

# Supporting Information

## Ultra-low volume oxygen tolerant photoinduced Cu-RDRP

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## Experimental

### Materials

Methyl acrylate (MA, 99%), *n*-butyl acrylate (*n*-BA, ≥99%), *tert*-butyl acrylate (*t*-BA, 98%), ethylene glycol methyl ether acrylate (EGA, 98%), hexyl acrylate (HA, 98%), lauryl acrylate (LA, 90%) 2,2,2-trifluoroethyl acrylate (TFEA, 99%), ethyl  $\alpha$ -bromoisobutyrate (EBiB, 98%), copper(II) bromide (Cu(II)Br<sub>2</sub>, 99%) and all the solvents were purchased from Sigma-Aldrich and used as received. 2,2,2-trifluoroethyl methacrylate (TFEMA) was purchased from Cornelius and used as received. Tris-(2-(dimethylamino)ethyl)amine (Me<sub>6</sub>Tren) was synthesized according to the literature and stored in the fridge.<sup>1</sup>

### Instrumentation

<sup>1</sup>H Nuclear Magnetic Resonance. <sup>1</sup>H NMR spectra were recorded on Bruker DPX-300 or DPX-400 spectrometers in deuterated chloroform (CDCl<sub>3</sub>) or deuterium oxide (D<sub>2</sub>O) obtained from Sigma-Aldrich. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Monomer conversions were determined via <sup>1</sup>H NMR spectroscopy by comparing the integrals of monomeric vinyl protons to polymer signals.

*Size Exclusion Chromatography.* SEC measurements were carried out using THF as the eluent with an Agilent 390-LC MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light scatter (LS) 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  $\mu$ m guard column. The eluent was THF with 2 % TEA (triethylamine) and 0.01 % BHT (butylated hydroxytoluene) additives. Samples were run at 1 mL / min at 30°C. Poly(methyl methacrylate) standards (Agilent EasyVials) were used to create a third order calibration between 550 gmol<sup>-1</sup> and 1,568,000 gmol<sup>-1</sup>. Analytical samples were filtered through a GVHP membrane with 0.22  $\mu$ m pore size before injection. Respectively, experimental molar mass ( $M_{n,SEC}$ ) and dispersity ( $\mathcal{D}$ )

values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software (version A.02.01).

*Matrix-assisted laser desorption/ionization time-of-flight* (MALDI-ToF-MS) measurements were 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 (THF) (50  $\mu\text{L}$ ) of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene] malononitrile (DCTB) as a matrix (saturated solution), sodium iodide as the cationization agent (1.0 mg mL<sup>-1</sup>) and sample (1.0 mg mL<sup>-1</sup>) were mixed, and 0.7  $\mu\text{L}$  of the mixture was applied to the target plate. Spectra were recorded in reflectron mode calibrated with poly(ethylene glycol) monomethyl ether (PEG-Me) 1900 kDa.

*Oxygen Probe.* Pocket Oxygen Meter - FireStingGO2 (from Pyro Science): The solvent-resistant oxygen probe OXSOLV measures oxygen partial pressure in most polar and nonpolar solvents. It is based on optical detection principles (REDFLASH technology) and can be used both in pure and complex organic solvents. The fiber-optic oxygen sensor tip is covered with a stainless steel tube 1.5 mm in diameter and 150 (or 40) mm in length. The analysis of the data was conducted with the FireStingGO2 Manager software.

*UV Source.* A UV nail gel curing lamp ( $\lambda_{\text{max}} \sim 365$  nm) with four 9 Watt bulbs was used.

## Experimental Procedures

### Typical 8 mL scale deoxygenation-free photoinduced Cu-RDRP of MA (targeted DP<sub>n</sub>=50) in DMSO

An 8 mL total volume capacity glass vial was charged with Cu(II)Br<sub>2</sub> (4.0 mg, 0.02 eq.) and DMSO (4 mL). Me<sub>6</sub>Tren (28.3  $\mu\text{L}$ , 0.12 eq.) was added through a microliter syringe and the solution was vortexed for  $\sim 1$  minute. MA (4 mL, 50 eq.), EBiB (129  $\mu\text{L}$ , 1 eq.) and a stirrer bar were added and the vial was septum-sealed. The polymerization was allowed to commence for 2 hours under a UV nail lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using <sup>1</sup>H NMR in CDCl<sub>3</sub> and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

### Typical deoxygenation-free photoinduced Cu-RDRP of MA (targeted DP<sub>n</sub>=50) in DMSO or TFE or Toluene-MeOH

A stock solution of Cu(II)Br<sub>2</sub> (1.0 mg, 0.02 eq.), Me<sub>6</sub>Tren (9.5  $\mu\text{L}$ , 0.12 eq.) and the solvent (1 mL of DMSO or 1 mL of TFE or Toluene (0.8 mL) -MeOH (0.2 mL) ) was prepared. The solution was vortexed for  $\sim 1$ min (or sonicated for  $> 10$  min when TFE was used) and MA (1 mL, 50 eq.) and EBiB (32  $\mu\text{L}$ , 1 eq.) were added. Aliquots of 200  $\mu\text{L}$ - 5 $\mu\text{L}$  were charged in vial inserts and

sealed with NMR-tube lids. The polymerization reactions were placed for 2 hours under a UV nail lamp ( $\lambda_{\text{max}} \sim 360$  nm) and conversions were measured through  $^1\text{H}$  NMR in  $\text{CDCl}_3$ . SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts. For targeted  $\text{DP}=100$  the reaction was left for 4 hours (99% conversion), 12 hours for  $\text{DP}=200$  (92% conversion) and for  $\text{DP}=400$  the polymerization was left to commence overnight (82% conversion).

#### **Typical deoxygenation-free photoinduced Cu-mediated RDRP of (*t*-BA) with targeted $\text{DP}_n=50$ in toluene-MeOH (4 : 1).**

A stock solution of  $\text{Cu(II)Br}_2$  (0.61 mg, 0.02 eq.), toluene (0.8 mL)-MeOH (0.2 mL) and  $\text{Me}_6\text{Tren}$  (4.4  $\mu\text{L}$ , 0.12 eq.) was prepared and vortexed for  $\sim 1$  minute. *t*-BA (1 mL, 50 eq.) and EBiB (20  $\mu\text{L}$ , 1 eq.) were added and aliquots of 100  $\mu\text{L}$  and 10  $\mu\text{L}$  were charged in vial inserts and sealed with NMR-tube lids. The polymerizations were allowed to commence for 10 hours under a UV lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using  $^1\text{H}$  NMR in  $\text{CDCl}_3$  and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

#### **Typical deoxygenation-free photoinduced Cu-mediated RDRP of (HA) with targeted $\text{DP}_n=50$ in TFE**

A stock solution of  $\text{Cu(II)Br}_2$  (0.51 mg, 0.02 eq.), TFE (1 mL) and  $\text{Me}_6\text{Tren}$  (3.7  $\mu\text{L}$ , 0.12 eq.) was prepared and sonicated for  $>10$  minutes. HA (1 mL, 50 eq.) and EBiB (17  $\mu\text{L}$ , 1 eq.) were added in the solution and aliquots of 100  $\mu\text{L}$  and 10  $\mu\text{L}$  were charged in vial inserts and sealed with NMR-tube lids. The polymerizations were allowed to commence overnight under a UV lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using  $^1\text{H}$  NMR in  $\text{CDCl}_3$  and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

#### **Typical deoxygenation-free photoinduced Cu-mediated RDRP of EGA with targeted $\text{DP}_n=50$ in DMSO**

A stock solution of  $\text{Cu(II)Br}_2$  (0.675 mg, 0.02 eq.), DMSO (1 mL) and  $\text{Me}_6\text{Tren}$  (5  $\mu\text{L}$ , 0.12 eq.) was prepared and vortexed for  $\sim 1$  min. EGA (1 mL, 50 eq.) and EBiB (22.8  $\mu\text{L}$ , 1 eq.) were added in the solution and aliquots of 100  $\mu\text{L}$  and 10  $\mu\text{L}$  were charged in vial inserts and sealed with NMR-tube lids. The polymerizations were allowed to commence for 2 hours under a UV lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using  $^1\text{H}$  NMR in  $\text{CDCl}_3$  and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

### **Typical deoxygenation-free photoinduced Cu-mediated RDRP of PEGA<sub>480</sub> with targeted DP<sub>n</sub>= 20 in DMSO**

A stock solution of Cu(II)Br<sub>2</sub> (0.5 mg, 0.02 eq.), DMSO (1 mL) and Me<sub>6</sub>Tren (3.7 μL, 0.12 eq.) was prepared and vortexed for ~ 1 minute. PEGA<sub>480</sub> (1 mL, 20 eq.) and EBiB (16.8 μL, 1 eq.) were added in the solution and aliquots of 100 μL and 10 μL were charged in vial inserts and sealed with NMR-tube lids. The polymerizations were allowed to commence for 2 hours under a UV lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using <sup>1</sup>H NMR in D<sub>2</sub>O and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

### **Typical photoinduced Cu-mediated RDRP of TFEA with targeted DP<sub>n</sub>= 50 in TFE**

A stock solution of Cu(II)Br<sub>2</sub> (0.7 mg, 0.02 eq.), TFE (1 mL) and Me<sub>6</sub>Tren (5 μL, 0.12 eq.) was prepared and sonicated for >10 minutes. TFEA (1 mL, 50 eq.) and EBiB (23 μL, 1 eq.) were added in the solution and aliquots of 100 μL and 10 μL were charged in vial inserts and sealed with NMR-tube lids. The polymerizations were allowed to commence for 24 hours under a UV lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using <sup>1</sup>H NMR in CDCl<sub>3</sub> and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

### **Typical photoinduced Cu-mediated RDRP of TFEMA with targeted DP<sub>n</sub>= 50 in TFE**

A stock solution of Cu(II)Br<sub>2</sub> (0.63 mg, 0.02 eq.), TFE (1 mL) and Me<sub>6</sub>Tren (4.5 μL, 0.12 eq.) was prepared and sonicated for >10 minutes. TFEMA (1 mL, 50 eq.) and MBPA (22 μL, 1 eq.) were added in the solution and aliquots of 100 μL and 10 μL were charged in vial inserts and sealed with NMR-tube lids. The polymerizations were allowed to commence for 19 hours under a UV lamp ( $\lambda_{\text{max}} \sim 360$  nm). Conversions were measured using <sup>1</sup>H NMR in CDCl<sub>3</sub> and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

### **Typical photoinduced Cu-mediated RDRP of PMA macroinitiator with DP<sub>n</sub>= 42 in DMSO**

MA (12 mL or 11.46 g, 50 eq.), EBiB (0.391 mL, 1 eq.), Cu(II)Br<sub>2</sub> (11.9 mg, 0.02 eq.) and DMSO (12 mL) were added to a septum sealed vial and the mixture was subsequently deoxygenated by bubbling with nitrogen for 15 minutes. Me<sub>6</sub>Tren (86 μL, 0.12 eq.) was then introduced in the vial *via* a gas-tight syringe and the polymerization was allowed to commence under UV irradiation for 45 minutes. SEC analysis was conducted in THF after the sample having been passed through neutral alumina for the removal of dissolved copper salts. The polymer was isolated *via* three precipitations in MeOH:H<sub>2</sub>O (70% MeOH), and dried under vacuum. The degree of polymerization of the PMA was calculated by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

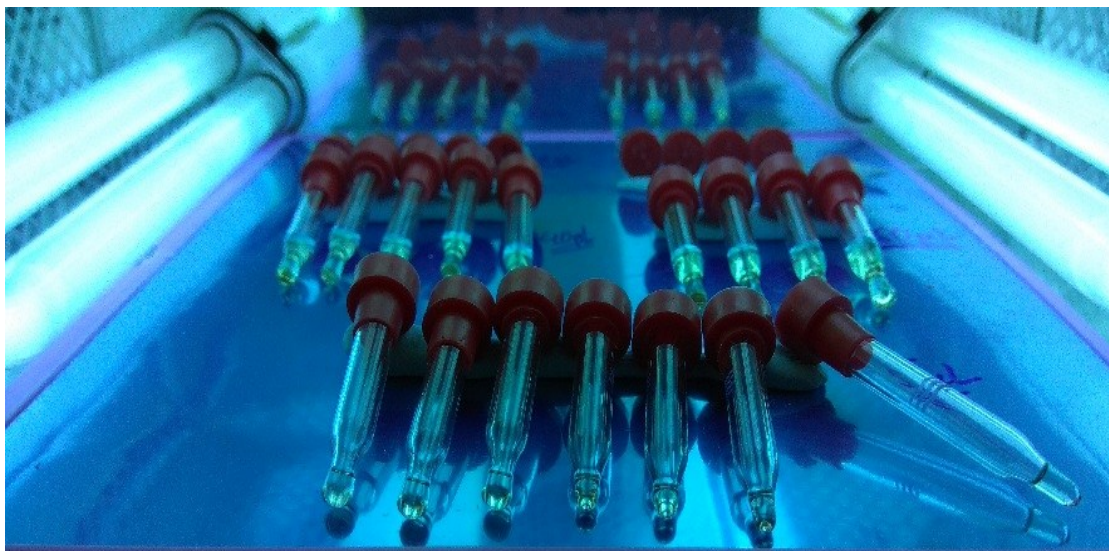
### **Typical chain extension of PMA with EGA *via* photoinduced Cu-mediated RDRP**

A stock solution of CuBr<sub>2</sub> (2.48 mg, 0.02 eq.) and Me<sub>6</sub>Tren (17.8 μL, 0.12 eq.) was prepared in DMSO (1 mL). 100 μL of this catalyst solution (0.02 equiv. CuBr<sub>2</sub> and 0.12 equiv. Me<sub>6</sub>Tren), PMA macroinitiator (0.25 g, DP<sub>n</sub> = 42, 1 eq.) dissolved in DMSO (0.5 mL) and EGA (0.357 mL, 42 eq.) were mixed and a 200 μL aliquot of this solution was added to a capped vial insert prior to UV irradiation for 7 hours. Conversions were measured using <sup>1</sup>H NMR in CDCl<sub>3</sub> and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

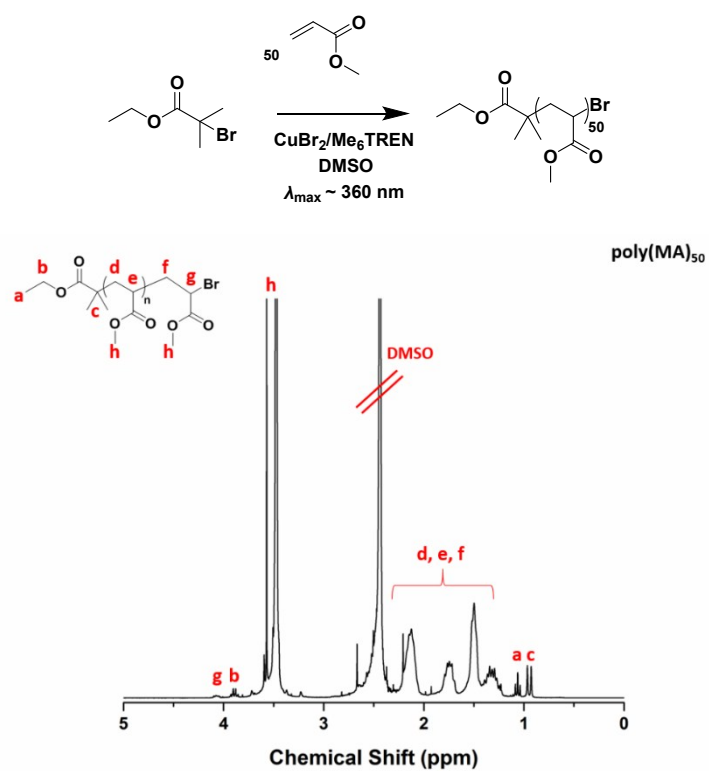
### **High-scale deoxygenation-free photoinduced Cu-mediated RDRP of MA with targeted DP<sub>n</sub> = 50 in DMSO or TFE**

A 0.5 L round bottom flask (RBF) was charged with Cu(II)Br<sub>2</sub> (250 mg, 0.02 eq.) and DMSO or TFE (250 mL). Me<sub>6</sub>Tren (1.769 mL, 0.12 eq.) was added and the solution was sonicated for ~ 15 minutes. MA (250 mL, 50 eq.), EBiB (8.063 mL, 1 eq.) and stirrer bar were added. The RBF was septum-sealed and an exit needle was added and maintained throughout the whole duration of the polymerization in order to facilitate gas-pressure release. The polymerization was allowed to commence overnight under a custom made UV box with λ<sub>max</sub> ~ 360 nm. Conversions were measured using <sup>1</sup>H NMR in CDCl<sub>3</sub> and SEC analysis was conducted in THF after the samples having been passed through neutral alumina for the removal of copper salts.

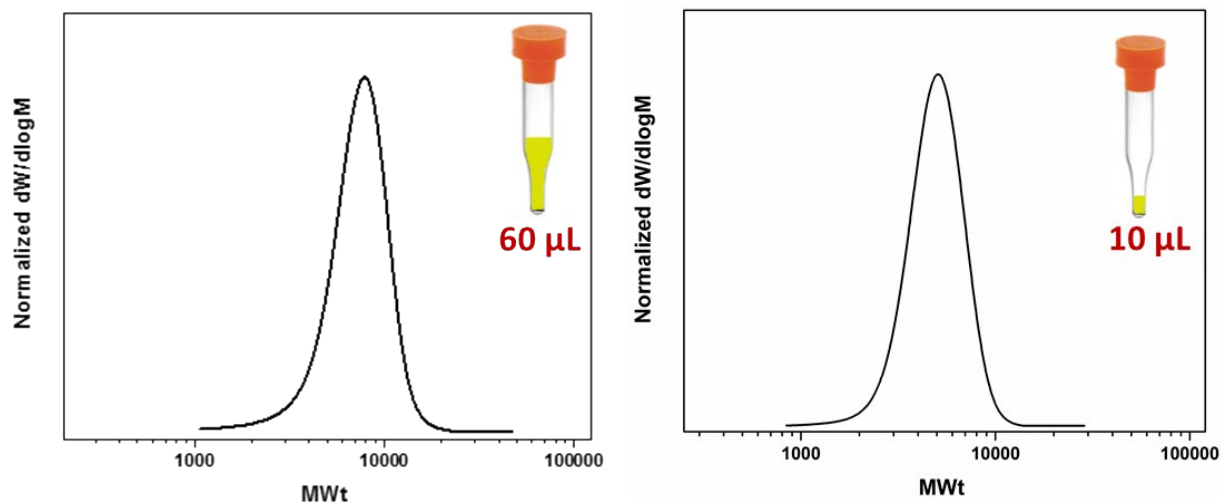
## Supplementary figures



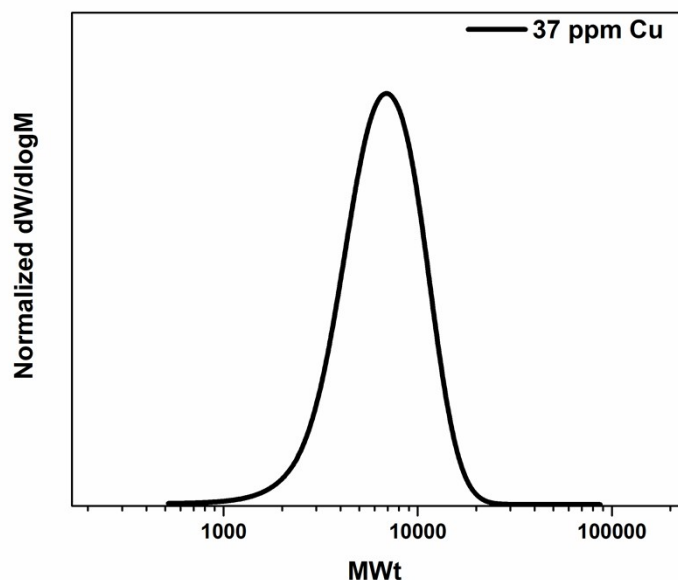
**Figure S1.** UV nail lamp reaction setup for the ultra-low volume polymerizations conducted in commercially available vial inserts ( $\lambda_{\text{max}} \sim 360 \text{ nm}$ ).



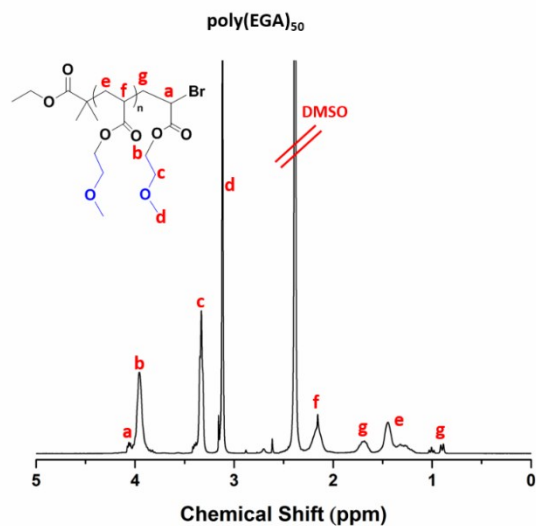
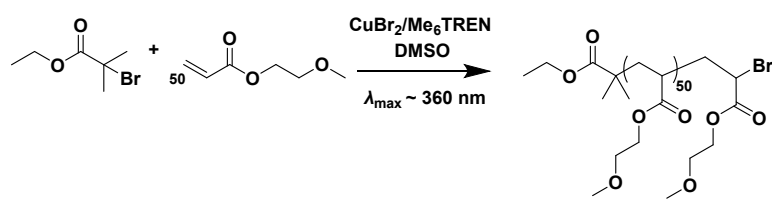
**Figure S2.** Reaction scheme and  $^1\text{H}$  NMR in  $\text{CDCl}_3$  for the low volume oxygen tolerant photoinduced Cu-mediated RDRP of MA with  $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{Tren}] = [50]:[1]:[0.02]:[0.12]$  in 50 % v/v DMSO.



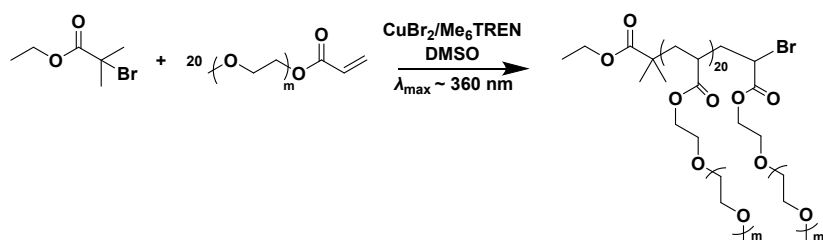
**Figure S3.** SEC traces for  $\text{PMA}_{50}$  synthesized in 60  $\mu\text{L}$  and 10  $\mu\text{L}$  *via* deoxygenation-free photoinduced Cu-RDRP using a UV lamp with broad band  $\lambda_{\text{max}} \sim 360$  nm.



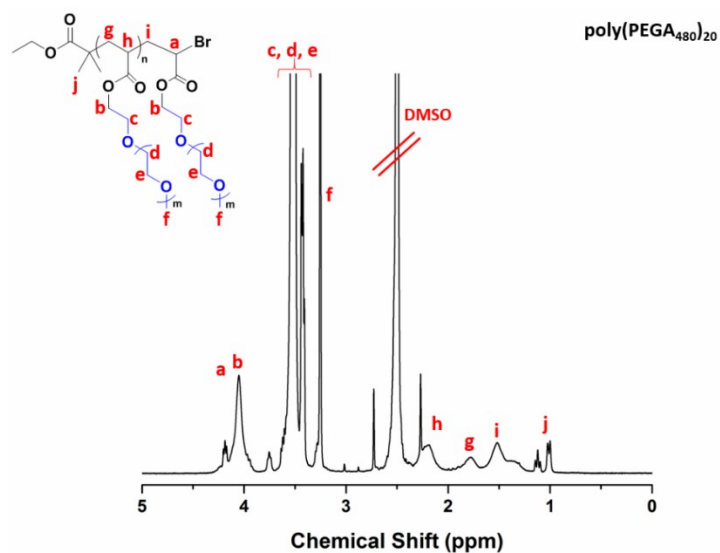
**Figure S4.** SEC trace for  $\text{PMA}_{50}$  synthesized on a 10  $\mu\text{L}$  scale *via* deoxygenation-free photoinduced Cu-RDRP utilizing 37 ppm of copper and using a UV lamp with broad band  $\lambda_{\text{max}} \sim 360$  nm.



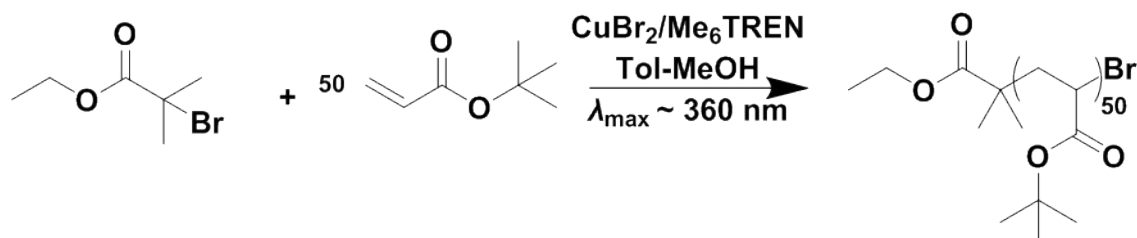
**Figure S5.** Reaction scheme and <sup>1</sup>H NMR in CDCl<sub>3</sub> for the oxygen tolerant photoinduced Cu-mediated RDRP of EGA on a 10 μL scale with [EGA]:[EBiB]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>Tren] = [50]:[1]:[0.02]:[0.12] in 50 % v/v DMSO.

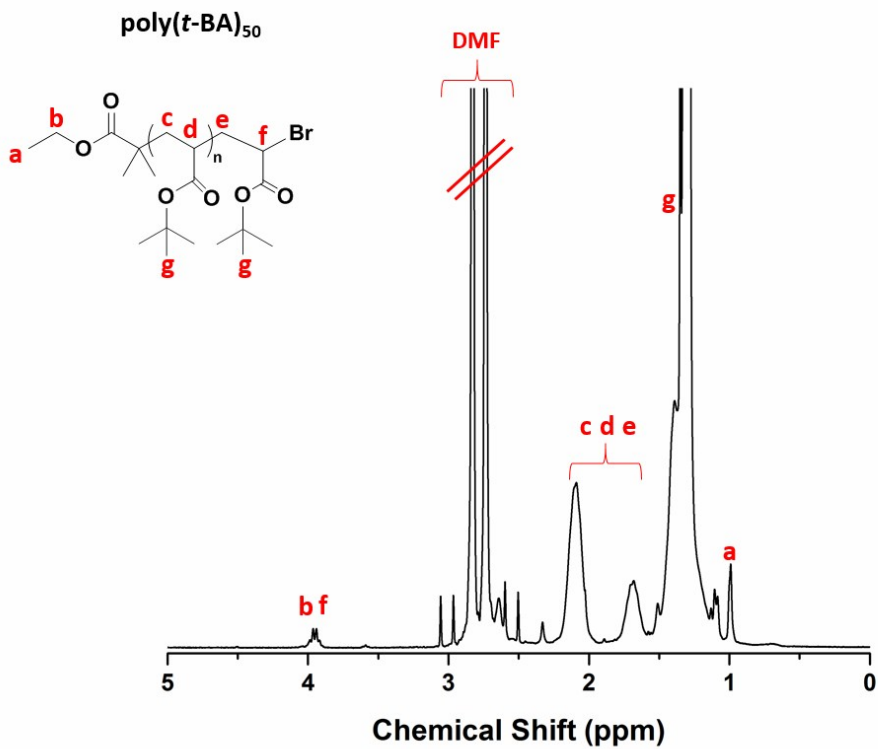




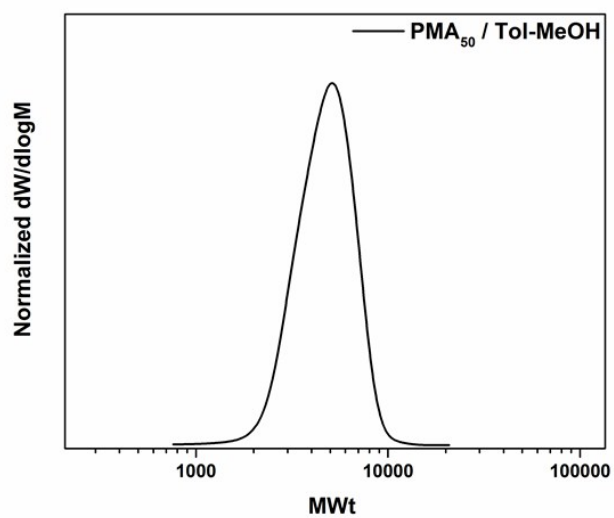


**Figure S6.** Reaction scheme and  $^1\text{H}$  NMR in  $\text{D}_2\text{O}$  for the oxygen tolerant photoinduced Cu-mediated RDRP of  $\text{PEGA}_{480}$  on a  $10\ \mu\text{L}$  scale with  $[\text{PEGA}_{480}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{Tren}] = [20]:[1]:[0.02]:[0.12]$  in 50 % v/v DMSO.





**Figure S7.** Reaction scheme and <sup>1</sup>H NMR in CDCl<sub>3</sub> for the oxygen tolerant photoinduced Cu-RDRP of *t*-BA on a 100 μL scale with [*t*-BA]:[EBiB]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>Tren] = [50]:[1]:[0.02]:[0.12] in 50 % v/v Toluene-MeOH (4:1).

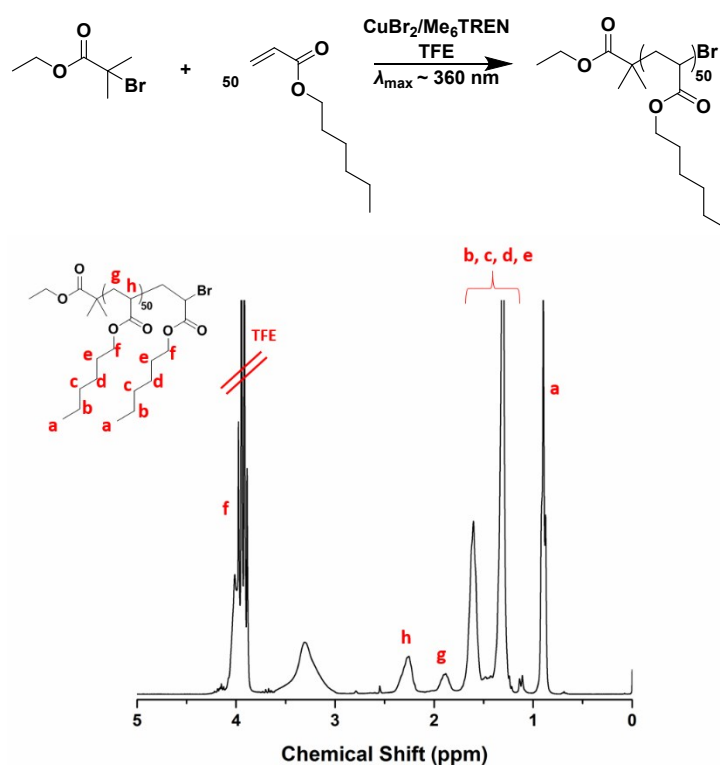


**Figure S8.** SEC trace for PMA<sub>50</sub> synthesized on a 100  $\mu\text{L}$  scale *via* oxygen tolerant photoinduced Cu-RDRP utilizing MeOH-Toluene (1:4) as solvent system using a UV lamp with broad band  $\lambda_{\text{max}} \sim 360 \text{ nm}$ .

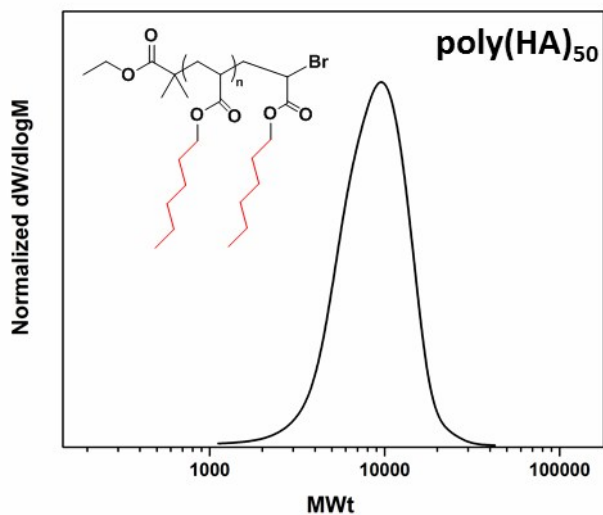
**Table S1.** <sup>1</sup>H NMR and SEC analysis for PMA<sub>50</sub> obtained through photoinduced Cu-RDRP without any type of deoxygenation in TFE and toluene-MeOH (4:1) as solvent systems.<sup>a</sup>

Polymer	Scale ( $\mu\text{L}$ )	Headspace ( $\mu\text{L}$ )	Solvent	Conversion <sup>1</sup> H NMR (%)	$M_{n, \text{theory}}$ ( $\text{g mol}^{-1}$ )	$M_{n, \text{SEC}}^b$	$\bar{D}$
PMA50	100	-	TFE	99	4,400	5,700	1.13
<<	100	-	Tol-MeOH	98	4,400	4,400	1.12

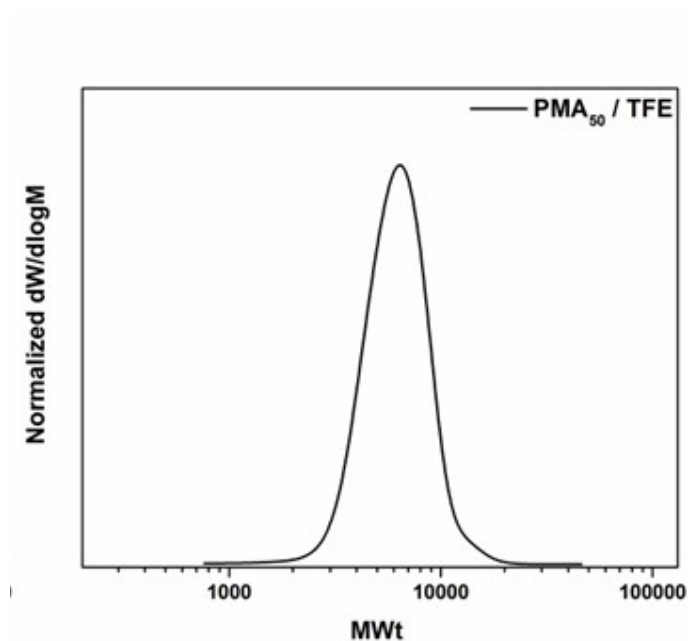
<sup>a</sup> In all polymerizations, the volume ratio of monomer to solvent(s) was maintained at 1:1 and conversion was calculated *via* <sup>1</sup>H NMR. <sup>b</sup> Determined by THF SEC analysis and expressed as molecular weight equivalents to PMMA standards.



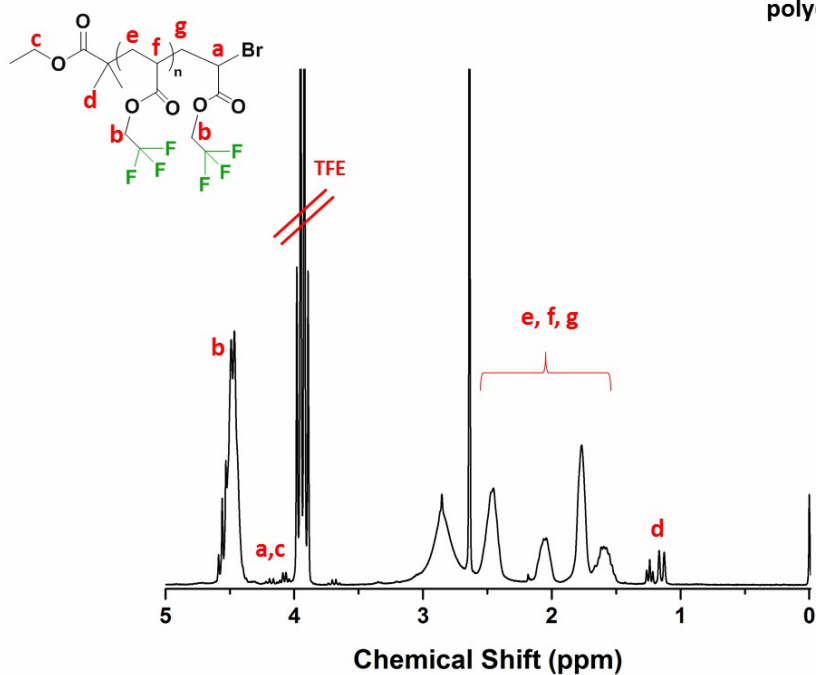
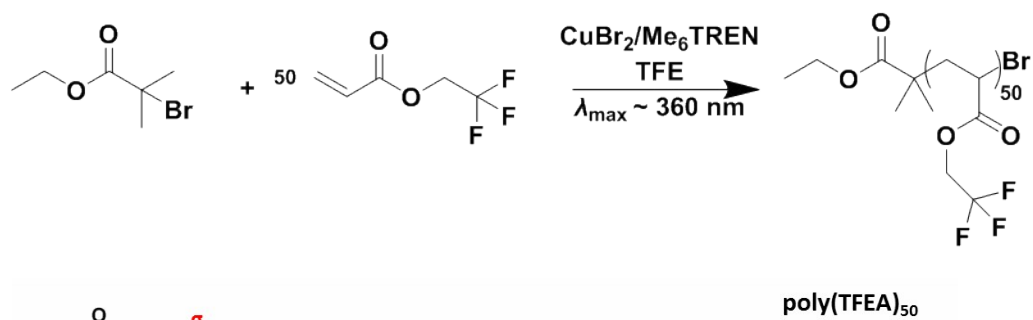
**Figure S9a.** Reaction scheme and  $^1\text{H}$  NMR in  $\text{CDCl}_3$  for the oxygen tolerant photoinduced Cu-RDRP of HA on a 100  $\mu\text{L}$  scale with  $[\text{HA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{Tren}] = [50]:[1]:[0.02]:[0.12]$  in 50 % v/v TFE.



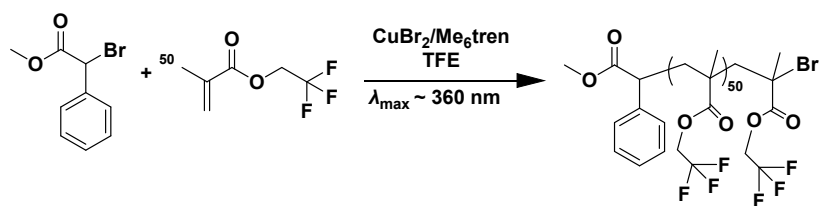
**Figure S9b.** SEC trace for PHA<sub>50</sub> synthesized on a 100  $\mu\text{L}$  scale *via* oxygen tolerant photoinduced Cu-RDRP in TFE using a UV lamp with broad band  $\lambda_{\text{max}} \sim 360$  nm.

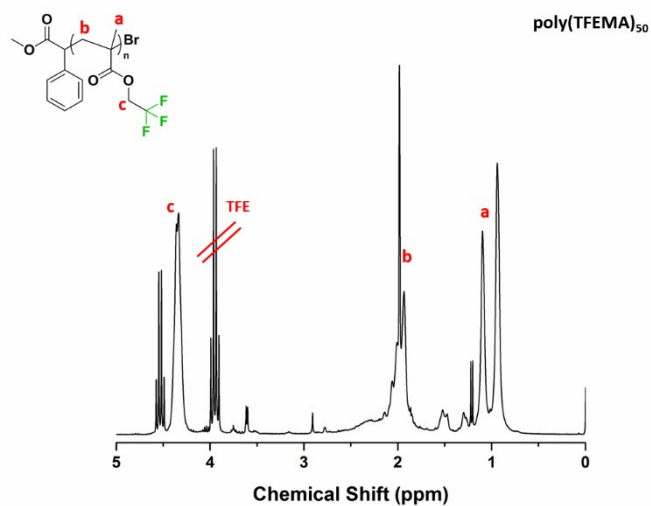


**Figure S10.** SEC trace for PMA<sub>50</sub> synthesized on a 100/100  $\mu\text{L}$  scale *via* oxygen tolerant photoinduced Cu-RDRP in TFE using a UV lamp with broad band  $\lambda_{\text{max}} \sim 360$  nm.

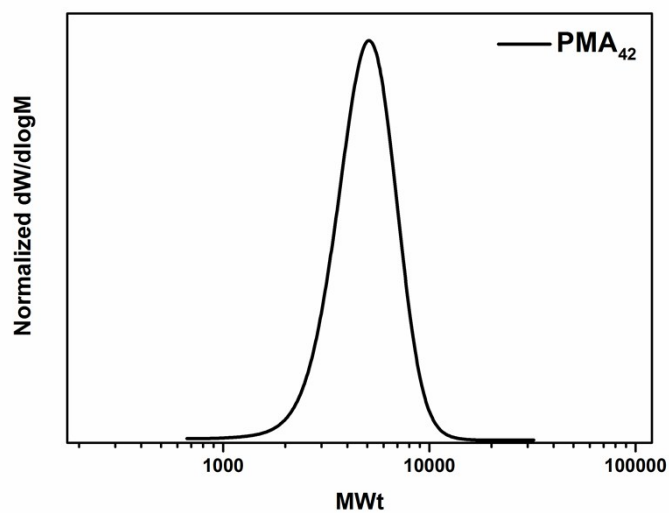


**Figure S11.** Reaction scheme and  $^1\text{H}$  NMR in  $\text{CDCl}_3$  for the oxygen tolerant photoinduced Cu-mediated RDRP of TFEA on a 100  $\mu\text{L}$  scale with  $[\text{TFEA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{Tren}] = [50]:[1]:[0.02]:[0.12]$  in 50 % v/v TFE.



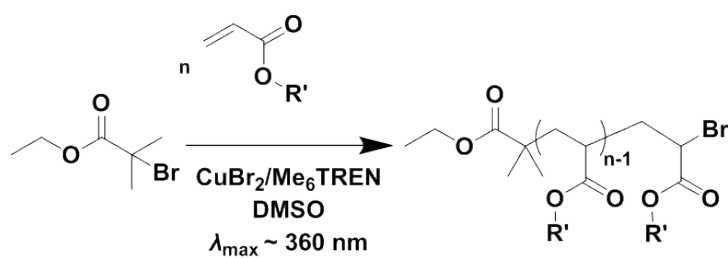


**Figure S12.** Reaction scheme and  $^1\text{H}$  NMR in  $\text{CDCl}_3$  for the oxygen tolerant photoinduced Cu-mediated RDRP of TFEMA on a 10  $\mu\text{L}$  scale with  $[\text{TFEMA}]:[\text{MBPA}]:[\text{CuBr}_2]:[\text{Me}_6\text{Tren}] = [50]:[1]:[0.02]:[0.12]$  in 50 % v/v TFE.

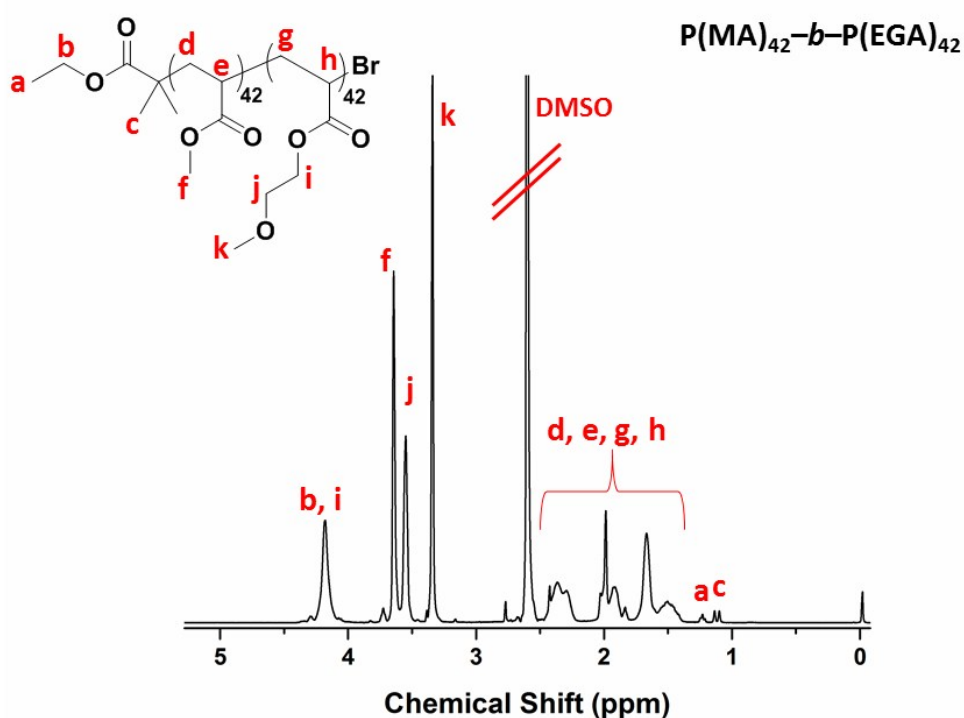
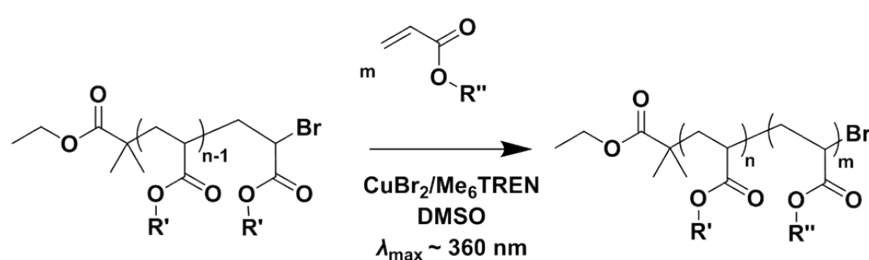


**Figure S13.** SEC trace for the PMA<sub>42</sub> macroinitiator synthesized *via* photoinduced Cu-RDRP in DMSO using a UV lamp with broad band  $\lambda_{\text{max}} \sim 360$  nm.

## PMA<sub>42</sub> macroinitiator synthesis

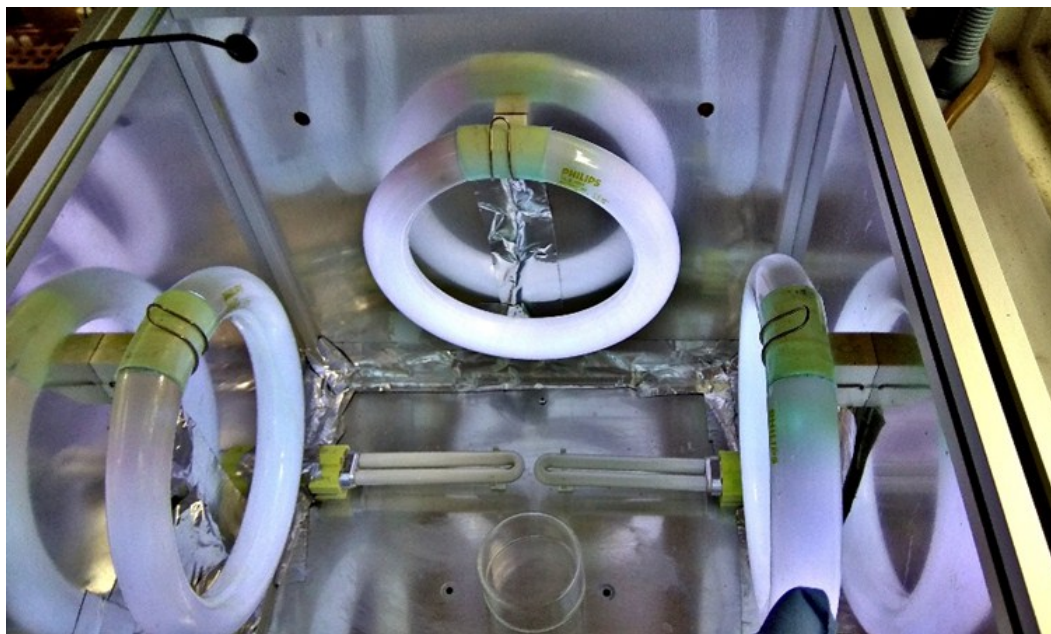


## P(MA)<sub>42</sub>-*b*-P(EGA)<sub>42</sub> synthesis



**Figure S14.** Reaction scheme and  $^1\text{H}$  NMR in  $\text{CDCl}_3$  for the diblock  $\text{P(MA)}_{42}\text{-}b\text{-P(EGA)}_{42}$  synthesized via low-volume oxygen tolerant photoinduced Cu-mediated RDRP. For the

macroinitiator [MA]:[EBiB]:[CuBr<sub>2</sub>]:[Me<sub>6</sub>Tren] = [42]:[1]:[0.02]:[0.12] in 50 % v/v DMSO. The block copolymerization was achieved upon re-irradiation of PMA<sub>42</sub> in the presence of EGA.



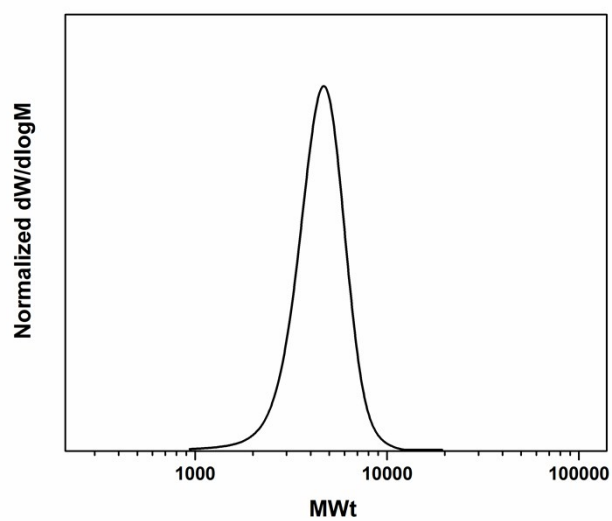
**Figure S15.** Custom-made UV box setup for the high-scale polymerizations with  $\lambda_{\text{max}} \sim 360$  nm.

**Table S2.** <sup>1</sup>H NMR and SEC analysis for the high scale deoxygenation-free copper-mediated photoinduced RDRP of MA with targeted DP<sub>n</sub>=50 <sup>a</sup>

Scale (mL)	Conversion <sup>1</sup> H NMR (%)	$M_{n, \text{theory}}$ (g mol <sup>-1</sup> )	$M_{n, \text{SEC}}^b$	$\bar{D}$
100	94	4,200	4,200	1.12
250	91	4,100	4,300	1.10
500	91	4,100	5,100	1.19

<sup>a</sup> In all polymerizations, the volume ratio of monomer to solvent(s) was maintained at 1:1 and conversion was calculated *via* <sup>1</sup>H NMR. <sup>b</sup> Determined by THF SEC analysis and expressed as molecular weight equivalents to PMMA standards.





**Figure S16.** SEC trace for PMA<sub>50</sub> synthesized on a 250 mL scale *via* oxygen tolerant photoinduced Cu-RDRP in TFE under a UV lamp with broad band  $\lambda_{\text{max}} \sim 360$  nm.

## References

1. M. Ciampolini and N. J. I. c. Nardi, 1966, **5**, 41-44.