Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

for

Poly(acrylates) *via* SET-LRP in a continuous flow reactor

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Materials and apparatus

Ethyl 2-bromoisobutyrate (EBiB, Aldrich, 98 %), copper(II) bromide ($CuBr_2$, Sigma_Aldrich, 99 %), dimethyl sulfoxide (DMSO, Aldrich, AR) were all used as received. Copper wire (diameter = 1.25 mm) was activated by washing in sulfuric acid for 10 min. Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesised according to literature procedures[1] and stored under nitrogen prior to use. ^{1}H NMR spectra were recorded on a Bruker DPX-300 or DPX-400 spectrometers in $CDCl_3$ unless otherwise stated. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane.

Size exclusion chromatography (SEC) measurements were conducted using an Agilent 1260 GPC-MDS fitted with differential refractive index (DRI), light scattering (LS) and viscometry (VS) detectors equipped with 2 x PLgel 5 mm mixed-D columns (300 x 7.5 mm), 1 x PLgel 5 mm guard column (50 x 7.5 mm) and autosampler. Narrow linear poly(methyl methacrylate) (PMMA) standards in range of 200 to 1.0 x 10^6 g mol^{-1} were used to calibrate the system. All samples were passed through 0.45 µm PTFE filter before analysis. The mobile phase was chloroform with 2 % triethylamine eluent at a flow rate of 1.0 mL min^{-1}. SEC data was analysed using Cirrus v3.3 with calibration curves produced using Varian Polymer laboratories Easi-Vials linear PMMA standards (200-4.7 x 10^5 g mol^{-1}).

At-line gel permeation chromatography (GPC) measurements were conducted using an Agilent GPC50 with differential refractive index (DRI) and light scattering (LS) detectors equipped with 1 x PLgel 3 µm mixed-E column (300 x 7.5 mm), and 1 x PLgel 5 mm guard column (50 x 7.5 mm). The same calibration procedure as above was taken place then for the 1260 GPC-MDS. The mobile phase was tetrahydrofuran at a flow rate of 1.0 mL min^{-1}. GPC data was analysed using Cirrus v3.2 with calibration curves produced using Varian Polymer laboratories Easi-vials PMMA standards (200-4.7 x 10^5 g mol^{-1}).

MALDI-TOF mass spectrometry was conducted using a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an acceleration voltage of 25 kV. Solutions in tetrahydrofuran (50 µL) of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propylidene] malonitrile (DCTB) as a matrix (saturated solution), sodium iodide as cationization agent (1.0 mg mL^{-1}) and sample (1.0 mg mL^{-1}) were mixed and 0.7 µL of the mixture was applied to the target plate. Spectra were recorded in reflectron mode calibration PEG-Me 1100 kDa.

Continuous tubular reactor setup

A 50 mL gas tight syringe was used to store the deoxygenated reaction mixture, which is connected to a piece of 1/8 ” diameter PTFE tubing. The reaction was kept in a fume hood and run at ambient

temperature (20°C) and the flow rate controlled using a syringe pump. The resultant polymer eluting from the reactor was collected and analysed in aliquots using SEC, ^{1}H NMR and MALDI-TOF MS. Samples for SEC were first percolated through a short alumina column to remove any solid impurities.

Synthesis of p(MA) using continuous flow reactor

Methyl acrylate (20 g, 2.44 mol), DMSO (20 g, 1.15 mol), Me_6TREN (0.046 g, 0.244 mmol), $CuBr_2$ (0.005 g, 24.6 mmol), and EBiB (4.08 g, 24.4 mmol) were combined in a 100 mL round bottom flask for a ratio of reactants $[MA]_0$:$[EBiB]_0$:$[Me_6TREN]_0$:$[CuBr_2]_0$ of 35 : 1 : 0.08: 0.02. The initial procedure targeted a degree of polymerization = 50, a number-average molecular weight (M_n) of 4300 g mol^{-1} and a polymer content of 50 wt% at full conversion. The feed solution was stirred and purged with nitrogen for approximately 20 min before the start of polymerization. At the same time, copper wire was "activated" by soaking in conc. H_2SO_4 for 15 minutes and threaded through the PTFE reactor. The reactor was then flushed with nitrogen for 30 minutes to minimize inhibition from the presence of oxygen in the system. The feed solution was then drawn into a 50 ml gas tight syringe, connected to the tubing and inserted into the syringe pump.

time (min)	M_n (g mol^{-1})	PDi	conv. (%)	end group fidelity (%)
300-330	1600	1.4	82	87
270-300	1600	1.3	83	81
240-270	1600	1.3	90	87
210-240	1500	1.4	90	75
180-210	1400	1.4	90	73
120-150	1400	1.4	80	82
90-120	1400	1.4	77	86
60-90	1400	1.4	65	90
0-60	1300	1.3	74	72

Table S1: Number-average molecular weight, dispersity, conversion and end group fidelity as a function of time for the SET-LRP of MA using a continuous tubular reactor with 20 cm reactor length

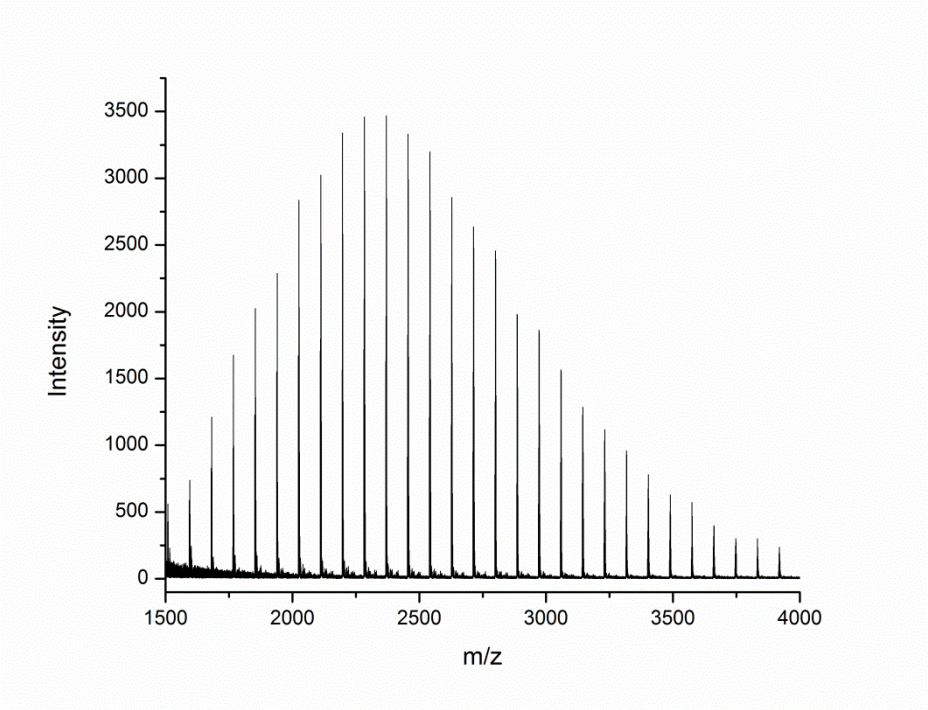

Figure S1: MALDI-TOF MS spectrum of poly(MA) (Polymer B3)

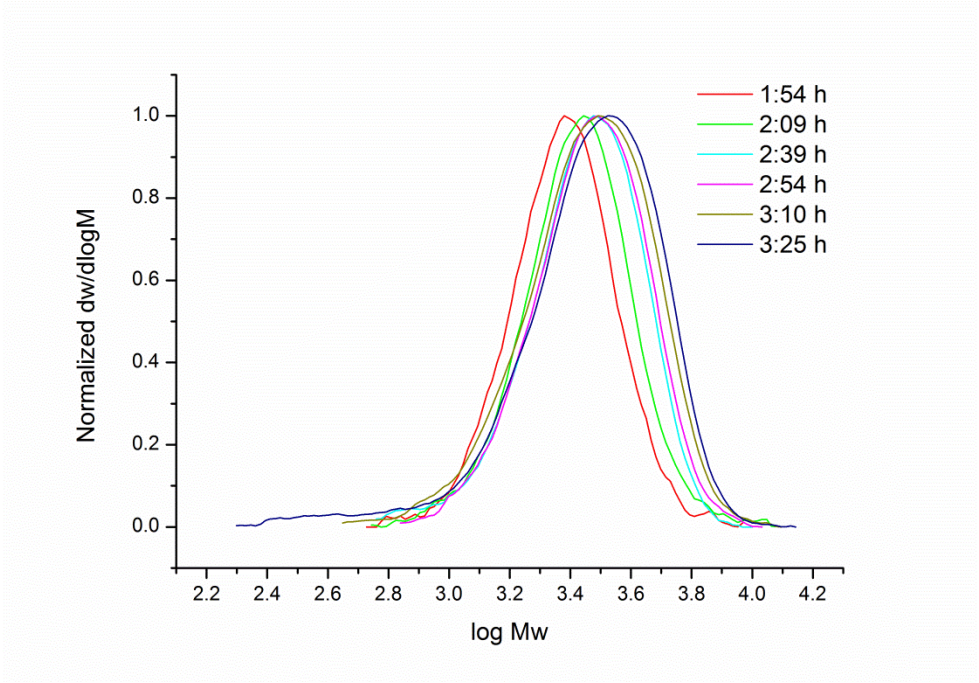

Figure S2 Molecular weight distributions for the SET-LRP of MA using continuous flow reactor monitored using at-line GPC

time (h)	M_n (g mol^{-1})	PDi
3.25	2500	1.3
3.10	2600	1.2
2.54	2500	1.2
2.39	2500	1.2
2.09	2400	1.2
1.54	2200	1.2

Table S2 M_n's and dispersities as a function of time for the SET-LRP of MA using continuous flow reactor, monitored using at-line GPC

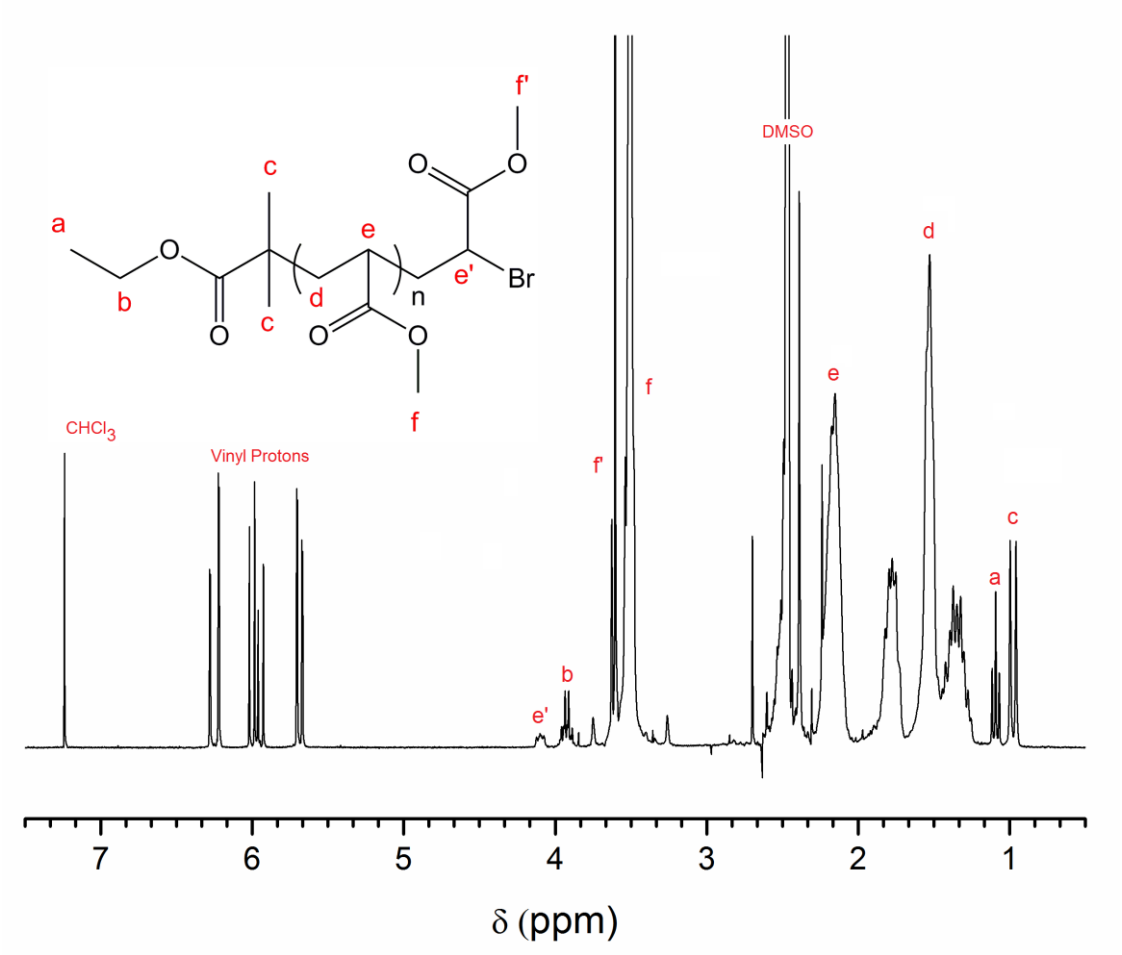

Figure S3 ^{1}H NMR spectrum of poly(MA) obtained via SET-LRP using continuous tubular reactor, non-consumed monomer seen clearly in the vinyl region. End-group fidelity (%CH-Br) is estimated by comparing the integral of the CH-Br proton (4.1 ppm, e') with the integral of the CH_2O protons (3.9 ppm b)

(1) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1966**, *5*, 41.