Supporting Information to

Alcohol-based PISA in Batch and Flow: Exploring the Role of Photoinitiators

Neomy Zaquen,[a,b,c] Wan. A. A. W. Azizi,[a] Jonathan Yeow,[a,b] Rhiannon. P. Kuchel,[d] Tanja Junkers,[c,e]* Per B. Zetterlund[a]* and Cyrille Boyer[a,b]*

[a] Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

[b] Australian Center for Nanomedicine, The University of New South Wales, Sydney, NSW 2052, Australia

[c] Organic and Bio-Polymer Chemistry (OBPC), Universiteit Hasselt, Agoralaan Building D, 3590 Diepenbeek, Belgium

[d] Mark Wainwright Analytical Centre, University of New South Wales, Sydney, NSW 2052, Australia.

[e] Polymer Reaction Design Group, School of Chemistry, Monash University, VIC 3800, Melbourne, Australia

Contents

Experimental Part

Materials

Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO, >99%, Sigma Aldrich), 4,4'-Bis(diethylamino)benzophenone (BDB, >99%, Sigma Aldrich), Eosin Y Disodium salt (>99%, Sigma Aldrich), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959 or PP-OH, >99%, Sigma Aldrich), Campherquione (CQ, >99%, Sigma Aldrich), ethyl 4-dimethylaminobenzoate (EDB, 99% Sigma Aldrich), triethanolamine (TEtOHA, >98%, TCI) were used as received. 2,2'-azobis(isobutyronitrile) (AIBN, 98% Fluka) was crystallized from methanol prior to use. Oligo (ethylene glycol) methyl ether methacrylate (OEGMA, M_n = 300 g·mol^{-1}, 99%, Sigma Aldrich), oligo (ethylene glycol) methyl ether acrylate (OEGA, M_n = 480 g·mol^{-1}, 99% Sigma Aldrich), dimethyl acrylamide (DMAA, 99%, Sigma Aldrich), isobornyl acrylate (IBA, 99%, Sigma Aldrich), benzyl methacrylate (BzMA, 99%, Sigma Aldrich) were de-inhibited by passing through a column of basic alumina. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA) and 2-(n-butyltrithiocarbonate)-propionic acid (BTPA) were synthesized according to literature procedure.[68, 69] All other reagents were used as received without further purification unless stated otherwise. Deionized (DI) water was obtained using a MilliQ reverse osmosis system with a resistivity of > 18 mΩ·cm^{-1}. Formvar coated copper grids (400 mesh) were purchased from ProSciTech.

Characterization

Nuclear Magnetic Resonance (NMR) Spectrometry: All NMR spectra were obtained using a Bruker Avance 400 spectrometer (400 MHz). All chemical shifts were recorded in ppm (δ) relative to tetramethylsilane (δ = 0 ppm), referenced to the chemical shifts of residual solvent resonances (1H). The multiplicities are referred to using the following abbreviations: s for singlet, d for doublet, t for triplet, m for multiplet and bs for broad signal.

Size Exclusion Chromatography (SEC): The molecular weight and polydispersity of synthesized polymers were analyzed via size exclusion chromatography (SEC). A Shimadzu modular system containing a DGU-12A degasser, an LC-10AT pump, an SIL-10AD automatic injector, a CTO-10A column oven and a RID-10A refractive index detector was used. A 50x7.8 mm guard column and three 300x7.8 mm linear columns (500, 103, 104, 105 Å pore size, 5 μm particle size) were used for analysis. Dimethylacetamide (DMAc) containing 0.03% w/v LiBr and 0.05% w/v 2,6-dibutyl-4-methylphenol (BHT) with a flow rate of 1 mL·min^{-1} at 50 °C was used as the mobile phase. The injection volume was 50 μL. The samples were prepared by dissolving 2-3 mg.mL^{-1} of the analyte in DMAc, followed by

filtration through a 0.45 µm filter. The unit was calibrated using commercially available linear poly(methyl methacrylate) (PMMA) standards (0.5-1000 kDa, Polymer Laboratories). Chromatograms were processed using Cirrus 2.0 software (Polymer Laboratories).

Dynamic Light Scattering (DLS): Particle sizes (the average diameters and size distributions) were determined using a Malvern Zetaplus particle size analyzer (laser, 35mW, $\lambda = 632$ nm, angle = 90°). Samples (1 droplet of latex; approx. 250 mg) were prepared in ethanol for DLS analysis. The count rate was kept in between 100 and 500 kcps, thereby highly diluting the latex samples, leading to almost translucent solutions. DLS measurements were performed on all samples in fivefold of which the average value was given. As DLS is based on scattering by light from 1 single angle, different results with respect to average diameter can be obtained for non-spherical particles, depending on the position of the particle relative to the laser light of the DLS. Therefore, particle size values obtained from DLS were only valid for spherical particles.

Ultraviolet Visible Spectroscopy (UV-Vis): UV-Vis spectra were recorded on a Varian Cary 300 UV-Vis-NIR spectrophotometer (scan rate 600 nm·min⁻¹, continuous run from 200 to 800 nm) equipped with a temperature controller. 1 Droplet of latex (250 mg) was prepared in ethanol for UV Analysis.

Transmission Electron Microscopy (TEM): A JEOL1400 TEM operating at 100 kV was used to characterize the morphology and shape of the nanoparticles. Samples were prepared by diluting the final latexes in ethanol. One Drop of the diluted latex (concentration range of $0.2–0.5$ mol·L⁻¹) was deposited onto a Formvar coated copper grid and left to dry for 1 minute. The samples were then stained for 5 minutes with a 2% uranyl acetate solution functioning as a negative stain. Staining was used to improve the visibility of the particle on the grid.

Wavelength of emission: The wavelength of the LED strips and UV bulb was obtained by using a HR4000 Ocean Optics Spectrometer, with an optical cable pointed directly at the lamp. A background was taken at a similar position with the lamp off. Emission spectra of all colors were recorded at the same moderate intensity (to avoid maxing out the receptor). Data was collected over the wavelength range from 189-1036 nm, with a fairly low resolution.

Flow Reactor set-up

A custom-made tubular reactor was built, consisting of fluorinated gastight PFA tubing (John Morris Group, 1/16″ OD, 1.0 mm ID) wrapped around a metal framework and placed in between two glass crystalizing dishes. On the inside of the large crystallizing dish (ID=190 mm) and on the outside of the small crystallizing dish (ID = 115 mm) were two LED strips placed (5050 SMD, 60 LEDs per meter, 460 nm, 14.4 W, 12-24 V) both facing the PFA tubing. Reactor volumes were adapted by varying the length of the reactor tubing. Reaction solutions were pumped into the reactor via Asia syringe pumps, using ASIA blue syringes (flow rates adjustable between 10 µL·min^{-1} to 2.5 mL·min^{-1}). In this study, a single 3 mL tubular reactor was employed for synthesis of nanoparticles, this lead to a maximum residence time of 300 min when employing the ASIA blue syringes. The intensity of blue light at the surface of the PFA tubing was measured to be approximately 0.8 mW·cm^{-2} per LED strip using a Newport 843-R power meter. Due to the use of LED strips and the accompanying heat generated by the lamps, all reactions were performed at 37°C (Figure S1 and S2).
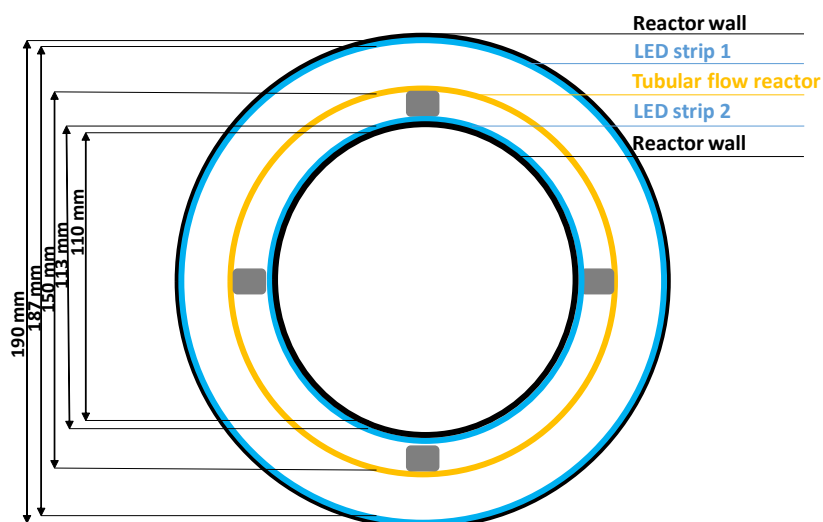

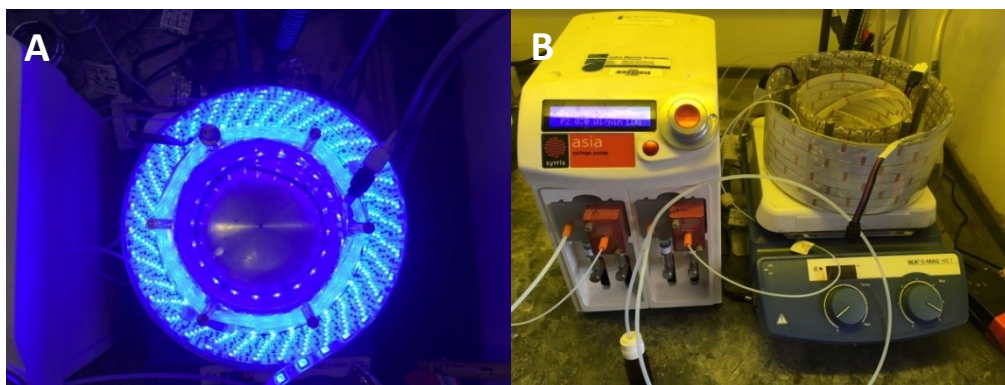**Figure S1:** Schematics of the flow reactor including all dimensions.

Figure S2: Photoflow reactor used for implementation of all methacrylate-based photo-PISA under flow conditions. Top view of the reactor with LED on (A) and picture of complete setup as used for the reaction with light off (B) in which an aluminum lid was used to prevent light inference of the surroundings.

Synthesis

Synthesis of POEGMA macro-RAFT via RAFT Polymerization

A typical procedure to synthesize POEGMA macro-RAFT via RAFT polymerization was prepared as follows;[31] OEGMA$_{300}$ (6.0 g, 0.02 mol, 71.4 equiv.), CDTPA (0.1612 g, 2.8 x 10^{-4} mol, 1 equiv.), AIBN (8.21 mg, 5 x 10^{-5} mol, 0.179 equiv.) and 25 mL toluene were added to a 50 mL round bottom flask which was sealed with a rubber septum and purged with nitrogen for 20 minutes at 0°C. The polymerization was conducted for 5 h at 70 °C, after which the reaction was quenched in liquid nitrogen and exposed to air. The resulting polymer was purified by precipitation in a mixture of petroleum spirit / diethylether (70/30 v/v%). The theoretical molecular weight ($M_{n,theory}$) was calculated using the following equation:

$$M_{n, theory} = MW_{CDTPA} + [\alpha \times \left(\frac{[M]_0}{[CDTPA]_0}\right) \times MW_{OEGMA}]$$

where MW_{CDTPA} is the molecular weight of the RAFT agent, α is the monomer conversion, $[M]_0$ is the initial concentration of monomer, $[CDTPA]_0$ is the initial concentration of the RAFT agent and MW_{OEGMA} is the molecular weight of OEGMA (300 g·mol^{-1}). The conversion of the monomer via ^{1}H-NMR was calculated as follows: $\alpha = 100 \times [p / (p+m)]$, where m = ∫I 5.8-5.5 ppm and p = [(∫I 4.5-4.0 ppm / 2) - (∫I 5.8-5.5 ppm)].

A similar procedure was followed when synthesizing POEGA-CDTPA and POEGA-BTPA macro-CTA. In that case, OEGA (M_n = 480 g·mol^{-1}) and either CDTPA or BTPA was chosen as RAFT agent. Polymerizations were carried out at 70°C for 5 h.

Synthesis of POEGMA-*b*-PBzMA nanoparticles via RAFT PISA Dispersion Polymerization in batch

A typical procedure for the synthesis of POEGMA-*b*-PBZMA with [BzMA]:[POEGMA] = 200, total solid content = 15 % and 70:30 v/v% EtOH : MeCN, was carried out as follows; POEGMA macro-CTA (M_n = 7 700 g·mol^{-1}; 0.03 g, 3.75 x 10^{-6} mol, 1 equiv.), BzMA (0.137 g, 7.79 x 10^{-4} mol, 200 equiv.), 0.95 g of solvents (70 v/v% of EtOH and 30 v/v% of MeCN) and TPO (2.71 x 10^{-4} g, 7.79 x 10^{-7} mol) were added to a 4 mL glass vial. The glass vial was sealed with a rubber septum and purged with nitrogen at 0°C for 20 minutes. The vial was then irradiated with blue LED light (λ_{max} = 460 nm) at room temperature for 24h, before it was quenched by exposure to air and stored in the dark. Conversion of BzMA was determined via ^{1}H NMR using the following equation α = 100 × ∫I 5.0-4.7 ppm / (∫I 5.17 ppm + ∫I 5.0-4.7 ppm) where ∫I 5.0-4.7 ppm and (∫I 5.17 ppm correspond to the intensities from the methylene protons adjacent to the ester linkage in the BzMA polymer and monomer respectively. The theoretical molecular weight ($M_{n,theory}$) was calculated using the following equation: $M_{n,NMR}$ = DP$_{POEGMA}$ × MW$_{OEGMA}$ + DP$_{POEGMA}$ × MW$_{BzMA}$ × [(∫I5.0-4.7 ppm)/(∫I4.3-3.9 ppm)] where DP$_{OEGMA}$ is the degree of polymerization of the macro-CTA, MW$_{OEGMA}$ is the molecular weight of the macro-CTA, MW$_{BzMA}$ is the molecular weight of BzMA (176.21 g·mol^{-1}) and ∫I 5.0-4.7 ppm and ∫I 4.3-3.9 ppm correspond to the intensities from the methylene protons adjacent to the PBzMA and POEGMA ester linkages respectively. ^{1}H NMR as well as SEC samples were taken to determine the conversion as well as molecular weight of the samples respectively. An aliquot of polymer was taken and diluted with milliQ water to an appropriate concentration for DLS as well as TEM analysis.

Similar reaction procedures were followed when different photoinitiators (BDB, QC/EDB, PP-OH, Eosin Y/TEtOHA) were used to initiate the reaction. The ratio between the macro-CTA and photoinitiator was varied between 0.05 – 0.5 equivalents. The light intensity was varied between 0.8 and 3.2 mW·cm^{-2} when using blue LED (λ_{max} = 460 nm) and between 21 – 109 mW·cm^{-2} when using UV light (λ_{max} = 405 nm). Ethanol as used as a standard solvent for all reactions. Co-solvents were added in relative volume fractions (v/v%)

A similar procedure was followed when synthesizing POEGMA-*b*-PIBA nanoparticles and POEGMA-*b*-PDMAA block copolymers respectively. In that case, IBA (M_n = 208.30 g·mol^{-1}) or DMAA (M_n = 99.13 g·mol^{-1}) were added as a monomer for the chain extension reaction under blue LED. Upon synthesis of POEGA-*b*-PBzMA, POEGA-*b*-PIBA

or POEGA-*b*-PDMAA a similar procedure as above was used. In this case POEGA-CDTPA or POEGA-BTPA was used as a macro-CTA, after which the appropriate monomer was added for chain extension.

Synthesis of POEGMA-*b*-PBzMA nanoparticles via RAFT PISA Dispersion Polymerization in flow

A typical procedure to synthesize POEGMA-*b*-PBzMA using a solid content of 15 wt% was as follows; POEGMA macro-CTA (M_n = 7 700 g·mol^{-1}; 0.03 g, 3.75 x 10^{-6} mol, 1 equiv.), BzMA (0.137 g, 7.79 x 10^{-4} mol, 200 equiv.) and TPO (2.71 x 10^{-4} g, 7.79 x 10^{-7} mol) were dissolved in 0.95 g of solvents (70 v/v% of EtOH and 30 v/v% of MeCN) in a sealed amber colored vial. Next, the vial was purged with nitrogen for 20 minutes, after which the solutions were pumped into the reactor via ASIA syringe pumps. A 3 mL tubular reactor was employed for the particle formation under illumination of blue light (460 nm) with a maximum residence time of 240 min (0.0125 mL·min^{-1} flow rate). Monomer conversions were determined via ^{1}H NMR and molecular weight distributions were analyzed via SEC. Lower molecular weights could be reached by changing the degree of polymerization (DP) of the second block at similar residence times in the reactor. An aliquot of polymer was taken and diluted with ethanol to an appropriate concentration for DLS as well as TEM analysis.

Additional Results and Discussion

Photoiniferter vs. Photoinitiator Pathway

From photoiniferter to photoinitiator pathway

Table S1: Polymerization conditions all methacrylate-based photo-PISA generating POEGMA-*b*-(PBzMA)x particles at varying initiator concentration and light intensity under blue LED irradiation.[a]

Entry	TPO[b] Eq.	Intensity mW·cm^{-2}	Time h	α[c] %	$M_{n,th}$[d] g·mol^{-1}	M_n[e] g·mol^{-1}	Đ[e]	DP	D_n[f] nm	PDI
A1[g]	0			51	8 200	7 700	1.18			
B1	0.05	1.6	4	41	22 100	20 300	1.49	82	78 ± 4	0.11
B2	0.05	1.6	6	45	23 600	21 400	1.65	90	100 ± 9	0.10
B3	0.05	1.6	7	61	29 200	23 400	1.47	122	82 ± 7	0.42
B4	0.05	1.6	17	95	41 200	28 700	1.94	190	105 ± 7	0.07
B5	0.05	1.6	24	98	42 200	39 800	2.23	196	78 ± 2	0.19
C1	0.1	1.6	4	40	21 800	28 500	1.51	80	31 ± 1	0.25
C2	0.1	1.6	6	52	26 000	22 200	1.54	104	83 ± 5	0.44
C3	0.1	1.6	7	61	39 800	29 400	2.1	182	429 ± 24	0.17
C4	0.1	1.6	17	99	42 600	40 300	1.83	198	133 ± 11	0.06
C5	0.1	1.6	24	99	42 600	24 400	2.12	198	77 ± 3	0.17
D1	0.2	1.6	4	22	15 500	11 300	1.45	44	52 ± 2	0.26
D2	0.2	1.6	6	49	25 000	21 100	1.49	98	51 ± 2	0.17
D3	0.2	1.6	7	52	26 100	21 400	1.38	104	60 ± 2	0.06
D4	0.2	1.6	17	98	42 300	35 700	1.47	196	137 ± 11	0.39
D5	0.2	1.6	24	99	42 600	39 600	1.57	198	88 ± 5	0.51
E1	0.5	1.6	4	45	23 600	23 700	1.6	90	83 ± 6	0.39
E2	0.5	1.6	6	86	38 000	30 500	1.91	172	108 ± 8	0.05
E3	0.5	1.6	7	99	42 600	33 000	1.79	198	89 ± 7	0.04
E4	0.5	1.6	17	99	41 900	30 500	1.97	194	138 ± 14	0.19
E5	0.5	1.6	24	99	42 600	41 900	1.87	198	102 ± 11	0.08
F1	0.2	0.8	4	46	23 900	21 400	1.58	92	68 ± 7	0.05
F2	0.2	0.8	6	68	31 700	27 000	1.7	136	90 ± 7	0.21
F3	0.2	0.8	7	79	35 500	27 100	1.76	158	177 ± 17	0.17
F4	0.2	0.8	17	96	41 500	32 300	1.8	192	106 ± 8	0.10
F5	0.2	0.8	24	97	41 900	36 700	1.71	194	155 ± 13	0.15
G1	0.2	3.2	4	44	23 200	18 100	1.62	88	84 ± 4	0.08
G2	0.2	3.2	6	66	31 000	25 100	1.88	132	119 ± 8	0.05
G3	0.2	3.2	7	62	29 600	24 100	1.78	124	111 ± 7	0.14
G4	0.2	3.2	17	93	40 500	23 200	2.05	186	84 ± 6	0.07
G5	0.2	3.2	24	98	42 200	30 400	1.94	196	121 ± 7	0.04

[a] Experimental conditions: solvent, EtOH/MeCN 70/30 v/v% ; light source, blue LED light (λ_{max} = 460 nm), 15 wt% solids content with a target DP of 200. [b] The amount of TPO was varied in equivalents relative to the macroRAFT. [c] Monomer conversions were determined via ^{1}H NMR spectroscopy (CDCl$_3$) by comparting the intensities from the methylene protons adjacent to the ester linkage in the BzMA monomer (5.17 ppm) and polymer (5.0 – 4.7 ppm) respectively. [d] Theoretical molecular weight was calculated using the following equation: $M_{n,th}$ = [M]$_0$/[POEGMA] x MW^M x α + MW^{POEGMA}, where [M]$_0$, [POEGMA], MW^M, α and MW^{POEGMA} correspond to the initial monomer concentration, initiator macroRAFT concentration, molar mass of the monomer, conversion determined by ^{1}H NMR and the molar mass of the macroRAFT respectively. [e] Molecular weight and polydispersity (Đ) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards. [f] Particle diameter and polydispersity index (PDI) were determined by DLS analysis in ethanol; [g] MacroRAFT used in this work.
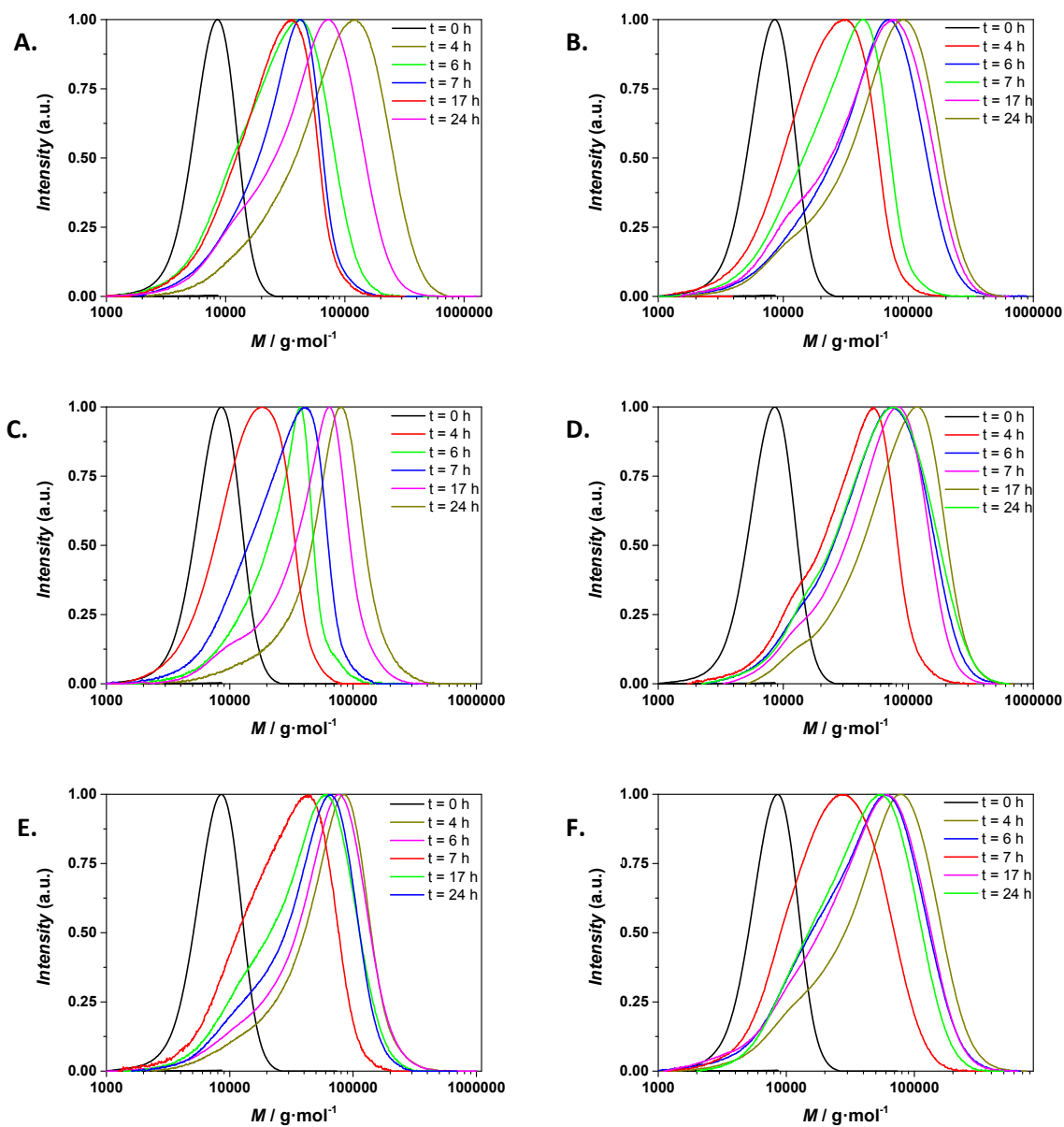
Figure S3: Molecular weight distributions at different monomer conversions all methacrylate-based photo-PISA of BzMA using a POEGMA-based macroRAFT agent in batch using the reaction conditions specified in Table S1. (A) entriesB1-B5, (B) entries C1-C5, (C) entries D1-D5, (D) entries E1-E5, (E) entries F1-F5 and (F) entries G1-G5 defined in Table S1.
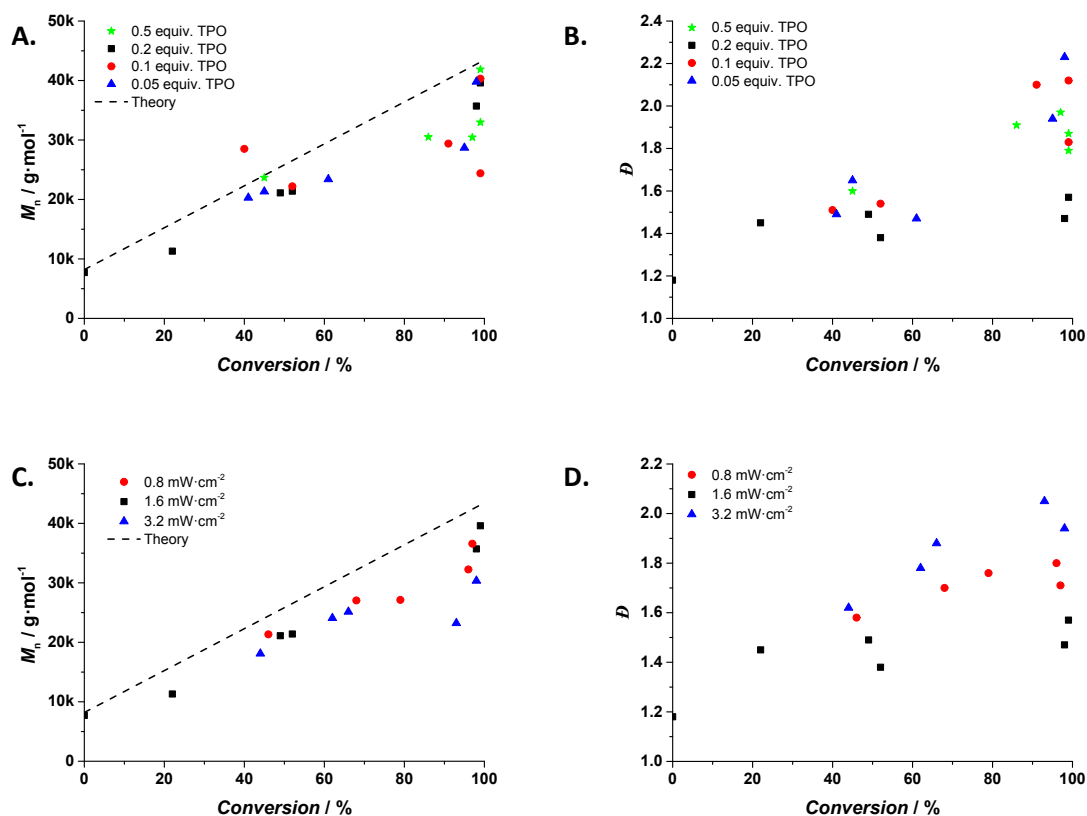
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Figure S4: Effect of variations in TPO concentration and light intensity on the M_n (A and C) and $Đ$ (B and D) upon polymerizing POEGMA-*b*-PBzMA block copolymers. Reaction conditions are specified in Table S1.
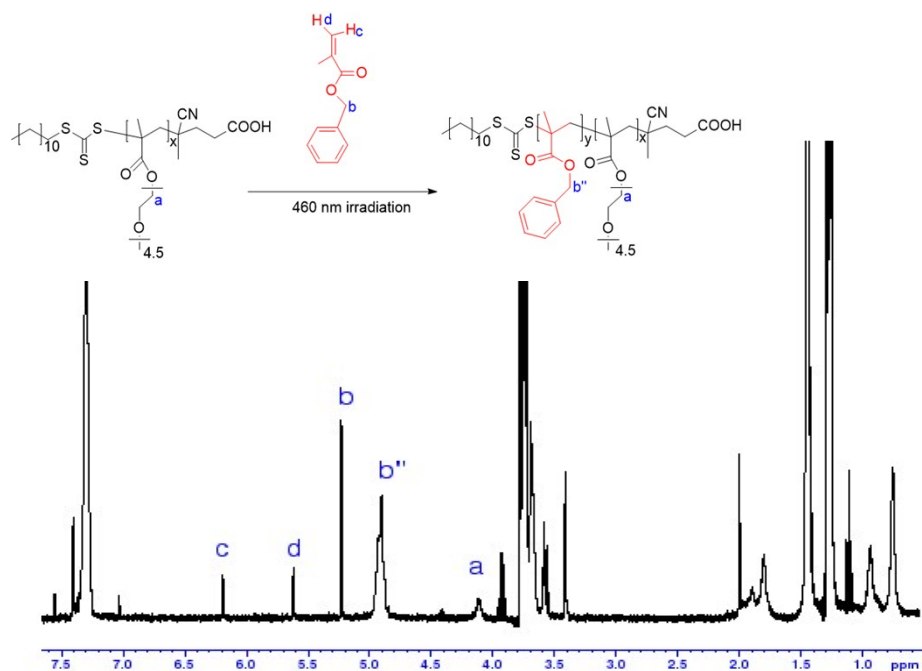

Figure S5: Typical ^1H-NMR spectra of POEGMA-*b*-PBzMA block copolymers with characteristic peaks of each blocks assigned in the NMR spectrum.
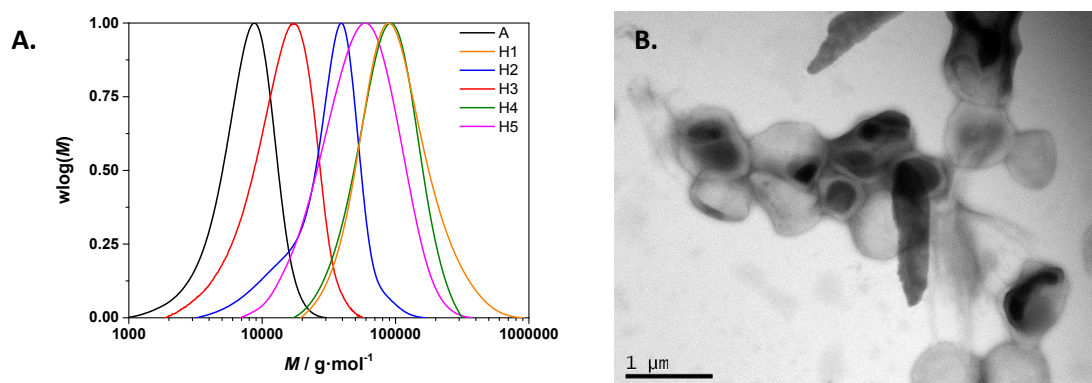
Effect of solvent on polymerization kinetics

Figure S6: (A) Molecular weight distributions of polymers prepared by photo-PISA of BzMA using a POEGMA-based macroRAFT agent in batch using the reaction conditions specified in Table 1 in different solvents. Use of EtOH (H1), EtOH / MeCN 90/10 v/v% (H2), EtOH / MeCN 70/30 v/v% (H3), EtOH / DMSO 90/10 v/v% (H4) or EtOH / DMSO 70/30 v/v% (H5) as solvent; (B) Representative TEM images of POEGMA-*b*-PBzMA block copolymer (experiment H4) defined in Table S1.

Table S2: Polymerization conditions all methacrylate-based photo-PISA generating POEGMA-b-(PBzMA)x particles using different photoinitiator systems under blue or green LED irradiation upon 4h of reaction.[a]

Entry	Initiator[b] Eq.	Initiator	α[c] %	$M_{n,th}$[d] g·mol^{-1}	M_n[e] g·mol^{-1}	$Đ$[e]	DP	D_n[f] nm	PDI
A1[g]	0	-	51	8 200	7 700	1.18	-	-	-
I1	0	-	88	57 700	77 900	1.40	160	267 ± 15	0.28
I2	0.2	TPO	98	48 900	68 900	1.43	196	297 ± 11	0.29
I3	0.2	BDB	98	65 700	76 000	1.53	196	215 ± 8	0.26
I4	1	QC/EDB	98	36 000	19 900	2.03	196	304 ± 24	0.34
I5	0.01	Eosin /TEtOHA	77	34 200	44 800	1.48	154	257 ± 19	0.31
I6	0.5	TPO	98	84 571	92 900	1.63	196	284 ± 16	0.26
I7	0.5	BDB	98	62 750	69 200	1.45	196	360 ± 14	0.29

[a] Experimental conditions: solvent, EtOH/DMSO 90/10 v/v% ; light source, blue LED light (λ_{max} = 460 nm and light intensity of 1.6 mW·cm^{-2}) for all reactions except for Eosin Y. In this case a green LED (λ_{max} = 530 nm) was used at a light intensity of 0.4 mW·cm^{-2}, 15 wt% solids content with a target DP of 200. [b] The amount of initiator was varied in equivalents relative to the macroRAFT. [c] Monomer conversions were determined via ^{1}H NMR spectroscopy (CDCl$_3$) by comparting the intensities from the methylene protons adjacent to the ester linkage in the BzMA monomer (5.17 ppm) and polymer (5.0 – 4.7 ppm) respectively. [d] Theoretical molecular weight was calculated using the following equation: $M_{n,th}$ = [M]$_0$/[POEGMA] x MW^M x α + MW^{POEGMA}, where [M]$_0$, [POEGMA], MW^M, α and MW^{POEGMA} correspond to the initial monomer concentration, initiator macroRAFT concentration, molar mass of the monomer, conversion determined by ^{1}H NMR and the molar mass of the macroRAFT respectively. [e] Molecular weight and polydispersity ($Đ$) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards. [f] Particle diameter and polydispersity index (PDI) were determined by DLS analysis in ethanol; [g] MacroRAFT used in this work.

Table S3: Polymerization conditions all methacrylate-based photo-PISA generating POEGMA-b-(PBzMA)$_x$ particles at varying blue LED source via the photoiniferter and photoinitiator pathway. [a]

Entry	TPO[b] Eq.	*Wavelength* nm	*Time* h	α[c] %	M_T[e] g·mol^{-1}	M_n[e] g·mol^{-1}	Đ[e]
A1[f]	0			51	8 200	7 700	1.18
I8	0	460	1	42	15 000	14 400	1.30
I9	0	460	2	54	23 900	25 900	1.47
I10	0	460	3	79	32 700	33 500	1.57
I11	0	460	4	93	41 500	50 800	1.45
I12	0.2	460	1	38	15 000	15 500	1.24
I13	0.2	460	2	54	23 900	26 800	1.56
I14	0.2	460	3	76	32 700	33 000	1.83
I15	0.2	460	4	95	41 500	42 100	1.36
I16	0	405	1	47	15 000	11 700	1.36
I17	0	405	2	53	23 900	17 300	1.50
I18	0	405	3	65	32 700	26 700	1.54
I19	0	405	4	91	41 500	53 500	1.44
I20	0.2	405	1	48	15 000	9 100	1.45
I21	0.2	405	2	65	23 900	14 400	1.39
I22	0.2	405	3	71	32 700	24 300	1.55
I23	0.2	405	4	92	41 500	43 600	1.45

[a] Experimental conditions: solvent, EtOH/DMSO 90/10 v/v% ; light source, blue LED light (λ_{max} = 460 nm and light intensity of 1.6 mW·cm^{-2}) or UV LED (λ_{max} = 405 nm and light intensity of 21 mW·cm^{-2}). [b] The amount of initiator was varied in equivalents relative to the macroRAFT. [c] Monomer conversions were determined via ^{1}H NMR spectroscopy (CDCl$_3$) by comparting the intensities from the methylene protons adjacent to the ester linkage in the BzMA monomer (5.17 ppm) and polymer (5.0 – 4.7 ppm) respectively. [d] Theoretical molecular weight was calculated using the following equation: $M_{n,th}$ = [M]$_0$/[POEGMA] x MW^M x α + MW^{POEGMA}, where [M]$_0$, [POEGMA], MW^M, α and MW^{POEGMA} correspond to the initial monomer concentration, initiator macroRAFT concentration, molar mass of the monomer, conversion determined by ^{1}H NMR and the molar mass of the macroRAFT respectively. [e] Molecular weight and polydispersity (Đ) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards; [f] MacroRAFT used in this work.

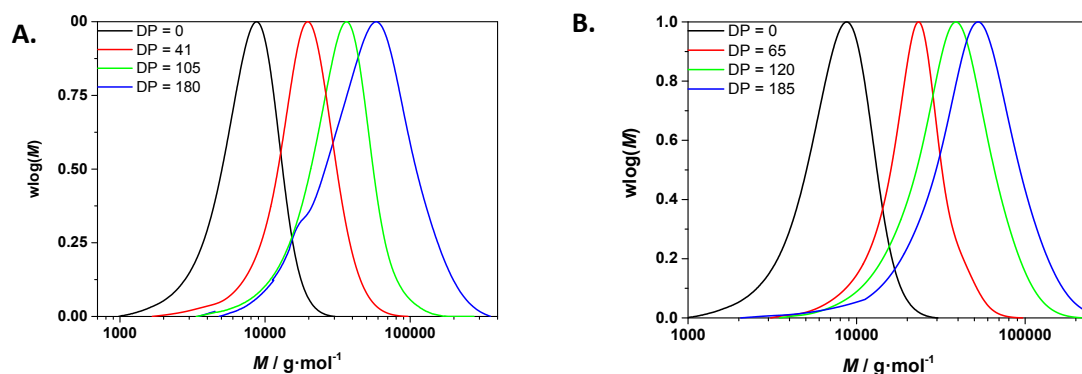## Synthesis of POEGMA-*b*-PBzMA nanoparticles in flow

Figure S7: Molecular weight distributions at different monomer conversions for all methacrylate-based photo-PISA polymerization of BzMA using a POEGMA-based macroRAFT agent in flow using the reaction conditions specified in Table 2. (A) entries O1-O3, (B) entries P1-P3.

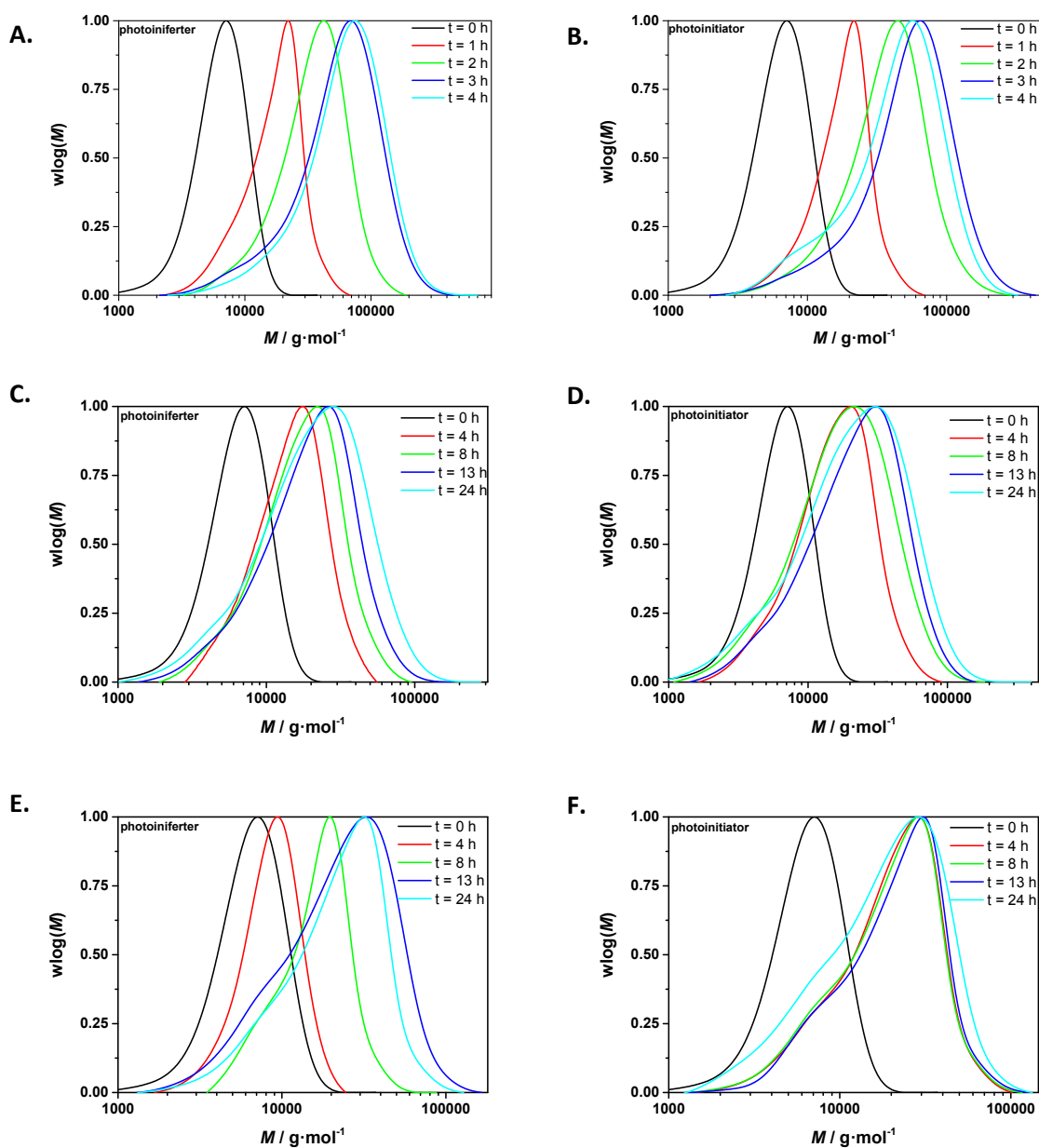# A closer look into the initiation mechanism via the photoinitiator / photoiniferter route

Figure S8: Molecular weight distributions at different monomer conversions for alcoholic photoPISA RAFT (dispersion) polymerization using a POEGMA-based macroRAFT agent in batch using the reaction conditions specified in Table 3. (A) entries L1-L4, (B) entries L5-L8, (C) entries L9-L12, (D) entries L13-L16, (E) entries L17-L20, (F) entries L21-L24.
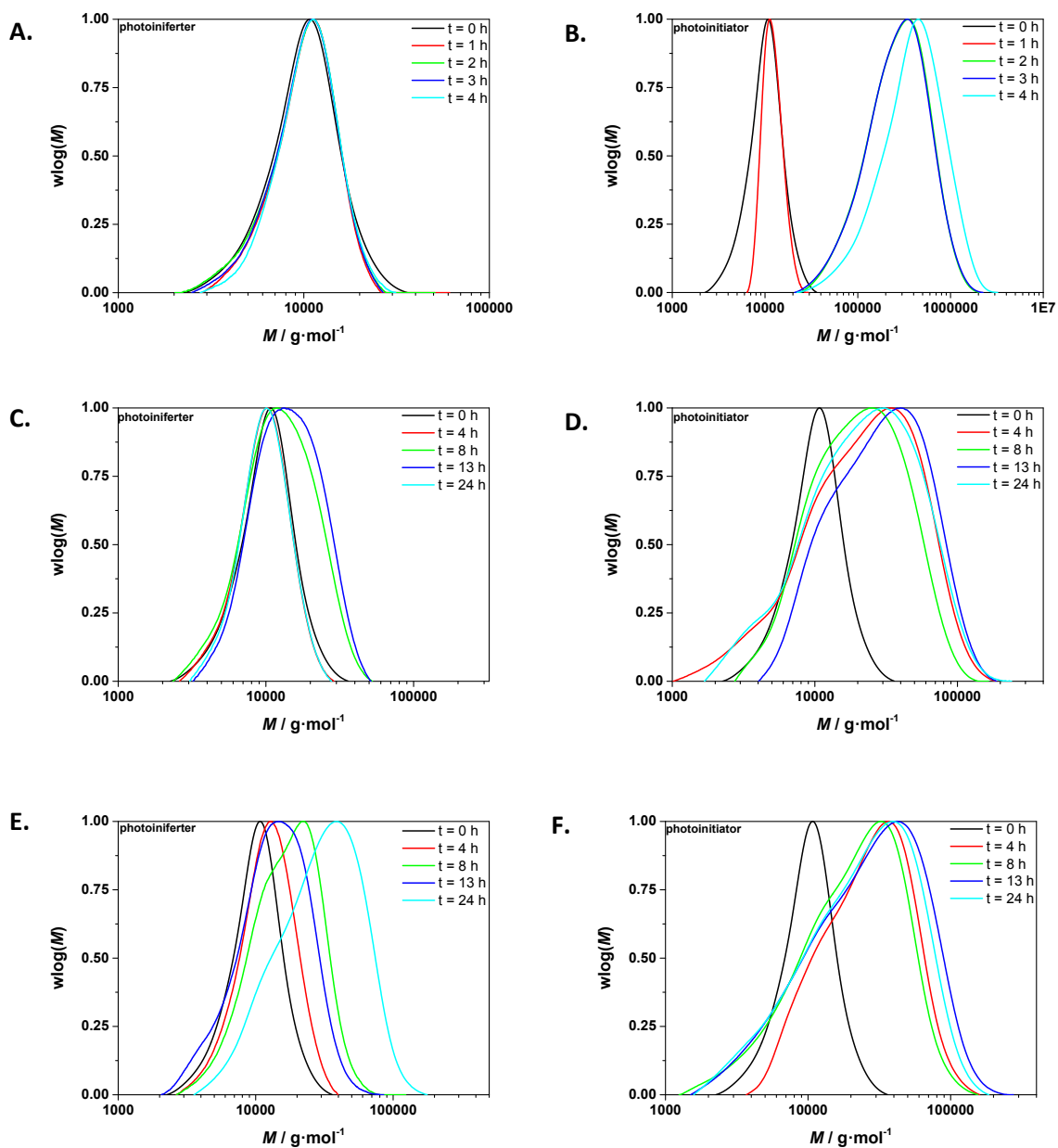
Figure S9: Molecular weight distributions at different monomer conversions for alcoholic photoPISA RAFT (dispersion) using a POEGA-based macroRAFT agent in batch via the reaction conditions specified in Table 3. (A) entries M1-M4, (B) entries M5-M8, (C) entries M9-M12, (D) entries M13-M16, (E) entries M17-M20, (F) entries M21-M24.
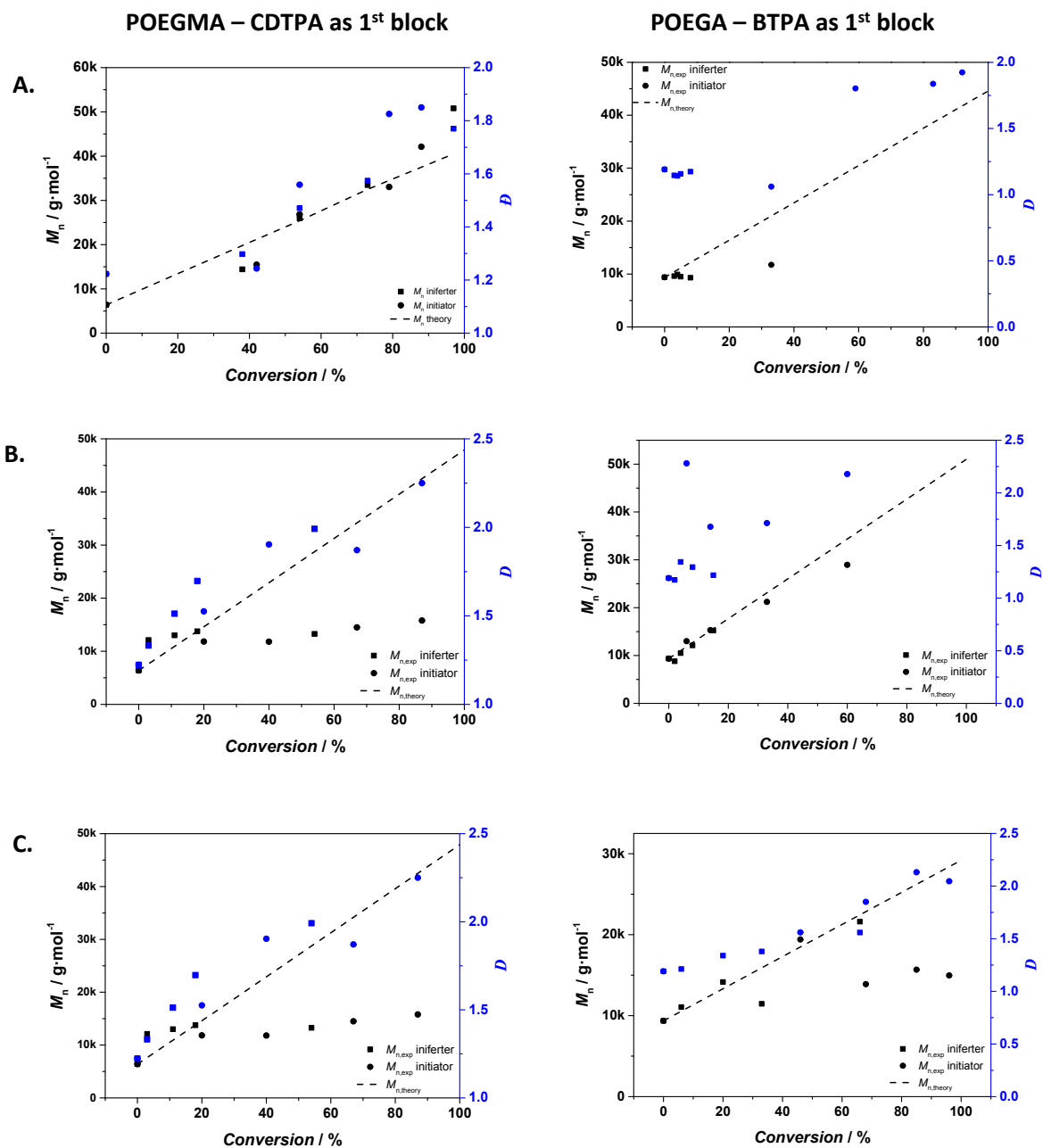
Figure S10: Polymerization reactions when using POEGMA (left) or POEGA (right) as first block, showing the M_n and $Đ$ with increasing monomer conversion using (A) BzMA (B) IBA or (C) DMAA as second block, specified in Table 3.

Table S4: Characterization of POEGA-*b*-PBzMA block copolymers synthesized via the photoiniferter route using POEGA-CDTPA as first block.[a]

Entry	*Time*	$M_{\text{n,theo}}$[b]	$M_{\text{n,exp}}$[c]	*Đ*[c]	α[d]
	h	**g·mol⁻¹**	**g·mol⁻¹**		**%**
A3[e]		9 900	10 700	1.23	49
N1	1	12 500	12 700	1.25	5
N2	2	12 800	13 000	1.24	6
N3	3	13 500	11 400	1.30	8
N4	4	14 200	14 400	1.19	10
N5	8	14 600	12 500	1.22	11

[a] Experimental conditions: solvent, EtOH/DMSO 90/10 v/v% ; light source, blue LED light (λ_{max} = 460 nm, 1.6 mW·cm⁻²), 15 wt% solids content. [b]Theoretical molecular weight was calculated using the following equation: $M_{\text{n,th}}$ = $[M]_0$/[POEGA] x MW$^{\text{M}}$ x α + MW$^{\text{POEGA}}$, where $[M]_0$, [POEGA-CDTPA], MW$^{\text{M}}$, α and MW$^{\text{POEGA-CDTPA}}$ correspond to the initial monomer concentration, initiator macroRAFT concentration, molar mass of the monomer, conversion determined by ¹H NMR and the molar mass of the macroRAFT respectively. [c] Molecular weight and polydispersity (*Đ*) were determined by SEC analysis calibrated to poly(methyl methacrylate) standards. [d] Monomer conversions were determined via ¹H NMR spectroscopy (CDCl₃) by comparing the intensities from the methylene protons adjacent to the ester linkage in the BzMA monomer (5.17 ppm) and polymer (5.0 – 4.7 ppm) respectively; [e] MacroRAFT used in this work.
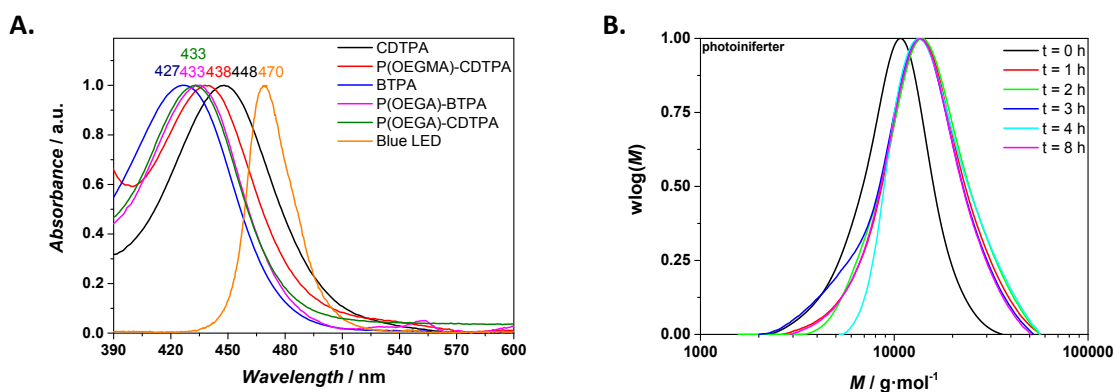

Figure S11: (A) UV Vis spectra performed in DMSO showing the maximum absorbance of the RAFT agents and the macroRAFT agents; (B) Molecular weight distributions at different monomer conversions for alcoholic RAFT (dispersion) polymerization of BzMA using a POEGA-CDTPA macroRAFT via the reaction conditions specified in Table S4 (entries N1-N5).