Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Cu(0)-RDRP of methacrylates in DMSO: the importance of the initiator

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Experimental

Materials and instrumentation

All materials were purchased from Sigma Aldrich and used as recieved unless otherwise stated. Tris[2-(dimethylamino)ethyl]-amine (Me_6TREN) was synthesized according to literature procedure[1] and stored under nitrogen and refrigerated prior to use. Cu(0) (gauge 0.25 mm) wire was purchased from Comax Engineered wires and was treated by immersion in conc. HCl prior to use. ^1H NMR spectra were recorded on Bruker AV-300, HD-300 and HD-400 MHz spectrometers at 25 °C using deuterated chloroform as the solvent. The Agilent 390-LC MDS instrument was equipped with differential refractive index (DRI) and dual wavelength UV detectors. The system was equipped with 2 x PLgel Mixed C columns (300 x 7.5 mm) and a PLgel 5 µm guard column. The eluent was either THF with 2 % TEA (triethylamine) and 0.01 % BHT (butylated hydroxytoluene) additives run at 1 ml/min at 30°C or DMF with 5 mmol NH_4BF_4 additive run at 1 ml/min at 50°C. Poly(methyl methacrylate) (Agilent Polymethyl Methacrylate EasiVials between 550 and 1.5 million g mol-1) and polystyrene standards (Agilent Polystyrene Medium EasiVials between 162 and 364,000 g mol-1) were used for calibration and fitted with a second order polynomial. Analyte samples were filtered through a GVHP membrane with 0.22 µm pore size before injection. Respectively, experimental molar mass ($M_{n\ \mathrm{SEC}}$) and dispersity ($Đ$) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software.

Methods

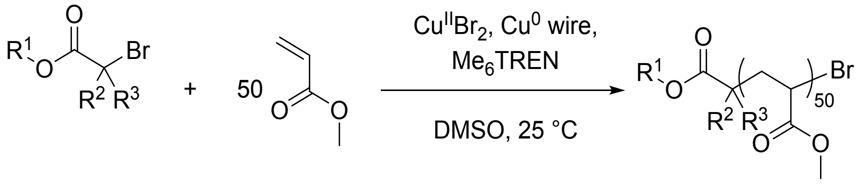
Typical Cu(0) mediated polymerization of MMA in DMSO

$Cu(II)Br_2$ (8.4 mg, 0.037 mmol, 0.05 eq.) was charged to a 25 mL glass vial and dissolved in 4 mL of DMSO. MMA (4 mL, 37.4 mmol, 50 eq.) was added and MBPA (118 µL, 0.75 mmol, 1 eq.) was carefully transferred into the reaction vessel *via* microliter syringe. Concurrently, in a separate vial, a stirrer bar wrapped with 5 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed into the reaction vessel, sealed with a rubber septum, and degassed by bubbling with nitrogen for 15 minutes in an oil bath at 25 °C. After this time a degassed aliquot of Me_6Tren (36 µL, 0.13 mmol, 0.18 eq.) was injected into the vial *via* microliter syringe. The reaction was left to proceed overnight and samples were taken and analysed via ^1H NMR and SEC.

Example of Cu(0) mediated polymerization of MMA in DMSO with online FT-NIR monitoring

$Cu(II)Br_2$ (16 mg, 71 µmol, 0.05 eq.) was charged to a 25 mL Schlenk tube and dissolved in 7.5 mL of DMSO. MMA (7.5 mL, 71 mmol, 50 eq.) was added and Me_6Tren (68 µL, 0.25 mmol, 0.18 eq.) was added *via* microliter syringe. Finally, MBPA (223 µL, 1.41 mmol, 1 eq.) was added. Concurrently, in a separate vial, a stirrer bar wrapped with 10 cm of copper wire was immersed in 37% HCl, stirred for 15 minutes, washed sequentially with water and acetone, and dried. The stirrer bar was then placed in the Schlenk tube, suspended above the reaction mixture using a magnet. The Schlenk tube was sealed using a ground glass stopper fitted with a septum through which the fibre optic FT-NIR probe was fitted. The reaction mixture was then degassed by three freeze-pump-thaw cycles, placed into an oil bath at 25 °C and the magnet removed, resulting in the stirrer bar dropping into the monomer/DMSO mixture and the reaction starting. Online monitoring of polymerizations *via* Fourier transform near-infrared (FT-NIR) spectroscopy was conducted on a Bruker vector 22/N-F spectrometer equipped with a HELLMA fibre-optic probe (3 mm) with 64 scans performed sequentially every 30 minutes between 6000 and 6300 wavenumbers. Conversions were calculated via integration of the $\gamma(=CH_2)$ absorption peak (6170 cm^{-1}), in comparison to the integration at time zero.

SEC Spectra of Poly(methyl acrylate)



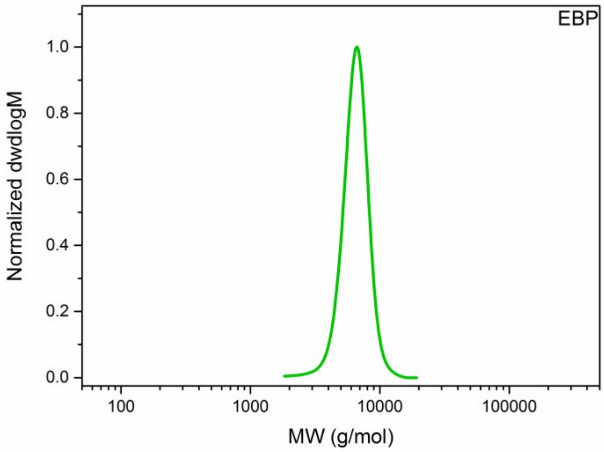


Figure S1: SEC spectra of poly(MA) synthesized using EBP initiator

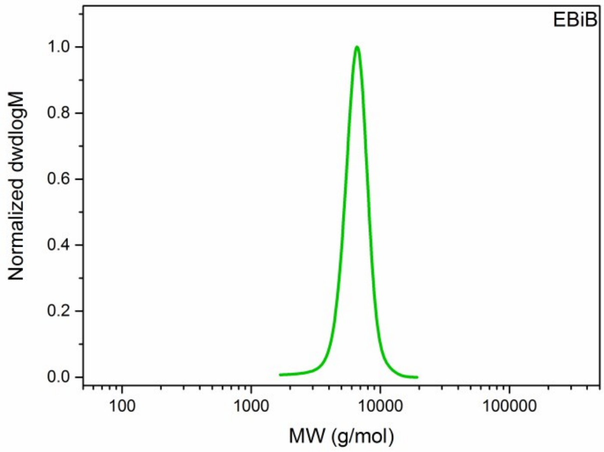


Figure S2: SEC spectra of poly(MA) synthesized using EBiB initiator

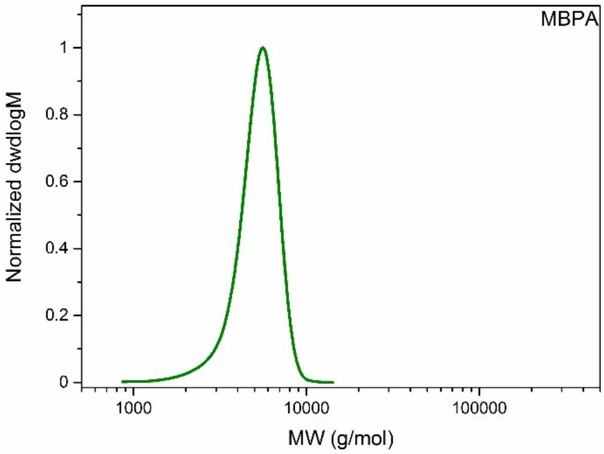


Figure S3: SEC spectra of poly(MA) synthesized using MBPA initiator

Table S1: chain extensions of poly(MA)

Entry	Initiator	Time (hours)	Conversion	$M_{n\,(Theo.)}$ ($g\ mol^{-1}$)	$M_{n\,(SEC)}$ ($g\ mol^{-1}$)	*Đ*
1	EBP	3	>99%	4500	4400	1.10
2		24	84%	9000	9200	1.10
3	MBPA	24	55%	4000	4900	1.09
4		24	23%		5800	1.10

NMR Spectra of Poly(methyl acrylate) (MBPA)

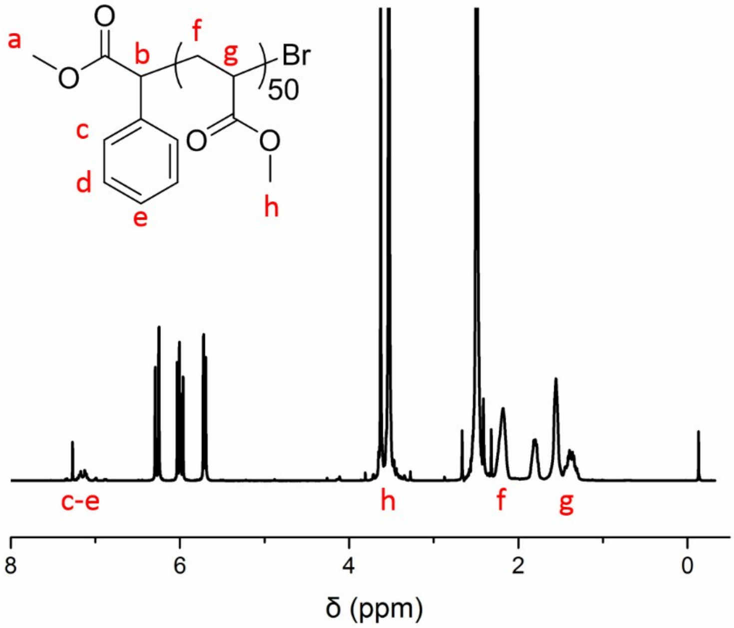


Figure S4: NMR of reaction mixture of polymerization of methyl acrylate. Conversion calculated by integration of methyl protons (h) with vinyl protons ~6 ppm.

Table S2: the effect of Cu(II)Br$_2$ concentation on PMMA synthesis

Entry	**[I]: [Cu(II)Br$_2$]: [Me$_6$Tren]**	**Time (hours)**	**Conversion**	**M$_{n (Theo.)}$ (g mol^{-1})**	**M$_{n (SEC)}$ (g mol^{-1})**	***Đ***
1	1:0:0.18	24	95	5000	9900	1.21
2	1:0.05:0.18	24	96	5000	8900	1.17
3	1:0.10:0.18	24	96	5000	7400	1.18
4	1:0.20:0.18	24	98	5200	7100	1.16
5	1:0.20:0.72	24	98	5200	11300	2.88

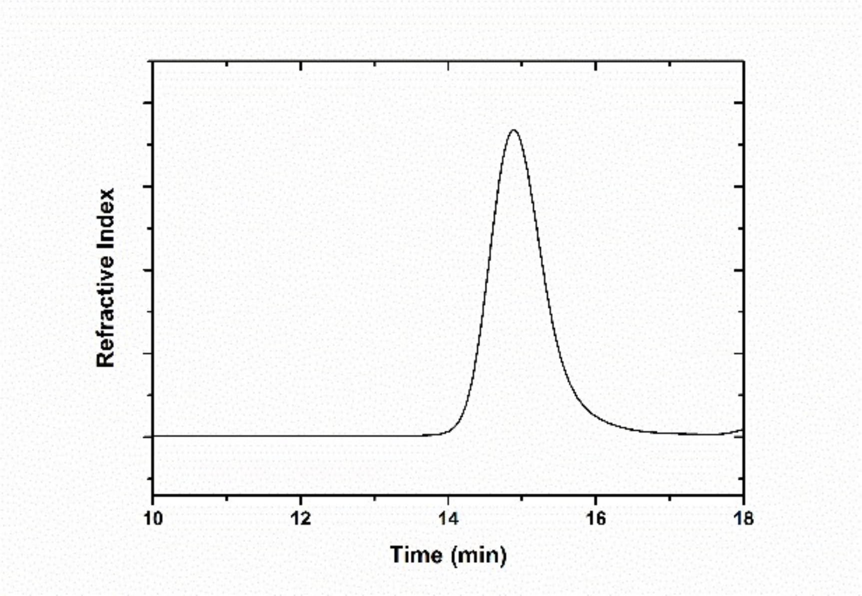


Figure 5a: SEC spectra of poly(MMA) synthesized using 0% Cu(II)Br$_2$ with respect to initiator.

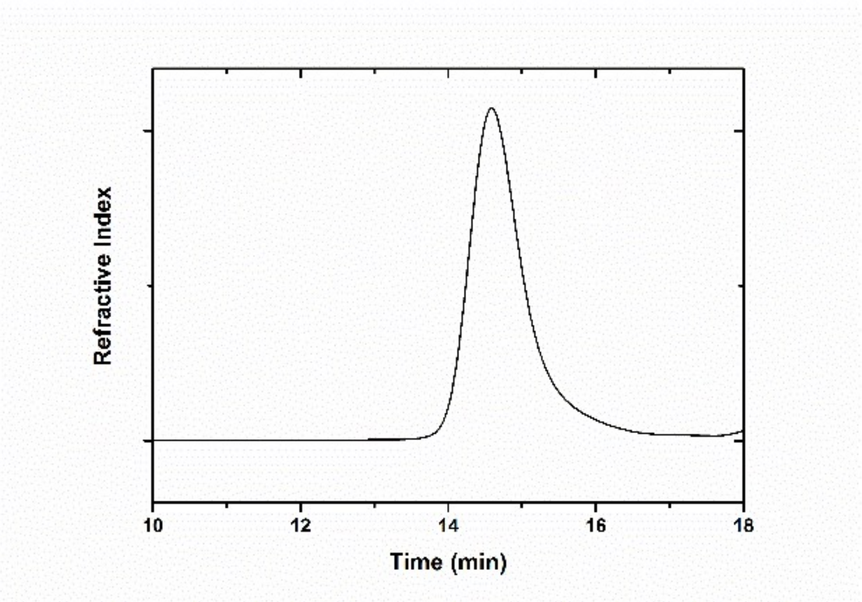


Figure 5b: SEC spectra of poly(MMA) synthesized using 5% Cu(II)Br$_2$ with respect to initiator.

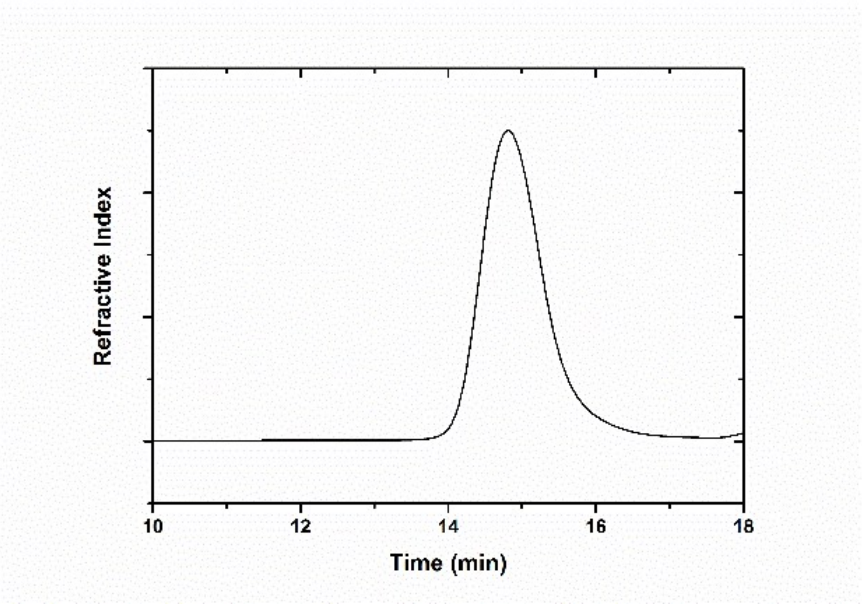


Figure 5c: SEC spectra of poly(MMA) synthesized using 10% Cu(II)Br_2 with respect to initiator.

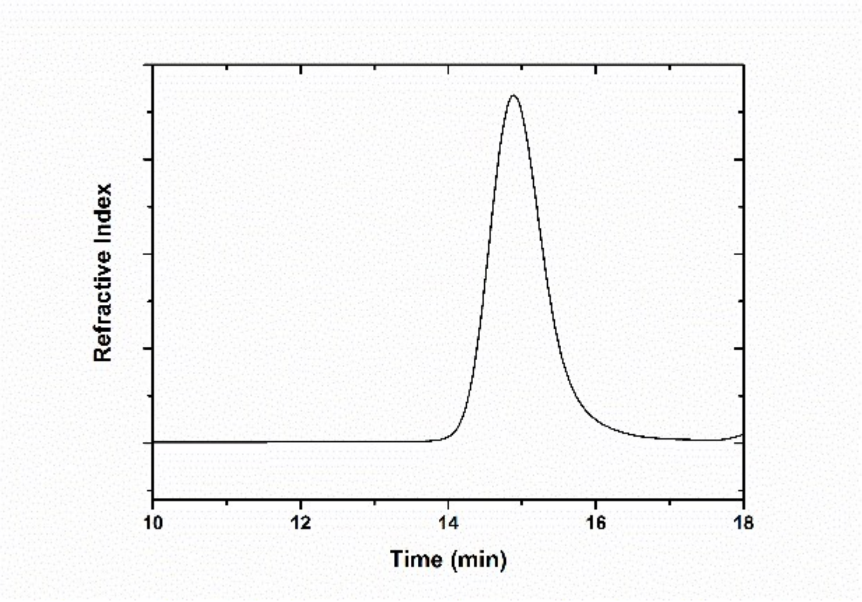


Figure 5d: SEC spectra of poly(MMA) synthesized using 20% Cu(II)Br_2 with respect to initiator.

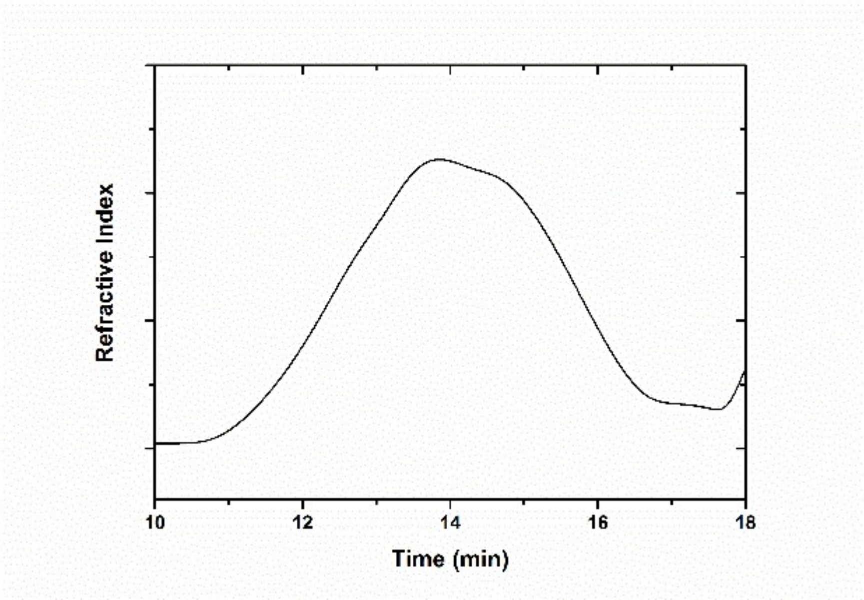


Figure 5e: SEC spectra of poly(MMA) synthesized using 20% Cu(II)Br_2 and 72% Me_6Tren with respect to initiator.

Note Figures 5a-5e were analysed on $CHCl_3$GPC at UCSB calibrated with PS standards.

NMR Spectra of Poly(methyl methacrylate) (MBPA)

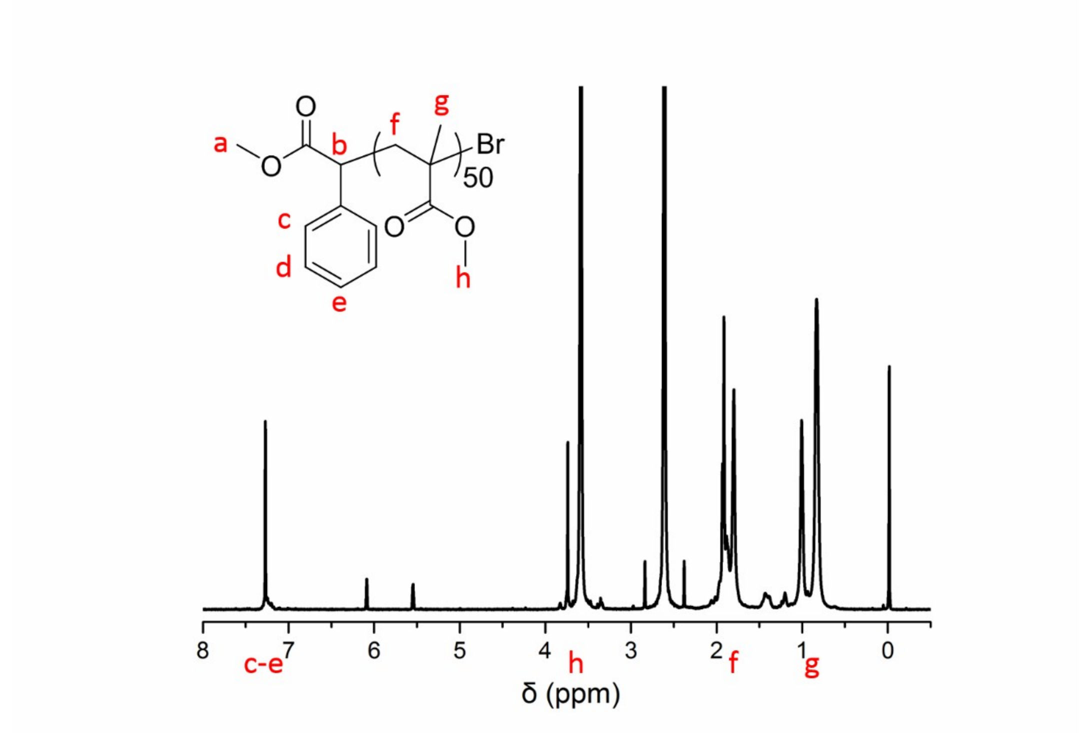


Figure S6: NMR of reaction mixture of polymerization of MMA. Conversion calculated by integration of methyl protons (h) with vinyl protons ~6 ppm.

The effect of temperature on the polymerization of MMA ($DP_n = 50$)

The polymerization of MMA under the optimized conditions was repeated at three different temperatures, in order to ascertain whether increased temperature could yield greater polymerization rates and higher conversions whilst maintaining the good degree of control over MWDs. At 50 °C it was found that the reaction proceeds much faster, with conversion found to be 65% by ^{1}H NMR after three hours, compared to just 5% at 25 °C. However after 24 hours the reaction had only reached a marginally higher conversion (94% compared to 90% at 25 °C), and furthermore the dispersity was significantly broader (*Đ =1.30* at 50 °C, compared to 1.10 at 25 °C). At 75 °C, this trend is further illustrated with conversion reaching almost 90% in 3 hours, but an even broader dispersity. All subsequent reactions were performed at ambient temperature to minimise the termination events occurring at higher temperatures.

Table S3: Polymerization of methyl acrylate using MBPA initiator with varying temperature.

Entry	Monomer	Temperature (°C)	Time (hours)	Conversion	$M_{n\ (Theo.)}$ (g mol^{-1})	$M_{n\ (SEC)}$ (g mol^{-1})	Đ
1	**Methyl Methacrylate**	25	3	5%	-	-	-
2			24	90%	4700	10800	1.10
3		50	3	65%	3400	6100	1.18
4			24	94%	4900	9900	1.30
5		75	3	86%	4500	8900	1.60
6			24	91%	4800	11200	1.50

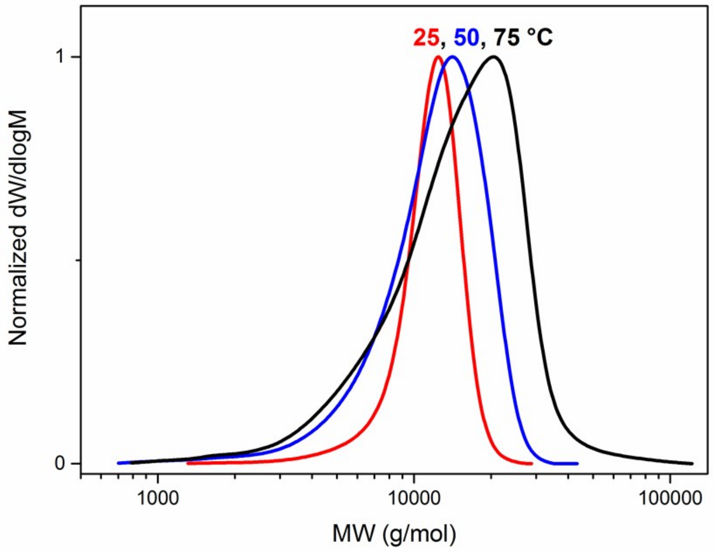


Figure S7: SEC spectra of PMMA synthesized at different temperatures

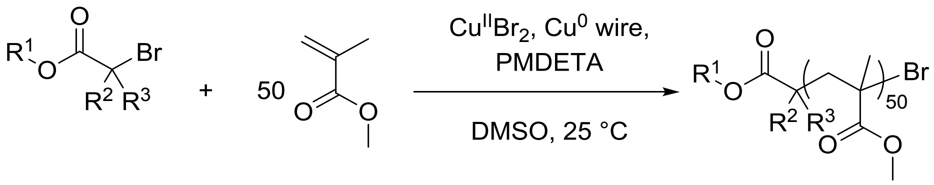
Polymerization of MMA using PMDETA as ligand (DP_n = 50)

Previous studies investigating the Cu(0) mediated polymerization of methacrylate monomers have highlighted the choice of ligand as an important parameter for achieving a desired controlled process.[2, 3] With this in mind polymerizations of MMA with the three initiators described previously were repeated using PMDETA as the ligand. As can be seen from table 2, EBP and EBiB in conjunction with PMDETA yielded higher conversions, but molecular weight distributions were similarly broad to reactions carried out utilizing Me_6Tren. For the phenyl acetate derived initiator, MBPA, conversion is similar to the reaction with Me_6Tren, however, there is interestingly a marked increase in dispersity observed (1.40 compared to 1.10), with noticeable low molecular weight tailing observed in the SEC trace, suggestion termination events were occurring. This termination has previously been reported by Voit and coworkers who illustrated termination in the ATRP of MMA when PMDETA was utilised as the ligand. This shows that ligand selection is important in combination with the highly active MBPA initiator, ([MBPA]:[Cu(II)Br_2]:[Me_6Tren]:[MMA] = [1]:[0.05]:[0.18]:[50]) to synthesize poly(methyl methacrylate) to high conversions whilst maintaining narrow molecular weight distributions.

Table S4: MMA polymerizations with different initiators and PMDETA as the ligand.

Entry	Initiator	Time (hours)	Conversion	$M_{n\ (Theo.)}$ (g mol^{-1})	$M_{n\ (SEC)}$ (g mol^{-1})	Đ
1	EBP	24	86%	4500	11300	2.04
2	EBiB	24	84%	4400	7400	1.52
3	MBPA	24	90%	4700	11500	1.40

SEC Spectra of PMMA synthesized using PMDETA



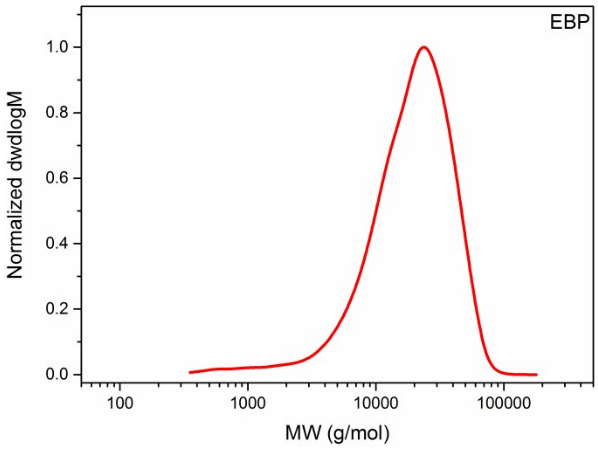


Figure S8: SEC spectra of PMMA synthesized using EBP initiator with PMDETA

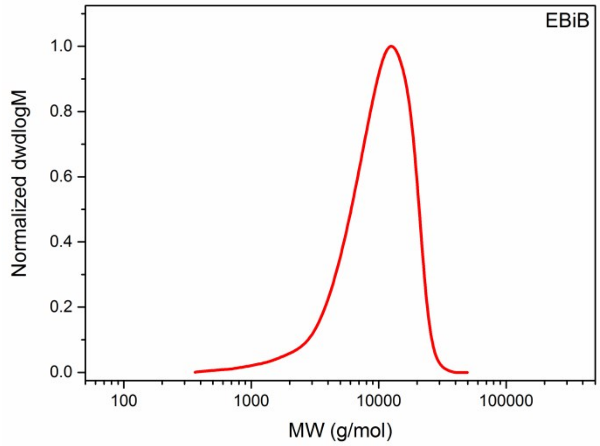


Figure S9: SEC spectra of PMMA synthesized using EBiB initiator with PMDETA

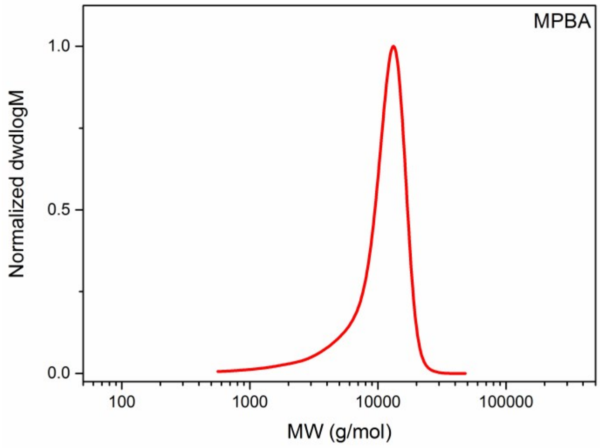


Figure S10: SEC spectra of PMMA synthesized using MBPA initiator with PMDETA

Photographs of FT-NIR spectrometer and experimental set up.

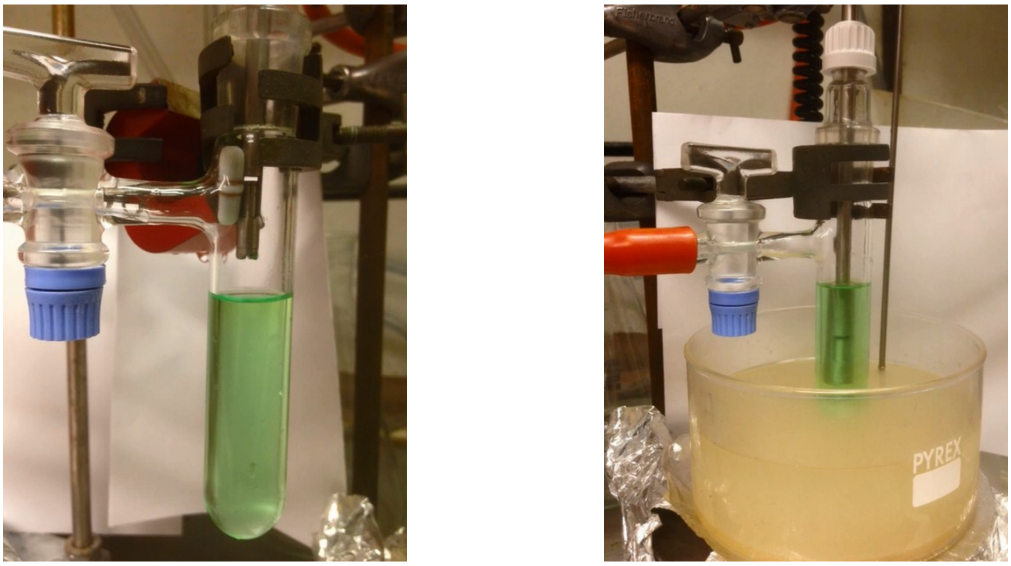


Figure S11: Left: photograph showing experimental set-up for NIR monitoring of polymerization, stirrer bar with copper wire is suspended by a magnet during degassing. Right: Experimental set-up showing probe immersed in reaction mixture.

Chain extension of $PMMA_{50}$ with MMA (25 eq.)

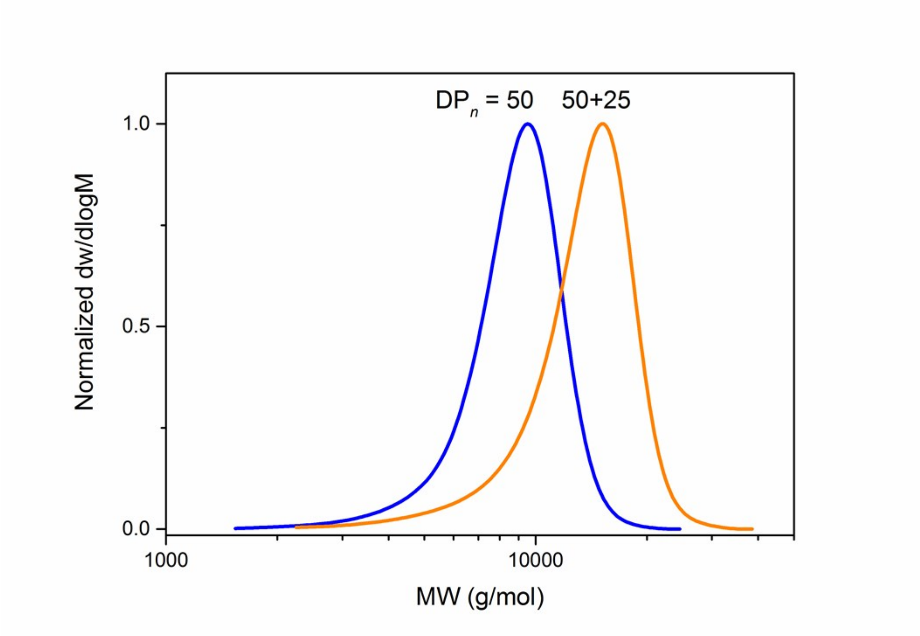
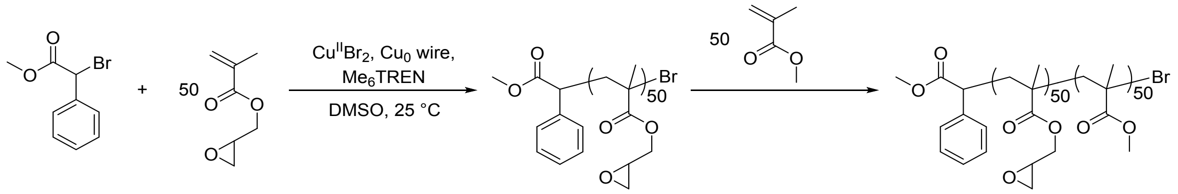


Figure S12: SEC trace of in-situ chain extension of PMMA.

Table S5: Data for in-situ chain extension from figure S11.

Entry	Targeted DP$_n$	Time (hours)	Conversion	M$_{n\ (Theo.)}$ (g mol^{-1})	M$_{n\ (SEC)}$ (g mol^{-1})	Đ
1	50	18	90%	4700	8200	1.10
2	25 (75 total)	18	91%	7700	12400	1.13

Chain extension of PGMA with MMA



Scheme S1: One-pot block copolymerization of PGMA-(b)-PMMA

SEC spectra of functional poly(methacrylates)

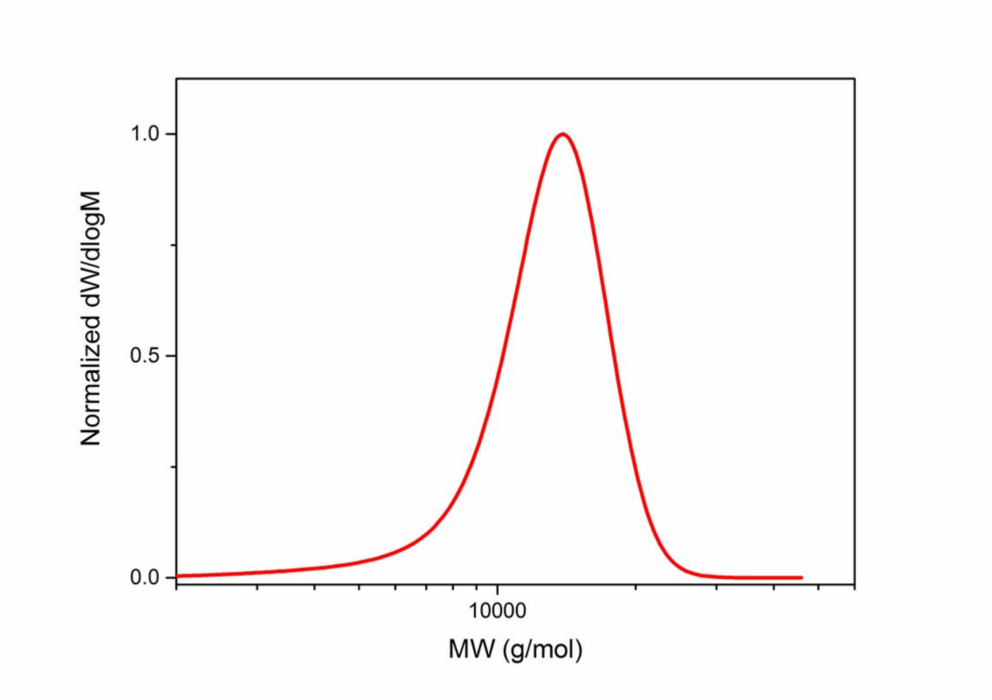


Figure S13: SEC of poly(ethyl methacrylate)

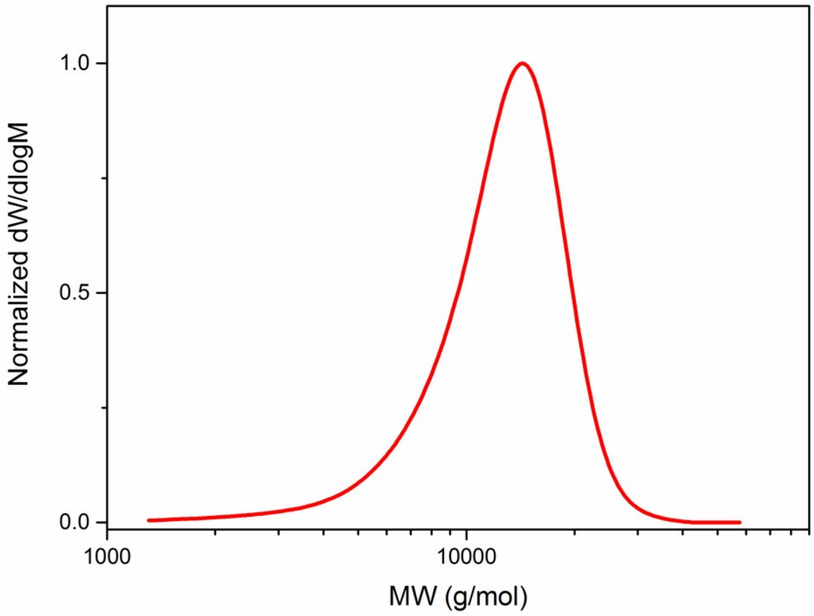


Figure S14: SEC of poly(benzyl methacrylate)

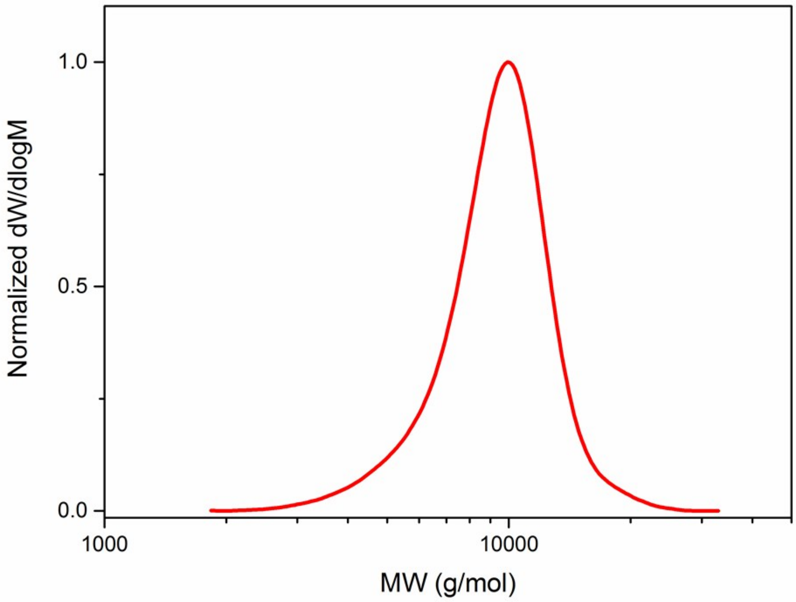


Figure S15: SEC of poly(glycidyl methacrylate)

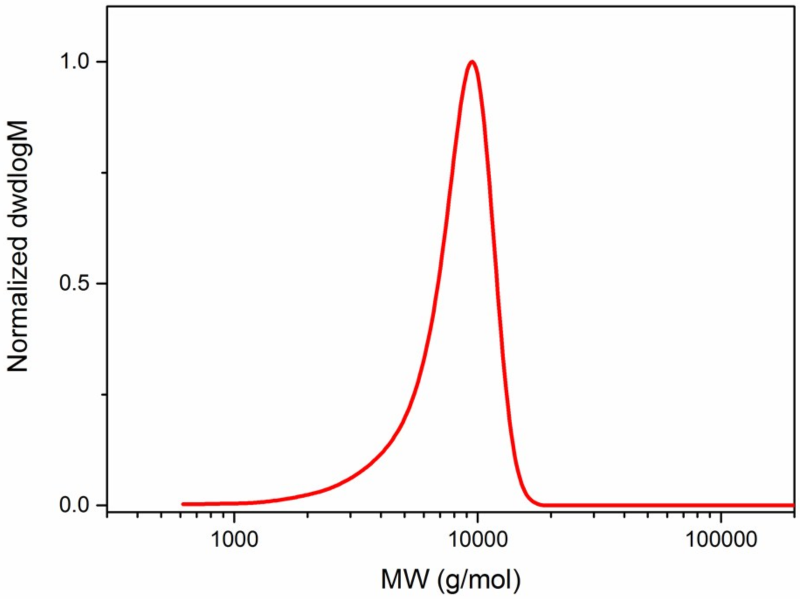


Figure S16: SEC of poly(ethylene glycol methyl ether) methacrylate

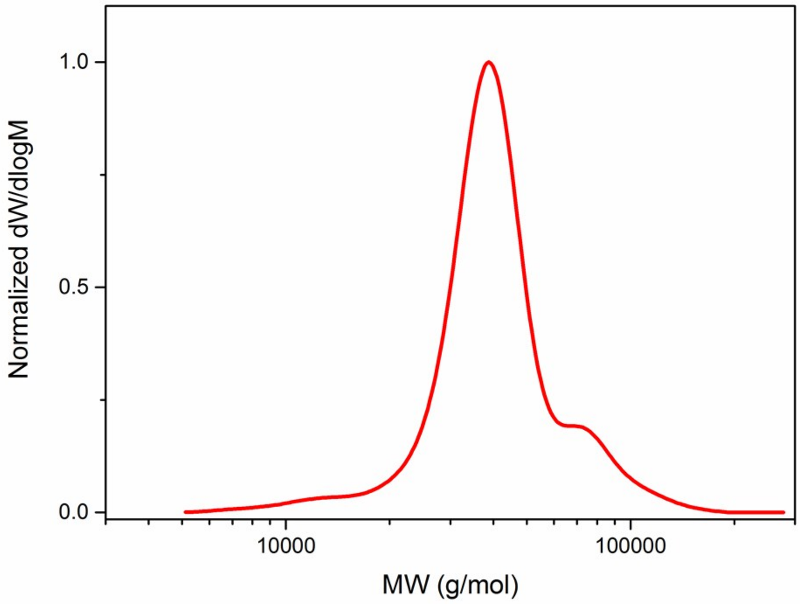


Figure S17: SEC of PEG methacrylate

[1] M. Ciampolini, N. Nardi, *Inorganic Chemistry* **1966**, *5*, 41.
[2] A. Anastasaki, C. Waldron, P. Wilson, R. McHale, D. M. Haddleton, *Polymer Chemistry* **2013**, *4*, 2672.
[3] A. Simula, V. Nikolaou, F. Alsubaie, A. Anastasaki, D. Haddleton, *Polymer Chemistry* **2015**.