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# **Copper mediated RDRP of Thioacrylates and their Combination with Acrylates and Acrylamides**

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## **Materials**

All reactions involving air- and/or moisture-sensitive substances were carried out under an inert atmosphere (argon or nitrogen) using standard Schlenk techniques. Solvents were dried and degassed using standard laboratory techniques.

All monomers, solvents and chemicals were purchased from Sigma-Aldrich (UK) at highest purity available unless stated otherwise. Commercially available monomers were destabilized by passing through a short column of basic aluminium oxide prior to polymerization.

## **Instruments**

### **Gel permeation chromatography (GPC)**

Molecular weight averages and polymer dispersity of obtained polymers were determined by GPC in THF. Measurements were performed on an Agilent 390-LC system equipped with a PL-AS RT autosampler, 2PLgel 5  $\mu\text{m}$  mixed-C columns (300 $\times$ 7.5 mm), a PLgel 5 mm guard column (50 $\times$ 7.5 mm), and a differential refractive index (DRI). The system was eluted with THF containing 2% trimethylamine (TEA) at a flow rate of 1 mL min<sup>-1</sup> and the DRI was calibrated with linear narrow poly(methyl methacrylate) standards in range of 1010 to 2136000 g/mol. All samples were passed through neutral aluminium oxide to remove any catalyst residues and filtered using 0.2  $\mu\text{m}$  PTFE filters before analysis.

### **Nuclear magnetic resonance (NMR)**

<sup>1</sup>H NMR spectra were recorded on a Bruker AV-400 or Bruker Avance 600 spectrometer at 303K. The resonance signal at 7.26 ppm (<sup>1</sup>H) was used as residual CDCl<sub>3</sub> or for (CD<sub>3</sub>)<sub>2</sub>CO at 2.05 ppm peak for the chemical shift ( $\delta$ ). For <sup>13</sup>C NMR spectra were referenced relative to the solvent signal (77.16 ppm).

### **Mass spectrometry (MS)**

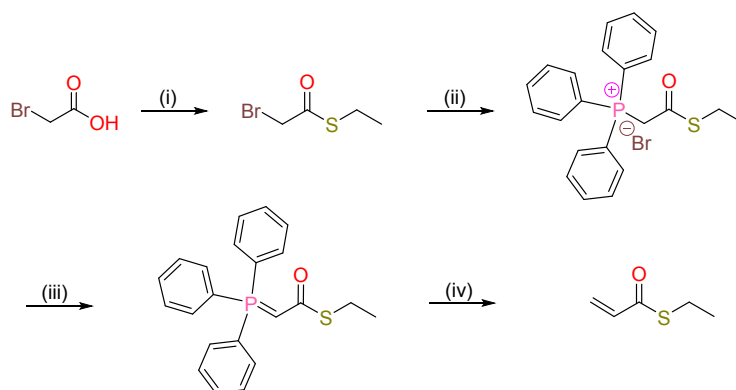
High-resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2-Si High Definition Mass Spectrometry system using a solvent gradient (0- $\rightarrow$ 100% Acetonitrile in Water + 0.1% Formic acid) in positive electrospray ionisation (ESI+) mode equipped with an Acquity UPLC BEH C18 column (2.1 x 50 mm; 130Å). The instrument was tuned using a Leucin Enkephalin mix to optimum resolution and signal intensity and was calibrated using a Waters Major Mix IMS/ToF in a range of m/z 50-1200.

## Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS)

MALDI-TOF MS was performed using a Bruker Daltonics Autoflex MALDI-ToF mass spectrometer, equipped with a nitrogen laser at 337 nm with positive ion ToF detection. Polymer samples were measured as follows; solutions in THF of trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB,  $\geq 98\%$ ) as matrix (30 mg/ml), silver trifluoroacetate (AgTFA) as cationisation agent (10 mg/ml) and sample (10 mg/ml) were mixed together in a 9:1:1 volume ratio for a total volume of 75  $\mu\text{L}$ . 2  $\mu\text{L}$  of the mixture was applied to the target plate. Spectra were recorded in reflectron mode and the mass spectrometer was calibrated with a peptide mixture up to 6000 Da.

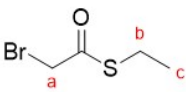
## Experimental

### Experimental Procedure for ethylthioacrylate (ETA) monomer

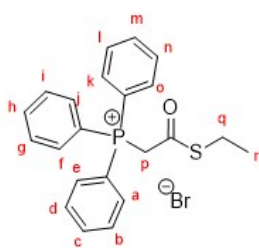


**Scheme S1:** Synthesis of *S*-Ethyl 2-bromoethanethioate (7), Reagents and conditions: (i) ethanethiol, DCC/DMAP,  $\text{CH}_2\text{Cl}_2$ , 0 °C to rt, 16 h. (ii) Triphenylphosphine, benzene, reflux, 30 min. (iii) 10 wt%  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_2\text{Cl}_2$ , rt, 30 min. (iv) paraformaldehyde,  $\text{CH}_2\text{Cl}_2$ , reflux, 1 h.

### Synthesis of *S*-ethyl bromoethanethioate (1)

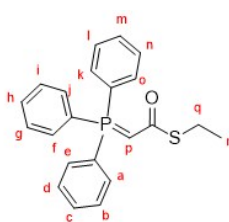
 A two-necked 5-L round bottom flask was charged with bromoacetic acid (200 g, 1.44 mol), ethanethiol (140 mL, 189 mmol) and a catalytic amount of DMAP (17.6 g, 0.144 mol). 1 L of DCM was added and the solution was cooled to 0 °C with stirring under an atmosphere of nitrogen. DCC (17.6 g, 144 mmol) was diluted in 200 mL of DCM and added dropwise and the solution slowly warmed to room temperature overnight until esterification was complete. The solution was then filtered through Silica and the filtercake was washed several times with DCM. The filtrate was washed with saturated  $\text{NaHCO}_3$  solution, water and brine and was dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent in *vacuo* gave a yellowish oil. (Yield = 181,68 g, 70%)  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  = 4.01 (s, 2H,  $\text{H}_a$ ), 2.94 (q,  $J$  = 7.5 Hz, 2H,  $\text{H}_b$ ) and 1.27 (t,  $J$  = 7.4 Hz, 3H,  $\text{H}_c$ ).

## Synthesis of (2-(ethylthio)-2-oxoethyl)triphenylphosphonium bromide (2)



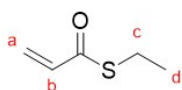
**Product 1** (181 g, 0.99 mol) and triphenylphosphine (337 g, 1.28 mol) in 750 mL of benzene was heated to reflux under nitrogen for one hour. The solvent was evaporated under reduced pressure to yield white crystals after filtering and washing with toluene.  $^1\text{H NMR}$  ( $(\text{CH}_3)_2\text{SO}$ , 600 MHz)  $\delta = 7.93\text{--}7.70$  (m, 15H,  $\text{H}_a - \text{H}_o$ ), 5.71 (d,  $J = 14.5$  Hz, 2H,  $\text{H}_p$ ), 2.82 (q,  $J = 7.3$  Hz, 2H,  $\text{H}_q$ ) and 1.04 (t,  $J = 7.3$  Hz, 3H,  $\text{H}_r$ ).

## Synthesis of S-ethyl 2-(triphenyl- $\lambda$ 5-phophanylidene) ethanethioate (3)



**Product 2** was then dissolved in 500 mL of DCM and vigorously stirred with 200 mL of 10% aqueous  $\text{K}_2\text{CO}_3$  solution for 30 min. The organic layer was separated and the aqueous layer was extracted twice with DCM. The combined organic phases were dried over magnesium sulfate and partially concentrated in *vacuo* and diluted in pentane which afforded 7b (259 g, 72% yield) of light-brown crystals after 24h.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta = 7.70\text{--}7.40$  (m, 15H,  $\text{H}_a - \text{H}_o$ ), 3.66 (d,  $J = 22.7$  Hz, 1H,  $\text{H}_p$ ), 2.84 (q,  $J = 7.4$  Hz, 2H,  $\text{H}_q$ ) and 1.25 (t,  $J = 7.4$  Hz, 3H,  $\text{H}_r$ ).

## Synthesis of S-ethyl prop-2-enethioate (Ethyl thioacrylate, ETA)



In a 1-L two-necked flask equipped with a cooling system and magnetic stirrer, (100 g, 270 mmol) of Wittig reagent **3** were introduced into 700 mL of DCM. Then, (41.7 g, 1.37 mol) of paraformaldehyde was poured into the solution. The mixture was heated for 1 hour under then concentrated in *vacuo* and the residue was suspended in cold pentane (250 mL) and filtered over silica. The filtercake was washed with cold (10:90  $\text{Et}_2\text{O}$ /pentane). Hydroquinone was added to the solution to prevent polymerisation. The solution was distilled over  $\text{CaH}_2$  (2 g/L) at reduced pressure (11 mbar/80°C) to yield (17,96 g, 57% yield) of a colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz),  $\delta = 6.32$  (dd,  $J = 17.2, 9.7$  Hz, 1H,  $\text{H}_{a1}$ ), 6.28 (dd,  $J = 17.2, 1.6$  Hz, 1H,  $\text{H}_{a2}$ ), 5.59 (dd,  $J = 9.8, 1.6$  Hz, 1H,  $\text{H}_b$ ), 2.89 (q,  $J = 7.4$  Hz, 2H,  $\text{H}_c$ ), 1.21 (t,  $J = 7.4$  Hz, 3H,  $\text{H}_d$ ).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 190.1, 135.1, 125.9, 23.1, 14.6.

## General Polymerisation Procedure for Homopolymerisation of ETA with EBiB

General polymerisation procedure will be exemplified on **P1**. For a typical polymerisation,  $\text{CuBr}_2$  (0.10 eq., 4.23mg, 18.9  $\mu\text{mol}$ ), DMSO (0.88 mL),  $\text{Me}_6\text{TREN}$  (0.19 eq., 9.60  $\mu\text{L}$ ,

36.0  $\mu\text{mol}$ ), ETA (20.0 eq., 0.44 g, 3.79 mmol) and EBiB (1 eq., 27.8  $\mu\text{L}$ , 189  $\mu\text{mol}$ ) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire was preactivated in 10 mL HCl (conc. 37%) for 15 minutes, then washed with deionised water and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire defines  $t = 0$ ).

### Synthesis of star P(ETA) with PE-Br<sub>4</sub> (P2)

For a typical polymerisation, CuBr<sub>2</sub> (0.4 eq., 12.8 mg, 0.04 mmol), DMSO (4.00 mL), Me<sub>6</sub>TREN (29.1  $\mu\text{L}$ , 0.11 mmol), ETA (60 eq., 1.00 g, 8.61 mmol), mesitylene (2.5%,  $v/v$ ) and PEB-Br<sub>4</sub> (1.0 eq., 105 mg, 0.14 mmol) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire was preactivated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire defines  $t=0$ ).

### General Polymerisation Procedure for Homopolymerisation of EA, DP=10

**Table S1:** Overview of the amounts used for the polymerisation of P17-P20.

Polymer	EA (g)	EBiB ( $\mu\text{L}$ )	Me <sub>6</sub> TREN ( $\mu\text{L}$ )	Metal halide (mg)	DMSO (mL)
P17	1.00	147	50.7	CuBr <sub>2</sub> : 22.3	2.00
P18	1.00	147	50.7	FeBr <sub>2</sub> : 21.5	2.00
P19	1.00	147	50.7	FeBr <sub>3</sub> : 29.5	2.00
P20	1.00	147	50.7	CuBr: 14.2	2.00

Polymerisation condition: [EA] : [EBiB] : [metal halide]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19.

For a typical polymerisation, metal halide (0.4 eq.), DMSO (1:2  $v/v$ ), Me<sub>6</sub>TREN (0.19 eq.), EA (10 eq.), mesitylene (2.5%,  $v/v$ ) and EBiB (1.0 eq.) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire was preactivated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water

and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire defines  $t=0$ ).

### General Polymerisation Procedure for Homopolymerisation of ETA, DP=10

**Table S2:** Overview of the amounts used for the polymerisation of P21-P24.

Polymer	ETA (g)	EBiB ( $\mu$ L)	Me <sub>6</sub> TREN ( $\mu$ L)	Metal halide (mg)	DMSO (mL)
P21	0.44	55.6	19.0	CuBr <sub>2</sub> : 8.40	0.88
P22	0.88	111	38.0	FeBr <sub>2</sub> : 16.3	1.76
P23	0.88	111	38.0	FeBr <sub>3</sub> : 22.3	1.76
P24	0.58	73.3	25.0	CuBr: 7.15	1.16

Polymerisation condition: [ETA]:[EBiB]:[metal halide]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19.

For a typical polymerisation, metal halide (0.4 eq.), DMSO (1:2 v/v), Me<sub>6</sub>TREN (0.19 eq.), ETA (10 eq.), mesitylene (2.5%, v/v) and EBiB (1.0 eq.) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire was preactivated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire defines  $t=0$ ).

### General Polymerisation Procedure for Homopolymerisation of DMA, DP = 10

**Table S3:** Overview of the amounts used for the polymerisation of **P25-P27**.

<b>Polymer</b>	<b>DMA (g)</b>	<b>EBiB (<math>\mu</math>L)</b>	<b>Me<sub>6</sub>TREN (<math>\mu</math>L)</b>	<b>Metal halide (mg)</b>	<b>DMSO (mL)</b>
P25	0.375	55.6	19.0	CuBr <sub>2</sub> : 8.40	0.74
P26	0.375	55.6	19.0	FeBr <sub>2</sub> : 8.13	0.74
P27	0.375	55.6	19.0	FeBr <sub>3</sub> : 11.2	0.74
Polymerisation condition: [DMA]:[EBiB]:[metal halide]:[Me <sub>6</sub> TREN] = 10:1:0.1:0.19.					

For a typical polymerisation, metal halide (0.4 eq.), DMSO (1:2 *v/v*), Me<sub>6</sub>TREN (0.19 eq.), DMA (10 eq.), mesitylene (2.5%, *v/v*) and EBiB (1.0 eq.) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire was preactivated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire defines  $t = 0$ ).

#### **Homopolymerisation of MA (P28)**

For a typical polymerisation, CuBr<sub>2</sub> (0.1 eq., 16.8 mg, 0.07 mmol), DMSO (1.30 mL), Me<sub>6</sub>TREN (0.19 eq., 38.4  $\mu$ L, 16.1 mmol), DMA (20 eq., 0.652 g, 7.58 mmol), mesitylene (2.5%, *v/v*) and EBiB (1.0 eq., 111  $\mu$ L, 0.38 mmol) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire was preactivated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire defines  $t = 0$ ).

#### **Homopolymerisation of MA (P29)**

For a typical polymerisation, FeBr<sub>2</sub> (0.1 eq., 16.3 mg, 0.07 mmol), DMSO (1.30 mL), Me<sub>6</sub>TREN (0.19 eq., 38.4  $\mu$ L, 16.1 mmol), MA (20 eq., 0.652 g, 7.58 mmol), mesitylene (2.5%, *v/v*) and EBiB (1.0 eq., 111  $\mu$ L, 0.38 mmol) were added to a Schlenk tube containing a stirrer bar. The Schlenk tube was subsequently sealed with a rubber septum, lowered into an oil bath set to 25 °C and degassed with argon for 30 minutes. At the same time, the copper wire

was preactivated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper wire was then transferred to the Schlenk tube containing the polymerisation mixture to start the reaction (the addition of the copper wire define  $t = 0$ ).

#### **Chain extension of P(MA) with ETA (P31)**

The general procedure for homopolymerisation described above was followed (**P1**). Upon detection of >99% conversion a 1:2 mixture of degassed ETA and DMSO was added to the reaction mixture *via* degassed syringe. Additional ligand (0.19 eq) and FeBr<sub>2</sub> (0.10 eq.) were added to Sample was taken after 16 hours and conversions was measured using <sup>1</sup>H NMR and GPC analysis.

#### **Chain extension of P(MA) with ETA (P32)**

The general procedure for homopolymerisation described above was followed (**P1**). Upon detection of >99% conversion at 140 minutes, a 1:2 mixture of degassed ETA (5.00 eq.) and DMSO was added to the reaction mixture *via* degassed syringe. Sample was taken after 16 hours and conversions was measured using <sup>1</sup>H NMR and GPC analysis.

#### **Chain extension of P(ETA) with MA (P34)**

The general procedure for homopolymerisation described above was followed (**P1**). Upon detection of >99% conversion at 360 minutes, a 1:2 mixture of degassed MA (60 eq.) and DMSO was added to the reaction mixture *via* degassed syringe. Sample was taken after 24 hours and conversions was measured using <sup>1</sup>H NMR and GPC analysis.

#### **Synthesis of all-acrylic block copolymer (P37)**

The general procedure for P(MA<sub>20</sub>-*b*-ETA<sub>10</sub>) chain extension was followed (**P31**). Sample was taken after 24 hours and conversions was measured using <sup>1</sup>H NMR and GPC analysis. Polymer was purified by dialysis. 475 mg of purified **P36** was added to a vial, 2.00 mL of THF was added. BzNH<sub>2</sub>, PhSH and TEA were subsequently added and the reaction was stirred for 24 h. The polymer was precipitated in cold H<sub>2</sub>O/MeOH (1:2). Degree of amidation was measured using <sup>1</sup>H NMR and GPC analysis.

**Table S4:** Amidation conditions used to obtain the all acrylic block copolymer **P37**.

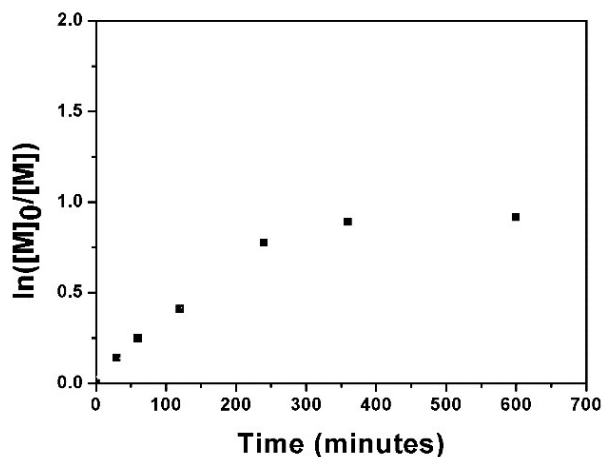
<b>P36</b>	<b>PhSH</b>	<b>BzNH<sub>2</sub></b>	<b>TEA</b>	<b>Solvent</b>
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<b>eq.</b>	1.00	2.00	2.50	2.00	
<b>used</b>	475 mg	270 $\mu$ L	360 $\mu$ L	370 $\mu$ L	2.00 mL

Amidation condition: room temperature.

## Additional Characterisation of polymers

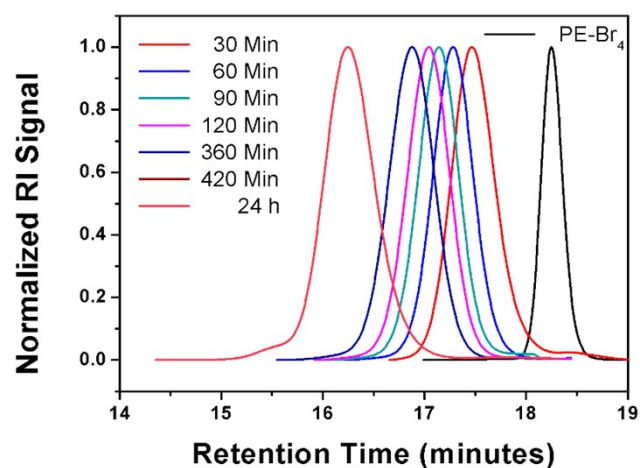


**Figure S1:**  $\ln([M]_0:[M])$  vs. time plot for **P1**.

**Table S5:** Experimental details of the homopolymerisation of ETA with linear initiator (EBiB) at DP = 60 in DMSO, **P1**.

<b>Time</b> <b>(min)</b>	$M_{n,theo}$ <b>(g/mol)</b>	$M_{n,GPC}^{[b]}$ <b>(g/mol)</b>	<b>PDI</b> <sup>[b]</sup>	<b>Conv.</b> <sup>[a]</sup> <b>(%)</b>
30	1200	1100	1.15	13
60	1800	1700	1.11	22
120	2800	2600	1.07	34
240	4000	4000	1.11	54
360	4300	4300	1.09	59
600	4400	4400	1.10	60

[ETA]:[EBiB]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 60:1:0.1:0.19. <sup>[a]</sup>Conversion measured by <sup>1</sup>H NMR spectroscopy. <sup>[b]</sup> THF eluent, linear PMMA standard.



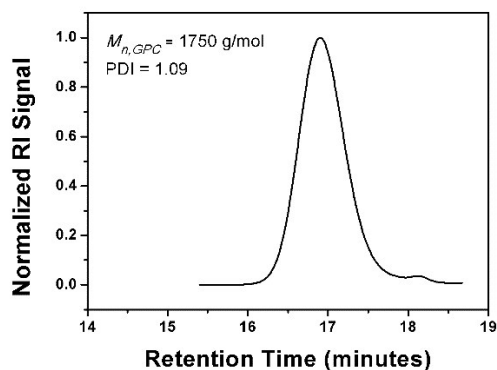
**Figure S2:** GPC traces of the homopolymerisation of ETA with 4-arm initiator PE-Br<sub>4</sub>.

**Table S6:** Experimental details of the homopolymerisation of ETA with 4-arm initiator (PE-Br<sub>4</sub>) at DP = 60 in DMSO, **P2**.

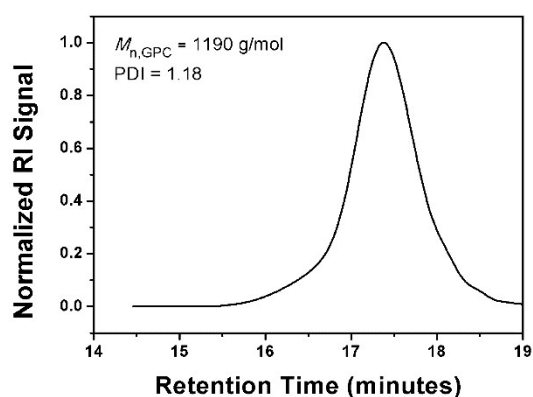
Time (min)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}^{[b]}$ (g/mol)	PDI <sup>[b]</sup>	Conv. <sup>[a]</sup> (%)
30	1300	1100	1.08	8
60	2000	1400	1.04	18
90	2200	1600	1.04	21
120	2700	1800	1.04	28
360	3200	2000	1.05	36
420	3600	2200	1.08	41
24 h	5300	3300	1.08	65

[ETA]:[PEB-Br<sub>4</sub>]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 60:1:0.4:0.76. <sup>[a]</sup>Conversion measured by <sup>1</sup>H NMR spectroscopy. <sup>[b]</sup> THF eluent, linear PMMA standard.

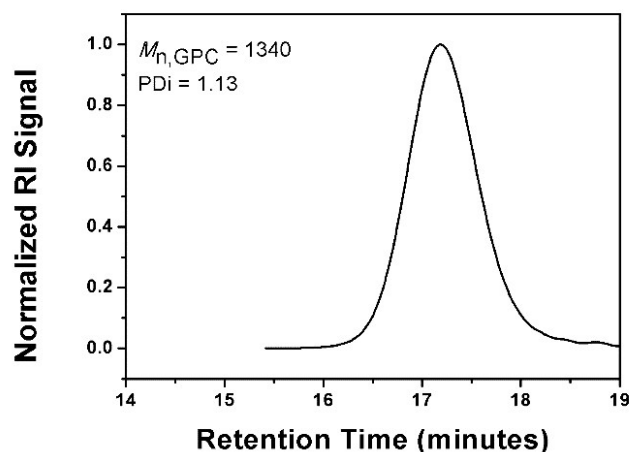
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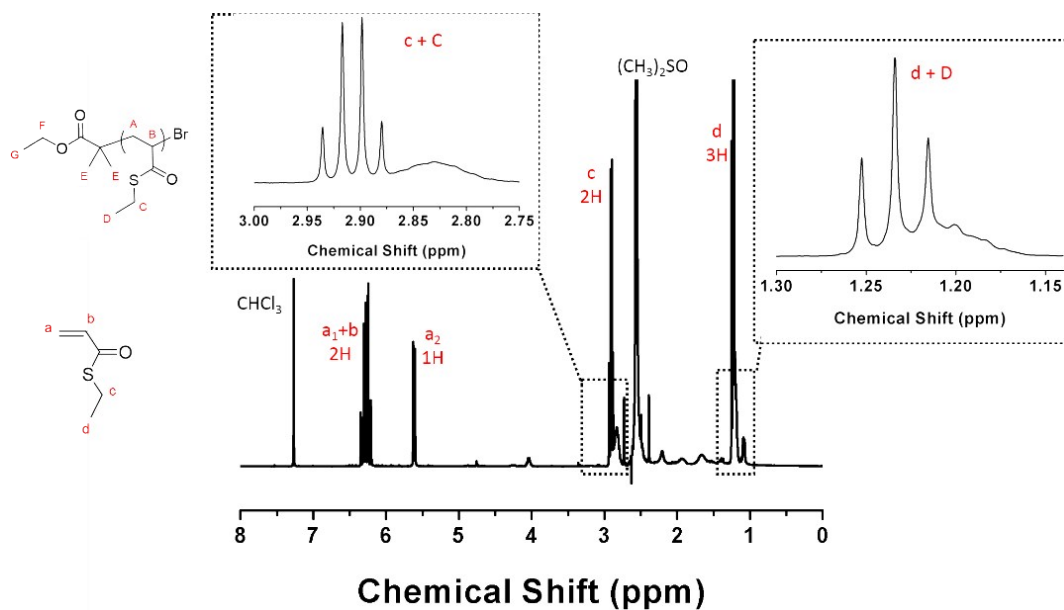
b)



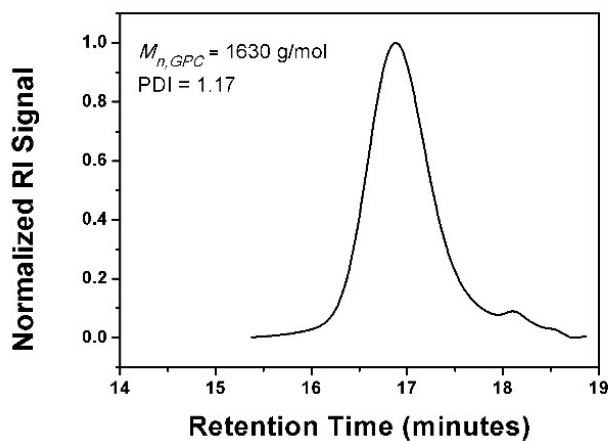
**Figure S3:** GPC traces obtained from the homopolymerisation of ETA with  $[I]:[CuBr_2]:[Me_6TREN] = 1:0.1:0.19$  **a)** DP = 20, showing an  $M_{n,GPC} = 1800$ , PDI = 1.09 and 80% conversion, **P3**. **b)** DP = 10, showing an  $M_{n,GPC} = 1200$ , PDI = 1.18 and 92% conversion, **P4**.



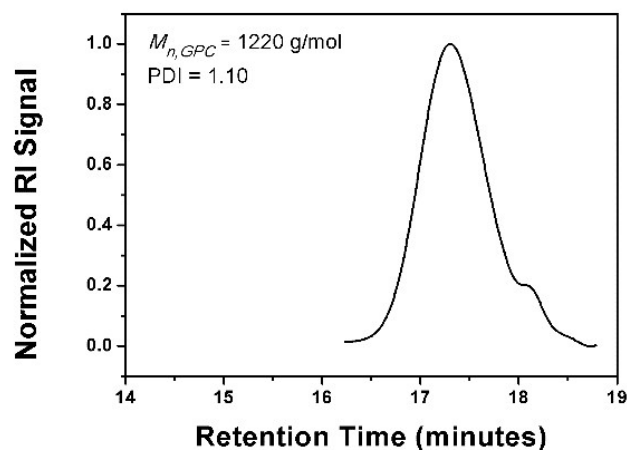
**Figure S4a:** GPC trace obtained from the homopolymerisation of ETA with  $[ETA]:[I]:[CuBr_2]:[Me_6TREN] = 20:1:0.2:0.19$ , showing an  $M_{n,GPC} = 1300$ , PDI = 1.13 and 50% conversion, **P5**.



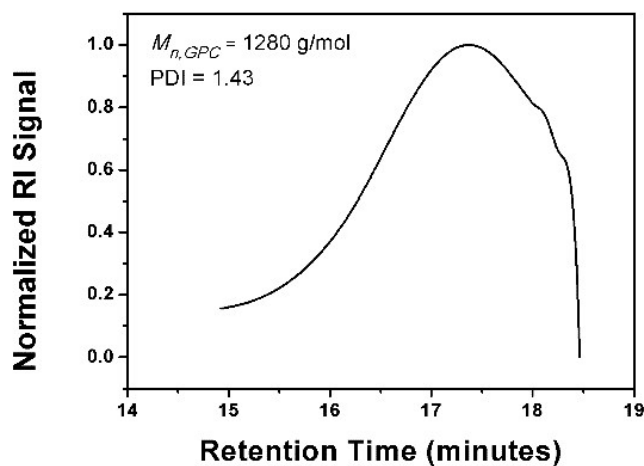
**Figure S4b:**  $^1\text{H}$  NMR spectrum of P(ETA), **P5** ( $\text{CDCl}_3$ , 400 MHz, 303 K) at 16 h.



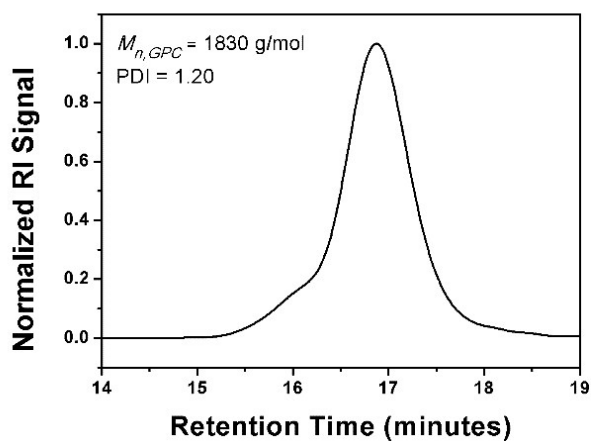
**Figure S5:** GPC trace obtained from the homopolymerisation of ETA with  $[\text{ETA}]:[\text{I}]:[\text{CuBr}_2]:[\text{Me}_6\text{TREN}] = 20:1:0.1:0.38$ , showing an  $M_{n,\text{GPC}} = 1600$ ,  $\text{PDI} = 1.17$  and 81% conversion, **P6**.



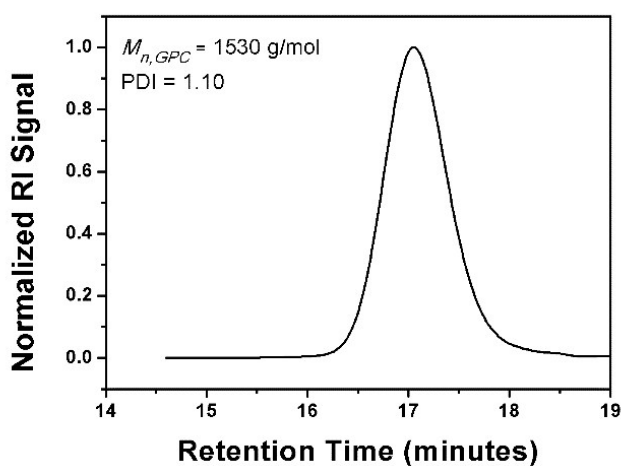
**Figure S6:** GPC traces obtained from the homopolymerisation of ETA with [ETA]:[I]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 20:1:0.1:0.19 with DMSO (8:1 v/v) showing an  $M_{n, GPC} = 1200$ , PDI = 1.10 and 80% conversion (**P7**).



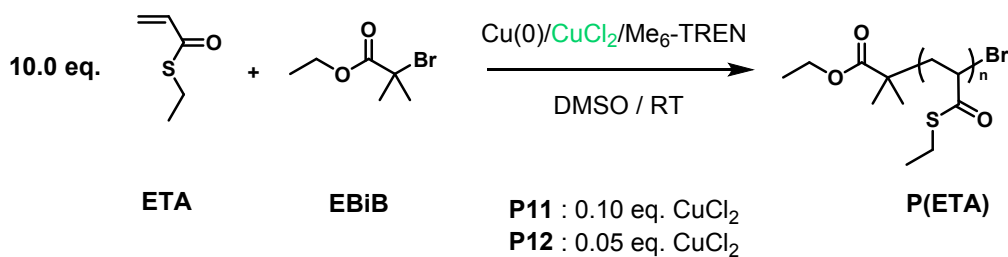
**Figure S7:** GPC traces obtained from the homopolymerisation of ETA with [ETA]:[I]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 20:1:0.1:0.19 with TFE, showing an  $M_{n, GPC} = 1300$ , PDI = 1.43 and 80% conversion (**P8**).



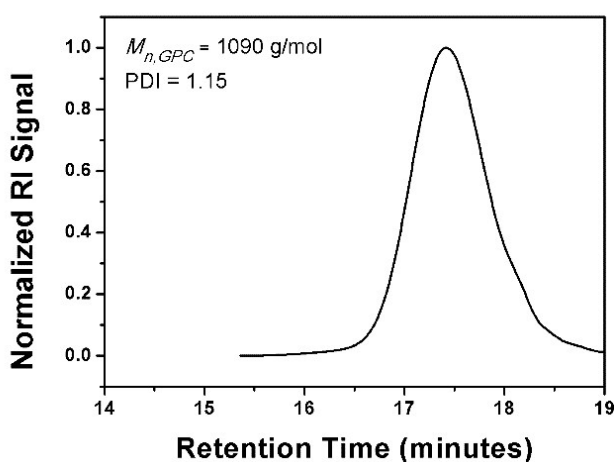
**Figure S8:** GPC traces obtained from the homopolymerisation of ETA with [ETA]:[I]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 20:1:0.1:0.19 at 40 °C, showing  $M_{n, GPC} = 1800$ , PDI = 1.20 and 91% conversion, **P9**.



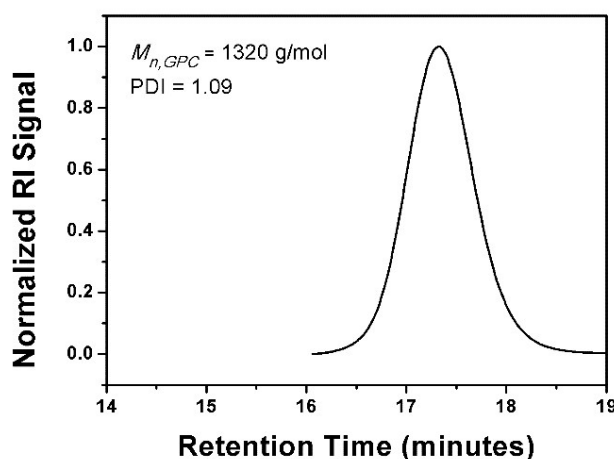
**Figure S9:** GPC traces obtained from the homopolymerisation of ETA with [ETA]:[I]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 20:1:0.1:0.19 with 10 cm Cu(0) wire, showing an  $M_{n, GPC} = 1500$ , PDI = 1.10 and 90% conversion, **P10**.



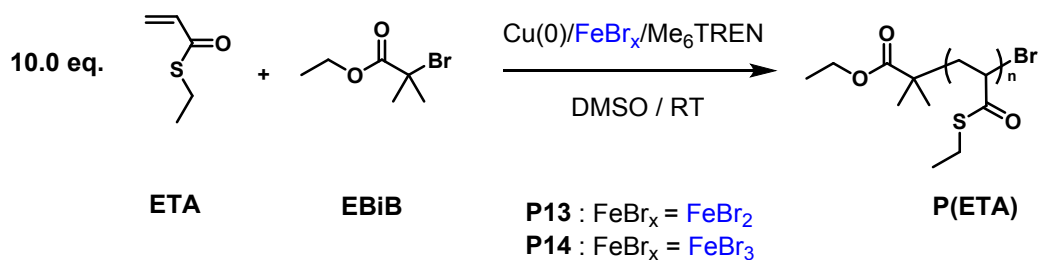
**Scheme S2:** General conditions for the polymerisation of ETA with EBiB *via* SET-LRP with  $[\text{ETA}]:[\text{I}]:[\text{Me}_6\text{TREN}] = 10:1:0.19$  using  $\text{CuCl}_2$ .



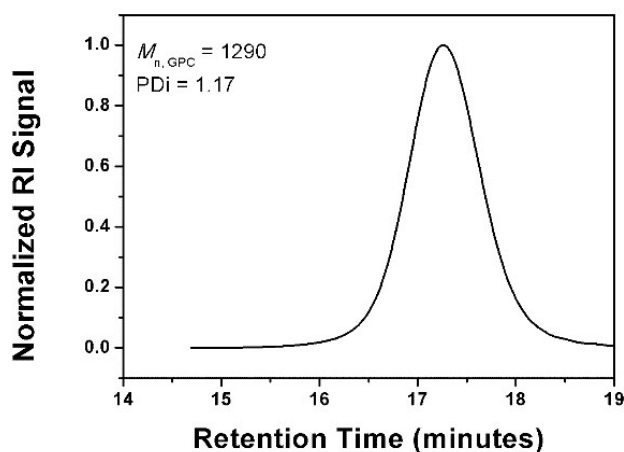
**Figure S10:** GPC traces obtained from the homopolymerisation of ETA with  $[\text{ETA}]:[\text{I}]:[\text{Me}_6\text{TREN}] = 10:1:0.19$  a) with 0.10 eq.  $\text{CuCl}_2$ , showing  $M_{n, \text{GPC}} = 1100$ ,  $\text{PDI} = 1.15$  and 86% conversion, **P11**.



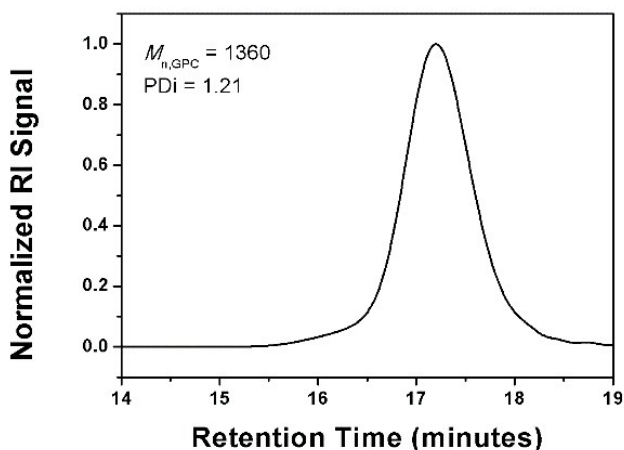
**Figure S11:** GPC traces obtained from the homopolymerisation of ETA with  $[\text{ETA}]:[\text{I}]:[\text{Me}_6\text{TREN}] = 10:1:0.19$  with 0.05 eq.  $\text{CuCl}_2$ , showing an  $M_{n, \text{GPC}} = 1300$ ,  $\text{PDI} = 1.09$  and 86% conversion, **P12**.



**Scheme S3:** General conditions for the polymerisation of ETA with EBiB *via* SET-LRP with  $[\text{ETA}]:[\text{I}]:[\text{FeBr}_x]:[\text{Me}_6\text{TREN}] = 10:1:0.1:0.19$ .

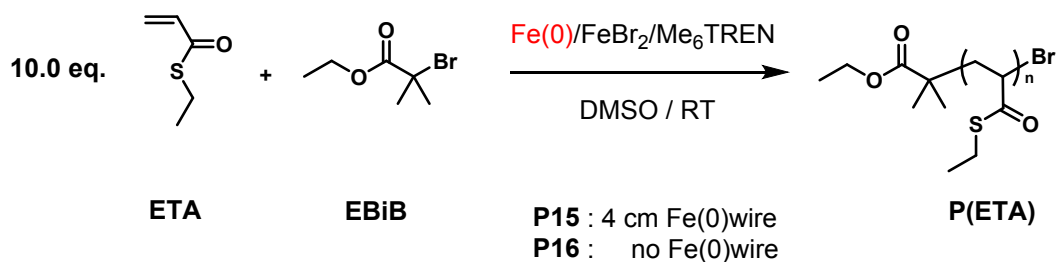


**Figure S12:** GPC traces obtained from the homopolymerisation of ETA with  $[\text{ETA}]:[\text{I}]:[\text{Me}_6\text{TREN}] = 10:1:0.19$  with 0.10 eq.  $\text{FeBr}_2$  showing  $M_{n,\text{GPC}} = 1300$ ,  $\text{PDI} = 1.17$  and 99% conversion, **P13**.

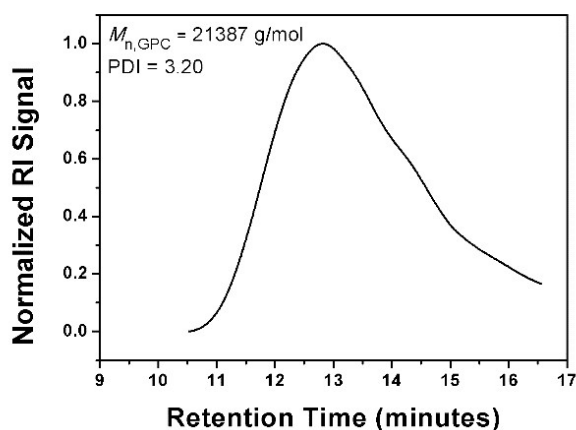


**Figure S13:** GPC traces obtained from the homopolymerisation of ETA with  $[\text{ETA}]:[\text{I}]:[\text{Me}_6\text{TREN}] = 10:1:0.19$  with 0.10 eq.  $\text{FeBr}_3$  showing an  $M_{n,\text{GPC}} = 1400$ ,  $\text{PDI} = 1.21$  and 99% conversion, **P14**.

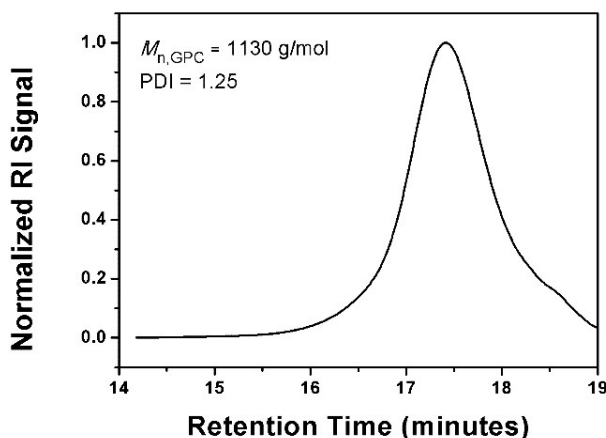




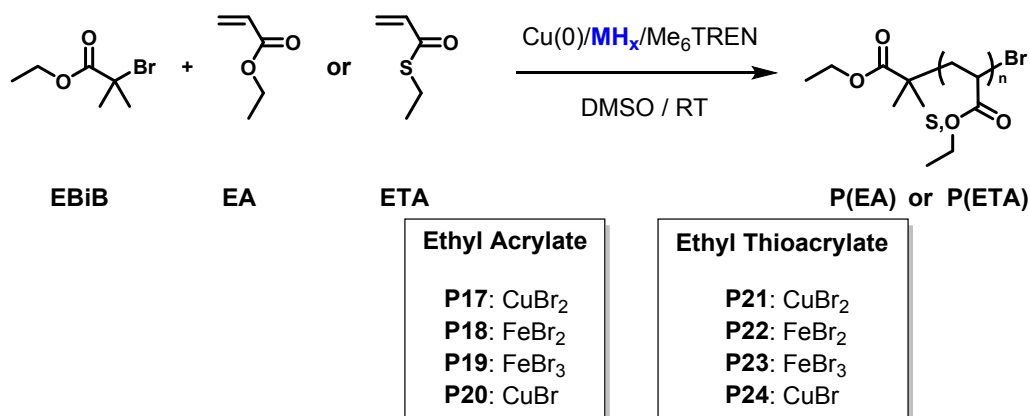
**Scheme S4:** General conditions for the polymerisation of ETA with EBiB *via* SET-LRP with [ETA]:[I]:[FeBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19 with Fe(0)-wire for **P15** and without for **P16**.



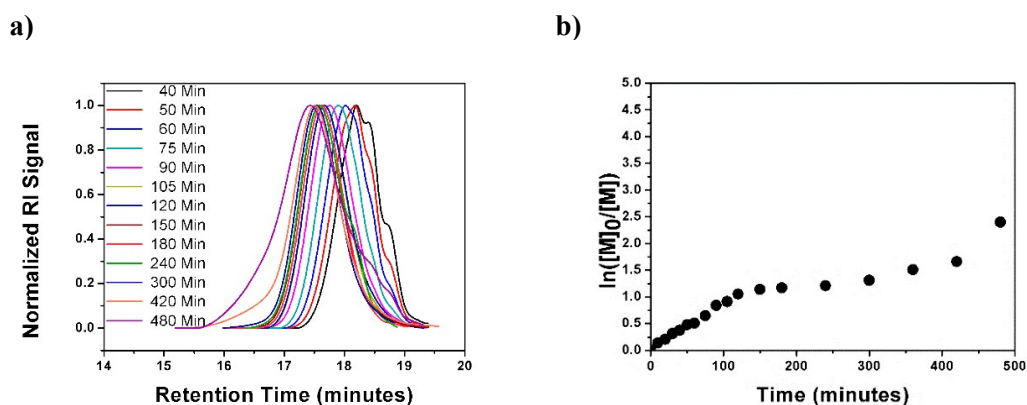
**Figure S14:** GPC traces obtained from the homopolymerisation of ETA with [ETA]:[I]:[FeBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19 with Fe(0)-wire, showing an  $M_{n,GPC} = 21400$ ,  $PDI = 3.22$  and 30% conversion, **P15**.



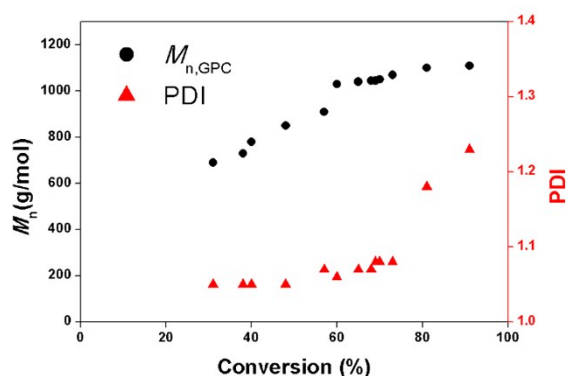
**Figure S15:** GPC traces obtained from the homopolymerisation of ETA with [ETA]:[I]:[FeBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19 with no Fe(0)-wire, showing an  $M_{n,GPC} = 1100$ ,  $PDI = 1.25$  and 87% conversion, **P16**.



**Scheme S5:** General conditions for the polymerisation of EA or ETA with EBiB *via* SET-LRP with [EA]:[I]:[MH<sub>x</sub>]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19 with Cu(0)-wire and different metal halides (MH<sub>x</sub>).

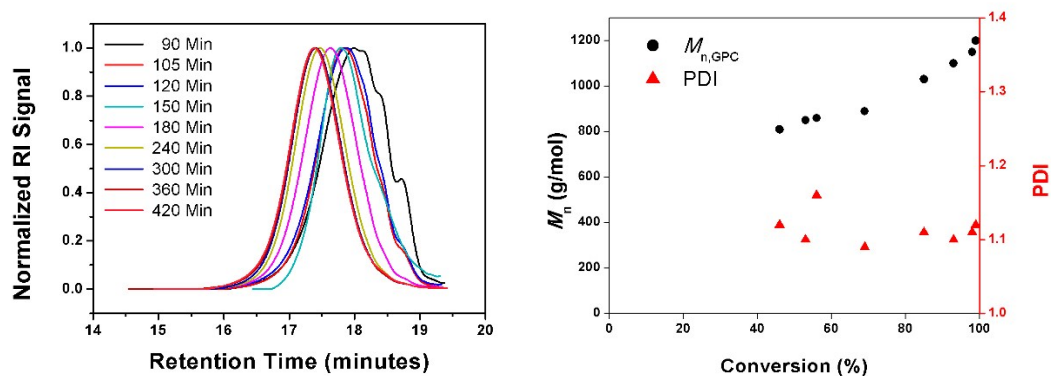


**Figure S16:** Homopolymerisation of ETA *via* SET-LRP with [ETA]:[I]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>TREN] = 10:1:0.1:0.19 **a)** GPC traces of the homopolymerisation of ETA, **P21**. **b)** Ln([M]<sub>0</sub>/[M]) vs. time plot for **P21**.

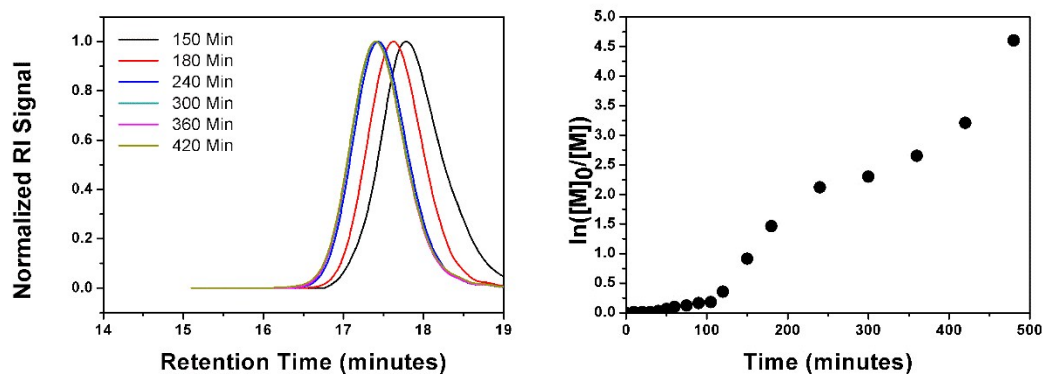


**Figure S17:**  $M_n$  vs. conversion plot for **P21**. Black circles represent  $M_{n,GPC}$  and red triangles represent their corresponding dispersity.

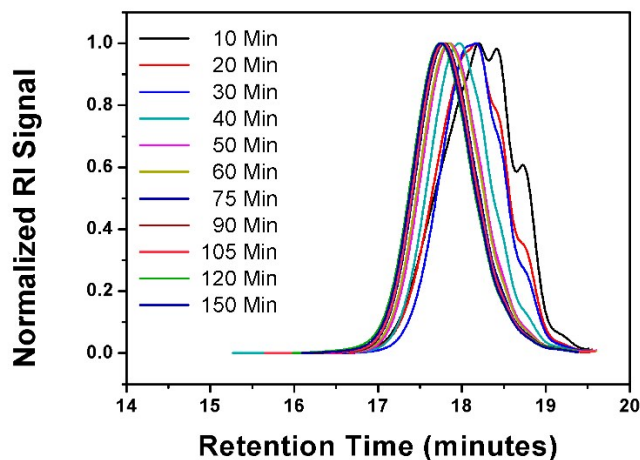
**a)** **b)**



**Figure S18:** Homopolymerisation of ETA *via* SET-LRP with  $[ETA]:[I]:[FeBr_2]:[Me_6TREN] = 10:1:0.1:0.19$  a) GPC traces of the homopolymerisation of ETA, **P22**. b)  $M_n$  vs. conversion plot for **P22**. Black circles represent  $M_{n,GPC}$  and red triangles represent their corresponding dispersity.

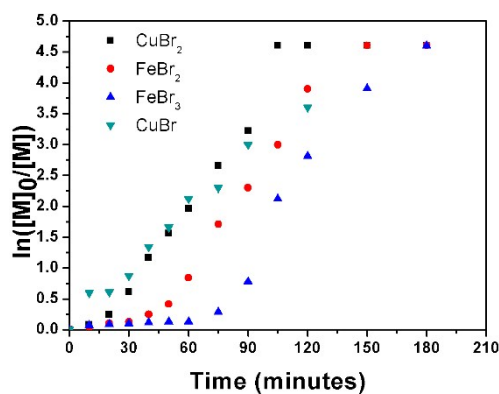


**Figure S19:** Results obtained from the homopolymerisation of ETA *via* SET-LRP with  $[ETA]:[I]:[FeBr_3]:[Me_6TREN] = 10:1:0.1:0.19$ . a) GPC traces of the homopolymerisation of ETA, **P23**. b)  $\ln([M]_0/[M])$  vs. time plot for the in **P23**.

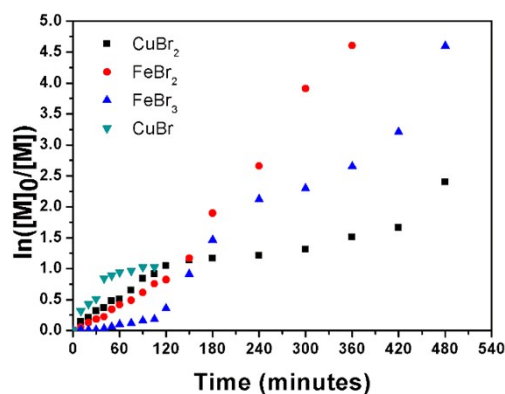


**Figure S20:** GPC traces of the homopolymerisation of ETA *via* SET-LRP with  $[ETA]:[I]:[CuBr]:[Me_6TREN] = 10:1:0.1:0.19$  in **P24**.

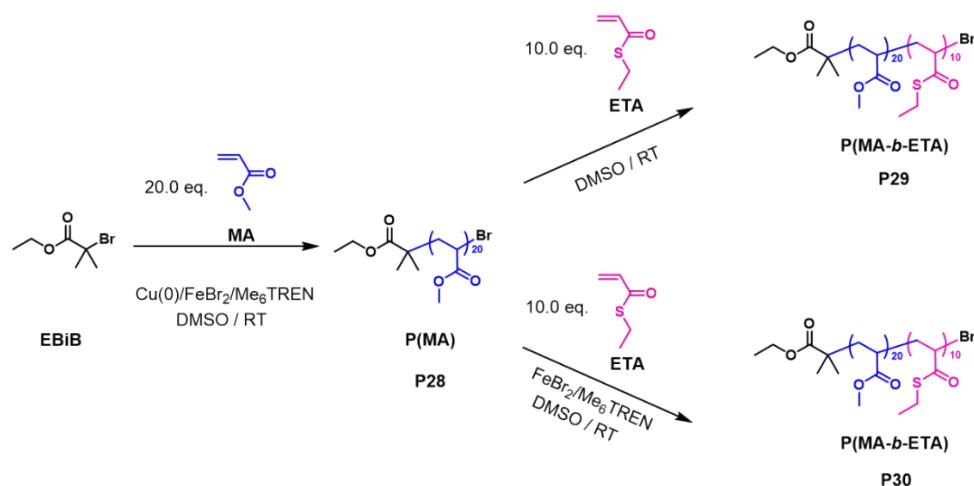
a) Ethyl acrylate



b) Ethyl thioacrylate

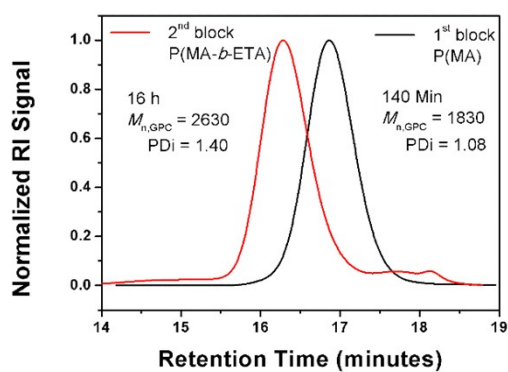


**Figure S21:** First order kinetic plot of different deactivators (0.1 equivalents) for [Monomer]:[EBiB]:[Me<sub>6</sub>TREN]=10:1:0.19, **a)** using ethyl acrylate and **b)** ethyl thioacrylate.

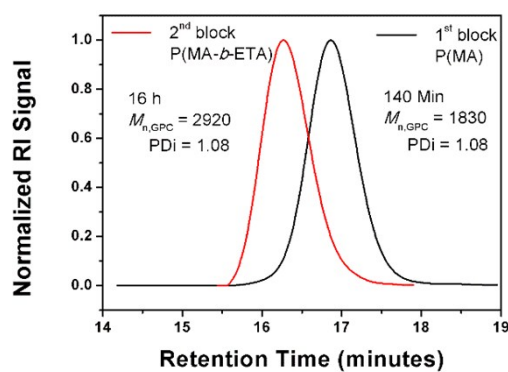


**Scheme S6:** Block copolymers of MA and ETA obtained *via* conventional chain extension (**P29**) and additional FeBr<sub>2</sub>/Me<sub>6</sub>TREN (**P31**).

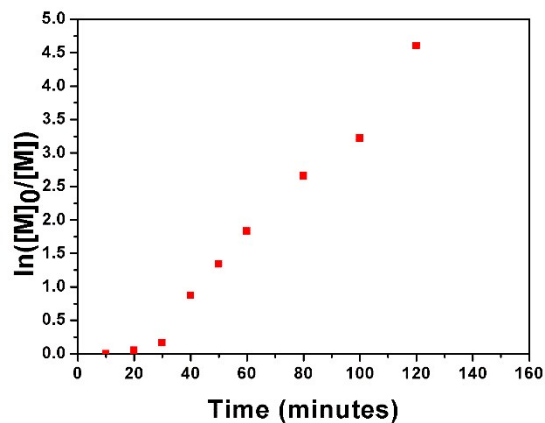
a)



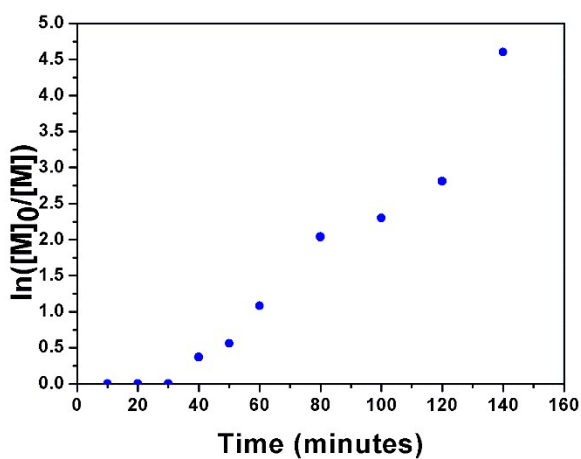
b)



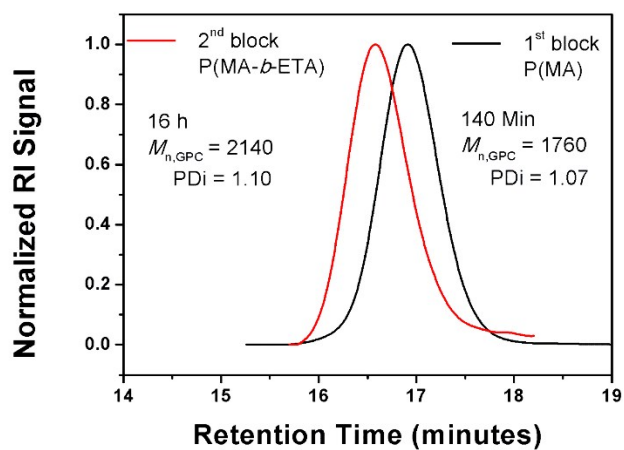
**Figure S22:** Overlay of the GPC traces for **a)** P28 and P29, and **b)** P28 and P30.



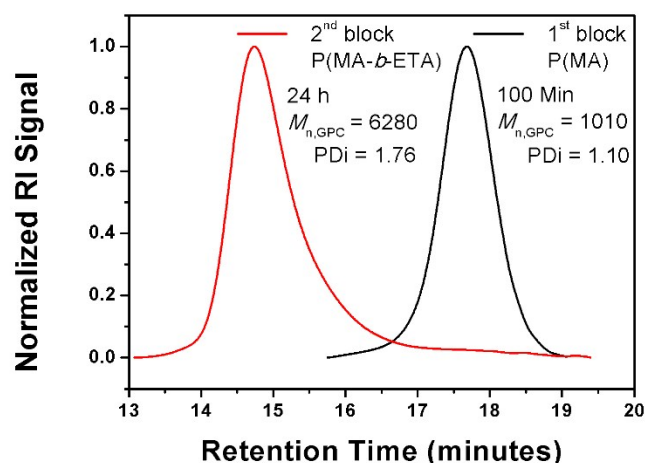
**Figure S23:** First order kinetic plot for the polymerisation of MA (**P28**).



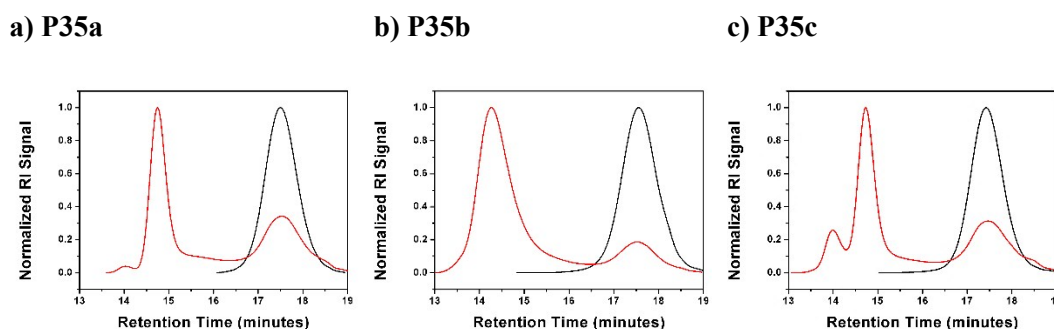
**Figure S24:** First order kinetic plot for the polymerisation of MA (**P29**).



**Figure S25:** Overlay of the GPC traces for **P31** (black) and **P32** (red).



**Figure S26:** Overlay of the GPC traces for **P32** (black) and **P33** (red).



**Figure S27:** Overlay of the GPC traces for **a) P34a** and **P35a**, **b) P34b** and **P35b**, and **c) P34c** and **P35c**.

**Table S7:** Overview of the obtained GPC results for the synthesis of **P36** and its amidation product **P37**.

Entry	$M_{n,theo}$ (g/mol)	$M_{n,GPC}^{[b]}$ (g/mol)	PDI <sup>[b]</sup>	Composition
<b>P36</b> 1 <sup>st</sup> block	1920	1540	1.10	P(MA) <sub>20</sub>
<b>P36</b> 2 <sup>nd</sup> block	2960	2390	1.20	P(MA <sub>20</sub> - <i>b</i> -ETA <sub>9</sub> )
<b>P37</b>	3190	3150	1.20	P(MA <sub>20</sub> - <i>b</i> -ETA <sub>4</sub> - <i>r</i> -BzAm <sub>5</sub> )

<sup>[a]</sup> Conversion measured by <sup>1</sup>H NMR spectroscopy. <sup>[b]</sup> THF eluent, linear PMMA standard.