ELECTRONIC SUPPORTING INFORMATION

SET-LRP of acrylates catalyzed by a 1 penny copper coin

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1   Materials

Monomers (MA, EA, eDEGA, OEGA$_{480}$), 2-ethyl isobromobutyrate (EBiB, 98%), Triethylamine (TEA, ≥99%), DMSO and other chemicals were obtained from Sigma Aldrich at highest purity available. The 1 penny coins were used as received from the Royal Mint. All monomers were passed over a short column of basic aluminium oxide to remove the inhibitor prior to use.

Tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN)[1,2] and PE-Br$_4$ initiator[3] were synthesized according to literature procedures and stored at 4°C prior to use. Conversion was calculated by comparing the change of the monomer:mesitylene integrals ratio of a desired time, with the monomer:mesitylene integrals ratio of the t = 0 sample taken 5 minutes prior to polymerization initiation with a degassed syringe. The respective surface area of a copper wire was calculated via Equation 1:

$$A_{cylinder} = 2\pi r^2 + 2\pi rh \qquad \text{(Eq. 1)}$$

The authors declare that no financial interest was gained from this work. Defacing or destroying British currency was under no circumstance intended or was expected in any procedure described. The coins were used only for research purposes. The coin retains throughout every stage of experimentation its original condition. Pictures before and after the HCl wash; and after the polymerization are depicted below in Image S1.

2   Instruments and analysis

NMR Spectroscopy

Proton nuclear magnetic resonance (^{1}HNMR) spectra were recorded on a Bruker AV III 400 in $CDCl_3$ at 303 K. All samples taken were immediately diluted with $CDCl_3$ for analysis.

Gas Chromatography

Gas chromatography – flame ionisation detection (GC-FID) analysis was performed using Agilent Technologies 7820A. An Agilent J&W HP-5 capillary column of 30 m x 0.320 mm, film thickness 0.25 µm was used. The oven temperature was programmed as follows: 40 °C (hold for 1 minute) increase at 30 °C min^{-1} to 300 °C (hold for 2.5 minutes). The injector was operated at 250 °C and the FID was operated at 320 °C. Nitrogen was used as carrier gas at a flow rate of 6.5 mL min-1 and a split ratio of 1:1 was applied. Chromatographic data was processed using OpenLab CDS ChemStation Edition, version C.01.05. Conversions were obtained by the comparing the integral of the monomer with the solvent.

Gel permeation chromatography

Gel permeation chromatography (GPC) measurements were conducted on an Agilent 1260 infinity system operating in THF with TEA (2% v/v) and equipped with refractive index detector and variable wavelength detector, 2 PLgel 5 µm mixed-C columns (300×7.5mm), a PLgel 5 mm guard column (50x7.5mm) and an autosampler. The instrument was calibrated with linear narrow poly(methyl methacrylate) standards in range of 550 to 46890 g/mol. All samples were passed through neutral aluminium oxide to remove any catalyst residues and filtered using 0.2 µm Nylon 66 filters before analysis.

MALDI-ToF MS

Matrix assisted laser desorption/ionisation – time of flight mass spectroscopy (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, ≥98%) as matrix (30 mg·mL−1), potassium trifluoroacetate (KTFA) as cationisation agent (10 mg·mL⁻¹) and sample (10 mg·mL−1) were mixed together in a 9:1:1 volume ratio for a total volume of 75 µL. 2 µL 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.

3 Synthesis

3.1 Synthesis of Pentaerythritol tetrakis(2-bromoisobutyrate) (PE-Br₄)

Into a 500 mL round-bottom flask, 100 mL of THF (dried over MgSO4 and filtered prior to addition), 12 g (0.12 mol) of triethylamine (TEA) and 3.7 g (27 mmol) of pentaerythritol (PE) were successively added and placed in an ice bath to be cooled down to 0°C. Then, a solution containing 26 g (0.12 mol) of α-bromoisobutyryl bromide (BiBB) and 40 mL dry THF was prepared and added dropwise under moderate stirring. The mixture was allowed to heat up to room temperature and stirred overnight. The mixture was transferred into a 1 L separatory funnel containing 300 mL of ether and successively extracted with 200 mL of H_2O, 200 mL of saturated aqueous $NaHCO_3$ (3x) and 200 mL of H_2O. The organic phase was dried over $MgSO_4$ and filtered and dried *in vacuo*. The crude product was redissolved and passed through a silica column using EtOAc:Hexane (1:9, *v/v*) as eluent. The eluent was removed and a white powder was obtained by crystallizing twice from diethyl ether (11.2 g, 57 %).

^{1}H NMR (CDCl₃, 400 MHz) δ: 4.33 (s, 8H, C-**CH₂**-O), 1.94 (s, 24H, C-**(CH₃)₂**-Br) ppm
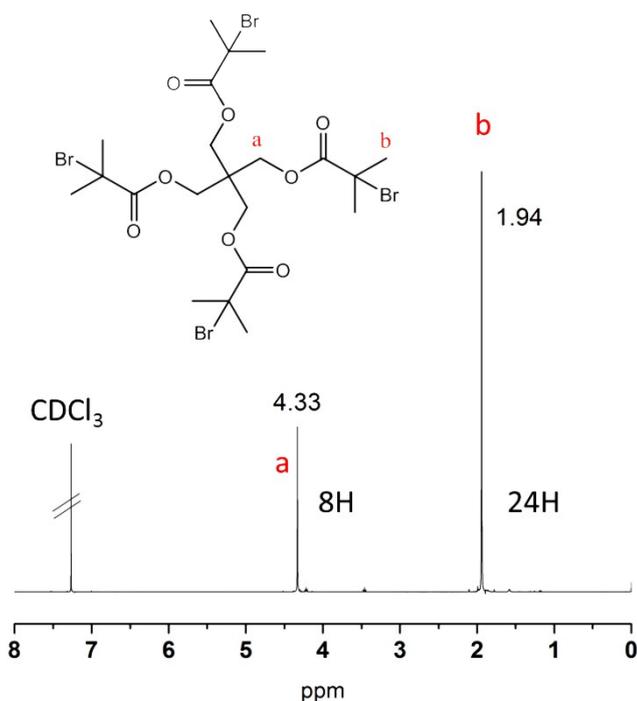
Figure S1: ^{1}H NMR spectrum of the obtained PE-Br$_4$ initiator in CDCl$_3$.

3.2   SET-LRP conditions for polymers P1-P10

For a typical polymerization, CuBr$_2$ (9.2 mg, 0.04 mmol), DMSO, Me$_6$TREN (21 µL, 0.076 mmol), monomer (20 equiv.), mesitylene (2.5%, *v/v*) and initiator (1 equiv.) 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, a copper coin was pre-activated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper coin was then transferred to the Schlenk tube containing the polymerization mixture to start the reaction (the addition of the copper coin defines t = 0). The exact amounts of DMSO, monomer and initiator used are given in the following table (Table S1).

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Table S1: Overview of the amounts used for the polymerization of **P1**-**P13**

| Polymer		Initiator	Monomer	DMSO
		EBiB		
P1	PMA$_{20}$	61 μL	0.75 mL	3.0 mL
P2	PEA$_{20}$	61 μL	0.90 mL	3.6 mL
P3	PDEGA$_{20}$	61 μL	1.50 mL	6.0 mL
P4	POEGA$_{20}$	61 μL	3.70 mL	14.6 mL
		PE-Br$_4$		
P5	PMA$_{20}$	304.6 mg	0.75 mL	3.0 mL
P6	PEA$_{20}$	304.6 mg	0.90 mL	3.6 mL
P7	PDEGA$_{20}$	304.6 mg	1.50 mL	6.0 mL
P8	POEGA$_{20}$	304.6 mg	3.70 mL	14.6 mL
		EBiB		
P9	PEA$_{40}$	61 μL	1.50 mL	6.0 mL
P10	PEA$_{80}$	61 μL	3.00 mL	12.0 mL
		EBiB		
P11 (50 g)	PEA$_{80}$	3.40 mL	50 mL	200 mL
		EBiB		
P12	PEA$_{20}$	61 μL	0.90 mL	3.6 mL
P13	PEA$_{20}$	61 μL	0.90 mL	3.6 mL

3.3 SET-LRP conditions for polymer P11

A 200 mL DMSO containing round-bottom flask was fitted with a stirrer bar and sealed to be degassed with argon overnight at 25 °C. The next day, CuBr$_2$ (92 mg, 0.4 mmol), Me$_6$TREN (210 μL, 0.76 mmol), ethyl acrylate (50 mL, 458 mmol), mesitlyene (5 mL) and initiator (1.01 mL, 5.73 mmol) were subsequently added under a positive flow of argon. The mixture was degassed for further 2 hours. At the same time, a copper coin was pre-activated in 10 mL HCl (conc. 37%) for 20 minutes, then washed with deionised water and acetone and dried under argon. The activated copper coin was then transferred to the round-bottom flask containing the polymerization mixture to start the reaction (the addition of the copper coin defines t = 0).

3.4   SET-LRP conditions for polymers P12-P13

The polymerization was carried out as described above in section **3.1** for **P2** with identical amounts of materials used. However, instead of a copper coin, wires of 5 cm and 9.6 cm were used. The activation of the copper wires and the polymerization initiation is as described above.

4   GPC traces, ^{1}H-NMR spectra, MALDI-ToF MS spectra and experimental pictures
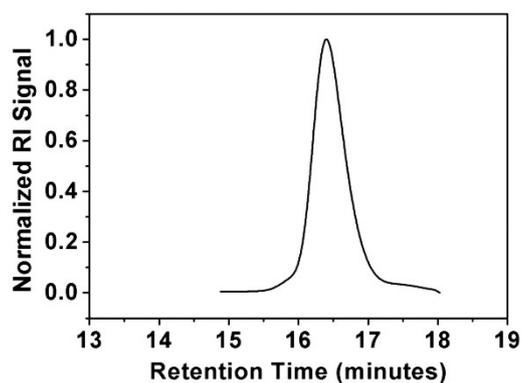
Comparison of GPC traces for different amounts of solvent used for the SET-LRP of PMA
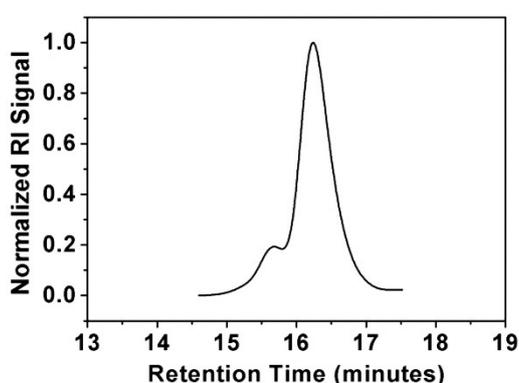
Figure S2: GPC trace obtained from the SET-LRP of MA_{40} in monomer:DMSO = 1:1 (*v/v*). $M_{n,GPC}$ = 4200 g mol^{-1}, PDI = 1.18, ρ = 97%.
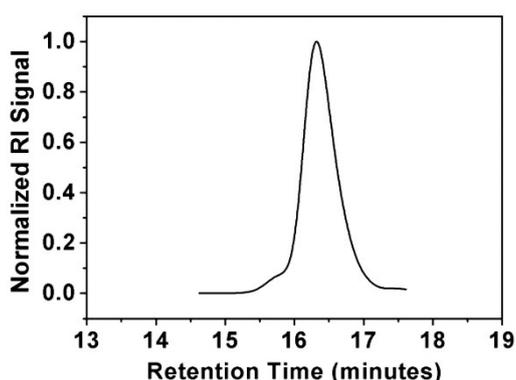
Figure S3: GPC trace obtained from the SET-LRP of MA_{40} in monomer:DMSO = 1:4 (*v/v*). $M_{n,GPC}$ = 4000 g mol^{-1}, PDI = 1.18, ρ = 97%.
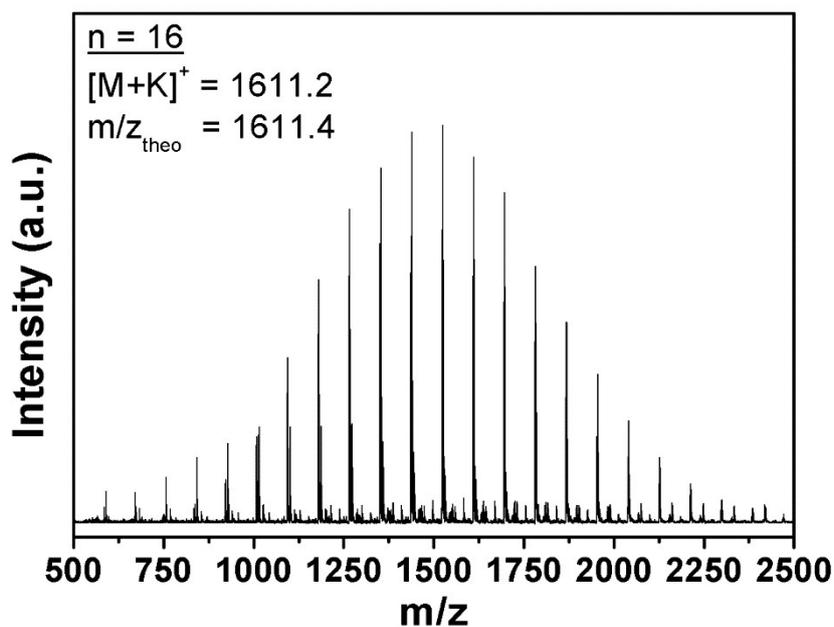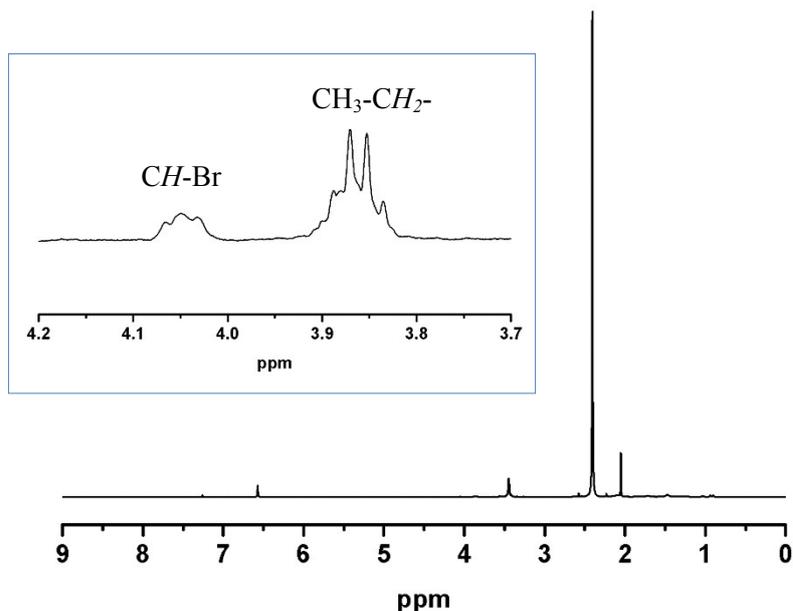
Figure S4: GPC trace obtained from the SET-LRP of MA_{40} in monomer:DMSO = 1:10 (*v/v*). $M_{n,GPC}$ = 3600 g mol^{-1}, PDI = 1.18, ρ = 87%.

Full MALDI-ToF MS spectrum of P1

Figure S5: Full MALDI-ToF MS spectrum of **P1**, PMA_{20}.
$M_{n,GPC}$ = 2000 g mol^{-1}, PDI = 1.10, ρ = 97%.

Full and zoomed ^{1}H NMR spectrum for P1

Figure S6: Full ^{1}H NMR spectrum of **P1** used to determine 81% chain end fidelity from the comparison of C*H*-Br (ω-terminus) integral between 4.09-4.00 ppm and CH$_3$-C*H*$_2$- (initiator) integral between 3.92-3.80 ppm.

M_n vs. conversion plot for the star shaped polymers P5-P8
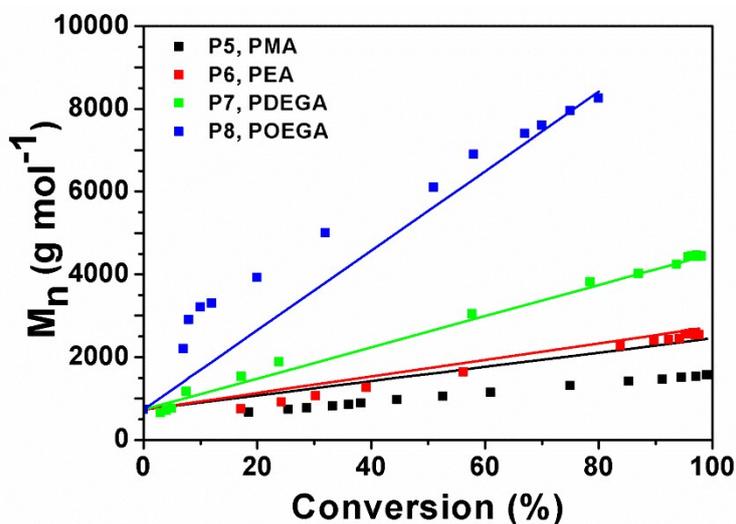
Figure S7: Evolution of M_n for **P5**-**P8** over conversion. Coloured symbols represent M_n obtained from GPC; lines represent theoretical M_n calculated from corresponding conversions.

GPC trace of the 1 penny mediated SET-LRP of PEA$_{80}$ at 50 g scale
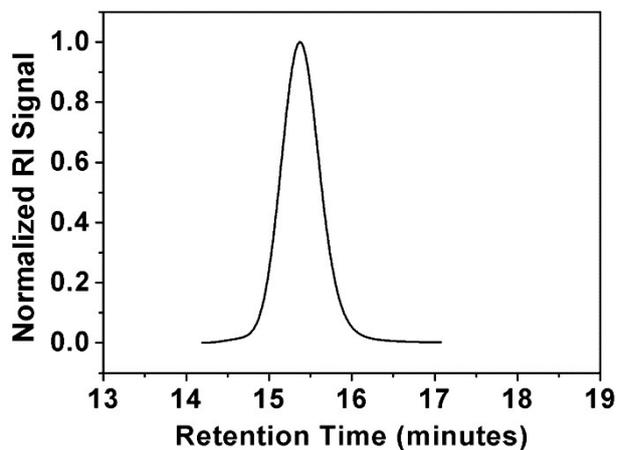
Figure S8: GPC trace obtained from the SET-LRP of PEA$_{80}$ (**P11**) at 50 g scale. $M_{n,GPC}$ = 8300 g mol^{-1}, PDI = 1.06, ρ = 100%.
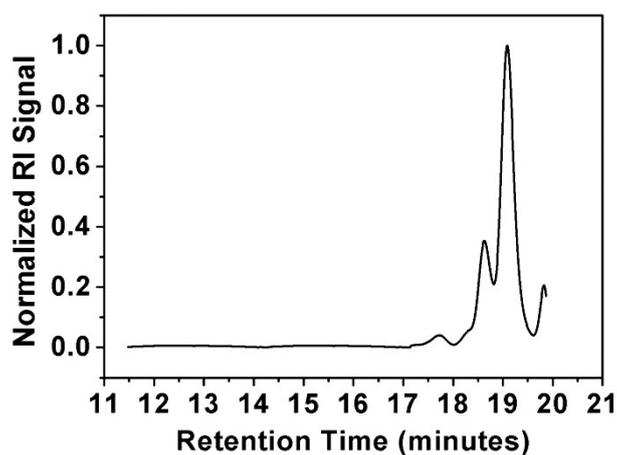
Figure S9: Normalized RI signal for the failed polymerization of DEGA, showing no polymer trace (12 – 17 minutes). Conversion was determined to be only 7% by ^{1}H NMR spectroscopy.

A)

B)

Figure S10: Comparison of the obtained GPC traces for PMA_{20}. **A)** mediated *via* 1 penny coin dated 1986 ($M_{n,GPC}$ = 2200 g mol^{-1}, PDI = 1.10, ρ = 100%) **B)** mediated *via* 1 penny coin dated 2015 ($M_{n,GPC}$ = 2000 g mol^{-1}, PDI = 1.10, ρ = 100%)

Results obtained for kinetic experiments of P1-P8

Table S2: Results obtained from kinetic experiments for **P1**.

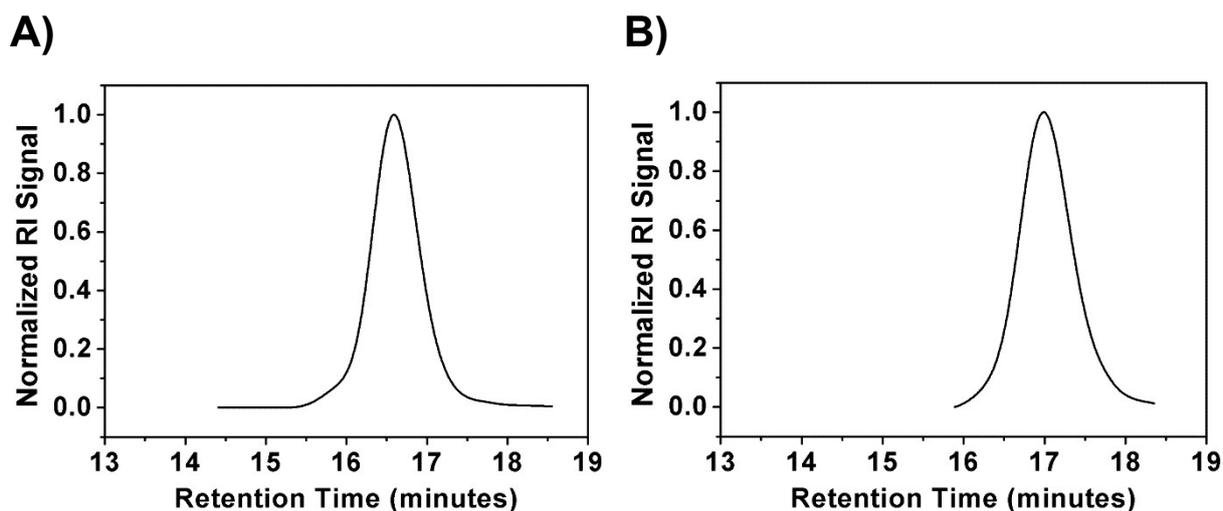| Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	480	-	-	16
10	690	-	-	28
20	1200	840	1.12	58
25	1400	1100	1.11	70
30	1500	1200	1.11	76
40	1700	1300	1.10	84
50	1800	1400	1.11	89
60	1800	1500	1.10	92
75	1800	1600	1.10	94
90	1800	1600	1.11	95
105	1900	1700	1.12	96
120	1900	1800	1.11	96
150	1900	1900	1.11	97
180	1900	2000	1.10	97

Table S3: Results obtained from kinetic experiments for **P2**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	500	-	-	18
10	600	-	-	25
15	700	-	-	27
20	800	1600	1.10	33
25	800	1900	1.09	35
30	800	2000	1.09	37
40	1000	2200	1.09	44
50	1100	2400	1.09	51
60	1200	2400	1.09	60
75	1500	2500	1.09	75
90	1700	2500	1.10	85
105	1800	2500	1.09	91
120	1900	2500	1.12	95
150	2100	2500	1.10	97
180	2200	2600	1.10	99

Table S4: Results obtained from kinetic experiments for **P3**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	800	-	-	16
10	1600	-	-	37
20	2500	1700	1.10	61
25	2500	3000	1.10	65
30	2800	3400	1.10	70
40	3200	3700	1.10	80
50	3400	3900	1.10	86
60	3600	4100	1.08	89
75	3700	4200	1.10	92
90	3800	4300	1.10	94
105	3800	4300	1.11	96
120	3900	4400	1.12	97
150	3900	4500	1.11	98
180	3900	4500	1.11	98

Table S5: Results obtained from kinetic experiments for **P4**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	0	-	-	0
10	480	-	-	3
15	770	-	-	6
20	1200	-	-	10
25	1500	-	-	14
30	1800	3000	1.08	17
40	2800	5200	1.12	27
50	6000	6800	1.06	60
60	7000	7600	1.06	71
75	7900	8100	1.07	80
90	8200	8300	1.06	83
105	8500	8700	1.07	87
120	8700	8800	1.07	89
150	8900	9100	1.07	91
180	9200	9200	1.07	93
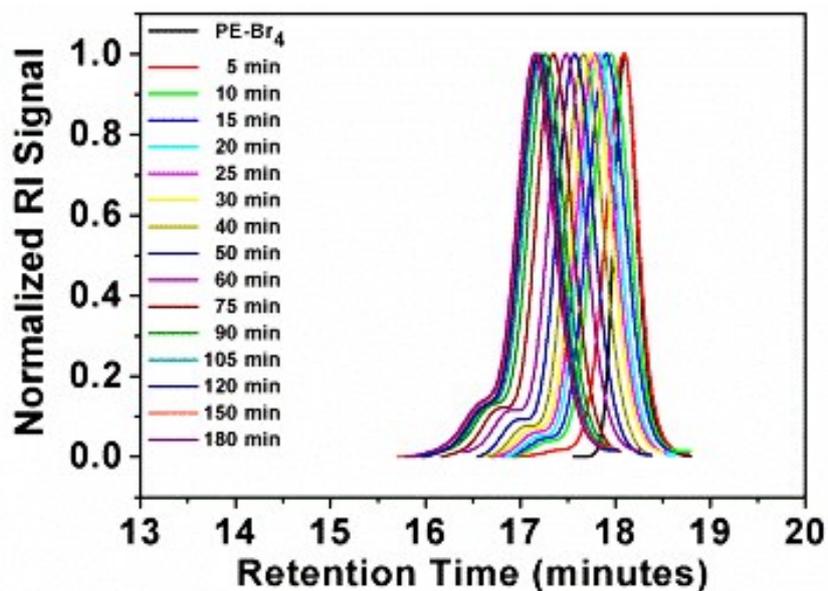
Figure S11: GPC traces of PMA (**P5**) obtained from periodic kinetic sampling.

Table S6: Results obtained from kinetic experiments for **P5**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	1000	700	1.03	18
10	1200	800	1.05	25
15	1200	800	1.05	27
20	1300	800	1.05	33
25	1300	900	1.05	35
30	1400	900	1.06	38
40	1500	1000	1.06	44
50	1600	1100	1.06	51
60	1800	1200	1.06	60
75	2000	1300	1.06	75
90	2200	1400	1.06	85
105	2300	1500	1.06	91
120	2300	1500	1.07	95
150	2400	1500	1.07	97
180	2400	1600	1.07	98
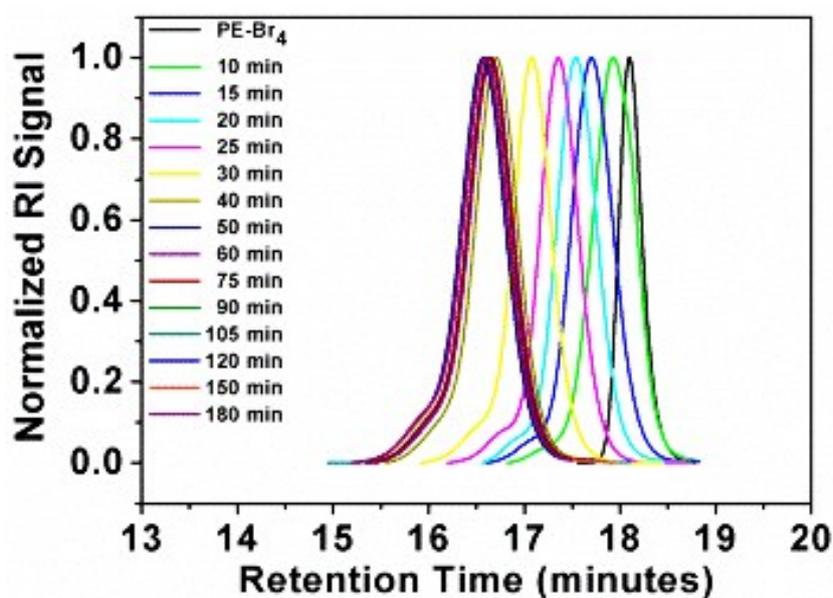
Figure S12: GPC traces of PEA (**P6**) obtained from periodic kinetic sampling.

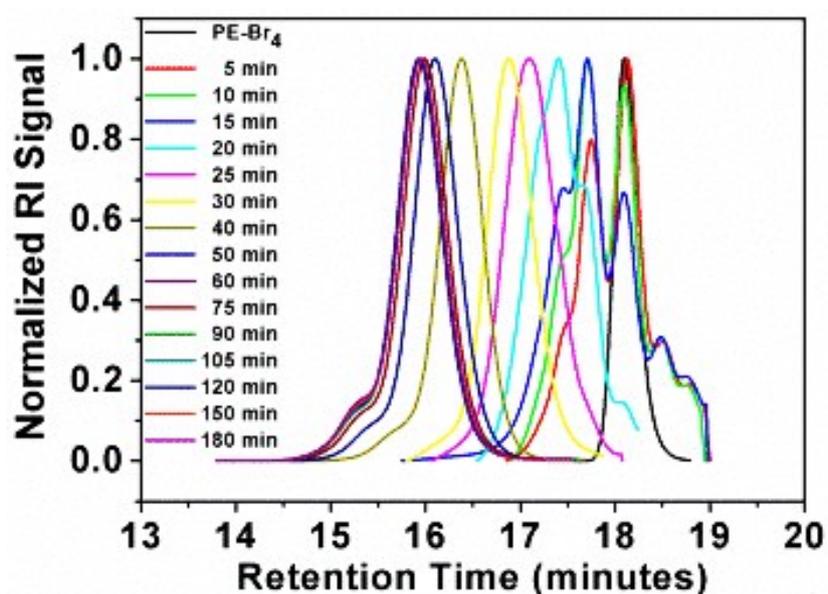**Table S7:** Results obtained from kinetic experiments for **P6**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	1000	700	1.03	15
10	1100	700	1.05	17
15	1200	900	1.06	24
20	1500	1100	1.05	40
25	1600	1300	1.06	45
30	1900	1600	1.06	56
40	2200	2300	1.07	74
50	2500	2400	1.06	90
60	2600	2400	1.06	92
75	2600	2400	1.07	94
90	2600	2600	1.08	95
105	2700	2600	1.08	96
120	2700	2600	1.08	97
150	2700	2600	1.07	97
180	2700	2600	1.08	99

Figure S13: GPC traces of PDEGA (**P7**) obtained from periodic kinetic sampling.

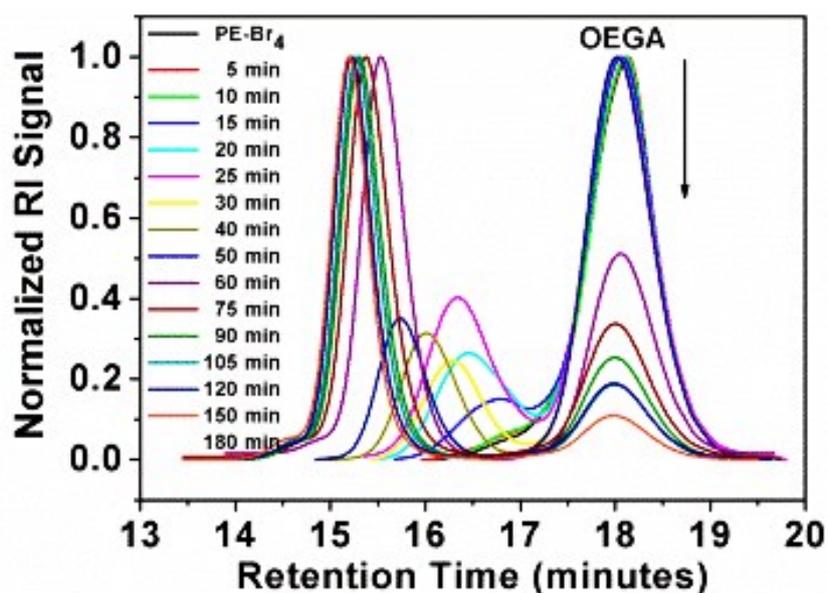**Table S8:** Results obtained from kinetic experiments for **P7**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	900	-	-	3
10	900	-	-	4
15	900	-	-	5
20	1000	1200	1.09	8
25	1400	1500	1.07	17
30	1600	1900	1.07	24
40	2900	3000	1.07	57
50	3700	3800	1.08	79
60	4000	4000	1.09	87
75	4300	4200	1.09	94
90	4300	4400	1.09	96
105	4400	4400	1.09	96
120	4400	4400	1.09	97
150	4400	4400	1.09	97
180	4400	4400	1.09	97

Figure S14: GPC traces of POEGA (**P8**) obtained from periodic kinetic sampling.

Table S9: Results obtained from kinetic experiments for **P8**.

Time (min)	$M_{n,theo}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	Conversion (%)
5	0	-	-	0
10	0	-	-	0
15	1300	-	-	6
20	1400	2200		7
25	1500	2900		8
30	1700	3200		10
40	1900	3300	1.05	12
50	2700	3900	1.06	20
60	3800	5000	1.05	32
75	5600	6100	1.06	51
90	6300	6900	1.06	58
105	7200	7400	1.06	67
120	7500	7600	1.06	70
150	7900	8000	1.05	75
180	8400	8300	1.06	80

Pictures of one of the British 1 penny coin used at different stages (from P11)

A)   **B)**   **C)**

Figure S15: A) British 1 penny before HCl wash (dirty), **B)** British 1 penny after HCl wash (clean and shiny) and **C)** British 1 penny after polymerization was stopped (still

clean and shiny). Neither **B)** nor **C)** shows any macroscopic physical damage, defacing or destruction to the coin.

5 References

1. Ciampolini, M.; Nardi, N. *Inorganic Chemistry*, **1966**, *5*, 41.
2. Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules,* **2000**, *33*, 8629.
3. K. Matyjaszewski, P. J. Miller, J. Pyun, G. Kickelbick and S. Diamanti, *Macromolecules*, **1999**, *32*, 6526.