Supporting Information

for

The importance of ligand reactions in Cu(0)-mediated living radical polymerisation of acrylates

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Materials and apparatus

n-Butyl acrylate (BA), methyl acrylate (MA), ethyl 2-bromopropionate and Cu(II)Br$_2$ were purchased from Aldrich and used as received. Me$_6$-Tren[1] and EbBiB[2] were synthesised according to previously reported literature. Cu(0) (gauge 0.25 mm) wire was purchased from Comax Engineered wires and was treated by immersion in conc. HCl prior to use. Solvents were purchased from Fisher Scientific and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300, DPX-400 or DRX-500 spectrometers in CDCl$_3$ unless otherwise stated. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Size exclusion chromatography (SEC) measurements of were conducted using an Agilent 1260 GPC-MDS fitted with differential refractive index (DRI), light scattering (LS) and viscometry (VS) detectors equipped with 2 × PLgel 5 mm mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm) and autosampler. Narrow linear poly(methyl methacrylate) standards in range of 200 to 1.0×10^6 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. SEC data was analyzed using Cirrus v3.3 with calibration curves produced using Varian Polymer laboratories Easi-Vials linear poly(methyl methacrylate) standards (200-4.7×10^5 g/mol). Infrared absorption spectra were recorded on a Bruker VECTOR-22 FTIR spectrometer using a Golden Gate diamond attenuated total reflection cell. High Resolution Mass Spectrometry (HR-MS) were conducted on a Bruker UHR-Q-ToF MaXis with electrospray ionization. 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 accelerating 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) and sample (1.0 mg/mL) were mixed, and 0.7 μL of the mixture was applied to the target plate. Spectra were recorded in reflectron mode calibrating PEG-Me 1100 kDa.

General procedure for the homo-polymerisation of MA

Filtered MA (2 mL, 22.2 mmol, 35 eq), EBiB (94 μL, 0.6 mmol, 1 eq), CuBr$_2$ (6.7 mg, 30 μmol, 0.05 eq), Me$_6$-Tren (0.09-0.18 eq) and DMSO (2 mL) were degassed by purging with nitrogen for 30 mins, during which time, Cu(0)-wire (5 cm) was immersed in conc. HCl. The

Cu-wire was removed and thoroughly rinsed with acetone and water then air dried. Polymerisation commenced upon addition of the Cu-wire to the degassed reaction mixture. Samples were taken periodically and conversions were measured using ^{1}H NMR and GPC analysis. Upon completion, the reaction mixture was diluted with THF then passed through an alumina column to removed traces of remaining copper and ligand. The filtrate was concentrated and the polymers isolated by precipitation into MeOH/H_2O mixtures.

General procedure for *in-situ* chain extension reactions

The general procedure for MA homo-polymerisation was followed. Upon detection of >99% conversion a 1 : 1 mixture of degassed MA and DMSO was added to the reaction mixture *via* degassed syringe. Where necessary, additional ligand (0.18 eq) was added to the monomer/solvent mixture prior to degassing and additional Cu(0)-wire (5 cm) was activated by immersion in conc. HCl. Samples were taken periodically and conversions were measured using ^{1}H NMR and GPC analysis.

General procedure for the telechelic polymerisation of BA

Filtered BA (2 mL, 14.0 mmol, 35 eq), EbBiB (144 mg, 0.4 mmol, 1 eq), CuBr$_2$ (4.4 mg, 20 μmol, 0.05 eq), Me$_6$-Tren (0.09-0.36 eq) and DMSO (2 mL) were degassed by purging with nitrogen for 30 mins, during which time, Cu(0)-wire (5 cm) was immersed in conc. HCl. The Cu-wire was removed and thoroughly rinsed with acetone and water then dried. Polymerisation commenced upon addition of the Cu-wire to the degassed reaction mixture. Samples were taken periodically and conversions were measured using ^{1}H NMR and GPC analysis. Upon completion, the reaction mixture was diluted with THF then passed through an alumina column to remove traces of remaining copper salts and ligand. The filtrate was concentrated and the pure polymers were isolated by precipitation into MeOH/H_2O mixtures.

General procedure for the quaternisation of EBP

EBP (1 eq) and Me$_6$-Tren (1 eq) were dissolved in d$_6$-DMSO and placed in an NMR tube. Reaction progress was followed by ^{1}H NMR and ^{13}C NMR; δ (^{1}H/^{13}C 400/100 MHz) Figure S3; υ (cm^{-1}) 2955, 2826, 1733, 1624, 1467, 1204, 1023, 1004, 762; HR-ESI-MS C$_{17}$H$_{39}$N$_4$O$_2^+$ found 331.3068, expected 331.3068.
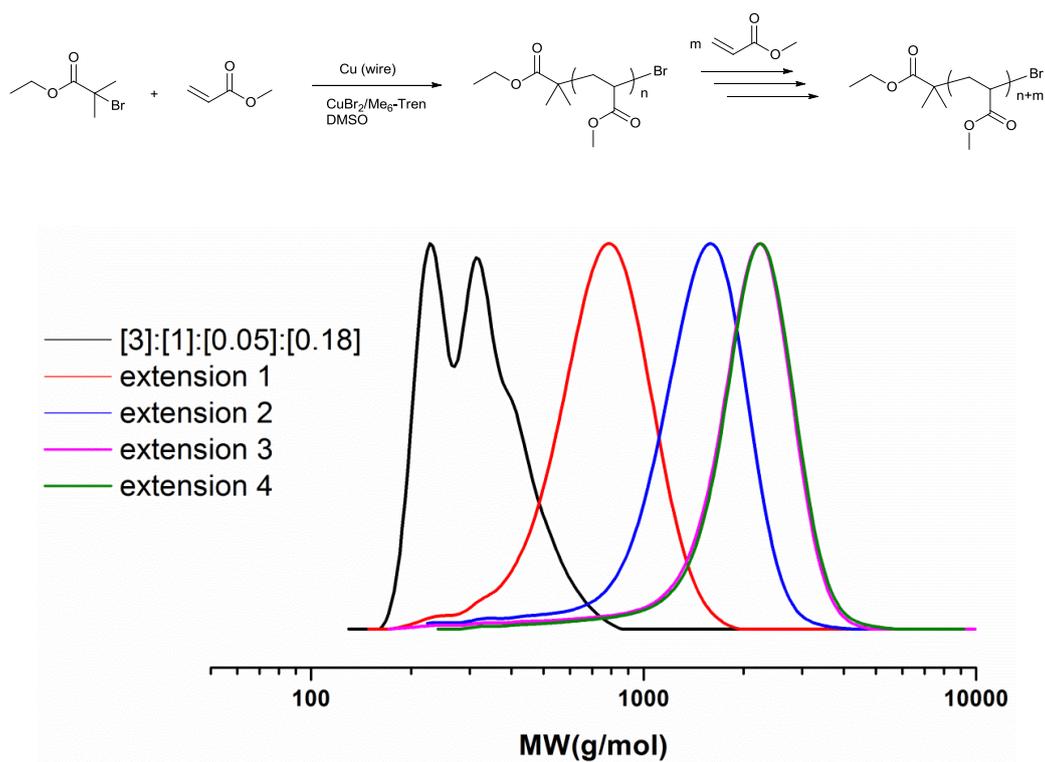
Supplementary Figures

Fig S1. *In-situ* chain extension of PMA which becomes dormant after 3 successful extensions.

expected mass(Na$^+$):2283.9
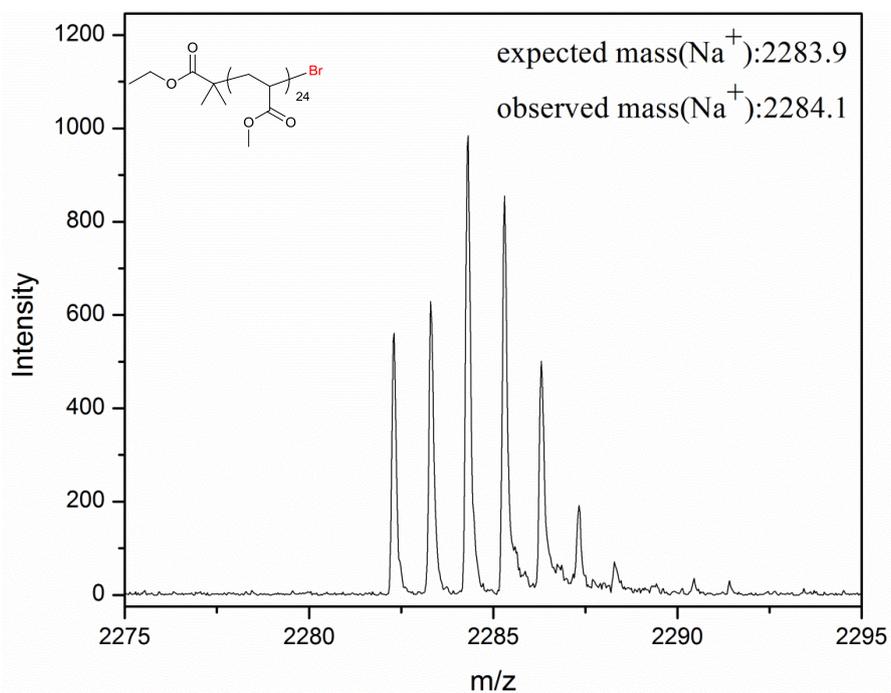
observed mass(Na$^+$):2284.1

Fig S2. MALDI-TOF analysis of the 'dormant' polymer after four attempted chain extensions which indicates high end-group fidelity as seen by the excellent agreement between observed and calculated isotopic distributions.
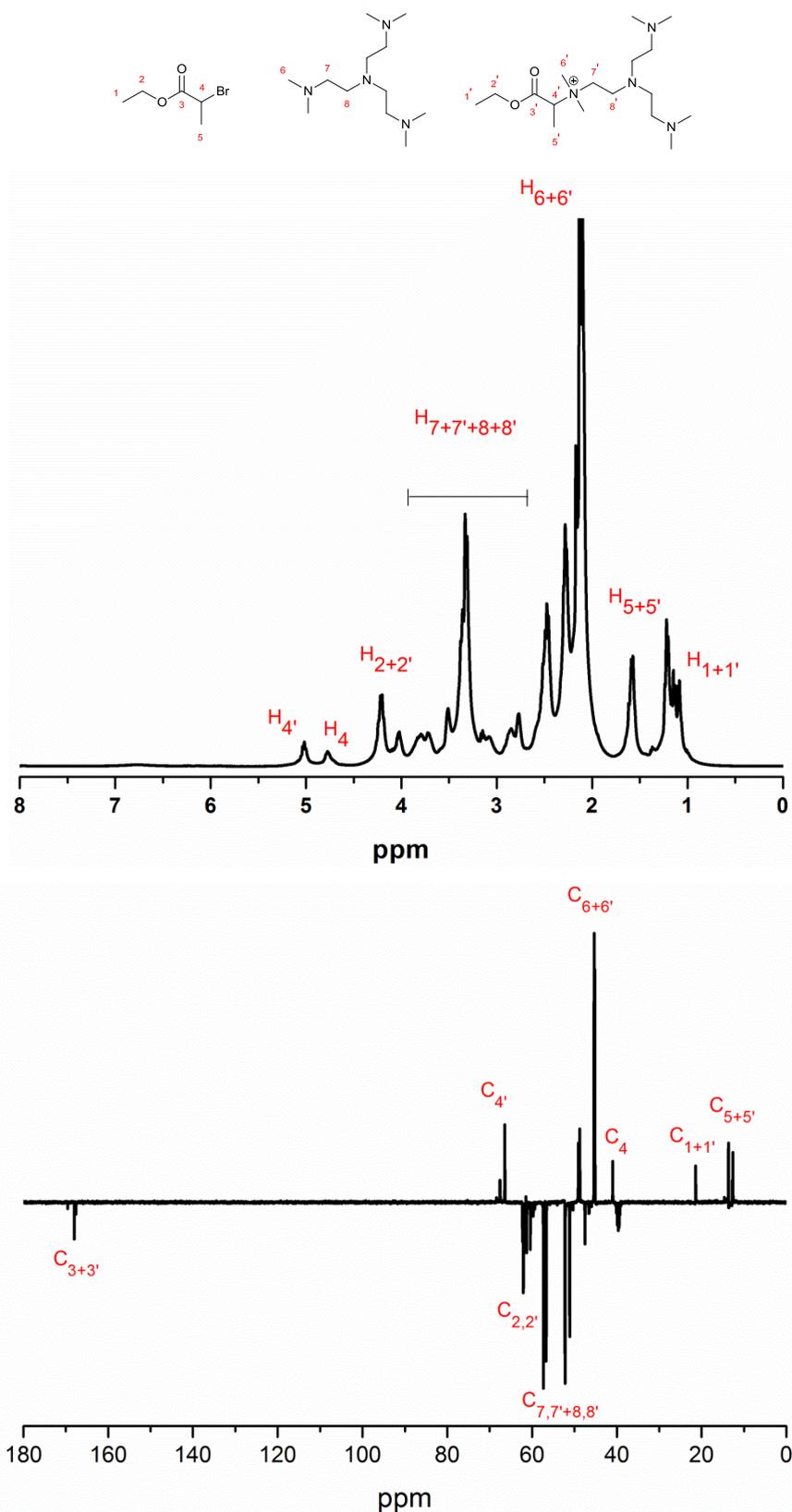
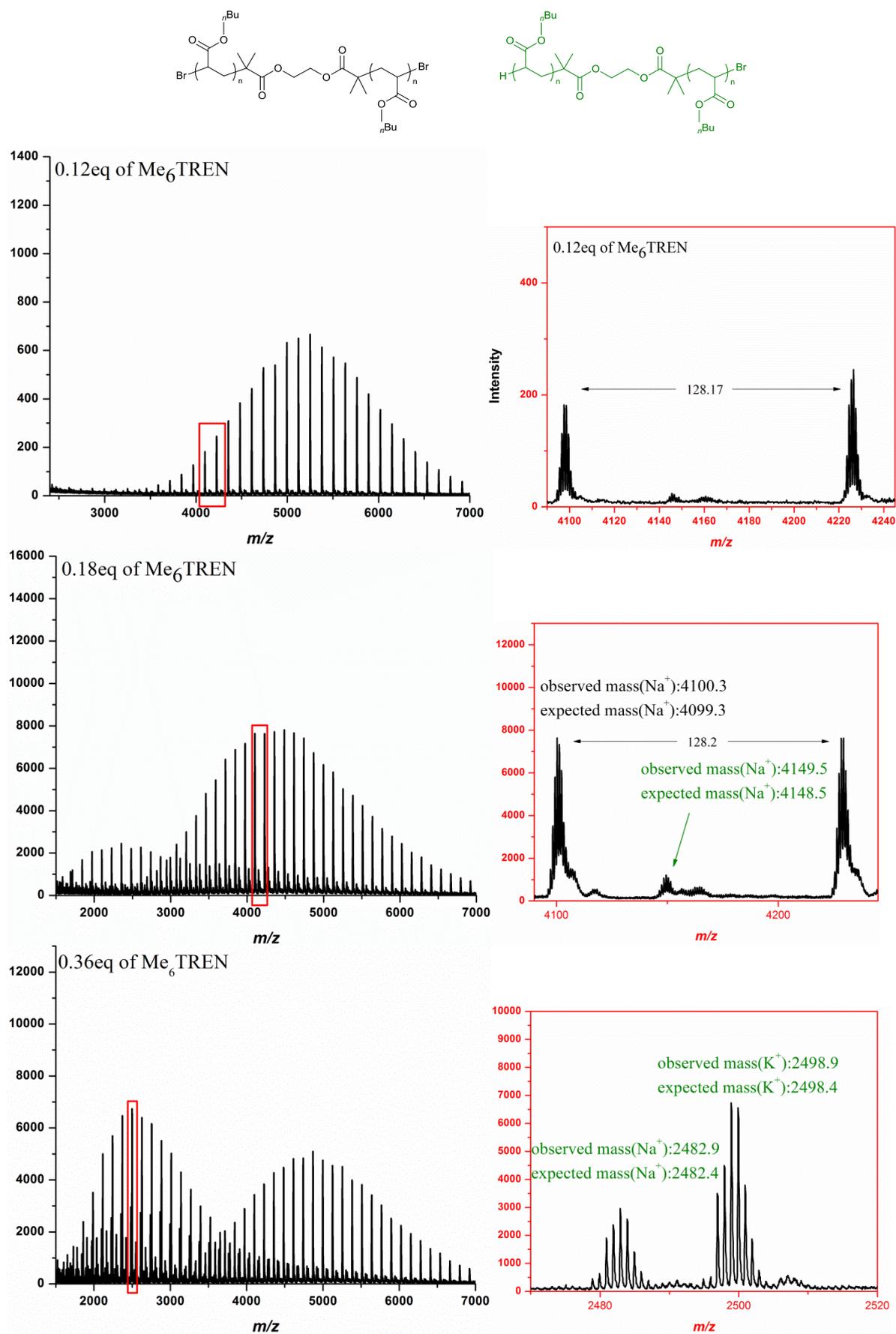**Fig S3. ¹H and ¹³C NMR of EBP the quaternisation reaction mixture.**

Fig S4 MALDI-TOF analysis of telechelic PBA prepared with various loadings of Me$_6$-Tren.
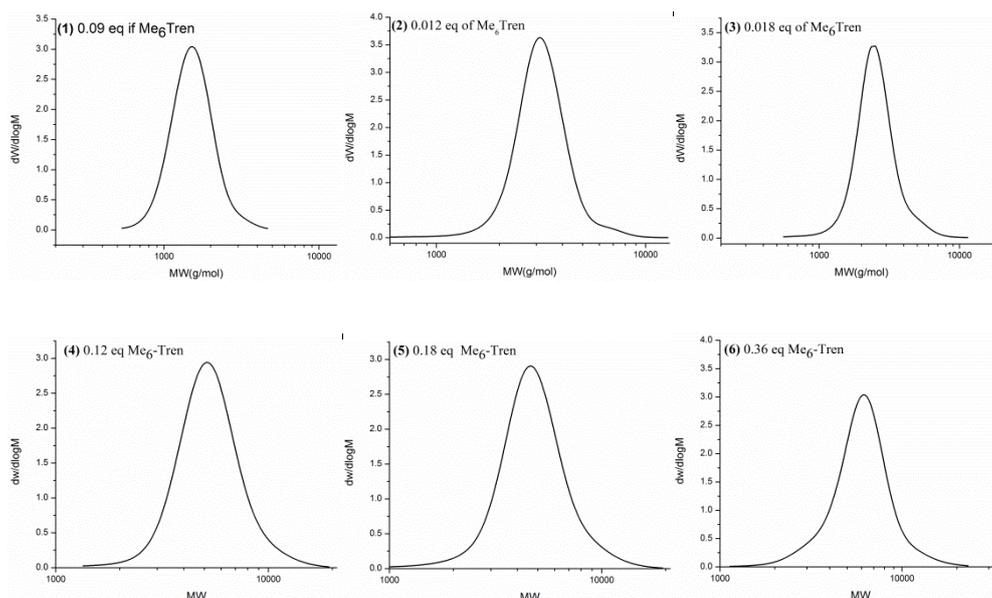
Fig S5. GPC (CHCl$_3$, DRI) for PMA and telechelic PBA prepared with various loadings of Me$_6$-Tren.

Table S1. Homo- and telechelic polymerisation of MA and BA respectively with various ligand loadings.

Entry	Initiator	[M]:[I]:[CuBr$_2$]:[L]	Conv.	$M_{n,th}$	$M_{n,GPC}$	PDi
1		20:1:0.05:0.09	>99%	1900	1500	1.09
2	EBiB	35:1:0.05:0.12	>99%	3200	3000	1.09
3		35:1:0.05:0.18	>99%	3200	2400	1.11
4		35:1:0.05:0.12	>99%	4800	4900	1.13
5	EbBiB	35:1:0.05:0.18	>99%	4800	4300	1.16
6		35:1:0.05:0.36	>99%	4800	5500	1.15

Table S2. MALDI-TOF mass data for polymers 1-4 (from Fig 2).

Polymer	1	2	3	4
[M+Na]$^+_{calc}$	2456.0	2463.1	2318.0	2497.2
[M+Na]$^+_{obs}$	2456.1	2463.2	2318.2	2497.2

(1)   Ciampolini, M.; Nardi, N. *Inorganic Chemistry* 1966, *5*, 41.

(2)   Boyer, C.; Atme, A.; Waldron, C.; Anastasaki, A.; Wilson, P.; Zetterlund, P. B.; Haddleton, D.; Whittaker, M. R. *Polymer Chemistry* 2012.