | 1 |
| 0.0232 | | 2.02 ≈ 2 |
| 0.0339 | | 2.95 ≈ 3 |
| 0.0465 | | 4.04 ≈ 4 |
| 0.0601 | | 5.22 ≈ 5 |
| 0.0796 | | 6.92 ≈ 7 |
| 0.0934 | | 8.11 ≈ 8 |
| 0.1036 | | 9.00 = 9 |

## 9. Differential Scanning Calorimetry (DSC)

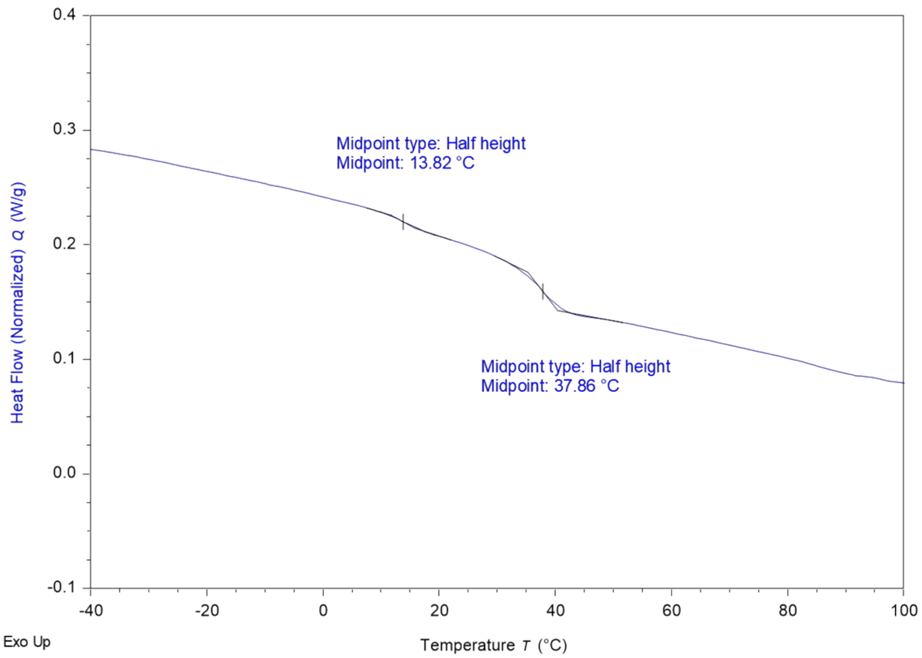


**Figure S31**: DSC curve of poly(*t*BA-*b*-MA-*b*-*t*BA) for the second heating cycle in a heat-cool-heat method. $T_g$ values were determined from the curve's inflection points (Table S1, Entry 3).

## 10. Diffusion-ordered Spectroscopy (DOSY)

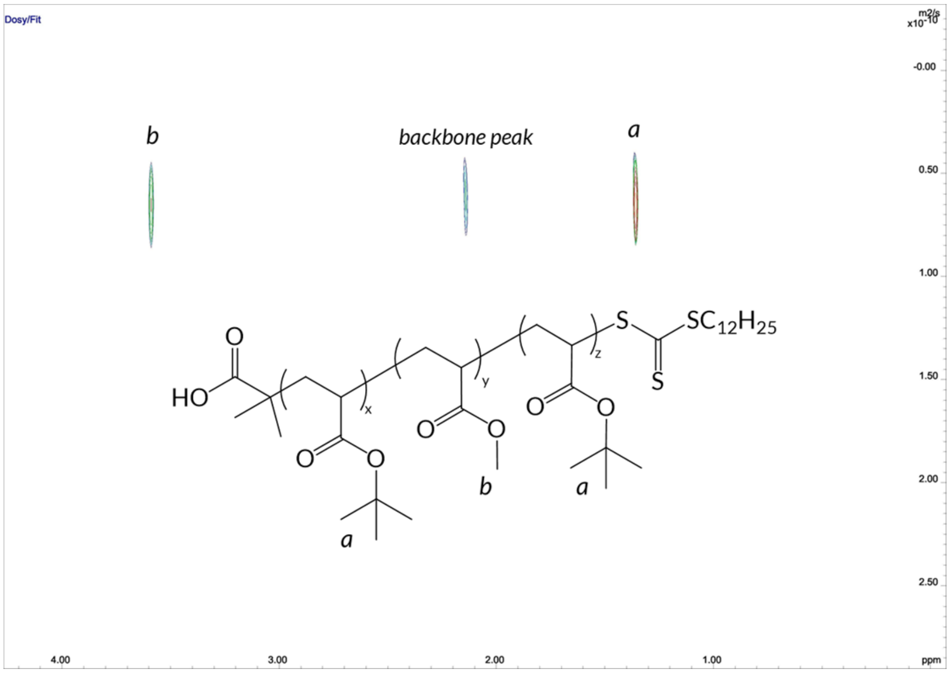


**Figure S32**: DOSY spectrum of ABA poly(*t*BA-*b*-MA-*b*-*t*BA) (**Table 1**, entry 1). Big Delta = 350 ms. The resonance at δ 1.4 ppm corresponds to the *tert*-butyl protons. The resonance at δ 2.2 ppm corresponds to a polymer backbone proton. The resonance at δ3.6 ppm corresponds to the $CH_3$ of MA.

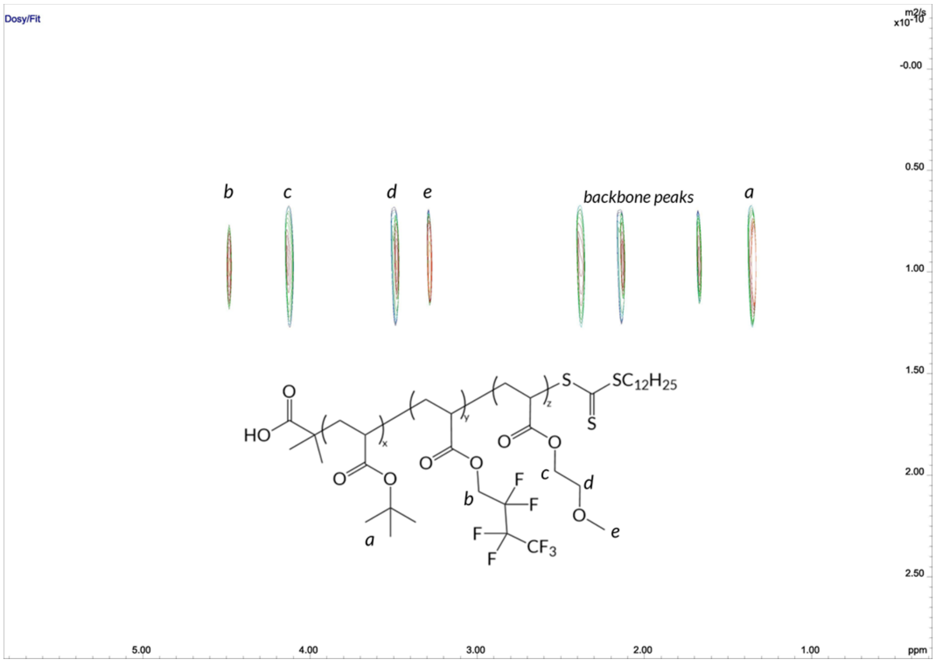


**Figure S33**: DOSY spectrum of ABC poly(*t*BA-*b*-HFBA-*b*-2-MEA) (**Table 2**, entry 1). Big Delta = 300 ms.

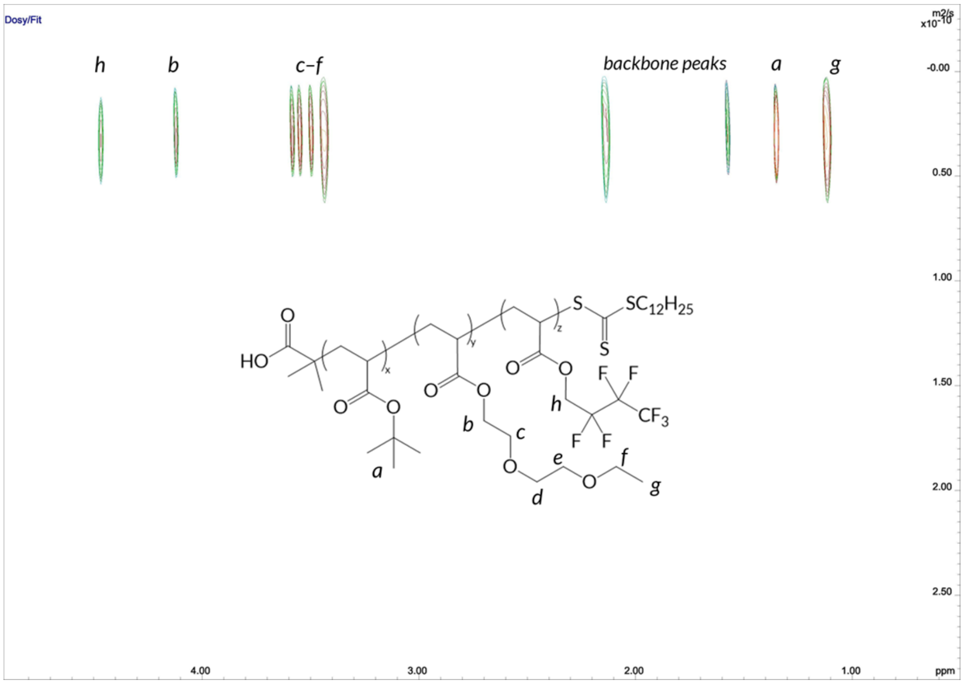


**Figure S34**: DOSY spectrum of ABA poly(*t*BA-*b*-DEGEEA-*b*-HFBA) (**Table 2**, entry 2). Big Delta = 350 ms.

# 11. References

1. P. Chakma, S. M. Zeitler, F. Baum, J. Yu, W. Shindy, L. D. Pozzo and M. R. Golder. *Angew. Chem. Int. Ed.* 2023, **62**, e202215733.