Supporting Information

Application of Oxygen Tolerant PET-RAFT to

Polymerization-Induced Self-Assembly

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EXPERIMENTAL SECTION

Materials

Benzyl methacrylate (BzMA, Aldrich) was deinhibited by passing through a column of basic alumina. Oligo(ethylene glycol) methyl ether methacrylate (OEGMA) (M_n = 300 g mol^{-1}) (Sigma-Aldrich) was used as received. 2,2'-azobis(isobutyronitrile) (AIBN, Fluka, 98%) was purified by recrystallization from methanol. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA, Boron Molecular), 5,10,15,20-Tetraphenyl-21H,23H-porphine (ZnTPP, Sigma-Aldrich), 9,10-dimethylanthracene (DMA, Sigma-Aldrich), L-ascorbic acid (AscA, Sigma-Aldrich, 99%), 3-methyl-3-butene-1-ol (Sigma-Aldrich, 97%), (R)-(+)-limonene (Lim, Sigma-Aldrich, 97%), 9-anthracenemethanol (9-AM, Sigma-Aldrich, 97%), 1,2-epoxybutane (Epoxy, Sigma-Aldrich, 99%), β-carotene (Sigma-Aldrich, 97%) were used as received. All other reagents were used as received unless otherwise specified.

Instrumentation

All ^{1}H-NMR spectra were recorded using a Bruker 300 or 400 MHz spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances.

The molecular weight and dispersity of the prepared polymers were measured by GPC. The eluent was DMAc (containing 0.03% w/v LiBr and 0.05% w/v 2,6-dibutyl-4-methylphenol (BHT)) at 50 °C (flow rate of 1 mL/min) with a Shimadzu modular system comprising an SIL-10AD auto-injector, a Polymer Laboratories 5.0 μm bead-size guard column (50×7.5 mm^2) followed by four linear PL (Styragel) columns (10^5, 10^4, 10^3, and 500 Å) and an RID-10A differential refractive-index (RI) detector and UV-Vis detector. The calibration of the system was based on narrow molecular weight distribution of polystyrene standards with molecular weights of 200–10^6 g mol^{-1}.

DLS measurements were performed using a Malvern Zetasizer Nano Series running DTS software and using a 4 mW He−Ne laser operating at a wavelength of 633 nm and an avalanche photodiode (APD) detector. The scattered light was detected at an angle of 173°.

TEM studies of self-assembled block copolymers were conducted using a Transmission Electron Microscope at an accelerating voltage of either 100 kV (JEOL-1400) or 200 kV (FEI Tecnai G2 20). The polymerization dispersions were diluted with ethanol (or water for aqueous dispersions) to give 0.2 - 0.5 wt% dispersions and deposited onto carbon-coated copper grids. Uranyl acetate staining was applied to all samples.

Online Fourier transform near-infrared (FTNIR) spectroscopy was used to determine monomer conversions by following the decrease of the vinylic C–H stretching overtone of the monomer at ∼6100 cm. A Bruker Vertex 70 Fourier transform spectrometer equipped with a CaF_2 beam splitter, and room temperature DLaTGS detector was used. Spectra were analyzed with OPUS software (Version 7.5).

Photopolymerization reactions were carried out in the reaction vessel where the reaction mixtures are irradiated by RS Component PACK LAMP RGB red LED lights (5 W, λ_{max} = 635 nm (red), 3.0 mW/cm²) as shown below. The distance of the samples to the light source was 5 cm. The light intensity was measured using a light meter Newport Power Meter Model 843-R. The RGB multi-colored LED light bulb with remote control was purchased from RS Components Australia.

PET-RAFT polymerization in the presence of quenchers and without deoxygenation

A typical experiment ([BzMA]:[CDTPA]:[ZnTPP] = 200:1:0.01 and DMA as quencher ([Q] = 16.2 mM) was set up as follows: ZnTPP (146.2 μg, 2.16×10^{-7} mol, 146.20 μL of a 1 mg/mL tetrahydrofuran (THF) stock solution) was added to a 21 mL glass vial. After evaporating the residual THF under a stream of nitrogen, CDTPA (8.7 mg, 2.16×10^{-5} mol), BzMA (759.5 mg, 4.32×10^{-3} mol), DMA (5 mg, 2.4×10^{-5} mol) and 0.773 mL DMF ([M] = 50 w/w%) were further added to the vial. 1.5 mL of the reaction mixture was subsequently transferred to a 1.6 mL glass vial which was subsequently sealed with a rubber septum and parafilm. The polymerization mixture was irradiated with red LED light (λ_{max} = 635 nm, 3.0 mW/cm²) at room temperature for 14 h before it was quenched by exposure to air (and storage in the dark). ¹H NMR (CDCl₃) of the crude polymerization mixture was used to measure the monomer conversion by comparing the relative intensities of the (P)BzMA methylene protons adjacent to the ester bond in the monomer (5.17 ppm) and polymer (5.0-4.7 ppm) respectively. GPC analysis was also used to determine the molecular weight ($M_{n,GPC}$) and polymer dispersity (Đ).

Note: For all experiments, ZnTPP stock solutions were first prepared in THF and the residual THF removed before addition of RAFT, monomer and solvent.

Kinetic studies of oxygen tolerant PET-RAFT polymerization in the presence of quenchers

For FTNIR kinetic studies, a typical polymerization mixture ([BzMA]:[CDTPA]:[ZnTPP] = 200:1:0.01 and DMA as quencher ([Q] = 27 mM)) was set up as follows. ZnTPP (84.0 μg, 1.24×10^{-7} mol, 84.0 μL of a 1 mg/mL tetrahydrofuran (THF) stock solution) was added to a 21 mL glass vial After evaporating the residual THF under a stream of nitrogen, CDTPA (5 mg, 1.24×10^{-5} mol), BzMA (436.5 mg, 2.48×10^{-3} mol), DMA (5 mg, 2.4×10^{-5} mol) and 0.442 mL DMF ([M] = 50 w/w%) were further added to the vial. 900 μL of the reaction mixture was transferred to an 0.9 mL FTNIR quartz cuvette (1 cm × 2 mm) which was sealed with a rubber septum irradiated with red LED light (λ_{max} = 635 nm, 3.0 mW/cm²) at room temperature. At predetermined time points, the cuvette was transferred from the reactor to the sample holder

for FTNIR measurement. The monomer conversions were calculated using the ratio of the integral of the wavenumber region 6220 - 6140 cm-1 at different time points relative to the integral of the initial polymerization mixture (0% monomer conversion). At regular intervals, a degassed syringe was used to extract ~0.05 mL aliquots for GPC analysis.

Synthesis of POEGMA macro-CTA via RAFT polymerızatıon

A typical synthesis of a POEGMA macro-CTA by RAFT polymerization was set up as follows: OEGMA (12.0 g, 0.04 mol), CDTPA (0.3224 g, 5.6×10^{-4} mol), AIBN (16.4 mg, 1×10^{-4} mol) and 50 mL toluene were added to a 200 mL round bottom flask which was sealed with a rubber septum and purged with nitrogen for 30 min at 0 °C. The polymerization was carried out for 5 h at 70 °C before quenching in an ice bath and exposing to air. The resulting polymer was purified by precipitation in a diethyl ether and petroleum spirit (boiling range of 40-60 °C) mixture (30:70, v/v). GPC analysis using DMAc as a mobile solvent and polystyrene standards indicated $M_{n,GPC} = 9\ 100$ g mol^{-1}, Đ = 1.15. ^{1}H NMR indicated a monomer conversion of 55 % which was calculated using the following equation $\alpha = 100 \times [p\ /\ (p+m)]$, where $m = \int I$ $^{5.8\text{-}5.5\ ppm}$ and $p = [(\int I\ ^{4.5\text{-}4.0\ ppm}\ /\ 2) - (\int I\ ^{5.8\text{-}5.5\ ppm})]$. The theoretical molecular weight was determined to be $M_{n,theo} = 8\ 700$ g/mol using the following equation: $M_{n,theo} = MW_{CDTPA} + [\alpha \times [M]_0/[CDTPA]_0 \times MW_{OEGMA}]$ where MW_{CDTPA} is the molecular weight of the RAFT agent, α is the monomer conversion, $[M]_0$ is the initial monomer concentration, $[CDTPA]_0$ is the initial concentration of the RAFT agent and MW_{OEGMA} is the molecular weight of OEGMA (300 g/mol).

PET-RAFT dispersion polymerization under red light and without deoxygenation

A typical experiment ([BzMA]:[POEGMA]:[ZnTPP] = 100:1:0.01 and total solids content of 10 wt%) was set up as follows: POEGMA macro-CTA ($M_{n,\ theo} = 8\ 700$ g mol^{-1} and Đ = 1.15) (43 mg, 4.9×10^{-6} mol) was added to a 21 mL glass vial followed by ZnTPP (33.5 µg, 4.94×10^{-8} mol, 33.5 µL of a 1 mg/mL tetrahydrofuran (THF) stock solution). After evaporating the residual THF under a stream of nitrogen,

BzMA (87.1 mg, 4.94×10^{-4} mol and 1.483 mL EtOH (90 wt%) were further added to the vial which was subsequently sealed with a rubber septum and irradiated with red LED light (λ_{max} = 635 nm, 3.0 mW/cm^2) at room temperature for 24 h before it was quenched by exposure to air (and storage in the dark). ^{1}H NMR (CDCl$_3$) of the crude polymerization mixture was used to measure the monomer conversion by comparing the relative intensities of the (P)BzMA methylene protons adjacent to the ester bond in the monomer (5.17 ppm) and polymer (5.0-4.7 ppm) respectively. The number average molecular weight ($M_{n, NMR}$) of POEGMA-PBzMA block copolymers was found by comparing the same PBzMA peak (5.0-4.7 ppm) with the POEGMA methylene protons at 4.1 ppm. GPC chromatograms were also used to determine the molecular weight ($M_{n,GPC}$) and polymer dispersity. Finally, TEM (and DLS for spherical nanoparticles) analysis were used to determine the size and the morphology of the self-assembled block copolymers.

(A)

Entry	Quencher	Conversion	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	Đ
P1	DMA (deoxygenated)	97	34 600	24 300	1.29
P2	None (deoxygenated)	98	32 100	25 000	1.29

(B)
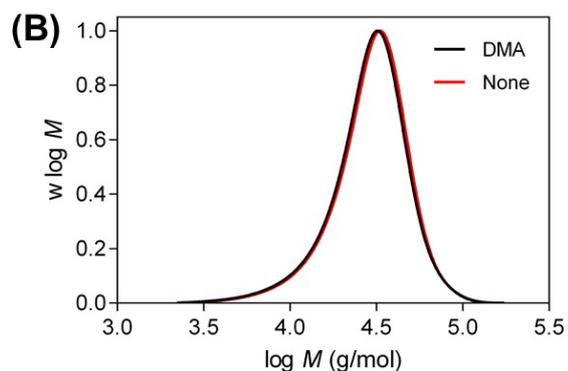
Figure S1. PET-RAFT polymerization of BzMA performed under deoxygenated conditions in DMF. **(A)** Experimental and characterization data and **(B)** molecular weight distributions of polymers synthesized using [BzMA]:[CDTPA]:[ZnTPP] = 200:1:0.01 under red light (λ_{max} = 635 nm, 3.0 mW/cm^2) for 14 h and in the presence ([Q] = 16.2 mM) and absence of DMA ([Q] = 0 mM).
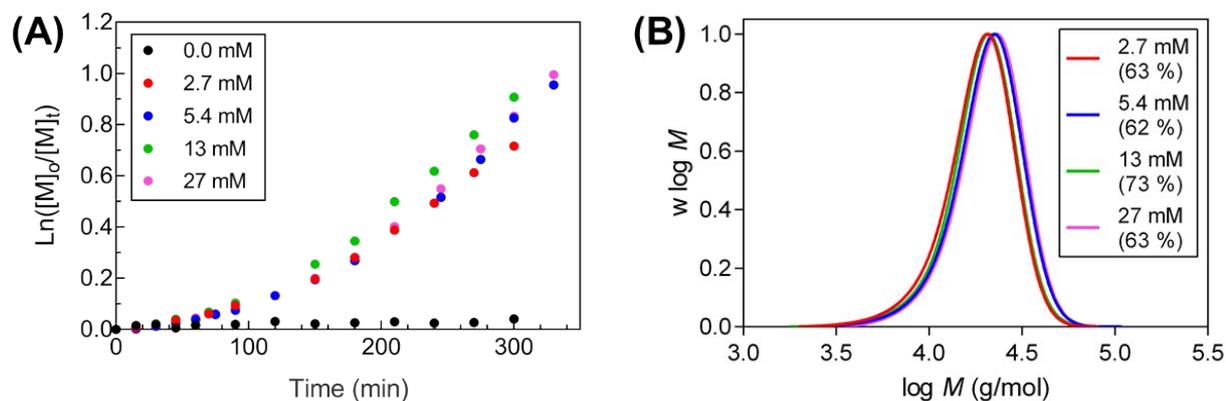
Figure S2. (A) Evolution of $\ln([M]_0/[M]_t)$ with irradiation time and **(B)** molecular weight distributions of polymers in the presence of varying concentrations of DMA ($[Q]$ = 2.7 - 27 mM) as a singlet oxygen quencher. The monomer conversions for each GPC trace are given in parenthesis. Polymerizations were performed under red light (λ_{max} = 635 nm, 3.0 mW/cm^2) using a [BzMA]:[POEGMA]:[ZnTPP] = 200:1:0.01.
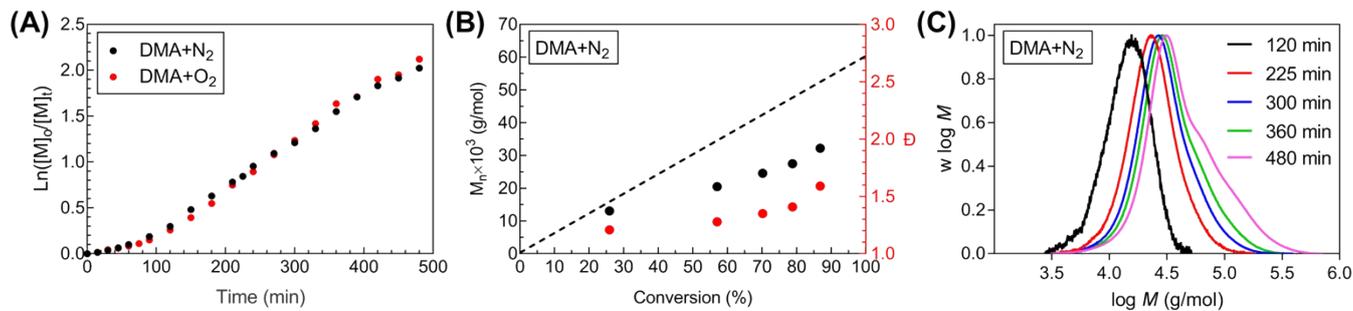
Figure S3. Polymerization kinetics of OEGMA in EtOH and in the presence of DMA ([Q] = 27 mM). Photopolymerization was performed under red light (λ_{max} = 635 nm, 3.0 mW/cm^2) under deoxygenated conditions using a [BzMA]:[CDTPA]:[ZnTPP] = 200:1:0.01: variation of **(A)** ln([M]$_0$/[M]$_t$) with irradiation time (non-deoxygenated kinetics from **Figure 4A** are overlaid for clarity), **(B)** GPC derived molecular weight (black dot) and dispersity (red dot) with conversion and **(C)** corresponding molecular weight distributions at varying irradiation time.

Entry	Solvent (50 wt%)	Conversion	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	Đ
P3	Tetrahydrofuran	89	31 800	25 300	1.23
P4	1,4-Dioxane	92	32 800	24 800	1.20
P5	Dimethylacetamide	93	33 200	21 600	1.25
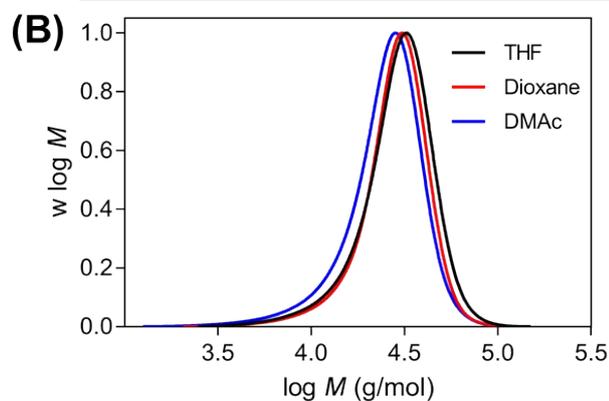
Figure S4. PET-RAFT polymerization of BzMA performed in different solvents in the presence of DMA as a singlet oxygen quencher. **(A)** Experimental and characterization data and **(B)** molecular weight distributions of polymers synthesized without deoxygenation using [BzMA]:[CDTPA]:[ZnTPP] = 200:1:0.01 under red light (λ_{max} = 635 nm, 3.0 mW/cm^2) for 14 h and in the presence of DMA ([Q] = 16.2 mM).
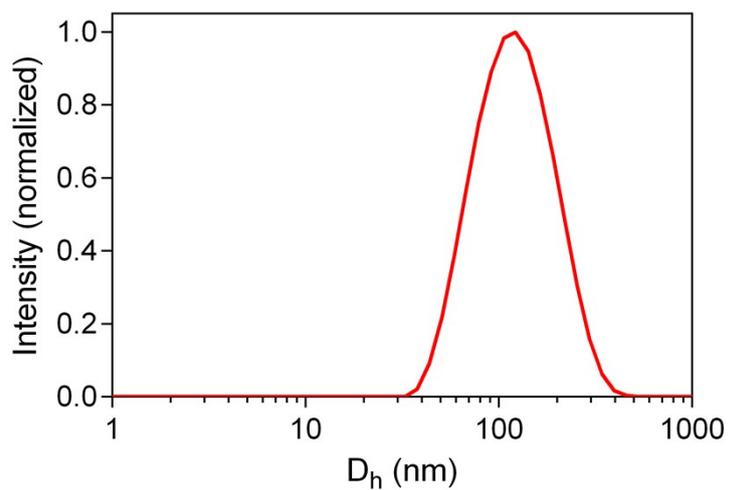
Figure S5. Particle size distribution (intensity-based) of nanoparticles synthesized under oxygen tolerant PET-RAFT dispersion polymerization. Polymerization was performed using [BzMA]:[POEGMA]:[ZnTPP] = 100:1:0.01 under red light (λ_{max} = 635 nm, 3.0 mW/cm^2) for 9.5 h.

(A) Entry	DMA (mM)	Time (h)	α (%)	$M_{n,Theo}$ (g/mol)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	Đ	D_h (nm)	DLS PDI
POEGMA	-	5	55	8 700	-	9 100	1.15	-	-
PISA-1	0.0	24	< 5	-	-	-	-	-	-
PISA-2	3.2	24	94	25 300	24 800	21 200	1.18	55	0.07
PISA-3	8.1	24	99	26 100	29 100	22 100	1.21	56	0.06
PISA-4	16	24	93	25 100	25 500	21 100	1.21	62	0.10
PISA-5*	16	24	94	25 300	26 800	22 900	1.22	55	0.10
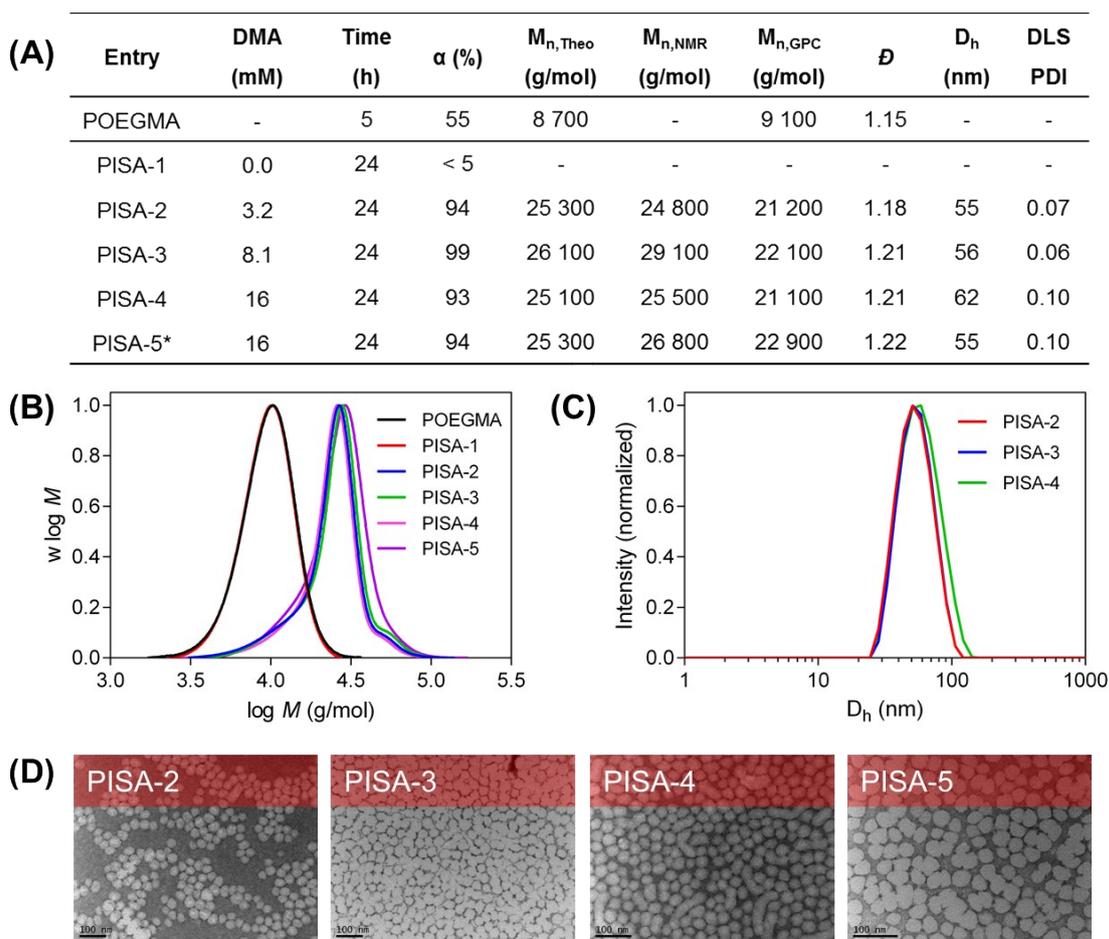
Figure S6. Oxygen tolerant PET-RAFT dispersion polymerization of BzMA conducted in the presence of varying amounts of DMA as a singlet oxygen quencher: **(A)** experimental and characterization data, **(B)** molecular weight distributions and **(C)** corresponding particle size distributions (intensity-based) as determined by DLS analysis. Polymerizations were performed under red light (λ_{max} = 635 nm, 3.0 mW/cm^2) using a [BzMA]:[POEGMA]:[ZnTPP] = 100:1:0.01 at a total solids content of 10 wt%. *Polymerization performed after sparging with nitrogen for 20 min at 0 °C.