Supporting information:

Effect of polymerization components on

oxygen-tolerant photo-ATRP

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Experimental

Materials

All chemicals were used as received, unless otherwise stated. Tris(2-aminoethyl)amine (TREN, 96%), N,N,N',N'-tetramethylethylenediamine (99%) and butyl acrylate (BA, 99+%) were obtained from Acros Organics. N,N,N',N",N"-Pentamethyldiethylenetriamine (PMDETA, 99%), N,N,N',N'',N''',N'''-hexamethyltriethylenetetramine (HMTETA, 97%), diethylenetriamine (DETA, 99%), 2-bromopropionitrile (BPN, 97%), N,N-dimethylformamide (DMF, >99%), ethyl acrylate (EA, 99%), hexyl acrylate, (HA, 98%), pentaerythritol tetrakis(2-bromoisobutyrate) (4f-BiB, 97%) and benzyl bromide (BnBr, 98%) were bought from Sigma Aldrich. Triethylenetetramine (TETA, \geq 97.0% GC) was purchased from Fluka. Triethylamine (TEA, \geq 99%), Dimethylsulfoxide, (DMSO), acetonitrile (MeCN), methanol (MeOH), acetone, ethanol (EtOH), and isopropanol (iPrOH) were obtained from VWR chemicals. Ethyl 2bromoisobutyrate (EBiB, 98%), ethyl 2-bromopropionate (EBP, 98%), ethyl bromoacetate (EBA, 98%), methyl acrylate (MA, 99%) and 2-hydroxyethyl acrylate (HEA, 97%) were acquired from ABCR. Methyl α -bromophenylacetate, (MBPA, > 97.0%) was procured from Tokyo Chemical Industries. 2,2,2-Trifluoroethyl acrylate (TFEA, 98%) was obtained from Apollo Scientific. Tris-(2-(dimethylamino)ethyl)amine (Me6TREN, vacuum distilled before use)¹, and 2,3-dihydroxypropyl 2-bromoisobutyrate (GlyBiB²) were prepared following literature procedures.

Instrumentation

¹H NMR spectra were measured in CDCl₃ (99.8 %, ReseaChem) DMSO-d₆ or D₂O (99%, ReseaChem) on a Avance-300 spectrometer (Bruker). Chemical shifts are given in ppm and are referenced to residual solvent proton signals. To obtain monomer conversion for poly(methyl acrylate) (PMA) synthesis, the monomer vinyl proton peaks were integrated against combined monomer and polymer ester signals.

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SEC was measured on Shimadzu equipment comprising a CBM-20A system controller, an LC-20AD pump (flow rate at 1 mL min⁻¹), an SIL-20A automatic injector, a 10.0 μ m bead-size guard column (50 × 7.5 mm) followed by three KF-805L columns (300 × 8 mm, bead size: 10 μ m, pore size maximum: 5000 Å), an SPD-20A ultraviolet detector, and an RID-20A differential refractive index detector. The columns' temperature was maintained at 40 °C using a CTO-20A oven. *N*,*N*-dimethylacetamide was used as eluent (HPLC grade, Acros, with 0.03% w/v LiBr). Molecular weights were determined according to calibration with commercial narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 5000 to 1.5 × 10⁶ g mol⁻¹ (Agilent technology). Before injection, all samples were passed through 0.45 μ m filters.

MALDI-ToF-MS was conducted using a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 10 ns laser pulses at 337 nm with positive ion ToF detection performed using an acceleration voltage of 25 kV. Tetrahydrofuran of dithranol as the matrix (40 mg mL⁻¹), sodium trifluoroacetate as the cationization agent (1.0 mg mL⁻¹) and sample (10 mg mL⁻¹) were prepared. 10 µL of matrix solution was mixed with 2 µL of cationization agent solution and 10 µL of sample solution, and 0.7 µL of the mixture was applied to the target plate. Spectra were obtained in reflectron mode calibrated with a monomethoxy PEG standard (M_n = 1900 g mol⁻¹).

ESI mass spectra were recorded by the MoBiAs service (ETH Zurich) using DCM as the solvent on a maXis ESI-Qq-TOF-MS (Bruker).

All oxygen consumption data was collected with an Optical Solvent-Resistant Oxygen Probe connected to a pocket oxygen meter purchased from Pyroscience. All data was collected with the FireStingGO2 manager software. Oxsolv-PTS solvent resistant fiber optic oxygen sensor with protected tip.

UV-vis spectra were recorded on a V670 two-beam spectrophotometer (Jasco) equipped with a temperature-controlled sample cell holder maintained at 25 °C by a recirculating water cooler (Krüss) and an ETC-717 Peltier temperature controller (Jacso). Spectra were typically recorded form 400 nm to 1200 nm at a rate of 400 nm min⁻¹.

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General Procedures for oxygen concentration measurements and polymerization

Procedure 1.1: Oxygen probe measurements to study ligand effects

For all measurements, a total volume of 5.4 mL was used. In particular, DMSO (5.4 mL) and CuBr₂ (3 mg, 0.02 equiv.) were introduced into a glass vial fitting 6 mL. Ligand (0.12 equiv. or equiv.= (number of Nitrogen*0.12)/4, normalized with respect to Me₆TREN) was then added using a microlitre pipette. Lastly, EBiB (88.1 µL, 1 equiv.) was added, before the vial was sealed with a septum and rapidly placed under a UV nailbox (36 W, λ_{max} = 360 nm). The oxygen probe was inserted into the solution through a hole in the top of the UV box, and measurement proceeded for 1 hour or until oxygen was completely consumed. The stirring rate for all experiments was fixed at 550 rpm. The same procedure was followed for different ligands, solvents and initiators by using the same concentration and adjusting the calculations accordingly. In addition, for oxygen consumption measurements longer than 1 hour, we gently insert the probe at specific times, record the value and remove it from the solution until the next measurement was taken.

Procedure 1.2: General procedure for methyl acrylate polymerization with different Ligands

For all the polymerizations, a total volume of 6 mL was used (unless specified otherwise). In particular, DMSO (3 mL), methyl acrylate (MA, 3 mL, 50 equiv.), ligand (0.12 equiv., 21.3 μ L when Me₆TREN is used) and CuBr₂ (3 mg, 0.02 equiv.) were introduced into a 6 mL glass vial. Lastly, EBiB (88.1 μ L, 1 equiv.) was added before closing the vial with a septum. The solution was rapidly placed under UV nailbox (36 W, λ_{max} = 360 nm) at a stirring rate of 550 rpm. The polymerizations were stopped by removing the vial from UV irradiation and opening it to air. It was sampled in order to determine the conversion *via* ¹H NMR, the molecular weight and dispersity *via* SEC measurements (samples were passed though basic alumina to removed copper). The same procedure was followed for different ligands, solvents and initiators by using the same amount of monomer and adjusting the calculations accordingly (same equivalents where used).

Procedure 1.3: UV-vis experiments

Samples were prepared by diluting a stock solution of CuBr₂ in DMSO (2.08 mg mL⁻¹) with an appropriate volume of DMSO and then adding stock solutions of the ligand (L, ~50 mg mL⁻¹) to final concentrations of [CuBr₂] \approx 2.2 mM and [L] \approx 13.4 mM. The resulting solutions were shaken, then immediately filled into quartz cuvettes. Experiments were conducted without degassing and minimal head space was left in the cuvettes, which were tightly stoppered and additionally wrapped with parafilm before immediately recording a first spectrum (t = 0). After recording the initial spectra, samples were exposed to UV light ($\lambda_{max} \approx$ 360 nm) under a nail curing lamp. The same lamp was used for all experiments reported here, as using a different lamp revealed some dependence of reaction kinetics on the specific model, likely related to photon flux. For measurements of further spectra, the cuvettes were removed from under the lamp (T \approx 50 °C) after the targeted time of UV exposure had elapsed, and the cell was permitted to thermally equilibrate with the cell holder before a spectrum was recorded.

Procedure 1.4: Procedure for PMA chain extension using TREN as ligand

A stock solution containing DMSO (3 mL) and CuBr₂ (3 mg, 0.02 equiv.) was introduced into a 20 mL glass vial. Ligand (0.12 equiv.) was added with a 100 µL pipette, followed by the addition of MA (3 mL, 50 equiv.). Lastly, EBiB (88.1 µL, 1 equiv.) was added before closing the vial with a septum (2/3 headspace remaining). The solution was rapidly placed under UV nailbox (36 W, λ_{max} = 360 nm) and reaction was allowed to proceed without stirring. After 2.5 h of polymerization, a preprepared mixture of MA, TREN, CuBr₂ and DMSO (100 µl) was added to the polymerisation in order to completely fill the vial. Once the addition was completed, the stirring rate was raised to 550 rpm. The vial was irradiated with UV for 15 h, and was, finally, sampled in order to determine the conversion *via* ¹H NMR and the molecular weight and dispersity *via* SEC measurements.





Figure S1 : a). Experimental setup of all oxygen consumption measurements, comprising of a UV nail box, a stirrer (550 rpm) and a Pyroscience oxygen probe. b). Zoomed in vial showing the insertion of the probe into the solution.



Figure S2: Oxygen consumption control experiments, with various combinations of DMSO, EBiB, CuBr₂ and Me₆TREN. The ratio of components was maintained at EBiB : CuBr₂ : $Me_6TREN = 1 : 0.02 : 0.12$ in all cases.



Figure S3 : Oxygen consumption control experiments in the dark of Me₆TREN + DMSO + CuB_{r2} + EBiB where the ratio of components was maintained constant at EBiB : $CuBr_2$: Me₆TREN = 1 : 0.02 : 0.12.



Figure S4 : Oxygen consumption control experiment with a near equimolar ratio of $CuBr_2$ to Me_6TREN (EBiB : $CuBr_2$: $Me_6TREN = 1 : 0.02 : 0.018$). a) Over a period of one hour, b) Over a period of 3 hours.



Figure S5 : The effect of ATRP ligands on oxygen consumption measured by oxygen probe without normalization (compare Fig. 1a).



Figure S6: Oxygen consumption experiments to analyze the effect of ligand when the number of nitrogen (rather than the ligand concentration) was kept constant. The ratio of components was maintained at EBiB : $CuBr_2$: L = 1 : 0.02 : (number of Nitrogen*0.12)/4, normalized with respect to Me₆TREN) in all cases.



Figure S7 : Time resolved UV-vis spectra of $CuBr_2 + L$ ([$CuBr_2$] : [L] = 1 : 6, L = a) TMEDA b) PMDETA, c) HMTETA, d) Me₆TREN, in DMSO, recorded after the given time of exposure to 360 nm UV light with negligible headspace and no prior degassing.



Figure S8 : Time resolved UV-vis spectra of $CuBr_2 + L$ ([$CuBr_2$] : [L] = 1 : 6, L = a) DETA b) TETA, c) TREN, in DMSO, recorded after the given time of exposure to 360 nm UV light with negligible headspace and no prior degassing.



Figure S9: Oxygen consumption control experiments, with various combinations of DMSO, EBiB, MA, CuBr₂ and TREN. The ratio of components was maintained at an EBiB : CuBr₂ : L : MA of 1 : 0.02 : 0.12 : 50 throughout, with results illustrated a) under UV light and b) in the dark and compared to analogous Me₆TREN data.



Figure S10 : Oxygen consumption control experiments, with various ligand (TREN, TETA, DETA, Me₆TREN, PMDETA), EBiB and DMSO, under UV irradiation. The ratio of components was maintained at an I : $CuBr_2 : L$ of 1 : 0.02 : 0.12.



6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2

Figure S11 : a) Side reaction between TREN and EBiB in order of relevance (1. Alkylation, 2. Amidation, 3. Elimination). b) ¹H NMR spectrum (DMSO-d₆, 300 MHz) of TREN + EBiB where the following ratio was chosen 1 : 10 in order to mimic the polymerization conditions and to show the side reactions between TREN and EBiB.



4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9

Figure S12 : Stacked ¹H NMR spectra (DMSO- d_6 , 300 MHz) of EBiB (grey spectrum) and TREN + EBiB (black spectrum) where the following ratio was chosen 10 : 1 to highlight the main side reaction between TREN and EBiB which is the alkylation.



Figure S13 : Electrospray ionization (ESI) mass spectrum of TREN + EBiB (1 : 10) showing the products of the side reactions (single and multiple alkylation and single amidation).



Figure S14 : Oxygen consumption control experiments with TREN and three molecules (BnBr, CHCl₃, ethyl acetate) mimicking different functionalities of EBiB in order to identify the reaction responsible for consuming the oxygen when TREN and EBiB are present. The ratio of components was maintained at an I : $CuBr_2$: TREN of 1 : 0.02 : 0.12.



Figure S15 : Oxygen consumption control experiments with TREN and primary (EBA), secondary (EBP) and tertiary (EBiB) initiators. The ratio of components was maintained at I : $CuBr_2 : TREN = 1 : 0.02 : 0.12$.

Table S1: List of control experiments of various combination of Ligand, MA, DMSO, $CuBr_2$ without degassing, where the following ratios were maintained: EBiB : $CuBr_2$: TREN : MA = 1 : 0.02 : 0.12 : 50.

| Time | Components | Conversion ¹ H | M _n (g mol ⁻¹) | Ð |
|------|--|---------------------------|---------------------------------------|-----|
| (h) | | NMR (%) | | |
| 1 | TREN MA DMSO | 2 | | |
| 1 | TREN MA DMSO CuBr ₂ | 3 | | |
| 1 | MA DMSO | 1 | | |
| 1 | MA DMSO EBIB | 2 | | |
| 1 | Me ₆ TREN MA DMSO | <1 | | |
| 1 | Me ₆ TREN MA DMSO CuBr ₂ | <1 | | |
| 15 | TREN MA DMSO | 42 | 440 000 | 2.3 |
| 15 | TREN MA DMSO CuBr ₂ | 22 | 131 000 | 2.3 |
| 15 | MA DMSO | | Insoluble gel | |
| 15 | MA DMSO EBIB | 96 | 1 000 000 | 2.1 |
| 15 | TREN MA DMSO EBIB | 94 | 131 400 | 4.1 |

Table S2 : Conversion and SEC data of photo-ATRP chain extension without degassing, using TREN as ligand. For the first block, the following ratios were maintained: EBiB : $CuBr_2$: TREN : MA = 1 : 0.02 : 0.12 : 50 and for the second block, $CuBr_2$: TREN : MA = 0,01 : 0,06 : 50. The first block was not stirred and upon the addition of the second block the stirring rate was raised to 550 rpm.

| Entry | Block | <i>Time</i> (h) | Conversion by NMR (%) | M _{n,SEC} (g mol ⁻¹) | Ð |
|-------|-------|--------------------|--------------------------|--|------|
| 1 | 1 | 2.5 | 96 | 6100 | 1.11 |
| 2 | 2 | 15 | 32 | 7500 | 1.18 |



Figure S16 : SEC traces of chain extension of poly(methyl acrylate) using TREN as ligand, non-degassed. For the first block, the following ratios were maintained: EBiB : $CuBr_2$: TREN : MA = 1 : 0.02 : 0.12 : 50 and for the second block, $CuBr_2$: TREN : MA = 0,01 : 0,06 : 50.

Table S3 :Conversion and SEC data of photo-ATRP comparing degassed and non-
degassed reactions with samples taken after 1 h and 15 h. The ratio of MA : EBiB : $CuBr_2$:
TREN was maintained at 50 : 1 : 0.02 : 0.12.

| Entry | Degas/No Degas | Time (h) | Conversion by NMR (%) | M _{n,SEC} (g mol⁻¹) | Ð |
|-------|-------------------|-------------|--------------------------|---------------------------------|------|
| 1 | Degassed | 15 | >99 | 5900 | 1.10 |
| 2 | Non- degassed | 15 | >99 | 6000 | 1.10 |



Figure S17 : SEC traces of poly(methyl acrylate) synthesized using the ligand TREN, comparing degassed and non-degassed procedures. The ratio of MA: EBiB : $CuBr_2$: TREN = 50 : 1 : 0.02 : 0.12 and samples were taken after 1 and 15 hours of polymerization.

Table S4 : Conversion and SEC data of photo-ATRP using TETA and DETA as ligands, without degassing with samples taken after 1 h. The ratio of MA : EBiB : $CuBr_2$: L was maintained at 50 : 1 : 0.02 : 0.12.

| Entry | Ligand | Time (h) | Conversion by NMR (%) | M _{n,SEC} (g mol⁻¹) | Ð |
|-------|--------|-------------|--------------------------|---------------------------------|------|
| 1 | TETA | 1 | 91 | 19000 | 2.02 |
| 2 | DETA | 1 | 91 | 6500 | 1.41 |



Figure S18 : SEC traces of poly(methyl acrylate) synthesized using the ligand a) DETA and b) TETA. Both reactions were not degassed and reaction vials were filled to minimize headspace. The ratio of MA: EBiB : $CuBr_2$: L was 50 : 1 : 0.02 : 0.12 and samples were taken after 1 hour of polymerization.



Figure S19 : a). Oxygen consumption of $CuBr_2$: TEA = 0.02 : 0.12 eq. in DMSO in 1 hour measurement, no degassing. b). Time-resolved UV-vis spectra of $CuBr_2$: TEA = 0.02 : 0.12 eq. (no degassing) in DMSO, recorded after the given time of exposure to 360 nm UV light.

| Table | e S5: Con | version | and S | SEC | data | of no | degassing | photo-ATRP | synthesis o | f poly(meth | yl |
|--------|------------|----------|---------|-------|-------------------|-------|-----------|------------|-------------|-------------|----|
| acryla | ate) using | differen | t ratio | os of | Me ₆ T | REN | : TEA. | | | | |

| Entry | Time | EBiB | MA | CuBr ₂ | Me ₆ TREN | TEA | Conversion by | M _n (g/mol) | Ð |
|-------|------|------|------|-------------------|------------------------------------|------|---------------|------------------------|------|
| | (h) | (eq) | (eq) | (eq) | (eq) | (eq) | NMR (%) | | |
| 1 | 12 | 1 | 50 | 0.02 | 0.018 | 0 | 0 | | |
| 2 | 12 | 1 | 50 | 0.02 | 0.018 | 0.4 | >99 | 6500 | 1.08 |
| 3 | 12 | 1 | 50 | 0.02 | 0.018 | 0.12 | >99 | 6300 | 1.06 |
| 4 | 12 | 1 | 50 | 0.02 | 0 | 0.12 | >99 | 7100 | 1.52 |



Figure S20 : SEC traces of poly(methyl acrylate) synthesized using different ratio of $Me_6TREN : TEA$. The reactions were not degassed. The ratio of MA : EBiB : CuBr₂ was 50 : 1 : 0.02 and the amount of TEA and Me₆TREN was varied : a). CuBr₂ : Me₆TREN : TEA (0.02 : 0.018 : 0.4), b). CuBr₂ : Me₆TREN : TEA (0.02 : 0.018 : 0.1) c). CuBr₂ : Me₆TREN : TEA (0.02 : 0 : 0.12). The reaction was sampled after 12 hours of reaction.



Figure S21 : *In-situ* oxygen consumption and kinetics of poly(methyl acrylate) synthesis using TREN as ligand. The ratio of EBiB : TREN : $CuBr_2$: MA was maintained as follow 1 : 0.12 : 0.02 : 50 and the total volume of reaction was 5.4 mL a time 0 (2.7 mL of DMSO and 2.7 mL of monomer). The reaction was conducted in the absence of external deoxygenation.



Figure S22 : *In-situ* oxygen consumption and kinetics of poly(methyl acrylate) synthesis using Me_6TREN as ligand. The ratio of EBiB : Me_6TREN : $CuBr_2$: MA was maintained as follow 1 : 0.12 : 0.02 : 50 and the total volume of reaction was 5.4 mL at time 0 (2.7 mL of DMSO and 2.7 mL of monomer). The reaction was conducted in the absence of external deoxygenation.



Figure S23 : *In-situ* oxygen consumption and kinetics of poly(methyl acrylate) synthesis using PMDETA as ligand. The ratio of EBiB : PMDETA : $CuBr_2$: MA was maintained as follow 1 : 0.12 : 0.02 : 50 and the total volume of reaction was 5.4 mL at time 0 (2.7 mL of DMSO and 2.7 mL of monomer). The reaction was conducted in the absence of external deoxygenation.



Figure S24 : *In-situ* oxygen consumption and kinetics of poly(methyl acrylate) synthesis using HMTETA as ligand. The ratio of EBiB : HMTETA : $CuBr_2$: MA was maintained as follow 1 : 0.12 : 0.02 : 50 and the total volume of reaction was 5.4 mL at time 0 (2.7 mL of DMSO and 2.7 mL of monomer). The reaction was conducted in the absence of external deoxygenation.

Table S6: ¹H NMR and SEC data of poly(methyl acrylate) polymerization using different ligands (TREN, Me_6TREN , PMDETA, HMTETA) without deoxygenation. In all cases the ratio of MA : EBiB : CuBr₂ : Ligand was maintained at 50: 1 : 0.02 : 0.12, the total volume of reaction was kept at 5.4 ml (2.7 ml of DMSO and 2.7 ml of monomer) and the headspace was minimized. The samples were taken during the kinetic study of figure S21, S22, S23, S24.

| Entry | Time (h) | Ligand | Conversion by NMR (%) | M _{n,SEC} (g mol ⁻¹) | Ð |
|-------|----------|----------------------|--------------------------|--|------|
| 1 | 1 | TREN | 90 | 5800 | 1.12 |
| 2 | 1 | Me ₆ TREN | 50 | 3200 | 1.08 |
| 3 | 1 | PMDETA | <1 | | |
| 4 | 9 | PMDETA | 80 | 5200 | 1.09 |
| 5 | 1 | HMTETA | <1 | | |
| 6 | 7.75 | HMTETA | 97 | 6600 | 1.21 |



Figure S25 : SEC traces of poly(methyl acrylate) synthesized using the ligand a) TREN, 1 h, b) Me_6TREN , 1 h, c) PMDETA, 9 h and d) HMTETA, 7 h 45 min. In all cases, the ratio of MA : EBiB : CuBr₂ : Ligand was maintained at 50 : 1 : 0.02 : 0.12, the total volume of reaction was kept at 5.4 ml (2.7 ml of DMSO and 2.7 ml of monomer) and the headspace was minimized. The samples were taken after 1 hour of polymerization during the kinetic study of figure S21.



Figure S26 : The effect of increasing the ligand concentration on oxygen consumption. The ratio used was: EBiB : $CuBr_2 : L = 1 : 0.02 : 0.6$ (5 times higher concentration of ligand than standard experiments). In all cases, the oxygen consumption was significantly accelerated. For instance, in the case of Me₆TREN the oxygen was fully consumed within ~ 1 min (rather than ~ 5 min previously), and ~ 1 min for TREN (rather than ~ 2.5 min). PMDETA at 0.6 equivalent consumed the oxygen in ~ 6 min (rather than ~ 25 min).

Table S7 : ¹H NMR and SEC data illustrating the effect of ligand choice (TREN, Me₆TREN, PMDETA and HMTETA) on the synthesis of poly(methyl acrylate) in the absence of external deoxygenation. In all cases the ratio of MA : EBiB : $CuBr_2$: Ligand was maintained at 1 : 0.02 : 0.60 : 50 and samples were taken after specific times of polymerization.

| Time | Ligand (eq) | Conversion by NMR (%) | Targeted DP | M _n (g mol⁻¹) | Ð |
|--------|----------------------------|--------------------------|----------------|--------------------------|------|
| 15 min | TREN : 0.6 | 93 | 50 | 5800 | 1,32 |
| 7 h | PMDETA : 0.6 | 94 | 50 | 6000 | 1,10 |
| 1 h | Me ₆ TREN : 0.6 | 90 | 50 | 6400 | 1.09 |
| 4 h | HMTETA : 0.6 | 96 | 50 | 6500 | 1.24 |



Figure S27 : SEC traces of poly(methyl acrylate) synthesised using the ligands a) TREN, b) PMDETA, c) Me₆TREN and d) HMTETA. The reaction vials were not degassed and were filled to minimize the headspace. The ratio was maintained at MA: EBiB : $CuBr_2 : L : MA = 50 : 1 : 0.02 : 0.60$ and samples were taken at specific reaction time (Table S7).



Figure S28 : Oxygen consumption over a 3 h 30 min period using EBA : $CuBr_2 : Me_6TREN$ (1 : 0.02 : 0.12).



Figure S29 : ¹H NMR of EBA quaternization with TREN inhibiting the oxygen consumption and the polymerization. Experiment conditions: EBA : Me_6TREN : $CuBr_2$ (1 : 0.12 : 0.02) in DMSO-d₆.



Figure S30 : Photograph illustrating the complexation of GlyBiB with Cu(II) in DMSO.

Table S8 : ¹H NMR and SEC data illustrating the effect of solvent choice (acetonitrile, isopropanol, ethanol, acetone, DMF and methanol) on the synthesis of poly(methyl acrylate) in the absence of external deoxygenation. In all cases, the ratio of MA : EBiB : $CuBr_2$: Ligand was maintained at 50 : 1 : 0.02 : 0.12 and samples were taken after 15 hours of polymerization.

| Solvent | Conversion by NMR (%) | M _n (g mol⁻¹) | Ð | |
|-------------------|--------------------------|-----------------------------|------|--|
| MeCN | 97 | 6000 | 1.05 | |
| ⁱ PrOH | 96 | 5400 | 1.05 | |
| EtOH | 99 | 5900 | 1.08 | |
| Acetone | 78 | 6100 | 1.05 | |
| DMF | 95 | 6000 | 1.05 | |
| MeOH | 99 | 6200 | 1.05 | |



Figure S31 : SEC traces of poly(methyl acrylate) synthesised in different solvents: a) Acetonitrile, b) Isopropanol , c) Ethanol, d) Acetone e) DMF and f) Methanol. The reactions were not degassed and reaction vials were filled to avoid headspace. The ratio of MA: EBiB : $CuBr_2 : L : MA = 50 : 1 : 0.02 : 0.12$ and samples were taken after 15 hours of polymerization.



Figure S32 : Effect of monomer on oxygen consumption. In all cases, the ratio of EBiB : $CuBr_2 : Me_6TREN$ was maintained at 1 : 0.02 : 0.12 in a mixture of DMSO/monomer : 50/50 (v/v).



Figure S33 : Photograph illustrating the complexation of Cu(II) with 2-hydroxyethyl acrylate in DMSO.

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