Copper(II) gluconate (a non-toxic food supplement/dietary aid) as a precursor catalyst for effective photo-induced living radical polymerisation of acrylates

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**Figure S1:** Typical set up for **photo-induced** polymerisation.
Figure S2: Molecular weight distribution of poly(methyl acrylate), $M_n = 5500\text{g/mol}$; $D = 2.30$; 96% conversion. [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v.

Figure S3: Molecular weight distribution of poly(methyl acrylate), $M_n = 5400\text{g/mol}$; $D = 1.80$; 98% conversion. [MA]:[EBiB]:[Cu(II) gluconate (pure)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v.
Figure S4: Molecular weight distribution of poly(methyl acrylate), $M_n = 5000\text{g/mol}$; $D = 1.50$; 98% conversion. $[\text{MA}]:[\text{EBiB}]:[\text{Cu}^{(II)} \text{ gluconate (tablet)}]:[\text{Me}_6\text{-Tren}] = [50]:[1]:[0.02]:[0.12]$ in DMSO 50% $\text{v/v}$, pre-mixing of the Cu$^{(II)}$ gluconate/Me$_6$-Tren complex for 2 h.

Figure S5a: Molecular weight distribution of poly(methyl acrylate), $M_n = 5500\text{g/mol}$; $D = 1.19$; 96% conversion. $[\text{MA}]:[\text{EBiB}]:[\text{Cu}^{(II)} \text{ gluconate (tablet)}]:[\text{Me}_6\text{-Tren}] = [50]:[1]:[0.02]:[0.12]$ in DMSO 50% $\text{v/v}$, pre-mixing of the Cu$^{(II)}$ gluconate/Me$_6$-Tren complex for 2 weeks.
**Figure S5b**: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate), obtained from photo-mediated polymerisation: [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me₆-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, **pre-mixing of the Cu(II) gluconate/Me₆-Tren complex for 2 weeks.**
Figure S5c: Monitoring effect of UV irradiation on Cu(II) gluconate/Me₆-Tren in DMSO complex as a function of time by UV–vis spectroscopy.

Figure S6: Molecular weight distribution of poly(methyl acrylate), $M_n = 5400$ g/mol; $D = 1.38$; 97% conversion. [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me₆-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me₆-Tren complex for 1 week.
**Figure S7a:** Molecular weight distribution of poly(methyl acrylate), $M_n = 4900$ g/mol; $D = 1.15$; 97% conversion. [MA]:[EBiB]:[Cu(II) gluconate (pure)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me$_6$-Tren complex for 2 h under UV irradiation.
Figure S7b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate), obtained from the photo-mediated polymerisation: [MA]:[EBiB]:[Cu(II) gluconate (pure)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me$_6$-Tren complex for 2 h under UV irradiation.

Figure S8a: Molecular weight distribution of poly(methyl acrylate), $M_n = 5600$ g/mol; $D = 1.16$; 98% conversion. [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me$_6$-Tren complex for 2 h under UV irradiation.
Figure S8b: $^1$H NMR (400MHz, CDCl$_3$) of poly(methyl acrylate) obtained from UV experiment: [MA]:[EBiB]:[Cu$^{(II)}$ gluconate]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v.

Figure S9: Molecular weight distribution of poly(methyl acrylate), $M_n = 3900$g/mol; $D = 1.33$; 70% conversion. [MA]:[EBiB]:[Cu$^{(II)}$ gluconate (pure)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu$^{(II)}$ gluconate/Me$_6$-Tren complex for 2 h under UV irradiation at 15 °C.
**Figure S10:** Molecular weight distribution of poly(methyl acrylate), $M_n = 4200 \text{ g/mol}$; $D = 1.40$; 75% conversion. [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me$_6$-Tren complex for 2 h under UV irradiation at 15 °C.

**Figure S11a:** Molecular weight distribution of poly(methyl acrylate), $M_n = 4300 \text{ g/mol}$; $D = 1.18$; 90% conversion. [MA]:[EBiB]:[Cu(II) gluconate (pure)]:[Me$_6$-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me$_6$-Tren complex for 2 h at 60 °C.
Figure S11b: MALDI-ToF-MS reflectron mode spectrum, of poly(methyl acrylate), obtained for the photo-mediated polymerisation: [MA]:[EBiB]:[Cu(II) gluconate (pure)]:[Me₆-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me₆-Tren complex for 2 h at 60 °C.
Figure S12a: Molecular weight distribution of poly(methyl acrylate), \( M_n = 5200 \text{g/mol} \); \( D = 1.19 \); 95% conversion. \([\text{MA}]:[\text{EBiB}]:[\text{Cu}^{(II)} \text{ gluconate (tablet)}]:[\text{Me}_6\text{-Tren}] = 50:[1]:[0.02]:[0.12]\) in DMSO 50% v/v, *pre-mixing of the Cu\(^{(II)}\) gluconate/Me\(_6\)-Tren complex for 2 h at 60 °C.*
Figure S12b: MALDI-ToF-MS reflectron mode spectrum, of poly(methyl acrylate), obtained for the photo-mediated polymerisation: [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% v/v, pre-mixing of the Cu(II) gluconate/Me_6-Tren complex for 2 h at 60 °C.

Figure S13a: Molecular weight distribution of poly(methyl acrylate), $M_n = 5400$ g/mol; $D = 1.15$; 99% conversion. [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me_6-Tren]:[NaBr] = [50]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% v/v.
**Figure S13b**: MALDI-ToF-MS reflectron mode spectrum, of poly(methyl acrylate), obtained for the photo-mediated polymerisation: [MA]:[EBiB]:[Cu(II) gluconate (tablet)]:[Me₆-Tren]:[NaBr] = [50]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% v/v.
Figure S14a: Molecular weight distribution of poly(methyl acrylate), $M_n = 5100$ g/mol; $D = 1.12$; 98% conversion. [MA]:[EBiB]:[Cu$^{II}$] gluconate (pure):[Me$_6$-Tren]:[NaBr] = [50]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% v/v.
**Figure S14b:** MALDI-ToF-MS reflectron mode spectrum, obtained from the photo-mediated polymerisation: \([\text{MA}]:[\text{EBiB}]:[\text{Cu(II)} \text{ gluconate (pure)}]:[\text{Me}_6\text{-Tren}]:[\text{NaBr}] = [50]:[1]:[0.02]:[0.12]:[0.04]\) in DMSO 50% v/v.

**Figure S15:** \(^1\text{H NMR}\) poly(methyl acrylate), 95% conversion. \([\text{MA}]:[\text{EBiB}]:[\text{Cu(II)} \text{ gluconate (tablet)}]:[\text{Me}_6\text{-Tren}]:[\text{NaBr}] = [200]:[1]:[0.02]:[0.12]:[0.04]\) in DMSO 50% v/v.
Figure S16: \(^1\)H NMR for the block copolymerization from a PMA macroinitiator. Initial conditions: \([\text{MA}]:[\text{EBiB}]:[\text{Cu}^{(II)} \text{ gluconate (tablet)}]:[\text{Me}_6\text{-Tren}]:[\text{NaBr}] = [50]:[1]:[0.02]:[0.12]:[0.04]\), DMSO (50%, v/v). Chain extension achieved upon addition of an aliquot of PEGA (15 equiv.) in DMSO (33%, v/v).

Experimental

Materials

All materials were purchased from Sigma Aldrich or Fisher Scientific unless otherwise stated. The dietary supplement (purchased on the internet from “BioCare” with a stated 1.1 mg Cu per pill (110% RDA)), the analytical pure copper\(^{II}\) gluconate and ethyl 2-bromoisobutyrate (EBiB) were used as received. Methyl acrylate was passed through a basic \(\text{Al}_2\text{O}_3\) chromatographic column prior to use. Tris-(2-(dimethylamino)ethyl)amine (Me\(_6\)-Tren) was synthesised according to previously reported literature.\(^1\)

Apparatus

\(^1\)H NMR spectra were recorded on 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 SEC-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 the range of 200 to $1.0 \times 10^6$ 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 analysed using Cirrus v3.3 software with calibration curves produced using Varian Polymer laboratories Easi-Vials linear poly(methyl methacrylate) standards (200-4.7×10$^5$ g/mol). 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 cationisation 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 reflector mode calibrating PEG-Me 1100 kDa. UV/Vis spectra were recorded on Agilent Technologies Cary 60 UV-Vis spectrophotometer in the range of 200-1100 nm using a cuvette with 10 mm path length. A nail lamp was purchased online (λ~365 nm) and used as the main UV source.

**General procedure for the homopolymerisation of MA**

Appropriate amounts of EBiB (1 eq.), MA (DP$_n$ eq), Cu(II) gluconate (0.02 eq.), Me$_6$-Tren (0.12eq.) and DMSO (50% v/v) were placed in a polymerisation flask, which was equipped with a magnetic stir bar and fitted with a rubber septum. The reaction mixture was degassed via bubbling with nitrogen for 20 min. The polymerization was allowed to proceed for 2 h under irradiation at λ~365 nm. Samples were taken periodically for conversion and molecular weight analyses. The polymerisation mixture was initially dissolved in THF and then passed through a small basic Al$_2$O$_3$ chromatographic column to remove the copper salts. The resulting solution was precipitated in methanol.

**In situ block copolymerisation**

Filtered MA (1 mL, 11.1 mmol, 50 eq), EBiB (32 μL, 0.22 mmol, 1 eq), Cu(II) gluconate (tablet) (1.0 mg, 4.4μmol, 0.02 eq), Me$_6$-Tren (7 μL, 22.0 μmol, 0.12 eq) and DMSO (1 mL)
were added to a septum sealed vial and degassed by purging with nitrogen for 15 mins. Polymerisation commenced upon addition of the degassed reaction mixture to the UV lamp. After 90 min a 1: 0.5 mixture of degassed PEGA (15 eq) used for block copolymerization and DMSO was added to the reaction mixture via degassed syringe. Samples were taken periodically and conversions were measured using $^1$H NMR and SEC analysis.

References